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BENZENE AND TOLUENE LEVELS IN THE UPPER ST. CLAIR RIVER

by

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Environment Canada

Management Perspective

Title: Benzene and toluene levels in the upper St. Clair River

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Date: November, 1987

Perspective:

This manuscript reports new research results on the occurrence and distribution of benzene, toluene, and a number of aliphatic hydrocarbons in water samples collected in November 1985 from 60 stations on 20 transects in the upper St. Clair River. The results indicate (i) sources of benzene and toluene in the upper St.Clair R. downstream from Sarnia and, (ii) the presence of aliphatic hydrocarbons, which are thought to be gasoline related substances, in most of the samples on either side of the river. The aliphatic hydrocarbons are strongly varying in composition and relative concentration, with some samples showing essentially only one, others up to 35 related components.

The benzene and toluene concentrations were found to be in the range of <100 to 4300 (mean of 38 samples 560) $ng.L^{-1}$ and <100 to 2200 (mean of 32 samples 710) $ng.L^{-1}$, respectively. These levels are well below those known to produce any acute toxic effects to humans and aquatic species. Insufficient data exist to evaluate their long-term exposure effects at these levels.

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Analyse de gestion

Titre : Teneurs en benzène et toluène dans le cours supérieur de la rivière Sainte-Claire

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Date : Novembre 1987

Analyse : Le présent manuscrit présente de nouveaux résultats de recherche sur la présence et la répartition du benzène, du toluène et d'un certain nombre d'hydrocarbures aliphatiques dans des échantillons d'eau, prélevés en novembre 1985, dans 60 stations, sur 20 transects, dans le cours supérieur de la rivière Sainte-Claire. Les résultats indiquent (i) des sources de benzène et de toluène dans le cours supérieur de la rivière Sainte-Claire, en aval de Sarnia, et (ii) la présence d'hydrocarbures aliphatiques que l'on croit être des substances apparentées à l'essence dans la plupart des échantillons des deux côtés de la rivière. Les hydrocarbures aliphatiques varient considérablement en ce qui a trait à leur composition et à leur concentration relative, certains échantillons présentant seulement un élément dérivé et d'autres jusqu'à 35.

Les concentrations de benzène et de toluène variaient respectivement entre moins de 100 et 4 300 (moyenne de 38 échantillons, 560) $ng.L^{-1}$ et entre moins de 100 et 2 200 (moyenne de 32 échantillons, 710) $ng.L^{-1}$. Ces teneurs sont bien inférieures à celles qui produisent des effets toxiques aigus chez l'être humain et les espèces aquatiques. Nous ne possédons pas suffisamment de données pour évaluer leurs effets d'exposition à long terme à ces teneurs.

TENEURS EN BENZÈNE ET TOLUÈNE DANS LE COURS SUPÉRIEUR DE LA RIVIÈRE SAINTE-CLAIRE

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RÉSUMÉ

Les analyses des échantillons d'eau de fond, prélevés dans la rivière Sainte-Claire le long de 20 transects, comprenant chacun 3 stations à 10 m, 25 m et 100 m au large, indiquent des apports de benzène et de toluène dans la zone littorale, le long d'une région fortement industrialisée en aval de Sarnia (Ontario). Les charges minimales de 10 kg.jour^{-1} de benzène et 15 kg.jour^{-1} de toluène sont calculées à partir des concentrations observées. De plus, un certain nombre d'autres hydrocarbures volatils étaient présents dans la plupart des échantillons et ont été identifiés provisoirement comme des alcanes ramifiés, portant 5 à 6 atomes de carbone.

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ABSTRACT

Analyses of St. Clair River bottom water samples along 20 transects, each comprising three stations at 10 m, 25 m, and 100 m offshore, show inputs of benzene and toluene in the nearshore zone along the highly industrialized area below Sarnia, Ontario. Minimum loadings of 18 $kg \cdot day^{-1}$ benzene and 15 $kg \cdot day^{-1}$ toluene are calculated from the observed concentrations. In addition, a number of other volatile hydrocarbons were present in most samples and were tentatively identified as five to six carbon atom containing branched alkanes.

