

**BENZENE in the AMBIENT AIR of
CANADIAN URBAN AREAS**

SOURCES and EXPOSURES

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**July 1987
(PMD File - 4024-6)**

EXECUTIVE SUMMARY

There appears to be no disagreement over the fact that benzene is a human carcinogen with most estimates of lifetime risk of cancer in the range of 22 to 170 cases per million population per ppb of lifetime benzene exposure. In the absence of other information, it is recommended that benzene be treated as a carcinogen that may act at all doses without any threshold level. Benzene has been formally listed as a toxic air pollutant by both the U.S. EPA and the California Air Resources Board.

Recent Canadian monitoring data for benzene show that mean concentrations range from 0.9 to 6.0 ppb with the highest concentrations measured near point sources. Using CO monitoring data from 51 sites and a derived benzene/CO relationship from recent measurement data, mean benzene levels in Canadian urban areas are estimated to be 3.0 ppb. This value is the same as to the mean benzene exposure level of 3.0 ppb calculated for the State of California and is within the range of recent mean benzene concentrations reported for major U.S. urban areas. Benzene exposures will be higher for commuters, for drivers who routinely use self-serve gas stations and for populations dwelling near point sources.

Tailpipe and evaporative emissions from light duty gasoline-powered vehicles are the largest source of benzene and account for the majority of population exposure to benzene. Benzene emissions are decreased substantially by catalyst control technology; emission decreases, however, can be offset by increasing fuel benzene content. It is estimated that LDV benzene emissions in Canada will decrease by 27% between 1984 and the year 2000.

Major point source emitters of benzene are poorly characterized and are not currently subject to any emission control requirements. Major sources are concentrated in three urban areas, Montreal, Sarnia and

Edmonton. Based on existing monitoring data for Montreal, point sources can have a major impact on locally measured ambient benzene concentrations.

Potential control measures for benzene have been reviewed by California. By adopting gasoline benzene limits and improved vapor recovery at all bulk and retail gasoline marketing sources, overall individual risk to benzene exposures in the State can be reduced by 50% by the year 2000. A U.S. EPA regulation for fugitive benzene emissions is designed to reduce maximum individual risks to benzene exposure. Most control measure costs are in the range of \$2 to \$200 per Kg of benzene reduced. Point source fugitive benzene emission control is one of the most cost-effective control measures.

Based on existing Canadian ambient air monitoring data and estimated risk values for benzene, it can be concluded that reductions in benzene levels are warranted to prevent harm to public health. Although some reduction will take place as a result of vehicular HC control measures, additional controls will be necessary, especially on point sources to reduce risk to currently acceptable values. Without regulation there is also no certainty regarding the future benzene content of gasoline. Increases in benzene fuel content will offset some of the expected LDV emission reduction.

RESUME

Il ne semble pas y avoir de désaccord au sujet des effets cancérigènes du benzène sur l'homme; en effet, d'après les estimations, les risques à vie sur une population d'un million de personnes exposées durant toute leur vie sont de 22 à 170 cas pour chaque partie par billion en concentration de benzène. En l'absence d'autres données, il est recommandé que le benzène soit considéré comme une substance cancérigène qui peut avoir des effets à toutes les concentrations. Le benzène a été inscrit officiellement sur la liste des polluants atmosphériques toxiques par l'EPA américain ainsi que par le California Air Resources Board.

Les mesures récemment effectuées au Canada indiquent que les concentrations moyennes de benzène varient entre 0,9 et 6,0 ppb; les plus hautes valeurs ont été relevées près de sources ponctuelles. A l'aide des données sur le CO recueillies à 51 postes d'échantillonnage, on a calculé, d'après un rapport établi entre les quantités de benzène et de CO récemment mesurées, que la concentration moyenne de benzène dans les régions urbaines du Canada était d'environ 3,0 ppb. Cette valeur est la même que celle calculée pour l'exposition moyenne au benzène en Californie (3,0 ppb), et elle correspond aux concentrations moyennes de benzène mesurées dans les principales régions urbaines des Etats-Unis. L'exposition au benzène est plus élevée dans le cas des banlieusards, des conducteurs d'automobile qui font régulièrement le plein eux-mêmes et des personnes qui demeurent près de sources ponctuelles.

Les gaz d'échappement et les vapeurs qui se dégagent des véhicules légers fonctionnant à l'essence constituent la plus importante source d'émission de benzène et d'exposition de la population à ce composé chimique. Les émissions de benzène sont considérablement réduites par les convertisseurs catalytiques, mais cette diminution peut être contrebalancée

par une augmentation de la teneur en benzène du carburant. On estime que les émissions de benzène produites par les véhicules légers au Canada diminueront de 27 % au cours de la période de 1984 à l'an 2000.

Les sources ponctuelles majeures d'émission de benzène sont très peu définies, et aucun objectif de qualité de l'air n'a été fixé à leur égard. Elles sont concentrées dans trois régions urbaines: Montréal, Sarnia et Edmonton. D'après les données recueillies à Montréal, les sources ponctuelles peuvent avoir un effet important sur les concentrations de benzène dans l'air ambiant mesurées à certains endroits.

L'Etat de Californie a étudié les mesures qui pourraient être prises pour réduire la pollution causée par le benzène. Grâce à l'adoption de limites pour la teneur en benzène de l'essence et à une récupération accrue des vapeurs se dégageant à tous les points de vente en gros et au détail de l'essence, les risques d'exposition au benzène pourraient en général être réduits de 50 % d'ici l'an 2000. Un règlement de l'EPA américain concernant les émissions fugitives de benzène a pour but de réduire le plus possible les risques individuels d'exposition à cette substance. Les coûts entraînés par la plupart des mesures de dépollution varient entre 2 \$ et 200 \$ par kg de benzène éliminé. L'une des mesures les plus rentables consiste à réduire les émissions fugitives de benzène provenant de sources ponctuelles.

