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Site de l'Île-aux-Chats - Projet de restauration des sédiments
Étude d'impact environnemental

VOLUME 3

Annexes (A à K)

Décembre 1997

TECSULT

Tecsult Environnement Inc.
experts-conseils
85, RUE STE-CATHERINE OUEST, MONTRÉAL (QUÉBEC) CANADA

en collaboration avec

EVS ENVIRONMENT CONSULTANTS

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ANNEXE A

Reclassification de l'Île-aux-Chats par le MEF

N°.: 06-3-15-A
Catégorie: III R

CELLULES DE CONFINEMENT SÉCURITAIRES DE LA COMPAGNIE DE PRODUITS CHIMIQUES ALLIED DU CANADA INC.

PROPRIÉTAIRE: Produits Chimiques Général du Canada ltée

LOCALISATION: Salaberry-de-Valleyfield, Ile-Aux-Chats

NATURE DES DÉCHETS: Gypse, boues d'alun et cendres de pyrite

IMPACTS POTENTIELS: Contamination de la nappe d'eau souterraine et contamination sectorielle du lac Saint-François

La compagnie Produits Chimiques Général Canada Limitée (PCGL) exploite actuellement une usine de fabrication d'alun sur l'Ile-aux-Chats (anciennement Ile Clark) située dans le lac Saint-François près de Valleyfield. Le site, autrefois la propriété de la compagnie Allied Chemicals, comprenait des installations de production d'acide sulfurique, d'acide fluorhydrique et une usine de produits chimiques. Ces dernières installations ne sont plus en opération sauf en ce qui a trait à la production d'alun liquide. L'île contenait jusqu'en 1990 quatre bassins de boues et d'eaux usées qui ont été exploités sur une superficie d'environ 14 hectares pour l'élimination d'une partie des déchets produits par la compagnie. Les bassins de sédimentation de la compagnie étaient classés catégorie I dans l'inventaire GERLED.

Ces bassins étaient identifiés 5a, 5b, 7a et "swimming pool". Le fond des bassins 5a, 5b et 7a était constitué de cendres de pyrite. Par la suite, les bassins 5a et 5b ont reçu les résidus de gypse de la compagnie et récemment des boues d'alun. Dans le bassin 7a, on avait placé les sédiments contenus dans un bassin de décantation connu sous le nom de "swimming pool" qui recevait un effluent d'acide contaminé entre autres par du mercure, des fluorures, de l'arsenic et du sélénium.

La restauration du site qui a débuté en 1990 a consisté en l'élimination de toutes sources de contamination pouvant dégrader l'état de l'environnement. À cet effet, la compagnie a construit une cellule sécuritaire à simple membrane d'une capacité de 60 000 m³ afin d'y confiner les sols contaminés au-dessus du critère C qui étaient présents sur l'île, puis une cellule sécuritaire d'une capacité de 118 000 m³ afin d'y permettre l'enfouissement des déchets de cendres de pyrite (déchets dangereux), des mélanges de sols et de déchets dangereux et des sols contaminés à des concentrations supérieures au critère C de la Politique de réhabilitation des terrains contaminés.

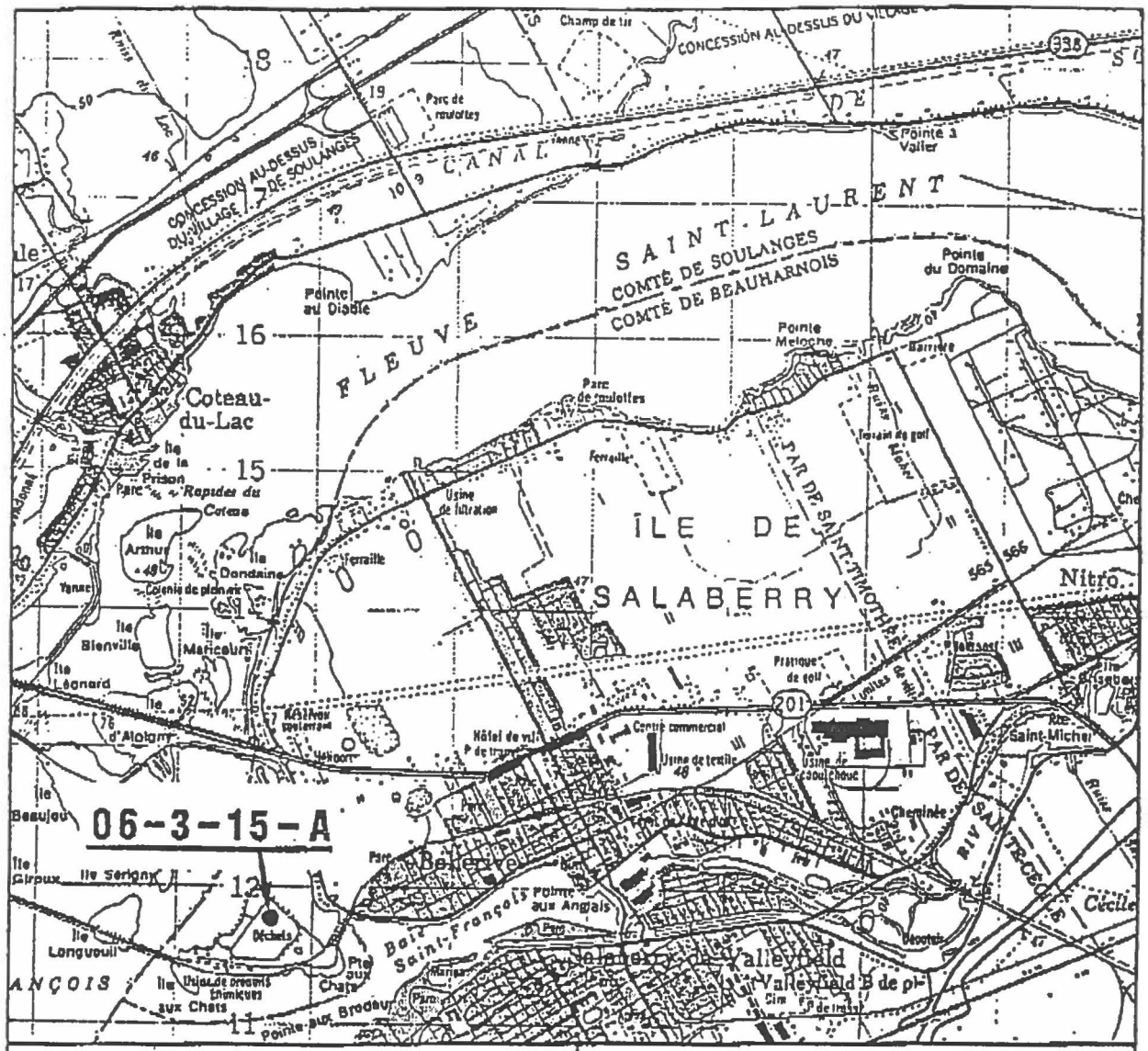
Les déchets de gypse/alun (déchets dangereux) ont également été excavés puis entreposés sur le site avant de servir pour la construction des digues de ceinture des cellules de confinement et comme matériaux de remblai pour l'aménagement final de la zone du bassin 5B; la zone de leur entreposage a été complètement recouverte à la fin 1992 d'une géomembrane imperméable. En mai et juin 1993, l'aménagement paysagé et la revégétation de l'île furent complétés.

L'ancien propriétaire du lieu, Allied Signal inc. demeure responsable de l'entretien et de la surveillance environnementale des cellules ainsi que du suivi environnemental des eaux souterraines des eaux de surface et des poissons.

Étant donné le confinement adéquat des déchets et des sols contaminés enfouis dans les cellules, ce lieu présente actuellement un faible potentiel de risque pour l'environnement et aucun pour la santé publique. Toutefois, un suivi annuel devra être réalisé sur le terrain. Il est donc classé dans la catégorie IIIR.

94/08/23

CELLULES DE CONFINEMENT SÉCURITAIRES DE LA COMPAGNIE DE PRODUIT CHIMIQUES ALLIED DU CANADA INC.



Gouvernement du Québec
Ministère de l'Environnement
et de la Faune

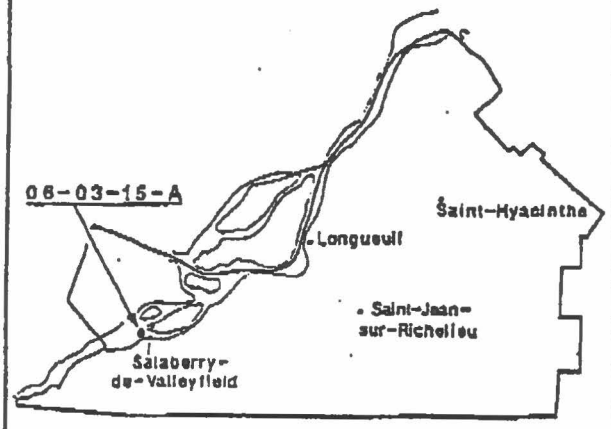
Échelle

1 : 50 000

1000 0 1000 2000 m

Source: Carte topographique 31 G/8,
Énergie, Mines et Ressources
Canada

RÉGION 16 MONTÉRÉGIE



ANNEXE B

Directive pour la préparation de l'étude d'impact environnemental du Projet de restauration des sédiments sur le pourtour de l'Île-aux-Chats

MINISTÈRE DE L'ENVIRONNEMENT ET DE LA FAUNE

DIRECTIVE

PROJET DE RESTAURATION DES SÉDIMENTS SUR LE POURTOUR DE L'ÎLE AUX CHATS, LAC SAINT-FRANÇOIS, FLEUVE SAINT-LAURENT

PAR LA COMPAGNIE ALLIEDSIGNAL CANADA INC.

Dossier 3211-02-146

JANVIER 1996

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INTRODUCTION

La directive ministérielle a pour but d'indiquer à l'initiateur du projet la nature, la portée et l'étendue de l'étude d'impact sur l'environnement qu'il doit préparer en vue d'obtenir du Gouvernement l'autorisation de réaliser son projet de restauration des sédiments autour de l'île aux Chats, tel que prévu à l'article 31.2 de la Loi sur la qualité de l'environnement (L.R.Q., c. Q-2).

Le projet est assujetti en vertu des dispositions de l'article 2b) du Règlement sur l'évaluation et l'examen des impacts sur l'environnement (R.R.Q., c. Q-2, r. 9 modifié par les décrets 1002-85 du 29 mai 1985, 879-88 du 8 juin 1988, 586-92 du 15 avril 1992 et 1529-93 du 3 novembre 1993). Le contenu de l'étude d'impact doit se conformer à la section III de ce règlement. L'étude doit être préparée avec une méthode scientifique et satisfaire les exigences du Ministre. Son envergure est fonction de la nature des activités constituant le projet et de l'importance des impacts appréhendés.

L'initiateur du projet doit envisager la réalisation de l'étude d'impact comme un exercice de planification pour son projet, en vue d'améliorer son insertion dans le milieu récepteur. En ce sens, l'initiateur doit tout au long de la réalisation de l'étude porter une attention particulière aux réglementations, aux orientations et aux préoccupations émanant des diverses instances gouvernementales concernées, tant sur le plan national, régional ou local. Le projet doit notamment être conforme aux objectifs du schéma d'aménagement de la Municipalité régionale de comté de Beauharnois-Salaberry et respecter les règlements d'urbanisme de la municipalité de Grande-Île. Il doit également prendre en considération les préoccupations et les intérêts des autres organismes et des citoyens préoccupés par le projet.

L'initiateur du projet peut utiliser toutes les données pertinentes dont il dispose déjà relativement à son projet. Il devra cependant préciser le contexte dans lequel elles ont été obtenues, les actualiser ou justifier la pertinence de les utiliser telles quelles.

Cette directive est préparée en fonction des renseignements contenus dans l'avis de projet. Si des éléments importants du projet sont modifiés, le Ministre doit en être informé. La directive pourra être réajustée en conséquence.

1. MISE EN CONTEXTE DU PROJET

Cette section a pour but de présenter les éléments de planification qui sont à l'origine du projet. Elle vise à présenter le projet et ses objectifs, à définir le contexte de réalisation du projet dans la réalité actuelle et future et à percevoir les relations avec d'autres projets. Elle inclut également un résumé de la démarche réalisée par l'initiateur du projet en vue de choisir la solution qu'il propose.

1.1 Nature et raison d'être du projet

L'étude d'impact doit décrire les grandes caractéristiques du projet et exposer les objectifs à atteindre. Elle doit faire état des besoins qui seront satisfaits et des problèmes qui seront résolus suite à la réalisation du projet. Elle doit préciser en fonction de quels usages actuels, prévus et probables de l'eau et du milieu aquatique, le projet de restauration des sédiments est conçu.

Afin que le public soit en mesure de juger de l'importance relative du niveau de contamination du site, l'étude d'impact doit situer le projet dans le cadre de la problématique générale de la contamination des sédiments du fleuve Saint-Laurent et dans le contexte de l'Entente Saint-Laurent Vision 2000.

1.2 Contexte social et enjeux

Afin de donner une perception d'ensemble du projet, l'étude d'impact doit faire état de l'intérêt, des préoccupations ou de la controverse que le projet suscite. Ainsi, l'initiateur pourra réaliser une démarche d'information et de consultation par le biais des organismes du milieu pour identifier au début de l'étude d'impact les éléments de l'environnement jugés importants ou sensibles par les milieux concernés et les enjeux significatifs qu'ils reconnaissent au projet.

1.3 Projets connexes et phases futures

Les relations pouvant exister entre le projet et tout autre projet en cours de planification ou d'exécution devront être présentées le cas échéant. Cet exercice doit permettre de déterminer, dans la mesure du possible, les effets cumulatifs ou les interactions potentielles avec le projet proposé. De plus, si l'initiateur prévoit des phases de développement futures, il devra en faire état.

2. MILIEU RÉCEPTEUR

Cette section de l'étude d'impact doit décrire l'état de l'environnement à l'endroit d'insertion du projet en accordant une attention particulière à la dynamique des écosystèmes et en utilisant toutes les données pertinentes à cette fin.

2.1 Zone d'étude

L'initiateur du projet doit identifier une zone d'étude et en justifier les limites. Elle doit être suffisamment vaste pour couvrir tous les territoires susceptibles d'être directement touchés ou d'être influencés par les interventions projetées. La zone d'étude peut être subdivisée en distinguant les zones d'effets directs des zones d'effets indirects du projet sur les milieux naturel et humain.

2.2 Description du milieu

L'étude d'impact doit présenter une description de l'état de l'environnement tel qu'il se présente dans la zone d'étude avant la réalisation du projet.

Cette description doit inclure les composantes physiques et biologiques du milieu naturel susceptibles d'être perturbées par le projet. Elle doit aussi exposer les relations entre ces composantes notamment pour identifier les écosystèmes présentant un intérêt particulier en terme de diversité biologique, de productivité ou d'habitat pour une ou plusieurs espèces d'intérêt.

Cette description doit inclure également les composantes du milieu humain reliées à l'utilisation actuelle, prévue et probable de la zone d'étude, lorsque celles-ci peuvent être modifiées par le projet.

La sélection des composantes à étudier et l'extension donnée à leur description doivent correspondre au degré d'influence que le projet exerce sur celles-ci, de même qu'à leur valeur ou à leur importance dans la zone d'étude. L'importance d'une composante est estimée en tenant compte :

- de sa sensibilité par rapport à l'aménagement proposé;
- de sa dimension et de son aire d'influence;
- de sa rareté ou de son unicité;
- de la perte de diversité qui pourrait être causée par sa disparition ou sa modification;
- de la valeur de cette composante pour la population;
- de l'offre et de la demande quant à une ressource;
- de sa reconnaissance formelle par une loi, une politique, une réglementation ou une décision officielle (parc, réserve, espèces menacées, etc.).

L'étude d'impact doit présenter l'image de la zone d'étude la plus actuelle possible. Si les données disponibles sont insuffisantes ou trop anciennes ou si elles indiquent par exemple que l'on peut retrouver un habitat d'une espèce menacée ou vulnérable ou susceptible d'être ainsi désignée, l'initiateur doit réaliser les inventaires appropriés et indiquer les méthodes utilisées.

2.2.1 Composantes physiques

La présentation du milieu physique doit comprendre sans s'y limiter une description des éléments suivants :

- le régime hydrologique (débits, niveaux d'eau, bathymétrie, hydrodynamique ...);
- le régime des glaces (formation du couvert, embâcle, débâcle ...);
- le régime sédimentologique (nature et épaisseur des sédiments, secteurs d'érosion, de transport et de sédimentation ...);

Sédiments

Puisqu'il s'agit de la restauration d'un site contaminé, l'étude d'impact doit contenir une évaluation détaillée portant sur les sédiments et leurs effets sur l'écosystème aquatique et la santé humaine. Les éléments suivants seront analysés :

- la qualité de l'eau du fleuve à proximité de l'île aux Chats;
- les niveaux de contamination des sédiments;
- la toxicité des sédiments pour la vie aquatique;
- les risques pour la santé humaine liés à la présence des sédiments contaminés.

· Échantillonnage

Le plan d'échantillonnage des sédiments doit permettre la collecte d'informations nécessaires à l'évaluation des différentes solutions de restauration et à la justification de la solution retenue. Les méthodes employées doivent être décrites et les marges d'erreur précisées.

Les niveaux de contamination, l'étendue et le volume de sédiments contaminés doivent être définis de manière à en obtenir une représentation visuelle. Cette représentation doit comprendre la zone contaminée à un niveau compris entre le niveau 2 (seuil d'effets mineurs) et le niveau 3 (seuil d'effets néfastes) et la zone contaminée à un niveau supérieur au niveau 3. Ces niveaux sont définis dans le document intitulé *Critères intérimaires pour l'évaluation de la qualité des sédiments du Saint-Laurent*, Environnement Canada et ministère de l'Environnement du Québec, avril 1992.

L'échantillonnage doit également permettre une collecte d'informations plus poussée, en tenant compte des usages actuels, prévus et probables de la zone contaminée. La toxicité des sédiments pour les communautés aquatiques doit être évaluée à partir des tests toxicologiques appropriés. Afin d'évaluer les risques pour la santé humaine liés à l'exposition des personnes aux sédiments contaminés une démarche d'analyse de risque doit être entreprise.

· Paramètres

L'évaluation de la qualité des sédiments doit être basée sur l'analyse des paramètres physico-chimiques suivants[1]:

---

1 Des critères de qualité applicables aux sédiments du Saint-Laurent ont été proposés pour plusieurs de ces substances. À l'exception des critères relatifs au fer et au sélénium, ces critères sont présentés dans le document intitulé Critères intérimaires pour l'évaluation de la qualité des sédiments du Saint-Laurent, Environnement Canada et ministère de l'Environnement du Québec, avril 1992. Les critères pour le fer sont présentés dans le document intitulé Guidelines for the Protection and Management of Aquatic Sediment Quality in Ontario, ministère de l'Environnement et de l'Énergie de l'Ontario, août 1993. Les critères pour le sélénium sont présentés dans le document intitulé First Report Of Canada Under The 1987 Protocol To The 1978 Great Lakes Water Quality Agreement, Commission mixte internationale, 1988.

- granulométrie;
- carbone organique total;
- arsenic, cadmium, chrome, cuivre, nickel, plomb et zinc extractibles, mercure total;
- sélénium;
- fer;
- HAP totaux;
- HAP : benzo(a)anthracène, benzo(b)fluoranthène, benzo(j)fluoranthène, benzo(k)fluoranthène, benzo(g,h,i)pérylène, benzo(c)phénanthrène, benzo(a)pyrène, chrysène, dibenzo(ah)anthracène, dibenzo(a,h)pyrène, dibenzo(a,i)pyrène, dibenzo(a,l)pyrène, diméthyl-7,12 benzanthracène-nel,2, fluoranthène, indéno(1,2,3,c,d)pyrène, méthyl-3 cholanthrène, acénaphtène, acénaphtylène, anthracène, fluorène, pyrène, naphthalène, phénanthrène;
- BPC : arochlore 1016, arochlore 1242, arochlore 1248, arochlore 1254, arochlore 1260.

Si certains paramètres ne sont pas mesurés, l'initiateur du projet devra expliquer quelles sont les raisons qui l'ont conduit à procéder ainsi. Les résultats obtenus par l'initiateur du projet antérieurement au dépôt de l'avis de projet au Ministère pourront être utilisés dans l'étude d'impact.

· Méthodes d'analyses

Pour toute analyse réalisée après l'émission de cette directive, l'initiateur du projet doit faire approuver par le ministère de l'Environnement et de la Faune les méthodes qu'il entend utiliser. Pour les paramètres physico-chimiques, il pourra se référer au *Guide méthodologique de caractérisation des sédiments*, publié en 1992 par le Centre Saint-Laurent en collaboration avec le ministère de l'Environnement du Québec.

· Dépôt de sédiments contaminés en milieu terrestre

Si l'initiateur du projet prévoit déposer des sédiments contaminés en milieu terrestre, sur un site autre qu'un site déjà autorisé par le ministère de l'Environnement et de la Faune, la description du milieu devra comprendre:

- la localisation et la délimitation du site et des couloirs de transport;
- la géologie, la topographie et le drainage dans le secteur du site de dépôt;
- la qualité physico-chimique du sol récepteur.

2.2.2 Composantes biologiques

Végétation

Les communautés végétales terrestres, riveraines et aquatiques de la zone d'étude doivent être décrites lorsqu'elles sont susceptibles d'être affectées par le projet. On doit porter attention aux communautés végétales peu communes au niveau régional ou national.

Faune

Les espèces fauniques terrestres, semi-aquatiques et aquatiques utilisant la zone d'étude et susceptibles d'être affectées par le projet doivent être décrites. L'étude doit tenir compte des différents types d'habitats (zone de reproduction, d'alevinage, d'alimentation et de repos ...) et de l'utilisation spatio-temporelle de ces habitats (cycles saisonniers, patron migratoire ...).

Espèces menacées ou vulnérables

Les espèces fauniques ou floristiques menacées ou vulnérables ou susceptibles d'être ainsi désignées figurent dans une liste officielle dressée en vertu de la Loi sur les espèces menacées ou vulnérables. Ces espèces doivent faire l'objet d'une attention particulière lors de la réalisation de tout projet susceptible d'affecter leurs populations ou leurs habitats. L'étude d'impact doit faire état des connaissances disponibles dans ce domaine. L'initiateur doit consulter les documents suivants :

- dans le cas de la flore : LAVOIE, G. *Plantes vasculaires susceptibles d'être désignées menacées ou vulnérables au Québec*, Direction de la conservation et du patrimoine écologique, ministère de l'Environnement du Québec, février 1992, 180 pages;

- dans le cas de la faune : BEAULIEU, H. *et al. Liste des espèces de la faune vertébrée susceptibles d'être désignées menacées ou vulnérables*, ministère du Loisir, de la Chasse et de la Pêche du Québec, 1992, 108 pages.

L'initiateur peut également consulter au ministère de l'Environnement et de la Faune, la Direction de la conservation et du patrimoine écologique (espèces floristiques) et la Direction régionale de la Montérégie (espèces fauniques).

2.2.3 Milieu humain

La description du milieu humain doit comprendre, sans s'y limiter, les éléments suivants. Chacun de ces éléments doit être traités en se restreignant aux aspects significatifs en regard du projet :

- l'utilisation actuelle et potentielle du territoire en se référant aux politiques, schémas et règlements municipaux et régionaux de développement et d'aménagement;
- les aires naturelles vouées à la protection et à la conservation ou présentant un intérêt pour leurs aspects récréatifs, esthétiques, historiques, scientifiques et éducatifs;
- les caractéristiques de la population;
- les habitudes de vie des résidants et leurs activités de loisirs en relation avec le milieu aquatique et riverain;
- les infrastructures de transport;
- les services municipaux et autres;

- les éléments significatifs du patrimoine archéologique et culturel;
- les paysages et les éléments visuels d'intérêt local et touristique.

3. CHOIX DU SECTEUR D'INTERVENTION

En utilisant l'information des chapitres précédents, l'initiateur doit présenter le cheminement qu'il a effectué pour choisir parmi différentes solutions possibles, le secteur d'intervention qui répond le mieux aux objectifs du projet et aux attentes du milieu.

3.1 Description des solutions possibles

L'étude d'impact doit présenter les solutions de restauration possibles en incluant leurs caractéristiques sur les plans technique, économique, et environnemental.

Lorsque l'on intervient dans un but de restauration, la mise en place d'une solution de type permanente doit être favorisée par rapport à une solution de type temporaire.

L'élaboration des solutions doit prendre en considération tous les usages actuels, prévus et probables du milieu aquatique et riverain. L'initiateur du projet doit préciser si la restauration sera totale ou partielle pour chacun de ces usages et justifier le choix effectué.

L'élaboration des solutions doit prendre en considération tous les secteurs ou la contamination des sédiments est supérieure au seuil d'effets néfastes soit le niveau 3 décrit dans le document intitulé *Critères intérimaires pour l'évaluation de la qualité des sédiments du Saint-Laurent*.

3.2 Choix de la meilleure solution

La sélection du secteur d'intervention doit s'effectuer au terme d'un exercice d'évaluation et de comparaison effectué à l'aide de critères explicites. Cette analyse doit être présentée dans l'étude d'impact. Le lecteur doit comprendre en quoi la solution sélectionnée est la plus pertinente, la plus souhaitable ou la plus acceptable selon l'initiateur du projet. Le processus décisionnel proposé par l'initiateur du projet devra respecter le processus décisionnel général exposé dans le document *Critères intérimaires...*

4. CONCEPTION DES VARIANTES DE RÉALISATION

Cette section de l'étude d'impact comprend l'identification des variantes de réalisation possibles, la sélection à priori des variantes les plus pertinentes au contexte observé, puis la description des caractéristiques techniques de chacune des variantes sélectionnées.

4.1 Identification des variantes possibles

L'initiateur doit identifier dans l'étude d'impact toutes les variantes possibles et raisonnables du projet. Dans le cas du présent projet les variantes doivent être conçues selon des techniques reconnues de restauration des sédiments.

Pour l'identification des variantes possibles, il importe de tenir compte de l'information recueillie dans les chapitres précédents ainsi que des critères suivants :

- chaque variante possède a priori une faisabilité technique et permet la réalisation du projet à des coûts jugés abordables par l'initiateur;
- chaque variante permet de répondre aux objectifs du projet et aux attentes du milieu;
- chaque variante permet de limiter a priori l'ampleur des impacts néfastes pendant la construction et à long terme en plus de maximiser les retombées positives.

4.2 Sélection des variantes réalisables

L'initiateur doit effectuer une sélection parmi les variantes possibles, en comparant leurs caractéristiques sur les plans technique, économique et environnemental et en insistant sur les avantages et inconvénients de chacune d'elles. Toutes les variantes doivent être présentées, c'est-à-dire les variantes dites permanentes et les variantes dites temporaires. À l'aide de critères explicites, l'étude doit, finalement, démontrer en quoi les variantes sélectionnées sont aptes à être considérées dans l'étude pour les fins de l'analyse détaillée des impacts prévue à la section suivante.

Pour qu'une variante soit écartée à ce stade de l'étude, il doit être évident qu'elle est inacceptable pour des motifs techniques, socio-économiques, ou à cause de l'ampleur de certains impacts environnementaux qui lui sont associés.

Il se peut que le présent exercice aboutisse au choix d'une seule variante réalisable sur laquelle portera l'analyse détaillée des impacts. L'étude expliquera alors en quoi celle-ci se distingue nettement des autres variantes envisagées et en quoi celles écartées ne sont pas aptes à être retenues pour l'analyse détaillée.

4.3 Description des variantes sélectionnées

Une fois les variantes sélectionnées, l'étude d'impact doit présenter les caractéristiques de chacune d'elles, en insistant sur celles qui s'avèrent distinctives. Il importe de décrire les caractéristiques susceptibles d'intervenir dans le processus d'analyse des impacts et dans le choix subséquent de la

variante préférable. Cela comprend les activités, les aménagements et travaux prévus à chacune des phases de réalisation, ainsi que les technologies et les équipements utilisés, de même que les intrants et les extrants prévus.

Les caractéristiques à décrire doivent être adaptées à chaque variante sélectionnée. Dans le cas de la variante proposée dans l'avis de projet, les caractéristiques à décrire peuvent être énumérées de la façon suivante :

- la localisation précise du site d'intervention (MRC, municipalité, lots, rangs);
- le régime de propriété des lots requis (droits de propriétés ou d'usages ou démarches réalisées pour les acquérir)[2];
- le plan d'ensemble à une échelle appropriée;
- les différentes composantes des structures qui seront construites;
- les activités de mobilisation;
- la séquence des procédures de construction incluant l'utilisation des équipements (méthode de mise en place des jetées provisoires, du rideau étanche, du géotextile et des matériaux de recouvrement, utilisation de machinerie lourde, d'embarcations etc.);
- les matériaux utilisés, leur volume et leur provenance;
- les modes de collecte et de transport des matériaux (type de véhicules, fréquence, horaires, etc.) et les modes d'entreposage;
- l'excavation et la mise en dépôt hors site des sols contaminés nécessaires pour l'ancrage du géotextile (cendres de pyrite non considérées lors de la restauration de la partie terrestre de l'île situées entre les palplanches d'acier des cellules de confinement et la rive);
- les rejets (effluents, émissions, déchets) et les nuisances (bruit, poussières);
- les profondeurs d'eau après le recouvrement ainsi que les profils de pente des nouvelles zones riveraines;
- la remise en état du site en milieu terrestre;
- la restauration d'un habitat favorable à la vie aquatique;
- le calendrier de réalisation incluant l'entretien et le suivi;
- l'efficacité et la fiabilité des structures de recouvrement;
- l'efficacité et la fiabilité des moyens de restauration d'un habitat favorable à la vie aquatique;
- la durée de vie des installations et les solutions envisagées au terme de cette durée de vie;
- la responsabilité de l'initiateur du projet par rapport aux installations pendant et après la durée de vie prévue;
- les phases futures de développement, s'il y a lieu;
- les coûts estimatifs du projet incluant les coûts d'entretien et de suivi.

---

2 Si les lots requis pour le projet relèvent du domaine hydrique public, l'initiateur du projet doit obtenir la légalisation de leur occupation auprès du Service de la gestion du domaine hydrique public du ministère de l'Environnement et de la Faune. Cette légalisation est requise en vertu du Règlement sur le domaine hydrique public (R.R.Q., c. R-13, r. 2) découlant de la Loi sur le régime des eaux (L.R.Q., c. R-13).

5. ANALYSE DES IMPACTS

5.1 Identification et évaluation des impacts

L'identification et l'évaluation des impacts constitue le coeur même de l'étude d'impact. Cette étape doit permettre de comprendre comment l'environnement et les ressources seront modifiées par le projet et comment ces modifications toucheront l'utilisation du territoire par les populations concernées.

L'identification des impacts consiste à déterminer la nature, l'intensité, l'étendue, la durée et la fréquence des changements causés aux éléments importants de l'environnement. Diverses techniques et méthodes sont disponibles pour l'identification des impacts (tableaux synoptiques ou matrices, listes de vérification, cartes superposées, etc.). Celles utilisées doivent être objectives, concrètes et reproductibles. Le lecteur doit pouvoir suivre facilement le raisonnement de l'initiateur pour identifier et mesurer les impacts. La méthodologie retenue et les échelles utilisées, de même que les incertitudes ou les biais qui s'y rattachent, doivent être expliqués.

Après avoir identifié et mesuré les impacts, l'étude doit présenter l'évaluation de l'importance de ces impacts. Alors que la mesure des impacts est plutôt factuelle, leur évaluation peut faire référence aux valeurs des citoyens concernés à l'égard des ressources affectées et des impacts appréhendés. Elle peut donc comporter un jugement de valeur. Le raisonnement et les critères utilisés pour effectuer cette évaluation doivent être expliqués.

Certains impacts devront faire l'objet d'une attention particulière, par exemple, et de façon non limitative:

- l'impact de la remise en suspension des cendres de pyrites, entres autres, sur les prises d'eaux et sur les chaînes de traitement de l'eau aux usines de filtration avoisinantes;
- la circulation routière, le bruit, la poussière et la sécurité des résidents affectés durant les travaux;
- les impacts de la présence des ouvrages sur les accès au plan d'eau ainsi que sur les usages du plan d'eau et de la rive;
- les impacts sur la circulation et la sécurité des bateaux pendant et après la construction.

5.2 Mesures d'atténuation

L'initiateur doit présenter les mesures d'atténuation prévues pour réduire certains impacts sur l'environnement. Il doit préciser les actions, les ouvrages, les correctifs ou les ajouts de même que les mesures de prévention, de contrôle ou sécurité à mettre en place aux différentes phases de réalisation des variantes retenues. L'efficacité des mesures d'atténuation retenues doit être prouvée. Ces mesures devront être inscrites ultérieurement dans les plans et devis de construction.

L'étude doit aussi présenter et évaluer les impacts résiduels des variantes retenues après l'intégration des mesures d'atténuation.

5.3 Choix de la variante préférable

En utilisant les informations contenues dans les chapitres précédents, l'initiateur doit présenter un bilan comparatif des variantes retenues en indiquant le degré de discrimination réelle des variantes, c'est-à-dire la netteté avec laquelle chacune se distingue des autres.

L'initiateur doit, par la suite, choisir la variante optimale de réalisation soit celle qui répond le mieux aux objectifs et qui s'insère le plus harmonieusement dans l'environnement biophysique et socio-économique. L'étude présentera le raisonnement et les critères justifiant ce choix.

5.4 Synthèse du projet

L'étude doit faire la synthèse du projet proposé en spécifiant notamment ses modalités de réalisation, les mesures d'atténuation proposées ainsi que la nature et l'importance des impacts résiduels après l'application des mesures d'atténuation. Cette description sommaire vise à préciser les éléments importants à inclure aux plans et devis.

5.5 Mesures de compensation et de mise en valeur

L'étude d'impact doit présenter les démarches réalisées par l'initiateur du projet dans le but d'évaluer et de sélectionner des mesures de compensation pour certains impacts résiduels difficiles à évaluer ou à atténuer. Afin de rendre le projet plus souhaitable ou plus attrayant d'un point de vue environnemental global, des mesures de mise en valeur pourront également être proposées.

6. PROGRAMME DE SURVEILLANCE ET DE SUIVI

L'étude d'impact doit exposer les modalités de conception et de réalisation des programmes de surveillance et de suivi du projet. Elle doit préciser sous quelle forme et selon quel calendrier les résultats de ces programmes parviendront au ministère de l'Environnement et de la Faune et identifier les personnes responsables.

6.1 Surveillance

L'initiateur du projet doit décrire le programme de surveillance qu'il entend mettre de l'avant pendant la construction pour s'assurer du respect des mesures proposées dans l'étude d'impact et dans les plans et devis, et du respect des autorisations obtenues (décret, certificat d'autorisation), des normes, lois et

règlements applicables. L'initiateur doit aussi indiquer toutes les conditions particulières auxquelles il entend souscrire afin de protéger adéquatement les milieux humain et naturel tout en répondant aux objectifs qui sont à l'origine de son projet. Ces conditions pourront être de nature technique, opérationnelle, administrative, économique ou autre.

6.2 Suivi

L'initiateur du projet doit élaborer un programme de suivi destiné à observer et à mesurer, sur une période de temps déterminée, la nature et l'envergure de certains impacts, tant positifs que négatifs du projet, notamment ceux qui dans l'étude présentent un niveau de risque ou d'incertitude. Les objectifs et les méthodologies proposés doivent être clairement exposés de même que la période de temps durant laquelle s'effectuera ce suivi.

Un tel programme devra comprendre, sans s'y limiter :

- les modalités de suivi et d'entretien des structures de recouvrement de façon à observer leur comportement en relation avec les processus naturels d'érosion et de sédimentation et à corriger s'il y a lieu certains points faibles;
- le suivi de l'évolution de la qualité de l'eau en période d'agitation par les vagues;
- le suivi de l'efficacité des aménagements effectués dans le but de restaurer la vie aquatique.

CONSIDÉRATIONS MÉTHODOLOGIQUES

La directive expose les éléments qui doivent constituer l'étude d'impact. La présentation de ces éléments suit une séquence linéaire; toutefois, l'initiateur du projet est libre d'en modifier l'ordre de présentation dans l'étude d'impact. Il peut aussi arriver que les résultats de l'étude d'un aspect puissent avoir une influence sur un ou plusieurs autres et en ce sens, la réalisation de l'étude peut impliquer un processus itératif. En conséquence, l'initiateur du projet doit donc s'assurer que tous les renseignements pertinents sur les relations entre les éléments traités sont clairement présentés dans l'étude d'impact et qu'ils sont intégrés à l'étape de l'évaluation finale afin de tenir compte des découvertes et des changements survenus en cours de route.

L'étude d'impact doit être présentée d'une façon claire et concise; elle doit se limiter aux éléments pertinents à la bonne compréhension du projet. Ce qui peut être schématisé ou cartographié doit l'être et ce, à des échelles adéquates. Les méthodes utilisées doivent être présentées et explicitées. En ce qui a trait aux inventaires, on doit retrouver les éléments permettant d'apprécier la qualité de ces derniers, dont la localisation des stations, les dates d'inventaire, les techniques et les méthodes utilisées incluant leur fiabilité et leurs limites

d'interprétation. Toutes les sources de renseignements doivent être données en référence. Le nom, la profession et la fonction des personnes responsables de la réalisation de l'étude doivent être indiqués.

Considérant que l'étude d'impact doit être mise à la disposition du public pour information, l'initiateur du projet doit fournir un résumé vulgarisé des éléments essentiels et des conclusions de l'étude ainsi que tout autre document qu'il juge nécessaire pour compléter l'examen du dossier. Ce résumé, publié séparément, doit inclure un plan général du projet et un schéma illustrant les impacts, les mesures d'atténuation et les impacts résiduels.

Lors du dépôt officiel de l'étude d'impact au ministre, l'initiateur du projet doit fournir trente (30) copies du dossier complet et une copie sur disquette en format « WordPerfect IBM PC sur DOS » version 5.1 ou supérieure. Il est suggéré qu'au cours de la préparation de l'étude, l'initiateur du projet demeure en contact régulier avec le ministère de l'Environnement et de la Faune. Il est également conseillé de déposer, en version préliminaire, des copies de l'étude d'impact et une copie informatique, pour consultation interministérielle avant son dépôt officiel.

Pour fins de clarté dans l'identification des différents documents qui sont soumis et pour faciliter leur archivage dans les banques informatisées, la page titre de l'étude doit contenir les informations suivantes: le nom du projet avec le lieu de réalisation, le titre du dossier incluant les termes « étude d'impact sur l'environnement soumise au ministre de l'Environnement et de la Faune », le sous-titre du document (ex. : résumé, rapport principal, annexe 1), la mention « Version préliminaire » ou « Version finale », le nom de l'initiateur du projet le nom du consultant s'il y a lieu, et la date.

ANNEXE C

AQ/CQ du laboratoire pour le résultats chimiques
des échantillons de sédiments - 1996

ZÉNON
LABORATOIRES

QA/QC REPORT

CHEMICAL ANALYSES FOR THE

CLARK ISLAND ENVIRONMENTAL STUDY, 1996

Prepared for :

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Judit Vass, M.Sc., Chemist

MARCH 1997

ZENON LABORATOIRES

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Project Manager and QA/QC Scientist :	Judit Vass, M.Sc., Chemist
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Secretaries :	Sylvie Lefebvre Manon Paulin

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1.0 INTRODUCTION

As part of an environmental impact study in the Clark Island area conducted by Tecsult Inc., Zenon Laboratories received 65 sediment and 30 water samples.

The major objective of Zenon Laboratories is to produce high quality data. In order to produce such data, it is essential to maintain extensive quality control procedures throughout the project, to ensure the traceability of measurements and to use validated methods which are referenced to known organizations.

2.0 DATA TRACKING

Zenon uses a VAX based LIMS system for data and task management. This is a secure system which tracks a sample's movement step by step throughout the laboratory form receipt to report.

Lab manager is the operational software used by the LIMS to function as a complete laboratory manager and provide all of the functions required to handle analytical data and perform manipulations on a daily basis.

3.0 SAMPLE MANAGEMENT

3.1 BOTTLE REQUESTS

After confirmation by Tecsult Inc. (see **APPENDIX A**) for bottle requests, new containers were sent to Tecsult Inc. These containers were either cleaned by Zenon laboratories or purchased as precleaned containers. The description of the containers used are detailed in **TABLE 1**.

TABLE 1. SAMPLE CONTAINERS

PARAMETERS	VOLUME (mL)	CONTAINER	PRESERVATIVE
Metals, Solids (Total and Volatile)	500 mL	Plastic, cleaned by Zenon	none
PAHs, PCBs, Total Organic Carbon and Ammonia	500 mL	Glass amber, precleaned certified	none
Total Sulfides	125 mL	Glass, cleaned by Zenon	2N Zinc Acetate
Sieve and Hydrometer Analysis		Plastic bag (provided by Tecsult Inc.)	none

To ensure that no contamination results from washing the containers or from the sample preservative (sulfides only), a container was analyzed for metals and sulfides after each batch of cleaning. The results of this proofing is presented in **APPENDIX B**.

3.2 SAMPLE RECEIVING

Upon receipt of samples, the sample reception staff checked that all containers received were in good condition. The chain of custody form was signed off by Tecsult Inc. and the sample receptionist (date, time and signature). A copy of the chain of custody was given to Tecsult Inc. and the other copies were kept with the samples.

Sample reception staff checked to make sure that the number of sample bottles, dates and sample ID's agree with the chain of custody. The samples were then entered into the LIMS with the following information :

- Client ID
- Sample matrix
- Zenon lab number (unique number)
- Zenon certificate number (unique number per batch of samples received)
- Date of sampling
- Date of sample reception
- Tests required
- Project ID
- Initials of Zenon's project manager
- Number of containers received and container type
- Special considerations

Samples were than labeled with unique numbers assigned by the LIMS and sent to the lab or to the refrigerated storage area. All paperwork was given to the project manager who checked the samples logged sheets against chain of custody/submission forms foanr y inconsistencies. The project manager than sent the analysis confirmation to Tecsult Inc. Copies of the chain of custody forms and the confirmation sheets are included in **APPENDIX C**. A summary of the samples received is given in **TABLE 2**.

3.3 SUBCONTRACTING

Samples for the following analyses were subcontracted : Major Elements by XRS [(1)], Sulfur [(1)], Sieve and Hydrometer analysis [(2)] and Total organic carbon [(3)]. Once the samples were registered into the LIMS, they were shipped to the subcontractors listed below via the courier Swiftsure (to Centre de Recherches Minérales and to Fondatec) or MemoPresto (to Barringer Laboratories). Copies of the chain of custody forms are included in **APPENDIX D.**

Subcontractor :
[(1)] Centre de Recherches Minérales, 2700 Einstein, Ste-Foy, Québec.
[(2)] Fondatec, 883 Bériault, Longueuil, Québec.
[(3)] Barringer Laboratories, a Division of Philip Analytical Services, 5735 McAdam Road, Mississauga, Ontario

TABLE 2. Summary of samples received at Zenon Laboratories for the Clark Island Project, 1996.

Date received	Number of samples received	Matrix	Zenon certificate number	Corresponding Zenon Sample Numbers
96/09/23	5	Sediments	6I0304	015705-015709
96/09/25	4	Sediments	6I0322	016133-016136
96/10/03	30	Water	6J0047	018011-018040
96/10/09	4	Sediments	6J0146	018562-018565
96/10/11	13	Sediments	6J0214	019100-019112
96/10/15	12	Sediments	6J0215	019113-019124
96/10/15	4	Filters	6J0268	019886-019889
96/10/17	10	Sediments	6J0246	019443-019452
96/10/18	17	Sediments	6J0272	019894-019910

4.0 ANALYTICAL PROCEDURES

The references of the methods used for the Clark Island project are given in **TABLE 3**. These methods were used throughout the whole project.

TABLE 3. ANALYTICAL METHODS

Parameters	Methods (*)
Ammonia	EPA 350.3
Arsenic (by hydride generation)	EPA 3050B and SM 3114C
Major Elements by XRS	CRM, 89-PR-05
Metals by ICP : Aluminum, Arsenic, Cadmium, Chromium, Copper, Iron, Lead, Nickel and Zinc	EPA 3050B and EPA 6010B
Sieve and Hydrometer analysis	BNQ 2560-040 and BNQ 2501-025
PAHs	EPA 8270
PCBs	MENVIQ 95.05/408 BPC 2.0 and Centre St-Laurent, section 13
Percent moisture	EPA 160.3
Sulfur	LECO Instruments
Total organic carbon	LECO Instruments
Total solids	EPA 160.3
Total sulfides	EPA 376.2
Total volatile solids	Standard Methods, 2540E

(*) Definition of Methods:

EPA : methods published by the United States Environmental Protection Agency.
MENVIQ : methods published by the Ministry of Environment of Quebec.
Standard Methods: Standard Methods for the Examination of Water and Wastewater, 19th edition.
Centre St Laurent : Guide méthodologique de caractérisation des sédiments, Environnement Canada, Centre Saint Laurent en collaboration avec le Ministere de l'Envrionnement du Québec, Avril 1992.
BNQ : Bureau du Normalisation de Québec.
CRM : Centre de recherche Minérale.

5.0 LABORATORY DATA MANAGEMENT

5.1 ORIGINAL TEST DATA

All original test data including QC data were recorded in a permanent form (i.e. note book, work sheet, instrument print out or magnetic media) at the time observations were made.

5.2 DATA REPORTING

All data, including QC data, was entered into the LIMS manually by the analyst. The following information was entered at the same time :

- date of extraction (digestion) and extractors initials
- date of instrumental analysis and analysts initials
- test comments (special test related information)

Results were checked by analysts and validated by senior analysts or lab managers. Validation sheets were printed by test parameter and signed off after acceptance by the analyst and the validator. The initialed data validation sheets were filed in the laboratory.

After validation of the data , the report (certificate of analysis) was generated by the LIMS. The project manager performed a final review of the the results and the report was signed by the lab manager and the project manager and sent to Tecsult Inc.

6.0 QUALITY CONTROL

Control samples were analyzed in order to demonstrate that each analytical system was in statistical control for in-lab contamination, bias, recovery and in-run precision. These controls included : method blanks, duplicates, reference materials, matrix spikes and surrogates (if applicable). The results are presented in the data package summary presented in **APPENDIX E**.

6.1 METHOD BLANKS AND PROOFING

Method blanks (all reagents used in the processing of samples and the same quantities) were processed along with and in the same manner as the samples. They were analyzed to assess possible laboratory contamination at all stages of sample preparation and analysis. A minimum of one method blank was analyzed for every extraction batch or for approximately every 10 samples. A method blank is considered free of contamination if the analysis yields results less than the method detection limit for inorganic parameters or generally less than 3 times the method detection limit for organic parameters. All method blanks, except 2 blanks for iron, were free from contamination (see **APPENDIX E**). The two iron blanks contained however only 4 mg Fe/kg (see certificate 6J0215) and 1 mg Fe/kg (see certificate 6J0246) which are insignificant when compared to the sample results (> 7000 mg Fe/kg).

Prior to the start of this project, glassware was proofed and restricted for use on this project. The proofing results are presented in **APPENDIX F.** Positive results (0.02 and 0.03 mg/kg) were obtained for the compound Acenaphtene ; these values are however only 2-3 times the method detection limit and are considered acceptable. The results indicate no contamination for all other compounds. When applicable, each sample was analyzed using a numbered set of glassware to ensure data traceability to previous sample contents. No proofing was done for metals, since disposable plasticware was used for digestions and analyses.

6.2 REFERENCE MATERIALS

Reference materials were either bought or prepared by spiking Ottawa sand or sodium sulfate (for organic analysis) with a standard purchased from a separate source from the calibration standards. The analysis of a reference standard is a check on the accuracy of the calibration standards and gives an indication of the accuracy of a method without the effects that a more complex matrix may introduce.

Reference materials were analyzed for every extraction batch. The percent recoveries of the reference materials, which are acceptable, are presented in **APPENDIX E** and in **TABLE 4**.

TABLE 4. SUMMARY OF % RECOVERIES FOR REFERENCE MATERIALS

Parameter	Average Recovery (%)	Standard Deviation	Minimum Value	Maximum Value	N
SiO2	96.5	9.2	90	103	2
Al2O3	101.0	2.8	99	103	2
Fe2O3 (total)	96.0	0.0	96	96	2
MgO	122.5	27.6	103	142	2
CaO	99.0	1.4	98	100	2
Na20	88.0	11.3	80	96	2
K2O	120.0	32.5	97	143	2
TiO2	100.5	10.6	93	108	2
MnO	90.0	14.1	80	100	2
P2O5	100.5	10.6	93	108	2
Sulfur	103.5	2.1	102	105	2
Ammonia (as N)	93.7	9.6	85	104	3
Sulphides	101.3	2.9	98	107	7
Total organic carbon	95.0	1.2	93	96	5
Metals					
Aluminium	100.6	1.3	99	102	5
Arsenic	106.4	2.7	102	109	5
Cadmium	98.2	1.1	97	100	5
Chromium	96.4	0.9	95	97	5
Copper	97.2	1.8	94	98	5
Iron	101.6	2.2	98	103	5
Lead	98.6	0.9	98	100	5
Nickel	96.4	0.9	96	98	5
Zinc	99.0	0.7	98	100	5
Total PCBs	85.8	14.3	64	100	5
PAHs					
Naphthalene	59.1	19.0	29	81	7
Acenaphthylene	83.1	8.7	70	95	7
Acenaphthene	84.7	8.6	71	94	7
Fluorene	88.9	5.0	83	93	7
Phenanthrene	96.6	11.5	85	110	7
Anthracene	75.1	4.0	71	81	7
Fluoranthene	85.7	3.3	80	89	7
Pyrene	87.9	3.3	82	92	7
Chrysene	85.9	5.5	77	91	7
Benzo(a)anthracene	102.1	9.3	93	118	7
Benzo (b+k+j) fluoranthene	88.1	7.2	74	95	7
Benzo (a) pyrene	87.3	9.6	72	100	7
Indeno (1,2,3-cd) pyrene	93.7	9.1	79	108	7
Dibenzo(ah)anthracene	95.7	9.1	82	107	7
Benzo (g,h,i) perylene	90.9	9.4	74	102	7
1,2-Benzanthracene-7,12-dimethyl	38.9	19.4	16	75	7
3-Methylcholanthrene	95.7	11.2	84	117	7
Dibenzo(a,h)pyrene	89.6	12.9	70	107	7
Dibenzo(a,i)pyrene	105.7	12.3	92	123	7
Dibenzo(a,l)pyrene	94.4	9.9	85	115	7
Benzo(c)phenanthrene	91.1	4.4	84	97	7

6.3 DUPLICATES

A laboratory duplicate or replicate is a sample, duplicated in the laboratory from a separate aliquot of sample, that is processed through all steps of the analytical procedure. The results of analysis of laboratory duplicate samples give an indication of precision of the data obtained for the matrix analyzed. One duplicate was analyzed for approximately every ten samples and the summary of the percent relative difference for the duplicates for the various parameters is given in **TABLE 5**. The precision of the data is acceptable since the percent relative difference is less than 25% for inorganic parameters and less than 40% for organic parameters (except for a few compounds close to the method detection limit).

TABLE 5. SUMMARY OF % RSDs FOR DUPLICATES

Parameter	Average %RSD	Standard Deviation	Minimum Value	Maximum Value	N
Moisture	0	0	0	0	2
Sulphides	6.7	5.9	0	14	4
Total organic carbon	2.4	2.3	0	5.6	4
Total solids (wet basis)	3.6	3.7	0	8.5	4
Total volatile solids	0.4	0.7	0	1.4	4
Metals					
Ammonia (as N)	5.7	6.7	0	13	4
Aluminium	1.1	1.3	0	2.7	6
Arsenic (ICP)	1.2	1.0	0	1.9	3
Arsenic (Hydride generation)	0.8	1.3	0	2.3	3
Cadmium	1.5	2.4	0	5.7	6
Chromium	1.8	2.5	0	6.5	6
Copper	0.7	1.1	0	2.4	6
Iron	0.4	1.1	0	2.6	6
Nickel	2.2	2.1	0	5.4	6
Lead	4.6	8.5	0	21(*)	6
Zinc	2.3	1.5	0	4.1	5
Total PCBs	0	0	0	0	5
PAHs					
Naphthalene	0	0	0	0	5
Acenaphthylene	0	0	0	0	5
Acenaphthene	0	0	0	0	5
Fluorene	0	0	0	0	5
Phenanthrene	12.8	23.0	0	53(*)	5
Anthracene	0	0.0	0	0	5
Fluoranthene	8.8	9.6	0	22(*)	5
Pyrene	6	9.2	0	21	5
Benz(a)anthracene	3.4	7.6	0	17	5
Chrysene	5.8	7.9	0	15(*)	5
Benzo(b,k,j)fluoranthene	6.8	10.0	0	22	5
Benzo(a)pyrene	9.6	17.3	0	40(*)	5
Indeno(1,2,3-cd)pyrene	0	0	0	0	5
Dibenzo(ah)anthracene	0	0	0	0	5
Benzo(ghi)perylene	0	0	0	0	5
1,2-Benzanthracene-7,12-Dimethly	0	0	0	0	5
3-Methlycholanthrene	0	0	0	0	5
Dibenzo(a,h)pyrene	0	0	0	0	5
Dibenzo(a,i)pyrene	0	0	0	0	5
Dibenzo(a,l)pyrene	0	0	0	0	5
Benzo(c)phenanthrene	0	0	0	0	5
Elements by XRS					
SiO2	0.8	1.4	0	2.5	3
Al2O3	0.4	0.5	0	0.9	3
Fe2O3 (total)	0.5	0.6	0	1.2	3
MgO	1.1	1.9	0	3.3	3
CaO	7.3	11.0	0	20	3
Na20	2.4	4.1	0	7.1	3
K2O	0.5	0.9	0	1.5	3
TiO2	2.5	2.5	0.9	5.3	3
MnO	0.0	0.0	0	0	3
P2O5	0.1	0.2	0	0.4	3
Sulfur	0.3	0.5	0	0.7	2
Loss on ignition (1150 deg C)	0.0	0.0	0	0	2

(*) value close to detection limit

6.4 MATRIX SPIKES

A matrix spike was a separate aliquot of a randomly chosen sample which has had some or all of the analytes of interest added prior to sample preparation and analysis. The analysis of matrix spikes gave an indication of the recovery efficiency obtained for the particular matrix being analyzed and was also a measure of the applicability of the method for that particular matrix. A spiked sample was analyzed at a frequency of approximately one in every ten samples. The percent recoveries for the various parameters are acceptable and are summarized in **TABLE 6**.

TABLE 6. SUMMARY OF MATRIX SPIKE RECOVERIES

Parameter	Average Recovery (%)	Standard Deviation	Minimum Value	Maximum Value	N
Ammonia (as N)	79.3	7.5	90	74	4
Sulphides	88	7.6	84	99	4
Metals					
Aluminium	109.0	10.5	94	120.0	6
Arsenic (ICP)	83.3	12.1	72	96.0	3
Arsenic (Hydride generation)	100.3	9.5	91	110.0	3
Cadmium	88.0	6.7	80	96.0	6
Chromium	78.8	10.1	66	93.0	6
Copper	92.2	8.0	78	99.0	6
Iron	117.5	13.3	95	130.0	6
Nickel	72.2	11.4	60	120.0	6
Lead	75.0	12.2	60	90.0	6
Zinc	80.5	13.2	65	97.0	4
Total PCBs	72.0	6.9	64	83	5
PAHs					
Naphthalene	63	10.6	49	73	5
Acenaphthylene	75	9.3	64	87	5
Acenaphthene	77.4	10.0	67	91	5
Fluorene	84.2	8.0	74	95	5
Phenanthrene	92.4	12.4	81	112	5
Anthracene	77.6	3.6	73	82	5
Fluoranthene	83.6	6.2	74	89	5
Pyrene	85.8	9.9	73	97	5
Chrysene	77.6	14.4	66	99	5
Benz(a)anthracene	94	9.8	84	110	5
Benzo(b,k,j)fluoranthene	77.6	12.9	60	89	5
Benzo(a)pyrene	73.2	12.7	55	88	5
Indeno(1,2,3-cd)pyrene	82.2	13.8	61	95	5
Dibenzo(ah)anthracene	80.8	16.1	56	95	5
Benzo(ghi)perylene	81.4	14.0	61	99	5
1,2-Benzanthracene-7,12-Dimethly	45.6	13.2	36	66	5
3-Methlycholanthrene	65.2	19.9	36	91	5
Dibenzo(a,h)pyrene	59.6	19.7	37	75	5
Dibenzo(a,i)pyrene	80.4	27.4	35	104	5
Dibenzo(a,l)pyrene	81.2	16.5	54	91	5
Benzo(c)phenanthrene	81.8	5.4	77	91	5

6.5 SURROGATES

A surrogate standard is a compound, not expected to be found in a sample and which behaves similarly to the analytes of interest during sample preparation and analysis. Surrogate standards were added to all samples and quality control samples for PAH and PCB analysis before sample preparation and analysis. The surrogate standard recovery upon analysis gives a measure of the accuracy of the method for that particular sample.

The summary of the surrogate recoveries is presented in **TABLE 7**. Surrogate recoveries for PCBs and PAHs indicate acceptable accuracy for all samples. Recoveries for Perylene-d12 were slightly low, although acceptable, for some of the samples (29% to 35%).This was possibly due to the high sulfur content of the samples.

TABLE 7. SUMMARY OF SURROGATE RECOVERIES

Surrogate	Average Recovery (%)	Standard Deviation	Minimum Value	Maximum Value	N
Pentachlorobiphenyle	78.4	10.2	60	99	62
Trichlorobiphenyle	75.4	10.0	52	103	62
Naphthalene-d8	70.4	9.3	55	101	62
Acenaphthene-d10	75.9	8.8	57	105	62
Phenanthrene-d10	79.6	8.7	60	105	62
Chrysene-d12	72.9	12.4	52	110	62
Perylene-d12	64.0	15.8	29	94	62

6.6 INSTRUMENT CALIBRATION

6.6.1 Inorganic Analysis

Initial calibration was achieved for sulfides, ammonia, arsenic and metals (by ICP) with the number of standards indicated in **TABLE 8**. All calibration data was acceptable since R was greater than 0.995 for all standard curves. The calibration data is presented in **APPENDIX G.**

TABLE 8. NUMBER OF CALIBRATION STANDARDS USED FOR INORGANIC PARAMETERS

PARAMETER	NUMBER OF STANDARDS FOR INITAL CALIBRATION	NUMBER OF STANDARDS FOR 2nd and 3rd CALIBRATIONS (IF APPLICABLE)
SULFIDE	7 (including a blank)	7 (including a blank)
AMMONIA	6	6
ARSENIC (HYD. GENERATION)	4 (including a blank)	1 (control check)
METALS (ICP)	3 to 4 (including a blank)	1 (control check)

6.6.2 Organic Analysis

PCB Analysis

Initial calibration for PCB (Arochlor) analysis was achieved with 4 concentration levels for each Arochlor at a frequency of every 4 to 8 weeks. Daily calibration checks were performed with one concentration level. The summary for the calibration data is presented in **APPENDIX G**. All calibration data is considered valid since the relative percent standard deviation for each multiple calibration and the percentage difference for the daily calibration standard are less than 20%.

PAH Analysis

Initial calibration for PAH analysis was achieved daily with 5 concentration levels for each compound. A calibration check was performed at the end of the run or every twelve hours, whichever was more frequent. The summary for the calibration data is presented in **APPENDIX G**. All initial calibration data is considered valid since the relative percent standard deviation for each multiple calibration is less than 20%. The percentage difference for the calibration checks deviated by less than 30% (acceptance level) for at least 90% of analytes in a single calibration check except in one case. In this batch (Zenon numbers 19110-19116) 7 compounds (the heavier PAHs) exceed the usual acceptance level. This is possibly due to the high sulfides content of some of the samples.

ANNEXE D

Tableau-synthèse des relevés pour la végétation riveraine

Summary Table of Data for Riparian Vegetation of Clark Island

Plant Community Types	Marsh			Wet Meadows																Riparian Herbaceous Communities											
	Cattail Type			Aquatic Sedge Type						Pectinate Spartina Type			Common Reed-Grass Type	Snakeroot, Goldenrod and Bleu-joint Type						Touch-me-not and Loosestrif							Willow Type	Dogwood and Willow Type		Dogwood and Willow Type	
Cartographic Segment	1A	2A	22A	9A	18B	20B	1B	3B	36B	68B	48A	45B	27A	7B	8B	4B	42B	37B	35B	34B	9A	13A	24A	25A	26A	31A	42A	41A	4	8A	9B	13B
Species																																
TREES																																
Fraxinus pennsylvanica																			1	1												
Salix nigra	1																															
Ulmus americana																				1							1	1				
Acer saccharinum																			1											1		
Acer negundo																											1					
Betula populifolia															D														1			
Tilia americana									1																							
Acer rubrum																																
Populus tremuloides																																
Prunus serotina																																
YOUNG TREES																																
Betula populifolia	1																							1								
Fraxinus pennsylvanica										1						1																
Populus balsamifera																								1								
SHRUBS																																
Cornus stolonifera										1				1	1					1	1					1		D		D	D	D
Rubus idaeus										1				1	1			1									1	1				
Prunus virginiana																																
Sambucus pubens															1	1		1									1					
Rhus typhina																											1					
Salix sp.																										1	1		D			
Crataegus sp.																																
Spiraea tomentosa	1	1						1							1																	
Salix bebbiana															1														1	1		
Salix discolor																															1	SD
Sambucus canadensis								1																					1			
Salix petiolaris																														1		

Summary Table of Data for Riparian Vegetation of Clark Island

Plant Community Types	Marsh			Wet Meadows																		Riparian Herbaceous Communities											
	Cattail Type			Aquatic Sedge Type						Pectinate Spartina Type			Common Reed-Grass Type	Snakeroot, Goldenrod and Bleu-joint Type								Touch-me-not and Loosestrif								Willow Type	Dogwood and Willow Type		Dogwood and Willow Type
Cartographic Segment	1A	2A	22A	9A	18B	20B	1B	3B	36B	68B	48A	45B	27A	7B	8B	4B	42B	37B	35B	34B	9A	13A	24A	25A	26A	31A	42A	41A	4	8A	9B	13B
Viburnum lentago																																
Amelanchier arborea																																
Cornus alternifolia																																
Myrica gale																								1								
Rubus odoratus																																
Salix interior																															1	
Salix myricoides																													1			
HERBACEOUS SPECIES																																
Impatiens capensis	1	1		D	SD	1							1			1			1		1	D	D	D	D		D	1	D	1		
Eupatorium rugosum									SD				1	1	SD	D	SD	SD	D	D	1						1	1	1			1
Lythrum salicaria	1	1	1	1				SD		1			1	1							1	SD	1	SD	SD	D	1	1	SD	1		
Calamagrostis canadensis								SD		D	1		1					D	SD	D				1		1	1		1			
Equisetum arvense				1				1					1	SD	SD	SD	D		SD	SD							SD	1	1			
Convolvulus sepium													1								1			1		SD			1			
Verbena hastata		1						1					1			1											1	1	1	1		
Echinocystis lobata																			1				1	1					1			1
Onoclea sensibilis		1						1							1															D		
Solidago rugosa								1						D	D	SD	1			D											1	
Carex aquatilis				SD	D	D	D	D	D																							
Cuscuta gronovii						1																	1	SD	SD							
Iris versicolor				1				1																						1		
Linaria vulgaris										1	1		1		1		1							1						1		
Solanum dulcamara																								1					1			1
Xanthium strumarium																							SD	1	1				1			
Bidens frondosa		1														SD											1	1				
Phragmites communis													D										1	1								
Steironema ciliatum																			1													
Teucrium occidentale													1																			
Solidago canadensis													1								1											1
Parthenocissus quinquefolius										1																						1

Summary Table of Data for Riparian Vegetation of Clark Island

Plant Community Types	Marsh			Wet Meadows																		Riparian Herbaceous Communities											
	Cattail Type			Aquatic Sedge Type						Pectinate Spartina Type			Common Reed-Grass Type	Snakeroot, Goldenrod and Bleu-joint Type								Touch-me-not and Loosestrif								Willow Type	Dogwood and Willow Type		Dogwood and Willow Type
Cartographic Segment	1A	2A	22A	9A	18B	20B	1B	3B	36B	68B	48A	45B	27A	7B	8B	4B	42B	37B	35B	34B	9A	13A	24A	25A	26A	31A	42A	41A	4	8A	9B	13B
Polygonum lapathifolium																							1	1								
Scirpus cyperinus	SD		1					1							1																	
Vitis riparia																																1
Achillea millefolium													1								1									1		
Asclepias syriaca										1					1		1															
Circaea lutetiana														1																		
Cirsium vulgare				1						1					1																	
Lycopus americanus																													1	1		
Poa palustris													1								1									1		
Poa pratensis															SD						1									1		
Polygonum punctatum				1				1																								
Spartina pectinata										SD	D	D																				
Typha angustifolia	D	D					1																									
Typha latifolia			D																			1										
Urtica dioica ssp gracilis																													1			
Agrostis alba															1																	
Agrostis stolonifera																								1								
Apios americana																													1			
Arctium minus										1																						1
Butomus umbellatus																																
Carex projecta															1															1		
Chelone glabra																														1		
Dryopteris spinulosa															1																	
Epilobium hirsutum				1										1																		
Epilobium leptophyllum	1							1																								
Festuca rubra										1																						
Geum aleppicum																		1														
Mentha canadensis																								1								
Muhlenbergia mexicana																													1	1		
Oenothera biennis				1																	1											
Rumex sp				1				1																								

Summary Table of Data for Riparian Vegetation of Clark Island

Plant Community Types	Marsh			Wet Meadows																Riparian Herbaceous Communities											
	Cattail Type			Aquatic Sedge Type						Pectinate Spartina Type			Common Reed-Grass Type	Snakeroot, Goldenrod and Bleu-joint Type						Touch-me-not and Loosestrif								Willow Type	Dogwood and Willow Type		Dogwood and Willow Type
Cartographic Segment	1A	2A	22A	9A	18B	20B	1B	3B	36B	68B	48A	45B	27A	7B	8B	4B	42B	37B	35B	34B	9A	13A	24A	25A	26A	31A	42A	41A	4	8A	9B	13B
Scirpus fluviatilis																													1			
Scutellaria lateriflora																								1								
Triadenum virginicum	1	1																														
Viola sp																																
Agrostis scabra												1																				
Alisma plantago-aquatica			1																													
Aster umbellatus				1																												
Athyrium filix-femina																														1		
Boehmeria cylindrica																																
Brassica kaber																							1									
Campanula aparinoides		1																														
Carex rosea																																
Dennstaedtia punctilobula																																
Dryopteris cristata																																
Eleocharis smallii							1																									
Eupatorium maculatum																								1								
Fragaria virginiana																																
Glechoma hederacea																																
Juncus tenuis															1																	
Leersia oryzoides				1																												
Lycopus uniflorus																													1			
Rhus radicans																																
Sagittaria latifolia			1																													
Scirpus lacustris			1																													
Scutellaria epilobiifolia																														1		
Sedum purpureum																																
Solidago altissima														SD																		
Solidago graminiifolia																								1								
Sonchus arvensis																																
Stachys palustris																																
Thalictrum pubescens																																

Summary Table of Data for Riparian Vegetation of Clark Island

Plant Community Types	Marsh			Wet Meadows																	Riparian Herbaceous Communities											
	Cattail Type			Aquatic Sedge Type						Pectinate Spartina Type			Common Reed-Grass Type	Snakeroot, Goldenrod and Bleu-joint Type							Touch-me-not and Loosestrif								Willow Type	Dogwood and Willow Type	Dogwood and Willow Type	
Cartographic Segment	1A	2A	22A	9A	18B	20B	1B	3B	36B	68B	48A	45B	27A	7B	8B	4B	42B	37B	35B	34B	9A	13A	24A	25A	26A	31A	42A	41A	4	8A	9B	13B
Thelypteris palustris	1																															
Tussilago farfara																								1								
Vicia cracca																					1											
Viola nephrophylla																																

Summary Table of Data for Riparian Vegetation of Clark Island

Plant Community Types	Shrub Communities															Forest Communities													
		Red-Osier Dogwood Type							Staghorn Sumach and Dogwood Type		Choke Cherry Type				Rasberry Type	Ash, Sedge, Touch-me-not and Loosestrife Type					Ash and Ulm Type	Ash and Snakeroot Type		Black Willow & Snakeroot T			Silver Maple Type		Gray Birch Type	
Cartographic Segment	50A	7C	28A	29A	3A	68C	46A	44A	7A	58A	49A	47A	45A	37A	61A	18A	20A	21A	4A	43A	34A	4C	33A	68A	57A	39A	23A	16A	15A	
Species																														**total**
TREES																														
Fraxinus pennsylvanica		1					SD	1		1	1	1				SD	D	SD	SD	SD	D	D	D	1					1	**18**
Salix nigra	1				1					1									1					D	D	1	SD	1	1	**12**
Ulmus americana		1					1					1								1	SD					D				**9**
Acer saccharinum			1													1	1										SD	D	1	**8**
Acer negundo			1																								1			**3**
Betula populifolia																1													D	**4**
Tilia americana										1													1							**3**
Acer rubrum																									SD					**1**
Populus tremuloides																							1							**1**
Prunus serotina																									1					**1**
YOUNG TREES																														
Betula populifolia												1																		**3**
Fraxinus pennsylvanica						1																								**3**
Populus balsamifera																														**1**
SHRUBS																														
Cornus stolonifera	SD	D	D	D	D	D	D	SD	D	1		1		1	1			1	1		1			1			1		1	**29**
Rubus idaeus		1						1		1					D								1	1	1					**13**
Prunus virginiana										1	1	D	D	D												1				**6**
Sambucus pubens													1												1					**6**
Rhus typhina		1							SD	D		1																		**5**
Salix sp.	D												1																	**5**
Crataegus sp.								1		1	1		1																	**4**
Spiraea tomentosa																														**4**
Salix bebbiana																														**3**
Salix discolor																											1			**3**
Sambucus canadensis																		1												**3**
Salix petiolaris									1																					**2**

Summary Table of Data for Riparian Vegetation of Clark Island

Plant Community Types	Shrub Communities															Forest Communities														
				Red-Osier Dogwood Type					Staghorn Sumach and Dogwood Type		Choke Cherry Type				Rasberry Type			Ash, Sedge, Touch-me-not and Loosestrife Type					Ash and Ulm Type	Ash and Snakeroot Type		Black Willow & Snakeroot T			Silver Maple Type		Gray Birch Type	
Cartographic Segment	50A	7C	28A	29A	3A	68C	46A	44A	7A	58A	49A	47A	45A	37A	61A	18A	20A	21A	4A	43A	34A	4C	33A	68A	57A	39A	23A	16A	15A	
Viburnum lentago										1	1																			**2**
Amelanchier arborea										1																				**1**
Cornus alternifolia		1																												**1**
Myrica gale																														**1**
Rubus odoratus															1															**1**
Salix interior																														**1**
Salix myricoides																														**1**
HERBACEOUS SPECIES																														
Impatiens capensis	1				1			1				SD		1		D	1	D	D	SD				1	SD	1	D		1	**32**
Eupatorium rugosum	1			1			1	1	1	D		D		1	1				SD	1	1	SD	D	SD	D	D			1	**32**
Lythrum salicaria				1	1							1				SD	1	1	1	1				1	1		1		1	**30**
Calamagrostis canadensis										1		1		1			1	1						1	SD	SD		1	D	**21**
Equisetum arvense		1	1					1	1			1													1	1				**19**
Convolvulus sepium				1				1				1		1		1	1		1						1	1	1			**15**
Verbena hastata								1				1						1	1					1						**13**
Echinocystis lobata														1		1		1							1				1	**10**
Onoclea sensibilis				1					1									1	1								1		1	**10**
Solidago rugosa										1													1	1						**10**
Carex aquatilis																		1		D							1			**9**
Cuscuta gronovii														1			1	1												**7**
Iris versicolor																			1					1			1		1	**7**
Linaria vulgaris																														**7**
Solanum dulcamara				1								1							1					1						**7**
Xanthium strumarium																1		1									1			**7**
Bidens frondosa							1					1																		**6**
Phragmites communis				SD												1													SD	**6**
Steironema ciliatum								1		1														1	1	1				**6**
Teucrium occidentale												1				1								1	1		1			**6**
Solidago canadensis																1		1												**5**
Parthenocissus quinquefoliu															1									1						**4**

Summary Table of Data for Riparian Vegetation of Clark Island

Plant Community Types	Shrub Communities															Forest Communities														
		Red-Osier Dogwood Type							Staghorn Sumach and Dogwood Type		Choke Cherry Type				Rasberry Type	Ash, Sedge, Touch-me-not and Loosestrife Type					Ash and Ulm Type	Ash and Snakeroot Type		Black Willow & Snakeroot T			Silver Maple Type		Gray Birch Type	
Cartographic Segment	50A	7C	28A	29A	3A	68C	46A	44A	7A	58A	49A	47A	45A	37A	61A	18A	20A	21A	4A	43A	34A	4C	33A	68A	57A	39A	23A	16A	15A	
Polygonum lapathifolium																1		1												4
Scirpus cyperinus																														4
Vitis riparia	1														1			1												4
Achillea millefolium																														3
Asclepias syriaca																														3
Circaea lutetiana																									1	1				3
Cirsium vulgare																														3
Lycopus americanus																								1						3
Poa palustris																														3
Poa pratensis																														3
Polygonum punctatum																1														3
Spartina pectinata																														3
Typha angustifolia																														3
Typha latifolia																1														3
Urtica dioica ssp gracilis																								1		1				3
Agrostis alba																		1												2
Agrostis stolonifera																													1	2
Apios americana	1																													2
Arctium minus																														2
Butomus umbellatus																											1		1	2
Carex projecta																														2
Chelone glabra																			1											2
Dryopteris spinulosa																									1					2
Epilobium hirsutum																														2
Epilobium leptophyllum																														2
Festuca rubra																			1											2
Geum aleppicum										1																				2
Mentha canadensis																											1			2
Muhlenbergia mexicana																														2
Oenothera biennis																														2
Rumex sp																														2

Summary Table of Data for Riparian Vegetation of Clark Island

Plant Community Types	Shrub Communities															Forest Communities														
		Red-Osier Dogwood Type							Staghorn Sumach and Dogwood Type		Choke Cherry Type				Rasberry Type	Ash, Sedge, Touch-me-not and Loosestrife Type					Ash and Ulm Type	Ash and Snakeroot Type		Black Willow & Snakeroot T			Silver Maple Type			Gray Birch Type	
Cartographic Segment	50A	7C	28A	29A	3A	68C	46A	44A	7A	58A	49A	47A	45A	37A	61A	18A	20A	21A	4A	43A	34A	4C	33A	68A	57A	39A	23A	16A	15A	
Scirpus fluviatilis																											1			2
Scutellaria lateriflora																	1													2
Triadenum virginicum																														2
Viola sp										1														1						2
Agrostis scabra																														1
Alisma plantago-aquatica																														1
Aster umbellatus																														1
Athyrium filix-femina																														1
Boehmeria cylindrica																										1				1
Brassica kaber																														1
Campanula aparinoides																														1
Carex rosea										1																				1
Dennstaedtia punctilobula																			1											1
Dryopteris cristata					1																									1
Eleocharis smallii																														1
Eupatorium maculatum																														1
Fragaria virginiana										1																				1
Glechoma hederacea																								1						1
Juncus tenuis																														1
Leersia oryzoides																														1
Lycopus uniflorus																														1
Rhus radicans								D																						1
Sagittaria latifolia																														1
Scirpus lacustris																														1
Scutellaria epilobiifolia																														1
Sedum purpureum																								1						1
Solidago altissima																														1
Solidago graminiifolia																														1
Sonchus arvensis																											1			1
Stachys palustris																	1													1
Thalictrum pubescens																											1			1

Summary Table of Data for Riparian Vegetation of Clark Island

Plant Community Types	Shrub Communities														Forest Communities													
		Red-Osier Dogwood Type							Staghorn Sumach and Dogwood Type		Choke Cherry Type				Rasberry Type	Ash, Sedge, Touch-me-not and Loosestrife Type					Ash and Ulm Type	Ash and Snakeroot Type		Black Willow & Snakeroot T			Silver Maple Type		Gray Birch Type	
Cartographic Segment	50A	7C	28A	29A	3A	68C	46A	44A	7A	58A	49A	47A	45A	37A	61A	18A	20A	21A	4A	43A	34A	4C	33A	68A	57A	39A	23A	16A	15A	
Thelypteris palustris																														1
Tussilago farfara																														1
Vicia cracca																														1
Viola nephrophylla																								1						1

ANNEXE E

Tableau-synthèse des relevés
pour la végétation aquatique peu profonde

Summary Table of Da r Shallow Aquatic Vegetation

	Emergent Vegetation (Marsh)																				
Cartographic section	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
Substratum[1]	Si	R	R	Si	R	R, S	R, S	R	R	R	Py	Py	Py	i, P	Si, C	Si, C	SSi, R	R	R	R	
Density[2]	4	0	0	4	0	0	3	0	0	0	1	2	3	3	4	3	4	0	0	0	
Species																					**Sub-total**
Alisma gramineum	1																				1
Carex canescens													1		1						2
Ceratophyllum demersum																					0
Chara																					0
Eleocharis smallii														CD	1						2
Elodea canadensis														1			1				2
Elodea americana																					0
Equisetum fluviatile														CD							1
Heteranthera dubia																					0
Lemna minor	1						1														2
Lemna trisulca	1																				1
Myriophyllum sibiricum														1							1
Najas flexilis														1			1				2
Nymphaea odorata	1													CD							2
Phragmites communis											1										1
Potamogeton bupleuroides																					0
Potamogeton gramineus																					0
Potamogeton illinoensis														1							1
Potamogeton natans																					0
Potamogeton pusillum																					0
Potamogeton sp																					0
Sagittaria cuneata														1							1
Sagittaria graminea															1	1	1				3
Sagittaria latifolia														1	1						2
Sagittaria rigida							1														1
Scirpus validus							D					CD	CD	CD	1		CD				6
Sparganium eurycarpum	D															CD	CD				3
Typha angustifolia											D	CD		1	D	CD					5
Typha latifolia													CD			CD	1				3
Vallisneria americana												1		1			1				3

(1) R= Rock; S= Sand; Si= Silt; C= Clay; Py= Pyrite cinders

(2) Density classes spread from 1 (very low density) to 5 (very high density and maximal covering of substratum). Zero marks the absence of vegetation.
D= Dominant species; CD= codominant species; SD= Sub-dominant species

Summary Table of Data for Shallow Aquatic Vegetation

	Floating or Reaching Surface Vegetation																				
Cartographic section	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
Substratum[1]	Si	Si, R	R	-	R, S, Si	R, S, Si	R	R	R	R	Py	Py	Si, Py	Si, Py	Si,	Si,	S, Si, R	R	S, R	R	
Density[2]	4	3	2	-	2	1-2	1-2	0-1	1	1	1	2	2	3	3-4	4	4	0	3	0	
Species																					**Sub-total**
Alisma gramineum			CD		D	SD	1	D	D	1	CD				CD	1	CD				11
Carex canescens																					0
Ceratophyllum demersum	1					1					1	1		1	1	1	1		1		9
Chara		CD													CD	CD	CD		CD		5
Eleocharis smallii																					0
Elodea canadensis	1														1	1	1		1		5
Elodea americana									1												1
Equisetum fluviatile																					0
Heteranthera dubia							CD								1						2
Lemna minor																					0
Lemna trisulca																					0
Myriophyllum sibiricum	1		1		1	1	1									1	1		1		8
Najas flexilis																					0
Nymphaea odorata							CD								CD		CD				3
Phragmites communis																					0
Potamogeton bupleuroides																1					1
Potamogeton gramineus					1																1
Potamogeton illinoensis		1												1		1					3
Potamogeton natans																					0
Potamogeton pusillum			1								1										2
Potamogeton sp																					0
Sagittaria cuneata																					0
Sagittaria graminea																					0
Sagittaria latifolia																					0
Sagittaria rigida																					0
Scirpus validus																					0
Sparganium eurycarpum																					0
Typha angustifolia																					0
Typha latifolia																					0
Vallisneria americana	CD	1	CD		1	D	1	1	1	D	CD	D	D	D	CD	CD	CD		CD		17

(1) R= Rock; S= Sand; Si= Silt; C= Clay; Py= Pyrite cinders

(2) Density classes spread from 1 (very low density) to 5 (very high density and maximal covering of substratum). Zero marks the absence of vegetation.
D= Dominant species; CD= codominant species; SD= Sub-dominant species

Summary Table of Da[illegible]r Shallow Aquatic Vegetation

	Submerged Vegetation																				
Cartographic section	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
Substratum[1]	Si	-	R	S, R	R, S, S	R, S	R	S, R	S, R	R, S	Py	Py	Si, Py	Si	Si, C	-	S, Si,	S, R	S, R	S, R	
Density[2]	4	3	3	2	3	1-2	1-2	1-2	2	3	3	3	3	3-4	3-4	4	4	3	3	3	
Species																					**Sub-total**	**Total**
Alisma gramineum		1	1	CD	CD	1	1	1	1						CD	1	1				11	23
Carex canescens																					0	2
Ceratophyllum demersum		1			CD	CD	1	1	1				SD	1	1	1	1		1	1	13	22
Chara	CD		SD	CD						CD	CD			CD	CD	CD	CD	CD	CD	CD	12	17
Eleocharis smallii																					0	2
Elodea canadensis	1	CD				CD									1	1	1		1	1	8	15
Elodea americana																					0	1
Equisetum fluviatile																					0	1
Heteranthera dubia	CD					CD	CD	CD	CD						1					1	6	8
Lemna minor																					0	2
Lemna trisulca						1															1	2
Myriophyllum sibiricum		1			1	1															3	12
Najas flexilis																					0	2
Nymphaea odorata																					0	5
Phragmites communis																					0	1
Potamogeton bupleuroides					1	1				1			1	1							5	6
Potamogeton gramineus																1	1		1	1	4	5
Potamogeton illinoensis																					0	4
Potamogeton natans																1	1				2	2
Potamogeton pusillum					1							1	1						1		4	6
Potamogeton sp										1											1	1
Sagittaria cuneata																					0	1
Sagittaria graminea																					0	3
Sagittaria latifolia																					0	2
Sagittaria rigida																					0	1
Scirpus validus																					0	6
Sparganium eurycarpum																					0	3
Typha angustifolia																					0	5
Typha latifolia																					0	3
Vallisneria americana	1	CD	D	CD	CD	CD	CD	CD	CD	CD	CD	D	D	CD	CD	CD	CD	CD	CD	CD	20	40

[1] R= Rock; S= Sand; Si= Silt; C= Clay; Py= Pyrite cinders

[2] Density classes spread from 1 (very low density) to 5 (very high density and maximal covering of substratum). Zero marks the absence of vegetation.
D= Dominant species; CD= codominant species; SD= Sub-dominant species

ANNEXE F

Tableau-synthèse des relevés pour les transects d'échantillonnage des herbiers profonds

APPENDIX F

List of Species Sampled in the Northeast Bay (Zone B)

Transects E1 to E13

	E1		E2		E3 PPP		E4		E5		E6		E7		E8		E9		E10		E11		E12 01		E13 north		Number of Stations
	sa.	vi.	sa.	vi.	sa.	vi.	sa.	vi.	sa.	vi.	sa.	vi.	sa.	vi.	sa.	vi.	sa.	vi.	sa.	vi.	sa.	vi.	sa.	vi.	sa.	vi.	
Valisneria americana		√		√	+	√		√		√	+	√		√	+	√	+	√	+	√	+	√	+	√	+	√	13
Ceratophyllum demersum											+	√	+	√	+		+	√	+	√		√	+	√	+	√	8
Elodea canadensis		√			+					√	+	√	+	√	+			√	+	√	+	√	+				10
Myriophyllum exalbescens		√			+	√		√		√	+	√		√		√		√	+	√		√				√	11
Heteranthera dubia		√		√		√		√		√		√		√		√		√		√					+		11
Potamogeton pectinatus					+												+										2
Potamogeton bupleuroides															+		+		+						+		4
Potamogeton illinaensis					+								+		+		+		+								5
Potamogeton zosteriformis													+														1
Potamogeton gramineus																	+		+								2
Potamogeton spp.		√				√		√		√		√		√		√		√		√		√		√		√	12
Zannichellia palustris					+	√		√		√		√	+	√										√			6
Chara													+		+		+		+								4

Legend:
sa.: sample of vegetation taken using a weighted rake
vi.: vegetation observed using an underwater camera

APPENDIX F

List of Species Sampled West of the Northeast Bay (Zone C and Fluvial Section)

Transects N1 to N10

	N1		N2		N3		N4		N5		N6		N7		N8		N9		N10		Number of Stations
	sa.	vi.	sa.	vi.	sa.	vi.	sa.	vi.	sa.	vi.	sa.	vi.	sa.	vi.	sa.	vi.	sa.	vi.	sa.	vi.	
Valisneria americana		√	+	√		√		√		√		√		√		√		√		√	10
Ceratophyllum demersum		√	+	√	+	√	+	√		√		√			+	√				√	8
Elodea canadensis						√	+	√						√		√					4
Myriophyllum exalbescens		√	+	√		√	+	√		√	+	√	+	√	+	√		√		√	10
Heteranthera dubia			+	√		√	+	√		√	+	√		√		√		√	+	√	9
Alisma gramineum							+			√						√		√	+		5
Potamogeton pectinatus									+												1
Potamogeton bupleuroides			+				+						+								3
Potamogeton illinoensis			+										+								2
Potamogeton zosteriformis			+				+								+						3
Potamogeton gramineus							+														1
Potamogeton spp.		√		√				√		√		√		√		√		√		√	9
Lemma trisulca					+																1

Legend:
sa.: sample of vegetation taken using a weighted rake
vi.: vegetation observed using an underwater camera

APPENDIX F

List of Species Sampled in the Fluvial Section West of Île-aux-Chats

Transects W1 to W14

	W1	W2	W3	W4	W5	W6	W7	W8	W9	W10	W11	W12	W13	W14	Number of Stations
	vi.	vi.	vi.	vi.	vi.	vi.	vi.	vi.	vi.	vi.	vi.	vi.	vi.	vi.	
Valisneria americana				√	√	√	√	√	√	√	√		√	√	10
Ceratophyllum demersum	√	√	√	√	√	√	√	√	√	√	√			√	12
Elodea canadensis			√												1
Myriophyllum exalbescens				√	√	√	√	√	√	√					7
Heteranthera dubia				√		√	√	√	√	√	√	√	√	√	10
Potamogeton spp.	√	√		√	√	√	√	√	√	√	√	√	√	√	13
Alisma gramineum						√	√	√		√					4

Legend:
vi.: vegetation observed using an underwater camera

ANNEXE G

Rapport d'Environnement Illimité Inc.

APPENDIX G.1

Caractérisation biologique (décembre 1996)

environnement illimité inc.
consultants en écologie et environnement

RESTAURATION DES SÉDIMENTS

AUTOUR DE L'ÎLE AUX CHATS

Caractérisation biologique

Rapport présenté à

Tecsult inc.

Décembre 1996

1453, Saint-Timothée, Montréal, Québec, H2L 3N7 Tél. : (514) 849-7281 Fax : (514) 849-6770

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Annexe 2 Données brutes des pêches réalisées autour de l'Île aux Chats au début de l'automne 1996

1.0 INTRODUCTION

Dans le cadre du projet de restauration des sédiments contaminés autour de l'Île aux Chats (lac Saint-François), le promoteur Allied Signal, a confié la réalisation de l'étude d'impact à la firme Tecsult inc. Environnement Illimité inc. a été mandaté par cette dernière pour réaliser le volet ichtyologique de l'étude ainsi qu'un échantillonnage complémentaire d'organismes aquatiques (tels que poissons, moules et plantes) pour les analyses écotoxicologiques.

Le présent document traite spécifiquement des activités relatives à l'étude de la faune ichtyenne. On y présente une description des objectifs et de la méthodologie, suivi des principaux résultats. Tout d'abord, une caractérisation des habitats aquatiques riverains a été réalisée à partir de paramètres physiques et biologiques. Cette caractérisation visait l'identification de stations homogènes afin d'établir une stratégie d'échantillonnage de la faune ichtyenne adaptée au milieu. L'échantillonnage des poissons a été réalisé à l'aide de plusieurs techniques de pêche afin d'établir un portrait représentatif de l'utilisation automnale du milieu. Finalement, une analyse des données est réalisée de façon à permettre une appréciation de la valeur des habitats pour la faune ichtyenne dans les différents secteurs de la zone d'étude.

2.0 OBJECTIFS

Le but principal des travaux est de réaliser une description de la faune ichtyenne de la zone d'étude et de son habitat. Cette information servira d'intrant à une évaluation des impacts sur l'environnement des travaux de restauration des sédiments autour de l'Île aux Chats. Les objectifs détaillés de l'étude sont les suivants :

- Réaliser une description de la végétation aquatique riveraine autour de l'Île aux Chats ;
- Réaliser des mesures d'oxygène dissous ;
- Réaliser l'inventaire de la faune ichtyenne à l'aide d'une pêche électrique, d'une seine de rivage et de filets maillants à une cinquantaine de stations autour de l'Île aux Chats ;
- Évaluer l'abondance et la diversité de la faune ichtyenne de la zone d'étude ;
- Évaluer le potentiel de la zone d'étude comme habitat pour la faune ichtyenne.

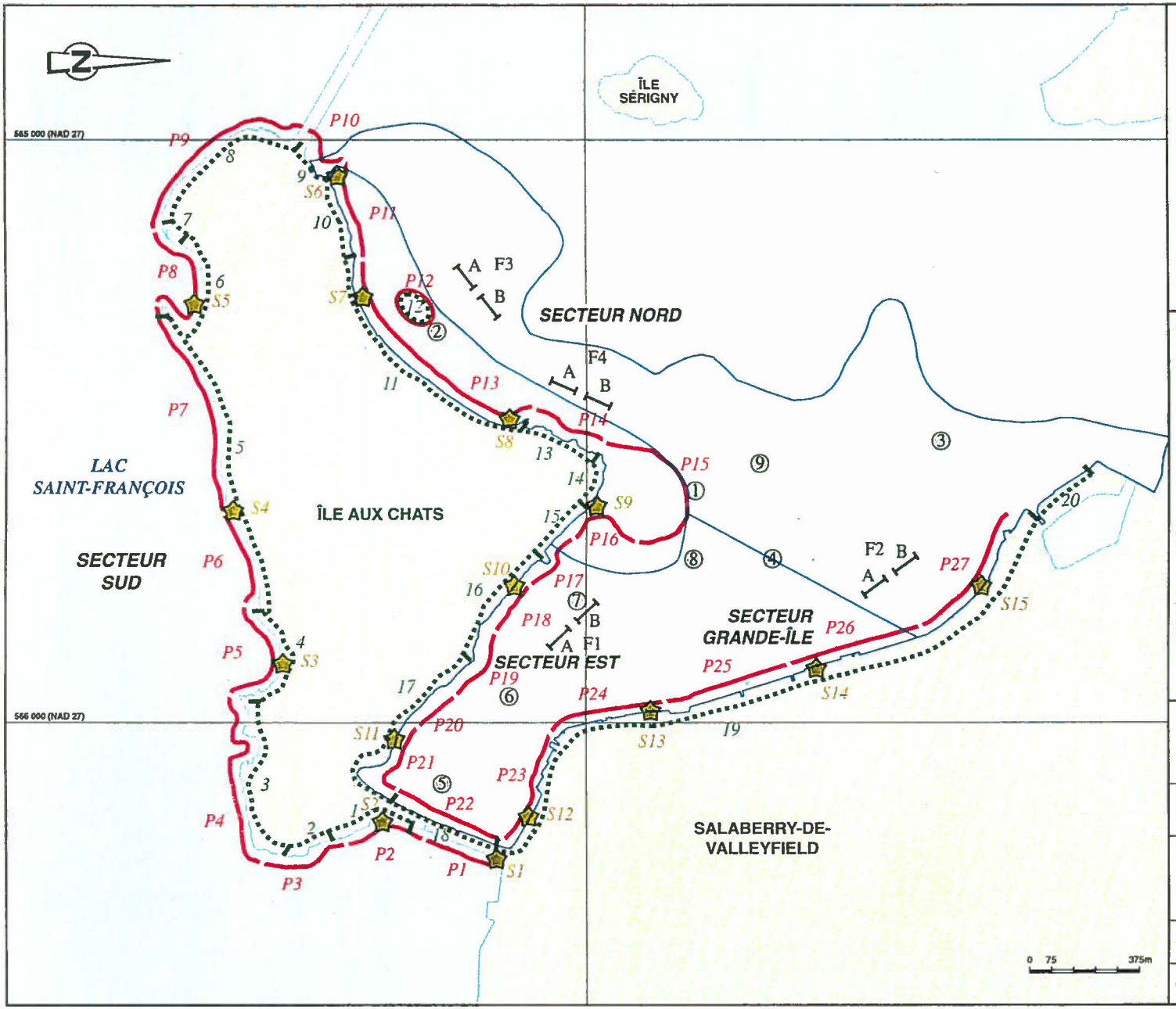
3.0 MATÉRIEL ET MÉTHODES

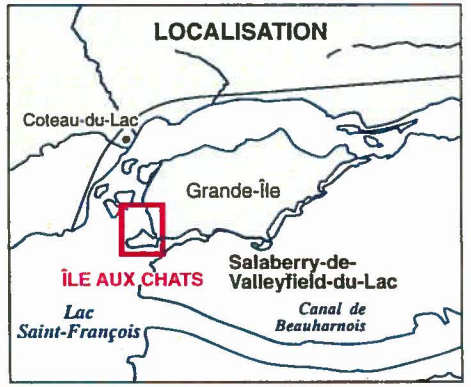
Les travaux d'inventaires comportaient deux principaux volets : la caractérisation de l'habitat, en fonction de la végétation aquatique riveraine et de certains paramètres physico-chimiques et l'échantillonnage de la faune ichtyenne. La méthodologie et les équipements utilisés sont décrits dans les lignes qui suivent.

3.1 Caractérisation des herbiers aquatiques riverains

La caractérisation des habitats aquatiques a principalement été réalisée lors d'un inventaire de la végétation riveraine réalisé en embarcation motorisée, le 23 août 1996. Ces travaux ont fait l'objet d'un rapport d'inventaire dont les principaux éléments sont repris dans le présent document. Cette information a été complétée par des observations ponctuelles obtenues lors des échantillonnages en plongée sub-aquatique pour la récolte de plantes et d'autres organismes nécessaires au volet écotoxicologique.

Les rives de l'Île aux Chats ont été subdivisées en 20 sections dont la délimitation est présentée à la fin de l'annexe 1. Les critères retenus pour segmenter le pourtour de l'île sont : la configuration de la rive (baie, pointe, jetée), le type de substrat, l'exposition aux vents et aux vagues et la présence d'herbiers aquatiques. Dans chacune des sections, la toposéquence des espèces végétales a été caractérisée en fonction de trois zones. La première zone se caractérise par la présence d'espèces ; la deuxième, par l'absence d'espèces émergentes et la présence d'espèces à feuilles flottantes ou d'espèces dont au moins une partie de la plante atteint la surface de l'eau ; la troisième zone se compose essentiellement de taxons entièrement submergés. Les deux dernières zones ont généralement plusieurs espèces communes et la délimitation correspond davantage à un changement bathymétrique plutôt qu'à une modification de la composition du substrat.





1 Végétation aquatique

P1 Pêche électrique

S1 Seine de rivage

A F1 B Filet maillant

① Mesure d'oxygène dissous

Allied Signal
ENGINEERED MATERIALS

SITE DE L'ÎLE AUX CHATS PROJET DE RESTAURATION DES SÉDIMENTS / CLARK ISLAND SITE SEDIMENT REHABILITATION PROJECT

CARACTÉRISATION BIOLOGIQUE

LOCALISATION DES STATIONS D'ÉCHANTILLONNAGE

DATE: DÉC. 1996 PROJET/PROJECT: 5804

TECSULT FIGURE: 1

environnement illimité inc.

Dans chacune des zones, les espèces présentes ont été identifiées sur le terrain ou récoltées dans des sacs de plastique pour une identification ultérieure à notre laboratoire de Montréal. Au total, 35 échantillons ont été conservés pour confirmer l'identification des spécimens. Celle-ci a été réalisée à l'aide d'une loupe binoculaire et basée sur les clés d'identification de la Flore Laurentienne (Rouleau, 1964) et du Gray's Manual of Botany (Fernald, 1950). Sur le terrain, la densité des herbiers fut évaluée en fonction d'une échelle de 0 à 5. Une valeur de zéro (0) signifiant qu'aucune plante n'a été observée alors qu'un herbier dont la valeur est de un (1) a une très faible densité, un indice de densité de cinq (5) correspond à une formation végétale dont le recouvrement du substrat est maximal.

Les données telles que le type de substrat et la profondeur de l'eau des sites d'échantillonnage ont également été notées. L'ensemble des données biotiques et abiotiques ont été enregistrées sur les fiches de terrains présentées à l'annexe 1.

Mesure d'oxygène dissous

Des mesures d'oxygènes dissous ont été réalisées à 9 stations réparties dans les zones III et IV (figure 1). Ces données ont été prises à l'aide d'un oxymètre de marque YSI muni d'une sonde de 10 m.

3.2 Échantillonnage de la faune ichtyenne

Les travaux d'inventaire de la faune ichtyenne ont été réalisés entre le 26 septembre et le 4 octobre 1996. Selon les habitudes connues des espèces présentes, à cette période il n'existe aucun rassemblement de fraie, ce qui favorise la capture de spécimens résidant dans le milieu.

Trois techniques de pêche ont été utilisées soit la pêche électrique, la seine de rivage et le filet maillant expérimental. La méthodologie relative à ces travaux est décrite ci-après.

Pêche électrique

L'ensemble du pourtour de l'Île aux Chats ainsi qu'une portion de la rive ouest de Grande d'Île ont été échantillonnés à l'aide d'une pêche électrique à haut voltage (modèle : *Electrofisher type V*) montée sur une embarcation d'aluminium de 5,5 m de longueur. Le système est muni de deux anodes circulaires (0,5 m de diamètre) installées à l'avant de l'embarcation, tandis que la cathode est directement branchée sur la coque du bateau. L'équipe est composée d'un conducteur et de deux pêcheurs installés de chaque côté de l'embarcation de façon à capturer simultanément les poissons à l'aide d'épuisettes (diamètre de mailles : 1 cm). Le système peut générer jusqu'à 7 ampères, mais généralement une intensité de deux ampères était suffisante pour attirer et immobiliser les poissons sans les blesser. Les poissons capturés étaient déposés dans un bac rempli d'eau pour être identifiés, mesurés et remis à l'eau. La zone d'étude a été divisée en 27 sections de rive de longueur variant généralement entre 90 m et 260 m. Les résultats de pêche ont été ajustés pour une longueur de 200 m. Les résultats de pêche ont été regroupés en fonction de cinq secteurs, soit les secteurs sud, I, II, III et IV (figure 1). Ce dernier, comportant essentiellement des zones plus profondes (3 m et plus), n'a été échantillonné qu'au filet maillant expérimental.

Seine de rivage

La zone d'étude a également été échantillonnée à l'aide d'une seine de rivage de 12 m de longueur par 2 m de hauteur, munie d'une poche de 2 x 2 x 2 m et constituée de maille de 1 mm de diamètre. Notons qu'une seine similaire a été utilisée par le MEF pour échantillonner l'ensemble du lac Saint-François au cour de l'automne 1996.

À chacune des stations, deux coups de seine ont été donnés, espacés d'environ 25 m, de façon à permettre une évaluation de la variabilité des résultats. La seine était étirée perpendiculairement à la rive sur toute sa longueur jusqu'à une profondeur d'environ 1,25 m, puis ramenée vers le bord en suivant un arc de cercle. Une fois la seine fermée, une troisième personne ramenait la ralingue de fond de façon à emprisonner les poissons dans la poche centrale. Certaines caractéristiques des stations étaient notées, soit la profondeur maximale, la distance de la rive, le type de substrat ainsi que la végétation dominante.

Quinze stations ont été réparties dans les même secteurs cités précédemment, soit 5 dans le secteur sud, 4 dans le secteur Nord, 2 dans le secteur Est et 4 dans le secteur Grande Île. Tous les poissons ont été identifiés, dénombrés et mesurés. Notons que les spécimens de petites tailles ont été dénombrés en fonction de classes de longueur.

Filet maillant expérimental

Des filets maillants expérimentaux ont été utilisés pour échantillonner les zones plus profondes des secteurs III et IV. Ces filets possèdent une dimension de 46 m de longueur par 1,8 m de hauteur et sont composés de huit panneaux dont la taille des mailles varie de 2,54 à 15,25 mm. Quatre stations dont la profondeur variait entre 4 et 7 m, ont été échantillonnées à l'aide de deux filets attachés bout-à-bout par une corde de 20 m. Notons que cette méthode a été utilisée par le MEF pour échantillonner l'ensemble du lac Saint-François au cours de l'automne 1996. L'effort de pêche a été exprimé en nombre de poissons/filet-nuit.

3.3 Assurance et contrôle de qualité

Échantillonnage

Un protocole de terrain détaillé a été élaboré avec le responsable de terrain, spécifiant l'entretien, la calibration et l'utilisation adéquate des engins de pêche, les données qui devraient être notées et la façon de les obtenir. Tous les appareils de mesure et d'échantillonnage ont été vérifiés et pré-calibrés avant les travaux. Toutes les données d'inventaire ont été notées sur des formulaires conçus pour ces types de mesures. L'équipe de terrain était constituée de biologistes et de techniciens d'expérience pour ce type d'échantillonnage, l'identification et les prises de mesures sur les poissons. Les poissons capturés ont été identifiés à l'espèce selon la clef d'identification de Scott et Crossman (1974).

Traitement des données

Les données d'inventaire et d'analyse ont été saisies sur une base de données (4e Dimension) spécialement conçue pour les analyses requises dans cette étude. La saisie informatique des données a été vérifiée par une autre personne que celle qui a fait la saisie initiale pour en vérifier sa concordance avec les données originales. Des copies de sauvegarde des fichiers de données et d'analyse ont été réalisées de façon à préserver l'intégrité des données. L'ensemble des fiches de pêche et d'analyse ainsi que les rapports informatiques des différents traitements des données ont été classés pour référence éventuelle.

4.0 RÉSULTATS

Les résultats sont présentés en trois volets, soit les données relatives à la caractérisation de la végétation aquatique et des paramètres physico-chimiques mesurés, et celles provenant de l'échantillonnage de la faune ichtyenne. Par la suite, un chapitre sur l'interprétation des résultats orientés vers une évaluation du potentiel de la zone d'étude comme habitat d'alimentation, d'alevinage et de reproduction est présenté.

4.1 Caractérisation des herbiers aquatiques

Les herbiers à végétation émergeante

Dans l'ensemble du territoire étudié, la zone d'herbiers riverains occupée par la végétation émergeante est généralement très étroite. D'ailleurs, ces espèces sont absentes dans 10 sections visitées (sections 2, 3, 5, 6, 8, 9, 10, 18, 19 et 20) (tableau 1). La correspondance entre les sections de caractérisation de la végétation et les stations de pêche électrique est présentée au tableau 1. Dans les sections 14, 15, 16 et 17 qui se situent à l'est de l'Île aux Chats, les herbiers émergents sont diversifiés et occupent une plus grande surface, en particulier la section 14 constituée d'un herbier à scirpe pouvant s'étendre jusqu'à 100 m de la rive. En général, l'espèce dominante est *Typha angultifolia*. Les taxons tels que *Scirpus validus*, *Eleocharis Smallii*, *Valisneria americana* et *Sparganium eurycarpum* sont également abondants par endroit. D'autre part, au niveau des sections 1, 4, 7, 11, 12, 13, ce type d'herbier est composé de peu d'espèces et réduit à une mince bande près de la rive.

Dans le secteur Nord où l'on retrouve une accumulation de pyrite de fer, soit les sections 11, 12 et 13, les espèces dominantes sont : *Typha angustifolia* et *Scirpus validus*. Notons que la composition végétale de chacune des sections est présentée à l'annexe I.

Tableau 1 Caractéristiques de la végétation aquatique autour de l'île aux Chats, été 1996

Section	Station de pêche	Végétation émergeante			Végétation atteignant la surface			Végétation submegée		
		Substrat	espèce	densité	Substrat	espèce	densité	Substrat	espèce	densité
1	P2	Limon	Sparganium	4	Limon	Elodea et valisneria	4	Limon	Chara, heteranthra	4
2	P3	Rocheux	Nil	0	Limon et roche	Chara, valisneria	3	Limon et roche	Valisneria, Elodea	3
3	P4	Rocheux	Nil	0	Rocheux	Valisneria, alisma	2	Rocheux	Valisneria, chara	3
4	P5	Limon	Sparganium, typha	4	Nil	Nil	Nil	Sable et roche	Valisneria, chara, alisma	2
5	P6, P7	Rocheux	Nil	0	Rocheux, sable et limon	Alisma	2	Roche, sable et limon	Valisneria, ceratophyllum	3
6	P8	roche et sable	Nil	0	Roche, sable et limon	Valisneria, alisma	1-2	Roche et sable	Valisneria, ceratophyllum	1-2
7	P8	Roche, sable	Sparganium	3	Rocheux	Nymphea, heteranthera	1-2	Rocheux	Valisneria, heteranthera	1-2
8	P9	Rocheux	Nil	0	Rocheux	Alisma	0-1	Sable et roche	Valisneria, heteranthera	1-2
9	P10	Rocheux	Nil	0	Rocheux	Alisma	1	Sable et roche	Valisneria, heteranthera	2
10	P11	Rocheux	Nil	0	Rocheux	Valisneria	0-1	Roche et sable	Chara, valisneria	3
11	P13	Pyrite	Typha	1-3	Pyrite	-	0	Pyrite	Valisneria, chara	3
12	P12	Pyrite	Scirpus	2	Pyrite	Valisneria	2	Pyrite	Valisneria	3
13	P14	Pyrite	Typha, scirpus	3	Pyrite	Valisneria	2	Pyrite	Valisneria, ceratophyllum	3
14	P15	Pyrite, limon	Scirpus, Eleocharis, Equisetum	3	Silt et pyrite	Valisneria	3	Silt et pyrite	Valisneria, chara	3-4
15	P16	Limon, argile	Typha	4	Limon, argile	Valisneria, alisma, chara	3-4	Limon, argile	Valisneria, alisma, chara	3-4
16	P17, P18	Limon, argile	Typha, sparganium	3	Limon, argile	Valisneria, chara	4	Limon	Valisneria, chara	4
17	P19-P21	Sable, limon, roche	Sparganium, scirpus	4	Sable, liomon, roche	Valisneria, chara	4	Sable, limon, roche	Valisneria, chara	4
18	P22	Bloc	Nil	0	Bloc	Nil	0	Sable et roche	Chara, valisneria	3
19	P23-P27	Rocheux	Nil	0	Sable et roche	Valisneria, chara	3	Sable, roche, limon	Valisneria, chara	3
20		Rocheux	Nil	0	Rocheux	Nil	0	Sable, roche	Valisneria, chara	3

Les herbiers à végétation flottante ou atteignant la surface

Les herbiers de cette zone sont présents dans 17 des 20 sections échantillonnées (tableau 1). *Valisneria americana* est la seule espèce présente dans chacune de ces 17 sections. *Alisma gramineum* et *chara* sont les deux autres espèces les plus fréquentes, on les rencontre respectivement dans onze (11) et sept (7) sections.

On observe que les densités les plus faibles (0 à 2) ont été observées dans les sections à fond nettement rocheux (sections 3, 4, 5, 6, 7, 8, 9, 10, 18 et 20). Les sections dont le substrat est dominé par du limon, de l'argile et/ou du sable avec ou sans roches (sections 1, 2, 11, 12, 13, 14, 15, 16, 17 et 19) ont des herbiers de plus forte densité (3 à 4).

Au niveau des sections 11, 12 et 13, contaminées par la pyrite, la densité des herbiers composés de végétation flottante est faible (densité = 2) et dominée par *Valisneria americana*, notamment dans la section 13 où seule cette espèce a été observée et, dans la section 12, où elle n'est accompagnée que de *Ceratophyllum demersum.*

Les herbiers à végétation submergée

Des herbiers à végétation submergée sont présents dans les vingt sections étudiées. Ils constituent des formations végétales denses (densité 3 ou 4) et très variées au niveau des quinze sections suivantes : 1, 2, 3, 5, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19 et 20. Dans la grande majorité de ces sections, le substrat est principalement composé de matières fines (sable, argile, limon). La densité demeure élevée même dans les sections 11, 12 et 13 où l'on retrouve de la pyrite de fer. D'autre part, dans les sections 4, 6, 7, 8 et 9, les densités sont plus faibles (1 ou 2) ; le substrat y est davantage rocheux.

Valisneria americana a été observée dans chacun de ces herbiers et est généralement l'espèce dominante. On retrouve également le *chara*, particulièrement abondant dans le

secteur Est, l'alisma, principalement dans le secteur sud, ainsi qu'heteranthera et ceratophyllum.

4.2 Mesure de l'oxygène dissous

Des mesures d'oxygène dissous ont été réalisées à 9 stations dans les secteurs I, III et IV de la zone d'étude (figure 1). À chacune des stations, ces mesures ont été prises en surface, à mi-profondeur et à 0,5 m du fond. Les résultats montrent des concentrations en oxygène variant entre 9,4 et 9,8 dans l'ensemble de la zone d'étude ce qui indique un niveau excellent pour la faune aquatique (tableau 2).

4.3 Caractérisation de la faune ichtyenne

Les résultats relatifs à la faune ichtyenne sont présentés en fonction des trois types d'engin de pêche utilisés. Ces résultats sont décrits pour chacune des stations ainsi que pour les cinq secteurs de la zone d'étude. De plus, les résultats de pêche exploratoire dans quelques sites de référence seront présentés à titre indicatif ; ces pêches visaient la capture de spécimens pour l'étude écotoxicologique et les efforts n'ont pas été répartis avec la même intensité que dans la zone d'étude. Finalement, une section *interprétation des résultats* présente une appréciation générale des habitats d'alimentation, de reproduction et d'alevinage pour les quatre secteurs à l'étude.

Globalement, l'inventaire de la faune ichtyenne dans la zone d'étude a permis la capture de 22 espèces pour un total de 4 888 poissons. La liste de l'ensemble des espèces capturées ainsi que les données brutes des pêches sont listées à l'annexe 2.

Tableau 2 - Mesures d'oxygènes dissous (mg/l) autour de l'Île aux Chats, automne 1996

Station	Profondeur (m)	Temp. (°C)	Oxygène dissous (mg/l)
1	surface	15	9,8
	1,5 m	15	9,8
	3,5 m	15	9,6
2	surface	16	9,6
	2,0 m	16	9,5
	4,5 m	16	9,4
3	surface	16	9,7
	2,0 m	16	9,6
	3,5 m	16	9,6
4	surface	16	9,9
	1,0 m	16	9,9
	2,0 m	16	9,9
5	surface	14	9,8
	1,5 m	14	9,6
	3,0 m	14	9,6
6	surface	14	9,6
	2,0 m	14	9,6
	4,0 m	14	9,5
7	surface	14	9,6
	2,0 m	14	9,5
	4,5 m	14	9,6
8	surface	15	9,7
	2,5 m	15	9,7
	5,0 m	15	9,7
9	surface	15	9,6
	2,5 m	15	9,5
	5,5 m	15	9,4

Pêche électrique

L'échantillonnage à la pêche électrique a été effectué le long de la rive de l'Île aux Chats ainsi que le long d'une portion de la rive de Grande Île. Les résultats de pêche ont été regroupés en fonction de 27 transects établis le long de ces rives. La délimitation des

transects a été basée sur les caractéristiques d'habitat établies lors de la caractérisation de la végétation aquatique riveraine. La longueur des stations varie entre 90 et 260 m et sont représentées à la figure 1. Afin de comparer les résultats de pêche, les données ont été ajustées pour des transects de 200 m.

Au total, l'échantillonnage de la zone d'étude à la pêche électrique a permis la capture de 16 espèces de poissons dont les plus abondantes sont la perchaude (PEFL) et le crapet soleil (LEGI) qui représentent respectivement 58,0 et 19,2 % des captures (tableau 3). La liste des espèces capturées, incluant les noms français et latin, leur abbréviation, ainsi que les secteurs et les engins de capture, est présentée à l'annexe 2. Les rendements de pêche varient de 0 à 63,6 poissons par transects de 200 m, selon les stations. On observe que les stations les plus riches en terme de nombre d'espèces et d'abondance de poissons sont localisées dans les zones d'herbiers, en particuliers, les secteurs III (stations P17 à P21), sud (P02 et P08) et II (station P23).

Les valeurs de diversité (Shannon) ont été calculées pour chacune des stations et pour chaque secteur. Ce paramètre est indicateur de la répartition de l'abondance observée entre les espèces. Une valeur faible indique une dominance d'une ou de quelques espèces, tandis qu'une valeur élevée révèle une forte répartition de l'abondance entre les espèces. De façon générale, les valeurs de ce paramètre sont relativement faibles (inférieures à 0,6), ce qui est le reflet d'une dominance de une ou quelques espèces à chacune des stations.

L'analyse comparative entre les quatre secteurs à l'étude révèle des écarts importants au niveau du nombre et de l'abondance des espèces capturées. Le secteur Est montre les valeurs les plus élevées avec la présence de 12 espèces et un rendement moyen de 34,0 spécimens/200 m. Les secteurs sud et II présentent des valeurs comparables avec 8 et 10 espèces et des rendements de pêche de 7,7 et 6,0 spécimens/200 m, respectivement. Le secteur Nord possède des rendements de pêche très faibles (3,5 spécimens/200 m), bien que 7 espèces y aient été capturées.

Tableau 3 Abondance numérique (valeurs ajustées pour un transect de 200 m) et abondance relative (%) des poissons capturés à la pêche électrique autour de l'île aux Chats, durant l'automne 1996

Espèces	Abondance numérique																															Total		Moyenne par Secteur			
	Secteur Sud									Secteur Nord								Secteur Est												Secteur Grande Île								
	P01	P02	P03	P04	P05	P06	P07	P08	P09	P10	P11	P12	P13	P14	P15	P16	P16a	P17	P17a	P18	P18a	P19	P19a	P20	P20a	P21	P21a	P22	P23	P24	P25	P26	P27			sud	1	3	2
Long. (m)	150	120	120	240	180	210	260	210	240	90	150	120	410	150	150	150	150	110	110	110	110	110	110	110	110	110	110	210	210	240	210	210	260	5540		1730	1370	970	920
AMRU	1.3	0	0	0	0	0	0	0	0	0	1.3	0	0	0	0	0	0	0	3.6	1.8	0	1.8	0	0	0	5.5	5.45	2.9	0	0.8	3.8	0	0	28.3	5.7%	0.1	0.2	1.9	0.9
ANRO	1.3	0	0	0	1.1	0	0	0	0	0	1.3	1.7	0	0	0	0	1.3	0	0	0	0	1.8	0	0	0	0	0	0	0	0	0	0	0	8.6	1.7%	0.3	0.5	0.2	0.0
CACO	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1.3	0	0	0	0	1.8	0	0	0	0	1.8	0	0	0	0	0	0	1	0.8	6.7	1.3%	0.0	0.2	0.3	0.3
CYCA	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1.8	0	0	0	0	0	0	0	0	0	0	0	0	0	1.8	0.4%	0.0	0.0	0.2	0.0
ESLU	0	1.7	0	0	0	0	0	0	0	0	0	1.7	0	1.3	0	0	0	0	0	0	0	0	0	1.8	0	0	0	0	0	0	1	0	0.8	8.2	1.6%	0.2	0.4	0.2	0.3
ESMA	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1.3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1.3	0.3%	0.0	0.2	0.0	0.0
ETNI	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1.8	0	1.8	0	0	0	0	0	7.27	0	0	0	0	1	0	11.9	2.4%	0.0	0.0	1.0	0.2
ICNE	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	1.8	0	0	0	0	0	0	0	0	0	1	0	0	0	0	3.7	0.7%	0.1	0.0	0.2	0.2
ICPU	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1.8	0	0	0	0	0	0	0	0	0	0	0	1.8	0.4%	0.0	0.0	0.2	0.0
LEGI	4	8.3	0	0	0	0	0	1	0	0	0	0	0	2.7	0	2.7	0	1.8	0	13	1.8	5.5	15	0	3.6	15	10.9	3.8	7.6	0.8	0	0	0	96.3	19.2%	1.5	0.7	6.3	1.7
MIDO	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.8	0.8	0.2%	0.0	0.0	0.0	0.2
MISA	2.7	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1.8	0	1.8	0	0	0	1.8	0	0	0	1	1	0	0	0	0	10.0	2.0%	0.3	0.0	0.6	0.2
NOCR	0	1.7	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2.6	0.5%	0.3	0.0	0.0	0.0
PEFL	4	17	8.3	0.8	1.1	0	0	13	0	0	0	1.7	0	1.3	1.3	1.3	5.3	9.1	20	22	0	18	55	7.3	22	44	25.5	4.8	1	0.8	2.9	1.9	2.3	290.7	58.0%	4.9	1.4	20.6	1.8
PINO	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	27	0	0	0	0	0	0	0	0	0	0	0	0	27.3	5.4%	0.0	0.0	2.5	0.0
PONI	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	1.0	0.2%	0.0	0.0	0.0	0.2
Total	13.3	28.3	8.3	0.8	2.2	0.0	0.0	16.2	0.0	0.0	2.7	5.0	0.0	5.3	2.7	4.0	8.0	12.7	27.3	41.8	30.9	29.1	69.1	10.9	27.3	63.6	49.1	12.4	11.4	2.5	7.6	3.8	4.6	501.1	100%	7.7	3.5	34.0	6.0
Nb espèce	5	4	1	1	2	0	0	4	0	0	2	3	0	3	2	2	3	3	4	6	3	5	2	3	3	3	4	4	5	3	3	3	4	16		8	7	12	10
Diversité	0.65	0.44	0.00	0.00	0.30	0.00	0.00	0.29	0.00	0.00	0.30	0.48	0.00	0.45	0.30	0.28	0.38	0.35	0.37	0.48	0.19	0.49	0.22	0.38	0.27	0.35	0.52	0.55	0.48	0.48	0.42	0.45	0.54	0.65		0.51	0.72	0.59	0.69

À titre indicatif, les résultats de pêche électrique réalisés dans 3 stations du secteur Pointe Mouillée, situé sur la rive nord du lac Saint-François de part et d'autre du ruisseau Sutherland à environ 12 km à l'amont de l'Île aux Chats, sont présentés ci-dessous.

