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Ambient Air Measurements of Benzene in Canada (1989-1998)

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ABSTRACT

The Analysis and Air Quality Division of the Environmental Protection Service, Environment Canada (EC) has operated a field measurement program for benzene and other volatile organic compounds (VOCs) in ambient air since 1989. With the cooperation of provincial and municipal environmental agencies, samples have been collected at over 50 urban and rural monitoring sites across the country. Samples are normally collected over 24-h sampling periods once every six days. Ambient air samples are collected in stainless steel canisters and analyzed using a cryogenic pre-concentration technique with a high-resolution gas chromatograph and quadropole mass-selective detector (GC-MSD). An extensive database of ambient air benzene observations is available for Canada for the 1989 to 1998 time period. Mean benzene concentrations (using data for all years) ranged from $9.0 \mu\text{g}/\text{m}^3$ at an urban site influenced by emissions from a chemical manufacturer (Montreal) to $0.3 \mu\text{g}/\text{m}^3$ at a rural remote site (Kejimikujik National Park in Nova Scotia). Mean and median benzene concentrations are highest at urban-street sites and at sites influenced by industrial sources and lowest at rural and suburban sites. For the most recent years of measurements (1996 to 1998), mean concentrations at the urban/suburban sites ranged from 1.0 to $2.8 \mu\text{g}/\text{m}^3$ with most sites recording mean concentrations of less than $2.5 \mu\text{g}/\text{m}^3$. Most sites recorded decreases in benzene concentrations between 1990 and 1998. Using the composite results for urban sites with complete data there was a 34% reduction in annual mean benzene concentrations between 1990 and 1998. Emission inventory data suggests that most of the reduction in ambient air levels was due to reduced emissions from light duty vehicles.

INTRODUCTION

The Analysis and Air Quality Division of the Environmental Protection Service, Environment Canada (EC) has operated a field measurement program for benzene and other volatile organic compounds (VOCs) in ambient air since 1989. With the cooperation of provincial and municipal environmental agencies, samples have been collected at over 50 urban and rural monitoring sites across the country. The collected data from the monitoring program are used to assess population exposure to benzene and other air toxics as well as to support photochemical oxidant assessment and control activities. Recently the data have been used to support the development of a Canada Wide Standard for Benzene.¹ Previous reports and publications have been prepared and

distributed². Sites are compared based on location (rural, suburban and urban) and in terms of source influences (transportation and industrial). Seasonal variations in benzene concentrations are examined and trends in benzene levels over the period are analyzed for sites with complete data.

METHODS

Sampling Sites and Schedules

A listing of the benzene sampling sites is provided in Table 1. The table includes the start date for sampling, the number of samples collected, the location of the site (urban, rural or suburban) and an indication of potential industrial source influences. Sampling began at most sites between 1989 and 1992 and benzene data are currently available through. Monitoring data are available from fifty-six individual sites with forty-seven of those sites still active. Most of the sites are situated in urban or suburban areas but nine active sites are in rural locations. The Ottawa-Slater, Montreal-Maisonneuve and Vancouver-Robson Square sites are located close to street level in the urban core and are categorized as urban-street sites. The Toronto-Evans Ave. site is located within 50 m of a major expressway and is also categorized as an urban-street site. Nine of the sites are potentially impacted by industrial emissions of benzene. Trend analysis was performed on a subset of urban and suburban monitoring sites that had complete data for 1990 to 1998. These sites are identified in the table. The final column of the table shows the short-form identification of the site in subsequent figures. Locations of sites in the east are shown in Figure 1.

Samples are normally collected over 24-h sampling periods once every six days. At many sites, more intensive VOC sampling campaigns have been carried out (to support the ground level ozone science program) with samples collected over three, four or twelve hour sampling periods.

Sampling and Analysis Methods

Ambient air samples are collected in 6-L stainless steel SummaTM polished canisters (Scientific Instrumental Specialists, Inc. or BRC Rasmussen). The canisters are cleaned and evacuated before shipment to the sampling sites. Sixteen canisters are cleaned simultaneously by evacuation to a vacuum of < 700 Pa with a two-stage vacuum pump and a liquid nitrogen trap. While under vacuum, the canisters are heated to 80 °C. The canisters are then pressurized to 200 kPa with humidified zero air from a pure air generator (AADCO Corp.). This cycle is repeated six to ten times. Two to three canisters of each batch of sixteen are analyzed for VOC to verify that the canisters are clean before the final evacuation.

In the field, ambient air samples are collected in canisters using whole air samplers. Many of the samplers were built in house and are based on the US Environmental Protection Agency (EPA) "R-Type" design³. In recent years, samplers have been purchased from Xontech, Inc. (Model 910). Before use, all samplers are cleaned and certified according to the procedures described in EPA method TO-14.⁴

The samplers are programmed to begin drawing ambient air at least 3 min prior to the 24-hour scheduled sample collection period. This is done to purge the sample lines and the pump with ambient air. The pump draws air at a flow-rate of 1 to 2 L/min. The sample flow is split to a mass flow controller that allows a constant flow of 10 to 15 mL/min to the canister with the remaining air exhausted. Canister samples are shipped to the laboratory and typically arrived under 70 to 140-kPa pressure.