Compte tenu des données recueillies sur la quantité de benzène présente dans l'air ambiant au Canada et des valeurs calculées pour les risques que comporte l'exposition à ce produit, il est permis de conclure que la réduction des concentrations de benzène est justifiée si l'on veut protéger la santé publique. Les émissions de benzène diminueront quelque peu en raison des restrictions imposées sur les hydrocarbures produits par les véhicules, mais d'autres mesures seront nécessaires, notamment dans le cas des sources ponctuelles, afin de réduire les risques à des valeurs

acceptables actuellement. En outre, si aucun règlement n'est adopté, il n'est pas certain que la teneur en benzène de l'essence demeurera la même, et, si elle augmente, certaines réductions prévues des émissions des véhicules légers n'auront aucun effet.

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ACKNOWLEDGEMENTS

The contribution of the following Environmental Protection staff members to the preparation and review of this report is gratefully acknowledged:

Pollution Measurement - Daniel Wang

Transportation Systems - François Lavallée, Doug Cope, Jonah Libman

Inventory Management - Art Jaques

Oil, Gas and Energy - Art Stelzig, Marie Louise Geadah

Benzene has received a good deal of attention over the past years primarily because of studies that have identified it as a human carcinogen. Despite this attention, no regulatory actions specifically aimed at reducing benzene emissions have been taken in Canada.

In 1977 in the United States, the U.S. EPA listed benzene as a hazardous air pollutant and in 1984 promulgated a national emission standard for fugitive emissions of benzene from processing equipment in the petroleum refining and chemical manufacturing industries that contain materials which have a benzene concentration of 10% or more by weight¹. EPA has also proposed a standard limiting benzene emissions from coke by-product recovery plants¹. Most recently, in January 1985, the State of California identified benzene as a toxic air contaminant and filed a proposed benzene control plan for the State^{2,3}. The basis for this action was a California Department of Health Services report on benzene which concluded that: (1) benzene is a human carcinogen; (2) benzene should be treated as a carcinogen that may act at all doses without any threshold level; and (3) under reasonably conservative estimates, the added lifetime (70 years) risk of cancer from exposure to benzene ranges between 22 and 170 cases per million population per ppb⁴.

Because of these recent actions aimed at regulating benzene as a toxic air pollutant, it was considered prudent to examine recent benzene monitoring data from Canadian urban areas and to contrast population exposure levels in Canada to those in the United States. An identification of major Canadian benzene emission sources was also made and U.S./Canada source characteristics and trends in emissions were compared.

2 BENZENE USES and EMISSIONS

Benzene is a natural component of crude oil and is also formed during gasoline production. Benzene is a major intermediary in the production of plastics, elastomers, phenolic resins and nylons. The benzene content of gasoline is typically in the 1-2% (by volume) range. Benzene in vehicle exhaust results from incomplete combustion of the benzene component of gasoline as well as through formation from other aromatics and hydrocarbons during combustion. Benzene is also emitted from vehicles through evaporative processes.

2.1 Existing Emission Inventory

The only benzene emission inventory for Canada was prepared for the year 1976⁵. Major emission sources and estimated yearly emissions are shown in Table 1. In 1976, gasoline-powered motor vehicles were the dominant source of benzene emissions accounting for 83% of the total. In the ten years since this inventory was prepared, motor vehicle benzene emissions should have declined; depending on changes in other source sectors the fraction of total emissions attributable to mobile sources may have declined also.

The emissions inventory prepared for California for the year 1984 estimated statewide benzene emissions to be 19,400 Mg/y with vehicular sources (exhaust and evaporation) accounting for 93% of the total³. In California, point source benzene emissions (refineries and petrochemical) accounted for less than 0.1% of the total, although this appears to be due to the absence of any significant production or use of benzene in the petrochemical industry in California and to stringent fugitive volatile organic (VOC) control requirements.

The U.S. EPA estimated in 1985 that total United States benzene emissions were 243,600 Mg/y with automobile emissions representing 78% of the total. Coke by-product plants accounted for 11% of the total and fugitive emissions from benzene production and processing operations accounted for 3% of the total (prior to regulation).

TABLE 1 - BENZENE EMISSIONS in CANADA, 1976

Source	Yearly Emissions (Mg)	% of Total
<u>Point Sources</u>		
Petroleum Refining		
(a) General	450	1.0
(b) Benzene Production	928	2.1
Chemical Processes Using Benzene and its Derivatives	3,103	6.8
Coke Ovens	124	0.3
Other	130	0.3
<u>Area Sources</u>		
Gasoline Powered Engines	37,405	82.9
Diesel Powered Engines	417	0.9
Benzene Loading/Unloading	102	0.2
Gasoline Marketing	660	1.5
Surface Coatings	1790	4.0
TOTAL	45,109	100.0

2.2 Benzene Emissions from Light Duty Vehicles (LDVs)

Benzene tailpipe emission factors for light duty gasoline-powered vehicles will vary depending on the technology used to control exhaust emissions and on the benzene content of gasoline. No Canadian specific data on tailpipe benzene emissions appear to be available; however, the California benzene report included a detailed review of benzene emissions relative to control technology. The sensitivity of exhaust benzene to the benzene content of fuel appears to vary among the dozens of engine/control combinations on the road; however, the California study indicates that within three broad categories of cars - no catalyst, oxidation catalyst and three-way catalyst - there are good correlations between exhaust benzene and the benzene content of gasoline. Predictive equations for the fraction (weight percent of benzene in exhaust hydrocarbon) versus the benzene content of gasoline are shown in Table 2. Also shown are the 1984 California benzene in gasoline fraction (volume %) and the estimated benzene fraction of exhaust hydrocarbons. Test data showed that other aromatic compounds in gasoline also contribute to benzene in exhaust; however, there is insufficient data to quantify the relationship between exhaust benzene and the total non-benzene aromatic content of gasoline. The relationship between benzene in gasoline and evaporative benzene emissions from automobiles is shown in Table 3. Some increase in benzene emissions with increasing Reid Vapor Pressure (RVP) would be expected, although no quantified relationship has been established.

Data on the aromatic and benzene content of Canadian gasolines is scarce; a Winter 1978/79 study of Ottawa/Hull area leaded gasoline and a Summer 1981 study of unleaded and super unleaded gasoline was carried out by the NRC^{6,7}. As shown in Table 4, only the benzene content of leaded gasoline was measured during the NRC studies; however, assuming there is a consistent relationship between aromatic content and benzene content for California and Canadian fuels, the benzene content of unleaded gasolines should have been in the 1.4-1.7% range and super unleaded in the 2-2.3% range. Two of the leaded gasolines studied in the Winter 1978/79 study were blended from super unleaded fuels and the NRC estimated their benzene content at 2.5%⁶. No data was available on the benzene content of gasolines refined from Tar Sands crude oil.