INTRODUCTION

Benzene and toluene are two chemicals classified as priority pollutants (US EPA, 1979) which are known to produce acute toxic effects in aquatic and terrestrial organisms (Kirk-Othmer, 1978/84, Vol. 3 and 23). Environmental tolerance levels for benzene and toluene are unspecified for Ontario waters since scientific data is insufficient for establishing water quality objectives, although both chemicals are of primary concern (MOE, 1978).

Benzene and toluene originate from petroleum feedstocks and are produced by catalytic cracking/reforming processes. Toluene production is primarily directed to the gasoline pool while benzene is mostly used in the synthesis of polystyrene plastics, synthetic rubber, phenolic resins, nylon, polyester resins, detergents and insecticides.

As most of the above manufacturing processes are present in the industrial area along the upper St. Clair River, near Sarnia, Ontario (CCN, 1986), it would not be unexpected to find these two materials in the surrounding environment.

EXPERIMENTAL

Single bottom water samples, 0.5 m off the bottom, were taken at the 60 stations on 20 transects in November 1985 with vertical Van Dorn samplers. In the sample descriptions, the letters a, b, and c denote sampling stations 10 m, 25 m, and 100 m offshore, respectively, along the transects denoted by numerals. The exact sampling dates and orders were: Nov. 19: transects 4, 5, 7, 9, 10, 6; Nov. 20: transect 20; Nov. 21: transects 12, 13, 14, 15, 16, 17, 18, 19, 20, 1, 3, 11; Nov. 22: transect 6; Nov. 26. The stations a, b, and c at each transect were sampled in that same order. The samples were transferred to 250 mL screwcap glass bottles, filled right to the top and were kept at or below room temperature until processing. The samples were processed at CCIW within two days from collection according to the procedure by Comba and Kaiser (1983) and some of our unpublished results which show the stability of such samples under such conditions.

For the analysis, a Varian 3700 gas chromatograph with a 30 m, SE-54 fused silica capillary column was used. The temperature regime was isothermal at 30°C with injections of 500 µL of sample head space using a split (15:1)/splitless mode of operation with an initial 0.2 min. hold in the splitless mode. Other instrument conditions were: injector temperature 80°C; flame ionization detector and carrier gas hydrogen at 1.0 $mL \cdot min^{-1}$. Detection limits for benzene and toluene under these conditions were 100 $ng \cdot L^{-1}$ (ppt).

RESULTS

Benzene and toluene were reported to be present in the effluents of Imperial Oil, Esso Chemical, Polysar, Dow and Suncor (King, 1986; King and Sherbin, 1986; Bonner and Meresz, 1981). Of the river water samples we analyzed, 65 and 54 percent contained measurable levels of benzene and toluene, respectively. The concentrations ranged from 100 to 4300 ng·L^{-1} benzene and from 100 to 2200 ng·L^{-1} toluene and are consistent with measured amounts of benzene in raw and treated waters at Walpole Island (Roberts et al., 1986). Along the eastern shore of the St. Clair River, increased levels were evident from the edge of the Imperial Oil property and downstream from there throughout the entire industrial area to the south of the Suncor property, as indicated in Figure 1.

