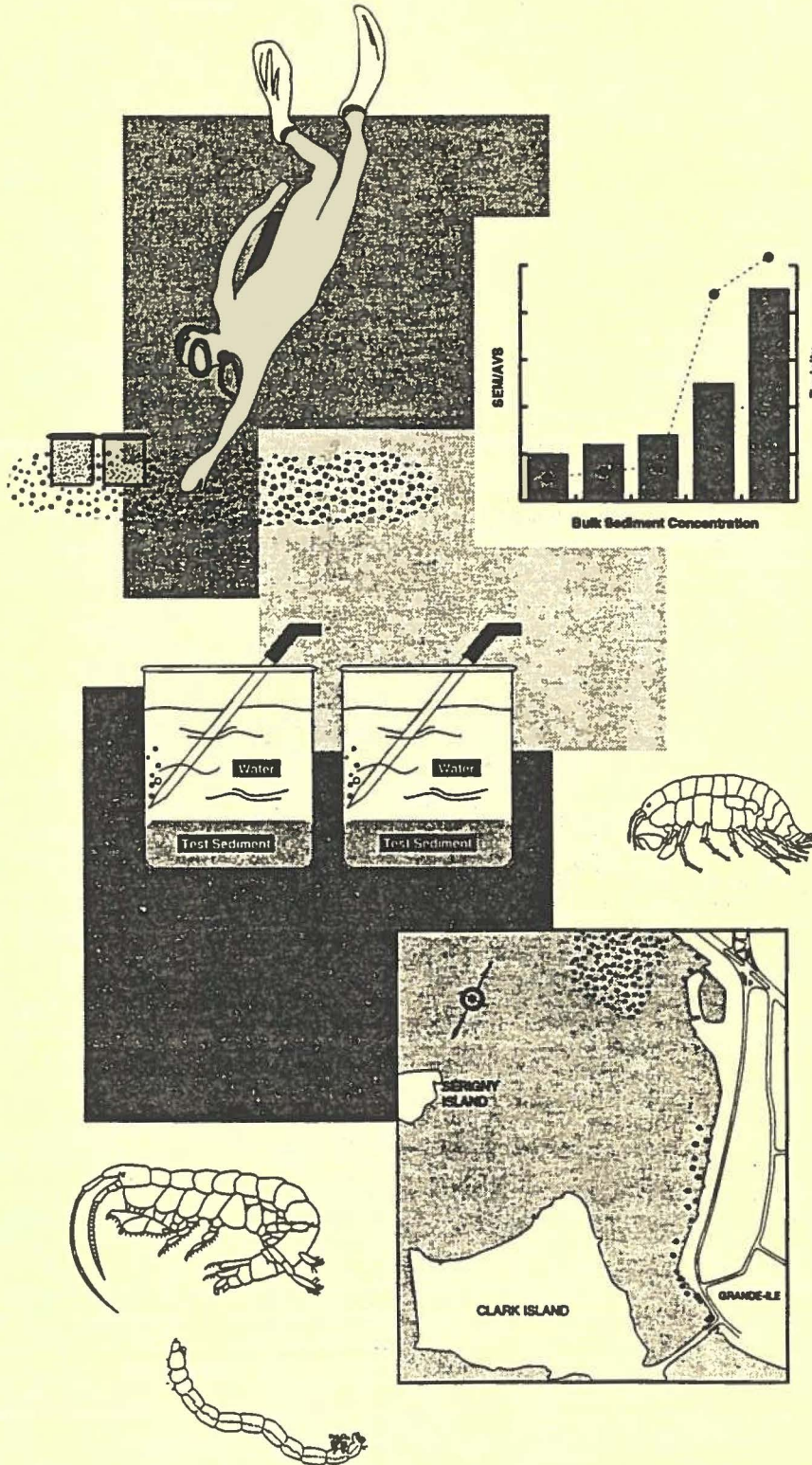




# Final Report

## Toxicity Characterization of Grande-Ile Shoreline Sediment: Data Report



Prepared for

AlliedSignal Inc.  
Morristown, NJ

May, 1994

**FINAL REPORT**

**CONFIDENTIAL**

**Toxicity Characterization of  
Grande-Ile Shoreline Sediment:  
Data Report**

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**May 1994**



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## 1.0 INTRODUCTION

This report address the toxicity of sediment near Clark Island, a small island in the St. Lawrence River, approximately 50 km southwest of Montréal, Québec, and 2 km east of downtown Salaberry-de-Valleyfield (Figure 1.1). Industrial activities on the island have resulted in contamination of river sediment by certain metals at concentrations identified as toxic by the Québec Ministry of the Environment (MENVIQ).

### 1.1 Site History

At present, the 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, including a sulfuric acid and oleum facility (operated between 1941 and 1983), a hydrofluoric acid production facility (which operated from 1956 until 1982), a chemicals production facility (operated from 1957 until 1985), and a bauxite grinding and alum production facility (began operations in 1946 and is still in operation). Except for the bauxite grinding and alum production facility, most of the production facilities were decommissioned and dismantled in the 1980s.

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-liner landfill, while all soils found to be contaminated were placed in a constructed on-site, single-liner landfill.

Past industrial activity on Clark Island has also resulted in the contamination of aquatic sediment. The degree of contamination is varied, 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. On occasion, the dikes failed. When this happened, cinders were lost into the river and nearby embayments. Pyrite cinders may have entered the river via a second source; until 1983, manufacturing effluents that could have contained pyrite cinders were discharged directly into the river.

Pyrite cinders presently overlay approximately 70,000 m<sup>2</sup> of native sediment along the northwest shoreline of the island. Sediment northeast of Clark Island also appears to have been contaminated by past industrial activities. Pyrite cinders, from the northwest shoreline, presumably transported by wave action and currents have mixed with native sediment, resulting in elevated metals concentrations. Pyrite cinder

wastes from the northwest shoreline of Clark Island are composed primarily of silt-sized iron particles (i.e., <80  $\mu\text{m}$  in diameter) containing trace metals and sulfides. Based on available data, the typical composition of the pyrite cinders, along the northwest shoreline of Clark Island, includes metals at the following range of concentrations (Tecsult, 1988; Tecsult, 1990; Tecsult, 1993b):

- 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 Québec Ministry of the Environment (MENVIQ) identified the need to assess sediment quality. As part of the assessment process, MENVIQ developed priority designations for areas around Clark Island. Priority Zone I areas are primarily associated with sediment directly offshore of northwest Clark Island and include those areas where pyrite cinders overlay native sediments. The Priority Zone II area is located along the shoreline of Grande-Ile. Priority Zone III and Priority Zone IV areas are located in deeper water to the northeast (e.g., between the Clark Island and Grande-Ile shorelines, and to the north, respectively).

## 1.2 Québec Sediment Quality Guidelines

Sediment quality and the need to potentially remediate contaminated sediments in the Clark Island area is primarily based on the concentration of contaminants observed in the sediment relative to numeric sediment quality guidelines published by the province. For the purpose of this report, the guidelines are used as criteria. In April 1992, Environmental Canada, the St. Lawrence Center, and MENVIQ published interim sediment guidelines for evaluating the quality of St. Lawrence River sediment (MENVIQ, 1992). Sediment quality guidelines have been developed for the following three management levels:

- Level 1: No Effect Level - Concentrations that will not cause chronic or acute effects to benthic organisms, and will not affect water quality or the uses normally associated with water
- Level 2: Minimal Effect Level - Concentrations expected to cause minimal effects in benthic organisms
- Level 3: Toxic Effect Level - Concentrations expected to cause significant effects in benthic organisms

Table 1.1 Sediment quality criteria for St. Lawrence River sediment (MENVIQ, 1992).

Parameter	Level 1 <sup>a</sup> (mg/kg)	Level 2 <sup>b</sup> (mg/kg)	Level 3 <sup>c</sup> (mg/kg)
Arsenic	3.0	7.0	17.0
Cadmium	0.2	0.9	3.0
Chromium	55.0	55.0	100.0
Copper	28.0	28.0	86.0
Mercury	0.05	0.2	1.0
Nickel	35.0	35.0	61.0
Lead	23.0	42.0	170.0
Zinc	100.0	150.0	540.0

- <sup>a</sup> No Effect Level: Background level, without acute or chronic effect on benthic organisms.
- <sup>b</sup> Minimal Effect Level: Level where effects might be expected but would be considered tolerable for the majority of benthic organisms.
- <sup>c</sup> Toxic Effect Level: Level where effects for the majority of benthic organisms might be expected.

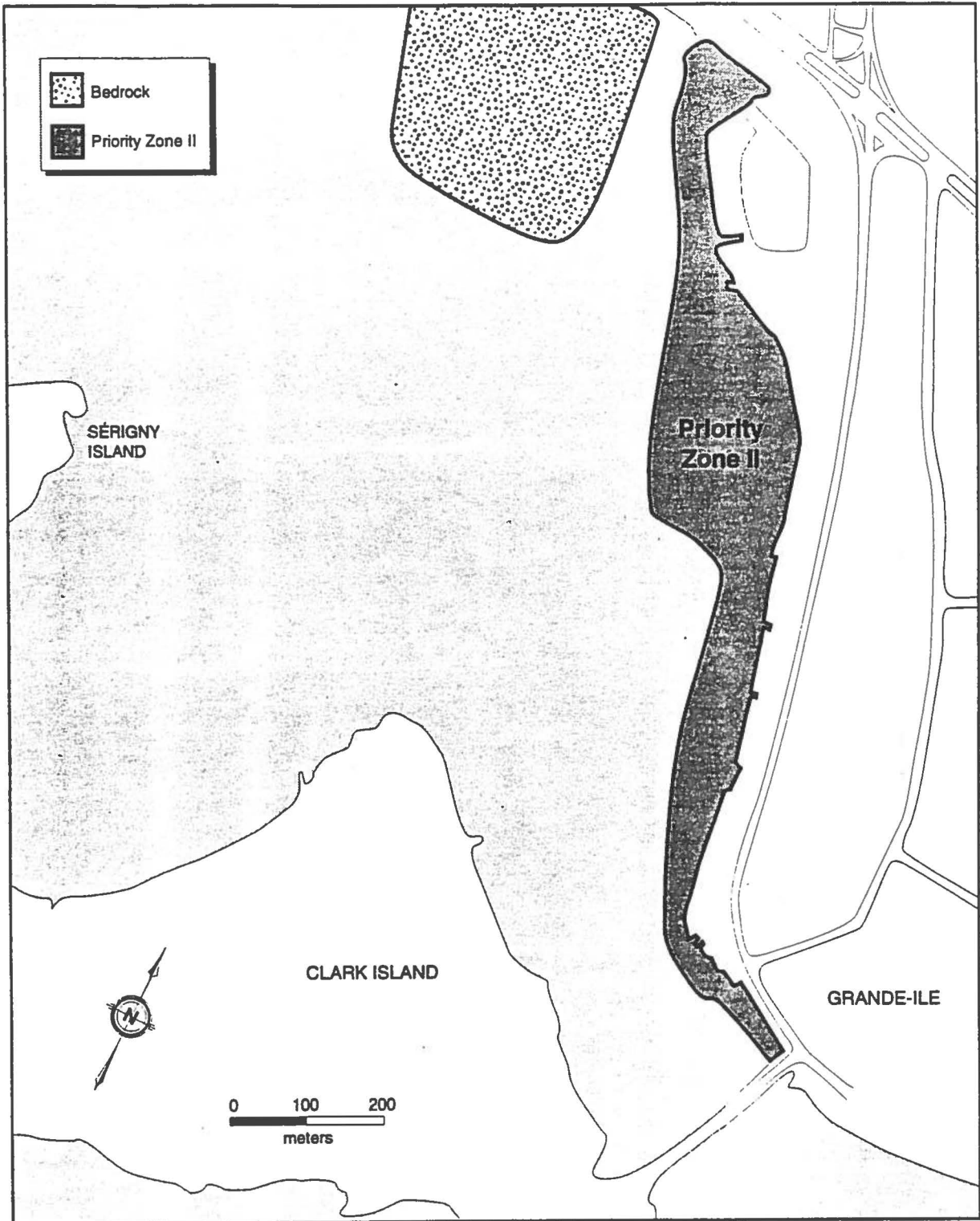
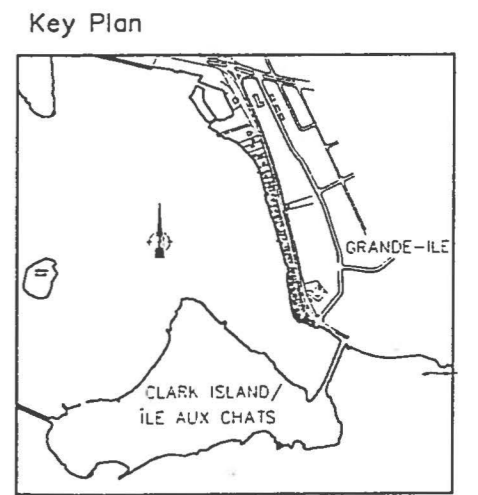
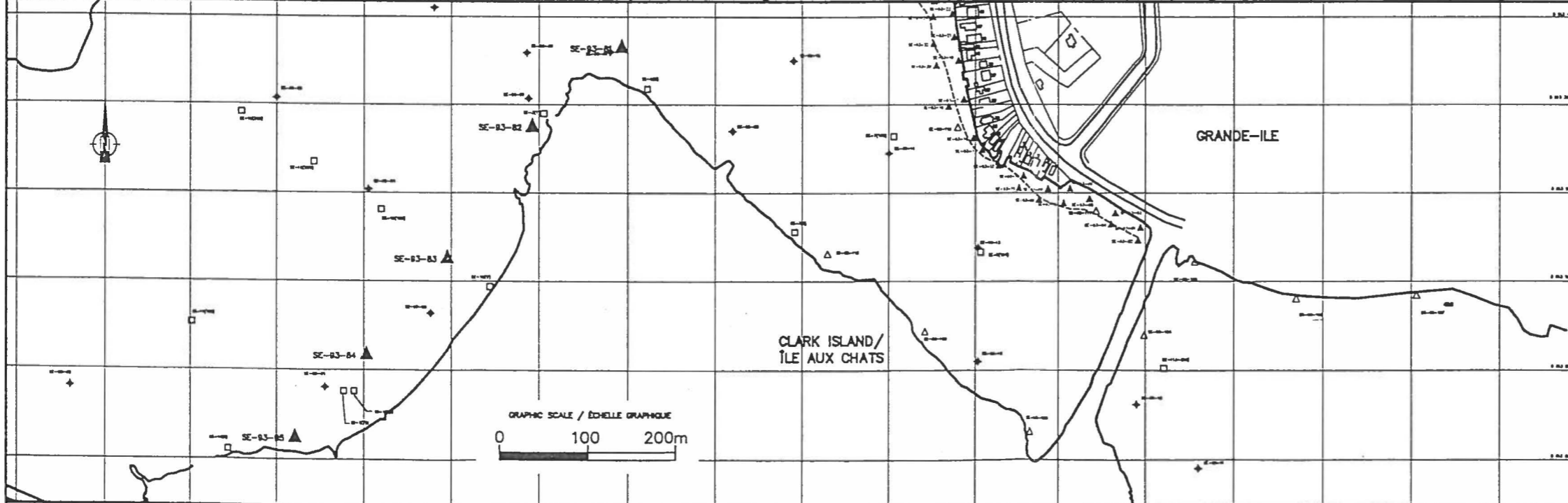
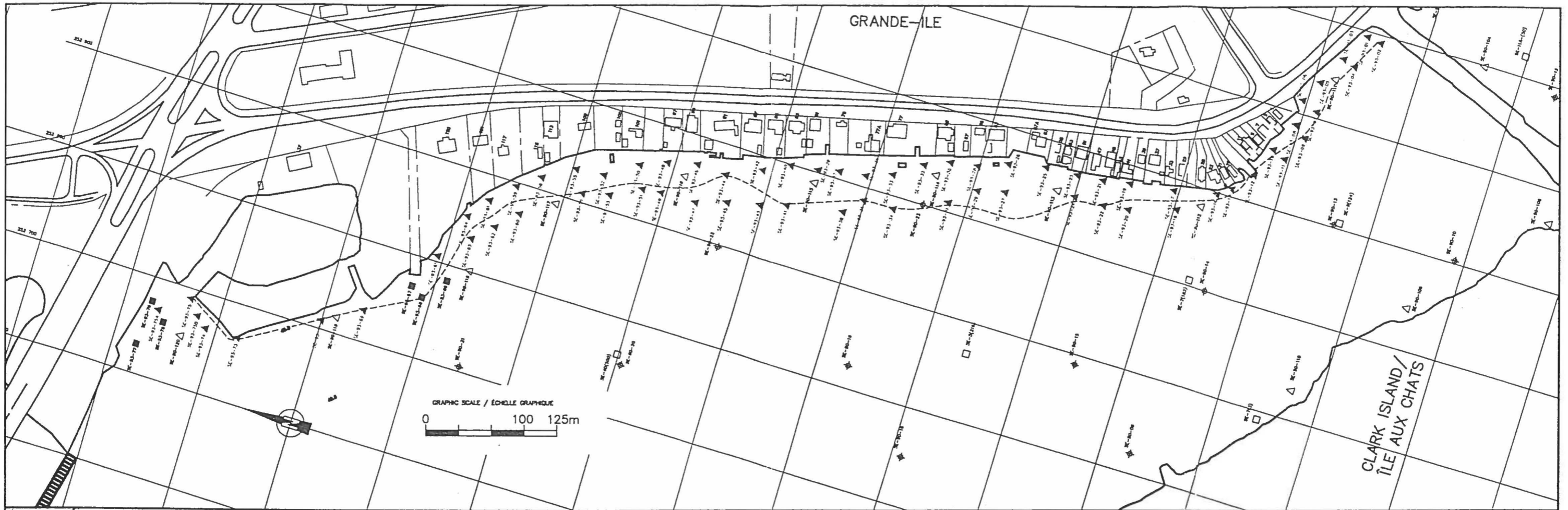


Figure 1.2 Location of Priority Zone II.