TABLE 2 - PREDICTED BENZENE in EXHAUST by GASOLINE BENZENE CONTENT and ENGINE CONTROL TECHNOLOGY

Engine Control Technology	Predictive Equation	California 1984	
		Benzene in Gasoline (Vol %)	Benzene in Exhaust (Weight %) ³
Diesel	----	----	2.30
Non-Catalyst	Bex = $2.57 + 0.943 \text{ Bg}$	1.15	3.65
Oxidation Catalyst	Bex = $2.32 + 0.719 \text{ Bg}$	1.58	3.46
3-Way Catalyst/Carburetor	1984 - CRC Test Data ¹ Later Years - $0.77 \text{ wt \%}/\text{vol \%}$ ²	1.58	3.10
3-Way Catalyst/Multi-Port Fuel Injection	1984 - CRC Test Data ¹ Later Years - $0.77 \text{ wt \%}/\text{vol \%}$ ²	1.58	4.20

Bex = Benzene in exhaust THC, weight % Bg = Benzene in gasoline, volume %

1 - 1984 number based on tests of 65 cars

2 - Increase in exhaust fraction per unit increase in benzene content of gasoline

3 - % of total THC emissions

TABLE 3 - EVAPORATIVE EMISSIONS from LIGHT DUTY VEHICLES

Gasoline	Predictive Equation	California 1984		
		Benzene in Gasoline (Vol %)	Aromatics in Gasoline (Vol %)	Benzene Fraction of Evaporative THC (Wt %)
Leaded	$\text{Bev} = 2.24 + 0.928 \text{ Bg} + 0.0822 \text{ Ag}$	1.15	28.0	1.13
Unleaded		1.58	35.0	2.10

Bev = Benzene in evaporative THC, weight %
 Bg = Benzene in gasoline, vol. %
 Ag = Other aromatics in gasoline, vol. %

TABLE 4 - PROPERTIES of AUTOMOTIVE GASOLINES in CANADA (OTTAWA/HULL)

Gasoline	Benzene (% vol)		Total Other Aromatics (% vol)	
	Mean	Range	Mean	Range
Regular Leaded	1.2	0.8 - 1.9	24.4	20.3 - 38.1
Unleaded	---		33.0	25.4 - 36.6
Super Unleaded	---		41.0	37.8 - 49.7

California Leaded	1.13	---	28.0	---
California Unleaded	1.58	---	35.0	---

2.3 Trends in LDV Benzene Emissions

Benzene emission factors for LDVs will vary as follows: (1) decrease with decreasing tailpipe and evaporative THC emissions; (2) increase with increasing benzene in gasoline; and (3) increase with change from oxidation catalyst to fuel-injected 3-way catalyst technology. Two major events will influence benzene vehicle emissions in Canada; namely, the implementation of new LDV emission regulations for the 1988 model year and the phase-out of leaded gasoline in 1991. Table 5 shows projected benzene in gasoline levels during the years 1984 to 2000^{8,9} and Table 6 shows derived benzene in exhaust concentrations for different exhaust control technology³. Table 7 gives the impact of changes in emission control technology and gasoline benzene content on benzene emission factors for the period 1984 to 2000. Vehicle miles travelled over this period are forecast to increase by 41%⁹ (no major fuel cost increase scenario) which would result in a net benzene emission change of -27%. Heavy duty diesel vehicles currently account for only a small fraction (1-2%) of THC emissions from mobile sources and a similarly small fraction of benzene emissions. Although the diesel truck fleet is predicted to grow substantially between 1984 and 2000, new THC emission standards will likely offset any increase in emissions¹⁰.

For California, total vehicular benzene emissions are forecast to decrease by 20% between 1984 and the year 2000³.

2.4 Other Sources of Benzene

Benzene emissions in refineries result from releases from process streams, from leaking pumps and flanges and from gasoline and other storage tanks containing benzene. In the 1976 inventory, refinery operations (excluding benzene production) accounted for only 1% of total benzene emissions⁵.

Benzene is an important intermediary chemical; total production in Canada was 412,000 m³ (360 Gg) in 1976. Benzene is produced from petroleum products by catalytic reforming, hydrodealkylation and pyrolysis;

TABLE 5 - PROJECTED GASOLINE BENZENE CONTENT

Year	Leaded		Unleaded		Super Unleaded		Pool Benzene (%)
	Market Share (%)	% Benzene (%)	Market Share (%)	Benzene (%)	Market Share (%)	Benzene (%)	
1984	44	1.2	46	1.6	10	2.3	1.5
1990	15	1.4	73	1.8*	12	2.5	1.8
1995	0	---	85	1.8	15	2.5	1.9
2000	0	---	85	1.8	15	2.5	1.9

* Projected increase based on California data

TABLE 6 - PROJECTED BENZENE in EXHAUST¹
(Wt % of THC)

Year	Non-Catalyst	Oxid. Catalyst	3-Way Catalyst
1984	3.65	3.46	3.10
1990	3.81	3.59	4.04 ³
1995	4.27 ²	3.59	4.20 ³
2000	4.27 ²	3.59	4.35 ³

¹ - Using equations from Table 2 and projected benzene in gasoline figures in Table 5

² - Assumes non-catalyst cars now burning unleaded gasoline

³ - Reflects changing fuel management technology as well as change in gasoline benzene content

TABLE 7 - PROJECTED BENZENE EMISSION FACTORS for LIGHT DUTY VEHICLES in CANADA

Year	Fleet Composite LDV Emissions Factors (g/mi)		Assumed Technology Penetration				Assumed Gasoline Benzene %	Fleet Composite Benzene in Exhaust (% of THC)		Calculated Benzene Emission Factors		Fleet* VMT Factor	VMT Factor x Emissions (mg/mi)
	Exhaust THC	Evap. THC	Oxidation Catalyst %	3-Way Catalyst %	No Catalyst %			Exhaust	Evap.	Exhaust (mg/mi)	Evap. (mg/mi)		
1984	3.12	1.81	38	9	53		1.5	3.53	1.73	110	31	1.0	141
1990	2.43	1.27	30	32	38		1.8	3.85	2.05	94	26	1.17	140
1995	1.75	0.78	18	60	22		1.9	4.11	2.30	72	18	1.29	116
2000	1.42	0.58	10	77	13		1.9	4.26	2.30	60	13	1.41	103