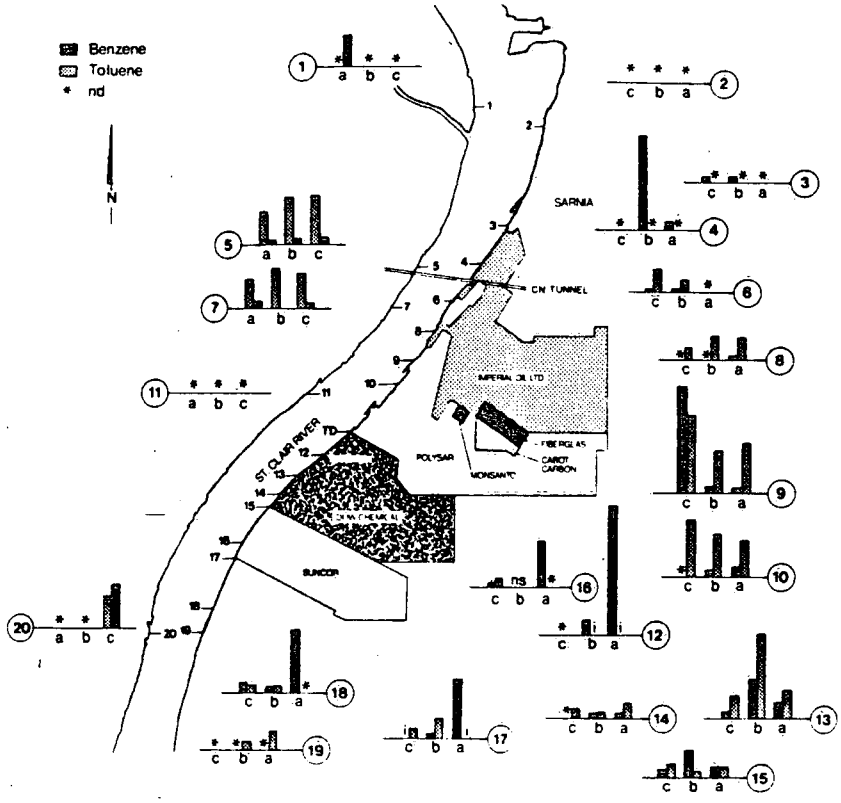

Figure 1 Benzene and toluene concentrations in bottom water samples of the St. Clair River, Sarnia, Ontario, 1985; TD denotes the Township Ditch tributary; data given in Table 1.

The upper St. Clair River is a relatively uniform channel which is 500 to 800 m wide and 9 to 15 m deep (Rukavina, 1986). Using a mean depth of 12 m, mean width of 600 m and a 6 km length for the sampled industrialized section of the river, the water in this part of the river represents approximately 10% of the total river volume. From the values in Table 1 (using zero for levels below detection limit), mean concentrations of 448 ng·L^{-1} benzene and 384 ng·L^{-1} toluene were calculated for stations 3,4,6,8,9,10,12, 13,14,15,16,17,18 and 19 along the Canadian shoreline. This represents loadings of approximately 18 kg·day^{-1} benzene and 15 kg·day^{-1} toluene for that sampling period based on a mean river velocity of 1.0 m·sec^{-1}. Effluent loadings derived for the same month (King, 1986) were significantly higher for benzene (176 kg·day^{-1}) and lower for toluene (4.7 kg·day^{-1}). The large discrepancy for benzene may partially be due to one unusually high value for the Dow, Third Street sewer, normally not contaminated with benzene, that accounted for 33 percent of this loading. Also, losses to the atmosphere depend on the temperature of the effluent, the river water and on the containment of the discharge. Our lower toluene values may be the result of our lower detection limits for that compound. King (1986) reported effluents as below a detection limit of 1 µg·L^{-1}.

Table 1. Benzene and toluene concentrations in nearshore waters of the upper St. Clair River, 1985. Concentrations in $ng \cdot L^{-1}$ (ppt).

Station Number	Benzene	Toluene	Station Number	Benzene	Toluene
1a	800	Nd	11a	Nd	Nd
b	Nd	Nd	b	Nd	Nd
c	Nd	Nd	c	Nd	Nd
2a	Nd	Nd	12a	4300	I
b	Nd	Nd	b	370	I
c	Nd	Nd	c	Nd	Nd
3a	Nd	Nd	13a	450	770
b	100	Nd	b	1000	2200
c	100	Nd	c	130	530
4a	100	Nd	14a	150	350
b	2400	Nd	b	100	100
c	Nd	Nd	c	Nd	260
5a	100	850	15a	200	210
b	100	1200	b	560	100
c	100	1200	c	190	260
6a	Nd	Nd	16a	1200	Nd
b	100	300	b	Ns	Ns
c	100	560	c	100	170
7a	100	700	17a	1500	I
b	Nd	910	b	100	500
c	100	900	c	I	330
8a	100	560	18a	1500	Nd
b	Nd	640	b	100	100
c	Nd	340	c	200	100
9a	100	1300	19a	400	Nd
b	100	1100	b	160	Nd
c	2600	2000	c	Nd	Nd
10a	280	910	20a	Nd	Nd
b	180	1100	b	Nd	Nd
c	Nd	1400	c	1100	700
			Township Ditch	1400	280

Nd - not detected (detection limits 100 $ng \cdot L^{-1}$).
I - Interfering peak, non-reliable quantitative determination.
Ns - no sample.