Station	ICPU	LEGI	MISA	PEFL	Total
BG06 (est)	0	3	6	1	10
BG06 (ouest #1)	0	1	5	0	6
BG08 (ouest #2)	4	6	16	3	29

Chacun des transects avait une longueur d'environ 200 m et l'herbier était principalement dominé par du carex, du sagitaire et du nymphéacée. Notons la présence de plusieurs jeunes de l'année d'achigan à grande bouche (MISA), ce qui suggère la présence d'une frayère pour cette espèce dans le secteur.

Seine

L'échantillonnage à la seine a permis la capture de 4 224 poissons répartie en 16 espèces, dont les plus abondantes sont le méné émeraude (NOAT), la chatte de l'est (NOCR), le ventre pourri (PINO), le fondule barré (FUDI) et la perchaude (PEFL) avec des abondances de 2 316, 975, 371, 211 et 149 spécimens, respectivement (tableau 3).

Tableau 4 Abondances numérique et relative des poissons capturés à la seine de rivage autour de l'île aux Chats, durant l'automne 1996

Espèce	Abondance numérique par secteur																															Abondance relative (%)				
	sud												Nord									Est							Grande Île			Total	Secteur				Total
	S01 *			S02			S03			S04			S05			S06	S07			S08			S09			S10			S11			S12			S13	S14	S15		Sud	Nord	Est	G-Î	
	a	b	tot.	a	b	tot.	a	b	tot.	a	b	tot.	a	b	tot.	tot.	a	b	tot.	a	b	tot.	a	b	tot.	a	b	tot.	a	b	tot.	a	b	tot.	tot.	tot.	tot.						
AMRU			0			0			0			0			0	6			0			0			0			0			0		2	2	0	0	0	8	0.0	0.3	0.2	0.0	0.2
CACO			0			0		1	1			0			0	0			0			0			0			0			0			0	0	0	0	1	0.2	0.0	0.0	0.0	0.0
CUIN			0			0			0			0			0	0			0			0			0			0		1	1	0	0	0	1	0.0	0.0	0.1	0.0	0.0
ESLU			0			0			0			0			0	0			0			0			0			0	2	1	3	0	0	0	3	0.0	0.0	0.2	0.0	0.1
ETNI			0		1	1	11		11			0			0	3	1	1	2		1	1			0	15	12	27	3	9	12			0	0	0	0	57	2.3	0.3	2.9	0.0	1.3
FUDI	1		1	13	19	32	3		3		27	27	2		2	2	6	17	23	9	1	10	25	1	26	40	18	58		6	6	15	5	20	1	0	0	211	12.2	2.6	6.3	2.9	5.0
ICPU			0			0			0			0			0	0			0			0			0			0		1	1			0	0	0	0	1	0.0	0.0	0.1	0.0	0.0
LASI	4	4	8			0			0	6		6			0	0			0			0			0			0	3	14	17			0	0	4	0	35	2.6	0.0	1.3	11.8	0.8
LEGI	2		2	1		1			0			0		1	1	2			0			0			0			0	11	17	28	21	27	48	1	0	0	83	0.8	0.1	5.7	2.9	2.0
MIDO			0			0			0			0			0	0			0			0			0			0		1	1			0	0	2	0	3	0.0	0.0	0.1	5.9	0.1
MISA			0			0			0			0			0	0			0			0			0			0	1		1	0	0	0	1	0.0	0.0	0.1	0.0	0.0
NOAT			0	1		1		20	20	1	150	151		1	1	0	377	1252	1629	204	310	514			0			0			0			0	0	0	0	2316	32.5	92.2	0.0	0.0	54.8
NOCR			0	75	13	88			0			0	4	1	5	50			0			0	12	8	20	12		12			0	500	300	800	0	0	0	975	17.4	3.0	60.9	0.0	23.1
NOHU			0			0			0			0			0	0			0			0			0	9		9			0			0	0	0	0	9	0.0	0.0	0.7	0.0	0.2
PEFL			0	1	6	7	2	1	3			0	1	3	4	0			0			0	1		1		1	1	69	37	106	2	8	10	15	0	2	149	2.6	0.0	8.8	50.0	3.5
PINO			0			0	30	21	51			0	2	104	106	10			0			0		25	25	55	40	95	40		40	15	20	35	0	9	0	371	29.5	1.5	12.8	26.5	8.8
TOTAL			11			130			89			184			119	73			1654			525			72			202			211			920	17	15	2	4224	100	100	100	100	100
Nb espèce			3			6			6			3			6	5			3			3			4			6			8			9	3	3	1	16	9	7	14	6	16
Diversité			0.33			0.38			0.52			0.24			0.22	0.37			0.04			0.05			0.50			0.57			0.63			0.25	0.19	0.40	0.00	0.59	0.34	0.24	0.48	0.20	0.59

* À chaque station, deux coups de seine espacés d'environ 20 m ont été réalisés (à l'exception des stations 6, 13, 14 et 15) et identifiés par les lettres a et b.

La répartition des espèces dans la zone d'étude est très hétérogène et généralement très localisée. Par exemple, chez le méné émeraude (NOAT), la chatte de l'est (NOCR), la perchaude (PEFL), le crapet soleil (LEGI) et le raseux-de-terre (ETNI), on retrouve entre 68 et 93 % des effectifs concentrés dans une ou deux stations (tableau 4). Par contre, le fondule barré (FUDI) et le ventre pourri (PINO) présentent une répartition plus large, bien que l'on observe des concentrations élevées à certaines stations. Notons que l'utilisation de la seine permet d'obtenir des résultats étroitement associés aux caractéristiques locales de la station, ce qui correspond souvent à la présence de micro-habitat. Cependant, certaines espèces présentent un comportement grégaire qui favorise la capture ponctuelle d'un grand nombre d'individus. Afin d'apprécier si une forte abondance de poissons est associée à un comportement grégaire ou à la présence d'un habitat recherché par l'espèce, l'échantillonnage a été réalisé en duplicata (a et b) dans la plupart des stations. Lorsque l'espèce est présente dans les deux sous-stations (a et b) celle-ci peut être associée à un habitat recherché dans cette station, tandis que si elle est présente dans une seule sous-station, une présence fortuite pourrait être considéré.

L'analyse comparative par secteur montre un nombre d'espèce et une abondance de poissons nettement supérieure dans la zone III. En effet, on y retrouve 14 espèces avec une abondance moyenne de 222 spécimens par coup de seine. Dans le secteur sud, on retrouve 9 espèces avec un rendement moyen de 53,3 spécimens/coup de seine sans pic d'abondance particulier, ce qui indique une certaine homogénéité de l'habitat. Dans le secteur Nord, on retrouve une forte concentration de méné émeraude (NOAT) aux station S07 et S08 avec la capture de 2 143 spécimens. Outre cette espèce, on y retrouve 6 espèces avec un rendement moyen de 25,9 spécimens/coup de seine. Le secteur Grande Île montre une faune ichtyenne très restreinte avec un rendement moyen de 11,3 spécimens/coup de seine. Ces derniers résultats sont associés au type d'habitat de ce secteur dont les rives ont été aménagées avec l'installation de murêts, ce qui a restreint les abris disponibles pour les petits poissons. Cette situation limite également le nombre de sites susceptibles d'être échantillonnés à la seine ; un seul coup de seine par station a été réalisé dans ce secteur.

À titre indicatif, les résultats obtenus dans les trois stations du secteur Pointe Mouillée sont présentés ci-après.

Station	ESLU	LASI	LEGI	MISA	PEFL	PINO	Total
BG06 (est)	0	5	5	0	5	40	55
BG07 (ouest #1)	1	5	20	3	0	75	104
BG08 (ouest #2)	0	2	10	5	2	40	59

La communauté ichtyenne de cet herbier est dominée par le ventre-pourri (PINO) et le crapet soleil (LEGI). L'abondance générale et le nombre d'espèces capturées est d'ordre moyen. Notons que cet herbier est constitué principalement de végétation émergeante (carex, sajitaire, nénuphare) dont la partie immergée est constitué de tige grossière offrant peu d'abris pour la faune ichtyenne.

Filet maillant

Quatre stations ont été échantillonnées à l'aide de deux filets maillants expérimentaux couplés bout-à-bout. Une station était localisée au centre de la baie du secteur Est et trois stations ont été réparties dans la zone IV, le long des rives de l'Île aux Chats et de Grande Île (figure 1). La perchaude (PEFL) et le grand brochet (ESLU) sont les deux espèces les plus abondantes avec la capture de 286 et 40 spécimens respectivement, ce qui représente 82,2 et 11,5 % de l'ensemble des captures (tableau 5).

Tableau 5 Abondance numérique, rendement de pêche et abondance relative des poissons capturés

Abondance numérique (N)

Espèces	Stations												Total
	F01			F02			F03			F04			
	a	b	tot.	a	b	tot.	a	b	tot.	a	b	tot.	
AMRU			0			0	2	1	3	2	1	3	6
CACO		1	1			0	1		1			0	2
ESLU	7	8	15	5	6	11			0	10	4	14	40
ICNE		2	2			0			0			0	2
LEGI	2	3	5	2	1	3			0			0	8
MISA		1	1			0			0			0	1
NOCR	2		2			0			0			0	2
PEFL	78	57	135	35	72	107	6	3	9	34	1	35	286
PEMA			0	1		1			0			0	1
TOTAL	89	72	161	42	79	122	9	4	13	46	6	52	348

Rendements numériques (poisson/filet-jour)

Espèces	Stations				Total
	F01	F02	F03	F04	
AMRU	0.0	0.0	1.5	1.5	0.8
CACO	0.5	0.0	0.5	0.0	0.3
ESLU	7.5	5.5	0.0	7.0	5.0
ICNE	1.0	0.0	0.0	0.0	0.3
LEGI	2.5	1.5	0.0	0.0	1.0
MISA	0.5	0.0	0.0	0.0	0.1
NOCR	1.0	0.0	0.0	0.0	0.3
PEFL	67.5	53.5	4.5	17.5	35.8
PEMA	0.0	0.5	0.0	0.0	0.1
TOTAL	80.5	61.0	6.5	26.0	43.5

Abondance relative (%)

Espèces	Stations				Total
	F01	F02	F03	F04	
AMRU	0.0	0.0	23.1	5.8	1.7
CACO	0.6	0.0	7.7	0.0	0.6
ESLU	9.3	9.0	0.0	26.9	11.5
ICNE	1.2	0.0	0.0	0.0	0.6
LEGI	3.1	2.5	0.0	0.0	2.3
MISA	0.6	0.0	0.0	0.0	0.3
NOCR	1.2	0.0	0.0	0.0	0.6
PEFL	83.9	87.7	69.2	67.3	82.2
PEMA	0.0	0.8	0.0	0.0	0.3
TOTAL	100	100	100	100	100

Les stations F01 et F02, localisées dans la baie du secteur Est entre l'Île aux Chats et Grande Île, montrent une faune ichtyenne nettement plus abondante avec des rendements de pêche de 80,5 et 61,0 spécimens/filet-nuit, respectivement. Les station F03 et F04 localisées au nord de l'Île aux Chats en bordure de la zone I montrent des rendements de pêche de 6,5 et 26,0 spécimens/filet-nuit, respectivement.

L'utilisation du filet maillant n'a pas révélé la présence d'autres espèces. Toutefois, le grand brochet (ESLU) présente une importance plus élevée et on observe que le crapet soleil (LEGI) se concentre dans la baie du secteur Est, tandis que le crapet de roche (AMRU) se retrouve davantage au large de l'Île aux Chats ; cette dernière espèce recherche habituellement un substrat rocheux.

Afin de présenter un appeçu de la taille moyenne des espèces composant la communauté ictyenne de la zone d'étude, on retrouve, au tableau 6, les valeurs moyenne, minimale et maximale de la longueur des spécimens pour chaque espèces capturés au filet maillant et à la pêche électrique.

Tableau 6 Taille des poissons capturés autour de l'île aux Chats et dans les sites de référence

Filet maillant (île aux Chats

Espèce	Nombre	Longueur (mm)		
		Min.	Max.	Moy.
AMRU	6	124	166	143
CACO	2	420	437	429
ESLU	40	345	760	534
ICNE	2	222	243	233
LEGI	8	111	220	152
MISA	1	-	-	185
NOCR	2	106	106	106
PEFL	286	100	273	173
PEMA	1			200

Pêche électrique (île aux Chats)

Espèce	Nombre	Longueur (mm)		
		Min.	Max.	Moy.
AMRU	20	90	195	139
ANRO	6	650	815	722
CACO	5	95	550	298
CYCA	1	-	-	82
ESLU	6	126	725	419
ESMA	1	-	-	159
ETNI	7	57	80	71
ICNE	3	65	175	128
ICPU	1	-	-	66
LEGI	62	36	210	116
MIDO	1	-	-	420
MISA	7	45	237	156
NOCR	2	65	87	79
PEFL	179	60	304	123
PONI	1	-	-	230

Pêche électrique dans les sites de référence (Pointe mouillée)

Espèce	Nombre	Longueur (mm)		
		Min.	Max.	Moy.
ESLU	3	400	600	500
ESMA	4	100	100	100
LEGI	10	85	200	156
MISA	26	70	300	117
PEFL	4	125	150	131

4.4 Interprétation des résultats

Caractéristiques générales de l'habitat du poisson

Dans ce chapitre, on retrouve une analyse descriptive de la qualité d'habitat qu'offre les cinq secteurs à l'étude pour la faune ichtyenne. Notons que dans cette étude, seul l'habitat d'alimentation a été analysé, étant donné la période automnale des inventaires. La reproduction des principales espèces de poissons du lac Saint-François a généralement lieu au printemps et au début de l'été, selon les espèces. Toutefois, les habitats potentiels de reproduction en rive ont été notés et certaines indications d'utilisation par les jeunes de l'années ont été relevées.

De façon générale, l'habitat constitué de la plaine d'inondation est très recherché pour la reproduction d'espèces printanières frayant dans la végétation riveraine. Cependant, dans le lac Saint-François, cet habitat est relativement réduit étant donné le type de gestion du lac caractérisé par le maintien d'un niveau très stable, même durant la crue printanière. Les zones de plaine d'inondation sont donc presqu'exclusivement situées à l'embouchure des tributaires. Sur les rives du lac, cette gestion du niveau d'eau favorise l'implantation d'espèce, telles que le typha et le scirpe qui sont peu utilisées pour la fraie des poissons. Ainsi, l'habitat de reproduction lacustre est probablement davantage concentré au niveau de la végétation aquatique riveraine à de faibles profondeurs, sur une végétation dominée par la vallisnérie.

L'habitat d'alevinage est généralement constitué de zone calme à l'intérieur de baies, qui offre un maximum d'abris, avec la présence d'une végétation aquatique dense, de faibles profondeurs et qui présente également une forte production primaire (plancton).

Les caractéristiques recherchées comme habitat d'alimentation varient selon les besoins de chaque espèce. Un habitat varié composé de végétation riveraine et de haut-fond rocheux avec la présence de zone profonde à proximité présente un bon potentiel.

Analyse descriptive par secteur

Dans les lignes suivantes, le lecteur trouvera une description générale des habitats de chacun des secteurs à l'étude associée à l'abondance et la diversité de la faune ichtyenne échantillonnée. Cette analyse descriptive vise à établir de façon qualitative la valeur biologique de ces secteurs ou portion de secteur afin de guider l'étude d'impact du projet de restauration des sédiments autour de l'Île aux Chats. Notons que pour l'ensemble de la zone d'étude, on retrouve à une profondeur de plus de deux mètres (pouvant aller jusqu'à 15 m dans le lac Saint-François) une végétation dense et très variée composée principalement de vallisnérie, de cératophylum, d'élodée, d'hétéranthère et de plusieurs espèces de potamot. La grande transparence de l'eau associée à une eau très conductrice et riche en éléments nutritifs sont des facteurs favorisant cette situation très particulière au Québec. Ainsi, les caractéristiques discriminantes entre les secteurs à l'étude concernent la zone littorale comprise entre 0 et 2 m de profondeur.

Secteur Sud

Le secteur sud est caractérisé par des rives généralement rocheuses jusqu'à une profondeur de deux mètres, situation causée par l'emprise des vents dominants et l'action des vagues. On retrouve peu d'abris, à l'exception de deux zones d'herbiers situées dans les stations P02 et P08. Ces deux sites montrent une plus grande abondance de poissons, en particulier la perchaude (PEFL) et le crapet soleil (LEGI). Parmi les petites espèces, la chatte de l'est (NOCR) domine la station S02, tandis que le ventre-pourri (PINO) est particulièrement abondant dans la station S05. Les stations P04, P06, P07 et P09 offrent peu d'abris et sont

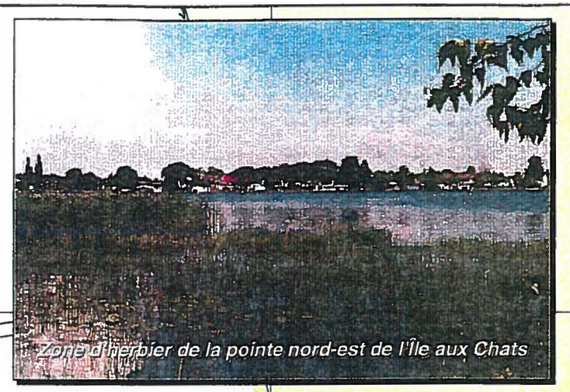
directement soumis à l'action des vagues ce qui se reflète dans les résultats de pêche qui présentent des rendements plus faibles.

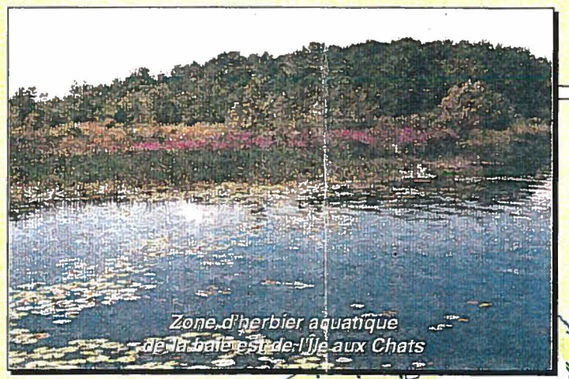
Ce secteur offre donc un potentiel d'habitat de reproduction et d'alevinage relativement faible, à l'exception de la section 1, qui présente un petit herbier dominé par la vallisnérie et l'élodée et à l'abri des vents dominants (figure 2). L'ensemble de ce secteur possède un habitat d'alimentation évalué à moyen.

Secteur Nord

Ce secteur est caractérisé par la présence d'un dépôt de pyrite de fer caractérisée par des particules très fines mais compactées sur une grande épaisseur. La pente de la rive est très faible et les profondeurs d'eau sont inférieures à 0,5 m sur une bonne distance de la rive. Une végétation très clairesemée y est observée, en particulier dans une petite zone (P12) composée de scirpes et de petits plants de vallisnérie. Dans la section 14, localisée à l'extrémité est du secteur, on retrouve un herbier d'une grande superficie également dominé par le scirpe jusqu'à une profondeur de près de 2 m et d'une petite zone de nymphea (nénuphar) (figure 2). Ce type de végétation offre peu de potentiel pour la reproduction, l'alevinage et l'alimentation. D'ailleurs, les résultats de pêche montrent une abondance et une diversité de la faune ichtyenne relativement faible. Aucun poisson n'a été capturé à la pêche électrique dans l'ensemble de la zone P13. Cependant, les deux stations de seinage (S07 et S08) ont montré une très forte abondance de méné émeraude (NOAT). Cette espèce pélagique recherche des milieux ouverts et est peu associée au substrat. Cependant, cette forte abondance observée nulle part ailleurs dans la zone d'étude indique que ce type d'habitat pourrait exercer un certain attrait pour cette espèce. Notons que celle-ci constitue une ressource alimentaire pour un grand nombre de poissons et d'oiseaux piscivores. D'autre part, on retrouve la chatte de l'est (NOCR) qui semble abondante aux deux extrémités du secteur Nord (S06 et S09), mais absente de la portion centrale (S07 et S08).

Vue aérienne de l'Île aux Chats


Zone d'herbier de la pointe nord-est de l'île aux Chats


Zone d'herbier aquatique de la baie est de l'Île aux Chats

ÎLE SÉRIGNY

LAC SAINT-FRANÇOIS

ÎLE AUX CHATS

SALABERRY-DE-VALLEYFIELD

SCI, ELE, EQU / densité: 3

VAL, ALI, NAJ / densité: 3-4

VAL / densité: 2

NOAT

VAL, ALI / densité: 0-1

PEFL
LEGI
ETNI
PINO
FUDI

VAL,NAJ / densité: 4

PEFL

VAL, CHA / densité: 3

CER, MYR, ALG / densité: 4

LASI
LEGI
NOCR

LEGI LASI
PEFL

LEGI
FUDI
NOCR

VAL, SCI, ALG / densité: 4

ELO, VAL / densité: 4

NAJ, VAL / densité: 2

VAL, ALI / densité: 2

SCI, VAL / densité: 2

NOAT

VAL / densité: 1

ALI / densité: 1

ALI / densité: 0-1

ALI / densité: 2

NOAT

VAL, ALI / densité: 1-2

NYM, HET / densité: 1-2

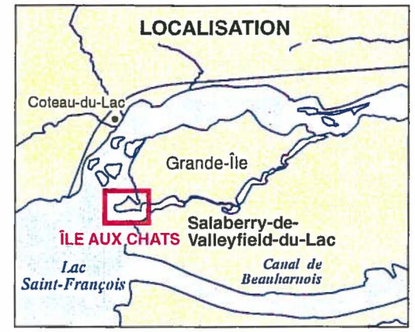
PEFL
PINO

0 50 250m

565 000 (NAD 27)

566 000 (NAD 27)

LOCALISATION



VÉGÉTATION

- Dominance de myriophylle et ceratophyllum
- Dominance de vallisneria et alisma
- Dominance de nymphea
- Dominance de scirpus

SUBSTRAT

- Pyrite
- Limon
- Rocheux

FAUNE ICHTYENNE

- Habitat potentiel de reproduction et d'alevinage

ELO	Elodea
VAL	Valisneria
NAJ	Najas
ALI	Alisma
NYM	Nymphea
HET	Heteranthera
SCI	Scirpus
ELE	Eleocharis
EQU	Equisetum

ESPÈCES ABONDANTES

ETNI	Raseux-de-terre
FUDI	Fondule barré
LASI	Crayon d'argent
LEGI	Crapet soleil
NOAT	Méné émeraude
NOCR	Chatte de l'est
PEFL	Perchaude
PINO	Ventre-pourri

Allied Signal
ENGINEERED MATERIALS

SITE DE L'ÎLE AUX CHATS PROJET DE RESTAURATION DES SÉDIMENTS / CLARK ISLAND SITE SEDIMENT REHABILITATION PROJECT

CARACTÉRISATION BIOLOGIQUE
DESCRIPTION DE LA ZONE RIVERAINE (0-2 M) DE L'ÎLE AUX CHATS

DATE: *DÉC. 1996* PROJET/PROJECT: *5804*

TECSULT FIGURE: *2*

environnement illimité inc.

Cette espèce est grégaire, recherche des eaux calmes, herbeuses et claires et occupe une place prépondérante dans le régime alimentaire de plusieurs espèces prédatrices.

Ce secteur est également soumis à l'emprise des vents d'ouest et offre donc peu d'abris pour les petits poissons. À l'exception des deux espèces mentionnées ci-haut, qui semblent retrouver un habitat d'alimentation automnale intéressant, le potentiel qu'offre le secteur Nord comme habitat de reproduction, d'alevinage et d'alimentation pour la faune ichtyenne est relativement faible.

Secteur Grande Île

Le secteur Grande Île est une zone dont les rives ont été particulièrement remaniées par de l'enrochement ou des murs de béton, ce qui a éliminé à toute fin pratique l'habitat riverain de ce secteur. Au pied de ces murs dont la hauteur varie entre 1,5 et 2,0 m, on retrouve un substrat plus ou moins modifié par l'ajout de sable, de toile et d'enrochement. La végétation submergée typique de la zone de profondeur de 2 m et plus, composée de vallisnérie, de chara, de ceratophyllum et de potamot, atteint les rives où le substrat plus limoneux subsiste. Ce secteur n'offre aucun habitat d'alimentation, de reproduction ou d'alevinage particulier pour la faune ichtyenne, à l'exception d'une petite zone située près de la jetée (station S12) qui présente une petite succession végétale riveraine, une profondeur moindre avec un substrat vaseux avec des blocs et débris ligneux. À ce site, un grand nombre de jeunes poissons ont été capturés, tels que le crapet soleil (LEGI), la chatte de l'est (NOCR), le ventre-pourri (PINO) et le fondule barré (FUDI).

Secteur Est

La portion riveraine du secteur Est, constituée de la partie est de l'Île aux Chats, est caractérisée par une variété et une qualité d'habitat pour la faune aquatique particulièrement élevées. En effet, bien que la pente de la beine soit relativement forte, on y retrouve une bonne succession d'herbiers émergeants et immergés, un haut-fond rocheux (près de la station P19) et une zone profonde à proximité qui offre un habitat d'alimentation pour une grande variété d'espèces de poisson et de faune aquatique en général. Les résultats de pêche à la seine et à la pêche électrique indiquent effectivement que ce secteur présente la plus grande richesse d'espèces et les plus grandes abondances. Certaines espèces y on été capturées de façon plus marquée, soit le raseux-de-terre (ETNI) (68 % des captures aux stations S10 et S11) et le crayon d'argent (LASI) (49 % des capture à la station S11).

La végétation riveraine est relativement dense et dominée par la vallisnérie, ce qui offre un bon potentiel de reproduction, en particulier pour la perchaude. De plus, ce secteur est à l'abri des vents dominants et devrait favoriser une bonne productivité planctonique, ce qui offre un bon potentiel d'habitat d'alevinage. D'ailleurs, plus d'une centaine de perchaudes (PEFL) de l'année y ont été capturées (station S11) ainsi que des ventres-pourris (PINO; N~50), crapets soleils (LEGI; N~20), fondules barrés (FUDI; N~20), raseux-de-terre (ETNI; N~10), queues à tache noire (NOHU; N~10), crayons d'argent (LASI; N~10) et barbottes brunes (ICNE; N=1).

5.0 CONCLUSION

L'analyse de la faune ichtyenne et son habitat dans la zone d'étude a permis d'identifier les élements suivants :

- Les inventaires ont permis d'identifier la présence de 22 espèces de poissons dont les principales sont : la perchaude (PEFL), le crapet soleil (LEGI), le grand brochet (ESLU), le crapet de roche (AMRU), le méné émeraude (NOAT), la chatte de l'est (NOCR), le ventre-pourri (PINO) et le fondule barré (FUDI) ;

- Le secteur Nord affecté par les dépôts de pyrite montre un habitat faiblement colonisé par la végétation aquatique dans la zone 0,25-2,0 m. De façon générale, cette zone montre un faible potentiel d'habitat pour la faune ichtyenne. Toutefois, on y retrouve aux extrémités des zones d'herbiers qui pourraient présenter un potentiel pour la reproduction de certaines espèces. Par ailleurs, on retrouve une forte concentration de méné émeraude (NOAT) et de chatte de l'est (NOCR) qui semblent y retrouver un attrait comme habitat d'alimentation automnale. Ces deux espèces grégaires et pélagiques composent le régime alimentaire de plusieurs espèces de poissons et d'oiseaux piscivores ;

- Le secteur Est présente un potentiel élevé comme habitat de reproduction, d'alevinage et d'alimentation, en particulier pour la perchaude et le crapet soleil, ainsi que cetaines petites espèces telles que le ventre-pourri, le fondule barré, le queue à tache noire et le crayon d'argent. Ce site pourrait être considéré comme une zone sensible pour la faune aquatique ;

- La zone littorale des secteurs Sud et Grande Île présente un potentiel d'habitat jugé de faible à moyen, à l'exception de la station P23, localisée à l'extrémité sud de la zone Grande Île, qui semble présenter des habitats de reproduction et d'alevinage recherchés

par la chatte de l'est (NOCR) et le crapet soleil (LEGI). La station P02, localisée dans le secteur Sud, montre également un potentiel pour cette espèce.

6. RÉFÉRENCES

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Annexe 1

Données brutes de l'inventaire de la végétation aquatique autour de l'Île aux Chats dans le lac Saint-François à la fin de l'été 1996

Liste des espèces végétales dominantes, sous-dominantes et co-dominantes

Végétation aquatique émergente

Secteur	Station de pêche	Typha angustifolia Typha latifolia	Scirpus validus	Sparganium eurycarpum	Eleocharis	Equisetum
1	P2	-	-	dominante	-	-
4	P5	co-dominante	-	co-dominante	-	-
7	P8	-	-	dominante	-	-
11	P13	dominante	-	-	-	-
12	P12	co-dominante	co-dominante	-	-	-
13	P14	co-dominante	co-dominante	-	-	-
14	P15	-	co-dominante	co-dominante	co-dominante	-
15	P16	dominante	-	-	-	-
16	P17,P18	co-dominante	-	co-dominante	-	-
17	P19-P21	-	co-dominante	co-dominante	-	-

Végétation flottante ou atteignant la surface

Secteurs		Elodea canadensis	Valisneria americana	Chara	Alisma gramineum	Nymphaea odorata	Heteranthera dubia
1	P2	co-dominante	co-dominante	-	-	-	-
2	P3	-	co-dominante	co-dominante	-	-	-
3	P4	-	co-dominante	-	co-dominante	-	-
5	P6,P7	-	-	-	dominante	-	-
6	P8	-	dominante	-	sous-dominante	-	-
7	P8	-	-	-	-	co-dominante	co-dominante
8	P9	-	-	-	dominante	-	-
9	P10	-	-	-	dominante	-	-
10	P11	-	dominante	-	-	-	-
11	P13	-	co-dominante	-	co-dominante	-	-
12	P12	-	dominante	-	-	-	-
13	P14	-	dominante	-	-	-	-
14	P15	-	dominante	-	-	co-dominante	-
15	P16	-	co-dominante	co-dominante	co-dominante	co-dominante	-
16	P17,P18	-	co-dominante	co-dominante	-	-	-
17	P19-P21	-	co-dominante	co-dominante	co-dominante	co-dominante	-
19	P23-P27	-	co-dominante	co-dominante	-	-	-

Végétation submergée

Secteurs		Elodea canadensis	Valisneria americana	Chara	Alisma gramineum	Ceratophyllum demersum	Heteranthera dubia
1	P2	-	-	co-dominante	-	-	co-dominante
2	P3	co-dominante	co-dominante	-	-	-	-
3	P4	-	dominante	sous-dominante	-	-	-
4	P5	-	co-dominante	co-dominante	co-dominante	-	-
5	P6,P7	-	co-dominante	-	co-dominante	co-dominante	-
6	P8	co-dominante	co-dominante	-	-	co-dominante	co-dominante
7	P8	-	co-dominante	-	-	-	co-dominante
8	P9	-	co-dominante	-	-	-	co-dominante
9	P10	-	co-dominante	-	-	-	co-dominante
10	P11	-	co-dominante	co-dominante	-	-	-
11	P13	-	co-dominante	co-dominante	-	-	-
12	P12	-	dominante	-	-	-	-
13	P14	-	dominante	-	-	sous-dominante	-
14	P15	-	co-dominante	co-dominante	-	-	-
15	P16	-	co-dominante	co-dominante	co-dominante	-	-
16	P17,P18	-	co-dominante	co-dominante	-	-	-
17	P19-P21	-	co-dominante	co-dominante	-	-	-
18	P22	-	co-dominante	co-dominante	-	-	-
19	P23-P28	-	co-dominante	co-dominante	-	-	-
20	-	-	co-dominante	co-dominante	-	-	-

d = espèce dominante
sd = espèce sous-dominante
cd = espèce co-dominante

FICHE DE TERRAIN

HERBIERS AQUATIQUES

ÎLE-AUX-CHATS, LAC SAINT-FRANÇOIS

SECTION: 1 (P02)

ZONE 1:

- SUBSTRAT: fond limoneux, profondeur < 0.5 m
- DENSITÉ: 4

Nymphaea odorata	Nymphéa odorant
Sparganium eurycarpum (d)	Rubanier à gros fruits
Alisma gramineum	Alisma graminoïde
Lemna minor	Lenticule mineure
Lemna trisulca	Lenticule trisulquée

ZONE 2

- SUBSTRAT: fond limoneux, profondeur 0.5 à 1.5 m
- DENSITÉ: 4

Elodea canadensis (cd)	Élodée du Canada
Valisneria americana (cd)	Valisnérie américaine
Ceratophyllum demersum	Cornifle d'eau
Myriophyllum exalbescens	Myriophylle blanchissant

ZONE 3

- SUBSTRAT: fond limoneux, profondeur > 1.5 m
- DENSITÉ: 4

Chara (cd)	Chara
Heteranthera dubia (cd)	Hétéranthère ligigieuse
Valisneria americana	Vallisnérie américaine
Elodea canadensis	Élodée du Canada

FICHE DE TERRAIN

HERBIERS AQUATIQUES

ÎLE-AUX-CHATS, LAC SAINT-FRANÇOIS

SECTION: 2 (P03)

ZONE 1

- SUBSTRAT: fond rocheux
- DENSITÉ: 0

ZONE 2

- SUBSTRAT: fond limoneux avec roches abondantes, profondeur 0.5 à 1m.
- DENSITÉ: 3

Chara (cd) Valisneria americana (cd) Potamogeton gramineum	Chara Vallisnérie américaine Potamot graminoide

ZONE 3

- SUBSTRAT: fond (donnée manquante) présence d'algues, profondeur > 1 m
- DENSITÉ: 3

Valisneria americana (cd) Elodea canadensis (cd) Myriophyllum exalbescens Ceratophyllum demersum Alisma gramineum	Valisnérie américaine Élodée du Canada Myriophylle blanchissant Cornifle nageante Alisma graminoide

FICHE DE TERRAIN

HERBIERS AQUATIQUES

ÎLE-AUX-CHATS, LAC SAINT-FRANÇOIS

SECTION: 3 (P04)

ZONE 1

- SUBSTRAT: boulders
- DENSITÉ: 0

ZONE 2

- SUBSTRAT: boulders, ± 1 m
- DENSITÉ: 2

Valisneria americana (cd) Potamogeton natans Alisma gramineum (cd) Myriophyllum exalbescens	Valisnérie américaine Potamogeton flottant Alisma graminoïde Myriophylle blanchissant

ZONE 3

- SUBSTRAT: boulders, > 1 m
- DENSITÉ: 3

Valisneria americana (d) Chara (sd) Alisma gramineum	Valisnérie américaine Chara Alisma graminoïde

FICHE DE TERRAIN

HERBIERS AQUATIQUES

ÎLE-AUX-CHATS, LAC SAINT-FRANÇOIS

SECTION: 4 (P05)

ZONE 1

- SUBSTRAT: limoneux, profondeur < 0.5 m
- DENSITÉ: 4

Sparganium eurycarpum (cd) Scirpus validus Typha angustifolia (cd)	Rubanier à gros fruits Scirpe vigoureux Typha à feuilles étroites

ZONE 2: inexistante

ZONE 3

- SUBSTRAT: sable et roches, profondeur de < 0.5 m à > 2 m
- DENSITÉ: 2

Valisneria americana (cd) Chara (cd) Alisma gramineum (cd)	Vallisnérie américaine Chara Alisma graminoïde

FICHE DE TERRAIN

HERBIERS AQUATIQUES

ÎLE-AUX-CHATS, LAC SAINT-FRANÇOIS

SECTION: 5 (P06, P07)

ZONE 1: inexistante

- SUBSTRAT: boulders
- DENSITÉ: 0

ZONE 2

- SUBSTRAT: boulders et un peu de sable et limon, profondeur < 0.6 m, algues sur roches
- DENSITÉ: 2

Alisma gramineum (d)	Alisma graminoïde
Valisneria americana	Valisnérie américaine
Myriophyllum exalbescens	Myriophylle blanchissant
Potamogeton bupleuroides	Potamot faux-buplèvre

ZONE 3

- SUBSTRAT: boulders et un peu de sable et limon, profondeur de < 0.6 m à > 2 m
- DENSITÉ: 3

Valisneria americana (cd)	Valisnérie américaine
Ceratophyllum demersum (cd)	Cornifle nageante
Alisma gramineum (cd)	Alisma graminoïde
Myriophyllum exalbescens	Myriophylle blanchissant
Potamogeton bupleuroides	Potamot faux-buplèvre
Potamogeton pusilum	Potamot nain

FICHE DE TERRAIN

HERBIERS AQUATIQUES

ÎLE-AUX-CHATS, LAC SAINT-FRANÇOIS

SECTION: 6 (P08)

ZONE 1: inexistante

- SUBSTRAT: rocheux, sablonneux
- DENSITÉ: 0

ZONE 2

- SUBSTRAT: rocheux, sablonneux avec un peu de limon
- DENSITÉ: 1 à 2

Valisneria americana (d)	Valisnérie américaine
Alisma gramineum (sd)	Alisma graminoïde
Ceratophyllum demersum	Cornifle d'eau
Myriophyllum exalbescens	Myriophylle blanchissant

ZONE 3

- SUBSTRAT: rocheux, sablonneux
- DENSITÉ: 1 à 2

Valisneria americana (cd)	Valisnérie américaine
Ceratophyllum demersum (cd)	Cornifle d'eau
Elodea canadensis (cd)	Élodée du Canada
Heteranthera dubia (cd)	Hétéranthère litigieuse
Potamogeton bupleuroides	Potamot faux-buplèvre
Myriophyllum exalbescens	Myriophylle blanchissant
Lemna trisulca	Lenticule trisulquée
Alisma gramineum	Alisma graminoïde

FICHE DE TERRAIN

HERBIERS AQUATIQUES

ÎLE-AUX-CHATS, LAC SAINT-FRANÇOIS

SECTION: 7 (P08)

ZONE 1:

- SUBSTRAT: fond rocheux avec sable
- DENSITÉ: 3

Sparganium eurycarpum (d)	Rubanier à gros fruits
Sagittaria rigida	Sagittaire dressée
Lemna minor	Lenticule mineure

ZONE 2

- SUBSTRAT: fond rocheux (boulder)
- DENSITÉ: 1 à 2

Nymphaea odorata (cd)	Nymphéa odorant
Heteranthera dubia (cd)	Hétéranthère litigieuse
Valisneria americana	Valisnérie américaine
Alisma gramineum	Alisma graminoïde
Myriophyllum exalbescens	Myriophylle blanchissant

ZONE 3

- SUBSTRAT: fond rocheux (boulder)
- DENSITÉ: 1 à 2

Valisneria americana (cd)	Valisnérie américaine
Heteranthera dubia (cd)	Hétéranthère litigieuse
Alisma gramineum	Alisma graminoïde
Ceratophyllum demersum	Cornifle nageante

FICHE DE TERRAIN

HERBIERS AQUATIQUES

ÎLE-AUX-CHATS, LAC SAINT-FRANÇOIS

SECTION: 8 (P09)

ZONE 1: inexistante

- SUBSTRAT: fond rocheux (boulders)
- DENSITÉ: 0

ZONE 2

- SUBSTRAT: fond rocheux (boulders)
- DENSITÉ: 0 à 1

Alisma gramineum (d) Valisneria americana	Alisma graminoïde Valisnérie américaine

ZONE 3

- SUBSTRAT: sable et roches
- DENSITÉ: 1 à 2

Valisneria americana (cd) Heteranthera dubia (cd) Alisma gramineum Ceratophyllum demersum	Valisnérie américaine Hétéranthère litigieuse Alisma graminoïde Cornifle nageante

FICHE DE TERRAIN

HERBIERS AQUATIQUES

ÎLE-AUX-CHATS, LAC SAINT-FRANÇOIS

SECTION: 9 (P10)

ZONE 1: inexistante

- SUBSTRAT: fond rocheux (boulders)
- DENSITÉ: 0

ZONE 2

- SUBSTRAT: fond rocheux (boulders)
- DENSITÉ: 1

Alisma gramineum (d) Valisneria americana Elodea americana	Alisma graminoïde Valisnérie américaine Élodée américaine

ZONE 3

- SUBSTRAT: sable et roches
- DENSITÉ: 2

Valisneria americana (cd) Heteranthera dubia (cd) Alisma gramineum Ceratophyllum demersum	Valisnérie américaine Hétéranthère litigieuse Alisma graminoïde Cornifle nageante

FICHE DE TERRAIN

HERBIERS AQUATIQUES

ÎLE-AUX-CHATS, LAC SAINT-FRANÇOIS

SECTION: 10 (P11)

ZONE 1: inexistante

- SUBSTRAT: fond rocheux (boulders)
- DENSITÉ: 0

ZONE 2

- SUBSTRAT: fond rocheux (boulders), profondeur ± 1.5 m
- DENSITÉ: 1

Valisneria americana (d) Alisma gramineum	Valisnérie américaine Alisma graminoïde

ZONE 3

- SUBSTRAT: fond rocheux (boulders) et sablonneux, profondeur > 1.5 m
- DENSITÉ: 3

Chara (cd) Valisneria americana (cd) Potamogeton bupleuroides Potamogeton sp	Chara Valisnérie américaine Potamot faux-buplèvre Potamot sp

FICHE DE TERRAIN

HERBIERS AQUATIQUES

ÎLE-AUX-CHATS, LAC SAINT-FRANÇOIS

SECTION: 11 (P13)

ZONE 1

- SUBSTRAT: pyrite de fer
- DENSITÉ: 1

Phragmites communis Typha angustifolia (d)	Roseau commun Typha à feuilles étroites

ZONE 2

- SUBSTRAT: pyrite de fer
- DENSITÉ: 1

Valisneria americana (cd) Alisma gramineum (cd) Ceratophyllum demersum Potamogeton pusillum	Valisnérie américaine Alisma graminoide Cornifle nageante Potamot nain

ZONE 3

- SUBSTRAT: pyrite de fer
- DENSITÉ: 3

Valisneria americana (cd) Chara (cd)	Valisnérie américaine Chara

FICHE DE TERRAIN

HERBIERS AQUATIQUES

ÎLE-AUX-CHATS, LAC SAINT-FRANÇOIS

SECTION: 12 (P12)

ZONE 1: herbier situé au large

- SUBSTRAT: pyrite de fer, profondeur ± 0.7 m
- DENSITÉ: 2

Scirpus validus (cd) Valisneria americana Typha angustifolia (cd)	Scirpe vigoureux Valisnérie américaine Typha à feuilles étroites

ZONE 2

- SUBSTRAT: pyrite de fer, profondeur de 0.7 à 1.2 m
- DENSITÉ: 2

Valisneria americana (d) Ceratophyllum demersum	Valisnérie américaine Cornifle nageante

ZONE 3

- SUBSTRAT: Pyrite de fer, profondeur > 1.2 m
- DENSITÉ: 3

Valisneria americana (d) Potamogeton pusillum	Valisnérie américaine Potamot nain

FICHE DE TERRAIN

HERBIERS AQUATIQUES

ÎLE-AUX-CHATS, LAC SAINT-FRANÇOIS

SECTION: 13 (P14)

ZONE 1

- SUBSTRAT: pyrite de fer
- DENSITÉ: 3

Typha latifolia (cd) Carex canescens Scirpus validus (cd)	Typha à feuilles larges Carex blanchâtre Scirpe vigoureux

ZONE 2

- SUBSTRAT: fond silteux, présence de pyrite, eau turbide
- DENSITÉ: 2

Valisneria americana (d)	Valisnérie américaine

ZONE 3

- SUBSTRAT: fond silteux, présence de pyrite, eau turbide
- DENSITÉ: 3

Valisneria americana (d) Ceratophyllum demersum (sd) Potamogeton bupleuroides Potamogeton pusillum	Valisnérie américaine Cornifle nageante Potamot faux-buplèvre Potamot nain

FICHE DE TERRAIN

HERBIERS AQUATIQUES

ÎLE-AUX-CHATS, LAC SAINT-FRANÇOIS

SECTION: 14 (P15)

ZONE 1

- SUBSTRAT: fond silteux, présence de pyrite de fer, eau noire, turbide, profondeur < 1 m
- DENSITÉ: 3

Scirpus validus (cd)	Scirpe vigoureux
Eleocharis Smallii (cd)	Éléocharide de Small
Equisetum fluviatile (cd)	Prêle fluviatile
Typha angustifolia	Typha à feuilles larges
Sagittaria latifolia	Sagittaire latifolié
Sagittaria cuneata	Sagittaire cunéaire
Nymphaea odorata (cd)	Nymphéa odorante
Potamogeton Illinoensis	Potamot de l'Illinois
Valisneria americana	Valisnérie américaine
Elodea canadensis	Élodée du Canada
Myriophyllum exalbescens	Myriophylle blanchissant
Najas flexilis	Naïas souple

ZONE 2

- SUBSTRAT: fond silteux, présence de pyrite, eau turbide, profondeur > 1 m
- DENSITÉ: 3

Valisneria americana (d)	Valisnérie américaine
Ceratophyllum demersum	Cornifle nageante
Potamogeton Illinoensis	Potamot de l'Illinois

ZONE 3

- SUBSTRAT: fond silteux, présence de pyrite de fer
- DENSITÉ: 3 à 4

Valisneria americana (cd)	Valisnérie américaine
Chara (cd)	Chara
Potamogeton bupleuroides	Potamot faux-buplèvre
Ceratophyllum demersum	Cornifle nageante

FICHE DE TERRAIN

HERBIERS AQUATIQUES

ÎLE-AUX-CHATS, LAC SAINT-FRANÇOIS

SECTION: 15 (P16)

ZONE 1

- SUBSTRAT: limon et argile
- DENSITÉ: 4

Typha angustifolia (d)	Typha à feuilles larges
Scirpus validus	Scirpe vigoureux
Eleochasis Smallii	Éléocharide de Small
Carex canescens	Carex blanchâtre
Sagittaria latifolia	Sagittaire latifoliée
Sagittaria graminea	Sagittaria graminoïde

ZONE 2

- SUBSTRAT: limon et argile
- DENSITÉ: 3 à 4

Valisneria americana (cd)	Valisnérie américaine
Alisma gramineum (cd)	Alisma graminoïde
Chara (cd)	Chara
Heteranthera dubia	Hétéranthère litigieuse
Elodea canadensis	Élodée du Canada
Nymphaea odorata (cd)	Nymphéa odorant
Ceratophyllum demersum	Cornifle nageante

ZONE 3

- SUBSTRAT: limon et argile
- DENSITÉ: 3 à 4

Valisneria americana (cd)	Valisnérie américaine
Alisma gramineum (cd)	Alisma graminoïde
Chara (cd)	Chara
Heteranthera dubia	Hétéranthère litigieuse
Elodea canadensis	Élodée du Canada
Ceratophyllum demersum	Cornifle nageante

FICHE DE TERRAIN

HERBIERS AQUATIQUES

ÎLE-AUX-CHATS, LAC SAINT-FRANÇOIS

SECTION: 16 (P17, P18)

ZONE 1

- SUBSTRAT: limon-argile, profondeur < 0.6 m
- DENSITÉ: 3

Typha latifolia (cd)	Typha à feuilles larges
Typha angustifolia (cd)	Typha à feuilles étroites
Sagittaria graminea	Sagittaire graminoïde
Sparganium eurycarpum (cd)	Rubanier à gros fruits

ZONE 2

- SUBSTRAT: limon-argile, profondeur > 0.6 m
- DENSITÉ: 4

Valisneria americana (cd)	Valisnérie américaine
Chara (cd)	Chara
Elodea canadensis	Élodée du Canada
Alisma gramineum	Alisma graminoïde
Ceratophyllum demersum	Cornifle nageante
Myriophyllum exalbescens	Myriophylle blanchissant
Potamogeton bupleuroides	Potamot faux-buplèvre
Potamogeton illinoensis	Potamot de l'Illinois

ZONE 3

- SUBSTRAT: donnée manquante
- DENSITÉ: 4

Valisneria americana (cd)	Valisnérie américaine
Chara (cd)	Chara
Elodea canadensis	Élodée du Canada
Alisma gramineum	Alisma graminoïde
Ceratophyllum demersum	Cornifle nageante
Potamogeton natans	Potamot flottant
Potamogeton gramineus	Potamot graminoïde

FICHE DE TERRAIN

HERBIERS AQUATIQUES

ÎLE-AUX-CHATS, LAC SAINT-FRANÇOIS

SECTION: 17 (P19-P21)

ZONE 1

- SUBSTRAT: sable limoneux avec roches
- DENSITÉ: 4

Sparganium eurycarpum (cd)	Rubanier à gros fruits
Typha latifolia	Typha à larges feuilles
Sagittaria graminea	Sagittaire graminoïde
Valisneria americana	Valisnérie américaine
Elodea canadensis	Élodée du Canada
Najas flexilis	Naïas souple
Scirpus validus (cd)	Scirpe vigoureux

ZONE 2

- SUBSTRAT: sable limoneux avec roches
- DENSITÉ: 4

Valisneria americana (cd)	Valisnérie américaine
Chara (cd)	Chara
Nymphaea odorata (cd)	Nymphéa odorant
Elodea canadensis	Élodée du Canada
Alisma gramineum (cd)	Alisma graminoïde
Ceratophyllum demersum	Cornifle nageante
Myriophyllum exalbescens	Myriophylle blanchissant

ZONE 3

- SUBSTRAT: sable limoneux avec roches
- DENSITÉ: 4

Valisneria americana (cd)	Valisnérie américaine
Chara (cd)	Chara
Elodea canadensis	Élodée du Canada
Alisma gramineum	Alisma graminoïde
Ceratophyllum demersum	Cornifle nageante
Potamogeton natans	Potamot flottant
Potamogeton gramineus	Potamot graminoïde

FICHE DE TERRAIN

HERBIERS AQUATIQUES

ÎLE-AUX-CHATS, LAC SAINT-FRANÇOIS

SECTION: 18 (P22)

ZONE 1: inexistante

- SUBSTRAT: remblaie rocheux
- DENSITÉ: 0

ZONE 2: inexistante

- SUBSTRAT: remblaie rocheux
- DENSITÉ: 0

ZONE 3

- SUBSTRAT: sable et roches
- DENSITÉ: 3

Chara (cd) Valisneria americana (cd)	Chara Valisnérie américaine

FICHE DE TERRAIN

HERBIERS AQUATIQUES

ÎLE-AUX-CHATS, LAC SAINT-FRANÇOIS

SECTION: 19 (P23-P27)

ZONE 1: inexistante

- SUBSTRAT: fond rocheux
- DENSITÉ: 0

ZONE 2

- SUBSTRAT: sable et roches, profondeur 0.3 à 1.3 m
- DENSITÉ: 3

Valisneria americana (cd)	Valisnérie américaine
Chara (cd)	Chara
Elodea canadensis	Élodée du Canada
Myriophyllum exalbescens	Myriophylle blanchissant
Ceratophyllum demersum	Cornifle nageante

ZONE 3

- SUBSTRAT: sable et roches, profondeur > 1.3 m
- DENSITÉ: 3

Valisneria americana (cd)	Valisnérie américaine
Chara (cd)	Chara
Potamogeton gramineus	Potamot graminoïde
Potamogeton pusillum	Potamot nain
Elodea canadensis	Élodée du Canada
Ceratophyllum demersum	Cornifle nageante

FICHE DE TERRAIN

HERBIERS AQUATIQUES

ÎLE-AUX-CHATS, LAC SAINT-FRANÇOIS

SECTION: 20

ZONE 1 et 2: inexistantes

- SUBSTRAT: fond rocheux, pente abrupte
- DENSITÉ: 0

ZONE 3

- SUBSTRAT: sable et roche, profondeur ± 2 m
- DENSITÉ: 3

Valisneria americana (cd)	Vallisnérie américaine
Chara (cd)	Chara
Elodea canadensis	Élodée du Canada
Heteranthera dubia	Hétéranthère litigieuse
Ceratophyllum demersum	Cornifle nageante
Potamogeton gramineus	Potamot graminoïde

Liste des espèces de poissons capturés autour de l'île aux Chats au cours de l'automne 1996

Espèce	Nom latin	Nom commun	Mode de capture			Secteur			
						sud	1	3	2
AMRU	Ambloplites rupestris	crapet de roche	P-E	S	F-M	x	x	x	x
ANRO	Anguilla rostrata	anguille d'amérique	P-E			x	x	x	
CACO	Catostomus commersoni	meunier noir	P-E	S	F-M	x	x	x	x
CUIN	Culaea inconstans	épinoche à cinq épines	S					x	
CYCA	Cyprinus carpio	carpe allemande	P-E					x	
ESLU	Esox lucius	grand brochet	P-E	S	F-M	x	x	x	x
ESMA	Esox masquinogy	masquinongé	P-E				x		
ETNI	Etheostoma nigrum	raseux-de-terre	P-E	S		x	x	x	x
FUDI	Fundulus diaphanus	fondule barré	S			x	x	x	x
ICNE	Ichtalurus nebulosus	barbotte brune	P-E	F-M				x	
ICPU	Ichtalurus punctatus	barbue de rivière	P-E	S				x	
LASI	Lapidesthes sicculus	crayon d'argent	S			x		x	x
LEGI	Lepomis gibbosus	crapet soleil	P-E	S	F-M	x	x	x	x
MIDO	Micropterus dolomieu	achigan à petite bouche	P-E	S				x	x
MISA	Micropterus salmoides	achigan à grande bouche	P-E	S	F-M	x		x	
NOAT	Notropis atterinoides	méné émeraude	S			x	x		
NOCR	Notemigonus chrysoleucas	chatte de l'est	P-E	S	F-M	x	x	x	
NOHU	Notropis hudsonius	queue à tache noire	S					x	
PEFL	Perca flavescens	perchaude	P-E	S	F-M	x	x	x	x
PEMA	Petromizon marinus	lamproie marine	F-M					x	
PINO	Pimephales notatus	ventre-pourri	P-E	S		x	x	x	x
PONI	Pomoxis nigromaculatus	marigane noire	P-E					x	
			Nombre d'espèce (total : 22)			13	14	20	10

P-E : pêche électrique
S : seine
F-M : filet maillant

Activités de pêche réalisés autour de l'île aux Chats et quelques sites de référence durant l'automne 1996

Date de pose	Station	Localisation	Code engin	Profondeur (m)	Effort (sec.)	Remarque
96-09-26	P16	Secteur III	Électrique	1	113	100 m
96-09-26	P17	Secteur III	Électrique	1	187	100 m
96-09-26	P18	Secteur III	Électrique	1	150	100 m
96-09-26	P19	Secteur III	Électrique	1	168	100 m
96-09-26	P21	Secteur III	Électrique	1	177	130 m
96-09-26	S09	Secteur I	Seine	1	-	12 m
96-09-26	S09	Secteur I	Seine	1	-	12 m
96-09-26	S10	Secteur III	Seine	1	-	15 m
96-09-26	S10	Secteur III	Seine	1.5	-	15 m
96-09-26	S11	Secteur III	Seine	1.5	-	15 m
96-09-26	S11	Secteur III	Seine	1.5	-	15 m
96-09-27	BG01	Pte aux Brodeurs	Électrique	1	356	-
96-09-27	BG02	Coteau Landing	Électrique	1	1346	-
96-09-27	BG03	Ile Lalonde	Électrique	1	1024	-
96-09-27	BG04	Ile Longueuil	Électrique	1	1265	-
96-09-27	BG05	Ile Grosse Pointe	Électrique	0	820	-
96-09-27	P16	Secteur I	Électrique	0.75	134	125 m
96-09-27	P17	Secteur III	Électrique	0.75	157	125 m
96-09-27	P18	Secteur III	Électrique	0.75	129	125 m
96-09-27	P19	Secteur III	Électrique	1	132	125 m
96-09-27	P20	Secteur III	Électrique	1	135	125 m
96-09-27	P21	Secteur III	Électrique	1	122	125 m
96-09-27	P22	Secteur III	Électrique	1.25	319	500 m
96-09-27	P23	Secteur II	Électrique	1.25	196	200 m
96-09-27	P24	Secteur II	Électrique	1.5	242	200 m
96-09-27	P25	Secteur II	Électrique	1.5	330	200 m
96-09-27	P26	Secteur II	Électrique	1.5	178	200 m
96-09-27	P27	Secteur II	Électrique	1.5	225	200 m
96-09-28	BG06	Pointe Mouillée	Électrique	0.75	400	200 m
96-09-28	BG06	Pointe Mouillée	Seine	1	-	2 coups de seine
96-09-28	BG07	Pointe Mouillée	Électrique	0.75	400	200 m
96-09-28	BG07	Pointe Mouillée	Seine	1	-	2 coups de seine
96-09-28	BG08	Pointe Mouillée	Électrique	0.75	400	100 m
96-09-28	BG08	Pointe Mouillée	Seine	1	-	2 coups de seine
96-09-28	BG09	Pointe Mouillée	Électrique	1.25	1700	500 m
96-09-28	BG10	Pointe Mouillée	Électrique	1.25	1200	500 m
96-09-30	P01	Secteur Sud	Électrique	2.5	253	200 m
96-09-30	P02	Secteur Sud	Électrique	1	155	100 m
96-09-30	P03	Secteur Sud	Électrique	1	145	100 m
96-09-30	P04	Secteur Sud	Électrique	1	246	150 m
96-09-30	P05	Secteur Sud	Électrique	0.75	94	100 m
96-09-30	P06	Secteur Sud	Électrique	1.25	175	100 m
96-09-30	P07	Secteur Sud	Électrique	1.5	237	150 m
96-09-30	P09	Secteur Sud	Électrique	1	60	50 m
96-09-30	P10	Secteur I	Électrique	1.5	130	70 m
96-09-30	P11	Secteur I	Électrique	1.5	211	100 m
96-09-30	P12	Secteur I	Électrique	0.75	98	25 m
96-09-30	P13	Secteur I	Électrique	0.75	140	150 m
96-09-30	P14	Secteur I	Électrique	1.25	297	150 m
96-09-30	P15	Secteur I	Électrique	1	250	150 m
96-09-30	S12	Secteur II	Seine	1.25	-	15 m
96-09-30	S12	Secteur II	Seine	1.25	-	15 m
96-09-30	S13	Secteur II	Seine	2	-	15 m
96-09-30	S14	Secteur II	Seine	3	-	10 m

Activités de pêche réalisés autour de l'île aux Chats et quelques sites de référence durant l'automne 1996

Date de pose	Station	Localisation	Code engin	Profondeur (m)	Effort (sec.)	Remarque
96-09-30	S15	Secteur II	Seine	2	-	10 m
96-10-01	F01	Secteur III	Filet maillant	7	28 hres	-
96-10-01	F01	Secteur III	Filet maillant	7	27 hres	-
96-10-01	F02	Secteur IV	Filet maillant	6	31 hres	-
96-10-01	F02	Secteur IV	Filet maillant	6	30 hres	-
96-10-02	F03	Secteur IV	Filet maillant	4.5	18 hres	-
96-10-02	F03	Secteur IV	Filet maillant	4.5	18 hres	-
96-10-02	F04	Secteur IV	Filet maillant	4.5	17 hres	-
96-10-02	F04	Secteur IV	Filet maillant	4.5	16 hres	-
96-10-04	S01	Secteur Sud	Seine	3.5	-	8 m
96-10-04	S01	Secteur Sud	Seine	3.5	-	8 m
96-10-04	S02	Secteur Sud	Seine	0.8	-	15 m
96-10-04	S02	Secteur Sud	Seine	0.8	-	15 m
96-10-04	S03	Secteur Sud	Seine	0.6	-	15 m
96-10-04	S03	Secteur Sud	Seine	0.8	-	20 m
96-10-04	S04	Secteur Sud	Seine	1	-	8 m
96-10-04	S04	Secteur Sud	Seine	0.5	-	10 m
96-10-04	S05	Secteur Sud	Seine	1	-	10 m
96-10-04	S05	Secteur Sud	Seine	1	-	15 m
96-10-04	S06	Secteur I	Seine	2	-	15 m
96-10-04	S06	Secteur I	Seine	1	-	15 m
96-10-04	S07	Secteur I	Seine	0.6	-	20 m
96-10-04	S07	Secteur I	Seine	0.6	-	20 m
96-10-04	S08	Secteur I	Seine	0.3	-	15 m
96-10-04	S08	Secteur I	Seine	0.4	-	15 m

Annexe 2

Données brutes des pêches réalisées autour de l'Île aux Chats
au début de l'automne 1996

Longueur des poissons capturés autour de l'île au Chat durant l'automne 1996

Station	Engin	Espèce	Nombre	Longueur (mm)
F01	Fillet maillant	CACO	1	437
F01	Fillet maillant	ESLU	1	345
F01	Fillet maillant	ESLU	1	420
F01	Fillet maillant	ESLU	1	426
F01	Fillet maillant	ESLU	1	435
F01	Fillet maillant	ESLU	1	440
F01	Fillet maillant	ESLU	1	482
F01	Fillet maillant	ESLU	1	483
F01	Fillet maillant	ESLU	1	490
F01	Fillet maillant	ESLU	1	496
F01	Fillet maillant	ESLU	1	514
F01	Fillet maillant	ESLU	1	533
F01	Fillet maillant	ESLU	1	620
F01	Fillet maillant	ESLU	1	660
F01	Fillet maillant	ESLU	1	695
F01	Fillet maillant	ESLU	1	745
F01	Fillet maillant	ICNE	1	222
F01	Fillet maillant	ICNE	1	243
F01	Fillet maillant	LEGI	1	111
F01	Fillet maillant	LEGI	1	140
F01	Fillet maillant	LEGI	1	140
F01	Fillet maillant	LEGI	1	143
F01	Fillet maillant	LEGI	1	195
F01	Fillet maillant	MISA	1	185
F01	Fillet maillant	NOCR	1	106
F01	Fillet maillant	NOCR	1	106
F01	Fillet maillant	PEFL	49	100
F01	Fillet maillant	PEFL	26	105
F01	Fillet maillant	PEFL	1	115
F01	Fillet maillant	PEFL	1	115
F01	Fillet maillant	PEFL	1	117
F01	Fillet maillant	PEFL	1	117
F01	Fillet maillant	PEFL	1	117
F01	Fillet maillant	PEFL	1	117
F01	Fillet maillant	PEFL	17	150
F01	Fillet maillant	PEFL	1	150
F01	Fillet maillant	PEFL	26	160
F01	Fillet maillant	PEFL	1	165
F01	Fillet maillant	PEFL	1	165
F01	Fillet maillant	PEFL	1	165
F01	Fillet maillant	PEFL	1	175
F01	Fillet maillant	PEFL	1	175
F01	Fillet maillant	PEFL	1	175
F01	Fillet maillant	PEFL	1	176
F01	Fillet maillant	PEFL	1	180
F01	Fillet maillant	PEFL	1	180
F01	Fillet maillant	PEFL	1	180
F01	Fillet maillant	PEFL	1	180
F01	Fillet maillant	PEFL	1	185
F01	Fillet maillant	PEFL	18	200
F01	Fillet maillant	PEFL	1	205
F01	Fillet maillant	PEFL	1	205
F01	Fillet maillant	PEFL	1	205
F01	Fillet maillant	PEFL	1	212
F01	Fillet maillant	PEFL	1	250
F01	Fillet maillant	PEFL	1	272
F02	Fillet maillant	ESLU	1	430

Longueur des poissons capturés autour de l'île au Chat durant l'automne 1996

Station	Engin	Espèce	Nombre	Longueur (mm)
F02	Fillet maillant	ESLU	1	470
F02	Fillet maillant	ESLU	1	490
F02	Fillet maillant	ESLU	1	517
F02	Fillet maillant	ESLU	1	520
F02	Fillet maillant	ESLU	1	528
F02	Fillet maillant	ESLU	1	595
F02	Fillet maillant	ESLU	1	620
F02	Fillet maillant	ESLU	1	680
F02	Fillet maillant	ESLU	1	760
F02	Fillet maillant	ESLU	1	760
F02	Fillet maillant	ESLU	1	760
F02	Fillet maillant	LEGI	1	116
F02	Fillet maillant	LEGI	1	153
F02	Fillet maillant	LEGI	1	220
F02	Fillet maillant	PEFL	20	100
F02	Fillet maillant	PEFL	13	105
F02	Fillet maillant	PEFL	1	110
F02	Fillet maillant	PEFL	1	110
F02	Fillet maillant	PEFL	1	110
F02	Fillet maillant	PEFL	1	120
F02	Fillet maillant	PEFL	1	120
F02	Fillet maillant	PEFL	1	120
F02	Fillet maillant	PEFL	36	140
F02	Fillet maillant	PEFL	11	155
F02	Fillet maillant	PEFL	1	165
F02	Fillet maillant	PEFL	1	165
F02	Fillet maillant	PEFL	1	165
F02	Fillet maillant	PEFL	1	165
F02	Fillet maillant	PEFL	1	170
F02	Fillet maillant	PEFL	1	185
F02	Fillet maillant	PEFL	1	185
F02	Fillet maillant	PEFL	1	185
F02	Fillet maillant	PEFL	1	185
F02	Fillet maillant	PEFL	1	190
F02	Fillet maillant	PEFL	1	190
F02	Fillet maillant	PEFL	1	190
F02	Fillet maillant	PEFL	1	190
F02	Fillet maillant	PEFL	1	195
F02	Fillet maillant	PEFL	1	195
F02	Fillet maillant	PEFL	1	195
F02	Fillet maillant	PEFL	1	195
F02	Fillet maillant	PEFL	1	195
F02	Fillet maillant	PEFL	1	205
F02	Fillet maillant	PEFL	1	215
F02	Fillet maillant	PEFL	1	235
F02	Fillet maillant	PEMA	1	200
F03	Fillet maillant	AMRU	1	137
F03	Fillet maillant	AMRU	1	150
F03	Fillet maillant	AMRU	1	166
F03	Fillet maillant	CACO	1	420
F03	Fillet maillant	PEFL	1	100
F03	Fillet maillant	PEFL	1	100
F03	Fillet maillant	PEFL	1	135
F03	Fillet maillant	PEFL	1	180
F03	Fillet maillant	PEFL	1	194
F03	Fillet maillant	PEFL	1	223
F03	Fillet maillant	PEFL	1	255

Longueur des poissons capturés autour de l'île au Chat durant l'automne 1996

Station	Engin	Espèce	Nombre	Longueur (mm)
F03	Fillet maillant	PEFL	1	260
F03	Fillet maillant	PEFL	1	273
F04	Fillet maillant	AMRU	1	124
F04	Fillet maillant	AMRU	1	135
F04	Fillet maillant	AMRU	1	145
F04	Fillet maillant	ESLU	1	425
F04	Fillet maillant	ESLU	1	425
F04	Fillet maillant	ESLU	1	425
F04	Fillet maillant	ESLU	1	440
F04	Fillet maillant	ESLU	1	465
F04	Fillet maillant	ESLU	1	465
F04	Fillet maillant	ESLU	1	465
F04	Fillet maillant	ESLU	1	490
F04	Fillet maillant	ESLU	1	490
F04	Fillet maillant	ESLU	1	510
F04	Fillet maillant	ESLU	1	510
F04	Fillet maillant	ESLU	1	515
F04	Fillet maillant	ESLU	1	660
F04	Fillet maillant	ESLU	1	685
F04	Fillet maillant	PEFL	12	100
F04	Fillet maillant	PEFL	1	115
F04	Fillet maillant	PEFL	1	120
F04	Fillet maillant	PEFL	1	120
F04	Fillet maillant	PEFL	1	120
F04	Fillet maillant	PEFL	1	155
F04	Fillet maillant	PEFL	1	175
F04	Fillet maillant	PEFL	1	175
F04	Fillet maillant	PEFL	1	190
F04	Fillet maillant	PEFL	1	190
F04	Fillet maillant	PEFL	1	190
F04	Fillet maillant	PEFL	1	195
F04	Fillet maillant	PEFL	1	195
F04	Fillet maillant	PEFL	1	220
BG09	Pêche électrique	ESLU	1	400
BG10	Pêche électrique	ESLU	1	500
BG09	Pêche électrique	ESLU	1	600
BG08	Pêche électrique	ICPU	1	100
BG08	Pêche électrique	ICPU	1	100
BG08	Pêche électrique	ICPU	1	100
BG08	Pêche électrique	ICPU	1	100
BG06	Pêche électrique	LEGI	1	85
BG06	Pêche électrique	LEGI	1	85
BG06	Pêche électrique	LEGI	1	85
BG07	Pêche électrique	LEGI	1	100
BG08	Pêche électrique	LEGI	1	200
BG08	Pêche électrique	LEGI	1	200
BG08	Pêche électrique	LEGI	1	200
BG08	Pêche électrique	LEGI	1	200
BG08	Pêche électrique	LEGI	1	200
BG08	Pêche électrique	LEGI	1	200
BG06	Pêche électrique	MISA	1	70
BG06	Pêche électrique	MISA	1	70
BG08	Pêche électrique	MISA	1	75
BG08	Pêche électrique	MISA	1	75
BG08	Pêche électrique	MISA	1	75
BG08	Pêche électrique	MISA	1	75
BG08	Pêche électrique	MISA	1	75

Longueur des poissons capturés autour de l'île au Chat durant l'automne 1996

Station	Engin	Espèce	Nombre	Longueur (mm)
BG08	Pêche électrique	MISA	1	75
BG08	Pêche électrique	MISA	1	75
BG08	Pêche électrique	MISA	1	75
BG08	Pêche électrique	MISA	1	75
BG08	Pêche électrique	MISA	1	75
BG08	Pêche électrique	MISA	1	75
BG08	Pêche électrique	MISA	1	75
BG08	Pêche électrique	MISA	1	75
BG08	Pêche électrique	MISA	1	75
BG08	Pêche électrique	MISA	1	75
BG07	Pêche électrique	MISA	1	80
BG07	Pêche électrique	MISA	1	80
BG07	Pêche électrique	MISA	1	175
BG07	Pêche électrique	MISA	1	175
BG07	Pêche électrique	MISA	1	175
BG06	Pêche électrique	MISA	1	230
BG06	Pêche électrique	MISA	1	230
BG06	Pêche électrique	MISA	1	230
BG06	Pêche électrique	MISA	1	230
BG08	Pêche électrique	MISA	1	300
BG08	Pêche électrique	PEFL	1	125
BG08	Pêche électrique	PEFL	1	125
BG08	Pêche électrique	PEFL	1	125
BG06	Pêche électrique	PEFL	1	150
P22	Pêche électrique	AMRU	1	90
P21	Pêche électrique	AMRU	1	101
P21	Pêche électrique	AMRU	1	104
P25	Pêche électrique	AMRU	1	112
P21	Pêche électrique	AMRU	1	120
P22	Pêche électrique	AMRU	1	120
P21	Pêche électrique	AMRU	1	125
P25	Pêche électrique	AMRU	1	125
P25	Pêche électrique	AMRU	1	128
P17	Pêche électrique	AMRU	1	134
P21	Pêche électrique	AMRU	1	146
P21	Pêche électrique	AMRU	1	153
P01	Pêche électrique	AMRU	1	164
P19	Pêche électrique	AMRU	1	164
P24	Pêche électrique	AMRU	1	166
P22	Pêche électrique	AMRU	1	170
P17	Pêche électrique	AMRU	1	192
P25	Pêche électrique	AMRU	1	195
P11	Pêche électrique	ANRO	1	650
P12	Pêche électrique	ANRO	1	680
P19	Pêche électrique	ANRO	1	712
P16	Pêche électrique	ANRO	1	725
P05	Pêche électrique	ANRO	1	750
P08	Pêche électrique	ANRO	1	815
P27	Pêche électrique	CACO	1	95
P17	Pêche électrique	CACO	1	256
P20	Pêche électrique	CACO	1	290
P26	Pêche électrique	CACO	1	550
P17	Pêche électrique	CYCA	1	82
P02	Pêche électrique	ESLU	1	126
P14	Pêche électrique	ESLU	1	365
P12	Pêche électrique	ESLU	1	371
P27	Pêche électrique	ESLU	1	510

Longueur des poissons capturés autour de l'île au Chat durant l'automne 1996

Station	Engin	Espèce	Nombre	Longueur (mm)
P25	Pêche électrique	ESLU	1	725
P16	Pêche électrique	ESMA	1	159
P21	Pêche électrique	ETNI	1	57
P17	Pêche électrique	ETNI	1	66
P21	Pêche électrique	ETNI	1	71
P21	Pêche électrique	ETNI	1	74
P21	Pêche électrique	ETNI	1	75
P18	Pêche électrique	ETNI	1	76
P26	Pêche électrique	ETNI	1	80
P17	Pêche électrique	ICNE	1	65
P20	Pêche électrique	ICNE	1	145
P23	Pêche électrique	ICNE	1	175
P19	Pêche électrique	ICPU	1	66
P20	Pêche électrique	LEGI	1	36
P18	Pêche électrique	LEGI	1	60
P17	Pêche électrique	LEGI	1	64
P21	Pêche électrique	LEGI	1	64
P21	Pêche électrique	LEGI	1	64
P21	Pêche électrique	LEGI	1	65
P19	Pêche électrique	LEGI	1	66
P19	Pêche électrique	LEGI	1	66
P21	Pêche électrique	LEGI	1	66
P22	Pêche électrique	LEGI	1	68
P21	Pêche électrique	LEGI	1	70
P21	Pêche électrique	LEGI	1	70
P21	Pêche électrique	LEGI	1	70
P17	Pêche électrique	LEGI	1	71
P17	Pêche électrique	LEGI	1	72
P20	Pêche électrique	LEGI	1	72
P19	Pêche électrique	LEGI	1	74
P21	Pêche électrique	LEGI	1	75
P22	Pêche électrique	LEGI	1	75
P22	Pêche électrique	LEGI	1	75
P21	Pêche électrique	LEGI	1	76
P19	Pêche électrique	LEGI	1	77
P22	Pêche électrique	LEGI	1	77
P17	Pêche électrique	LEGI	1	78
P17	Pêche électrique	LEGI	1	79
P19	Pêche électrique	LEGI	1	79
P02	Pêche électrique	LEGI	1	83
P20	Pêche électrique	LEGI	1	96
P23	Pêche électrique	LEGI	1	98
P24	Pêche électrique	LEGI	1	98
P01	Pêche électrique	LEGI	1	110
P02	Pêche électrique	LEGI	1	112
P23	Pêche électrique	LEGI	1	115
P21	Pêche électrique	LEGI	1	120
P23	Pêche électrique	LEGI	1	120
P23	Pêche électrique	LEGI	1	120
P02	Pêche électrique	LEGI	1	125
P17	Pêche électrique	LEGI	1	125
P19	Pêche électrique	LEGI	1	126
P02	Pêche électrique	LEGI	1	130
P06	Pêche électrique	LEGI	1	130
P17	Pêche électrique	LEGI	1	131
P02	Pêche électrique	LEGI	1	132
P06	Pêche électrique	LEGI	1	134

Longueur des poissons capturés autour de l'île au Chat durant l'automne 1996

Station	Engin	Espèce	Nombre	Longueur (mm)
P21	Pêche électrique	LEGI	1	134
P22	Pêche électrique	LEGI	1	135
P21	Pêche électrique	LEGI	1	136
P06	Pêche électrique	LEGI	1	137
P19	Pêche électrique	LEGI	1	137
P18	Pêche électrique	LEGI	1	139
P19	Pêche électrique	LEGI	1	140
P21	Pêche électrique	LEGI	1	140
P21	Pêche électrique	LEGI	1	140
P23	Pêche électrique	LEGI	1	140
P23	Pêche électrique	LEGI	1	140
P14	Pêche électrique	LEGI	1	141
P19	Pêche électrique	LEGI	1	141
P19	Pêche électrique	LEGI	1	142
P06	Pêche électrique	LEGI	1	145
P06	Pêche électrique	LEGI	1	145
P06	Pêche électrique	LEGI	1	148
P06	Pêche électrique	LEGI	1	148
P06	Pêche électrique	LEGI	1	150
P06	Pêche électrique	LEGI	1	150
P06	Pêche électrique	LEGI	1	150
P19	Pêche électrique	LEGI	1	150
P23	Pêche électrique	LEGI	1	155
P14	Pêche électrique	LEGI	1	156
P01	Pêche électrique	LEGI	1	158
P10	Pêche électrique	LEGI	1	158
P06	Pêche électrique	LEGI	1	170
P23	Pêche électrique	LEGI	1	172
P06	Pêche électrique	LEGI	1	189
P06	Pêche électrique	LEGI	1	190
P06	Pêche électrique	LEGI	1	191
P01	Pêche électrique	LEGI	1	210
P27	Pêche électrique	MIDO	1	420
P23	Pêche électrique	MISA	1	45
P18	Pêche électrique	MISA	1	85
P22	Pêche électrique	MISA	1	147
P08	Pêche électrique	MISA	1	189
P01	Pêche électrique	MISA	1	230
P01	Pêche électrique	MISA	1	237
P06	Pêche électrique	NOCR	1	65
P20	Pêche électrique	NOCR	1	86
P02	Pêche électrique	NOCR	1	87
P23	Pêche électrique	PEFL	1	60
P05	Pêche électrique	PEFL	1	80
P27	Pêche électrique	PEFL	1	81
P22	Pêche électrique	PEFL	1	83
P01	Pêche électrique	PEFL	1	86
P02	Pêche électrique	PEFL	1	91
P20	Pêche électrique	PEFL	1	92
P25	Pêche électrique	PEFL	1	92
P17	Pêche électrique	PEFL	1	94
P19	Pêche électrique	PEFL	1	94
P20	Pêche électrique	PEFL	1	94
P17	Pêche électrique	PEFL	1	95
P21	Pêche électrique	PEFL	1	95
P21	Pêche électrique	PEFL	1	95
P21	Pêche électrique	PEFL	1	95

Longueur des poissons capturés autour de l'île au Chat durant l'automne 1996

Station	Engin	Espèce	Nombre	Longueur (mm)
P19	Pêche électrique	PEFL	1	96
P20	Pêche électrique	PEFL	1	96
P20	Pêche électrique	PEFL	1	96
P21	Pêche électrique	PEFL	1	96
P17	Pêche électrique	PEFL	1	97
P19	Pêche électrique	PEFL	1	97
P22	Pêche électrique	PEFL	1	97
P19	Pêche électrique	PEFL	1	98
P19	Pêche électrique	PEFL	1	98
P17	Pêche électrique	PEFL	1	99
P18	Pêche électrique	PEFL	1	99
P19	Pêche électrique	PEFL	1	99
P19	Pêche électrique	PEFL	1	99
P20	Pêche électrique	PEFL	1	99
P20	Pêche électrique	PEFL	1	99
P21	Pêche électrique	PEFL	1	99
P22	Pêche électrique	PEFL	1	100
P22	Pêche électrique	PEFL	1	100
P27	Pêche électrique	PEFL	1	100
P12	Pêche électrique	PEFL	1	101
P16	Pêche électrique	PEFL	1	101
P18	Pêche électrique	PEFL	1	101
P17	Pêche électrique	PEFL	1	102
P19	Pêche électrique	PEFL	1	102
P19	Pêche électrique	PEFL	1	102
P19	Pêche électrique	PEFL	1	102
P20	Pêche électrique	PEFL	1	102
P26	Pêche électrique	PEFL	1	102
P17	Pêche électrique	PEFL	1	103
P19	Pêche électrique	PEFL	1	103
P19	Pêche électrique	PEFL	1	103
P19	Pêche électrique	PEFL	1	103
P21	Pêche électrique	PEFL	1	103
P19	Pêche électrique	PEFL	1	104
P20	Pêche électrique	PEFL	1	104
P21	Pêche électrique	PEFL	1	104
P21	Pêche électrique	PEFL	1	104
P02	Pêche électrique	PEFL	1	105
P08	Pêche électrique	PEFL	1	105
P16	Pêche électrique	PEFL	1	105
P18	Pêche électrique	PEFL	1	105
P19	Pêche électrique	PEFL	1	105
P21	Pêche électrique	PEFL	1	105
P21	Pêche électrique	PEFL	1	105
P21	Pêche électrique	PEFL	1	105
P21	Pêche électrique	PEFL	1	105
P21	Pêche électrique	PEFL	1	105
P25	Pêche électrique	PEFL	1	105
P19	Pêche électrique	PEFL	1	106
P19	Pêche électrique	PEFL	1	106
P19	Pêche électrique	PEFL	1	106
P20	Pêche électrique	PEFL	1	106
P20	Pêche électrique	PEFL	1	106
P20	Pêche électrique	PEFL	1	106
P20	Pêche électrique	PEFL	1	106
P08	Pêche électrique	PEFL	1	107
P16	Pêche électrique	PEFL	1	107

Longueur des poissons capturés autour de l'île au Chat durant l'automne 1996

Station	Engin	Espèce	Nombre	Longueur (mm)
P19	Pêche électrique	PEFL	1	107
P19	Pêche électrique	PEFL	1	108
P19	Pêche électrique	PEFL	1	108
P19	Pêche électrique	PEFL	1	108
P19	Pêche électrique	PEFL	1	109
P19	Pêche électrique	PEFL	1	109
P20	Pêche électrique	PEFL	1	109
P20	Pêche électrique	PEFL	1	109
P20	Pêche électrique	PEFL	1	109
P21	Pêche électrique	PEFL	1	109
P02	Pêche électrique	PEFL	1	110
P17	Pêche électrique	PEFL	1	110
P19	Pêche électrique	PEFL	1	110
P19	Pêche électrique	PEFL	1	110
P19	Pêche électrique	PEFL	1	110
P21	Pêche électrique	PEFL	1	110
P21	Pêche électrique	PEFL	1	110
P21	Pêche électrique	PEFL	1	110
P21	Pêche électrique	PEFL	1	110
P26	Pêche électrique	PEFL	1	110
P27	Pêche électrique	PEFL	1	110
P17	Pêche électrique	PEFL	1	111
P19	Pêche électrique	PEFL	1	111
P19	Pêche électrique	PEFL	1	111
P21	Pêche électrique	PEFL	1	111
P21	Pêche électrique	PEFL	1	111
P21	Pêche électrique	PEFL	1	111
P02	Pêche électrique	PEFL	1	112
P17	Pêche électrique	PEFL	1	112
P19	Pêche électrique	PEFL	1	112
P19	Pêche électrique	PEFL	1	112
P21	Pêche électrique	PEFL	1	112
P21	Pêche électrique	PEFL	1	112
P02	Pêche électrique	PEFL	1	113
P20	Pêche électrique	PEFL	1	113
P21	Pêche électrique	PEFL	1	113
P14	Pêche électrique	PEFL	1	114
P19	Pêche électrique	PEFL	1	114
P19	Pêche électrique	PEFL	1	114
P20	Pêche électrique	PEFL	1	114
P20	Pêche électrique	PEFL	1	114
P21	Pêche électrique	PEFL	1	114
P01	Pêche électrique	PEFL	1	115
P08	Pêche électrique	PEFL	1	115
P17	Pêche électrique	PEFL	1	115
P19	Pêche électrique	PEFL	1	115
P19	Pêche électrique	PEFL	1	115
P19	Pêche électrique	PEFL	1	115
P20	Pêche électrique	PEFL	1	115
P21	Pêche électrique	PEFL	1	115
P24	Pêche électrique	PEFL	1	115
P25	Pêche électrique	PEFL	1	115
P02	Pêche électrique	PEFL	1	116
P03	Pêche électrique	PEFL	1	116
P20	Pêche électrique	PEFL	1	116
P20	Pêche électrique	PEFL	1	116
P21	Pêche électrique	PEFL	1	116

Longueur des poissons capturés autour de l'île au Chat durant l'automne 1996

Station	Engin	Espèce	Nombre	Longueur (mm)
P21	Pêche électrique	PEFL	1	116
P20	Pêche électrique	PEFL	1	120
P21	Pêche électrique	PEFL	1	120
P22	Pêche électrique	PEFL	1	120
P02	Pêche électrique	PEFL	1	121
P17	Pêche électrique	PEFL	1	121
P21	Pêche électrique	PEFL	1	121
P17	Pêche électrique	PEFL	1	126
P10	Pêche électrique	PEFL	1	128
P21	Pêche électrique	PEFL	1	130
P03	Pêche électrique	PEFL	1	131
P08	Pêche électrique	PEFL	1	131
P10	Pêche électrique	PEFL	1	134
P17	Pêche électrique	PEFL	1	135
P21	Pêche électrique	PEFL	1	135
P20	Pêche électrique	PEFL	1	136
P08	Pêche électrique	PEFL	1	143
P06	Pêche électrique	PEFL	1	144
P17	Pêche électrique	PEFL	1	145
P18	Pêche électrique	PEFL	1	145
P02	Pêche électrique	PEFL	1	146
P21	Pêche électrique	PEFL	1	146
P21	Pêche électrique	PEFL	1	146
P17	Pêche électrique	PEFL	1	149
P05	Pêche électrique	PEFL	1	150
P02	Pêche électrique	PEFL	1	151
P05	Pêche électrique	PEFL	1	152
P19	Pêche électrique	PEFL	1	152
P16	Pêche électrique	PEFL	1	155
P17	Pêche électrique	PEFL	1	155
P17	Pêche électrique	PEFL	1	155
P21	Pêche électrique	PEFL	1	155
P08	Pêche électrique	PEFL	1	156
P21	Pêche électrique	PEFL	1	159
P17	Pêche électrique	PEFL	1	161
P17	Pêche électrique	PEFL	1	164
P06	Pêche électrique	PEFL	1	165
P17	Pêche électrique	PEFL	1	165
P03	Pêche électrique	PEFL	1	167
P03	Pêche électrique	PEFL	1	170
P01	Pêche électrique	PEFL	1	171
P19	Pêche électrique	PEFL	1	171
P18	Pêche électrique	PEFL	1	172
P19	Pêche électrique	PEFL	1	174
P19	Pêche électrique	PEFL	1	174
P17	Pêche électrique	PEFL	1	176
P04	Pêche électrique	PEFL	1	180
P21	Pêche électrique	PEFL	1	182
P03	Pêche électrique	PEFL	1	186
P10	Pêche électrique	PEFL	1	190
P08	Pêche électrique	PEFL	1	193
P02	Pêche électrique	PEFL	1	194
P05	Pêche électrique	PEFL	1	195
P10	Pêche électrique	PEFL	1	196
P17	Pêche électrique	PEFL	1	200
P20	Pêche électrique	PEFL	1	200
P21	Pêche électrique	PEFL	1	200

Longueur des poissons capturés autour de l'île au Chat durant l'automne 1996

Station	Engin	Espèce	Nombre	Longueur (mm)
P20	Pêche électrique	PEFL	1	206
P20	Pêche électrique	PEFL	1	238
P17	Pêche électrique	PEFL	1	304
P23	Pêche électrique	PONI	1	230
S01	Seine	FUDI	1	30
S01	Seine	LASI	1	60
S01	Seine	LASI	1	60
S01	Seine	LASI	1	60
S01	Seine	LASI	1	60
S01	Seine	LASI	1	60
S01	Seine	LASI	1	60
S01	Seine	LASI	1	60
S01	Seine	LASI	1	60
S01	Seine	LEGI	1	20
S01	Seine	LEGI	1	150
S02	Seine	ETNI	1	60
S02	Seine	FUDI	1	25
S02	Seine	FUDI	1	25
S02	Seine	FUDI	1	25
S02	Seine	FUDI	10	30
S02	Seine	FUDI	1	40
S02	Seine	FUDI	1	40
S02	Seine	FUDI	1	40
S02	Seine	FUDI	1	40
S02	Seine	FUDI	1	40
S02	Seine	FUDI	1	40
S02	Seine	FUDI	1	40
S02	Seine	FUDI	1	40
S02	Seine	FUDI	1	40
S02	Seine	FUDI	1	40
S02	Seine	LEGI	1	95
S02	Seine	NOAT	1	55
S02	Seine	NOCR	1	30
S02	Seine	NOCR	1	30
S02	Seine	NOCR	1	30
S02	Seine	NOCR	1	30
S02	Seine	NOCR	1	30
S02	Seine	NOCR	1	30
S02	Seine	NOCR	1	30
S02	Seine	NOCR	1	30
S02	Seine	NOCR	1	30
S02	Seine	NOCR	1	30
S02	Seine	NOCR	1	40
S02	Seine	NOCR	1	40
S02	Seine	NOCR	1	40
S02	Seine	NOCR	75	45
S02	Seine	PEFL	1	30
S02	Seine	PEFL	1	30
S02	Seine	PEFL	1	30
S02	Seine	PEFL	1	30
S02	Seine	PEFL	1	30
S02	Seine	PEFL	1	30
S02	Seine	PEFL	1	30
S02	Seine	PEFL	1	30
S02	Seine	PEFL	1	30
S02	Seine	PEFL	1	30
S02	Seine	PEFL	1	40

Longueur des poissons capturés autour de l'île au Chat durant l'automne 1996

Station	Engin	Espèce	Nombre	Longueur (mm)
S02	Seine	PEFL	1	40
S02	Seine	PEFL	1	40
S02	Seine	PEFL	1	40
S02	Seine	PEFL	1	40
S02	Seine	PEFL	1	40
S02	Seine	PEFL	1	40
S02	Seine	PEFL	1	40
S02	Seine	PEFL	1	40
S02	Seine	PEFL	1	110
S02	Seine	PEFL	1	110
S02	Seine	PEFL	1	110
S02	Seine	PEFL	1	110
S02	Seine	PEFL	1	120
S02	Seine	PEFL	1	120
S02	Seine	PEFL	1	190
S03	Seine	CACO	1	95
S03	Seine	ETNI	1	40
S03	Seine	ETNI	1	40
S03	Seine	ETNI	1	40
S03	Seine	ETNI	1	40
S03	Seine	ETNI	1	40
S03	Seine	ETNI	1	45
S03	Seine	ETNI	1	45
S03	Seine	ETNI	1	45
S03	Seine	ETNI	1	60
S03	Seine	ETNI	1	60
S03	Seine	ETNI	1	60
S03	Seine	FUDI	1	35
S03	Seine	FUDI	1	35
S03	Seine	FUDI	1	35
S03	Seine	NOAT	20	30
S03	Seine	PEFL	1	95
S03	Seine	PEFL	1	100
S03	Seine	PEFL	1	110
S03	Seine	PINO	1	80
S03	Seine	PINO	2	30
S03	Seine	PINO	30	20
S04	Seine	FUDI	1	25
S04	Seine	FUDI	1	25
S04	Seine	FUDI	25	40
S04	Seine	LASI	1	60
S04	Seine	LASI	1	60
S04	Seine	LASI	1	60
S04	Seine	LASI	1	60
S04	Seine	LASI	1	60
S04	Seine	LASI	1	60
S04	Seine	NOAT	1	20
S04	Seine	NOAT	150	25
S05	Seine	FUDI	1	35
S05	Seine	FUDI	1	50
S05	Seine	LEGI	1	30
S05	Seine	NOAT	1	40
S05	Seine	NOCR	1	30
S05	Seine	NOCR	1	30
S05	Seine	NOCR	1	30
S05	Seine	NOCR	1	30
S05	Seine	NOCR	1	45

Longueur des poissons capturés autour de l'île au Chat durant l'automne 1996

Station	Engin	Espèce	Nombre	Longueur (mm)
S05	Seine	PEFL	1	100
S05	Seine	PEFL	1	110
S05	Seine	PEFL	1	125
S05	Seine	PEFL	1	195
S05	Seine	PINO	1	30
S05	Seine	PINO	1	30
S05	Seine	PINO	1	40
S05	Seine	PINO	1	40
S05	Seine	PINO	1	40
S05	Seine	PINO	1	50
S05	Seine	PINO	100	30
S06	Seine	AMRU	1	25
S06	Seine	AMRU	1	40
S06	Seine	AMRU	1	40
S06	Seine	AMRU	1	40
S06	Seine	AMRU	1	40
S06	Seine	AMRU	1	40
S06	Seine	ETNI	1	40
S06	Seine	ETNI	1	40
S06	Seine	ETNI	1	50
S06	Seine	FUDI	1	25
S06	Seine	FUDI	1	25
S06	Seine	LEGI	1	30
S06	Seine	LEGI	1	30
S06	Seine	NOCR	50	35
S06	Seine	PINO	10	25
S07	Seine	ETNI	1	32
S07	Seine	ETNI	1	36
S07	Seine	FUDI	1	30
S07	Seine	FUDI	1	30
S07	Seine	FUDI	1	30
S07	Seine	FUDI	1	30
S07	Seine	FUDI	1	30
S07	Seine	FUDI	1	30
S07	Seine	FUDI	1	30
S07	Seine	FUDI	1	30
S07	Seine	FUDI	1	30
S07	Seine	FUDI	1	40
S07	Seine	FUDI	1	40
S07	Seine	FUDI	1	40
S07	Seine	FUDI	1	40
S07	Seine	FUDI	1	40
S07	Seine	FUDI	1	40
S07	Seine	FUDI	1	40
S07	Seine	FUDI	1	40
S07	Seine	FUDI	1	40
S07	Seine	FUDI	1	45
S07	Seine	FUDI	1	45
S07	Seine	FUDI	1	45
S07	Seine	FUDI	1	45
S07	Seine	FUDI	1	45
S07	Seine	NOAT	1	50
S07	Seine	NOAT	1	50
S07	Seine	NOAT	1	50
S07	Seine	NOAT	1	60
S07	Seine	NOAT	1600	20
S07	Seine	NOAT	25	30

Longueur des poissons capturés autour de l'île au Chat durant l'automne 1996

Station	Engin	Espèce	Nombre	Longueur (mm)
S08	Seine	ETNI	1	50
S08	Seine	FUDI	1	30
S08	Seine	FUDI	1	37
S08	Seine	FUDI	1	37
S08	Seine	FUDI	1	41
S08	Seine	FUDI	1	41
S08	Seine	FUDI	1	41
S08	Seine	FUDI	1	41
S08	Seine	FUDI	1	41
S08	Seine	FUDI	1	41
S08	Seine	FUDI	1	41
S08	Seine	NOAT	1	50
S08	Seine	NOAT	1	50
S08	Seine	NOAT	1	50
S08	Seine	NOAT	1	50
S08	Seine	NOAT	1	50
S08	Seine	NOAT	1	50
S08	Seine	NOAT	1	50
S08	Seine	NOAT	1	50
S08	Seine	NOAT	1	50
S08	Seine	NOAT	1	50
S08	Seine	NOAT	1	50
S08	Seine	NOAT	1	50
S08	Seine	NOAT	1	65
S08	Seine	NOAT	1	68
S08	Seine	NOAT	500	30
S09	Seine	FUDI	1	20
S09	Seine	FUDI	25	10-30
S09	Seine	NOCR	8	10-25
S09	Seine	NOCR	12	10-25
S09	Seine	PEFL	1	50
S09	Seine	PINO	25	5-20
S10	Seine	ETNI	12	25-55
S10	Seine	ETNI	15	20-55
S10	Seine	FUDI	18	20-35
S10	Seine	FUDI	40	20-55
S10	Seine	NOCR	12	20-30
S10	Seine	NOHU	9	15-25
S10	Seine	PEFL	1	45
S10	Seine	PINO	40	20-30
S10	Seine	PINO	55	15-25
S11	Seine	ETNI	3	35
S11	Seine	ETNI	4	30-40
S11	Seine	ETNI	5	50-60
S11	Seine	FUDI	6	20-55
S11	Seine	ICPU	1	25
S11	Seine	LASI	3	30-40
S11	Seine	LASI	14	45
S11	Seine	LEGI	11	20-60
S11	Seine	LEGI	17	20-40
S11	Seine	MIDO	1	50
S11	Seine	PEFL	1	200
S11	Seine	PEFL	36	40-50
S11	Seine	PEFL	69	55
S11	Seine	PINO	40	20-40
S12	Seine	AMRU	1	116
S12	Seine	AMRU	1	146

Longueur des poissons capturés autour de l'île au Chat durant l'automne 1996

Station	Engin	Espèce	Nombre	Longueur (mm)
S12	Seine	CUIN	1	30
S12	Seine	ESLU	1	124
S12	Seine	ESLU	1	150
S12	Seine	ESLU	2	455
S12	Seine	FUDI	5	50
S12	Seine	FUDI	15	20
S12	Seine	LEGI	24	20
S12	Seine	LEGI	20	40
S12	Seine	LEGI	1	75
S12	Seine	LEGI	1	138
S12	Seine	LEGI	1	171
S12	Seine	LEGI	1	145
S12	Seine	MISA	1	30
S12	Seine	NOAT	2	40
S12	Seine	NOCR	300	30-40
S12	Seine	NOCR	500	20-50
S12	Seine	PEFL	1	60
S12	Seine	PEFL	1	71
S12	Seine	PEFL	1	99
S12	Seine	PEFL	1	102
S12	Seine	PEFL	1	112
S12	Seine	PEFL	1	112
S12	Seine	PEFL	1	114
S12	Seine	PEFL	1	172
S12	Seine	PEFL	2	50-60
S12	Seine	PINO	15	20-25
S12	Seine	PINO	20	20-30
S13	Seine	FUDI	1	25
S13	Seine	LEGI	1	91
S13	Seine	PEFL	15	50-120
S14	Seine	LASI	4	50-60
S14	Seine	MIDO	2	30-40
S14	Seine	PINO	9	20-30
S15	Seine	PEFL	2	130
BG06	Seine	LASI	1	35
BG06	Seine	LASI	1	35
BG06	Seine	LASI	1	35
BG06	Seine	LASI	1	35
BG06	Seine	LASI	1	35
BG06	Seine	LEGI	1	65
BG06	Seine	LEGI	1	65
BG06	Seine	LEGI	1	65
BG06	Seine	LEGI	1	65
BG06	Seine	LEGI	1	65
BG06	Seine	PEFL	1	140
BG06	Seine	PEFL	1	140
BG06	Seine	PEFL	1	140
BG06	Seine	PEFL	1	140
BG06	Seine	PEFL	1	140
BG07	Seine	ESLU	1	350
BG07	Seine	LASI	1	35
BG07	Seine	LASI	1	35
BG07	Seine	LASI	1	35
BG07	Seine	LASI	1	35
BG07	Seine	LASI	1	35
BG07	Seine	LEGI	1	55
BG07	Seine	LEGI	1	55

Longueur des poissons capturés autour de l'île au Chat durant l'automne 1996

Station	Engin	Espèce	Nombre	Longueur (mm)
BG07	Seine	LEGI	1	55
BG07	Seine	LEGI	1	55
BG07	Seine	LEGI	1	55
BG07	Seine	LEGI	1	55
BG07	Seine	LEGI	1	55
BG07	Seine	LEGI	1	55
BG07	Seine	LEGI	1	55
BG07	Seine	LEGI	1	55
BG07	Seine	LEGI	1	55
BG07	Seine	LEGI	1	55
BG07	Seine	LEGI	1	55
BG07	Seine	LEGI	1	55
BG07	Seine	LEGI	1	55
BG07	Seine	LEGI	1	55
BG07	Seine	LEGI	1	55
BG07	Seine	LEGI	1	55
BG07	Seine	LEGI	1	55
BG07	Seine	LEGI	1	55
BG07	Seine	LEGI	1	55
BG07	Seine	MISA	1	50
BG07	Seine	MISA	1	50
BG07	Seine	MISA	1	50
BG08	Seine	LASI	1	35
BG08	Seine	LASI	1	35
BG08	Seine	LEGI	1	80
BG08	Seine	LEGI	1	80
BG08	Seine	LEGI	1	80
BG08	Seine	LEGI	1	80
BG08	Seine	LEGI	1	80
BG08	Seine	LEGI	1	80
BG08	Seine	LEGI	1	80
BG08	Seine	LEGI	1	80
BG08	Seine	LEGI	1	80
BG08	Seine	LEGI	1	80
BG08	Seine	MISA	1	35
BG08	Seine	MISA	1	35
BG08	Seine	MISA	1	35
BG08	Seine	MISA	1	35
BG08	Seine	MISA	1	35
BG08	Seine	PEFL	1	75
BG08	Seine	PEFL	1	75

APPENDIX G.2

Faune ichtyenne - Caractérisation des activités de reproduction et d'alevinage (septembre 1997)

environnement illimité inc.
consultants en écologie et environnement

RESTAURATION DES SÉDIMENTS AUTOUR DE L'ÎLE AUX CHATS

Faune ichtyenne
Caractérisation des activités de reproduction et d'alevinage

Rapport présenté à

Tecsult inc.

Septembre 1997

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ANNEXE 2 Données brutes des captures de poissons réalisées à la seine de rivage autour de l'Île aux Chats, au cours des mois d'avril à juillet 1997

1 INTRODUCTION

Dans le cadre du projet de restauration des sédiments contaminés autour de l'Île aux Chats (lac Saint-François), le promoteur Allied Signal, a confié la réalisation de l'étude d'impact à la firme Tecsult inc. Cette dernière a mandaté Environnement Illimité inc. pour réaliser le volet ichtyologique de l'étude. Une caractérisation de la faune ichtyenne et son habitat autour de l'Île aux Chats a été réalisée durant l'automne 1996 (Environnement Illimité inc., 1996). Les résultats relatifs à ces travaux indiquaient, entre autres, que plusieurs espèces de poissons semblaient se reproduire dans le secteur. Afin de préciser cette situation, une étude complémentaire a été initiée afin d'identifier les espèces qui utilisent la zone d'étude pour se reproduire et de localiser les principales frayères.

Le présent document traite spécifiquement des activités relatives à l'étude de la reproduction printanière de la faune ichtyenne autour de l'Île aux Chats, au cours du printemps 1997. Suite à une description des objectifs et de la méthodologie, les principaux résultats sont présentés sous la forme de tableaux et de cartes, afin de permettre une appréciation de la localisation et l'importance des activités de fraie observées.

2 OBJECTIFS

Bien que cette étude vise l'ensemble des espèces, une attention particulières est dirigée vers la présence d'espèces rares, telles que le brochet vermiculé, le suceur ballot et le dard gris, ainsi que vers le grand brochet, la perchaude, le crapet soleil et la carpe allemande, espèces pour lesquelles des indications de fraie ont été notées. Cette information servira d'intrant à l'évaluation des impacts sur l'environnement reliés aux travaux de restauration des sédiments autour de l'Île aux Chats et visera également à permettre d'adapter la conception des aménagements afin de favoriser la faune ichtyenne et d'atténuer les effets du projet sur son habitat. Les objectifs détaillés de l'étude sont les suivants :

- Réaliser un inventaire printanier de la faune ichtyenne autour de l'Île aux Chats ;
- Identifier les espèces frayant dans le secteur en notant le stade de maturité des captures et en suivant leur évolution ;
- Localiser les zones principales de fraie et en évaluer leur importance.

3 MATÉRIEL ET MÉTHODES

Les travaux d'inventaire de la faune ichtyenne ont été réalisés au cours de huit journées d'échantillonnage réparties comme suit :

Date	Température de l'eau	Filet troubleau	Pêche électrique	Seine de rivage	Plongée sub-aquatique
29 avril	7 °C	X	X		
12 mai	8 °C	X	X		
23 mai	10 °C		X	X	X
5 juin	14 °C		X	X	X
19 juin	17 °C		X	X	X
3 juillet	20 °C		X	X	
17 juillet	24 °C			X	X
24 juillet	22 °C		X	X	

Au cours des travaux, la température de l'eau est passée de 7 °C à 24 °C. Les inventaires ont principalement été réalisés à l'aide de la seine de rivage pour l'échantillonnage des petits poissons et de la pêche électrique pour la capture d'espèces de grande taille. Ces deux techniques présentent l'avantage d'être rapides et de minimiser les mortalités. De plus, le filet troubleau et la plongée sub-aquatique ont complété les inventaires.

Pêche électrique

La pêche électrique à haut voltage (modèle : *Electrofisher type V*) est montée sur une embarcation d'aluminium de 5,5 m de longueur. Le système est muni de deux anodes circulaires (0,5 m de diamètre) installées à l'avant de l'embarcation, tandis que la cathode est directement branchée sur la coque du bateau. L'équipe est composée d'un conducteur et de deux pêcheurs installés de chaque côté de l'embarcation de façon à capturer simultanément les poissons à l'aide d'épuisettes (diamètre de mailles : 1 cm). Le système peut générer jusqu'à sept ampères, mais généralement une intensité de deux ampères était suffisante pour attirer et immobiliser les poissons sans les blesser. Les poissons capturés étaient déposés dans un bac rempli d'eau pour les maintenir en vie.

Les spécimens étaient identifiés, mesurés et remis à l'eau. Le sexe et le stade de maturité ont été identifiés par pression abdominale et extrusion du produit de la fraie. Quelques spécimens étaient sacrifiés afin de confirmer l'état d'avancement de la maturité des gonades. La zone d'étude a été divisée en 17 sections de rive de longueur variant généralement entre 100 m et 150 m, à l'exception de la zone de pyrite (station P12) qui possède une longueur d'environ 700 m (figure 1).

Seine de rivage

La zone d'étude a également été échantillonnée à l'aide d'une seine de rivage de 12 m de longueur par 2 m de hauteur, munie d'une poche de 2 x 2 x 2 m et constituée de mailles de 1 mm de diamètre.

La seine était étirée perpendiculairement à la rive sur toute sa longueur jusqu'à une profondeur d'environ 1,25 m, puis ramenée vers le bord en suivant un arc de cercle. Une fois la seine fermée, une troisième personne ramenait la ralingue de fond de façon à emprisonner les poissons dans la poche centrale.

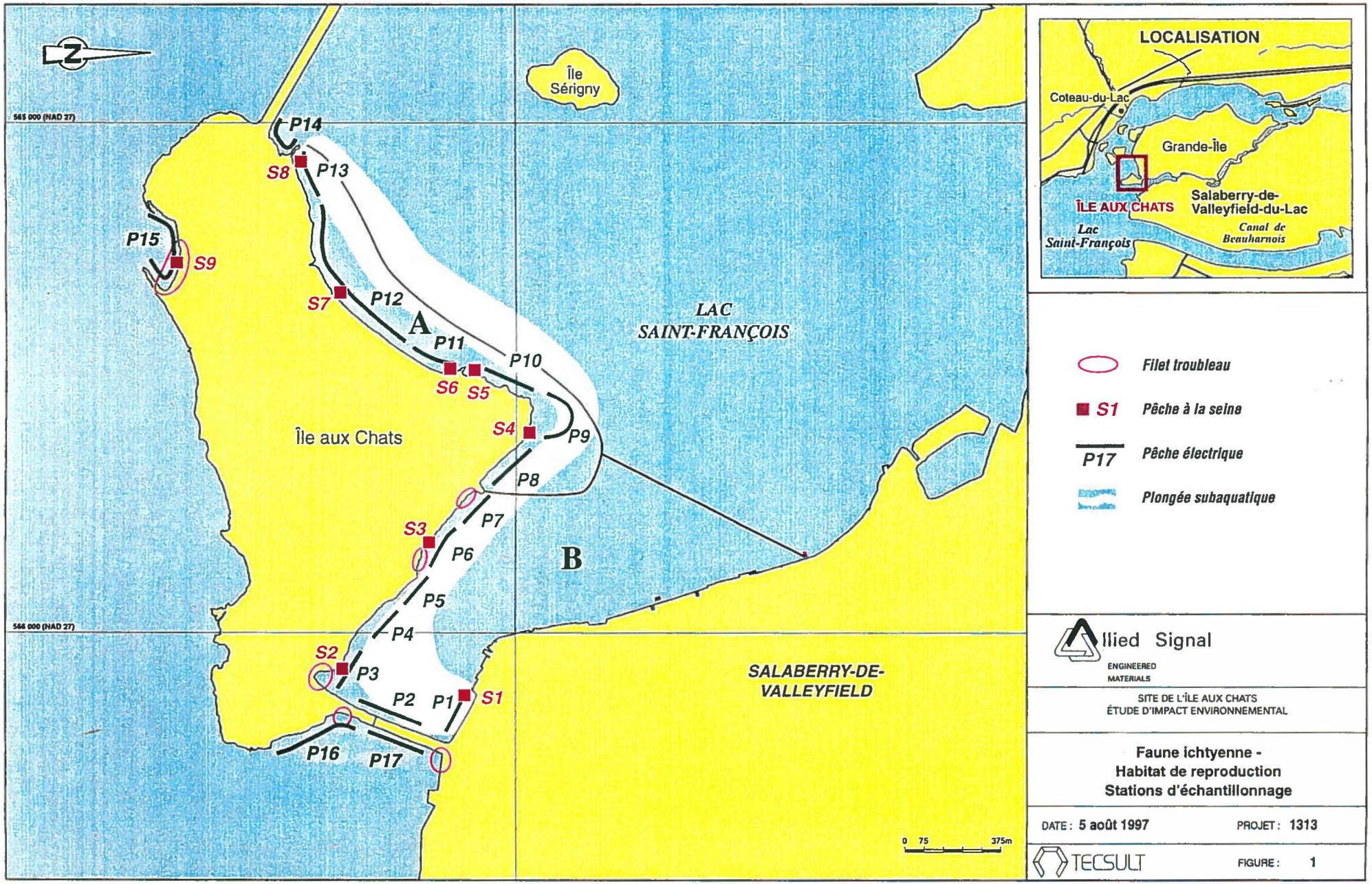
Neuf stations ont été réparties dans la zone d'étude dont deux dans la partie sud de l'île, zone non affectée par la contamination (figure 1). Tous les poissons ont été identifiés, dénombrés, mesurés et sexés. Les spécimens de petite taille ont été dénombrés en fonction de classes de longueur.

Filet troubleau

Le filet troubleau est généralement utilisé pour la recherche d'œufs dans les plaines d'inondation printanière et dans les herbiers de faible profondeur. Cette technique est efficace pour la recherche de frayères à grand brochet et à perchaude. Seul les habitats propices à la fraie de ces deux espèces ont été inventoriés à l'aide de cette méthode (figure 1).

Plongée sub-aquatique

La plongée sub-aquatique vise l'acquisition d'informations complémentaires sur l'habitat aquatique en général. De plus, cette technique permet de repérer les pontes de perchaude et les nids de crapet soleil à des profondeurs supérieures à 1 m. La zone littorale (1 à 3 m de profondeur) en bordure du secteur contaminé ainsi que dans la baie est de l'île aux Chats a été inventoriée (figure 1).



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4 RÉSULTATS

L'identification des zones de reproduction est basée sur les résultats d'échantillonnage au filet troubleau, à la pêche électrique, à la seine et en plongée sub-aquatique. Les résultats sont présentés en deux volets, soit une description des captures et des observations réalisées et une caractérisation des zones de reproduction et leur importance selon les espèces.

4.1 Description des captures

Au total, 21 espèces de poissons ont été capturés dans la zone d'étude (tableau 1). Une description des principaux résultats obtenus à l'aide de chaque technique d'échantillonnage décrite précédemment est présentée dans les lignes qui suivent.

Filet troubleau

Au cours de la première journée d'échantillonnage, la recherche d'habitats propices à la fraie de la perchaude et du grand brochet a révélé une très faible superficie d'herbiers inondés autour de l'Île aux Chats. Cette situation est causée par la gestion du niveau d'eau du lac Saint-François qui élimine à toute fin pratique l'augmentation du niveau d'eau généralement observée lors de la crue printanière. Les quelques petites zones d'herbiers terrestres inondés ont été échantillonnées sans succès (figure 1). Mentionnons également que l'habitat riverain n'offre aucune présence d'herbier aquatique à des profondeurs inférieures à 1,5 m. Cette situation limite considérablement la superficie d'habitat de reproduction généralement utilisé par ces deux espèces. Toutefois, six brochetons ont été capturés à l'aide du filet troubleau dans un petit canal près de la station S2, ce qui suggère la possibilité d'une activité de reproduction dans ce secteur.

Pêche électrique

L'utilisation de la pêche électrique visait la capture de géniteurs d'espèces de grande taille. Les résultats des captures de géniteurs et de spécimens immatures sont présentés pour chacune des journées d'échantillonnage (tableau 2). Au total, 3 987 poissons ont été capturés. Parmi les spécimens sexuellement matures (géniteurs), les principales espèces sont par ordre d'importance

TABLEAU 1 — Liste des espèces de poissons capturés autour de l'île aux Chats entre le 29 avril et le 24 juillet 1997

Espèce	Nom latin	Nom commun	Exploitation
AMRU	Ambloplites rupestris	Crapet de roche	Sportive
ANRO	Anguilla rostrata	Anguille d'Amérique	Commerciale
CACO	Catostomus commersoni	Meunier noir	Appât
CYCA	Cyprinus carpio	Carpe allemande	Sportive
ESLU	Esox lucius	Grand brochet	Sportive
ESMA	Esox masquinogy	Masquinongé	Sportive
ETEX	Etheostoma exile	Dard à ventre jaune	
ETNI	Etheostoma nigrum	Raseux-de-terre	
FUDI	Fundulus diaphanus	Fondule barré	
ICNE	Ichtalurus nebulosus	Barbotte brune	Sportive
LEGI	Lepomis gibbosus	Crapet soleil	Sportive
LEOS	Lepisosteus osseus	Lépisosté osseux	Sportive
MIDO	Micropterus dolomieu	Achigan à petite bouche	Sportive
MISA	Micropterus salmoides	Achigan à grande bouche	Sportive
NOAT	Notropis atterinoides	Méné émeraude	Appât
NOCR	Notemigonus chrysoleucas	Chatte de l'est	Appât
NOHU	Notropis hudsonius	Queue à tache noire	Appât
NOSP	Notropis spilopterus	Méné bleu	Appât
PECA	Percina caprodes	Fouille-roche	
PEFL	Perca flavescens	Perchaude	Sportive
PINO	Pimephales notatus	Ventre-pourri	

numérique la chatte de l'est, la perchaude, le crapet soleil, le queue à tache noire et la barbotte brune. Chez la perchaude, les géniteurs ont été capturés au début de la campagne d'échantillonnage, soit le 29 avril et le 12 mai. Les chattes de l'est ont été capturées en grand nombre le 29 avril et le 23 mai, tandis que le pic d'abondance des géniteurs de crapet soleil et de barbotte brune a eu lieu le 19 juin. Les données brutes présentées par station et par classe de longueurs sont listées à l'annexe 1.

TABLEAU 2 — Résultats cumulatifs des pêches réalisées à la pêche électrique autour de l'Île aux Chats, du 29 avril au 24 juillet 1997

		STATION							
Espèce	Stade	29 avril	12 mai	23 mai	05 juin	19 juin	03 juillet	24 juillet	Total
AMRU	géniteur	-	-	-	1	5	-	1	**7**
	immature	-	-	8	3	27	6	7	**51**
ANRO	immature	-	-	-	-	8	3	3	**14**
CACO	immature	-	-	2	-	-	1	1	**4**
CYCA	géniteur	-	-	-	-	1	4	1	**6**
ESLU	immature	5	3	3	5	1	-	-	**17**
ETEX	géniteur	-	-	-	-	-	-	-	**0**
	immature	-	-	-	-	-	-	-	**0**
ETNI	géniteur	-	-	2	-	1	-	-	**3**
	immature	10	-	17	-	-	-	2	**29**
FUDI	géniteur	-	-	-	-	-	-	-	**0**
	immature	1	-	4	1	-	-	-	**6**
ICNE	géniteur	-	-	1	3	18	6	-	**28**
	immature	6	3	-	30	31	4	12	**86**
LEGI	géniteur	-	-	6	15	62	1	1	**85**
	immature	20	25	62	39	13	6	11	**176**
MIDO	géniteur	-	-	-	-	1	-	-	**1**
	immature	-	-	-	-	1	2	-	**3**
MISA	immature	-	-	2	-	2	1	-	**5**
NOAT	géniteur	-	-	-	16	-	-	-	**16**
	immature	2	200	-	1	-	-	-	**203**
NOCR	géniteur	1 000	-	613	-	-	-	-	**1 613**
	immature	201	4	103	71	25	-	-	**404**
NOHU	géniteur	-	-	29	-	-	-	-	**29**
	immature	-	3	-	-	-	-	-	**3**
NOSP	géniteur	-	-	-	-	-	-	-	**0**
	immature	-	-	-	-	-	-	-	**0**
PECA	immature	-	-	-	-	-	-	-	**0**
PEFL	géniteur	31	54	4	6	-	-	-	**95**
	immature	19	20	39	17	38	15	91	**239**
PINO	géniteur	-	-	-	5	3	-	-	**8**
	immature	800	6	50	-	-	-	-	**856**

Seine de rivage

La seine de rivage a été utilisée dans neuf stations autour de l'Île aux Chats (figure 1). Au total, 17 246 poissons ont été capturés (excluant les 11 920 alevins non identifiés). Ceux-ci sont répartis au sein de 19 espèces, dont les plus abondantes en terme de géniteurs sont : le ventre-pourri, la chatte de l'est, le méné bleu, le fondule barré, le méné émeraude et le raseux-de-terre (tableau 3). Bien qu'en général la période de fraie de ces petites espèces soit assez étalée dans le temps, on observe des concentrations de géniteurs très marquées chez la chatte de l'est (23 mai et 5 juin), le ventre-pourri (5 juin) et le méné émeraude (17 et 24 juillet). Chez ces mêmes espèces, on observe également de très fortes concentrations de spécimens immatures, situation principalement reliée à leur comportement grégaire. Notons l'apparition de plusieurs milliers d'alevins non identifiés, le 5 juin et le 3 juillet, situation probablement associée à l'émergence respective des alevins de chatte de l'est et de ventre-pourri. Les données brutes présentées par station et par classe de longueurs sont listées à l'annexe 2.