* 2.7%/y growth 1984 - 1990
1.9%/y growth 1990 - 2000

emissions occur from atmospheric relief vents, pump valve seals and storage tanks. Benzene is used in the manufacture of ethylbenzene, cumene, cyclohexane, maleic anhydride and nitrobenzene; total Canadian consumption of benzene in 1976 was 290,500 m³ (225 Gg). Emission sources for these processes include process vents, storage tanks, and various other fugitive sources. Emissions from benzene production and chemical processing were estimated at 8.9% of total benzene emissions in 1976. Most of the benzene production and use occurs at only a few plants in Canada located in Montreal, Sarnia and Edmonton. A listing of major plants and 1979 production of benzene derivatives¹¹ is given in Table 8. In 1979, Gulf Canada also produced benzene but its refinery complex has since been closed down. In the United States, benzene production and consumption has decreased about 15% between 1979 and 1987; equivalent production change data for Canada were not available.

As discussed in Section 3.3, it appears that non-automotive sources are contributing 70-80% of the measured ambient benzene concentrations in Pointe-aux-Trembles. The situation appears similar in Sarnia, although the data base is very limited. The most likely point source of benzene in the Montreal/Pointe-aux-Trembles area is the Finachem (Polysar) facility located 1.5 km WSW of the monitoring site. California studies indicated a negligible point source impact on ambient benzene levels; the situation appears to be much different in Canada due to no mandated VOC controls at refineries and petrochemical plants. Major point source impacts on ambient benzene levels would be expected in Montreal and Sarnia due to the density of point source emissions. In terms of production capacity, the Polysar and Petrosar plants in Sarnia are much larger than the Finachem (Polysar) plant in Montreal.

The U.S. benzene fugitive emission source regulation applies to equipment containing materials with a benzene concentration of 10% or more by weight (sites producing or using 1,000 Mg/y of benzene or less are exempt¹). Equipment covered by the standard include new and existing valves, pumps, compressors, pressure relief devices, sampling connection system, open ended valves or lines, pipeline flanges, product accumulator vessels and closed vent systems and control devices used to comply with the

TABLE 8 - CANADIAN PETROCHEMICAL PRODUCTION
(BENZENE AND DERIVATIVES) in 1979

Plant	Product	Production (Gg/y)
<u>Montreal Area</u>		
Finachem (Polysar)*	Toluene	120
	Polybutene	11
	Benzene	160
	Xylene	190
Union Carbide	Ethylene	75
	Propylene	10
	Butadiene	7
	Polyethylene	225
<u>Sarnia Area</u>		
Dow Chemical	Styrene	80
	Polyethylene	118
Petrosar	Ethylene	450
	Propylene	275
	Butadiene	225
	Toluene/Xylene	125
Polysar	Butadiene	135
	Benzene	60
	Styrene	385
Esso	Benzene	96
	Ethylene	225
	Propylene	175
	Butadiene	20
Sunchem	Benzene	40
	Toluene	118
	Xylene	63

* 1985 Data¹²

vessels and closed vent systems and control devices used to comply with the standard. The regulations include the requirement for monthly leak detection and repair of all these process components.

Benzene emissions also result from benzene loading/unloading operations, from gasoline distribution and from gasoline marketing at service stations. In Canada, these sources were estimated to account for less than 2% of the total benzene emissions in 1976. In California, almost all of these sources are controlled using vapor recovery systems. Emissions from gasoline marketing operations will increase as the benzene level of gasoline increases. As discussed previously, exposure to benzene during vehicle refuelling can increase annual benzene exposure estimates.

Benzene emissions from surface coatings in 1976 were estimated at 4.0% of the total. These emissions were entirely due to evaporation from the application of industrial paints which contained benzene.

Benzene emissions from the coke by-product industry appear to account for a major portion of U.S. stationary source emissions. The importance of this source sector in Canada is not known.

3 EXPOSURE TO BENZENE

3.1 Measured Ambient Air Concentrations in Canada

Data on ambient air concentrations of benzene have been collected from sites in Canada during recent years as shown in Table 9. The characteristics of the monitoring sites and the length of the available data record are also included in the table. Monitoring is still continuing at the Montreal, Vancouver and Toronto (26 Breadalbane) locations.

The Montreal site is located within 2.5 km of two refineries and 1.5 km from a petrochemical plant. There are a number of small industries located near the Junction Triangle site but none of them were classified as major point source (greater than 50 Mg/y) emitters of volatile organics

TABLE 9 - BENZENE MONITORING SITES in CANADA (1983-1986)

NAPS Station No.	City	Address	Height Above Ground (m)	Point Source Influences	Data Record
61004	Sarnia	Centennial Park	3	Petrochemical	Aug. 83 to Sep. 83
----	Toronto	Junction Triangle	11	--	Aug. 84 to Mar. 86
50103	Montreal	Pointe aux Trembles	5	Petrochemical/ Refinery	Oct. 84 to Aug. 86
00111	Vancouver	Rocky Point Park	4	Refinery	Dec. 85 to Jul. 86
60417	Toronto	26 Breadalbane	16	--	Aug. 86 to Oct. 86

(VOC). The Vancouver site was approximately 2.5 km E of a small refinery (35,000 bbls/day) while the Sarnia site was located approximately 4 km N of a major petrochemical complex. None of the sites appeared to be unduly influenced by emissions from single nearby roadways; the two Toronto stations were located in the urban core. The sampling intake for the Toronto-Junction Triangle station was at a height of 11 m while the Breadalbane site intake was at 16 m; the other sites' intake heights ranged from 3 m to 5 m.

All data was collected as twenty-four hour average concentrations using a Tenax cartridge sampling system with analysis by gas chromatography/flame ionization/mass selective detection. Details of the sampling and analytical scheme employed are contained in Reference 13.