LEGEND / LÉGENDE :

- |           |   |                                                                                                                  |          |   |                                                                                                                                                     |
|-----------|---|------------------------------------------------------------------------------------------------------------------|----------|---|-----------------------------------------------------------------------------------------------------------------------------------------------------|
| SE-9(124) | □ | SURFACE SEDIMENTS SAMPLING STATION / STATION D'ÉCHANTILLONNAGE DES SÉDIMENTS DE SURFACE (JANUARY / JANVIER 1988) | SE-93-66 | ■ | SAMPLING STATION WHERE NO SEDIMENTS WERE RECOVERED / STATION D'ÉCHANTILLONNAGE DES SÉDIMENTS DE SURFACE SANS RÉCUPÉRATION (FEBRUARY / FÉVRIER 1993) |
| SE-90-13  | ⊕ | SEDIMENTS BOREHOLE / FORAGE AU TRAVERS DES SÉDIMENTS (FEBRUARY / FÉVRIER 1990)                                   | SE-93-01 | ▲ | SURFACE SEDIMENTS SAMPLING STATION / STATION D'ÉCHANTILLONNAGE DES SÉDIMENTS DE SURFACE (FEBRUARY / FÉVRIER 1993)                                   |
| SE-90-112 | △ | SURFACE SEDIMENTS SAMPLING STATION / STATION D'ÉCHANTILLONNAGE DES SÉDIMENTS DE SURFACE (JUNE / JUIN 1990)       |          |   |                                                                                                                                                     |



N° contrat / contract	Échelle / Scale	Date
4361-1000	INDICATED	FEB.1994

FEBRUARY 1993  
CHARACTERIZATION CAMPAIGN  
ALONG GRANDE-ÎLE SHORELINE  
SAMPLING STATIONS LOCATION

FIGURE : 1.3

In addition to determining the bulk sediment concentration of metals in Grande-Ile sediment, Tecslult (1993a) also analyzed a subset (i.e., 34 samples) of 1993 sediment samples for simultaneously extracted metals (SEM) and acid volatile sulfide (AVS) concentrations. The ratio of SEM/AVS was then used to estimate potential toxicity associated with bioavailable forms of metals. The ratio of SEM to AVS provides an indirect indication of the potential toxicity of metals in contaminated sediment (DiToro et al., 1992). An SEM/AVS ratio of less than 1 indicates that all available metals should be bound to the sediment sulfide, making the sediment nontoxic. If the SEM/AVS ratio is greater than 1, then some fraction of the metals will be in an available form (i.e., not bound as a sulfide), which may result in sediment toxicity. Recent studies indicate that sediments with ratios greater than 1 may also be nontoxic, depending upon a number of factors, including the presence of other metals-binding agents (Ankley et al., 1993). Further, Ankley et al. (1991a) presented data indicating that relatively low SEM/AVS ratios (e.g., >1, but <10) represent a "transition zone" in which toxicity may or may not be present, depending on sediment-specific characteristics.

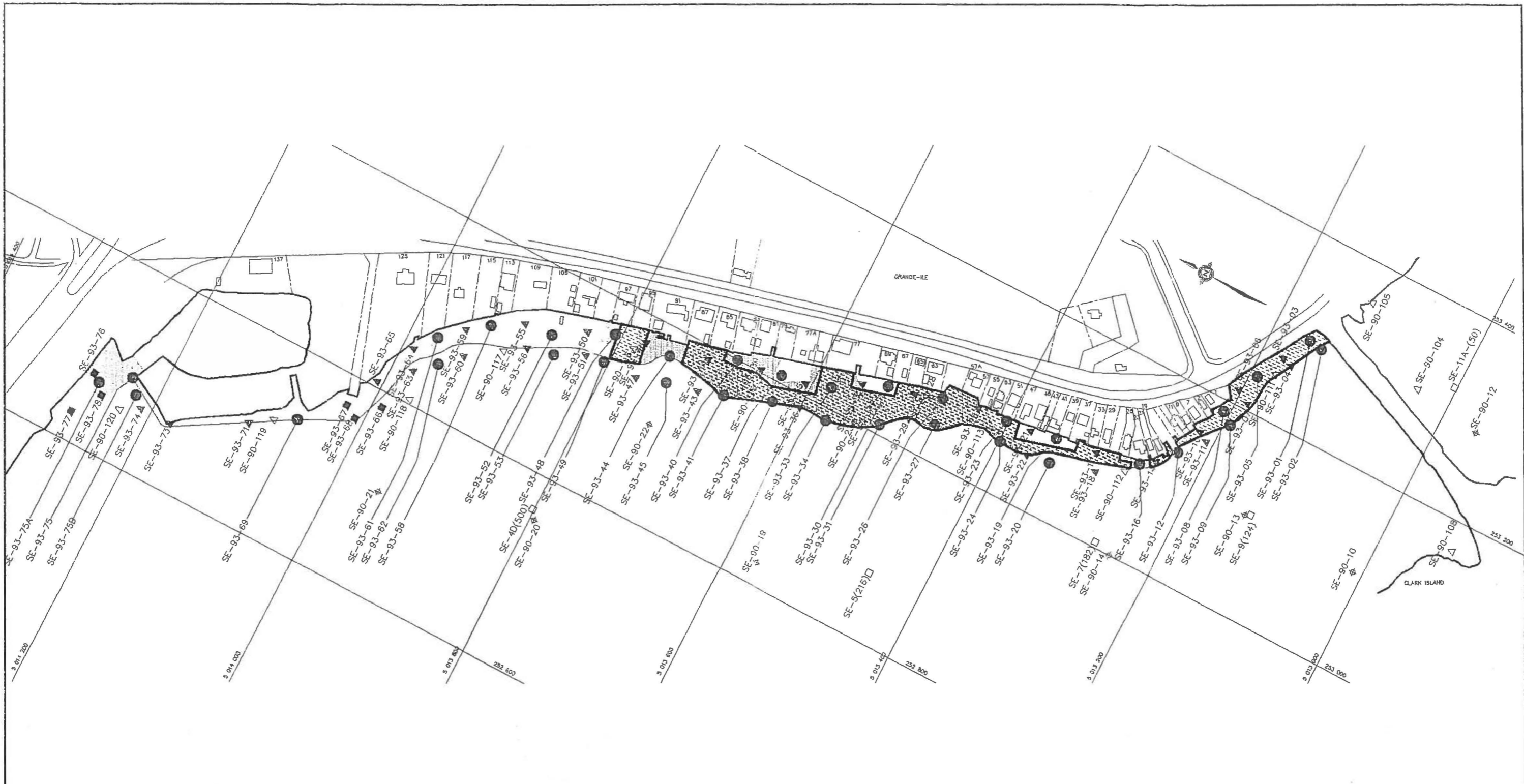
Tecslult (1993a) grouped the Grande-Ile sediment into three categories, based on the ratio of the summation of the individual simultaneously extracted metals to AVS ( $\Sigma$ SEM/AVS):

- Category 1 sediments -  $\Sigma$ SEM/AVS ratios <1
- Category 2 sediments -  $\Sigma$ SEM/AVS ratios 1 to 3
- Category 3 sediments -  $\Sigma$ SEM/AVS ratios >3

Figure 1.4 illustrates zones of potential toxicity as well as the extent of zinc contamination along Grande-Ile shoreline. As demonstrated by the work of DiToro et al. (1992) and Ankley et al. (1991a), the  $\Sigma$ SEM/AVS ratios for Grande-Ile sediment indicate that some sediment may be toxic, and some may not be. The ratios of SEM/AVS and  $\Sigma$ SEM/AVS represent predictions of sediment toxicity. These predictions can be verified only by direct testing of the sediment using standardized bioassay testing procedures.

#### 1.4 Study Objectives

Although the concentrations of metals in sediment from the Grande-Ile shoreline exceed the MENVIQ Level 3 guideline concentrations, the sediment may not represent a significant risk to aquatic species. Two factors support this position:



LEGEND / LÉGENDE :

SEM/AVS < 1.0

SEM/AVS 1-3

SEM/AVS > 3.0

ZINC CONCENTRATION ABOVE MENVQ LEVEL 3 CRITERION (FEBRUARY 1993)

SE-9(124) □ SURFACE SEDIMENTS SAMPLING STATION / STATION D'ÉCHANTILLONNAGE DES SÉDIMENTS DE SURFACE (JANUARY/JANVIER 1988)

SE-90-13 ⊕ SEDIMENTS BOREHOLE / FORAGE AU TRAVERS DES SÉDIMENTS (FEBRUARY/FÉVRIER 1990)

SE-90-112 △ SURFACE SEDIMENTS SAMPLING STATION / STATION D'ÉCHANTILLONNAGE DES SÉDIMENTS DE SURFACE (JUNE/JUIN 1990)

SE-93-03 ▲ SURFACE SEDIMENTS SAMPLING STATION / STATION D'ÉCHANTILLONNAGE DES SÉDIMENTS DE SURFACE (FEBRUARY/FÉVRIER 1993)

SE-93-66 ■ SAMPLING STATION WHERE NO SEDIMENTS WERE RECOVERED / STATION D'ÉCHANTILLONNAGE DES SÉDIMENT DE SURFACE SANS RÉCUPÉRATION (FEBRUARY/FÉVRIER 1993)

SE-93-01 ● SURFACE SEDIMENTS SAMPLING STATION WITH TOXICITY TEST / STATION D'ÉCHANTILLONNAGE DES SÉDIMENTS AVEC ANALYSES DE TOXICITÉ (FEBRUARY / FÉVRIER 1993)



N° contrat/contract  
4361-1000

Echelle / Scale  
1:4000

Date  
DEC. 1993

FEBRUARY 1993  
CHARACTERIZATION CAMPAIGN  
ALONG GRANDE-ÎLE SHORELINE  
TOXICITY ASSESSMENT AND  
EXTENT OF ZINC CONTAMINATION

FIGURE : 1.4

- Several of the sediment samples obtained from the Grande-Ile shoreline had  $\Sigma\text{SEM}/\text{AVS}$  ratios less than 1, indicating that the metals present are not biologically available (see Figure 1.4)
- Field staff, during reconnaissance surveys and sediment sampling, noted abundant biological activity (e.g., abundance of bivalves, snails, crustaceans, and rooted aquatic plants) along the Grande-Ile shoreline, suggesting that the sediment is not highly toxic.

The present study was undertaken to resolve the apparent inconsistency between high concentrations of metals (relative to the MENVIQ sediment quality criteria) and an abundant flora and fauna along the Grande-Ile shoreline. The study objective was to assess whether sediment containing metals at concentrations higher than Level 3 criteria and having  $\Sigma\text{SEM}/\text{AVS}$  ratios greater than 1 was toxic when tested using two species of benthic invertebrates. The results of the toxicity tests, along with the data on sediment metals concentrations, would then be used to determine if remediation of Grande-Ile shoreline is appropriate.

### **1.5 Report Format**

This report contains six sections plus seven appendices. Section 1.0 provides background information on the Clark Island site and the need for the current study. The study methods such as, study design, field collection methods, and testing procedures are detailed in Section 2.0. The results of the sediment testing are presented in Section 3.0. Section 4.0 discusses the sediment toxicity characterization. A summary of important conclusions is provided in Section 5.0, while Section 6.0 contains the literature cited in this report.

---

## 2.0 STUDY METHODS

### 2.1 Overall Study Design

The study was designed to assess the toxicity of sediment collected along the Grande-Ile shoreline. If sediment toxicity was evident for a given sediment sample, then a Phase I Toxicity Identification Evaluation (TIE) approach was used to determine if the observed toxicity was due to metals present in the sample or potentially due to other factors (e.g., sediment grain size or ammonia).

Sediment to be tested as part of this study was selected after reviewing the sediment chemistry data presented by Tecslut (1993b) and the assessment of potential toxicity based on  $\Sigma\text{SEM}/\text{AVS}$  ratios (Tecslut 1993a). A subset of stations was selected for resampling and toxicity testing. The factors used to select sediment sampling locations were:

- The concentration of at least one metal exceeded the Level 3 guideline (based on the results from previous sampling)

or

- The  $\Sigma\text{SEM}/\text{AVS}$  ratio for the sediment was greater than 1, indicating that there was some likelihood that the sediment would be toxic
- In addition, the station was representative of sediment characteristics (i.e., grain size, TOC concentration, metals concentration, and  $\Sigma\text{SEM}/\text{AVS}$  ratio) from nearby areas to allow use of test results as a predictive tool in defining the limits of remediation.

After reviewing the data presented by Tecslut (1993a and 1993b), and consulting with AlliedSignal and Tecslut staff, the stations listed in Table 2.1 along the Grande-Ile shoreline (Figure 2.1) were selected for toxicity testing. As shown in Table 2.1, the sediment selected for toxicity testing was expected to represent a range of metals contamination above the Level 3 guideline concentrations, and  $\Sigma\text{SEM}/\text{AVS}$  ratios ranging from 0.66 to 13.53. The distribution of proposed sampling stations provided suitable spatial coverage for the lower two-thirds of the Grande-Ile shoreline. Samples were not collected from the upper portion of the Grande-Ile shoreline because previous analyses of sediment samples from this portion indicated that metal concentrations were below the Level 3 guideline concentrations (Tecslut, 1993b). In addition to the sampling stations selected along the Grande-Ile shoreline, two stations were

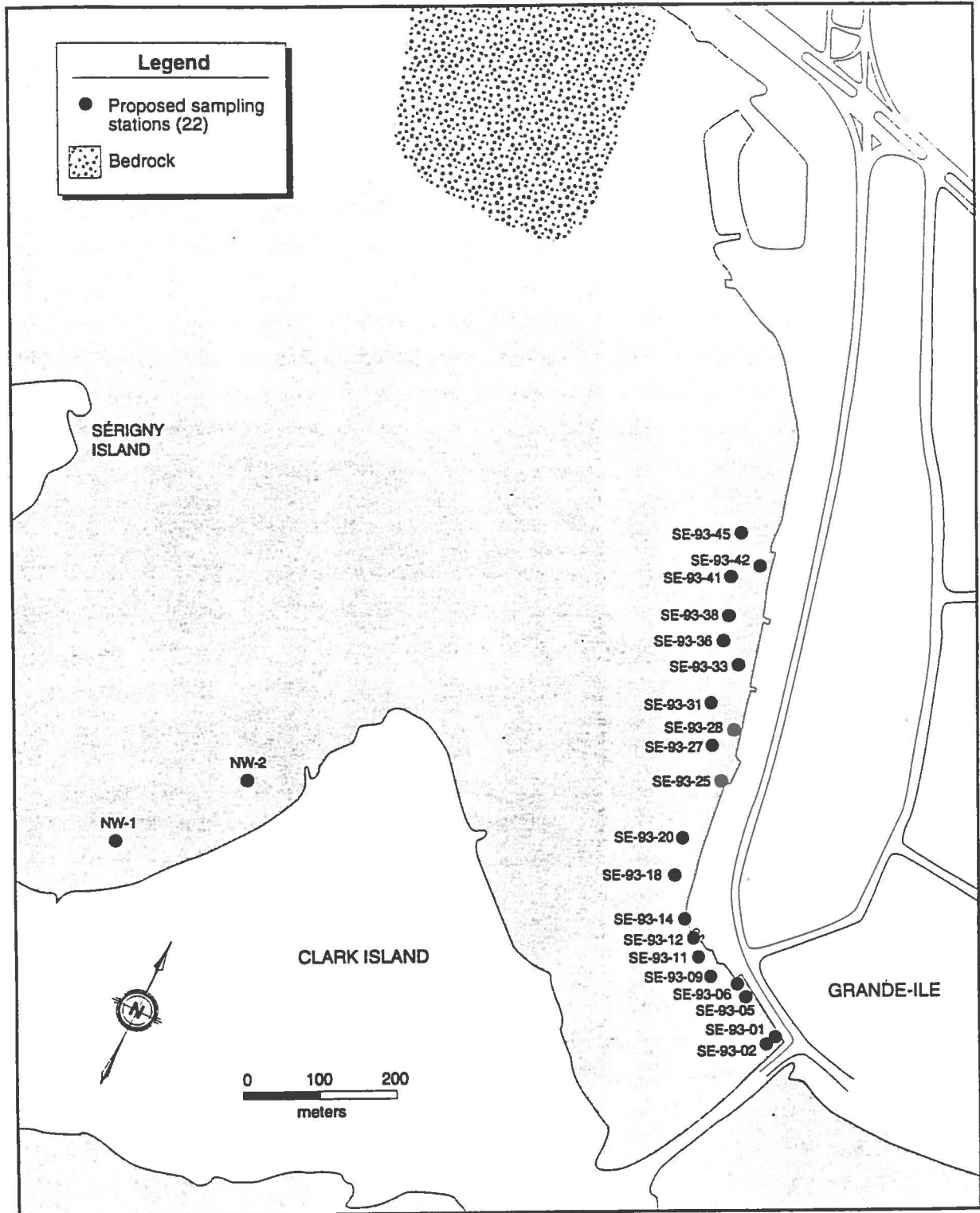
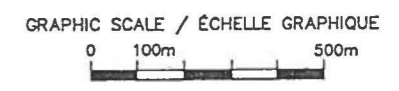
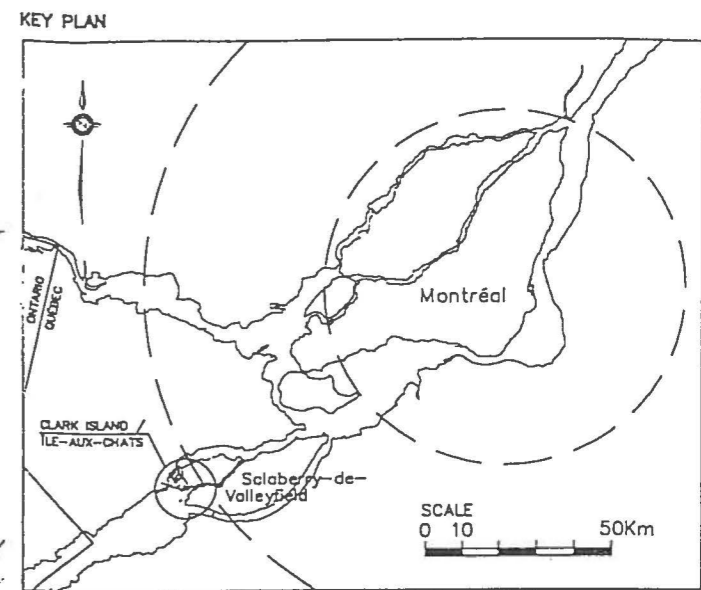
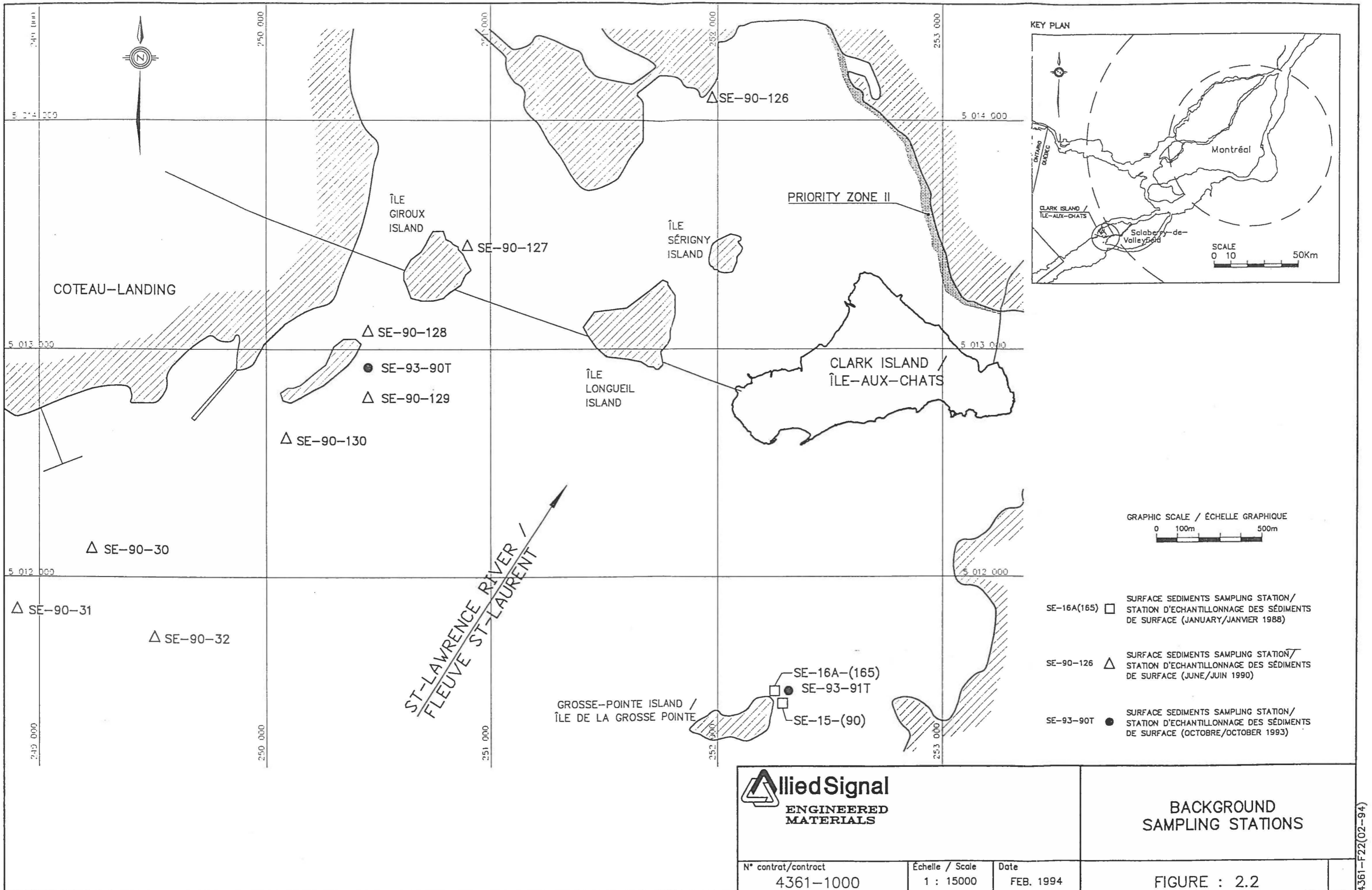