Plongée sub-aquatique

Les observations en plongée sub-aquatique ont été réalisées le long des rives nord et est de l'Île aux Chats. Cette activité visait d'une part, la recherche de rubans d'œufs de perchaude et de nids de crapet soleil et, d'autre part, une appréciation des concentrations de géniteurs des principales grandes espèces telles que la perchaude, le crapet soleil, la carpe allemande et la barbotte brune. Les plongées ont été réalisées à quatre reprises, soit le 23 mai, le 5 juin, le 19 juin et le 24 juillet.

Lors de la plongée du 23 mai, un peu plus d'une centaine de rubans d'œufs de perchaude ont été observés dans la baie est de l'Île aux Chats. Ceux-ci étaient concentrés principalement près des rives de l'Île aux Chats et de Grande-Île, le long des transects P1 à P8 (figure 1). Les plus fortes concentrations ont été observées le long des transects P1 et P3, avec respectivement 50 et 30 rubans d'œufs inventoriés. Une dizaine de pontes ont été localisées dans chacun des transects P2, P4 et P5, tandis que dans les transects P6 à P8, respectivement cinq, trois et un rubans d'œufs ont été identifiés.

En bordure des rives de l'Île aux Chats, les œufs étaient déposés directement sur le fond, dans un substrat constitué de sédiments fins, à une profondeur variant entre 0,5 et 1,5 m. Dans les zones de fortes concentrations, on retrouvait jusqu'à trois pontes par mètre carré. Notons que plusieurs pontes étaient recouvertes d'une fine couche de sédiments, ce qui limite probablement

TABLEAU 3 — Résultats cumulatifs des pêches réalisées à la seine de rivage autour de l'Île aux Chats, du 23 mai au 24 juillet 1997

		STATION						
Espèce	**Stade**	**23 mai**	**05 juin**	**19 juin**	**03 juillet**	**17 juillet**	**24 juillet**	**Total**
ALEVINS (sp.)	-	-	5 100	-	4 520	1 200	1 100	**11 920**
AMRU	géniteur	-	3	-	-	3	3	**9**
	immature	-	6	-	35	10	22	**73**
CACO	immature	-	-	-	11	370	100	**481**
ESLU	immature	-	1	-	-	-	1	**2**
ESMA	immature	-	-	-	-	-	3	**3**
ETEX	géniteur	4	7	-	-	6	-	**17**
	immature	-	2	1	6	5	1	**15**
ETNI	géniteur	35	36	5	27	10	2	**115**
	immature	27	16	75	23	63	29	**233**
FUDI	géniteur	-	32	-	31	122	80	**265**
	immature	107	178	55	93	112	61	**606**
ICNE	géniteur	-	-	-	-	-	-	**0**
	immature	3	-	-	1	1	-	**5**
LEOS	immature	-	-	-	-	5	2	**7**
LEGI	géniteur	1	26	1	3	6	1	**38**
	immature	-	27	33	20	4	7	**91**
MIDO	immature	-	-	-	2	-	5	**7**
MISA	immature	-	5	2	-	9	13	**29**
NOAT	géniteur	-	-	-	-	70	90	**160**
	immature	425	-	800	45	300	45	**1 615**
NOCR	géniteur	403	433	-	1	-	-	**837**
	immature	275	5 170	10	200	200	-	**5 855**
NOHU	géniteur	-	1	-	-	-	-	**1**
	immature	25	-	-	-	530	505	**1 060**
NOSP	géniteur	-	614	-	50	-	-	**664**
	immature	-	20	-	70	-	-	**90**
PECA	immature	-	-	-	-	1	-	**1**
PEFL	géniteur	9	-	-	-	-	-	**9**
	immature	-	101	33	29	117	52	**332**
PINO	géniteur	-	1 095	-	275	166	68	**1 604**
	immature	350	1 100	495	462	465	150	**3 022**

l'oxygénation des oeufs et leur taux de survie. Du côté de Grande-Île, les œufs étaient déposés entre 1,5 et 2,5 m de profondeur, sur une accumulation de plantes aquatiques jonchant le fond de la baie. Celles-ci étaient principalement composées de ceratophyllum, d'elodea et de potamoteton. Dans ce secteur, la survie des œufs semblait supérieure ; dans la deuxième plongée (5 juin), les rubans d'oeufs étaient moins colmatés et contenaient une moins grande proportion d'œufs morts (blancs) que ceux du secteur de l'Île aux Chats. Parallèlement à la recherche d'oeufs, les plongées ont montré une forte abondance de géniteurs de perchaude, principalement dans les secteurs P1 et P3.

Une trentaine de nids de crapet soleil ont été observés le long des rives des deux îles lors de la plongée du 19 juin. Du côté de l'Île aux Chats, les nids (n=24) étaient répartis uniformément sur une distance d'environ 800 m à partir de la digue, le long des transects P3 à P7 (figure 1). Le long des rives de Grande-Île, les nids (n=6) ont été observés sur une distance d'environ 200 m (transect P1). Ceux-ci étaient constitués d'une légère dépression dans les sédiments localisés entre 1 et 2 m de profondeur et facilement identifiables par le réseau radiculaire des plantes aquatiques mis à nu. Plusieurs centaines de spécimens de grande taille (géniteurs) ont été observés dans ces mêmes stations. Notons finalement qu'une quinzaine de barbottes brunes (géniteurs) ont été observées le long du transect P2.

Le 24 juillet, la plongée était davantage dirigée vers l'utilisation par la carpe allemande de la zone littorale de la rive nord de l'Île aux Chats. Un seul individu a été identifié en plongée tandis que quatre spécimens étaient observés à partir de la surface. Les observations dans ce secteur ont révélé que la zone écotone entre la plage (zone de cendres de pyrite) et les herbiers aquatiques (à partir de 1,5 m) était occupée par une faune ichtyenne abondante et diversifiée. Des bancs de petits poissons et plusieurs grands spécimens d'espèces telles que le grand brochet, l'achigan à grande bouche, l'achigan à petite bouche, l'anguille d'Amérique étaient observés (au large des stations P9, P10 et P11).

4.2 Localisation des zones de reproduction

L'analyse des résultats relatifs à la reproduction des principales espèces utilisant la zone d'étude est présentée dans les lignes qui suivent. La localisation et l'évaluation de l'importance d'une zone de fraie sont basées sur trois éléments, soit les abondances de géniteurs, d'alevins (ou de jeunes de l'année) et d'œufs (ou de nids). L'ensemble de ces informations a été synthétisé au tableau 4. Ces

Tableau 4 Résultats cumulatifs des captures et des observation de géniteurs (G), de jeune de l'année (J) et d'œufs (ou de nids) autour de l'ile aux Chats, du 29 avril au 24 juille 1997

		Station																								
Espèce	Stade	P1	S1	P2	P3	P4	S2	P5	P6	P7	S3	P8	P9	S4	P10	P11	S5	S6	P12	S7	P13	P14	S8	P15	S9	P16	P17	Total
ALEVINS (sp.	-	0	500	0	0	0	1 000	0	0	0	600	0	0	1 000	0	0	500	200	0	120	0	0	8 000	0	0	0	0	11 920
AMRU	géniteur	1	6	0	0	0	0	1	0	0	1	0	0	2	1	0	0	0	0	0	0	0	0	3	0	0	1	16
	jeune	0	17	0	0	0	1	0	0	0	0	0	0	1	0	0	14	1	0	0	0	0	1	0	0	0	0	35
CACO	jeune	0	10	0	0	0	40	0	0	0	100	0	0	211	0	0	5	10	0	0	0	0	105	0	0	0	0	481
CYCA	géniteur	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2	0	0	4	0	3	1	0	0	0	1	0	11
ESLU	jeune	0	0	0	0	0	6	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	6
ESMA	jeune	0	0	0	0	0	0	0	0	0	1	0	0	2	0	0	0	0	0	0	0	0	0	0	0	0	0	3
ETEX	géniteur	0	0	0	0	0	0	0	0	0	2	0	0	5	0	0	5	0	0	5	0	0	0	0	0	0	0	17
ETNI	géniteur	0	0	0	0	2	9	0	1	0	73	0	0	3	0	0	16	0	0	2	0	0	12	0	0	0	0	118
FUDI	géniteur	0	4	0	0	0	16	0	0	0	82	0	0	20	0	0	20	55	0	10	0	0	58	0	0	0	0	265
	jeune	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	10	0	0	0	3	0	2	0	16
ICNE	géniteur	6	0	10	1	2	0	1	2	3	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	11	1	38
LEOS	jeune	0	0	0	0	0	0	0	0	0	0	0	0	7	0	0	0	0	0	0	0	0	0	0	0	0	0	7
LEGI	géniteur	9	11	0	2	5	13	1	3	2	4	0	0	6	0	0	0	0	0	0	0	0	0	53	4	4	6	123
	nids	6	0	0	7	3	0	5	4	5	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	30
MIDO	jeune	0	0	0	0	0	0	0	0	0	2	0	0	0	0	0	0	1	0	0	0	0	0	0	2	0	0	5
MISA	jeune	0	4	0	0	0	0	0	0	1	0	0	0	6	0	0	1	0	0	0	0	0	8	0	0	0	0	20
NOAT	géniteur	0	0	2	0	0	0	0	0	11	0	3	0	30	0	0	40	50	0	40	0	0	0	0	0	0	0	176
NOCR	géniteur	1 000	400	8	600	63	7	10	0	0	420	0	0	10	0	0	0	0	0	0	0	0	0	3	0	0	0	2 521
NOHU	géniteur	0	0	0	0	0	0	19	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	10	0	0	0	30
	jeune	0	0	30	0	3	100	0	0	0	60	0	0	200	0	0	5	0	0	50	0	0	200	0	90	0	0	738
NOSP	géniteur	0	25	0	0	0	0	0	0	0	30	0	0	25	0	0	54	500	0	30	0	0	0	0	0	0	0	664
PEFL	géniteur	59	0	5	9	10	6	2	1	1	0	5	0	3	0	0	0	0	0	0	0	0	0	3	0	0	0	104
	ponte	50	0	10	30	10	0	10	5	3	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	119
PINO	géniteur	0	100	0	0	0	84	0	0	0	653	0	0	195	0	0	84	400	0	38	0	0	50	8	0	0	0	1 612

résultats indiquent que 18 espèces de poissons utilisent, de façon plus ou moins intense, la zone d'étude comme habitat de reproduction et/ou d'alevinage. En terme d'abondance de géniteurs, les espèces les plus abondantes sont : la chatte de l'est, le ventre-pourri, le méné bleu, le fondule barré, le méné émeraude, le crapet soleil, le raseux-de-terre et la perchaude. Parmi les espèces moins abondantes, on retrouve le crapet de roche, la barbotte brune, le dard à ventre jaune et la carpe allemande. Quant à l'abondance de jeunes de l'année, on retrouve principalement le queue à tache noire et le meunier noir, deux espèces dont peu de géniteurs ont été capturés. Parmi les autres espèces pour lesquelles seulement des jeunes de l'année ont été capturés, mentionnons la présence d'achigans à grande bouche, de lépisostés osseux et de masquinongés.

La localisation des principales zones de reproduction et les espèces qui y sont associées sont présentées à la figure 2. Notons que les délimitations des différentes zones de reproduction sont approximatives.

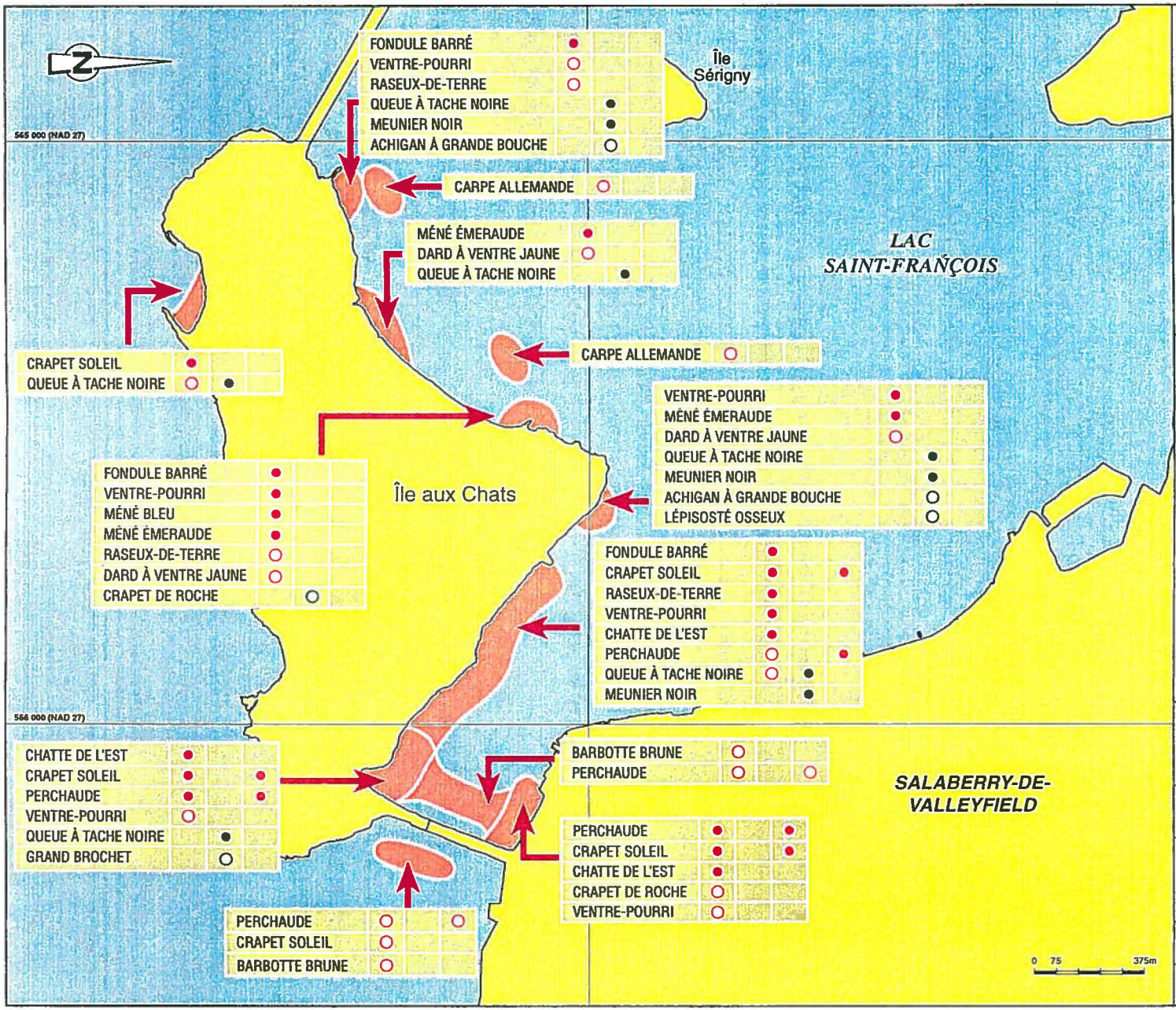
Rive nord

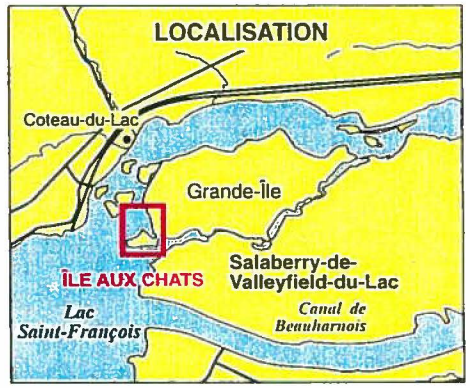
La rive nord de l'Île aux Chats (secteur contaminé) est caractérisée par la présence de six zones de reproduction (figure 1). Celles-ci ont été identifiées à partir de concentrations de géniteurs et d'alevins ; aucun oeuf n'y a été récolté.

On a observé à quelques reprises des carpes allemandes dauphinant à la surface de l'eau, le long de la limite nord de la zone de pyrite, caractérisée par une végétation abondante et des vitesses de courant relativement faibles (figure 2). Ce comportement est généralement caractéristique d'une activité de fraie. Cependant, l'abondance de géniteurs semblait relativement faible, car seulement six spécimens ont été capturés à la pêche électrique, quatre autres spécimens ont été observés à la surface de l'eau et un seul en plongée sub-aquatique.

Dans la portion ouest de la rive nord, on retrouve une petite pointe rocheuse en aval de laquelle on a observé une forte concentration de géniteurs de fondule barré ainsi que d'alevins de queue à tache noire et de meunier noir. Des géniteurs de ventre-pourri et des jeunes achigans à grande bouche ont également été capturés.

Dans la partie centrale de la zone contaminée, une quarantaine de géniteurs de méné émeraude, quelques géniteurs de dard à ventre jaune, espèce peu fréquente, ainsi qu'une concentration d'alevins de queue à tache noire ont été capturés.





ZONES D'ACTIVITÉS DE REPRODUCTION ET D'ALEVINAGE

ABONDANCE

Espèce de poisson	Géniteurs	Jeunes de l'année	Oeufs ou nids
CARPE ALLEMANDE	●	●	●

Abondance de géniteurs
- ● Élevée
- ○ *Moyenne*

Abondance des jeunes de l'année
- ● Élevée
- ○ *Faible*

Abondance d'oeufs ou de nids
- ● Forte
- ○ Moyenne

Allied Signal
ENGINEERED MATERIALS

SITE DE L'ÎLE AUX CHATS
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Faune ichtyenne - Habitat de reproduction Localisation des frayères

DATE : **5 août 1997** PROJET : **1313**

TECSULT FIGURE : **2**

C.M. 13130307.fh7

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Plus à l'est, on retrouve une seconde petite pointe rocheuse caractérisée par une forte concentration de géniteurs de méné bleu qui semblent privilégier ce site (tableau 4). On y retrouve également du ventre-pourri et du méné émeraude en abondance.

Près de l'extrémité nord de l'île, caractérisée par un herbier à cirpe, on retrouve sept espèces susceptibles de frayer à proximité, en particulier le ventre-pourri et le méné émeraude. Notons également la grande abondance d'alevins de meunier noir et de queue à tache noire, bien qu'aucun géniteur n'y ait été capturé, ainsi que quelques jeunes lépisostés osseux et achigans à grande bouche.

Baie est

La grande baie, localisée à l'est de l'Île aux Chats, peut être considérée comme une grande zone de reproduction multi-spécifique utilisée par une dizaine d'espèces, dont les principales sont la chatte de l'est, le ventre-pourri, la perchaude, le crapet soleil, le fondule barré et le raseux-de-terre (figure 2 et tableau 4).

Dans ce secteur, on retrouve quatre zones de fraie distinctes. La plus grande, couvrant la majorité de la zone littorale de la rive nord-est de l'Île aux Chats, est utilisée par huit espèces dont les plus caractéristiques sont le ventre-pourri, le fondule barré, le raseux-de-terre et le queue à tache noire. À l'extrémité est de l'île, près de la digue la reliant à Grande-Île, on retrouve une baie peu profonde utilisée principalement par la perchaude, le crapet soleil et la chatte de l'est. Dans la portion centrale de la baie, le long de la digue, on retrouve une concentration locale de géniteurs de barbotte brune observée en plongée. Finalement, la portion de la rive de Grande-Île, non occupée par des résidences, est utilisée par la perchaude, le crapet soleil et la chatte de l'est.

Secteur sud

Deux sites présentant les meilleurs potentiels comme frayères ont été inventoriés sur la rive sud de l'Île aux Chats. À l'extrémité ouest, on retrouve une baie peu profonde protégée par des brise-lames d'enrochement submergés, utilisée par le crapet soleil et le queue à tache noire. À l'extrémité est, près de la digue, on retrouve des concentrations de géniteurs de perchaude, de crapet soleil et de barbotte brune. Notons que quelques pontes de perchaude ont été observées à partir de la surface. Aucune plongée n'a été effectuée dans ce secteur.

5 SYNTHÈSE

Les activités de reproduction de la faune ichtyenne autour de l'Île aux Chats ont été caractérisées par huit campagnes de terrain réparties entre le 29 avril le 24 juillet. Plusieurs techniques d'échantillonnage ont été utilisées dont la pêche électrique à haut voltage, la seine de rivage, le filet troubleau et la plongée sub-aquatique.

Les résultats obtenus montrent que l'Île aux Chats, en particulier les rives nord et est, constitue un important habitat de fraie et d'alevinage multi-spécifique pour la faune ichtyenne. Au total, 18 espèces utilisent plus ou moins intensément ce secteur pour leur reproduction. La qualité de cet habitat est reliée, d'une part, à la position géographique de l'île qui offre une vaste zone d'abris de courant à la confluence d'une zone lacustre et lentique du lac Saint-François, et d'autre part, à la diversité d'habitats qu'on y retrouve, tels que des plages peu profondes, des pointes rocheuses, des herbiers aquatiques variés, quelques zones de gravier et d'autres constituées d'amoncellements de débris végétaux et ligneux.

La zone contaminée par la pyrite de fer, située en rive nord de l'Île aux Chats, est fréquentée par des géniteurs de plusieurs petites espèces telles que le fondule barré, le méné émeraude, le ventre-pourri et le méné bleu, ainsi qu'une forte concentration d'alevins de queue à tache noire et de meunier noir. On y retrouve aussi, en moins grande abondance des géniteurs de carpe allemande, de dard à ventre jaune et de raseux-de-terre ainsi que des jeunes de l'année d'achigan à grande bouche, de crapet de roche et de lépisosté osseux.

Ce secteur (correspondant à la zone A) est caractérisé par quatre types d'habitat distincts :

- des pointes rocheuses offrant des sites d'abris de courant et des placettes de gravier présentant un habitat de reproduction pour le fondule barré, le ventre-pourri, le méné bleu et le méné émeraude et d'alevinage pour le queue à tache noire, le meunier noir, l'achigan à grande bouche et le crapet de roche ;
- des plages peu profondes permettant aux jeunes poissons d'échapper aux prédateurs et offrant un habitat de croissance intéressant par le réchauffement rapide de l'eau ;
- des herbiers aquatiques denses en plus grande profondeur (> 1,5 m), soit à la lisière de la zone contaminée, soumis à une gradation de vitesse de courant en s'éloignant vers le large et offrant un excellent camouflage pour plusieurs prédateurs de tailles diverses. Cette zone semble également utilisée pour la reproduction de la carpe allemande ;

- des herbiers peu profonds à cirpe et à typha offrant un habitat de reproduction pour le ventre-pourri et le méné émeraude et d'alevinage pour plusieurs espèces dont le queue à tache noire et le meunier noir.

Les travaux et les aménagements associés à la réhabilitation du site (zone A) devraient viser la conservation de la diversité des habitats qu'on y retrouve afin de favoriser le maintien de l'utilisation du secteur par la faune ichtyenne.

La grande baie située au nord-est de l'île (correspondant à la zone B) a été subdivisée en quatre zones de fraie utilisées par un grand nombre de géniteurs d'espèces sportives, telles que la perchaude et le crapet soleil, et de petites espèces telles que le fondule barré, le raseux-de-terre, le ventre-pourri et la chatte de l'est. La barbotte brune, le crapet de roche et le queue à tache noire utilisent aussi ce secteur pour se reproduire, ainsi que dans une moindre mesure, le grand brochet.

On retrouve dans ce secteur quatre habitats distincts :

- la rive est de l'Île aux Chats possède un substrat constitué de sédiments fins avec certaines parcelles plus rocheuses et d'autres composées d'herbiers aquatiques clairsemés. La profondeur d'eau à 5 m de la rive oscille entre 0,5 et 1,0 m. Des géniteurs de plusieurs petites espèces telles que le fondule barré, le raseux-de-terre, le ventre-pourri, la chatte de l'est et le queue à tache noire s'y concentrent. Chez les espèces sportives, on retrouve une forte abondance de géniteurs et de nids de crapet soleil, ainsi que dans une moindre mesure de perchaude. Des alevins de queue à tache noire et de meunier noir y ont observés en grande abondance ;
- à l'extrémité est de la rive, on retrouve une baie peu profonde constituée de sédiments fins et colonisée par un grand herbier aquatique. Ce site est utilisé pour la reproduction de la perchaude, du crapet soleil, de la chatte de l'est et du ventre-pourri ;
- le long de la digue, on retrouve une pente rocheuse très abrupte complétée par un plateau de sédiments fins à une profondeur d'environ 2 à 2,5 m. Les géniteurs de barbotte brune sembleraient privilégier ce site. On y retrouve aussi des oeufs et des géniteurs de perchaude ;
- l'extrémité est de la digue est caractérisée par une pente abrupte et rocheuse ; la profondeur d'eau à 5 m de la rive est d'environ 2 m. On y retrouve un herbier aquatique assez dense utilisé pour la reproduction de la perchaude, du crapet soleil et de la chatte de l'est.

ANNEXE 1

Données brutes des captures de poissons réalisées à la pêche électrique autour de l'Île aux Chats, au cours des mois d'avril à juillet 1997

Résultats des pêches réalisées à la pêche électrique (nombre, sexe et maturité*) autour de l'Île aux Chats, le 29 avril 1997

	Station	P1	P2	P3	P4	P5	P6	P7	P8	P9	P10	P11	P12	P13	P14	P15	P16	P17
	Effort (sec.)	*75*	*175*	*107*	*90*	*143*	*91*	*60*	*105*					*107*		*175*	*80*	*100*
Espèce	**Long. (cm)**																	
NIL								X									X	
ANRO	70-80	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
AMRU	3-5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
AMRU	5-10	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
AMRU	10-15	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
AMRU	15-20	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
CACO	3-5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
CACO	5-8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
CACO	8-12	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
CACO	500-600	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
CYCA	70-80	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
ESLU	100-150	1I	-	-	2I	-	-	-	-	-	-	-	-	-	-	-	-	-
ESLU	20-30	-	-	-	2I	-	-	-	-	-	-	-	-	-	-	-	-	-
ESLU	10-15	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
ESLU	40-50	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
ETEX	15-20	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
ETEX	5-8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
ETEX	8-12	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
ETNI	3-5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
ETNI	5-8	-	-	-	2	3I	5I	-	-	-	-	-	-	-	-	-	-	-
ETNI	8-12	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
FUDI	3-5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
FUDI	5-8	-	-	-	-	-	1I	-	-	-	-	-	-	-	-	-	-	-
FUDI	8-12	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
ICNE	5-10	-	-	-	4I	-	-	-	-	-	-	-	-	-	-	-	-	-
ICNE	10-15	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
ICNE	15-20	-	1I	-	-	-	-	-	-	-	-	-	-	-	-	1I	-	-
ICNE	25-30	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
ICNE	30-35	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
LEGI	5-10	-	-	-	5I	-	-	-	-	-	-	-	-	-	-	-	-	-
LEGI	10-15	13I	-	-	2I	-	-	-	-	-	-	-	-	-	-	-	-	-
LEGI	15-20	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
LEGI	20-25	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
MIDO	5-10	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
MIDO	10-15	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
MIDO	25-30	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
MISA	5-10	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
MISA	10-15	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
MISA	15-20	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NOAT	3-5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NOAT	5-8	-	-	2	-	-	-	-	-	-	-	-	-	2I	-	-	-	-
NOAT	8-12	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NOCR	3-5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NOCR	5-8	-	-	200I	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NOCR	8-12	500F5/5M5	-	-	1I	-	-	-	-	-	-	-	-	-	-	-	-	-
NOHU	3-5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NOHU	5-8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NOHU	8-12	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NOSP	3-5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NOSP	5-8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NOSP	8-12	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PECA	3-5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PECA	5-8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PECA	8-12	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PEFL	3-5	-	-	5I	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PEFL	5-10	1I	-	-	-	-	3I	-	-	-	-	-	-	-	-	-	-	-
PEFL	10-15	5M5/6F5	-	1M5	5M5/6I	-	-	-	3M5/4I	-	-	-	-	-	-	-	-	-
PEFL	15-20	4M5	-	-	5M5	-	-	-	2M5	-	-	-	-	-	-	-	-	-
PEFL	20-25	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PINO	3-5	-	200	500I	-	-	-	-	-	-	-	-	-	-	-	100I	-	-
PINO	5-8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PINO	8-12	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

* Nombre, sexe et maturité :

Sexe : I : immature
F : femelle
M : mâle

Maturité :
5 le produit de la fraie s'écoule sous une forte pression abdominale
6 faible pression
7 s'écoule tout seul
8 fraye terminée

Résultats des pêches réalisées à la pêche électrique (nombre, sexe et maturité*) autour de l'Île aux Chats le 12 mai 1997

	Station	P1	P2	P3	P4	P5	P6	P7	P8	P9	P10	P11	P12	P13	P14	P15	P16	P17
	Effort (sec.)	*112*	*173*	*92*	*84*	*167*	*80*	*85*	*90*	*75*	*x*	*x*	*x*	*x*	*x*	*x*	*132*	*195*
Espèce	Long. (cm)																	
NIL							X											
ANRO	70-80	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
AMRU	3-5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
AMRU	5-10	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
AMRU	10-15	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
AMRU	15-20	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
CACO	3-5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
CACO	5-8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
CACO	8-12	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
CACO	500-600	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
CYCA	70-80	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
ESLU	100-150	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
ESLU	20-30	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
ESLU	10-15	-	-	1I	-	-	-	-	-	-	-	-	-	-	-	-	-	-
ESLU	40-50	-	-	1I	-	-	-	-	-	-	-	-	-	-	-	-	1I	-
ETEX	15-20	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
ETEX	5-8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
ETEX	8-12	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
ETNI	3-5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
ETNI	5-8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
ETNI	8-12	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
FUDI	3-5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
FUDI	5-8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
FUDI	8-12	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
ICNE	5-10	1I	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
ICNE	10-15	1I	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
ICNE	15-20	-	-	-	1I	-	-	-	-	-	-	-	-	-	-	-	-	-
ICNE	25-30	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
ICNE	30-35	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
LEGI	5-10	1I	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2I
LEGI	10-15	6I	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	9I
LEGI	15-20	-	2I	3I	-	-	-	-	-	-	-	-	-	-	-	-	-	1I
LEGI	20-25	-	1I	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
MIDO	5-10	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
MIDO	10-15	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
MIDO	25-30	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
MISA	5-10	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
MISA	10-15	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
MISA	15-20	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NOAT	3-5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NOAT	5-8	-	-	-	200I	-	-	-	-	-	-	-	-	-	-	-	-	-
NOAT	8-12	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NOCR	3-5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NOCR	5-8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NOCR	8-12	-	-	-	4I	-	-	-	-	-	-	-	-	-	-	-	-	-
NOHU	3-5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NOHU	5-8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NOHU	8-12	-	-	-	3I	-	-	-	-	-	-	-	-	-	-	-	-	-
NOSP	3-5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NOSP	5-8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NOSP	8-12	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PECA	3-5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PECA	5-8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PECA	8-12	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PEFL	3-5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PEFL	5-10	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PEFL	10-15	15M6/4I	-	1M6	-	3I	-	4I	5I	4I	-	-	-	-	-	-	2I	1I
PEFL	15-20	24M6	2M6	6M6	-	1M8	-	-	-	-	-	-	-	-	-	-	-	2I
PEFL	20-25	3M6	-	1M6	-	1F8	-	-	-	-	-	-	-	-	-	-	-	-
PINO	3-5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PINO	5-8	-	-	-	4I	-	-	-	-	-	-	-	-	-	-	-	-	-
PINO	8-12	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2I	-

* Nombre, sexe et maturité :

Sexe : I : immature
F : femelle
M : mâle

Maturité : 5. le produit de la fraie s'écoule sous une forte pression abdominale
6. faible pression
7. s'écoule tout seul
8. fraye terminée

Résultats des pêches réalisées à la pêche électrique (nombre, sexe et maturité*) autour de l'île aux Chats, le 23 mai 1997

	Station	P1	P2	P3	P4	P5	P6	P7	P8	P9	P10	P11	P12	P13	P14	P15	P16	P17
	Effort (sec.)	*143*	*170*	*60*	*92*	*114*	*80*	*80*	*70*	*60*	*60*	*45*	*150*	*50*	*50*	*100*	*95*	*150*
Espèce	**Long. (cm)**																	
NIL											X	X	X	X				
ANRO	70-80	1I	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
AMRU	3-5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
AMRU	5-10	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	5I
AMRU	10-15	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	3I
AMRU	15-20	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
CACO	3-5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
CACO	5-8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
CACO	8-12	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
CACO	20-30	-	1I	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
CACO	500-600	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
CYCA	70-80	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
ESLU	10-15	2I	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
ESLU	15-20	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
ESLU	40-50	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1I	-
ETEX	3-5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
ETEX	5-8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
ETEX	8-12	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
ETNI	3-5	-	-	-	-	-	-	5I	12I	-	-	-	-	-	-	-	-	-
ETNI	5-8	-	-	-	11 5 /1M5	-	-	-	-	-	-	-	-	-	-	-	-	-
ETNI	8-12	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
FUDI	3-5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
FUDI	5-8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2I	2I	-
FUDI	8-12	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
ICNE	5-10	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
ICNE	10-15	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
ICNE	15-20	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
ICNE	20-25	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
ICNE	25-30	-	-	1F5	-	-	-	-	-	-	-	-	-	-	-	-	-	-
ICNE	30-35	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
LEGI	5-10	17I	-	-	10I	-	4I	-	-	2I	-	-	-	-	-	-	-	9I
LEGI	10-15	5M5 / 1F5 / 7I	-	-	4I	-	-	-	-	-	-	-	-	-	-	-	-	8I
LEGI	15-20	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1I
LEGI	20-25	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
MIDO	5-10	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
MIDO	10-15	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
MIDO	25-30	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
MISA	5-10	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
MISA	10-15	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1I
MISA	15-20	-	-	-	1I	-	-	-	-	-	-	-	-	-	-	-	-	-
NOAT	3-5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NOAT	5-8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NOAT	8-12	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NOCR	3-5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NOCR	5-8	-	1F5 /1I	100F5 / 100M5 /50I	2I	50I	-	-	-	-	-	-	-	-	-	-	-	-
NOCR	8-12	-	-	200M5 /200F5	2F5	8M5 /2F5	-	-	-	-	-	-	-	-	-	-	-	-
NOHU	3-5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NOHU	5-8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NOHU	8-12	-	-	-	-	15M5 / 4F6	-	-	-	-	-	-	-	-	-	7M6 /3F6	-	-
NOSP	3-5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NOSP	5-8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
NOSP	8-12	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PECA	3-5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PECA	5-8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PECA	8-12	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PEFL	3-5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PEFL	5-10	2I	2I	-	6I	-	1I	3I	2I	1I	-	-	-	-	1I	-	-	-
PEFL	10-15	1M6 / 7I	-	2I	4I	-	-	-	-	2I	-	-	-	-	-	-	2I	2I
PEFL	15-20	-	1M7 /2F7 /1I	-	-	-	-	-	-	-	-	-	-	-	-	1I	-	-
PEFL	20-25	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PINO	3-5	-	-	-	-	-	-	5I	-	-	-	-	-	-	-	20I	-	-
PINO	5-8	-	-	-	3I	14I	-	-	-	-	-	-	-	-	-	-	-	-
PINO	8-12	-	-	-	-	-	-	-	-	-	-	-	-	-	-	8I	-	-

* Nombre, sexe et maturité :

Sexe : I : immature; F : femelle; M : mâle

Maturité : 5. le produit de la fraie s'écoule sous une forte pression abdominale; 6. faible pression; 7. s'écoule tout seul; 8. fraye terminée

Résultats des pêches réalisées à la seine de rivage (nombre, sexe et maturité*) autour de l'Île aux Chats, le 5 juin 1997

Espèce	Long. (cm)	S1	S2	S3	S4	S5
ALEVINS (sp.)		-	-	-	-	-
AMRU	3-5	-	-	-	-	-
AMRU	5-10	-	-	-	-	-
AMRU	10-15	-	-	-	-	-
AMRU	15-20	-	-	-	-	-
CACO	3-5	-	-	-	-	-
ESLU	200-250	-	-	-	-	-
ESLU	250-300	-	-	-	-	-
ESMA	5-7	-	-	-	-	-
ETEX	3-5	-	-	-	-	-
ETEX	5-8	-	-	-	-	1I
ETNI	1-3	-	-	-	-	-
ETNI	3-5	-	-	-	50I	-
ETNI	5-8	-	-	2M5/3F5	-	25I
ETNI	8-12	-	-	-	-	-
FUDI	1-3	-	-	-	-	-
FUDI	3-5	-	-	-	-	-
FUDI	5-8	50I	-	-	-	5I
FUDI	8-12	-	-	-	-	-
ICNE	5-10	-	-	-	-	-
ICNE	10-15	-	-	-	-	-
ICNE	15-20	-	-	-	-	-
LEGI	5-10	5I	8I	8I	4I	-
LEGI	10-15	-	3I	5I	1F5	-
LEGI	15-20	-	-	-	-	-
LEOS	5-10	-	-	-	-	-
MIDO	3-5	-	-	-	-	-
MIDO	5-10	-	-	-	-	-
MIDO	10-15	-	-	-	-	-
MIDO	15-20	-	-	-	-	-
MISA	2-5	-	-	-	-	-
MISA	10-15	-	-	2I	-	-
MISA	15-20	-	-	-	-	-
MISA	5-10	-	-	-	-	-
NOAT	3-5	-	-	-	-	-
NOAT	5-8	800I	-	-	-	-
NOCR	3-5	5I	-	-	-	5I
NOCR	5-8	-	-	-	-	-
NOCR	8-12	-	-	-	-	-
NOHU	1-3	-	-	-	-	-
NOHU	3-5	-	-	-	-	-
NOHU	5-8	-	-	-	-	-
NOSP	3-5	-	-	-	-	-
NOSP	5-8	-	-	-	-	-
PECA	3-5	-	-	-	-	-
PEFL	5-10	5I	-	-	25I	-
PEFL	10-15	-	3I	-	-	-
PEFL	15-20	-	-	-	-	-
PINO	3-5	-	-	-	-	250I
PINO	5-8	200I	-	-	25I	20I

* Nombre, sexe et maturité :

Sexe : I : immature
F : femelle
M : mâle

Maturité :
5. le produit de la fraie s'écoule sous une forte pression abdominale
6. faible pression
7. s'écoule tout seul
8. fraye terminée

Résultats des pêches réalisées à la seine de rivage (nombre, sexe et maturité*) autour de l'Île aux Chats, le 19 juin 1997

Espèce	Long. (cm)	S1	S2	S3	S4	S5	S6	S7	S8	S9
ALLVINS (sp.)		-	-	-	-	-	-	100I	5000I	-
AMRU	3-5	-	-	-	-	-	-	-	-	-
AMRU	5-10	-	-	-	-	-	-	-	-	-
AMRU	10-15	3F5/5I	-	-	-	-	-	-	-	-
AMRU	15-20	-	-	-	-	-	-	-	-	1I
CACO	3-5	-	-	-	-	-	-	-	-	-
ESLU	200-250	-	-	-	-	-	-	-	-	-
ESLU	250-300	-	-	-	-	1I	-	-	-	-
ESMA	5-7	-	-	-	-	-	-	-	-	-
ETEX	3-5	-	-	-	-	-	-	-	-	-
ETEX	5-8	-	-	1M5	3M6/2F6	1M5	-	-	2I	-
ETNI	1-3	-	-	-	-	-	-	-	-	-
ETNI	3-5	-	-	-	2I/3M5	-	-	2F6	-	-
ETNI	5-8	-	-	10F5/10M5/4I	-	5F5/4M6	10I	-	2F5	-
ETNI	8-12	-	-	-	-	-	-	-	-	-
FUDI	1-3	-	-	-	-	-	-	-	-	-
FUDI	3-5	-	-	-	-	-	100I	-	-	25I
FUDI	5-8	15I	-	10I	5F5	5M5	10F5/10F5	3I/2M5	-	25I
FUDI	8-12	-	-	-	-	-	-	-	-	-
ICNE	5-10		-	-	-	-	-	-	-	-
ICNE	10-15		-	-	-	-	-	-	-	-
ICNE	15-20		-	-	-	-	-	-	-	-
LEGI	5-10		-	-	-	3I	-	-	-	-
LEGI	10-15	5F5/5M5/4I	8F5/5M5/17I	3I/2F5	1F5	-	-	-	-	-
LEGI	15-20	-	-	-	-	-	-	-	-	-
LEOS	5-10	-	-	-	-	-	-	-	-	-
MIDO	3-5	-	-	-	-	-	-	-	-	-
MIDO	5-10	-	-	-	-	-	-	-	-	-
MIDO	10-15	-	-	-	-	-	-	-	-	-
MIDO	15-20	-	-	-	-	-	-	-	-	-
MISA	2-5	-	-	-	-	-	-	-	-	-
MISA	10-15	-	2I	-	-	-	-	-	-	-
MISA	15-20	2I	-	-	1I	-	-	-	-	-
MISA	5-10	-	-	-	-	-	-	-	-	-
NOAT	3-5	-	-	-	-	-	-	-	-	-
NOAT	5-8	-	-	-	-	-	-	-	-	-
NOCR	3-5	400OI	-	-	-	20I	100I	50I	-	1000I
NOCR	5-8	200M6/200F6	3M6	20M6	10M6	-	-	-	-	-
NOCR	8-12	-	-	-	-	-	-	-	-	-
NOHU	1-3	-	-	-	-	-	-	-	-	-
NOHU	3-5	-	-	-	-	-	-	-	-	-
NOHU	5-8	-	-	-	-	-	-	1M5	-	-
NOSP	3-5	-	-	-	-	-	-	-	-	-
NOSP	5-8	25F6	-	30F6	15F6/10M7	2M7/2F7	200M5/300F6	30F6/20I	-	-
NOSP	8-12	-	-	-	-	-	-	-	-	-
PECA	3-5	-	-	-	-	-	-	-	-	-
PEFL	5-10	-	-	-	1I	4I	-	-	-	-
PEFL	10-15	35I	59I	2I	-	-	-	-	-	-
PEFL	15-20	-	-	-	-	-	-	-	-	-
PINO	3-5	100I	-	-	-	-	-	-	-	1000I
PINO	5-8	100F6	-	250F7/250M6	15M5/10F6	20M5/10F7	200F6/200F7	12M6/15F6/11F7	1F5/1M5	-

* Nombre, sexe et maturité :

Sexe: I immature, F femelle, M mâle

Maturité: 5. le produit de la fraie s'écoule sous une forte pression abdominale; 6. faible pression; 7. s'écoule tout seul; 8. fraye terminée

Résultats des pêches réalisées à la seine de rivage (nombre, sexe et maturité*) autour de l'Île aux Chats, le 3 juillet 1997

Espèce	Long. (cm)	S1	S2	S3	S4	S5	S6	S7	S8
ALEVINS (sp.)		-	-	500	500	500	-	20	3000
AMRU	3-5	111	-	-	-	111	-	-	-
AMRU	5-10	81	-	-	-	21	-	-	-
AMRU	10-15	-	-	-	-	21	-	-	11
AMRU	15-20	-	-	-	-	-	-	-	-
CACO	3-5	-	-	-	111	-	-	-	-
ESLU	200-250	-	-	-	-	-	-	-	-
ESLU	250-300	-	-	-	-	-	-	-	-
ESMA	5-7	-	-	-	-	-	-	-	-
ETEX	3-5	-	-	51	-	-	-	-	-
ETEX	5-8	-	-	-	-	-	-	-	11
ETNI	1-3	-	-	-	-	-	-	-	-
ETNI	3-5	11	31	-	-	-	-	41	51
ETNI	5-8	-	2F5	25F5/10I	-	-	-	-	-
ETNI	8-12	-	-	-	-	-	-	-	-
FUDI	1-3	-	-	-	-	-	-	-	-
FUDI	3-5	-	22I	25F5	70I	-	-	-	-
FUDI	5-8	11	3F5/2F5/1F6	-	-	-	-	-	-
FUDI	8-12	-	-	-	-	-	-	-	-
LEGI	5-10	11	7I	-	-	2I	-	-	-
ICNE	10-15	-	-	-	-	-	-	-	-
ICNE	15-20	-	-	-	-	-	-	-	-
ICNE	20-25	11	-	-	-	-	-	-	-
LEGI	10-15	-	-	-	3M7	10I	-	-	-
LEGI	15-20	-	-	-	-	-	-	-	-
LEOS	5-10	-	-	-	-	-	-	-	-
MIDO	3-5	-	-	-	-	-	-	-	-
MIDO	5-10	-	-	-	11	-	-	-	-
MIDO	10-15	-	-	-	-	-	-	-	-
MIDO	15-20	-	11	-	-	-	-	-	-
MISA	2-5	-	-	-	-	-	-	-	-
MISA	5-10	-	-	-	-	-	-	-	-
MISA	10-15	-	-	-	-	-	-	-	-
MISA	15-20	-	-	-	-	-	-	-	-
NOAT	3-5	-	-	151	30I	-	-	-	-
NOAT	5-8	-	-	-	-	-	-	-	-
NOCR	3-5	200I	-	-	-	-	-	-	-
NOCR	5-8	-	1F7	-	-	-	-	-	-
NOCR	8-12	-	-	-	-	-	-	-	-
NOHU	1-3	-	-	-	-	-	-	-	-
NOHU	3-5	-	-	-	-	-	-	-	-
NOHU	5-8	-	-	-	-	-	-	-	-
NOSP	3-5	-	-	-	20I	50I	-	-	-
NOSP	5-8	-	-	-	-	30F6/20M5	-	-	-
PECA	3-5	-	-	-	-	-	-	-	-
PECA	5-8	-	-	-	-	-	-	-	-
PECA	8-12	-	-	-	-	-	-	-	-
PEFL	5-10	-	-	-	-	31	-	-	-
PEFL	10-15	11	111	-	-	71	-	-	-
PEFL	15-20	11	61	-	-	-	-	-	-
PINO	3-5	-	4F7/24I	351	100I	-	-	-	-
PINO	5-8	-	50F7/3I	50F7	150F7	300I/11F6/10M6	-	-	-

* Nombre, sexe et maturité :

Sexe : I : immature
F : femelle
M : mâle

Maturité :
5. le produit de la fraie s'écoule sous une forte pression abdominale
6. faible pression
7. s'écoule tout seul
8. fraye terminée

Résultats des pêches réalisées à la seine de rivage (nombre, sexe et maturité*) autour de l'Île aux Chats, le 24 juillet 1997

Espece	Long. (cm)	S1	S2	S3	S4	S5	S6	S7	S8	S9
ALLVINS (sp.)	1-2	-	1000I	100I	-	-	-	-	-	-
AMRU	3-5	5I	1I	-	-	3I	1I	-	-	-
AMRU	5-10	1I	1I	1I	1I	1I	-	-	-	-
AMRU	10-15	1I	2I	1F6	1F6/1M8	1I	-	-	-	1I
AMRU	15-20	-	-	-	-	1I	-	-	-	1I
CACO	3-5	10I	-	-	-	5I	10I	-	75I	-
ESLU	200-250	-	-	-	1I	-	-	-	-	-
ESLU	250-300	-	-	-	-	-	-	-	-	-
ESMA	5-7	-	-	1I	2I	-	-	-	-	-
ETEX	3-5	-	-	-	-	-	-	-	1I	-
ETEX	5-8	-	-	-	-	-	-	-	-	-
ETNI	1-3	-	5I	-	-	-	-	-	-	-
ETNI	3-5	1I	2M6/3I	10I	-	5I	-	5I	-	-
ETNI	5-8	-	-	-	-	-	-	-	-	-
ETNI	8-12	-	-	-	-	-	-	-	-	-
FUDI	1-3	-	-	-	-	-	-	10I	-	-
FUDI	3-5	1I	20I	3I	-	10I	-	-	-	2I
FUDI	5-8	-	-	3M7/4F7/2I	10I	15F6	3F6	-	25F6/3M7/12I	1I
FUDI	8-12	-	-	-	-	-	-	-	-	-
ICNE	5-10	-	-	-	-	-	-	-	-	-
ICNE	10-15	-	-	-	-	-	-	-	-	-
ICNE	15-20	-	-	-	-	-	-	-	-	-
ICNE	20-25	-	-	-	-	-	-	-	-	-
LEOS	5-10	-	-	-	2I	-	-	-	-	-
LEGI	5-10	1F7/4I	-	-	-	1I	-	-	-	-
LEGI	10-15	-	-	-	-	1I	1I	-	-	-
LEGI	15-20	-	-	-	-	-	-	-	-	-
MIDO	3-5	-	-	2I	-	-	1I	-	-	2I
MIDO	5-10	-	-	-	-	-	-	-	-	-
MIDO	10-15	-	-	-	-	-	-	-	-	-
MIDO	15-20	-	-	-	-	-	-	-	-	-
MISA	2-5	4I	-	1I	6I	1I	-	-	-	-
MISA	5-10	-	-	-	-	-	-	-	-	-
MISA	10-15	-	-	-	-	-	-	-	-	-
MISA	15-20	-	-	-	-	1I	-	-	-	-
NOAT	3-5	-	-	-	-	-	-	-	-	-
NOAT	5-8	-	-	-	-	40F6/15I	50F6/20I	10I	-	-
NOCR	3-5	-	-	-	-	-	-	-	-	-
NOCR	5-8	-	-	-	-	-	-	-	-	-
NOHU	1-3	30I	50I	30I	-	5I	-	50I	-	40I
NOHU	3-5	-	-	30I	20I	-	-	-	250I	-
NOHU	5-8	-	-	-	-	-	-	-	-	-
NOSP	3-5	-	-	-	-	-	-	-	-	-
NOSP	5-8	-	-	-	-	-	-	-	-	-
PECA	3-5	-	-	-	-	-	-	-	-	-
PEFL	5-10	1I	11I	14I	2I	-	-	-	-	1I
PEFL	10-15	1I	8I	7I	3I	1I	-	-	1I	1I
PEFL	15-20	-	-	-	-	-	1I	-	-	-
PINO	3-5	-	20I	-	10I	-	20I	-	20I	-
PINO	5-8	-	-	3F8/10I	10F6/20I	30F6/3M7/25I	-	-	20F6/2M6/25I	-

* Nombre, sexe et maturité :

Sexe: I immature, F femelle, M mâle

Maturité: 5 le produit de la frate s'ecoule sous une forte pression abdominale; 6 faible pression; 7 s'ecoule tout seul; 8 fraye terminee

ANNEXE 2

Données brutes des captures de poissons réalisées à la seine de rivage autour de l'Île aux Chats, au cours des mois d'avril à juillet 1997

Résultats des pêches réalisées à la seine de rivage (nombre, sexe et maturité*) autour de l'Île aux Chats, le 23 mai 1997

Espèce	Long. (cm)	S1	S2	S3	S4	S5	S6	S7	S8
ALEVINS (sp.)		-	-	-	-	-	-	-	-
AMRU	3-5	-	-	-	-	-	-	-	-
AMRU	5-10	-	-	-	-	-	-	-	-
AMRU	10-15	-	-	-	-	-	-	-	-
AMRU	15-20	-	-	-	-	-	-	-	-
CACO	3-5	-	-	-	-	-	-	-	-
ESLU	200-250	-	-	-	-	-	-	-	-
ESLU	250-300	-	-	-	-	-	-	-	-
ESMA	5-7	-	-	-	-	-	-	-	-
ETEX	3-5	-	-	-	-	4M5	-	-	-
ETEX	5-8	-	-	-	-	-	-	-	-
ETNI	1-3	-	-	-	-	-	-	-	-
ETNI	3-5	-	-	-	5I	-	-	15I	-
ETNI	5-8	-	3F5/2M5/2I	3M5/5F5/5F5/4I	-	5M5/2F5	1I	-	4F5/6M5
ETNI	8-12	-	-	-	-	-	-	-	-
FUDI	1-3	-	-	-	-	-	-	-	-
FUDI	3-5	-	-	2I	20I	-	-	75I	10I
FUDI	5-8	-	-	-	-	-	-	-	-
FUDI	8-12	-	-	-	-	-	-	-	-
ICNE	5-10	-	3I	-	-	-	-	-	-
ICNE	10-15	-	-	-	-	-	-	-	-
ICNE	15-20	-	-	-	-	-	-	-	-
LEGI	5-10	-	-	-	-	-	-	-	-
LEGI	10-15	-	-	1M5	-	-	-	-	-
LEGI	15-20	-	-	-	-	-	-	-	-
LEOS	5-10	-	-	-	-	-	-	-	-
MIDO	3-5	-	-	-	-	-	-	-	-
MIDO	5-10	-	-	-	-	-	-	-	-
MIDO	10-15	-	-	-	-	-	-	-	-
MIDO	15-20	-	-	-	-	-	-	-	-
MISA	2-5	-	-	-	-	-	-	-	-
MISA	5-10	-	-	-	-	-	-	-	-
MISA	10-15	-	-	-	-	-	-	-	-
MISA	15-20	-	-	-	-	-	-	-	-
NOAT	3-5	-	-	-	-	-	-	10I	-
NOAT	5-8	-	-	200I	200 I	10I	5I	-	-
NOCR	3-5	-	75I	-	200I	-	-	-	-
NOCR	5-8	-	-	400M5	-	-	-	-	-
NOCR	8-12	-	3M5	-	-	-	-	-	-
NOHU	1-3	-	-	-	-	-	-	-	-
NOHU	3-5	-	-	-	-	-	-	-	-
NOHU	5-8	-	-	-	25I	-	-	-	-
NOSP	3-5	-	-	-	-	-	-	-	-
NOSP	5-8	-	-	-	-	-	-	-	-
PECA	3-5	-	-	-	-	-	-	-	-
PEFL	5-10	-	6I	-	-	-	-	-	-
PEFL	10-15	-	-	-	3I	-	-	-	-
PEFL	15-20	-	-	-	-	-	-	-	-
PINO	3-5	-	-	20I	-	-	-	5I	-
PINO	5-8	-	-	300I	-	15I	5I	-	5I

* Nombre, sexe et maturité :

Sexe : I : immature
F : femelle
M : mâle

Maturité : 5. le produit de la fraie s'écoule sous une forte pression abdominale
6. faible pression
7. s'écoule tout seul
8. fraye terminée

Résultats des pêches réalisées à la seine de rivage (nombre, sexe et maturité*) autour de l'Île aux Chats, le 19 juin 1997

Espèce	Long. (cm)	S1	S2	S3	S4	S5	S6	S7	S8	S9
ALEVINS (sp.)		-	-	-	-	-	-	100I	5000I	-
AMRU	3-5	-	-	-	-	-	-	-	-	-
AMRU	5-10	-	-	-	-	-	-	-	-	-
AMRU	10-15	3I 5/5I	-	-	-	-	-	-	-	-
AMRU	15-20	-	-	-	-	-	-	-	-	1I
CACO	3-5	-	-	-	-	-	-	-	-	-
ESLU	200-250	-	-	-	-	-	-	-	-	-
ESLU	250-300	-	-	-	-	1I	-	-	-	-
ESMA	5-7	-	-	-	-	-	-	-	-	-
ETEX	3-5	-	-	-	-	-	-	-	-	-
ETEX	5-8	-	-	1M5	3M6/2F6	1M5	-	-	2I	-
ETNI	1-3	-	-	-	-	-	-	-	-	-
ETNI	3-5	-	-	-	2I/3M5	-	-	2F6	-	-
ETNI	5-8	-	-	10F5/10M5/4I	-	5F5/4M6	10I	-	2F5	-
ETNI	8-12	-	-	-	-	-	-	-	-	-
FUDI	1-3	-	-	-	-	-	-	-	-	-
FUDI	3-5	-	-	-	-	-	100I	-	-	25I
FUDI	5-8	15I	-	10I	5F5	5M5	10F5/10F5	3I/2M5	-	25I
FUDI	8-12	-	-	-	-	-	-	-	-	-
ICNE	5-10		-	-	-	-	-	-	-	-
ICNE	10-15		-	-	-	-	-	-	-	-
ICNE	15-20		-	-	-	-	-	-	-	-
LEGI	5-10		-	-	-	3I	-	-	-	-
LEGI	10-15	5F5/5M5/4I	8F5/5M5/17I	3I/2F5	1F5	-	-	-	-	-
LEGI	15-20	-	-	-	-	-	-	-	-	-
LEOS	5-10	-	-	-	-	-	-	-	-	-
MIDO	3-5	-	-	-	-	-	-	-	-	-
MIDO	5-10	-	-	-	-	-	-	-	-	-
MIDO	10-15	-	-	-	-	-	-	-	-	-
MIDO	15-20	-	-	-	-	-	-	-	-	-
MISA	2-5	-	-	-	-	-	-	-	-	-
MISA	10-15	-	2I	-	-	-	-	-	-	-
MISA	15-20	2I	-	-	1I	-	-	-	-	-
MISA	5-10	-	-	-	-	-	-	-	-	-
NOAT	3-5	-	-	-	-	-	-	-	-	-
NOAT	5-8	-	-	-	-	-	-	-	-	-
NOCR	3-5	4000I	-	-	-	20I	100I	50I	-	1000I
NOCR	5-8	200M6/200F6	3M6	20M6	10M6	-	-	-	-	-
NOCR	8-12	-	-	-	-	-	-	-	-	-
NOHU	1-3	-	-	-	-	-	-	-	-	-
NOHU	3-5	-	-	-	-	-	-	-	-	-
NOHU	5-8	-	-	-	-	-	-	1M5	-	-
NOSP	3-5	-	-	-	-	-	-	-	-	-
NOSP	5-8	25F6	-	30F6	15F6/10M7	2M7/2F7	200M5/300F6	30F6/20I	-	-
NOSP	8-12	-	-	-	-	-	-	-	-	-
PECA	3-5	-	-	-	-	-	-	-	-	-
PEFL	5-10	-	-	-	1I	4I	-	-	-	-
PEFL	10-15	35I	59I	2I	-	-	-	-	-	-
PEFL	15-20	-	-	-	-	-	-	-	-	-
PINO	3-5	100I	-	-	-	-	-	-	-	1000I
PINO	5-8	100F6	-	250F7/250M6	15M5/10F6	20M5/10F7	200F6/200F7	12M6/15F6/11F7	1F5/1M5	-

* Nombre, sexe et maturité :

Sexe : I immature
F femelle
M mâle

Maturité
5 le produit de la fraie s'écoule sous une forte pression abdominale
6 faible pression
7 s'écoule tout seul
8 fraye terminée

Résultats des pêches réalisées à la seine de rivage (nombre, sexe et maturité*) autour de l'Île aux Chats, le 3 juillet 1997

Espèce	Long. (cm)	S1	S2	S3	S4	S5	S6	S7	S8
ALEVINS (sp.)		-	-	500	500	500	-	20	3000
AMRU	3-5	111	-	-	-	111	-	-	-
AMRU	5-10	81	-	-	-	21	-	-	-
AMRU	10-15	-	-	-	-	21	-	-	11
AMRU	15-20	-	-	-	-	-	-	-	-
CACO	3-5	-	-	-	111	-	-	-	-
ESLU	200-250	-	-	-	-	-	-	-	-
ESLU	250-300	-	-	-	-	-	-	-	-
ESMA	5-7	-	-	-	-	-	-	-	-
ETEX	3-5	-	-	51	-	-	-	-	-
ETEX	5-8	-	-	-	-	-	-	-	11
ETNI	1-3	-	-	-	-	-	-	-	-
ETNI	3-5	11	31	-	-	-	-	41	51
ETNI	5-8	-	2F5	25F5/101	-	-	-	-	-
ETNI	8-12	-	-	-	-	-	-	-	-
FUDI	1-3	-	-	-	-	-	-	-	-
FUDI	3-5	-	221	25F5	701	-	-	-	-
FUDI	5-8	11	3F5/2F5/1F6	-	-	-	-	-	-
FUDI	8-12	-	-	-	-	-	-	-	-
LEGI	5-10	11	71	-	-	21	-	-	-
ICNE	10-15	-	-	-	-	-	-	-	-
ICNE	15-20	-	-	-	-	-	-	-	-
ICNE	20-25	11	-	-	-	-	-	-	-
LEGI	10-15	-	-	-	3M7	101	-	-	-
LEGI	15-20	-	-	-	-	-	-	-	-
LEOS	5-10	-	-	-	-	-	-	-	-
MIDO	3-5	-	-	-	-	-	-	-	-
MIDO	5-10	-	-	-	11	-	-	-	-
MIDO	10-15	-	-	-	-	-	-	-	-
MIDO	15-20	-	11	-	-	-	-	-	-
MISA	2-5	-	-	-	-	-	-	-	-
MISA	5-10	-	-	-	-	-	-	-	-
MISA	10-15	-	-	-	-	-	-	-	-
MISA	15-20	-	-	-	-	-	-	-	-
NOAT	3-5	-	-	151	301	-	-	-	-
NOAT	5-8	-	-	-	-	-	-	-	-
NOCR	3-5	2001	-	-	-	-	-	-	-
NOCR	5-8	-	1F7	-	-	-	-	-	-
NOCR	8-12	-	-	-	-	-	-	-	-
NOHU	1-3	-	-	-	-	-	-	-	-
NOHU	3-5	-	-	-	-	-	-	-	-
NOHU	5-8	-	-	-	-	-	-	-	-
NOSP	3-5	-	-	-	201	501	-	-	-
NOSP	5-8	-	-	-	-	30F6/20M5	-	-	-
PECA	3-5	-	-	-	-	-	-	-	-
PECA	5-8	-	-	-	-	-	-	-	-
PECA	8-12	-	-	-	-	-	-	-	-
PEFL	5-10	-	-	-	-	31	-	-	-
PEFL	10-15	11	111	-	-	71	-	-	-
PEFL	15-20	11	61	-	-	-	-	-	-
PINO	3-5	-	4F7/241	351	1001	-	-	-	-
PINO	5-8	-	50F7/31	50F7	150F7	3001/11F6/10M6	-	-	-

* Nombre, sexe et maturité :

Sexe : I : immature
F : femelle
M : mâle

Maturité : 5. le produit de la fraie s'écoule sous une forte pression abdominale
6. faible pression
7. s'écoule tout seul
8. fraye terminée

Résultats des pêches réalisées à la seine de rivage (nombre, sexe et maturité*) autour de l'Île aux Chats, le 5 juin 1997

Espèce	Long. (cm)	S1	S2	S3	S4	S5
ALEVINS (sp.)		-	-	-	-	-
AMRU	3-5	-	-	-	-	-
AMRU	5-10	-	-	-	-	-
AMRU	10-15	-	-	-	-	-
AMRU	15-20	-	-	-	-	-
CACO	3-5	-	-	-	-	-
ESLU	200-250	-	-	-	-	-
ESLU	250-300	-	-	-	-	-
ESMA	5-7	-	-	-	-	-
ETEX	3-5	-	-	-	-	-
ETEX	5-8	-	-	-	-	1I
ETNI	1-3	-	-	-	-	-
ETNI	3-5	-	-	-	5OI	-
ETNI	5-8	-	-	2M5/3F5	-	25I
ETNI	8-12	-	-	-	-	-
FUDI	1-3	-	-	-	-	-
FUDI	3-5	-	-	-	-	-
FUDI	5-8	5OI	-	-	-	5I
FUDI	8-12	-	-	-	-	-
ICNE	5-10	-	-	-	-	-
ICNE	10-15	-	-	-	-	-
ICNE	15-20	-	-	-	-	-
LEGI	5-10	5I	8I	8I	4I	-
LEGI	10-15	-	3I	5I	1F5	-
LEGI	15-20	-	-	-	-	-
LEOS	5-10	-	-	-	-	-
MIDO	3-5	-	-	-	-	-
MIDO	5-10	-	-	-	-	-
MIDO	10-15	-	-	-	-	-
MIDO	15-20	-	-	-	-	-
MISA	2-5	-	-	-	-	-
MISA	10-15	-	-	2I	-	-
MISA	15-20	-	-	-	-	-
MISA	5-10	-	-	-	-	-
NOAT	3-5	-	-	-	-	-
NOAT	5-8	80OI	-	-	-	-
NOCR	3-5	5I	-	-	-	5I
NOCR	5-8	-	-	-	-	-
NOCR	8-12	-	-	-	-	-
NOHU	1-3	-	-	-	-	-
NOHU	3-5	-	-	-	-	-
NOHU	5-8	-	-	-	-	-
NOSP	3-5	-	-	-	-	-
NOSP	5-8	-	-	-	-	-
PECA	3-5	-	-	-	-	-
PEFL	5-10	5I	-	-	25I	-
PEFL	10-15	-	3I	-	-	-
PEFL	15-20	-	-	-	-	-
PINO	3-5	-	-	-	-	250I
PINO	5-8	200I	-	-	25I	20I

* Nombre, sexe et maturité :

Sexe : I : immature
F : femelle
M : mâle

Maturité : 5. le produit de la fraie s'écoule sous une forte pression abdominale
6. faible pression
7. s'écoule tout seul
8. fraye terminée

Résultats des pêches réalisées à la seine de rivage (nombre, sexe et maturité*) autour de l'Île aux Chats, le 17 juillet 1997

Espece	Long. (cm)	S1	S2	S3	S4	S5	S6	S7	S8	S9
ALEVINS (sp.)		500	-	-	500	-	200	-	-	-
AMRU	3-5	1I	-	-	1I	-	-	-	-	-
AMRU	5-10	-	-	-	1I	-	-	-	-	-
AMRU	10-15	3M6	1I	2I	1I	-	-	-	3I	-
AMRU	15-20	-	-	-	-	-	-	-	-	-
CACO	3-5	-	40I	100I	200I	-	-	-	30I	-
ESLU	200-250	-	-	-	-	-	-	-	-	-
ESLU	250-300	-	-	-	-	-	-	-	-	-
ESMA	5-7	-	-	-	-	-	-	-	-	-
ETEX	3-5	-	-	-	-	-	-	3M5	2I	-
ETEX	5-8	-	-	1M7/1I	2I	-	-	2M5	-	-
ETNI	1-3	-	-	-	-	-	-	-	-	-
ETNI	3-5	-	25I	-	-	-	3I	-	-	-
ETNI	5-8	-	15I	20I	-	-	-	-	-	-
ETNI	8-12	-	-	10M5	-	-	-	-	-	-
FUDI	1-3	-	-	-	-	-	-	-	-	-
FUDI	3-5	4F6/7I	-	10I	-	-	5I	-	50I	10I
FUDI	5-8	-	10F6	40F7/10M7	15F7	-	5F5	2F6/30I	20F6/10M6	-
FUDI	8-12	-	-	-	-	-	-	3F6/3M6	-	-
ICNE	5-10	-	-	-	-	-	-	-	-	-
ICNE	10-15	-	-	-	-	-	-	-	-	-
ICNE	15-20	1I	-	-	-	-	-	-	-	-
ICNE	20-25	-	-	-	-	-	-	-	-	-
LEOS	5-10	-	-	-	5I	-	-	-	-	-
LEGI	5-10	-	-	1M7/1I	-	-	1I	1I	-	2M6
LEGI	10-15	-	1I	-	-	-	-	-	-	1M6
LEGI	15-20	-	-	-	1M7	-	-	-	-	1F6
MIDO	3-5	-	-	-	-	-	-	-	-	-
MIDO	5-10	-	-	-	-	-	-	-	-	-
MIDO	10-15	-	-	-	-	-	-	-	-	-
MIDO	15-20	-	-	-	-	-	-	-	-	-
MISA	2-5	-	-	-	-	-	-	-	8I	-
MISA	5-10	1I	-	-	-	-	-	-	-	-
MISA	10-15	-	-	-	-	-	-	-	-	-
MISA	15-20	-	-	-	-	-	-	-	-	-
NOAT	3-5	-	-	-	-	-	-	-	-	100I
NOAT	5-8	-	-	-	30F6	-	-	40F6	-	200I
NOCR	3-5	200I	-	-	-	-	-	-	-	-
NOCR	5-8	-	-	-	-	-	-	-	-	-
NOHU	1-3	-	50I	30I	200I	-	-	-	200I	50I
NOHU	3-5	-	-	-	-	-	-	-	-	-
NOHU	5-8	-	-	-	-	-	-	-	-	-
NOSP	3-5	-	-	-	-	-	-	-	-	-
NOSP	5-8	-	-	-	-	-	-	-	-	-
PECA	3-5	-	1I	-	-	-	-	-	-	-
PEFL	5-10	22I	34I	11I	-	-	-	-	-	-
PEFL	10-15	4I	4I	15I	8I	-	1I	2I	3I	8I
PEFL	15-20	4I	-	1I	-	-	-	-	-	-
PEFL	5-10	-	-	-	-	-	-	-	-	-
PINO	3-5	-	-	25I	50I	-	-	-	-	100I
PINO	5-8	-	30F6/50I	100F6	10F7	-	-	40I	1M6/25F6	200I

* Nombre, sexe et maturité :

Sexe: I immature, F femelle, M mâle

Maturité: 5 le produit de la fraie s'écoule sous une forte pression abdominale; 6 faible pression; 7 s'écoule tout seul; 8 fraye terminée

Résultats des pêches réalisées à la seine de rivage (nombre, sexe et maturité*) autour de l'Île aux Chats, le 24 juillet 1997

Espèce	Long. (cm)	S1	S2	S3	S4	S5	S6	S7	S8	S9
ALEVINS (sp.)	1-2	-	1000I	100I	-	-	-	-	-	-
AMRU	3-5	5I	1I	-	-	3I	1I	-	-	-
AMRU	5-10	1I	1I	1I	1I	1I	-	-	-	-
AMRU	10-15	1I	2I	1F6	1F6/1M8	1I	-	-	-	1I
AMRU	15-20	-	-	-	-	1I	-	-	-	1I
CACO	3-5	10I	-	-	-	5I	10I	-	75I	-
ESLU	200-250	-	-	-	1I	-	-	-	-	-
ESLU	250-300	-	-	-	-	-	-	-	-	-
ESMA	5-7	-	-	1I	2I	-	-	-	-	-
ETEX	3-5	-	-	-	-	-	-	-	1I	-
ETEX	5-8	-	-	-	-	-	-	-	-	-
ETNI	1-3	-	5I	-	-	-	-	-	-	-
ETNI	3-5	1I	2M6/3I	10I	-	5I	-	5I	-	-
ETNI	5-8	-	-	-	-	-	-	-	-	-
ETNI	8-12	-	-	-	-	-	-	-	-	-
FUDI	1-3	-	-	-	-	-	-	10I	-	-
FUDI	3-5	1I	20I	3I	-	10I	-	-	-	2I
FUDI	5-8	-	-	3M7/4F7/2I	10I	15F6	30F6	-	25F6/3M7/12I	1I
FUDI	8-12	-	-	-	-	-	-	-	-	-
ICNE	5-10	-	-	-	-	-	-	-	-	-
ICNE	10-15	-	-	-	-	-	-	-	-	-
ICNE	15-20	-	-	-	-	-	-	-	-	-
ICNE	20-25	-	-	-	-	-	-	-	-	-
LEOS	5-10	-	-	-	2I	-	-	-	-	-
LEGI	5-10	1I7/4I	-	-	-	1I	-	-	-	-
LEGI	10-15	-	-	-	-	1I	1I	-	-	-
LEGI	15-20	-	-	-	-	-	-	-	-	-
MIDO	3-5	-	-	2I	-	-	1I	-	-	2I
MIDO	5-10	-	-	-	-	-	-	-	-	-
MIDO	10-15	-	-	-	-	-	-	-	-	-
MIDO	15-20	-	-	-	-	-	-	-	-	-
MISA	2-5	4I	-	1I	6I	1I	-	-	-	-
MISA	5-10	-	-	-	-	-	-	-	-	-
MISA	10-15	-	-	-	-	-	-	-	-	-
MISA	15-20	-	-	-	-	1I	-	-	-	-
NOAT	3-5	-	-	-	-	-	-	-	-	-
NOAT	5-8	-	-	-	-	40F6/15I	50F6/20I	10I	-	-
NOCR	3-5	-	-	-	-	-	-	-	-	-
NOCR	5-8	-	-	-	-	-	-	-	-	-
NOHU	1-3	30I	50I	30I	-	5I	-	50I	-	40I
NOHU	3-5	-	-	30I	20I	-	-	-	25OI	-
NOHU	5-8	-	-	-	-	-	-	-	-	-
NOSP	3-5	-	-	-	-	-	-	-	-	-
NOSP	5-8	-	-	-	-	-	-	-	-	-
PECA	3-5	-	-	-	-	-	-	-	-	-
PEFL	5-10	1I	11I	14I	2I	-	-	-	-	1I
PEFL	10-15	1I	8I	7I	3I	1I	-	-	1I	1I
PEFL	15-20	-	-	-	-	-	1I	-	-	-
PINO	3-5	-	20I	-	10I	-	20I	-	20I	-
PINO	5-8	-	-	3F8/10I	10F6/20I	30F6/3M7/25I	-	-	20F6/2M6/25I	-

* Nombre, sexe et maturité :

Sexe: I immature; F femelle; M mâle

Maturité: 5 le produit de la fraie s'écoule sous une forte pression abdominale; 6 faible pression; 7 s'écoule tout seul; 8 fraye terminée

ANNEXE H

Noms français, anglais et latins des espèces citées

APPENDIX H

English, French and Latin Names of Species Cited

English Name	French Name	Latin Name
PLANTS		
American Bulrush	Scirpe d'amérique	*Scirpus americanus*
American Eel-grass	Vallisnérie d'amérique	*Vallisneria americana*
American Hackberry	Micocoulier occidental	*Celtis occidentalis*
Aquatic Sedge	Carex aquatique	*Carex aquatilis*
Arrowhead	Sagittaire latifoliée	*Sagittaria latifolia*
Aspen	Peuplier faux-tremble	*Populus tremuloides*
Balsam Poplar	Peuplier baumier	*Populus balsamifera*
Bindweed	Liseron	*Convolvulus sepium*
Black Willow	Saule noir	*Salix nigra*
Bladdernut	Staphylier à trois feuilles	*Staphylea trifolia*
Broad-fruited Bur-reed	Rubanier à gros fruits	*Sparganium eurycarpum*
Broad-leaved Arrow-leaf	Sagittaire latifoliée	*Sagittaria latifolia*
Broad-leaved Cattail	Quenouille à feuilles larges	*Typha latifolia*
Burr arrowhead	Sagittaire dressée	*Sagittaria rigida*
Button-bush	Céphalanthe occidental	*Cephalanthus occidentalus*
Canada blue joint	Calamagrostis du canada	*Calamagrostis canadensis*
Canada Nettle	Laportéa du canada	*Laportea canadensis*
Canada Water-weed	Élodée du canada	*Elodea canadensis*
Cap Touch-me-not	Impatiente du cap	*Impatiens capensis*
Chara	Chara sp.	*Chara*
Choke Cherry	Cerisier à grappes	*Prunus virginiana*
Common elodea	Élodée du canada	*Laportea canadensis*
Common reed-grass	Phragmite commun	*Phragmites communis*
Common Water-Plantain	Alisme commun	*Alisma triviale*
Common Willow	Saule blanc	*Salix alba*
Coontail	Cornifle nageante	*Ceratophyllum demersum*
Cork-Elm	Orme de Thomas	*Ulmus Thomasi*
Cottonwood	Peuplier à feuilles deltoïdes	*Populus deltoides*
Crack Willow	Saule fragile	*Salix fragilis*
Cut-leaved Toothwort	Dentaire laciniée	*Dentaria laciniata*
Grass-leaved Water-Plantain	Alisme graminoïde	*Alisma gramineum*
Great Bulrush	Scirpe des étangs	*Scirpus lacustris*
Gronovius' Dodder	Cuscute de gronovius	*Cuscuta gronovii*
Erect Arrow-leaf	Sagittaire dressée	*Sagittaria rigida*
Fern	Fougère	
Flowering Rush	Butome à ombrelles	*Butomus ombellatus*
Foxtail Sedge	Carex alopécoïde	*Carex alopecoides*
Fragant Water-Lily	Nymphée odorante	*Nymphea odorata*
Frog's bit hydrocarid	Hydrocharide grenouillette	*Hydrocharis morsus-ranae*

English Name	French Name	Latin Name
PLANTS (cont'd)		
Goldenrod	Verge d'or	*Solidago*
Grass-leaved Water-Plantain	Alisme graminoïde	*Alisma gramineum*
Gray Birch	Bouleau gris	*Betula populifolia*
Great Water-Dock	Rumex orbiculaire	*Rumex orbiculatus*
Horned Pondweed	Zannichellie palustre	*Zannichellia palustris*
Hornwort	Cornifle nageante	*Ceratophyllum demersum*
Icelandic Water-Cress	Rorippa d'Islande	*Rorippa islandica*
Illinois Pondweed	Potamot de l'illinois	*Potamogeton illinoensis*
Ivy-leaved Duckweed	Lenticule à trois pointes	*Lemna trisulca*
Larger Duckweed	Spirodèle polyrhize	*Spirodela polyrhiza*
Lesser Duckweed	Lenticule mineure	*Lemna minor*
Marsh Bedstraw	Gaillet palustre	*Galium palustre*
Marsh Shield-Fern	Thélyptéride palustre	*Thelypteris palustris*
Muskgrasses	Chara sp.	*Chara*
Narrowleaf water plantain	Alisme graminoïde	*Alisma gramineum*
Narrow-leaved Cattail	Quenouille à feuilles étroites	*Typha angustifolia*
Nitella	Nitalla sp.	*Nitella sp.*
Nuttall's Water-weed	Élodée de Nuttall	*Elodea nuttallii*
Ostrich Fern	Matteucie fougère-à-l'autruche	*Matteuccia Struthiopteris*
Pale Touch-me-not	Impatiente pâle	*Impatiens pallida*
Pectinate Pondweed	Potamot pectiné	*Potamogeton pectinatus*
Pectinate Spartina	Spartine pectinée	*Spartina pectinata*
Pointed Bulrush	Scirpe aigu	*Scirpus acutus*
Purple Loosestrife	Salicaire commune	*Lythrum salicaria*
Rasberry	Framboisier	*Rubus idaeus*
Red Ash	Frêne de pennsylvanie	*Fraxinus pennsylvanica*
Red-osier Dogwood	Cornouiller stolonifère	*Cornus stolonifera*
Reed-grass	Roseau commun	*Phragmites communis*
Reed Phalaris	Phalaris roseau	*Phalaris arundinacea*
Richardson's Pondweed	Potamot de richardson	*Potamogeton richardsonii*
River Bulrush	Scirpe des rivières, Scirpe fluviatile	*Scirpus fluviatilis*
River Horsetail	Prêle fluviatile	*Equisetum fluviatile*
Sandbar Willow	Saule de l'intérieur	*Salix interior*
Sensitive Fern	Onoclée sensible	*Onoclea sensibilis*
Silver maple	Érable argenté	*Acer saccharinum*
Slender Naias	Naïas souple	*Najas flexilis*
Small's Spike-rush	Éléocharide de small	*Eleocharis Smallii*
Sphagnum	Sphaigne	*Spagnum*
Staghorn Sumach	Sumac vinaigrier	*Rhus typhina*
Stalked Willow	Saule pétiolé	*Salix petiolaris*
Star duckweed	Lenticule à trois pointes	*Lemna trisulca*
Tuberous Water-Lily	Nymphée tubéreuse	*Nymphaea tuberosa*
Tufted Loosestrife	Lysimaque thyrsiflore	*Lysimachia thyrsiflora*

English Name	French Name	Latin Name
PLANTS (cont'd)		
Variable pondweed	Potamot de l'illinois	*Potamogeton illinoensis*
Violet	Violette	*Viola*
Wild Celery	Vallisnérie d'amérique	*Vallisneria americana*
Water Knotweed	Renouée ponctuée	*Poygonum punctatum*
Water Star-grass	Hétéranthère litigieuse	*Heteranthera dubia*
White Snakeroot	Eupatoire rugueuse	*Eupatorium rugosum*
Whitish Water-Milfoil	Myriophylle de sibérie	*Myriophyllum sibriricum*
Wild Rice	Zizanie aquatique	*Zizania aquatica*
Wild Rice	Zizanie des marais	*Zizania palustris*
FISH		
Alewife	Gaspareau	*Alosa pseudoharengus*
American Eel	Anguille d'Amérique	*Anguilla rostrata*
American Shad	Alose savoureuse	*Alosa sapidissima*
Banded Killifish	Fondule barré	*Fundulus diaphanus*
Blackchin Shiner	Menton noir	*Notropus heterodon*
Black Crappie	Marigane noire	*Pomoxis nigromaculatus*
Blacknose Shiner	Museau noir	*Notropis heterolepis*
Bluntnose Minnow	Ventre-pourri	*Pimephales notatus*
Bowfin	Poisson castor	*Amia calva*
Bridle Shiner	Méné d'herbe	*Notropus bifrenatus*
Brook Silverside	Crayon d'argent	*Labidesthes sicculus*
Brook Stickleback	Épinoche à cinq épines	*Culaea inconstans*
Brown Bullhead	Barbotte brune	*Ictalurus nebulosus*
Brown Trout	Truite brune	*Salmo trutta*
Burbot	Lotte	*Lota lota*
Carp	Carpe	*Cyprinus carpio*
Channel Catfish	Barbue de rivière	*Ictalurus punctatus*
Channel Darter	Raseux-de-terre (gris)	*Percina copelandi*
Chinook Salmon	Saumon Chinook	*Oncorhynchus tshawytscha*
Common Shiner	Méné à nageoires rouges	*Notropus cornutus*
Creek Chub	Mulet à cornes	*Semotilus atromaculatus*
Cutlips Minnow	Bec-de-lièvre	*Exoglossum maxillingua*
Emerald Shiner	Méné émeraude	*Notropus atherinoides*
Fallfish	Ouitouche	*Semotilus corporalis*
Fathead Minnow	Tête-de-boule	*Pimephales promelas*
Freshwater Drum	Malachigan	*Aplodinotus grunniens*
Golden Shiner	Chatte de l'est	*Notemigonus crysoleucas*
Golden Shiner	Méné jaune	*Notemigonus crysoleucas*
Greater Redhorse	Suceur jaune	*Moxostoma valenciennesi*
Iowa Darter	Dard à ventre jaune	*Etheostoma exile*
Johnny Darter	Raseux-de-terre (noir)	*Etheostoma nigrum*

English Name	French Name	Latin Name
FISH (cont'd)		
Lake Sturgeon	Esturgeon jaune	*Acipenser fulvescens*
Lamprey	Lamproie sp.	*Petromyzontidae spp.*
Largemouth Bass	Achigan à grande bouche	*Micropterus salmoides*
Logperch	Fouille-roche	*Percina caprodes*
Longnose Dace	Naseaux de rapides	*Rhinichthys cataractae*
Longnose gar	Lépisosté osseux	*Lepisosteus osseus*
Longnose Sucker	Meunier rouge	*Catostomus catostomus*
Mimic Shiner	Méné pâle	*Notropus volucellus*
Mooneye	Laquaiche argentée	*Hiodon tergisus*
Mottled Sculpin	Chabot tacheté	*Cottus bairdi*
Muskellunge	Maskinongé	*Esox masquinongy*
Northern Pike	Grand brochet	*Esox lucius*
Pumpkinseed	Crapet-soleil	*Lepomis gibbosus*
Quillback	Couette	*Carpiodes cyprinus*
Rainbow Smelt	Éperlan arc-en-ciel	*Osmerus mordax*
Rainbow Trout	Truite arc-en-ciel	*Salmo gairdneri*
River Redhorse	Suceur ballot	*Moxostoma carinatum*
Rock Bass	Crapet de roche	*Ambloplites rupestris*
Rosyface Shiner	Tête rose	*Notropis rubellus*
Sand Shiner	Méné paille	*Notropus stramineus*
Sauger	Doré noir	*Stizostedion canadense*
Sea lamprey	Lamproie marine	*Petromizon marinus*
Shorthead Redhorse	Suceur rouge	*Moxostoma macrolepidotum*
Silver Redhorse	Suceur blanc	*Moxostoma anisurum*
Smallmouth Bass	Achigan à petite bouche	*Micropterus dolomieui*
Spotfin Shiner	Méné bleu	*Notropus spilopterus*
Spottail Shiner	Queue à tache noire	*Notropis hudsonius*
Trout-perche	Omisco	*Percopsis omiscomaycus*
Walleye	Doré jaune	*Stizostedion vitreum*
White perch	Bar-perche	*Morone americana*
White Sucker	Meunier noir	*Catostomus commersoni*
Yellow Perch	Perchaude	*Perca flavescens*
BIRDS		
American Black Duck	Canard noir	*Anas rubripes*
American Wigeon	Canard siffleur d'amérique	*Anas americana*
Belted Kingfisher	Martin-pêcheur d'Amérique	*Ceryle alcyon*
Black-bellied Plover	Pluvier argenté	*Pluvialis squatarola*
Black-crowned Night-Heron	Bihoreau à couronne noire	*Nycticorax nycticorax*
Blue-Winged Teal	Sarcelle à ailes bleues	*Anas discors*
Bonaparte's Gull	Mouette de Bonaparte	*Larus philadelphia*
Bufflehead	Petit garrot	*Bucephala albeola*

English Name	French Name	Latin Name
BIRDS (cont'd)		
Canada Goose	Bernache du canada	*Branta canadensis*
Common Goldeneye	Garrot à oeil d'or	*Bucephala clangula*
Common loon	Huart à collier	*Gavia immer*
Common Merganser	Grand bec-scie	*Mergus merganser*
Common Tern	Sterne pierregarin	*Sterna hirundo*
Double-Crested Cormorant	Cormoran à aigrettes	*Phalacrocorax auritus*
Gadwall	Canard chipeau	*Anas strepera*
Great Blue Heron	Grand héron	*Ardea herodias*
Greater Black-Back Gull	Goéland à manteau noir	*Larus marinus*
Greater scamp	Grand morillon	*Athya marila*
Greater Yellowlegs	Grand chevalier	*Tringa melanoleucas*
Green Heron	Héron vert	*Butorides striatus*
Green-Winged Teal	Sarcelle à ailes vertes	*Anas crecca*
Hooded Merganser	Bec-scie couronnée	*Lophodytes cucullatus*
Killdeer	Pluvier kildir	*Charadrius vociferus*
Lesser scamp	Petit morillon	*Athya affinis*
Mallard	Canard colvert	*Anas platyrhynchos*
Northern Pintail	Canard pilet	*Anas acuta*
Northern Shoveler	Canard souchet	*Anas clypeata*
Red-Breasted Merganser	Bec-scie à poitrine rousse	*Mergus serrator*
RedHead	Morillon à tête rouge	*Athya americana*
Ring-billed Gull	Goéland à bec cerclé	*Larus delawarensis*
Ring-Necked Duck	Morillon à collier	*Athya collaris*
Spotted Sandpiper	Chevalier branlequeue	*Actitis macularia*
Wood Duck	Canard branchu	*Aix sponsa*
MAMMALS		
Beaver	Castor	*Castor canadensis*
Muskrat	Rat musqué	*Ondatra zibethicus*
REPTILES AND AMPHIBIANS		
American Toad	Crapeau d'Amérique	*Bufo americanus*
Blue-spotted Salamander	Salamandre à points bleus	*Ambystoma laterale*
Bullfrog	Ouaouaron	*Rana catesbeiana*
Common Garter Snake	Couleuvre rayée	*Thamnophis sirtalis*
Common Snapping Turtle	Chélydre serpentine	*Chelydra serpentina*
Eastern Newt	Triton vert	*Notophthalmus viridescens*
Green Frog	Grenouille verte	*Rana clamitans*

English Name	French Name	Latin Name
REPTILES AND AMPHIBIANS (cont'd)		
Mudpuppy	Necture tachetée	*Necturus maculosus*
Northern Leopard Frog Northern Spring Peeper	Grenouille léopard Rainette crucifère	*Rana pipiens* *Pseudacris crucifer*
Painted turtle	Tortue peinte	*Chrysemys picta*
Redbelly Snake	Couleuvre à ventre rouge	*Storeria occipitomaculata*
Tetraploid Gray Treefrog	Rainette versicolore	*Hyla versicolor*
Wood Frog Wood turtle	Grenouille des bois Tortue des bois	*Rana sylvatica* *Clemmys insculpta*

ANNEXE I

Commentaires du MEF concernant les méthodes d'analyse du sélénium dans les filets de poisson

Gouvernement du Québec
Ministère de l'Environnement et de la Faune
Direction des laboratoires
Service de gestion de la qualité et du développement

NOTE

DESTINATAIRE : Madame Chantal Dubreuil
Direction de l'évaluation environnementale des projets industriels et en milieu hydrique

EXPIDITEUR : Louis Martel

DATE : Le 15 mai 1997

OBJET : Analyse du sélénium dans les filets de poissons - Projet de restauration des sédiments - Site de l'Île-aux-Chats

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La présente fait suite aux correspondances de TECSULT (M.-C. Wilson, 2 avril 1997) et d'AlliedSignal (M. Vazquez, 18 avril 1997) concernant l'analyse du sélénium dans les filets de poissons. Les renseignements qui nous ont alors été transmis démontrent que les deux laboratoires impliqués dans ces analyses présentent un problème de précision interlaboratoires.

Comme convenu, nous avons procédé, avec la participation des responsables de l'analyse du sélénium de notre organisation, à l'examen des renseignements fournis.

L'analyse du sélénium dans la chair de poisson est effectuée dans nos laboratoires depuis plusieurs années. Bien que relativement délicate à réaliser, cette analyse peut, lorsque bien maîtrisée, générer des résultats dont la précision et l'exactitude sont satisfaisantes. À titre d'exemple, les résultats du contrôle de qualité effectué dans nos laboratoires en 1996 (trois séries d'analyses) sont annexés.

La méthode de digestion proposée dans le protocole NAQUADAT No 34601, et utilisée par le laboratoire Technitrol-Eco, consiste en un traitement de l'échantillon avec de l'acide nitrique, de l'acide perchlorique et de l'acide sulfurique. Tam et Lacroix (1982) mentionnent qu'une étude interlaboratoires (28 participants), où les échantillons étaient digérés de façon similaire au protocole NAQUADAT, a mis en évidence des problèmes de précision intra- et interlaboratoires.

...2

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Pour sa part, le laboratoire Brooks Rand applique la méthode EPA-200.2 pour la préparation des échantillons. Cette méthode utilise une digestion dans l'acide nitrique et l'acide phosphorique. Les mêmes problèmes que ceux rencontrés avec le mélange d'acides utilisé dans la méthode NAQUADAT No 34601 peuvent être suspectés. D'ailleurs, la méthode EPA-200.2 précise que son utilisation n'est pas recommandée lorsque le dosage des échantillons se fait par absorption atomique avec four au graphite (GFAA). C'est justement cette méthode de dosage (EPA-200.9) qui a été utilisée par Brooks Rand. Les renseignements fournis par ce laboratoire sur l'analyse de matériaux de référence certifiés ne permettent pas de juger de la justesse de leurs analyses puisqu'aucune indication de la concentration en sélénium de ces matériaux n'est présentée.

Des méthodes de digestion semblables à celles utilisées par les deux laboratoires ont déjà été testées dans nos laboratoires et n'ont pas été retenues. La méthode appliquée s'apparente à celle décrite par Tam et Lacroix (1982). Elle consiste en plusieurs étapes : les tissus sont minéralisés en milieu fortement oxydant; du nitrate de magnésium est ajouté afin d'assurer l'oxydation complète de la matière organique et de stabiliser les sels d'arsenic et de sélénium; l'échantillon est calciné, puis redissous dans l'acide chlorhydrique à chaud; le dosage est réalisé par absorption atomique avec génération d'hydrures. Certaines de ces étapes sont critiques, notamment la redissolution dans l'acide chlorhydrique. Néanmoins, la méthode apparaît bien maîtrisée. Les résultats des contrôles de qualité que nous avons obtenus vont d'ailleurs dans ce sens.

Ainsi, les méthodes de digestion des échantillons dans les mélanges d'acides n'ont pas été retenues dans nos laboratoires en raison des faibles performances obtenues lors de nos essais. Selon nos experts, ces méthodes ne semblent pas suffisamment stabilisantes pour garder les sels de sélénium en solution. Il ne nous est cependant pas possible de porter un jugement comparatif sur la validité des résultats générés par ces méthodes dans le cadre du projet de restauration des sédiments du site de l'Île-aux-Chats, puisque nous n'avons effectué aucune analyse de contrôle.

Le tableau 2 de la correspondance d'AlliedSignal du 18 avril 1997 mentionne que bien que les résultats obtenus par Brooks Rand soient de façon constante plus élevés que ceux de Technitrol-Eco, toutes les valeurs sont sous les critères généralement acceptés pour le risque écologique. Les valeurs de référence («Benchmarks») retenues pour le sélénium ne nous ont cependant pas été présentées. Nos calculs selon la méthodologie et les données toxicologiques de Sample *et al.* (1996) ne vont cependant pas dans ce sens. Il serait alors utile d'obtenir le détail des valeurs de référence auxquelles il est fait mention au tableau 2 afin que nous puissions compléter notre analyse.

...3

Le cas échéant, nous sommes disposés à effectuer quelques analyses de contrôle. Ces analyses pourraient se faire sur les échantillons composites utilisés pour l'étude interlaboratoires (No 3184, 3160 et 3215). Si cette proposition est reçue favorablement, nous apprécierions recevoir les échantillons avant le 15 juin 1997.

Nous demeurons disponible pour tout besoin d'information complémentaire.

LM/ct

p.j.

c.c. : *Pierrette Lelièvre*
Direction des laboratoires

Andrée Gendron
Direction des laboratoires

Marc Sinotte
Direction des écosystèmes aquatiques

ANNEXE A

PHYSICOCHIMIE DU MILIEU

CONTRÔLE DE LA QUALITÉ

Réseau toxique 1997 (poissons)

Se : 3 lots (ou séries d'analyses)

COURBES D'ÉTALONNAGE

	Pente unité/mg-L^{-1}	*Corrélation*
Lot 1	*2,04*	*0,9997*
Lot 2	*2,02*	*0,9981*
Lot 3	*1,98*	*0,9988*

BLANCS: <0,01 mg/L (3 lots)

DOUBLES

No labo	Lot	Se (1) mg/L	Se(2) mg/L	Écart mg/L
76134	1	0,40	0,35	0,05
76167	1	0,25	0,23	0,02
76177	2	0,38	0,35	0,03
76184	2	0,35	0,34	0,01
76186	3	0,20	0,19	0,01

POURCENTAGE DE RÉCUPÉRATION: 92 % (ajout dosé sur MAB-3)

MATÉRIAUX DE RÉFÉRENCE

Matériel	Lot	Se (obtenu) mg/L	Se (certifié) mg/L
MAB-3	1	1,38	1,35-1,70
DORM-2	1	1,38	1,40 ±0,09
MAB-3	2	1,44	1,35-1,70
DORM-1	2	1,38	1,40 ±0,09
MAB-3	3	1,28	1,35-1,70
DORM-1	3	1,38	1,40 ±0,09

Andrée Gendron, chimiste

ANNEXE B

RÉFÉRENCES

EPA, 1994. Methods for the Determination of Metals in Environmental Samples. Supplement 1. Environmental Monitoring Systems Laboratory. Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio. EPA-200.2 and -200.9.

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Tam, G.K.H. and Lacroix, G., 1982. Dry Ashing, Hydride Generation Atomic Absorption Spectrometric Determination of Arsenic and Selenium in Foods. Journal of the Association of Official Analytical Chemist, 65 (3) : 647-650.

ANNEXE J

Résultats analytiques sur les filets de poisson
(1989, 1993, 1996 et 1997)

ALLIEDSIGNAL - CLARK ISLAND SITE

1997 MORPHOMETRIC DATA OF FISH CAPTURED

YELLOW PERCHES

LOCATION	SAMPLE NUMBER	SEX	LENGTH (mm)	WEIGHT (g)
St-Anicet (upstream)	1	F	198,0	90,0
	2	M	212,0	120,0
	4	M	187,0	90,0
	5	M	193,0	82,0
	6	M	189,0	77,0
	7	M	195,0	90,0
	11	M	191,0	80,0
	15	F	193,0	84,0
	17	M	193,0	84,0
	32	F	201,0	85,0
	33 (duplicate of 32)	F	201,0	85,0
Clark Island	36	F	201,0	104,0
	37 (duplicate of 36)	F	201,0	104,0
	40	F	189,0	77,0
	43	M	192,0	78,0
	47	M	191,0	82,0
	49	M	193,0	76,0
	50	F	201,0	83,0
	51	F	211,0	105,0
	52	F	188,0	78,0
	53	M	190,0	78,0
	54	M	193,0	75,0

NOTES : F: female

I: immature

M: male

ALLIEDSIGNAL - CLARK ISLAND SITE

1997 MORPHOMETRIC DATA OF FISH CAPTURED

NORTHERN PIKE

LOCATION	SAMPLE NUMBER	SEX	LENGTH (mm)	WEIGHT (g)
St-Anicet (upstream)	21	M	735,0	2 450,0
	22 (triplicate of 21)	M	735,0	2 450,0
	23 (triplicate of 21)	M	735,0	2 450,0
	24	F	727,0	2 300,0
	25	F	651,0	1 400,0
	26	M	572,0	1 120,0
	27	F	668,0	1 690,0
	28	F	516,0	490,0
	29	M	611,0	1 520,0
	30	I	405,0	370,0
	31	M	647,0	910,0
Clark Island	56	F	710,0	2 090,0
	57 (triplicate of 56)	F	710,0	2 090,0
	58 (triplicate of 56)	F	710,0	2 090,0
	59	F	669,0	500,0
	60	M	578,0	840,0
	62	F	605,0	1 405,0
	63	M	647,0	1 580,0
	66	F	643,0	1 390,0
	68	F	512,0	720,0
	69	M	413,0	440,0
	70	I	753,0	2 630,0
	71	F	611,0	1 350,0

NOTES : F: female
I: immature
M: male

ALLIEDSIGNAL - CLARK ISLAND SITE

FISH FILLETS CHARACTERIZATION

YELLOW PERCHES - 1997 SAMPLE RESULTS

LOCATION	SAMPLE NUMBER	SEX	SELENIUM (wet weight)
St-Anicet (upstream)	1	F	0,4
	2	M	0,5
	4	M	0,5
	5	M	0,5
	6	M	0,6
	7	M	0,3
	11	M	0,5
	15	F	0,5
	17	M	0,6
	32	F	0,4
	33 (duplicate of 32)	F	0,4
	Geometric mean (1)	-	**0,47**
Clark Island	36	F	2,5
	37 (duplicate of 36)	F	2,7
	40	F	3,5
	43	M	1,2
	47	M	0,9
	49	M	0,7
	50	F	2,1
	51	F	0,4
	52	F	3,0
	53	M	0,7
	54	M	1,5
	Geometric mean (1)	-	**1,34**
	Detection limit	-	**0,2**

NOTES : F: female

I: immature

M: male

(1) : The geometric mean was calculated using the half detection limit value when the value was not detected

ALLIEDSIGNAL - CLARK ISLAND SITE

FISH FILLETS CHARACTERIZATION

NORTHERN PIKES - 1997 SAMPLE RESULTS

LOCATION	SAMPLE NUMBER	SEX	SELENIUM (wet weight)
St-Anicet (upstream)	21	M	0,4
	22 (triplicate of 21)	M	0,4
	23 (triplicate of 21)	M	0,4
	24	F	0,3
	25	F	0,3
	26	M	0,4
	27	F	0,5
	28	F	0,4
	29	M	0,5
	30	I	0,6
	31	M	0,2
	Geometric mean (1)	-	**0,38**
Clark Island	56	F	0,8
	57 (triplicate of 56)	F	0,8
	58 (triplicate of 56)	F	0,8
	59	M	1,5
	60	M	2,6
	62	M	2,1
	63	F	1,9
	66	F	0,7
	68	F	2,1
	69	M	2,1
	70		1,5
	71	M	0,8
	Geometric mean (1)	-	**1,47**
	Detection limit	-	**0,2**

NOTES : F: female

I: immature

M: male

(1) : The geometric mean was calculated using the half detection limit value when the value was not detected

ALLIEDSIGNAL - CLARK ISLAND SITE
1996 MORPHOMETRIC DATA OF FISH CAPTURED
YELLOW PERCH

SAMPLE NUMBER	SEX	LENGTH (cm)	WEIGHT (g)	SAMPLE NUMBER	SEX	LENGTH (cm)	WEIGHT (g)
PA-1	M	15.0	55.5	PC-31	F	14.0	43.5
PA-2	F	17.5	92.5	PC-32	F	18.0	86.4
PA-3	F	19.0	99.2	PC-33	F	12.5	42.5
PA-4	M	17.0	71.0	PC-34	F	17.0	74.7
PA-5	F	18.0	87.0	PC-35	M	13.0	38.8
PA-6	F	18.0	91.1	PC-36	M	14.6	44.8
PA-7	M	18.0	85.3	PC-37	M	15.0	50.0
PA-8	M	16.0	58.8	PC-38	M	15.2	57.4
PA-9	F	21.0	139.9	PC-39	J	13.5	41.0
PC-4	J	12.0	28.3	PC-40	F	14.0	49.0
PC-5	J	17.5	72.7	PC-41	F	15.0	55.4
PC-6	J	17.0	80.5	PC-42	M	14.5	43.6
PC-7	J	14.0	40.3	PC-43	F	14.5	47.7
PC-8	F	15.0	48.9	PC-44	M	13.8	37.8
PC-9	M	14.0	43.5	PC-45	F	13.5	45.6
PC-10	J	13.2	39.6	PC-46	F	16.5	66.1
PC-11	M	16.0	60.9	PC-47	F	16.0	55.9
PC-12	F	15.0	57.2	PC-48	J	13.5	38.2
PC-13	F	16.5	68.9	PC-49	M	14.5	41.6
PC-14	F	14.0	44.9	PC-50	F	15.0	55.5
PC-15	F	14.0	44.6	PC-51	F	12.0	38.3
PC-16	F	14.0	48.9	PC-52	M	16.0	58.5
PC-17	F	15.0	48.3	PC-53	F	15.7	54.2
PC-18	M	15.5	52.3	PC-54	F	13.5	42.6
PC-19	N/D	12.5	38.9	PC-55	F	17.0	70.6
PC-20	M	13.5	42.7	PC-56	F	14.0	47.9
PC-21	F	14.0	47.9	PC-57	F	16.2	65.8
PC-22	F	15.0	49.8	PC-58	F	15.2	58.7
PC-23	F	15.5	58.6	PC-59	M	14.5	48.7
PC-24	F	15.0	51.1	PC-60	M	14.0	43.1
PC-25	M	15.3	55.3	PC-61	F	14.0	42.8
PC-26	J	12.5	32.5	PC-62	M	13.8	39.1
PC-27	F	13.5	37.2	PC-63	M	14.0	46.9
PC-28	J	13.5	31.4	PC-64	M	14.3	44.0
PC-29	F	16.5	64.4	PC-65	N/D	15.0	70.1
PC-30	M	16.0	64.4				

NOTES : F: female
J: juvenile
M: male
N/D: sex not identified

PA : Perch from St- Anicet (upstream)
PC : Perch from Clark Island (Northeast bay)

ALLIEDSIGNAL - CLARK ISLAND SITE

1996 MORPHOMETRIC DATA OF FISH CAPTURED

NORTHERN PIKE

SAMPLE NUMBER	SEX	LENGTH (cm)	WEIGHT (g)
BA-1	F	57.0	1200.0
BA-5	F	75.0	2000.0
BA-6	J	28.0	200.0
BA-7	M	28.5	200.0
BA-8	F	56.5	1200.0
BA-10	J	31.5	400.0
BC-1	F	56.0	1000.0
BC-2	F	52.0	800.0
BC-3	F	53.5	1000.0
BC-7	F	42.0	500.0
BC-8	F	41.5	500.0
BC-9	F	71.0	2100.0
BC-14	F	56.0	1100.0
BC-16	F	53.0	1200.0
BC-17	M	39.5	500.0
BC-18	F	41.0	500.0
BC-21	J	24.0	200.0
BC-22	M	38.5	500.0
BC-23	M	36.0	400.0
BC-24	J	29.0	200.0
BC-27	F	55.0	1500.0
BC-28	F	56.0	1300.0
BC-29	F	36.0	500.0

NOTES : F: female
J: juvenile
M: male

BA : Pike from St- Anicet (upstream)
BC : Pike from Clark Island (Northeast bay)

ALLIEDSIGNAL - CLARK ISLAND SITE
FISH FILLETS CHARACTERIZATION
YELLOW PERCH - 1996 SAMPLE RESULTS

SAMPLE NUMBER	PARAMETERS (mg/kg wet base)								
	Sex	Moisture(%)	Arsenic	Cadmium	Copper	Lead	Mercury	Selenium	Zinc
PA-1+PA-4	M	80	<0.1	<0.002	0.5	0.02	0.11	<0.1	7.8
PA-7+PA-8	M	79	<0.1	<0.002	0.5	0.02	0.15	0.2	8.9
PA-2+PA-3	F	79	<0.1	<0.002	0.5	0.02	0.16	<0.1	6.9
PA-5+PA-6+PA-9	F	78	<0.1	<0.002	0.3	0.02	0.15	<0.1	6.5
PA-5+PA-6+PA-9 (dupl.)	F	78	<0.1	<0.002	0.3	0.02	0.17	<0.1	6.9
Geometric mean (1)	-	-	**<0.1**	**<0.002**	**0.44**	**0.02**	**0.14**	**0.07**	**7.47**
PC-9+PC-11+PC-18	M	77	<0.1	<0.002	0.5	0.02	0.13	0.4	8.6
PC-9+PC-11+PC-18 (dupl.)	M	77	<0.1	<0.002	0.6	0.03	0.12	0.2	9.1
PC-20+PC-25+PC-30	M	79	<0.1	<0.002	0.6	0.03	0.06	0.4	8.6
PC-35+PC-36+PC-37	M	78	<0.1	<0.002	0.5	0.02	0.16	0.2	6.4
PC-38+PC-42+PC-44	M	79	<0.1	<0.002	0.6	0.04	0.09	0.4	8.0
PC-49+PC-52+PC-59	M	79	<0.1	<0.002	0.5	0.01	0.12	0.3	7.5
PC-60+PC-62	M	79	<0.1	<0.002	0.5	0.02	0.12	0.5	9.1
[illegible]-63+PC-64	M	79	<0.1	0.003	0.6	0.03	0.18	<0.1	8.7
[illegible]-8+PC-12+PC-13	F	77	<0.1	<0.002	0.7	0.05	0.14	0.3	8.4
PC-8+PC-12+PC-13 (dupl.)	F	77	<0.1	<0.002	0.5	0.03	0.13	0.2	8.7
PC-14+PC-15+PC-16	F	80	<0.1	<0.002	0.5	0.01	0.12	0.3	7.5
PC-17+PC-21+PC-22	F	80	<0.1	<0.002	0.5	0.01	0.15	0.4	7.9
PC-23+PC-24+PC-27	F	78	<0.1	<0.002	0.4	0.08	0.07	0.3	8.3
PC-29+PC-31+PC-32	F	79	<0.1	<0.002	0.4	0.02	0.09	0.5	7.4
PC-33+PC-34+PC-40	F	79	<0.1	<0.002	0.4	0.07	0.12	0.3	7.6
PC-41+PC-45+PC-46	F	79	<0.1	<0.002	0.5	0.02	0.10	<0.1	8.0
PC-43+PC-53+PC-54	F	79	<0.1	<0.002	0.4	0.01	0.08	0.5	7.0
PC-47+PC-50+PC-51	F	78	<0.1	<0.002	0.5	0.09	0.10	0.4	8.2
PC-55+PC-56+PC-57	F	78	<0.1	<0.002	0.6	0.05	0.16	<0.1	7.7
PC-58+PC-61	F	79	<0.1	<0.002	0.5	0.04	0.13	<0.1	8.5
PC-28+PC-39+PC-48	J	78	<0.1	<0.002	0.4	0.02	0.16	<0.1	9.9
PC-4+PC-10+PC-26	J	78	<0.1	<0.002	0.5	0.03	0.11	0.2	9.2
PC-5+PC-6+PC-7	J	79	<0.1	<0.002	0.4	0.01	0.14	0.2	8.6
PC-19+PC-65	N/D	79	<0.1	<0.002	0.6	0.04	0.10	0.3	8.9
Geometric mean (1)	-	-	**<0.1**	**0.0010**	**0.50**	**0.03**	**0.12**	**0.22**	**8.14**
Detection limit	-	-	**0.1**	**0.002**	**0.05**	**0.01**	**0.02**	**0.1**	**0.01**

NOTES : F: female — PA : Perch from St- Anicet (upstream)
J: juvenile — PC : Perch from Clark Island (northeast bay)
M: male — N/D: sex not identified
dupl.: duplicate sample
(1) : The geometric mean was calculated using the half detection limit value when the value was not detected.