The mean, the standard deviation of the mean, and the maximum benzene concentrations for each of the sites are shown in Table 10. There was only a limited amount of sampling data available for the Sarnia and Toronto-Breadalbane stations; the other three sites had an eight-month to two-year data record. Of the sites with longer data records, Montreal had the highest mean benzene concentration of 5.7 ppb, followed by Vancouver with 3.2 ppb and Toronto-Junction Triangle with 2.8 ppb. The Sarnia site had a mean concentration of 6.0 ppb during the one-month period in 1983 when sampling was carried out. Mean benzene concentrations at the downtown Toronto site were less than 1 ppb during the sampling period. A more detailed discussion of benzene monitoring data for the 1984/85 period for the Montreal and Toronto-Junction Triangle sites is contained in Reference 13.

A summary of recently reported benzene data from U.S. monitoring sites is given in Table 11^{14,15}.

3.2 Relationships Between Benzene and Carbon Monoxide (CO)

Because the data base on measured ambient benzene concentrations in Canada is currently limited, it is useful to examine relationships between benzene and other pollutants such as carbon monoxide (CO) since the

TABLE 10 - SUMMARY of BENZENE CONCENTRATIONS (ppb) at CANADIAN MONITORING STATIONS

City	Address	Dates	No. of Samples	Mean	Std. Dev.	Maximum
Sarnia	Centennial Park	Aug.83-Sep.83	8	6.0	4.9	15.3
Toronto	Junction Triangle	Aug.84-Mar.86	105	2.8	1.6	11.6
Montreal	Pointe-aux-Trembles	Aug.84-Aug.86	83	5.7	4.8	25.1
Vancouver	Rocky Point Park	Dec.85-Jul.86	38	3.2	2.6	11.2
Toronto	26 Breadalbane	Aug.86-Oct.86	13	0.9	0.4	1.6

TABLE 11 - BENZENE CONCENTRATIONS in the UNITED STATES

City	No. of Obs.	Mean Concentration (ppb)	24 h Maximum Concentration (ppb)	Dates
El Monte, CA	310	4.6	15.6	Sep. 83 - Sep. 85
Riverside, CA	69	4.1	9.2	Sep. 83 - Dec. 84
Boston, MA	20	1.1	1.9	July 85 - Jan. 86
Chicago, IL	14	1.3	3.0	July 85 - Jan. 86
Houston, TX	23	2.2	9.3	Mar. 85 - July 85
Las Vegas, NV	18	3.2	6.7	Sep. 85 - Dec. 85
California*	--	3.3	---	1984
United States+	--	3.8	---	1978-82

* - Statewide population weighted annual mean 1984

+ - Estimated annual mean from 5 U.S. metropolitan areas (1978-1982 data)

data base for CO is much more extensive. As discussed in Section 2, the major source of benzene emissions in Canada is automobile exhaust; therefore in areas with no industrial emissions of benzene, measured CO levels should be a useful indicator of ambient benzene concentrations. The State of California used derived benzene/CO relationships to develop a statewide exposure estimate for benzene³.

Twenty-four hour average CO data were available for most benzene sampling days at each site and Table 12 summarizes benzene/CO relationships for each Canadian site. California data are also presented for comparison. Table 12 contains mean CO concentration (ppm), mean benzene concentration (ppb) and the slope, intercept and r^2 values for the linear equation:

$$\text{Benzene (ppb)} = B + A * \text{CO (ppm)}$$

As shown in Table 12, there was a wide variation in the coefficients of the linear equation and in the calculated r^2 values from site to site. Benzene/CO relationships will only be relevant if benzene at a site derives predominantly from auto exhaust. It has been shown that auto exhaust contains benzene and the aromatics-toluene, m,p-xylene, o-xylene and ethylbenzene in consistent proportions¹⁶. As shown in Table 13, extensive monitoring data from sites in the United States where automobiles were the dominant source of aromatics reveals benzene/ethylbenzene ratios of 0.9 to 2.5, toluene/ethylbenzene ratios of 3.2 to 7.0 and xylene/ethylbenzene ratios of 2.5 to 4.0^{17,18}. Mean concentrations of benzene and other aromatics normalized to ethylbenzene for the Canadian monitoring sites are given in Table 14. Benzene/ethylbenzene ratios at the two Toronto sites and the Vancouver site fell within the expected range if automobile exhaust was the primary source of benzene. At the Montreal and Sarnia site, a source of benzene other than the automobile is indicated.

As shown in Table 12, the slopes of the benzene/CO equation at the Toronto-Junction Triangle and Vancouver sites were similar to that calculated for the California data, although intercepts were approximately twice as high. The Toronto-Breadalbane site had the smallest calculated slope of all the sites although the data set is limited and an examination

TABLE 12 - RELATIONSHIP BETWEEN CO & BENZENE at MONITORING SITES

Site	N	Mean CO (ppm)	Mean Benzene (ppb)	Benzene = A*CO+B		
				A	B	r ²
Montreal	61	0.47	5.7	2.8	4.8	0.07
Toronto	13	0.87	0.9	0.6	0.4	0.48
Toronto (JT)	118	0.95	2.8	2.0	1.0	0.44
Vancouver	30	1.04	3.2	2.3	0.9	0.88
Sarnia	13	0.14	6.0	13.6	4.1	0.32
California (8 sites)	548	2.15	4.5	1.8	0.4	0.71

TABLE 13 - MEAN CONCENTRATIONS of AROMATIC HYDROCARBONS
NORMALIZED to ETHYLBENZENE
at U.S. MONITORING SITES

	Benzene/ Ethylbenzene	Toluene/ Ethylbenzene	Xylenes/ Ethylbenzene
Houston*	1.2	3.2	3.7
Philadelphia*	2.2	4.8	3.8
Baltimore*	1.6	6.1	3.9
Washington*	0.9	4.2	4.1
Newark*	1.1	4.7	2.7
Boston*	2.5	7.0	4.0
Milwaukee*	1.3	5.3	3.7
Lincoln Tunnel°	2.6	4.6	2.8
Average of 15 US Cities+	2.5	4.3	2.5

* 6-9 AM concentrations in Downtown Areas (Reference 17)

+ Spring/Summer concentrations in Urban Areas (Reference 18)

° Reference 16

TABLE 14 - MEAN CONCENTRATIONS of BENZENE and OTHER AROMATIC HYDROCARBONS
NORMALIZED to ETHYLBENZENE
at CANADIAN MONITORING SITES

City	Address	Benzene/ Ethylbenzene	Toluene/ Ethylbenzene	Xylenes/ Ethylbenzene
Sarnia	Centennial Park	7.9	5.0	3.0
Toronto	Junction Triangle	2.8	7.4	4.3
Montreal	Pointe-aux-Trembles	9.1	5.5	3.3
Vancouver	Rocky Point Park	3.2	5.4	3.0
Toronto	26 Breadalbane	2.5	10.0	3.5

of other VOC data collected at this site showed possible interferences from a nearby source.