The ambient air samples are analyzed using a cryogenic pre-concentration technique with a high-resolution gas chromatograph and quadrupole mass-selective detector (GC-MSD) as described in EPA Method TO-14. Two separate automated pre-concentration GC systems are used for analysis. One employs a Nutech 3550A pre-concentrator with auto-sampler (Nutech Corp., Research Triangle Park, N.C.). The other employs an Entech Model 2000 pre-concentrator with auto-sampler (Entech Corp., Calif.). The instruments used for species identification and quantification are a Hewlett Packard 5890 series II GC and a Hewlett Packard 5970 MSD. VOCs are separated on a 50 m, 0.32 mm ID fused silica capillary column with a 1.0- μ m film thickness of HP-1 bonded liquid phase.

Approximately 0.5 L of the canister sample is passed through a Nafion dryer to remove water vapour. A mass flow controller is used to measure sample volume and internal standards are added using an internal sample loop in the Nutech system. A cryogenic trap, held at -150 °C, is used to concentrate the air sample. Once the sample is concentrated, the trap is heated to 150°C and the sample is back-flushed onto a cryo-focus located at the head of the silica column. When the GC-MSD is ready, the cryo-focus is heated and the VOCs are injected into the GC. The initial column temperature of -60 °C is held for 3 minutes then raised to 250 °C at 8 °C/min. Operated in selected ion monitoring (SIM) mode, the GC-MSD acquires data for target compounds only and ignores all others. Peak identification is based on GC retention time and MSD confirmation. Benzene and approximately 110 other VOC species are quantified in the samples.

Typical method detection limits for benzene are 0.1 μ g/m³ for GC-MSD SIM analysis. Method precision as demonstrated by replicate analysis of canister samples is in the range of 5-8 % for concentrations greater than 0.25 μ g/m³. The static dilution standards prepared in the laboratory have been compared with a diluted National Institute of Standards and Technology (NIST) aromatic hydrocarbon standard and found to agree within +5%. The laboratory also has participated in the National Centre for Atmospheric Research (NCAR) inter-comparison study for 16 hydrocarbons (NOMHICE)⁵ and results for benzene agreed within 3%.

Table 1: List of benzene monitoring sites and summary of available data (as of Dec. 1998).

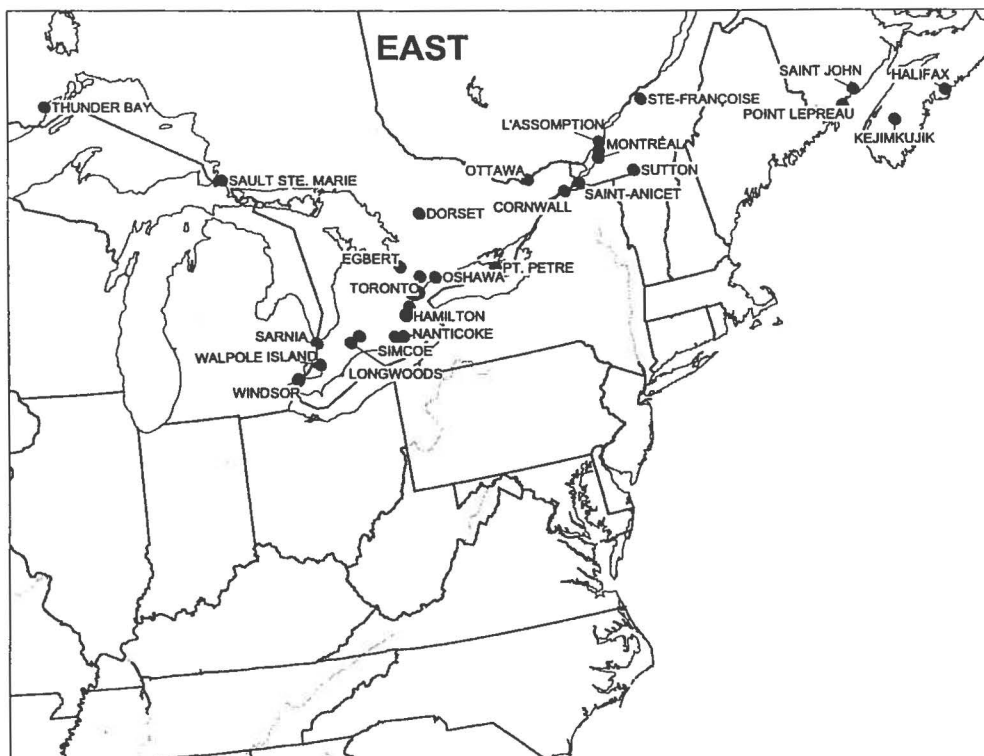
NAPS No.	City ¹	Address	Site Classification	Industrial Impact ²	Start Date	End Date	24h Sampling	3,4 or 12h Sampling	Trend Site	Figure 1 Site ID
30117	Halifax	Bedford Row P.O.	Urban		09-Jun-89	08-Oct-90	X			
30118	Halifax	1657 Barrington	Urban		07-Dec-90	13-Dec-98	X		92-98	Halifax
30501	Kejimikujik Nat. Park		Rural		06-Jun-94	22-Dec-98		X		Kejimikujik
40501	Pt. Lepreau	Main Gate	Rural		05-Jul-92	31-Dec-98	X	X	92-98	Lepreau
40203	Saint John	Forest Hills	Suburban	R	24-May-92	31-Dec-98	X	X	92-98	Saint John
50103	Montreal	Pte. aux Trembles	Suburban	R,C	16-Jan-89	31-Dec-98	X	X	92-98	Mon-PT
50104	Montreal	1125 Ontario St.	Urban		10-May-89	25-Dec-98	X		92-98	Mon-ONT
50115	Montreal	1001 Maisonneuve O.	Urban-Street		09-Jul-92	03-Aug-98	X	X	92-98	Mon-MAIS
50121	Montreal	Parc Oceanie, Brossard	Suburban		30-Jun-93	31-Dec-98	X			Mon-BROS
54101	Mount Sutton		Rural		06-Jun-94	31-Dec-98		X		Sutton
54301	Ste. Francoise		Rural		26-Feb-93	25-Nov-98		X		Ste. Francoise
54401	St. Anicet		Rural		15-Jun-94	22-Dec-98		X		St. Anicet
54501	L'Assomption		Rural		27-May-96	22-Dec-98		X		L'Assomption
60101	Ottawa	88 Slater St.	Urban-Street		28-May-89	31-Dec-98	X		92-98	Ott-SLA
60104	Ottawa	Rideau/Wurtemberg	Urban		22-Sep-93	31-Dec-98	X			Ott-WURT
60204	Windsor	467 University Ave.	Urban		04-Jan-89	08-Apr-94	X	X		Win-UNI
60302	Kingston	Napier St.	Urban		08-Oct-98	19-Dec-98	X			Kingston
60403	Toronto	Evans/Arnold	Urban-Street		18-Jun-95	31-Dec-98	X	X		Tor-EVAN
60424	Toronto	Bay/Grosvenor	Urban		06-May-92	18-Sep-95	X	X		
60422	Toronto	35 Edgar Ave.	Urban		04-Jan-89	25-Apr-93	X			
60418	Toronto	Junction Triangle	Urban		04-Jan-89	31-Dec-98	X		92-98	Tor-JT
60413	Toronto	Elmcrest Road	Suburban		01-May-93	31-Dec-98	X	X		Tor-ELM
60426	Mississauga	Clarkson Refinery	Suburban	R	02-Jul-96	31-Dec-98	X			Clarkson
60512	Hamilton	Elgin/Kelly	Urban	I&S	28-Jan-89	31-Dec-98	X		92-98	Ham-ELG
60903	London	900 Highbury Ave.	Urban		29-May-98	31-Dec-98	X			London
61004	Sarnia	Centennial Park	Suburban	R,C	10-Jan-89	31-Dec-98	X		92-98	Sarnia
61602	Oakville	Bronte Rd./Woburn Cres.	Suburban		27-Apr-95	02-Jun-96	X			Oakville
61901	Walpole Island		Rural		03-Feb-89	22-Mar-95	X			
62601	Simcoe	Experimental Farm	Rural		06-Feb-93	31-Dec-98	X	X		Simcoe
63301	Dorset		Rural		16-Jul-98	31-Dec-98	X			Dorset
63601	Longwoods	Longwoods Cons. Auth.	Rural		12-May-91	01-Nov-98	X			Longwoods
63201	Stouffville	Hwy 47 & Hwy 48	Suburban		10-Jan-89	31-Dec-98	X		92-98	Tor-STOU