ALLIEDSIGNAL - CLARK ISLAND SITE
FISH FILLETS CHARACTERIZATION
NORTHERN PIKE - 1996 SAMPLE RESULTS

SAMPLE NUMBER	PARAMETERS (mg/kg wet base)								
	Sex	Moisture(%)	Arsenic	Cadmium	Copper	Lead	Mercury	Selenium	Zinc
BA-7	M	85	<0.1	<0.002	0.4	0.14	0.08	<0.1	9.0
BA-1	F	86	<0.1	<0.002	0.8	0.04	0.73	<0.1	7.0
BA-5	F	83	<0.1	<0.002	0.3	0.06	1.91	<0.1	5.0
BA-8	F	84	<0.1	<0.002	0.4	0.03	0.48	<0.1	9.0
BA-8 (dupl.)	F	84	<0.1	<0.002	0.3	0.04	0.52	<0.1	10.0
BA-6	J	84	<0.1	<0.002	0.3	0.11	0.13	<0.1	10.0
BA-10	J	84	<0.1	<0.002	0.3	0.12	0.1	<0.1	10.0
Geometric mean (1)	-	-	**<0.1**	**<0.002**	**0.39**	**0.07**	**0.30**	**<0.1**	**8.11**
BC-17	M	84	<0.1	<0.002	0.3	0.01	0.15	0.2	7.0
BC-22	M	84	<0.1	<0.002	0.3	0.01	0.11	<0.1	5.0
BC-23	M	84	<0.1	<0.002	0.3	0.01	0.21	0.4	9.0
BC-1	F	81	<0.1	<0.002	0.3	0.11	0.52	<0.1	6.0
BC-2	F	85	<0.1	<0.002	0.2	0.02	0.29	0.2	6.0
BC-2 (dupl.)	F	85	<0.1	<0.002	0.2	0.03	0.27	<0.1	7.0
BC-3	F	78	<0.1	<0.002	0.3	0.01	0.47	<0.1	8.0
BC-7	F	84	<0.1	<0.002	0.3	0.03	0.16	<0.1	6.0
BC-8	F	80	<0.1	<0.002	0.3	0.01	0.09	<0.1	7.0
BC-9	F	79	<0.1	<0.002	0.3	0.02	0.74	<0.2	5.0
BC-9 (dupl.)	F	79	<0.1	<0.002	0.2	0.01	0.74	<0.2	5.0
BC-14	F	79	<0.1	<0.002	0.3	0.02	0.25	0.4	6.0
BC-16	F	80	<0.1	<0.002	0.3	0.01	0.3	<0.1	6.0
BC-18	F	79	<0.1	<0.002	0.3	0.01	0.15	0.2	9.0
BC-27	F	80	<0.1	<0.002	0.4	0.03	0.53	0.2	6.0
BC-28	F	83	<0.1	<0.002	0.4	0.03	0.32	0.4	6.0
BC-29	F	82	<0.1	<0.002	0.4	0.02	0.21	0.2	8.0
BC-21	J	79	<0.1	<0.002	0.4	0.02	0.15	<0.1	9.0
BC-24	J	80	<0.1	<0.002	0.3	0.01	0.13	0.3	9.0
Geometric mean (1)	-	-	**<0.1**	**<0.002**	**0.31**	**0.02**	**0.24**	**0.13**	**6.81**
Detection limit	-	-	**0.1**	**0.002**	**0.05**	**0.02**	**0.02**	**0.1 to 0.2**	**0.01**

NOTES : F: female
J: juvenile
M: male

BA : Pike from St- Anicet (upstream)
BC : Pike from Clark Island (northeast bay)

(1) : The average concentration was calculated using the half detection limit value when the value was not detected

ALLIEDSIGNAL – CLARK ISLAND
MORPHOMETRIC DATA OF FISH SAMPLES (1993)

GROUP	SAMPLE NUMBER	SEX	WEIGHT (g)	LENGTH (cm)
YELLOW PERCH	M1	MALE	62.22	16.5
	M2	MALE	92.03	19.5
	M3	MALE	83.40	19.0
	M9	MALE	41.08	15.0
	M14	MALE	31.14	13.5
	F7	FEMALE	51.58	15.5
	F8	FEMALE	28.55	13.0
	F10	FEMALE	107.07	20.5
	F14	FEMALE	130.22	20.5
	F17	FEMALE	176.79	22.1
	J1	JUVENILES	21.53	12.0
	J2	JUVENILES	22.41	12.0
	J3	JUVENILES	25.14	12.0
	J4	JUVENILES	36.58	13.5
	J6	JUVENILES	20.13	12.0
NORTHERN PIKE	M1	MALE	360.0	33.5
	M2	MALE	402.0	33.0
	F3	FEMALE	1234.0	49.0
	F5	FEMALE	502.6	36.0
	F7	FEMALE	424.0	33.0

ALLIEDSIGNAL – CLARK ISLAND
FISH CHARACTERIZATION
1993 SAMPLE RESULTS

GROUP	SAMPLE NUMBER	SEX	MEASURED CONCENTRATION (mg/kg)							
			ARSENIC	CADMIUM	COPPER	MERCURY	LEAD	SELENIUM	ZINC	FLUORIDES
DETECTION LIMIT			<0.1	<0.02	<0.5	<0.005	<0.05	<0.01	<0.1	<0.3
YELLOW PERCH	M1+M14 (1)	MALE	<0.1	<0.02	0.5	0.082	0.41	0.85	20.0	<0.3
	M2 (1)	MALE	<0.1	<0.02	1.0	0.114	0.12	0.90	12.5	<0.3
	M3 (1)	MALE	<0.1	<0.02	0.5	0.185	0.12	0.70	8.0	<0.3
	M9 (1)	MALE	<0.1	<0.02	0.5	0.050	<0.05	1.65	8.0	<0.3
	F7 (1)	FEMALE	<0.1	<0.02	1.0	0.074	0.13	1.40	6.0	–
	F8 (1)	FEMALE	<0.1	<0.02	0.5	0.066	0.10	0.80	7.0	<0.3
	F10 (1)	FEMALE	<0.1	<0.02	0.5	0.117	0.25	0.70	7.5	<0.3
	F14 (1)	FEMALE	<0.1	<0.02	0.5	0.118	0.45	0.45	7.0	<0.3
	F17 (1)	FEMALE	<0.1	<0.02	0.5	0.064	0.11	1.70	7.5	<0.3
	F17 (2)	FEMALE	<0.3	<0.01	2.1	0.040	<0.03	1.00	9.8	–
	J1+J2+J6 (1)	JUVENILES	<0.1	<0.02	0.5	0.080	0.19	2.20	9.0	<0.3
	J3 (1)	JUVENILES	<0.1	<0.02	0.5	0.066	0.26	0.40	9.0	–
	J4 (1)	JUVENILES	<0.1	<0.02	0.5	0.027	0.19	2.50	7.0	<0.3
NORTHERN PIKE	M1 (1)	MALE	<0.1	<0.02	0.5	0.117	0.35	2.10	6.5	<0.3
	M2 (1)	MALE	<0.1	<0.02	0.5	0.119	0.12	2.30	8.0	<0.3
	F3 (1)	FEMALE	<0.1	<0.02	0.7	0.117	0.14	2.70	5.0	<0.3
	F3 (2)	FEMALE	<0.3	<0.01	2.2	0.030	<0.03	1.40	7.5	–
	F5 (1)	FEMALE	<0.1	<0.02	0.5	0.061	0.21	3.40	8.0	<0.3
	F7 (1)	FEMALE	<0.1	<0.02	<0.5	0.110	0.09	2.30	7.0	<0.3
NUMBER OF OCCURRENCES			0/17	0/17	16/17	17/17	16/17	17/17	17/17	0/17
GEOMETRIC AVERAGE (1)			<0.1	<0.02	0.53	0.08	0.16	1.32	7.99	<0.3

NOTE : (1) RESULTS FROM ECO–CNFS LABORATORY; THE GEOMETRIC AVERAGE WAS CALCULATED USING 1/2 DETECTION LIMIT VALUE WHEN THE VALUE WAS NOT DETECTED
(2) RESULTS FROM ZENON LABORATORY

DONNEES MORPHOMETRIQUES POUR LES ECHANTILLONS DE PERCHAUDES (1989)

a) Mâles et femelles

Sexe	Date échantillonnée	Poids g	Longueur cm	Identification du laboratoire
Femelle	27-Feb-89	200	24.5	P-1
Femelle	27-Feb-89	140	21.1	P-2
Femelle	27-Feb-89	120	20.8	P-3
Femelle	27-Feb-89	85	18.9	P-6
Femelle	27-Feb-89	95	19.1	P-6
Femelle	28-Feb-89	135	21.2	P-4
Femelle	28-Feb-89	145	21.0	P-5
Femelle	28-Feb-89	95	19.7	NT
Femelle	28-Feb-89	100	19.5	NT
Male	27-Feb-89	115	20.6	P-11
Male	27-Feb-89	55	16.5	P-11
Male	27-Feb-89	110	20.2	P-14
Male	27-Feb-89	75	18.4	P-14
Male	27-Feb-89	85	18.6	P-15
Male	27-Feb-89	85	18.8	P-15
Male	27-Feb-89	75	18.3	
Male	27-Feb-89	55	16.2	
Male	27-Feb-89	95	18.4	
Male	27-Feb-89	135	21.5	
Male	27-Feb-89	85	18.6	
Male	28-Feb-89	115	20.5	P-16
Male	28-Feb-89	95	19.2	P-16
Male	28-Feb-89	155	22.1	P-17
Male	28-Feb-89	120	20.0	P-17
Male	28-Feb-89	120	20.8	P-18
Male	28-Feb-89	75	18.1	P-18

DONNEES MORPHOMETRIQUES POUR LES ECHANTILLONS DE PERCHAUDES (1989)

b) Jeunes

Sexe	Date échantillonnée	Poids g	Longueur cm	Identification du laboratoire
Jeune	27-Feb-89	60	16.8	P-21
Jeune	27-Feb-89	35	14.9	P-21
Jeune	27-Feb-89	55	16.3	P-21
Jeune	27-Feb-89	45	15.4	P-22
Jeune	27-Feb-89	95	19.0	P-22
Jeune	27-Feb-89	80	18.3	P-23
Jeune	27-Feb-89	70	18.7	P-23
Jeune	27-Feb-89	95	19.5	P-24
Jeune	27-Feb-89	75	18.3	P-24
Jeune	27-Feb-89	55	17.2	P-24
Jeune	27-Feb-89	45	15.5	
Jeune	27-Feb-89	35	14.4	
Jeune	28-Feb-89	45	15.4	P-25
Jeune	28-Feb-89	45	14.8	P-25
Jeune	28-Feb-89	60	17.5	P-25
Jeune	28-Feb-89	75	18.0	P-25
Jeune	28-Feb-89	45	16.3	P-26
Jeune	28-Feb-89	45	15.8	P-26
Jeune	28-Feb-89	35	14.6	P-26
Jeune	28-Feb-89	35	14.7	P-26
Jeune	28-Feb-89	60	17.1	
Jeune	28-Feb-89	45	15.5	
Jeune	28-Feb-89	45	15.1	
Jeune	28-Feb-89	35	15.1	
Jeune	28-Feb-89	60	16.7	
Jeune	28-Feb-89	30	13.9	
Jeune	28-Feb-89	35	14.8	
Jeune	28-Feb-89	65	17.9	

DONNEES MORPHOMETRIQUES POUR LES ECHANTILLONS DE BROCHETS (1989)

Sexe	Date échantillonnée	Poids g	Longueur cm	Identification du laboratoire
Femelle	27-Feb-89	1590	63.5	B-1
Femelle	28-Feb-89	455	42.5	B-2
Femelle	01-Mar-89	2730	73.0	B-3
Male	28-Feb-89	680	46.4	B-5
Male	01-Mar-89	485	41.9	B-4
Male	02-Mar-89	520	43.0	B-6

RESULTATS ANALYTIQUES OBTENUS DES ECHANTILLONS DE POISSONS (1989)

Groupe	Numéro d'échantillon Seuil de détection	Arsenic (0,01) (mg/kg)	Cadmium (0,1) (mg/kg)	Cuivre (0,5) (mg/kg)	Plomb (0,2) (mg/kg)	Mercure (0,005) (mg/kg)	Sélénium (0,01) (mg/kg)	Zinc (0,1) (mg/kg)	Fluoru (0,3 (mg/k
Perchaude femelle	P-1	--	--	--	--	0,107	--	1,02	--
	P-2	0,014	--	--	--	0,082	--	0,90	--
	P-3	--	--	--	--	0,076	--	0,47	--
	P-4	--	--	--	--	0,081	--	0,64	--
	P-5	--	--	--	--	0,091	--	0,93	--
	P-6	0,015	--	--	--	0,076	--	1,68	--
Perchaude mâle	P-11	0,017	--	--	--	0,102	--	1,02	--
	P-14	--	--	--	--	0,089	--	0,91	--
	P-15	0,019	--	--	--	0,112	--	1,19	--
	P-16	--	--	--	--	0,096	--	1,27	--
	P-17	--	--	--	--	0,087	--	1,29	--
	P-18	--	--	--	--	0,077	--	1,07	--
Perchaude jeune	P-21	--	--	--	--	0,017	--	1,07	--
	P-22	--	--	--	--	0,019	--	0,86	--
	P-23	--	--	--	--	0,026	--	1,11	--
	P-24	--	--	--	--	0,027	--	1,03	--
	P-25	--	--	--	--	0,011	--	1,09	--
	P-26	--	--	--	--	0,009	--	0,99	--
Brochet	B-1	0,013	--	--	--	0,570	--	1,50	--
	B-2	0,019	--	--	--	0,411	0,02	0,43	--
	B-3	--	--	--	--	0,713	--	0,98	--
	B-4	--	--	--	--	2,26	0,03	0,78	--
	B-5	0,015	--	--	--	0,87	--	0,98	--
	B-6	--	--	--	--	0,72	--	0,93	--
	Moyenne géométrique	0,007	0,05	--	--	0,101	0,006	0,96	--

SOMMAIRE DES RESULTATS DES ANALYSES DE TISSUS[1]

DE POISSONS (1989

Paramètre	Nombre d'analyse	Nombre d'occurence	Moyenne géométrique[2]	Concentration maximale mesurée
Arsenic	24	7	0,007	0,019
Cadmium	24	0	--[3]	--
Cuivre	24	0	--	--
Plomb	24	0	--	--
Mercure	24	13	0,101	2,26
Sélénium	24	2	0,006	0,03
Zinc	24	24	0,96	1,68
Fluorures	24	0	--	--

1 - Echantillons de poissons obtenus en février/mars 1989 dans la baie St-François
2 - Moyenne géométrique calculée en utilisant la moitié du seuil de détection lorsque non détecté
3 - Non détecté

ANNEXE K

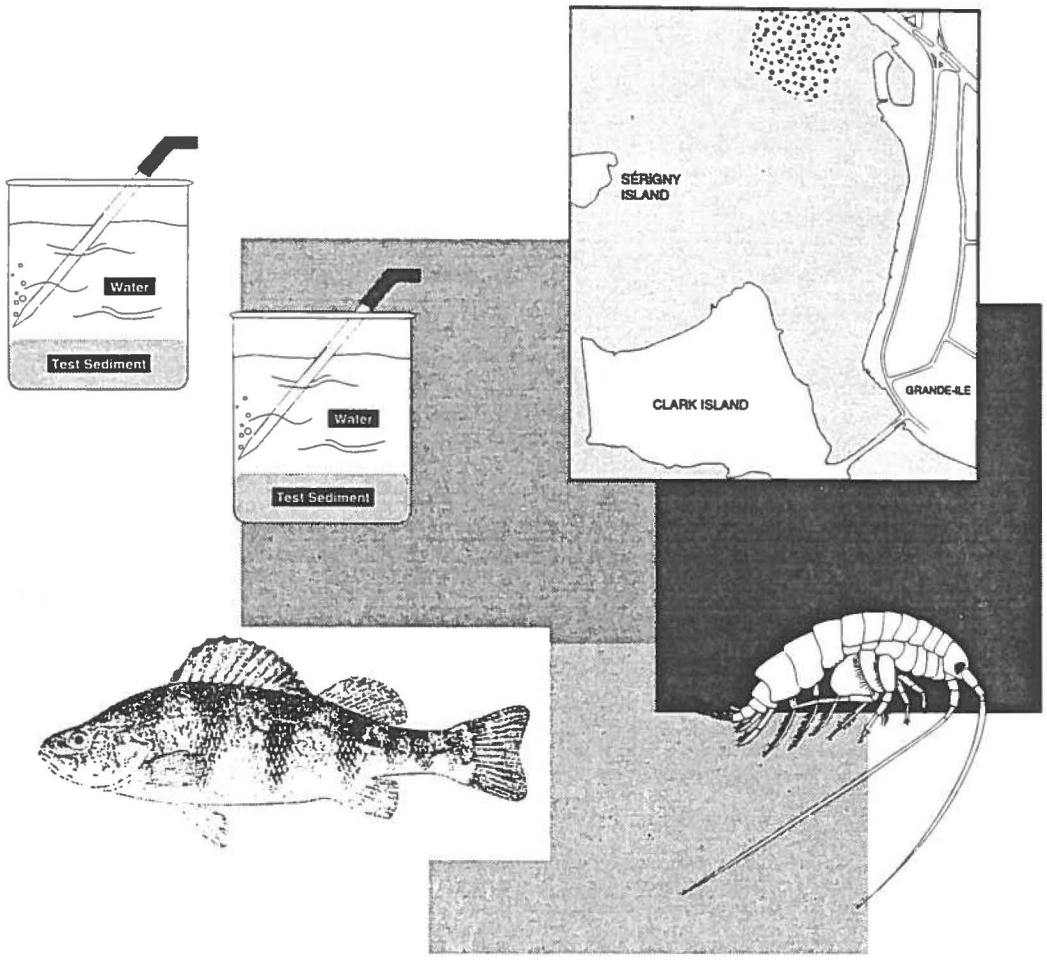
Programme d'échantillonnage et d'analyse (SAP/QAPP)

August 1996

DRAFT FINAL Volume 1 of 2

Clark Island

SAMPLING AND ANALYSIS PLAN



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SAMPLING AND ANALYSIS PLAN

VOLUME 1 OF 2

DRAFT FINAL

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AUGUST 1996

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LIST OF ACRONYMS

ASTM	American Society for Testing and Materials
AVS	acid volatile sulfide
COC	contaminant of concern
EIS	environmental impact study
ERA	ecological risk assessment
EVS	EVS Consultants
GPS	global positioning system
HSP	health and safety plan
MEF	Quebec Ministry of the Environment and Fauna
NOP	Notice of Project
PAH	polycyclic aromatic hydrocarbon
PCB	polychlorinated biphenyl
PSEP	Puget Sound Estuary Program
QA/QC	quality assurance/quality control
QAPP	quality assurance project plan
SAP	sampling and analysis plan
SEM	simultaneously extracted metals
SLC	screening level concentration
TIE	toxicity identification evaluation
TOC	total organic carbon

1.0
INTRODUCTION

1.1 SITE BACKGROUND

AlliedSignal Canada, Limited, plans to conduct an environmental impact study (EIS) that addresses sediments near Clark Island, a small island in the St. Lawrence River, approximately 50 km southwest of Montreal, Quebec, and 2 km east of downtown Salaberry-de-Valleyfield (Figure 1-1). This sampling and analysis plan (SAP) provides details on the field investigation that will be conducted to provide data regarding the sediments and aquatic habitats at the site. The additional data collected during this investigation will be used to support the ecological risk assessment (ERA), which will form one part of the EIS.

At present, Clark Island houses an alum manufacturing plant operated by General Chemical Canada, Limited. Previously, Clark Island was owned by Allied Chemical Canada, Incorporated, which operated several production facilities there, including a sulfuric acid facility (1941-1983), a hydrofluoric acid production facility (1956-1982), a chemicals production facility (1957-1985), and a bauxite grinding and alum production facility (1946-present). The facilities not currently in use have been decommissioned and dismantled.

Site-specific contamination on Clark Island was extensively remediated between 1991 and 1993. Hazardous wastes identified on the island were confined in a constructed, on-site double-lined landfill; contaminated soils were placed in a constructed on-site, single-lined landfill.

Past industrial activity on Clark Island has also resulted in the contamination of aquatic sediment. The degree of contamination varies, based on proximity to historical production operations, waste pits, and discharge outfalls. Pyrite cinders from the sulfuric acid production process were the major waste product disposed of on Clark Island. Pyrite wastes were sluiced and pumped into settling ponds in various locations on the island. These wastes were also used in the construction of dikes surrounding some settling ponds at the site. On occasion, the dikes failed, and cinders were lost into the river and nearby embayments. In addition, until 1983, manufacturing effluents that could have contained pyrite cinders were discharged directly into the river.

Pyrite cinders presently overlay approximately 70,000 m^2 of native sediment along the northwest shoreline of the island. Pyrite cinders from the northwest shoreline,

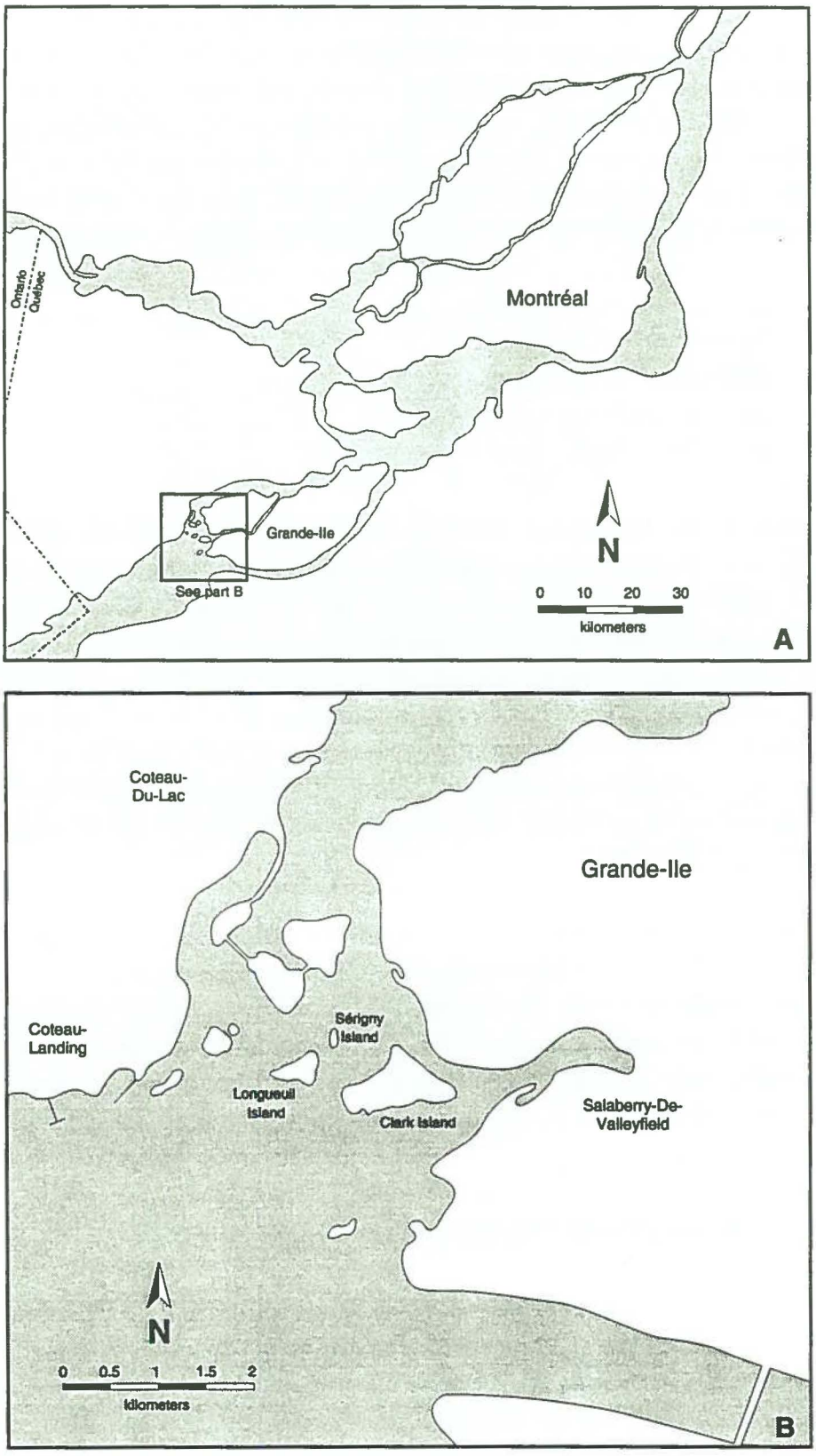

Figure 1-1. Location of Clark Island site

presumably transported by wave action and currents, have mixed with native sediment and have increased the metals concentrations in those sediments. These pyrite cinders are composed primarily of silt-sized particles (i.e., < 80 μm in diameter) containing iron oxides, selenium, trace metals, and sulfur. Based on available data, the typical composition of pyrite cinders found along the northwest shoreline of Clark Island includes metals in the following ranges of concentrations (Tecsult 1988, 1990, 1993a, b):

- Arsenic - 0.11 to 156 mg/kg
- Copper - 43 to 1,744 mg/kg
- Cadmium - 4 to 25.7 mg/kg
- Mercury - undetected to 50 mg/kg
- Zinc - 179 to 8,606 mg/kg

Concerned about potential contamination of the aquatic environment, the Quebec Ministry of the Environment and Fauna (MEF) identified the need to assess sediment quality. As part of the assessment process, MEF developed priority designations for areas around Clark Island. These priority designations have been modified in this SAP to reflect the results of previous sediment sampling and analysis. Figure 1-2 shows the modified priority designations. For this project, three study areas are designated: Study Area A corresponds to the area previously designated as Priority Zone I; Study Area B includes Priority Zone III and the southern portion of Priority Zone II; and Study Area C corresponds to the area previously designated as Priority Zone IV and the northern portion of Priority Zone II.

Initially, the area along the shoreline of Grand-Ile was delineated and subsequently evaluated for potential human health risks to nearby residential receptors. A quantitative baseline risk assessment clearly demonstrated that exposure to river bottom sediments would not result in significant human health risks. Therefore, subsequent sediment sampling and analysis will focus on obtaining and evaluating ecotoxological data, and the modified area designations reflect this focus.

1.2 RATIONALE FOR THE STUDY

In February 1995, AlliedSignal submitted a Notice of Project (NOP) for Clark Island sediments to the MEF. The NOP proposed remediation of the sediment contaminated with pyrite cinders (Study Area A). Because the proposed remediation involves the St. Lawrence River environment and covers an area of more than 5,000 m^2, MEF determined that AlliedSignal must submit an EIS, which evaluates the need to undertake remediation and the impact of any such action. The primary purpose of the Clark Island sediment

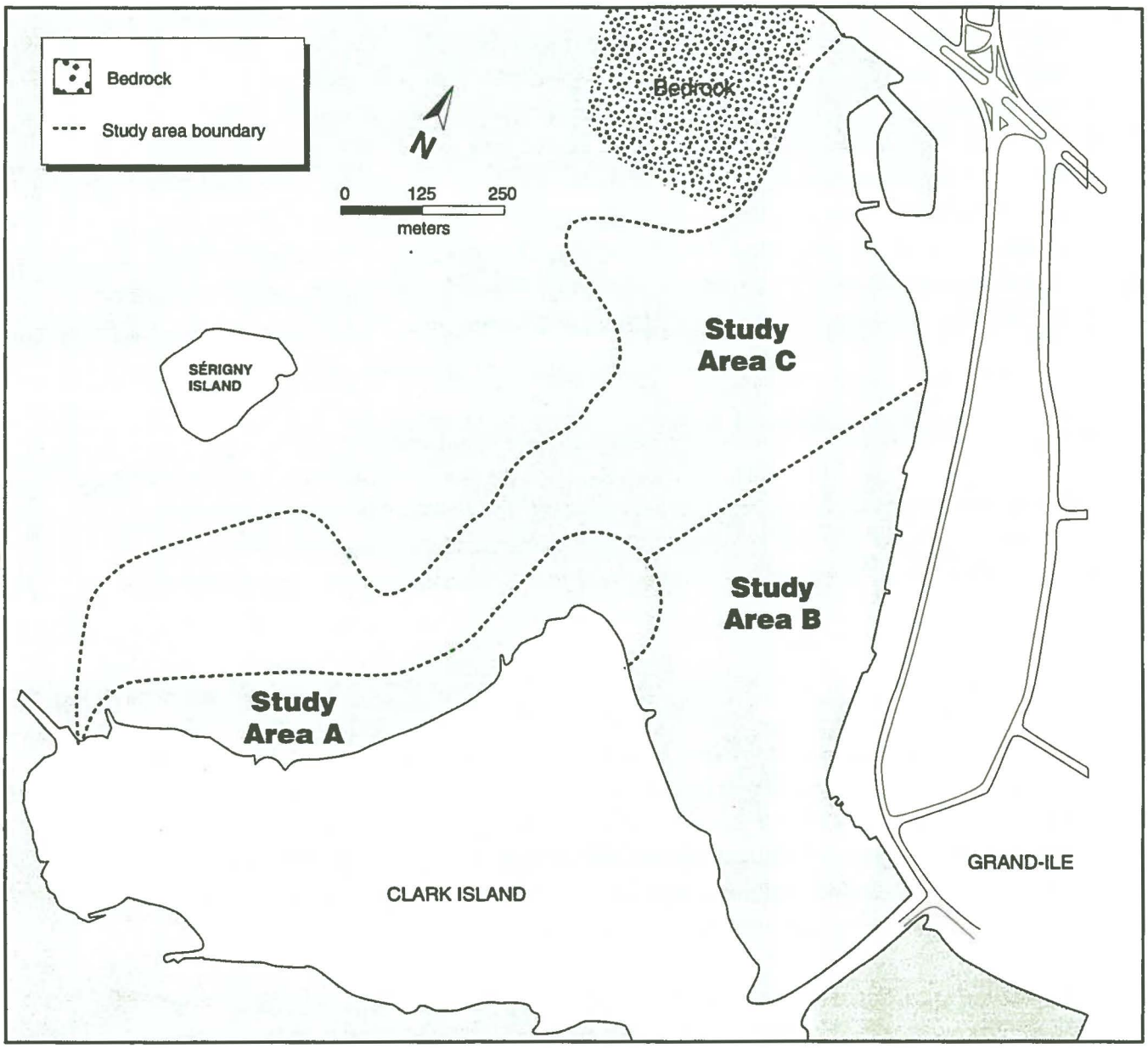

Figure 1-2. Delineation of study areas in the vicinity of Clark Island

studies described in this SAP is to support the environmental analysis required in the EIS. Specifically, the studies are designed to obtain data for Study Areas A, B, and C that can be used to evaluate the potential ecological impacts of contaminants associated with bedded sediment.

Data on the concentrations of contaminants of concern (COCs), sediment toxicity, and benthic community health will be used to determine risks posed to benthic communities in each of the newly designated study areas. In addition, data on tissue residue concentrations of COCs capable of biomagnifying through the food chain will be obtained for fish, benthic macroinvertebrates, and submerged plants from the vicinity of Clark Island to assess potential risks to terrestrial and avian species that use aquatic flora and fauna as a food source. COCs present in Clark Island sediments that may potentially biomagnify include mercury (as methylmercury) and selenium (as seleniomethionine). The data generated for this study will be combined with existing data for the site to justify proposed remedial actions for the Clark Island sediments.

1.3 OVERVIEW OF FIELD STUDIES AND ANALYSES

Field studies will consist of a reconnaissance survey followed approximately 1 month by the primary field survey. Table 1-1 lists the types of field samples that will be collected during each survey. The remainder of this section discusses the activities associated with each.

The field sampling program will begin with a reconnaissance survey to map habitat types, collect samples of plant tissue, benthic macroinvertebrate tissue, and fish tissue, and collect data for use in selecting background stations for the primary field survey. Whole fish were collected during a previous study and frozen for subsequent analysis; these samples may also be used for the tissue analysis portion of the study. Results of the reconnaissance survey will guide selection of final station locations, identify any additional samples needed for the project, and identify any other aspects of the field program that need to be addressed to fulfill the project objectives.

Samples to be collected during the primary field survey include sediments and benthic community samples. Sediment samples will be analyzed for selected metals, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and conventional parameters. Sediments will also be used in conducting 14-day toxicity tests using the amphipod *Hyalella azteca* and the chironomid *Chironomus tentans*. A companion study will examine the dose/response of *H. azteca* to variations in grain size and total organic carbon (TOC) in sediments. Should sediments fail toxicity testing, modified toxicity identification evaluations (TIEs) will be conducted using *H. azteca* and *C. tentans* by

Table 1-1. Summary of proposed sample types

Station	Surface Sediments	Plant Tissue	Benthic Macroinvertebrate Tissue	Benthic Community	Pore Water	Fish Tissue
Reconnaissance Survey						
All Field Stations		✓	✓			
Selected Field Stations						✓
Potential Background Stations	✓			observations only		
Primary Field Survey						
All Field Stations	✓			✓	✓[a]	
Background Stations	✓			✓		

[a] Pore water extraction from sediments is contingent upon toxicity testing results.

exposing them to pore water extracted from the sediment samples. Fish and benthic sample tissues will be analyzed for mercury and methylmercury. The benthic community will also be characterized by identifying and enumerating resident species collected in benthic community sampling.

Chemical and biological data will be integrated into a cohesive characterization of the environmental quality of the site, and will be used to conduct the ERA

Field methods and analyses used in the investigation of sediment quality will conform to guidelines published by Environment Canada and MEF (MEF 1992). The preparation and content of the EIS for this project will conform to guidelines provided by MEF (1995).

1.4 PROJECT ORGANIZATION AND TEAM RESPONSIBILITIES

Tecsult, Inc. will have lead responsibility for conducting the EIS. EVS Consultants (EVS) will have responsibility for the ERA that will form a portion of the EIS. Mr. Romeo Ciubotariu will be the Tecsult project manager and Dr. D. Michael Johns will be the EVS project manager. Mr. Manuel Vazquez will be the representative for AlliedSignal, with assistance from Dr. Erik Rifkin of Rifkin and Associates. Both project managers will be supported by skilled staff, and will be responsible for coordinating the joint participation of EVS and Tecsult in the field sampling effort, analysis of samples, interpretation of data, and production of deliverables. Figure 3-1 in the QAPP (Appendix A) shows the organizational structure and outlines the responsibilities of key team members.

Tecsult will provide the technical support needed for field sampling. Support will include addressing the logistics of the field sampling effort and supplying skilled field personnel for the various aspects of sample collection and handling. Tecsult will also be responsible for conducting the reconnaissance survey. During the reconnaissance survey, Tecsult will collect additional data along selected transects that will contribute to the EIS.

EVS will be responsible for identifying the sampling and analysis requirements to support the ERA. EVS will ensure that appropriate samples are collected that will adequately represent the ranges of contaminant concentrations at the site and the distribution of habitat types that may be affected. EVS will use these field data to perform the ERA.

1.5 REPORT ORGANIZATION

This SAP provides details of the field sampling program. The quality assurance project plan (QAPP), provided in Appendix A, describes field and laboratory quality assurance/quality control (QA/QC) procedures, provides data quality objectives, details laboratory protocols, and outlines procedures used to ensure that data are valid. Appendix B provides example field forms and sample labels, and Appendix C (bound separately as Volume 2) contains laboratory protocols for conducting the chemical and biological tests. Companion documents include an ERA work plan and a health and safety plan (HSP). The ERA work plan includes the problem formulation, the conceptual model, the assessment and measurement endpoints, and the study design. The HSP presents details and procedures for protecting personnel during field activities and provides an emergency response plan.

2.0
PROJECT FIELD STUDIES

Project field studies will occur in two phases: a reconnaissance survey and a primary field survey. The reconnaissance survey, which will provide information to guide subsequent field work and analysis, will consist of environmental sampling and general site observation. The primary field survey will include the collection of sediment samples and benthic macroinvertebrate specimens for benthic community analysis.

2.1 RECONNAISSANCE SURVEY

2.1.1 Site Habitat Characterization

The site habitat characterization will use both underwater video recording devices and divers. This portion of the study will begin with a habitat survey conducted using a towed, underwater video camera. The camera will be towed along transects 50 m apart and covering Study Areas A, B, and C. A manually operated winch controls the height of the camera above the bottom. The camera system transmits real-time images of the bottom along the transect to a monitor and recorder aboard the tow boat. Using a predetermined coding system for habitat types, a trained observer viewing the monitor keys in the habitat type in real time. The video tape recording is available for review after the transects are completed. An on-board navigation system continuously updates the boat position and integrates the position display with the underwater camera signal so that the recorded bottom image includes date, time, and position. The boat operator uses a separate monitor linked to the navigation system that plots the transect line to be followed and marks the boat's position along it. The system allows direct downloading of habitat type and distribution into a geographical database for immediate mapping.

Habitat maps produced by the underwater video camera survey will be used to select locations for collection of plant and benthic macroinvertebrate samples for tissue analysis. A pair of divers will collect plant specimens and will operate the Ekman grab sampler to collect sediment samples from which benthic macroinvertebrates will be sieved. One of the divers will be a trained biologist familiar with the local plant species. Divers will also confirm certain aspects of the habitat survey performed by underwater video recording. These aspects may include sediment grain size, benthic macroinvertebrate diversity and density, aquatic vegetation diversity and density, and bottom morphology.

The site habitat characterization along selected transects will include the following:

- Electrofishing, which will allow identification, counting, and sizing of caught fish; the location of the captured fish will be determined using the global positioning system (GPS)

- Fishing using nets, which will allow sampling of organisms living on macrophytes, particularly young fish and aquatic insects; this method could confirm the presence of spawning areas around the site

2.1.2 Plant Tissue Collection

All plant tissue samples for the project will be collected during the reconnaissance survey. Up to 24 reconnaissance survey sites that span the observed types and ranges of habitat will be chosen on the basis of the information gathered during the habitat survey. Samples of plants will be collected at these locations, with actual species collected determined on the basis of their role in the local food web. Section 5.2 presents procedures for collecting and handling plant tissue samples. Sample identification numbers will be ASR-01-PT-F to ASR-24-PT-F (the sample numbering system is discussed in detail in Section 7.1). Table 2-1 specifies the laboratory analyses to be requested; the QAPP lists targeted detection limits; and Appendix C contains protocols that will be used by the analytical laboratory. Procedures in Sections 7.0 and 8.0 will be followed in handling, tracking, and shipping the samples.

2.1.3 Benthic Macroinvertebrate Tissue Collection

At each reconnaissance survey site, grab samples of surface sediments containing benthic macroinvertebrates will be collected. Section 5.3 presents procedures for collecting and handling benthic macroinvertebrate tissue samples. Sample identification numbers will be ASR-01-BT-F up to ASR-24-BT-F. Table 2-1 specifies the laboratory analyses to be requested, the QAPP lists targeted detection limits, and Appendix C contains protocols that will be used by the analytical laboratory. Procedures in Sections 7.0 and 8.0 will be followed in handling, tracking, and shipping the samples.

2.1.4 Fish Tissue Collection

Selected specimens of fish collected by electrofishing will be used for tissue analysis. Locations will be determined by field personnel based on results of the habitat survey. Whole-body samples will be preserved and submitted for analysis for mercury, methylmercury, selenium, and selenate.

Table 2-1. Parameters for chemical analysis of samples collected during the reconnaissance survey

Analytes	Sediment[a]	Plant Tissue	Benthic Macroinvertebrate Tissue	Fish Tissue
Metals and Metalloids				
Aluminum	✓			
Arsenic	✓			
Cadmium	✓			
Chromium	✓			
Copper	✓			
Iron	✓			
Lead	✓			
Mercury	✓	✓	✓	✓
Methylmercury	✓	✓	✓	✓
Nickel	✓			
Selenium	✓	✓	✓	✓
Selenate	✓	✓	✓	✓
Zinc	✓			
PAHs				
Acenaphthene	✓			
Acenapthylene	✓			
Anthracene	✓			
1,2-Benzanthracene	✓			
Benz(a)anthracene	✓			
Benzo(a)pyrene	✓			
Benzo(b+k+j)fluoranthene	✓			
Benzo(c)phenanthrene	✓			
Benzo(g,h,i)perylene	✓			
Chrysene	✓			
Dibenz(a,h)anthracene	✓			
Dibenzo(a,h)pyrene	✓			
Dibenzo(a,j)pyrene	✓			
Dibenzo(a,l)pyrene	✓			
Fluoranthene	✓			
Fluorene	✓			
Indeno(1,2,3-cd)pyrene	✓			
3-Methylchloranthrene	✓			

Table 2-1. continued

Analytes	Sediment[a]	Plant Tissue	Benthic Macroinvertebrate Tissue	Fish Tissue
Naphthalene	✓			
Phenanthrene	✓			
Pyrene	✓			
Total PCBs	✓			
Conventional Parameters				
Grain size	✓			
Total solids	✓			
Total volatile solids	✓			
Total organic carbon	✓			
Total sulfides	✓			
AVS/SEM	✓			
Ammonia	✓			
Percent lipids				✓
Percent moisture		✓	✓	✓

NOTE: AVS/SEM - acid volatile sulfides/simultaneously extracted metals
PAH - polycyclic aromatic hydrocarbon
PCB - polychlorinated biphenyl

[a] Sediment samples are from potential background stations only.

The species and size classes to be collected will be presented in a technical memorandum prior to performing field activities. The technical memorandum will also contain procedures for handling the fish samples.

2.1.5 Background Station Investigation

Another component of the reconnaissance survey will be collecting data necessary to select background stations for the primary field survey. Potential background areas will be identified with the help of scientists familiar with the local area. Criteria for potential background station locations are that they are not near any known source of contamination and that they reflect the habitat types in the study area. Up to 16 potentialbackground station locations will be visited by the sampling team. The final number of background stations selected will be determined by the number of habitat types identified in the study area. At each location, a diver will survey the plant density and species composition and will note evidence of benthic macroinvertebrates. The diver will also record bottom depth. Position will be determined as described in Section 4.0 and recorded. A surface sediment sample will be collected using procedures outlined in Section 5.1 and submitted for the analyses listed in Table 2-1. The QAPP lists targeted detection limits, and Appendix C contains protocols that will be used by the analytical laboratory. Sample identification numbers will be ASR-01-SS-B up to ASR-16-SS-B. Procedures in Sections 7.0 and 8.0 will be followed in handling, tracking, and shipping the samples.

Data collected during the reconnaissance survey will be used to select the final background station locations to be sampled during the primary field survey. Up to four background stations will be selected. Selection will be guided by the need to provide reference sediments that cover the range of sediment parameters expected in the assemblage of primary field survey stations. Parameters include grain size distribution, TOC content, and benthic community structure and population.

2.2 PRIMARY FIELD SURVEY

The reconnaissance survey will provide a foundation for the primary field survey. The primary field survey will include final selection of station locations and collection and analysis of field samples.

2.2.1 Preliminary Selection of Station Locations

During the primary field survey, sediment and benthic community samples will be collected in the study areas near Clark Island. This section outlines the procedure that

will be used to make a preliminary selection of the number and distribution of sampling locations.

Data from previous studies will be reviewed and historical stations grouped using a multivariate statistical technique known as cluster analysis. This analysis will use the historical concentrations of arsenic, cadmium, copper, mercury, and zinc to define the clusters.

Once the geographic areas for the historical station groups are identified, the proposed station locations for the primary field survey will be selected using a stratified random sampling approach. Stratum definitions are based on areas of contaminant concentrations (the groups described above), and the station locations will be randomly selected within each stratum. The number of stations will be proportionally allocated so that each study area is sampled representatively.

The final locations and sample sizes will be selected in the field by project personnel using habitat survey maps and maps of concentration contours for the COCs.

2.2.2 Sample Types for the Primary Field Survey

At each of the primary field survey sampling locations, sediment samples and samples of benthic macroinvertebrates will be collected. Sediment samples will be used for chemical analysis and toxicity tests. Benthic macroinvertebrate samples will also be used for the benthic community analysis.

2.2.2.1 Sediment Samples

At each primary field survey station, and at each of the selected background stations, a grab sampler will be deployed to collect a sufficient volume of surface sediment for chemistry, bioassay, and benthic community analyses. Procedures to be followed are described in Section 5.1. Sample identification numbers will be ASF-01-SS-F to ASF-24-SS-F. Table 2-2 specifies the laboratory analyses to be requested; the QAPP lists targeted detection limits; and Appendix C contains protocols that will be used by the analytical laboratory. Procedures in Sections 7.0 and 8.0 will be followed in handling, tracking, and shipping the samples.

2.2.2.2 Benthic Community Analysis Samples

Five subsamples of sediment collected as described in Section 2.2.2.1 will be used for the analysis of the benthic macroinvertebrate community. Section 5.4 describes procedures for collecting and handling samples collected for benthic community analysis. Sample

Table 2-2. Parameters for chemical analysis of samples collected during the primary field survey

Analytes	Sediment	Pore Water[a]
Metals and Metalloids		
Aluminum	✓	✓
Arsenic	✓	✓
Cadmium	✓	✓
Chromium	✓	✓
Copper	✓	✓
Iron	✓	✓
Lead	✓	✓
Mercury	✓	✓
Methylmercury	✓	✓
Nickel	✓	✓
Selenium	✓	✓
Selenate	✓	✓
Zinc	✓	✓
PAHs		
Acenaphthene	✓	
Acenapthylene	✓	
Anthracene	✓	
1,2-Benzanthracene	✓	
Benz(a)anthracene	✓	
Benzo(a)pyrene	✓	
Benzo(b+k+j)fluoranthene	✓	
Benzo(c)phenanthrene	✓	
Benzo(g,h,i)perylene	✓	
Chrysene	✓	
Dibenz(a,h)anthracene	✓	
Dibenzo(a,h)pyrene	✓	
Dibenzo(a,j)pyrene	✓	
Dibenzo(a,l)pyrene	✓	
Fluoranthene	✓	
Fluorene	✓	
Indeno(1,2,3-cd)pyrene	✓	
3-Methylchloranthrene	✓	
Naphthalene	✓	

Table 2-2. continued.

Analytes	Sediment	Pore Water[a]
Phenanthrene	✓	
Pyrene	✓	
Total PCBs	✓	
Conventional Parameters		
Grain size	✓	
Total solids	✓	
Total volatile solids	✓	
Total organic carbon	✓	
Total sulfides	✓	
AVS/SEM	✓	
Ammonia	✓	

NOTE: AVS/SEM - acid volatile sulfides/simultaneously extracted metals
PAH - polycyclic aromatic hydrocarbon
PCB - polychlorinated biphenyl

[a] Pore water extraction and analysis are contingent upon toxicity test results.

identification numbers will be ASF-01-BC-F through ASF-24-BC-F. Section 9.3 contains procedures that will be used by the analytical laboratory to perform the benthic community analysis. Procedures in Sections 7.0 and 8.0 will be followed in handling, tracking, and shipping the samples.

2.2.2.3 Field Quality Control Samples

Two related types of field quality control samples will be used to evaluate the efficiency of field decontamination procedures: cross contamination blanks and filter blanks. Field duplicate samples will also be collected.

Cross Contamination Blanks — Cross contamination blanks consist of ashless filter paper used to wipe down the surfaces of any processing equipment (after decontamination) that has been in contact with the sample. Cross contamination blanks will be collected from the sediment homogenization equipment and the sieves used for separating benthic macroinvertebrates from sediments. To minimize contamination from gloves worn by sampling personnel, the filter paper will be held with stainless-steel forceps while wiping down the equipment. One cross contamination blank will be submitted for the analysis of metals, PAHs, and PCBs for every 20 field samples collected or per sampling event (any continuous sampling period not interrupted by more than 2 days), whichever is more frequent.

Filter Blanks — A filter blank consists of a piece of clean ashless filter paper (the same kind used for the cross contamination blanks) placed in a sampling jar. Analysis of the filter blank allows discrimination between contamination resident on the filter paper and contamination that might be due to residues left on the equipment after decontamination. One filter blank per filter lot will be submitted for analysis of metals, PAHs, and PCBs.

Field Duplicate Samples — Field duplicate samples will be collected for sediments, plant tissue, and benthic macroinvertebrate tissue. One of each type of field duplicate sample will be collected for each 10 field samples, and the duplicate samples will be submitted for the same analyses as the corresponding field samples. Duplicate samples will be collected from the same homogenized material as the corresponding field sample.

Additional splits of sediment samples will be also be collected. Splits will be provided to Eco Laboratories at Pointe-Claire and to the MEF laboratory. One set of sediment sample splits will be collected for each 10 field sediment samples, and the splits will be analyzed for the same parameters as the corresponding field samples.

2.2.3 Other Field Measurements

During the primary field survey, *in situ* measurements of pH, temperature, conductivity, and dissolved oxygen concentration will be made at the stations. At a portion of the stations, current velocity measurements will also be made. All measurements will be made while the boat is at the station collecting samples by lowering sensors to the desired depth and recording readings on log sheets.

3.0
SAMPLING PLATFORM AND CREW

For the reconnaissance survey, the sampling platform will be a Prince Craft (60 horsepower), equipped with a mechanical winch that will allow the use of heavy equipment for collecting samples. This type of boat is stable, has adequate working area and capacity to allow sampling with an Ekman grab sampler and the associated on-board sample handling, and can support the use of an underwater camera system or a pair of divers for conducting the site habitat characterization. An additional smaller boat will be used to transport equipment, samples, and personnel between the shore and the sample collection boat.

Findings of the reconnaissance survey will guide selection of a sampling platform for the primary field survey. Sediment volumes to be collected during the primary field survey are much greater than those collected during the reconnaissance survey. Therefore, the platform will likely be larger to provide adequate working area and will be equipped with an A-frame at the stern for deploying and recovering the sampler.

The crew will include a field work coordinator, biologist-divers, sediment collection personnel, a technician, and a surveyor plus assistant.

4.0
STATION POSITIONING

Station positioning will be accomplished with a combination of standard land-based surveying instruments and GPS aboard the sampling platform. For the land-based instrument method, buoys will be installed to mark the stations. The GPS system will be a Leica Controller CR-233 with Antenna SR-9400, which has an accuracy of 2 to 5 meters. Measured coordinates obtained with either the land-based surveying instruments or the GPS will be transformed into the geodesic coordinate system (NAD-27) with the help of the Montreal-area reference station of the Canadian Coast Guard.

5.0
FIELD SAMPLING METHODS

5.1 SEDIMENT SAMPLING

During the reconnaissance survey, sediment samples will be collected with an Ekman grab sampler. During the primary field survey, sediment samples will be collected with a modified van Veen sampler with hydraulically powered jaw closure. The type of sampler will dictate the boat size and the method for deploying, operating, and retrieving the sampler. Regardless of which type is used, the procedures to be followed after the sampler is on deck and the sample is exposed are the same.

5.1.1 Sample Collection and Containers

Collection of sediment samples will be accomplished by using existing, proven sample collection and handling techniques. The procedures to be followed for sediment collection and processing have been developed by the Puget Sound Estuary Program (PSEP) in the State of Washington, USA, and are documented in a series of guidance manuals (PSEP 1987).

Surface sediment samples for chemical analysis and laboratory bioassays will be collected using a stainless-steel grab sampler. For this study, the 0- to 10-cm sediment horizon will be collected to determine the concentration of contaminants throughout the predominantly biologically active zone of the sediments.

The grab sampler will be operated by a crew of two or three, depending on the type. Field technicians will handle deployment and retrieval of the sampler while the vessel operator controls the hydrowire winch. The general procedure for collecting sediment samples is as follows (Note: This procedure may be amended based on experience in the reconnaissance survey.):

1. Make logbook entries as necessary (see Appendix B) throughout the sampling process to ensure thorough recordkeeping.

2. Maneuver the sampling vessel to the proposed sampling location using the positioning procedures described in Section 4.0.

3.A If using the Ekman grab sampler, use the following procedure:

a. Cock open the sampler

b. Guide the sampler overboard and lower until just above the bottom

c. Upon signal from the diver, lower the sampler slowly to the bottom

d. The diver will place and trip the sampler and will signal the surface to retrieve it

e. Record the position

f. Retrieve the sampler at a vertical speed of approximately 0.3 m/s.

3.B If using the hydraulically operated van Veen grab sampler, use the following procedure (Note: the sampler will be open on the support cradle and decontaminated after the previous use.):

a. Guide the sampler overboard until it is clear of the side of the boat

b. Lower the sampler through the water column to the bottom at approximately 0.3 m/s

c. Signal the location control person to record the position when the sampler reaches the bottom

d. Actuate the hydraulic controls to close the jaws of the sampler

e. Signal the winch operator to begin retrieving the sampler and raise it at a speed of approximately 0.3 m/s.

4. Guide the sampler aboard the vessel and place it on the work table on the deck, taking care to avoid jostling that might disturb the integrity of the sample.

5. Examine the sample for the sediment acceptance criteria presented in Section 5.1.2. If sample acceptance criteria are not achieved, the sample will be rejected. If unable to obtain a sample that meets the appropriate acceptance criteria within 15.2 m (50 ft) of the proposed location, investigate

options for relocation and secure approval from the project manager for relocating the proposed sampling location.

6. Siphon off any standing water from the surface of the sediment using a hose primed with site water. Be careful during siphoning not to disturb the integrity of the sediment surface.

7. If acid volatile sulfide/simultaneously extracted metals (AVS/SEM) and/or total sulfides are to be determined for the sample, collect AVS/SEM and total sulfide samples, using a decontaminated stainless-steel spoon, before removing and homogenizing the sample. For AVS/SEM, place the sample into one 8-oz pre-cleaned glass sample container (leave no headspace), close the container, wipe it off, and place it in a cooler for temporary storage. For total sulfides, fill two 1.5-oz pre-cleaned glass sample containers leaving space for the preservative, add 2 mL of zinc acetate to each container (there should be no headspace left), close the containers, wipe them off, and place them in a cooler for temporary storage.

8. Collect the upper 10 cm of contents from the sampler using a stainless-steel scoop or equivalent implement. Take care not to include any material that has been in contact with any interior sampler surface. Place sediment into an appropriate-sized high-density polyethylene bucket or stainless-steel bowl, as volume dictates.

   If the sediment sample is to be used for either the benthic community analysis or the benthic macroinvertebrate tissue analysis, place the sediment from individual grabs in separate glass containers of the appropriate size, label them with the station identification and grab number, place them in a cooler, and set it aside for later transfer to shore for processing.

9. Thoroughly rinse the interior of the sampler until all loose sediment has been washed off.

10. Repeat the sampling process until sufficient sediment volume is obtained to satisfy the sampling requirements for the station. Collect successive grab samples within a radius of 3 m of the initial sampling location.

11. Place a latching cover over the bulk sediment container, label it with the station number, and set it aside for later transfer to shore and subsequent homogenization and distribution to sample containers.

12. Thoroughly decontaminate the sampler by following the procedure in Section 6.0.

13. Ensure that all logbook entries are complete.

14. Either proceed to the next proposed sampling location or proceed to shore to unload bulk sediment containers.

Onshore handling procedures are as follows:

15. Homogenize the bulk sediment with a heavy-duty, variable-speed drill with stainless-steel stirring paddle if in a bucket, or by hand if in a bowl, until the sediment appears uniform in color and texture.

16. Distribute the homogenized sediment to appropriate sample containers according to the sample requirements identified in Table 5-1 and ensure that sample labels are completely filled out and affixed to the containers.

17. Clean the exterior of all sample containers and store them in a cooled ice chest.

There may be contingencies during field activities that require modification of the general procedure outlined above. Modifications of procedure will be at the discretion of the field coordinators. All modifications will be recorded in the appropriate logbook.

5.1.2 Sample Acceptability and Field Quality Assurance

Only those grab samples that meet the following acceptability criteria will be retained for analysis:

- The sediment does not contain large foreign objects
- The sampler is not overfilled, which would cause the sediment surface to press against the top of the sampler
- The sampler is not leaking (there is overlying water and no visible leaks)
- The sample is not disturbed (overlying water shows little or no turbidity)
- The sample has not been winnowed (sediment has a relatively flat surface)

Table 5-1. Sample volume and containers for project samples collected during the reconnaissance and primary field surveys

Sample Matrix	Analysis	Quantity	Container Size	Type	Field Preservative	Laboratory
Surface Sediment	Metals	1	8 oz	glass	4°C	Zenon
	Mercury/methylmercury and selenium/selenate	1	8 oz	glass	4°C	Brooks Rand
	PAHs and PCBs	1	8 oz	glass	4°C	Zenon
	Conventional parameters	1	8 oz	glass	4°C	Zenon
	Grain size	1	1,000 g	plastic bag	4°C	Zenon
	Total sulfides	1	1.5 oz	glass	zinc acetate	Zenon
	AVS/SEM	1	1.5 oz	glass	4°C	ARI
	Amphipod bioassay	1	64 oz	glass	4°C	EVS
	Chironomid bioassay	1	64 oz	glass	4°C	EVS
	TIE	2	2 gallon	HDPE	4°C	Archive-EVS
	Benthic community analysis	5	32 oz	glass	4°C	EVS
Plant Tissue	Mercury/methylmercury and selenium/selenate	1	1 gallon	plastic bag	4°C	Brooks Rand
Benthic Macroinvertebrate Tissue	Mercury/methylmercury and selenium/selenate	1	50 g	plastic bag	4°C	Brooks Rand
Fish Tissue	Mercury/methylmercury and selenium/selenate	1	1 gallon	plastic bag	freeze	Brooks Rand
Pore Water Chemistry	Metals and organic compounds	2	1 L (from TIE)	plastic	acid	Archive-EVS

NOTE: AVS/SEM - acid volatile sulfides/simultaneously extracted metals
HDPE - high-density polyethylene
PAH - polycyclic aromatic hydrocarbon
PCB - polychlorinated biphenyl
TIE - toxicity identification evaluation

- The penetration depth is at least 10 cm for sediment to be composited for chemical analyses

5.1.3 Sample Handling and Preservation

Preservation for samples intended for analysis for total sulfides is described in Step 7 of the sediment sample collection procedure. If sample containers are filled aboard the sampling vessel, they will be stored aboard the boat in coolers with ice or frozen blue-ice packs prior to unloading to shore. On shore prior to shipping to the analytical laboratory, filled sample containers will be maintained in coolers with ice or frozen blue-ice packs, or if available, inside a suitable refrigerated storage facility.

5.2 PLANT TISSUE COLLECTION

5.2.1 Sample Collection and Containers

Divers will collect whole plants (both root and water-column portions) at each reconnaissance survey site. Sites will be predetermined to span a gradient of sediment contaminant concentrations. Under the direction of an on-site specialist, divers will subsample each habitat type within a specified sediment concentration gradient. It is anticipated that the typical number of subsamples will be five. Divers will visit each subsample location, collect whole plants that are within arm's reach, and place them in a plastic collection bag. Upon a signal from one of the divers, an attached line will be used to manually retrieve the sample bag to the surface, where the contents of the bag will be emptied into a suitable holding container. Equal portions of each subsample will be combined to form a composite sample for the site, and the remainder of each subsample will be archived until adequate sample material has been collected.

For both the composite sample and the subsamples to be archived, whole plants will be rinsed thoroughly with site water to remove attached sediment and any other foreign matter, including benthic and epibenthic organisms. Root sections will be separated from the rest of the plant body using a scalpel and working on a decontaminated surface. Both sections of the plant body will be rinsed a second time with site water and segregated directly into separate sample containers. Containers of composite samples will be weighed to ensure that a minimum of 200 g of tissue sample has been collected before the containers are sealed. Table 5-1 lists the sample container for plant tissue samples after they have been processed.

5.2.2 Sample Acceptability

Plants or plant parts collected by the diver will be examined at the surface by a qualified expert. This individual will confirm that the appropriate species have been collected and that there is no damage due to collection that would potentially allow contamination from an external source.

5.2.3 Sample Handling and Preservation

Each sample jar will be sealed, and a sample identification label will be affixed to the jar and covered with clear tape. A tag number will be attached to each container. Plant tissues will be preserved by freezing and holding frozen until shipping to the analytical laboratory.

5.3 Benthic Macroinvertebrate Tissue Collection

5.3.1 Sample Collection and Containers

Sediment samples that will provide benthic organisms for tissue analysis will be collected using a stainless-steel Ekman grab sampler. Subsamples will be collected, composited, and archived according to the same scheme described in Section 5.2.1 for plants. The composite sample for analysis and the respective subsamples will be sieved using site water and retained on a 0.5-mm mesh screen. Benthic macroinvertebrates remaining on the screen will be placed in the glass sample jar for analysis. Table 5-1 lists the container type and size. The amount of sample will be weighed, and the collection procedure repeated if more sample is needed.

5.3.2 Sample Acceptability

Sediment grab samples will be evaluated according to the acceptability criteria in Section 5.1.2. Benthic macroinvertebrate organisms to be used for tissue samples will be inspected for physical damage as they are collected. Those that are not intact will be rejected and returned to the site.

5.3.3 Sample Handling and Preservation

Each jar will be sealed, and a sample identification label will be affixed to the jar and wrapped with clear tape. A tag number will be attached to each container. Samples will be preserved by freezing.

5.4 BENTHIC COMMUNITY ANALYSIS

5.4.1 Sample Collection and Containers

Sediment samples for benthic community analysis will be collected concurrently with sediment samples using the hydraulically powered van Veen grab sampler. Five grab samples will be collected; these samples will not be composited. For each grab, the sample will be sieved using site water and retained on a 0.5-mm mesh screen. An end-of-line filter will be attached to the site water hose to prevent water column organisms (e.g., phytoplankton/zooplankton) from contaminating the benthic samples during sieving. Any biota or debris remaining on the screen will be placed in a glass jar for analysis. Table 5-1 lists sample container requirements for benthic community analysis samples. The sample collection/preparation procedures are as follows:

1. Deploy the sampler as described in Section 5.1.1, Steps 1 through 5

2. If the sample meets acceptability criteria, carefully empty the sample into a 0.5-mm sieve box, including the overlying water which is not siphoned off

3. Use filtered site water to gently flush the small-grain sediment matrix through the sieve; it is important to keep one corner of the sieve box clean of sediment so that water in the box does not overflow

4. Transfer the organisms and debris left behind on the screen by spoon and tweezer to an internally and externally labeled plastic sample container

5. Fill the sample jar no more than two-thirds full with organisms and debris and then fill with a 10-20 percent buffered formalin solution; samples with very high organic debris content require the higher (20 percent) formalin concentration

6. Tightly attach the lid and invert the sample jar repeatedly to ensure proper mixing of the sediment with the formalin solution

7. Log the sample on the chain-of-custody form and store at room temperature in a cooler or other container that will protect it from breakage

5.4.2 Sample Acceptability

Benthic community sediment samples will be accepted according to the criteria for acceptance of samples outlined in Section 5.1.2. Manually collected specimens will be inspected for physical damage, and those not intact will be rejected.

5.4.3 Sample Handling and Preservation

Samples of benthic macroinvertebrates to be used for benthic community analysis will be preserved as described in Section 5.4.1. Each sample jar will be sealed and a sample identification label will be affixed to the jar and covered with clear tape. A tag number will be attached to each container. Upon receipt of samples at the laboratory, the formalin will be replaced with 70 percent alcohol.

5.5 FISH TISSUE COLLECTION

5.5.1 Sample Collection and Containers

Whole fish samples will be collected by electrofishing during the reconnaissance survey. Stunned fish float to the surface and will be collected by net. The procedure for electrofishing and specimen selection will be provided in a technical memorandum prior to initiating field activities. Samples will be weighed to ensure adequate material for laboratory analysis. Table 5-1 gives requirements for containers and sample size.

5.5.2 Sample Acceptability

Whole fish will be inspected for lacerations or other damage that might occur during collection. Fish with lacerations or other damage that breaches the integrity of the skin will be rejected to avoid the potential of introducing contamination from an outside source.

5.5.3 Sample Handling and Preservation

Whole-body samples will be weighed to ensure adequate weight for the required analyses. Fish will be placed in the proper sample container and preserved by freezing.

5.6 PORE WATER EXTRACTION

5.6.1 Sample Collection and Containers

Pore water will be extracted and analyzed only for stations requiring TIEs, if any. Extraction will be by centrifuge, and the supernatant will be collected in clean glass jars. A portion of the pore water will be collected for chemical analysis, and the remainder will be reserved for the TIE. Table 5-1 lists the requirements for containers and sample size for pore water samples to be submitted for chemical analysis and for those to be used for TIEs.

5.6.2 Sample Acceptability

Pore water samples obtained by following the proper extraction procedure will be deemed acceptable.

5.6.3 Sample Handling and Preservation

Pore water will be decanted into proper containers. Preservation will be by maintaining at 4°C.

6.0
FIELD EQUIPMENT DECONTAMINATION

Sampling equipment, sample homogenization implements, and mixing containers will be decontaminated before use at each new station location and upon the completion of each day's sampling. The following decontamination procedure will be used:

1. Rinse with site water to remove any remaining sediment or organic matter

2. Scrub with brushes using an Alconox solution

3. Rinse and scrub with site water

4. Rinse with laboratory-grade deionized water to remove rinse water impurities

5. At the end of each day, protect and adequately store the decontaminated equipment for use the next day

6. Minimize the generation of decontamination fluids, collect spent fluids in a closable storage container, and dispose of spent fluids to the sanitary sewer

7.0
SAMPLE IDENTIFICATION, LABELS, DOCUMENTATION, AND CUSTODY

7.1 SAMPLE IDENTIFICATION

Each sample collected during the field effort will carry a unique alphanumeric identifier to facilitate identification and tracking. The sample identifier will be used for the duration of the project. The use of an alphanumeric identifier will allow data associated with each sample to be logically entered into a relational database system. This process will facilitate data analysis and report generation. The code will be as follows:

- First two digits, "AS" (for AlliedSignal), identify the project
- Third digit identifies the survey ("R" for reconnaissance survey and "F" for field survey) and is not separated by a dash from "AS"
- Next two digits identify the station number (e.g., "01" for Station 1)
- Next two digits identify the sample type using "FT" for fish tissue, "PT" for plant tissue, "BT" for benthic macroinvertebrate tissue, "BC" for benthic community sample, "SS" for sediment sample, and "PW" for pore water
- The last digit identifies the sample category using "B" for background, "F" for field sample, "D" for field duplicate sample, "W" for equipment wipe sample, and "R" for rinsate blank
- If the sample is one of the subsamples of plant specimens or benthic macroinvertebrate specimens, each one will be uniquely identified by appending "-Rx" to the sample identification number, where x is the subsample number (e.g., 1, 2, 3) for the given station

For example, the sample code "ASR-01-PT-B" identifies the plant tissue sample collected during the reconnaissance survey from Station 1 in the area identified as a background area. The sample code "ASF-17-SS-F" identifies the sediment sample collected during the field investigation at Station 17. The distinction between sediment samples used for chemical analysis and those used for bioassays will be apparent from the analysis requested on the chain-of-custody form that accompanies them.

7.2 SAMPLE LABELS

Sample labels will be made of waterproof material and will be self-adhering; an indelible pen will be used to fill out each label. Each sample label will contain the project number, sample identification number, preservation technique, date and time of collection, and initials of the person(s) preparing the sample. A completed sample label will be affixed to each sample container and clear tape will be wrapped over the label. A tag number will also be attached to each sample container. An example sample label is provide in Appendix B.

7.3 DOCUMENTATION

A complete record of all field activities will be maintained. This documentation will include:

- Records of all field activities
- Records of all samples collected for analysis
- Sample labels and tracking forms for all samples

The field coordinator or a designee will maintain a field logbook. The field logbook will provide a description of all sampling activities, personnel, weather conditions, and a record of all modifications to the procedures and plans identified in the SAP, the QAPP, and the HSP for this project. Daily entries regarding health and safety aspects will also be entered into the field logbook. The field logbook will be bound, with numbered pages. All entries will be made in indelible ink. The field logbook is intended to provide sufficient data and observations to enable participants to reconstruct events that occurred during the sampling period.

7.4 CHAIN OF CUSTODY

It is essential that the possession of samples be traceable from the time they are collected through analysis. Chain of custody will be established with documentation during all stages of this study.

Samples are considered to be "in custody" if they are: 1) in the custodian's possession or view, 2) retained in a secured place (locked) with restricted access, or 3) in a container that is secured with an official seal(s) such that the sample cannot be reached without breaking the seal(s). The principal documents used to identify each sample and to

document possession are chain-of-custody records, field logbooks, and field tracking forms. Chain-of-custody procedures will be used for all samples throughout the analytical process.

Chain-of-custody procedures will be initiated during sample collection. A chain-of-custody record will accompany each sample. Each person who has custody of the samples will sign the form and ensure that the samples are not left unattended unless properly secured. Minimum documentation of sample handling and custody will include:

- Project name and sample identification number
- Sample collection date and time
- Any special notations on sample characteristics or problems
- Initials of the person collecting the sample
- Date sample was sent to the laboratory

All chain-of-custody forms will be completed in indelible ink. The completed chain-of-custody form will be placed in a plastic envelope, which will be taped to the inside lid of the cooler containing the listed samples. The lid of the cooler will be sealed with chain-of-custody tape on two sides. Upon transfer and receipt of samples at the laboratory, the shipping container chain-of-custody seal will be broken. The chain-of-custody form will be signed by the persons transferring custody of the samples. The condition of the samples will be recorded by the receiver. Chain-of-custody records will be included in the analytical report prepared by the laboratory, and will be considered an integral part of that report.

Archived benthic community samples awaiting chemical results will be maintained under EVS custody until further notice.

8.0
SHIPPING AND ARCHIVING

8.1 SHIPPING REQUIREMENTS AND RECEIPT

The Field and QA Coordinators or their designees will be responsible for all sample tracking and chain-of-custody procedures for samples in the field, for final sample inventory, and for maintenance of chain-of-custody documentation. Prior to shipping, information on the sample labels will be checked against sample log entries and chain-of-custody forms, and samples will be recounted.

For shipping, sample containers will be wrapped in bubble wrap and securely packed inside the cooler with adequate ice packs to maintain the cooler temperature at 4°C until it reaches the analytical laboratory. Additional packing material should be placed in the cooler to prevent jostling of the sample containers against each other. Chain-of-custody forms will be placed in a zip-locked bag and taped to the inside lid of the cooler. Fiber tape will be wrapped completely around the cooler. On each side of the cooler a *This Side Up* arrow label will be appropriately attached, a *Glass—Handle with Care* label will be attached to the top of the cooler, and the cooler will be sealed with a chain-of-custody seal.

Samples for the various types of analyses will be shipped via overnight mail or delivered by hand courier to the appropriate laboratory. The point-of-contact and pertinent shipping information for each laboratory is provided below:

Tissue chemistry analyses (mercury, methylmercury, selenium, selenate, percent lipids, and percent moisture):

Colin Davies
Brooks Rand Ltd.
3950 Sixth Ave. N.W.
Seattle, WA 98107
Telephone: (206) 632-6206
Facsimile: (206) 632-6017

Sediment chemistry analyses (mercury, methylmercury, selenium, selenate, and percent solids):

Colin Davies
Brooks Rand Ltd.
3950 Sixth Ave. N.W.
Seattle, WA 98107
Telephone: (206) 632-6206
Facsimile: (206) 632-6017

Sediment chemistry analyses (acid volatile sulfides/simultaneously extracted metals [AVS/SEM]):

Kate Stegemoeller
Analytical Resources, Inc.
333 Ninth Ave. N.
Seattle, WA 98109
Telephone: (206) 621-6490
Facsimile: (206) 621-7523

Sediment chemistry analyses (metals [except mercury and selenium], polycyclic aromatic hydrocarbons [PAHs], polychlorinated biphenyls [PCBs], and conventional parameters):

Amr Rouchdy
Zenon Laboratory
10390 Lafontaine
Anjou, Quebec H1J 2T3
Telephone: (514) 493-4733
Facsimile: (514) 493-4725

Bioassay analyses (amphipod and chironomid larvae):

Jennifer Stewart
EVS Consultants
195 Pemberton
North Vancouver, B.C. V7P 2R4
Canada
Telephone: (604) 986-4331
Facsimile: (604) 662-8548

Benthic community analysis:

Gary Rosenthal
EVS Consultants
200 West Mercer St., Suite 403
Seattle, WA 98119
Telephone: (206) 217-9337
Facsimile: (206) 217-9343

Gary Lester
Eco-Analyst
105 East Second St., Suite. 2
Moscow, ID 83843
Telephone: (208) 882-2588
Facsimile: (208) 882-2588

The QA Officer at each laboratory will ensure that chain-of-custody forms are properly signed upon receipt of the samples and will note questions or observations concerning sample integrity on the chain-of-custody forms. The laboratories will contact the QA Coordinator immediately if discrepancies between the chain-of-custody forms and the sample shipment are discovered. The laboratory QA Officer will specifically note any coolers that do not contain ice packs or that are not sufficiently cold upon receipt. The laboratory will not dispose of the environmental samples for this project until notified in writing by the QA Coordinator.

8.2 SAMPLE ARCHIVING

Sufficient sediment will be collected at each field station to allow performance of a TIE, if necessary. Sediment samples for possible use in TIE studies will be archived at EVS. Archiving will be by storage at 4°C under nitrogen or with zero head space.

Plant and benthic macroinvertebrate tissue from site subsamples will also be archived. Archiving will be by freezing.

The laboratory will maintain chain-of-custody procedures and sample integrity while archived samples are in their possession. Archived samples will not be disposed of by EVS without written permission of AlliedSignal personnel.

9.0
LABORATORY ANALYSES

9.1 CHEMICAL ANALYSES

9.1.1 Sediment

Tables 2-1 and 2-2 list the parameters for which sediment samples collected during the reconnaissance and primary field surveys will be analyzed. The QAPP lists targeted detection limits, and Appendix C contains protocols that will be used by the analytical laboratory.

9.1.2 Plant Tissue

Plant samples collected during the reconnaissance survey will be analyzed for parameters listed in Table 2-1. The QAPP lists targeted detection limits, and Appendix C contains protocols that will be used by the analytical laboratory.

9.1.3 Benthic Macroinvertebrate Tissue

Tables 2-1 and 2-2 list the parameters for which tissue samples from benthic macroinvertebrates will be analyzed. The QAPP lists targeted detection limits, and Appendix C contains protocols that will be used by the analytical laboratory.

9.1.4 Fish Tissue

Table 2-1 lists the parameters for which fish tissues will be analyzed. The QAPP lists targeted detection limits, and Appendix C contains protocols that will be used by the analytical laboratory.

9.1.5 Pore Water

Should a TIE be performed for a particular field station, organisms will be exposed to pore water from the sediments archived for that station. Table 2-2 lists the parameters for which pore water samples will be analyzed. The QAPP lists targeted detection limits, and Appendix C contains protocols that will be used by the analytical laboratory.

9.1.6 Additives for Dose/Response Bioassays

Certain additives will be used to modify the surface sediments used in conducting dose/response bioassays. If additives are not accompanied by a certified analysis sheet, then they must be analyzed to ensure they do not contribute toxicity effects to the modified sediments. The parameters for which additive materials will be analyzed will be chosen on a case-by-case basis and will be recorded as part of the project documentation. The QAPP lists targeted detection limits, and Appendix C contains analytical protocols that will be used by the analytical laboratory.

9.2 BIOASSAYS

9.2.1 Amphipod Survival (*H. azteca*)

Adverse effects of potentially contaminated sediment will be evaluated by measuring survival in adult amphipods (*Hyalella azteca*). Amphipods will be exposed to the site-related sediment and the reference sediment for a 14-day period. Appendix C details the protocol to be used in conducting the *H. azteca* bioassay. The test and QA/QC performance standards are drawn from the American Society for Testing and Materials (ASTM 1994).

9.2.2 Chironomid Survival and Growth (*C. tentans*)

Adverse effects of potentially contaminated sediment will also be evaluated by measuring survival and growth in juvenile chironomids (*Chironomus tentans*). Larval chironomids will be exposed to whole sediment and the reference sediment for a 14-day period. Appendix C details the protocol to be used in conducting the *C. tentans* bioassay. This test and QA/QC performance standards are also drawn from ASTM (1994).

9.2.3 TOC and Grain Size Dose/Response Bioassays

The influence of different TOC concentrations and grain size distributions on amphipod survival and chironomid survival and growth will be examined. The study will be performed by formulating sediments to produce reference sediments containing a particular range of TOC concentrations and grain size distributions and then conducting amphipod and chironomid bioassays (see Sections 9.2.1 and 9.2.2) using these modified sediments. These bioassays will be run at the same time as those using field sample sediments, and the results will be evaluated in the same way. Appendix C contains the protocols for formulating the reference sediments and for conducting the bioassays.

9.3 BENTHIC COMMUNITY ENUMERATION

Upon arrival at the laboratory, all macroinvertebrate samples will be reinventoried and checked against chain-of-custody forms. If a sample consists of multiple containers, all containers will be processed as a group. Any irregularities indicating that sample integrity may have been compromised (e.g., evidence of tampering, loose lids, cracked jars) will be noted and the client-designated QA Coordinator will be contacted for further instructions.

Upon completion of reinventory and chain-of-custody checks, individual samples will be gently rinsed with fresh water into a 0.5-mm mesh screen to remove the formalin from the sample material. Screens will be only partially filled while rinsing a sample to maximize washing efficiency and prevent loss of material. All material retained on the screen will be transferred to a glass or plastic jar, covered with 70 percent ethanol, and gently agitated to ensure proper preservation of the material by the alcohol. All internal and external labels will be transferred to the sample jars. A rescreening log will be filled out as each sample is completed and will include sample identification number, date rescreened, and number of sample jars used.

Standard and accepted techniques will be used for sorting organisms from the sediments. Each sample container will be sorted in its entirety unless the laboratory manager determines that the sample should be split. It is standard practice to subsample a freshwater benthic sample if either sample volume is large or the abundance of organisms is high. Small fractions of a sample (or subsample) will be placed in a gridded petri dish under a 10 power magnification dissecting microscope. The petri dish will be scanned systematically and all organisms and fragments will be removed using fine-tipped forceps. Each petri dish will be sorted twice to ensure removal of all organisms. Sorted organisms will be placed in labeled vials prior to QA/QC testing.

All whole organisms will be counted and identified to the lowest practical taxonomic level, generally species. Oligochaetes will be left at Oligochaeta. If animal fragments are present, only anterior portions will be counted. Identifications will be performed by experienced taxonomic experts. Taxonomists will maintain a notebook with all data and information about a sample or a specimen. Questionable organisms will be compared against specimens in the EVS permanent reference collections and may be sent out for additional confirmation by other qualified taxonomic specialists.

The following QA/QC procedures for both sorting and taxonomy will be followed. Twenty percent of each processed sample will be randomly selected and resorted to check sorting efficiency. Sorting QA/QC will be done using 25 power magnification by someone other than the original sorter. A 95 percent sorting efficiency is proposed for

this study. A sample will pass if the number of organisms found during the 20 percent QA/QC check does not represent more than 5 percent of the total number of organisms found in the entire sample. If the number of organisms found is greater than 5 percent of the total number, the entire sample will be resorted. Taxonomic QA/QC will be achieved by sending representative specimens of questionable or uncertain organisms out for independent confirmation by a qualified regional expert.

A voucher collection representing all taxa collected during the survey will be prepared and archived by major taxonomic groups (i.e., arthropoda, mollusca, and miscellaneous taxa) for future reference.

9.4 TOXICITY IDENTIFICATION EVALUATION

TIE is a toxicity-based fractionation method used to characterize and identify compounds in aqueous samples (e.g., sediment pore water) that exhibit toxicity to aquatic organisms. TIE procedures are designed to address multiple toxicant interactions as well as matrix effects on bioavailability.

Phase I of the TIE isolates the compounds responsible for sample toxicity. Phase I TIE procedures using the amphipod *H. Azteca* will be conducted on sediment samples that fail the bioassay interpretive criteria. Modified U.S. Environmental Protection Agency protocols (U.S. EPA 1991), as outlined in Burgess et al. (1994) will be used. Appendix C contains the laboratory standard operating procedure for conducting the Phase I TIE.

Phase I of the TIE characterizes the physical and chemical properties of the sample toxicants by altering or rendering biologically unavailable generic classes of compounds. This is done by subjecting the sample to a series of manipulations and tests, as summarized below. Toxicity due to cationic metals is measured by adding a chelating agent, EDTA, and then testing for toxicity. The manipulation of sample pH is designed to determine if the sample is more or less toxic at different pHs or if other manipulations may affect sample toxicity differently at different pHs. In an aeration test, the sample is aerated for a period of time and then tested for toxicity to determine whether toxicity is due to a volatile or oxidizable compound. Filtration tests indicate whether toxicity is associated with filterable components of the sediment pore water. To test for non-polar organic compounds, the sample is passed over a C_{18} solid-phase extraction column and then tested for toxicity. Toxicity that is due to the presence of oxidizing agents is indicated by a reduction in toxicity following addition of the reducing agent sodium thiosulfate.

10.0
REDUCTION, VALIDATION, AND REPORTING OF ANALYTICAL RESULTS

The QAPP describes the requirements and approach for reducing, validating, and reporting laboratory analytical results.

11.0
DATA MANAGEMENT AND ANALYSIS

EVS will enter validated analytical results into its database system for organization and manipulation. Data will then be available for statistical evaluation of bioassay results and ultimate use in the ERA. This section provides specifics of data management and of the analyses used to evaluate test results.

11.1 DATA MANAGEMENT

FoxPro, a relational database software that creates Xbase files (i.e., files with .dbf extensions), will be used. These files are directly compatible with ARC/INFO® and other geographical information systems.

Data structures will be developed to provide the flexibility to meet known and predicted data analysis goals. Structures will be designed using database normalization techniques to minimize the number and size of the files, while considering effective methods of data manipulation for the requirements of data analysis and summarization. Typical files will include the following:

- Station file identifying where samples were collected, including station identifier numbers
- Sample file describing when and what samples were collected, including sample depth
- Analytical chemistry results, including concentrations, units of measure, and qualifiers
- Biological test results with identification of test organisms and test conditions

A library of routines will be used to translate typical electronic output from laboratory analytical systems and to generate data analysis reports. The use of automated routines ensures that all data are consistently converted into the desired data structures and that operator time is kept to a minimum. In addition, routines and methods for quality checks will be used to ensure that such translations are correctly applied. Final electronic files will be made available to the client in an agreed-upon format.

Written documentation will be used to clarify how field and laboratory duplicates and QA/QC samples were recorded in the data tables, and to provide explanations of other issues that may arise. The data management task will include keeping accurate records of field and laboratory QA/QC samples to provide study team members who use the data with appropriate documentation.

In addition to placing all data and identifiers into an electronic database, hard copies of all original analytical data or study records will be placed into a library filing system. Each analytical data set or document will be given a unique code (based on the original source of the data or information) and filed based on that code. A master list of all filed documents, sorted in order by filing code, will be maintained for easy retrieval from the library. Data management files will be stored on a secure computer or on a removable hard drive that can be secured.

11.2 DATA ANALYSIS

Laboratory results will be analyzed to determine if there is evidence of environmental degradation in the study areas. Analyses will include checking for distributions and/or outliers, computing 95 percent confidence limits for input to the food web model, determining statistical significance of bioassay results, and comparing results for field survey stations with appropriate background stations. The results of these data analyses will supplement the ecological risk analysis in achieving a thorough characterization of the study areas.

11.2.1 Bioassay Results

Bioassay test results for field survey station sediments will be compared against those for background station sediments. Data will be tested to determine whether they are normally or non-normally distributed. Depending on the outcome of the test for normality, the appropriate *t*-test will be applied to determine whether the toxicity of field survey station sediments differs statistically from that of the associated background station sediments. Results will be tabulated and used to determine whether TIEs should be conducted using respective sediments. Results will also be used to perform a triad analysis.

11.2.2 Triad Analysis

The sediment quality triad analysis will be used to evaluate the impact of chemical contamination in the vicinity of Clark Island. The sediment quality triad uses a weight-of-evidence approach to assess the effects of contamination by combining chemical and

biological measurements (Chapman 1992). Three complementary measures are used to identify pollution-induced degradation: sediment chemistry to determine contamination, sediment bioassays to determine toxicity, and *in situ* bioeffects (e.g., benthic infaunal community structure) to determine alteration of resident communities. The combination of these three separate measures will allow for the differentiation of effects related to contamination from natural variability and/or laboratory artifacts. In general, impacted or degraded habitats are those which have positive "hits" for all three measures. Summary statistics for the triad approach commonly include rankings or an index of severity for the respective measurement parameters, ratio-to-reference values, and generation of triaxial plots for the different indices. This process permits a station-by-station analysis to establish whether conditions at the station are degraded and whether the degradation is consistent among the independent measures.

In conducting the triad analysis for the primary survey area, stations will be placed into one of three classifications—affected, potentially affected, or unaffected—based on a qualitative evaluation of the data from each station. Following are definitions for the classification terms:

- ***Affected***: This classification is assigned if the sediments were toxic in at least one of the two toxicity tests **and** there were significant reductions in at least one of the benthic community indices **and** the chemical data from a station included contaminants at concentrations that were elevated at least two times above those at the background station.

- ***Potentially Affected***: This classification is assigned if **either** the sediments were toxic in at least one of the two toxicity tests and toxicity is confirmed by TIE **or** there were significant reductions in at least one of the benthic community indices. The overall classification is the same whether the chemical data from a station included contaminants at concentrations that (A) were elevated above those at the background station or (B) were not elevated above those at the background station.

  Status (B) is recognized because not all potential contaminants are analytically measured, and the responses measured during toxicity testing or reduction of benthic community indices may be due to one of these unmeasured contaminants.

- ***Unaffected***: This classification is assigned if there were no significant responses observed in any of the toxicity tests or if there were significant responses that were not confirmed by TIE **and** there were no significant reductions in any of the benthic community indices. The classification is the

same whether or not chemical data from a station included contaminants at concentrations above those at the background station.

Follow-up of positive toxicity responses with a TIE distinguishes whether or not the toxicity response is due to the COCs. If not, some other factor is producing the toxic response. The fact that the last two classifications are independent of the chemical data reflects the reliance on biological indices to assess ecological impacts. That is, even if chemical concentrations are elevated in sediments, it is the presence of biological effects that indicates actual *in situ* impacts.

The triad analysis will be performed on a station-by-station basis, and the results will be summarized in a classification matrix.

12.0
DELIVERABLES

The primary deliverable for the project will be the ERA. Secondary deliverables will be compilations of the chemical and biological test results. These compilations will contain summary tables of the data, laboratory analytical results sheets, QA/QC documentation for the samples, and validation reports. The anticipated report sequence is to produce draft, draft final, and final versions of the project deliverables.

13.0
SCHEDULE

The reconnaissance survey is tentatively scheduled for September 16, 1996 through September 28, 1996. The primary field survey is scheduled for October 15, 1996, through October 31, 1996. This schedule may be revised depending on site biological conditions.

14.0
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APPENDIX A

Quality Assurance Project Plan

SIGNATURE PAGE

CLARK ISLAND
QUALITY ASSURANCE PROJECT PLAN

Approved by: _____ _____

D. Michael Johns — Date
EVS Project Manager
EVS Environment Consultants

Approved by: _____ _____

Kim Magruder — Date
EVS QA Coordinator
EVS Environment Consultants

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LIST OF ACRONYMS

ARI	Analytical Resources, Inc.
ASTM	American Society for Testing and Materials
AVS	acid volatile sulfides
CVAFS	cold vapor atomic fluorescence spectrophotometry
DQO	data quality objective
ECD	electron capture detection
ERA	ecological risk assessment
EVS	EVS Environment Consultants, Inc.
GC	gas chromatography
GFAA	graphite furnace atomic absorption spectrometry
ICP	inductively coupled plasma atomic emission spectrometry
MDL	method detection limit
MS	mass spectrometry
PAH	polycyclic aromatic hydrocarbon
PCB	polychlorinated biphenyl
PSEP	Puget Sound Estuary Program
QAPP	quality assurance project plan
QA/QC	quality assurance/quality control
RPD	relative percent difference
%RSD	percent relative standard deviation
SAP	sampling and analysis plan
SEM	simultaneously extracted metal
SIM	selected ion monitoring
TDL	targeted detection limit
TIE	toxicity identification evaluation
TOC	total organic carbon
TRV	toxicity reference value

1.0
INTRODUCTION

This combined quality assurance project plan (QAPP) is designed to ensure data quality for the collection and analysis of sediment, plant tissue, and biological tissue samples, and for the analysis of sediments for toxicity and benthic community structure to support the ecological risk assessment (ERA) for the Clark Island site. A detailed description of the study design is provided in the associated sampling and analysis plan (SAP). This work will be conducted jointly by EVS Consultants (EVS) and Tecsult, Inc.

This QAPP describes the quality assurance and quality control (QA/QC) procedures that will be implemented to ensure that the data generated are of sufficient quality to be used in support of the Clark Island ERA. This QAPP has been prepared in general accordance with the *Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans* (U.S. EPA 1983), *Preparing Perfect Project Plans* (U.S. EPA 1989), and *EPA Requirements for Quality Assurance Project Plans for Environmental Data Operations* (U.S. EPA 1994).

2.0
PROJECT DESCRIPTION

A description of the Clark Island study area is provided in Section 1.0 of the SAP. The rationale for selection of station locations and a detailed discussion of the objectives for this study are provided in Section 2.0. A complete description of field sampling methods is provided in Section 5.0.

For the reconnaissance survey, up to 16 sediment samples will be collected from potential background stations and will be analyzed for the parameters listed in Table 2-1. Plant and benthic macroinvertebrate tissue samples collected from up to 24 stations near Clark Island will also be analyzed for the parameters listed in Table 2-1. For the primary field survey, fish tissue samples and up to 24 sediment samples will undergo the analyses listed in Table 2-2. In addition, sediment samples from the primary field study that are found to be toxic in either the amphipod or chironomid bioassays will have toxicity identification evaluations (TIEs) performed.

Table 2-1. Parameters for chemical analysis of samples collected during the reconnaissance survey

Analytes	Sediment[a]	Plant Tissue	Benthic Macroinvertebrate Tissue	Fish Tissue
Metals and Metalloids				
Aluminum	✓			
Arsenic	✓			
Cadmium	✓			
Chromium	✓			
Copper	✓			
Iron	✓			
Lead	✓			
Mercury	✓	✓	✓	✓
Methylmercury	✓	✓	✓	✓
Nickel	✓			
Selenium	✓	✓	✓	✓
Selenate	✓	✓	✓	✓
Zinc	✓			
PAHs				
Acenaphthene	✓			
Acenapthylene	✓			
Anthracene	✓			
1,2-Benzanthracene	✓			
Benz(a)anthracene	✓			
Benzo(a)pyrene	✓			
Benzo(b+k+j)fluoranthene	✓			
Benzo(c)phenanthrene	✓			
Benzo(g,h,i)perylene	✓			
Chrysene	✓			
Dibenz(a,h)anthracene	✓			
Dibenzo(a,h)pyrene	✓			
Dibenzo(a,j)pyrene	✓			
Dibenzo(a,l)pyrene	✓			
Fluoranthene	✓			
Fluorene	✓			
Indeno(1,2,3-cd)pyrene	✓			

Table 2-1. continued.

Analytes	Sediment[a]	Plant Tissue	Benthic Macroinvertebrate Tissue	Fish Tissue
3-Methylchloranthrene	✓			
Naphthalene	✓			
Phenanthrene	✓			
Pyrene	✓			
Total PCBs	✓			
Conventional Parameters				
Grain size	✓			
Total solids	✓			
Total volatile solids	✓			
Total organic carbon	✓			
Total sulfides	✓			
AVS/SEM	✓			
Ammonia	✓			
Percent lipids				✓
Percent moisture		✓	✓	✓

NOTE: AVS/SEM - acid volatile sulfides/simultaneously extracted metals
PAH - polycyclic aromatic hydrocarbon
PCB - polychlorinated biphenyl

[a] Sediment samples are from potential background stations only.

Table 2-2. Parameters for chemical analysis of samples collected during the primary field survey

Analytes	Sediment	Pore Water[a]
Metals and Metalloids		
Aluminum	✓	✓
Arsenic	✓	✓
Cadmium	✓	✓
Chromium	✓	✓
Copper	✓	✓
Iron	✓	✓
Lead	✓	✓
Mercury	✓	✓
Methylmercury	✓	✓
Nickel	✓	✓
Selenium	✓	✓
Selenate	✓	✓
Zinc	✓	✓
PAHs		
Acenaphthene	✓	
Acenapthylene	✓	
Anthracene	✓	
1,2-Benzanthracene	✓	
Benz(a)anthracene	✓	
Benzo(a)pyrene	✓	
Benzo(b+k+j)fluoranthene	✓	
Benzo(c)phenanthrene	✓	
Benzo(g,h,i)perylene	✓	
Chrysene	✓	
Dibenz(a,h)anthracene	✓	
Dibenzo(a,h)pyrene	✓	
Dibenzo(a,j)pyrene	✓	
Dibenzo(a,l)pyrene	✓	
Fluoranthene	✓	
Fluorene	✓	
Indeno(1,2,3-cd)pyrene	✓	
3-Methylchloranthrene	✓	
Naphthalene	✓	

Table 2-2. continued.

ANALYTES	SEDIMENT	PORE WATER[a]
Phenanthrene	✓	
Pyrene	✓	
Total PCBs	✓	
Conventional Parameters		
Grain size	✓	
Total solids	✓	
Total volatile solids	✓	
Total organic carbon	✓	
Total sulfides	✓	
AVS/SEM	✓	
Ammonia	✓	

NOTE: AVS/SEM - acid volatile sulfides/simultaneously extracted metals
PAH - polycyclic aromatic hydrocarbon
PCB - polychlorinated biphenyl

[a] Pore water extraction and analysis are contingent upon toxicity test results.

3.0
PROJECT ORGANIZATION AND RESPONSIBILITIES

The overall project organization and the names of individuals responsible for quality assurance are provided in Figure 3-1. Responsibilities of these personnel and of the QA Coordinators for specific laboratory and data analysis tasks are described in the following sections.

3.1 PROJECT MANAGEMENT

The Project Manager is responsible for overall project coordination, including the production of all project deliverables, and the collection and submittal of environmental samples to the designated laboratories for chemical and physical analyses as specified in this QAPP. The Project Managers are:

D. Michael Johns
EVS Consultants
200 W. Mercer St., Suite 403
Seattle, WA 98119
Telephone: (206) 217-9337
Facsimile: (206) 217-9343
E-mail: mikej@evs.wa.com

Romeo Ciubotariu
Tecsult, Inc.
85, Rue Ste-Catherine Ouest
Montreal, Quebec H2X 3P4
Telephone: (514) 287-8500
Facsimile: (514) 287-8643

3.2 QUALITY ASSURANCE

The Project QA Coordinator is responsible for preparing this QAPP, coordinating with the analytical and bioassay laboratories, ensuring data quality for chemical and bioassay analyses, overseeing data validation, and supervising project quality assurance coordination. The Project QA Coordinator is:

Kim Magruder
EVS Consultants
200 W. Mercer St., Suite 403
Seattle, WA 98119
Telephone: (206) 217-9337
Facsimile: (206) 217-9343
E-mail: kimm@evs.wa.com

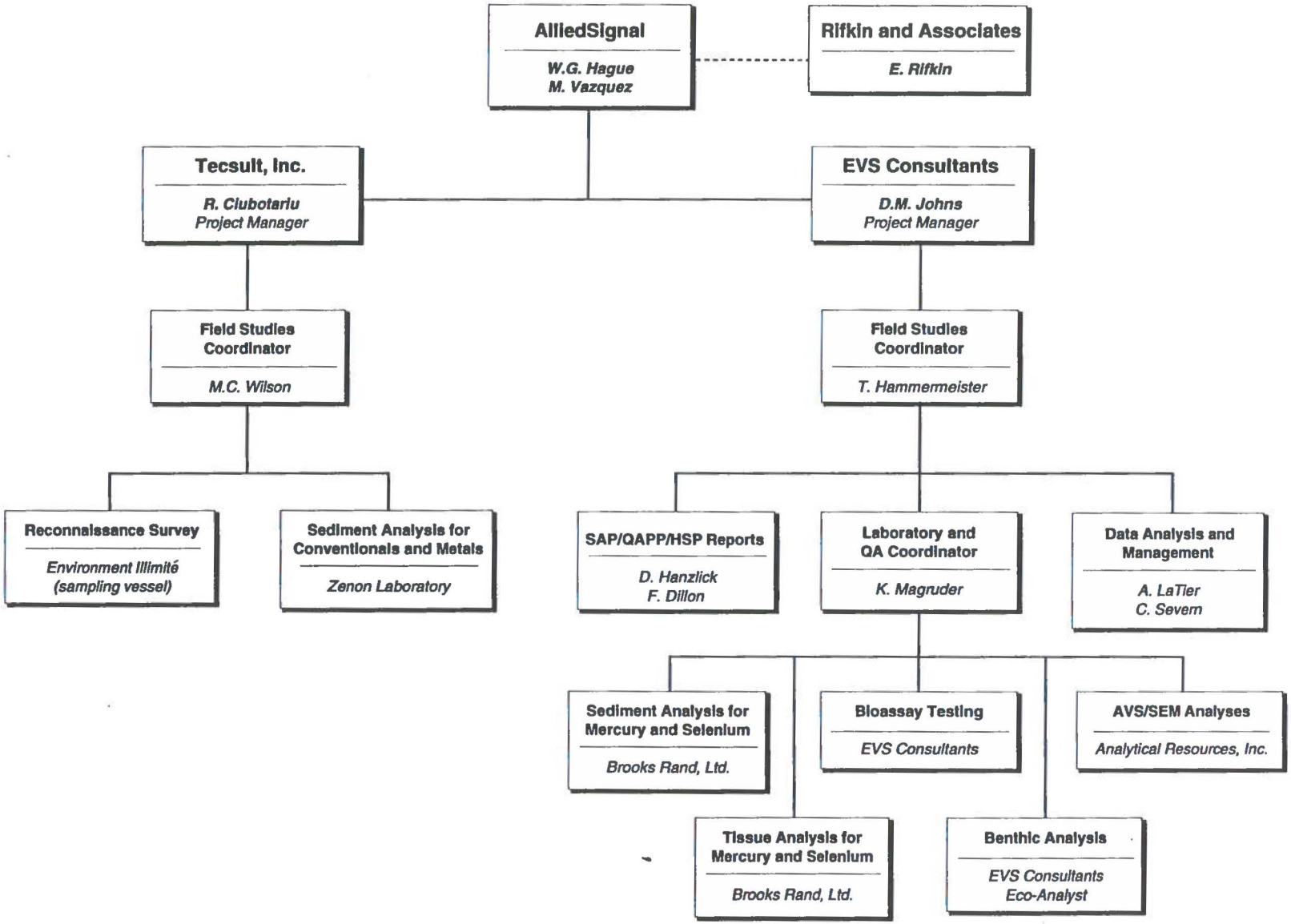

Figure 3-1. Project organization and team responsibilities

3.3 LABORATORY PROJECT MANAGEMENT

A project manager from each laboratory will provide analytical support to this project and is responsible for ensuring that all laboratory analyses meet the project data quality objectives and other specifications detailed in this QAPP. The laboratory project managers are:

Tissue chemistry analyses (mercury, methylmercury, selenium, selenate, percent lipids, and percent moisture):

Colin Davies
Brooks Rand Ltd.
3950 Sixth Ave. N.W.
Seattle, WA 98107
Telephone: (206) 632-6206
Facsimile: (206) 632-6017

Sediment chemistry analyses (mercury, methylmercury, selenium, selenate, and percent solids):

Colin Davies
Brooks Rand Ltd.
3950 Sixth Ave. N.W.
Seattle, WA 98107
Telephone: (206) 632-6206
Facsimile: (206) 632-6017

Sediment chemistry analyses (acid volatile sulfides/simultaneously extracted metals [AVS/SEM]):

Kate Stegemoeller
Analytical Resources, Inc.
333 Ninth Ave. N.
Seattle, WA 98109
Telephone: (206) 621-6490
Facsimile: (206) 621-7523

Sediment chemistry analyses (metals [except mercury and selenium], polycyclic aromatic hydrocarbons [PAHs], polychlorinated biphenyls [PCBs], and conventional parameters):

Amr Rouchdy
Zenon Laboratory
10390 Lafontaine
Anjou, Quebec H1J 2T3
Telephone: (514) 493-4733
Facsimile: (514) 493-4725

Bioassay analyses (amphipod and chironomid larvae):

Jennifer Stewart
EVS Consultants
195 Pemberton
North Vancouver, B.C. V7P 2R4
Canada
Telephone: (604) 986-4331
Facsimile: (604) 662-8548

Benthic community analysis:

Gary Rosenthal
EVS Consultants
200 West Mercer St., Suite 403
Seattle, WA 98119
Telephone: (206) 217-9337
Facsimile: (206) 217-9343

Gary Lester
Eco-Analyst
105 East Second St., Suite. 2
Moscow, ID 83843
Telephone: (208) 882-2588
Facsimile: (208) 882-2588

The contract laboratories are expected to meet the following minimum technical requirements as specified in their negotiated contracts with EVS and Tecsult:

- Adhere to the methods outlined in the statement of work, including those methods referenced for each analytical procedure
- Provide a per analysis price and total price for the analytical services (including any additional costs for electronic data files)
- Deliver electronic data files as specified
- Meet reporting requirements
- Implement QA/QC procedures, including the QAPP data quality requirements, method requirements, and performance evaluation testing requirements
- Allow AlliedSignal, EVS, and Tecsult to perform laboratory and data audits, if deemed necessary
- Follow documentation, chain-of-custody, and sample logbook procedures
- Meet turnaround times for deliverables

Deviations from the laboratory procedures specified in the QAPP will not be permitted without written documentation of the intended change and the rationale. All changes must be approved in advance by the EVS QA Coordinator.

4.0
QUALITY ASSURANCE OBJECTIVES

The overall quality assurance objective for this project is to develop and implement procedures that will ensure the collection of representative data of known, acceptable, and defensible quality. Table 4-1 summarizes quality assurance objectives for each analysis type. Targeted detection limits (TDLs) shown in Table 4-2 for tissue and sediment are based on contaminant of concern-specific toxicity reference values (TRVs). Interferences in individual samples may result in an increase in the reported detection limits. To achieve the required low detection limits, some modifications to the methods are necessary. The method modifications are presented in Section 7.1.3.

The data quality parameters used to assess the acceptability of the data are precision, accuracy, representativeness, comparability, and completeness. These parameters are discussed below.

4.1 PRECISION

Precision is the measure of the reproducibility among individual measurements of the same property, usually under similar conditions, such as multiple measurements of the same sample. Precision goals can be defined for all parameters of this project (chemical and biological). Precision is assessed by performing multiple analyses on a sample and is expressed as a relative percent difference (RPD) when duplicate analyses are performed and as a percent relative standard derivation (%RSD) when more than two analyses are performed on the same sample (i.e., triplicates). Precision is assessed by duplicate analyses for all parameters except when reference materials are not available or spiking of the matrix is inappropriate; in these cases, precision is assessed by triplicate analyses. Precision measurements can be affected by the nearness of a chemical concentration to the method detection limit, where the percent error (expressed as either %RSD or RPD) increases. The equations used to express precision are as follows:

$$RPD = \frac{|\text{measured value} - \text{measured duplicate value}|}{(\text{measured value} + \text{measured duplicate value})/2} \times 100$$

Table 4-1. Summary of data quality objectives

Parameter	Units	Method Detection Limit	Sample Volume	Precision	Accuracy	Completeness	Method	Reference	Container	Holding Time	Preservation Method
Sediments											
Total metals	mg/kg (dry weight)	0.1-10	10 g	±35%	±35%	95%	ICP/GFAA	Environment Canada	Plastic	6 months	Freeze
Total mercury	mg/kg (dry weight)	0.060	10g	±35%	±35%	95%	Gold trap/ CVAFS	Brooks Rand Laboratory Method BR-0002	Glass	28 days	Cool/4°C
Methylmercury	mg/kg (dry weight)	0.060	10 g	±35%	±40%	95%	GC/CVAFS	Brooks Rand Laboratory Method BR-0011	Glass	28 days	Cool/4°C
Selenium	mg/kg (dry weight)	0.042	10 g	±35%	±35%	95%	HGAA	Brooks Rand Laboratory Method BR-0020	Glass	6 months	Freeze
Selenate	mg/kg (dry weight)	0.042	10 g	±35%	±35%	95%	HGAA	Brooks Rand Laboratory Method BR-0022	Glass	6 months	Freeze
PAHs	mg/kg (dry weight)	0.02-0.10	60 g	±50%	±50%	95%	GC/MS-SIM	U.S. EPA Method 3540;8270	Glass	6 months	Freeze
PCBs	mg/kg (dry weight)	0.1-1.0	from PAH extract	±50%	±50%	95%	GC/ECD	Centre St. Laurent Method 13	Glass	6 months	Freeze
Acid-volatile sulfides	µmole/g	0.9	10 g	±30%	±25%	95%	Distillation, titration	Allen et al. 1991	Glass	14 days	No headspace cool/4°C/dark

Table 4-1. continued

Parameter	Units	Method Detection Limit	Sample Volume	Precision	Accuracy	Completeness	Method	Reference	Container	Holding Time	Preservation Method
Simultaneously extracted metals	µmole/g	0.02-0.5	From AVS extract	±35%	±35%	95%	ICP/GFAA	Modified CLP after extraction	na	14 days	na
Grain size	na	na	1000 g	±30%	na	95%	Sieve	ASTM	Plastic bag	14 days	Cool/4°C
pH	std units	0.1	From total solids	±10%	±20%	95%	Electrometric	U.S. EPA Method 9045	Glass	14 days	Freeze
Total solids	%	0.1	50 g	±10%	±20%	95%	Combustion	U.S. EPA Method 160.3	Glass	6 months	Freeze
Total volatile solids	%	0.1	from metals	±20%	±20%	95%	Gravimetric	Centre St. Laurent Method 6	Plastic	6 months	Freeze
Total organic carbon	% (dry weight)	0.05	from PAHs	±20%	±20%	95%	Combustion	LECO Instruments	Glass	6 months	Freeze
Total sulfides	mg/kg (dry weight)	1	5 g	±20%	±25%	95%	Colorimetric	U.S. EPA Method 376.2	Glass	7 days	2*N* Zn acetate; dark;4°C
Ammonia	mg/kg (dry weight)	1	40 g	±20%	±25%	95%	Potentiometric	U.S. EPA Method 350.3	Glass	28 days	Cool/4°C
Chironomus tentans	% survival and growth	na	2000 g	na	na	95%	14-day static exposure	ASTM Method E1383-94	Glass	56 days	Cool/4°C/ dark/nitrogen atmosphere
Hyalella azteca	% survival and growth	na	2000 g	na	na	95%	14-day static exposure	ASTM Method E1383-94	Glass	56 days	Cool/4°C/ dark/nitrogen atmosphere

Table 4-1. continued

Parameter	Units	Method Detection Limit	Sample Volume	Precision	Accuracy	Completeness	Method	Reference	Container	Holding Time	Preservation Method
Tissue											
Total mercury	µg/kg (wet weight	5	1 g	±35%	±35%	95%	Gold trap/ CVAFS	Brooks Rand Laboratory Method BR-0002	Plastic	1 year	Freeze
Methylmercury	µg/kg (wet weight	5	1 g	±35%	±40%	95%	GC/CVAFS	Brooks Rand Laboratory Method BR-0011	Plastic	1 year	Freeze
Selenium	mg/kg (dry weight)	0.042	5 g	±35%	±35%	95%	HGAA	Brooks Rand Laboratory Method BR-0020	Plastic bag	6 months	Freeze
Selenate	mg/kg (dry weight)	0.042	5 g	±35%	±35%	95%	HGAA	Brooks Rand Laboratory Method BR-0022	Plastic bag	6 months	Freeze
Percent lipids	%	na	100 g	±30%	na	95%	Gravimetric	Bligh and Dyer 1989	Glass	1 year	Freeze
Percent moisture	%	0.1	10 g	±10%	±20%	95%	Gravimetric	Brooks Rand Laboratory Method BR-1501	Glass	1 year	Freeze

Note: CVAFS - cold vapor atomic fluorescence spectrophotometry
GC/MS -SIM - gas chromatography/mass spectrometry-selected ion monitoring
GC/ECD - gas chromatography/electron capture detection
GFAA - graphite furnace atomic absorption spectrometry
HGAA - hydride generation-atomic absorption spectrometry
ICP - inductively coupled plasma atomic emmision spectrometry
na - not applicable, please see Section 8.1.2

Table 4-2. Analytes, methods, and targeted detection limits

Analytes	Method	Targeted detection limits for Tissue	Targeted Detection Limits for Sediments
CHEMICAL PARAMETERS		(wet weight)	(dry weight)
Metals in mg/kg			
Arsenic	ENV-02-2500	na	0.1
Aluminum	ENV-02-2451	na	10
Cadmium	ENV-02-2451	na	0.2
Chromium	ENV-02-2451	na	5
Copper	ENV-02-2451	na	5
Iron	ENV-02-2451	na	5
Lead	ENV-02-2451	na	10
Mercury	BR-0002/BR-0011	0.060	0.005
Methylmercury	BR-0002/BR-0011	0.060	0.005
Nickel	ENV-02-2451	na	5
Selenium	BR-0020	0.042	0.042
Selenate	BR-0022	0.042	0.042
Zinc	ENV-02-2451	na	5
PAHs in mg/kg			
Naphthalene	U.S. EPA Method 8270	na	0.03
2-Methylnaphthalene	U.S. EPA Method 8270	na	0.02-0.1
Acenaphthylene	U.S. EPA Method 8270	na	0.04
Acenaphthene	U.S. EPA Method 8270	na	0.07
Fluorene	U.S. EPA Method 8270	na	0.03
Phenanthrene	U.S. EPA Method 8270	na	0.03
Anthracene	U.S. EPA Method 8270	na	0.02
Fluoranthene	U.S. EPA Method 8270	na	0.02
Pyrene	U.S. EPA Method 8270	na	0.03
Benz(a)anthracene	U.S. EPA Method 8270	na	0.02
Chrysene	U.S. EPA Method 8270	na	0.03
Benzo(a)pyrene	U.S. EPA Method 8270	na	0.05
Dibenz(a,h)anthracene	U.S. EPA Method 8270	na	0.04
Indeno(1,2,3-cd)pyrene	U.S. EPA Method 8270	na	0.06
1,2-Benzanthracene	U.S. EPA Method 8270	na	0.10

Table 4-2. continued

Analytes	Method	Targeted Detection Limits for Tissue	Targeted Detection Limits for Sediments
3-Methylcholanthrene	U.S. EPA Method 8270	na	0.10
Dibenzo(a,h)pyrene	U.S. EPA Method 8270	na	0.10
Debenzo(a,i)pyrene	U.S. EPA Method 8270	na	0.10
Dibenzo(a, l)pyrene	U.S. EPA Method 8270	na	0.10
Benzo(c)phenanthrene	U.S. EPA Method 8270	na	0.10
Benzo(g,h,i)perylene	U.S. EPA Method 8270	na	0.10
PCBs in mg/kg	Centre St. Laurent Method 13	na	0.1-1
CONVENTIONAL PARAMETERS			
Percent lipids (%)	Bligh and Dyer (1959)	0.1	na
Percent moisture (%)	BR-1501	0.1	na
Total solids (%)	U.S. EPA Method 160.3	na	0.1
Grain size (%)	ASTM-D422-63	na	0.01
pH (std units)	U.S. EPA Method 9045	na	0.1
Acid volatile sulfides (µ moles/g)	Allen et al. 1991	na	0.9
Total volatile solids (%)	Centre St. Laurent Method 6	na	0.1
Total organic carbon (%)	LECO Instruments	na	0.05
Total sulfides (mg/kg dry)	U.S. EPA Method 376.2	na	1
Ammonia (mg/kg dry)	U.S. EPA Method 350.3	na	1

NOTE: na - not applicable

$$\%RSD = (SD / D_{ave}) \times 100$$

$$\text{Where: } SD = \sqrt{\left(\frac{\sum_{n=3} (D_n - D_{ave})^2}{(n-1)} \right)}$$

where:

D = sample value #
D_{ave} = average sample value #
n = number of samples

4.2 ACCURACY

Accuracy is an expression of the degree to which a measured or computed value represents the true value. Accuracy measurements apply only to the chemical analysis portion of this project; accuracy measurements cannot be assessed for toxicity or benthic sorting because true values do not exist. However, the use of positive and negative controls in toxicity testing provides evidence that the measurement system was properly calibrated. For benthic analyses, taxonomic identification will be verified by an independent taxonomist. Accuracy may be expressed as the percent difference between two measured values, as a percentage of the true or reference value, or as a percent recovery in those analyses where reference materials are not available and spiked samples are analyzed. The equations used to express accuracy are as follows:

$$\text{Percent difference} = \frac{(\text{measured value} - \text{true value})}{\text{true value}} \times 100$$

$$\text{Percent recovery (true vs. measured)} = \frac{\text{measured value}}{\text{true value}} \times 100$$

$$\text{Percent recovery (spiked vs. unspiked)} = \frac{(\text{spiked sample result} - \text{unspiked sample result})}{\text{amount of spike added}} \times 100$$

4.3 REPRESENTATIVENESS

Representativeness expresses the degree to which data accurately and precisely represent an environmental condition. For this program, the substances selected for analysis have been identified as the potential hazardous substances related to the Clark Island site. For bioassays, the toxicity of the sediments tested represents the toxicity of those sediments to the particular species employed and perhaps to closely related species and life stages in the study area.

4.4 COMPARABILITY

Comparability expresses the confidence with which one data set can be evaluated in relation to another data set. For the Clark Island investigation, comparability of data will be established through the use of program-defined general methodologies and reporting formats and the use of common traceable calibration and reference materials from the National Institute of Standard and Technology or other established sources.

4.5 COMPLETENESS

Completeness is a measure of the amount of data that is determined to be valid in proportion to the amount of data collected. Completeness will be calculated as follows:

$$\text{Completeness} = \frac{\text{number of valid measurements}}{\text{total number of data points planned}} \times 100$$

The data quality objective for completeness for all components of this project is 95 percent. Data that have been qualified as estimated because the quality control criteria were not met will be considered valid for the purpose of assessing completeness. Data that have been qualified as rejected will not be considered valid for the purpose of assessing completeness.

5.0
SAMPLING PROCEDURES

Sampling procedures for this investigation are described in detail in Section 5.0 of the SAP.

5.1 SAMPLE ACCEPTABILITY

Samples will be considered acceptable for analysis unless they fail to meet the sample acceptability criteria described in Section 5.1.2 of the SAP for sediment samples, Section 5.2.2 of the SAP for plant samples, Section 5.3.2 of the SAP for benthic macroinvertebrate grab samples, Section 5.4.2 of the SAP for benthic community samples, and Section 5.5.2 of the SAP for fish samples.

5.2 FIELD QUALITY CONTROL CRITERIA

Although validation guidelines have not been established for field quality control samples, their analysis is useful in identifying possible problems resulting from sample collection or sample processing in the field. All field quality control samples will be documented in the field logbook and verified by the QA Coordinator or a designee. The field quality control samples that will be collected during this investigation are discussed in the following sections.

5.2.1 Certified Reference Materials

Analysis of reference materials and certified reference materials provides information on the accuracy of the analysis and the performance of the laboratory. At least one reference material will be analyzed for each analyte group, contingent on availability and at the discretion of the QA Coordinator.

5.2.2 Field Blanks

Field blanks are used to assess whether the samples have been contaminated during sample collection. The field blanks discussed below will be collected throughout the sampling event for this investigation.

5.2.2.1 Cross Contamination Blanks

Cross contamination blanks are used to assess whether and to what degree contamination is crossing from one sample to the next during sample collection or processing. A cross contamination blank is created by wiping the sample processing equipment with ashless filter paper after it has undergone decontamination procedures. Because the sediment in contact with the sampling device will not be collected, cross contamination blanks will not be prepared for the sampling device. A minimum of one cross contamination blank will be submitted for the analysis of metals, PAHs, and PCBs for every 20 samples processed in the field or per sampling event, whichever is most frequent.

5.2.2.2 Filter Blanks

Filter blanks are used in conjunction with the cross contamination blanks to assist in verifying the source of contamination (e.g., if an analyte is detected in the cross contamination blank but not in the filter blank then the contamination could be a result of insufficient decontamination procedures or poor field technique). One filter blank will be submitted for the analysis of metals, PAHs, and PCBs per box of filter papers used.

5.2.2.3 Field Duplicate Samples

Field duplicate samples will be collected for sediments, plant tissue, and benthic macroinvertebrate tissue. One of each type of field duplicate sample will be collected for each 10 field samples, and the duplicate samples will be submitted for the same analyses as the corresponding field samples. Duplicate samples will be collected from the same homogenized material as the corresponding field sample.

Additional splits of sediment samples will be also be collected. Splits will be provided to Eco Laboratories at Pointe-Claire and to the MEF laboratory. One set of sediment sample splits will be collected for each 10 field sediment samples, and the splits will be analyzed for the same parameters as the corresponding field samples.

6.0
SAMPLE HANDLING AND CUSTODY

Sample custody is a critical aspect of environmental investigations. Sample possession and handling must be traceable from the time of sample collection, through laboratory and data analysis, to the time sample results are ready to be introduced as evidence. Documentation procedures for sampling are provided in greater detail in the SAP. This section describes the minimum program requirements for sample handling and chain-of-custody procedures.

6.1 FIELD SAMPLING OPERATIONS

Field sampling operations and documentation are discussed in detail in Section 5.0 and 7.0 of the SAP. Station log and field logbook entries will be completed for each station occupied and each sample taken. Sample containers will be labeled with the client name, survey number, sample number, sampling date and time, sample tag number, required analyses, and initials of the individual processing the sample. The QA Coordinator or designee will check all container labels, chain-of-custody form entries, and logbook entries for completeness and accuracy at the end of each sampling day.

6.2 SAMPLE PRESERVATION

The requirements for preserving sample aliquots destined for each type of analysis are listed in Table 4-1. In brief, immediately after the samples are placed in sample containers, the containers will be placed in the appropriate coolers with a sufficient number of ice packs (or crushed ice) to keep them cold through the completion of that day's sampling and transport to the laboratories. The samples will be stored as indicated in Table 4-1.

6.3 SAMPLE CHAIN OF CUSTODY

Samples are considered to be "in custody" if they are: 1) in the custodian's possession or view; 2) in a secured place (under lock) with restricted access; or 3) in a container that is secured with an official seal(s) such that the sample cannot be reached without breaking the seal(s). The principal documents used to identify samples and to document possession are chain-of-custody records, field logbooks, and field tracking forms. Chain-

of-custody procedures will be used for all samples at all stages in the analytical or transfer process and for all data and data documentation whether in hard copy or electronic format.

6.4 SAMPLE SHIPMENT

The EVS QA Coordinator and Field Coordinator or their designees will be responsible for all sample tracking and chain-of-custody procedures in the field. The QA Coordinator or a designee will be responsible for final sample inventory and will maintain chain-of-custody documentation. At the end of each day, and prior to transfer, chain-of-custody entries will be made for all samples. Finally, information on the sample labels will be checked against sample logbook entries and chain-of-custody forms, and samples will be recounted. All samples will be accompanied by chain-of-custody forms; the forms will be signed at each point of transfer and will include sample numbers. All chain-of-custody forms will be completed in indelible ink. Copies of all forms will be retained by EVS and will be included as appendices to QA/QC reports.

Before shipping, sample containers will be wrapped in bubble wrap and securely packed inside the cooler with ice packs or crushed ice. The original, signed chain-of-custody forms will be placed in a sealable plastic bag, which will be taped to the inside of the cooler lid. Fiber tape will be wrapped completely around the cooler. On each side of the cooler a *This Side Up* arrow label will be appropriately attached, and a *Glass—Handle with Care* label will be attached to the top of the cooler (as appropriate). The cooler will be sealed with custody seal tape, which will be dated and initialed.

All samples will be shipped via Federal Express to the appropriate laboratories as indicated in Section 3.3 of this QAPP.

6.5 SAMPLE RECEIPT

The Laboratory Project Managers at each laboratory will ensure that chain-of-custody forms are properly signed upon receipt of the samples and will note questions or observations concerning sample integrity on the chain-of-custody forms. The laboratories will contact the Project QA Coordinator immediately if discrepancies are discovered between the chain-of-custody forms and the sample shipment upon receipt. The Laboratory Project Manager will specifically note any coolers that do not contain ice packs or that are not sufficiently cold (4°C ± 2°) upon receipt.

6.6 INTRA-LABORATORY SAMPLE TRANSFER

The Laboratory Project Manager will ensure that a sample-tracking record is maintained that follows each sample through all stages of laboratory processing. The sample-tracking record must contain at a minimum the name/initials of responsible individuals performing the analyses, dates of sample extraction/preparation and analysis, and the type of analysis being performed.

6.7 ARCHIVED SAMPLES

All excess samples remaining after laboratory analysis will be archived. The laboratories will maintain chain-of-custody procedures and sample integrity for the entire time that the samples are in their possession. All laboratories will store the excess samples for 1 year following completion of data validation. The laboratories will not dispose of the environmental samples for this project until they notify the Project QA Coordinator.

7.0
CHEMISTRY ANALYSES AND QUALITY CONTROL PROCEDURES

7.1 SAMPLE ANALYSES

Prior to analysis of the samples, the laboratory must provide written protocols for the analytical methods to be used, calculate method detection limits (MDLs) for each analyte in each matrix of interest, and establish an initial calibration curve for all analytes. The laboratory must demonstrate their continued proficiency by participation in interlaboratory comparison studies and through repeated analysis of certified reference materials, calibration checks, laboratory reagent blanks, and spiked samples.

7.1.1 Analytical Methods and Targeted Detection Limits

The methods of analysis and associated TDLs are identified in Table 4-2.

7.1.2 Determination of Method Detection Limits

The MDL is defined as the lowest concentration of an analyte or compound that a method can detect in either a sample or a blank with 99 percent confidence. Brooks Rand, Ltd. and Analytical Resources, Inc. (ARI) determine MDLs using standard procedures outlined in 40 CFR, Part 136, Appendix B. In summary, seven replicate samples are fortified at 1 to 5 times (but not to exceed 10 times) the level expected to be the MDL. The MDL is then determined by calculating the standard deviation of the replicates and multiplying by 3.14. Zenon Laboratory determines their MDLs by analyzing 10 replicates fortified at 5 to 10 times the level expected to be the MDL. The MDL is then determined by calculating the standard deviation of the replicates and multiplying by 3. Brooks Rand, Zenon Laboratory, and ARI conduct MDL studies on an annual basis.

7.1.3 Method of Analysis

Based on the project data quality objectives (DQOs), the level of support requested of the laboratory for this project will consist of using modified standard methods with sufficient documentation to enable full validation of the data. Modifications will be made where applicable and appropriate.

7.1.3.1 Polycyclic Aromatic Hydrocarbons

Analysis of PAHs will follow U.S. EPA Method 8270 protocols. PAHs and PCBs will be coextracted using U.S. EPA Method 3550. PAH concentrations will be determined using gas chromatography/mass spectrometry-selected ion monitoring (GC/MS-SIM) instead of full scan MS, as indicated in U.S. EPA Method 8270.

7.1.3.2 Polychlorinated Biphenyls

Analysis of PCBs will follow *Guide Méthodologique de Charactérisation des Sédiments* (Environment Canada 1992) protocols. To remove interferents from the sample extracts, all PCB extracts will undergo cleanup on a water deactivated silica gel column. PCBs will be measured by high-resolution gas chromatography/electron capture detection (GC/ECD) with dual column confirmation.

7.1.3.3 Metals

Analysis of metals (except for mercury and methylmercury) will follow Environment Canada standard methods (Environment Canada 1992). Sediment samples will be dried at 105°C, then sieved through an 80-mesh sieve. One gram of sediment will then be digested with nitric acid, hydrochloric acid, and hydrogen peroxide. Arsenic and selenium will be determined by hydride generation inductively coupled plasma atomic emission spectrometry (ICP). Cadmium and lead will be determined by graphite furnace atomic absorption spectrometry (GFAA). Aluminum, chromium, copper, iron, nickel, and zinc will be determined by ICP.

7.1.3.4 Total Mercury and Methylmercury

Sediment and tissue samples will be analyzed for total mercury by Brooks Rand Method BR-0002. The samples are subjected to a digestion with nitric/sulfuric acid and further oxidized with bromine chloride in order to convert all mercury species to mercury (II). Samples are then reduced with stannous chloride, forming volatile mercury or elemental mercury, and purged and concentrated on a gold trap. The gold trap is heated, thermally desorbing the mercury, which is then analyzed by cold vapor atomic fluorescence spectrophotometry (CVAFS).

Sediment and tissue samples will be analyzed for methylmercury by Brooks Rand Method BR-0011. The samples are ethylated forming a methyl-ethyl mercury derivative. The mercury is then released using a percolation trap, followed by heating under a flow of inert gas. The mercury species are then separated using gas chromatography, pyrolitically broken down to elemental mercury, and analyzed by CVAFS.