In order to predict benzene concentrations from CO data at other Canadian sites, it seemed most appropriate to use a composite of the Vancouver and Toronto-Junction Triangle data resulting in a final relationship as follows:

$$\text{Benzene (ppb)} = 0.9 + 2.09 \text{ CO (ppm)}, r^2 = 0.59 \quad (\text{Equation 1})$$

This relationship, of course, will not account for benzene from sources other than automobiles. The higher intercept in the above equation versus the California equation may be due in part to the much better controls on fugitive VOC (and benzene) emissions from miscellaneous sources such as solvent use and gasoline marketing in California³.

In Canada, there are currently 51 CO monitoring sites reporting data to the NAPS network¹⁹. These sites were located in cities with a combined total population in 1981 of 17.8 million people. The distribution of sites in terms of scale of representativeness was as follows: (1) neighbourhood scale (not immediately adjacent to major roads) - 35%; (2) middle scale (may be affected by specific nearby roadways) - 61%; and (3) micro-scale (very close to roadways) - 4%. The network thus probably overestimates city-wide CO levels and may overestimate population exposures to ambient concentrations.

Table 15 provides annual mean CO data for the sites in the network with the highest mean concentrations in 1985. Also included is the calculated benzene concentrations using Equation 1. The composite (average of all sites) Canadian annual mean is also shown, as is the California (1984) composite mean, the California population weighted mean and the California calculated population weighted benzene exposure. Annual mean CO levels (using all data for the year) are also shown for the Canadian benzene monitoring sites, as are the benzene concentrations calculated using Equation 1.

TABLE 15 - 1985 ANNUAL MEAN CO LEVELS at SELECTED CANADIAN MONITORING SITES
and CALCULATED BENZENE CONCENTRATIONS+

NAPS Stn. No.	City	Address	1985 Annual Mean CO (ppm)	Calculated Benzene Conc. (ppb)
50115	Montreal	Boul. Maisonneuve	1.8	4.7
60101	Ottawa	88 Slater	1.8	4.7
60415	Toronto	Queensway/Hurontario	1.9	4.9
60416	Toronto	381 Yonge	3.7	8.6
90130	Edmonton	104th Street	1.5	4.0
90227	Calgary	1611 4th Street	1.7	4.5
00108	Vancouver	250 West 70th	1.4	3.8
00112	Vancouver	Robson/Hornby	2.5	6.1
-----	Toronto	Junction Triangle	0.9	2.8
60417	Toronto	26 Breadalbane	1.1	3.2
50103	Montreal	Pointe-aux-Trembles	0.3	1.5
00111	Vancouver	Rocky Point Park	1.0	3.0
Canadian Composite Annual Mean (51 sites)			1.0	3.0

California Composite (67 sites - 1984)			1.4	3.0*
California Populated Weighted			1.6	3.3*

+ Using Equation 1

* Using California equation (Table 11)

The calculated Canadian composite mean benzene concentration of 3.0 ppb was identical to that derived for California. No attempt was made to calculate a population weighted mean although, as noted above, 75% of the Canadian population resides in the urban areas included in the NAPS CO monitoring program. As discussed previously, mean concentrations calculated from network CO monitors may be an overestimate of urban CO exposures.

People living close to major roadways will obviously be exposed to higher levels of benzene than the average. Commuters on busy highways have been shown to experience higher cumulative CO exposures and hence higher benzene exposures than would be represented by fixed monitors.

3.3 Exposure to Benzene from Non-Automotive Sources

It was calculated in California that the maximum ground level impact due to point sources would be 1.1 ppb³; it was also determined that, since point sources accounted for less than 0.1% of the States total benzene emissions, point sources would have little impact on total benzene exposures. Minimal point source emissions of benzene in California are due to two factors: (a) limited production and use of benzene in the State petrochemical industry; and (b) stringent fugitive VOC controls on all point sources due to ozone attainment regulations. In Canada, there are no mandated fugitive VOC emission controls on refinery or petrochemical processes. Two provinces, Alberta and Quebec, have regulations governing VOC emissions from storage facilities.

In Sarnia and Montreal, there are large petrochemical manufacturing facilities. In Montreal, based on benzene/ethylbenzene ratios, it was calculated that 70-80% of the benzene (mean concentration 5.7 ppb) was due to point source emissions¹³. The situation appears similar in Sarnia, although the data base was quite limited. Total population exposures to point source benzene emissions are difficult to quantify without additional monitoring data.

Customers who refuel their own cars at self-serve gas stations will also be exposed to benzene in gasoline vapors for short periods. Studies in California have shown that customers are typically exposed to 1 ppm of benzene for two minutes during fueling at stations with no vapor recovery. Assuming 104 refuellings a year, this could add 0.4 ppb to an individual's annual average benzene exposure³. Typical exposures in Canada are possibly lower because of lower average temperatures and hence reduced benzene volatilization, although this may be compensated by longer periods of use of winter fuels with correspondingly higher Reid Vapor Pressure. Attendants at full serve stations may be subject to significantly higher exposures than average.

A number of studies have shown that indoor exposures to benzene are significant and benzene levels are often higher indoors than out. Data from California and Montreal suggest indoor levels average 0.8 to 1.5 ppb above outdoor levels^{3,20}. Outdoor benzene concentrations, however, appear to account for baseline indoor concentrations since benzene is quite stable in the atmosphere and most homes have an air infiltration rate in the range of 0.25 to 2.5 exchanges per hour. Additional sources in the home account for the higher indoor levels over the outdoor baseline. This suggests that any reduction in ambient benzene concentration reductions should result in equivalent or near equivalent indoor benzene reductions. Therefore, risk calculations based on twenty-four hour averaged ambient benzene exposures need not be discounted for time spent indoors^{2,3}.