Table 1: List of benzene monitoring sites and summary of available data (as of Dec. 1998).

NAPS No.	City ¹	Address	Site Classification	Industrial Source Impact ¹	Start Date	End Date	24h Sampling	3,4 or 12h Sampling	Trend Site (Years)	Figure 1 Site ID
64401	Egbert	CARE	Rural		14-Jun-94	31-Dec-98		X		Egbert
64601	Point Petre		Rural		25-Aug-96	31-Dec-98	X			Point Petre
70119	Winnipeg	65 Ellen St.	Urban		24-Dec-89	31-Dec-98	X		92-98	Winnipeg
90121	Edmonton	17 St./105 Ave.	Suburban	R,C	27-Aug-90	31-Dec-98	X		92-98	Edm-EIMU
90130	Edmonton	10255-104th St.	Urban		18-May-91	31-Dec-98	X		92-98	Edm-EDMU
90227	Calgary	611-4TH ST. SW	Urban		09-Aug-90	25-Dec-98	X		92-98	Calgary
90701	Fort McMurray	MacDonald Drive	Suburban		03-Apr-95	31-May-95	X			
90601	Fort Saskatchewan	100 Ave. & 98th St.	Suburban		28-Dec-94	02-Feb-95	X			
90901	Vegreville	Royal Park	Rural		01-Aug-96	02-Nov-96	X			Vegreville
91001	Esther		Rural		25-Sep-96	30-Nov-96	X			Esther
100112	Vancouver	Robson Square	Urban-Street		28-Jan-89	31-Dec-98	X	X		Van-T1
100118	Vancouver	2550 W 10TH Ave.	Urban		26-Jul-93	06-Aug-93	X			
100110	Vancouver	Kensington Park	Urban	R	04-Jan-89	05-Apr-98	X	X		Van-T4
100121	Vancouver	75 Riverside Dr.	Urban		22-Sep-93	09-Mar-94		X		
100111	Vancouver	Rocky Point Park	Urban	R	04-Jan-89	01-Dec-98	X	X	92-98	Van-T9
100127	Vancouver	Surrey East	Suburban		10-Jan-89	31-Dec-98	X			Van-T15
101201	Vancouver	Pitt Meadows Airport	Suburban		15-Sep-92	03-Sep-95		X		Van-T16
100128	Vancouver	Richmond South	Suburban		22-Jan-89	30-Dec-97	X	X		Van-T17
100133	Vancouver	7815 Shellmount St.	Suburban	T	18-Mar-90	31-Dec-98	X			Van-T22
100132	Vancouver	Mahon Park	Urban		23-May-90	11-Apr-98	X			Van-T26
100134	Vancouver	International Airport	Suburban		05-May-98	25-Dec-98	X			Hope
101301	Vancouver	52nd. Ave. Langley	Suburban		12-Jul-93	29-Apr-98	X	X		Van-T27
101101	Chilliwack	Works Yard	Suburban		16-Jun-98	25-Dec-98	X			Chilliwack
101401	Hope	Airport	Rural		03-Aug-98	13-Dec-98	X			

¹ R-Refinery, C-Chemical Manufacturing, I&S- Iron & Steel, T-Pipeline Transfer

Figure 1: Monitoring site locations in eastern Canada.