The mean river loadings derived here are similar to loadings of volatile halocarbon contaminants reported earlier for these samples (Kaiser and Comba, 1986). For example, 22 $kg \cdot day^{-1}$ carbon tetrachloride, 32 $kg \cdot day^{-1}$ tetrachloroethylene, and 3 $kg \cdot day^{-1}$ 1,1,1-trichloroethane.

Benzene and toluene levels were also observed in St. Clair River water along the American shoreline near station 1 (see Figure 1), the discharge area of the Port Huron water pollution control plant, and at stations 5, 7, and 20. The likely sources of these materials are gasoline products, however, their exact origin cannot be determined. The observed concentrations near the train tunnel (station 5 and 7) could result from railway barge operations in this area. Also, the possibility of seepage from abandoned oil wells cannot be excluded.

In addition to the benzene and toluene contaminants observed, most samples contained other non-halogenated volatile hydrocarbons at much higher levels. Attempts to identify these materials were unsuccessful for lack of suitable standards. However, most of these compounds eluted in the five to six carbon atom containing alkane region of the chromatogram and are thought

to be branched pentanes and hexanes related to gasoline blends. Relative concentrations of these compounds are shown in Figure 2. In the northern reach of the river, above Polysar, their concentrations are dominated mainly by one compound. Their relative concentrations begin to change south of station 10, and also at stations 1 and 20 on the American shoreline. We surmise that the contaminants of stations which are dominated by one compound are related to "gasoline inputs", while the others indicate more complex industrial discharges. This hypothesis would support the contaminant patterns observed at station 1, the Port Huron WPCP, and would suggest that gasoline losses from railway operations in the area of stations 5 and 7 are also the source of the benzene and toluene levels observed there. The contaminant pattern at station 20c, 100 m from shore may be interpreted as originating from station 1.

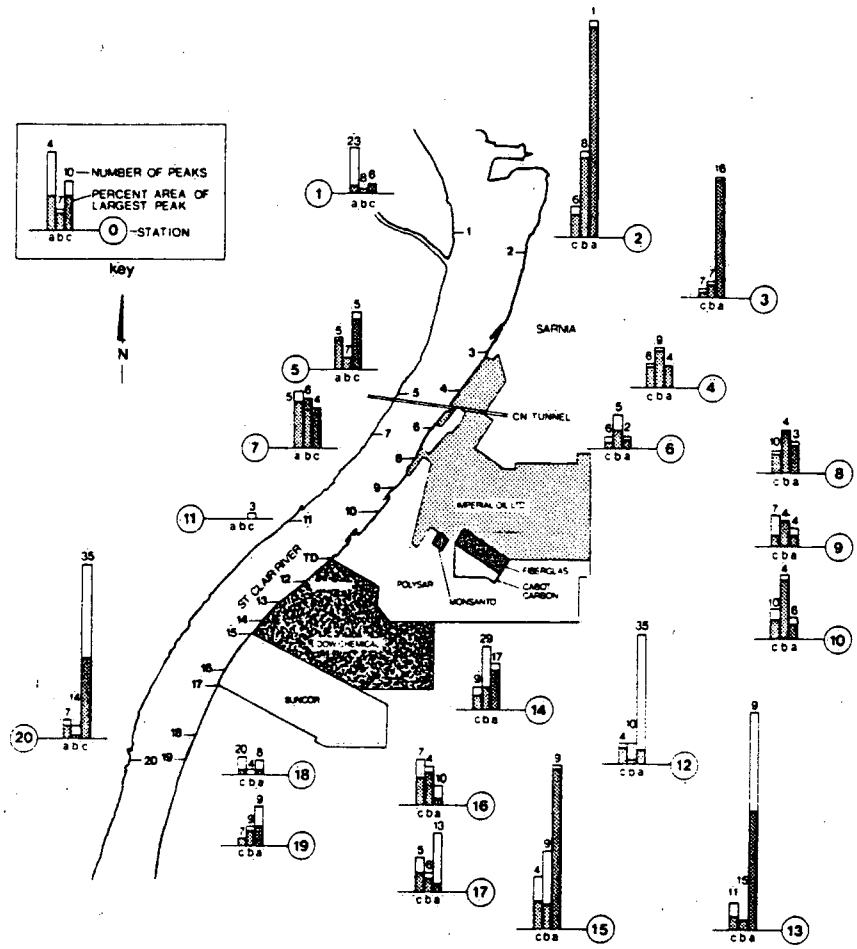

Figure 2 Relative concentrations in percent of highest observed concentrations of unidentified, non-halogenated volatile hydrocarbons in bottom water samples of the St. Clair River, Sarnia, Ontario, 1985.