Figure 2.1 Proposed sediment sampling stations for Priority Zone II .



- SE-16A(165) □ SURFACE SEDIMENTS SAMPLING STATION / STATION D'ÉCHANTILLONNAGE DES SÉDIMENTS DE SURFACE (JANUARY/JANVIER 1988)
- SE-90-126 △ SURFACE SEDIMENTS SAMPLING STATION / STATION D'ÉCHANTILLONNAGE DES SÉDIMENTS DE SURFACE (JUNE/JUIN 1990)
- SE-93-90T ● SURFACE SEDIMENTS SAMPLING STATION / STATION D'ÉCHANTILLONNAGE DES SÉDIMENTS DE SURFACE (OCTOBER/OCTOBRE 1993)

**AlliedSignal**  
ENGINEERED MATERIALS

**BACKGROUND SAMPLING STATIONS**

N° contrat/contract 4361-1000	Échelle / Scale 1 : 15000	Date FEB. 1994
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FIGURE : 2.2

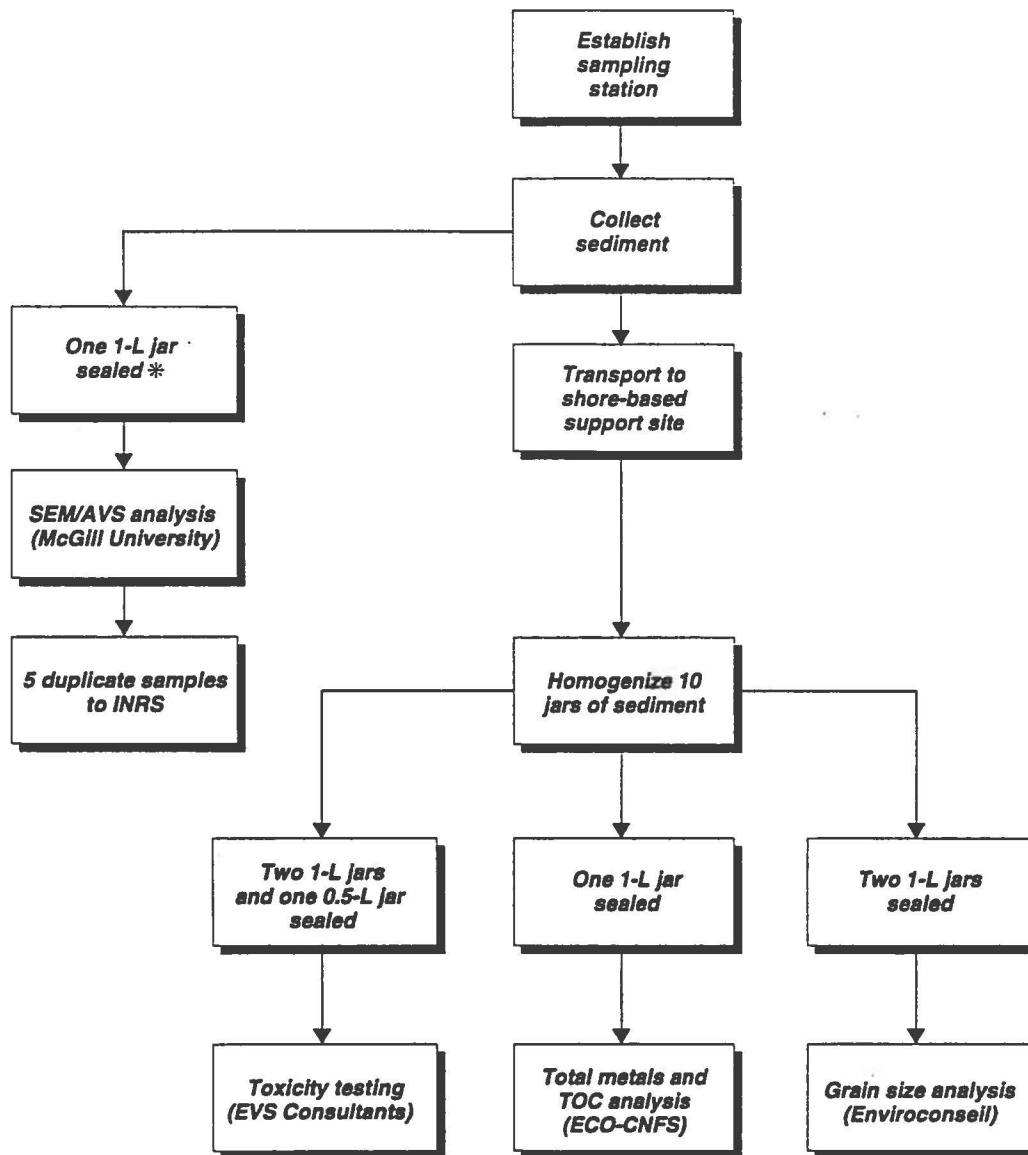
4361-F22(02-94)

Table 2.2 Range of concentrations (mg/kg) of contaminants found in sediment collected at background stations upstream of Clark Island

Sampling Date	Grosse Pointe Island		Coteau Landing		Longueuil & Giroux Islands	Lake St-Francois
	Oct 87 - Jan 88	Oct 93	Feb 90	Oct 93	June 90	Serodes (1978)
No. Samples	2	1	3	1	5	—
Arsenic	0.17-0.25	1.80	4.7-5.0	1.60	0.5-5.4	3.3
Cadmium	<1.0-1.3	<0.03	<1.0	1.90	0.7-4.3	—
Copper	9.3-12.0	8.0	42.0-45.0	7.0	8.0-59.0	37.0
Mercury	0.26-0.52	0.19	1.30-1.94	0.10	0.15-1.17	0.22
Lead	7.5-8.2	—	56.0-60.0	—	6.1-47.7	18.0
Selenium	0.14-0.25	—	15.3-19.4	—	0.2-1.1	—
Zinc	81.0-87.0	52.0	35.0-279.0	79.0	49.0-384.0	105.0

Table 2.3 Actual stations sampled in October 1993.

Proposed Station	Actual Station	Analysis				Duplicate Analysis
		Bioassays	Metals	SEM/AVS	Sediment Conventionals	SEM/AVS
SE-93-01						
SE-93-02	SE-93-02T	✓	✓	✓	✓	
	SE-93-03T	✓	✓	✓	✓	
SE-93-05						
SE-93-06	SE-93-06T	✓	✓	✓	✓	
SE-93-09	SE-93-09T	✓	✓	✓	✓	✓
SE-93-11	SE-93-11T	✓	✓	✓	✓	
SE-93-12	SE-93-12T	✓	✓	✓	✓	
SE-93-14	SE-93-14T	✓	✓	✓	✓	
SE-93-18	SE-93-18T	✓	✓	✓	✓	✓
SE-93-20	SE-93-20T	✓	✓	✓	✓	
SE-93-25	SE-93-25T	✓	✓	✓	✓	
SE-93-27	SE-93-27T	✓	✓	✓	✓	✓
SE-93-28	SE-93-28T	✓	✓	✓	✓	
SE-93-31	SE-93-31T	✓	✓	✓	✓	
SE-93-33	SE-93-33T	✓	✓	✓	✓	✓
SE-93-36	SE-93-36T	✓	✓	✓	✓	
SE-93-38	SE-93-38T	✓	✓	✓	✓	
SE-93-41	SE-93-41T	✓	✓	✓	✓	
SE-93-42	SE-93-42T	✓	✓	✓	✓	✓
SE-93-45	SE-93-45T	✓	✓	✓	✓	
NW-1	SE-93-86T	✓	✓	✓	✓	
NW-2	SE-93-87T	✓	✓	✓	✓	
Background 1	SE-93-90T	✓	✓	✓	✓	
Background 2	SE-93-91T	✓	✓	✓	✓	

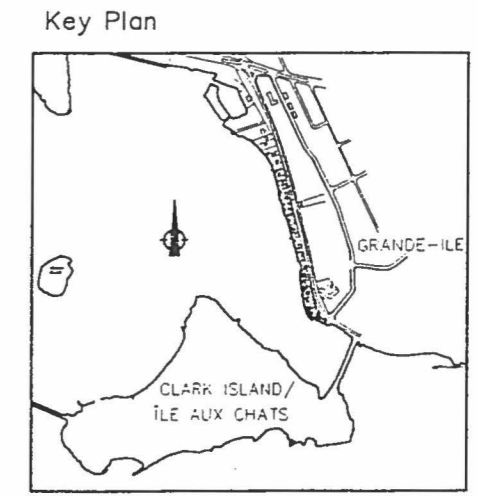
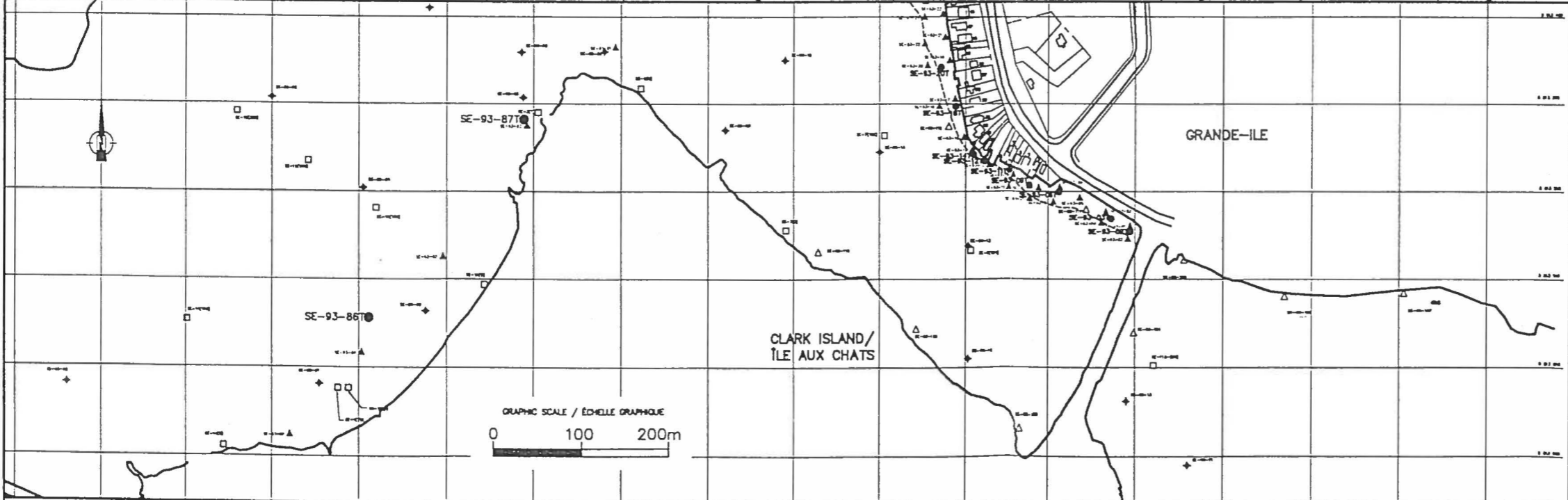
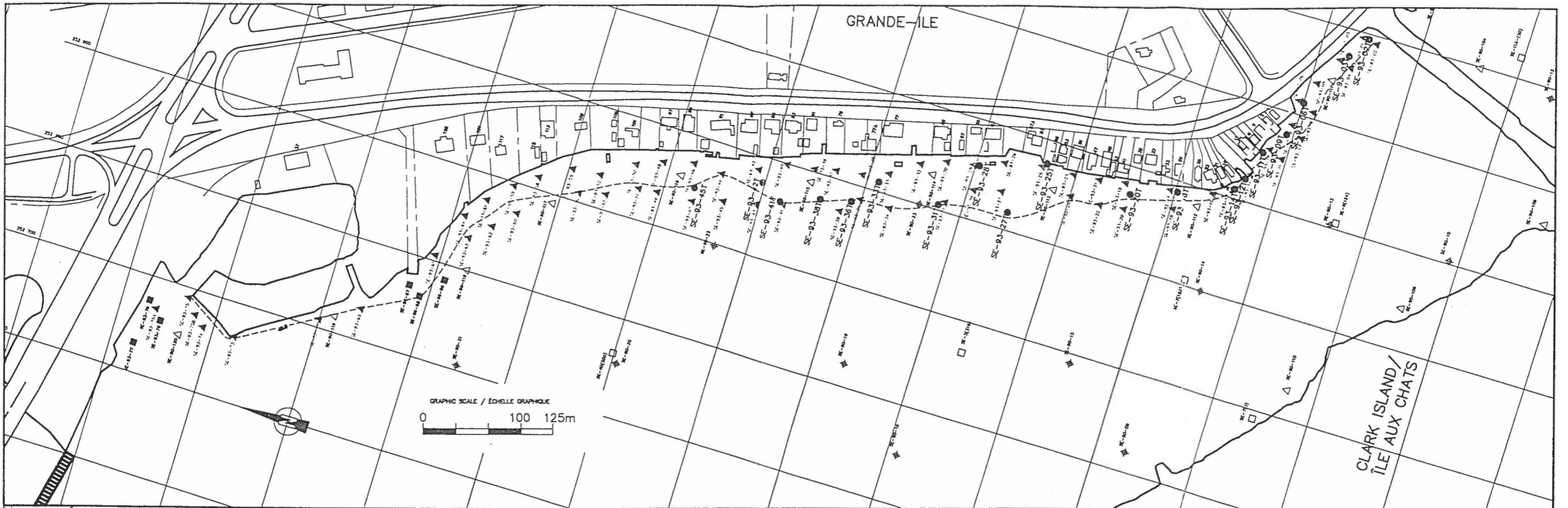


\* The first 1-L jar of sediment collected

Figure 2.3 Schematic of the distribution of sediment collected at each station for analysis.


Table 2.4 Sampling station coordinates in SCOPQ system.

Sampling Station	SCOPQ System	
	X	Y
SE-93-02T	253294.5	5013154.3
SE-93-03T	253271.9	5013169.0
SE-93-06T	253212.7	5013199.6
SE-93-09T	253177.1	5013207.0
SE-93-11T	253152.7	5013224.6
SE-93-12T	253122.2	5013234.7
SE-93-14T	253109.2	5013242.0
SE-93-18T	253088.6	5013297.3
SE-93-20T	253072.1	5013341.9
SE-93-25T	253076.3	5013431.2
SE-93-27T	253017.8	5013455.3
SE-93-28T	253054.5	5013496.1
SE-93-31T	253005.3	5013524.3
SE-93-33T	253009.5	5013588.1
SE-93-36T	252982.5	5013609.1
SE-93-38T	252975.2	5013640.4
SE-93-41T	252961.0	5013679.5
SE-93-42T	252974.6	5013702.9
SE-93-45T	252948.2	5013769.6
SE-93-86T	252411.4	5013056.4
SE-93-87T	252588.7	5013282.2



**LEGEND / LÉGENDE :**

SE-9(124) □	SURFACE SEDIMENTS SAMPLING STATION / STATION D'ÉCHANTILLONNAGE DES SÉDIMENTS DE SURFACE (JANUARY / JANVIER 1988)	SE-93-66 ■	SAMPLING STATION WHERE NO SEDIMENTS WERE RECOVERED / STATION D'ÉCHANTILLONNAGE DES SÉDIMENTS DE SURFACE SANS RÉCUPÉRATION (FEBRUARY / FÉVRIER 1993)
SE-90-13 ⊕	SEDIMENTS BOREHOLE / FORAGE AU TRAVERS DES SÉDIMENTS (FEBRUARY / FÉVRIER 1990)	SE-93-01 ▲	SURFACE SEDIMENTS SAMPLING STATION / STATION D'ÉCHANTILLONNAGE DES SÉDIMENTS DE SURFACE (FEBRUARY / FÉVRIER 1993)
SE-90-112 △	SURFACE SEDIMENTS SAMPLING STATION / STATION D'ÉCHANTILLONNAGE DES SÉDIMENTS DE SURFACE (JUNE / JUIN 1990)	SE-93-02T ●	SURFACE SEDIMENTS SAMPLING STATION WITH TOXICITY TEST / STATION D'ÉCHANTILLONNAGE DES SÉDIMENTS DE SURFACE AVEC ANALYSE DE TOXICITÉ (OCTOBER / OCTOBRE 1993)

 <b>AlliedSignal</b> ENGINEERED MATERIALS	N° contrat / contract	Échelle / Scale	Date
	4361-1000	INDICATED	FEB.1994

<b>OCTOBER 1993          CHARACTERIZATION CAMPAIGN          ALONG GRANDE-ILE SHORELINE          SAMPLING STATIONS LOCATION</b>
<b>FIGURE : 2.4</b>

4361-F24(02-94)

## 2.4 Sediment Analytical and Testing Methods

As discussed previously, sediment collected from the Grande-Ile shoreline was subjected to a number of analytical and testing procedures. To meet the analytical and testing requirements, subsamples of sediment were shipped to different laboratories. Table 2.5 lists the testing laboratories and the type of analysis performed by each. The volume of sediment sent to each laboratory, and the type of testing undertaken by each laboratory are identified in Figure 2.3.