RESULTS AND DISCUSSION

Ambient Air Benzene Concentrations

There were approximately 19,000 individual benzene observations in the database as of December 1998. Table 2 provides frequency distributions, maximum, mean, standard deviation and median benzene concentrations ($\mu\text{g}/\text{m}^3$) for selected sites using all data collected between 1989 to 1998. The sites were selected based on length of data record. For most of the sites, the statistics are based on 24-h data but for some of the rural sites, shorter time period observations are used.

Mean benzene concentrations (using data for all years) ranged from $9.0 \mu\text{g}/\text{m}^3$ at the Montreal Pte. aux Trembles site to $0.3 \mu\text{g}/\text{m}^3$ at the Kejimikujik site in Nova Scotia. The highest 24-h average benzene concentration of $126 \mu\text{g}/\text{m}^3$ was measured at the Montreal-Trembles site in 1993. Mean and median benzene concentrations are highest at urban-street sites and at sites influenced by industrial sources and lowest at rural and suburban sites.

As discussed later in the paper, there has been a decrease in benzene recorded at most of the urban monitoring sites between 1989 and 1998. In Figure 2, sites are compared in terms of current (1996/98) benzene concentrations using a boxplot presentation. The rural sites are shown separately from urban/suburban sites, as are the four sites with the highest mean concentrations (average greater than $3.0 \mu\text{g}/\text{m}^3$). For the rural sites mean

concentrations ranged between 0.4 and 1.0 $\mu\text{g}/\text{m}^3$ with 90th percentile concentrations ranging between 0.7 and 2.1 $\mu\text{g}/\text{m}^3$. The highest concentrations were measured at the rural sites closest to cities such as l'Assomption (near Montreal), Simcoe and Longwoods (in southwestern Ontario). Rural concentrations appear higher at sites in Ontario and Quebec than at sites in the Atlantic and Prairie regions, although there are very few observations from rural western sites. Mean concentrations at the urban/suburban sites ranged from 1.0 to 2.8 $\mu\text{g}/\text{m}^3$ with most sites (20 out of 28) recording mean concentrations of less than 2.5 $\mu\text{g}/\text{m}^3$. Ninetieth percentile concentrations at these sites ranged from 1.5 to 5.8 $\mu\text{g}/\text{m}^3$ with most sites (18 out of 28) recording 90th percentile concentrations of less than 4.0 $\mu\text{g}/\text{m}^3$. For the highest concentration sites, mean benzene concentrations ranged from 3.1 to 10.0 $\mu\text{g}/\text{m}^3$ and 90th percentile concentrations varied from 4.0 to 26.0 $\mu\text{g}/\text{m}^3$.

Seasonal Variations

Seasonal variations in ambient benzene concentrations are determined by seasonal differences in emission rates, in meteorology (primarily wind speed, temperature and mixing depth) and in the rate of removal of benzene from the atmosphere. Benzene is considered of low reactivity in the atmosphere, and is removed only slowly by reaction with the OH radical. Residence times (defined as the time at which concentration is 37 % of original value) of benzene in urban atmospheres have been estimated to be 5 days in July and 120 days in January at 40°N latitude.⁶ The difference is due to the much greater abundance of OH radicals in the summer. Residence times will be longer outside urban areas and at higher latitudes.

Monthly variations in benzene concentrations for eight rural sites with complete data for 1994/1998 (two data sets for Simcoe are shown – one is from 24 h 1-in-6-day sampling, the other from 12 and 4 hour sampling) are illustrated in Figure 3. All sites showed a typical seasonal pattern with minimum concentrations measured during June and July and maximum concentrations during January and February. Winter to summer ratios were approximately 3 at all sites. The Pt. Lepreau (eastern New Brunswick), Kejimikujik and Mount Sutton (elevated site near Montreal) sites recorded the lowest benzene concentrations with the smallest variability. The Simcoe and Longwoods site showed the greatest variability in the summer months reflecting the impact of local sources. The January/February mean concentration of 0.8 $\mu\text{g}/\text{m}^3$ and June/July mean of 0.2 $\mu\text{g}/\text{m}^3$ at Pt. Lepreau are similar to a winter maximum benzene value of 0.8 $\mu\text{g}/\text{m}^3$ and a summer minimum of 0.1 $\mu\text{g}/\text{m}^3$ recorded in the free troposphere over the North Atlantic ocean.⁷

In Figure 4, monthly variations in benzene concentrations are shown for 12 urban sites (composite of 1990 to 1998 data). The Winnipeg, Calgary and Vancouver sites show the largest and most distinct seasonal variations in benzene concentrations. Most of the other urban sites recorded lower benzene concentrations in summer than in winter but variability is very large. The point source influenced sites show site-specific seasonal patterns probably resulting from monthly variations in predominant wind directions.

Table 2: Summary statistics for benzene ($\mu\text{g}/\text{m}^3$) for selected sites: 1989 – 1998.