7.1.3.5 Total Selenium and Selenate

Sediment and tissue samples will be analyzed for total selenium by Brooks Rand Method BR-0020. The samples are subjected to a digestion with nitric/perchloric acid. All forms of selenium are then converted to Se(IV). Selenium is then determined by hydride generation-atomic absorption spectrometry.

Sediment and tissue samples will be analyzed for selenate by Brooks Rand Method BR-0022. The samples are extracted with sodium hydroxide. The samples are first analyzed directly to determine Se(IV), then in a second set of aliquots Se(VI) is reduced to Se(IV). Selenate [Se(VI)] is determined by difference of the Se(IV + VI) and Se(IV) results.

7.1.3.6 Percent Lipids

Percent lipids will be determined using a method developed by Bligh and Dyer (1959). The tissue samples are extracted with chloroform and methanol, then the percent lipids are determined gravimetrically.

7.1.4 Laboratory Quality Control Criteria

Results of the quality control samples from each sample group will be reviewed by the analyst immediately after a sample group has been analyzed. The quality control sample results will then be evaluated to determine if control limits have been exceeded. If control limits are exceeded in the sample group, the Project QA Coordinator will be contacted immediately, and corrective action (e.g., method modifications followed by reprocessing the affected samples) will be initiated prior to processing a subsequent group of samples.

All primary chemical standards and standard solutions used in this project will be traceable to the National Institute of Standards and Technology, Environmental Resource Associates, National Research Council of Canada, or other documented, reliable, commercial sources. Standards will be validated to determine their accuracy by comparison with an independent standard. Any impurities found in the standard will be documented.

The following sections summarize the procedures that will be used to assess data quality throughout sample analysis. A summary of the associated control limits for precision and accuracy is presented in Table 4-1.

7.1.4.1 Initial Calibration

Multipoint initial calibration will be performed on each instrument at the start of the project, after each major interruption to the analytical instrument, and when any ongoing calibration does not meet control criteria. Ongoing calibration will be performed every 12 hours for metals and organic analyses, and conventional parameters when applicable, to track instrument performance.

Instrument blanks or continuing calibration blanks provide information on the stability of the baseline established. Continuing calibration blanks will be analyzed immediately prior to continuing calibration verification at a frequency of one continuing calibration blank for every 10 samples analyzed at the instrument for inorganic analyses and one blank every 12 hours for organic analyses. If the ongoing calibration is out of control, the analysis must come to a halt until the source of the control failure is eliminated or reduced to meet control specifications. All project samples analyzed while instrument calibration was out of control will be reanalyzed.

7.1.4.2 Standard Reference Materials

Analysis of standard reference materials and certified reference materials provides information on the accuracy of the analysis and the performance of the laboratory. At least one reference material will be analyzed for conventional parameters per 10 samples or per group of samples, whichever is more frequent. All results of analyses of certified reference materials must fall within the acceptance ranges established for the reference material.

7.1.4.3 Matrix Replicates

Analytical replicates provide information on the precision of the analysis and are useful in assessing potential sample heterogeneity and matrix effects. Analytical replicates are subsamples of the original sample that are prepared and analyzed as a separate sample assuming sufficient sample matrix is available. A minimum of one replicate will be analyzed per sample group or for every 10 samples, whichever is more frequent. If insufficient material is available for matrix replicates and spikes, standard reference materials will be substituted.

7.1.4.4 Matrix Spikes and Matrix Spike Duplicates

Analysis of matrix spike samples provides information on the extraction efficiency of the method on the sample matrix. By performing duplicate matrix spike analyses, information on the precision of the method is also provided for organic analyses. A

minimum of one matrix spike will be analyzed for every sample group or for every 10 samples, whichever is more frequent, when possible. A standard reference material will be used to assess method accuracy for those parameters that cannot be spiked.

7.1.4.5 Surrogate Spikes

All project samples analyzed for organic compounds will be spiked with appropriate surrogate compounds as defined in the analytical methods. Surrogate recoveries will be reported by the laboratories; however, no sample results will be corrected for recovery using these values.

7.1.4.6 Method Blanks

Method blanks are analyzed to assess possible laboratory contamination at all stages of sample preparation and analysis. A minimum of one method blank will be analyzed for every extraction batch or for every 10 samples, whichever is more frequent.

7.2 DATA DELIVERABLES

Laboratories will be responsible for internal checks on data reporting and will correct errors identified during the quality assurance review. Close contact will be maintained with the laboratories to resolve any quality control problems in a timely manner. Brooks Rand, Zenon Laboratory, and ARI will be required to report the following:

1. ***Project Narrative***: This summary, in the form of a cover letter, will discuss any problems encountered during any aspect of analysis. This summary should discuss, but not be limited to, quality control, sample shipment, sample storage, and analytical difficulties. Any problems encountered, actual or perceived, and their resolutions will be documented in as much detail as necessary.

2. ***Chain-of-Custody Records***: Legible copies of the chain-of-custody forms will be provided as part of the data package. This documentation will include the time of receipt and condition of each sample received by the laboratory. Additional internal tracking of sample custody by the laboratory will also be documented.

3. ***Sample Results***: The data package will summarize the results for each sample analyzed. The summary will include the following information when applicable:

   - Field sample identification code and the corresponding laboratory identification code
   - Sample matrix
   - Date of sample extraction/digestion
   - Date and time of analysis
   - Weight and/or volume used for analysis
   - Final dilution volumes or concentration factor for the sample
   - Percent moisture in the sediment and plant tissue samples
   - Percent lipids in the fish tissue samples
   - Identification of the instrument used for analysis
   - Method reporting and quantitation limits
   - Analytical results reported to appropriate significant figures with reporting units identified
   - All data qualifiers and their definitions
   - A computer diskette containing all of the data

4. ***Quality Assurance/Quality Control Summaries***: This section will contain the results of all QA/QC procedures. Each QA/QC sample analysis will be documented with the same information required for the sample results (see above). No recovery or blank corrections will be made by the laboratory (except for methylmercury). The required summaries are listed below; additional information may be requested.

   - **Calibration data summary**: Report the concentrations of the initial calibration and daily calibration standards and the date and time of

analysis. List the response factor, %RSD, percent difference, and retention time for each analyte as appropriate. Report results for standards to indicate instrument sensitivity.

- **Internal standard area summary**: Report the stability of internal standard areas as appropriate.

- **Method blank analysis**: Report the method blank analyses associated with each sample and the concentration of all compounds of interest identified in these blanks.

- **Surrogate spike recovery**: Report all surrogate spike recovery data for PAHs and PCBs. List the name and concentration of all compounds added, percent recoveries, and range of recoveries.

- **Matrix spike recovery**: Report all matrix spike recovery data for metals, PAHs, PCBs, and conventional parameters (as appropriate). List the name and concentration of all compounds added, percent recoveries, and range of recoveries. Report the RPD for all duplicate analyses.

- **Matrix duplicate**: Report the RPD for all matrix duplicate analyses.

- **Relative retention time**: Report the relative retention time of each analyte detected in the samples for both primary and confirmational analyses as appropriate.

5. ***Original Data***: Legible copies of the original data generated by the laboratory will include the following:

   - Sample extraction/digestion, preparation, and cleanup logs

   - Instrument specifications and analysis logs for all instruments used on days of calibration and analysis

   - Reconstructed ion chromatograms for all samples, standards, blanks, calibrations, spikes, replicates, and reference materials

   - Enhanced spectra of detected compounds with associated best-match spectra for each sample

- Printouts and quantitation reports for each instrument used, including reports for all samples, standards, blanks, calibrations, spikes, replicates, and reference materials

- Original data quantification reports for each sample

- Original data for blanks and samples not reported

No recovery or blank corrections will be made by the laboratory, with the exception of methylmercury.

8.0
BIOASSAY ANALYSES AND QUALITY CONTROL PROCEDURES

8.1 SAMPLE ANALYSES AND QUALITY CONTROL CRITERIA

The bioassay procedures for this study are described in detail in Appendix C. Up to 24 sediment samples will be submitted to the EVS laboratory for bioassay analyses. The following sections discuss the components of the QA/QC program.

8.1.1 Project-Specific Standard Operating Procedures

The following two sediment toxicity tests will be used in this study:

Amphipod Bioassay: Short-term adverse effects of potentially contaminated sediment will be evaluated by measuring survival and growth in adult amphipods (*Hyalella azteca*). Amphipods will be exposed to the site-related and reference sediment for a 14-day period. The test will be performed according to the procedures and QA/QC performance standards described in American Society for Testing and Materials (ASTM) Method E1383-94 (ASTM 1994).

Chironomid Larvae Bioassay: Chironomid larvae will be used to evaluate the toxicity of the sediments by measuring the survival and growth of the larvae. *Chironomus tentans* larvae will be used in the present study. Chironomids will be exposed to the site-related and reference sediment for a 14-day period. Test protocols and QA/QC performance standards will be in accordance with ASTM Method E1383-94 (ASTM 1994).

8.1.2 Dose/Response Studies using Total Organic Carbon and Grain Size

In order to establish the effects of total organic carbon (TOC) and grain size on the toxic response of the organisms used in the bioassays, dose/response studies for TOC and grain size will be conducted. The dose/response studies will consist of setting up multiple test chambers for each organism, with one variable remaining constant throughout the test chambers while the second variable varies among the test chambers. For determining the effects of varying TOC content on the organisms, the grain size will be kept constant

while the TOC content will range from 0.2-15 percent. For determining the effects of varying grain size distribution on the organisms, TOC content will be held constant at 2 percent, and grain size will be varied from 90 percent sand/10 percent fines to 10 percent sand/90 percent fines. These studies will be conducted for both the amphipod and chironomid larval bioassays. Test protocols are presented in Appendix C.

8.1.3 Test Quality Control

Both sediment toxicity tests to be used in the study will incorporate standard QA/QC procedures to ensure that the test results are valid. Standard QA/QC procedures include the use of a negative control, a positive control, reference sediment samples, and measurement of water quality during testing.

Negative Control — A negative control for a sediment toxicity test consists of a clean, inert material and the same diluent seawater used in testing sediment toxicity. For the tests to be used in this study, the negative control will be fine silica sand (#30) obtained from Ocean Construction Supply Ltd., in Vancouver, B.C. The negative control should not exhibit greater than 10 percent mortality.

Positive Control — In a positive control for a sediment toxicity test, a reference toxicant is used to establish the relative sensitivity of the test organism. The positive control for sediment tests is typically conducted with diluent seawater and without sediment. Reference toxicants used in this study will include zinc sulphate for *H. azteca* and sodium chloride for *C. tentans*. Specific reference toxicants and test methods for the bioassays to be conducted for this study are described in the referenced methods. The positive control should fall within the range of the laboratory mean plus or minus 2 times the standard deviation.

In addition to the positive control described above, an additional positive control will be conducted using ammonia. Ammonia is often present in marine sediments and may be a significant cause of toxicity observed in toxicity tests. The purpose of the ammonia positive control is to determine the toxicity of ammonia to the test organisms being used in this study. Both the amphipod and the larval stages of the chironomid can be sensitive to environmental concentrations of ammonia. For this reason, a positive control will be conducted for the amphipod and chironomid larval tests. The positive control with ammonia will be accomplished using control sediment spiked with ammonia at varying concentrations. The target range of ammonia concentrations used will bracket the expected LC50. A 14-day exposure period will be used for the ammonia positive control.

Reference Sediment — A reference sediment will also be included with each bioassay. Reference sediments provide toxicity data that can be used to separate toxicant

effects from unrelated effects, such as those of sediment grain size. Sediment samples selected to be the test reference sediment should be collected from an area that represents background concentrations of contaminants and the range of important natural, physical, and chemical characteristics of the test sediments (e.g., sediment grain size and TOC). Appropriate reference sediments will be selected from the background stations sampled during the reconnaissance survey.

Water Quality Variables — Bioassays require that proper water quality conditions be maintained to ensure survival of the organisms, and to ensure that undue stress is not exerted on the organisms unrelated to test sediments. Water quality variables, including measurements of salinity, dissolved oxygen, pH, ammonia, sulfides, and temperature, are measured during testing.

8.1.4 Test Quality Control Checklists

Quality control checklists recommended by the U.S. Army Corps of Engineers (U.S. EPA and ACOE 1993) will be used by the laboratory to ensure that all test procedures are followed and that all data are recorded. Laboratory staff are required to complete all elements of the checklists.

8.2 DATA DELIVERABLES

The laboratories will be responsible for internal checks on data reporting and will correct errors identified during the quality assurance review. The bioassay laboratories for this study will be required to report results that are supported by all information recommended by ASTM protocols for quality assurance review, including:

- Cover letter discussing analytical problems (if any) and procedures
- Test methods used for bioassay testing and statistical analyses
- Results for survival, growth, reburial, abnormalities, water quality parameters, reference toxicants, and statistical analyses
- Original data sheets for water quality, survival, growth, reburial, abnormalities, reference toxicant, and statistics
- Original quality control checklists
- Chain-of-custody records

- Computer diskette containing an electronic file of the data

Close contact with the laboratory will be maintained to resolve any quality control problems in a timely manner.

9.0
BENTHIC COMMUNITY ANALYSES

9.1 SAMPLE ANALYSES AND QUALITY CONTROL CRITERIA

Approximately 120 sieved benthic samples (5 replicates from approximately 24 stations) will be submitted to the EVS laboratory for sorting and taxonomic identification. The following sections outline the quality control procedures to be used for this program, which are based on Puget Sound Estuary Program (PSEP) protocols (U.S. EPA 1987).

9.1.1 Sample Sorting

To determine sorting efficiency, 20 percent of each sample will be re-sorted. Prior to re-sorting the sample will be homogenized to ensure the aliquot is representative of the entire sample. A sample is considered to have passed quality control if the number of organisms found in the re-sort does not differ from the original count by more than 5 percent. Complete records of sorting and re-sorting of each station will be permanently maintained.

9.1.2 Identification of Organisms

Consistency and accuracy of identification of organisms will be checked. Internal quality control will be maintained by checking identifications against verified voucher specimens. External verification and quality control will be maintained by having 5 percent of all samples re-identified by another equally qualified taxonomist. Specimen identification will be at least 95 percent accurate. Complete records on identification will be permanently maintained.

9.1.3 Data Validation

EVS will perform data validation and verification of methods for benthic infauna. Reports will be reviewed to ensure that all quality control requirements have been met and that completeness is acceptable.

9.2 DATA DELIVERABLES

The laboratory will be responsible for internal checks on data reporting and will correct errors identified during the quality assurance review. The laboratory will be required to report results supported by all information recommended by PSEP protocols for quality assurance review, including:

- Cover letter discussing problems (if any) and procedures
- Summary report for taxonomy
- Spreadsheet containing replicate abundance data
- Quality assurance results for 20 percent re-sorting
- Original data sheets
- Screening logs
- Chain-of-custody forms and transfer logs

Close contact with the laboratory will be maintained to resolve any quality control problems in a timely manner.

10.0
TOXICITY IDENTIFICATION EVALUATION ANALYSES

10.1 SAMPLE ANALYSES AND QUALITY CONTROL CRITERIA

The TIE procedures for this study are described in detail in Appendix C. In general, analysis will consist of a modified Phase I TIE. Phase I characterizes the physical and chemical properties of the sample toxicants by altering or rendering biologically unavailable generic classes of compounds. This is done by subjecting the sample to a series of manipulations. These manipulations include:

- C_{18} solid-phase extraction
- pH adjustments
- Addition of the chelating agent EDTA

Sediment samples that fail either the *Hyalella* or the Chironomid bioassays will be submitted to the EVS laboratory for TIE analysis.

To ensure the generation of technically defensible data, a QA/QC program will be instituted before initiating the tests. This program will include preparation of a QAPP by the testing laboratory. In addition, the QA/QC program will include project-specific quality control checklists and data bench sheets. The following sections discuss the components of the QA/QC program.

10.1.1 Project-Specific Laboratory Procedures

Project-specific procedures to be used by the laboratories are provided in Appendix C.

10.1.2 Test Quality Control Checklists

Quality control checklists recommended for use by the U.S. Army Corps of Engineers (U.S. EPA and ACOE 1993) have been modified for the TIE testing and will be used by the laboratory to ensure that all procedural and data elements of the tests are followed and recorded. Laboratory staff are required to complete all elements of the checklists.

10.2 DATA DELIVERABLES

The laboratories will be responsible for internal checks on data reporting and will correct errors identified during the quality assurance review. The TIE laboratory for this study will be required to report all results necessary for a complete quality assurance review, including:

- A cover letter discussing analytical problems (if any) and procedures
- Test methods used for bioassay testing and statistical analyses
- Results for survival, growth, water quality parameters, and statistical analyses
- Original data sheets for water quality, survival, growth, reference toxicant, and statistics
- Original quality control checklists
- Chain-of-custody records

Close contact with the laboratories will be maintained to resolve any quality control problems in a timely manner.

11.0
LABORATORY AND FIELD PERFORMANCE AUDITS

Laboratory and field performance audits consist of on-site reviews of quality assurance systems and equipment for sampling, calibration, and measurement. Laboratory audits will not be conducted as part of this study; however, all laboratory audit reports will be made available to the EVS QA Coordinator upon request. All laboratories are required to have written procedures addressing internal QA/QC; these procedures have been submitted to EVS and will be reviewed by the Project QA Coordinator to ensure compliance with the QAPP. All laboratories and QA Coordinators are required to ensure that all personnel engaged in sampling and analysis tasks have appropriate training.

12.0
CORRECTIVE ACTION PROCEDURES

12.1 CORRECTIVE ACTION FOR FIELD SAMPLING

The Field Coordinator, or a designee, will be responsible for correcting equipment malfunctions throughout the field sampling effort. The EVS QA Coordinator will be responsible for resolving situations in the field that may result in nonconformance or noncompliance with the QAPP. All corrective measures will be immediately documented in the field logbook. Corrective action for the field sampling efforts is described in greater detail in Section 5.0 of the SAP.

12.2 CORRECTIVE ACTION FOR LABORATORY ANALYSES

All laboratories are required to comply with the standard operating procedures previously submitted to the Project QA Coordinator. The Laboratory Project Managers will be responsible for ensuring that appropriate corrective actions are initiated as required for conformance with this QAPP. All laboratory personnel will be responsible for reporting problems that may compromise the quality of the data.

The EVS QA Coordinator will be notified immediately if any quality control sample exceeds the project-specified control limits (Table 4-1). The analyst will identify and correct the anomaly before continuing with the sample analysis. The Laboratory Project Manager will document the corrective action taken in a memorandum submitted to the Project QA Coordinator within 5 days of the initial notification. A narrative describing the anomaly, the steps taken to identify and correct the anomaly, and the treatment of the relevant sample batch (i.e., recalculation, reanalysis, reextraction) will be submitted with the data package in the form of a cover letter.

13.0
DATA AND DATA DOCUMENTATION

All original data and documentation generated by the laboratories will be kept in a secure location for 7 years after the data have been validated. Chain-of-custody procedures will be followed for all laboratory data and data documentation, whether in hard copy or electronic format. All laboratory data and data documentation, including electronic data files in a format specified by EVS, will be submitted to EVS, as appropriate, for the validation of chemistry data and bioassay results. All data and data documentation are the responsibility of the Project Manager and will be marked "Confidential."

14.0
DATA REDUCTION AND DATA MANAGEMENT

14.1 DATA REDUCTION

Data reduction is the process by which original data (analytical measurements) are converted or reduced to a specified format or unit to facilitate analysis of the data. Data reduction requires that all aspects of sample preparation that could affect the test result (such as sample volume analyzed or dilutions required) be taken into account in the final result. It is the laboratory analyst's responsibility to reduce the data, which are subjected to further review by the Laboratory Project Manager, the EVS Project Manager, EVS QA Coordinator, and independent reviewers. Sediment results will be reported on a dry-weight basis, with percent moisture noted. Tissue results will be reported on a wet-weight basis, with percent lipids noted. The data will be generated in a form amenable to review and evaluation. Data reduction may be performed manually or electronically. If performed electronically, all software used must be demonstrated to be true and free from unacceptable error.

14.2 DATA MANAGEMENT

FoxPro, a relational database software that creates Xbase files (i.e., files with .dbf extensions), will be used. These files are directly compatible with ARC/INFO® and other geographical information systems.

Data structures will be developed to provide the flexibility to meet known and predicted data analysis goals. Structures will be designed using database normalization techniques to minimize the number and size of the files, while considering effective methods of data manipulation for the requirements of data analysis and summarization. Typical files will include the following:

- Station file identifying where samples were collected, including station identifier numbers

- Sample file describing when and what samples were collected, including sample depth

- Analytical chemistry results, including concentrations, units of measure, and qualifiers

- Biological test results with identification of test organisms and test conditions

A library of routines will be used to translate typical electronic output from laboratory analytical systems and to generate data analysis reports. The use of automated routines ensures that all data are consistently converted into the desired data structures and that operator time is kept to a minimum. In addition, routines and methods for quality checks will be used to ensure such translations are correctly applied. Final electronic files will be made available to the client in an agreed-upon format.

Written documentation will be used to clarify how field and laboratory duplicates and QA/QC samples were recorded in the data tables, and to provide explanations of other issues that may arise. The data management task will include keeping accurate records of field and laboratory QA/QC samples so that study team members who use the data will have appropriate documentation.

In addition to placing all data and identifiers in an electronic database, hard copies of all original analytical data or study records will be placed in a library filing system. Each analytical data set or document will be given a unique code (based on the original source of the data or information) and filed based on that code. A master list of all filed documents, sorted in order by filing code, will be maintained for easy retrieval from the library. Data management files will be stored on a secure computer or on a removable hard drive that can be secured.

15.0
DATA VALIDATION

Data validation, initiated in the laboratory, is a process in which data are reviewed and evaluated by supervisory personnel or quality assurance specialists within the laboratory. The laboratory analyst is responsible for ensuring that the analytical data are correct and complete, the appropriate procedures have been followed, and the quality control results are within the acceptable limits. The EVS QA Coordinator is responsible for ensuring that all analyses performed by Brooks Rand and EVS are correct, properly documented, and complete, and that they satisfy the project DQOs for sediment toxicity bioassays and for the collection and analysis of mercury and methylmercury in tissue and sediment samples. Tecsult is responsible for ensuring that all analyses performed by Zenon are correct, properly documented, and complete, and that they satisfy the project DQOs specified in this QAPP.

All discrepancies and requests for additional, corrected data will be discussed with the laboratories prior to issuing the formal data validation report. All contacts with the laboratories will be documented on a communication report. Review procedures used and findings made during data validation will be documented on worksheets. A validation report will be prepared for each matrix; that report will summarize quality control results, qualifiers, and possible data limitations. Only validated data with appropriate qualifiers will be released for general use.

Quality assurance review of the benthic and bioassay data will be performed by EVS in the context of DQOs specified in this QAPP.

16.0
DATA REPORTING

Data are not considered final until validated. All data, including laboratory and field quality control sample results, will be summarized in a quality assurance summary report. The quality assurance summary reports will focus on data that did not meet the DQOs specified in Table 4-1. The quality assurance summary reports will be included as an appendix to the final ERA document. In addition, EVS will include a summary of the sampling event, including deviations from this QAPP and actions taken to address those deviations.

17.0
REFERENCES

Allen, H.E., F. Gongmin, W. Boothman, D. Ditoro, and J.D Mahony. 1991. Determination of acid volatile sulfides and simultaneously extracted metals in sediments. U.S. Environmental Protection Agency, Office of Science and Technology, Washington, DC. 17 pp.

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Environment Canada, Centre Saint-Laurent en collaboration avec le Ministére de l'Environment du Québec. Avril 1992. Guide méthodologique de charactérisation des sédiment. Ministre des Approvisionnements et Services Canada 1991, No de catalogue Em 40-418/1991F.

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U.S. EPA. 1987. Recommended protocols for sampling and analyzing subtidal benthic macroinvertebrate assemblages in Puget Sound. Prepared for Puget Sound Estuary Program, U.S. Environmental Protection Agency, Region 10, Office of Puget Sound, Seattle, WA.

U.S. EPA. 1989. Preparing perfect project plans. U.S. Environmental Protection Agency, Risk Reduction Engineering Laboratory, Cincinnati, OH.

U.S. EPA. 1994. EPA requirements for quality assurance project plans for environmental data operations. Draft interim final, August 1994. EPA QA/R-5. U.S. Environmental Protection Agency, Quality Assurance Division, Washington, DC.

U.S. EPA and ACOE. 1993. Evaluation of dredged material proposed for discharge in inland and near coastal waters - testing manual (draft). U.S. Environmental Protection Agency, Office of Water and Office of Science and Technology, Washington, DC, and Department of the Army, U.S. Army Corps of Engineers, Washington, DC.

APPENDIX B

Examples of Field Data Forms and Sample Labels

EVS ENVIRONMENT CONSULTANTS

Sample Information

Project No.:

Sample I.D.:

Date: Time:

Analyze for:

Sampled by:

Preservative:

200 West Mercer St.
Suite 403
Seattle, WA 98119

Tel: (206) 217-9337
Fax: (206) 217-9343

Sample Identification

EVS ENVIRONMENT CONSULTANTS

Field Record for Surface Sediment Grab Samples

Station ID: _____ **Sampling Date:** _____

Project Name: Clark Island EIS **EVS Project Number:** 2/612-02.32 **On-site Director:** _____

Time at Station: _____ **Target Station Coordinates:** _____

Weather: _____

Grab No: _____ **Bottom depth:** _____ **Penetration depth:** _____ **Time:** _____

Sediment type:	*Sediment color:*	*Sediment odor:*	
cobble	D.O.	none	H_2S
gravel	gray	slight	Petroleum
sand C M F	black	moderate	Other:
silt clay	brown	strong	
wood chips	brown surface	overwhelming	

GPS Coordinates: N _____ E _____

Sediment Sample? Y N

Benthic Community Subs Sample? Y N

Subsample No: _____ **ID** _____

Grab No: _____ **Bottom depth:** _____ **Penetration depth:** _____ **Time:** _____

Sediment type:	*Sediment color:*	*Sediment odor:*	
cobble	D.O.	none	H_2S
gravel	gray	slight	Petroleum
sand C M F	black	moderate	Other:
silt clay	brown	strong	
wood chips	brown surface	overwhelming	

GPS Coordinates: N _____ E _____

Sediment Sample? Y N

Benthic Community Subs Sample? Y N

Subsample No: _____ **ID** _____

Grab No: _____ **Bottom depth:** _____ **Penetration depth:** _____ **Time:** _____

Sediment type:	*Sediment color:*	*Sediment odor:*	
cobble	D.O.	none	H_2S
gravel	gray	slight	Petroleum
sand C M F	black	moderate	Other:
silt clay	brown	strong	
wood chips	brown surface	overwhelming	

GPS Coordinates: N _____ E _____

Sediment Sample? Y N

Benthic Community Subs Sample? Y N

Subsample No: _____ **ID** _____

Grab No: _____ **Bottom depth:** _____ **Penetration depth:** _____ **Time:** _____

Sediment type:	*Sediment color:*	*Sediment odor:*	
cobble	D.O.	none	H_2S
gravel	gray	slight	Petroleum
sand C M F	black	moderate	Other:
silt clay	brown	strong	
wood chips	brown surface	overwhelming	

GPS Coordinates: N _____ E _____

Sediment Sample? Y N

Benthic Community Subs Sample? Y N

Subsample No: _____ **ID** _____

Grab No: _____ **Bottom depth:** _____ **Penetration depth:** _____ **Time:** _____

Sediment type:	*Sediment color:*	*Sediment odor:*	
cobble	D.O.	none	H_2S
gravel	gray	slight	Petroleum
sand C M F	black	moderate	Other:
silt clay	brown	strong	
wood chips	brown surface	overwhelming	

GPS Coordinates: N _____ E _____

Sediment Sample? Y N

Benthic Community Subs Sample? Y N

Subsample No: _____ **ID** _____

Recorded by: _____

EVS ENVIRONMENT CONSULTANTS

Field Record for Aquatic Plant Collection

Station ID: _____ Sampling Date: _____

Project Name: Clark Island EIS EVS Project Number: 2/612-02.32 On-site Director: _____

Time at Station: _____ Target Station Coordinates: _____

Weather: _____

Subsample No: _____ Assigned Subsample ID: _____ Water Depth: _____ m

Time: _____ Subsample Location coordinates: N _____ E _____

Species Collected:	No. of Specimens	Roots? (✓)	Stems and Leaves? (✓)

Subsample No: _____ Assigned Subsample ID: _____ Water Depth: _____ m

Time: _____ Subsample Location coordinates: N _____ E _____

Species Collected:	No. of Specimens	Roots? (✓)	Stems and Leaves? (✓)

Subsample No: _____ Assigned Subsample ID: _____ Water Depth: _____ m

Time: _____ Subsample Location coordinates: N _____ E _____

Species Collected:	No. of Specimens	Roots? (✓)	Stems and Leaves? (✓)

Subsample No: _____ Assigned Subsample ID: _____ Water Depth: _____ m

Time: _____ Subsample Location coordinates: N _____ E _____

Species Collected:	No. of Specimens	Roots? (✓)	Stems and Leaves? (✓)

Subsample No: _____ Assigned Subsample ID: _____ Water Depth: _____ m

Time: _____ Subsample Location coordinates: N _____ E _____

Species Collected:	No. of Specimens	Roots? (✓)	Stems and Leaves? (✓)

Recorded by:

EVS ENVIRONMENT CONSULTANTS

Field Record for Sediment Grabs to be used for Benthic Tissue Analysis

Station ID: _____ Sampling Date: _____

Project Name: Clark Island EIS EVS Project Number: 2/612-02.32 On-site Director: _____

Time at Station: _____ Target Station Coordinates: _____

Weather: _____

Subsample No. _____ **Assigned Subsample ID:** _____

Time: _____ **Water Depth:** _____ m **Penetration depth:** _____ cm

Sediment type:	*Sediment color:*	*Sediment odor:*	
cobble	D.O.	none	H_2S
gravel	gray	slight	Petroleum
sand C M F	black	moderate	Other:
silt clay	brown	strong	
wood chips	brown surface	overwhelming	

Location Coordinates: N _____ E _____

Comments:

Subsample No. _____ **Assigned Subsample ID:** _____

Time: _____ **Water Depth:** _____ m **Penetration depth:** _____ cm

Sediment type:	*Sediment color:*	*Sediment odor:*	
cobble	D.O.	none	H_2S
gravel	gray	slight	Petroleum
sand C M F	black	moderate	Other:
silt clay	brown	strong	
wood chips	brown surface	overwhelming	

Location Coordinates: N – E _____

Comments:

Subsample No. _____ **Assigned Subsample ID:** _____

Time: _____ **Water Depth:** _____ m **Penetration depth:** _____ cm

Sediment type:	*Sediment color:*	*Sediment odor:*	
cobble	D.O.	none	H_2S
gravel	gray	slight	Petroleum
sand C M F	black	moderate	Other:
silt clay	brown	strong	
wood chips	brown surface	overwhelming	

Location Coordinates: N _____ E _____

Comments:

Subsample No. _____ **Assigned Subsample ID:** _____

Time: _____ **Water Depth:** _____ m **Penetration depth:** _____ cm

Sediment type:	*Sediment color:*	*Sediment odor:*	
cobble	D.O.	none	H_2S
gravel	gray	slight	Petroleum
sand C M F	black	moderate	Other:
silt clay	brown	strong	
wood chips	brown surface	overwhelming	

Location Coordinates: N _____ E _____

Comments:

Subsample No. _____ **Assigned Subsample ID:** _____

Time: _____ **Water Depth:** _____ m **Penetration depth:** _____ cm

Sediment type:	*Sediment color:*	*Sediment odor:*	
cobble	D.O.	none	H_2S
gravel	gray	slight	Petroleum
sand C M F	black	moderate	Other:
silt clay	brown	strong	
wood chips	brown surface	overwhelming	

Location Coordinates: N _____ E _____

Comments:

Recorded by: _____

CHAIN-OF-CUSTODY/TEST REQUEST FOR OR SEDIMENT AND WATER SAMPLE(S)*

Client Name: _____ Ship to: _____

Contact Name: _____ _____

Sampled By: _____ Attn: _____ Shipping Date: _____

Sample Collection Date (d/m/y)	Time (am/pm)	Sample Identification	Volume of Sample/# of Containers	Test(s) Requested (check test(s) required)							Comments/Instructions

1) Released by: Date/Time:	2) Released by: Date/Time:	3) Released by: Date/Time:	To be completed by EVS Laboratory upon sample receipt: EVS Project #:	EVS W.O. #
1) Rec'd by: Date/Time:	2) Rec'd by: Date/Time:	3) Rec'd by: Date/Time:	Date of Receipt: Condition Upon Receipt:	Time of receipt: Received by:

* Instructions for completion of Chain-of-Custody/Test Request Form on back.
* Distribution: White and yellow copies accompany shipment; pink-consignor's copy; white-consignee return with results; yellow-consignee's copy.

EVS ENVIRONMENT CONSULTANTS

- 195 Pemberton Avenue
  North Vancouver,B.C.
  Canada, V7P 2R4
  Tel: (604) 986-4331
  Fax: (604) 662-8548
- 200 West Mercer Street
  Suite 403
  Seattle, WA 98119
  Tel: (206) 217-9337
  Fax: (206) 217-9343

EVS ENVIRONMENT CONSULTANTS

Sample Tracking Form

Station ID: _____

Date Collected: _____ Date Processed: _____ Date Shipped: _____

Project Name: **Clark Island EIS** EVS Project No.: **2/612-02.32** Shipped Via: _____

TAG #	Sample ID	Analyses	Lab

Comments:

Recorded by: _____

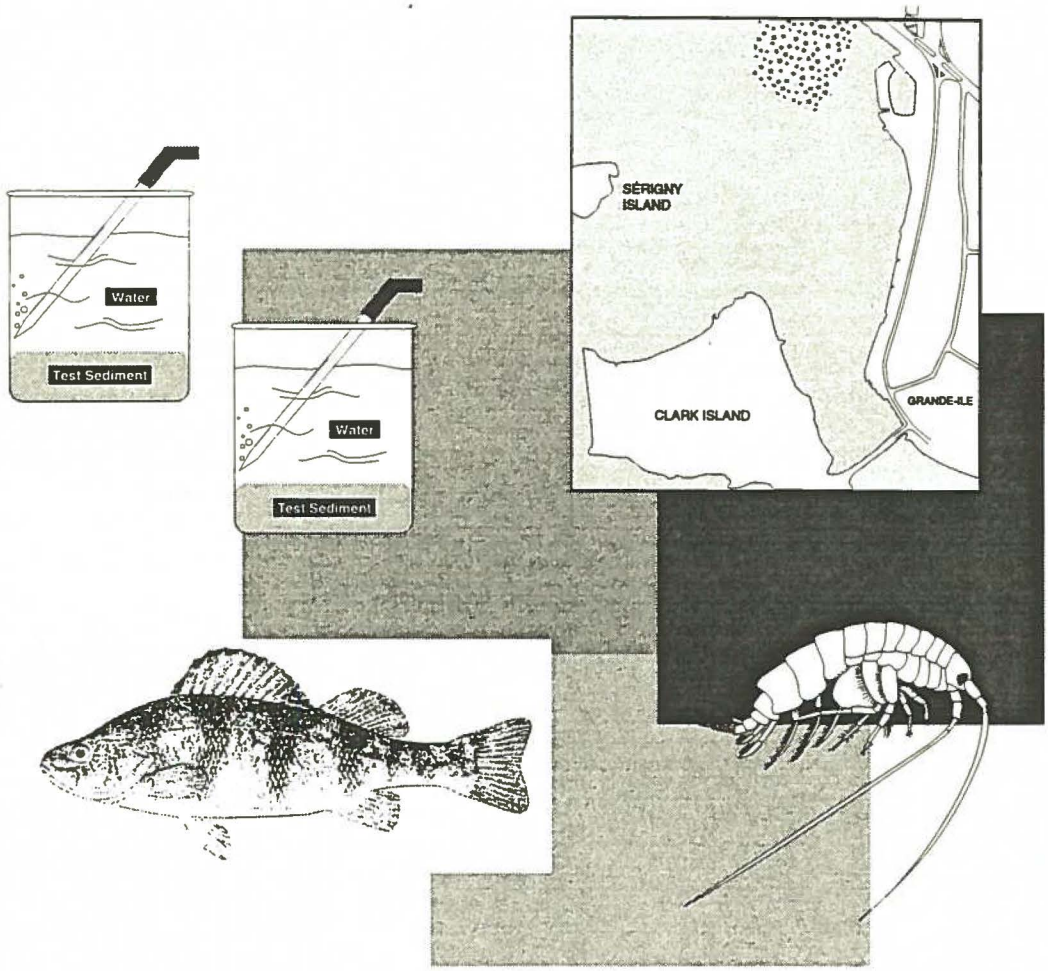
August 1996

DRAFT FINAL Volume 2 of 2

Clark Island

SAMPLING AND ANALYSIS PLAN

Appendix C – Laboratory Procedures



PREPARED FOR:

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Morristown, New Jersey

PREPARED BY:

EVS ENVIRONMENT CONSULTANTS

Seattle, Washington

TECSULT

Montréal, Québec, Canada

Clark Island

SAMPLING AND ANALYSIS PLAN

VOLUME 2 OF 2

DRAFT FINAL

Prepared for

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EVS Project No.

2/612-02

AUGUST 1996

APPENDIX C

Laboratory Procedures

Zenon Laboratory

Ms. Kim Magrouder
EVS CONSULTANTS
200 West, Mercer Street,
Suite 403
Seatle, Washington
98119

RE: SOP for sediment - Allied Signals

Please find enclosed copies of the SOP used by our lab in reference to the required analysis by Tecsult on the allied signals projects.

Hoping that you find everything to your satisfaction.

Truly yours,

Amr Rouchdy
General Manager - Quebec

Zénon Laboratoires Environnementaux
10 390, L.-H.-Lafontaine, Anjou, Québec, Canada H1J 2T3 Tél.: (514) 493-4733 Fax: (514) 493-4725

III-104

SOLS, SÉDIMENTS ET BOUES
DÉTERMINATION DES MÉTAUX PAR ICP

Auteure: Judit Vass
Révisée par: Judit Vass

préparée pour

ZÉNON LABORATOIRES ENVIRONNEMENTAUX

Approbation:

Amr Rouchdy, Directeur général

Judit Vass, Directrice - Assurance qualité

Jean-François Alary, Directeur - Laboratoire Inorganique

Révision No.: 1
Date effective: 26 avril 1996

Cette procédure d'opération standard a été préparée pour l'utilisation ultime de Zénon Laboratoires Environnementaux et ne peut être applicable aux activités de d'autres organisations.

INTRODUCTION

La présence des métaux dans l'environnement est due à l'action des agents atmosphériques sur les roches et à l'action de l'eau sur les sédiments, au lessivage des sols par les eaux de précipitations et aux rejets industriels.

Certains métaux sont indispensables à la croissance des plantes et à l'alimentation animale (Ca, Fe, K, etc.). Cependant lorsque la concentration d'un élément est supérieure à la capacité d'absorption d'une espèce présente dans un milieu, cet élément peut devenir toxique pour l'espèce et pour le milieu dans lequel il évolue. De plus, plusieurs métaux toxiques pour l'homme (Cd, Cr, Pb) ont tendance à s'accumuler dans la chaîne alimentaire.

La présence de concentrations anormalement élevées d'éléments métalliques dans l'environnement permet d'identifier des sources de pollution inorganiques.

1. EMPLACEMENT

Salle d'instrumentation de chimie inorganique.

2. DOMAINE D'APPLICATION

Cette méthode s'applique pour la détermination des métaux totaux extractibles dans les sols, sédiments et boues.

Le domaine d'application se situe entre la limite de détection et la concentration maximale de la courbe d'étalonnage, respectives à chaque métal. La limite supérieure du domaine d'application peut être plus élevée, mais une dilution est alors nécessaire pour que la concentration lue se trouve environ au milieu du domaine d'application initial.

2.1 PRINCIPE ET THÉORIE

Dans une première étape, l'échantillon est minéralisé en milieu acide et oxydant.

Par la suite, le dosage est effectué à l'aide d'un spectrophotomètre d'émission atomique au plasma d'argon (type ICP). L'échantillon est entraîné dans le plasma d'argon par l'intermédiaire d'une pompe péristaltique et d'un nébuliseur. Les métaux contenus dans l'échantillon sont atomisés dans le plasma et à cette haute température (≈ 10 000°C), ils émettent de l'énergie lumineuse à des longueurs d'onde qui leur sont spécifiques. La lumière émise est séparée à l'aide d'un réseau dispersif qui se positionne en fonction de chaque longueur d'onde spécifique et son intensité est mesurée à l'aide d'un détecteur photo-électrique dans le cas du spectrophotomètre ARL. En ce qui concerne le spectrophotomètre TJA, l'intensité de la lumière émise et séparée également à l'aide d'un réseau est mesurée par un détecteur de type CID qui permet la lecture du spectre à plusieurs longueurs d'onde simultanément.

Les concentrations des éléments sont déterminées par comparaison entre les intensités lumineuses respectives de l'échantillon et des solutions-étalons.

3. FIABILITÉ

3.1 INTERFÉRENCES

Les interférences les plus fréquentes sont les interférences inter-éléments et les déplacements de ligne de base. Ces deux types d'interférences peuvent être corrigés à l'aide du logiciel informatique contrôlant le spectrophotomètre. Si une concentration d'argent supérieure à 10 mg/L solution (ou 500 mg/L) est suspectée ou attendue, une préparation spéciale est requise (voir section 9.3).

3.2 LIMITE DE DÉTECTION ET LIMITE DE QUANTIFICATION

Voir tableaux de validation en ANNEXE I.

3.3 SENSIBILITÉ

Voir tableaux de validation en ANNEXE I.

3.4 FIDÉLITÉ ET JUSTESSE

Voir tableaux de validation en ANNEXE I.

4. RÉFÉRENCES

4.1 Principaux codes d'analyse dans le système de gestion d'information de laboratoire "LIMS":

METALS-S	ICPQ-S	ICPQT-S
ICP-S	ICP2-S	"Abréviation du métal" - S

4.2 Ministère de l'environnement, Gouvernement du Québec, Sols- Détermination des métaux, méthode par spectrométrie d'émission au plasma d'argon, MENVIQ. 90.05/304 - Mét 1.2.

4.3 Ministère de l'environnement, Gouvernement du Québec, Boues- Détermination des métaux, méthode par spectrométrie d'émission au plasma d'argon, MENVIQ. 89.12/304 - Mét 1.3.

4.4 Raymond, N., 1995, Guide de procédures, Assurance et contrôle de la qualité pour les travaux analytiques contractuels en chimie, Ministère de l'environnement, Gouvernement du Québec.

4.5 American Public Health Association, American Water Works Association and Water Pollution Control Federation, Standard Methods for the Examination of water and wastewater, 18th Edition, 1992.

4.6 Procédure I-104, "SOP for Quality Control and Quality Assurance";
Procédure ZEL-102, "SOP for Control Charting".

5. PRÉLÈVEMENT ET CONSERVATION

Les échantillons de sols, sédiments et boues doivent être prélevés dans des récipients de verre ou de polyéthylène à large ouverture. Les échantillons de sols doivent être conservés à environ 4°C et les échantillons de sédiments, à environ -10°C. Le délai de conservation entre le prélèvement et l'analyse ne doit pas excéder 6 mois.

6. APPAREILLAGE

6.1. Bloc chauffant pour tube de 50 mL (BRAN & LUBBE BD-40).

6.2 Tubes gradués en verre de 50 mL.

6.3 Mortier et pilon.

6.4 Tamis de nylon d'une ouverture de 2 mm .

6.5 Tubes gradués en polypropylène de 50 mL, avec bouchons ("tubes Falcon").

6.6 Dispensettes Brinkman 0-10 mL.

6.7 Pipettes automatiques:

Pipette Eppendorf, 10 -100 µL
Pipette Nichiryo, 40 - 200 µL
Pipette Nichiryo, 200 - 1000 µL
Pipette Nichiryo, 1000 - 5000 µL
Pipette Oxford, 1 - 5 mL

6.8 Fioles jaugées de 100 mL et de 1000 mL.

6.9 Étuve fixée à une température de 105° C.

6.10 Spectrophotomètre d'émission atomique à plasma d'argon de marque ARL, modèle 3510ICP; Détecteur séquentiel.

6.10.1 Auto-échantillonneur de marque ISCO, modèle "ISIS autosampler".

6.10.2 Pompe péristaltique de marque Gilson, modèle minipuls 3.

6.11 Spectrophotomètre d'émission atomique à plasma d'argon de marque Thermo Jarrell Ash (TJA), modèle IRIS/AP; détecteur type "C.I.D."

6.11.1 Auto-échantillonneur de marque thermo Jarrell Ash.

7. RÉACTIFS ET ÉTALONS

Tous les réactifs commerciaux utilisés sont de grade «trace metal», à moins d'indication contraire.

L'eau utilisée est de l'eau déminéralisée par osmose inverse.

7.1 Acide nitrique concentré, de qualité "trace metal" de la compagnie fisher.

7.1.1. Acide nitrique 5%

Ajouter doucement 50 mL d'acide nitrique dans 950 mL d'eau déminéralisée. **Attention: corrosif!** Voir la fiche signalétique correspondante.

7.2 Solutions-étalons primaires de 10000 mg/L de grade ICP

7.3 Solutions-étalons primaires de 1000 mg/L de grade ICP

7.4 SOLUTIONS-ÉTALONS POUR LA MÉTHODE SOLMTX^D (ICP ARL) — ANNEXE II

Codes d'analyse associés: METALS-S; "abréviation du métal" - S

7.4.1 Standard 1 (Blanc, HNO_3 5%)

Voir section 7.1.1. pour la préparation.

7.4.2 Standard 2 (1 mg Cd/L, 5 mg Cr/L, 5 mg Cu/L, 5 mg Ni/L, 10 mg Fe/L, 10 mg Pb/L, 10 mg Zn/L dans du HNO_3 5%)

Voir le tableau à la section 7.4.3.

7.4.3 Standard 3 (10 mg Cd/L, 25 mg Cr/L,25 mg Cu/L, 25 mg Ni/L, 50 mg Fe/L, 50 mg Pb/L, 50 mg Zn/L dans du HNO_3 5%)

Dans une fiole jaugée de 500 mL ajouter environ 150 mL d'eau déminéralisée et 25 mL d'acide nitrique concentré. Ensuite, introduire à l'aide de pipettes automatiques les solutions-étalons suivantes:

SOLUTION-ÉTALON	STANDARD #2		STANDARD #3	
	VOLUME PIPETTÉ	CONCENTRATION FINALE	VOLUME PIPETTÉ	CONCENTRATION FINALE
Cadmium 10 000 mg/L	50 µL	1 mg Cd/L	500 µL	10 mg Cd/L
Chrome 10 000 mg/L	250 µL	5 mg Cr/L	1.25 mL	25 mg Cr/L
Cuivre 10 000mg/L	250 µL	5 mg Cu/L	1.25 mL	25 mg Cu/L
Nickel 10 000 mg/L	250 µL	5 mg Ni/L	1.25 mL	25 mg Ni/L
Fer 10 000 mg/L	500 µL	10 mg Fe/L	2.5 mL	50 mg Fe/L
Plomb 10 000 mg/L	500 µL	10 mg Pb/L	2.5 mL	50 mg Pb/L
Zinc 10 000 mg/L	500 µL	10 mg Zn/L	2.5 mL	50 mg Zn/L

Compléter au trait de jauge avec de l'eau déminéralisée.

7.4.4 Standard 4 (100 mg Fe/L dans du HNO_3 5%)

Dans une fiole jaugée de 100 mL, introduire à l'aide d'une pipette automatique, 1000 µL de la solution-étalon de fer de 10 000 mg Fe/L et 5 mL d'acide nitrique concentré et compléter au trait de jauge avec de l'eau.

7.4.5 Standard 5 (200 mg Fe/L dans du HNO_3 5%)

Dans une fiole jaugée de 100 mL, introduire à l'aide d'une pipette volumétrique, 2,00 mL de la solution-étalon de fer de 10 000 mg Fe/L et 5 mL d'acide nitrique concentré et compléter au trait de jauge avec de l'eau.

7.5 SOLUTIONS-ÉTALONS POUR LA MÉTHODE ICP QUE^D (ICP ARL)—ANNEXE III

Codes d'analyse associés: METALS-S; ICPQ-S; "abréviation du métal" -S

7.5.1 Standard 1 (Blanc, 5% HNO_3)
Voir section 7.1.1. pour la préparation.

7.5.2 Standard 2 (dans du HNO_3 5%)
1 mg /L: Baryum,Cadmium et Cobalt;
5 mg/L: Cuivre, Chrome, Nickel,Molybdène, Étain et Arsenic et Sélénium;
10 mg/L: Fer, Plomb et Zinc.

*Voir le tableau à la section 7.5.3

7.5.3 Standard 3 (dans du HNO_3 5%)
10 mg /L: Baryum,Cadmium, Cobalt, Arsenic et Sélénium;
25 mg/L: Cuivre, Chrome, Nickel,Molybdène et Étain;
50 mg/L: Fer, Plomb et Zinc.

Dans une fiole jaugée de 1000 mL ajouter environ 300 mL d'eau déminéralisée et 50 mL d'acide nitrique concentré. Ensuite, introduire à l'aide de pipettes automatiques les solutions-étalons suivantes:

SOLUTION-ÉTALON	STANDARD #2		STANDARD #3	
	VOLUME PIPETTÉ	CONCENTRATION FINALE	VOLUME PIPETTÉ	CONCENTRATION FINALE
Baryum 10 000 mg/L	100 µL	1 mg Ba/L	1 mL	10 mg Ba/L
Arsenic 1 000 mg/L	5 mL	5 mg As/L	10 mL	10 mg As/L
Cadmium 10 000 mg/L	100 µL	1 mg Cd/L	1 mL	10 mg Cd/L
Cobalt 10 000 mg/L	100 µL	1 mg Co/L	1 mL	10 mg Co/L
Chrome 10 000 mg/L	500 µL	5 mg Cr/L	2.5 mL	25 mg Cr/L
Cuivre 10 000mg/L	500 µL	5 mg Cu/L	2.5 mL	25 mg Cu/L
Nickel 10 000 mg/L	500 µL	5 mg Ni/L	2.5 mL	25 mg Ni/L
Molybdène 10 000 mg/L	500 µL	5 mg Mo/L	2.5 mL	25 mg Mo/L
Étain 10 000 mg/L	500 µL	5 mg Sn/L	2.5 mL	25 mg Sn/L
Sélénium 1 000 mg/L	5 mL	.5 mg Se/L	10 mL	10 mg Se/L
Fer 10 000 mg/L	1000 µL	10 mg Fe/L	5 mL	50 mg Fe/L
Plomb 10 000 mg/L	1000 µL	10 mg Pb/L	5 mL	50 mg Pb/L
Zinc 10 000 mg/L	1000 µL	10 mg Zn/L	5 mL	50 mg Zn/L

Compléter au trait de jauge avec de l'eau déminéralisée.

7.5.4 Standard 4 (1 mg Ag/L dans du HNO_3 5%)

Dans une fiole jaugée de 500 mL, introduire à l'aide d'une pipette automatique, 50 µL de la solution-étalon d'argent de 10 000 mg Ag/L et 25 mL d'acide nitrique concentré et compléter au trait de jauge avec de l'eau.

7.5.5 Standard 5 (10 mg Ag/L dans du HNO_3 5%)

Dans une fiole jaugée de 500 mL, introduire à l'aide d'une pipette volumétrique, 500 µL de la solution-étalon d'argent de 10 000 mg Ag/L et 25 mL d'acide nitrique concentré et compléter au trait de jauge avec de l'eau.

7.6 SOLUTIONS-ÉTALONS POUR LA MÉTHODE ALCALI^D (ICP ARL) - ANNEXE IV

Codes d'analyse associés: CATION-S; "abréviation du métal" - S

7.6.1 Standard 1 (Blanc, HNO_3 5%)

Voir section 7.1.1. pour la préparation.

7.6.2 Standard 2 (dans du HNO_3 5%)

25 mg /L: Calcium, Magnésium, Sodium, Potassium, Phosphore et Soufre

Voir le tableau à la section 7.6.3.

7.6.3 Standard 3 (dans du HNO_3 5%)

50 mg/L: Calcium, Magnésium, Sodium, Potassium, Phosphore et Soufre

Dans une fiole jaugée de 500 mL ajouter environ 150 mL d'eau déminéralisée et 25 mL d'acide nitrique concentré. Ensuite, introduire à l'aide de pipettes automatiques les solutions-étalons suivantes:

SOLUTION-ÉTALON	STANDARD #2		STANDARD #3	
	VOLUME PIPETTÉ	CONCENTRATION FINALE	VOLUME PIPETTÉ	CONCENTRATION FINALE
Calcium 10 000 mg/L	1,25 mL	25 mg Ca/L	2,5 mL	50 mg Ca/L
Magnésium 10 000 mg/L	1,25 mL	25 mg Ma/L	2,5 mL	50 mg Ma/L
Sodium 10 000 mg/L	1,25 mL	25 mg Na/L	2,5 mL	50 mg Na/L
Potassium 10 000 mg/L	1,25 mL	25 mg K/L	2,5 mL	50 mg K/L
Phosphore 10 000 mg/L	1,25 mL	25 mg P/L	2,5 mL	50 mg P/L
Soufre 10 000 mg/L	1,25 mL	25 mg S/L	2,5 mL	50 mg S/L

Compléter au trait de jauge avec de l'eau déminéralisée.

7.6.4 Standard 4 (dans du HNO_3 5%)

100 mg /L: Calcium, Potassium, Magnésium, Sodium, Phosphore et Soufre;.

Voir le tableau à la section 7.6.5.

7.6.5 Standard 5 (dans du HNO_3 5%)

200 mg /L: Calcium, Potassium, Magnésium, Sodium, Phosphore et soufre.

Dans une fiole jaugée de 1000 mL ajouter environ 300 mL d'eau déminéralisée et 50 mL d'acide nitrique concentré. Ensuite, introduire à l'aide de pipettes automatiques les solutions-étalons suivantes:

SOLUTION-ÉTALON	STANDARD #4		STANDARD #5	
	VOLUME PIPETTÉ	CONCENTRATION FINALE	VOLUME PIPETTÉ	CONCENTRATION FINALE
Calcium 10 000 mg/L	5 mL	100 mg Ba/L	10 mL	200 mg Ba/L
Potassium 10 000 mg/L	5 mL	100 mg Be/L	10 mL	200 mg Be/L
Magnésium 10 000 mg/L	5 mL	100 mg Mg/L	10 mL	200 mg Mg/L
Sodium 10 000 mg/L	5 mL	100 mg Na/L	10 mL	200 mg Na/L
Phosphore 10 000 mg/L	5 mL	100 mg P/L	10 mL	200 mg P/L
Soufre 10 000 mg/L	5 mL	100 mg S/L	10 mL	200 mg S/L

Compléter au trait de jauge avec de l'eau déminéralisée.

7.7 SOLUTIONS-ÉTALONS POUR LA MÉTHODE ICPOFE (ICP TJA) - ANNEXE V

Codes d'analyse associés: ICPQT-S; ICPQ-S; METALS-S; "abréviation du métal" - S

7.7.1 Standard 1 (Blanc, HNO_3 5%)

Voir section 7.1.1. pour la préparation.

7.7.2 Standard 2 (ICPO1) (dans du HNO_3 5%)

1 mg /L: Baryum, Cadmium, Cobalt, Chrome, Cuivre, Molybdène, Nickel, Plomb, Zinc et Fer;
2,5 mg/L: Arsenic, Sélénium et Étain;
5 mg/L: Aluminium.

7.7.3 Standard 3 (ICPO2) (dans du HNO_3 5%)

5 mg /L: Baryum, Cadmium, Cobalt, Chrome, Cuivre, Molybdène, Nickel, Plomb, Zinc, Étain, Arsenic, Sélénium et Fer;
10 mg/L: Aluminium.

Dans une fiole jaugée de 1000 mL ajouter environ 300 mL d'eau déminéralisée et 50 mL d'acide nitrique concentré. Ensuite, introduire à l'aide de pipettes automatiques les solutions-étalons suivantes:

SOLUTION-ÉTALON	STANDARD #2 (ICPQ1)		STANDARD #3 (ICPQ2)	
	VOLUME PIPETTÉ	CONCENTRATION FINALE	VOLUME PIPETTÉ	CONCENTRATION FINALE
Baryum 10 000 mg/L	100 µL	1 mg Ba/L	500 µL	5 mg Ba/L
Arsenic 1 000 mg/L	2,5 mL	2,5 mg As/L	10 mL	5 mg As/L
Sélénium 1 000 mg/L	2,5 mL	2,5 mg Se/L	5 mL	5 mg Se/L
Cadmium 10 000 mg/L	100 µL	1 mg Cd/L	500 µL	5 mg Cd/L
Cobalt 10 000 mg/L	100 µL	1 mg Co/L	500 µL	5 mg Co/L
Chrome 10 000 mg/L	100 µL	1 mg Cr/L	500 µL	5 mg Cr/L
Cuivre 10 000mg/L	100 µL	1 mg Cu/L	500 µL	5 mg Cu/L
Nickel 10 000 mg/L	100 µL	1 mg Ni/L	500 µL	5 mg Ni/L
Molybdène 10 000 mg/L	100 µL	1 mg Mo/L	500 µL	5 mg Mo/L
Étain 10 000 mg/L	250 µL	2,5 mg Sn/L	500 µL	5 mg Sn/L
Aluminium 10 000 mg/L	500 µL	5 mg Al/L	1000 µL	10 mg Se/Al
Fer 10 000 mg/L	100 µL	1 mg Fe/L	500 µL	5 mg Fe/L
Plomb 10 000 mg/L	100 µL	1 mg Pb/L	500 µL	5 mg Pb/L
Zinc 10 000 mg/L	100 µL	1 mg Zn/L	500 µL	5 mg Zn/L

Compléter au trait de jauge avec de l'eau déminéralisée.

7.7.4 Standard 4 (ICPQ3) (dans du HNO_3 5%)

10 mg /L: Cuivre, Plomb et Zinc;
25 mg/L: Baryum, Chrome, Molybdène, Nickel, Aluminium et Fer.

Dans une fiole jaugée de 1000 mL ajouter environ 300 mL d'eau déminéralisée et 50 mL d'acide nitrique concentré. Ensuite, introduire à l'aide de pipettes automatiques les solutions-étalons suivantes:

SOLUTION-ÉTALON	STANDARD #4 (ICPQ3)	
	VOLUME PIPETTÉ	CONCENTRATION FINALE
Baryum 10 000 mg/L	2,5 mL	25 mg Ba/L
Chrome 10 000 mg/L	2,5 mL	25 mg Cr/L
Cuivre 10 000mg/L	100 µL	10 mg Cu/L
Nickel 10 000 mg/L	100 µL	1 mg Ni/L
Molybdène 10 000 mg/L	2,5 mL	25 mg Mo/L
Aluminium 10 000 mg/L	2,5 mL	25 mg Al/L
Fer 10 000 mg/L	2,5 mL	25 mg Fe/L
Plomb 10 000 mg/L	1000 µL	10 mg Pb/L
Zinc 10 000 mg/L	1000 µL	10 mg Zn/L

Compléter au trait de jauge avec de l'eau déminéralisée.

7.7.5 Standard 5 (ICPO4) (dans du HNO_3 5%)

25 mg /L: Cuivre;
50 mg/L: Plomb, Zinc, Aluminium, Fer et Soufre.

Voir le tableau à la section 7.7.6.

7.7.6 Standard 6 (ICPO5) (dans du HNO_3 5%)

100 mg /L: Plomb et Zinc;
200 mg/L: Aluminium, Fer et Soufre.

Dans une fiole jaugée de 1000 mL ajouter environ 300 mL d'eau déminéralisée et 50 mL d'acide nitrique concentré. Ensuite, introduire à l'aide de pipettes automatiques les solutions-étalons suivantes:

SOLUTION-ÉTALON	STANDARD #5 (ICPQ4)		STANDARD #6 (ICPQ5)	
	VOLUME PIPETTÉ	CONCENTRATION FINALE	VOLUME PIPETTÉ	CONCENTRATION FINALE
Cuivre 10 000mg/L	2,5 mL	25 mg Cu/L	—	—
Soufre 10 000 mg/L	5 mL	50 mg S/L	20 mL	200 mg S/L
Aluminium 10 000 mg/L	5 mL	50 mg Al/L	20 mL	200 mg Al/L
Fer 10 000 mg/L	5 mL	50 mg Fe/L	20 mL	200 mg Fe/L
Plomb 10 000 mg/L	5 mL	50 mg Pb/L	20 mL	100 mg Pb/L
Zinc 10 000 mg/L	5 mL	50 mg Zn/L	20 mL	100 mg Zn/L

Compléter au trait de jauge avec de l'eau déminéralisée.

7.8 SOLUTIONS-ÉTALONS POUR LA MÉTHODE SCAN (ICP TJA) - ANNEXE VI

Codes d'analyse associés:

ICP-S ICP2-S "abréviation du métal" - S
ICPQT-S ICPQ-S

7.8.1 Standard 1 (Blanc, HNO_3 5%)

Voir section 7.1.1 pour la préparation.

7.8.2 Standard 2 (S1) (dans du HNO_3 5%)

0,25 mg/L: Béryllium;
0,50 mg/L: Manganèse, Strontium et Lithium;
1 mg/L: Baryum, Bore, Cadmium, Cobalt, Chrome, Cuivre, Fer, Molybdène, Nickel, Plomb, Silice, Titane, Vanadium, Zinc et Zirconium;
2,5 mg/L: Sodium, Antimoine, Tellure, Thallium, Arsenic et Sélénium;
10 mg/L: Aluminium, Calcium, Magnésium, Potassium et Phosphore.

Voir le tableau à la section 7.8.3.

7.8.3 Standard 3 (S2) (dans du HNO_3 5%)

0,5 mg/L: Béryllium;
1 mg/L: Manganèse, Strontium et Lithium;
5 mg/L: Bore, Baryum, Cadmium, Cobalt, Chrome, Cuivre, Fer, Molybdène, Nickel,Plomb, Silice, Titane, Vanadium, Zinc, Zirconium, Sodium, Antimoine, Étain,Tellure, Thallium, Arsenic et Sélénium;
25 mg/L: Aluminium, Calcium, Magnésium, Potassium et Phosphore.

SOLUTION-ÉTALON	STANDARD S1		STANDARD S2	
	VOLUME	CONCENTRATIO	VOLUME	CONCENTRATION
Aluminium 10 000 mg/L	1000 µL	10 mg Al/L	2,5 mL	25 mg Al/L
Antimoine 10 000 mg/L	250 µL	2,5 mg Sb/L	500 µL	5 mg Sb/L
Arsenic 1 000 mg/L	2,5 mL	2,5 mg As/L	5 mL	5 mg As/L
Baryum 10 000 mg/L	100 µL	1 mg Ba/L	500 µL	1 mg Ba/L
Béryllium 10 000 mg/L	25 µL	0,25 mg Be/L	50 µL	0,5 mg Be/L
Bore 10 000 mg/L	100 µL	1 mg B/L	500 µL	5 mg B/L
Cadmium 10 000 mg/L	100 µL	1 mg Cd/L	500 µL	5 mg Cd/L
Calcium 10 000 mg/L	1000 µL	10 mg Ca/L	2,5 mL	25 mg Ca/L
Chrome 10 000 mg/L	100 µL	1 mg Cr/L	500 µL	5 mg Cr/L
Cobalt 10 000 mg/L	100 µL	1 mg Co/L	500 µL	5 mg Co/L
Cuivre 10 000mg/L	100 µL	1 mg Cu/L	500 µL	5 mg Cu/L
Étain 10 000 mg/L	250 µL	2,5 mg Sn/L	500 µL	5 mg Sn/L
Fer 10 000 mg/L	100 µL	1 mg Fe/L	500 µL	5 mg Fe/L
Lithium 10 000mg/L	50 µL	0,5 mg Li/L	100 µL	1 mg Li/L
Manganèse 10 000 mg/L	50 µL	0,5 mg Mn/L	100 µL	1 mg Mn/L
Magnésium 10 00 mg/L	1000 µL	10 mg Mg/L	2,5 mL	25 mg Mg/L
Molybdène 10 000 mg/L	100 µL	1 mg Mo/L	500 µL	5 mg Mo/L
Nickel 10 000 mg/L	100 µL	1 mg Ni/L	500 µL	5 mg Ni/L
Plomb 10 000 mg/L	100 µL	1 mg Pb/L	500 µL	5 mg Pb/L
Phosphore 10 000 mg/L	1000 µL	10 mg P/L	2,5 mL	25 mg P/L
Potassium 10 000 mg/L	1000 µL	10 mg K/L	2,5 mL	25 mg K/L
Sélénium 1 000 mg/L	2,5 mL	2,5 mg Se/L	5 mL	5 mg Se/L
Silice 10 000 mg/L	100 µL	1 mg Si/L	500 µL	5 mg Si/L
Sodium 10 000 mg/L	250 µL	2,5 mg Na/L	500 µL	5 mg Na/L
Strontium 10 000 mg/L	50 µL	0,5 mg Sr/L	100 µL	1 mg Sr/L
Tellure 10 000 mg/L	250 µL	2,5 mg Te/L	500 µL	5 mg Te/L
Thallium 10 000 mg/L	250 µL	2,5 mg Tl/L	500 µL	5 mg Tl/L
Titane 10 000 mg/L	100 µL	1 mg Ti/L	500 µL	5 mg Ti/L
Vanadium 10 000 mg/L	100 µL	1 mg V/L	500 µL	5 mg V/L
Zinc 10 000 mg/L	100 µL	1 mg Zn/L	500 µL	5 mg Zn/L
Zirconium 10 000 mg/L	100 µL	1 mg Zr/L	500 µL	5 mg Zr/L

Compléter au trait de jauge avec de l'eau déminéralisée.

7.8.4 Standard 4 (S3) (dans du HNO_3 5%)

10 mg/L: Manganèse, Baryum, Cuivre et Zinc;
25 mg/L: Chrome, Fer, Molybdène, Nickel, Plomb, Silice, Aluminium et Calcium.

Dans une fiole jaugée de 1000 mL ajouter environ 300 mL d'eau déminéralisée et 50 mL d'acide nitrique concentré. Ensuite, introduire à l'aide de pipettes automatiques les solutions-étalons suivantes:

SOLUTION-ÉTALON	STANDARD #4 (S3)	
	VOLUME PIPETTÉ	CONCENTRATION FINALE
Baryum 10 000 mg/L	1000 µL	10 mg Ba/L
Calcium 10 000 mg/L	2,5 mL	25 mg Ca/L
Chrome 10 000 mg/L	2,5 mL	25 mg Cr/L
Cuivre 10 000mg/L	1000 µL	10 mg Cu/L
Nickel 10 000 mg/L	2,5 mL	25 mg Ni/L
Manganèse 10 000 mg/L	1000 µL	10 mg Mn/L
Molybdène 10 000 mg/L	2,5 mL	25 mg Mo/L
Aluminium 10 000 mg/L	2,5 mL	25 mg Al/L
Fer 10 000 mg/L	2,5 mL	25 mg Fe/L
Silice 10 000 mg/L	2,5 mL	25 mg Si/L
Plomb 10 000 mg/L	2,5 mL	25 mg Pb/L
Zinc 10 000 mg/L	1000 µL	10 mg Zn/L

Compléter au trait de jauge avec de l'eau déminéralisée.

7.8.5 Standard 5 (S4) (dans du HNO_3 5%)

25 mg/L: Manganèse, Cuivre et Zinc;
50 mg/L: Fer, Sodium, Aluminium, Calcium, Magnésium, Potassium, Phosphore et Soufre.

Voir le tableau à la section 7.8.6.

7.8.6 Standard 6 (S5) (dans du HNO_3 5%)

100 mg/L: Magnésium, Phosphore, Soufre et Zinc;
200 mg/L: Fer, Sodium, Aluminium, Calcium et Potassium.

Dans une fiole jaugée de 1000 mL ajouter environ 300 mL d'eau déminéralisée et 50 mL d'acide nitrique concentré. Ensuite, introduire à l'aide de pipettes automatiques les solutions-étalons suivantes:

SOLUTION-ÉTALON	STANDARD #5 (S4)		STANDARD #6 (S5)	
	VOLUME PIPETTÉ	CONCENTRATION FINALE	VOLUME PIPETTÉ	CONCENTRATION FINALE
Cuivre 10 000mg/L	2,5 mL	25 mg Cu/L	—	—
Calcium 10 000 mg/L	5 mL	50 mg Ca/L	20 mL	200 mg Ca/L
Sodium 10 000 mg/L	5 mL	50 mg Na/L	20 mL	200 mg Na/L
Potassium 10 000 mg/L	5 mL	50 mg K/L	20 mL	200 mg K/L
Manganèse 10 000 mg/L	2,5 mL	25 mg Mn/L	—	—
Magnésium 10 000 mg/L	5 mL	50 mg Mg/L	10 mL	100 mg Mg/L
Soufre 10 000 mg/L	5 mL	50 mg S/L	10 mL	100 mg S/L
Aluminium 10 000 mg/L	5 mL	50 mg Al/L	20 mL	200 mg Al/L
Fer 10 000 mg/L	5 mL	50 mg Fe/L	20 mL	200 mg Fe/L
Phosphore 10 000 mg/L	5 mL	50 mg P/L	10 mL	100 mg P/L
Zinc 10 000 mg/L	2,5 mL	25 mg Zn/L	10 mL	100 mg Zn/L

Compléter au trait de jauge avec de l'eau déminéralisée.

7.8.7 Standard 7 (2,5 mg Ag/L dans du HNO_3 5%)

Dans une fiole jaugée de 1000 mL, ajouter environ 300 mL d'eau déminéralisée et 50 mL d'acide nitrique concentré. Ensuite, introduire à l'aide d'une pipette automatique 2,5 mL de la solution-étalon d'argent de 10 000 mg Ag/L et compléter au trait de jauge avec de l'eau.

7.8.8 Standard 8 (5 mg Ag/L dans du HNO_3 5%)

Dans une fiole jaugée de 1000 mL, ajouter environ 300 mL d'eau déminéralisée et 50 mL d'acide nitrique concentré. Ensuite, introduire à l'aide d'une pipette automatique 5 mL de la solution-mère d'argent de 10 000 mg Ag/L et compléter au trait de jauge avec de l'eau.

7.9 SOLUTIONS-CONTRÔLES «BWMS » ET «FORTIFIÉES»

7.9.1 Solution #2 (BWMS #2 et «SPIKE»#2)

Dans une fiole jaugée de 1000 mL ajouter environ 300 mL d'eau déminéralisée et 50 mL d'acide nitrique concentré. Ensuite, introduire à l'aide de pipettes automatiques les solutions-étalons suivantes:

SOLUTION-ÉTALON	SOLUTION #2		
	VOLUME PIPETTÉ (mL)	CONCEN-TRATION FINALE (mg/L)	CONCENTRA-TION ÉQUIVALENTE EN mg/Kg AU DOSAGE*
Ba (10 000 mg/L)	5	50	50
Cd (10 000 mg/L)	2.5	25	25
Cr (10 000 mg/L)	5	50	50
Co (10 000 mg/L)	2.5	25	25
Sn (10 000 mg/L)	1.25	12.5	12.5
Cu (10 000 mg/L)	5	50	50
Pb (10 000 mg/L)	5	50	50
Mo (10 000 mg/L)	2.5	25	25
Ni (10 000 mg/L)	5	50	50
Zn (10 000 mg/L)	10	100	100
As (1000 mg/L)	12.5	12.5	12.5
Se (1000 mg/L)	12.5	12.5	12.5

* Voir les sections 8.2 et 8.4 pour la préparation.

7.9.2 Solution #A (BWMS #A et «SPIKE»#A)

Dans une fiole jaugée de 100 mL ajouter environ 10 mL d'eau déminéralisée et 5 mL d'acide nitrique concentré. Ensuite, introduire à l'aide de pipettes automatiques les solutions-étalons suivantes:

SOLUTION-ÉTALON	VOLUME PIPETTÉ	CONCENTRATION FINALE	CONCENTRATION ÉQUIVALENTE EN mg/kg AU DOSAGE*
Ba (10 000 mg/L)	500 µL	50 mg/L	50
Be (10 000 mg/L)	100 µL	10 mg/L	10
B (10 000 mg/L)	500 µL	50 mg/L	50
Cd (10 000 mg/L)	250 µL	25 mg/L	25
Cr (10 000 mg/L)	500 µL	50 mg/L	50
Co (10 000 mg/L)	250 µL	25 mg/L	25
Cu (10 000 mg/L)	500 µL	50 mg/L	50
Pb (10 000 mg/L)	500 µL	50 mg/L	50
Mn (10 000 mg/L)	500 µL	50 mg/L	50
Mo (10 000 mg/L)	500 µL	50 mg/L	50
Ni (10 000 mg/L)	500 µL	50 mg/L	50
Si (10 000 mg/L)	500 µL	50 mg/L	50
Sr (10 000 mg/L)	500 µL	50 mg/L	50
Tl (10 000 mg/L)	500 µL	50 mg/L	50
Ti (10 000 mg/L)	500 µL	50 mg/L	50
V (10 000 mg/L)	500 µL	50 mg/L	50
Zn (10 000 mg/L)	500 µL	50 mg/L	50
Zr (10 000 mg/L)	500 µL	50 mg/L	50
Li (10 000 mg/L)	500 µL	50 mg/L	50
Sb (10 000 mg/L)	500 µL	50 mg/L	50
Sn (10 000 mg/L)	500 µL	50 mg/L	50
Te (10 000 mg/L)	500 µL	50 mg/L	50
As (10 000 mg/L)	25 mL	25 mg/L	25
Se (10 000 mg/L)	25 mL	25 mg/L	25

* Voir les sections 8.2 et 8.4 pour la préparation.

7.9.3 Solution #B (BWMS #B et «SPIKE»#B)

Dans une fiole jaugée de 100 mL ajouter environ 10 mL d'eau déminéralisée et 5 mL d'acide nitrique concentré. Ensuite, introduire à l'aide de pipettes automatiques les solutions-étalons suivantes:

SOLUTION-ÉTALON	VOLUME PIPETTÉ	CONCENTRATION FINALE	CONCENTRATION ÉQUIVALENTE EN mg/kg AU DOSAGE*
Ca (10 000 mg/L)	10 mL	1000 mg/L	1000
Mg (10 000 mg/L)	10 mL	1000 mg/L	1000
Na (10 000 mg/L)	10 mL	1000 mg/L	1000
K (10 000 mg/L)	10 mL	1000 mg/L	1000
Al (10 000 mg/L)	10 mL	1000 mg/L	1000
Fe (10 000 mg/L)	10 mL	1000 mg/L	1000
P (10 000 mg/L)	5 mL	500 mg/L	500
Ag (10 000 mg/L)	0.5 mL	50 mg/L	50
S (10 000 mg/L)	5 mL	500 mg/L	500

* Voir les sections 8.2 et 8.4 pour la préparation.

7.10 ÉTALONS CERTIFIÉS

7.10.1 Étalon pour les sols: PriorityPollutnT/CLP Quality Control Standard de la compagnie Environmental Resource Associates, Arvada, Colorado 80002.

7.10.2 Étalon pour les boues: SewageSludG Quality Control Standard de la compagnie Environmental Resource Associates, Arvada, Colorado 80002.

7.10.3 Étalon pour les sédiments: MESS-2 ou PACS-1 du Conseil national de recherches Canada, Ottawa, Canada, K1A 0R6.

7.10.4 Étalon certifié pour le contôle de qualité d'analyse seulement: WasteWatR/Quality Control Standard, no. de catalogue WW-11 ("Trace metals") de la compagnie Environmental Resource Associates, Arvada, Colorado, 80002.

8. CONTRÔLE DE LA QUALITÉ

Voir les procédures "SOP for Quality Control and Quality Assurance" "SOP for Control Charting" pour avoir plus de détails.

8.1 SOLUTION TÉMOIN(Blanc de méthode)—CQ de préparation et CQ d'analyse

Analyser une solution témoin d'analyse (eau déminéralisée) sur une base quotidienne et à chaque série d'au plus 20 déterminations (voir la fréquence du contrôle de qualité lors de l'analyse en ANNEXE VII), en plus des blancs de préparation suivant ceux préparés (voir la fréquence de préparation en ANNEXE VIII)

Les résultats des blancs d'analyse sont enregistrés dans le "LIMS", et ceux des blancs de préparation également lorsque le résultat est requis.

8.2 CONTRÔLE «BWMS» — CQ de préparation

Analyser le contrôle «BWMS» (voir les sections 7.9.1 à 7.9.3) sur une base quotidienne suivant ceux préparés (voir fréquence du contrôle de qualité lors de la préparation en ANNEXE VIII)

Préparer ce contrôle comme suit:

Ajouter 1 mL de la solution-contrôle BWMS/SPIKE désirée (voir les sections 7.9.1 à 7.9.3) et 1 mL d'eau dé-ionisée dans un tube de digestion et suivre intégralement toutes les étapes de la minéralisation tel qu'indiqué à la section 9.3.

Calculer la récupération avec l'équation suivante:

$$(\%)\ \text{récupération} = \frac{C_o \times 100}{C_a}$$

où

C_o : concentration obtenue
C_a : concentration attendue

Les % de récupération obtenus doivent se situer entre 85% et 115%.

Enregistrer les résultats dans le «LIMS».

8.3 DUPLICATA PRÉPARÉ EN LABORATOIRE — CQ de préparation

Analyser un échantillon en duplicata suivant ceux préparés (voir la fréquence de préparation en ANNEXE VIII).

Le % d'écart est calculé d'après l'équation suivante:

$$\%\ \text{d'écart} = \frac{\text{Résultat de l'échantillon - Résultat du duplicata}}{\text{Résultat de l'échantillon + Résultat du duplicata} \ / \ 2} \times 100$$

Le % d'écart devrait être inférieur ou égal à 25%.

Enregistrer les résultats dans le «LIMS».

8.4 ÉCHANTILLONS FORTIFIÉS — CQ de préparation

Ce contrôle est effectué en suivant la fréquence décrite en ANNEXE VIII.

Ajouter 1 mL de la solution-contrôle «BWMS/SPIKE» désirée (voir les sections 7.9.1 à 7.9.3) à 1 g de sol dans un tube de digestion et suivre intégralement toutes les étapes de la minéralisation tel qu'indiqué à la section 9.3.

Calculer la récupération avec l'équation suivante:

$$(\%)\ \text{récupération} = \frac{(C_f - C) \times 100}{C_a}$$

OÙ

C_f: concentration de l'échantillon fortifié
C: concentration de l'échantillon non fortifié
C_a: concentration de l'ajout

Les % de récupération obtenus doivent généralement se situer entre 80% et 120%.

Les résultats sont enregistrés dans le «LIMS».

8.5 ÉCHANTILLON DE CONTRÔLE DE SOURCE INTERNE — CQ de préparation

Analyser un échantillon de contrôle de sols de source interne , suivant ceux préparés (voir la fréquence du contrôle de qualité lors de la préparation en ANNEXE VIII).

Les résultats obtenus doivent se situer dans un intervalle de ± 20 % de la valeur théorique.

8.6 ÉTALONS CERTIFIÉS — CQ de préparation

Analyser un étalon certifié (voir les sections 7.10.1 à 7.10.3) suivant la fréquence du contrôle de qualité lors de la préparation en ANNEXE VIII.

Les résultats obtenus pour le cadmium, le chrome, le cuivre, le nickel, le plomb et le zinc sont tracés sur des chartes de contrôles et doivent se situer entre les limites définies par chacune de ces chartes. Pour les autres métaux, les résultats doivent se situer entre les limites définies par l'organisme de certification.

8.7 ÉCHANTILLONS DE CONTRÔLE DE SOURCE INTERNE — CQ d'analyse

Ces échantillons sont analysés pour vérifier la performance instrumentale et l'étalonnage à une fréquence décrite en ANNEXE VII, pendant les analyses.

Les résultats du contrôle "CTL 1" pour le cadmium, le chrome, le cuivre, le nickel, le plomb et le zinc sont tracés sur des chartes de contrôles et doivent se situer entre les limites définies par chacune de ces chartes. Les résultats du contrôle "CTL 1" pour les métaux et les résultats des autres contrôle de source interne doivent se situer dans un intervalle de ± 15 % de la valeur théorique.

8.8 ÉTALONS CERTIFIÉS — CQ DE L'ANALYSE

Analyser un étalon certifié WW-11 (voir la section 7.10.4) suivant la fréquence décrite en ANNEXE VII.

Les résultats obtenus doivent se situer entre les limites définies par l'organisme de certification.

9. PROTOCOLE ANALYTIQUE

9. 1 NETTOYAGE DE LA VERRERIE

Rincer les tubes de digestion (en verre) à l'eau chaude et laisser tremper dans l'eau savonneuse pendant environ une (1) heure.

Nettoyer, à l'aide d'une brosse, à l'eau chaude savonneuse.

Rincer abondamment à l'eau du robinet afin d'enlever le savon.

Laisser les tubes de verre tremper dans une solution d'acide nitrique (grade A.C.S.) 20% v/v pendant une nuit.

Rincer (3) trois fois à l'eau déminéralisée.

Laisser sécher.

9.2 PRÉPARATION DES ÉCHANTILLONS

Note: L'utilisation du terme "sols" inclue les sols, les boues et les sédiments.

Homogénéiser l'échantillon de sol (en entier).

Prélever une portion représentative (environ 30 g) de sols et placer à l'étuve à 105°C durant au moins 4 heures.

Broyer l'échantillon sec à l'aide d'un mortier et d'un pilon afin de briser les agrégats mais sans altérer les particules.

Tamiser l'échantillon broyé sur un tamis de nylon d'une ouverture de 2 mm et transférer dans un sac en plastique bien identifié. Conserver à la température ambiante jusqu'au moment de l'analyse.

9.3 MINÉRALISATION DE L'ÉCHANTILLON

La préparation de la solution témoin et les contrôles doivent être préparés de la même façon que les échantillons.

Introduire environ 1,0 g de sol (séché et tamisé) dans les tubes de digestion.

Noter l'identification et le poids de l'échantillon dans le cahier «digestion de sols» (voir en ANNEXE VIII) pour les exemples du contenu de ce cahier.

À l'aide d'une dispensette, ajouter 2 mL d'acide nitrique (grade «trace metal») et laisser reposer l'échantillon s'il y a de l'effervescence.

À l'aide d'une dispensette , ajouter 6,0 mL d'acide chlorhydrique (grade «trace metal»). Si une concentration supérieure à 10 mg/kg (0,2 mg/L solution) est suspectée ou attendue pour l'argent et que cette analyse est demandée, une 2e minéralisation pour l'échantillon pour la détermination de l'argent uniquement doit être effectuée en remplaçant ce 6,0 mL d'acide chlorhydrique par 6,0 mL d'acide nitrique (minéralisation spéciale pour l'argent). Il est toutefois essentiel d'effectuer quand même la minéralisation régulière sur une 2e portion du même échantillon si l'analyse d'autres métaux est requise.

Par la suite, ajouter environ 2 mL d'eau déminéralisée et mélanger à l'aide du «vortex».

Placer les tubes dans le bloc digesteur et chauffer pendant une heure à 60° C et pendant 2 1/2 heures à 95° C en ajustant les conditions d'opération du bloc digesteur de la façon suivante:

i) Placer l'interrupteur du contrôleur à «auto»
ii) Ajuster le bouton «LOW TEMP.TIME» à «1»
iii) Ajuster le bouton «LOW TEMP.» à «60° C»
iv) Ajuster le bouton «TOTAL CYCLE TIME» à «4»
v) Ajuster le bouton «HIGH TEMP.» à «95° C.

Laisser refroidir les tubes pendant environ 30 minutes et ajouter environ 15 mL d'eau déionisée.

Transvider le tout dans un tube "falcon" de 50 mL en polypropylène, jauger à 50 mL et bien agiter.

Laisser décanter ou filtrer, s'il y a lieu, sur papier filtre Whatman #40, ou l'équivalent d'une porosité de 8 µm, et procéder au dosage.

9.4 DOSAGE

9.4.1 Mise en opération du spectrophotomètre d'émission atomique à plasma d'argon:

Pour l'utilisation du spectrophotomètre à plasma ICP ARL, voir la vérification journalière décrite en ANNEXE IX.

Pour l'utilisation du spectrophotomètre à plama ICP TJA, voir la procédure décrite en ANNEXE X.

9.4.2. Conditions instrumentales

9.4.2.1 Conditions du spectrophotomètre à plasma ICP ARL

Ajuster les conditions instrumentales de l'appareil de la façon suivante:

NÉBULISEUR	TYPE "NOORDERMEER"	TYPE "MEINHARD"
Puissance incidente (For ward power)	1,2 kW	1,2 kW
Puissance réfléchie (Reflected watts)	0 - 10 W	0 - 10 W
Débit du gaz pour la torche/plasma (Gas flow auxiliary)	20 psi	20 psi
Débit du gaz auxiliaire (Gaz flow auxillary)	30 psi	30 psi
Débit du gaz au nébulisateur (Gaz flow nebuliser)	(*)	(*)
Débit d'échantillonnage (Sample flow rate)	2 mL/min.	2 mL/min.
Vide (Vaccum)	<30 millitor	<30 millitor
Profile reading on micromètre	355.431 ± 0,02 nm	355.431 ± 0,02 nm

* Selon l'optimisation de chaque méthode (voir sous "lect. bullomètre" dans le cahier de bord de l'instrument i.e. ANNEXE XI.

Les longueurs d'onde utilisées sont celles mentionnées respectivement dans chaque méthode (ANNEXES II À VI).

9.4.2.2 Conditions du spectrophotomètre à plasma ICP TJA:

Voir dans chaque méthode sous "Plasma Conditions" (Les exemples dans les ANNEXES V À VI).

9.4.3 Étalonnage de la méthode

Étalonner l'appareil tous les jours en utilisant les solutions-étalons décrites aux sections 7.4 à 7.8 en suivant la méthode d'analyse et le spectrophotomètre à plasma ICP utilisé.

9.4.4 Vérification et entretien de l'appareil

9.4.4.1 Spectrophotomètre à plasma ICP ARL:

À chaque utilisation, noter les intensités des blancs (première solution-étalon de la courbe i.e. 0 ppm) et des étalons pour les éléments suivants (selon les méthodes utilisées)et inscrire les valeurs obtenues dans le cahier de bord (voir l'ANNEXE XI).

Ba 455,403 nm	Cu 324,754 nm	Pb 220,353 nm
Cd 228,880 nm	Ni 231,604 nm	Sn 189,989 nm
Cr 267,716 nm	P 214,914 nm	Zn 213,856 nm

9.4.4.2 Spectrophotomètre à plasma ICP TJA:

À chaque utilisation, noter les intensités des blancs (première solution-étalon de la courbe i.e. 0 ppm) et d'un autre étalon pour les éléments suivants pour lesquels l'étalonnage a été effectué, et inscrire les valeurs obtenues dans le cahier de bord (voir l'ANNEXE XII).

As 189,0 nm	Cu 324,754 nm	Pb 220.353 nm
Cd 228,880 nm	Ni 231,604 nm	Zn 206,2 nm
Cr 267,716 nm	P 214,914 nm	

10. CALCUL ET EXPRESSION DES RÉSULTATS

La valeur de la prise d'échantillon ainsi que le volume final sont enregistrés dans le système informatisé (voir la feuille de calcul «informatisée» à l'ANNEXE XI); les résultats d'analyse sont obtenus à l'aide de ce système. Les résultats d'analyse sont exprimés en mg/kg pour chacun des métaux dosés.

10.1 INTERPRÉTATION DES RÉSULTATS

Inscrire l'intensité des signaux des étalons d'éléments choisis au début du cahier de bord du spectrophotomètre de TJA ou ARL sur les feuilles comme celles données en exemple en ANNEXE XII ET XIII.

Vérifier un à un le coefficient de corrélation des courbes d'étalonnage à plus de 2 points de chacun des éléments. Ils doivent généralement être ≥ 0,995 pour le spectrophotomètre TJA alors que le "RMS ERROR" doit être <5% pour le spectrophotomètre ARL.

Inscrire les valeurs obtenues pour les contrôles choisis sur les chartes dans le cahier de contrôle de qualité. Vérifier si les résultats obtenus se trouvent dans les écarts acceptables de chaque charte de contrôle.

Les résultats des blancs et des échantillons de contrôle "BWMS" sont entrés dans le système informatique"LIMS" selon le code d'analyse choisi:

METALS-W	ICPQT-S	ICP-W
METALS-S	ICPQ-S	ICP2-W
METAL-WD	ICPQT-W	ICP-S
	ICPQT-WD	ICP2-S

Le % de récupération de l'échantillon de contrôle "BWMS" est calculé par rapport à la valeur théorique et aussi entré dans le "LIMS".

Les résultats d'analyse pour les échantillons sont aussi entrés dans le "LIMS" selon le code d'analyse demandé par l'analyste.

Une liste de validation des résultats est imprimée et les résultats inscrits pour les échantillons sont vérifiés par un deuxième analyste.

Une personne autorisée vérifie et valide les résultats dans le "LIMS".

11. ARCHIVAGE

Les résultats d'analyses sont enregistrés dans le "LIMS" par l'analyste. Ils sont validés par le superviseur avant d'être transmis au client par le chargé de projet.

Les données de résultats et de contrôle de la qualité sont archivées pour un minimum de trois (3) ans.

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12. LISTE DES ANNEXES

ANNEXE I: TABLEAUX DE VALIDATION
ANNEXE II: "PRINT-OUT" MÉTHODE SOLMTX^D
ANNEXE III: "PRINT-OUT" MÉTHODE ICPQUE^D
ANNEXE IV: "PRINT-OUT" MÉTHODE ALCALI^D
ANNEXE V: "PRINT-OUT" MÉTHODE ICPQFE
ANNEXE VI: "PRINT-OUT" MÉTHODE SCAN
ANNEXE VII: CQ D'ANALYSE
ANNEXE VIII: CQ DE PRÉPARATION
ANNEXE IX: PROCÉDURE ARL
ANNEXE X: PROCÉDURE TJA
ANNEXE XI: EXEMPLE DE FEUILLE DE CALCUL
ANNEXE XII: CAHIER DE BORD ARL
ANNEXE XIII: CAHIER DE BORD TJA

Number: METHOD 02-2451

Title: METHOD FOR THE ANALYSIS OF EXTRACTABLE METALS IN SEDIMENT BY HYDROCHLORIC ACID EXTRACTION AND ATOMIC ABSORPTION SPECTROSCOPY

Version Number: 1 Date Authorized: October 4, 1994

Background Information:

With the advent of the industrial revolution and especially during the 20th Century, metals and metalloids have been mined, industrially processed and used in numerous applications. This has led to regional and global redistribution and to a significant increase of their concentrations in the upper part of earth's crust. This increase in concentrations has occurred in the plough-layer of soils, in plants, biota, lakes, rivers, estuaries, oceanic and arctic regions, foodstuffs and human beings and has caused various harmful effects to the ecosystem.

Although some elements, such as Fe, Zn, Cu and Mn, are considered to be essential for human health, most are not.

Al, As, Be, Cd, Co, Cr, Hg, Ni, Pb, Se and Tl are among the elements that are toxic to humans and most other living organisms. Some of these elements are toxic only at high concentrations.

Certain elements, such as Al, have been implicated in a number of neurological diseases, such as Alzheimer's senile and pre-senile dementia, amyotropic lateral sclerosis, and Parkinson's dementia of Guam. Some elements are more toxic when combined with organic molecules (organo metals), such as alkyl lead and organo mercury compounds [1,2].

Scope:

This method provides the analytical and supporting methodology necessary for the detection and quantitation of metals, including aluminum, cadmium, chromium, cobalt, copper, iron, lead, manganese, nickel, zinc, molybdenum and vanadium, in sediments by atomic absorption spectroscopy (AAS).

The method detection limit (MDL) is defined as the lowest concentration of analyte in Type I reagent grade water that the method can detect reliably and which is statistically different from the response obtained from a blank carried through the complete method, including chemical extraction or pretreatment of the sample [3]. The method detection limits for the respective analytes are provided in **Table 02-2451:1** and are based on a sample size of 5.0 grams. With appropriate dilution, samples having higher concentrations can be determined within this analytical working range.

Procedure:

1. Scope and Application

1.1 This method may be used to analyze suspended and bottom sediment for the determination of extractable or non-residual metal constituents. The range varies, depending on the abundance of the metal normally found. Upper limits are provided in **Table 02-245:1**.

2. Summary of Method

2.1 A sediment sample is received dried, ground and homogenized. The sample is dissolved in hydrochloric acid and filtered. The filtrate is analyzed by atomic absorption spectroscopy after the addition, in certain cases, of appropriate matrix modifiers. Additional interferences are removed or compensated for by background correction.

2.2 Non-residual metal in sediment is defined as the fraction of the metal that is not part of the silicate matrix of the rock from which the sediment is derived. This includes insoluble metal salts adsorbed on the sediment particles, such as organic matter.

2.3 Non-residual metal analysis provides more information than total metal analysis in the detection of pollution, since adsorption, complexation and precipitation are the main forms in which metals from polluted waters are retained in sediments.

2.4 Hydrochloric acid solution is used to liberate metals from organic matter, dissolve precipitated salts and extract adsorbed as well as all easily-extractable metals from sediments. This solution gives no reflection of the rock from which the sediment is derived and thus provides a measure of non-residual [4,5,6] metal in sediment.

2.5 The non-residual metal content of sediments is a function of its particle size distribution (surface area). It has been found [7] that below a particle size of 80 mesh, the dependence of metal content on surface area is removed. Therefore, if this portion of the sediment is used, the analysis with respect to sample type (i.e. sand, silt, or clay) is normalized. It has also been found [7] that the highest contrast between anomalous and background samples is obtained when the 80 mesh portion is used.

3. Interferences

3.1 Matrix effects are controlled by matching the viscosity of the samples and standards through the addition of acid or noninterfering salt to the standard. This is controlled by making standards with the same acid concentration as the sample.

3.2 Background absorption can be eliminated by the use of background correction.

3.3 Ionization interferences are eliminated or compensated for by the addition of easily-ionized elements, such as sodium or ammonium chloride, to both samples and standards. Ionization effects can also be controlled by keeping the flame temperature as low as possible.

3.4 Element-specific interferences and corrections include the following:

3.4.1 Aluminum: Aluminum is easily ionized in the flame. This is controlled by adding 0.1 mL 25% NaCl to 5.0 mL of sample and standard.

3.4.2 Chromium: The absorption of chromium is suppressed by iron in the air-acetylene flame. Iron interference is controlled by the addition of 0.3 mL of 30% NH_4Cl to 5.0 mL of sample and standard.

3.4.3 Molybdenum: The absorbtion of molybdenum is suppressed by calcium, barium, cadmium and cerium. This chemical interference is removed by the addition of 0.3 mL of 30% NH_4Cl to 5.0 mL of sample and standard.

3.4.4 Vanadium: Vanadium is easily ionized in the flame and can be controlled by adding 0.1 mL of 25% NaCl to 5.0 mL of sample and standard.

4. Safety

4.1 Hydrochloric acid is a strong acid and can cause severe burns to exposed skin. The fumes can cause irritation to the eyes and lungs. Work must be carried out in a well-ventilated area, and protective clothing, such as lab coats, gloves and safety glasses, must be worn when handling concentrated acids. For further information on first aid and preventive measures, consult the corresponding Material Safety Data Sheet.

4.2 Safety regulations require that the acetylene and nitrous oxide gas cylinders must be secured and in an upright position. Damage to the burner system by acetone, a common contaminant in acetylene, can be prevented by replacing the acetylene cylinder when it reaches a pressure of 100 psi. Flashback at the burner, caused by a reduction in nitrous oxide flow through a frozen regulator, can be prevented by fitting the nitrous oxide cylinder with a special nonfreezable regulator or by wrapping a heating coil around an ordinary regulator. (Some atomic absorption instruments have an automatic gas control system that will safely shut down a nitrous oxide-acetylene flame in the event of a reduction in nitrous oxide flow rate.)

4.3 When using atomic absorption instruments, make certain that the safety precautions listed in the accompanying manuals are followed. Some of these precautions include proper ventilation, handling of compressed gasses, installation of various burner heads, fuel settings and general setup. Other safety issues include making sure there is enough water in the drain trap and that all the proper interlocks are in place.

5. Apparatus, Equipment and Materials

5.1 Atomic absorption spectrometer equipped with background correction, Perkin-Elmer 4000. Models 603, 503, 403, 5000, 5100 or equivalent may also be used. For set-up, refer to the manufacturer's manual for instrument optimization. Refer to **Table 02-2451:2** for a summary of instrumental conditions.

5.2 Acetylene and nitrous oxide tanks with gauges and necessary plumbing.

5.3 Electronic analytical balance, certified to accurately weigh to 0.0001 gram.

5.4 Mechanical shaker with external timer.

5.5 Suction filtration apparatus, WHATMAN glass fiber filter (4.25 cm GF/C).

5.6 Automatic diluter.

5.7 Vortex mixer.

5.8 Wide-mouth polyethylene or polypropylene bottles, 125 mL. Store sample bottles filled with 5% HCl. Bottles to be used are emptied and rinsed three times with Type I water (see **Section 6.1**) and allowed to air dry. After analysis, rinse the bottles well with Type I water and store filled with 5% HCl.

5.9 Labware: volumetric flasks, funnels, beakers, 100 mL graduated cylinder, volumetric pipettes for making up standards and adding spikes, 20 mL test tubes for dilution and/or modifier additions, 5.0 mL pipetter for aliquot uptake, 10 mL and 50 mL dispensers. All labware should be washed with 10% nitric acid and rinsed thoroughly with Type I water.

6. Reagents and Consumable Materials

6.1 ASTM Type I grade reagent water [8] should be used throughout the procedure for the preparation of solutions, for dilutions, and for rinsing glassware. Type I water is prepared by the initial treatment of feed water by reverse osmosis. The resultant product should average a conductivity of less than 10 micromhos/cm. It is then passed through a 0.2 micrometer membrane filter and polished with a mixed bed ion exchanger. (Manufacturer SYBRON/BARNSTEAD). The electrical resistivity of the polished water should be monitored on a per use basis, and the water should be used only if the reading is greater than 16.7 megohms-cm.

6.2 Hydrochloric acid (concentrated), spectroscopy grade or better.

6.3 HCl extracting solution: Prepare by adding 100 mL of concentrated HCl to a 2.0 litre flask containing Type I water. For safety, add the acid to the water. Gently swirl to mix and bring to final volume with Type I water. Repeat this dilution to prepare enough solution for analysis. Additional solution should also be prepared to serve as baseline water during instrumental analysis and also to serve as the calibration blank.

6.4 Stock metal solutions: Commercially-prepared stock standards of 1,000 ppm and 10,000 ppm are available for all of the metals in this method. Certification should state that the starting material is of a purity of 99.99% or better.

6.5 Intermediate stock solution: The intermediate is a mixed solution consisting of 500 mg/L of Al and Fe and 50 mg/L of all other metals in this method. To

a 500 mL volumetric flask, add 100 mL Type I water and 25 mL concentrated HCl. Then add 25 mL of each 1000 ppm stock standard: Cu, Mn, Pb, V, Zn, Cd, Co, Cr, Mo and Ni. Add 25 mL of 10,000 ppm Al and 25 mL of 10,000 ppm Fe stock standards and bring the final volume up to 500 mL with Type I water.

6.6 Calibration standards. These mixed standards are prepared using the intermediate standard. Refer to **Table 02-2451:3** and add the indicated volume of intermediate solution to a 250 mL volumetric flask. Also note the volume of HCl required to give a final 5% HCl concentration. Bring the final volume up to 250 mL with Type 1 water. Store each prepared standard in a clean polyethylene bottle.

6.7 Control standard: An additional set of certified stocks is obtained commercially from a second source. This control standard should be prepared to contain a metal concentration equivalent to the mid-range of the calibration standards used. To a 1.0 litre flask, add 50 mL concentrated HCl and add the volume and concentration of stock as shown in **Table 02-2451:4.** Dilute to volume with Type I water. Refer to **Table 02-2451:4** for the final metal concentrations of this control standard.

6.8 Verification standard: For a verification standard, use the mid-level calibration standard for the element being analyzed.

6.9 Spiking solution A: Follow **Table 02-2451:5** to prepare spiking solution A. Add the appropriate volume of stock standards indicated to a 500 mL volumetric flask and swirl the flask as each is added. Bring the final volume up to 500 mL with Type I water. No additional acid is required, as the acid concentration of the stock standards is sufficient. Refer to **Table 02-2451:5** for the final metal concentrations of this spiking solution.

6.10 Spiking solution B: To a 500 mL volumetric flask, add 90 mL of 10,000 ppm stock Al standard, 185 mL of 10,000 ppm stock Fe standard and 25 mL concentrated HCl. Bring the final volume up to 500 mL with Type I water. This will produce a spiking solution of 1800 ppm Al and 3700 ppm Fe.

6.11 Sodium chloride solution (25%): Weigh 25 grams NaCl and transfer to a 100 mL volumetric flask. Make up to 100 mL with Type I water.

6.12 Ammonium chloride solution (30%): Weigh 30 grams of NH_4Cl and transfer to a 100 mL volumetric flask. Make up to 100 mL with Type I water.

7. Sample Collection, Preservation and Handling

7.1 Sediment samples are received air-dried or freeze-dried, ground and homogenized. All debris, such as leaves, twigs, and large stones, is removed. Samples are stored at room temperature in glass or plastic containers. No preservation is necessary.

8. Sample Receiving

8.1 Samples are received by the NLET from the client, checked and logged into ECOLIMS (NLET's Laboratory Information Management System) by the sample receiving group. This group is responsible for the storage of the samples until collected by the analyst.

9. Quality Assurance/Quality Control (QA/QC)

9.1 Analyst Certification: All analysts involved in the analysis of metals in sediments must obtain a certification of operator competence. Certification is described in **Chapter 1** in quality assurance and quality control.

9.2 Method Detection Limits: The method detection limits, as shown in **Table 02-2451:1**, were calculated according to the procedure described in **Chapter 1**, on quality assurance and quality control.

9.3 Calibration Curves: An external standard calibration procedure is used to quantitate the metal concentrations. Quantification is done using regression analysis, as described in **Section 11**.

9.4 Method Accuracy: Analyze two reference samples of different concentration levels, preferably covering the low and high ends of the operating range, with each run of 40 samples. The data should fall within the established control limits as listed in **Table 02-2451:6 and Table 02-2451:7**. Take corrective actions as described in **Section 9.11** if the data are indicated to be out of control. Document all non-conformances and the corrective actions taken.

9.5 Method Precision: Replicate two references or randomly selected samples, as described in **Chapter 1**, for within run duplicates with each run of 40 samples. The data should fall within the established control limits as listed in **Table 02-2451:8**. Take corrective actions as described in **Section 9.11** if the data are indicated to be out of control. Document all non-conformances and the corrective actions taken.

9.6 Matrix Interference: Randomly select two samples from the batch of samples and spike an aliquot with an appropriate volume of spiking solution, as described in **Chapter 1**. Analyze the sample and take corrective actions as described in **Section 9.11.** If the data are indicated to be out of control for expected spike recoveries (see **Table 02-2451:9**), document all non-conformances and the corrective actions taken.

9.7 Method Blank: To assess contamination, analyze two blanks together with the unknown samples.

9.8 Control Charts: Keep ongoing control charts on two sets of parameters: reference samples and within run duplicates.

9.9 X - (Shewhart) Chart for Reference Samples: Calculate control limits and construct a control chart for each reference sample, as described in **Chapter 1**. Immediately after analyzing the reference samples, plot the values on the respective control charts. If the plot indicates the data point to be out of control, take corrective actions as described in **Section 9.11**. Document all non-conformances and the corrective actions taken.

9.10 X - (Shewhart) Chart for Within Run Duplicates: Calculate control limits and construct a control chart for the duplicates, as described in **Chapter 1**. Immediately after analyzing the duplicates, plot the differences on the control chart. If the plot indicates the data point to be out of control, take corrective actions as described in **Section 9.11**. Document all non-conformances and the corrective actions taken.

9.11 Corrective Actions: If the warning and control limits on a control chart are set at 2 S_d and 3 S_d (standard deviation), respectively, it is expected that 1 out of 20 and 1 out of 100 data points will exceed the warning and controls limits, respectively. On careful examination of the control charts, the following guide will indicate when to intervene and take appropriate action to correct the problems.

9.11.1 Control Limit: If one data point exceeds the control limit, repeat that sample immediately to confirm that the next data point is within control limits. If the next data point also exceeds control limits, discontinue the analysis [9].

9.11.2 Warning Limit: If two out of three successive data points exceed warning limits, analyze another sample. If the next data point is within the warning limits, continue the analysis; otherwise, discontinue until the problem is corrected [9].

9.11.3 Standard Deviation: If four out of five successive data points exceed $1S_d$ or are in increasing or decreasing order, analyze another sample. If the next data point is within 1 S_d or changes the order, continue the analysis; otherwise, discontinue until the problem is corrected [9].

9.11.4 Centre Line: If six successive data points are on one side of the centre line, analyze another sample. If the next data point is on the opposite side of the centre line, continue the analysis. If the next data point is on the same side, discontinue the analysis until the problem is corrected [9].

9.12 Internal Performance Audits: Blind performance audits are conducted biannually by the NLET QA chemist. These audits consist of the submission of sediment samples with known metal concentrations. These concentrations are within the working range of the analytical method. The QA chemist reviews the complete analytical report and highlights any abnormal deviations from expected results. The chemist in charge is responsible for taking appropriate corrective action and for submitting a full report, documenting the corrective actions taken, to the QA chemist.

9.13 Interlaboratory Performance Audits: In addition to several special interlaboratory studies, NLET participates in two regular external performance audits. The Federal Provincial Inorganic QA Study is conducted by the quality assurance group of the National Water Research Institute of Canada (NWRI) [10]. This audit consists of the annual submission of 10 sediment samples. The West Enviro-Agricultural Laboratory Association Round Robin Study is conducted by the Energy Resource Conservation Board (ERCB). This audit requires the submission of 5 sediment samples annually. The NLET QA chemist receives the reports from these audits, highlights any significant deviations from the expected results and circulates the report to staff members for appropriate corrective actions.

9.14 Accreditation: The Canadian Association of Environmental Analytical Laboratories (CAEAL) [11] is the accrediting organization for NLET. NLET participates in all CAEAL studies that are necessary to assure accreditation of its methods.

10. Preparation and Procedure

10.1 Sample Preparation:

10.1.1 Weigh 5.0 grams of the representative sample into a clean 125 mL bottle.

10.1.2 Repeat this weighing step for additional duplicates, spikes and references.

10.1.3 Carry two method blanks through the procedure and subject them to the same process as the sediment samples.

10.1.4 Add the appropriate spiking solutions to the designated samples selected. That is, add 1.0 mL of spiking solution A and 10 mL of spiking solution B. Refer to **Table 02-2451:10** for a summary of the liquid spike concentrations in mg/L and the corresponding solid spike concentrations in mg/Kg based on 5.0 grams of sample and a final volume of 100 mL.

10.1.5 Using the reagent dispenser, add enough 5% HCl solution to obtain a final volume of 100 mL. If bubbling of CO_2 occurs when HCl is added, allow the solution to stand for a few minutes until the reaction ceases before capping. The bubbling is the result of $CaCO_3$ in the sediment.

10.1.6 Cap the bottles tightly and securely place them on the mechanical shaker length-wise.

10.1.7 Shake the samples overnight (16 hours), at room temperature.

10.1.8 Filter the sample solution by suction using a Whatman glass fiber filter (4.25 cm GF/C) and discard the leached sediment. Place the filtrate in a clean bottle. The solution will now be ready for analysis by atomic absorption spectroscopy.

10.2 Instrument Calibration:

10.2.1 Optimization: Set up the instrument as shown in **Table 02-2451:2**. Align the burner head and hollow cathode lamp position and adjust the nebulizer flow rate to achieve the greatest signal to noise ratio, as described in **Section 10.2.2**.

10.2.2 Sensitivity Check: Immediately after optimization, aspirate a standard solution of known concentration (verification standard) to achieve an absorbance equal to the instrument specification for the analyzed elements.

10.2.3 Calibration: This is the process of adjusting system functions to produce output from a set of standards, and construction of calibration curves to relate the output to the known concentration of the elements contained within the standards. Unknowns can then be determined by referring the output from the sample to the calibration curve. The process also involves establishing a stable baseline, confirming the accuracy of the calibration standards, correcting for baseline drift and recalibrating when sensitivity drift is outside normal tolerances.

10.2.4 When using the Perkin-Elmer AA 4000, push down the "HOLD", "CONCENTRATION", and "PRINT" buttons to ensure proper set-up for the display of integrated data, expansion factor, and electronic data transfer to ECOLIMS for later data processing and storage.

10.2.5 Establish a baseline at 5% of recorder output by aspirating baseline water (5% HCl) and AUTO ZERO the instrument.

10.2.6 Establish the upper range at 95% of recorder output for the highest standard in the calibration set.

10.2.7 Set up the ECOLIMS system for direct data capture from the instrument.

10.2.8 Aspirate the calibration standard solutions. Measure and store the absorbance readings. These will be used later for generation of the calibration curve.

10.3 Measurement:

10.3.1 Analyze all unknown samples and quality control aliquots by following the sequence shown in **Table 02-2451:11**.

10.3.2 Wait for the peak signal for each sample and depress the READ button. Once the integrated value is sent to the computer, continue the analysis, aspirating a wash between each sample aliquot.

10.3.3 After completion of the analytical run, use ECOLIMS to calculate the concentration of the metals in the unknowns as specified in **Section 11.1**.

10.3.4 Return all system components to non-operational status.

11. Calculations

11.1 A second degree equation is generated by ECOLIMS from computerized curve fitting of the calibration standard data using regression analysis. The method uses a least-squares fitting, which is designed to minimize the sum of squares of the deviations of the actual data points from the second degree line of best fit. This line is described by the equation $y = ax^2 + bx + c$, where "a" and "b" are coefficients of the curve and "c" is the y-intercept. The concentration of metals in the unknowns is determined in relationship to their respective line. The unknowns in the tray pattern are bracketed by calibration standards, usually in groups of 40 samples, and quantitation and recalibration is carried out at these intervals. The integrity of the calibration curve is assessed by evaluation of the control standard, calibration blank, and verification standard.

11.2 The concentration of metal in the sediment is calculated as follows:

$$M = \frac{C \times V}{W}$$

M = concentration of metal in sediment (mg/Kg)
C = concentration of metal in solution (mg/L)
V = volume of solution (L)
W = weight of sample (Kg)

12. Method Performance

12.1 Accuracy information from reference material was not available for this method.

12.2 Recovery data on spikes yielded the QC data shown in **Table 02-2451:9**.

12.3 Precision is expressed as the coefficient of variation (CV), and is defined by the following equation:

$$CV\ (\%) = \frac{\text{standard deviation}}{\text{mean concentration}} \times 100$$

12.4 For this method, between run precision was calculated using 2 different reference samples. The coefficients of variation, at specified levels of respective analytes, obtained by a single laboratory (National Laboratory for Environmental Testing), are shown in **Tables 02-2451:6** and **02-2451:7**. Within run precision was calculated from the differences of duplicates of natural samples. Refer to **Table 02-2451:8** for within run precision data generated by this method.

13. Reporting of Data

13.1 The following records of the analytical methods are maintained: analyst's daily quality control log, control charts, daily work book and instruments log.

13.2 Hard copies of analytical data, QA/QC data and report logs are maintained by NLET for 5 years from the date of analysis.

13.3 Magnetic copies of all data and associated QA/QC information are maintained permanently by NLET.

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7. H. E. Hawkes and J. S. Webb, *Geochemistry in Mineral Exploration*, Harper and Row, New York, 1962, p. 9-12.

8. R. A. Shorer (Editor), *Annual Book of ASTM Standards, D1193-77 Standard Specification for Reagent Water*, ASTM, Easton MD, 1991, Vol. 11.01, p. 45.

9. A. E. Greenberg et al. (Editors), *Standard Methods For The Examination Of Water And Wastewater*, 18th Edition, American Public Health Association, Washington, DC, 1992, Part 1000, p. 1-6.

10. National Water Research Institute of Canada, 867 Lakeshore Road, Burlington, Ontario L7R 4A6.

11. The Canadian Association for Environmental Analytical Laboratories (CAEAL), Suite 532, 1 Nicholas Street, Ottawa, Ontario K1N 7B7.

APPENDIX A

Table 02-2451:1: Method Codes, Method Detection Limits and Upper Limits

PARAMETER	ENVIRODAT CODE	ECOLIMS CODE	MDL (mg/Kg)	UPPER LIMIT (mg/Kg)
Aluminum	013054	A0425	2.0	2000
Cadmium	048054	A0426	0.2	20
Chromium	024054	A0427	0.2	100
Cobalt	027054	A0428	0.4	40
Copper	029054	A0429	0.2	100
Iron	026054	A0430	1.0	4000
Lead	082054	A0431	1.0	100
Manganese	025054	A0432	0.2	400
Nickel	028054	A0433	0.6	40
Zinc	030054	A0434	0.2	200
Molybdenum	000075	A1019	1.0	100
Vanadium	000070	A1020	1.0	100

Table 02-2451:2: Instrument Set-Up

PARAMETER	WAVELENGTH (nm)	BURNER HEAD N_2O/AIR	OXIDANT
Aluminum	309.3	N_2O	N_2O
Cadmium	228.8	Air	Air
Chromium	357.9	Air	Air
Cobalt	240.7	Air	Air
Cupper	324.7	Air	Air
Iron	248.3	Air	Air
Lead	217.0*	Air	Air
Manganese	279.5	Air	Air
Nickel	232.0	Air	Air
Zinc	213.9	Air	Air
Molybdenum	313.3	N_2O	N_2O
Vanadium	318.4	N_2O	N_2O

* A wavelength of 217.0 nm is recommended for instruments with background correction. For elevated levels of lead, a wavelength of 283.3 nm offers good stability.

Table 02-2451:3: Calibration Standards for Direct Aspiration

CALIBRATION STANDARD (mg/L)*	VOLUME OF INTERMEDIATE (mL)	VOLUME OF HCL (mL)
0	0	12.5
.01	.05	12.5
.02	0.1	12.5
.05	.25	12.5
0.1	0.5	12.5
0.2	1.0	12.5
0.5	2.5	12.4
1.0	5.0	12.3
2.0	10	12.0
5.0	25	11.3
10	50	10.0
20	100	7.5

* The concentrations for Al and Fe are ten times higher than indicated due to the fact that the intermediate standard used contained ten times the amount of Al and Fe.