### 2.4.1 Metals Analysis

Sediment samples were analyzed for the bulk concentrations of the following metals: arsenic, cadmium, copper, mercury, and zinc. The decision to measure the concentrations of only these five metals was based on the previous sediment characterization studies conducted on Grande-Ile sediment by Tecslut (1990, 1993b). Previous sediment analyses have indicated that four of these five metals (i.e., all but arsenic) most frequently exceed the MENVIQ guideline concentrations. Arsenic was measured to update the existing database. Samples were analyzed according to standard methods (see Table 2.6). The analytical work was conducted by ECO-CNFS of Pointe-Claire, Québec. Detection limits of the methods used ranged from 0.02 to 1.0 mg/kg, depending upon the analyte (Table 2.6). A successful external QA/QC program had been conducted during the February 1993 sampling event to verify analytical methodologies and laboratory practices; because the analytical methods have not changed since that time, an external QA/QC program was not conducted for this (October 1993) sampling event.

### 2.4.2 Conventional Sediment Parameters

Total organic carbon and grain size were measured for each of the sediment samples. TOC was determined by ECO-CNFS using methods proposed by Environment Canada (1980). Partial grain size distribution was analyzed by Enviroconseil of Montréal, using 5-mm and 80- $\mu$ m sieves, according to the BNQ (Québec Normalization Board) 25560-040 Method.

### 2.4.3 SEM and AVS Analysis

The concentrations of SEM and AVS were measured in bulk sediment samples by McGill University using the methods described by Allen et al. (1991) for the U.S. Environmental Protection Agency (U.S. EPA). The procedure for determining SEM and AVS includes the conversion of AVS to hydrogen sulfide (H<sub>2</sub>S).

Table 2.6 Analytical methods and detection limits used in determining total heavy metal and organic carbon content in sediment collected from the Grande-Ile shoreline.

Parameter	Digestion Method	Analytical Method	Detection Limit (mg/kg)
Arsenic	HNO <sub>3</sub> +H <sub>2</sub> O <sub>2</sub>	STM-3112 <sup>a</sup>	.1
Cadmium	HNO <sub>3</sub> +H <sub>2</sub> O <sub>2</sub>	STM-3113 <sup>a</sup>	.03
Copper	HNO <sub>3</sub> +H <sub>2</sub> O <sub>2</sub>	STM-3120 <sup>a</sup>	.0
Mercury	HNO <sub>3</sub> +H <sub>2</sub> SO <sub>4</sub> + +KMnO <sub>4</sub> +K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	BEST-1979 <sup>b</sup>	.02
Zinc	HNO <sub>3</sub> +H <sub>2</sub> O <sub>2</sub>	STM-3120 <sup>a</sup>	.0
Total Organic Carbon	HCl	Environment Canada <sup>c</sup>	.01 percent

<sup>a</sup> STM: *Standard Methods for the Examination of Water and Wastewater*, 17th edition, 1989.

<sup>b</sup> BEST: Study Board on Toxic Substances, MENVIQ

<sup>c</sup> Environment Canada (1980)

Table 2.7 Analytical methods and detection limits used in determining SEM and AVS concentrations in sediment collected from the Grande-Ile shoreline.

Parameter	Method <sup>a</sup>	Detection Limit
AVS	Allen et al., 1991	0.05 $\mu$ mole/g
SEM [Cd]	Allen et al., 1991	0.0001 mg/L
SEM [Cu]	Allen et al., 1991	0.001 mg/L
SEM [Hg]	Allen et al., 1991	0.0001 mg/L
SEM [Zn]	Allen et al., 1991	0.002 mg/L

<sup>a</sup> Method developed by Allen et al. (1991) for the U.S. Environmental Protection Agency.

individual was considered moribund if there was no movement of antennae or other body appendages when viewed under a dissecting microscope.

For logistical reasons, the *H. azteca* tests were split into two approximately equal lots and initiated on separate days (see Table 2.8). Each test lot included a negative (i.e., clean) control and a positive (i.e., reference toxicant) control. The negative control consisted of five replicates containing fine silica sand. Test organisms were exposed to the silica sand for the entire 10-day period. Survival data from the negative controls were used to assess the performance of the test organisms. The positive (i.e., reference toxicant) control consisted of a dilution series of the reference toxicant zinc sulfate and a 96-hour exposure period. Following the exposure period, the number of surviving organisms was counted and the 96-hour LC<sub>50</sub> was calculated by statistical analysis (U.S. EPA, 1985b). Data from the positive control were used to assess the sensitivity of test organisms.

#### 2.4.4.2 *Chironomus tentans* Toxicity Test

The assessment using *C. tentans* followed the procedures described by ASTM (1991). Sediment was prepared as previously described for the *H. azteca* test. Following the 24-hour equilibration period, 10 second-instar chironomid larvae (approximately 9-10 d post-hatching at 23-25°C) were added to the sediment and the exposure chambers monitored for the next 10 days. Test animals were fed 0.2 mL of Tetra-Min Fishfood preparation and 0.5 mL of d-YCTF/Algae Food mixture per replicate jar on days 0, 2, 4, 6, and 8. The tests were conducted as previously described for *H. azteca*.

For logistical reasons, the *C. tentans* tests also were split into two approximately equal lots and initiated on separate days (see Table 2.8). Each of the test lots included both a negative and a positive control. The negative (i.e., clean) control consisted of five replicates containing fine silica sand. Test organisms were exposed to the silica sand for the entire 10-day period. Survival data from the negative controls were used to assess performance of the test organisms. The positive control consisted of a dilution series of the reference toxicant potassium chloride and a 96-hour exposure period. Following the exposure period, the number of surviving organisms was counted and the 96-hour LC<sub>50</sub> calculated. Data from the positive controls were used to assess the sensitivity of test organisms.

At the conclusion of the 10-d exposure period, the sediments were carefully sieved and sorted. Final counts of total larvae recovered and surviving larvae were made. Surviving larvae from each replicate were transferred to pre-weighed aluminum pans and dried at 60°C for 24 hours for determination of total

dry weight. Larvae which had begun to pupate, were counted as survivors but were not included in the determination of dry weight. The larvae were weighed to an accuracy of 0.1 mg to obtain final dry weights. Mean individual dry weights were obtained by dividing the final dry weight of each replicate by the number of larvae weighed.

#### 2.4.5 Phase I Toxicity Identification Evaluations

Sediment found to be toxic on the basis of statistically significant mortality in either the *H. azteca* or *C. tentans* tests relative to mortality in background sediment was evaluated using modified Phase I TIE procedures described by Mount and Anderson-Carnahan (1988). The Phase I TIE was conducted using fresh sediment porewater, which was obtained from the 0.5-L bulk sediment sample by centrifugation at 4000 X g at 4°C for 45 minutes. Following centrifugation, the collected porewater was decanted into a clean glass container and stored at 4°C until used in testing.

To determine whether or not the toxicity observed in the whole sediment was due to metals, subsamples of porewater were treated with varying concentrations of the chelating agent ethylenediaminetetraacetate (EDTA). A 0.055 M stock solution of EDTA was prepared and added to a porewater sample in the following dilution series: 1 mL, 0.8 mL, 0.6 mL, 0.4 mL, 0.2 mL, 0.1 mL, 0.05 mL, 0.025 mL, and 0.0125 mL. Final test concentrations of EDTA were 1.86 g/L, 1.52 g/L, 1.16 g/L, 0.78 g/L, 0.39 g/L, 0.20 g/L, 0.1 g/L, 0.05 g/L, and 0.03 g/L. A porewater blank (i.e., a porewater subsample with no EDTA added) was also included with each dilution series.

Potential toxicity due to ammonia was evaluated using pH adjustments of a porewater subsample prior to toxicity testing. Ammonia exists in two forms: ionized ( $\text{NH}_4^+$ ) and un-ionized ( $\text{NH}_3$ ). Ammonia toxicity is due to the un-ionized form (U.S. EPA, 1985a). The portion of total ammonia in the un-ionized form is controlled primarily by pH and temperature (Emerson et al., 1975). Three aliquots (30 mL) of porewater were prepared. The first aliquot was adjusted to pH 7.5 using 0.12 and 0.012 N HCl (if the initial sample pH was above 7.5) or 0.1 and 0.01 N NaOH (if the initial sample pH was below 7.5). Caution was taken to minimize the volume of acid or base added to the test solution. One aliquot was adjusted to pH 6.5, and the third aliquot was adjusted to pH 8.5.

The test chambers were filled until the sample extended slightly above the edge of the container. After the test organisms were introduced (see below), the test containers were sealed with Parafilm<sup>®</sup>. Parafilm<sup>®</sup> was used to minimize shifts in pH due to the adsorption and desorption of  $\text{CO}_2$  from air. Care was taken to prevent loss of test organisms and to achieve zero headspace in the chamber.

## 3.0 RESULTS

### 3.1 Conventional Sediment Characteristics

Grande-Ile sediment characteristics (e.g., color, odor, and layering) were noted in the field based on visual inspection, while partial sediment grain size distribution and TOC were determined in the laboratory. A description of the collected sediment samples, based on a visual description of sediment cores collected at each station, is compiled in Table 3.1.

The depth of the unconsolidated layer of surface sediment (i.e., sediment overlaying the gray clay prevalent in the area) ranged from 4 to 60 cm. Sediment from the unconsolidated layer was characterized as predominated by either silt or sand. Most of the sediment cores also had evidence of biological activity, such as aquatic vegetation, shell fragments, and benthic fauna. Exceptions were the samples collected from the northwest end of Clark Island (i.e., pyrite cinders from Priority Zone I), in which the sediment was characterized as being silty, and red in color with little evidence of biological activity (see Stations SE-93-86T and SE-93-87T).

Results of the laboratory analyses for sediment grain size and TOC are presented in Table 3.2. The TOC content of the samples ranged from 0.20 to 12.47 percent. Sediment organic carbon content was between 4.41 and 12.47 percent for the area between Stations SE-93-02T and SE-93-12T. These measurements are comparable to the values obtained during the February 1993 sampling (Tecsult, 1993a). For all other stations, including the two located along the northwest shoreline of Clark Island, TOC ranged from 0.2 to 0.9, percent which is comparable to values measured during the February 1993 sampling (Tecsult, 1993b).

Based on the field descriptions and the interpretation of the geotechnical test results, sediment collected in this study can be divided in three categories:

- Pyrite cinders (Priority Zone I)
- Fine sediments (Priority Zone II)
- Coarse sediments (Priority Zone II)

Table 3.2 Partial grain size and total organic carbon characteristics of sediment collected from the Grande-Ile shoreline.

Station No.	Water Depth (m)	River Bottom Elevation (m)	Grain Size (%)			Total Organic Carbon %
			Clay + Silt (<80 $\mu$ m)	Sand (<5 mm & >80 $\mu$ m)	Gravel (>5 mm)	
SE-93-02T	1.45	45.05	90.5	9.5	0.0	12.47
SE-93-03T	1.40	45.10	87.7	12.3	0.0	8.77
SE-93-06T	1.40	45.10	91.8	8.2	0.0	6.55
SE-93-09T	1.45	45.05	83.2	16.8	0.0	5.89
SE-93-11T	1.40	45.10	88.2	11.8	0.0	6.17
SE-93-12T	1.40	45.10	36.6	63.4	0.0	4.41
SE-93-14T	1.50	45.00	8.7	91.3	0.0	0.32
SE-93-18T	1.30	45.20	2.5	97.5	0.0	0.32
SE-93-20T	1.30	45.20	8.0	92.0	0.0	0.52
SE-93-25T	1.30	45.20	6.4	88.5	5.1	0.20
SE-93-27T	1.45	45.05	4.8	94.4	0.8	0.26
SE-93-28T	1.20	45.30	10.3	89.7	0.0	0.26
SE-93-31T	1.50	45.00	73.5	26.5	0.0	2.1
SE-93-33T	1.30	45.20	65.8	34.2	0.0	0.65
SE-93-36T	1.45	45.05	68.5	31.5	0.0	0.43
SE-93-38T	1.50	45.00	79.1	20.4	0.5	0.62
SE-93-41T	1.50	45.00	66.3	33.7	0.0	0.41
SE-93-42T	1.45	45.05	88.1	11.9	1.2	0.26
SE-93-45T	1.50	45.00	50.9	48.0	1.1	0.9
SE-93-86T	1.10	45.40	64.7	35.3	0.0	0.74
SE-93-87T	0.90	45.60	80.3	19.7	0.0	0.57
SE-93-90T	ND	ND	46.1	16.0	37.9	0.85
SE-93-91T	1.30	45.20	23.4	69.0	7.6	0.28

## 3.2 Bulk Sediment Metals

As previously mentioned, all sediment samples (i.e., 23 surface samples and one subsurface sample) were analyzed for bulk concentrations of arsenic, cadmium, copper, mercury, and zinc. Analytical results are presented in Table 3.3. These results are comparable to those measured from the same sites in February 1993 (Tecsult, 1993b). The results of the internal QA/QC program implemented by ECO-CNFS laboratory on four samples are presented in Appendix A. The internal QA/QC results exhibited general agreement. To facilitate an assessment of sediment quality based on the presence of metal contamination, the Level 3 criteria proposed by MENVIQ were used to assess the significance of the measured sediment concentrations.

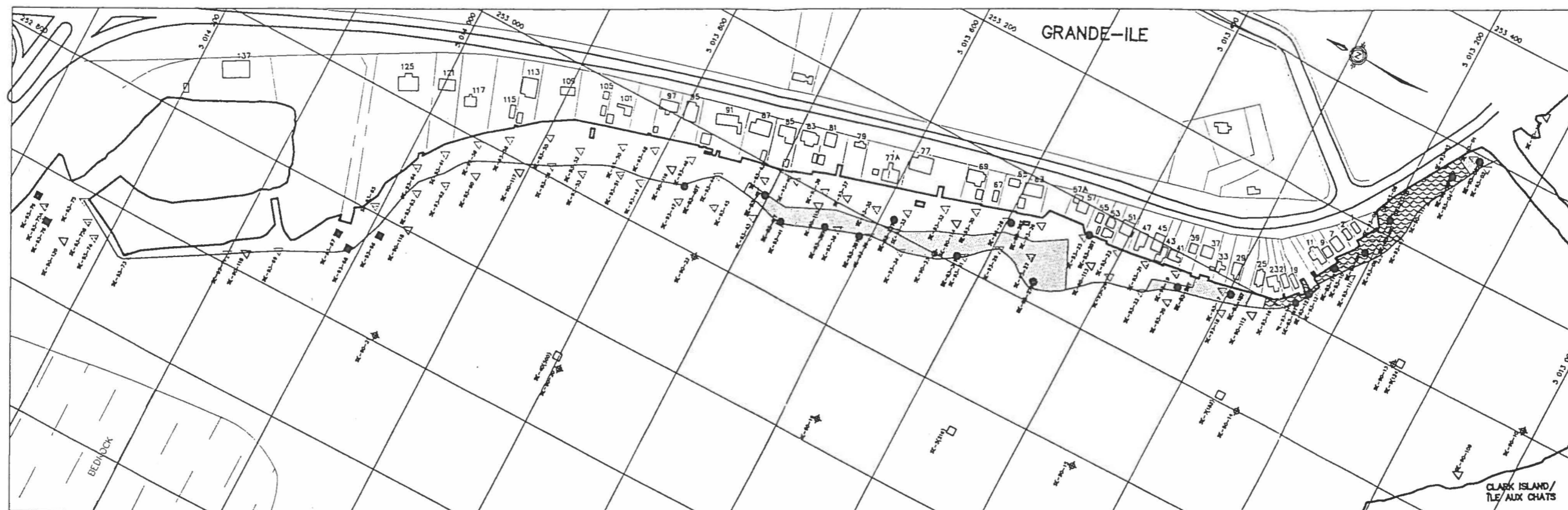
### 3.2.1 Arsenic

Arsenic concentrations along the Grande-Ile shoreline varied from 1.9 to 49 mg/kg, with an average concentration of 17.1 mg/kg. The highest arsenic concentration (i.e., 49.0 mg/kg) in Priority Zone II was found in Sample SE-93-09T (e.g., taken from the northeast portion of the bay near the causeway).


Arsenic was found above the MENVIQ Level 3 criterion of 17 mg/kg in 26 percent of the samples collected from the Grande-Ile shoreline. In addition, all Grande-Ile sediment samples contained arsenic in concentrations above the concentrations (i.e., 1.6 mg/kg and 1.8 mg/kg) observed in sediment collected from the background stations (i.e., Stations SE-93-90T and SE-93-91T). Eight stations found to exceed MENVIQ Level 3 criteria during the February 1993 sampling were found, in this study, to have As concentrations below the Level 3 criteria. Four of the stations are located in an area of recent sand deposition.


The extent of the surface area along Priority Zone II containing arsenic above the MENVIQ Level 3 criterion (i.e., 17 mg/kg) is illustrated in Figure 3.1 for both the February and October 1993 sampling events. It should be noted that the extent of arsenic contamination based on the October 1993 sampling event was less accurate than that represented by the February 1993 study because the number of stations sampled in October is about half the number of stations sampled in February.


In both samples collected from the pyrite cinder along the northwest shoreline of Clark Island (i.e., Priority Zone 1), arsenic concentrations (55 and 67 mg/kg) exceeded the MENVIQ Level 3 criterion.