The only other known non-industrial route of exposure to benzene would be through drinking water. Based on California data, it was calculated that the public breathes in 350 times more benzene than they would drink from water contaminated at the detection level³.

3.4 Exposure and Risks

A summary of the California Department of Health Services (DHS) report on the health effects of benzene is contained in Reference 3. The

findings of a Scientific Review Panel which reviewed the DHS report is also contained in this reference.

The Review Panel recommended that benzene be listed as a toxic air contaminant having no threshold level. They agreed that the following DHS propositions were prudent interpretations of the available evidence:

- 1) Benzene is a human carcinogen.
- 2) Benzene should be treated as a carcinogen that may act at all doses without any threshold level.
- 3) Health effects, other than cancer, are not anticipated at current ambient exposure levels.
- 4) Under reasonable conservative estimates, the added lifetime cancer risk from ambient exposures is not negligible.

Exposure to an air pollutant is usually calculated by multiplying ambient concentration by the total population of the area represented by the ambient measurements. This results in a unit of millions of ppb-persons and is usually averaged over one year. When multiplied by the risk factor determined by DHS of 22 to 170 excess cancers per ppb among a million people exposed for 70 years, each unit of exposure (10^6 ppb-persons) corresponds to 22 to 170 "theoretical cancers" occurring prematurely during 70-year lifetimes³. There are, of course, many uncertainties in making estimates of cancer occurrence over 70-year lifetimes; however, the Scientific Review Panel concluded that there was a reasonable scientific basis for regulatory action regarding benzene.

For California in 1984, it was calculated that 25.8 million people were exposed to an average benzene concentration of 3.3 ppb resulting in a total exposure of 84.1×10^6 ppb-persons. Multiplying this times the risk factor results in a 70-year estimated cancer risk ranging from about 1,900 to 14,500 excess cancers for California³. Using Canadian data based on benzene/CO relationships in urban areas which include a

population of 17.8 million people, and assuming a benzene level equivalent to the background concentration of 0.8 ppb benzene in other areas³, total Canadian exposure would be approximately 58×10^6 ppb-persons. Using the DHS risk estimate, these exposures over 70 years would result in 1,000 to 10,000 excess cancers for Canada. However, as discussed in Sections 3.2 and 3.4, there is a good deal of uncertainty in the Canadian benzene ambient concentration estimates.

3.5 Air Quality Trends

Because vehicular emissions of hydrocarbons and benzene have decreased dramatically since the late 1960s and early 1970s, ambient benzene concentrations are also assumed to have declined. Limited sampling (9 days) conducted during the summer of 1971 in downtown Toronto resulted in a mean measured benzene concentration of 9 ppb with a maximum of 98 ppb, substantially higher than any recent monitoring results²¹. For California, it was estimated that emissions had declined 50% from 1964 to 1984 and that ambient benzene concentrations during rush hour in the early 1960s used to reach 40 ppb³. To predict future levels of benzene requires development of a projected emission trend as discussed in Section 2.

4 AVAILABLE CONTROL MEASURES

Available benzene control measures were identified in the California control plan and were categorized according to technical feasibility, potential emission reduction and cost per pound of benzene reduction³. A summary of these control measures is given in Table 16. As noted in the table, the costs of many of the vehicular control measures have been attributed to criteria pollutant control needs.

The California measures may not be directly applicable to Canadian sources and the cost-effectiveness calculations may be significantly different, especially for point sources. No control measures for organic chemical manufacture are included since this source is insignificant in California.

TABLE 16 - SUMMARY of BENZENE CONTROL MEASURES (CALIFORNIA)

	Technical Feasibility	Statewide Emission Reduction* 2000 (tons/yr)	% of Total	Cost* (\$/lb. Benzene Reduced)	Priority for Measure Development
A. Motor Vehicles					
1. Oxygen Sensor Durability/ On-Board Diagnostics	A	290	1.6	n/a	Adopted 4/85
2. Modifier-Certified New Vehicle Regulations	A	180	1.0	n/a	Adopted 12/85
3. More Stringent Exhaust HC Standard+	B	1,900	10.6	n/a	High
4. More Stringent Evaporative HC Standard	B	37	0.2	n/a	High
5. Other HC Measures	B	2,400	13.3	n/a	High
6. Exhaust Emission Benzene Limit	C	1,500	8.3	\$5 - \$25	High
7. Alternative Fuels	B	700	3.9	n/a	High
B. Non-Vehicular					
1. Gasoline Marketing					
a) Vapor Recovery at Service Stations	A	130	0.7	\$19	High
b) Vapor Recovery at Bulk Plants	A	36	0.2	\$28	High
c) Afterburners at Bulk Terminals	A	40	0.2	\$23	High
2. Gasoline Specifications					
a) 1.4 vol. % benzene limit	B	1,400	7.8	\$53	High
b) 1.0 vol. % benzene limit	B	2,800	15.6	\$49	High
3. Refinery Sources					
a) Vapor Recovery on Benzene Tanks	A	11	0.1	\$1 - \$2	High
b) Improve Seals on Benzene Tanks	A	7	0.1	\$1	High
c) Vapor Recovery on Marine Loading	B	23	0.1	\$75 - \$520	Low
d) Improve Seals on Gasoline Tanks	A	2.3	0.1	\$22 - \$33	High
e) Replace Riveted Benzene Tank	A	7.4	0.1	\$11	High
f) Replace Gasoline Tanks	A	.3	0.1	\$700 - \$2800	Low

- A - Presently available control technology; available and proven control method
 B - Technically feasible but not available commercially at present; more development time is needed
 C - Advanced control method which requires additional research and/or time to develop technology prior to commercial applications
 * - The emission reductions are not additive since implementation of some measures will affect other measures' costs and emission reductions
 n/a - Not applicable, potential vehicular control measures planned for criteria pollutant control
 No cost is attributed to benzene control
 + - More stringent than Canadian 1988 LDV standards

Control measure A6 in Table 16, for exhaust emission benzene limit, would require manufacturers to achieve a 50% reduction in benzene emissions from the average emissions of current (U.S./California specification) catalyst-equipped vehicles. Although the average exhaust benzene level for catalyst-equipped vehicles is approximately 4%(Wt % of THC), some new catalyst vehicles have exhaust benzene levels as high as 10%³. The technical feasibility of benzene specific control measures is still under investigation in California. The most effective control measure (in terms of tons/ year benzene reduction) in the California summary was a 1% limit on the benzene content of gasoline. The cost of this measure was estimated at 1.8 cents per U.S. gallon³.