Table 02-2451:4: Preparation of Control Standard

PARAMETER	STOCK CONCENTRATION (mg/L)	STOCK VOLUME (mL)	FINAL CONCENTRATION (mg/L)
Aluminum	1,000	50	50
Iron	1,000	100	100
Copper	1,000	2.5	2.5
Manganese	1,000	10	10
Lead	1,000	2.5	2.5
Vanadium	1,000	2.5	2.5
Zinc	1,000	5.0	5.0
Cadmium	1,000	0.5	0.5
Chromium	1,000	2.5	2.5
Cobalt	1,000	1.0	1.0
Molybdenum	1,000	2.5	2.5
Nickel	1,000	1.0	1.0

Table 02-2451:5: Preparation of Spiking Solution A

PARAMETER	STOCK CONCENTRATION (mg/L)	STOCK VOLUME (mL)	FINAL CONCENTRATION (mg/L)
Aluminum	10,000	100	2,000
Iron	10,000	150	3,000
Copper	10,000	5	100
Manganese	10,000	25	500
Lead	10,000	5	100
Vanadium	10,000	5	100
Zinc	10,000	10	200
Cadmium	1,000	10	20
Chromium	1,000	50	100
Cobalt	1,000	25	50
Molybdenum	1,000	25	50
Nickel	1,000	25	50

Table 02-2451:6: Reference 1 Data for HCl Extractable Metals in Sediment

METAL	MEAN mg/Kg	STANDARD DEVIATION mg/Kg	COEFFICIENT OF VARIATION %	UPPER CONTROL LIMIT mg/Kg	UPPER WARNING LIMIT mg/Kg	LOWER CONTROL LIMIT mg/Kg	LOWER WARNING LIMIT mg/Kg
Al	2648	230	8.7	3338	3108	1958	2188
Co	2.19	0.56	25.6	3.87	3.31	0.51	1.07
Cr	6.26	0.76	12.1	8.54	7.78	3.98	4.74
Cu	6.72	0.35	5.2	7.77	7.42	5.67	6.02
Fe	5680	673	11.9	7699	3661	4334	7026
Mn	44.1	4.8	10.9	59	53.7	30	34.5
Ni	7.29	1.23	16.9	11	9.75	4	4.83
Pb	17	0.9	5.3	20	18.8	14	15.2
Zn	45.6	2.3	5	52.5	50.2	38.7	41

Table 02-2451:7: Reference 2 Data for HCl Extractable Metals in Sediment

METAL	MEAN mg/Kg	STANDARD DEVIATION mg/Kg	COEFFICIENT OF VARIATION %	UPPER CONTROL LIMIT mg/Kg	UPPER WARNING LIMIT mg/Kg	LOWER CONTROL LIMIT mg/Kg	LOWER WARNING LIMIT mg/Kg
Al	3444	810	23.5	5874	5064	1014	1824
Cd	2.02	0.29	14.4	2.89	2.6	1.15	1.44
Co	6.6	0.6	13.2	9.21	8.34	3.99	4.86
Cr	37.5	4	10.7	49.5	45.5	25.5	29.5
Cu	55.3	3.2	5.8	64.9	61.7	45.7	48.9
Fe	11907	2378	20	19041	16663	4773	7151
Mn	727	58	8	901	843	553	611
Ni	25.4	1.8	7.1	30.8	29	20	21.8
Pb	93.2	3.9	4.2	104.9	101	81.5	85.4
Zn	543	28	5.2	627	599	459	487

Table 02-2451:8: Duplicate Data for HCl Extractable Metals in Sediment

METAL	MEAN mg/Kg	STANDARD DEVIATION mg/Kg	UPPER CONTROL LIMIT mg/Kg	UPPER WARNING LIMIT mg/Kg	LOWER CONTROL LIMIT mg/Kg	LOWER WARNING LIMIT mg/Kg
Al	189	165	684	519	-684	-519
Cd	0.052	0.054	0.214	0.16	-0.214	-0.16
Co	0.27	0.28	1.11	0.83	-1.11	-0.83
Cr	0.69	0.74	2.91	2.17	-2.91	-2.17
Cu	0.82	0.91	3.55	2.64	-3.55	-2.64
Fe	405	344	1437	1093	-1437	-1093
Mn	31.5	38.5	147	109	-147	-109
Ni	0.55	0.53	2.14	1.61	-2.14	-1.61
Pb	1.16	1.2	4.8	3.6	-4.8	-3.6
Zn	3.7	4.5	17.2	12.7	-17.2	-12.7

Table 02-2451:9: Spike Data for HCl Extractable Metals in Sediment

METAL	MEAN %	STANDARD DEVIATION %	UPPER CONTROL LIMIT %	UPPER WARNING LIMIT %	LOWER CONTROL LIMIT %	LOWER WARNING LIMIT %
Al	92.6	9.1	119.9	110.8	65.3	74.4
Cd	96	3.5	106.5	103	85.5	89
Co	95.8	4.2	108.4	104.2	83.2	87.4
Cr	93.2	8.4	118.4	110	68	76.4
Cu	94.9	3.6	105.7	102.1	84.1	87.7
Fe	96.3	14.7	140.4	125.7	52.2	66.9
Mn	98.3	16.5	147.8	131.3	48.8	65.3
Ni	94.7	3.1	104	100.9	85.4	88.5
Pb	93.2	3.9	104.9	101	81.5	85.4
Zn	93.2	7.9	117	109	69.5	77.4

Table 02-2451:10: Final Liquid and Solid Spike Concentrations

PARAMETER	LIQUID SPIKE mg/L	SOLID SPIKE mg/Kg
Aluminum	200	4000
Cadmium	0.2	4
Cobalt	0.5	10
Chromium	1.0	20
Copper	1.0	20
Iron	400	8000
Manganese	5.0	100
Molybdenum	1.0	20
Nickel	0.5	10
Lead	1.0	20
Vanadium	1.0	20
Zinc	2.0	40

Table 02-2451:11: Sample Tray Arrangement and Analysis Sequence

Position Number	Sample ID Sample Type	Position Number	Sample ID Sample Type
1	Blank	41	Verification Standard
2	Standard 1	42-51	10 Samples
3	Standard 2	52	Blank
4	Standard 3	53	Calibration Blank
5	Standard 4	54	Verification Standard
6	Standard 5	55-64	10 Samples
7	Standard 6	65	Method Blank 2
8	Blank	66	Duplicate Within 2
9	Control Standard	67	Reference 1B
10	Blank	68	Reference 2B
11-20	10 Samples	69	Spike 2
21	Blank	70	Blank
22	Calibration Blank	71	Standard 1
23	Varification Standard	72	Standard 2
24-33	10 Samples	73	Standard 3
34	Method Blank 1	74	Standard 4
35	Duplicate Within 1	75	Standard 5
36	Reference 1A	76	Standard 6
37	Reference 2A	77	Blank
38	Spike 1 Blank	78	
39	Blank	79	
40	Calibration Blank	80	

Number: METHOD 02-2500

Title: METHOD FOR THE ANALYSIS OF ARSENIC AND SELENIUM IN SEDIMENT BY INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROSCOPY-HYDRIDE GENERATION

Version Number: 1 **Date Authorized:** October 6, 1994

Background Information:

With the advent of the industrial revolution and especially during the 20th Century, metals and metalloids have been mined, industrially processed and used in numerous applications. This has led to regional and global redistribution and to a significant increase of their concentrations in the upper part of earth's crust. This increase in concentrations has occurred in the plough-layer of soils, in plants, biota, lakes, rivers, estuaries, oceanic and arctic regions, foodstuffs and human beings and has caused various harmful effects to the ecosystem.

While some arsenic compounds can have beneficial effects on human and animal life, certain arsenic compounds are toxic and can cause acute and chronic poisoning. Among arsenic compounds common in the environment, arsenite is the most toxic.

Selenium also has a toxic/essential duality, being necessary for animal and human health at low concentrations and leading to health impairment and even death at higher toxic doses. Allowable concentrations in drinking water in Canada and the United States are 50 µg total As/L and 10 µg total Se/L [1,2].

Scope:

This method provides an analytical procedure for the quantitation of arsenic and selenium in sediments and soils by hydride generation Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES).

The method detection limit (MDL) is defined as the lowest concentration of analyte in Type I reagent grade water that the method can detect reliably and which is statistically different from the response obtained from a blank

carried through the complete method, including chemical extraction or pretreatment of the sample [3]. The MDLs for this method are provided in **Table 02-2500:1.**

Procedure:

1. Scope and Application

1.1 This method is applicable to the determination of arsenic and selenium in sediment and soil samples. The analytical range in the final solution is 0.001 to 0.250 mg/L with a sample size of 0.5 g. This gives a sample concentration range of 0.2 to 50 mg/Kg. With appropriate dilution of the digest, samples of higher concentration can be determined.

2. Summary of Method

2.1 A sediment sample is dried, ground and homogenized. The sample is weighed in a zirconium crucible, digested with nitric acid and then placed in a muffle furnace to allow for the extraction of arsenic and selenium by fusion with sodium hydroxide. The solidified melt is dissolved and further digested using sodium borohydride in hydrochloric acid. Arsenic and selenium hydrides are formed. The samples are analyzed by atomic emission spectroscopy using inductively coupled argon plasma as an excitation source [4,5,6].

2.2 Preliminary digestion with nitric acid eliminates reducing conditions which result in low recoveries for selenium.

2.3 Inorganic forms of arsenic and selenium are digested with hydrochloric acid. All forms of arsenic and selenium are converted to arsenate (AsO_4^{3-}) and selenate (SeO_4^{2-}) by the acid. HCl also reduces the selenate to selenite (SeO_3^{2-}). Sodium borohydride ($NaBH_4$) is needed to reduce the arsenate to arsenite (AsO_3^{3-}).

2.4 Hydrides of arsenic and selenium are formed by the action of sodium borohydride ($NaBH_4$) in an acidic medium. The hydrides, arsine (AsH_3)and selenium hydride (H_2Se) are analysed.

3. Interferences

3.1 Concentrations of copper over 100 mg/L in solution (equivalent to 20,000 mg/Kg copper in the sediment) will decrease selenium recovery. If high levels are present, correct by diluting the sample.

4. Safety

4.1 Safety attire, such as lab coats, gloves and safety glasses, must be worn. The use of most laboratory reagents and the digestion of samples is restricted to fumehoods. Any analyst working in the laboratory should be familiar with the laboratory safety manual describing proper safety practices. For more specific information concerning the handling and disposal of chemicals used in this method, the analyst should refer to the Material Safety Data Sheets.

4.2 This method requires the use of relatively large amounts of concentrated inorganic acids. Hydrochloric and nitric acids are highly corrosive and should be handled with care. Strong acids cause severe burns and skin irritation. The inhalation of vapours may cause coughing, chest pains, difficulty in breathing or unconsciousness.

4.3 Sodium hydroxide is a strong base, which will cause severe irritation or burn when in contact with skin or eyes.

4.4 Sodium borohydride reacts strongly with water and acids, liberating hydrogen, and can be an explosion hazard, especially when heated.

4.5 Exposure to arsenic compounds can cause disorders of the nervous and gastrointestinal systems, mucous membranes and skin. The ingestion of arsenic compounds can be poisonous, leading to death. Arsenic compounds are known to be carcinogens.

4.6 Exposure to selenium may cause abdominal pains, diarrhea, vomiting, chest pains, coughing and difficulty in breathing. Inhalation may cause lung irritations. Skin contact may cause dermatitis.

5. Apparatus, Equipment and Materials

5.1 Autoanalyzer unit, consisting of the following:

5.1.1 Technicon Sampler IV with glass tubes and 20-1:2 cam (20 samples per hour and 1:2 sample to wash ratio);

5.1.2 Proportioning Pump, Carlo Erba, 20 Channel or equivalent;

5.1.3 Gas flow regulator, 0-250 mL/min;

5.1.4 Manifold, as shown in **Figure 02-2500:1** [7]; and

5.1.5 Phase separator, as shown in **Figure 02-2500:2.**

5.2 Atomic Emission Spectrometer, model ARL, QA-137 or equivalent, under microprocessor control and with dedicated data capture

5.3 Hot plate, model Thermolyne type 2200.

5.4 Zirconium crucible, 25 mL.

5.5 Muffle furnace.

5.6 Centrifuge, model IEC Centra -7, with 50 mL centrifuge tubes.

5.7 Micropipette , 0-1000 µL, with disposable tips.

5.8 Glassware: 150 mL beakers, 250 mL erlenmeyer flasks, pipettes, 100 mL volumetric flasks, glass rods and funnels. All glassware should be washed in hot tap water and with a laboratory grade soap, rinsed with hot tap water, followed by a 5% nitric acid soak and three rinses with Type I water (see **Section 6.1**).

5.9 Sample containers: Store the freeze-dried sample in a suitably-sized polyethylene, glass or teflon container. The sample container should be cleaned and container blanks should be prepared and analyzed to verify that the container is not a source of arsenic and selenium contamination. The NLET procedure for sample bottle washing requires that bottle and caps be soaked for at least 3 days in dilute HNO_3 and rinsed 3 times with Type I water.

5.10 Electronic Balance, Sartorius Model 1652 or equivalent, capable of measuring to 0.0001 decimal places.

6. Reagents and Consumable Materials

6.1 ASTM Type I grade reagent water [7] should be used throughout the procedure for the preparation of solutions, for dilutions, and for rinsing glassware. Type I water is prepared by the initial treatment of feed water by reverse osmosis. The resultant product should average a conductivity of less than 10 micromhos/cm. It is then passed through a 0.2 micrometer membrane filter and polished with a mixed bed ion exchanger. (Manufacturer SYBRON/BARNSTEAD). The electrical resistivity of the polished water

should be monitored on a per use basis, and the water should be used only if the reading is greater than 16.7 megohms-cm.

6.2 Sodium hydroxide (NaOH), pellets, ACS grade.

6.3 Hydrochloric acid (HCL), concentrated, ACS grade.

6.4 Nitric acid (HNO_3), concentrated, ACS grade.

6.5 Sodium borohydride ($NaBH_4$) solution, 2.5% w/v, ACS grade: Dissolve 25 g of $NaBH_4$ and 40 g of NaOH in 1L of Type I water.

6.6 Argon, prepurified

6.7 Stock standard solutions: These should be obtained commercially as certified stocks at concentrations of 1000 mg/L. The certificate should specify that the starting material is of a purity of 99.99% or better.

6.8 Intermediate stock solution (ISA): The intermediate is a mixed solution consisting of 10 mg/L As and 0.5 mg/L Se. To prepare, pipette 10 mL of As stock solution, 0.5 mL of Se stock solution, and 300 mL of concentrated hydrochloric acid into a 1L volumetric flask. Dilute to volume with Type I water.

6.9 Calibration standard solutions: To prepare the calibration standards, pipette appropriate volumes of the mixed intermediate stock, as shown in **Table 02-2500:2,** to 100 mL volumetric flasks. In addition, add 30 mL of concentrated HCl to each volumetric flask and dilute to volume with Type I water.

6.10 Control standard: An additional set of certified stocks should be obtained commercially from a second source. An intermediate solution (ISB) identical to the solution described in **Section 6.8** is prepared from these stocks. The control standard is prepared from this intermediate and compared to a level equivalent to the mid range of the calibration curve. To prepare the control standard, add 10 ml of intermediate solution (ISB) to 100 mL volumetric flask. Also add 30 mL of concentrated HCl and dilute to volume with Type I water.

6.11 Verification standard: Prepare a suitable quantity for a daily run, usually 500 mL. Add 150 mL HCl to 250 mL Type I water in a 500 mL volumetric flask, let cool, add .5 mL of intermediate stock solution (ISA) and bring to volume.

6.12 Calibration blank: Prepare a suitable quantity for a daily run, usually 200 mL. Add 60 mL HCl to 100 ml of Type I water in a 200 mL volumetric flask, let cool, and bring to volume.

6.13 Spiking solution: The intermediate solution (ISA), as described in **Section 6.8,** is used for spiking unknowns.

6.14 Baseline reagent (33 % HCl): To prepare, mix a 1:2 (v/v) concentrated HCl to Type I water in a 20 L pyrex container. Let cool to room temperature before use.

7. Sample Collection, Preservation and Handling

7.1 Sediment samples should be freeze-dried, ground and homogenized in clean polyethylene or teflon containers. The dried samples require no preservation and are stored at room temperature.

7.2 Wet samples received from the field are drained and stored in refrigerated polyethylene bags or bottles at -20°C. The samples are freeze-dried (where a freeze-drier is not available, they are air-dried at room temperature in petri dishes) and sieved through a 20 mesh sieve to remove leaves, twigs, large stones and any other debris. The entire dried sample is ground with a mortar and pestle until a homogenous sample is obtained. The sample should be able to pass through a 200 mesh sieve. Store the sample in clean containers as described in **Section 5.9.**

8. Sample Receiving

8.1 Samples are received by the NLET from the client, checked and logged into ECOLIMS (NLET's Laboratory Information Management System) by the sample receiving group. This group is responsible for the storage of the samples until collected by the analyst.

9. Quality Assurance/Quality Control (QA/QC)

9.1 Analyst Certification: All analysts involved in the analysis of arsenic and selenium in sediments must obtain a certification of operator competence. Certification is described in **Chapter 1** in quality assurance and quality control.

9.2 Method Detection Limits: The method detection limits, as shown in **Table 02-2500:1**, were calculated according to the procedure described in **Chapter 1,** on quality assurance and quality control.

9.3 Calibration Curves: An external standard calibration procedure is used to quantitate the arsenic and selenium concentrations. Quantification is done using regression analysis, as described in **Section 11**.

9.4 Method Accuracy: Analyze two certified reference samples of different concentration levels, preferably covering the low and high ends of the operating range, with each run of 40 samples. The data should fall within the established control limits as listed in **Tables 02-2500:3 and 02-2500:4.** Take corrective actions as described in **Section 9.11** if the data are indicated to be out of control. Document all non-conformances and the corrective actions taken.

9.5 Method Precision: Replicate two references or randomly selected samples, as described in **Chapter 1**, for within run duplicates with each run of 40 samples. The data should fall within the established control limits as listed in **Tables 02-2500:3 and 02-2500:4**. Take corrective actions as described in **Section 9.11** if the data are indicated to be out of control. Document all non-conformances and the corrective actions taken.

9.6 Matrix Interference: Randomly select two samples from the batch of samples and spike an aliquot with an appropriate volume of arsenic and selenium intermediate (ISA), as described in **Chapter 1**. Analyze the sample and take corrective actions as described in **Section 9.11** if the data are indicated to be out of control. Document all non-conformances and the corrective actions taken.

9.7 Method Blank: To assess contamination, process two blanks using a procedure identical to the steps carried out for the samples, including exposure to all glassware, equipment and reagents.

9.8 Control Charts: Keep ongoing control charts on two sets of parameters: reference samples and within run duplicates.

9.9 X - (Shewhart) Chart for Reference Samples: Calculate control limits and construct a control chart for each reference sample, as described in **Chapter 1**. Immediately after analyzing the reference samples, plot the values on the respective control charts. If the plot indicates the data point to be out of control, take corrective actions as described in **Section 9.11**. Document all non-conformances and the corrective actions taken.

9.10 X - (Shewhart) Chart for Within Run Duplicates: Calculate control limits and construct a control chart for the duplicates, as described in **Chapter 1**.

Immediately after analyzing the duplicates, plot the differences on the control chart. If the plot indicates the data point to be out of control, take corrective actions as described in **Section 9.11**. Document all non-conformances and the corrective actions taken.

9.11 Corrective Actions: If the warning and control limits on a control chart are set at 2 S_d and 3 S_d (standard deviation), respectively, it is expected that 1 out of 20 and 1 out of 100 data points will exceed the warning and controls limits, respectively. On careful examination of the control charts, the following guide will indicate when to intervene and take appropriate action to correct the problems.

9.11.1 Control Limit: If one data point exceeds the control limit, repeat that sample immediately to confirm that the next data point is within control limits. If the next data point also exceeds control limits, discontinue the analysis [8].

9.11.2 Warning Limit: If two out of three successive data points exceed warning limits, analyze another sample. If the next data point is within the warning limits, continue the analysis; otherwise, discontinue until the problem is corrected [8].

9.11.3 Standard Deviation: If four out of five successive data points exceed 1S_d or are in increasing or decreasing order, analyze another sample. If the next data point is within 1 S_d or changes the order, continue the analysis; otherwise, discontinue until the problem is corrected [8].

9.11.4 Centre Line: If six successive data points are on one side of centre line, analyze another sample. If the next data point is on the opposite side of the centre line, continue the analysis. If the next data point is on the same side, discontinue the analysis until the problem is corrected [8].

9.12 Internal Performance Audits: Blind performance audits are conducted biannually by the NLET QA chemist. These audits consist of the submission of sediment samples with known concentrations of arsenic and selenium. These concentrations are within the working range of the analytical method. The QA chemist reviews the complete analytical report and highlights any abnormal deviations from expected results. The chemist in charge is responsible for taking appropriate corrective action and for submitting a full report, documenting the corrective actions taken, to the QA chemist.

9.13 Interlaboratory Performance Audits: In addition to several special studies NLET participates in two regular external performance audits. The Federal Provincial Inorganic QA Study is conducted by the quality assurance group of the National Water Research Institute of Canada (NWRI) [9]. This audit consists of the annual submission of 10 sediment samples. The West Enviro-Agricultural Laboratory Association Round Robin Study is conducted by the Energy Resource Conservation Board (ERCB). This audit requires the submission of 5 sediment samples annually. The NLET QA chemist receives the reports from the audits, highlights any significant deviations from the expected results and circulates the report, through the chemist in charge, to staff members for appropriate corrective actions.

9.14 Accreditation: The Canadian Association of Environmental Analytical Laboratories (CAEAL) [10] is the accrediting organization for NLET. NLET participates in all CAEAL studies that are necessary to assure accreditation of this method.

10. Preparation and Procedure

10.1 Sample Preparation:

10.1.1 Weigh 0.5 g of the representative sample into a clean zirconium crucible.

10.1.2 Add 4 mL of concentrated HNO_3 and place on a hot plate set at 80° to 90° C. Heat until dry. If foaming continues, add another 4 mL of concentrated HNO_3 and heat until dry.

10.1.3 Cool the zirconium crucible and add 4.5 g of NaOH pellets.

10.1.4 Cover the crucible with a lid and place into a 150 mL beaker. Place the entire assembly into a muffle furnace at room temperature.

10.1.5 Increase the temperature of the muffle furnace 50°C every 15 minutes until a temperature of 350°C is reached.

10.1.6 Maintain a temperature of 350°C for at least 4 hours or overnight.

10.1.7 Allow the muffle furnace and melts to cool to room temperature.

10.1.8 Add 50 mL of Type I water to the cold beaker and heat on a hot plate at 90°C until the contents of the crucible are dislodged. Employ a stirring rod to accelerate this process.

10.1.9 Transfer the contents of the crucible and beaker to a 250 mL Erlenmyer flask.

10.1.10 Rinse the crucible with 5 mL of Type I water and transfer to the 250 mL Erlenmyer flask. Rinse the crucible again but with 12 mL of concentrated HCl acid. **Caution : The reaction is very vigorous.**

10.1.11 Repeat the rinsing with 30 mL of concentrated HCl and transfer to the Erlenmyer flask. Heat at 90°C for 1 hour.

10.1.12 While still hot, transfer the solution to a 100 mL volumetric flask. Allow the solution to cool to room temperature and fill to volume with Type I water.

10.1.13 Centrifuge 25 mL of sample at a speed of 3500 rpm for 10 minutes. All non-dissolved silicates will be settled at the bottom of the tube.

10.2 Instrument Calibration:

10.2.1 Prepare the manifold as shown in **Figure 02-2500:1.**

10.2.2 Set the conditions of operation as listed in **Table 02-2500:5**.

10.2.2 Connect the manifold to the spectrometer and light the plasma; allow the system to stabilize before optimization.

10.2.3 Set up the spectrometer data acquisition system to print intensity readings.

10.2.4 Optimization involves adjustment of the torch position and profile positioning of the primary slit to obtain maximum intensity signal to noise ratio.

10.2.5 Adjustment of the torch position involves running a mid level arsenic and selenium solution (verification standard) and adjusting the torch position to obtain maximum reading of the intensity. This is usually necessary only when the torch is

replaced; the solution is analysed daily to confirm that the intensity is within expected tolerances.

10.2.6 Profile positioning is the process of adjusting the primary slit in order to locate the "line peak", or the position where spectral light is centred on the secondary slits. The solution described in **Section 10.2.5** is read with each incremental adjustment of the primary slit dial. The maximum reading on the profile produced locates the dial position for the primary slit. Changes in "line peak" are due to changes in the system's ambient environment. Changes are usually very small because the optical chamber is insulated and stabilized by a constant temperature water bath.

10.2.7 Calibration is the process of adjusting system functions to produce output from a set of standards, and construction of calibration curves to relate the output to the known concentration of the elements contained within the standards. Unknowns can then be determined by referring the output from the sample to the calibration curve. The process also involves establishing the baseline zero, confirming the accuracy of the calibration standards, correcting for baseline drift and recalibrating when sensitivity drift is outside normal tolerances.

10.2.8 Establish that the baseline is stable by taking 5 readings of the baseline reagent. The relative standard deviation should be less than 2%.

10.2.9 Establish that the raw intensity readings are within expected levels by taking an additional reading of the verification standard.

10.2.10 Fill the appropriate sample tubes with the calibration standards and place them on the sample tray in accordance with the tray pattern scheme shown in **Table 02-2500:6**. Start the autosampler and initiate the spectrometer data capture system, which will then store the calibration standard data for later calculation.

10.3 Measurement:

10.3.1 Fill the remaining sample tubes with the unknown samples and quality control aliquots, place them on the sample tray in

accordance with the tray pattern scheme shown in **Table 02-2500:6,** and proceed with the analysis.

10.3.2 After completion of the analytical run, save all data files for later calculation of arsenic and selenium in the liquid unknowns.

10.3.3 Return all system components to non-operational status and transfer the raw data collected to ECOLIMS for data regression as described in **Section 11**.

11. Calculations

11.1 A second degree equation is generated by ECOLIMS from computerized curve fitting of the calibration standard data using regression analysis. The method uses a least-squares fitting, which is designed to minimize the sum of squares of the deviations of the actual data points from the second degree line of best fit . This line is described by equation $y = ax^2 + bx + c$, where a and b are coefficients of the curve and c is the y-intercept. The concentration of arsenic and selenium in the unknowns is determined in relationship to their respective line. The unknowns in the tray pattern are bracketed by calibration standards , usually in groups of 40 samples, and quantitation and recalibration is carried out at these intervals. The integrity of the calibration curve is assessed by evaluation of the control standard, calibration blank, and verification standard.

11.2 The concentration of metal in the sediment is calculated as follows:

$$M = \frac{C \times M}{W}$$

M = concentration of metal in sediment (mg/Kg)
C = concentration of metal in solution (mg/L)
V = volume of solution (digest)(L)
W = weight of sample(Kg)

12. Method Performance

12.1 The accuracy of the method is expressed as % Error (E) and is a measure of the bias from the expected value of a certified reference sample. It is defined by the following equation:

$$\% \ E = \frac{\text{measured value - certified value}}{\text{certified value}} \times 100$$

For accuracy data generated by this method refer to **Tables 02-2500: 7 and 02-2500:8.**

12.2 The recovery of added analytes, which is an indication of trueness, is defined as follows:

$$\text{Average recovery (\%)} = \frac{\text{mean recovered concentration}}{\text{true concentration}} \times 100$$

In a single laboratory (National Laboratory for Environmental Testing) the average recoveries of method analytes obtained from spiking a variety of natural waters are shown in **Tables 02-2500: 3** and **02-2500:4.**

12.3 Precision is expressed as the coefficient of variation (CV) and is defined by the following equation:

$$\text{CV (\%)} = \frac{\text{standard deviation}}{\text{mean concentration}} \times 100$$

12.4 For this method, the between run precision was calculated using two different reference samples and the within run precision was calculated from the differences between duplicates of natural samples. Refer to **Section 9.5**. The coefficients of variation, at specified levels of respective method analytes, obtained by a single laboratory (National Laboratory for Environmental Testing), are shown in **Tables 02-2500:3 and 02-2500:4**.

13. Reporting of Data

13.1 The following records of the analytical methods are maintained: analyst's daily quality control log, control charts, daily work book and instruments log.

13.2 Hard copies of analytical data, QA/QC data and report logs are maintained by NLET for 5 years from the date of analysis.

13.3 Magnetic copies of all data and associated QA/QC information are maintained permanently by NLET.

References

1 M. Stoepper (Editor), *Hazardous Metals in the Environment,* Elsevier Science, Amsterdam, 1992, Vol. 12, p. IX.

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4 R. Bock, *A Handbook of Decomposition Methods in Analytical Chemistry*, John Wiley and Sons, New York - Toronto, 1979, p. 101.

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6 P. D. Goulden, D. H. Anthony and K. D. Austen, *Anal. Chem.*, 53 (1981) 2027.

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8 A. E. Greenberg et al. (Editors), *Standard Methods for the Examination of Water and Wastewater,* 18th Edition, American Public Health Association, Washington, DC, 1992, Part 1000, pp. 1-6.

9 National Water Research Institute of Canada, 867 Lakeshore Road, Burlington, Ontario L7R 4A6.

10 The Canadian Association for Environmental Analytical Laboratories (CAEAL), Suite 532, 1 Nicolas Street, Ottawa, Ontario K1N 7B7.

APPENDIX A

Table 02-2500:1: Method Codes and Method Detection Limits for Arsenic and Selenium in Sediments

PARAMETER	ENVIRODAT CODE	ECOLIMS CODE	METHOD DETECTION LIMIT mg/Kg
ARSENIC	033052	A0524	0.2
SELENIUM	034052	A0525	0.2

Table 02-2500:2: Preparation of Calibration Standard Solutions for Arsenic and Selenium in Sediments.

Arsenic mg/L	Selenium mg/L	Volume of Intermediate(ISA) mL
0	0	0
.02	.001	.2
.05	.0025	.5
.1	.05	1
.2	.01	2
.5	0.025	5

Table 02-2500:3: Quality Control Data for Arsenic in Sediments

ALIQUOT TYPE	MEAN	STANDARD DEVIATION	COEFFICIENT OF VARIATION	UPPER CONTROL LIMIT	UPPER WARNING LIMIT	LOWER CONTROL LIMIT	LOWER WARNING LIMIT
REFERENCE SAMPLES	**mg/Kg**	**mg/Kg**	**%**	**mg/Kg**	**mg/Kg**	**mg/Kg**	**mg/Kg**
Low	10.7	.7	6.5	12.8	12.1	8.6	9.3
High	21.6	.9	4.2	24.3	23.4	18.9	19.8
DUPLICATES	**mg/Kg**	**mg/Kg**		**mg/Kg**	**mg/Kg**	**mg/Kg**	**mg/Kg**
Within Run (Difference)	.35	.39	-	1.53	1.14	-1.53	-1.14
SPIKES	**%**	**%**		**%**	**%**	**%**	**%**
Recovery	102.9	6.8	-	123	117	83	89

Table 02-2500:4: Quality Control Data for Selenium in Sediments

ALIQUOT TYPE	MEAN	STANDARD DEVIATION	COEFFICIENT OF VARIATION	UPPER CONTROL LIMIT	UPPER WARNING LIMIT	LOWER CONTROL LIMIT	LOWER WARNING LIMIT
REFERENCE SAMPLES	**mg/Kg**	**mg/Kg**	**%**	**mg/Kg**	**mg/Kg**	**mg/Kg**	**mg/Kg**
Low	.39	.06	15.4	.57	.51	.21	.27
High	1.02	.11	7.8	1.35	1.24	.80	.69
DUPLICATES	**mg/Kg**	**mg/Kg**		**mg/Kg**	**mg/Kg**	**mg/Kg**	**mg/Kg**
Within Run (Difference)	.102	.118	-	.456	.338	-.456	-.338
SPIKES	**%**	**%**		**%**	**%**	**%**	**%**
Recovery	93.9	8.6	-	120	111	68	77

Table 01-1050:5: Instrumental Operating Conditions for the Analysis of Arsenic and Selenium in Sediments

PARAMETERS	SETTINGS
Flow of argon:	
Before separator	0.12 Litre/min
After separator	0.22 Litre/min
Cooling gas	12.0 Litres/min
Plasma gas	0.12 Litre/min
Injector gas	0.34 Litre/min
Flow of air:	1.5 mL/min
ICP operating parameters:	
Forward power	1600 Watts
Reflected power	10 Watts
Pre-integration time	50 seconds
Integration time	30 seconds

Table 02-2500:6: Tray Pattern Scheme for the Analysis of Arsenic and Selenium in Sediments

Position #	Sample ID / Sample Type	Position #	Sample ID / Sample Type
1	Blank	41	Verification Standard
2	Standard 1	42-51	10 Samples
3	Standard 2	52	Blank
4	Standard 3	53	Calibration Blank
5	Standard 4	54	Verification Standard
6	Standard 5	55-64	10 Samples
7	Standard 6	65	Method Blank 2
8	Blank	66	Duplicate With-in 2
9	Control Standard	67	Reference 1B
10	Blank	68	Reference 2B
11-20	10 Samples	69	Spike2
21	Blank	70	Blank
22	Calibration Blank	71	Standard 1
23	Verification Standard	72	Standard 2
24-33	10 Samples	73	Standard 3
34	Method Blank1	74	Standard 4
35	Duplicate With-in 1	75	Standard 5
36	Reference 1A	76	Standard 6
37	Reference 2A	77	Blank
38	Spike1	78	
39	Blank	79	
40	Calibration Blank	80	

Table 02:2500:7 Arsenic and Selenium as Measured in the National Research Council Canada MESS-1, Estuarine Sediment Reference Material.

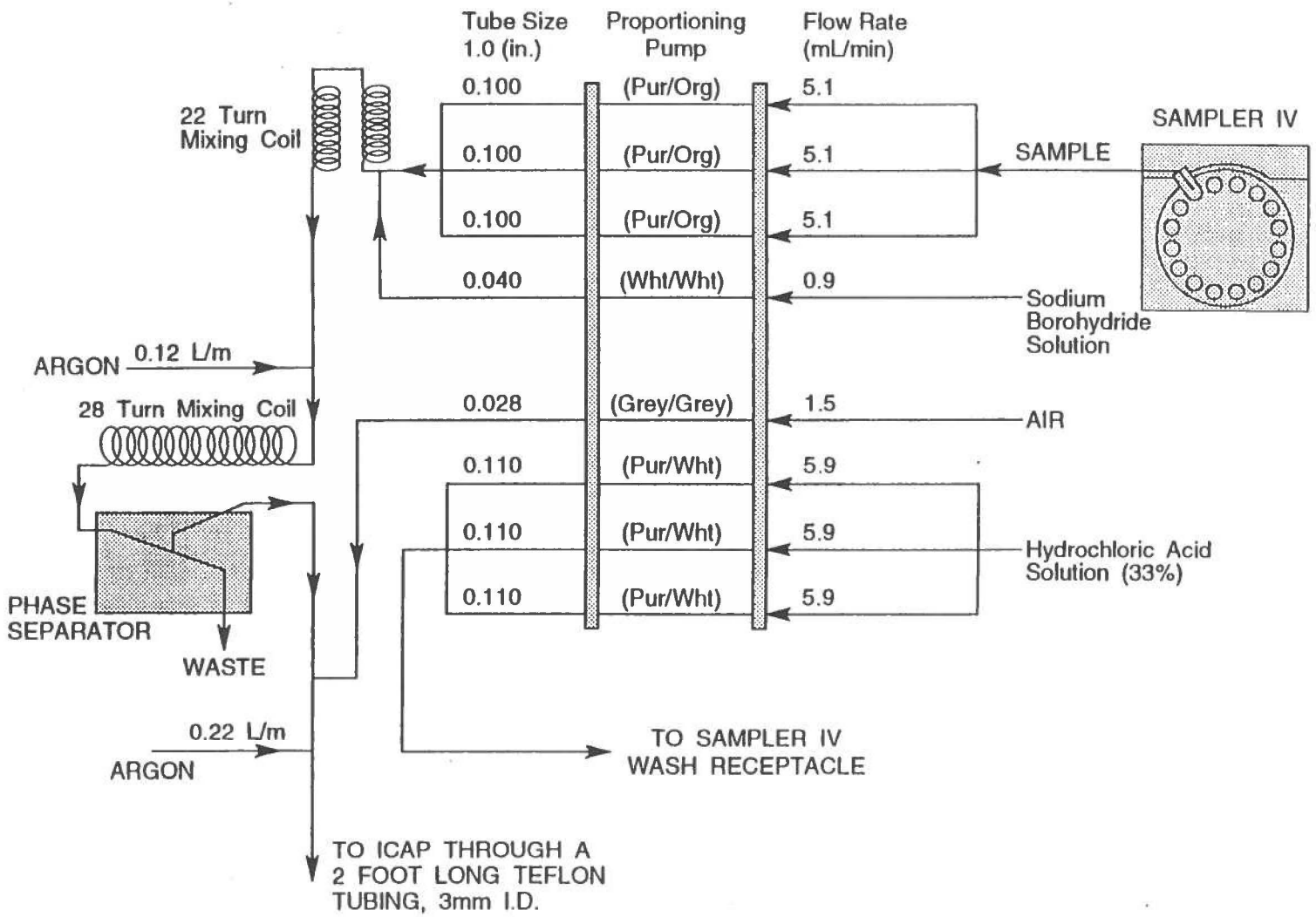
METAL	CERTIFIED VALUE mg/Kg	MEASURED VALUE mg/Kg	BIAS mg/Kg	% ERROR
Arsenic	10.6	10.7	0.1	0.9
Selenium	0.34	0.39	0.05	14.7

Table 02:2500:8 Arsenic and Selenium as Measured in National Institute of Standards and Technology 2704, River Sediment Reference Material.

METAL	CERTIFIED VALUE mg/Kg	MEASURED VALUE mg/Kg	BIAS mg/Kg	% ERROR
Arsenic	23.4	21.6	-1.8	-7.7
Selenium	1.1*	1.02	-.08	-7.3

* Tentative value

APPENDIX B



02-2500-26

FIGURE 02:2500:1: FLOW DIAGRAM FOR ARSENIC AND SELENIUM IN WATER

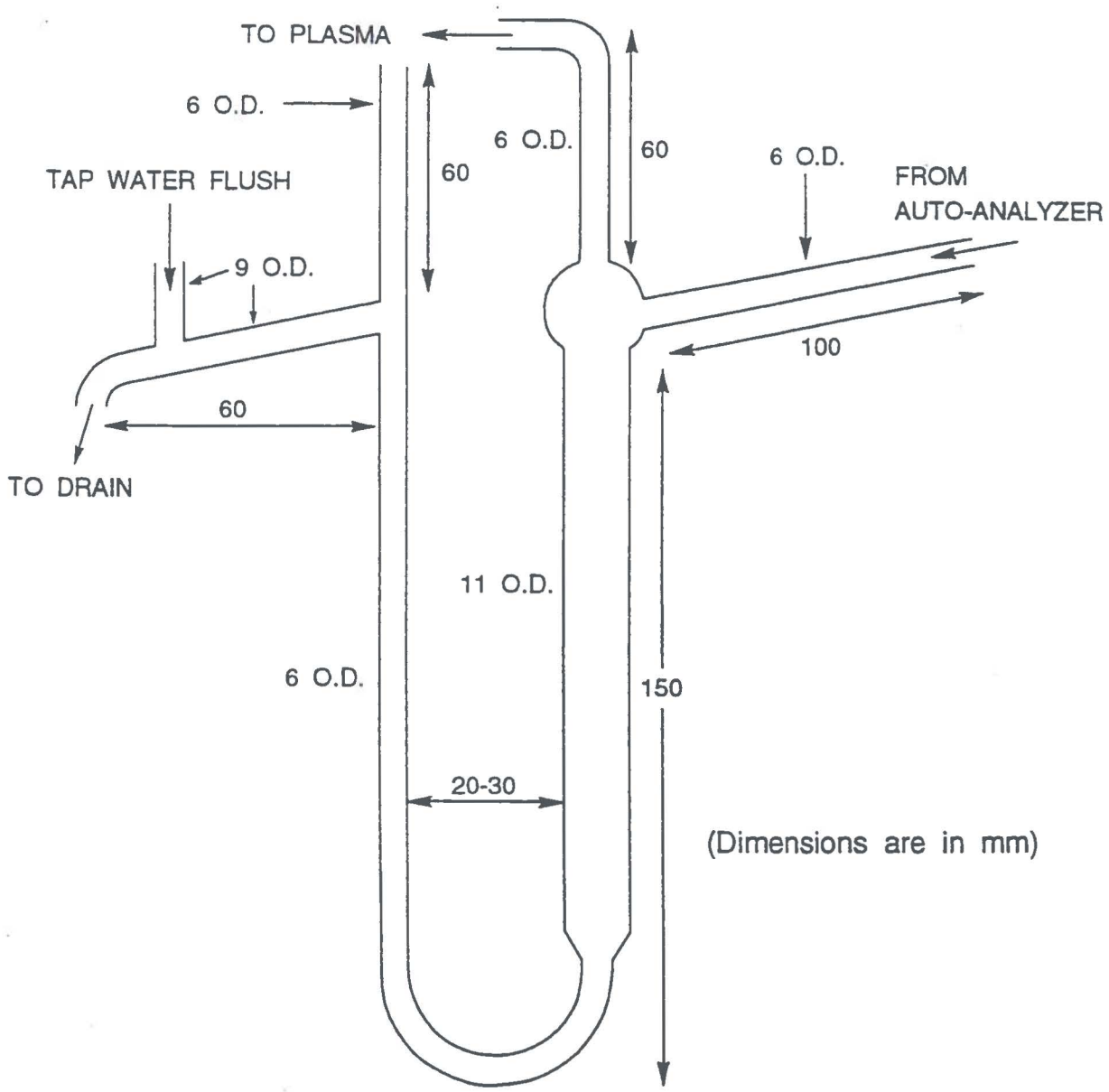


FIGURE 02-2751:2: PHASE SEPARATOR FOR ARSENIC AND SELENIUM IN SEDIMENT

13 POLYCHLOROBIPHÉNYLES (PCB), PESTICIDES ORGANOCHLORÉS ET HEXACHLOROBENZÈNE (HCB)

13.0 Généralités

Les polychlorobiphényles (PCB) sont produits synthétiquement par la chloration du biphényle. Les PCB sont des mélanges complexes d'isomères connus sous le nom commercial d'Aroclor 1221, 1232, 1242, 1248, 1254 et 1260; les deux derniers chiffres de ces nombres indiquent le pourcentage pondéral de chlore dans le mélange d'isomères (1). Leur résistance à la chaleur et leur grande stabilité en ont fait un produit de choix pour la fabrication de peintures, de vernis, de plastifiants, d'encres d'imprimerie, d'huiles de transformateur, etc..

La concentration des PCB, dans un environnement aquatique, est généralement beaucoup plus élevée dans les sédiments que dans les eaux qui les recouvrent. Les PCB ont une grande affinité pour les matières solides en suspension, surtout celles ayant de fortes teneurs en carbone organique (2).

La quantité maximale de PCB admise dans les matériaux de dragage a été fixée à 0,1 mg/kg de sédiments secs pour les projets d'immersion de déchets en mer (3).

Le terme "pesticides" regroupe une grande variété de composés organiques utilisés surtout en agriculture pour contrôler les infestations de toutes sortes. On regroupe ces composés en différentes classes dont les organochlorés. Les pesticides organochlorés se dégradent lentement dans le milieu naturel et se transforment en plusieurs composés homologues qui présentent généralement le même degré de toxicité que les composés dont ils sont issus.

Les PCB et les pesticides organochlorés, bien que différents par leur nature chimique, possèdent des caractéristiques physiques semblables et sont quantifiés par les mêmes méthodes d'analyse.

La quantité maximale de pesticides organochlorés totaux et d'hexachlorobenzène admise dans les matériaux de dragage a été fixée à 0,1 mg/kg de sédiments secs (3).

13.1 Méthode d'analyse (chromatographie en phase gazeuse - détecteur à capture d'électrons)

Les protocoles relatifs à la méthode utilisée pour l'analyse des PCB, des pesticides organochlorés et du HCB dans les sédiments figurent ci-dessous.

N°	PROTOCOLES
a	"Sols - Détermination de pesticides de type organochlorés. Extraction avec de l'hexane et purification avec florisil. Dosage par chromatographie en phase gazeuse". MENVIQ. n° 89.07/410 - P.Oc. 1.1
b	"Analyse des BPC dans les déchets industriels et les sols". MENVIQ, 1985
c	"Polychlorinated Biphenyls". Environnement Canada, Région du Pacifique et du Yukon, ver. 3.0, octobre 1990

13.2 Domaine d'application

Cette méthode permet le dosage des résidus de pesticides organochlorés, du HCB et des PCB énumérés au tableau 13-1.

TABLEAU 13-1 DOMAINE D'APPLICATION DE L'ANALYSE DES PCB, DES PESTICIDES ORGANOCHLORÉS ET DU HCB

COMPOSÉ	GAMME DE CONCENTRATIONS (mg/kg)
HCB	0,0002 - 0,02
Lindane	0,0002 - 0,02
Heptachlore	0,0004 - 0,04
Aldrine	0,0004 - 0,04
Époxyde d'heptachlore	0,0004 - 0,04
p,p-méthoxychlore	0,001 - 0,1
Dieldrine	0,0004 - 0,04
p,p' - DDE	0,0004 - 0,04
p,p' - DDD	0,0004 - 0,04
o,p - DDD	0,0004 - 0,04
p,p' - DDT	0,0004 - 0,04
o,p - DDT	0,0004 - 0,04
α - BHC	0,0002 - 0,02
β - BHC	0,0002 - 0,02
Cis - chlordane	0,001 - 0,1

TABLEAU 13-1 DOMAINE D'APPLICATION DE L'ANALYSE DES PCB, DES PESTICIDES ORGANOCHLORÉS ET DU HCB (fin)

COMPOSÉ	GAMME DE CONCENTRATIONS (mg/kg)
Trans - Chlordane	0,001 - 0,1
α - Endosulfan	0,001 - 0,1
β - Endosulfan	0,001 - 0,1
Endrine	0,0004 - 0,04
Mirex	0,001 - 0,1
Aroclor 1242	0,02 - 2,00
Aroclor 1254	0,02 - 2,00
Aroclor 1260	0,02 - 2,00

13.3 Principe et théorie

Les PCB et les pesticides organochlorés sont extraits des sédiments avec un mélange de solvants organiques appropriés. L'extrait obtenu est ensuite lavé à l'eau, concentré à l'aide d'un évaporateur rotatif, purifié et fractionné à l'aide d'une colonne d'adsorbant et de solvants de différentes polarités. Les fractions recueillies sont concentrées à faible volume et analysées en phase gazeuse à l'aide d'un chromatographe muni d'une colonne capillaire et d'un détecteur à capture d'électrons (4 et 5).

13.4 Fiabilité

13.4.1 Interférences.- Du soufre élémentaire ou des composés sulfurés réactifs se trouvent souvent dans les extraits de sédiments. Le soufre peut être éliminé en le faisant réagir avec du cuivre métallique en poudre ou avec du mercure.

Des impuretés provenant du matériel utilisé et des réactifs, peuvent être la cause d'interférences avec les composés étudiés. Des méthodes de nettoyage adéquates et l'emploi de réactifs purifiés permettent de réduire ces interférences.

Les plastiques tels le polyéthylène, le polypropylène et le chlorure de polyvinyle sont une autre source possible d'interférences et leur usage doit être proscrit. Il est

préférable d'éviter que des instruments de plastique entrent en contact avec l'échantillon de sédiments lors de son prélèvement, de son transfert, de son entreposage ou de son analyse.

D'autres résidus de pesticides et leurs produits de dégradation, ainsi que plusieurs autres composés organiques, peuvent interférer lors de l'analyse.

13.4.2 Seuil de détection.- Le seuil de détection a été fixé entre 0,0002 mg/kg et 0,001 mg/kg pour l'ensemble des pesticides organochlorés, à 0,02 mg/kg pour les PCB et à 0,0002 mg/kg pour le HCB, lorsqu'on effectue l'extraction sur une portion de 10 à 15 g d'échantillon.

13.4.3 Exactitude et précision de la méthode.- Aucune donnée statistique n'est disponible.

13.5 Prélèvement et conservation

Les échantillons de sédiments destinés au dosage des PCB, des pesticides organochlorés et du HCB doivent être recueillis dans des contenants de métal ou de verre.

S'ils ne sont pas analysés dans un délai de 48 heures, les échantillons doivent être conservés à –20 °C, à l'abri de la lumière, pendant une période maximale de 6 mois à compter de la date du prélèvement.

13.6 Préparation des échantillons

Les échantillons de sédiments que reçoivent les laboratoires contiennent généralement beaucoup d'eau libre. Il est important d'éliminer cette eau sans entraîner de particules de sédiments. Le surnageant est retiré par décantation et les échantillons sont homogénéisés de la façon décrite à la section 2.1.

13.7 Contrôle de la qualité

Des mesures de contrôle de la qualité doivent être appliquées lors de l'analyse des PCB, des pesticides organochlorés et du HCB dans les sédiments. Ces mesures sont de trois ordres et sont décrites aux sections 13.7.1 à 13.7.3.

13.7.1 Mesures d'ordre général

La pureté de chaque nouveau lot de solvants utilisés doit être vérifiée en injectant ceux-ci dans le chromatographe, après concentration d'un volume approprié. Les valeurs obtenues ne doivent pas dépasser le seuil de détection.

La capacité d'élution des colonnes de purification doit être vérifiée en éluant un mélange d'étalons d'Aroclor et de pesticides. La quantité d'éluant et/ou la quantité d'adsorbant dans la colonne doivent être réajustées si la séparation désirée n'est pas adéquate ou si le total de la récupération de chaque composé n'atteint pas 90 p. 100.

Des étalons frais doivent être préparés tous les 6 mois. Ces étalons doivent être comparés à ceux que l'on désire remplacer, afin de déceler toute détérioration dans la qualité des anciens étalons et d'erreur dans la préparation de nouveaux.

13.7.2 Validation de la performance du chromatographe

La reproductibilité des appareils doit être vérifiée en injectant plusieurs fois la même quantité d'un étalon. La variation du facteur de réponse ne doit pas dépasser 10 p. 100.

Le domaine de linéarité doit être vérifié périodiquement.

Un étalon de chacun des pesticides organochlorés, de chaque Aroclor et de HCB doit être injecté toutes les 5 analyses ou pour chaque série d'analyses si le nombre de ces dernières est inférieur à 5.

La concentration des étalons doit être du même ordre de grandeur que celle des échantillons pour obtenir une bonne quantification.

La performance du chromatographe doit être vérifiée périodiquement en analysant un mélange contenant tous les composés organochlorés énumérés au tableau

13-1, à l'exception des Aroclor, à une concentration proche de la limite de détection. Il faut aussi vérifier la séparation des BPC en analysant individuellement les différents Aroclor.

13.7.3 Vérification de la performance

Tous les 10 échantillons et/ou pour chaque série de moins de 10 échantillons, il faut effectuer une analyse d'un blanc de méthode et une analyse par ajout dosé.

Un échantillon doit être analysé en duplicata tous les 20 échantillons et/ou pour chaque lot de moins de 20 échantillons.

Un matériau de référence certifié doit être analysé tous les 20 échantillons et/ou pour chaque lot de moins de 20 échantillons. Le tableau 13-2 donne, à titre de suggestion, quelques-uns de ces matériaux ainsi que le nom de leur fournisseur.

TABLEAU 13-2 MATÉRIAUX DE RÉFÉRENCE CERTIFIÉS POUR L'ANALYSE DES PCB, HCB ET PESTICIDES ORGANOCHLORÉS

IDENTIFICATION DES SÉDIMENTS	COMPOSÉS CERTIFIÉS	FOURNISSEUR
Sédiments de rivage marin CS-1	PCB	CNRC
Sédiments portuaire HS-1	PCB (Aroclor 1254) les 10 isomères des PCB	CNRC
Sédiments portuaire HS-2	PCB (Aroclor 1254) les 10 isomères des PCB	CNRC
Sédiments de lacs EC-2	Composés organochlorés PCB, chlorobenzènes	CCEI

CNRC = Conseil national de recherche du Canada
CCEI = Centre Canadien des eaux intérieures
Les adresses des fournisseurs sont données au chapitre 3 du guide.

13.8 Calcul et expression des résultats

13.8.1 Dosage des pesticides et du HCB

Les teneurs en pesticides organochlorés et en HCB dans les sédiments sont exprimées en mg/kg de sédiments secs. Ces teneurs sont déterminées en comparant les aires des pics des composés trouvés dans les échantillons à celles des étalons et

sont calculées à l'aide de la formule 13.1. Cette formule suppose que l'on injecte un volume identique de solution dans le chromatographe pour l'étalon et pour l'extrait d'échantillon.

Le seuil de détection doit être rapportée lorsqu'un composé n'est pas détecté. Il est à noter que la mention "ND" (non-détecté) dans le rapport ne peut être acceptée.

$$C_x = \frac{A_{éch} \times C_{ét} \times V_{ext}}{A_{ét} \times P_{éch}} \times \frac{100}{100 - \% \, hum} \qquad (13.1)$$

où

C_x = Concentration du composé *x* dans l'échantillon de sédiments calculée sur une base sèche (mg/kg);

$A_{éch}$ = Aire du pic du composé *x* dans l'extrait d'échantillon;

$A_{ét}$ = Aire du pic du composé *x* dans la solution étalon;

$C_{ét}$ = Concentration du composé *x* dans la solution étalon (µg/mL);

V_{ext} = Volume de l'extrait final (mL);

$P_{éch}$ = Poids de la portion d'échantillon humide extraite (g);

% hum = Pourcentage d'humidité calculé à partir d'une autre portion d'échantillon, selon la procédure décrite au chapitre 4.

13.8.2 Dosage des PCB

La quantification est effectuée habituellement en utilisant la procédure de la "somme totale des surfaces sous les pics" décrite à la référence 6, et à l'aide de la formule 13.2. Il faut noter cependant une exception lorsque l'échantillon contient plus d'un Aroclor. Il faut alors inclure à la somme correspondant à un Aroclor donné uniquement les pics qui ne peuvent être assignés qu'à cet Aroclor.

$$C_x = \frac{A_{T_{éch}} \times C_{ét} \times V_{ext}}{A_{T_{ét}} \times P_{éch}} \times \frac{100}{100 - \% \, hum} \qquad (13.2)$$

où

C_x = Concentration de l'Aroclor *x* dans l'échantillon de sédiments calculée sur une base sèche (mg/kg); où *x* = 1221, 1232, 1242, 1248, 1254 ou 1260.

$A_{Téch}$ = Somme des aires des pics choisis pour la quantification de l'Aroclor *x* dans l'extrait d'échantillon;

$A_{Tét}$ = Somme des aires des pics choisis correspondant à ceux de l'échantillon pour la solution étalon de l'Aroclor *x*;

$C_{ét}$ = Concentration de l'Aroclor *x* dans la solution étalon (µg/mL);

V_{ext} = Volume de l'extrait final (mL);

$P_{éch}$ = Poids de la portion d'échantillon humide utilisé pour effectuer l'extraction (g);

% hum = Pourcentage d'humidité calculé à partir d'une autre portion d'échantillon, selon la procédure décrite au chapitre 4.

La quantification doit se faire avec une solution étalon dont la concentration se rapproche de celle de l'extrait d'échantillon. Par exemple, pour un échantillon inconnu dont la concentration serait inférieure à 0,25 µg/mL, une solution étalon de 0,1 µg/mL serait adéquate pour la doser et, pour une concentration supérieure à 0,25 µg/mL, une solution étalon de 1,0 µg/mL pourrait être utilisée si le domaine de linéarité du détecteur le permet.

Si la distribution des pics d'un échantillon ne correspond pas à celle d'un Aroclor connu, ou si on est en présence de concentrations élevées de plusieurs Aroclor qui se superposent, il est suggéré d'utiliser la méthode de quantification de Webb & McCall (7).

Pour ce faire il faut derminer les temps de rétention relatif (TRR) au p,p'-DDE des différents pics de chacun des Aroclor et ensuite faire le choix des bons étalons de comparaison à l'aide du schéma décisionnel de la figure 13-1. Nous pouvons alors effectuer le calcul de la concentration par la même formule que celle utilisée pour quantifier les Aroclor (formule 13.2).

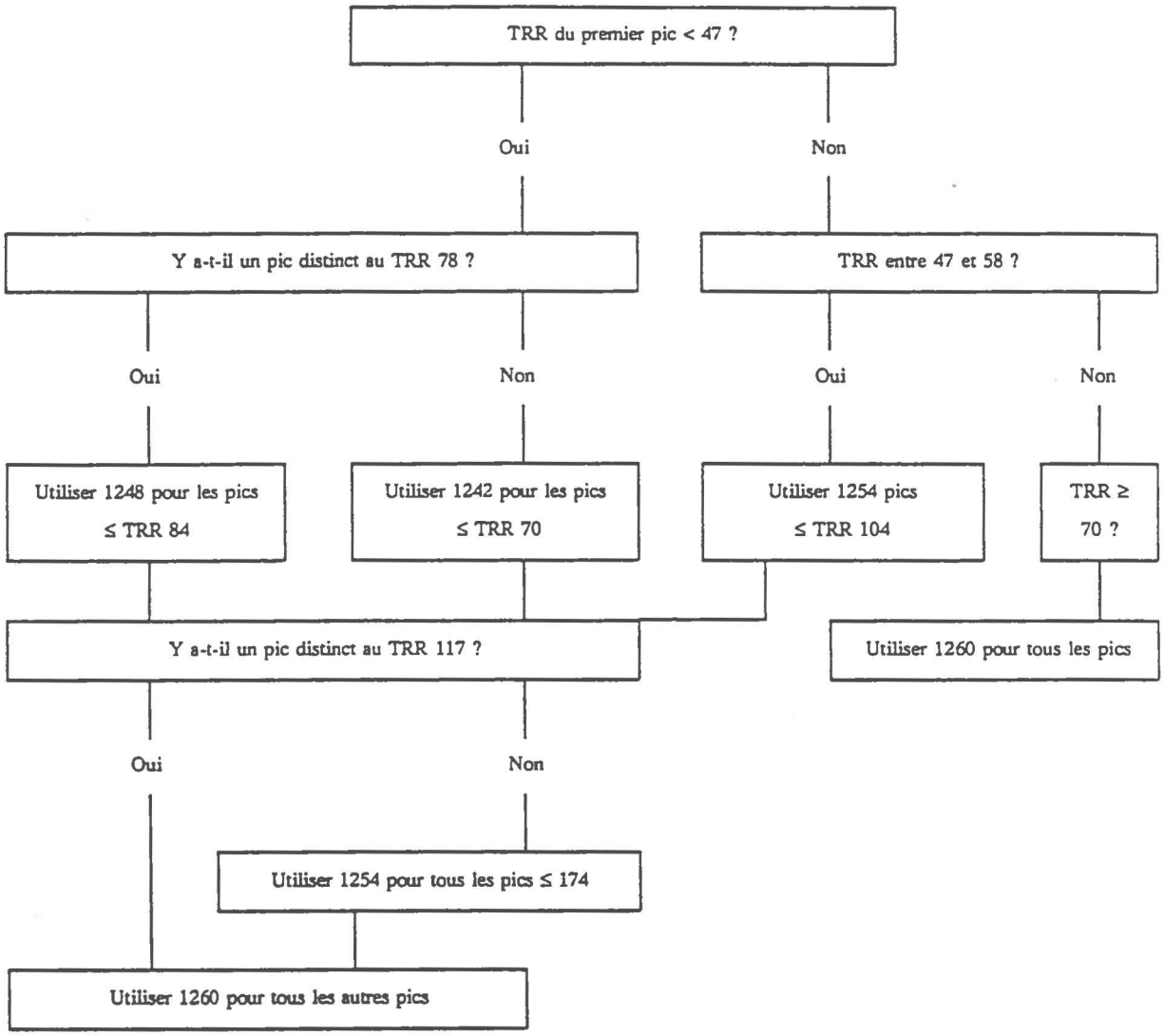


FIGURE 13-1 SCHÉMA DÉCISIONNEL POUR LES CALCULS D'AROCLOR SELON LA MÉTHODE DE WEBB AND McCALL

La teneur en BPC totaux s'obtient en effectuant la somme des teneurs en Aroclor de l'échantillon.

En ce qui concerne les résultats de BPC totaux qui doivent être rapportés en vertu de la Loi canadienne sur la protection de l'environnement (LCPE), ils ne doivent pas inclure la teneur en chlorobiphényles possédant 1 ou 2 atomes de chlore. Ce résultat est

obtenu en utilisant les facteurs de correction indiqués au tableau 13-3 pour chaque Aroclor identifié dans l'échantillon. Ces facteurs de correction sont dérivés des poids moyens exprimés en pourcentage, que représentent les groupes de congénères composant chaque Aroclor (6).

TABLEAU 13-3 FACTEURS DE CORRECTION POUR LE CALCUL DES BPC TOTAUX EN VERTU DE LA LCPE (6)

Aroclor 1221	multiplier par 0,038
Aroclor 1232	multiplier par 0,394
Aroclor 1016	multiplier par 0,793
Aroclor 1242	multiplier par 0,811
Aroclor 1248	pas de correction
Aroclor 1254	pas de correction
Aroclor 1260	pas de correction

RÉFÉRENCES

1) "Biphényles polychlorés", Nicole Goyer, ministère de l'Environnement du Québec, Bureau d'étude sur les substances toxiques, 1980, pages 6-7

2) "Recommandations pour la qualité des eaux au Canada", Groupe de travail sur les recommandations pour la qualité des eaux, Conseil canadien des ministres des ressources et de l'environnement, 1987, pages 6-144 à 6-147 et 6-176 à 6-201

3) "Limites des substances réglementées par l'annexe I de la loi sur l'immersion de déchets en mer - Aperçu général - Immersion de déchets en mer - Rapport n° 3 F", Swiss J.J., Addison R.F., Meleese D.W., Payne J.F., Pêches et Océans Canada, 1982, pages 13 à 23

4) "Détermination des biphényles polychlorés - Extraction solide-liquide et purification avec C-18, Si, Cu-Dosage par chromatographie gazeuse", ministère de l'Environnement du Québec, 1989, méthode n° 89.11/405 - BPC 1.5

5) "Sols - Détermination de pesticides de type organochlorés - Extraction avec l'hexane et purification avec Florisil - Dosage par chromatographie gazeuse", ministère de l'Environnement du Québec, 1989, méthode n° 89.07/410 - P.Oc 1.1

6) "Polychlorinated Biphenyls". Environnement Canada, région du Pacifique et du Yukon, ver. 3.0, octobre 1990

7) "Quantitative PCB Standards for Electron Capture Gas Chromatography, R.G. Webb et A.C. McCall, 1973, J. Chrom. Sci., vol. 11, pages 366 à 373.

15 HYDROCARBURES AROMATIQUES POLYCYCLIQUES (HAP)

15.0 Généralités

Les hydrocarbures aromatiques polycycliques (HAP) sont des composés formés par combustion incomplète ou inefficace de matières organiques, par diagenèse ou biosynthèse. Les HAP peuvent être d'origine naturelle (feux de forêts, activités volcaniques, diagenèse etc.) ou d'origine anthropique (centrales thermiques, moteurs à explosion, etc.). Ce sont des composés constitués de deux ou de plusieurs noyaux benzéniques adjacents se partageant au moins deux atomes de carbone.

Les concentrations de HAP dans les sédiments des écosystèmes aquatiques sont généralement élevées. Elles sont moyennes dans les organismes aquatiques et faibles dans l'eau. Étant donné leur faible solubilité dans l'eau et leur nature hydrophobe, les HAP sont plus susceptibles de s'associer à la matière organique et inorganique des sédiments en suspension et des sédiments de fond que de demeurer en solution dans l'eau.

Dans le cas où des sédiments sont analysés dans le cadre du programme d'immersion de déchets en mer, les résultats d'analyse des hydrocarbures aromatiques polycycliques doivent être rapportés en deux groupes : les HAP à faible poids moléculaire (2 et 3 noyaux benzéniques) et les HAP à poids moléculaire élevé (plus de 3 noyaux benzéniques). Mentionnons que, en vertu de ce programme, les teneurs maximales permises actuellement dans les sédiments sont les suivantes : 2,5 mg/kg pour les HAP totaux à faible poids moléculaire et 50 mg/kg pour les HAP à poids moléculaire élevé (1).

Les deux méthodes d'analyse proposées pour quantifier les HAP dans les sédiments emploient la chromatographie en phase gazeuse couplée à la spectrométrie de masse (CPG/SM). Cette technique a été retenue pour améliorer la sélectivité du dosage des HAP car, suite aux traitements effectués sur les échantillons, une quantité importante de coextractants demeure présente dans l'extrait purifié.

15.1 Analyse des HAP (chromatographie en phase gazeuse - spectrométrie de masse)

Les protocoles relatifs à la méthode utilisée pour l'analyse des HAP dans les sédiments figurent ci-dessous.

N°	PROTOCOLES
a	"Methodology for organic analysis - NITEP/Québec combustion tests", Division de la chimie, Centre de technologie environnementale de River Road, Conservation et Protection, Environnement Canada, 1987*
b	"Test Methods for Evaluating Solid Waste - Physical and Chemical Methods", USA Environmental Protection Agency, 1986, méthode n° 8270*

* Utiliser 10 à 30 grammes d'échantillon

15.2 Domaine d'application

Cette méthode permet de séparer, identifier et quantifier les HAP énumérés aux tableaux 15-1 et 15-2.

15.3 Principe et théorie

Avant l'extraction des HAP, l'échantillon de sédiments est d'abord enrichi de HAP marqués avec des isotopes, puis il est mélangé avec du sulfate de sodium. Par la suite, on effectue une extraction des substances organiques avec un solvant approprié (p. ex. du dichlorométhane) dans un extracteur de type "Soxhlet" ou par agitation ultrasonique.

L'extrait est séché et concentré. Il est ensuite purifié à l'aide d'une colonne d'adsorbant (p. ex. du gel de silice) pour enlever les coextractants. Le volume de l'éluat qui contient les HAP est finalement réduit par une procédure appropriée (p. ex. à l'aide d'un évaporateur rotatif) et une quantité connue d'un HAP marqué avec des isotopes lui est ajoutée pour corriger la variation obtenue lors des injections dans l'appareil d'analyse.

TABLEAU 15-1 DOMAINE D'APPLICATION DE L'ANALYSE DES HAP (LISTE 1)

Composé	Gamme de concentration (1) (mg/kg)
Naphtalène	0,03 à 2,50
Acénaphtylène	0,03 à 2,50
Acénaphtène	0,03 à 2,50
Fluorène	0,03 à 2,50
Phénanthrène	0,03 à 2,50
Anthracène	0,03 à 2,50
Fluoranthène	0,03 à 2,50
Pyrène	0,03 à 2,50
Benzo(a)anthracène	0,03 à 2,50
Chrysène	0,03 à 2,50
Benzo(b)fluoranthène et benzo(j)fluoranthène	0,03 à 2,50
7,12-diméthylbenz(a)anthracène	0,03 à 2,50
Benzo(k)fluoranthène	0,03 à 2,50
Benzo(e)pyrène	0,03 à 2,50
Benzo(a)pyrène	0,03 à 2,50
3-méthylcholanthrène	0,03 à 2,50
Indéno(1,2,3-cd)pyrène	0,03 à 2,50
Dibenzo(a,h)anthracène	0,03 à 2,50
Benzo (g,h,i)périylène	0,03 à 2,50
Dibenzo(a,e)pyrène	0,05 à 2,50
Dibenzo(a,h)pyrène	0,05 à 2,50
Dibenzo(a,i)pyrène	0,05 à 2,50
Dibenzo(a,j)acridine[2]	
7H-Dibenzo(c,g)carbazole[2]	
5-méthylchrysène	

(1) Les domaines d'application sont estimés en fonction de la sensibilité des instruments et du facteur de concentration de l'échantillon. Ces domaines s'appliquent aux sédiments et sont basés sur l'analyse d'un extrait provenant de 10 g d'échantillon (poids sec), et dont le volume final, avant l'analyse, est de 5 ml.

(2) Composés aromatiques polycycliques ayant un ou des atomes de N, S ou O.

TABLEAU 15-2 LISTE DES HAP QUI DOIVENT ÊTRE ANALYSÉS LORS D'UN PROGRAMME D'IMMERSION DE DÉCHETS EN MER (LISTE 2)

TYPE	COMPOSÉ	ABRÉVIATION
1	Naphtalène	NAP
	Acénaphthylène	ACY
	Fluorène	FLU
	Acénaphthène	ACE
	Phénanthrène	PHE
	Anthracène	ANT
2	Fluoranthène	FLA
	Pyrène	PYR
	Benzo (a) anthracène	BAN
	Chrysène	CRY
	*Benzo (b) fluoranthène+	BBF
	*Benzo (k) fluoranthène	BKF
	Benzo (a) pyrène	BAP
	**Indéno (1,2,3-cd) pyrène +	IND
	**Dibenzo (a,h) anthracène	DBA
	Benzo (g,h,i) pérylène	BGP

Type 1 : HAP à faible poids moléculaire
Type 2 : HAP à poids moléculaire élevé

* Les pics correspondant à ces composés peuvent ne pas être complètement résolus par chromatographie en phase gazeuse, il est donc acceptable de rapporter la somme des teneurs en BBF et BKF.

** Les pics correspondant à ces composés peuvent ne pas être complètement résolus par chromatographie en phase gazeuse, il est donc acceptable de rapporter la somme des teneurs en IND et DBA.

Les HAP sont séparés et analysés par chromatographie en phase gazeuse à l'aide d'une colonne capillaire couplée à un spectromètre de masse à basse résolution (LRMS). Le spectromètre de masse peut être opéré dans le mode acquisition de spectre (SCAN) ou dans le mode fragmentométrie de masse (SIM), selon la sensibilité recherchée. L'analyse doit être effectuée avec un minimum de deux ions caractéristiques choisis dans le spectre de chaque analyte. La présence de l'analyte est confirmée lorsque les ions cibles sont présents dans le bon rapport isotopique et pour un bon temps de rétention.

La purification de l'extrait organique à l'aide d'une colonne de gel de silice suffit généralement à éliminer une partie importante des substances coextractibles pour que l'analyse par CPG/SM soit adéquate.

Ainsi le mode acquisition de spectre (SCAN) permet d'atteindre un seuil de détection de 2 µg par composé injecté dans le chromatographe. Ce seuil est supérieur

aux exigences de la loi. Toutefois, le mode fragmentométrie de masse (SIM) permet de détecter 100 pg de chacun des composés et devra être employé pour atteindre le seuil de détection requis pour vérifier la conformité à la Loi canadienne sur la protection de l'environnement.

15.4 Fiabilité

15.4.1 Interférences. - Les interférences peuvent provenir des solvants, des réactifs et de la verrerie. L'utilisation de solvants et de réactifs de grande pureté et des méthodes de nettoyage adéquates permettent de les réduire.

Des interférences peuvent aussi être attribuées à des substances coextractibles présentes dans la matrice des sédiments. L'importance de ce type d'interférences varie d'un échantillon de sédiments à un autre. La purification de l'extrait organique à l'aide d'une colonne de gel de silice suffit généralement à éliminer une partie importante des substances coextractibles pour que l'analyse par CPG/SM soit adéquate.

15.4.2 Seuil de détection. - La méthode d'analyse acceptable pour les projets de vérification de conformité à la partie VI de la Loi canadienne sur la protection de l'environnement doit avoir un seuil de détection confirmé d'au moins 0,1 mg/kg pour chaque composé mesuré.

15.4.3 Exactitude et précision de la méthode.- Aucune donnée statistique n'est disponible.

15.5 Prélèvement et conservation

Les échantillons de sédiments destinés à l'analyse des HAP doivent être conservés dans des contenants de métal ou de verre, à l'obscurité et à environ – 20 °C. Le délai entre le prélèvement de l'échantillon et son analyse ne doit pas excéder 6 mois.

15.6 Préparation des échantillons

Les échantillons de sédiments que reçoivent les laboratoires, contiennent généralement beaucoup d'eau libre. Il faut éliminer cette eau sans entraîner de particules de sédiments avant de traiter l'échantillon. L'eau surnageante est donc retirée par décantation et les échantillons sont homogénéisés de la façon décrite à la section 2.1.

La suite du traitement de l'échantillon sera effectuée sur une portion humide de sédiments homogénéisés.

15.7 Contrôle de la qualité

15.7.1 Validations à effectuer

15.7.1.1 Validation de la méthode. - La documentation sur la validation complète de tous les aspects de la méthode utilisée doit être disponible, maintenue à jour et fournie à l'autorité scientifique sur demande.

Cette validation doit comporter un estimé de la performance de la méthode, c'est-à-dire de la précision et de l'exactitude des mesures des composés analysés. De plus, des données de récupération concernant l'analyse des échantillons enrichis par des composés naturels ou des composés marqués avec des isotopes doivent faire partie de la documentation servant à la validation de la méthode. Ces données doivent être générées pour des niveaux d'enrichissement situés près des limites de détection et près des limites supérieures de quantification de l'appareil. On procédera à la validation de la méthode, de la performance du chromatographe, ainsi qu'à la validation de l'identification et de la quantification des composés.

15.7.1.2 Validation de la performance du chromatographe. - La séparation des composés d'intérêt doit répondre aux critères suivants : la séparation de la paire phénanthrène/anthracène doit produire un vallon inférieur à 1 p. 100 du plus grand pic de la paire et celle de la paire benzo(a)anthracène/chrysène un vallon inférieur à 25 p. 100 du plus grand pic de cette paire. Cette information doit être rapportée sous

forme de tableau pour les étalons et les matériaux de référence qui accompagnent chaque lot d'échantillons.

15.7.1.3 Validation de l'identification des composés au spectromètre de masse. -Si les échantillons sont analysés au SM dans le mode SIM, les informations suivantes devront être fournies : 1°) la masse des ions choisis pour l'analyse de chaque composé; 2°) l'intensité des signaux obtenus pour chacun de ces ions; 3°) le rapport entre l'intensité des signaux de ces ions; 4°) l'écart toléré entre ce rapport et la valeur théorique qui sert à déterminer si le composé est présent ou absent de l'échantillon; 5°) la quantité minimale requise pour obtenir une identification positive.

Si, par contre, les échantillons sont analysés dans le mode SCAN, la corrélation obtenue après recherche informatique dans une banque de données de spectres de masse, ainsi que la quantité minimale requise pour une identification positive devront être indiquées pour chacun des composés recherchés.

15.7.1.4 Validation de la quantification des composés par spectrométrie de masse. - Cette validation est faite par l'analyse des solutions diluées en série d'un mélange contenant les composants présentant de l'intérêt. Les données recueillies doivent permettre de déterminer le seuil de détection, le domaine de quantification, le domaine de linéarité et le facteur de réponse correspondant à chacun des composés que l'on veut analyser.

15.7.2 Étalonnage et quantification.

a) Critères d'opération dans le mode SCAN

- Atteindre un seuil de détection de 0,1 µg/g, ou mieux, pour chacun des composés d'intérêt;
- Effectuer la collecte des données sur l'abondance des ions dont les masses sont comprises entre 50 et 400 amu;
- Identifier le ou les ions de quantification (un à trois ions);

- Établir une courbe d'étalonnage avec au moins deux points, ne comprenant pas le point d'origine, pour chacun des composés d'intérêt;
- Utiliser des composés marqués avec des isotopes pour enrichir l'aliquot analysé (méthode des ajouts dosés) et obtenir des données de récupération pour chacun des échantillons. Compiler les résultats de récupération sous forme de tableau en indiquant les composés utilisés, la quantité utilisée pour enrichir l'aliquot et la récupération obtenue. Ne pas rapporter les résultats d'analyse corrigés en fonction des pourcentages de récupération.

b) Critères d'opération dans le mode SIM.

- Atteindre un seuil de détection de 0,01 µg/g, ou mieux, pour chacun des composés d'intérêt;
- Faire l'acquisition des données pour trois ions de chacun des composés d'intérêt. Un tableau qui présente la liste des ions choisis regroupés pour chacun des composés d'intérêt, leur abondance relative théorique et observée aux instruments doit être compilé;
- Identifier le ou les ions utilisés pour quantifier les composés d'intérêt présents dans les échantillons;
- Quantifier les composés d'intérêt à l'aide d'une courbe d'étalonnage à plusieurs points, établie pour chacun des composés d'intérêt, avec un minimum de deux points, à l'exclusion du point d'origine;
- Utiliser des composés marqués avec des isotopes pour enrichir l'aliquot analysé (méthode des ajouts dosés) et obtenir des données de récupération pour chacun des échantillons. Compiler les résultats de récupération sous forme de tableau en indiquant les composés utilisés, la quantité utilisée pour enrichir l'aliquot et la récupération obtenue. Ne pas rapporter les résultats d'analyse corrigés en fonction des pourcentages de récupération.

15.7.3 Vérification de la performance. - Le laboratoire des entrepreneurs doit appliquer un programme interne d'assurance de la qualité. Il doit :

a) Analyser un blanc de méthode tous les 10 échantillons et/ou pour chaque série de moins de 10 échantillons.

b) Analyser en duplicata de 15 à 20 p. 100 des échantillons de sédiments. Si le nombre d'échantillons du lot est inférieur à 5, il doit analyser en duplicata au moins un échantillon

c) Analyser au moins un matériau de référence par série d'échantillons. Ces matériaux peuvent être obtenus au CNRC sous le nom de HS-3, HS-4, HS-5 ou HS-6. Les seuls substituts acceptables sont les matériaux de référence du CCEI suivants : EC-1, EC-2, EC-3, EC-4, EC-5, EC-6 et/ou EC-7. La teneur en HAP des matériaux choisis doit être du même ordre de grandeur que celle des échantillons à analyser.

d) Conserver toute la documentation ayant rapport aux analyses des échantillons ainsi qu'aux procédures de contrôle de la qualité pour vérification éventuelle par l'autorité scientifique.

TABLEAU 15-3 MATÉRIAUX DE RÉFÉRENCE CERTIFIÉS POUR L'ANALYSE DES HAP

IDENTIFICATION DES SÉDIMENTS	FOURNISSEUR
Sédiments portuaires HS-3	CNRC
Sédiments portuaires HS-4	CNRC
Sédiments portuaires HS-5	CNRC
Sédiments portuaires HS-6	CNRC
Sédiments EC-1, EC-2, EC-3, EC-4, EC-5, EC-6 et EC-7	CCEI

CCEI : Centre canadien des eaux intérieures
CNRC : Conseil National de Recherche du Canada
Voir l'adresse du fournisseur au chapitre 3.

15.1.8 Calcul et expression des résultats. - Les teneurs en HAP des sédiments sont exprimées en mg/kg de sédiments secs. Elles sont calculées à l'aide des formules 15.1 et 15.2. Le rapport doit indiquer les résultats obtenus pour chaque HAP identifié au tableau 15-1. Dans le cas des projets d'immersion de déchets en mer, on doit rapporter le résultat obtenu pour chaque HAP identifié au tableau 15-2 et le total des HAP de poids

moléculaire faible et élevé. Le seuil de détection doit être rapportée lorsqu'un composé n'est pas détecté. Il est à noter que la mention "ND" (non-détecté) dans le rapport ne peut être acceptée.

$$FR_x = \frac{C_{ét}}{A_{ét}} \times V_{étinj} \qquad (15.1)$$

FR_x = Facteur de réponse de l'étalon *x*;

$A_{ét}$ = Aire du pic produit par l'ion de quantification de l'étalon *x*;

$C_{ét}$ = Concentration de l'étalon (µg/mL);

$V_{étinj}$ = Volume de solution étalon injectée (µL).

$$C_x = A_{éch} \times FR_x \times \frac{V_{ext}}{P_{éch}} \times \frac{1}{V_{extinj}} \times \frac{100}{100 - \% hum} \qquad (15.2)$$

où

C_x = Concentration de l'HAP *x* dans l'échantillon de sédiments, calculée sur une base sèche (mg/kg);

$A_{éch}$ = Aire du pic produit par l'ion de quantification du HAP *x* dans l'échantillon;

FR_x = Facteur de réponse de l'étalon *x*;

V_{ext} = Volume de l'extrait final (mL);

$P_{éch}$ = Poids de la portion d'échantillon humide extraite (g);

V_{extinj} = Volume de l'extrait final injecté (µL);

% hum = Pourcentage d'humidité calculé à partir d'une autre portion d'échantillon selon la procédure décrite au chapitre 4.

RÉFÉRENCES

1) "Interim Contaminant Testing Guidelines for Ocean Disposal", Environnement Canada, Conservation et protection, Région du Pacifique et du Yukon, février 1990, page 3

2) "Tests Methods for Evaluating Solid Waste - Physical and Chemical Methods", USA Environmental Agency, 1986, méthode n° 8270

3) "Quality Assurance Guidelines for Contract Determination of Polycyclic Aromatic Hydrocarbons in Sediment Samples Proposed for Ocean Disposal", Environnement Canada, Conservation et protection, Région du Pacifique et du Yukon, version 2.0, septembre 1990

Title: LECO-TOTAL CARBON ANALYZER

Weighing of sediment samples

The Carbon Analyzer is only capable of measuring small quantities of CO_2, released after combustion of the sample. Therefore, it is important that the correct quantity of sample is weighed out for analysis. The following chart lists the sample weights used at C.C.I.W.

Note: for samples containing over 40% carbon, weighing should be to five or six decimal places, and analysis should be carried out in triplicate.

Expected carbon % of sample	Appropriate weight for analysis
0 - 5.0% carbon	~ 0.2000 gm
5.0 - 10.0% carbon	~ 0.1000 gm
10.0 - 30.0% carbon	~ 0.0500 gm
30.0 - 40.0% carbon	~ 0.0200 gm
above 40.0% carbon	~ 0.010000 gm

Analytical Procedure

Analysis should be carried out in duplicate, or singly when a large number of samples is required. In the latter case it is suggested that every tenth sample be done in duplicate.

1) Weigh the ground and homogenized sediment sample into two separate crucibles: one for total carbon analysis, one for organic carbon analysis.
2) Cover with crucible lids until next step.

3) Organic carbon samples:

A. Add 5cc sulphurous acid to crucible in the fume hood, one drop at a time. If vigorous bubbling occurs, stop and wait until bubbling subsides, then continue to add acid slowly again so that no material will bubble out of crucible.

B. Stir each sample with a clean spatula to get each particle into suspension.

C. In case of samples with a high carbonate carbon content and hence appreciable bubbling, add 5 additional cc's of sulphurous acid slowly again so that no material will be lost.

D. Allow samples to dry under fume hood.

Note: Samples take from 12 to 48 hours to dry, depending on sediment type and amount of sulphurous acid added.

E. When dry, carefully scrape each sample with a clean spatula so that the sediment is well pulverized and mixed in the crucible.

F. Add 2 scoops of iron chip accelerator; mix well with sample. Cover the mixture with 1 scoop of copper metal accelerator.

G. Cover samples with crucible lids until time of burning.

4) Total carbon samples:

Carry out steps F and G from 3) above, on the homogenized, dried sediment.

5) Combustion of weighed and prepared samples:

Follow procedures outlined in Leco manual.

Calculations of results

The volume of CO_2 from the sediment is determined after the sample has burned, the CO_2 has been absorbed in the caustic solution and the buret stopcock is in the lock position. The reading of the buret is taken on the left side of the calibrated tube. The reading is corrected for temperature and pressure using Correction Factor Chart #501-154 and then divided by the weight of the sample thus:

$$\frac{\text{BURET READING X CORRECTION FACTOR}}{\text{WEIGHT OF SAMPLE}} = \% \text{ CARBON}$$

To find the percentage of carbonate carbon, subtract the organic carbon % from the total carbon % thus:

TOTAL CARBON % - ORGANIC CARBON % = CARBONATE CARBON %

To find the percentage of organic matter, multiply the organic carbon % by 1.72[2], thus:

ORGANIC CARBON % X 1.72 = % ORGANIC MATTER

To find the percentage of carbonate carbon figured as calcium carbonate, multiply carbonate carbon % by 8.33 (molecular weight of $CaCO_3$) thus:

CARBONATE CARBON % X 8.33 = % CO_3C figured as $CaCO_3$

Note: It is possible that dolomite or other carbonates may be present in sediment and this calculation will be meaningless.

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2. Jackson, M.L., 1958. Soil Chemical Analysis. Prentice-Hall Inc., Englewood Cliffs, N.J.

NOTES:

Precision

Standard deviations (σ) were found to vary from 0.06 to 0.005 for total carbon and 0.22 to 0.017 for organic carbon. Tests were carried out on thirty-three Great Lakes sediment samples with total carbons ranging from 0.0 to 16.0%, organic carbons from 0.0 to 9.0%. The precision and maximum deviations were worse for samples having less than 1.0% carbon and were best at the higher carbon concentrations.

Operator time

Barring machine breakdown or peculiarity of sediment samples, the entire process, beginning with weighing of samples and including calculations of results, should allow a single experienced operator to complete approximately sixty samples per thirty-five hour week.

Burning of the total carbon samples can be done while the organic carbon samples are drying in the fume hood. An experienced operator can mix samples with accelerator and calculate some of the initial results during the combustion cycle.

Cautions:

In the case of high carbonate samples, great care must be taken not to lose any of the sediment material due to the bubbling of the acid within the crucible.

The very best crucibles should be used due to the high temperature needed for the carbon analysis.

Due to the porosity of the crucibles, the sulphurous acid sometimes leaks through. This leakage was not found to affect the results of the analysis.

Some sediments have a high sulphur content so it is advisable to frequently check the manganese dioxide in the sulphur trap on Carbon Analyzer. This should be done every time the machine is cleaned. At that time, any blackened manganese dioxide from the bottom of the trap should be discarded and fresh manganese dioxide should be added to the top of sulphur trap.

It is desirable that the plate count on the induction furnace should be between 400 and 500 for complete combustion of material.

Note: We have a rheostat plugged into the induction furnace to regulate plate current.

Hydrocarbons or high organic matter content in the sediments can cause an explosion during combustion. It is best to have a good supply of combustion tubes, pedestals and plugs in this situation.

Total Carbon

1. Dry the unknown samples at 105°C for at least one hour.

2. Run three (3) determinations of one scoop Cu accelerator in order to determine the blank for the Cu and the 528-016 crucible.

3. Calibrate the CR-12 Analyzer with three (3) 1.000 gram samples of a standard, i.e. NBS 10a plus one scoop of Cu in the 528-016 crucible, setting the slope pot to the quoted value each time. Set the slope pot to the average value.

4. Weigh out several samples of other standards, i.e. NBS 16c for a periodic calibration check.

5. Run three (3) determinations of one scoop Fe chip plus one scoop Cu in the 528-030 crucible for the blank.

6. Weigh into the 528-016 crucible 0.25 grams of unknown sample.

7. Add one scoop Cu plus one scoop Fe and analyze.

8. The total % C = (DVM reading - blank)/sample weight

II. Organic Carbon by HCl Evolution

Follow steps one through six of the Total Carbon Analysis using the 528-030 filter crucible.

7. Place the sample in a filtering apparatus taking care to avoid rubbing any rubber into the crucible. A tight wrapping of a piece of thin plastic bag works very well.

8. Moisten the sample with 1 or 2 drops of hot distilled water.

9. Add five (5) 2 ml portions of 6N HCl, taking care to avoid violent evolution of the CO_2 which could cause splashing and loss of sample. Let the previous portion get sucked out of the crucible before adding the next portion.

10. Add five (5) 2 ml portions of distilled water.

11. Dry in a 105°C oven for at least one hour.

12. Add one scoop Cu and one scoop Fe chip and analyze.

13. The organic carbon (DVM reading - blank)/sample weight

III. Carbonate Carbon by Burning off Organic Carbon

Repeat steps one through five of Total Carbon Analysis using the 528-016 crucible.

6. Weigh 0.25 grams of sample into a quartz liner from the graphite enclosed crucible 528-132.

7. Place the liner with the quartz crucible in an induction furnace which has been calibrated to give a temperature of 500°C in three minutes in an oxygen stream. This calibration can be done by using pellets of known melting point.

8. Transfer the heated sample from the quartz liner to a 528-016 crucible.

9. Add one scoop Cu plus one scoop Fe chip and analyze.

10. The carbonate carbon is (DVM reading - blank)/sample weight.

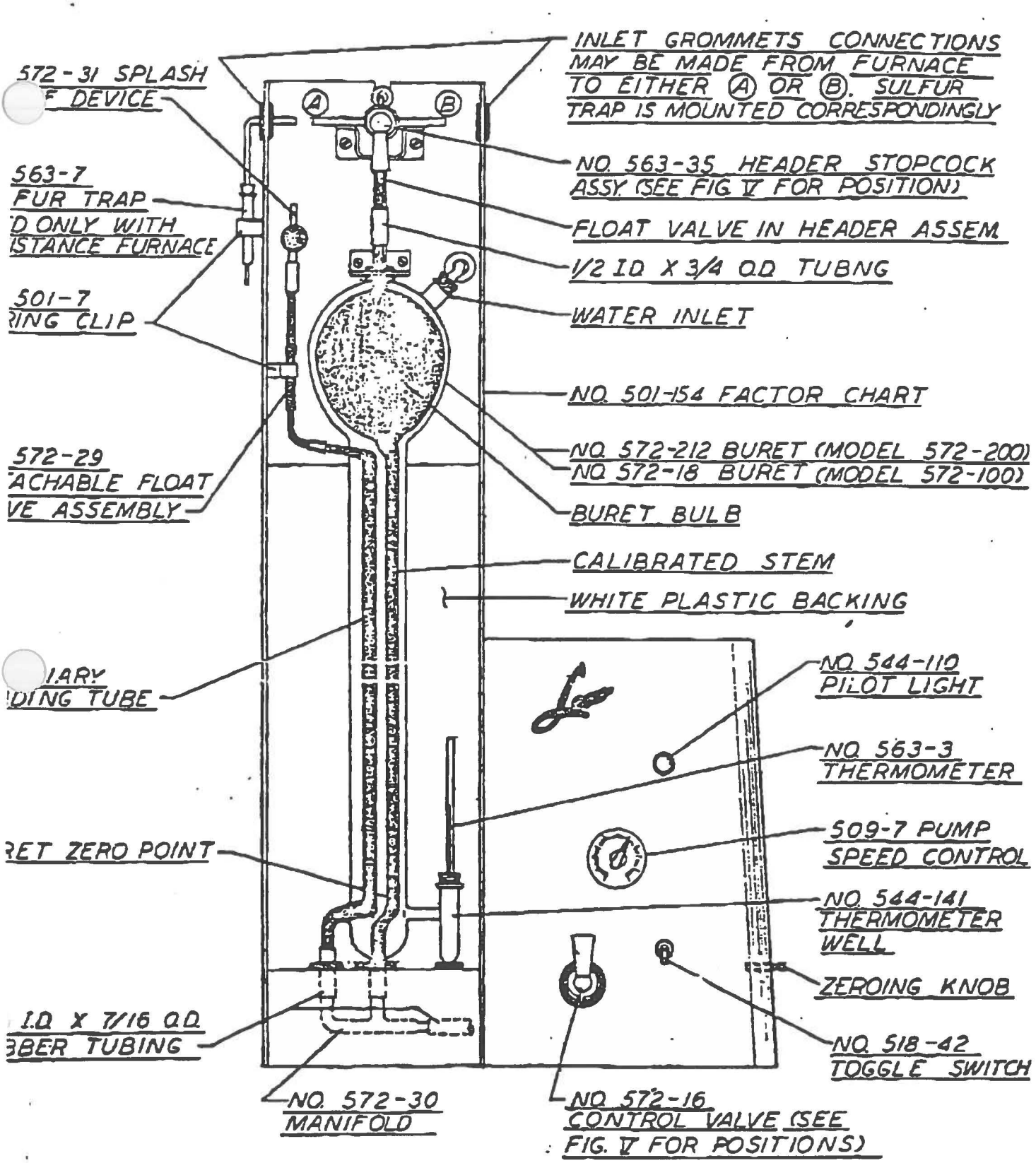

FIG. I FRONT VIEW NO. 572-100 & 572-200 CARBON DETERMINATORS

Brooks Rand Ltd.

SOP #BR-0002

Determination of Total Mercury in Solids by Cold Vapor Atomic Fluorescence Spectrophotometry (CVAFS)

Brooks Rand, Ltd.

Revision 003
Revised 12/94

Reviewed _____

COPY #003 for EVS

_____ 12/5/94
President Date

CONFIDENTIAL

_____ 12/2/94
Lab Director Date

_____ 12.02.94
Senior Scientist Date

Total Mercury In Solids By Cold Vapor Atomic Fluorescence Spectrophotometry

1. SCOPE AND APPLICATION

1.1. Method BR-0002 is a peer-reviewed, published procedure for the determination of total mercury in a wide range of biological and geological matrices. All samples must be subject to an appropriate digestion step prior to analysis.

2. SUMMARY OF METHOD

2.1. Prior to analysis, the solid samples must be prepared according to the procedure discussed in this method.

2.2. Method BR-0002 is a cold vapor atomic fluorescence technique, based upon the emission of 253.7 nm radiation by excited Hg^0 atoms in an inert gas stream. Mercuric ions in the oxidized sample are reduced to Hg^0 with $SnCl_2$, and then purged onto gold-coated sand traps as a means of preconcentration. Mercury vapor is thermally desorbed into the fluorescence cell. Fluorescence (peak height or area) is measured as a function of total mercury collected, which is converted to concentration by the size of the aliquot purged.

2.3. The typical detection limit for this method is 1 $ng \cdot g^{-1}$ as Hg (or 1 ppb) calculated as 3 times the standard deviation of complete method blanks.

3. INTERFERENCES

3.1. Due to the strong oxidation step there are no observed interferences with this method.

3.2. The potential exists for destruction of the gold traps (and consequently, low values) if free halogens are purged onto them, or if they are overheated (>500° C). When these instructions are followed accurately, neither of these outcomes is likely.

3.3. Water vapor may collect in the gold traps, and be released into the fluorescence cell where it condenses, giving a false peak due to scattering of the excitation radiation. This can be avoided with the use of a soda lime pre trap.

3.4. As always with atomic fluorescence, the fluorescent intensity is strongly dependent upon the inertness of the carrier gas. It is the analyst's responsibility to ensure high purity inert carrier gas and a leak-free analytical train.

4. APPARATUS AND MATERIALS

4.1. Atomic fluorescence spectrophotometer or equivalent. To achieve the low detection levels and small, interference-free aliquots claimed by this method, a very sensitive CVAFS detector is required. Such systems are built at Brooks Rand, Ltd. (BRL Model II and Model III) based on the principals discussed by Bloom and Fitzgerald(1988). Other mercury specific detectors such as atomic absorption or plasma emission may be used, but detection limits would be 10-100 times higher. The CVAFS detector contains the four major components:

4.1.1. Four watt low pressure mercury vapor lamp

4.1.2. Far UV quartz flow-through fluorescence cell 12 mm x 12 mm x 45 mm long, with a 10 mm path length.

4.1.3. UV Visible photomultiplier: Sensitive to <230 nm. This PMT is isolated from outside light with a 254 nm interference filter.

4.1.4. Flowmeter: flowmeter with needle valve capable of reproducibly keeping carrier gas flow at 30 $mL \cdot min^{-1}$.

4.2. Flow meter/needle valve: Capable of controlling and measuring gas flow to the purge vessel at 200-500 $mL \cdot min^{-1}$.

4.3. Teflon® fittings: Connections between components and traps are made using 3.2 mm O.D. precleaned Teflon® FEP tubing, and Teflon® friction-fit or threaded tubing connectors.

4.4. Acid-fume and moisture pretrap: A 10 cm x 0.9 cm diameter Teflon® tube containing 2-3 grams of reagent grade, non-indicating 8-12 mesh soda lime, packed in between wads of silanized glass wool. This trap is purged of Hg by placing on the output of a clean cold vapor generator, filled with double deionized water (DDW), and purging for 20 minutes with N_2 at 100 $mL \cdot min^{-1}$.

4.5. Cold vapor generator: A 250 mL or 125 mL florence flask with standard taper 24/40 neck, fitted with a spurging stopper having a coarse glass frit which extends to within 0.2 cm of the flask bottom.

4.6. Gold-coated sand traps: Made from 10 cm lengths of 6.5 mm O.D. x 4 mm I.D. quartz tubing, with a circular indentation 2.0 cm from one end. The tube is filled with 2.5 cm of gold-coated ashed (800° C for 6 hours) quartz sand (60/80 mesh). The end is then plugged with quartz wool. Gold is applied to the sand as a coating several·atoms thick using an ion discharge gilding apparatus such as is employed to coat electron microscopy samples. Traps are heated to 450°-500° C (a barely visible red glow when the room is darkened) with a coil consisting of 78.75 cm of 22 ga nichrome wire at a potential of 10

VAC. Potential is applied and finely adjusted with an autotransformer. Traps should be heated for 5 minutes and cooled, after construction and before their first use.

4.7. Recorder: Any integrator with 0.1-5.000 mV input.

4.8. Pipetters: All plastic pneumatic fixed volume and variable pipetters in the range of 10 µL to 5.0 mL.

4.9. Refluxing digestion flask. 100 mL volumetric flasks with acid-cleaned 1 inch diameter glass marbles over the mouth. When the flasks are placed on a hot plate (about 125°-150° C) the contents will reflux, the marbles acting as pressure relief valves. Loosely capped Teflon® vials can be used instead of volumetric flasks.

5. REAGENTS

5.1. Water: 18 megohm ultrapure deionized water (ASTM type I) starting from a pre-purified (distilled, R.O., etc.) source. As a final mercury and organic removal step, the activated carbon cartridge on the 18 megohm system is placed between the final ion exchange bed and the 0.2 µM filter. Water should be monitored for Hg -- especially after ion exchange beds are changed.

5.2. Nitric/sulfuric acid: Carefully add 300 mL of pre-analyzed low mercury (<10 $ng \cdot L^{-1}$ Hg) concentrated sulfuric acid to 700 mL pre-analyzed, low mercury (<10 $ng \cdot L^{-1}$ Hg) concentrated nitric acid in a Teflon bottle, with constant stirring.

Caution: This mixture gets hot and emits caustic fumes!

5.3. Stannous Chloride: A solution containing 200 g of $SnCl_2 \cdot 2H_2O$ and 200 mL concentrated HCl is brought to 1.0 L with high purity water. This solution is purged overnight with mercury-free N_2 at 500 $mL \cdot min^{-1}$ to remove all traces of Hg.

5.4. Bromine monochloride: 27 g of KBr are added to a 2.5 L bottle of concentrated pre-analyzed HCl found to be low in Hg (<5 $ng \cdot L^{-1}$ Hg). A clean magnetic stir bar is placed in the bottle, and it is stirred for 1 hour in a fume hood. Next, 38 g of pre-analyzed, low Hg $KBrO_3$ are slowly added to the acid with stirring.

Caution: This process generates copious quantities of free Cl_2 which are released from the bottle. Add the $KBrO_3$ slowly and in a well operating fume hood! The fumes from this reagent, like chlorine or bromine, are very irritating and corrosive.

When all of the $KBrO_3$ has been added, the solution should have gone from yellow to red to orange. Loosely cap the bottle, and allow to stir another hour before tightening the lid. Store tightly capped, and in the dark. This reagent usually has a Hg concentration in the range of 25-40 ng/L.

5.5. Stock mercury standard: A commercially available 1000 $mg \cdot L^{-1}$ mercury atomic absorption standard that is traceable to NIST is used. Alternatively, 0.1354 g of high purity $HgCl_2$ may be dissolved in 75 mL of water, 5 mL of bromine monochloride solution added, and the volume brought to 100.0 mL in a class A volumetric flask. This stock standard should be replaced by the manufacturer's expiration date.

5.6. Intermediate mercury standard solution: 0.100 mL of the stock solution is diluted to 100.0 mL of water containing 5 mL of bromine monochloride. This solution contains 1.00 $\mu g \cdot mL^{-1}$ Hg. Keep in a tightly closed Teflon® bottle. This solution should be replaced yearly.

5.7. Mercury working standards: 1.00 mL of the intermediate mercury standard is diluted to 100.0 mL with high purity water containing 1% by volume bromine monochloride solution, to make a 10.0 $ng \cdot mL^{-1}$ working solution. Also, a 1.00 $ng \cdot mL^{-1}$ working standard should be made with 0.100 mL of the intermediate mercury standard diluted to 100.0 mL with high purity water containing 1% by volume BrCl solution. Both working standards should be replaced monthly.

5.8. Nitrogen: Grade 4.5 (standard laboratory grade) nitrogen which has been further purified by the removal of Hg using a gold-coated sand trap.

5.9. Helium or argon: Grade 5.0 (ultra high purity, G.C. grade) inert gas which has been further purified by the removal of Hg using a gold-coated sand trap.

6. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1. Samples should be collected into acid-cleaned Teflon® container or glass containers with Teflon® lids. Under no circumstances should polyethylene, polypropylene, or vinyl containers be used.

6.2. Samples are to be frozen at <-10° C (standard freezer on coldest setting) until use. A maximum holding time of 1 year at <-10° C is recommended.

6.3. All dissection, homogenization, and other handling of the samples is to occur by clean-room gloved personnel in either a class-100 clean station with mercury removal filters or in a clean room atmosphere.

7. PROCEDURE

7.1. Sample Preparation: Dissect and/or homogenize the sample or a greater than 10 g aliquot (if available) with acid-washed stainless steel tools. An approximately 1.0 gram aliquot of the homogenized sample is weighed directly into the volumetric flask. If necessary, up to 2-3 mL of high purity water may be used to rinse the sample down to the bottom. 10.0 mL of the HNO_3/H_2SO_4 mixture are pipetted in, and the sample swirled. The marble is placed over the mouth, and the samples are allowed to predigest at room

temperature for about 1 hour. Samples are next placed on a hot plate, and brought up to a refluxing boil in temperature increments. This is to avoid excessive foaming, especially common with tissue samples. Samples are digested at 105° C (hot plate temperature) for an hour and then refluxed at a hot plate temperature 150° C for 2 hours, or until all organic matter is dissolved, the solution looks substantially colorless or light yellow, and the brown gas above the liquid has almost disappeared. Sediment samples, especially sandy ones, may take less time. The samples are allowed to cool on the hot plate, and the marbles collected and rinsed in a beaker of water. Samples are diluted to the 100.0 mL mark with high purity water containing 1.0% BrCl. The original volumetric flask caps are replaced, and the samples thoroughly homogenized prior to analysis. Experience and numerous intercalibrations show that undigested rock material or animal fat does not affect the accuracy of this digestion for Hg, because these fractions are both very low in initial Hg content, and are effectively leached by the boiling acid. As a substitute, 25.6 Teflon® vials may be used instead. If Teflon® vials are used the caps should be loosened about 1/4 turn after the threads make good contact before heating, to allow the samples to vent. After digestion the vials should be allowed to cool, and 0.5 mL of BrCl should be added and the volume brought up to 25.6 mL.

7.2. Analysis: The sequence of steps for analysis is shown graphically in Figure 1. 100 mL of water is placed in the bubblers, and 1.0 mL of $SnCl_2$ solution added. The bubbler is purged with N_2 at 300 $mL \cdot min^{-1}$ for 20 minutes, and then a gold-coated sand trap is connected to the soda lime pretrap and purged for another 12 minutes. This value is the bubbler blank or calibration blank used for calibration. To analyze samples, 0.5 mL of $SnCl_2$ and an aliquot of the digestate, usually in the range of 0.25-1.0 mL, are pipetted into each bubbler. The caps are replaced, the vessel gently swirled, and gold-coated sand traps placed onto the soda lime pretrap outlet, and the sample bubbled for 12 minutes. New samples may then be added to the bubblers, with additional aliquots of $SnCl_2$. After 10 samples standards should be analyzed and then bubbler blanks should be measured. Then the water in the bubblers is replaced with fresh ultrapure water, and the above sequence is repeated.

To analyze the mercury contained on a gold trap, the nichrome wire coil is placed around the trap, and the trap is inserted in between the incoming Hg-free argon (or helium) and the analyzer. Electrical current (10 VAC) is then applied to the coil for 2.5 minutes (or 1 minute after returning to the base line), thermally desorbing the Hg as Hg^0, which is carried by the He to the analyzer. At the same time the data acquisition device (integrator) is turned on.

Following the recording of the peak, the coil on the gold trap is turned off, and the cooling fan directed at it. The gold trap is now removed from the gas stream, and the Teflon® end plugs replaced until it is needed to collect another sample. The next sample trap is placed in line, and the procedure repeated.

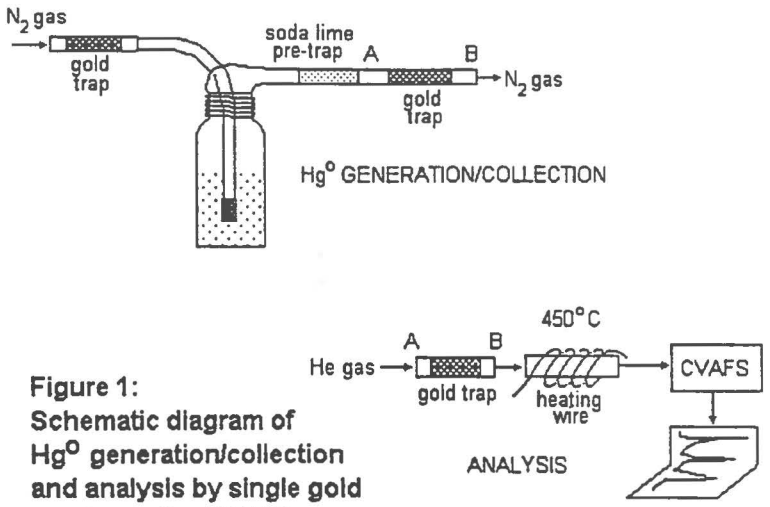

Figure 1: Schematic diagram of Hg^0 generation/collection and analysis by single gold amalgamation/CVAFS

Peaks generated using this technique should be very sharp and almost symmetrical. The peak comes off at approximately 1 minute, and has a half-height width of about 5 seconds. Broad or asymmetrical peaks are indicative of an analytical problem, possibly including: low gas flow, water vapor on the trap, or the trap being damaged by chemical fumes or overheating. The last possibility is definitely the case if following a sharp peak, a secondary small broad peak is observed. If the gold trap has been damaged, it and the Teflon® tubing downstream from it should be discarded, due to the possibility of gold migration on downstream surfaces.

7.3. Cold Vapor Atomic Fluorescence for mercury is linear over at least 5 orders of magnitude (Bloom and Fitzgerald, 1988). However, it is required that at least a 3 point calibration curve be prepared each day prior to analysis to verify linearity. Standards to be analyzed for calibration should include one standard at 100 pg, one at 500 or 1000 pg and one at 5000 pg.

7.4. To run standards, aliquots of working standard solution are injected into a purged bubbler containing a fresh 0.5 mL aliquot of $SnCl_2$, and the analysis run as a sample.

7.5. Gold-coated sand traps should be tracked by unique identifiers, so that any trap producing poor results can be quickly recognized and discarded. A log book should be maintained documenting initial trap testing and any questionable trap behavior. Occasionally due to inadvertent contact with halogen fumes, bubbler solution, organic fumes, or overheating, a sampling trap will become damaged, giving low and irreproducible results. Suspect traps should be checked with at least two consecutive standard runs before continued use.

7.6. The major cause of analytical problems with this method is from using the soda lime pretraps too long. These traps should be purged for at least 20 minutes as described and

then used for only one day's analytical work. Longer use risks irreproducibility, as the traps may begin retarding the flow of Hg^0. Also, as they become very wet, there is a risk of NaOH-saturated water drops coming out onto the gold trap. If sample aliquots with much acid (i.e. 5 mL) are being analyzed, it is recommended that the soda lime pretraps are changed every two or three samples. The acid fumes in combination with water vapor, when trapped in soda lime pretraps seem to start trapping Hg^0 and therefore low recoveries may result.

7.7. Duplicates, spiked samples, method blanks and check standards should be routinely analyzed, as discussed in section 8.

7.8. Calculations are made by the following method:

a) Divide each standard amount (pg of Hg) by each net standard result (peak area of standard minus mean peak area of bubbler blanks or CB) in the calibration, to yield the "pg Hg/peak area." Pool all of the "pg Hg/peak area" values for a given calibration, to obtain a mean "pg Hg/peak area" value called the calibration coefficient (C). (C) is also functionally the equal to the slope of the regression of the standard curve. Linear regression is used to calculate a correlation coefficient (r). The r value should be greater than 0.995 for sample analysis to commence.

b) Pool the calibration blank values to obtain a mean "calibration blank peak area" (CB).

c) To calculate the amount of total mercury measured in the sample aliquot analyzed (P), employ the following formula:

$$P = Hg \text{ (in pg)} = C(A-CB)$$

Where A is the gross sample area. If blank correction is not desired by a customer, CB is not subtracted out.

d) To determine the concentration of total mercury in a sample, the calculation is performed as follows:

$$Hg \text{ (in ng/g or ppb)} = [(P/v)V - p]/M$$

Where V is the final dilution volume of the digestate in mL (in this case, 100 mL) v is the volume of digestate analyzed in mL, M is the digested sample mass, in milligrams and p is the mean pg from the preparation of the method blanks. If blank correction is not desired by a customer, p is not subtracted out.

e) To determine the pg from the preparation of the method blanks (p), use the following formula for each method blank:

$$p = [(MB - CB)C \cdot V]/v$$

Where MB is the peak area of the method blank, V is the final dilution volume of the method blank and v is the volume of the method blank analyzed.

d) The limit of detection is considered to be 3 times the standard deviation of the picograms in the entire method blanks. The picograms in the method blanks is calculated in the following manner:

$$\text{Hg in method blank (in pg)} = (MB \bullet C \bullet V)/v$$

To determine if a sample is detectable, the limit of detection should be multiplied by V and divided by v using volume amounts specific for that sample. If a sample is below the detection limit it should be qualified as such.

8. QUALITY CONTROL

8.1. All quality control data should be maintained and available for easy reference or inspection.

8.2. Calibration data must be composed of a minimum of 3 calibration (or bubbler) blanks and 3 standards (preferably four of each). Such a calibration should be run at least once per day, or every 20 samples, whichever comes first. If work performed is research level, more than 20 samples may be analyzed in a batch at the discretion of the lab director.

8.3. Samples containing high analyte concentrations may be run either following dilution, or on a separate run at lower instrumental sensitivity provided the instrument is calibrated at this sensitivity. All peak areas obtained for samples must ultimately fall below the peak area obtained from the highest standard analyzed in the calibration curve.

8.4. Calibration checks must be analyzed after instrument calibration, after every ten samples and at the end of the analytical batch. Calibration checks shall consist of a mid-level standard (500 or 1000 pg) and a bubbler blank. The calibration check standard must be within 20% of the calibration and the calibration check blank must be within 100% of the calibration blanks.

8.5. A minimum of 2 method blanks per batch of 20 samples must be run. To obtain a meaningful value for the reporting limits of detection, the standard deviation must be estimated from at least 7 sets of method blanks. Method blanks should consist of all reagents used for a sample and should be carried through the entire method as a sample. To estimate the standard deviation from multiple sets of duplicate method blanks, the following formula is used:

$$\text{Estimated Standard Deviation} = \sqrt{[\sum(d \cdot d)]/2m}$$

where d is the difference between within batch determinations of the method blanks and m is the number of duplicate blank determinations.

8.6. Analysis of split samples should be run once every 10 samples or once per batch, whichever comes first. Split samples are defined as a homogeneous sample that is split into two aliquots, and then each aliquot is carried through the entire preparation and analytical procedure. Criteria for split sample results are determined by control charts. If control charts are not available then the split sample results must have a relative percent difference of 35% or less for the analysis to be considered valid. Sample results not meeting this criteria shall be reprepared and analyzed or qualified at the discretion of the lab director.

8.7. NRC or NBS certified reference materials for mercury in tissues and sediments should be analyzed at a frequency of once per 10 samples or once per batch, whichever comes first. Criteria for CRMs are determine by control charts. If control charts are not available then CRM results should be within 25% of the certified value for the analysis to be considered valid. CRM sample results not meeting this criteria shall be reprepared and analyzed or qualified at the discretion of the lab director.

8.8. Procedural spike recoveries are analyzed at the request of the client, or in the absence of a suitable certified sample as determined by the lab director.

9. REFERENCES

Bloom, N.S. and Crecelius, E.A. (1983). "Determination of Mercury in Seawater at Subanogram per Liter Levels." *Mar. Chem.* 14:49.

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SOP #BR-0003

Determination of Total and "Acid-Labile" Mercury in Aqueous Samples by Cold Vapor Atomic Fluorescence Spectrophotometry (CVAFS)

Brooks Rand, Ltd.

Revision 003
Revised 11/94

Reviewed

COPY #003 for EVS

Colin O

President	12/5/94 Date
Lab Director	12/2/94 Date
Senior Scientist	12.02.94 Date

CONFIDENTIAL

Determination of Total and "Acid-Labile" Mercury in Aqueous Samples by Cold Vapor Atomic Fluorescence Spectrophotometry (CVAFS)

1. SCOPE AND APPLICATION

1.1. Method BR-0003 is a peer-reviewed, published procedure for the determination of total mercury in a wide range of aqueous samples, ranging from pristine seawater to sewage effluent.

2. SUMMARY OF METHOD

2.1. Prior to analysis, the aqueous samples must be prepared according to the procedure discussed in this method.

2.2. Method BR-0003 is a cold vapor atomic fluorescence technique, based upon the emission of 253.7 nm radiation by excited Hg^0 atoms in an inert gas stream. Mercuric ions in the oxidized sample are reduced to Hg^0 with $SnCl_2$, and then purged onto gold-coated sand traps as a means of preconcentration. Mercury vapor is thermally desorbed into the fluorescence cell. Fluorescence (peak height or area) is measured as a function of total mercury collected, which is converted to concentration by the size of the aliquot purged.

2.3. The typical detection limit for the method is 0.4 $ng \cdot L^{-1}$ as Hg (or 0.4 ppt) calculated as three times the standard deviation of the complete method blanks.

3. INTERFERENCES

3.1. Due to the BrCl oxidation step, there are no observed interferences with the total Hg methodology when properly carried out. The "acid labile" mercury, however, is operationally quantifying an interference, i.e.; the partial complexation of Hg by organic matter. Thus, it is critical to follow the instructions for standardization accurately. Also, when "acid labile" Hg samples are analyzed, most of the Hg may be in non-labile forms, which then can adsorb to the bubbler walls. It is critical, therefore, to clean the bubblers at least daily, and always between "acid labile" and total mercury determinations as described below. FAILURE TO DO SO WILL RESULT IN CARRY-OVER OF MERCURY AND IRREPRODUCIBLE RESULTS. This problem does not exist during the analysis of only total mercury samples. The cleaning procedure is as follows:

a) Fill bubblers with 10% KOH in water, and let sit for 10 minutes.

b) Fill bubblers with concentrated HCl, and bring to boil in fume hood. continue heating, while filled with HCl, for 30 minutes.

c) Fill bubblers with clean deionized water plus 1 mL of BrCl solution. Let sit for 10 minutes.

d) Neutralize BrCl with 0.5 mL NH_2OH solution, discard, and rinse the entire bubbler apparatus with copious quantities of ultra-pure water.

e) Fill with 1% HCl and purge with N_2 at about 25 $mL \cdot min^{-1}$ until further use.

3.2. The potential exists for destruction of the gold traps (and consequently, low values) if free halogens are purged onto them, or if they are overheated (>500° C). When these instructions are followed accurately, neither of these outcomes is likely.

3.3. Water vapor may collect in the gold traps, and be released into the fluorescence cell where it condenses, giving a false peak due to scattering of the excitation radiation. This can be avoided with the use of a soda lime pre trap.

3.4. As always with atomic fluorescence, the fluorescent intensity is strongly dependent upon the inertness of the carrier gas. This technique eliminates quenching due to trace gases, but it still remains the analyst's responsibility to ensure high purity inert carrier gas and a leak-free analytical train.

4. APPARATUS AND MATERIALS

4.1. Atomic fluorescence spectrophotometer or equivalent. To achieve the low detection levels and small, interference-free sample aliquots claimed by this method, a very sensitive CVAFS detector is required. Such systems are built at Brooks Rand, Ltd. (BRL Model II and Model III) based on the principals discussed in Bloom and Fitzgerald (1988). Other mercury specific detectors such as atomic absorption or plasma emission may be used, but detection limits would be 10-100 times higher. The CVAFS detector contains the following four major components:

4.1.1. Four-watt low pressure mercury vapor lamp.

4.1.2. Far UV quartz flow-through fluorescence cell 12 mm x 12 mm x 45 mm long, with a 10 mm path length.

4.1.3. UV visible photomultiplier: Sensitive to <230 nm. This PMT is isolated from outside light with a 254 nm interference filter.

4.1.4. Flowmeter: flowmeter with needle valve capable of reproducibly keeping carrier gas flow at 30 $mL \cdot min^{-1}$.

4.2. Flow meter/needle valve: Capable of controlling and measuring gas flow to the purge vessel at 200-500 $mL \cdot min^{-1}$.

4.3. Teflon fittings: Connections between components and traps are made using 3.2 mm O.D. pre-cleaned Teflon® FEP tubing, and Teflon® friction-fit or threaded tubing connectors.

4.4. Acid-fume pre-trap: A 10 cm x 0.9 cm diameter Teflon® tube containing 2-3 grams of reagent grade, non-indicating 8-12 mesh soda lime chunks, packed in between wads of silanized glass wool. This trap is purged of Hg by placing the output of a clean cold vapor generator, filled with double deionized water (DDW), and purging for 20 min. with N_2 at 300 $mL \cdot min^{-1}$.

4.5. Cold vapor generator: A 250 mL or 125 mL florence flask with a standard taper 24/40 neck, fitted with a spurging stopper having a coarse glass frit which extends to within 0.2 cm of the flask bottom.

4.6. Gold coated sand traps: Made from 10 cm lengths of 6.5 mm O.D. x 4 mm I.D. quartz tubing, with a circular indentation 2.0 cm from one end. The tube is filled with 2.5 cm of gold-coated ashed (800° C for 6 hours) quartz sand (60/80 mesh). The end is then plugged with quartz wool. Gold is applied to the sand as a coating several atoms thick using an ion discharge gilding apparatus such as is employed to coat electron microscopy samples. Traps are heated to 450-500° C (a barely visible red glow when the room is darkened) with a coil consisting of 78.75 cm of 22 ga nichrome wire at a potential of 10 VAC. Potential is applied and finely adjusted with an autotransformer.

4.7. Recorder: Any integrator with 0.1-5.000 mV input is acceptable.

4.8. Pipetters: All plastic pneumatic fixed volume and variable pipetters in the range of 10 µL to 5.0 mL.

4.9. Sampling and Oxidation Bottles: It is imperative for accurate $ng \cdot L^{-1}$ mercury work that appropriately cleaned Teflon® bottles with tight-fitting lids be used for all steps contacting the aqueous sample. It is good practice to use 1000 mL or 500 mL bottles to collect the samples in, and 125 mL bottles to perform the BrCl oxidation step. New Teflon® bottles are cleaned by heating to >95° C in concentrated HNO_3 for at least 48 hours. The bottles are cooled, rinsed 3 times with ultra-clean water, and then filled with ultra-clean water containing 1% HCl. These bottles are capped and placed in a clean oven at 50° overnight. After cooling, they are rinsed 3 more times, filled with ultra-pure water plus 0.4% HCl, and placed in a mercury-free class 100 clean-air station until dry. The bottles are then tightly capped (with a wrench if necessary) and double bagged in new polyethylene zip-loc bags until needed. After the initial cleaning, bottles are cleaned by heating overnight in 50% HCl or heating for 6 hours in HNO_3. After removing the Teflon® bottles from the acid vats, the bottles should be rinsed 3 times, and filled with high purity 1% HCl solution. For further information on cleaning (or decontaminating) Teflon® bottles see SOP BR-0400.