LEGEND / LÉGENDE :


 ARSENIC CONCENTRATION ABOVE MENVQ LEVEL 3 CRITERION (FEBRUARY 1993)


 ARSENIC CONCENTRATION ABOVE MENVQ LEVEL 3 CRITERION (OCTOBER 1993)


SE-9(124)  SURFACE SEDIMENTS SAMPLING STATION / STATION D'ÉCHANTILLONNAGE DES SÉDIMENTS DE SURFACE (JANUARY / JANVIER 1988)

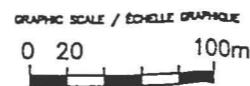
SE-90-13  SEDIMENTS BOREHOLE / FORAGE AU TRAVERS DES SÉDIMENTS (FEBRUARY / FÉVRIER 1990)

SE-90-112  SURFACE SEDIMENTS SAMPLING STATION / STATION D'ÉCHANTILLONNAGE DES SÉDIMENTS DE SURFACE (JUNE / JUIN 1990)

SE-93-66  SAMPLING STATION WHERE NO SEDIMENTS WERE RECOVERED / STATION D'ÉCHANTILLONNAGE DES SÉDIMENTS DE SURFACE SANS RÉCUPÉRATION (FEBRUARY / FÉVRIER 1993)

SE-93-01  SURFACE SEDIMENTS SAMPLING STATION / STATION D'ÉCHANTILLONNAGE DES SÉDIMENTS DE SURFACE (FEBRUARY / FÉVRIER 1993)

SE-93-02T  SURFACE SEDIMENTS SAMPLING STATION WITH TOXICITY TEST / STATION D'ÉCHANTILLONNAGE DES SÉDIMENTS DE SURFACE AVEC ANALYSE DE TOXICITÉ (OCTOBER / OCTOBRE 1993)



 **Allied Signal**  
 ENGINEERED MATERIALS

EXTENT OF SEDIMENTS CONTAMINATION ALONG GRANDE-ILE SHORELINE ARSENIC

N° contrat / contract  
 4361-1000

Échelle / Scale  
 1 : 4000

Date  
 FEB. 1994

FIGURE : 3.1

### 3.2.2 Cadmium

Cadmium concentrations along the Grande-Ile shoreline ranged from 0.28 to 48 mg/kg, with an average concentration of 14.9 mg/kg. The highest cadmium concentration (48 mg/kg) in Priority Zone II was found near the causeway (i.e., Stations SE-93-02T and SE-93-03T). Cadmium was found above the MENVIQ Level 3 criterion of 3 mg/kg in 37 percent of the samples collected along the Grande-Ile shoreline. In addition, approximately 84 percent of the Grande-Ile sediment samples contained cadmium at concentrations above the concentrations (i.e., 1.9 and <0.03 mg/kg) observed in sediment collected from the background stations. Five stations found to exceed MENVIQ Level 3 criteria during the February 1993 sampling were found, in this study, to have Cd concentrations below the Level 3 criteria. All five stations are located in an area of recent sand deposition.

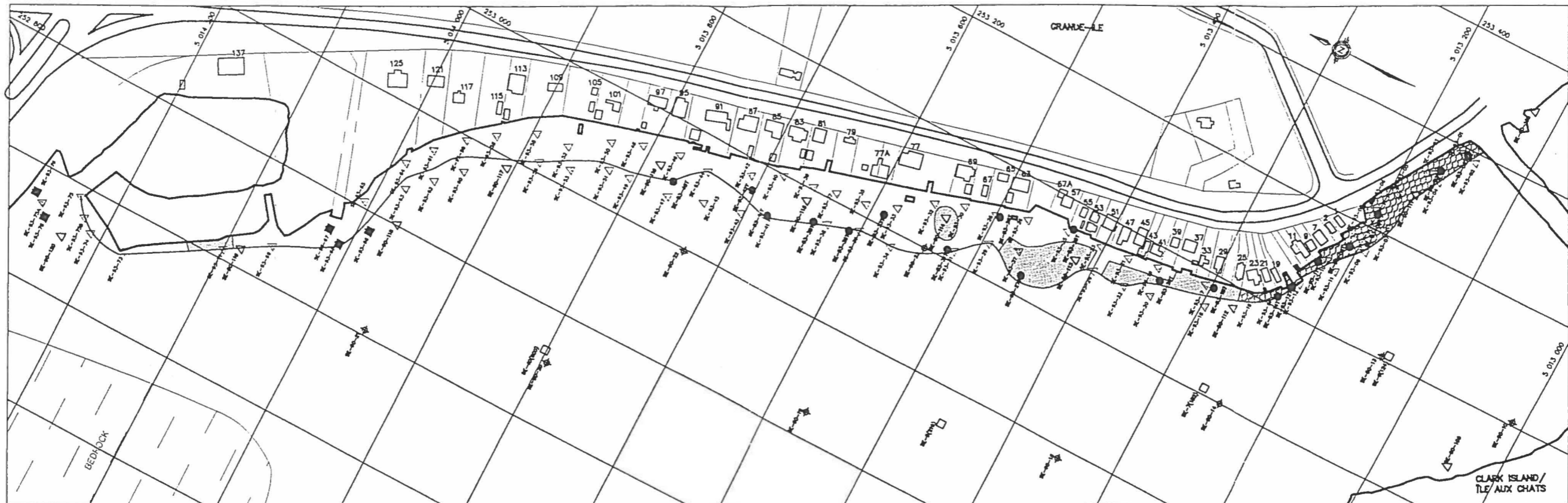
The extent of surface area along Priority Zone II containing cadmium above the MENVIQ Level 3 criterion (i.e., 3 mg/kg) is illustrated in Figure 3.2 for the February and October 1993 sampling events. It should be noted that the extent of cadmium contamination represented by the October 1993 data was probably less accurate than that represented by the February 1993 data since the number of stations sampled in October was about half the number of stations sampled in February.

In both pyrite cinder samples collected from the northwest shoreline of Clark Island (i.e., Priority Zone I), cadmium concentrations (24 and 27 mg/kg) exceed the MENVIQ Level 3 criterion.


### 3.2.3 Copper


Copper concentrations along Grande-Ile shoreline ranged from 7 to 341 mg/kg with an average concentration of 112.7 mg/kg. The highest copper concentration (341 mg/kg) in Priority Zone II was found near the causeway (i.e., Station SE-93-09T).


Copper was found above the MENVIQ Level 3 criterion of 86 mg/kg in 37 percent of the samples collected along the Grande-Ile shoreline. In addition, all but one station, Station SE-93-18T, had copper concentrations that were higher than the concentrations found at the background stations (i.e., 7 and 8 mg/kg). One station found to exceed MENVIQ Level 3 criteria during the February 1993 sampling was found, in this study, to have Cu concentrations below the Level 3 criteria. This station is located in an area of recent sand deposition.





LEGEND / LÉGENDE :


 CADMIUM CONCENTRATION ABOVE MENVIQ LEVEL 3 CRITERION (FEBRUARY 1993)


 CADMIUM CONCENTRATION ABOVE MENVIQ LEVEL 3 CRITERION (OCTOBER 1993)


SE-9(124)  SURFACE SEDIMENTS SAMPLING STATION / STATION D'ÉCHANTILLONNAGE DES SÉDIMENTS DE SURFACE (JANUARY / JANVIER 1988)

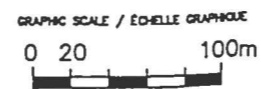
SE-90-13  SEDIMENTS BOREHOLE / FORAGE AU TRAVERS DES SÉDIMENTS (FEBRUARY / FÉVRIER 1990)

SE-90-112  SURFACE SEDIMENTS SAMPLING STATION / STATION D'ÉCHANTILLONNAGE DES SÉDIMENTS DE SURFACE (JUNE / JUIN 1990)

SE-93-66  SAMPLING STATION WHERE NO SEDIMENTS WERE RECOVERED / STATION D'ÉCHANTILLONNAGE DES SÉDIMENTS DE SURFACE SANS RÉCUPÉRATION (FEBRUARY / FÉVRIER 1993)

SE-93-01  SURFACE SEDIMENTS SAMPLING STATION / STATION D'ÉCHANTILLONNAGE DES SÉDIMENTS DE SURFACE (FEBRUARY / FÉVRIER 1993)

SE-93-02T  SURFACE SEDIMENTS SAMPLING STATION WITH TOXICITY TEST / STATION D'ÉCHANTILLONNAGE DES SÉDIMENTS DE SURFACE AVEC ANALYSE DE TOXICITÉ (OCTOBER / OCTOBRE 1993)



 **AlliedSignal**  
 ENGINEERED  
 MATERIALS

EXTENT OF SEDIMENTS  
 CONTAMINATION ALONG  
 GRANDE-ILE SHORELINE  
 CADMIUM

N° contrat / contract  
 4361-1000

Échelle / Scale  
 1:4000

Date  
 DEC. 1993

FIGURE : 3.2

The extent of the surface area along Priority Zone II containing copper above the MENVIQ Level 3 criterion (86 mg/kg) is illustrated in Figure 3.3 for both the February and October 1993 sampling events. As mentioned previously, the extent of copper contamination represented by the October 1993 data was probably less accurate than that represented by the February 1993 data, because the number of stations sampled in October was about half the number of stations sampled in February.

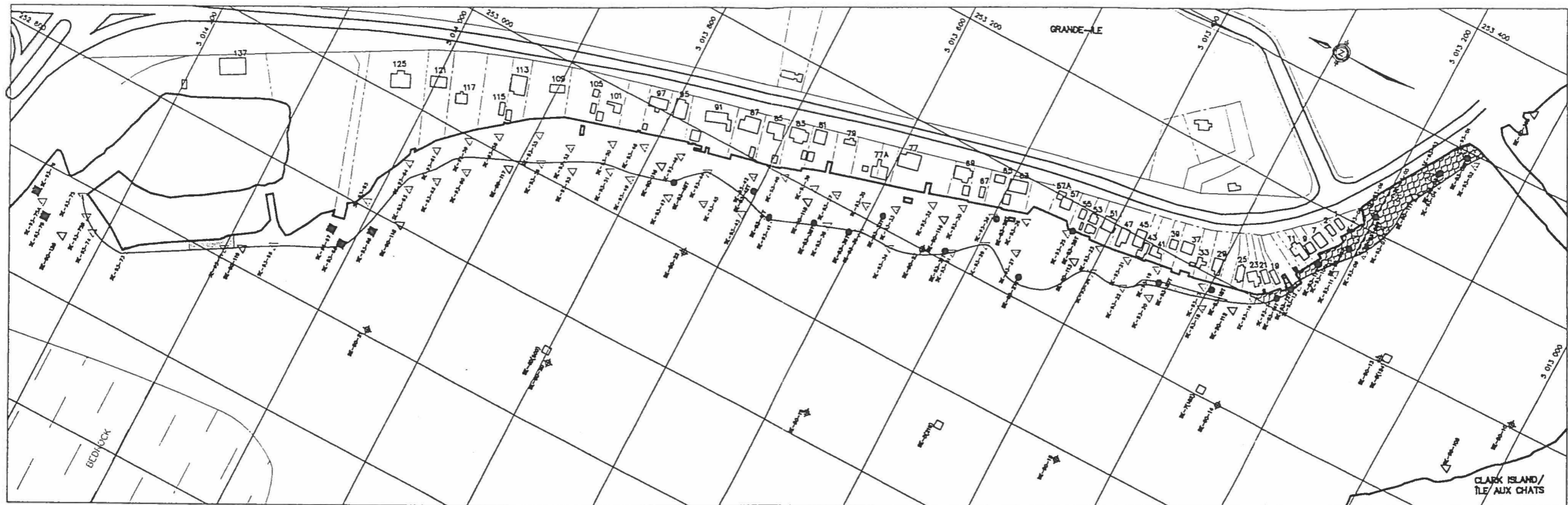
In both pyrite cinder samples collected along the northwest shoreline of Clark Island (i.e., Priority Zone I), copper concentrations (1,030 to 1,390 mg/kg) exceeded the MENVIQ Level 3 criterion.

#### 3.2.4 Mercury


Mercury concentrations along Grande-Ile shoreline (i.e., Priority Zone II) varied from 0.02 to 71.7 mg/kg, with an average concentration of 4.6 mg/kg. The highest mercury concentration (i.e., 71.7 mg/kg) in Priority Zone II was found at Station SE-93-45T, located along the northern portion of Grande-Ile shoreline. This value is not comparable the February 1993 value (0.59 mg/kg). There is no explanation for this high concentration since no recent industrial activity on Clark Island has involved mercury, and no effluent was directed into the river. With the exception of the high concentration observed at Station SE-93-45T, mercury concentrations range from 0.02 to 3.73 mg/kg with an average concentration of 1.06 mg/kg.


Mercury was found above the MENVIQ Level 3 criterion of 1 mg/kg in 37 percent of the samples. In addition, approximately 53 percent of the samples collected from the Grande-Ile shoreline had mercury concentrations above the concentrations (i.e., 0.1 mg/kg and 0.19 mg/kg) observed at the background stations. Three stations found to exceed MENVIQ Level 3 criteria during the February 1993 sampling had Hg concentrations below the Level 3 criteria. All three stations are located in an area of recent sand deposition.


The extent of the surface area along Priority Zone II containing mercury above the MENVIQ Level 3 criterion is illustrated in Figure 3.4 for both the February and October 1993 sampling events. It should be noted that the extent of mercury contamination represented by the October 1993 data was probably less accurate than that represented by the February 1993 data, because the number of stations sampled in October was about half the number of stations sampled in February.





LEGEND / LÉGENDE :


 COPPER CONCENTRATION ABOVE MENVIQ LEVEL 3 CRITERION (FEBRUARY 1993)


 COPPER CONCENTRATION ABOVE MENVIQ LEVEL 3 CRITERION (OCTOBER 1993)


SE-9(124)  SURFACE SEDIMENTS SAMPLING STATION / STATION D'ÉCHANTILLONNAGE DES SÉDIMENTS DE SURFACE (JANUARY / JANVIER 1988)

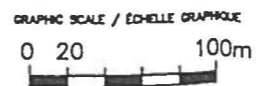
SE-90-13  SEDIMENTS BOREHOLE / FORAGE AU TRAVERS DES SÉDIMENTS (FEBRUARY / FÉVRIER 1990)

SE-90-112  SURFACE SEDIMENTS SAMPLING STATION / STATION D'ÉCHANTILLONNAGE DES SÉDIMENTS DE SURFACE (JUNE / JUIN 1990)

SE-93-66  SAMPLING STATION WHERE NO SEDIMENTS WERE RECOVERED / STATION D'ÉCHANTILLONNAGE DES SÉDIMENT DE SURFACE SANS RÉCUPÉRATION (FEBRUARY / FÉVRIER 1993)

SE-93-01  SURFACE SEDIMENTS SAMPLING STATION / STATION D'ÉCHANTILLONNAGE DES SÉDIMENTS DE SURFACE (FEBRUARY / FÉVRIER 1993)

SE-93-02T  SURFACE SEDIMENTS SAMPLING STATION WITH TOXICITY TEST / STATION D'ÉCHANTILLONNAGE DES SÉDIMENTS DE SURFACE AVEC ANALYSE DE TOXICITÉ (OCTOBER / OCTOBRE 1993)



 **Allied Signal**  
 ENGINEERED MATERIALS

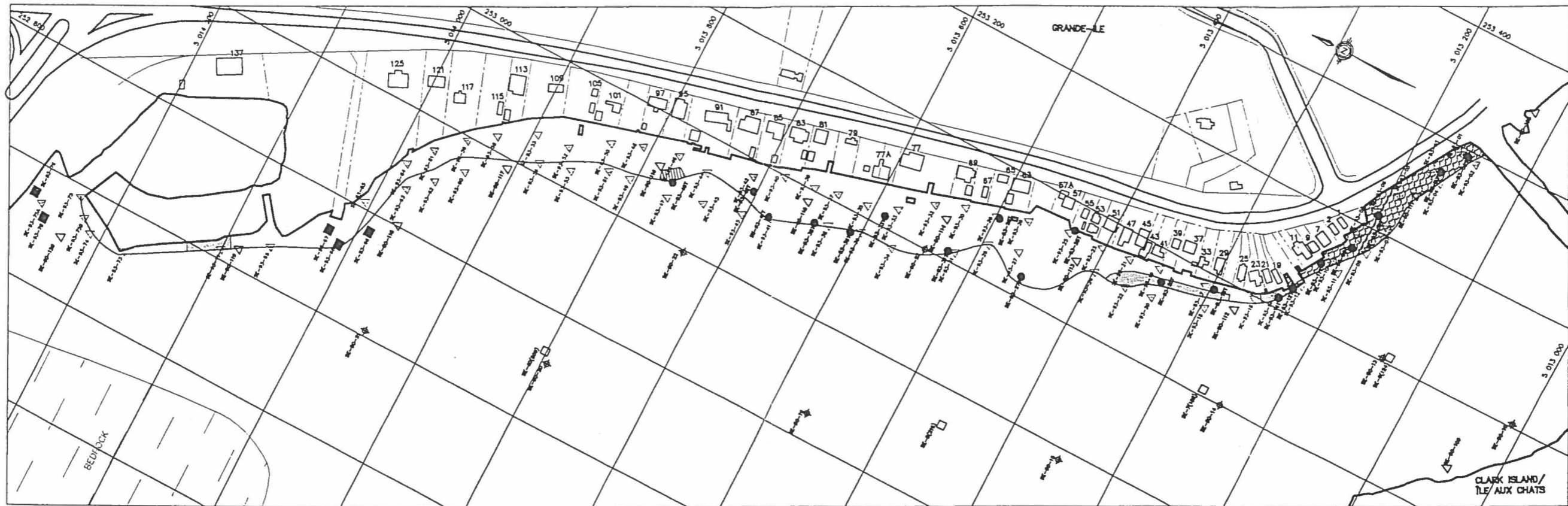
EXTENT OF SEDIMENTS CONTAMINATION ALONG GRANDE-ILE SHORELINE COPPER

N° contrat/contract  
4361-1000


Échelle / Scale  
1:4000


Date  
DEC. 1993


FIGURE : 3.3





LEGEND / LÉGENDE :


 MERCURY CONCENTRATION ABOVE MENVQ LEVEL 3 CRITERION (FEBRUARY 1993)


 MERCURY CONCENTRATION ABOVE MENVQ LEVEL 3 CRITERION (OCTOBER 1993)


SE-9(124)  SURFACE SEDIMENTS SAMPLING STATION / STATION D'ÉCHANTILLONNAGE DES SÉDIMENTS DE SURFACE (JANUARY/JANVIER 1988)

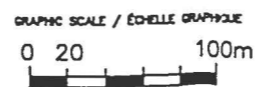
SE-90-13  SEDIMENTS BOREHOLE / FORAGE AU TRAVERS DES SÉDIMENTS (FEBRUARY/FÉVRIER 1990)

SE-90-112  SURFACE SEDIMENTS SAMPLING STATION / STATION D'ÉCHANTILLONNAGE DES SÉDIMENTS DE SURFACE (JUNE/JUIN 1990)

SE-93-66  SAMPLING STATION WHERE NO SEDIMENTS WERE RECOVERED / STATION D'ÉCHANTILLONNAGE DES SÉDIMENTS DE SURFACE SANS RÉCUPÉRATION (FEBRUARY/FÉVRIER 1993)

SE-93-01  SURFACE SEDIMENTS SAMPLING STATION / STATION D'ÉCHANTILLONNAGE DES SÉDIMENTS DE SURFACE (FEBRUARY/FÉVRIER 1993)

SE-93-02T  SURFACE SEDIMENTS SAMPLING STATION WITH TOXICITY TEST / STATION D'ÉCHANTILLONNAGE DES SÉDIMENTS DE SURFACE AVEC ANALYSE DE TOXICITÉ (OCTOBER / OCTOBRE 1993)



 **Allied Signal**  
 ENGINEERED MATERIALS

EXTENT OF SEDIMENTS CONTAMINATION ALONG GRANDE-ILE SHORELINE MERCURY

N° contrat/contract  
 4361-1000

Échelle / Scale  
 1:4000

Date  
 DEC. 1993

FIGURE : 3.4

In both pyrite cinder samples collected from the northwest shoreline of Clark Island (i.e., Priority Zone I), mercury concentrations (10.3 and 11.7 mg/kg) exceeded the MENVIQ Level 3 criterion.