City	Address	Start Date	Stop Date	Avg. Time	No. of Samples	Mean	Std. Dev.	Median	90 th Perc.	Max.
Pt. Lepreau	Main Gate	05-Jul-92	11-May-98	24	299	0.4	0.2	0.4	0.7	1.2
Saint John	Forest Hills	24-May-92	31-Dec-98	24	320	1.5	1.0	1.3	2.8	6.1
Halifax	1657 Barrington	07-Dec-90	13-Dec-98	24	426	3.4	1.8	3.0	5.6	13.8
Kejimikujik		06-Jun-94	22-Dec-98	3,4,12	851	0.3	0.3	0.3	0.6	3.6
Ste. Francois		26-Feb-93	05-May-98	24	247	0.6	0.4	0.5	1.1	2.9
Montreal	Pte. aux Trembles	16-Jan-89	31-Dec-98	24	519	9.0	9.3	6.0	20.3	126.3
Montreal	1125 Ontario St.	10-May-89	25-Dec-98	24	497	3.6	2.0	3.1	6.1	14.8
Montreal	1001 Boul Maisonneuve	09-Jul-92	31-Dec-98	24	368	5.5	2.3	5.0	8.5	16.6
Montreal	Parc Oceanie, Brossard	30-Jun-93	31-Dec-98	24	279	1.3	1.2	1.0	2.4	14.2
Mount Sutton		06-Jun-94	31-Dec-98	3,4,12	893	0.4	0.3	0.3	0.7	3.2
St. Anicet		15-Jun-94	31-Dec-98	3,4,12	841	0.5	0.6	0.4	1.1	7.0
L'Assomption		27-May-96	22-Dec-98	3,4,12	427	1.0	0.9	0.7	2.1	7.9
Ottawa	88 Slater St.	28-May-89	31-Dec-98	24	523	3.7	2.1	3.2	6.3	15.4
Ottawa	Rideau/Wurtemberg	22-Sep-93	31-Dec-98	24	303	1.8	1.1	1.6	3.1	8.6
Point Petre		25-Aug-96	31-Dec-98	24	138	0.6	0.3	0.5	0.9	2.0
Toronto	Perth/Ruskin	04-Jan-89	31-Dec-98	24	493	2.5	1.5	2.1	3.9	16.6
Toronto	Elmcrest Road	01-May-93	31-Dec-98	24	235	2.0	1.3	1.7	3.6	10.7
Toronto	Stouffville	10-Jan-89	31-Dec-98	24	465	1.4	3.8	0.9	2.0	77.1
Toronto	Evans/Arnold	18-Jun-95	31-Dec-98	24	188	2.2	1.4	1.8	3.8	10.5
Egbert	CARE	14-Jun-94	31-Dec-98	3,4,12	906	0.5	0.4	0.4	1.0	3.8
Hamilton	Elgin/Kelly	28-Jan-89	31-Dec-98	24	485	3.7	3.4	2.3	8.0	25.9
Simcoe	Experimental Farm	18-Jun-94	31-Dec-98	3,4,12	754	0.7	0.5	0.6	1.2	4.4
Longwoods	Longwoods Cons. Auth.	12-May-91	23-May-98	24	349	0.8	0.4	0.7	1.3	2.8
Sarnia	Centennial Park	10-Jan-89	31-Dec-98	24	514	3.5	4.5	1.8	8.7	37.4
Windsor	College/Prince	29-May-90	31-Dec-98	24	468	2.3	1.5	1.9	4.1	13.0
Winnipeg	65 Ellen St.	24-Dec-89	31-Dec-98	24	508	1.9	1.0	1.7	3.0	11.9
Edmonton	17 St./105 Ave.	27-Aug-90	31-Dec-98	24	475	2.6	1.9	2.0	4.5	19.3
Edmonton	10255-104th St.	18-May-91	31-Dec-98	24	447	3.1	1.8	2.5	5.4	13.5
Calgary	611-4TH ST. SW	09-Aug-90	25-Dec-98	24	481	3.3	2.1	2.8	6.0	16.8
Vancouver	Rocky Point Park	04-Jan-89	01-Dec-98	24	545	4.1	2.9	3.2	7.9	21.5
Vancouver	Pitt Meadows Airport	15-Sep-92	03-Sep-95	24	196	1.1	0.9	0.7	2.3	4.3
Vancouver	Burmount	18-Mar-90	31-Dec-98	24	198	2.5	1.8	1.9	5.1	11.4

Figure 2: Mean, 10th and 90th percentile benzene concentrations by site (1996-1998).