5. REAGENTS

5.1. Water: 18 megohm ultra-pure deionized water starting from a pre-purified (distilled, R.O., etc.) source. As a final mercury and organic removal step, the activated carbon cartridge on the 18 megohm system is placed between the final ion exchange bed and the 0.2 μM filter. Water should be monitored for Hg--especially after ion exchange beds are changed.

5.2. Air. For best results doing low level aquatic mercury research, it is very important that the laboratory air be low in both particulate and gaseous mercury. This is generally not the case for existing laboratories, as years of broken thermometers, use of Hg salts as reagents, and mercury preserved paints on the walls have permanently elevated room air levels to hundreds of $ng \cdot m^{-3}$. Ideally, mercury work should be conducted in a new laboratory, with mercury-free paint on the walls. Outside air, which is very low in Hg, should be brought directly into the class-100 clean air station intakes. If this is impossible, air coming into the clean air stations can be cleaned for mercury by placing a gold-coated cloth pre-filter over the intake. This is made as follows:

> Soak several square meters of cotton gauze in 100 mL of 10% gold chloride solution at pH 7. In a hood, add 100 mL of 30% $NH_2OH \cdot HCl$ solution, and homogenize into the cloth with gloved hands. The material will turn black as colloidal gold is precipitated. Allow the mixture to sit for several hours, then rinse with a copious amount of deionized water. Considerable colloidal gold will be washed out, so you may wish to collect and settle the rinse water to recover it. Squeeze dry the rinsed cloth, and spread flat on newspapers to air-dry. When dry, fold and place over the intake pre-filter of your laminar flow hood. CAUTION: THIS PROCESS IS MESSY, SO GREAT CAUTION SHOULD BE TAKEN TO AVOID SPREADING GOLD DUST ALL OVER THE LABORATORY. THIS COULD RESULT IN INTERFERENCES WITH ANALYSIS IF GOLD BECOMES INCORPORATED IN THE SAMPLES. THE GILDING PROCEDURE SHOULD BE DONE IN A REMOTE LABORATORY IF POSSIBLE.

5.3. Hydrochloric Acid. Trace-metal purified reagent HCl is purchased and pre-analyzed for Hg before use. In general, it is possible to obtain acid containing less than 5 $pg \cdot mL^{-1}$ Hg. When a lot number meeting this specification is found, several cases are purchased and stored in a low Hg atmosphere (i.e.; in clean lab or outside the building). Generally, lower values can be obtained in this manner than by re-distilling acid in the laboratory. So-called ULTRA-PURIFIED acids are often to most irreproducibly contaminated (for mercury) grade of acid commercially available, and should be avoided.

5.4. Hydroxylamine Hydrochloride. Dissolve 300 grams of $NH_2OH \cdot HCl$ in ultra-pure water to make 1.0 L. This solution should be purified by purging overnight at 500 $mL \cdot min^{-1}$ with Hg-free N_2.

5.5. Stannous Chloride: A solution containing 200 g of $SnCl_2 \cdot 2H_2O$ and 200 mL concentrated HCl is brought to 1.0 L with high purity water. This solution is purged overnight with mercury-free N_2 at 500 $mL \cdot min^{-1}$ to remove all traces of Hg.

5.6. Bromine monochloride: 27 g of KBr are added to a 2.5 L bottle of concentrated pre-analyzed HCl found to be low in Hg (<5 $ng \cdot mL^{-1}$ Hg). A clean magnetic stir bar is placed in the bottle, and it is stirred for 1 hour, in a fume hood. Next, 38 g of pre-analyzed, low Hg $KBrO_3$ are slowly added to the acid with stirring.

Caution: *This process generates copious quantities of free halogens (Cl_2, Br, BrCl) which are released from the bottle. Add the $KBrO_3$ slowly and in a well operating fume hood! The fumes from this reagent, like chlorine or bromine, are very irritating and corrosive!*

When all of the $KBrO_3$ has been added, the solution should have gone from yellow to red to orange. Loosely cap the bottle, and allow to stir another hour before tightening the lid. Store tightly capped, and in the dark. This reagent usually has a Hg concentration in the range of 25-40 ng/L.

5.7. Stock mercury standard: A commercially available 1000 $mg \cdot L^{-1}$ mercury atomic absorption standard that is traceable to NIST is used. Alternatively, 0.1354 g of high purity $HgCl_2$ may be dissolved in 75 mL of water, 5 mL of bromine monochloride solution added, and the volume brought to 100.0 mL in a class A volumetric flask. This stock standard should be replaced by the manufacturer's expiration date.

5.8. Intermediate mercury standard solution: 0.100 mL of the stock solution is diluted to 100.0 mL of water containing 5 mL of bromine monochloride. This solution contains 1.00 $\mu g \cdot mL^{-1}$ Hg. Keep in a tightly closed Teflon® bottle. This solution should be replaced yearly.

5.9. Mercury working standard. 1.00 mL of the mercury secondary standard is diluted to 100.0 mL with high purity water containing 1% by volume bromine monochloride solution, to make a 10.0 $ng \cdot mL^{-1}$ working solution. Also, a 1.00 $ng \cdot mL^{-1}$ working standard should be made with 0.100 mL of the intermediate mercury standard diluted to 100 mL with high purity water containing 1% by volume BrCl solution. Both working standards should be replaced monthly.

5.10. Nitrogen. Grade 4.5 (standard laboratory grade) nitrogen which has been further purified by the removal of Hg using a gold coated sand trap.

5.11. Helium or Argon. Grade 5.0 (ultra high purity, G.C. grade) inert gas which has been further purified by the removal of Hg using a gold-coated sand trap.

6. SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1. Samples should be collected only into rigorously cleaned Teflon® bottles. Under no circumstances should ordinary plastic (i.e.; polyethylene, polypropylene, or vinyl) containers be used, as they are very diffusive to Hg^0 gas from the air. Ashed or rigorously acid cleaned Borosilicate or quartz glass bottles with Teflon® caps may be used if Teflon® bottles are not available or if samples are expected to be high (100+ ng/L) in Hg. It is critical that the bottles have very tightly sealing caps to avoid diffusion of atmospheric Hg through the threads (Gill and Fitzgerald, 1985). As an added precaution, clean bottles are filled with high purity 0.4% HCl and the bottle threads dried, capped, and double-bagged in new zip-loc bags in the clean-room or in a class-100 laminar flow hood, and stored in plastic boxes until use.

6.2. Samples are collected using rigorous ultra-clean protocols (Gill and Fitzgerald, 1985) which are summarized as follows:

a) At least two persons wearing fresh clean-room gloves at all times, are required on a sampling crew.

b) One person ("dirty hands") pulls a bagged bottle from the box, and opens the outer, dirty bag, avoiding touching inside that bag.

c) The other person ("clean hands") reaches in, opens the inner bag, and pulls out the sample bottle.

d) The bottle is opened with a plastic shrouded dedicated wrench, and the acidified water is discarded downstream of the sampling site.

e) The bottle is rinsed once with sample water, and then filled.

f) Preservative (i.e.; 0.8% by volume of high purity HCl) may be added at this time, or the samples should be kept on ice and preserved in the clean laboratory within twenty four hours of receipt.

g) The cap is replaced with the wrench, and the bottle re-bagged in the opposite order from which it was removed.

h) Clean-room gloves are changed between samples and whenever something not know to be clean is touched.

i) Water samples are best obtained by surface grab, using gloved hands, and facing into a flowing body of water (i.e.; looking upstream or off the bow of a moving boat). If samples are to be taken from depth, the only non-contaminating method generally available is pumping. Two methods have been found to work in this regard. The first is to use rigorously acid-cleaned Teflon® tubing, and a peristaltic pump with

FRESHLY cleaned (heating to 70° C in 5% HCl + 5% CH_3COOH) silicon tubing. Beware that once cleaned, silicon tubing quickly absorbs Hg from the air. The other method involves high-volume pumping (i.e.; 50 $L \cdot min^{-1}$) through neoprene hose. If this method is used, it is best to clean the system first by pumping several hundred liters of 5% HCl solution, and then pumping clean water for several hours. This second technique works largely because the rate of flow is so fast that the contamination becomes imperceptibly diluted.

j) DISCRETE SAMPLERS (i.e.; Niskin, GoFlo, and Kemerer bottles) ARE TO BE AVOIDED, AS UNDER EVEN THE BEST OF CONDITIONS THEY ARE OFTEN FOUND TO GROSSLY CONTAMINATE SAMPLES AT THE $ng \cdot L^{-1}$ LEVEL.

6.3. Samples may be preserved by adding 8 $mL \cdot L^{-1}$ of concentrated HCl (to allow both "acid-labile" and total mercury analysis), or 5 $mL \cdot L^{-1}$ BrCl solution, if only total mercury is to be analyzed. Samples may also be sent back to the laboratory unpreserved if they are 1) collected in Teflon® bottles, 2) filled to the top with no head space, and 3) sent at 1° C by overnight mail. The samples should be acid preserved soon after arrival at the laboratory (within 24 hours) FREEZING IS NOT AN ACCEPTABLE TECHNIQUE FOR TOTAL Hg, AS UPON THAWING, MUCH Hg(II) IS CONVERTED TO VOLATILE Hg^0.

6.4. All handling of the samples in the lab should be undertaken in a mercury-free clean air bench, after rinsing the outside of the bottles in low Hg water, and drying in the clean air hood.

7. PROCEDURE

7.1. Sample preparation. The value obtained for "acid-labile" mercury is somewhat dependent upon the length of time the sample is stored with acid. The amount of "acid-labile" mercury recovered levels off after about 3 weeks of aging, at a level which may be twice that observed in a fresh sample. Thus, greatest reproducibility is obtained by storage for 1 month before analysis, but this is often not feasible. Currently, no uniform protocol exists clearly defining the acidification parameter for "acid-labile" Hg.

For total Hg, a 100 mL aliquot should be poured from a thoroughly shaken, acidified sample, into a 125 mL Teflon® bottle. 0.5 mL of BrCl is added, the bottle is capped, and it is placed in a UV radiation box. The UV lamps should then be turned on for 30 minutes. If the yellow color disappears, more BrCl should be added and the UV process repeated until a permanent yellow color is obtained. Some highly organic matrices such as sewage effluent will require a high level of BrCl (i.e. 5 mL/100 mL of sample), and longer oxidation times, or elevated temperatures (i.e. place sealed bottles in an oven at 50°C for 3 hours). In all cases the oxidation must be conducted until a permanent yellow color remains.

7.2. Analysis: The sequence of steps for analysis is shown graphically in Figure 1. 100 mL of DI water is placed in each bubbler, and 1.0 mL of $SnCl_2$ is added. The bubbler is purged with Hg-free N_2 for 20 minutes at 300-400 $mL \cdot min^{-1}$. A gold/sand trap is then connected to the output of the soda lime pre-trap, and the water purged another 12 minutes to obtain a bubbler blank. Standards are then analyzed by the addition of 0.1-5.0 ng aliquots of Hg standard, and 0.5 mL $SnCl_2$ to the bubblers, swirling to mix, and purging as above.

For "acid-labile" mercury, place 100-200 mL of acidified sample into a clean bubbler, determining the volume by weight difference. Add 0.5 mL of $SnCl_2$ solution, replace the bubbler cap, and swirl to mix. Place a clean gold/sand column on the output of the soda-lime trap and purge for 30 minutes with Hg-free N_2 at 300-400 $mL \cdot min^{-1}$.

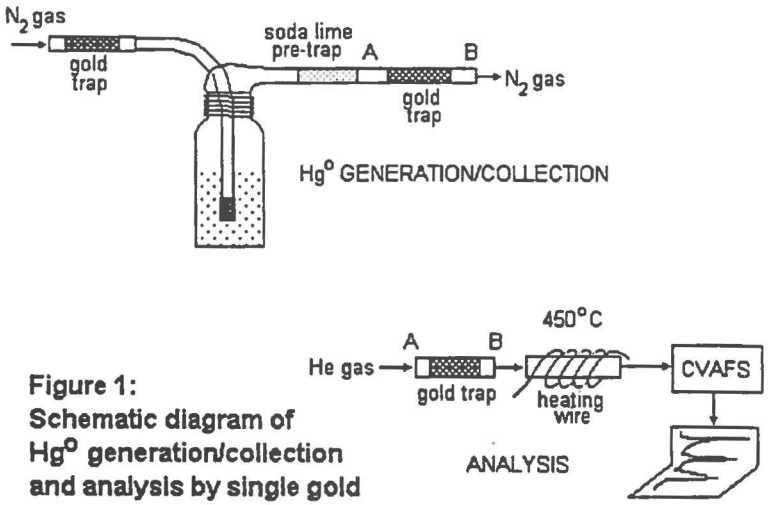

Figure 1: Schematic diagram of Hg^0 generation/collection and analysis by single gold amalgamation/CVAFS

Please note that "acid-labile" Hg is an operationally defined fraction of the total, and hence the bubbling time is a defining parameter. The longer the sample is bubbled, the greater the amount recovered will be. Thus, reproducibility in the bubbling time is critical. Also, since most of the total Hg remains in the sample after bubbling, multiple samples must be not added to the same water in the bubbler; the bubbler must be completely emptied between samples. SAMPLES TOO SMALL TO FILL THE BUBBLER ABOVE THE FRIT, AND STANDARDS, MUST BE RUN ON $SnCl_2$ PURGED DEIONIZED WATER -- NOT ON TOP OF PURGED NATURAL WATER SAMPLES!

Total mercury may be analyzed after acid-labile values have been run, only after cleaning the bubblers as described in section 3.1. To the BrCl oxidized sample in the 125 mL Teflon® bottles, 50 µL of 30% NH_2OH is added, the bottle capped, and the sample swirled. The yellow color will disappear, indicating the destruction of the BrCl. The sample is allowed to react for 5 minutes to be sure that no trace of halogens remain. PURGING OF FREE HALOGENS ONTO THE GOLD TRAPS WILL RESULT IN

DAMAGE, AND LOW IRREPRODUCIBLE RESULTS THEREAFTER. Once the sample has been pre-reduced with NH_2OH, it may be analyzed as described for acid-labile Hg. When running total mercury samples, however, the recovery is quantitative, and organic interferents are destroyed. Thus, standards and bubbler blanks may be run directly on top of past purged samples.

To analyze the mercury contained on a gold trap, the nichrome wire coil is placed around the trap, and the trap is inserted in between the incoming Hg-free argon (or helium) and the analyzer. Electrical current (10 VAC) is then applied to the coil for 2.5 minutes (or 1 minute after returning to the base line), thermally desorbing the Hg as Hg^0, which is carried by the He to the analyzer. At the same time the data acquisition device (integrator) is turned on.

Following the recording of the peak, the coil on the gold trap is turned off, and the cooling fan directed at it. The gold trap is now removed from the gas stream, and the Teflon® end plugs replaced until it is needed to collect another sample. The next sample column is placed in line, and the procedure repeated.

Peaks generated using this technique should be very sharp and almost symmetrical. The peak comes off at approximately 1 minute, and has a half-height width of about 5 seconds. Broad or asymmetrical peaks are indicative of an analytical problem, possibly including: low gas flow, water vapor on the trap, or the trap being damaged by chemical fumes or overheating. The last possibility is definitely the case if following a sharp peak, a secondary small broad peak is observed. If the gold trap has been damaged, it and the Teflon® tubing downstream from it should be discarded, due to the possibility of gold migration on downstream surfaces.

7.3. Cold Vapor Atomic Fluorescence for mercury is linear over at least 5 orders of magnitude (Bloom and Fitzgerald, 1988). However, it is required that at least a 3 point calibration curve be prepared each day prior to analysis to verify linearity. Standards to be analyzed for calibration should include one standard at 100 pg, one at 500 or 1000 pg and one at 5000 pg.

7.4. To run standards, aliquots of working standard solution are injected into a purged bubbler containing a fresh 0.5 mL aliquot of $SnCl_2$, and the analysis run as a sample.

7.5. Gold-coated sand traps should be kept track of by unique identifiers, so that any trap producing poor results can be quickly recognized and discarded. A log book should be maintained documenting initial trap testing and any questionable trap behavior. Occasionally due to inadvertent contact with halogen fumes, bubbler solution, organic fumes, or overheating, a sampling trap will become damaged, giving low and irreproducible results. Suspect traps should be checked with at least two consecutive standard runs before continued use.

7.6. The major cause of analytical problems with this method is from using the soda lime pretraps too long. These traps should be purged for at least 20 min. as described and then used for only one day's analytical work. Longer use risks irreproducibility, as the traps may begin retarding the flow of Hg^0. Also, as they become very wet, there is a risk of NaOH-saturated water drops coming out onto the gold trap. If samples aliquots containing much acid (i.e. 5 mL) are being analyzed, it is recommended that the soda lime pretraps are changed after every two or three samples. The acid fumes in combination with water vapor, when trapped in the soda lime pretraps seem to start trapping Hg^0 and therefore low recoveries may result.

7.7. Duplicates, spiked samples, method blanks and check standards should be analyzed, as discussed in section 8.

7.8. Calculations are made by the following method:

a) Divide each standard amount (pg of Hg) by each net standard result (peak area of standard minus mean peak area of bubbler blanks or CB) in the calibration, to yield the "pg Hg/peak area." Pool all of the "pg Hg/peak area" values for a given calibration, to obtain a mean "pg Hg/peak area" value called the calibration coefficient (C). (C) is also functionally the equal to the slope of the regression of the standard curve. Linear regression is used to calculate a correlation coefficient (r). The r value should be greater than 0.995 for sample analysis to commence.

b) Pool the calibration blank values to obtain a mean "calibration blank peak area" (CB).

c) To calculate the amount of total mercury measured in a sample, employ the following formula:

$$P = Hg \text{ (in pg)} = C(A-CB)$$

Where A is the gross sample area. If blank correction is not desired by a customer, CB is not subtracted out.

d) To determine the concentration of total mercury in a sample, the calculation is performed as follows:

$$Hg \text{ (in ng/L or ppt)} = [(P/v)V - p]/ V_o - (\text{pg/mL of Hg in excess BrCl})$$

Where V is the final dilution volume of the sample in mL (in this case, 100 mL) v is the volume of sample analyzed in mL, V_o is the prepared sample volume, in mL and p is the mean pg from the preparation of the method blanks. The concentration of any excess BrCl (the amount of BrCl added to the sample minus the amount added to the method blanks) must be subtracted if any excess BrCl was added. If blank correction is not desired by a customer, p and pg/mL of Hg in excess BrCl are not subtracted out.

e) To determine the pg from the preparation of the method blanks (p), use the following formula for each method blank:

$$p = [(MB - CB)C \cdot V]/v$$

Where MB is the peak area of the method blank, V is the final dilution volume of the method blank and v is the volume of the method blank analyzed.

d) The limit of detection is considered to be 3 times the standard deviation of the picograms in the entire method blanks. The picograms in the method blanks is calculated in the following manner:

$$\text{Hg in method blank (in pg)} = (MB \cdot C \cdot V)/v$$

To determine if a sample is detectable the limit of detection should be multiplied by V and divided by v using volume amounts specific for that sample. If a sample is below the detection limit it should be qualified as such.

8. QUALITY CONTROL

8.1. All quality control data should be maintained and available for easy reference or inspection.

8.2. Calibration data must be composed of a minimum of 3 calibration (or bubbler) blanks and 3 standards (preferably four of each). Such a calibration should be run at least once per day, or every 20 samples, whichever comes first. If work performed is research level, more than 20 samples may be analyzed in a batch at the discretion of the lab director.

8.3. Samples containing high analyte concentrations may be run either following dilution, or on a separate run at lower instrumental sensitivity provided the instrument is calibrated at this sensitivity. All peak areas obtained for samples must ultimately fall below the peak area obtained from the highest standard analyzed in the calibration curve.

8.4. Calibration checks must be analyzed after instrument calibration, after every ten samples and at the end of the analytical batch. Calibration checks shall consist of a mid-level standard (500 or 1000 pg) and a bubbler blank. The calibration check standard must be within 20% of the calibration and the calibration check blank must be within 100% of the calibration blanks.

8.5. A minimum of 2 method blanks per batch of 20 samples must be run. To obtain a meaningful value for the reporting limits of detection, the standard deviation must be estimated from at least 7 sets of method blanks. Method blanks should consist of all reagents used for a sample and should be carried through the entire method as a sample. To estimate the standard deviation from multiple sets of duplicate method blanks, the following formula is used:

$$\text{Estimated Standard Deviation} = \sqrt{[\sum (d \cdot d)]/2m}$$

where d is the difference between within batch determinations of the method blanks and m is the number of duplicate blank determinations.

8.6. Analysis of split samples should be run once every 10 samples or once per batch, whichever comes first. Split samples are defined as a homogeneous sample that is split into two aliquots, and then each aliquot is carried through the entire preparation and analytical procedure. Criteria for split sample results are determined by control charts. If control charts are not available then the split sample results must have a relative percent difference of 35% or less for the analysis to be considered valid. Sample results not meeting this criteria shall be reprepared and analyzed or qualified at the discretion of the lab director.

8.7. NRC or NBS certified reference materials for mercury in tissues and sediments should be analyzed at a frequency of once per 10 samples or once per batch, whichever comes first. Criteria for CRMs are determine by control charts. If control charts are not available then CRM results should be within 25% of the certified value for the analysis to be considered valid. CRM sample results not meeting this criteria shall be reprepared and analyzed or qualified at the discretion of the lab director.

8.8. Procedural spike recoveries are analyzed at the request of the client, or in the absence of a suitable certified sample as determined by the lab director.

9. REFERENCES

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SOP #BR-0011

Determination of Methylmercury by Aqueous Phase Ethylation, Trapping Pre-Collection, Isothermal GC Separation, and CVAFS Detection

Brooks Rand, Ltd.

Revision 003
Revised 8/95

Reviewed _____

COPY #003 for EVS

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Determination of Methylmercury by Aqueous Phase Ethylation, Trapping Pre-Collection, Isothermal GC Separation, and CVAFS Detection

1. DESCRIPTION

1.1. Mono-methylmercury (MMHg) is determined by an improved method (Liang, Bloom, and Horvat 1994). The MMHg is first ethylated with sodium tetraethylborate (BEt_4^-) and collected by purging with dry, Hg free Nitrogen onto a column filled with either Carbotrap™ or Tenax. The ethyl mercury derivatives are then thermally desorbed and transferred to a GC column held in an oven at 96° C, and the species are chromatographically separated by the GC column. The organo-Hg compounds are decomposed at 900° C to Hg^0, then quantified by a cold vapor atomic fluorescence spectrometer (CVAFS). The detection limits (DL, as Hg) for the technique are about 0.6 pg for MMHg. The method can be applied for the determination of MMHg in a variety of samples and it has been demonstrated as being a very sensitive, precise, and accurate method. Very good results were obtained for the determination of MMHg in reference standard materials and hair, blood, and brain intercalibration samples (Liang, Bloom, and Horvat 1994).

2. APPARATUS AND MATERIAL

2.1. Cold vapor atomic fluorescence spectrometer (CVAFS) made at Brooks Rand, Ltd.

2.2. Chromatographic peak integrator (Lab Data Control I-400)

2.3. Reaction and purge vessels: A 150 mL flat bottom bottle with 24/40 tapered fitting is used as the reaction vessel. A special 4-way valve sparging-tube cap-assembly is used. This valve assembly allows the water sample to react initially with the ethylating reagent, without bubbling, then to be purged onto the trapping column, and finally to be bypassed, so that water vapor adsorbed onto the column may be evaporated by the direct flow of dry carrier gas.

2.4. Trapping column: A column for the collection of purged organomercury species is constructed from a 10 cm length of 6.4 mm outside diameter x 4.0 mm inside diameter silanized quartz tubing with a coarse quartz frit 2.5 cm from one end. The column is prepared by packing either 180 mg of Carbotrap™ or 80 mg of Tenax TA, using silanized glass wool to hold the packing in place (see figure 1). The layer of glass wool to the end A should be thin, just for blocking up grains of filling material, while the layer to the end B should be packed in a manner that makes a glass wool stopper about

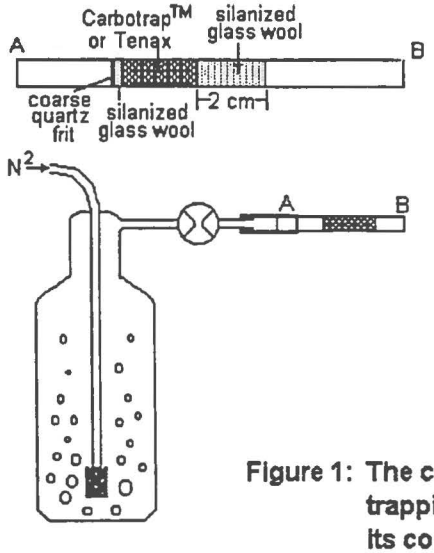

Figure 1: The construction of trapping column and its connection with a reaction vessel

2 cm length, and then placed into the quartz tubing as tightly as possible. Compress the packing again, carefully making filling grains tight, but do not crush them. Figure 1 also shows the connection of the column and a reaction vessel.

2.5. Isothermal gas chromatography system: Illustrated in figure 2 is a schematic diagram. A GC column is prepared by packing 65 cm length of preconditioned 15% OV-3 on chromasorb W-AW-DMCS, 60/80 mesh into a silanized 80 cm total length 6.4 mm outside diameter x 4.0 mm inside diameter borosilicate glass chromatography U-tube within a sealed glass sheath, and the OV-3 column is held in place with silanized glass wool plugs. Under a 50 mL/min flow of high purity helium, organomercury species desorbed from a trapping column were carried by gas passing through a GC column held at 96° C in a cylindrical oven and eluted. Separated species were decomposed in a thermal decomposition tube and finally detected by CVAFS.

3. REAGENTS, GASES, AND WATER

3.1. MMHg Standard solutions

a) Stock solution: 1 mg/mL MMHg, as Hg. Dissolve 0.1252 g CH_3HgCl (95%+) in 100 mL of isopropanol.

b) Intermediate stock solution: 1 µg/mL MMHg, as Hg. Dilute 1.00 mg/mL stock solution in isopropanol. This solution is stable at least for one year if stored in refrigerator.

c) Working solution. 1 ng/mL MMHg, as Hg. Dilute 1.00 ng/mL stock solution in 1% HCl. This solution is stable for at least 3 weeks when stored out of direct light at room temperature.

3.2. Sodium tetraethylborate ($NaBEt_4$) solution: Dissolve one gram of $NaBEt_4$ in 100 mL of 2% NaOH solution stored previously in refrigerator. The solution is then divided into several smaller Teflon small mouth bottles. These small bottles are stored frozen. Since this reagent is extremely air sensitive, the preparation must be performed quickly. Defrost the solution prior to use. Frozen aliquots may lose effectiveness after 2 weeks.

3.3. Sodium acetate buffer: A 2M acetate buffer is prepared by dissolving 272 g of reagent grade sodium acetate and 118 mL of glacial acetic acid in DDW to a final volume of 1 L. This solution is purified of trace mercury by the addition of 5 g of 1 N HCl-rinsed sulthydoxyl chelating resin (Sumitomo Q-10R) to the bottle and agitation. The solution is stored in a Teflon FEP bottle and filtered prior to use.

3.4. Potassium hydroxide methanol solution: Dissolve 250 g of reagent grade KOH pellets in high purity methanol to a final volume of 1 L. The solution is stored in a Teflon FEP bottle.

3.5. Gases: Helium used as a GC carrier gas is laboratory grade. Nitrogen used as a purge gas for sweeping derivatives from a bubbler is also laboratory grade. Both are passed through a gold-coated sand trap to remove traces of mercury prior to use.

3.6. Water: Double Deionized Water (DDW) from a Millipore System was used throughout.

4. ANALYSIS

Standards, typically 0, 10, 50, 100, 500 pg for MMHg, and samples (for sample preparation see section 6) to be analyzed are added into reaction vessels containing 50-100 mL of DDW and 200 µl of 2M acetate buffer. An aliquot of 50 µl of $NaBEt_4$ is added, the 4-way valve-cap inserted and the vessel swirled to rinse. The mixture is allowed to react without purging for 12 minutes A trapping column is placed in an orientation shown in Figure 1, and then is purged with N_2 at a flow rate of 250 $mL \cdot min^{-1}$ for 12 minutes. The organomercury compounds are swept and collected onto the trapping column. Then the valve is switched to pass dry gas over the column for 5 minutes, to remove residual water condensation from the trap. The trapping column is then connected in-line with the GC column (Fig. 2)

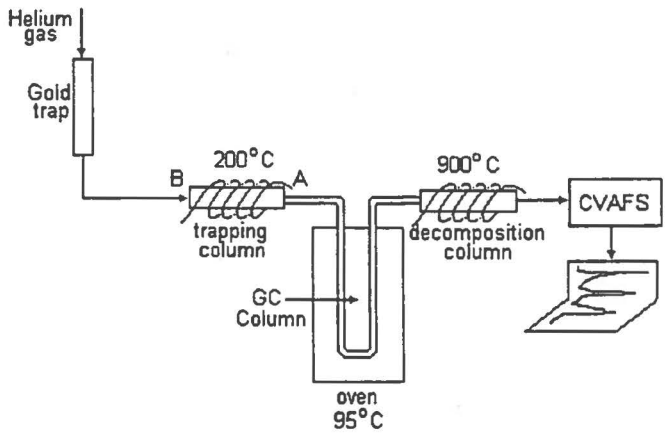

FIGURE 2: A schematic diagram of isothermal gas chromatograph system

When a carbotrap is used, special attention must be paid to the orientation of the trap shown in Figure 2. The trap is placed so that the end facing the bubbler output is now facing the GC column input to avoid the organomercury species passing through the entire length of the heating trap column and decomposing to Hg^0 (Liang, Bloom, and Bloom 1994). Under a helium flow rate of 80 mL·min the column is heated to reach 200° C from room temperature within 30 seconds, controlled by switching on a timer connected in-line, while turning on the integrator or chart recorder. The organomercury species were desorbed and carried to pass through the GC column held in an oven at 96° C. The species are eluted in an order of increasing molecular weight and carried through the thermal (900° C) decomposition tube where all organomercury species are converted into Hg^0 and detected by CVAFS, and fluorescence signals are recorded by an integrator as peak area or by a chart recorder as peak heights, and are measured manually with a millimeter ruler.

5. CALCULATIONS

Calculations may be made by reading off the (linear) standard curve, or by the following method, which is functionally the same.

Calculate a mean (B) "peak height (mm) of the calibration (bubbler) blank".
Calculate a mean coefficient (C)

$$C = \frac{pgHg}{PH - B}$$

where PH is a peak height of aliquot of standard in mm.

Calculate the concentration of each species in sample by the following formula:

For aqueous samples:

ng of Hg/L = $\{[C\cdot(S-B)\cdot V_2/V_1]-MB\}/V_3$

where S is the peak height of sample aliquot in mm, V_1 is the analyzed sample aliquot size in mL, V_2 is the final dilution volume of the distillate in mL, MB is the total picograms of the method blank and V_3 is the original sample volume distilled in mL.

$MB = C\cdot(S-B)\cdot V_2/V_1$

where S is the peak height of method blank in mm, V_1 is the analyzed method blank aliquot size in mL, and V_2 is the final dilution volume of the method blank distillate in mL.

For solid samples:

Solid samples are calculated in the same manner as above except that V_3 is the original sample weight digested or distilled in mg, with the result being in ng/g

6. SAMPLE PREPARATION

Depending on the purposes and definitions of investigations of mercury biogeochemistry cycling, samples are prepared in the following methods prior to analysis.

6.1. The following two isolation methods, distillation and solvent extraction, have been used in our labs for the determination of MMHg in aqueous samples. Good agreement was obtained in the comparison of the two methods for most water samples studied: for organic rich and/or high level sulfide containing samples, the distillation showed some advantages over the solvent extraction method with higher recoveries (85 ± 4%, Horvat, Bloom, and Liang, 1993). In addition, extraction consumes a lot of organic solvent and results in environmental contamination. Therefore, distillation is preferred.

6.1.1. Distillation:

Reagents: 20% KCl in L-Cysteine, 8M H_2SO_4, 0.05% $NH_2OH\cdot HCl$

Distillation devices: Vials and caps for distillation and distillate collection are made of Teflon obtained by Savillex Corporation, USA. Caps have 1/8" ports for friction fit 1/8" Teflon tubing. Instead of Teflon, a glass distillation still may also be used (Horvat and Stoeppler, 1988).

Distillation procedures: An aliquot of water sample, typically 45 mL, is transferred into a 60 mL Teflon vial (for high MMHg concentration samples, small sample size should be used, but bring the final volume to a known volume with DDW). Add 0.2 mL of 20% KCl and 0.5 mL of 8M H_2SO_4. Start the distillation immediately after addition of reagents at a nitrogen flow rate of 60 $mL\cdot min^{-1}$ and at a heating

block temperature of 145° C. The distillate is collected into a 60 mL Teflon vial containing 3-5 mL of 0.05% $NH_2OH{\cdot}HCl$ in DDW, which is cooled in an ice-water bath. The distillation is finished when approximately 85% of distillate is collected after taking 3-4 hours. Bring the final volume to 58 mL with DDW in receiving vial. Depending on its MMHg concentration, the whole or an aliquot of the distillate is added into the methylation reaction vessel for analysis as described in section 4. Some acid can be carried over during distillation. Adjust pH in the bubbler to 3.5-5.5 by adding 20% KOH and/or 1:1 HAC solutions before adding buffer.

6.1.2. Solvent extraction

Reagent: 30% KCl (saturated), methylene chloride (large blanks in MMHg determination occasionally result from this solvent. Therefore, different brands and lot numbers should be examined to minimize this contamination.)

Extraction procedure: An extraction procedure described by Bloom (1989) was used. Depending on its concentration, weigh an approximate volume of the sample acidified to a pH of 2-5, typically 50 mL into a 125 mL Teflon bottle. If a smaller sample size is used, bring the final volume to 50 mL with DDW. Add 5 mL of 30% KCl, and swirl the bottle to mix. Add 40 mL of methylene chloride. Shake the bottle for 1-2 h with a mechanical shaker to reach a distribution equilibrium of MMHg between aqueous and solvent phases, then allow the two phases to separate. Remove the upper phase (aqueous phase) by pipetting. Add about 50 mL of DDW to the methylene chloride, and place the bottle in a hot water bath at 60° C until all of the CH_2Cl_2 has boiled away. The water is then purged for 2-3 minutes at 250 $mL{\cdot}min^{-1}$ with N_2 to remove any residual solvent. The MMHg is transferred to the DDW matrix, which is ready for ethylation as described above. At least 2 reagent blanks and 2 spikes are run each day of extraction/analysis. Usually, 10% of samples are used for spike recovery evaluation. The mean recovery is calculated, which is used to correct all sample results.

6.2. Determination of MMHg and Hg(II) in biological materials and sediments

6.2.1. Alkaline digestion: About one gram of biological materials or sediments (wet, homogenous) is weighed into a 30 mL Teflon vial. 10 mL of 25% KOH methanol solution is then added to the vial, which is then tightly closed with a cap. The sample is digested in an oven at 65° C for 3-4 hours. After digestion, bring the final volume to 25.6 mL with methanol prior to analysis. Analyze an appropriate aliquot, depending on the sample's concentration of MMHg and Hg(II).

6.2.2. Distillation: If the MMHg concentration compared to Hg(II) is low, matrix interference on ethylation reaction caused by using large volumes of alkaline

digestate will occur. This interference is avoided by distillation (Horvat, Bloom, and Liang, 1993). A sediment sample can be distilled directly by weighing an appropriate amount into a 30 mL Teflon vial and adding 10 mL of DDW, followed by the distillation procedure mentioned above (6.1.1). For biological samples (Liang, Bloom, and Horvat 1994) the MMHg bound on protein must be distilled out completely; therefore, a sample should be distilled after alkaline digestion by taking 0.5 mL of alkaline digestion, adding 10 mL DDW into a 30 mL vial, and following section 6.2.1.

7. SAMPLE COLLECTION, STORAGE, AND HANDLING, AQUEOUS, SEDIMENTS, AND BIOLOGICAL MATERIALS.

7.1. Water

7.1.1. Samples should be collected only into rigorously cleaned Teflon bottles. Under no circumstances should ordinary plastic (i.e.; polyethylene, polypropylene, or vinyl) containers be used, as they are very diffusive to gaseous Hg^0 from the air. Ashed or rigorously acid cleaned Borosilicate or quartz glass bottles with Teflon caps may be used as well. It is critical that the bottles have very tightly sealing caps to avoid diffusion of atmospheric Hg through the threads (Gill and Fitzgerald, 1985). As an added precaution, clean bottles are filled with high purity 1% HCl solution and dried, capped, and double-bagged in new zip-loc bags in the clean-room, and stored in wooden or plastic boxes until use.

7.1.2. Samples are collected using rigorous ultra-clean protocols (Gill and Fitzgerald, 1985; and EPA Method 1669 "Sampling Ambient Water for Trace Metals At EPA Water Quality Criteria Levels", April 1995) which are summarized as follows:

a) At least two persons wearing fresh clean-room gloves at all times, are required on a sampling crew.

b) One person ("dirty hands") pulls a bagged bottle from the box, and opens the outer, dirty bag, avoiding touching inside that bag.

c) The other person ("clean hands") reaches in, opens the inner bag, and pulls out the sample bottle.

d) The bottle is opened with a plastic shrouded dedicated wrench, and the acidified water is discarded downstream of the sampling site.

e) The bottle is rinsed once with sample water, and then filled.

f) Preservative (i.e.; 0.8% by volume of high purity HCl) may be added at this time, or within several hours after receipt at the clean laboratory.

g) The cap is replaced with the wrench, and the bottle rebagged in the opposite order from which it was removed.

h) Clean-room gloves are changed between samples and whenever something not known to be clean is touched.

i) Water samples are best obtained by surface grab, using gloved hands, and facing into a flowing body of water (i.e.; looking upstream or of the bow of a moving boat). If samples are to be taken from depth, the only non-contaminating method generally available is pumping. Two methods have been found to work in this regard. The first is to use rigorously acid-cleaned Teflon tubing, and a peristaltic pump with *freshly cleaned* (heating to 70° C in 5% HCl + CH_3COOH) silicon tubing. Beware that once cleaned, silicon tubing quickly absorbs Hg from the air The other method involves high-volume pumping (i.e.; 50 $L \cdot min^{-1}$) through neoprene hose. If this method is used, it is best to clean the system first by pumping several hundred liters of 5% HCl solution, and then pumping clean water for several hours. This second technique works largely because the rate of flow is so fast that the contamination becomes imperceptibly diluted.

j) DISCRETE SAMPLERS, i.e.; Niskin, GoFlo, and Kemerer BOTTLES, ARE TO BE AVOIDED, AS EVEN UNDER THE BEST OF CONDITIONS THEY ARE OFTEN FOUND TO GROSSLY CONTAMINATE SAMPLES AT THE $ng \cdot L^{-1}$ LEVEL.

7.1.3. Samples may be preserved by adding 8 $mL \cdot L^{-1}$ of concentrated HCl (if only total methylmercury is to be analyzed), or frozen if labile and methylmercury are to be analyzed. Samples may also be sent back to the laboratory unpreserved if they are 1) collected in Teflon bottles, 2) filled to the top with no head space, and 3) sent at 1° C by overnight mail. The samples should be preserved and analyzed soon after arrival at the laboratory (within 24 hours). FREEZING IS NOT AN ACCEPTABLE TECHNIQUE FOR TOTAL INORGANIC Hg, AS UPON THAWING, MUCH Hg(II) IS CONVERTED TO VOLATILE Hg^0.

7.1.4. All handling of the samples in the lab is to occur by clean-room gloved personnel in a class-100 clean room station with mercury removal filters, after rinsing the outside of the bottles in low Hg water, and drying in the clean air hood.

7.2. Solids

7.2.1. Samples should be collected only into rigorously cleaned Teflon containers or glass containers with Teflon lined lids. Under no circumstances should polyethylene, polypropylene, or vinyl containers be used.

7.2.2. Samples are to be frozen at <-10°C (standard freezer on coldest setting) until use. A holding time of 1 year at <-10°C is recommended.

7.2.3. All dissection, homogenization, and other handling of the samples is to occur by clean-room gloved personnel in a class-100 clean room station with mercury removal filters.

8. QUALITY CONTROL

8.1. All quality control data should be maintained and available for easy reference or inspection.

8.2. Calibration data must be composed of a minimum of 3 calibration (or bubbler) blanks and 3 standards (preferably four of each). Such a calibration should be run at least once per day, or every 20 samples, whichever comes first. If work performed is research level, more than 20 samples may be analyzed in a batch at the discretion of the lab director.

8.3. Samples containing high analyte concentrations may be run either following dilution, or on a separate run at lower instrumental sensitivity provided the instrument is calibrated at this sensitivity. All peak areas obtained for samples must ultimately fall below the peak area obtained from the highest standard analyzed in the calibration curve and above the lowest standard if possible.

8.4. Calibration checks must be analyzed after instrument calibration, after every ten samples and at the end of the analytical batch. Calibration checks shall consist of a mid-level standard and a bubbler blank. The calibration check standard must be within 20% of the calibration and the calibration check blank must be within 100% of the calibration blanks.

8.5. A minimum of 2 method blanks per batch of 20 samples must be run. To obtain a meaningful value for the reporting limits of detection, the standard deviation must be estimated from at least 7 sets of method blanks. Method blanks should consist of all reagents used for a sample and should be carried through the entire method as a sample. To estimate the standard deviation from multiple sets of duplicate method blanks, the following formula is used:

$$\text{Estimated Standard Deviation} = \sqrt{[\sum(d \cdot d)]/2m}$$

where d is the difference between within batch determinations of the method blanks and m is the number of duplicate blank determinations.

8.6. Analysis of split samples should be run once every 10 samples or once per batch, whichever comes first. Split samples are defined as a homogeneous sample that is split into two aliquots, and then each aliquot is carried through the entire preparation and analytical procedure. Criteria for split sample results are determined by control charts. If

control charts are not available then the split sample results must have a relative percent difference of 25% or less for water and 35% or less for solids for the analysis to be considered valid. Sample results not meeting this criteria shall be reprepared and analyzed or qualified at the discretion of the lab director.

8.7. NRC or NBS certified reference materials for mercury in tissues and sediments should be analyzed at a frequency of once per 10 samples or once per batch, whichever comes first. Criteria for CRMs are determine by control charts. If control charts are not available then CRM results should be within 25% of the certified value for the analysis to be considered valid. CRM sample results not meeting this criteria shall be reprepared and analyzed or qualified at the discretion of the lab director.

8.8. Procedural spike recoveries are analyzed at the request of the client, or in the absence of a suitable certified sample as determined by the lab director.

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SOP #BR-0020

Determination of Selenium and Arsenic in Environmental Samples by Hydride Generation-Atomic Absorption with Cryogenic Trap Preconcentration

Brooks Rand, Ltd.

Written 2/28/93

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Revised 12/94

Reviewed

COPY #003 for EVS

CONFIDENTIAL

President — Date 12/2/94

Lab Director — Date 12/2/94

Senior Scientist — Date 12/2/94

Determination of Selenium and Arsenic in Environmental Samples by Hydride Generation-Atomic Absorption with Cryogenic Trap Preconcentration

1. DESCRIPTION

The procedure for the determination of total Selenium/Arsenic in fresh/sea water, sediment, and biological materials is based on a method described in peer reviewed literature (Liang *et. al.*, 1994; Crecilius *et. al.*, 1986). For the determination of As in water, organic As is oxidized into As(III) and/or As(V) by the addition of a $KBrO_3$/KBr/HCl solution and UV irradiation. In the presence of NH_2OHHCl, As(V) in 4 M HCl is quantitatively reduced to As(III) by heating until boiling (without boiling time dependence) in a conventional kitchen microwave oven. For the determination of Se in water, the sample must first be preconcentrated by reducing the volume at an elevated temperature (without boiling), then the sample is treated the same as sediment and biological samples. For the determination of As and Se in sediment and biological materials, samples are digested with $HNO_3/HClO_4$ in a sand bath. The organo-Se, Se(II) and Se(O) are oxidized to Se(IV) and/or Se(VI), and then the Se(VI) is reduced to Se(IV) with NH_2OHHCl and heating in a conventional kitchen microwave oven. Arsenic is reduced in the same manner. Se and As are then determined by Hydride Generation-Atomic Absorption (HGAA) with cryogenic trap preconcentration and H_2/Air flame quartz furnace decomposition.

2. APPARATUS AND MATERIALS

2.1. Detector: A Perkin-Elmer 703 Atomic Absorption Spectrophotometer (AAS) with a selenium electrodeless discharge lamp, fitted with a quartz tube furnace (1.0 cm I.D. and 7.0 cm long) in which an air-hydrogen flame burns.

2.2. Integrator: Chromatographic peak integrator (Spectra Physics, SP4290).

2.3. Hydride generation system: The hydride generation system, cryogenic trap precollection and AA detection systems are shown in Figure 1. Flat bottom glass bottles (150, 100, 30 mL) with sparging-tube cap assembly and a silicone bubbler septum injection port serve as reaction vessels and strippers. A peristaltic pump (Cole-Parmer Instrument Company, 7570-10) is used for pumping the $NaBH_4$ solution. A trap immersed in liquid nitrogen (LN) for the collection of SeH_2/AsH_3 is constructed from a 30 cm length of 6.2 mm outside diameter x 4.0 mm inside diameter Pyrex glass tubing, and packed with 5 cm of 3% OV-3 on Chromasorb W-AW-DMCS, 60/80 mesh. The OV-3 column is held in place with glass wool plugs. A cylindrical oven is used for rapidly heating the trap to quickly release hydrides. All connections are made with Teflon connectors and Teflon tubing.

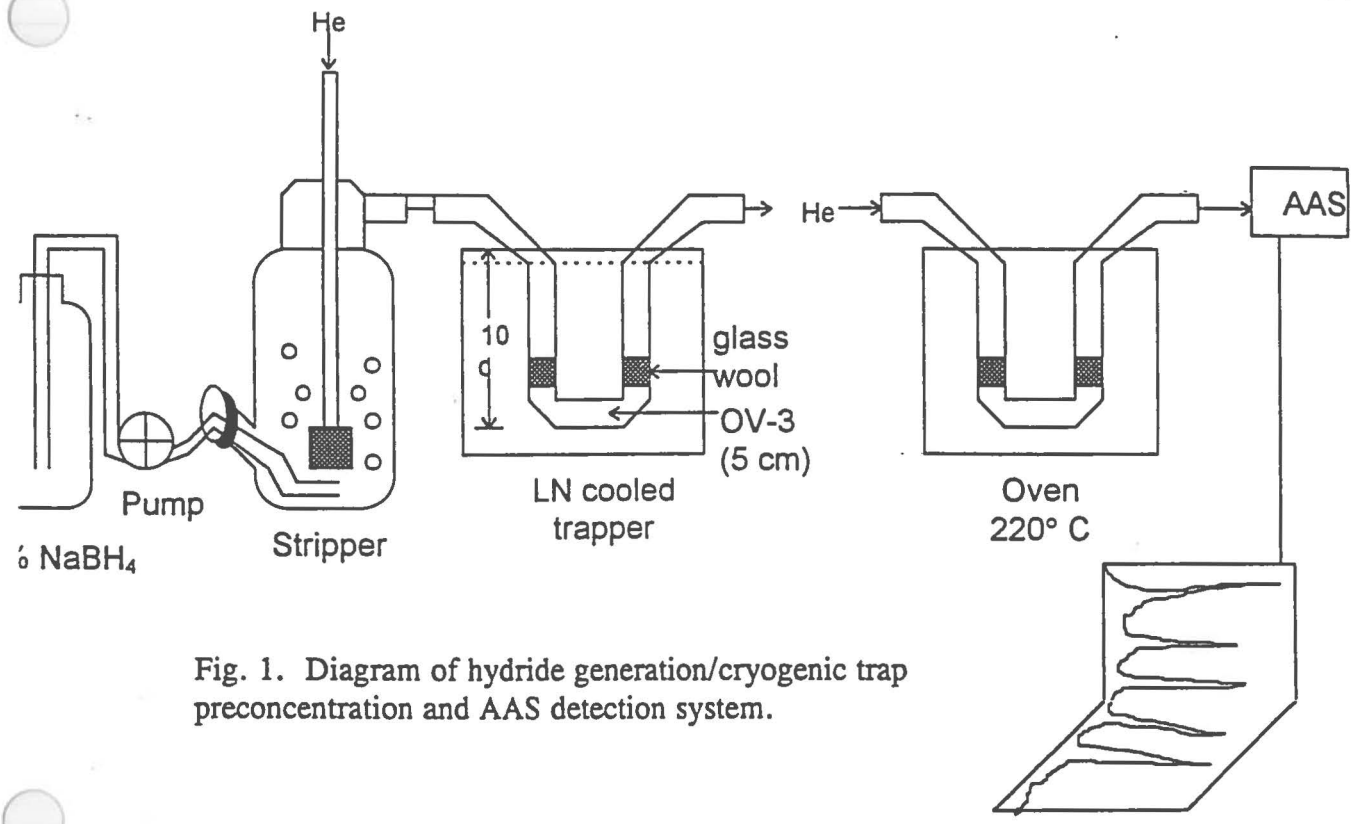

Fig. 1. Diagram of hydride generation/cryogenic trap preconcentration and AAS detection system.

2.4. Microwave: A microwave oven used for boiling solution is a conventional kitchen microwave oven.

2.5. UV irradiation box: A UV irradiation box is used for pretreatment of water samples for As.

2.6. Sand bath: Sand-bath with a temperature control is used for digestion of solid samples and Se in water.

3. REAGENTS, GASES, AND WATER

3.1. All reagents are analytical grade. All gases are laboratory grade. Double deionized water (DDW) from a Millipore System is used throughout.

3.2. Standards: Se(IV) stock solution, 1000 µg/mL in 2% HCl (v/v) (High Purity Standards, P.O. Box 30188 Charleston, SC, 29417; Catalog Number 291103), and As stock solutions, 1000 µg/mL in 2% HCl (v/v) (High Purity Standards; Catalog Numbers 290512, 290708) are used for preparation of diluted working standards.

3.3. Reducing agent: The reducing solution of 4% $NaBH_4$ (w/v) is prepared by dissolving $NaBH_4$ (98% purity) in 0.2% KOH (w/v).

3.4. $KBrO_3$/KBr/HCl solution: 27g of KBr is dissolved in a 2.5 L bottle of concentrated HCl. 38 g of $KBrO_3$ is added slowly to the solution with stirring. The solution is used as an oxidant for the determination of total As in water.

3.5. 30% NH_2·OH·HCl (w/v) solution.

3.6. HNO_3/$HClO_4$ (4:1, v/v): Baker Instra-Analyzed acids (J.T. Baker Chemical Co., Phillipsburg, NJ) are used.

4. PROCEDURES

4.1 Se Determination

4.1.1 Aqueous sample preparation. A 50 mL aliquot of sample is poured from a thoroughly shaken, acidified sample, into a 125 conical flask. 0.5 mL of HNO_3 is added, and the sample is heated in the sand bath at 90-120°C but without bringing the sample to a boil. When the volume of sample is reduced to about 5 mL (after about 5 hours) the sample is treated as a solid sample for further preparation.

4.1.2. Solid sample preparation. A 1 gram aliquot of wet homogeneous sample or 0.2-0.4 g of dry sample is weighed into a 125 mL conical flask. For Se in water, leave the entire concentrated sample aliquot from 4.1.1 in the flask. Ten mL of a mixture (4:1) of HNO_3 and $HClO_4$ is then added.

WARNING: *The use of $HClO_4$ in sample digestion is potentially very dangerous. The analyst must pay attention to the digestion process which must be carried out in a fume hood.*

A glass funnel is placed in the flask, and a glass ball is used to cover the neck of the funnel. The sample is then digested in a sand bath set at 200°C. The temperature of the surface of the sand bath should be about 140°C, and the bottom at about 200°C. At the beginning, the flask should be inserted about 5 mm below the surface of the sand, to maintain a gentle boiling for four hours. The flask is then inserted into the bottom of the sand bath and the funnel removed to speed up the decomposition and/or vaporization of HNO_3. The digestion should continue until about 0.5 mL of sample remains, making sure not to allow the digestates to dry. After decomposition of $HClO_4$ the digestate is cooled and then diluted with 17 mL of HCl and the total volume is brought to 50 mL with DD water. This diluted sample is then transferred to a pre-weighed Teflon bottle. 50 µL of the 30% NH_2·OH·HCl solution is added to the bottle,

and the bottle loosely capped. The loosely capped sample is heated in a microwave oven until boiling. The volume should be corrected with DDW to the original volume after microwave boiling. The sample should then be cooled in a cold water bath to room temperature. If an ice water bath is used and the sample is cooled to below room temperature, allow it to return to room temperature. The hydride generation reaction can be conducted only when the sample temperature is at room temperature. Reagent blanks should be done as samples.

4.1.3 Hydride Generation. For water samples, 20 mL (or half the sample) is transferred to the hydride generation vessel. The vessel is connected in-line with the liquid nitrogen (LN) trap/AA system. The $NaBH_4$ solution was pumped to the vessel at a speed of 1 mL/min. for five minutes. Helium is the purging gas (N_2 can also be used). Remove the vessel from the line while the He gas is connected to the LN trap. The trap is then moved from the LN container to the cylindrical oven set at 180°C to release the SeH_2 quickly to the quartz furnace using a hydrogen air flame. The SeH_2 is decomposed and then detected by AA. Standards of 0, 5, 15, and 30 ng of Se are added directly to the hydride generation vessel containing HCl at a concentration above 1N to make a standard curve for calibration. The AAS conditions are listed in Table 1.

Table 1: AAS Conditions for Se Determination

Lamp Current	6W
Wavelength	196.0 nm
Slit	0.7 mm
Signal mode	Peak area
Gas flow rates	H_2:He: Air = 225:90:375 mL/min.

4.1.4 Calculation of Results: Calculations are performed as follows:

(a) Calibration Blank (B_C) is the mean peak area signal of blanks from the hydride generation vessel.

(b) Coefficient $C_1 = \frac{D_1}{(A_1 - B_C)}$ ng / unit peak area

where D is the amount of standard in ng and A is the peak area signal of the standard.

The Coefficient (C) is then calculated as the average of C_1, C_2, C_3, etc.

(c) Se concentration of water sample $= \frac{C(S_1 - B_M)}{V_1} \mu g / L$

here, S_1 is the peak area signal of the sample measured, V_1 is the volume of the sample measured in mL, and B_M is the adjusted peak area of the method blank

where $B_M = \frac{B_{Mo} \times V_1}{V_{Bm}}$

B_{Mo} is the measured peak area of the method blank, and V_{Bm} is the volume of the method blank

(d) Se concentration of solid sample (or diluted water sample)

$$= \frac{C(S-B)V_1}{V_2 \cdot W \cdot 1000} \mu g / g(\text{or L})$$

where, V_1 is the final dilution volume of the sample digestate in mL; V_2 is the analyzed volume in mL; S is the peak area signal of the sample aliquot analyzed; W is the sample weight in g (or the sample volume in L).

4.2 As Determination

4.2.1 Aqueous sample preparation. An aliquot of sample, typically 40 mL, is poured from a thoroughly shaken, acidified sample, into a 125 mL Teflon bottle. 0.3 mL of the $KBrO_3$/KBr/HCl solution is added, and the bottle closed. The bottle is placed in the UV box and irradiated for 20 minutes to oxidize the sample. If the yellow color disappears, more $KBrO_3$/KBr/HCl solution should be added, until a permanent yellow color is obtained. Some organic-rich water will require a larger volume of the $KBrO_3$/KBr/HCl solution and longer oxidation time. After oxidation is complete, 30% NH_2·OH·HCl is added to the bottle until the yellow color disappears. The bottle is loosely capped and heated in the microwave oven until boiling prior to the hydride generation. The sample volume should now be corrected, if necessary, to the original sample volume with DD water. The sample must be allowed to return to room temperature prior to hydride generation.

4.2.2 Solid sample preparation. The same digestate solution mentioned in section 4.1.2 for Se determination is used. If only As determination is required, the same procedure described in 4.1.2 can be used for sample digestion, but the concentration of HCl used for digestate dilution is not as critical as for Se. About 1N HCl can be used.

4.2.3. Hydride generation. Depending on the expected concentrations, either part of the sample or the entire sample should be used. If the sample concentration is expected to be too high to analyze the entire sample then after microwave oven heating, the total volume of the sample has to be adjusted to the original sample volume. For solid samples an appropriately sized aliquot of the digestate solution is used. The same procedure for hydride generation used for Se determination in 4.1.3, is used for As determination. Standards of 0, 5, 10, and 20 ng of As are added directly to the hydride generation vessel containing HCl at a concentration above 1N to make a standard curve for calibration.

Table 2: AAS Conditions for As Determination

Lamp Current	6W
Wavelength	193.7 nm
Slit	0.7 mm
Signal mode	Peak area
Gas flow rates	H_2:He: Air = 225:90:375 mL/min.

4.2.4. Calculation. The same method described in 4.1.4 for Se was used for As concentration calculation.

5. QA/QC

5.1 Calibration

5.1.1 Instrument and Method Calibration-The instrument calibration consists of analyzing at least three standards covering at least one order of magnitude (one near the upper limits of linearity within the calibration curve, one in the middle and one at the low end) and a calibration blank. See the analytical sections for standard amounts to be analyzed. These standards should cover the expected range of analyte concentrations in the samples. The correlation coefficient of the initial calibration must be ≥0.990. The initial calibration check, consisting of one standard at the mid-point of the calibration curve and one calibration blank, is performed immediately following this initial calibration, after every ten samples and at the end of each batch. After analysis of a batch (maximum 20 samples), the instrument must be recalibrated before use. Calibration criteria for instrument linearity and sensitivity must be met before samples are analyzed. Initial and continuing calibration checks are used to establish whether ongoing instrument calibration is acceptable. Initial and continuing calibration checks must be within 20% of the instrument calibration.

All standards used to prepare the calibration standard solution are obtained from chemical suppliers and are of high purity and concentration. The standards are routinely checked by the laboratory for traceability to National Research Council of Canada (NRCC) or National Institute of Standards and Technology (NIST) Standard Reference materials. These commercial standards are used as stock standards. Working standards are made from the stock standards at appropriate concentrations to cover the linear range of the calibration curve as outlined in the individual procedures. The working standards used for initial calibration curves are independent of calibration check standards and spiking solutions. Preparation of all standards is recorded in a bound laboratory logbook (as described in SOP BR-0500).

All solutions are labeled as follows: name of solution, concentration of solution, date prepared, analyst's initials.

5.1.2 Calibration Checks-Calibration check standards are used to verify the standard calibration curve and assess instrument drift. A calibration check consists of a mid-level standard and a calibration blank. Calibration checks are performed immediately after the calibration curve, after every ten samples and at the end of the analytical batch. Calibration check standards are prepared in the laboratory from standards traceable to the NRCC or NIST. The experimental results of the check sample are compared with the true values, and the percent recovery of the check standard is calculated. If the percent recovery falls within the acceptance range of 80-120%, then sample analysis proceeds. However, if the percent recovery does not fall within the acceptance range, the problem is identified and corrected, and the instrument calibration sequence begins again.

5.2 Quality Assurance Samples

5.2.1 Standard and Certified Reference Materials-All Reference Materials are preferably obtained from either the National Resource Council of Canada (NRCC) or the National Institute of Standards and Technology (NIST). When necessary SRMs/CRMs may be obtained from other sources including the community Bureau of Reference under the Commission of the European Communities (BCR), South African Bureau of Standards (SABS), the International Atomic Energy Agency (IAEA), or others. Most standard reference materials are used directly in audit studies and will reflect performance in both quality and usage. SRMs to be used for Se and As are found in Table 1.

A Reference Material shall be analyzed once for every ten samples to ensure sample recoveries and to show method bias. Results must be within 20% of the certified value.

5.2.2 Performance Evaluation Samples-As an external check performance evaluation samples are analyzed. EPA performance samples (WP study) and USGS intercalibration samples are analyzed semiannually. If any results from these studies are not within the control limits established by the study then an investigation of the methodology and analyst shall be performed, and followed by appropriate corrective action.

5.3 Method Blanks and Limits of Detection

5.3.1 Method Blanks-A method blank is a sample of reagent water (ASTM Type I) that is treated as a sample in that it undergoes the same analytical process as the corresponding field samples. Method blanks are used to monitor laboratory performance, contamination introduced during the analytical

procedure, and for determining method detection limits. Two method blanks are required per analytical batch (maximum of 20 field samples).

Table 1. - CRMs certified for As and Se

Name of SRM	Description/Matrix	Certified concentration for As in ug/g	Certified concentration for Se in ug/g
NRCC DORM-1	Dogfish Muscle	17.7 ± 2.1	1.62 ± 0.12
NRCC DOLT-2	Dogfish Liver	16.6 ± 1.1	6.06 ± 0.49
BCR No. 40	Coal	13.2 ± 1.1	N/A
BCR No. 181	Coking Coal	27.7 ± 1.2	1.15 ± 0.05
NRCC NASS-4	Open Ocean Seawater	1.26 ± 0.09	0.018*
NRCC BCSS-1	Marine Sediment	11.1 ± 1.4	0.43 ± 0.06
NRCC MESS-2	Marine Sediment	20.7 ± 0.8	0.72 ± 0.09
NRCC PACS-1	Marine Sediment	211 ± 11	1.09 ± 0.11
NRCC TORT-1	Lobster Hepatopancreas	24.6 ± 2.2	6.88 ± 0.47
NRCC DORM-2	Dogfish Muscle	18.0 ± 1.1	1.40 ± 0.09
SABS SARM 20	Coal	4.7 ± 1.3	0.8 ± 0.2
NIST 1632b	Coal	3.72 ± 0.09	1.29 ± 0.11
NIST 1643c	Water	82.1 ± 1.2	12.7 ± 0.7
NIST 1633a	Fly Ash	145 ± 15	10.3 ± 0.6

*Not certified, informational value only
All ± values are at the 95% confidence level or 2 standard deviations

5.3.2 Method Detection Limits and Quantitation Limits-The method detection limit (MDL) is the minimum concentration of an analyte of interest that can be measured and reported, with 95 percent confidence, that the value is above zero. MDLs are determined by analyzing duplicate method blanks with each batch of samples. A minimum of seven duplicate method blanks must be analyzed for determination of the MDL. The MDL is then calculated as three times the estimated standard deviation. When evaluating an MDL, the method blank must be carried through the entire method. By analyzing duplicate method blanks with each batch, the MDL is constantly updated.

The quantitation limit (QL) is the concentration of an analyte of interest at which the relative confidence in the measured value is ± 30% at the 95% confidence level. QLs are determined by analyzing duplicate method blanks with each batch of samples. A minimum of seven duplicate method blanks must be analyzed for determination of the QL. The QL is then calculated as ten times the estimated standard deviation.

5.4 Split samples

Split samples or replicate samples provide information about sampling and analysis precision. Replicate samples are true field replicates of two or more samples collected from a common sampling location in two or more independent sampling events; these samples should, hypothetically, have identical compositions and therefore they can be used to evaluate overall precision, including both analytical error and sampling error. Split samples are one or more sub-samples of a primary homogenous sample and are used to evaluate the precision of analysis. The frequency of replicate sample collection and analysis is specified in the contract with the client. One split sample is analyzed per 10 field samples collected.

Results of split sample analyses are used to calculate the relative percent difference (RPD). RPD is then used to estimate analytical precision. Criteria for split sample results is determined by control charts. If no control charts are available, the criteria for the calculated RPD is 25% for aqueous samples and 35% for solid matrices.

5.5 Matrix spikes

Spiked samples are only analyzed at the request of clients. Both samples and method blanks can be spiked with a known amount of analyte. Both samples and spiked samples are then analyzed. Bias is then estimated by calculating the percent recovery of the known amount.

Percent recovery = 100(spiked sample result - sample result)/(known amount spiked)

Spiked samples are used to monitor the analytical method and the effect of the sample matrix on analytical technique.

5.6 Preventative Maintenance

Instrument logbooks are maintained for all equipment. These logbooks contain a complete history of past performance and maintenance. When QC criteria are not met from an analysis, all instrumentation is thoroughly checked and appropriate maintenance is taken.

5.7 Supplies and Reagents

All supplies (i.e., glassware, chemicals, reagents) are of the best possible quality to ensure proper instrument calibration and to avoid contamination. All reagents used are prepared from Analytical Reagent Grade (AR) chemicals or higher purity grades, unless such purity is not available. Reagent water is prepared by double deionization of tap water. Each reagent is clearly labeled with the composition, concentration, date prepared, initials of preparer, expiration date, and special storage requirements, if any.

Reagent solutions are stored in appropriate glass or plastic containers, under conditions designed to maintain their integrity (refrigerated, dark, etc.). Shelf life is listed on the label, and the reagent is discarded after it has expired. Water used in the laboratory is deionized (ASTM Type I water) and periodically checked for purity. All acids used are either glass-distilled or special grade for trace metal analysis. Reagent solutions are checked for contamination by employing reagent blanks before use in any analysis.

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SOP #BR-0022

Extraction of Soil, Sediment, and Biota Samples for the Determination of Selenium Species

Brooks Rand, Ltd.

Written 08/05/96

Revision 000

Reviewed _____

COPY #001 for EVS

DRAFT

President _____ Date _____

Lab Director _____ Date _____

Senior Scientist _____ Date _____

CONFIDENTIAL

Extraction of Soil, Sediment, and Biota Samples for the Determination of Selenium Species

1. DESCRIPTION

The procedure for the determination of selenium species in soil, sediment, and biological materials is based in part on a method described in peer reviewed literature (EPRI, 1986), and on method development work conducted at BRL. Soil and sediments are extracted using a weak sodium hydroxide solution followed by agitation on a shaker table, while homogenized biota is extracted using a more concentrated sodium hyroxide solution (2M) in a hot-water bath. Each matrix is first mixed thoroughly using ultrasonic disruption.

The sample aliquots are first analyzed directly to determine Se(IV), then in a second set of aliquots Se(VI) is reduced to Se(IV) using $NH_2OH{\cdot}HCl$ and heating in a conventional kitchen microwave oven. Selenium species content is then determined by Hydride Generation-Atomic Absorption (HGAA) with cryogenic trap preconcentration and H_2/Air flame quartz furnace decomposition. Total Se is determined afterward by HGAA or Graphite furnace Atomic Absorption, following approved BRL SOPs. For HGAA the prereduction step is critical; only Se(IV) forms volatile hydrides. Selenium (VI) is determined by difference of the Se(IV + VI) and Se(IV) results.

2. APPARATUS AND MATERIALS

2.1. Water bath: A standard laboratory water bath capable of maintaining a temperature of 90 ± 3°C. The bath should have a shaker tray with an agitation rate of 30-60 rpm.

2.2. Shaker table: A vibration-dampened platform suitable for agitating sample extraction vessels. Agitation rate should be adjustable between 60 - 200 rpm.

2.3. Analytical balance: A standard laboratory balance suitable for sample preparation (0-300g; ±0.001g).

2.4. Microwave oven, variable power: A microwave oven used for heating the digestate to near-boiling, a conventional kitchen microwave oven may be used.

2.5. Ultrasonic disrupter and horn: Minimum 400W, 20kHz ultrasonic disrupter with horn and power supply (preferred);
OR
Ultrasonic bath with countdown timer.

3. REAGENTS, GASES, AND WATER

3.1. All reagents are analytical grade; it may be desirable to use double-distilled acids. All gases are laboratory grade. Double deionized water (DDW) from a Millipore System is used throughout.

3.2. Matrix spike standards: Prepare Se(IV) stock solution, 1000 µg/mL in 2% HCl, by dissolving an appropriate amount of sodium selenite (Alfa AESAR; Catalog Number 12585 or equivalent), and Se(VI) stock solutions, 1000 µg/mL in 2% HNO_3 (v/v) (Catalog Number 14239 or equivalent) are used for preparation of matrix spike standards - refer to the relevant analytical SOPs for preparation.

3.3. Sodium hydroxide: Analytical reagent-grade sodium hydroxide (Baker 3722-04 or equivalent)

4. PROCEDURES

4.1 Se Determination

4.1.1. Determine appropriate spiking levels and number/type of quality control samples required for the extraction lot/project. Prepare spiked samples and other quality control samples using the procedure described below.

4.1.2. Solid sample preparation. Between 0.5 - 2 g of wet homogeneous sample or 0.25 - 1 g of dry sample is accurately weighed into a 50 mL centrifuge tube. Between 10 - 30 mL of 2M NaOH solution (4M for biota) is added, the tube capped tightly, and the contents sonicated for 3 minutes using either the sonic horn disrupter or the sonicator bath. Each of these should be operated according to manufacturer's instructions.

4.1.3. Place the tubes horizontally on either the shaker table or water bath tray and agitate between 30-60 rpm for 2 hours.

4.1.4. Remove the tubes from the table or tray and cetrifuge for four minutes. Decant the extract.

4.1.5. Add 5-10 mL of the appropriate NaOH to the tube, cap, and shake to breaak-up the pellet which formed during centrifugation.

4.1.6. Repeat steps 4.1.2 - 4.1.4 and bring the final extract to an appropriate volume prior to analysis.

5. QA/QC

5.1 Calibration

5.1.1. All standards used to prepare the calibration standard solution are obtained from chemical suppliers and are of high purity and concentration. The standards are routinely checked by the laboratory for traceability to National Research Council of Canada (NRCC) or National Institute of Standards and Technology (NIST) Standard Reference materials. These commercial standards are used as stock standards. Working standards are made from the stock standards at appropriate concentrations to cover the linear range of the calibration curve as outlined in the individual procedures. The working standards used for initial calibration curves are independent of calibration check standards and spiking solutions. Preparation of all standards is recorded in a bound laboratory logbook (as described in SOP BR-0500).

All solutions are labeled as follows: name of solution, concentration of solution, date prepared, analyst's initials.

5.1.2 Calibration Checks-Calibration check standards are used to verify the standard calibration curve and assess instrument drift. A calibration check consists of a mid-level standard and a calibration blank. Calibration checks are performed immediately after the calibration curve, after every ten samples and at the end of the analytical batch. Calibration check standards are prepared in the laboratory from standards traceable to the NRCC or NIST. The experimental results of the check sample are compared with the true values, and the percent recovery of the check standard is calculated. If the percent recovery falls within the acceptance range of 80-120%, then sample analysis proceeds. However, if the percent recovery does not fall within the acceptance range, the problem is identified and corrected, and the instrument calibration sequence begins again.

5.2 Quality Assurance Samples

5.2.1 Standard and Certified Reference Materials-All Reference Materials are preferably obtained from either the National Resource Council of Canada (NRCC) or the National Institute of Standards and Technology (NIST). When necessary SRMs/CRMs may be obtained from other sources including the community Bureau of Reference under the Commission of the European Communities (BCR), South African Bureau of Standards (SABS), the International Atomic Energy Agency (IAEA), or others. Most standard reference materials are used directly in audit

studies and will reflect performance in both quality and usage. SRMs to be used for Se are found in Table 1.

A Reference Material shall be analyzed once for every ten samples to ensure sample recoveries and to show method bias. Results must be within 20% of the certified value.

5.2.2 Performance Evaluation Samples-As an external check performance evaluation samples are analyzed. EPA performance samples (WP study) and USGS intercalibration samples are analyzed semiannually. If any results from these studies are not within the control limits established by the study then an investigation of the methodology and analyst shall be performed, and followed by appropriate corrective action.

5.3 Method Blanks and Limits of Detection

5.3.1 Method Blanks-A method blank is a sample of reagent water (ASTM Type I) that is treated as a sample in that it undergoes the same analytical process as the corresponding field samples. Method blanks are used to monitor laboratory performance, contamination introduced during the analytical procedure, and for determining method detection limits. Two method blanks are required per analytical batch (maximum of 20 field samples).

Table 1. - CRMs certified for Se

Name of CRM	Description/Matrix	Certified concentration for Se in ug/g
NRCC DORM-1	Dogfish Muscle	1.62 ± 0.12
NRCC DOLT-2	Dogfish Liver	6.06 ± 0.49
BCR No. 40	Coal	N/A
BCR No. 181	Coking Coal	1.15 ± 0.05
NRCC NASS-4	Open Ocean Seawater	0.018*
NRCC BCSS-1	Marine Sediment	0.43 ± 0.06
NRCC MESS-2	Marine Sediment	0.72 ± 0.09
NRCC PACS-1	Marine Sediment	1.09 ± 0.11
NRCC TORT-1	Lobster Hepatopancreas	6.88 ± 0.47
NRCC DORM-2	Dogfish Muscle	1.40 ± 0.09
SABS SARM 20	Coal	0.8 ± 0.2
NIST 1632b	Coal	1.29 ± 0.11
NIST 1643c	Water	12.7 ± 0.7
NIST 1633a	Fly Ash	10.3 ± 0.6

*Not certified, advisory value only.

5.3.2 Method Detection Limits and Quantitation Limits-The method detection limit (MDL) is the minimum concentration of an analyte of interest that can be measured and reported, with 95 percent confidence, that the value is above zero. MDLs are determined by analyzing duplicate method blanks with each batch of samples. A minimum of seven duplicate method blanks must be analyzed for determination of the MDL. The MDL is then calculated as three times the estimated standard deviation. When evaluating an MDL, the method blank must be carried through the entire method. By analyzing duplicate method blanks with each batch, the MDL is constantly updated.

The quantitation limit (QL) is the concentration of an analyte of interest at which the relative confidence in the measured value is ± 30% at the 95% confidence level. QLs are determined by analyzing duplicate method blanks with each batch of samples. A minimum of seven duplicate method blanks must be analyzed for determination of the QL. The QL is then calculated as ten times the estimated standard deviation.

5.4 Split samples

Split samples or replicate samples provide information about sampling and analysis precision. Replicate samples are true field replicates of two or more samples collected from a common sampling location in two or more independent sampling events; these samples should, hypothetically, have identical compositions and therefore they can be used to evaluate overall precision, including both analytical error and sampling error. Split samples are one or more sub-samples of a primary homogenous sample and are used to evaluate the precision of analysis. The frequency of replicate sample collection and analysis is specified in the contract with the client. One split sample is analyzed per 10 field samples collected.

Results of split sample analyses are used to calculate the relative percent difference (RPD). RPD is then used to estimate analytical precision. Criteria for split sample results is determined by control charts. If no control charts are available, the criteria for the calculated RPD is 25% for aqueous samples and 35% for solid matrices.

5.5 Matrix spikes

Spiked samples are analyzed either at the request of client or the lab manager. Both samples and method blanks can be spiked with a known amount of analyte. Both samples and spiked samples are then analyzed. Bias is then estimated by calculating the percent recovery of the known amount.

Percent recovery = 100 * (spiked sample result - sample result)
/ (amount spiked)

Spiked samples are used to monitor the analytical method and the effect of the sample matrix on analytical technique.

5.6 Preventative Maintenance

Instrument logbooks are maintained for all equipment. These logbooks contain a complete history of past performance and maintenance. When QC criteria are not met from an analysis, all instrumentation is thoroughly checked and appropriate maintenance is taken.

5.7 Supplies and Reagents

All supplies (i.e., glassware, chemicals, reagents) are of the best possible quality to ensure proper instrument calibration and to avoid contamination. All reagents used are prepared from Analytical Reagent Grade (AR) chemicals or higher purity grades, unless such purity is not available. Reagent water is prepared by double deionization of tap water. Each reagent is clearly labeled with the composition, concentration, date prepared, initials of preparer, expiration date, and special storage requirements, if any.

Reagent solutions are stored in appropriate glass or plastic containers, under conditions designed to maintain their integrity (refrigerated, dark, etc.). Shelf life is listed on the label, and the reagent is discarded after it has expired. Water used in the laboratory is deionized (ASTM Type I water) and periodically checked for purity. All acids used are either glass-distilled or special grade for trace metal analysis. Reagent solutions are checked for contamination by employing reagent blanks before use in any analysis.

6.0. Analyze extracts by HGAA in acordance with SOP BR-0020. Se(IV) determinations are performed directly on the extract following pH adjustment, whereas Se(IV+VI) determinations are made after a separate aliquot of the extract is carried through a reduction step using hydroxylamine hydrochloride and hydrochloric acid. Se(VI) is then determined by difference of these two analytical results.

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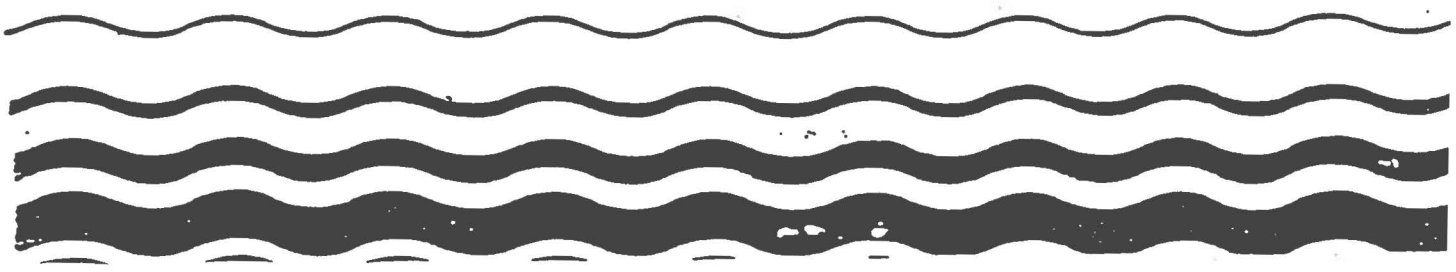
EPA xxx/x-xx-xxx
August 1991

WATER

Draft Analytical Method

for Determination of Acid

Volatile Sulfide in Sediment



DETERMINATION OF ACID VOLATILE SULFIDES AND SIMULTANEOUSLY EXTRACTABLE METALS IN SEDIMENT

1. SCOPE AND APPLICATION

1.1 This method describes procedures for the determination of acid volatile sulfides (AVS) and for metals that are solubilized during the acidification step (simultaneously extracted metal, SEM). The conditions used have been reported to measure amorphous or moderately crystalline monosulfides (1). As a precipitant of toxic heavy metals, sulfide is important in controlling the bioavailability of metals in anoxic sediments (2). If the molar ratio of toxic metals measured by SEM to AVS exceeds one, the metals are potentially bioavailable. Because the relative amounts of AVS and SEM are important in the prediction of potential metal bioavailability, it is important to use the SEM procedure for sample preparation for metal analysis. This uses the same conditions for release of both sulfide and metal from the sediment and thus provides the most predictive means of assessing the amount of metal associated with sulfide.

2. SUMMARY OF METHOD

2.1 The AVS in the sample is first converted to hydrogen sulfide (H_2S) by acidification with hydrochloric acid at room temperature. The H_2S is then purged from the sample and trapped. The amount of sulfide that has been trapped is then determined. The SEM are metals liberated from the sediment during the acidification. These are determined after filtration of the sample.

2.2 Two types of apparatus for sample purging and trapping of H_2S are described. One uses a series of Erlenmeyer flasks while the other uses flasks and traps with ground glass stoppers. The former is less costly. The latter is less prone to leakage that causes low recovery of AVS. The latter is recommended when higher degrees of precision are desired and for samples containing low levels of AVS.

2.3 Three means of quantifying the H_2S released by acidifying the sample are provided. In the gravimetric procedure, the H_2S is trapped in silver nitrate. The silver sulfide that is formed is determined by weighing (2,3). This procedure is recommended for samples with moderate or high AVS concentrations. In the colorimetric method, the H_2S is trapped in sodium hydroxide. The sulfide is converted to methylene blue that is measured (4). This procedure is recommended for samples that have low to moderate AVS concentrations. In an alternative procedure the H_2S is trapped in an antioxidant buffer before using an ion-selective electrode (5,6).

4. INTERFERENCES

4.1 Oxygen in the reagents and apparatus is the primary interference reported. Special precautions must be taken to insure that the analytical system is adequately purged with oxygen-free nitrogen. Argon may be substituted for nitrogen if it is important that an even lower level oxygen concentration be maintained (4).

4.2 The pH of the sample after the addition of the acid and during the purge process must be below 3. Typically, the pH is below 2.

5. SAFETY

5.1 The toxicity or carcinogenicity of reagents used in this method have not been fully established. Each chemical and environmental sample should be regarded as a potential health hazard and exposure should be minimized. Each laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets should be available to all personnel involved in the chemical analysis.

5.2 Hydrogen sulfide is a highly poisonous, gaseous compound having a characteristic odor of rotten eggs. It is detectable in air by humans at a concentration of approximately 0.002 ppm. Handling of acid samples should be performed in a hood or well ventilated area. If hydrogen sulfide is detected in the air by the laboratory staff, sample handling procedures must be corrected.

6. APPARATUS AND EQUIPMENT

6.1 Glassware

6.1.1 AVS evolution and H_2S trapping - Glassware in Section 6.1.1.1 is recommended. Glassware in Section 6.1.1.2 may be used, but will not provide as high precision or accuracy for samples.

6.1.1.1 For highest precision and low AVS levels - For each analytical train 500 mL gas washing bottles, one 250 mL round bottom flask with a septum (Ace Glass 6934 or equivalent), 100 or 250 mL impingers. The round bottom flask contains the sediment and acid is introduced to it by a syringe inserted through the septum. The flasks are connected by plastic tubing. In all cases the inlets are below the liquid level and the outlets are above the liquid levels. The apparatus is assembled as shown in Figure 1 and more than one analytical train can be connected to a single cylinder of nitrogen if flow controllers are installed in the

6.5 Gravimetric method

6.5.1 Filtering flask.

6.5.2 Filter holder for 47 mm filter.

6.6 Colorimetric method

6.6.1 Spectrophotometer - Capable of measuring absorbance at 670 nm.

6.6.2 Spectrophotometer cells.

6.7 Ion-selective electrode method

6.7.1 Electrometer, pH meter or ion-selective meter - Compatible with the use of ion-selective electrodes.

6.7.2 Sulfide selective electrode.

6.8 Atomic absorption or inductive couple plasma spectrophometer for the determination of SEM.

7. REAGENTS AND CONSUMABLE MATERIALS

7.1 All water and reagents used in this method must be free of dissolved oxygen and sulfides. Freshly prepare and use deaerated, deionized water, DDIW, by purging dissolved oxygen from the deionized water by vigorously bubbling with oxygen free nitrogen for approximately one hour. Deaerate reagents by purging with nitrogen.

7.2 Sodium sulfide standard - Required for quality assurance and calibration.

7.2.1 Sulfide stock standard solution, approximately 0.05M or 50 µmoles/mL.

7.2.1.1 Place a few crystals of $Na_2S \cdot 9H_2O$ in a beaker. Wash them with distilled water and dry them by blotting with filter paper. Weigh about 12 gram of $Na_2S \cdot 9H_2O$ and dissolve it in 1,000 mL of DDIW. Store in a brown bottle.

7.2.1.2 Standardize against thiosulfate solution.

7.2.1.2.1 Pipette 10.00 mL of 0.025N standard iodine solution (Section 7.2.2) into each of two 125-mL Erlenmeyer flasks.

7.2.1.2.2 Pipette 2.00 mL of sulfide stock standard solution into one flask. Pipette 2.00 mL of DDIW, as a laboratory reagent blank, into the other flask.

7.2.3.2.3 Calculate the thiosulfate concentration as follows:

$$N\left(S_2O_3^{2-}\right) = \frac{g\ K_2CrO_7}{mL\ S_2O_3^{2-}} \times \frac{1\ mole\ K_2CrO_7}{294.19\ g\ K_2CrO_7} \times \frac{6\ equiv\ K_2CrO_7}{1\ mole\ K_2CrO_7} \times \frac{1000\ mL}{1\ L}$$

7.2.4 Starch indicator - Dissolve 1.0 gram soluble starch in 100 mL boiling deionized water.

7.2.5 Sulfide working standards - Prepare sulfide working standards using the sulfide stock standard solution in Section 7.2.1. The concentrations of the following standards will depend on the exact concentration of the sulfide stock standard determined in Section 7.2.1.2.5. Correct concentrations of the the standards in the following part of this section and the amount of sulfide in standards used in the colorimetric method in Section 12.2.5 by multiplying by a factor of the concentration determined in Section 7.2.1.2.5 divided by 50 µmoles/mL.

7.2.5.1 Prepare sulfide working standard A by diluting 1.00 mL of sulfide stock standard to 100.0 mL. This solution contains 0.5 µmole sulfide/mL, if the concentration of the sulfide stock standard is exactly 0.05M.

7.2.5.2 Prepare sulfide working standard B by diluting 10.00 mL of sulfide stock standard to 100.0 mL. This solution contains 5.0 µmole sulfide/mL, if the concentration of the sulfide stock standard is exactly 0.05M.

7.3 AVS evolution

7.3.1 Hydrochloric acid 6M - Dilute 500 mL of concentrated hydrochloric acid (sp. gr. 1.19) to 1L with deionized water.

7.3.2 Nitrogen gas, oxygen free, with regulator and flow controller. An oxygen gas scrubber may be required and is available commercially or deoxygenating solutions may be placed in the flask or gas washing bottle placed first in the analytical train.

7.3.3 Plastic hypodermic syringe, 30 mL, and needle.

7.4 Gravimetric method

7.4.1 Potassium acid phthalate, 0.05M - Dissolve 10.2 g of potassium acid phthalate, $KHC_8H_4O_4$, in DDIW and dilute to 1L.

7.4.2 Silver nitrate, 1M - Dissolve 17 g of silver nitrate, $AgNO_3$, in DDIW and dilute to 1L. Store in a dark bottle.

7.4.3 Glass fiber filters, 1.2 micron - Predry filters at 102°C.

8.4 Samples should be cooled to 4°C as soon as possible after collection. Samples maintained at 4°C have been found to have no significant loss of AVS for storage periods up to 2 weeks (4). Anoxic sediments stored at 4°C for 20 days show significant changes in metal partitioning, suggestive of oxidation of the sediment (9). Holding time for samples should not exceed 14 days.

9. CALIBRATION AND STANDARDIZATION

9.1 Calibrate the photometer with a minimum of four standards and a blank that cover the expected range of the samples. Prepare a calibration graph relating absorbance to the µmoles of sulfide taken.

9.2 Calibrate the sulfide electrode system with a minimum of three standards that cover the expected range of the samples. Standards must be made up in SAOB diluted 1+1 with DDIW. Follow the manufacturer's instructions for use of the electrode.

9.3 Overall sulfide recovery is determined by analysis of a known amount of sodium sulfide standard added to DDIW from which the sulfide is liberated in the analysis train (LFB). Recoveries of 95% ± 10% are expected.

10. QUALITY CONTROL

10.1 Each laboratory using this method is required to operate a formal quality control (QC) program. The minimum requirement of this program consists of an initial demonstration of laboratory capability, and the analysis of laboratory reagent blanks, fortified blanks and samples as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of data thus generated.

10.2 INITIAL DEMONSTRATION OF PERFORMANCE

10.2.1 The initial demonstration of performance is used to characterize instrument performance, method detection limits, and linear calibration ranges.

10.2.2 Method detection limit (MDL) - The method detection limit should be established for the analyte, using DDIW (blank) fortified at a concentration two to five times the estimated detection limit (10). To determine MDL values, take seven replicate aliquots of the fortified reagent water and process through the entire analytical method. Perform all calculations and report the concentration values in the appropriate units. Calculate the MDL as follows:

$$MDL = t \times s$$

where, t = students' t value for a 99% confidence level and a standard deviation

10.4 ASSESSING ANALYTE RECOVERY - LABORATORY FORTIFIED SAMPLE MATRIX

10.4.1 The laboratory must fortify a minimum of 10% of the routine samples or one fortified sample per set, whichever is greater. Ideally, the concentration should at least double the background concentration. Over time, samples from all routine sample sources should be fortified.

10.4.2 Calculate the percent recovery for the analyte, corrected for background concentrations measured in the unfortified sample, and compare these values to the control limits established in Section 10.3.3 for the analyses of LFBs. Spike recovery calculations are not required if the spike concentration is less than 10% of the sample background concentration. Percent recovery may be calculated in units appropriate to the matrix, using the following equation:

$$R = \frac{(C_s - C_b)}{S} \times 100$$

where

R = percent recovery,

C_s = fortified sample concentration,

C_b = sample background concentration, and

S = concentration equivalent of the fortified sample.

10.4.3 If the recovery of the analyte in the fortified sample falls outside the designated range, and the laboratory performance on the LFB for the analyte is shown to be in control (Section 10.3) the recovery problem encountered with the fortified sample is judged to be matrix related, not system related.

11. GENERATION OF H_2S

11.1 Assemble glassware according to the detection method to be used. The setup in Figure 1 should be followed as a general guide. In all cases a flask or gas washing bottle containing a deoxygenating solution may be placed in the sample train between the nitrogen tank and the first flask. Glassware is specified in Section 6.1.1. It is recommended that nitrogen be controlled by a flow-controller, but an equivalent flow rate may be regulated by a clamp and bubble rate determined. In all cases the glassware will minimally consist of a H_2S generating flask and a series of traps.

11.1.1 Gravimetric method - The first flask contains the sediment sample or standard. The second flask contains 175-200 mL of potassium hydrogen phthalate reagent

12. ANALYSIS OF SULFIDE

12.1 Gravimetric method

12.1.1 Insure that the final trap, the second silver nitrate trap, contains no precipitate.

12.1.2 Filter the silver sulfide contained in the first sulfide trap through a preweighed 1.2 micron filter. Dry at 102 °C and weigh.

12.1.3 Calculate the amount of silver sulfide as the difference between the weight of silver sulfide and the filter and the weight of the predried filter.

12.1.4 Calculate the amount of sulfide in the sample:

$$\text{Sulfide in wet sediment (}\mu\text{moles)} = \frac{\text{g } Ag_2S}{247.8} \times 10^6$$

12.2 Colorimetric method

12.2.1 If the AVS concentration is low, add 10 mL of the mixed diamine reagent (MDR) directly to the NaOH solution in each trap tube to develop the color. Transfer this solution to a 100 mL volumetric flask and dilute to the mark with DDIW. If the sulfide contained in the NaOH in the tube trap exceeds 18 µmoles, transfer the NaOH in each tube trap to a 100 mL volumetric flask. Rinse the trap with deaerated 0.5M NaOH and dilute to volume with NaOH. An appropriate volume aliquot of this solution is used for the analysis. In this case, the aliquot is transferred to a 100 mL. Sufficient 0.5M NaOH is added so that the total volume is 80 mL, 10 mL MDR is added and the solution is diluted to 100 mL with DDIW. Use of sediment samples smaller than 1-2 grams is not recommended due to sulfide oxidation and sample heterogeneity.

12.2.2 After 30 minutes, measure the absorbance of light at 670 nm using a half-inch diameter or 1 cm rectangular spectrophotometer cell.

12.2.3 If the absorbance of the sample is greater than 0.6, dilute 10-fold with 1.0M H_2SO_4 and compare to the high range calibration curve.

12.2.4 Normally, the sulfide concentration in second trap tube is close to the blank value in this procedure and is not significant in calculating the concentration of sulfide. If a significant color is developed, the flow rate and amount of sulfide in the standard or sediment should be checked

12.2.5 Preparation of calibration curve - The indicated amounts of sulfide are based on a 0.05 M concentration of the sulfide stock standard solution. The procedure indicated in Section 7.2.5 should be used to calculate the exact amount of sulfide in each of the standards.

point calibration has been performed. If the readings are in millivolts, convert millivolts to concentration using the calibration curve obtained from standard solutions.

12.3.6 Calculate the amount of sulfide (µmoles) in the sample.

13. CALCULATION OF AVS CONCENTRATION IN SEDIMENTS

13.1 The sediment dry weight/wet weight ratio (R) must be determined separately. Acid volatile sulfides can be oxidized or altered to non-volatile forms during drying.

13.2 Transfer an aliquot of the sediment to a tared 100-mL tared evaporating dish. Weigh the dish plus the wet sediment. Calculate the wet weight of the sample. Dry the sediment at 104 °C and weigh. Calculate the dry weight of sediment.

13.3 Determine the ratio of dry weight to wet weight for the sediment sample:

$$R = \frac{W_d}{W_w}$$

where R = ratio of dry weight to wet weight,

W_d = dry weight of sediment sample (g), and

W_w = wet weight of sediment sample (g).

Also, the weight of water, W_{water}, taken in a sample for AVS analysis can be calculated. If the weight of the wet sediment sample taken for the AVS analysis is W_{s+w}, the weight of water contained in the sediment sample would be

$$W_{water} = W_{s+w} - (R \times W_{s+w})$$

The volume of water in the sample equals the weight of water, assuming the density is near unity.

13.4 Compute the sulfide concentration per gram dry weight of sediment:

$$AVS\ (\mu moles / g) = \frac{S}{R \times W_w}$$

where S = the amount of AVS in sediment (µmoles) from Section 12.1.4, 12.2.6, or 12.3.6, as appropriate,

R = ratio of dry weight to wet weight from Section 13.3, and

W_w = wet weight of sediment (g) taken for AVS analysis.

3. Morse, J.W., F.J. Millero, J.C. Cornwell and D. Rickard, "The Chemistry of the Hydrogen Sulfide and Iron Sulfide System in Natural Waters", *Earth Science Review*, 1987, 24, 1-42.

4. Allen, H.E., G. Fu and B. Deng, "Determination of Acid Volatile Sulfide (AVS) in Sediment", Report to Environmental Protection Agency Office of Water Regulations and Standards, Washington, December 1990, 26 pages.

5. Boothman, W.S., "Acid-volatile Sulfide Determination in Sediments Using Sulfide-specific Electrode Detection", U.S. Environmental Protection Agency Environmental Research Laboratory, Narragansett, R.I., undated, 8 pages.

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7. U.S. Environmental Protection Agency. "Methods for Chemical Analysis of Water and Wastes", EPA-600/4-79-020, revised March 1983.

8. "Standard Methods for the Examination of Water and Wastewater", 17th edition, APHA, AWWA, WPCF, 1989.

9. Rapin, F., A. Tessier, P.G.C. Campbell and R. Carignan, "Potential Artifacts in the Determination of Metal Partitioning in Sediments by a Sequential Extraction Procedure", *Environmental Science and Technology*, 1986, 20, 836-840.

10. Code of Federal Regulations 40, Ch. 1, Pt. 136, Appendix B.

EVS Consultants

Procedure for Formulating Test Sediments with Specified Ranges of Percent Sand and Percent Fines (Silt and Clay) and with a Constant Total Organic Carbon Content of 2 Percent

This procedure follows procedures outlined by Walsh et al. 1991 as modified[a] by the National Biological Service, Midwest Science Center, Columbia, Missouri.

TEST SEDIMENT PREPARATION

1. Select the desired sand/fines mixture from the table below to determine quantities of ingredients. Note all quantities are in grams dry weight.

	MIXTURE				
INGREDIENTS	90% SAND 10% FINES	70% SAND 30% FINES	50% SAND 50% FINES	30% SAND 70% FINES	10% SAND 90% FINES
Sand (g)	1,314.9	1,022.7	730.5	438.3	146.1
Silt and Clay (g)	146.1	438.3	730.5	1,022.7	1,314.9
Dolomite (g)	7.5	7.5	7.5	7.5	7.5
Humic Acid (g)	0.15	0.15	0.15	0.15	0.15
∝-cellulose (g)	489.6	489.6	489.6	489.6	489.6

2. Use sand with a grain size range of 0.25 to 0.5 mm.

3. Wash the sand with tap water until water runs clear, rinse 5 times with deionized water, and spread out on clean aluminum foil to dry.

4. Combine the ingredients in a 4-L glass jar, cover the mouth of the jar with parafilm, and duct tape the parafilm on the outside of the jar.

5. Roll each jar of test sediment on a rolling mill for 1 hour. Sediment may be stored in a sealed plastic bucket.

6. Hydrate the test sediment with overlying water for 24 hours before using in tests.

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[a] Personal communication with N. Kemble. National Biological Service manuscript is presently in review.

Procedure for Formulating Test Sediments with Specified Ranges of Percent Total Organic Carbon (TOC) and with a Constant Content of 50 Percent Sand and 50 Percent Fines (Silt and Clay)

This procedure follows procedures outlined by Walsh et al. 1991 as modified[a] by the National Biological Service, Midwest Science Center, Columbia, Missouri.

TEST SEDIMENT PREPARATION

1. Select the desired sand/fines mixture from the table below to determine quantities of ingredients. Note all quantities are in grams dry weight.

	PERCENT TOC					
INGREDIENTS	0.2%	4%	8%	10%	12%	15%
∝-cellulose (g)	7.4	163.2	367.2	489.6	629.4	881.2
Sand (g)	730.5	730.5	730.5	730.5	730.5	730.5
Silt and Clay (g)	730.5	730.5	730.5	730.5	730.5	730.5
Dolomite (g)	7.5	7.5	7.5	7.5	7.5	7.5
Humic Acid (g)	0.15	0.15	0.15	0.15	0.15	0.15

2. Use sand with a grain size range of 0.25 to 0.5 mm.

3. Wash the sand with tap water until water runs clear, rinse 5 times with deionized water, and spread out on clean aluminum foil to dry.

4. Combine the ingredients in a 4-L glass jar, cover the mouth of the jar with parafilm, and duct tape the parafilm on the outside of the jar.

5. Roll each jar of test sediment on a rolling mill for 1 hour. Sediment may be stored in a sealed plastic bucket.

6. Hydrate the test sediment with overlying water for 24 hours before using in tests.

Reference and a list of suppliers for test sediment ingredients are attached.

LIST OF SUPPLIERS FOR RECONSTITUTED SEDIMENT

Cow Manure
A.H. Hoffman Inc.
77 Cooper Ave.
Landisville, PA 17538
1-800-877-0848 or (717) 828-2461
Fax: (717) 898-3190

Sphagnum Peat Moss
Mellinger's
2319 West South Range Rd.
North Lima, OH 44452-9731

Algae Feast Chlorell Powder
Earthrise Farms
P.O.Box 719
Calipatria, CA 92233
(619) 348-2685
Ron Hensen
Fax: (619) 349-2895

ASP 400 (Silt/Clay)
Mozel
4003 Pach Ave.
St. Louis, MO 63110
(314) 865-3115

Sand #1 dry, #2, #3
New England Silica Inc.
1370 John Fitch Blvd.
South Windsor, CT 06074-0185
(203) 289-7778
Fax: (203) 282-9885

Maple Leaves
Ye Olde Maple Tree

Alpha-Cellulose
Sigma Chemical Company
P.o. Box 14508
St. Louis, MO 63178-9916
1-800-325-3010

Dolomite (Part of Sand Blasting Package)
Ward's Natural Science Establishment
P.O. Box 92912
Item #28E2566 (In the Earth Science Catalog)
Rochester, NY 14692-9012
1-800-962-2660

REFERENCE

Walsh, G.E., D.E. Weber, F.L. Simon, L.K. Brashers. 1991. Toxicity test of effluents with march plants in water and sediment. Envir. Toxicol. and Chem., Vol. 10, pp 517-525.

9.0 STANDARD OPERATING PROCEDURES TOXICITY IDENTIFICATION EVALUATION METHOD FOR PHASE I

Toxicity identification evaluation (TIE) for use on sediment samples has been adapted from methods described by U.S. EPA (1988).

9.1 BACKGROUND INFORMATION

The first phase of a TIE involves a series of chemical and physical manipulations designed to characterize the substances responsible for sediment toxicity. The characterization information gathered in Phase I forms the basis and direction for Phase II identification of the specific toxicants or may be useful for remedial evaluations. In Phase I, simple toxicity removal or alteration is performed on the sediment porewater. The objectives of the toxicity characterization phase is to determine the physical and the chemical characteristics of the toxicant(s).

Each of the manipulations described in the Phase I TIE SOP is designed to change the toxicity of groups of constituents. Toxicity before and after the manipulation will indicate for which groups the toxicity was changed. All but one of these tests are performed at the same time in order to minimize confounding effects resulting from sample degradation over time. While it is not critical that each manipulation be performed at exactly the same time, the toxicity test should be initiated at approximately the same time.

Day 1 is when the porewater is extracted from the test sediment in the laboratory. On day 1 initial physical/chemical measurements are taken for the porewater sample. Aliquots of the sample are adjusted to pH 3 and 11, filtered, aerated, and/or chromatographed using a C_{18} solid phase extraction (SPE) column. Following these manipulations, each aliquot is readjusted to the initial pH (pH_I) of the porewater. These aliquots and the remainder of the porewater are then held at 4°C overnight. This procedure allows pH adjusted porewater aliquots more time to stabilize, and additional pH adjustments can be made as necessary.

On the second day the aliquots of porewater prepared on day 1 are diluted and subsequently tested for toxicity. Other toxicity tests involving the addition of chelating and reducing agents and less severe pH adjustments are also conducted. A toxicity test is

begun using unaltered porewater, now 24 hours old. The results of this and subsequent whole porewater tests are referred to as the "Baseline".

Toxicity test results are read on subsequent testing days and depending on the outcome of the Phase I test series, additional toxicity tests designed to further define or confirm the nature of the toxicants are conducted.

Several Phase I characterization test are relatively broad in scope, intended to include more than one class of toxicants. Therefore, if a significant change in porewater toxicity is seen following these characterization procedures, additional test are needed to further delineate the nature of the toxicity. The amount of testing beyond the initial characterization of the sample will depend on the nature of the toxicity. A "significant reduction" in toxicity between aliquots of the whole porewater and treated porewater must be decided based upon the laboratory's test precision. Usually a change in the EC50 equal to one concentration interval can be considered significant but when precision is good smaller differences can be used. None of these test by themselves are conclusive, so the danger of type I or type II errors is not great. If not all toxicity is removed, other groups of toxicants (not addressed in Phase I procedures) may be present in the effluent or a single toxicant may be present in the porewater at such high concentrations that only partial toxicity removal is achieved. Additional testing to resolve these findings involves applying the successful Phase I test at a higher level (i.e., increased degradation time, increased aeration, larger C_{18} SPE column volume, increased reagent concentrations).

Another outcome of the Phase I characterization test series may be that several test succeed in partially removing porewater toxicity. In this situation, one may be dealing with several toxicants, each with different physical/chemical characteristics, or a single toxicant of such a nature as to be removed by more than one Phase I test. These results may be resolved by treating a single aliquot of the sample with all of the characterization tests that significantly reduced the baseline toxicity of the porewater. If porewater toxicity removal is enhanced as compared to the reduction provided by individual characterization tests, the sample may contain more than on type of toxicant. If the final toxicity removal at the end of the series of characterization tests is approximately the same as that provided by the most efficient single Phase I test, than it is likely that all of the test methods involved are successful in reducing the same toxicant to varying extents. This outcome is also suggested when one or more Phase I tests completely remove toxicity while some number of other tests partially reduce toxicity. Phase I tests overlap somewhat in their abilities to remove groups of toxicants. For example, increasing pH may cause a metal to precipitate, and EDTA may also remove its toxicity. In any case, results of this nature are useful in selecting Phase II options.

When several treatments are applied to the same sample, tests must be designed to ensure that toxicity does not result from the additives used (acid, base, EDTA) rather than from the porewater toxicants. The assumption must not be made that toxicants are either additive or synergistic. The independent action (one or more of multiple toxicants act independently of the rest, as though the others were not present) is not uncommon in sediments.

There are two types of checks that can be used to detect artifact toxicity. A "toxicity blank" consists of performing the same (Phase I) test on dilution water and measuring to determine whether any toxicity is added by the test procedure. A toxicity blank, however, does poorly in identifying artifact toxicity if toxicity is affected by the porewater matrix. For example, the toxicity of a Phase I reagent, EDTA, may be completely different in dilution water and in porewater. If so, a toxicity blank is inappropriate for the chelation test. A "toxicity control", on the other hand, involves a comparison of the test solution and the Baseline porewater. In this case the comparison must demonstrate that the porewater test solution has not become more toxic than the unaltered porewater. If it has, the test procedure has produced artifactual toxicity. For some treatments, valid blanks or toxicity controls cannot be made.

No procedure should be assumed to be free of artifactual toxicity. Many of the Phase I toxicity tests involve relatively severe and unorthodox manipulations. Blanks and controls must be consistently and conscientiously used to detect the introduction of toxic artifacts or other changes to the effluent that increase sample toxicity.

9.1.1 Reference Literature

American Public Health Association, American Water Works Association Water Pollution Control Federation. 1980. Standard methods for the examination of water and wastewater. 15th Edition. American Public Health Association, Washington, DC.

Dowden, B.F. and H.J. Bennett. 1965. Toxicity of selected chemicals to certain animals. J. Water Pollut. Control Fed., 37(9):1308-1316.

Horning, W. and C.I. Weber, (Eds.). 1985. Short-term methods for estimating the chronic toxicity of effluents and receiving waters to freshwater organisms. U.S. Environmental Protection Agency, Cincinnati, OH. EPA-600/4-85-014.

Magnuson, V.R., D.K. Harriss, M.S. Sun, D.K. Taylor, and G.E. Glass. 1979. Relationships of activities of metal-ligand species to aquatic toxicity. In: ACS Symposium Series, No. 93. "Chemical Modeling in Aqueous Systems, (E.A. Jenne; editor), pp.635-656.

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U.S. EPA. 1985. Ambient water quality criteria for ammonia. Environmental Protection Agency, Environmental Research Laboratory-Duluth, Duluth, MN, and the Criteria and Standards Division, Washington, DC. EPA-440/5085-001.

U.S. EPA. 1988. Methods for aquatic toxicity identification evaluations; phase I toxicity characterization procedures. U.S. Environmental Protection Agency, Environmental Research Laboratory, Duluth, MN. EPA-600/3-88/034.

9.1.2 Equipment Needed

- disposable one ounce test chambers,
- 8-25 mL graduated cylinders
- 12-30 mL beakers
- 6-50 mL beakers
- 6-50 mL wide graduated cylinders
- 6-250 mL graduate cylinders
- 6-250 mL beakers
- 2-500 mL beakers,
- 2-500 mL graduated cylinders
- 6 glass diffusers
- 1 mL glass pipettes
- automatic pipette (10 mL)
- disposable pipette tips (10 mL)
- 10 and 100 microliter syringes
- burettes for acid and base titrations
- burettes for EDTA addition
- glass stirring rods
- stir plate
- stir bars (perfluorocarbon)
- pump with sample reservoir
- pH meter and probe
- perfluorocarbon (Teflon) tubing
- in-line filter housing
- filter stand
- ring stands
- clamps
- stainless steel forceps
- vacuum flask

- vacuum tubing
- water aspirator or vacuum pump
- glass-fiber filters (nominal size 1.0 µm, without organic binder)
- aeration device or compressed air system with a molecular sieve
- 3-3 mL C_{18} SPE columns (200 mg sorbent)
- Parafilm® or 3-600 mL beakers, wire mesh test chambers,
- eye dropper or wide bore pipette
- light box, and/or microscope (optional)

9.2 OBTAINING TEST ORGANISMS

A number of test organisms including marine and freshwater fish, invertebrates, and algae are available for TIE testing. The appropriate species and organism age will depend on study-specific specifications. For this study juvenile (≤7 days old) *Hyalella azteca* will be used.

Test organisms should normally be obtained from the in-house *Hyalella* cultures; however, animals can also be purchased from commercial suppliers. Each tank of 100 brood adults can be expected to yield approximately 100-150 juveniles after 7 d. Juveniles collected from the breeding cultures can be used as ≤ 7 d old neonates for aqueous-phase toxicity tests.

There should be a minimum 30% surplus of animals of the appropriate age and size available for test initiation. Before beginning a toxicity test, confirm that there are enough animals of acceptable size and quality available. Juvenile amphipods can be isolated in 1-L beakers (200/beaker) and kept in the dark with gentle aeration for up to 24 h before test initiation.

9.3 TEST PROCEDURES

9.3.1 Porewater Extraction

Sediment porewater will be used for the TIE manipulations. Sediment porewater is obtained via centrifugation. A large volume refrigerated centrifuge is required. Porewater extraction is done using the following procedures.

- Since settling may occur following storage, sediments are first homogenized in the storage container with a stainless steel spoon.

- Homogenized sediment is placed in Teflon centrifuge tubes designed for the specific centrifuge configuration to be used.

- The centrifuge jars should not be completely filled to avoid seepage during centrifugation.

- The prepared sample is then centrifuged at 4000 X g at 40C for 45 minutes.

- Following centrifugation the separated porewater is decanted into a clean Cubitainer.

- The sample is stored at 4°C with zero head space until testing.

9.3.2 Initial or Baseline Sediment Porewater Toxicity Test

The major purpose of the initial or baseline porewater toxicity test is to provide an estimate of the 24 hour EC50 for purposes of setting exposure concentrations in Phase I tests.

9.3.2.1 Volume Required

Initial toxicity test is performed in duplicate exposure, and 40 mL of porewater is needed.

9.3.2.2 Test Organisms

Test organisms, 60 or more, of the same age and species.

9.3.2.3 Procedure (Day 1)

A concentration series using 10 mL in duplicate of 100%, 50%, 25%, 12.5%, 6.25% porewater, and a control will suffice for most samples. Obviously more toxic sediments will require a lower range of porewater dilutions. If nothing is known about the toxicity, more concentrations should be included.

9.3.4 pH Adjustment Test

The pH has a substantial effect on the toxicity of many compounds found in sediments. Therefore pH adjustment is used throughout Phase I to provide more information on the nature of the toxicants. Changes in pH can affect the solubility, polarity, volatility, stability, and speciation of a compound, thereby affecting its bioavailability as well as its toxicity.

The effects of pH on the ratio of the ionized and unionized forms of acids and bases has a number of impacts on Phase I results. First, compounds may be more toxic in the un-ionized form as compared to the ionized form. For example, NH_3 is generally recognized as the toxic form of ammonia while NH_4^+ is of far less concern. A second implication of this effect relates to toxicant solubility. Unionized forms of acids and bases can be considered less polar than their ionized forms, which interact to a greater extent with water molecules. Consequently, un-ionized forms of acids and bases can be more easily stripped from water using aeration or extraction with non-polar solvents or solid phase column techniques. Likewise, changes in compound solubility with pH change may mediate removal through filtration.

Regardless of the speciation effect on toxicity, changes in solution pH may affect the toxicity of any given compound. The pH of the test solution may affect membrane permeability at the respiratory surface as well as the chemistry of the toxicant. One might expect that changing the pH, only to return it to its original pH in a short time, would not alter toxicity. However, this adjustment sometimes results in reduction or loss of toxicity. If the kinetics of the pH driven reaction (on return to the original pH) are slow or irreversible, pH adjustment alone may be effective in evidencing toxicants affected by pH change. Some organics may also degrade due to pH change.

Another purpose of the "pH Adjustment Test" is to provide a blank for subsequent Phase I pH adjustment tests performed in combination with other operations. This test will demonstrate whether toxic concentrations of ions have been reached as a result of the addition of acid and base.

Toxicity blanks for sample ionic strength increases which are based on adding the same volumes and strengths of the acid and base to dilution water, do not give comparable results when added to the porewater. Sediment porewaters already contain substantial concentrations of major anions and cations, which are not found in dilution water. Further, the volumes and strengths of the acid and base necessary, for example, to lower porewater to pH 3 and raise it back to pH 7.6 are not likely to result in the same final pH when added to dilution water.

9.3.4.1 Volume Required

600 mL are needed to make pH adjustments. A 300 mL aliquot of the day 1 porewater sample is lowered to pH 3 with four exposure concentrations, and the second 300 mL sample is raised to pH 11. Approximately 30 mL will be needed for the test but the actual amount depends on the 24 hour EC50 of the initial porewater test. The remaining 270 mL of each of these solutions is reserved for the pH Adjustment/Filtration, pH Adjustment/Aeration and pH Adjustment/C_{18} SPE Phase I tests.

9.3.4.2 Reagents

1.0, 0.1, and 0.01 NaOH, 1.2, 0.12, and 0.012 N HCl (ACS grade in high purity water) and buffers for pH meter calibration.

9.3.4.3 Test Organisms

Test organisms, 40 or more, of the same age and species.

9.3.4.4 Procedure (Day 1)

Using a burette, and stirring constantly, 1.0 N NaOH is added dropwise to a 300 mL aliquot day 1 porewater until the solution pH nears 11.0. (Note: overshooting results in the addition of more salts and volume may cause toxicant decomposition and should be avoided.) In order to minimize any over-adjustment of pH, 0.1 N NaOH is added dropwise in the latter stages to bring the porewater aliquot to pH 11. The solution should be allowed to equilibrate after each incremental addition of base. The amount of time necessary for pH equilibration will depend on the buffering capacity of the porewater. Caution should be taken to prevent any solution pH of greater than 11.0. If pH 11 is exceeded, 0.12 N HCl must be used to lower the pH to 11.0. The goal of the pH adjustment step is to reach pH 11, while minimizing both the change in aliquot volume and the increase in ionic strength. Volumes and strengths of base (and any acid added) should be recorded. A 30 mL volume is held for the same length of time it takes to complete other Phase I manipulations (performed on day 1) with pH 11 porewater. Once other work has been completed with the total volume of the pH 11 porewater, the 30 mL volume at pH 11 is returned to the initial pH (pH_I) of the day 1 porewater. (The other aliquots of pH 11 porewater are also returned to pH_I at this time.) This is accomplished by the slow, dropwise addition of 0.12 N HCl first and later 0.012 N HCl as the pH of the stirred solution nears pH_I. If pH_I is exceeded, the pH must be appropriately increased with 0.01 NaOH. Again, the volumes and strengths of acid and any base added should be recorded.

The pH of the solution should be checked periodically throughout the remainder of the work day and readjusted as necessary. Changes in the total volume of acids and bases added should be recorded.

This entire procedure is repeated with a second 300 mL aliquot of porewater, using 1.2 N and 0.12 N HCl to lower the pH to 3. As with the pH 11 porewater, 270 mL of the pH 3 porewater is used for the pH Adjustment/Filtration, pH Adjustment/Aeration and pH Adjustment/C_{18} SPE Phase I tests. The remaining 30 mL of the pH 3 porewater is held until the first day's work on all of the pH 3 porewater has been completed. At this point,

the pH of the 30 mL volume of pH 3 porewater is readjusted to pH_I by the dropwise addition of 0.1 N and 0.01 N NaOH. Maintenance of pH_I must be assured through periodically checking and readjusting the sample throughout the day. All volumes and strengths of acid and base added should be recorded.

(Day 2): At the beginning of the work day (on the day after the extraction of the porewater from the sediment in the laboratory), the pH of both the 30 mL volumes is again checked to ensure the pH_I has been maintained. Any additional pH adjustments are made and recorded. The toxicity of each pH-adjusted solution is tested. Test solution pH should be measured and recorded every 24 hours.

9.3.4.5 Interferences/Controls and Blanks

Controls prepared for the initial or baseline toxicity test act as a check on the organisms, dilution water, and test chambers for the test as well.

The initial or baseline porewater test acts as a control for the pH Adjustment test, indicating whether the addition of NaCl in the form of the acid and base has increased porewater toxicity. The pH Adjustment test acts as the control for other Phase I tests entailing pH adjustment. In addition to serving as a control for other pH adjustment tests, increased toxicity following pH adjustment, not as a result of NaCl concentration, indicates a pH effect on toxicity.

9.3.4.6 Results/Subsequent Tests

If either the pH 3 or pH 11 adjusted porewater tests have significantly greater toxicity than the Baseline porewater test, two possible sources of toxicity exist: 1) the ions (Na^+, Cl^-) added by the acid and base have resulted in a solution with an ionic strength intolerable to the test organism; or 2) chemical reactions driven by the pH change have not reversed upon readjusting to pH_I. Neither of these phenomena would be detected through the use of a dilution water-based blank. The minimum concentration of NaCl in the test solution (i.e., not including the concentration of NaCl originally present in the porewater) can be calculated from the volumes and strengths of the acid and base added and final solution volume. The toxicity of the added NaCl is best determined by adding that amount to the porewater and see if the addition increased porewater toxicity.

If pH 3 and/or pH 11 adjustment results in a significant decrease in porewater toxicity, it could result from volume changes by acid and base addition or chemical reactions driven by pH change may not have been re-established or are irreversible. These two possibilities can be checked by adding a volume of dilution water equivalent to the total volume of acid and base added to the 30 mL porewater volume. If a similar loss in

toxicity of the diluted porewater occurs, the pH Adjustment test should be repeated using more concentrated acid and base.

A reduction or loss of toxicity may also be the result of the degradation of toxicant at the altered pH values. Both organics and inorganics can be so changed with a probable loss in toxicity. In some cases, the toxicity could also be increased if the degradation product is more toxic than the original compound.

For most of the Phase I combination pH adjustment tests, the pH Adjustment test will act as an equivalent or "worst case" control for changes in test solution ionic strength and volume. In effect, most of the operations applied to the pH adjusted porewater will not affect pH or will serve to drive it closer to pH_I. This may not be the case for the pH Adjustment/Aeration test, however. Because pH 3 and 11 must be maintained throughout the aeration process and because the loss of volatiles may result in pH shifts towards pH_I, more acid and/or base may be added to these test solutions as compared to the pH adjustment only solutions.

9.3.5 pH Adjustment/Filtration Test

The filtration experiment provides information on sediment porewater toxicants associated with filterable material. Toxic pollutants associated with particles may be less biologically available. Aquatic organisms can be exposed to these pollutants through ingestion of the particles, however. The degree to which any compound exists sorbed or in solution depends on a number of factors including particle surface charge (or lack thereof), surface area, compound polarity and charge, solubility and the porewater matrix. By filtering particles from the porewater, both a source and sink of toxic chemicals may be removed.