ENVIRONMENTAL AND HEALTH ASPECTS

Long- and short-term occupational exposure to benzene can cause toxic and chronic effects, hematological disorders and leukemia in humans (Kirk-Othmer 1978/84, Vol. 3; Mehlman, 1983).

Insufficient information is available to establish effects of sublethal levels to humans or aquatic life, however, benzene is a suspected carcinogen. At present, no Canadian levels are set for finished drinking water (Health & Welfare Canada, 1978). A review of benzene carcinogenity and toxicity estimates a 10^{-5} lifetime risk fo leukemia for ambient water concentrations of 6.6 $\mu g \cdot L^{-1}$ (ppb) (Mehlman, 1983).

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Toluene has acute toxic effects, but exhibits no evidence of chronic health effects to blood formation as is known for benzene (Kirk-Othmer, 1978/84, Vol. 23). Carp exposed to sublethal concentrations of toluene (100 ppb) demonstrated significant effects on six biological functions that produce toxic responses as characterized by the phenomenom of stress (Gluth and Hanke, 1985).

The pentanes (isopentane, n-pentane, neopentane) and hexanes (2-methylpentane, 3-methylpentane, 2,2-dimethylbutane, 2,3-dimethylbutane and n-hexane) are principal components of gasoline (Kirk-Othmer 1978/84, Vol. 12) and display moderate toxicity.

In laboratory experiments, petroleum hydrocarbons in general display some degree of carcinogenity, however, this has been linked to the aromatic fraction of the crude oils (Mehlman, 1983). Prolonged exposure to gasoline vapors produces human hexacarbon neurotoxicity, the causative agent of which is now believed to be n-hexane (Spencer et al., 1980).

Data on ambient water concentrations of these compounds is limited and the effects of long-term exposure to sublethal concentrations is unknown. For the mean water concentrations of benzene (448 $ng \cdot L^{-1}$) and toluene (384 $ng \cdot L^{-1}$) measured, the daily human intake from water related consumption would be less than 1 percent of that from atmospheric sources (Mehlman, 1983). The effect on aquatic organisms of prolonged exposure at these levels is not known. As is the case for sublethal levels of pesticides, it is thought that the deleterious effects to fish are subtle alterations in their behaviour and morphological status which changes their ability to withstand stress (Murty, 1986). Isolated incidences of fish toxicity could occur for those species that tend to inhabit the nearshore zones in the warmer waters of the discharge plumes that have, on occasion, had high concentrations of these chemicals (King, 1986; Bonner and Meresz, 1981). The undetermined volatile hydrocarbons, thought to be of a "gasoline nature" may pose a more significant threat because of their significantly greater concentrations.

CONCLUSIONS

Concentrations of benzene and toluene in 60 bottom water samples of the upper St. Clair River near Sarnia, Ontario were found to be in the range of <100 to 4300 $ng \cdot L^{-1}$ (mean of 38 samples 560 $ng \cdot L^{-1}$) for benzene and <100 to 2200 $ng \cdot L^{-1}$ (mean of 32 samples 710 $ng \cdot L^{-1}$) for toluene, respectively. These concentrations do not appear to pose any significant health risk for potable water as comparative exposure from atmospheric concentrations is much higher. These concentrations are well below those producing any acute toxic effects on aquatic organisms, but insufficient toxicological data exist to determine the possibility of chronic effects.

In addition to benzene and toluene, a variety of other hydrocarbons, tentatively identified as five to six carbon atom alkanes, were observed in most water samples. These compounds generally appear to be present at concentrations higher than benzene or toluene and are thought to be gasoline type products.

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