### 3.2.5 Zinc

Zinc concentrations along Grande-Ile shoreline (i.e., Priority Zone II) ranged from 229 to 13,000 mg/kg, with an average concentration of 4,092 mg/kg. The highest zinc concentration (i.e., 13,000 mg/kg) in Priority Zone II was found near the causeway (i.e., Station SE-93-02T). Zinc was found above the MENVIQ Level 3 criterion of 540 mg/kg in 79 percent of the samples collected along the Grande-Ile shoreline. In addition, all of the samples exhibited zinc concentrations above background values (i.e., 79 and 52 mg/kg). At five stations, zinc levels dropped from above the MENVIQ Level 3 criterion in February 1993 to below it in this study. All five of the stations are located in an area of recent sand deposition.

The extent of the surface area along Priority Zone II containing Zn above the MENVIQ Level 3 criterion is illustrated in Figure 3.5 for both the February and October 1993 sampling events. It should be noted that the extent of zinc contamination represented by the October 1993 data was probably less accurate than that represented by the February 1993 data, because the number of stations sampled in October was about half the number of stations sampled in February.

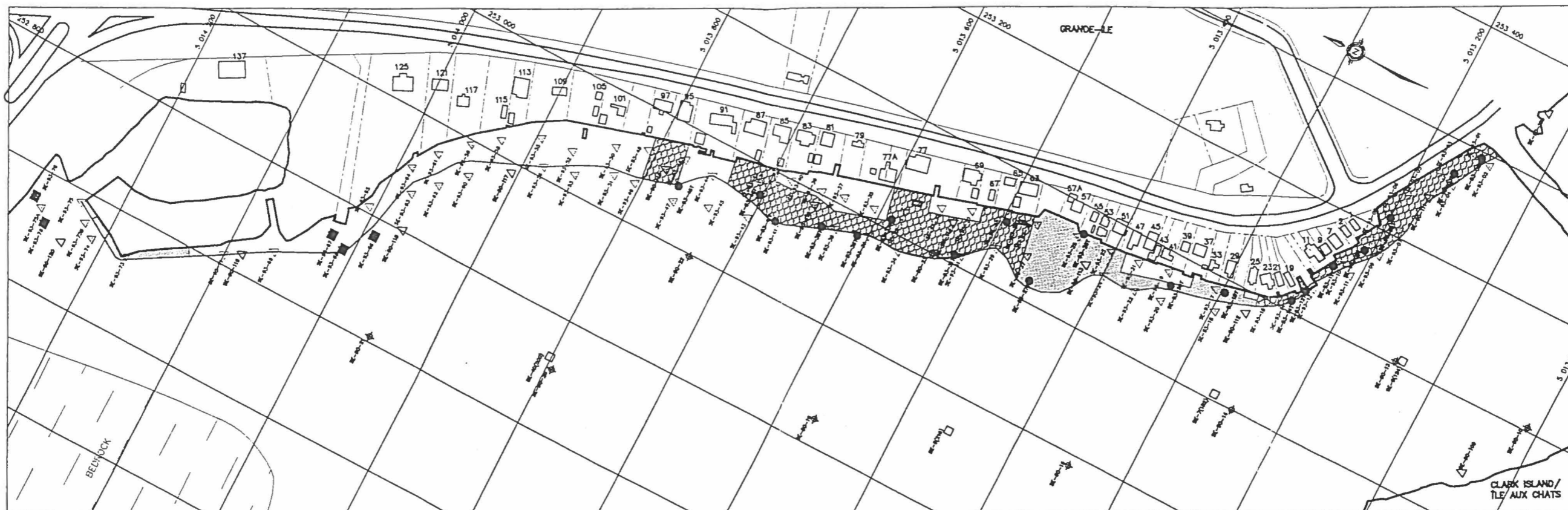
In both pyrite cinder samples collected from the northwest shoreline of Clark Island (i.e., Priority Zone I), zinc concentrations (4,140 to 4,220 mg/kg) exceeded the MENVIQ Level 3 criterion.

### 3.3 SEM and AVS Concentrations


The 23 sediment samples were analyzed to determine the concentration of SEM and AVS. Results of these analyses are presented in Table 3.4. Data are presented on the molar concentrations of the four metals (cadmium, copper, mercury, and zinc) and AVS. The ratio of  $\sum$ SEM (for the four metals analyzed) to AVS is also presented.


The results of the internal QA/QC program implemented by McGill University, and the external QA/QC program by INRS (Scientific National Research Institute) are presented in Appendix A. For the external QA/QC program, field duplicates, and not split samples, were submitted to the two laboratories.


This approach was taken because AVS measurements should be performed on sediment that has not been exposed to ambient air and splitting samples would have exposed the sediment to ambient air. Within the





LEGEND / LÉGENDE :


 ZINC CONCENTRATION ABOVE MENVIQ LEVEL 3 CRITERION (FEBRUARY 1993)


 ZINC CONCENTRATION ABOVE MENVIQ LEVEL 3 CRITERION (OCTOBER 1993)


SE-9(124)  SURFACE SEDIMENTS SAMPLING STATION / STATION D'ÉCHANTILLONNAGE DES SÉDIMENTS DE SURFACE (JANUARY / JANVIER 1988)

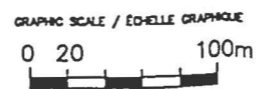
SE-90-13  SEDIMENTS BOREHOLE / FORAGE AU TRAVERS DES SÉDIMENTS (FEBRUARY / FÉVRIER 1990)

SE-90-112  SURFACE SEDIMENTS SAMPLING STATION / STATION D'ÉCHANTILLONNAGE DES SÉDIMENTS DE SURFACE (JUNE / JUIN 1990)

SE-93-66  SAMPLING STATION WHERE NO SEDIMENTS WERE RECOVERED / STATION D'ÉCHANTILLONNAGE DES SÉDIMENT DE SURFACE SANS RÉCUPÉRATION (FEBRUARY / FÉVRIER 1993)

SE-93-01  SURFACE SEDIMENTS SAMPLING STATION / STATION D'ÉCHANTILLONNAGE DES SÉDIMENTS DE SURFACE (FEBRUARY / FÉVRIER 1993)

SE-93-02T  SURFACE SEDIMENTS SAMPLING STATION WITH TOXICITY TEST / STATION D'ÉCHANTILLONNAGE DES SÉDIMENTS DE SURFACE AVEC ANALYSE DE TOXICITÉ (OCTOBER / OCTOBRE 1993)



 **Allied Signal**  
**ENGINEERED MATERIALS**

EXTENT OF SEDIMENTS CONTAMINATION ALONG GRANDE-ILE SHORELINE ZINC

N° contrat / contract  
4361-1000

Échelle / Scale  
1:4000

Date  
DEC. 1993

FIGURE : 3.5

4361-F35(1e93)

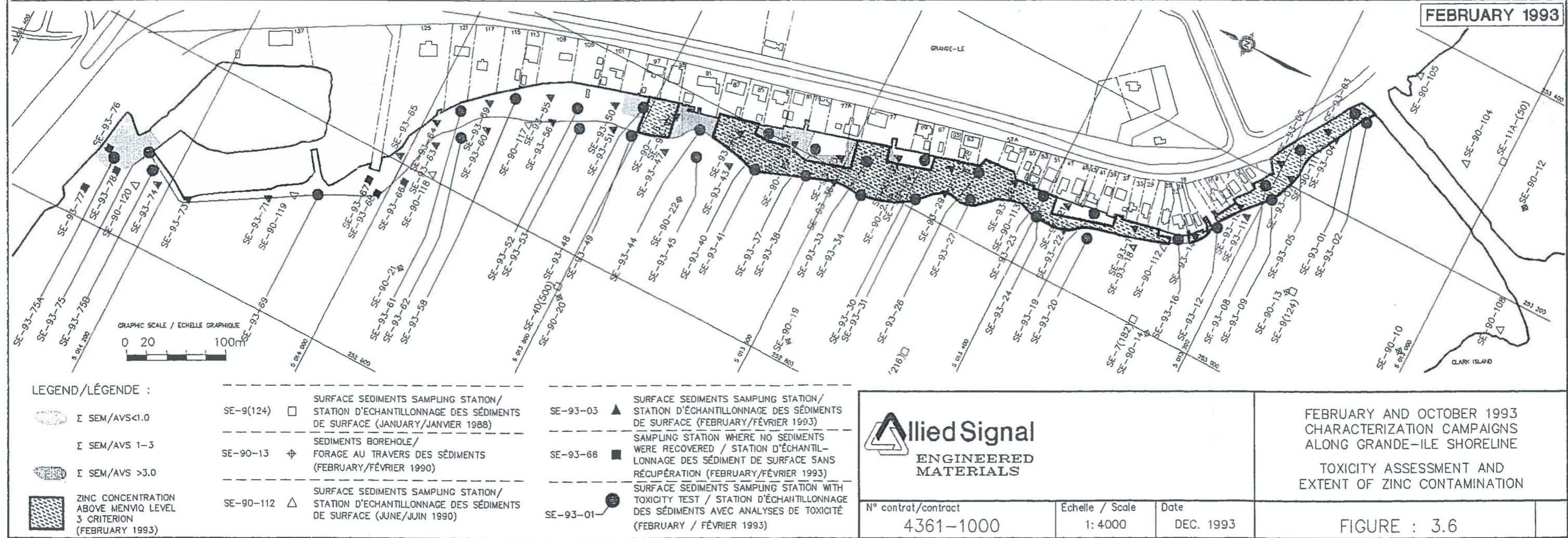
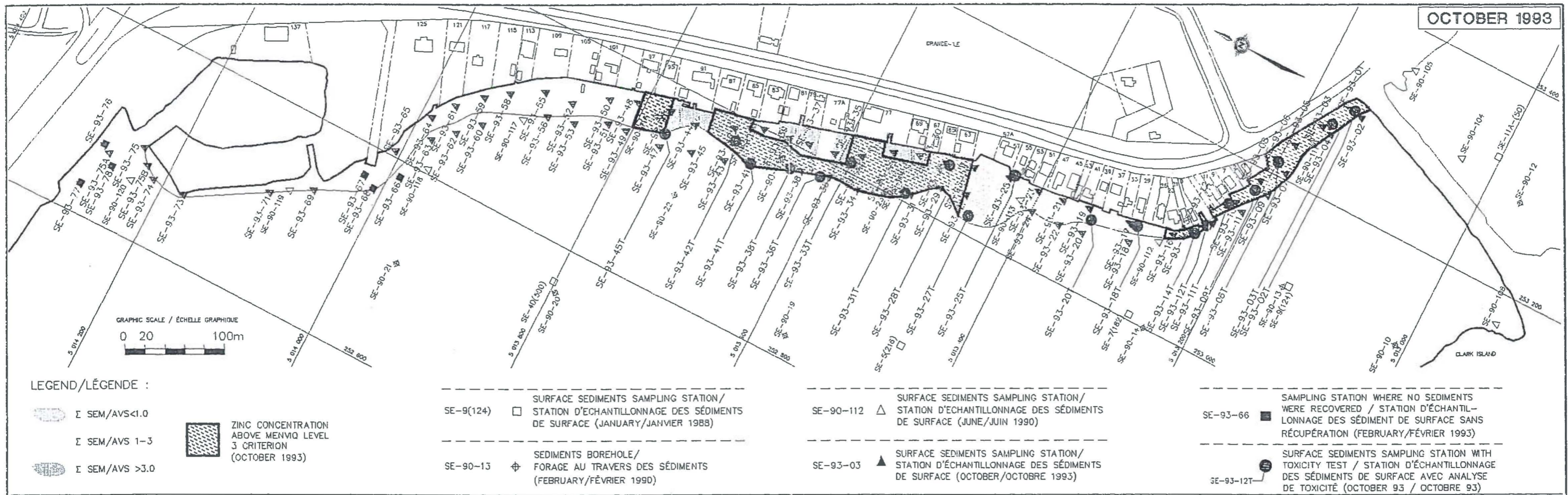
Table 3.4 Results of simultaneously extracted metals (SEM) and acid volatile sulfide (AVS) analysis on sediment collected from the Grande-Ile shoreline.

Sample No.	Water Depth (m)	River Bottom Elevation (m)	Simultaneously Extracted Metals ( $\mu\text{mole/g}$ )					Acid Volatile Sulfides ( $\mu\text{mole/g}$ )	$\Sigma\text{SEM} / \text{AVS}$
			SEM[Cd]	SEM[Cu]	SEM[Hg] <sup>a</sup>	SEM[Zn]	$\Sigma\text{SEM}^b$		
SE-93-02T	1.45	45.05	0.634	8.791	<0.0001	279.611	289.04	147.10	1.96
SE-93-03T	1.40	45.10	0.603	4.522	<0.0001	218.998	224.12	96.69	2.32
SE-93-06T	1.40	45.10	0.355	2.556	<0.0001	116.969	119.88	40.86	2.93
SE-93-09T	1.45	45.05	0.493	3.662	<0.0001	164.603	168.76	92.64	1.82
SE-93-11T	1.40	45.10	0.387	2.512	<0.0001	141.558	144.46	78.54	1.84
SE-93-12T	1.40	45.10	0.275	1.439	<0.0001	93.506	95.22	60.64	1.57
SE-93-14T	1.50	45.00	0.010	0.020	<0.0001	4.259	4.29	2.12	2.02
SE-93-18T	1.30	45.20	0.022	0.029	<0.0001	1.301	1.35	3.28	0.41
SE-93-20T	1.30	45.20	0.064	0.178	<0.0001	7.541	7.78	7.14	1.09
SE-93-25T	1.30	45.20	0.030	0.062	<0.0001	4.721	4.81	8.61	0.56
SE-93-27T	1.45	45.05	0.032	0.115	<0.0001	2.743	2.89	7.33	0.39
SE-93-28T	1.20	45.30	0.012	0.068	<0.0001	10.575	10.66	5.80	1.84
SE-93-31T	1.50	45.00	0.061	0.476	<0.0001	37.496	38.03	6.24	6.10
SE-93-33T	1.30	45.20	0.011	0.289	<0.0001	45.411	45.71	7.08	6.46
SE-93-36T	1.45	45.05	0.024	0.385	<0.0001	18.344	18.75	11.07	1.69
SE-93-38T	1.50	45.00	0.037	0.432	<0.0001	40.947	41.42	12.07	3.43
SE-93-41T	1.50	45.00	0.035	0.357	<0.0001	0.002	0.39	7.70	0.05
SE-93-42T	1.45	45.05	0.022	0.511	<0.0001	21.707	22.24	4.99	4.46
SE-93-45T	1.50	45.00	0.018	0.332	<0.0001	28.441	28.79	4.46	6.46
SE-93-86T	1.10	45.40	0.049	3.600	<0.0001	11.903	15.55	6.74	2.31
SE-93-87T	0.90	45.60	0.084	3.526	0.0174	33.843	37.47	0.30	125.32
SE-93-90T	ND	ND	0.044	0.121	<0.0001	1.197	1.36	1.47	0.93
SE-93-91T	1.30	45.20	0.001	1.928	<0.0001	0.767	2.70	3.74	0.72

<sup>a</sup> A value of one-half of the detection limit was used to calculate  $\Sigma\text{SEM}$  when Hg was not detected

<sup>b</sup>  $\Sigma\text{SEM}$  = Sum of SEM[Cd], SEM[Cu], SEM[Hg], and SEM[Zn].

ND Not Determined



N° contrat/contract 4361-1000  
Echelle / Scale 1:4000  
Date DEC. 1993

FEBRUARY AND OCTOBER 1993  
CHARACTERIZATION CAMPAIGNS  
ALONG GRANDE-ILE SHORELINE  
TOXICITY ASSESSMENT AND  
EXTENT OF ZINC CONTAMINATION

FIGURE : 3.6

- Background Station SE-93-91T (predominantly coarse particles)

SE-93-12T      SE-93-20T      SE-93-28T

SE-93-14T      SE-93-25T

SE-93-18T      SE-93-27T

Bioassay test results are expressed as the mean of five replicate exposures.

#### 3.4.1 *Hyalella azteca*

*Hyalella azteca* survival was significantly reduced at nine of the 21 sample stations relative to the background (Table 3.5). The spatial distribution of test responses is shown in Figures 3.7 and 3.9. Stations exhibiting statistically significant responses were clustered in two areas. Three stations, SE-93-02T, SE-9-09T, and SE-93-11T, were located in the area just north of the causeway and three stations, SE-93-25T, SE-93-27T, and SE-93-31T, were located in the middle of the Priority Zone II study area. A single station (i.e., SE-93-45T) located at the northern end of the study area also exhibited toxicity. In addition, the two stations (i.e., SE-93-86T, and SE-93-87T) located in Priority Zone I (pyrite cinders) were toxic relative to the background stations. Mean mortality from all stations ranged from 0 to 96 percent. Samples from stations located in the pyrite cinders produced the highest mortalities (i.e., 90 and 96 percent). Observed mortality was much lower for the sites within the Priority Zone II (i.e., 0 to 66 percent).