In addition to determining the effect of filtration on the toxicity of the porewater, the effects of pH adjustment in combination with filtration are also assessed. Changes in pH can result in the formation of insoluble complexes of metals. Similarly, organic acids and bases existing in ionic form can be transformed into the non-ionic form by pH adjustment. Shifts in porewater pH can also act to drive dissolved toxicants onto particles in the porewater (e.g., shifting the dissolved/adsorbed equilibrium away from the free form). Changes in toxicant polarity resulting from solution pH change can make some particle/toxicant interactions stronger. In other cases, the increase in porewater ionic strength resulting from the shift in pH may force non-polar organic compounds onto uncharged surfaces to a greater extent.

By filtering pH adjusted aliquots of porewater, those compounds typically in solution at unadjusted pH but insoluble or associated with particles to a greater extent at more

extreme pHs, are removed. By removing the toxicant contaminated particles or precipitated compounds prior to readjustment of the sample to pH_I, these toxicants are no longer available for dissolution in the porewater. The pH change may also destroy or dissolve the particles thereby removing the sorption surfaces or drive the dissolved/sorbed equilibrium in the opposite direction.

Positive pressure filtration is recommended. Use of a vacuum to draw the sample through the filter may result in a loss of volatile compounds by degassing the solution during filtration. This problem is potentially worsened in pH adjusted porewater if toxicants become more volatile as a result of pH changes. If vacuum filtration is used and porewater toxicity is reduced, subsequent tests must be performed to define the nature of the toxicity loss.

The solid phase extraction characterization test requires the use of filtered porewater. Without knowledge of the effect of filtering on the porewater toxicity, it is not possible to tell whether or not the column or the filtration removed the toxicity. Filtering may also be useful in connection with other Phase I tests.

9.3.5.1 Volume Required

A 235 mL aliquot of pH_I, day 1, porewater is filtered. Also, 235 mL each of pH 3 and pH 11 porewater aliquots are filtered. The remaining 35 mL of each is reserved for the pH Adjustment /Aeration Tests. A maximum volume of 30 mL of each of these three solutions is needed to perform the filtration toxicity tests. Each test requires four exposure concentrations (10 mL each). The exact porewater volume required for the toxicity tests will be a function of the porewater toxicity. The remaining filtered porewater volumes (200+ mL) of pH 3, pH 11, and the pH_I solution are each reserved for the C_{18} SPE tests. Excess volume has been included to cover losses occurring during the filtration operation.

9.3.5.2 Reagents

Solvents and high purity water for cleaning pump reservoir and filter,0.1 and 0.01 NaOH, 0.12 and 0.012 N HCl (ACS grade in high purity water) and buffers for pH meter calibration.

9.3.5.3 Test Organisms

Test organisms, 75 or more, of the same age and species.

9.3.5.4 Procedure (Day 1)

The first step for the Filtration test is filter preparation. First the filters are prepared, then the blanks, and finally porewater samples at three pH's are filtered. Use of glass-fiber rather than cellulose-based filters should minimize the adsorption and loss of dissolved non-polar organic compounds from the porewater sample. Adsorption of toxic dissolved organic compounds onto the filter can lead to spurious results.

9.3.5.5 Filter Preparation

To prepare the 1.0 µm glass-fiber filter for use, wash two 50 mL volumes of high purity water through the filter. For pH 3 effluent filtration test, the filter should be washed with high purity water adjusted to pH 3 using HCl. Likewise, the filter used with pH 11 porewater samples should first be washed with high purity water adjusted to pH 11 using a concentrated NaOH solution. Washing the filters with water adjusted to the same pH as the porewater should preclude sample contamination with water soluble toxicants contained on the filters.

9.3.5.6 Blank Preparation

The next step is to prepare filter blanks using dilution water. These blanks are used to detect the presence of any water soluble toxicants which may remain on the filter following the washing process. The pH_I filtration blank is simply prepared by passing 220 mL of pH unadjusted dilution water through a prepared filter. The filtered dilution water is collected and 200 mL of this volume is reserved for the C_{18} SPE test blank. the remaining 20 mL is used on day 2 as a blank in a toxicity test. Again, excess is included to cover any possible loss during rinses.

The procedures to prepare the pH 3 and 11 filtration blanks are some what different. To prepare the pH 3 filtration blank, 255 mL of dilution water is adjusted to pH 3 with 0.12 and 0.012 N HCl, caution being taken to minimize the increase in dilution water ionic strength. Of the pH 3 dilution water, 35 mL is reserved for use as a blank in the Aeration test. The remaining 220 mL of pH 3 dilution water is passed through a filter previously washed with pH 3 rinse water. The pH 3 dilution water is collected and 200 mL of this volume is reserved for the pH 3 C_{18} SPE test blank. The remaining 20 mL is readjusted to the initial pH of the dilution water (pH_o) using 0.01 N NaOH, again taking care not to exceed pH_o (pH_o symbolizes the equilibrium pH of the dilution water) during the readjustment process. This solution is used on day 2 in a single exposure toxicity test.

9.3.5.7 Sample Preparation

The same filter used to prepare the pH_o filtration blank is now used to filter a 235 mL aliquot of the pH_I porewater. Porewater passed through the filter is collected and 200 mL is reserved for the C_{18} SPE test. The remaining volume is held overnight for toxicity tests initiated on day 2.

Using the same filter used to prepare the pH 3 filtration blank, 235 mL of pH 3 porewater is filtered and collected. The filtered pH 3 porewater is split into 200 mL and 35 mL aliquots. The 200 mL aliquot is used in the pH 3 C_{18} SPE test. The 35 mL aliquot is readjusted to pH_I using 0.1 and 0.01 N NaOH. Care must be taken to minimize both an increase in aliquot volume and ionic strength. The pH readjusted 35 mL aliquot is held for the day 2 toxicity testing.

Finally, the filtration step is repeated using 235 mL of the pH 11 porewater and the filter originally used to filter pH 11 dilution water. Again, 200 mL of the pH 11 filtered porewater is used in the basic C_{18} SPE test; 30 mL is readjusted to the pH_I of the porewater with 0.12 n NaOH and 0.012 N HCl and used to conduct a toxicity test on day 2.

The pH of the pH adjusted blanks and porewater aliquots, designated for day 2 toxicity test, should be checked periodically throughout the work day. Adjustments should be made as necessary in order to maintain pH_o and pH_I, respectively, of these solutions.

(Day 2): Prior to initiating the toxicity tests, the pH of the pH 3 and 11 blanks and filtered porewater aliquots should be measured and readjusted to the pH_o and pH_I, respectively. Toxicity tests performed on all three (pH 3, pH_I, and pH 11) filtration blanks involve testing without dilution. Based on the 24 hour Initial EC50 of the day 1 porewater, toxicity tests performed on the porewater aliquots filtered at pH 3, pH_I, and pH 11 are set up using the dilution series identified by the initial testing. Measurement of exposure pH should be made daily on the highest tested concentration, concurrently with survival readings.

9.3.5.8 Interferences/Controls and Blanks

Controls prepared for the Baseline toxicity test serve as a check on the quality of organisms, dilution water and test conditions.

Results of the pH Adjustment test will indicate whether or not toxic levels of NaCl have been produced through pH adjustment. Results of the porewater filtration test at each pH to determine the validity of the toxicity test outcome. No significant mortality should

occur in any of the filtration blanks. If unacceptable mortality of control organisms occurs in either or both of the pH adjusted filtration blanks, further investigation will be necessary to determine whether lethality resulted from toxicants leached from the filter at pH 3 and/or 11, or whether the increase in dilution water ionic strength (via acid and base addition) is responsible for the problem. This can be accomplished by repeating the filtration step on pH adjusted dilution water providing a pH adjustment blank (i.e., pH adjusted unfiltered dilution water). Additionally, if the pH 3 and/or 11 filtration, aeration, and C_{18} SPE dilution water blanks have approximately the same final concentration of acid and base, any ionic strength related toxicity should be detected in them.

If a filtration blank shows unacceptable acute toxicity but the corresponding filtered porewater is equally or less toxic than the Baseline porewater, it is possible that the dilution water blank removed the final traces of toxic filter artifacts. In some cases, the porewater matrix may have also prevented the artifacts from leaving the filter or masked their presence. Alternatively the observed filtered porewater toxicity may represent the net effect of toxicant removal via filtration plus contamination by filter artifacts.

9.3.5.9 Results/Subsequent Tests

The EC50s for the aliquots of pH 3, pH_I, and pH 11 filtered porewater are compared to the Baseline porewater EC50 to determine whether any of these processes resulted in a significant change in porewater toxicity.

If any or all of these pH/filtration combinations result in less porewater toxicity (which cannot be attributed to the effects of pH adjustment alone), it may be possible to confirm the findings of the test. This can be attempted through a transfer of the solids contained on the filter back into the filtrate at pH_I. This can be done by reversing the flow of the filtrate through the filter or rinsing the solids off the filter with the filtrate. The toxicity exhibited by this solution should be similar to the original porewater, provided that the final concentration of solids in the test solution approximates the solids level in the sample that was filtered. For precipitates formed as a result of pH changes or for contamination of suspended solids facilitated by pH adjustment, time must be allowed for the precipitate to redissolve in the pH_I filtrate or for a new equilibrium to be set up between the contaminants on the solids and in solution. The results of this test are not likely to be quantitative due to the recovery problems inherent in the process.

In order to determine whether the porewater matrix affects the toxicity of filterable particles (e.g., its ionic strength, dissolved organic carbon content), the filtered material can also be added to a volume of pH_I dilution water equal to the volume of porewater that was passed through the filter. The toxicity of this dilution water, spiked with porewater

solids, can be compared to the toxicity of the unfiltered (Baseline) porewater and the filtrate spiked with its own solids.

9.3.6 pH Adjustment/Aeration Test

The Aeration test is designed to determine how much sediment porewater toxicity can be attributed to volatile or oxidizable compounds. The test is performed with pH-adjusted and unadjusted porewater. By comparing the toxicity test results for aerated acidic, pH_I, and basic samples, toxicity may be changed and this knowledge con be used for further characterization. Some compounds can be removed or oxidized most easily at one pH, whereas others are most easily removed or oxidized at a different pH. Thus, the aeration is performed at several pH values.

Whether a constituent is completely removed, or sufficiently removed to reduce toxicity, depends on many chemical/physical conditions. At a minimum, one must be certain that the geometry of the sparging process is always the same and that the duration is constant. Otherwise, the test is of little value. The pH may change, sometimes rapidly, during sparging and so pH must be frequently checked and maintained during the entire aeration period.

Air is used for sparging so that oxidation is included. Subsequent tests with nitrogen may be used to separate sparging from oxidation. Oxidation can change many constituents in many ways and one must determine if oxidation or sparging is the mechanism before additional tests can be designed. Water soluble constituents such as ammonia and cyanide are not readily stripped by this test and one should not assume that they will be removed.

9.3.6.1 Volume Required

Thirty-five mL volumes of pH 3, pH 11 and pH_I porewater are needed for this test. A maximum volume of 30 mL of each of these solutions is required for the toxicity tests on aerated solutions. An excess volume has been provided to allow for losses without removing it from the aeration vessel. Each toxicity test utilizes four exposure concentrations (10 mL each). The exact volume required for the toxicity test on each pH adjusted or unadjusted aerated solution will depend on the toxicity of the porewater (the 24 hour Initial EC50).

9.3.6.2 Reagents

0.01 NaOH, 0.012 N HCl (ACS grade in high purity water), and buffers for pH meter calibration.

9.3.6.3 Test Organisms

Test organisms, 75 or more, of the same age and species.

9.3.6.4 Procedure (Day 1)

Six different solutions are aerated in this test; pH 3, pH_I, and pH 11 porewater and pH 3, pH_o, and pH 11 dilution water. Each sample is transferred to a 50 mL cylinder containing a small perfluorocarbon stir bar. The diameter and length of the pH probe must be such that it can be placed into the solution during aeration. The taller the water column and the smaller the bubbles, the better the stripping will be. Each solution should be moderately aerated (~10 mL air/minute) for a standard time such as 60 minutes. Formation of precipitates should be noted.

The pH of the acidic and basic porewater and dilution water aliquots is checked every 10 minutes thereafter. If the pH of any solution had drifted more than 0.2 pH units, it must be readjusted back to the nominal. The volume and concentration of additional acid and/or base added to the solution should be recorded so that the final concentration of Na^+ and Cl^- in each solution can be calculated following final pH readjustment. Solutions should be stirred during any pH readjustment. Again, precautions must be taken in order to minimize the amount of acid and base added. Aeration time does not include the time intervals during which aeration is temporarily discontinued to readjust pH. A constant pH is not maintained in the "pH_I' porewater because this solution represents the generalized effects of aeration on the porewater without regard to pH. Only slight changes in the pH of the pH_o dilution water are likely since such water is usually brought to air equilibrium.

Air contaminated with oil (droplets or vapor), natural gas, or any other substance is not acceptable. Contaminated air is probable from air lines containing oil or in cases where the source of air is contaminated (e.g., boiler rooms). Small air pumps, sold for home aquaria are adequate, if the room air is free of chemicals. Chemistry laboratories where concentrated chemicals are used often do not have suitable air quality. Following aeration, the pH of each solution (including the 35 mL portions of pH unadjusted porewater and dilution water) is returned to the pH of the initial porewater or dilution water using the necessary volumes of 0.01 N NaOH and 0.012 N HCl. Returning all porewater solutions to the initial pH will ensure that a valid comparison can be made with the Baseline EC50. The pH of each sample must be periodically checked throughout the remaining work day and readjusted as necessary. If stable pH can be attained prior to toxicity test initiation, the pH during the test is likely to change less.

(Day 2): Prior to initiating the toxicity tests, the pH of all the aerated porewater and blank solutions should be checked and adjusted to pH_I or pH_o. Toxicity tests are performed on a single 100 % concentration of all three dilution water blanks (pH 3, pH_o, and pH 11). These blanks will provide information on toxic artifacts resulting from aeration.

Based on the 24 hour Initial EC50 of the day 1 porewater, toxicity tests are performed on each aerated porewater solution using an appropriate dilution series The pH of each test concentration should be measured and recorded daily.

9.3.6.5 Interferences/Controls and Blanks

Controls prepared for the Baseline toxicity test also act as controls on organisms, dilution water, and test conditions for this test. Results of the pH adjustment test will suggest whether or not toxic levels of NaCl may have been reached as a result of the addition of acids and bases to the porewater.

No significant mortality should occur in any of the three aeration blanks. If there is significant mortality, the cause must be found and corrected before the test can be meaningful. Blank toxicity, especially in all three, suggests contaminated air. Other possible causes include contaminated equipment, such as electrodes or glassware (especially where low or high pH solutions were in contact), or the addition of too much acid or base. To determine which of these factors resulted in blank toxicity, the toxicity of pH adjusted aerated dilution water can be compared to that in the same pH adjusted unaerated dilution water. Approximately the same quantities and concentrations of acid and base should be added to both these samples of dilution water to make them comparable. Another approach to this question involves observing the pH Adjustment/Filtration and pH Adjustment/C_{18} SPE blanks. Assuming the concentration of acid and base in the final blank solution is approximately the same in all dilution waters for the three tests, toxicity in the aeration blanks but not in the filtration or C_{18} SPE blanks suggests that the aeration rather than pH adjustment has led to contamination. Compare the toxicity from the Baseline test to the toxicity of all three aerated porewater samples. When the Baseline toxicity is significantly less than that of any one of the aerated samples, toxicity was added or created during porewater manipulations. This check is especially important because pH adjustment of aerated porewater may have required larger quantities of acid and base as compared to the pH adjustment test.

Dissolved oxygen depletion is likely to be caused by nitrogen stripping. If a relatively large surface-to-volume ratio is used (such as 10 mL volume in a one ounce plastic cup) during the overnight holding period, DO should not be a problem.

9.3.6.6 Results/Subsequent Tests

The EC50s for the aliquots of pH 3, pH_I, and pH 11aerated porewater are compared to the Baseline porewater EC50 to determine whether any of these processes resulted in significant change in porewater toxicity. If a substantial reduction in toxicity is seen for any or all of the three aerated porewater solutions, one must next determine whether the separation of effects was caused by sparging or oxidation. This is done by repeating those tests in which toxicity was reduced, substituting nitrogen for air in the stripping process. If side-by-side porewater stripping tests with air and nitrogen provide the same results, toxicant removal is probably caused by the sparging process. If only the test(s) conducted by air succeed(s) in reducing or removing toxicity, oxidation is a probable cause. A porewater sample may contain toxicants removed through sparging and oxidation. An example would be where aeration at pH 3 and pHI reduces toxicity, but nitrogen stripping removes the toxicity only in the pH 3 porewater.

9.3.7 pH Adjustment/C_{18} Solid Phase Extraction Test

The solid phase extraction (SPE) test is designed to determine the extent of porewater toxicity caused by those organic compounds and metal chelates that are relatively non-polar. The porewater is passed through a small column packed with octadecyl (C_{18}) sorbent. Compounds in the porewater interact through solubility and polarity with the sorbent and are extracted from the porewater onto the sorbent. This type of chromatography in which the mobile phase (the effluent) is polar and the solid phase (C_{18} sorbent) is non-polar, is referred to as reverse phase, SPE. Any organic compound present in water can be considered "soluble" by virtue of its presence in the water. Obviously relative degrees of water solubility exist. Many highly toxic pollutants found in sediment porewater at very low concentrations are not considered water soluble despite the fact they are present in toxic concentrations.

Compounds extracted by the C_{18} sorbent from a neutral aqueous solution are usually soluble in hexane or chloroform. The C_{18} sorbent can also be used to extract acids and bases as organic acids and bases can be made polar by shifting the equilibrium to the un-ionized species. By adjusting the porewater to a low pH and a high pH, some of these compounds will exist predominately in the un-ionized form and will sorb to the C_{18} column. Because of C_{18} column degradation, the use of pHs above 10 and below 2 are not used. To ensure column integrity, pH of the porewater will be lowered only to 3 and raised only to 9 (not 11) in this test. Manufacturer's data should be consulted for tolerable column pH ranges and for exact column conditioning procedures which must be done to get proper performance.

9.3.7.1 Volume Required

A maximum of 35 mL of solution at each pH is required for the pH adjustment/filtration toxicity testing and an additional 200 mL volume is pumped through the C_{18} column. The remaining 200 mL volumes of filtered pH 3, pH 11, and pHI porewater from Section 6.0 are used in this test. Each toxicity test is conducted on four exposure concentrations (10 mL each). The exact volume required for the toxicity test on each pH adjusted or pHI post-column porewater will depend on the toxicity of the porewater (the 24 hour Initial EC50).

9.3.7.2 Reagents

HPLC grade methanol and high purity water, 0.01 NaOH, 0.012 N HCl (ACS grade in high purity water), buffers for pH meter calibration, and solvents for cleaning the pump and reservoir..

9.3.7.3 Test Organisms

Test organisms, 135 or more, of the same age and species.

9.3.7.4 Procedure (Day 1)

The first step in the test involves conditioning the solid phase extraction column. Column conditioning procedures may vary with the manufacturer of the column. the procedures described in this document are modifications of the conditioning steps used with the Baker® C_{18} SPE columns (J.T. Baker Chemical Company, Phillipsburg, NJ).

Using a flow rate of 10 mL/min., 25 mL of HPLC grade methanol is pumped through the column and discarded. Next, 25 mL of high purity water, adjusted to pH 3 with HCl, is placed in the sample reservoir. Care must be taken in timing the addition of solutions after the methanol has passed through the column. While the mixing of methanol with subsequent solutions must be minimized, the column must also be prevented from going dry following the methanol wash. The amount of time needed between introduction of solutions to prevent any column drying will be unique to each investigator's apparatus. This timing should be determined before performing this procedure with actual porewater samples. If the column dries at any time after the introduction of the methanol, the column must be reconditioned (with methanol).

As the last volume of pH 3 high purity water is entering the column, the filtered pH 3 dilution water is placed into the reservoir. Again, the column must not be allowed to dry before the pH 3 dilution water enters the column. The pH 3 high purity water passing

from the column should be measured to determine the point at which the dilution water begins to leave the column. The pH 3 high purity water used to condition the column is discarded. The full 200 mL of the filtered pH dilution water is collected, and a 10 mL aliquot is taken for the toxicity blank to detect toxicity leached from the column. This 10 mL aliquot is readjusted to the initial pH of the dilution water using 0.01 NaOH and reserved for day 2 toxicity testing. Care should be taken to minimize changes in sample volume and ionic strength during pH readjustment.

As the last several mL of filtered pH dilution water are entering the column, the 200 mL volume of filtered pH 3 porewater is placed in the sample reservoir. Again, the column sorbent must not be allowed to dry between the dilution water blank and the porewater. Collect a 30 mL aliquot of column effluent after the 25 mL of the porewater passes through the system. A second 30 mL aliquot is collected after a total of 150 mL of the porewater passes through the column. Collection of the first post-column porewater sample after 25 mL of porewater has passed through the column ensures that any dilution water left in the system will not be present in the post-column porewater sample. The second sample of post-column porewater provides information on column overloading and toxicant breakthrough. Both of these 30 mL aliquots are readjusted to the initial pH of the porewater using the drop-wise addition of 0.01 N NaOH. The total volume of NaOH necessary for pH adjustment should be recorded. these aliquots are reserved for day 2 toxicity testing. Columns are not re-used but should be saved for subsequent elution.

If a dilution water is used, for example receiving water, in which trace organic contaminants may be present or in which organics such as humic acid may be present, the same column should not be used for the porewater. Rather, a new column should be conditioned and in place of the 200 mL dilution water blank, 200 mL of a synthetic dilution water should be used. It should be checked for toxicity in the same way. The pH should be adjusted to the same value as that of the porewater sample.

The above procedure is repeated using a new conditioned 3 mL C_{18} column and the filtered pH_I porewater. Prior to attaching a new column to the apparatus, the reservoir and pump must be cleaned with acetone and high purity water. After the samples are started through the column, the pH of the aliquots of dilution water and porewater collected should be checked. It is unlikely however, that the pH readjustment to pH_o and pH_I (respectively) will be necessary. If pH adjustment is necessary it should be performed using 0.012 N HCl or 0.01 N NaOH, recording all volumes added.

In the final C_{18} column test, pH 9 (not 11) dilution water and porewater are chromatographed as described above. While use of pH 11 porewater offers the likely advantage of shifting a larger number of basic organic compounds farther towards the

predominantly unionized form, and therefore removal, the C_{18} column will not withstand a pH above 10. for this reason, the pH 11 filtered dilution water and porewater aliquots previously prepared are readjusted to pH 9 with 0.12 N HCl and 0.012 N HCl before application to the column. The 25 mL of high purity water used to rinse the column following methanol conditioning must also be adjusted to pH 9 with NaOH. The single 10 mL aliquot of post-column pH 9 dilution water and both 30 mL aliquots of post-column pH 9 porewater are further adjusted to pH_o and pH_I respectively, prior to toxicity testing. The total volume of acid added for pH readjustment is recorded. The pH of all aliquots of the chromatographed dilution water and porewater should be checked and readjusted as appropriate throughout the remainder of the work day.

(Day 2): The pH of all of the post-column dilution water and porewater aliquots should be checked and readjusted if pH has drifted over night. Toxicity tests are performed on a single 100% concentration of all three of the dilution water blanks collected. These blanks will provide information on the presence of toxicity leached from the C_{18} column at different pHs.

The six 30 mL post-column porewater aliquots are tested for toxicity using an exposure series based on the 24 hour EC50 of the original effluent. Chromatographed effluent aliquots are tested using an appropriate dilution series. The pH of each solution tested should be measured daily and recorded along with the organism survival.

9.3.7.5 Interferences/Controls and Blanks

Controls on test organism performance, dilution water quality, and such are provided by the control from the Baseline toxicity test. The pH Adjustment and Filtration tests provide information on the effects of pH adjustment and filtration on porewater toxicity apart from any additional changes caused by C_{18} SPE. Porewater and blank results from these two tests must be consulted prior to interpreting the results of the C_{18} SPE test, both in terms of identifying any toxic artifacts added during filtration and pH adjustment and in allocating toxicity reduction to the three components potentially impacting porewater toxicants in the C_{18} SPE test.

The C_{18} technique is, of those methods so far discussed, the most dependent on more manipulations. More problems are likely to be encountered with toxic blanks because in addition to those associated with pH adjustment and filtering, the C_{18} method involves use of resin and methanol as well. Blanks for toxicity must be checked in the same manner as before for acid and base addition, filter toxicity, pH drift, as well as toxicity from the C_{18} column.

If toxicity is not reduced in post-column porewater, not too much credence should be placed on the results. Going back and sorting through the possible causes can be very time consuming.

If the post-column porewater is not toxic, then considerable weight can be attached to the results. The next step is to go on to Phase II C_{18} procedures for that toxicity removed by the column. Some checking should be done to assure that the C_{18} column has not just served as a smaller pore size filter than the glass filter used to filter the sample before passing it through the column. This caution is especially applicable to the samples in which pH was adjusted.

9.3.8 Oxidant Reduction Test

This test is designed to determine to what extent constituents reduced by sodium thiosulfate are responsible for porewater toxicity. In this test, varying quantities of sodium thiosulfate ($Na_2S_2O_3$), are added to aliquots of the porewater to produce increasing ratios of reducing agent/total thiosulfate reducible constituents. Frequently, the reduced form of the toxicant has a much lower toxicity.
The approach is to add a concentration (at the highest addition) that is approximately equal to the $Na_2S_2O_3$ EC50 of the test species. If the EC50 for the preferred test species is unknown, an $Na_2S_2O_3$ EC50 will have to be determined.

For cases where oxidants account for only part of the toxicity, sodium thiosulfate may only reduce the toxicity as opposed to completely eliminating it. Time to mortality must be measured rather than observing mortality at a fixed time. Time to mortality measurements are necessitated as there are no dilutions from which to calculate an EC50. The endpoint is the estimated concentration that will kill half of the organisms in a specified time. In time to mortality tests, the concentration is fixed and the time required to kill 50% of the organisms is measured. Obviously, to do so requires frequent mortality observation. Since toxicity is a function of tine and concentration, both EC50s and ET50s (time to 50% effects) are measures of the same property.

9.3.8.1 Volume Required

A maximum volume of 100 mL porewater is required for the Oxidant Reduction Test. The exact volume required will depend on the 24 hour Initial EC50. The test requires 10 porewater aliquots at 100%.

9.3.8.2 Reagents

The sodium thiosulfate stock concentration should be 10X the $Na_2S_2O_3$ EC50 concentration for the test species being used. The stock solution should be prepared in freshly boiled water.

9.3.8.3 Test Organisms

Test organisms, 50 or more, of the same age and species.

9.3.8.4 Procedure (Day 2)

To perform the test, put 10 mL aliquots of porewater diluted to 4X-EC50 (or 100%) in 10 test chambers. Add 1.0, 0.8, 0.6, 0.4, 0.2, 0.1, 0.05, 0.025, and 0.012 mL to nine aliquots (mix), and do not add any to the tenth. The treatment receiving 1 mL should contain the approximate concentration of sodium thiosulfate equal to the EC50 of the test species.

9.3.8.5 Interferences/Controls and Blanks

Controls prepared for the initial or baseline toxicity test act as a check on the general health of test organisms, dilution water quality and test conditions. By comparing the time to mortality in the various $Na_2S_2O_3$ exposure concentrations with that in the treatment without thiosulfate, one can determine whether the addition of $Na_2S_2O_3$ increased time to mortality at some thiosulfate concentration. If, in all of the porewater exposures, time to mortality decreases as the volume of sodium thiosulfate added increases the test should be repeated with a 10 times weaker $Na_2S_2O_3$ solution. If a significant loss in porewater toxicity is apparent over the first 24 hour period after porewater extraction in the laboratory (i.e., Initial EC50 < Baseline EC50), it may be necessary to conduct future Oxidant Reduction tests immediately upon the samples extraction from the test sediment.

9.3.8.6 Results/Subsequent Tests

If oxidants are causing toxicity, time to mortality should increase somewhere in the range of tested thiosulfate additions. No change in toxicity suggest either no oxidant toxicity or not enough thiosulfate was added. The experiment should be repeated, increasing the concentration of thiosulfate added.

9.3.9 EDTA Chelation Test

To determine the extent to which porewater toxicity is caused by certain cationic metals, increasing amounts of a chelating agent (EDTA) are added to aliquots of the porewater sample. The form of the metal has a major effect on its toxicity to aquatic organisms (Magnuson et al., 1979) and specific metal forms may be more important in aquatic toxicity than the total quantity of the metal.

Addition of the ethylenediaminetetraacetate ligand (EDTA), a strong chelating agent, will produce relatively non-toxic complexes with many metals. The success of EDTA in removing metal toxicity is a function of solution pH, the type and speciation of the metal, other ligands in the solution, and the binding affinity of EDTA for the metal versus the affinity of the metal for the tissues of the organism (Stumm and Morgan, 1981). Because of its complexing strength, EDTA-metal complexes will often displace other soluble forms such as chlorides and oxides of many metals. Among the cations typically chelated by EDTA are aluminum, barium, cadmium, cobalt, copper, iron, lead, manganese ($^{+2}$), nickel, strontium, and zinc. EDTA will not complex anionic forms of metals such as selenides, chromates, and hydrochromates and forms relatively weak chelates with arsenic and mercury. For those metals with which it forms relatively strong complexes, the toxicity of the metal to aquatic organisms is frequently reduced.

Since EDTA will complex relatively non-toxic metals (e.g., calcium, magnesium) as well as more toxic heavy metals, fairly concentrated solutions are needed. The mass of chelating agent required should be approximated because EDTA can become toxic when present above a certain concentration. The range of EDTA concentrations that will adequately bind the metals but not be toxic appears to be smaller than that for sodium thiosulfate and oxidants.

By measuring the hardness and salinity of the porewater, the range of EDTA concentrations that should not be toxic in a porewater sample can be estimated. "Salinity" not due strictly to NaCl will have different effects on toxicity. This calculation, for prediction of the EDTA concentration is more involved than is first apparent. Previously collected data (Horning and Weber, 1985) has indicated that over the physiological range of hardness and salinity, hardness affects the toxicity of EDTA more than does sodium chloride. The usual methods for measurement of salinity (conductivity meter, salinometer, or refractometer) do not specifically measure sodium chloride. the choice of EDTA concentrations should always be based first on hardness and second on salinity *only* when the salinity is known. The particular combination of hardness and salinity present in a porewater sample may have to be tested to get an accurate EDTA EC50. If the salinity is composed of ions other than sodium and chloride, the hardness of the dilution water should be made equal to the porewater hardness and the

additional "salinity" added in the form of other major cations and anions such as potassium, sulfate, and carbonate.

An EDTA EC50 value can be derived in a standard toxicity test water is likely to be much lower than the EC50 for EDTA in porewater. The toxic concentration of EDTA in one porewater will not be the same as the concentration causing toxicity in a different porewater or even a different sample of the same porewater. For this reason, the concentrations of EDTA added to the porewater aliquots should bracket the expected EC50 based on clean water with a similar salinity and hardness value.

As in the pH Adjustment and Oxidant Reduction tests, the porewater itself is used as a control rather than the blank based on dilution water. By adding increasing concentrations of EDTA to each aliquot, at some addition the metals will be chelated but unbound EDTA will not be present at toxic concentrations. The goal of this test is to add enough EDTA to reduce metal toxicity. This is most easily achieved by adding insufficient EDTA in the lowest EDTA additions so metal toxicity is not removed. In the midrange of EDTA additions, the metals will be rendered non-toxic by the EDTA, and at the high end of the range of EDTA additions, the unreacted EDTA is itself toxic. By using a porewater concentration of 100% if the EC50 is greater than 25%, the potential for exceeding the binding capability of the added EDTA is lessened, especially for very toxic porewaters (EC50 < 10%).

9.3.9.1 Volume Required

A volume of 100 mL porewater usually is required for the EDTA Chelation test. The exact volume needed will depend on the 24 hour Initial EC50 and the particular option chosen to determine the EDTA concentration series required.

9.3.9.2 Reagents

EDTA stock solution, reagents for determination of porewater hardness and salinity.

9.3.9.3 Test Organisms

Test organisms, 50 or more, of the same age and species.

9.3.9.4 Procedure (Day 1)

Set the EDTA concentration at the midrange of EDTA toxicity, equal to the EDTA EC50 concentration. Choice of the EDTA EC50 must be based on porewater hardness (and

salinity). It may be necessary to determine the EDTA EC50 for the particular combination of porewater salinity, hardness, and test organism used.

(Day 2): To perform the test, 10 aliquots (or more depending on the option chosen) of the porewater are prepared at a concentration equal to 100% porewater where the EC50 is greater than 25% (where the EC50 value is calculated from the 24 hour Initial toxicity test results). Next, 1.0 mL of the EDTA stock is added to the first 10 mL aliquot of the porewater. To the second 10 mL sample of porewater, 0.8 mL is added, to the third, 0.6 mL, and so on until the fifth 10 mL porewater sample has received 0.2 mL. Continue the procedure with four more 10 mL aliquots of the 100% porewater using 0.1, 0.05, 0.025, and 0.012 mL of EDTA stock. The tenth is a blank used to compare treatment effects on time to mortality. A microliter syringe will be needed for the smaller additions. If more than 1 mL of EDTA is required, a stronger stock concentration of EDTA should be used. If the porewater has a low toxicity (EC50 = 50-100%) a series of dilution blanks may be necessary to check for the dilution effect of the EDTA stock addition. No more than 10% dilution of the porewater aliquots should be allowed unless a dilution blank series is included. Special care must be taken to mix the contents of each chamber before introducing the test organisms.

9.3.9.5 Interferences/Controls and Blanks

Controls prepared for the initial or baseline Toxicity test provide quality control for test organisms, dilution water, and test conditions. The untreated aliquot acts as a blank for use in determining the presence of EDTA toxicity. Time to mortality at each EDTA addition is compared to the untreated aliquot. If time to mortality is shorter in all treatments, repeat the test using a lower EDTA range. If time to mortality is not reduced in any treatment, repeat using a higher range of EDTA concentrations. Erratic patterns in mortality cannot be used. If this occurs it suggests that this test is not useful for the particular porewater being studied.

9.3.9.6 Results/Subsequent Tests

If the appropriate EDTA concentration range is utilized, the time to mortality will not change from that seen in the exposure of unaltered porewater at low additions of EDTA. In the midrange, toxicity will be reduced and at high additions of EDTA, toxicity will be as high or higher due to unbound EDTA toxicity and porewater toxicants other than chelatable metals if present. Time to mortality must be used to detect partial toxicity removal.

Toxicity may be removed at all exposures if the lowest addition of EDTA removes metal toxicity and the highest addition does not cause EDTA toxicity. If toxicity is not reduced

in any treatment, either the porewater has no chelatable metal toxicity or not enough EDTA was added. Increased toxicity over untreated porewater suggests EDTA toxicity and a lower EDTA range should be tested.

9.3.10 Graduated pH Test

This test is designed to determine whether porewater toxicity can be attributed to ammonia. The test will not confirm ammonia as a toxicant but will indicate whether its presence in the porewater should be further investigated.

Total ammonia concentration in a porewater sample does not relate very well to the toxicity because the toxicity of ammonia is a function of DO, pH and temperature. The pH has a very large effect on ammonia toxicity, pH rises upon contact with air such as in a toxicity test. Literature data can be used only as a general guide because of the large effect of very small pH changes. These are usually not reported fully enough to be useful.

One might expect ammonia to be removed during the pH/Aeration test. Ammonia is not readily reduced below concentrations toxic to aquatic organisms. Other techniques which can be used to remove ammonia-related toxicity may also displace other toxicants with completely different physical and chemical characteristics. For example, ion exchange resins (e.g., zeolite) in addition to removing ammonia, may also remove toxic organic compounds through adsorption. For this reason, a specific test to address toxicity related to this common pollutant is useful.

Ammonia acts as a basic compound in water. The un-ionized, more toxic form, NH_3, predominates above pH 9.3 and the ionized, essentially non-toxic form, NH_4^+, is most abundant below this pH at 25°C. Through the pH range from 7.0-8.0, the percent of total ammonia in the toxic form increases rapidly. It is important to note that the toxicity of the toxic form decreases with increasing pH (EPA, 1985). Therefore, the increase in the concentration of the toxic form is partially compensated by the decrease in toxicity. As pH increases, the percentage in the toxic form is greater but the toxicity of the toxic form is less. As pH decreases, the percentage of total ammonia as NH_3 decrease, but the toxicity of NH_3 increases. Temperature also affects dissociation of ammonia but since it is usually held constant in toxicity tests, it can be ignored for purposes here. The increase in the percent of total ammonia occurring in the toxic form with increasing pH is greater than the decrease in its toxicity. The net result is an increase in toxicity, based on total ammonia in the sample.

These opposing effects of pH change can be used to detect the presence of ammonia toxicity. By diluting aliquots of porewater to their 24 hour Initial EC50 and adjusting each aliquot to a different pH value, porewater toxicity can be greatly enhanced or

completely eliminated. For example, at pH 6 and 25°C, 0.0568% of the total ammonia in solution is present in the toxic form. At pH 7 and 25°C, 0.566% of the total ammonia is present as NH_3 and at pH 8, 5.38% is present in the un-ionized form. Similar changes in percent NH_3 for pHs 6, 7, and 8 occur at other temperatures, if a test temperature different from 25°C is needed. This difference in the percent of un-ionized ammonia is enough to make the same amount of total ammonia about 3 times more toxic at pH 8 as at pH 6. Whether or not toxicity will be eliminated at pH 6 and the extent to which toxicity will increase at pH 8 will depend on the total ammonia concentration. But if a dilution of porewater equal to the EC50 is used for pH adjustment, this should "normalize" the total ammonia concentration and one should see toxicity differences between pH 6 and 8. Either pH 8 will have a higher toxicity than the unadjusted porewater EC50 or pH 6 will have a lower toxicity depending on the pH of the unaltered porewater.

Perhaps the greatest challenge faced in this test is that of maintaining a constant solution pH. This is a necessity if the concentration of un-ionized ammonia is to remain constant and the test results are to be valid. In conducting toxicity test on porewater, it is not unusual to see the pH of the test solutions with high porewater concentration drift 1 to 2 units greater over a 48 to 96 hour period.

9.3.10.1 Volume Required

Depending on the method chosen for pH stabilization, 120 mL to 1,500 mL of porewater is required for this test. The volume used is split into three aliquots and tested at the 24 hour Initial EC50 concentration, without dilution or replication.

9.3.10.2 Reagents

1.0 and 0.1 N NaOH or 0.1 N and 0.01 N NaOH, 1.2 N and 0.12 N HCl or 0.12 N and 0.012 N HCl.

9.3.10.3 Test Organisms

Test organisms, 15 or more, of the same age and species.

9.3.10.4 Procedure (Day 2)

If the dissolved oxygen content of the porewater is adequate and BOD is not high, the following small volume pH stabilization procedure should be tried. An aliquot of porewater is diluted to the 24 hour Initial EC50 concentration using dilution water for a final volume of 120 mL. A 40 mL portion of this solution is adjusted to pH 7 using 0.12 and 0.012 N HCl or 0.1 and 0.01 N NaOH. Caution must be taken to minimize the

volume of acid or base solution should be subrogated with the addition of the weaker solution of acid or base. Approximately half of this volume is transferred into a one ounce disposable transparent test chamber and five test organisms are added. The remaining volume is transferred into the test chamber until the volume of pH 7 porewater rises slightly above the edge of the container. A section of Parafilm® slightly larger in area than the mouth of the test chamber, is laid on top of the porewater. The Parafilm® is carefully pulled down around the edges of the test chamber, caution being taken to prevent test organism loss at this time. Care must also be used to exclude any air bubbles during the sealing process.

This procedure is repeated with the other two 33 mL aliquots of the porewater adjusted to pH 6 and pH 8. Test organisms can be observed through the transparent test chamber. The Parafilm® cover should only be removed at the end of the test period in order to measure test solution pH and dissolved oxygen.

If the above method does not hold pH or if oxygen is too low, the following large volume pH stabilization procedure may be tried.

9.3.10.5 Interferences/Controls and Blanks

Blanks prepared for the initial or baseline test act as a check on the general health of test organisms, dilution water quality, and test conditions. The initial or baseline test acts as a control for the detection of problems (especially in the small volume pH stabilization method) and problems associated with acid base addition. If the Baseline porewater pH is close to the pH of any of the pH adjusted test solutions, the toxicity should be similar. Significantly greater toxicity suggests that an interference from other factors. Other compounds with toxicities that increase directly with pH may lead to confounding results or may give results similar to ammonia.

9.3.10.6 Results/Subsequent Test

When ammonia is present in the porewater at toxic levels, the pH 6 test solution should be less toxic than the pH 7 solution, which, in turn, should be less toxic than the pH 8 solution. However, ammonia is not the only possible cause. Using the pH at Baseline porewater EC50, the relative toxicity of each pH adjusted solution can be predicted if ammonia is the sole cause. For example, if, for the baseline porewater, the average pH in the 100% concentration in which no organisms survived, the estimated pH at the EC50 (71%) could be approximated as 7.7. One would expect greater than 50% mortality in the pH 8 test solution and significantly less lethality in the pH 7 solution. One should then proceed to Phase II for identification. If ammonia is one of several toxicants in porewater

this procedure may pose problems. For this reason, if total ammonia levels are greater than 20 mg/L, it may be appropriate to include a pH 6 porewater treatment interfaced with other Phase I tests.

12.0 FRESHWATER SEDIMENT TOXICITY TESTS

12.1 *Hyalella azteca* 14-d Sediment Toxicity Test

12.1.1 Background Information

The procedure described below is a modification of EVS SOP 1073-1, which is a 10-d sediment toxicity test. The modification is a change from a 10-d test to a 14-d test.

This static, acute toxicity test can be used to determine the relative toxicity of sediments using the freshwater amphipod, *Hyalella azteca*. This test is not appropriate for marine sediments. The amphipods are exposed to whole sediments in 1-L jars for a 14-d period to determine effects on survival and growth. The response of amphipods to test sediments is compared with the response of amphipods exposed to clean control sediment or a reference sediment.

Read the entire SOP before beginning any tasks relating to this test. This SOP is organized into separate sections describing preparation activities, instructions for obtaining and culturing test organisms, testing the sample(s) and running regular reference toxicant tests. The procedures described are for routine sample testing only and describe tests as they are currently conducted. Other options (e.g., use of flow-through systems) may be valid if in accordance with reference protocols and approved by the Laboratory Manager. If additional controls or different types of samples are to be tested, the Laboratory Manager may also specify other modifications to this SOP.

Reference Literature

ASTM (American Society for Testing and Materials). 1994. Standard guide for conducting sediment toxicity tests with freshwater invertebrates. Method E1383-94. In: 1994 Annual Book of ASTM Standards, Volume 11.04. American Society for Testing and Materials, Philadelphia, PA.

Equipment

Culture Maintenance

- constant environment room: 23 or 25 ± 1°C; 16:8 h L:D photoperiod; light intensity approximately 500 ft candles
- aeration supply, airlines, pasteur pipettes, airstones
- thermometer, pH, DO and SCT meters
- clean, fine silica sand
- 13-L glass aquaria, with covers
- reconstituted "moderately hard" water, prepared from dechlorinated water

- 20-L carboys for water storage
- dried maple leaves
- Nitex mesh cones
- sieves and sorting trays
- light source (e.g., light table)
- squirt bottle of culture water
- inverted pasteur pipettes, with bulbs
- Tetra-Min® flake fish food
- blender
- top-loading balance, weighboats and scoops
- d-YCT/*Selenastrum*, prepared in 1:1 ratio (*Ceriodaphnia* diet)

Test Equipment

- juvenile *Hyalella* (2nd instar, 2 - 3 mm long)
- constant environment room: 23 or 25 ± 1°C; 16:8 h L:D photoperiod; light intensity at approximately 50 ft candles
- aeration supply, air lines, pasteur pipettes, airstones
- thermometer, pH, DO and SCT meters
- clean 1-L glass jars, w/lids with airline holes - 5 for control, 5 for each test sediment
- 10% nitric acid
- acetone
- reconstituted "moderately hard" water, prepared from dechlorinated water (5 L per sediment)
- scoops for measuring sediments
- balances: top-loading and analytical
- sieves, sieving tubs
- small weighboats (1 per test jar, plus extras)
- squirt bottle of culture water
- Pyrex trays and inverted pasteur pipettes with bulbs for sorting sediments
- light source (e.g., light table)
- Tetra-Min® flake fish food
- d-YCT/*Selenastrum*, prepared in 1:1 ratio (*Ceriodaphnia* diet)
- numbered, pre-weighed foil pans (for dry weights)
- drying oven @ 60°C (for dry weights) and desiccator

Reference Toxicant Equipment

- 10 mg/L Zn stock solution
- 100-mL graduated cylinder
- 150-mL glass beakers - 9 per test

- Eppendorf pipettors (0.1 - 1 mL, 1 - 10 mL capacity)
- weighboats
- inverted pasteur pipettes, with bulbs

Sample Details

Sample required: A minimum of 2 L of test sediment should be collected (approximately 1 L is used for testing).

Sample storage: Collect sediments in new, precleaned glass jars with teflon-lined lids (e.g., I-Chem® jars). Fill the jars completely to exclude any air. Store the samples at 4°C in the dark until used for testing. The maximum holding time is 14 d from sediment collection. Store unused sample at 4°C until the test is completed and the client has received the report.

Time Requirements

Culture maintenance:	3 h/week
Glassware preparation:	1 h/test sediment
Sediment preparation (Day -1):	1.5 h/test sediment
Test initiation (Day 0):	1 h/test sediment
Daily monitoring for 14 d:	0.25 h/d/test sediment
Test termination:	1.5 h/test sediment
Reference toxicant test:	3-4 h
Data analysis, report preparation:	3 h

12.1.2 Culturing Test Organisms

Test organisms are obtained from an in-house culture which is maintained on a continuous basis in the EVS laboratory, or they may be purchased from commercial suppliers. Detailed instructions for culture maintenance, including food preparation, and for obtaining organisms for use in tests are described in this section of the SOP.

Hyalella azteca (Saussure), Amphipoda, is a small freshwater crustacean which has received considerable attention for use in screening the toxicity of contaminated sediments. It is common throughout lakes and streams of temperate North America. It has many desirable characteristics of a test species, including: short generation time, widespread and abundant distribution, ecological importance, and a wide tolerance of sediment grain size. Although *H. azteca* is usually found in

waters of low or medium hardness, it is tolerant of hard waters. Most importantly, it is a sensitive indicator of the presence of contaminants associated with sediments. *H. azteca* is an epibenthic detritivore and herbivore and will burrow in the sediment surface in the search of food.

The life-cycle of *H. azteca* can be divided into three distinct stages: an immature stage, consisting of the first 5 instars; a juvenile stage, including instars 6 and 7; and an adult stage, covering the 8th and older instars. Growth is indeterminate, so older adults should be larger than younger adults. *H. azteca* can complete one life-cycle in approximately 4 weeks at 26 - 28°C, but individuals may live for up to 12 - 16 weeks. Animals usually begin to form mating pairs in 3 - 4 weeks. Once mating pairs are evident, neonates will soon begin to appear. Development is somewhat delayed at lower temperatures. Brood size is dependent on the size of the adult female, which is greatest at lower temperatures (e.g., 10 - 15°C).

Starter Cultures and Commercial Suppliers

New "starter" cultures of *Hyalella* can be obtained from several sources, such as other private laboratories, government laboratories, universities and commercial suppliers. A "starter" culture usually consists of 50 - 100 amphipods of similar age which can be used to establish a new in-house laboratory culture or supplement an existing one. If larger numbers of amphipods are required (i.e., if tests are being conducted with purchased rather than cultured animals), a commercial supplier should be used. *Hyalella* have been obtained from the following sources in the past.

Margaret Stinson
Washington Department of Ecology
Manchester Laboratory
7411 Beach Drive East
Port Orchard, WA 98366-8204
Tel: (206) 871-8821
Fax: (206) 871-8850

Stan Stinitski
Aquatic Research Organisms (ARO)
P.O. Box 1271
Hampton, NH 03842
Tel: (603) 926-1650
Fax: (603) 926-5278

Margaret Stinson may be able to supply small "starter" cultures at no cost other than shipping. ARO charges $0.25 per amphipod plus shipping.

Organisms obtained from external sources must be acclimated slowly to EVS laboratory conditions. To do this, gradually change the water in which amphipods were transported to 100% EVS culture water over a period of no less than 8 h. Adjust the water temperature to the desired temperature no faster than 2°C per 24-h period. Measure the dissolved oxygen (DO) concentration; it should be close to 100% saturation (≈8-9 mg/L at 20-25°C).

Glassware Cleaning

Glassware used for culture maintenance should be kept separate from that which is used for testing and for general laboratory use. All glassware and plasticware used for culture and testing must be cleaned prior to use. Wash all glassware with non-phosphate detergent, rinse twice with dechlorinated water, allow to dry and then check for cleanliness. Rinse glassware once with 10% nitric acid, twice with distilled or deionized water, once with full-strength acetone, and then five times with deionized water (if there is a shortage of deionized water, then use distilled water for all but the last two rinses). New plasticware must be soaked in dilution water at least overnight before its first use; after that, normal washing procedures are followed.

Dilution/Control Water

"Moderately hard" reconstituted water (80 - 100 mg/L as $CaCO_3$) is used for culturing *Hyalella* and for dilution and control water during testing. Throughout this SOP, "dilution/control" water or "culture" water refers to this type of reconstituted water. Prepare the water at least one day before use and discard it if not used within two to three weeks. Since the same water is used for *Chironomus tentans* culture and testing, the same storage container(s) can be used. Instructions for preparing reconstituted water are provided in Section 8.1 of this Manual; dechlorinated water is used as the dilution medium. Make sure the chemicals are fully dissolved in a small volume of dechlorinated water before adding them to the larger volume. Do not rely on aeration to dissolve the chemicals. Place an airstone in the carboy and make sure it is aerating vigorously. Cover the container and aerate it for 24 - 48 h before use. Before using the reconstituted water, measure and record the temperature, DO, pH, conductivity, hardness and alkalinity to make sure they are within acceptable limits (see Section 8.1). The dilution/control water DO should be 90 - 100% saturation.

Culture Sediment

Fine silica sand is used as the substrate for culture tanks and as control sediment for toxicity tests. Sand can be obtained from a hardware store (sandblasting sand) or from a pet store (canary sand). An 80-lb sack of #30 silica sand can be purchased from:

Ocean Construction Supply Ltd., Masonry Division
1280 W. 77th Avenue
Vancouver, B.C.
Tel: 261-2211

Always rinse the sand several times before use, first with dechlorinated tap water and finally with culture water. Although sand makes it harder to collect animals, it seems to improve the quality of the culture.

Preparation of Culture Tanks

Two types of *Hyalella* cultures can be prepared: a stock culture which contains animals of mixed ages, and a breeding culture prepared specifically for the collection of young animals of known age for use in toxicity testing. All culture tanks need to be prepared one day before they are needed; that is, before animals are added.

Stock Cultures

To prepare *Hyalella* stock culture tanks, place a 2- to 3-cm layer of pre-rinsed silica sand in a 13-L aquarium and add about 10 L of culture water. Each aquarium should also contain several small leaves or bits of leaves (as too many leaves can cause fouling of the test chamber). Various species, including maple, alder, birch, and poplar, work well (we normally use dry maple leaves). Leaves should be presoaked in culture water for 4-7 d and then rinsed well to remove tannins and other inhibitory/toxic compounds before they are added to the culture tanks. In addition to the dried leaves, Nitex mesh cones should be provided as a substrate. The cones are prepared from 0.5-mm Nitex mesh and are approximately 5 cm deep and 8 cm in diameter. Place 2 - 3 cones in each culture tank. (**NOTE**: mesh cones are preferable to the cotton gauze used by other researchers as they do not rot.)

After the addition of the mesh and leaves, add 100 mL of d-YCT/*Selenastrum* and 20 mL of a Tetra-Min® fish food slurry (preparation instructions are described below). Provide gentle aeration to each culture tank by means of a Pasteur pipette attached to an air line. Cover tanks with a sheet of plexiglass and leave undisturbed overnight. Food is added one day before introducing the amphipods to allow it to build up on the mesh and leaves to provide an adequate food supply for breeding adults. On the following day, add 50 - 100 animals of mixed age to each tank.

Breeding Cultures

Breeding tanks are prepared in the same manner as the stock culture tanks, except that no sand is added. To prepare *Hyalella* breeding culture tanks, place 10 L of culture water in a 13-L aquarium. Add the mesh cones, presoaked leaves, d-YCT/*Selenastrum* and Tetra-Min® slurry as described above. After overnight aeration, add approximately 100 breeding pairs (joined adults) from the stock culture tank(s) to each new breeding tank.

Feeding

Hyalella cultures should be fed three times per week (i.e., Monday, Wednesday, Friday) with a combination of two foods:

1. the same d-YCT/*Selenastrum* diet used for feeding in-house *Ceriodaphnia* cultures,

2. a prepared slurry of Tetra-Min® flake fish food.

Instructions for preparation of the d-YCT/*Selenastrum* food are provided in the *Ceriodaphnia* SOP (Section 14.2, Water). A 1:1 ratio of d-YCT and *Selenastrum* should be used. If d-YCT is not available, YCT can be substituted.

To prepare the Tetra-Min® fish food slurry, weigh 20 g of Tetra-Min® flake fish food and add it to 200 mL of culture water in a blender. Blend the mixture for at least 3 min, then pour into a 250-mL Erlenmeyer flask. Stopper the flask, label it with the preparation date and keep it in the 4 °C room. The food should last for a few weeks; monitor odour for signs of fouling and discard if this occurs. Always swirl the contents of the flask before using to resuspend the food particles. Prepare a double volume when multiple culture tanks are being maintained. This Tetra-Min® slurry is also used for the *Chironomus tentans* culture, so the same batch of prepared food can be shared.

Except for the initial addition of food to newly prepared culture tanks, each 13-L culture vessel should receive the following: 20 mL of d-YCT/*Selenastrum* and 6 mL of Tetra-Min® slurry. If the water turns cloudy, appears too green, or smells foul, reduce the amount of food or the frequency of feedings. Modifications are made at the technician's discretion, but all changes and amounts of food provided must be recorded in the *Hyalella* culture logbook.

Culture Maintenance and Renewal

Hyalella cultures should be maintained at 23 or 25 ± 1 °C under a photoperiod of 16:8 h light:darkness. The light intensity should be approximately 500 ft candles for culture. The DO level in the culture water should be near saturation (8.6 mg/L at 23 °C). To maintain *H. azteca* in good condition and avoid unnecessary stress, crowding and rapid changes in temperature and water quality should be avoided. Maintenance of a healthy culture is indicated by the following:

- frequent and conspicuous pairing
- females mating and releasing live young every 8 ± 1 d

- females producing 3-20 young/moult (but do not expect >5-10 young/moult/female)
- individuals completing life-cycle in 27-30 d.

Stock cultures require little regular maintenance; once every 1 - 2 weeks carefully siphon off and replace half the culture water in each tank and thin the *Hyalella* population if needed. Breeding culture tanks require regular maintenance and should be renewed once per week (usually Fridays) as described below. Renewal can be less frequent if no tests are expected. Additional presoaked maple leaves should be added to all culture tanks as old ones decompose and are eaten.

To renew a breeding tank, transfer about 1 L of culture water from the tank to a glass baking dish. Transfer all the leaves and mesh cones to the baking dish and shake them gently under water to remove/dislodge the amphipods. Large leaf pieces can be kept and later returned to the breeding tank.

After removing the leaves and mesh cones from the baking dish, count the adults and transfer them to a new breeding culture tank which contains about 5 L of culture water. Count the juvenile *Hyalella* and transfer them to a 600-mL beaker containing about 400 mL of old culture water from their breeding tank. Transfer animals with an inverted Pasteur pipette, taking care to release the amphipods carefully underwater to avoid injury or trapping of air under the carapace. Juveniles are extremely small (≈ 1 mm) so take care that they are not overlooked when renewing cultures. Check all the water in the old breeding tank by pouring small amounts into the glass dish and removing adults and young by pipette. Keep half the culture water from the old tank and add this to the new breeding tank to bring the volume to 10 L. The juvenile amphipods are either set aside for use in toxicity tests, or added to the stock culture tank(s).

Measure hardness, pH, temperature and DO of both the old and new culture water. Record the culture renewal date, water quality data, and numbers of adults and juveniles counted in the *Hyalella* culture logbook. Minor adult mortalities in the breeding tanks can be replaced with adults from the stock culture; high mortalities require a review of culturing procedures. Also label each breeding tank with the date that adults were added or cultures renewed. This tank should be checked again in 7-10 d; juveniles recovered at that time can be used in toxicity tests.

Regardless of whether toxicity tests are scheduled, breeding-size adults should be combined in one or two new tanks every 1-2 weeks. This will ensure that the culture continues to grow in size and that young animals will be available within 1-2 weeks in case a test is scheduled. If no tests are planned, all young should still be removed and transferred to the stock culture tanks. Always record the number of young collected in the culture logbook.

Obtaining Test Organisms

Test organisms should normally be obtained from the in-house *Hyalella* cultures, however animals can also be purchased from commercial suppliers. Each tank of 100 brood adults can be expected to yield approximately 100 - 150 juveniles after 7 d. Juveniles collected from the breeding cultures can be used as ≤7 d old neonates for aqueous-phase toxicity tests, or allowed to mature for an additional 7 d to be used as 7-14 d old juveniles in sediment toxicity tests. Organisms used for 14-d sediment tests are typically 7-10 d old and approximately 2 mm in length.

A 14-d sediment toxicity test requires 50 juvenile amphipods (5 replicates of 10 animals) for each test sediment, plus an additional 50 amphipods for the negative (clean) control. The reference toxicant test requires 90 test organisms. There should be a minimum 30% surplus of animals of the appropriate age and size available for test initiation. Before beginning a toxicity test, confirm that there are enough animals of acceptable size and quality available. Juvenile amphipods can be isolated in 1-L beakers (200/beaker) and kept in the dark with gentle aeration for up to 24 h before test initiation.

12.1.3 Test Procedure

Experimental Design

Tests should be initiated (i.e., Day -1 sediment preparation) on a Monday or a Thursday to avoid having to begin or complete a test on the weekend.

Amphipods are exposed to sediments in 1-L jars for 14 d. There are five replicates for each treatment, each containing 10 juvenile amphipods. This test involves preparing the sediments and overlying water one day and allowing them to equilibrate overnight. The following day (Day 0), the amphipods are counted and distributed to the test containers. Test conditions are monitored throughout the 14-d exposure period. On Day 14, amphipods are sieved from the sediments to determine mean survival. If growth is also being used as an endpoint, dry weight measurements are performed on surviving amphipods. For amphipods obtained from in-house cultures, a static 48-h LC50 test with the standard reference toxicant, zinc sulphate, is performed once a month. If amphipods were obtained from another source, a reference toxicant test is performed for each batch of animals, concurrently with the sediment toxicity tests. Test conditions are summarized in Table 12.1.

Glassware Cleaning

All glassware and plasticware used to perform the toxicity tests must be cleaned prior to use following the cleaning procedures given in Section 12.1.2.

Dilution/Control Water and Control Sediment

The water which is added to each test container as overlying water, and used as dilution water for the reference toxicant test, is reconstituted "moderately hard" water (80 - 100 mg/L as $CaCO_3$), the same water used for *Hyalella* culture. Follow the instructions in Section 12.1.2 for preparing this type of water. Always prepare enough water so that all tests can be set up using the same batch of dilution water.

For each series of sediment toxicity tests, there must be a negative (clean) control which consists of clean sediment and dilution/control water. The control sediment is clean silica sand, from the same source used for the *Hyalella* stock cultures. Rinse the sand thoroughly, first with dechlorinated water and then with culture water, before use and do not re-use control sediment.

Sediment Preparation (Day -1)

1. Ensure that all equipment is working correctly and that supplies are available, well in advance of the test initiation date. Prepare five 1-L jars for each sediment and the control and nine 150-mL beakers for the reference toxicant test. Label test containers with sample name and replicate.

2. Transfer the sediment from the container in which it was shipped to a large glass sorting pan. If the sediments were collected properly, any water on the sediment surface should just be interstitial water which has appeared because of settling during storage. This water should be mixed back into the sediments. Visually inspect the sediment and record observations of colour, grain size, odour, etc. on the sediment description datasheet (Figure 12.1). The sediment is put into a large glass sorting tray and hand-picked to remove rocks and large organic debris. If the average particle size is >3 mm then this test will not work as well since *Hyalella* should be able to burrow into the top layer of sediment. At this time, carefully inspect the sediment for the presence of native amphipods or other large organisms. If amphipods are present, remove these from the sample.

3. After removing any large particles and indigenous organisms, homogenize the sediment in the glass tray by thorough hand mixing. Afterwards, carefully transfer homogenized wet sediment directly into each 1-L jar. Add enough test sediment to each jar to make a 2-cm deep layer. For replicates, the weight of sediment necessary to make a 2-cm layer (about 175 mL) in the first jar is added to the other replicates. **Do this in a well-ventilated area.** (Some samples may require preparation in the fume hood; if the balance won't work in the fume hood, the 2-cm layer must be determined visually for each replicate.) The same procedure applies to the negative control. Record weight of sediment in each replicate on sample weight record sheet (Figure 12.2).

4. Make sure there is no sediment left around the rims of the test jars. It is also important that the sediment is relatively evenly distributed over the entire bottom surface of the jar.

5. Return unused sediment to its storage container, check the lid is tightly sealed, and return it to 4°C storage. Using a clean scoop, repeat this process for each test sediment.

6. Add approximately 800 mL of dilution/control water to each test container. Fill the jars to halfway up the "shoulder" of the jar, with all of them at the same level. Take care not to disturb the sediments when adding the water.

7. Cover each jar with a plastic lid that has an airline hole in the centre. Do not tighten the lids; they are opened frequently for water quality measurements. Place the jars in the constant environment chamber. Allow the sediment and water to equilibrate overnight before starting the test.

8. Gently aerate the water in each test jar. Set up an airline to each jar with gentle aeration (1-2 bubbles/sec) through a Pasteur pipette, so that the sediment is not disturbed. Aeration systems require a lot of adjustment to get an even, gentle flow of air to all containers.

Test Initiation (Day 0)

1. Prepare datasheets for recording water quality (Figure 12.3) and survival data (Figure 12.4). Randomly select two of the five replicates from each treatment for monitoring water quality. Measure and record temperature, DO, pH, and conductivity in these containers. The DO concentration should be >40% and ≤100% saturation (3.6 - 9.1 mg/L at 20°C; 3.4 - 8.6 mg/L at 23°C; 3.3 -8.3 mg/L at 25°C). Hardness and alkalinity should only be measured in composite samples collected on Days 0 and 10.

2. Following water quality measurements, the amphipods are added to the test containers. Since there are 5 replicates per treatment, 50 juvenile amphipods are needed per treatment. All animals used in a test must be from the same source, and be approximately the same size and age. Do not use organisms which are obviously different in size. To ensure that amphipods are randomly added to the various test jars, first collect them all in a large crystallizing dish. Screen the amphipods for consistency in size and set aside any which are too small or too large. Set out one weighboat per test container plus several extra ones, and place a small amount of culture water in each one. Randomly transfer 10 juvenile *Hyalella* (approximately 2 mm long; 7 - 10 d old) to each weighboat. Use an inverted Pasteur pipette and always release the amphipods below the water surface; discard animals that are dropped or contact dry surfaces. Transfer amphipods individually, making sure that all weighboats get one amphipod before getting the second, third, etc. Keep the amphipods at 23 °C during sorting.

3. Confirm that each weighboat contains exactly 10 amphipods (preferably have a second person check the counts) and that they are appear healthy. Randomly select groups of five weighboats for each of the test or control sediments and set them aside. Also set aside an additional five weighboats of amphipods for initial dry weight measurements. Gently pour the contents of one weighboat to one test container. A squirt bottle of culture water may be used to facilitate this. Check that no amphipods remain on the weighboat. This can also be done using a pipette and bulb, transferring one organism at a time into each jar. Gently resubmerge any which become trapped at the air-water interface. To ensure that each jar is seeded only once, clip a plastic clothespin to the aeration line as you seed each jar, and check them when you finish. Test jars should be inspected within 2 h of seeding. Any amphipods which continue to remain at the air-water interface at that time should be removed and replaced.

4. For large setups, test containers should be seeded in batches (i.e., several sediments at a time or all of one replicate at a time). To avoid seriously stressing the organisms, ensure that the amphipods are not held without sediment for more than 4 h. Furthermore, ensure that the ambient temperature is similar to the test temperature (e.g., sort organisms directly in the environmental chamber where the test will be conducted). If the ambient temperature is substantially different from the test temperature, then the water temperature in the sorting pan and holding container(s) could easily change, thereby stressing the animals. Frequent replacement of this water can minimize this stress.

5. If growth is being measured, do not weigh individual test animals prior to introduction into test beakers. This will place unnecessary stress on the amphipods and invalidate the test. Use the extra five sets of 10 amphipods that were set aside during the seeding process to

determine the mean initial dry weight of the test organisms. Weigh five numbered foil pans using clean gloves and the analytical balance (to 0.1 mg) and record the information on the dry weight datasheet (Figure 12.5). Transfer the amphipods to a pre-weighed foil pan. Dry the amphipods at 60°C for 24 h (to constant weight). Allow the pans to cool in a desiccator and re-weigh them using the same analytical balance. Mean individual dry weight is obtained by dividing the total amphipod weight by the number of animals weighed for that replicate.

Feeding and Daily Observations

1. Juvenile *Hyalella* are fed every other day during 14-d sediment toxicity tests. On Days 0, 2, 4, 6, 8, 10, and 12, add 0.6 mL of Tetra-Min® slurry and 2 mL of d-YCT/*Selenastrum* to each test jar.

2. Monitor cloudiness of the overlying water. If the water is excessively green or turbid, reduce the amount of algae or Tetra-Min® slurry added. If too much food accumulates, a fungal or bacterial growth may form on the sediment surface; in this case feeding should be suspended for one or more days. A drop in DO concentration to 40% saturation might also indicate that all of the food added to the water is not being consumed. In such a case, suspend feeding for the amount of time necessary to increase the DO concentration to ≥70%. Record all adjustments in feeding.

3. Measure and record temperature, DO, pH, and conductivity in the water quality replicates daily. The DO concentration should be >40% and ≤100% saturation (3.6 - 9.1 mg/L at 20°C; 3.4 -8.6 mg/L at 23°C; 3.3 - 8.3 mg/L at 25°C). Hardness and alkalinity should only be measured on Days 0 and 14. If any measurements fall outside acceptable limits, advise the Laboratory Manager.

4. If the water level drops during the test, new culture water can be added to bring the level back to the 800-mL mark.

5. If growth is being measured, pre-weigh foil pans while the test is in progress. One pan will be required for each test container. Use the analytical balance and clean gloves and weigh to 0.1 mg. Number the pans and record their weights on the "Dry Weight" datasheets. Store the pans in a plastic bag to protect from dust if they will not be used right away.

Test Termination (Day 14)

1. Survival and growth are the most commonly measured endpoints. There is not enough information known about the basic biology of these animals to look at reproduction as an endpoint (Bob Hoke, pers. comm.). It may be difficult to obtain reliable estimates of growth with the small size of amphipods presently used for 14-d sediment toxicity tests. Confirm with the Laboratory Manager whether growth is to be measured before initiating the test.

2. On Day 14, record water quality measurements (including hardness and alkalinity) for each test container.

3. Tear down the negative controls first to determine whether the test was valid. Mean control survival must be ≥80%.

4. Process each replicate individually. Transfer all the amphipods from the test container to a weighboat containing water only. Many of the surviving amphipods can be pipetted from the water column before sieving the sediments. After removing all organisms swimming in the water column, decant two thirds of the water and gently swirl the jar to resuspend the top sediment layer in the remaining volume of water. Pour this slurry through a 300-μm sieve and collect any remaining amphipods. Sieve the remaining sediment through the 300-μm screen and collect remaining amphipods. Record the number of live, dead and missing amphipods on the datasheet (Figure 12.4). If growth is being measured, treat the live amphipods recovered as described in Step 5.

5. Growth (expressed as dry weight) is only measured for organisms surviving the 14-d exposure period. Process each replicate separately. Once all amphipods have been retrieved from a set of test jars, discard any dead organisms. Transfer these amphipods to the pre-weighed foil pans, and record the pan number, sample and replicate identification on the dry weight datasheets (Figure 12.5). Record the number of animals weighed for each replicate. (This should equal the number of survivors unless animals are lost in transfer to the pans.) Use one weighing pan per replicate. Place the pans in a drying oven at 60°C for 24 h to obtain a constant weight. Allow the pans to cool in a desiccator and weigh each pan with its contents. Use the same analytical balance as used to pre-weigh the aluminum pans (to 0.1 mg). Record the total dry weight for each replicate on the dry weight datasheets. Do not weigh individual organisms.

Statistical Analysis

1. A standardized LOTUS spreadsheet has been developed for calculation of total and average individual dry weights for each replicate, as well as mean survival and dry weight for each treatment (Figure 12.6). Copy the spreadsheet template from "H:\TRANSFER\LOTUS.LAB\SEDWT.WK1" to your user or a diskette and then enter the raw data. Use the spreadsheet, rather than hand-calculation, to facilitate QA/QC review of the data. It will be necessary to re-enter the data for further statistical calculations.

2. Requirements for statistical analysis may vary between clients and various regulatory agencies. Before proceeding with analysis, confirm whether statistical comparisons are to be made to a control or a reference sediment. Some agencies only use the control to determine test validity, and use a reference sediment to compare treatment responses. Confirm what statistical analyses are required (e.g., paired comparisons using *t*-tests or multiple comparisons using an analysis of variance [ANOVA]). Data for survival and growth are analyzed separately. If survival was significantly different, growth data for that treatment are not included in statistical analysis. Guidance on the use of software programs for statistical analysis is provided in Section 9.0 of this Manual.

3. If individual comparisons are to be made using t-tests, use the STATISTIX software package. Use one-tailed two-sample t-tests to determine whether the treatment is significantly different from the control ($P<0.05$). Data transformation is not required since t-values are automatically calculated for both equal and unequal variances.

4. If multiple comparisons are to be made, use the TOXSTAT software program. With TOXSTAT, enter survival data as a proportion (e.g., 99% becomes 0.99) and then transformed using an arcsine square-root transformation. Growth data are entered directly and do not normally require transformation. Data are analysed for normality (Shapiro-Wilk's test) and homogeneity of variance (Bartlett's test) prior to detailed statistical analyses. If data pass these tests, an ANOVA and Dunnett's or Bonferroni's t-test are performed, depending on the number of replicates in each treatment. If the data fail tests for normality or homogeneity of variance, either Steel's Many-One Rank test or a Wilcoxon Rank Sum test is performed, depending on replicate numbers.

5. Prepare a summary table showing mean (±SD) survival and growth responses for each test, reference and control sediment. Where statistically significant differences in survival or

growth were identified, indicate that in the table by placing an asterisk after the mean response. The summary table will be included in the final report and forms part of the data package along with the rest of the statistical printouts.

12.1.4 Reference Toxicant Test

A reference toxicant test, or positive control, is tested on a regular basis to monitor the relative health and sensitivity of the *Hyalella*. This is a static, acute 48-h LC50 test performed without sediment. For amphipods obtained from in-house cultures, this test is performed at least once per month. If amphipods were obtained from another source, a reference toxicant test must be performed for each batch of animals, concurrently with the sediment toxicity tests. The standard reference toxicant used is zinc sulphate. Concentrations are expressed as the amount of zinc ion, not the metal salt (zinc sulphate).

1. The test is conducted in 150-mL glass beakers containing 100 mL of dilution/control water and various amounts of zinc stock solution. Sediment is not added. Eight zinc concentrations and one negative control are tested, with one replicate each. As more reference toxicant data are collected, the number of test concentrations may be reduced. A total of 90 juvenile amphipods (10 per treatment) are required. The test is run for 48 h and survival is the only endpoint measured.

2. Test solutions are prepared from a 10 mg/L Zn stock solution. Since this concentration of stock solution is also used for other reference toxicant tests in the laboratory, one 1-L common supply should be made up for general use and stored at 4°C. Do not prepare a fresh stock solution for each test. When a new stock solution is prepared, have the zinc concentration verified by chemical analysis (send to ASL prior to use and when current stock is 75% used). To prevent contamination of the stock solution, always pour the amount needed into a separate container and prepare dilutions from there. (Instructions for preparation of new stock solutions are provided in Section 8.9 of this Manual.)

3. The test solution concentrations used to obtain the 48-h LC50 are: 10, 32, 56, 100, 180, 320, 560 and 1,000 μg/L Zn. The volumes of 10 mg/L Zn stock solution (diluted to 100 mL with dilution/control water) required to obtain these concentrations are: 0.1, 0.32, 0.56, 1.0, 1.8, 3.2, 5.6 and 10.0 mL, respectively. Starting with the lowest concentration, transfer the appropriate amount to a 100-mL graduated cylinder, top this up to 100 mL with

dilution/control water and transfer the solution to the appropriate test beaker. Use an Eppendorf pipettor (0.1 - 1.0 mL capacity) for the smaller volumes. The negative control contains 100 mL of dilution/control water.

4. Measure and record initial water quality (temperature, pH, DO, conductivity) in each test container at 0 h. Randomly transfer ten 7-10 d old juvenile amphipods to each of the nine beakers. Cover the beakers to reduce evaporation. Do not provide aeration or feed the amphipods during the 48-h test.

5. After 24 h, record the survival in each concentration.

6. After 48 h, record water quality and percent survival in each treatment. For the test to be valid, control survival must be ≥90%. If the 48-h LC50 result appears to be outside control limits, send samples of the high, medium and low solutions to ASL to verify test concentrations. For reference toxicant tests, mortality data are used to calculate the 48-h LC50 value. This estimate is determined using the EFFL software program. Compare the 48-h LC50 value to the control limits (mean ± 2SD) and control chart established for *Hyalella* testing in the EVS laboratory. This information is used to assess the relative sensitivity of each batch of test organisms. If the control failed or the LC50 value was outside the control limits, report this to the Laboratory Manager and QA/QC Manager.

7. Add the results of each LC50 test to the control chart and recalculate the mean ± 2SD as more data are obtained.

8. File a copy of the LC50 datasheet and computer printout in the *Hyalella* reference toxicant file and include the originals with the data package for that project.

Table 12.1 Summary of recommended test conditions for *Hyalella azteca* 14-d sediment test.

Test Parameter		Test Condition
1.	Test type	Static, non-renewal
2.	Temperature (°C)	23 or 25 ± 1 °C
3.	Water hardness	80 - 100 mg/L as $CaCO_3$
4.	Light quality	Ambient laboratory light
5.	Light intensity	500 ft candles for culture 50 ft candles for testing
6.	Photoperiod	16:8 h light:darkness
7.	Test vessel size	1-L glass jar
8.	Test material volumes	2-cm layer of sediment; 800 mL of overlying dilution water
9.	Replicates/treatment	5
10.	Test organisms/replicate	10
11.	Size/age of test organisms	approximately 2 mm (7 - 10 d old)
12.	Feeding regime	2 mL of d-YCT/*Selenastrum* and 0.6 mL of Tetra-Min® slurry/ test container on Days 0, 2, 4, 6, 8 and 10
13.	Aeration	Gentle bubbling to maintain DO above 6 mg/L
14.	Dilution water	Moderately hard reconstituted dechlorinated water (80 - 100 mg/L as $CaCO_3$)
15.	Test duration	14 d
16.	Effects measured	Survival and growth
17.	Test acceptability criteria	≥80% mean control survival

EVS CONSULTANTS
SEDIMENT DESCRIPTION AND CHARACTERIZATION

Page ____ of ____

Client: _____ Test Species: _____

EVS Project No.: _____ Test Type/Duration: _____

EVS W.O. No.: _____ Day 0: _____

Sample I.D.	Colour	Grain Size	Smell	Shells/ Debris	Other Observations	Tech. Initial

Be descriptive when you characterize the sediments. Colour and grain size information must be complete. If the sediment has an odour, describe the type of smell. Note any shells or debris that are present. Be sure to record anything else in the Observations section.

Data Certified By: _____ Date Certified: _____

Forms\Lab\Datashts\SEDIMENT.DES

Figure 12.1 Sediment description and characterization datasheet.

Page ____ of ____

EVS CONSULTANTS
SEDIMENT WEIGHT RECORD

Date: _____ Client: _____
EVS Project No.: _____ EVS W.O. No.: _____
Test Type and Species: _____
Balance Model and Serial Number: _____

Sample I.D.	Rep.	Tare Weight (g)	Gross Weight (g)	Final Weight (Gross-Tare)	Technician's Initials

Data Certified By: _____ Date Certified: _____

Forms\Lab\Datashts\SEDIMENT.WT

Figure 12.2 Sample weight record sheet.

EVS CONSULTANTS Page No. _____

14-d FRESHWATER SEDIMENT TOXICITY TEST - DAILY WATER QUALITY MONITORING

Water Quality Instruments Used

D.O. Meter _____
pH Meter _____
Conductivity _____
Temperature _____

Client: _____
EVS Project No.: _____
EVS W.O. No.: _____
Day 0: _____
Day 14: _____
Test Species: _____
Source/Collection Date: _____

Sample I.D.	Temperature (°C)															Dissolved Oxygen (mg/L)													
	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Technician's Initials																														

Comments/Adjustments Made: _____

Data Certified By: _____ Date Certified: _____

Forms\Lab\Datasht\SEDWQFW.10d (P.1)

Figure 12.3 Daily water quality monitoring datasheet.

EVS CONSULTANTS Page No. _____

14-d FRESHWATER SEDIMENT TOXICITY TEST - DAILY WATER QUALITY MONITORING

Water Quality Instruments Used

D.O. Meter _____
pH Meter _____
Conductivity _____
Temperature _____

Client: _____
EVS Project No.: _____
EVS W.O. No.: _____
Day 0: _____
Day 14: _____
Test Species: _____
Source/Collection Date: _____

Sample I.D.	Conductivity (µmhos/cm)															pH														
	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Technician's Initials																														

Comments/Adjustments Made: _____

Data Certified By: _____ Date Certified: _____

Forms\Lab\Datasht\SEDWQFW.10d (P.2)

Figure 12.3 continued.

Page No. ___

EVS CONSULTANTS
SEDIMENT TOXICITY TESTS - SURVIVAL AND FINAL WATER QUALITY DATA

Client: _____
EVS Project Number: _____
EVS W.O. No.: _____

Test Type: _____
Test Species: _____
Start Date (Day 0): _____
End Date: _____

Sample I.D.	Rep.	Pan No.	No. Alive	No. Dead	Total Recovered	No. Missing	Tech. Init.		D.O. (mg/L)	Temp. (°C)	pH	Cond. (µmhos/cm) ☐ Salinity (ppt) ☐
						Technician's Initials						

W.Q. Instruments Used: Temperature _____ pH _____ DO _____ Cond./Sal. _____
Data Certified By: _____ Date Certified: _____

Forms\Lab\Datasht\SURVIVAL.SED

Figure 12.4 Survival and final water quality datasheet.

Page No. _____

EVS CONSULTANTS
SEDIMENT TOXICITY TESTS - DRY WEIGHT DATA

ient : _____ Test Type : _____

/S Project Number : _____ Test Species : _____

/S W.O. Number: _____ Start Date (Day 0): _____

ılance Type/Serial Number: _____

Sample I.D.	Rep.	Pan No.	Pan Weight (g)	Final Weight (g) (pan + biomass)	Number of Survivors	Number Weighed	Comments	Tech'n Initials

ata Certified By: _____ Date Certified: _____

ms\Lab\Datashts\SEDDRY.WT

Figure 12.5 Dry weight datasheet.

EVS CONSULTANTS

Sediment Toxicity Test -- Dry Weight Data

Client: _____ Test Species: _____
Project #: _____ Date Initiated: _____
Work Order: _____ Date Terminated: _____
Test Type: _____ Number of Animals/rep: _____

Sample ID	Rep	# of Survivors	# of Animals Weighed	Pan Weight (g)	Final Weight (pan + animals) (g)	Total Animal Dry Weight (mg)	Average Individual Dry Weight by Replicate (mg)	Mean Survival (%)	Mean Individual Dry Weight[1] (mg)
Initial Weights (Day 0)	A	NA						NA	0.00
	B	NA							
	C	NA							
	D	NA							
	E	NA							
Control Sediment	A							ERR	0.00
	B								
	C								
	D								
	E								
Sample A	A							ERR	0.00
	B								
	C								
	D								
	B								
Sample B	A							ERR	0.00
	B								
	C								
	D								
	E								

[1] Mean of the average individual dry weight by replicate for each treatment.

Figure 12.6 Sample Lotus spreadsheet for test data.

12.2 *Chironomus tentans* 14-d Sediment Toxicity Test

12.2.1 Background Information

The procedure described below is a modification of EVS SOP 1074-1, which is a 10-d sediment toxicity test. The modification is a change from a 10-d to a 14-d test.

This static, acute toxicity test can be used to determine the relative toxicity of freshwater sediments using larvae of the midge, *Chironomus tentans*. This test is not appropriate for marine sediments. The larvae are exposed to whole sediments in 1-L jars for a 14-d period to determine effects on survival and growth. The response of chironomid larvae to test sediments is compared with the response of chironomids exposed to clean control sediment or a reference sediment.

Read the entire SOP before beginning any tasks relating to this test. This SOP is organized into separate sections describing preparation activities, instructions for obtaining and culturing test organisms, testing the sample(s) and running regular reference toxicant tests. The procedures described are for routine sample testing only and describe tests as they are currently conducted. Other options (e.g., use of flow-through systems) may be valid if in accordance with reference protocols and approved by the Laboratory Manager. If additional controls or different types of samples are to be tested, the Laboratory Manager may also specify other modifications to this SOP.

Reference Literature

ASTM (American Society for Testing and Materials). 1994. Standard guide for conducting sediment toxicity tests with freshwater invertebrates. Method E1383-94. In: 1994 Annual Book of ASTM Standards, Volume 11.04. American Society for Testing and Materials, Philadelphia, PA.

Equipment

Culture Maintenance

- constant environment room: 23 or 25 ± 1 °C; 16:8 h L:D photoperiod
- aeration supply, airlines, pasteur pipettes, airstones
- thermometer, pH, DO and SCT meters
- clean, fine silica sand (#30)
- 13-L glass aquaria, with fitted mesh covers
- 4-L glass jars for hatching egg masses
- "bug sucker"
- reconstituted "moderately hard" water, prepared from dechlorinated water
- 20-L carboys for water storage

- sieves and sorting trays
- squirt bottle of culture water
- inverted pasteur pipettes, with bulbs
- Tetra-Min® flake fish food
- blender
- top-loading balance, weighboats and scoops
- d-YCT/*Selenastrum*, prepared in 1:1 ratio (*Ceriodaphnia* diet)

Test Equipment

- 2nd instar chironomid larvae (approximately 14-d post-hatch)
- constant environment room: 23 or 25 ± 1°C; 16:8 h L:D photoperiod
- aeration supply, air lines, pasteur pipettes, airstones
- thermometer, pH, DO and SCT meters
- clean 1-L glass jars, w/lids with airline holes - 5 for control, 5 for each test sediment
- 10% nitric acid
- acetone
- reconstituted "moderately hard" water, prepared from dechlorinated water (5 L per sediment)
- Pyrex trays and artist's paint brush for sorting sediments
- scoops for measuring sediments
- balances: top-loading and analytical
- sieves, sieving tubs
- small weighboats (1 per test jar, plus extras)
- squirt bottle of culture water
- inverted pasteur pipettes, with bulbs
- light source (e.g., light table)
- Tetra-Min® flake fish food
- d-YCT/*Selenastrum*, prepared in 1:1 ratio (*Ceriodaphnia* diet)
- numbered, pre-weighed foil pans (for dry weights)
- drying oven @ 60°C (for dry weights) and desiccator

Reference Toxicant Equipment

- 20 g/L KCl stock solution
- 100-mL graduated cylinder
- 30-mL plastic vials, 10 per concentration (60 in total)
- 6 - 150-mL glass beakers
- Eppendorf pipettors (0.1 - 1 mL, 1 - 10 mL capacity)
- weighboats
- inverted pasteur pipettes, with bulbs

Sample Details

Sample required:	A minimum of 2 L of test sediment should be collected (approximately 1 L is used for testing).
Sample storage:	Collect sediments in new, precleaned glass jars with teflon-lined lids (e.g., I-Chem® jars). Fill the jars completely to exclude any air. Store the samples at 4°C in the dark until used for testing. The maximum holding time is 14 d from sediment collection. Store unused sample at 4°C until the test is completed and the client has received the report.

Time Requirements

Culture maintenance:	3 h/week
Glassware preparation:	1 h/test sediment
Sediment preparation (Day -1):	1.5 h/test sediment
Test initiation (Day 0):	1 h/test sediment
Daily monitoring for 14 d:	0.25 h/d/test sediment
Test termination:	1.5 h/test sediment
Reference toxicant test:	3-4 h
Data analysis, report preparation:	3 h

12.2.2 Culturing Test Organisms

Test organisms are obtained from an in-house culture which has been maintained on a continuous basis in the EVS laboratory since April 1990. The original source of this culture was the U.S. EPA laboratory in Duluth, MN. The in-house culture consists of one or more main culture tanks containing chironomid populations of mixed age, and larval rearing tanks containing chironomid larvae of a specific age. The larval rearing tanks are only needed when test organisms are needed for toxicity tests. The EVS culture should be the source of all larvae used for tests. External sources should only be used to start new cultures if the existing ones crash or appear unhealthy. Detailed instructions for culture maintenance, including food preparation, and for obtaining organisms for use in tests are described in this section of the SOP.

Chironomus tentans (Fabricius) is a non-biting midge, whose larvae are common in eutrophic ponds, lakes, and sloughs. The larvae are benthic filter feeders and will eat almost any organic material of appropriate size. In addition, they are an important food source for many fish and waterfowl species. The larvae are most frequently found in fine sediment and detritus, but can inhabit sediments with

a mean particle size ≤2 mm. Chironomid larvae usually penetrate a few centimetres into the sediment. Here they pupate and later emerge from the water as adults. Adults usually breed within 24 h of emergence and die soon after. Females extrude a gelatinous strand of eggs into the water, but are not selective with respect to oviposition site. Larvae will hatch and move into the sediment within 2 - 3 d of egg mass deposition, go through four instar stages (each approximately one week long), pupate, and emerge as adults in 24-28 d at 20°C.

C. tentans has been used frequently and successfully in freshwater sediment toxicity tests because it is a fairly large midge with a short generation time, is easily cultured in the laboratory, and the larvae have direct contact with the sediment where they burrow to build cases. It has been shown to be sensitive to many contaminants associated with sediments. Its response to test sediments provide information concerning the bioavailability of contaminants associated with the sediment to benthic, burrowing organisms.

Starter Cultures

Chironomid cultures are started from egg masses, which can be obtained from several sources, such as other private laboratories, government laboratories, universities and commercial suppliers. Each egg mass should provide about 200 organisms, so only a small number are needed to start a culture. Chironomid egg masses may be obtained from the following sources:

Bob Hoke	Jeff Denny or Kurt Meed	Stan Stinitski
AScI Corporation	U.S. EPA	Aquatic Research Organisms (ARO)
Duluth, MN	Duluth, MN	Hampton, NH 03842
(218) 720-5618	(218) 720-5518	(603) 926-1650

Bob, Jeff or Kurt may occasionally be able to supply a small number of egg masses at no cost. Stan Stinitski (ARO) charges $75.00 US per egg mass (approximately 200 organisms). Regardless of the source, expect to have to wait at least two weeks before any order for egg masses can be met.

Upon arrival, egg masses must be acclimated to EVS culture conditions (specifically, water and temperature). Gradually change the water in which the egg masses were transported to 100% EVS culture water over a period of 8 h. Change the water temperature to the desired temperature no faster than 2°C in a 4-h period. Acclimation may occur directly in the culture tank if eggs are shipped in a small volume of water (i.e., 100-200 mL). Measure the dissolved oxygen concentration; it should be near 100% saturation (about 8-9 mg/L). After acclimation, very carefully decant egg masses under water directly onto the sand substrate of the culture tank. Instructions for handling the egg masses and culturing the larvae are described under "Obtaining Test Organisms".

If testing-size larvae are required, they may be obtained as a last resort from the following source (minimum of one week's notice required):

Ryan Warbritton
ABC Labs
Columbia, MO 65202
(314) 474-8579

Ryan can supply larvae if available at approximately $150.00 per 1,000 larvae (plus shipping costs).

Glassware Cleaning

Glassware used for culture maintenance should be kept separate from that which is used for testing and for general laboratory use. All glassware and plasticware used for culture and testing must be cleaned prior to use. Wash all glassware with non-phosphate detergent, rinse twice with dechlorinated water, allow to dry and then check for cleanliness. Rinse glassware once with 10% nitric acid, twice with distilled or deionized water, once with full-strength acetone, and then five times with deionized water (if there is a shortage of deionized water, then use distilled water for all but the last two rinses). New plasticware must be soaked in dilution water at least overnight before its first use; after that, normal washing procedures are followed.

Dilution/Control Water

"Moderately hard" reconstituted water (80 - 100 mg/L as $CaCO_3$) is used for culturing *Chironomus* and for dilution and control water during testing. Throughout this SOP, "dilution/control" water or "culture" water refers to this type of reconstituted water. Prepare the water at least one day before use and discard it if not used within two to three weeks. Since the same water is used for *Hyalella azteca* culture and testing, the same storage container(s) can be used. Instructions for preparing reconstituted water are provided in Section 8.1 of this Manual; dechlorinated water is used as the dilution medium. Make sure the chemicals are fully dissolved in a small volume of dechlorinated water before adding them to the larger volume. Do not rely on aeration to dissolve the chemicals. Place an airstone in the carboy and make sure it is aerating vigorously. Cover the container and aerate it for 24 - 48 h before use. Before using the reconstituted water, measure and record the temperature, DO, pH, conductivity, hardness and alkalinity to make sure they are within acceptable limits (see Section 8.1). The dilution/control water DO should be 90 - 100% saturation.

Culture Sediment

Chironomid larvae require the presence of a substrate. If they are allowed to migrate out of the mucous sheath of the egg mass without a substrate, they become attached to the tank glass and are difficult to dislodge; cannibalism also becomes a problem. Fine silica sand is used as the substrate for culture tanks and as control sediment for toxicity tests. Sand can be obtained from a hardware store (sandblasting sand) or from a pet store (canary sand). An 80-lb sack of #30 silica sand can be purchased from:

Ocean Construction Supply Ltd., Masonry Division
1280 W. 77th Avenue
Vancouver, B.C.
Tel: 261-2211

Always rinse the sand several times before use, first with dechlorinated tap water and finally with culture water.

Preparation of Culture Tanks

The EVS culture usually consists of one or two main culture tanks, containing a chironomid population of mixed age, plus additional culture tanks containing larvae of known age being reared for use in toxicity tests. Culture tanks need to be prepared one day before their intended use. Place a 1- to 2-cm layer of pre-rinsed fine silica sand in a 38-L aquarium and add enough culture water (about 7 - 8 L) to provide an 8 - 10-cm layer of water over the substrate. The volume and depth of substrate is critical; too much makes it very difficult and time-consuming to find the larvae, and with too little, the animals are exposed to cannibalism.

Aerate the tank gently with an airstone or glass pipette. Cover the tank with a fitted mesh cover and leave it undisturbed for 24 h before introducing any egg masses. Check that the pH, hardness and DO of the culture water are within acceptable ranges before adding egg masses. (Other researchers have used ground paper towel as a substrate, however this is more time consuming to prepare and can be toxic to the cultures if not done properly or with the wrong type of paper towel.)

Feeding

Chironomus cultures should be fed three times per week (i.e., Monday, Wednesday, Friday) with a combination of two foods:

1. the same d-YCT/*Selenastrum* diet used for feeding in-house *Ceriodaphnia* cultures,

2. a prepared slurry of Tetra-Min® flake fish food.

Instructions for preparing the d-YCT/*Selenastrum* food are provided in the *Ceriodaphnia* SOP (Section 14.2, Water). Use a 1:1 ratio of d-YCT and *Selenastrum*. If d-YCT is not available, YCT can be substituted.

To prepare the Tetra-Min® fish food slurry, weigh 20 g of Tetra-Min® flake fish food and add it to 200 mL of culture water in a blender. Blend the mixture for at least 3 min, then pour into a 250-mL Erlenmeyer flask. Stopper the flask, label it with the preparation date and keep it in the 4°C room. The food should last for a few weeks; monitor odour for signs of fouling and discard if this occurs. Always swirl the contents of the flask before using to resuspend the food particles. This Tetra-Min® slurry is also used for the *Hyalella azteca* culture, so the same batch of prepared food can be shared.

Mix the slurry well to resuspend the food particles and add 40 mL to each active 38-L *Chironomus* culture tank. Overfeeding can lead to the growth of fungus in the aquaria and will necessitate more frequent water changes. If too little food is added, larvae will be observed on the sediment surface searching for food. Normally, the larvae should not be seen outside their burrows.

Feeding of the chironomid cultures should begin the day that larvae are observed to hatch (Day 1), which is usually 1-3 d after addition of the egg masses. The following is a proposed feeding schedule for a 38-L aquarium:

Day 1	10 mL Tetra-Min® slurry + 40 mL d-YCT/*Selenastrum*
Day 3	10 mL Tetra-Min® slurry
Day 5	10 mL Tetra-Min® slurry + 40 mL d-YCT/*Selenastrum*
Day 7	10 mL Tetra-Min® slurry
Day 9	10 mL Tetra-Min® slurry + 40 mL d-YCT/*Selenastrum*
Day 11	10 mL Tetra-Min® slurry
Day 13	10 mL Tetra-Min® slurry + 40 mL d-YCT/*Selenastrum*
Day 15	10 mL Tetra-Min® slurry
Day 17	etc.

If smaller aquaria (i.e., 20-L) are used for cultures, a proportionally smaller amount of food is required. Feeding should still follow the above schedule, but only 6 mL of Tetra-Min® slurry and 20 mL of d-YCT/*Selenastrum* are needed.

Monitor colour and cloudiness of the water. The chironomids seem to do best when the water is light green and slightly turbid (i.e., lots of food present). If water is excessively turbid or very green or smells foul on a scheduled feeding day, reduce the amount fed or postpone feeding until following day. Conversely, if larvae are visible in large numbers on the sediment surface between feedings, then the amount fed should be increased. Always record the date and amount fed in the *Chironomus* culture logbook.

Culture Maintenance

Chironomid cultures should be maintained at 23 or 25 ± 1 °C under a 16:8 h light:dark photoperiod. Culture tanks require little regular maintenance. Partial replacement of the culture water in the main culture tank(s) may be required periodically. It should not be necessary to change culture water in the larval rearing tanks over the 2-wk period that larvae are being reared for toxicity tests. If it becomes necessary to do so because of fouling, carefully siphon off the water to avoid disturbing sediments and chironomids (do not pour off water). Add new water very carefully to prevent re-suspension of sediments.

If no tests are scheduled and adults are not being collected to obtain egg masses, the culture density should be controlled by periodically removing emerging adults from the tanks before they can deposit egg masses. Adults not needed for egg mass production should be removed from the culture tank(s) and sacrificed. An anoxic gas (e.g., carbon dioxide or nitrogen) should be blown into the aspirating flask for approximately 1 min to immobilize the adults. Immobilized adults are then wrapped in a paper towel, squashed, and discarded.

It is very important to keep the fitted mesh covers in place on the culture tanks so that adult chironomids cannot escape. When removing adults with the aspirating flask, just lift the cover up enough to insert the aspirating tube and try to capture the adults as quickly as possible.

When a culture tank has been depleted of larvae, the sand should be sieved through a 710-μm screen to remove the larger organic matter, then thoroughly rinsed with dechlorinated tap water and autoclaved for 1 h. The sand can either be dried for storage (storing wet sand will result in a bacterial buildup) or reused to start new culture tanks.

Obtaining Test Organisms

Toxicity tests must be started with larvae of the same age and size (second instar, preferably 14-d post-hatch). Test organisms should not be taken directly from the main culture tank. New cultures need to be started with freshly collected egg masses so that larvae can be reared to a specific age and

size. A minimum of two weeks' notice is required to collect egg masses and rear the larvae to the correct age. Most larvae will remain as second instars through the 16th day (approximately 14-d old larvae). Larvae that are ≥16-d old should not be used for 14-d sediment toxicity tests because they may start to pupate or metamorphose to adults. Whenever possible, use larvae that are 14-d post-hatch. Because of the effort involved and the relatively narrow range when larvae are an acceptable age for testing, it is very important to confirm proposed sample collection and test initiation dates with the Project Manager.

A 14-d sediment toxicity test requires 50 chironomid larvae (5 replicates of 10 animals) for each test sediment, plus an additional 50 larvae for the negative (clean) control. The reference toxicant test requires 60 test organisms. There should be a minimum 30% surplus of animals of the appropriate age and size available for test initiation. Before beginning a toxicity test, confirm that there are enough animals of acceptable size and quality available.

To obtain new egg masses, carefully transfer 10 to 15 newly emerged adult chironomids to a 4-L glass jar containing approximately 2 to 3 cm (about 350 mL) of culture water in which two regular sugar cubes have been dissolved. Although adult chironomids do not normally feed, they will consume liquid carbohydrates. The consumption of energy-rich sugars presumably maximizes the potential for the successful completion of egg production.

Transfer of adults is best accomplished using a dry aspirating flask (a 1-L Erlenmeyer flask equipped with two suction tubes; one attached to the side-arm of the flask, the other inserted through a hole in the rubber stopper). By inhaling with short, sharp breaths through the tube attached to the side-arm, adult chironomids can be drawn into the flask through the other tube. This second tube must be held very close to the adult midge to work. The internal diameter of the tube should be approximately 1 cm to avoid injuring the adults.

The sex ratio of collected adults should be approximately 2:3 or 3:4 females to males, although ratios of approximately 1:2 or 1:3 females to males will also work. There should be more males than females if possible. Males can be distinguished by their plumose antennae while females have a much darker abdomen. In new cultures, males will begin to hatch approximately one week before females. About 10 - 15 adults/jar are needed to obtain 2 - 3 egg cases.

Once the adults have been transferred to the glass jar, cover the opening with fine-meshed screen to allow air in, but confine the adults. Feeding is not necessary. Egg masses should appear in 1 - 3 d. If none have been deposited by Day 4, discard all the adults as they must be assumed to be unhealthy. Also, discard remaining live adults and unused egg masses.

Once egg masses are seen, immediately transfer them to a newly prepared culture tank for rearing (only 1-2 egg masses/tank). Monitor the egg masses carefully over the next few days. Note the day when hatching begins (Day 1); this should occur approximately 2 - 3 d after introduction of the egg masses. Under a dissecting microscope, larvae will be visible and can be seen feeding on the mucous sheath of the egg case. The larvae will appear transparent and should be moving around slightly. As soon as hatching begins, start the feeding schedule described previously.

Chironomid larvae should be handled as little as possible. When handling is necessary, it should be done as gently and quickly as possible so that the midges are not unnecessarily stressed. Larvae should be carefully transferred with a wide-bore (7-mm ID) glass pipette or a fine artist's paint brush. Coax individual larvae out of their sand cases with a soft, fine-point artist's paint brush; gently tapping one end of the sand case with the paint brush usually provides sufficient coaxing. Midges should be introduced into solution beneath the water surface. Any midges that touch dry surfaces, are dropped, or injured during handling should be discarded.

After all larvae needed for a test have been collected and the test initiated, remaining larvae can be left in the culture tank and allowed to continue development, thereby serving as a potential source of adults and new egg masses for future tests.

12.2.3 Test Procedure

Experimental Design

Tests should be initiated (i.e., Day -1 sediment preparation) on a Monday or a Thursday to avoid having to begin or complete a test on the weekend.

Chironomid larvae are exposed to sediments in 1-L jars for 14 d. There are five replicates for each treatment, each containing 10 second instar larvae. This test involves preparing the sediments and overlying water one day and allowing them to equilibrate overnight. The following day (Day 0), the chironomids are counted and distributed to the test containers. Test conditions are monitored throughout the 14-d exposure period. On Day 14, chironomids are sieved from the sediments to determine mean survival. Growth (expressed as dry weight) is also measured for surviving chironomids. A static 96-h LC50 test with the standard reference toxicant, potassium chloride, is performed once a month for in-house cultures, and on each batch of chironomids purchased from other sources. Test conditions are summarized in Table 12.2.

Glassware Cleaning

All glassware and plasticware used to perform the toxicity tests must be cleaned prior to use following the cleaning procedures given in Section 12.2.2.

Dilution/Control Water and Control Sediment

The water which is added to each test container as overlying water, and used as dilution water for the reference toxicant test, is reconstituted "moderately hard" water (80 - 100 mg/L as $CaCO_3$), the same water used for *Chironomus* culture. Follow the instructions in Section 12.2.2 for preparing this type of water. Always prepare enough water so that all tests can be set up using the same batch of dilution water.
For each series of sediment toxicity tests, there must be a negative (clean) control which consists of clean sediment and dilution/control water. The control sediment is clean silica sand, from the same source used for the *Chironomus* stock cultures. Rinse the sand thoroughly, first with dechlorinated water and then with culture water, before use and do not re-use control sediment.

Sediment Preparation (Day -1)

1. Ensure that all equipment is working correctly and that supplies are available; do this well before the test initiation date. Prepare five 1-L jars for each sediment and the control and all glassware for the reference toxicant test. Label test containers with sample name and replicate.

2. Transfer the sediment from the container in which it was shipped to a large glass sorting pan. If the sediments were collected properly, any water on the sediment surface should just be interstitial water which has appeared because of settling during storage. This water should be mixed back into the sediments. Visually inspect the sediment and record observations of colour, grain size, odour, etc. on the sediment description datasheet (Figure 12.1). The sediment is put into a large glass sorting tray and hand-picked to remove rocks and large organic debris. If the average particle size is >3 mm then this test will not work as well since chironomids need to be able to burrow into the sediment to build cases. At this time, carefully inspect the sediment for the presence of native chironomids or other large organisms. If chironomids are present, remove these from the sample.

3. After removing any large particles and indigenous organisms, homogenize the sediment in the glass tray by thorough hand mixing. Afterwards, carefully transfer homogenized wet sediment directly into each 1-L jar. Add enough test sediment to each jar to make a 2-cm

deep layer. For replicates, the weight of sediment necessary to make a 2-cm layer (about 175 mL) in the first jar is added to the other replicates. **Do this in a well-ventilated area.** (Some samples may require preparation in the fume hood; if the balance won't work in the fume hood, the 2-cm layer must be determined visually for each replicate.) The same procedure applies to the negative control. Record weight of sediment in each replicate on sample weight record sheet (Figure 12.2).

4. Make sure there is no sediment left around the rims of the test jars. It is also important that the sediment is relatively evenly distributed over the entire bottom surface of the jar.

5. Return unused sediment to its storage container, check the lid is tightly sealed, and return it to 4°C storage. Using a clean scoop, repeat this process for each test sediment.

6. Add approximately 800 mL of dilution/control water to each test container. Fill the jars to halfway up the "shoulder" of the jar, with all of them at the same level. Take care not to disturb the sediments when adding the water.

7. Cover each jar with a plastic lid that has an airline hole in the centre. Do not tighten the lids; they are opened frequently for water quality measurements. Place the jars in the constant environment chamber. Allow the sediment and water to equilibrate overnight before starting the test.

8. Gently aerate the water in each test jar. Set up an airline to each jar with gentle aeration (1-2 bubbles/sec) through a Pasteur pipette, so that the sediment is not disturbed. Aeration systems require a lot of adjustment to get an even, gentle flow of air to all containers.

Test Initiation (Day 0)

1. Prepare datasheets for recording water quality (Figure 12.3), survival (Figure 12.4) and dry weight data (Figure 12.5). Randomly select two of the five replicates from each treatment for monitoring water quality. Measure and record temperature, DO, pH, and conductivity in these containers. The DO concentration should be >40% and ≤100% saturation (3.3 - 8.3 mg/L at 25°C). Hardness and alkalinity should only be measured in composite samples collected on Days 0 and 10.

2. Following water quality measurements, the chironomid larvae are added to the test containers. Since there are 5 replicates per treatment, 50 second instar larvae are needed per treatment. All animals used in a test must be from the same source and be approximately the

same size and age. Do not use organisms which are obviously different in size. To ensure that chironomids are randomly added to the various test jars, first collect them all in a large crystallizing dish. Screen the larvae for consistency in size and set aside any which are too small or too large. Set out one weighboat per test container plus several extra ones, and place a small amount of culture water in each one. Randomly transfer 10 chironomid larvae to each weighboat. Larvae must first be coaxed out of their sand cases using a soft, fine-point artist's paint brush. Use an inverted Pasteur pipette to transfer the larvae and always release them below the water surface. Discard any larvae that are injured, dropped or touch dry surfaces. Transfer the larvae individually, making sure that all weighboats get one chironomid before getting the second, third, etc. Keep the chironomids at the test temperature during the sorting and seeding process.

3. Confirm that each weighboat contains exactly 10 chironomids (preferably have a second person check the counts) and that they are appear healthy. Randomly select groups of five weighboats for each of the test or control sediments and set them aside. Also set aside an additional five weighboats of chironomids for initial dry weight measurements. Gently pour the contents of one weighboat to one test container. A squirt bottle of culture water may be used to facilitate this. Check that no larvae remain on the weighboat. Gently resubmerge any which become trapped at the air-water interface. To ensure that each jar is seeded only once, clip a plastic clothespin to the aeration line as you seed each jar, and check them when you finish. Test jars should be inspected within 2 h of seeding. Any chironomids which continue to remain at the air-water interface at that time should be removed and replaced.

4. For large setups, test containers should be seeded in batches (i.e., several sediments at a time or all of one replicate at a time). To avoid seriously stressing the organisms, ensure that the chironomids are not held without sediment for more than 4 h. Furthermore, ensure that the ambient temperature is similar to the test temperature (e.g., sort organisms directly in the environmental chamber where the test will be conducted). If the ambient temperature is substantially different from the test temperature, then the water temperature in the sorting pan and holding container(s) could easily change, thereby stressing the larvae. Frequent replacement of this water can minimize this stress.

5. For determination of the growth response, do not weigh individual test animals prior to introduction into test beakers. This will place unnecessary stress on the chironomids and invalidate the test. Use the extra five sets of 10 chironomids that were set aside during the seeding process to determine the mean initial dry weight of the test organisms. Weigh five numbered foil pans using clean gloves and the analytical balance (to 0.1 mg) and record the information on the "Dry Weight" datasheet. Use an artist's paint brush to transfer the

chironomids to a pre-weighed foil pan. Dry the chironomids at 60°C for 24 h (to constant weight). Allow the pans to cool in a desiccator and re-weigh them using the same analytical balance. Mean individual dry weight is obtained by dividing the total chironomid weight for that replicate by the number of larvae weighed for that replicate.

Feeding and Daily Observations

1. Chironomid larvae are fed every other day during 14-d sediment toxicity tests. On Days 0, 2, 6, and 10, add 0.6 mL of Tetra-Min® slurry and 1.5 mL of d-YCT/*Selenastrum* to each test jar. On Days 4, 8, and 12, just add 0.6 mL of Tetra-Min® slurry to each test jar. Do not feed the chironomids on Day 14.

2. Monitor cloudiness of the overlying water. If the water is excessively green or turbid, reduce the amount of d-YCT/*Selenastrum* or Tetra-Min® slurry added. If too much food accumulates, a fungal or bacterial growth may form on the sediment surface; in this case feeding should be suspended for one or more days. A drop in DO concentration to 40% saturation might also indicate that all of the food added to the water is not being consumed. In such a case, suspend feeding for the amount of time necessary to increase the DO concentration to ≥70%. Record all adjustments in feeding.

   The amount of food provided is slightly more than what has been used by other researchers, but this is necessary when using silica sand as the control sediment as the sand contains no organic matter which can serve as a food source for the chironomids. Also, although ASTM (1994) does not mention the use of algae as a supplementary food source, results obtained in the EVS laboratory suggest that the use of algae is the main reason for good culture health.

3. Measure and record temperature, DO, pH, and conductivity in the water quality replicates daily. The DO concentration should be >40% and ≤100% saturation (3.3 - 8.3 mg/L at 25°C). Hardness and alkalinity should only be measured on Days 0 and 14. If any measurements fall outside acceptable limits, advise the Laboratory Manager.

4. If the water level drops during the test, new culture water can be added to bring the level back to the 800-mL mark.

5. For growth measurement, pre-weigh foil pans while the test is in progress. One pan will be required for each test container. Use the analytical balance and weigh to 0.1 mg. Number the pans and record their weights on the dry weight datasheets (Figure 12.5). Store the pans in a plastic bag to protect from dust if they will not be used right away.

Test Termination (Day 14)

1. Survival and growth (dry weight) are the most commonly measured endpoints. Larval length and adult emergence have also been used by other researchers.

2. On Day 14, record water quality measurements (including hardness and alkalinity) for each test container.

3. Tear down the negative controls first to determine whether the test was valid. Mean control survival must be ≥70%. In general, control survival should be >85% and responses below that indicate that the test organisms may have been stressed or unhealthy.

4. Process each replicate individually. Carefully collect all the chironomids from a test container either by pouring the entire contents of the jar through a 500- to 700-μm screen (for fine-grained sediments) or by pouring the contents into a glass sorting pan and carefully removing the chironomids with an artist's paint brush and a glass pipette (for sandy sediments). Carefully transfer all the live chironomids from one replicate to a weighboat containing culture water only. Record the number of live, dead and missing chironomids on the datasheet. Occasionally larvae will have begun to pupate or even emerge as adults; this should also be recorded on the datasheets (Figure 12.4). Only the surviving chironomid larvae are used for growth measurements.

5. Growth (expressed as dry weight) is only measured for larvae that survived the 14-d exposure period. If an organism survived the sediment exposure but was accidentally killed during test termination, it should still be included in the dry weight measurement. Chironomids that have pupated should be counted as survivors but not included in dry weight measurements.

   Process each replicate separately. Once all the surviving chironomid larvae have been retrieved from a set of test jars, use an artist's paint brush to transfer the larvae to the pre-weighed foil pans, and record the pan number, sample and replicate identification on the dry weight datasheets. Record the number of animals weighed for each replicate. (This should equal the number of survivors unless animals had pupated or were lost in transfer to the pans.) Use one weighing pan per replicate. Place the pans in a drying oven at 60°C for 24 h to obtain a constant weight. Allow the pans to cool in a desiccator and weigh each pan with its contents. Use the same analytical balance as used to pre-weigh the aluminum pans (to

0.1 mg). Record the total dry weight for each replicate on the dry weight datasheets. Do not weigh individual organisms. (**NOTE**: average Day 0 dry weights should be approximately 0.3-0.4 mg and average Day 14 dry weights approximately 2-3 mg).

Statistical Analysis

1. A standardized LOTUS spreadsheet has been developed for calculation of total and average individual dry weights for each replicate, as well as mean survival and dry weight for each treatment (Figure 12.6). Copy the spreadsheet template from "H:\TRANSFER\LOTUS.LAB\SEDWT.WK1" to your user or a diskette and then enter the raw data. Use the spreadsheet, rather than hand-calculation, to facilitate QA/QC review of the data. It will be necessary to re-enter the data for further statistical calculations.

2. Requirements for statistical analysis may vary between clients and various regulatory agencies. Before proceeding with analysis, confirm whether statistical comparisons are to be made to a control or a reference sediment. Some agencies only use the control to determine test validity, and use a reference sediment to compare treatment responses. Confirm what statistical analyses are required [e.g., paired comparisons using *t*-tests or multiple comparisons using an analysis of variance (ANOVA)]. Data for survival and growth are analysed separately. If survival was significantly different, growth data for that treatment are not included in statistical analyses. Guidance on the use of software programs for statistical analysis is provided in Section 9.0 of this Manual.

3. If individual comparisons are to be made using t-tests, use the STATISTIX software package. Use one-tailed two-sample t-tests to determine whether the treatment is significantly different from the control ($P<0.05$). Data transformation is not required since t-values are automatically calculated for both equal and unequal variances.

4. If multiple comparisons are to be made, use the TOXSTAT software program. With TOXSTAT, enter survival data as a proportion (e.g., 99% becomes 0.99) and then transformed using an arcsine square-root transformation. Growth data are entered directly and do not normally require transformation. Data are analysed for normality (Shapiro-Wilk's test) and homogeneity of variance (Bartlett's test) prior to detailed statistical analyses. If data pass these tests, an ANOVA and Dunnett's or Bonferroni's t-test are performed, depending on the number of replicates in each treatment. If the data fail tests for normality or homogeneity of variance, either Steel's Many-One Rank test or a Wilcoxon Rank Sum test is performed, depending on replicate numbers.

5. Prepare a summary table showing mean (±SD) survival and growth responses for each test, reference and control sediment. Where statistically significant differences in survival or growth were identified, indicate that in the table by placing an asterisk after the mean response. The summary table will be included in the final report and forms part of the data package along with the rest of the statistical printouts.

12.2.4 Reference Toxicant Test

A reference toxicant test, or positive control, is tested on a regular basis to monitor the relative health and sensitivity of the chironomid culture. This is a static, acute 96-h LC50 test. For chironomids obtained from in-house cultures, this test is performed at least once per month using second instar larvae obtained in the same manner as for sediment toxicity tests. The standard reference toxicant used is potassium chloride. Concentrations are expressed in terms of the amount of potassium chloride (KCl).

1. The test is conducted in 50-mL plastic vials containing approximately 25 mL of test solution (either dilution/control water or various dilutions of potassium chloride stock solution) and a very thin (2-mm) layer of control sediment. Five concentrations and one negative control are tested, with ten replicates each. A total of 60 chironomid larvae (1 per vial, 10 per concentration) are required. The test is run for 96 h and survival is the only endpoint measured. Water quality is measured in six 150-mL beakers containing the five test concentrations and a negative control. A 2-mm layer of sediment is also added to these beakers for consistency.

2. The test solution concentrations used to obtain the 96-h LC50 are: 1.25, 2.5, 5, 10, and 20 g/L KCl. To prepare the highest concentration, weigh 20.00 g KCl and add this to 1 L of dilution water in a 1-L volumetric flask. Dispense 25 mL of this solution to each of the appropriate test vials (labelled 20 g/L KCl), and 150 mL to the corresponding water quality beaker. Transfer 500 mL of the remaining solution to a 1-L graduated cylinder and add 500 mL of dilution water; the result will be a 1-L volume of 10 g/L KCl solution. Dispense 25 mL of this solution to each of the appropriate test vials (labelled 10 g/L KCl), and 150 mL to the corresponding water quality beaker. Add 500 mL of dilution water to 500 mL of the remaining 10 g/L KCl solution and repeat this process. Continue until all five concentrations are prepared. The negative control consists of 25 mL of dilution/control water in 10 replicate vials, plus a 150-mL water quality beaker.

3. Measure and record initial water quality (temperature, pH, DO, conductivity) in each water

quality beaker at 0 h. Randomly transfer one second instar larvae to each test vial. Cover the vials and beakers to reduce evaporation. Do not provide aeration during the 96-h test.

4. The larvae are fed 2 drops of Tetra-Min® slurry at test initiation (0 h) and at 48 h. Throughout the 96-h test, water-quality measurement and survival are reported daily.

5. After 96 h, record water quality and percent survival in each treatment. For the test to be valid, control survival must be ≥90%. For reference toxicant tests, mortality data are used to calculate the 96-h LC50 value. This estimate is determined using the EFFL software program. Compare each 96-h LC50 value obtained to the control limits (mean ± 2SD) and control chart established for *Chironomus tentans* testing in the EVS laboratory. This information is used to assess the relative sensitivity of each batch of test organisms. If the control failed or the LC50 value was outside the control limits, report this to the Laboratory Manager and QA/QC Manager.

6. Add the results of each LC50 test to the control chart and recalculate the mean ± 2SD as more data are obtained.

7. File a copy of the LC50 datasheet and computer printout in the *Chironomus tentans* reference toxicant file and include the originals with the data package for that project.

Table 12.2 Summary of recommended test conditions for *Chironomus tentans* 14-d sediment test.

Test Parameter		Test Condition
1.	Test type	Static, non-renewal
2.	Temperature (°C)	23 or 25 ± 1°C
3.	Water hardness	80 - 100 mg/L as $CaCO_3$
4.	Light quality	Ambient laboratory light
5.	Light intensity	50 ft candles (538 lux)
6.	Photoperiod	16:8 h light:darkness
7.	Test vessel size	1-L glass jar
8.	Test material volumes	2-cm layer of sediment; 800 mL of overlying dilution water
9.	Replicates/treatment	5
10.	Test organisms/replicate	10
11.	Size/age of test organisms	Second instar larvae (preferably 14-d post-hatch)
12.	Feeding regime	1.5 mL of d-YCT/*Selenastrum* and 0.6 mL of Tetra-Min® slurry/test container on Days 0, 2 and 6; 0.6 mL of Tetra-Min® slurry on Days 4 and 8
13.	Aeration	Gentle bubbling to maintain DO above 6 mg/L
14.	Dilution water	Moderately hard reconstituted dechlorinated water (80 - 100 mg/L as $CaCO_3$)
15.	Test duration	14 d
16.	Effects measured	Survival and growth
17.	Test acceptability criteria	≥70% mean control survival