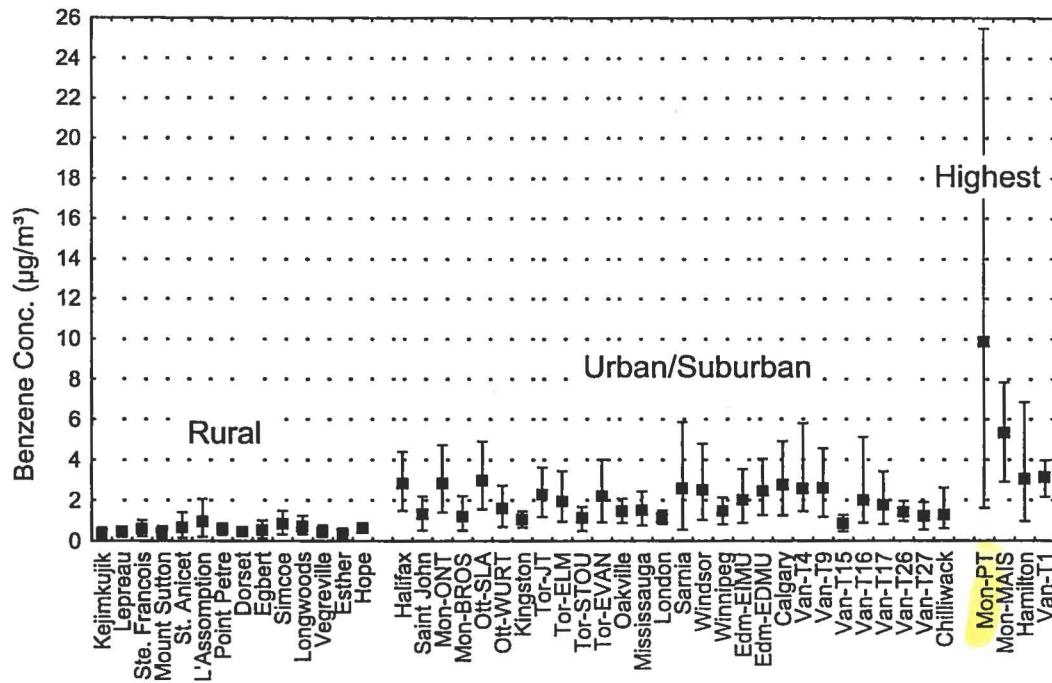


Figure 3: Monthly variation in benzene at rural sites (1994-1998).

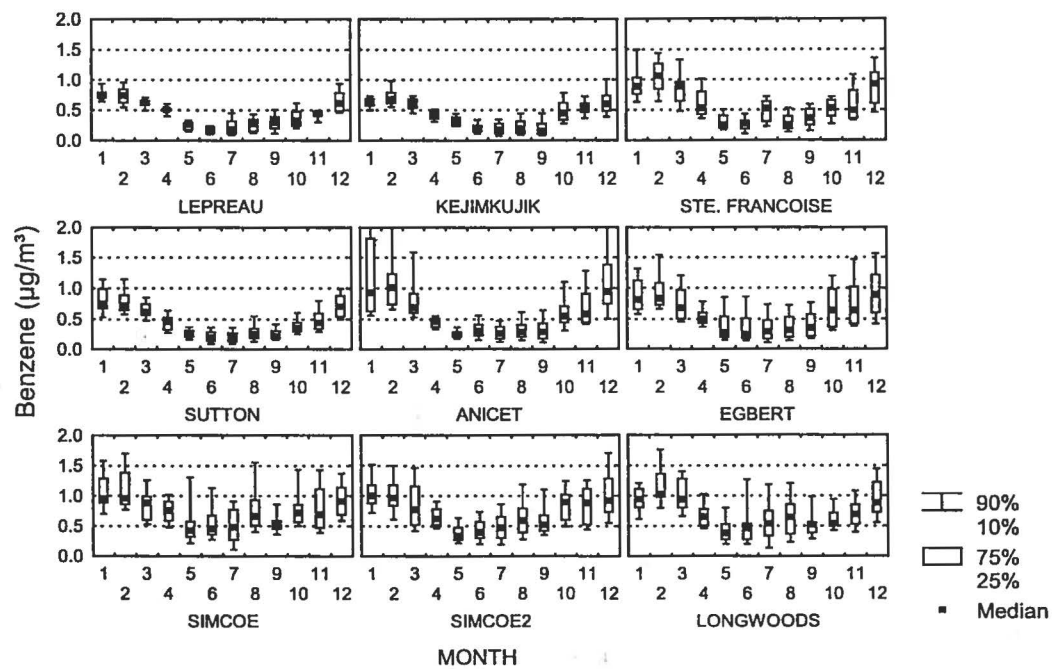
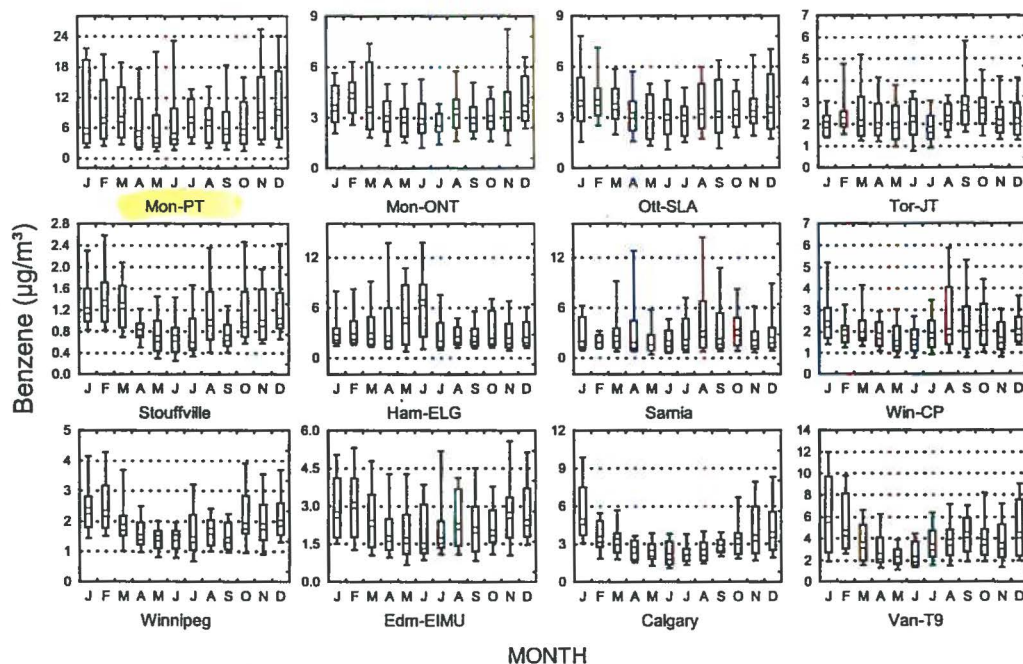


Figure 4: Monthly variation in benzene at urban sites (1994-1998) - median, 10th, 25th, 75th, 90th percentiles.