#### 3.4.2 *Chironomus tentans*

Chironomid survival was significantly reduced at four of the 21 stations relative to the background stations (Table 3.5). The spatial distribution of test responses is shown in Figures 3.8 and 3.9. Three of the stations, SE-93-31T, SE-93-36T, and SE-93-41T, considered to be toxic were found in the northern end of the Priority Zone II study area. A single station (i.e., Station SE-93-06T) was located in the area just north of the causeway. Mean chironomid mortality from all stations ranged from 2 to 36 percent. Because of the relatively low mean mortality at the stations determined to be statistically different from background, further analysis was conducted on the chironomid data.

An ANOVA was conducted on the data to determine if all the stations were considered to represent the same statistical population. This procedure was undertaken because the data suggested that the identified

Table 3.5 Responses measured in *Hyalella azteca* and *Chironomus tentans* bioassays.

Station No.	<i>Hyalella azteca</i>		<i>Chironomus tentans</i>	
	Percent Mortality <sup>a</sup>	Toxic <sup>b</sup>	Percent Mortality <sup>a</sup>	Toxic <sup>b</sup>
SE-93-02T	60 (±10)	✓	14 (±6.7)	
SE-93-03T	10 (±10)		12 (±8.3)	
SE-93-06T	26 (±29)		36 (±11)	✓
SE-93-09T	42 (±27)	✓	2 (±4.5)	
SE-93-11T	66 (±24)	✓	14 (±17)	
SE-93-12T	8 (±11)		6 (±5.5)	
SE-93-14T	0 (±0)		14 (±9)	
SE-93-18T	10 (±7)		10 (±12)	
SE-93-20T	4 (±5.5)		6 (±9)	
SE-93-25T	30 (±14)	✓	4 (±5.5)	
SE-93-27T	48 (±22)	✓	6 (±9)	
SE-93-28T	16 (±17)		10 (±14)	
SE-93-31T	34 (±28)	✓	14 (±5.5)	✓
SE-93-33T	12 (±16)		6 (±9)	
SE-93-36T	0 (±0)		22 (±8)	✓
SE-93-38T	0 (±0)		14 (±21)	
SE-93-41T	12 (±8)		20 (±7)	✓
SE-93-42T	4 (±5.5)		10 (±10)	
SE-93-45T	36 (±23)	✓	2 (±4.5)	
SE-93-86T	96 (±5.5)	✓	10 (±10)	
SE-93-87T	90 (±22)	✓	8 (±15)	
Background Stations				
SE-93-90T	6 (±5.5)		6 (±5.5)	
SE-93-91T	6 (±5.5)		8 (±13)	

<sup>a</sup> Mean of five replicate exposures.

<sup>b</sup> Stations noted as toxic had statistically significant increases in percent mortality compared to background as determined by a *t*-test at the  $\alpha=0.05$  level.

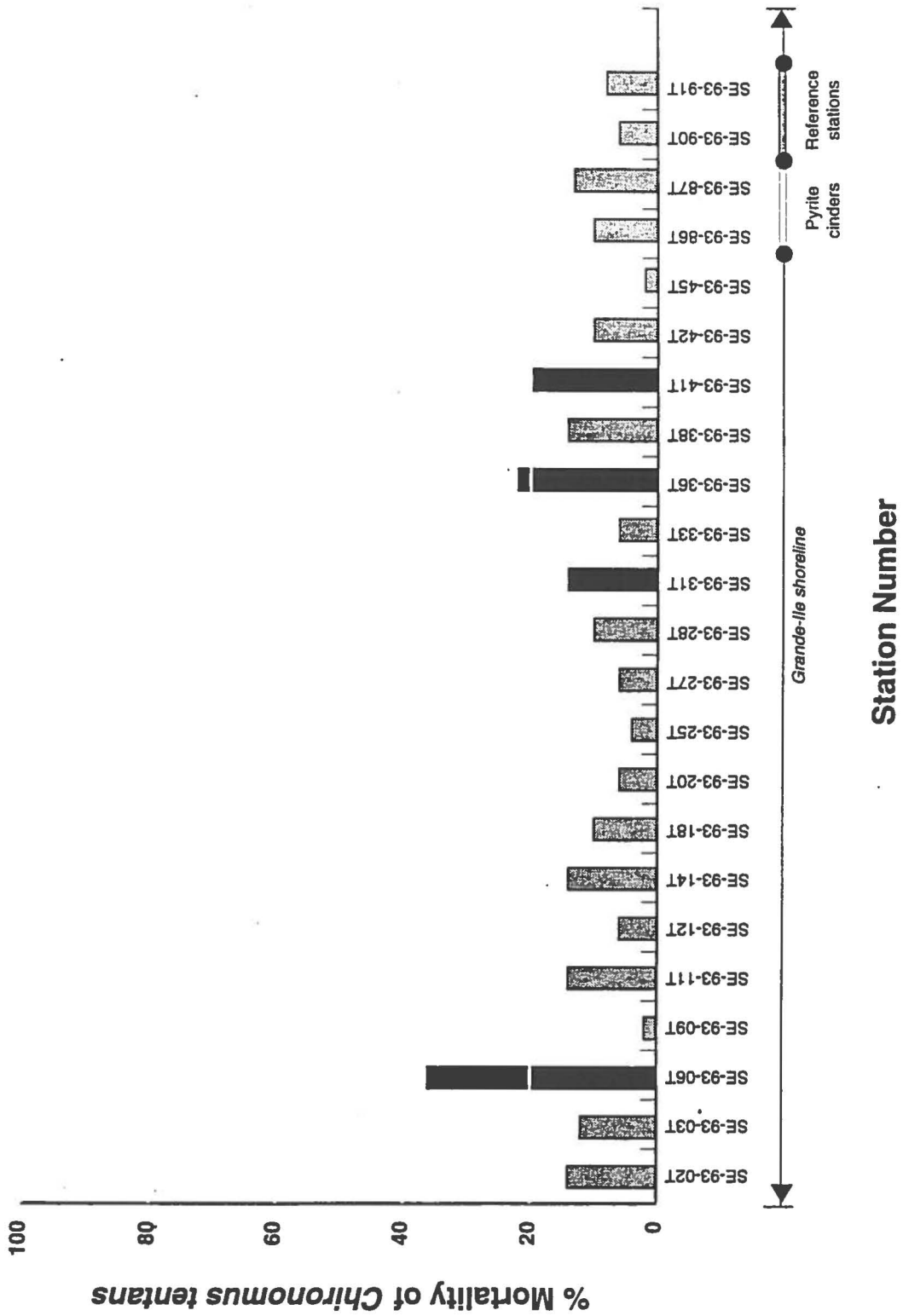


Figure 3.8 Spatial distribution of response in *Chironomus tentans* bioassay.

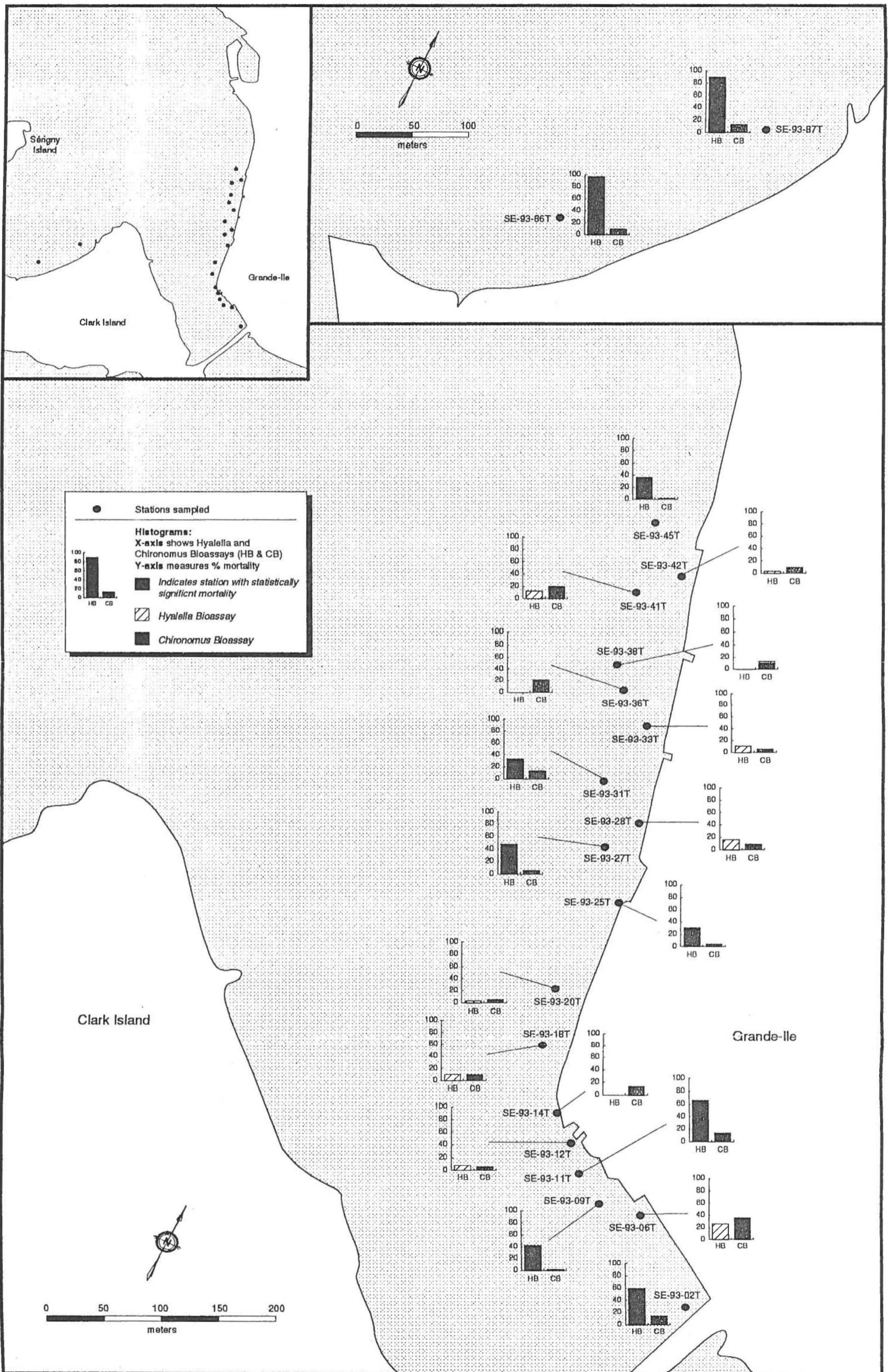


Figure 3.9 Spatial distribution of sediment toxicity in Priority Zone II.

differences may have been statistical artifacts due to the low variance observed in mortality of the replicate exposures at the background stations. The results of the ANOVA conducted on the complete chironomid data set indicated that the sample population was statistically different at the  $\alpha = 0.05$  level. An *a posteriori* analysis was performed using Fisher's LSD test to identify which station (or stations) were different. Analysis indicated that Station SE-93-06T was the only station with mortality statistically different from the sample population as a whole. Additional analysis was done on the data set after omitting Station SE-93-06T, which had the highest mean mortality at 36 percent. In this case, the ANOVA indicated that there was no statistical difference in the sample population at the  $\alpha = 0.05$  level. This analysis indicates that only Station SE-93-06T caused significant mortality to *C. tentans* relative to background.

Larval growth ranged from 242 percent for Station SE-93-87T to 987 percent for Station SE-93-14T (Table 3.6). Statistical analysis indicates the mean percent weight gain at twelve (12) stations was significantly reduced compared to the background. However, growth was equal or significantly greater at all but a single station relative to growth measured in the control exposures (i.e., clean silica sand) (Table 3.7). Further statistical analysis was undertaken to compare growth in the samples with the appropriate control growth. To be conservative, sample stations were compared with the lower of the two control growth rates with the same test date. This analysis indicated that only Station SE-93-87T had growth rates significantly lower than those measured in the control exposures (see Table 3.7).

### 3.4.3 Toxicity Identification Evaluation

TIE procedures were conducted on sediment porewater from the 12 stations identified as toxic by either the *H. azteca* or *C. tentans* bioassay. Porewater from only Station SE-93-31T was toxic to *Ceriodaphnia dubia* (Table 3.8). The EDTA manipulation on the sample from Station SE-93-31T showed a reduction in toxicity at higher EDTA additions, indicating the toxicity was due to cationic metals (Table 3.9). For samples not exhibiting porewater toxicity, mortality was observed at the highest concentrations of EDTA. This is consistent with the expected response as the range of EDTA additions used in the TIE brackets the  $LC_{50}$  of EDTA (0.41 g/L) for *C. dubia*. This pattern (toxicity at highest EDTA concentrations) was not observed in five of the manipulations (i.e., samples from Stations SE-93-06T, SE-93-31T, SE-93-36T, SE-93-41T, and SE-93-86T) and is most likely the result of interference due to the hardness (i.e., the  $Mg^{++}$  and  $Ca^{++}$  concentrations) of the porewater sample. This interference did not affect the evaluation of the porewater in that four of the sites had no toxicity in the untreated porewater. The fifth sample, SE-93-31T, in which porewater was toxic, showed reduction and/or removal of toxicity at the highest EDTA additions, indicating that an adequate amount of EDTA was available to bind any toxic metals in the porewater.

Table 3.7 Larval growth for *Chironomus tentans* compared with controls.

Station No.	Test Date	Percent Weight Gain <sup>a</sup>	Reduced Relative To Control <sup>b</sup>
SE-93-87T	11/05/93	242 (NC)	✓
Control 1	11/02/93	326 (±50)	
SE-93-86T	11/02/93	430 (±42)	
Control 3	11/05/93	431 (±91)	
Control 4	11/05/93	462 (±15)	
SE-93-42T	11/02/93	483 (±59)	
Control 2	11/02/93	500 (±52)	
SE-93-31T	11/02/93	622 (±50)	
SE-93-36T	11/02/93	622 (±58)	
SE-93-45T	11/05/93	638 (±56)	
SE-93-38T	11/02/93	657 (±53)	
SE-93-09T	11/05/93	662 (±132)	
SE-93-33T	11/05/93	677 (±33)	
SE-93-02T	11/05/93	685 (±72)	
SE-93-91T	11/05/93	700 (±35)	
SE-93-12T	11/05/93	731 (±26)	
SE-93-06T	11/02/93	735 (±64)	
SE-93-25T	11/05/93	754 (±41)	
SE-93-41T	11/02/93	761 (±59)	
SE-93-18T	11/02/93	804 (±37)	
SE-93-20T	11/05/93	815 (±79)	
SE-93-11T	11/02/93	839 (±49)	
SE-93-03T	11/02/93	883 (±111)	
SE-93-90T	11/05/93	900 (±43)	
SE-93-28T	11/05/93	908 (±65)	
SE-93-27T	11/05/93	938 (±65)	
SE-93-14T	11/02/93	987 (±132)	

<sup>a</sup> Mean of five replicate exposures.

<sup>b</sup> Stations noted as reduced relative to control, are statistically significant reductions in growth relative to the appropriate control as determined by a *t*-test at the  $\alpha = 0.05$  level.

NC Standard deviation could not be determined.

Table 3.9 Results of EDTA chelation manipulations.

Station Number	Percent Survival of <i>Ceriodaphnia dubia</i> at 48 Hours									
	1.0 <sup>a</sup> (1.86 g/L)	0.8 (1.52 g/L)	0.6 (1.16 g/L)	0.4 (0.78 g/L)	0.2 (0.39 g/L)	0.1 (0.20 g/L)	0.05 (0.10 g/L)	0.025 (0.05 g/L)	0.0125 (0.03 g/L)	Blank
SE-93-02T	0% (6.95/8.1) <sup>b</sup>	0% (6.95/8.3)	0% (7.15/8.6)	100% (7.0/8.6)	100% (7.17/8.6)	100% (7.23/8.5)	100% (7.5/8.4)	100% (7.7/8.4)	100% (7.8/8.3)	100% (7.8/8.3)
SE-93-06T	100% (7.53/8.28)	100% (7.66/8.23)	100% (7.75/8.21)	100% (7.88/8.23)	100% (7.89/8.17)	100% (8.08/8.18)	100% (8.06/8.16)	100% (8.09/8.12)	100% (8.1/8.23)	100% (8.1/8.08)
SE-93-09T	0% (6.84/8.2)	0% (6.96/8.2)	0% (7.46/8.2)	100% (7.6/8.5)	100% (7.22/8.6)	100% (7.1/8.5)	100% (7.4/8.4)	100% (7.7/8.4)	100% (7.9/8.4)	100% (7.9/8.4)
SE-93-11T	0% (7.1/8.2)	0% (7.03/8.2)	0% (7.18/8.5)	100% (7.06/8.6)	100% (7.35/8.6)	100% (7.2/8.5)	100% (7.7/8.4)	100% (7.8/8.4)	100% (7.9/8.4)	100% (7.9/8.4)
SE-93-25T	NC	NC	NC	80% (6.55/8.4)	NC	NC	NC	NC	NC	100% (7.33/8.3)
SE-93-27T	0% (6.44/7.9)	NC	NC	100% (6.4/8.1)	NC	NC	NC	NC	NC	100% (7.8/8.3)
SE-93-31T	100% (7.54/8.14)	NC	60% (7.6/8.11)	20% (7.6/8.06)	40% (7.70/8.06)	NC	40% (7.70/8.02)	NC	NC	40% (7.90/8.0)
SE-93-36T	100% (7.36/8.29)	NC	100% (7.63/8.25)	100% (7.60/8.26)	100% (7.96/8.25)	100% (7.85/8.23)	100% (8.06/8.20)	NC	NC	100% (8.18/8.20)
SE-93-41T	100% (6.24/7.85)	NC	100% (6.75/7.97)	100% (7.0/8.04)	100% (7.10/8.11)	NC	100% (7.35/8.15)	NC	NC	100% (7.27/8.11)
SE-95-45T	0% (7.16/8.5)	NC	100% (7.24/8.7)	100% (6.95/8.6)	NC	100% (7.4/8.3)	NC	NC	NC	100% (8.0/8.3)
SE-93-86T	100% (7.20/8.4)	NC	100% (7.21/8.3)	100% (7.36/8.4)	100% (7.55/8.4)	100% (7.2/8.4)	100% (7.4/8.2)	NC	NC	100% (7.8/8.1)
SE-93-87T	0% (6.95/7.9)	NC	0% (6.65/7.9)	100% (7.2/8.4)	NC	100% (7.26/8.4)	100% (7.5/8.4)	NC	NC	100% (7.8/8.2)

<sup>a</sup> Milliliters of 0.055M EDTA added.