The U.S. EPA fugitive benzene control regulation affects 229 facilities emitting 7,900 Mg/y (14% of the stationary source total) in 1984 and was to result in a total emission reduction of 5,400 Mg. The calculated cost effectiveness (1984) of this measure was estimated at \$1.40/Kg¹ of benzene reduced. Attainment of this regulation is achieved by better maintenance and elimination of all process and vent leaks. A proposed regulation of benzene emissions from the coke by-product industry is under final review by EPA; this regulation would result in an annual 25,500 Mg benzene emission reduction at an estimated cost-effectiveness of \$3.30/Kg^{22,23}

5 SUMMARY and CONCLUSIONS

There appears to be no debate over the fact that benzene is a human carcinogen with most estimates of lifetime risk of cancer in the range of 22 to 170 x 10⁻⁶ per ppb of benzene exposure. In the absence of other information, it is recommended that benzene be treated as a carcinogen that may act at all doses without any threshold level. Benzene has been formally listed as a toxic air pollutant by both the U.S. EPA and the California Air Resources Board.

Recent Canadian monitoring data for benzene show that mean concentrations range from 0.9 to 6.0 ppb with the highest concentrations measured near point sources. Using CO monitoring data from 51 sites and a derived benzene/CO relationship from recent measurement data, mean benzene levels in Canadian urban areas are estimated to be 3.0 ppb. This value is the same as the mean benzene exposure level of 3.0 ppb calculated for the State of California and is within the range of recent mean benzene concentrations reported for major U.S. urban areas. Benzene exposures will be higher for commuters, for drivers who routinely use self-serve gas stations and for populations dwelling near point sources. Background levels of benzene are estimated to range from 0.1 to 0.8 ppb. Indoor levels are typically higher than outdoor levels but control of outdoor sources should reduce indoor exposures proportionately.

Tailpipe and evaporative emissions from light duty gasoline-powered vehicles are the largest source of benzene and account for the majority of population exposure to benzene. Benzene emissions are decreased substantially by catalyst control technology; emission decreases, however, can be offset by increasing fuel benzene content. It is estimated that LDV benzene emissions in Canada will decrease by 27% between 1984 and the year 2000.

Major point source emitters of benzene are poorly characterized and are not currently subject to any emission control requirements. Major sources are concentrated in three urban areas, Montreal, Sarnia and Edmonton. Based on existing monitoring data for Montreal, point sources can have a major impact on locally measured ambient benzene concentrations. Projecting future emission trends for point sources is not currently feasible. Most point sources of benzene in the U.S. have been required to reduce benzene emissions as a component of overall VOC reductions mandated by ozone control plans. Additionally, fugitive benzene emissions from benzene production facilities have been regulated since 1984.

Potential control measures for benzene were carefully reviewed by California. Current VOC control plans for vehicles (non-benzene specific) will result in a 20% reduction in benzene emissions (1984-2000) in California, similar to the projected 27% reduction for Canada. By adopting gasoline benzene limits and improved vapor recovery at all bulk and retail gasoline marketing sources, overall individual risk to benzene exposures in the State could be reduced by 50% by the year 2000. The U.S. EPA regulation of fugitive benzene emissions was designed to reduce maximum individual risks to benzene exposure. Most of the control measure costs were in the range of \$2 to \$200 per Kg of benzene reduced. Point source fugitive benzene emission control is one of the most cost-effective control measures as is the proposed benzene emission regulation for the coke by-product industry.

Based on existing Canadian ambient air monitoring data and estimated risk values for benzene, it can be concluded that reductions in benzene levels are warranted to prevent harm to public health. Although some reduction will take place as a result of vehicular HC control measures, additional controls will be necessary, especially on point sources to reduce risk to currently acceptable values (10^{-10} to 10^{-6}). Without regulation there is also no certainty regarding the future benzene content of gasoline. Increases in benzene fuel content will offset some of the expected LDV emission reduction.

6 RECOMMENDATIONS

Because of uncertainties in estimates used in the report on current exposure and risk and because of uncertainties related to emission-trend projections, the following work tasks are recommended.

6.1 Health Assessment

Health and Welfare Canada should review the DHS analysis of the health effects of benzene and assess the following: (a) Are the DHS risk estimates reasonable? (b) Does the risk posed by current ambient benzene levels in Canada warrant control actions?

6.2 Ambient Monitoring

A limited ambient benzene data base exists in Canada. Because of the utility of estimating benzene exposures from CO data, efforts should be made to validate CO/benzene relationships at additional sites. Exposures due to point source emissions should be better quantified; monitoring data from a residential area of Sarnia near the petrochemical complex would be useful. Long-term trend sites for benzene will be necessary to determine the impact of emission changes.

6.3 Source Characterization

Point sources such as refineries and petrochemical plants are very poorly characterized in regards to VOC emissions including benzene. Emission measurements should be carried out as soon as possible. A review of recent U.S. data should be carried out.

Canadian specific benzene tailpipe and evaporative emissions data should be gathered especially at cold temperatures. A review of the most recent U.S. test data should also be carried out.

6.4 Benzene in Fuels

Data on current and future gasoline benzene content appears critical to the accurate determination of automobile benzene emissions.

6.5 Emission Trends

The benzene emission projection developed in this report should be confirmed. The existing benzene emission inventory should be updated; better point and mobile source emission data as noted in Section 6.3 and benzene in fuel data (Section 6.4) will be needed.

6.6 Control Technology

A detailed review of U.S. data on control costs and control options, especially for the petrochemical industry, should be initiated. Data on current practices in the industry, in regards to control of fugitive emissions, is required. Developments in benzene specific control measures for California should be followed closely. Proposed new HC control measures such as fuel volatility reductions and more stringent automobile evaporative emission controls will also reduce benzene emissions and should be examined in detail.

6.7 Socio-Economic Considerations

The cost effectiveness of various control strategies should be evaluated. The benefits associated with reductions in ambient benzene levels should be identified.

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