Urban sites also show substantial day of the week variation in benzene concentrations with the lowest values typically recorded on Saturday and Sundays. Sites near street level or close to roadways can show a factor of two difference between weekend and mid-week benzene concentrations.

Trends in Benzene Concentrations

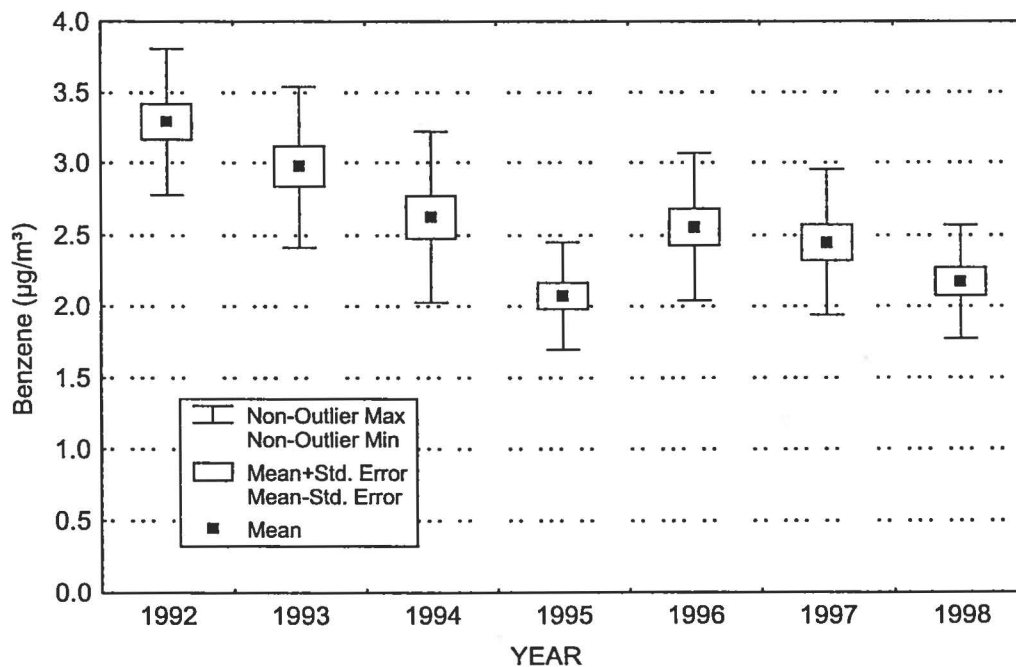
Annual mean benzene concentrations are shown in Table 3 for urban and suburban sites that met data completeness criteria for the period 1992 to 1998 (at least 20 observations in each year and 6 out of 7 years of data). Composite results for these sites (Montreal – Trembles not included in composite results) are shown in the form of a boxplot in Figure 5.

Between 1992 to 1998 composite annual means decreased by 34% for the sites. The decline was quite linear with exception of 1995, which had the lowest annual mean value in the period. This was likely due to lower economic activity in 1995. All but three of the sites showed declines in benzene between 1992 and 1998 with percentage decreases ranging from 5 to 47%. Of the three sites showing an increase, the Montreal site is influenced by a chemical plant producing benzene, the Windsor site is impacted by emissions from coke production at a US facility and the Stouffville site is in a suburban area that has experienced rapid housing and roadway development.

Table 3: Annual mean benzene concentrations ($\mu\text{g}/\text{m}^3$) for 1992 to 1998 for urban and suburban sites.

City		1992	1993	1994	1995	1996	1997	1998	% Change (97/98 vs. 92/93)
Saint John	Forest Hills	1.9	1.7	1.6	1.3	1.3	1.9	1.1	-17%
Halifax	1657 Barrington	4.5	4.1	3.3	2.5	2.9	3.0	2.6	-35%
Montreal	1125 Ontario St.	4.2	4.0	3.6	2.4	2.7	3.0	2.8	-30%
Montreal	Pte. aux Trembles	7.4	10.0	8.5	9.0	8.1	11.4	10.2	24%
Montreal	1001 Boul Maisonneuve	5.6	6.1	5.4	5.1	5.6	5.5	4.8	-12%
Montreal	Parc Oceanic, Brossard	-	1.8	1.7	1.1	1.3	1.3	0.9	-36%
Ottawa	88 Slater St.	4.1	4.0	3.9	2.9	3.3	3.2	2.4	-30%
Toronto	Perth/Ruskin	2.5	2.2	3.1	2.0	2.3	2.3	2.2	-5%
Toronto	Stouffville	1.1	1.0	1.3	2.6	1.1	1.4	1.0	14%
Hamilton	Elgin/Kelly	4.6	4.3	3.7	2.4	3.9	2.9	2.4	-40%
Sarnia	Centennial Park	3.6	2.6	4.2	2.0	3.2	2.4	2.2	-23%
Windsor	College/Prince	2.0	2.4	2.2	1.9	2.2	2.8	2.4	19%
Winnipeg	65 Ellen St.	2.4	2.1	1.8	1.7	1.5	1.5	1.5	-36%
Edmonton	17 St./105 Ave.	3.4	2.9	2.6	2.6	1.8	2.1	2.1	-33%
Edmonton	10255-104th St.	4.0	3.6	3.5	2.7	2.6	2.3	2.5	-38%
Calgary	611-4th St. SW	3.9	3.4	3.2	3.4	2.7	2.9	2.6	-23%
Vancouver	Rocky Point Park	4.4	4.7	3.6	3.7	2.8	2.8	2.1	-47%

Figure 5: Yearly variations in benzene for urban sites (1992-1998).