<sup>b</sup> Initial pH/final pH of test chamber.

NC Not conducted due to lack of sufficient volume of porewater.

Table 3.10 Results of graduated pH manipulations.

Station No.	Percent Survival at 48 Hours		
	pH 8.5	pH 7.5	pH 6.5
SE-93-02T	100% (8.5/8.0) <sup>a</sup>	100% (7.41/8.2)	100% (6.52/8.2)
SE-93-06T	100% (8.48/8.03)	100% (7.46/8.05)	100% (6.55/8.16)
SE-93-09T	100% (8.47/8.1)	100% (7.52/8.2)	100% (6.54/7.9)
SE-93-11T	100% (8.48/8.2)	100% (7.51/8.2)	100% (6.58/7.9)
SE-93-31T	60% (8.49/7.93)	60% (7.38/7.79)	50% (6.50/7.86)
SE-93-36T	100% (8.46/8.12)	80% (7.41/8.20)	100% (6.48/8.24)
SE-93-41T	100% (8.54/7.70)	100% (7.42/7.84)	80% (6.97/7.52)
SE-93-45T	100% (8.48/7.9)	100% (7.49/7.9)	100% (6.45/7.7)
SE-93-86T	100% (8.45/8.2)	100% (7.43/8.3)	100% (6.49/8.1)
SE-93-87T	0% (8.3/8.4)	100% (7.32/7.8)	100% (6.35/7.6)

<sup>a</sup> Initial pH/final pH of test chamber

### 3.5.2 Bulk Sediment Metals

Biological response data were correlated to the following bulk sediment metal concentrations: arsenic, cadmium, copper, mercury, zinc, and total metals. For the complete data set, statistically significant correlations existed between two biological responses and one metal (Table 3.13). *Hyaella* mortality and larval growth of *Chironomus* were significantly related to the bulk sediment concentrations of copper. No statistically significant correlations were found when comparing the biological response data to the data set containing only Priority Zone II and background area data (Table 3.14).

### 3.5.3 SEM/AVS

Biological response data were correlated to the SEM concentrations for cadmium, copper, mercury, zinc as well as  $\Sigma$ SEM, and the ratio of  $\Sigma$ SEM/AVS. For the complete data set, the best fit model for *Hyaella* mortality included simultaneously extracted copper, zinc, and the ratio of  $\Sigma$ SEM/AVS. Larval growth of *Chironomus* was found to be significantly correlated to the ratio of SEM/AVS (Table 3.15). No significant regressions were found in the comparisons based on the Priority Zone II and background area data (Table 3.16).

In order to investigate if sediment AVS is controlling metals bioavailability and therefore toxicity, *Hyaella* mortality was plotted against the  $\Sigma$ SEM/AVS ratio (Figure 3.10). Amphipod mortality was less than 10 percent when the ratio of  $\Sigma$ SEM/AVS was <1 at all but two stations (i.e., Stations SE-93-25T and SE-93-27T). Mortality at the stations where the  $\Sigma$ SEM/AVS ratio was >1 ranged from 0 to 96 percent.

Table 3.15 Partial correlation coefficients from stepwise multiple regression of biological responses and simultaneously extracted metals using the complete data set.

	Cd	Cu	Zn	$\Sigma$ SEM	SEM/AVS
<i>Hyalella azteca</i> Percent Mortality	0.254	<b>0.547</b>	<b>-0.472</b>	0.260	<b>0.462</b>
<i>Chironomus tentans</i> Percent Mortality	0.171	0.152	0.159	0.159	0.048
Larval Growth Percent Change	0.093	-0.277	0.029	0.021	<b>-0.626</b>

Shaded values are considered "best" fit at  $\alpha = 0.05$  (Systat, 1992).

Table 3.16 Partial correlation coefficients from stepwise multiple regression of biological responses and simultaneously extracted metals after omitting pyrite stations.

	Cd	Cu	Zn	$\Sigma$ SEM	SEM/AVS
<i>Hyalella azteca</i> Percent Mortality	-0.134	-0.148	-0.322	-0.145	-0.145
<i>Chironomus tentans</i> Percent Mortality	-0.087	-0.138	-0.271	-0.101	-0.102
Larval Growth Percent Change	0.021	-0.107	-0.179	-0.084	-0.084

Shaded values are considered "best" fit at  $\alpha = 0.05$  (Systat, 1992).

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## 4.0 DISCUSSION

### 4.1 General Site Conditions

Field observations of the physical characteristics of Priority Zone II sediment suggest that Grande-Ile sediment can be classified into three general areas based on sediment grain size and the presence of organic matter. One area, Area A, is located northwest of the Clark Island causeway, extending from Station SE-93-02T to Station SE-93-11T. This area is composed of fine surficial sediment that is black-brown in color and characterized by organic silts and some sand. In this area unconsolidated surficial sediment ranges from 25 to 60 cm in depth indicating that this is an active depositional zone. A second area, Area B, can be found farther up the shoreline, between Stations SE-93-12T and SE-93-28T. Sediment in this area is primarily sand with some silt, and is brown in color. A deep core collected at Station SE-93-14T indicates that the surficial sand overlays a silty layer. A comparison of geotechnical data from the February 1993 (Tecsult, 1993a) sampling and this study suggests that a sand layer has recently been deposited in the area between stations SE-93-12T and SE-93-28T. It is not known if the sand has been deposited by riverside residents or by natural sediment transport processes. The third area, Area C, includes Stations SE-93-31T to SE-93-45T, and is characterized by brown, sandy silt. The entire Priority Zone II is underlain by a consolidated gray clay layer.

A wide variety of biota naturally associated with sediment was observed in all three areas. All of Priority Zone II, as well as the entire bay between Clark Island and Grand-Ile, was densely vegetated by a variety of submerged macrophytes. The dominant type was wild celery, *Valissneria* sp.; *Elodea* sp. and several species of pondweed, *Potamogeton* sp. were also noted. The macrophyte beds were densest in Area A, just northwest of the causeway. Vegetation was sparser in the areas farther west along the shoreline, because the vegetation in those areas had already died back for the season.

The epibenthic community is typical of a vegetated area in that large numbers of gastropods were observed. Dense groups of leptocerid caddisflies were observed on most solid substrates, as were zebra mussels (*Dreissena polymorpha*). The infaunal benthic community included unionid mussels, consisting of at least two species, with the genus *Lampsilis* being the most common. Amphipods were also observed, often in high numbers (e.g., more than 10 observed in a 10-cm<sup>2</sup> area) in the sediment at some of the stations (e.g., SE-93-33T).

Overall, the general pattern observed in the Priority Zone II study area was that finer, organic-rich sediment tended to be found in the corner of the bay just west of the causeway (Area A). Circulation

### 4.3 Sediment Toxicity

The *Hyaella azteca* mortality test characterized seven Priority Zone II stations and two stations containing pyrite cinders (i.e., Priority Zone I) as having statistically significant toxicity. By contrast, only one station (i.e., Station SE-93-06T) was toxic on the basis of reduction in survival of *Chironomus tentans*. No significant reductions in larval growth were observed in *C. Tentans* exposed to Priority Zone II sediment. However, Station SE-93-87T, a Priority Zone I station, did exhibit reductions in growth. Although Station SE-93-06T sediment was found to be toxic, based on a statistical comparison to a background sediment, the mean survival was still 64 percent. Given that larval growth of *C. Tentans* exposed to sediment from this station resulted in a 735 percent weight gain, toxicity effects to native organisms are probably minimal.

Because the *C. tentans* data suggest that Grande-Ile sediment is not causing ecologically significant impacts, further discussion focuses on the *H. azteca* responses. The mortality response of *Hyaella* can be divided on the basis of the general site and sediment area classifications presented earlier. Stations SE-93-02T, SE-93-09T, and SE-93-11T, which exhibited the highest mean mortality (i.e., 60 percent, 42 percent, and 66 percent, respectively) are all found in Area A. Stations SE-93-25T and SE-93-27T, which are found in Area B, resulted in mean mortalities of 30 percent and 48 percent respectively. Two Stations, SE-93-31T and SE-93-45T, are located in Area C and have mean mortalities (i.e., 34 percent and 36 percent respectively) similar to the mortality observed at stations found in Area B.

In summary, the bioassay results indicate that only limited sediment toxicity appears to exist with Grande-Ile sediment. Only 8 of 19 (i.e., 42 percent) Priority Zone II stations exhibited significant responses to at least one of the two bioassays. The level of toxicity observed can be characterized as low to moderate (i.e., 24 to 66 percent mortality). Furthermore, no sediment sample was found to be toxic to both bioassays. Most regulatory decision makers generally prefer to have toxicity response agreement between two or more bioassays in order to have a high degree of certainty that toxicity does exist in a sediment sample. This is why most regulatory programs typically utilize a battery of two or more bioassays when characterizing sediment quality (Burton, 1991).

On the basis of two samples, SE-93-86T and SE-93-87T) Priority Zone I sediments are highly toxic (i.e., 90 percent and 96 percent mortality) to *H. azteca*, but are not toxic to *C. tentans*.

Of the 11 stations that did not corroborate the AVS theory, nine had ratios greater than 1 with no toxic sediment, and two had ratios less than 1 with toxic sediment. For the nine stations with ratios greater than 1 but no observed toxicity, the  $\Sigma\text{SEM}/\text{AVS}$  ratios were between 1 and 10, indicating that other factors affect metals availability. One potential factor is the presence of organic carbon, which may provide additional binding capacity for available metal. At Stations SE-93-25T and SE-93-27T, the sediment was toxic even though the  $\Sigma\text{SEM}/\text{AVS}$  ratios were less than 1. This strongly suggests that toxicity was due to factors other than metals.

As discussed previously, the TIE manipulations were designed to determine whether the toxicity observed in whole sediment was due to metals in the porewater. Results of the TIE manipulations indicate that a majority of the toxicity observed during whole sediment testing is not due to metals in porewater. The TIE manipulations also indicate that the toxicity observed in the whole sediment tests is not due to ammonia or other pH-dependent factors. The primary factors that could have caused toxicity in whole sediment, but not in extracted porewater, are grain size and TOC.

Only the porewater sample from Station SE-93-31T was found to be toxic as a result of the TIE manipulations. The results of the EDTA additions (i.e., reduced toxicity at greater additions of EDTA) indicate the toxicity may be due to metals. EDTA chelates metals and renders them biologically unavailable. Toxicity also was measured in the pore water from Station SE-93-31T during the graduated pH manipulations. The graduated pH manipulation is designed to identify toxicity due to pH dependent toxicants such as ammonia (U.S. EPA, 1985a) and metals (Schubauer-Berigan et al., 1993). The level of toxicity was consistent across the pH range (see Table 3.10), indicating the toxicant was not affected by pH. However, during the course of the test the pH of the individual adjustments drifted and equilibrated in the range of 7.8. pH drift is common in porewater samples (Ankley et al., 1991b; Dillon and Ross, 1992, Schubauer-Berigan et al., 1993), and in the case of Station SE-93-31T, may be the reason for a lack of a distinctive pattern of toxicity based on the initial pH manipulations.

Toxicity was also observed in the graduated pH test on the pyrite cinder sample from Station SE-93-87T. At pH 8.5, no *C. dubia* survived, indicating that toxicity was due to either metals whose toxicity increases with increasing pH (i.e., such as zinc or nickel); (Schubauer-Berigan et al., 1993) or to ammonia (U.S. EPA, 1985a). Further examination of the test results show that both the pH manipulation and the untreated porewater (which was not toxic) exhibited similar pH values (i.e., within 0.2 pH units) upon completion of testing (see Tables 3.9 and 3.10). It is unlikely that this small a difference in pH could have caused the difference in toxicity. Although the results of the TIE manipulations on the pore water samples from Station SE-93-87T are inconclusive, the lack of toxicity in the untreated porewater indicates that metals were not present in toxic amounts. In addition, toxicity was observed at pH 7.5 in porewater from

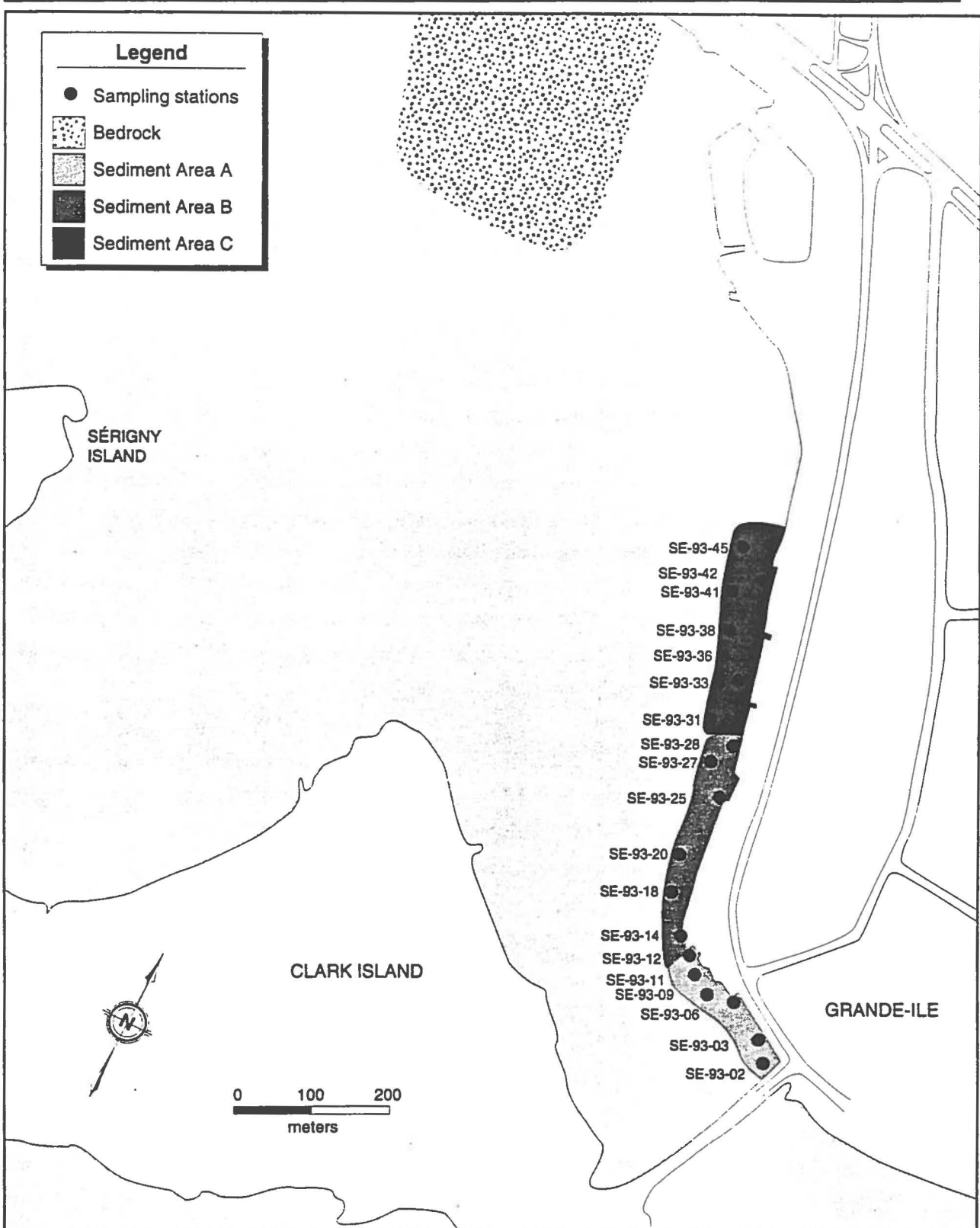


Figure 4.1 Locations of sediment areas found in Priority Zone II.

Table 4.1 Correlations coefficients between sediment characteristics, sediment metals concentrations, and sediment SEM and AVS.

	Percent Gravel	Percent Sand	Percent Silt & Clay	Percent Organic Carbon
As	-0.252	<b>-0.575</b>	<b>0.633</b>	0.407
Cd	-0.211	<b>-0.559</b>	<b>0.607</b>	<b>0.888</b>
Cu	-0.164	-0.337	0.375	0.148
Hg	-0.07	-0.054	0.07	-0.046
Zn	-0.264	<b>-0.617</b>	<b>0.678</b>	<b>0.942</b>
Total Metals	-0.27	<b>-0.626</b>	<b>0.687</b>	<b>0.922</b>
Cd (SEM)	-0.164	<b>-0.503</b>	<b>-0.54</b>	<b>0.972</b>
Cu (SEM)	-0.17	<b>-0.516</b>	<b>0.555</b>	<b>0.84</b>
Zn(SEM)	-0.212	<b>-0.549</b>	<b>-0.598</b>	<b>0.979</b>
$\Sigma$ SEM	-0.211	<b>-0.55</b>	<b>0.599</b>	<b>0.98</b>
$\Sigma$ SEM/AVS	-0.08	-0.191	0.209	-0.115

Shaded values are significant at  $\alpha = 0.05$  (Zar, 1974).

## 5.0 Conclusions

The following conclusions can be made concerning the quality of Grande-Ile sediment and pyrite cinders:

- The southeastern end of the Grande-Ile shoreline is predominated by fine-grained, organic rich sediment that contains metals at high concentrations (i.e., exceed the MENVIQ Level 3 criteria).
- Coarser sediment with relatively low metals concentrations is found along the remainder of the Grande-Ile shoreline.
- Pyrite cinders are characterized as being fine-grained sediment that contain metals at high concentrations (i.e., exceed the MENVIQ Level 3 criteria).
- Only one sediment sample (i.e., Station SE-93-06T) was found to be toxic to *Chironomus tentans*. However, this single data point suggests that toxic effects to native organisms are probably minimal.
- Seven of the Grande-Ile sediment samples were found to be toxic (i.e., mortality ranged from 24 to 66 percent) to *Hyaella azteca*, as were the two pyrite cinder samples (i.e., mortality ranged from 90 to 96 percent).
- Bioavailability tests (i.e., TIE manipulations) indicate that a factor (or factors) other than metals appears to be the cause of toxicity observed in both the Grande-Ile sediment and pyrite cinders, except at Station SE-93-31T. TIE manipulations indicate that cationic metals are the probable cause of toxicity at this station. Although not confirmed as part of this study, the causative factors appear to be sediment grain size and/or organic carbon content.
- The lack of agreement in toxic response between the two bioassays used in this study suggests that the toxicity observed in *H. azteca* is due to some sediment characteristic other than metals.
- The findings reported in this study indicate that there is a low probability for impacts (i.e., sediment toxicity) due to metals contamination and that a typical aquatic community appears to be supported in the area. Conclusions concerning the overall health of the Grande-Ile

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