BENZENE EMISSIONS

A summary of estimated Canadian benzene emissions for the years 1990, 1995 and 2000 are provided in Table 4.⁸ Light duty gasoline vehicles accounted for over 50% of total anthropogenic benzene releases in 1990 and they represented the dominant emission source in most urban areas. The reduction in emissions from this source is estimated to have been about 50% between 1990 and 2000 and undoubtedly accounts for most of the reduction in urban benzene concentrations. Although the overall trend in emissions matches the ambient trend, the emission inventory does not provide any explanation for the low ambient benzene concentrations in 1995. Further reductions in emissions from light duty vehicles are forecast through 2010 because of regulations limiting the benzene content of gasoline (1% in 1999), lower sulphur limits in gasoline (25 ppm in 2005), introduction of Tier 2 vehicles and continued fleet turnover.

Although point sources account for only a small fraction of emissions, they can have a large local impact. The highest benzene concentrations in the country were found at a site in Montreal, which is impacted by benzene releases from a nearby (2.5 km) chemical manufacturing plant. This site showed no reduction in benzene concentrations over the time period examined.

Table 4: Annual benzene emissions (kilotonne) by source category.

Sector	Type	1990	1995	2000
Petroleum Refining	Point	0.6	0.4	0.3
Chemical Production	Point	1.5	0.4	0.4
Iron and Steel	Point	1.7	1.2	0.4
Glycol Dehydrators	Area	5.7	8.7	3.1
Misc. Fuel Combustion	Area	4.0	4.7	4.8
Light Duty Gas Vehicles	Area	32.9	25.3	16.4
Off Road Gasoline	Area	3.4	2.6	2.7
Other Transportation	Area	2.7	3.3	3.4
Residential Wood Combustion	Area	10.5	10.7	11.0
Prescribed Burning	Area	0.5	0.5	0.4
Total Anthropogenic		63.5	57.8	42.9
Forest Fires	Area	8.1	58.0	27.0
Total		71.6	115.8	69.9

SUMMARY

An extensive database of ambient air benzene observations is available for Canada for the 1989 to 1998 time period. Mean benzene concentrations (using data for all years) ranged from 9.0 $\mu\text{g}/\text{m}^3$ at an urban site influenced by emissions from a chemical producer to 0.3 $\mu\text{g}/\text{m}^3$ at a rural remote site. For typical (i.e. not adjacent to roadways) urban site locations with no industrial source influences, mean benzene concentrations over the period were in the range of 1.0 to 2.8 $\mu\text{g}/\text{m}^3$. Mean and median benzene concentrations are highest at urban-street sites and at sites influenced by industrial sources and lowest at rural and suburban sites.

Most sites recorded decreases in benzene concentrations between 1992 and 1998. Using the composite results for urban sites with complete data there was a 34% reduction in annual mean benzene concentrations between 1992 and 1998. Results for individual sites were more variable with percentage changes between 1992 and 1998 ranging from a 47% decrease to a 24% increase.

The decline in ambient benzene levels at most urban sites is a result of improved VOC emission control technology on new motor vehicles plus the effect of reduced gasoline benzene levels. The lack of improvement in benzene levels at some sites with high concentrations is still of concern.

REFERENCES

1. Canadian Council of Ministers of the Environment, *Canada Wide Standard for Benzene: Phase 1*. CCME Web Document, http://www.ccme.ca/pdfs/benzene/benz_cwsp1_e.pdf.
2. Dann, T.F. and Wang, D.K., "Ambient Air Benzene Concentrations in Canada (1989-1993): Seasonal and Day of Week Variations, Trends and Source Influences." *J. Air & Waste Manage. Assoc.*, **1995**, 45: 695-702, 1995.
3. McClenny, W. A.; Pleil, J. D.; Lumpkin T. A.; Oliver K. D., *Toxics Monitoring with Canister-Based Systems*. Proceedings of the 80th Annual Meeting of the APCA, New York, N.Y., 1987.
4. Winberry Jr., W. T.; Murphy, N. T.; Riggan, R. M., *Method TO-14 and Method TO-13, Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*. U.S. Environmental Protection Agency 1988; EPA 600/4-89-017.
5. E. C. Apel, E.C.; Calvert, J. G.; Fehsenfeld, F.C.; "The nonmethane hydrocarbon intercomparison experiment (NOMHICE): Tasks 1 and 2". *J. Geophys. Res.* **1994**, 99, 16651.
6. *Motor Vehicle-Related Air Toxics Study*. U.S. Environmental Protection Agency 1993; EPA 420-R-93-005.
7. Penkett, S.; Blake, N.; Lightman, P.; Marsh, A.; Anwyl, P.; Butcher G., "The seasonal variation of nonmethane hydrocarbons in the free troposphere over the North Atlantic Ocean: possible evidence for extensive reaction of hydrocarbons with the nitrate radical". *J. Geophys. Res.* **1993**, 98, 2865.

8. Environment Canada. *Benzene Inventory Trend in Canada (1990-2010)*. Report prepared by Cheminfo Services Inc., 1999.

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Benzene, VOC, Monitoring, Trends, Emissions, Transportation.