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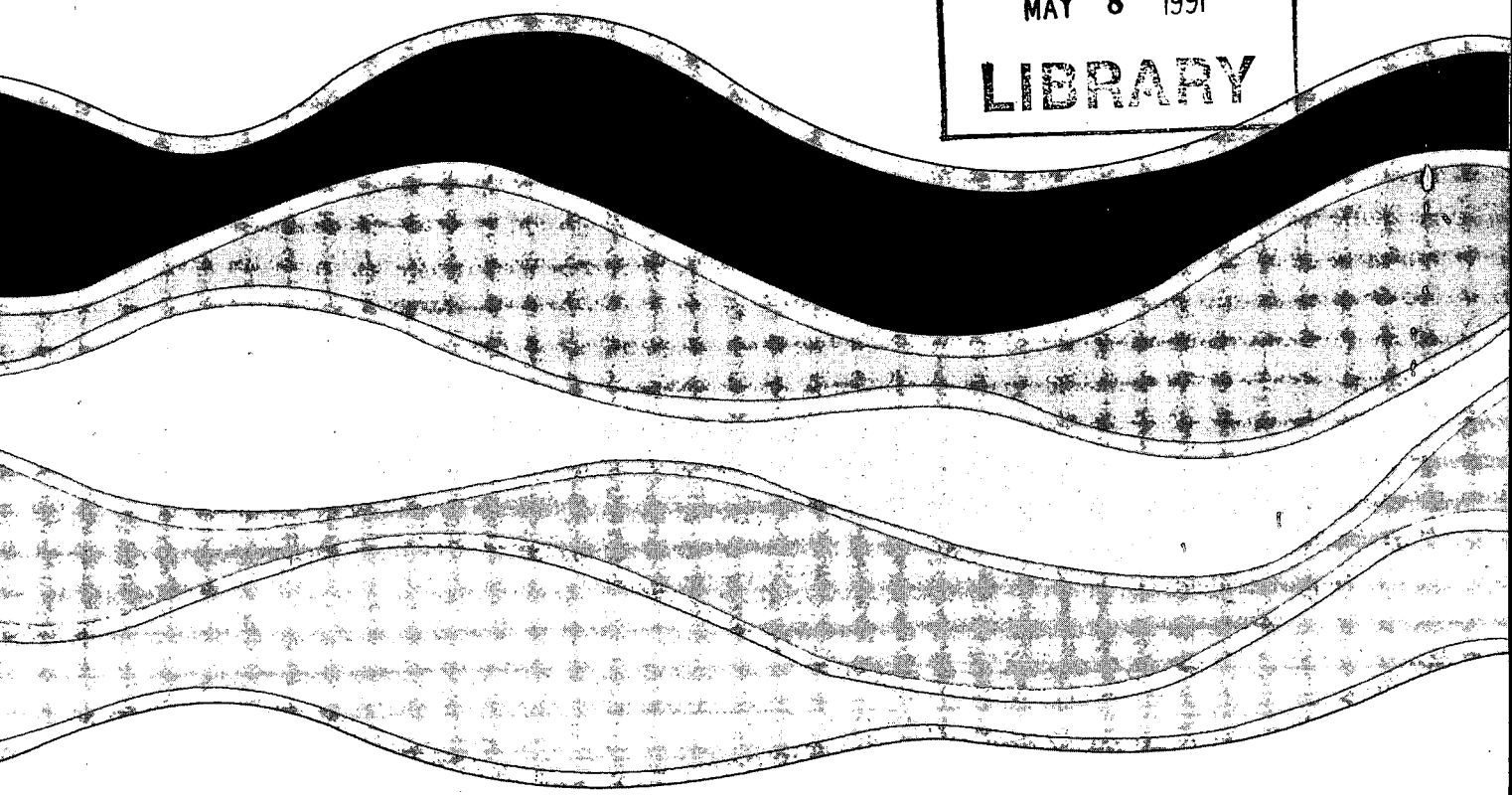

LONG RANGE CONTAMINATION AND TRANSPORT OF TOXIC ORGANIC CHEMICALS IN THE ST. LAWRENCE, FRASER AND MACKENZIE RIVERS OF CANADA

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LONG RANGE CONTAMINATION AND TRANSPORT OF TOXIC ORGANIC CHEMICALS IN THE ST. LAWRENCE, FRASER AND MACKENZIE RIVERS OF CANADA[1]

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MANAGEMENT PERSPECTIVE

Many of Canada's largest rivers, in terms of discharge and drainage area, are contaminated by toxic organic chemicals. For economic-population reasons, most of the toxic organic chemical transport and fate research on large rivers has been conducted on the high discharge "rivers" which connect the Great Lakes and the St. Lawrence River which drains the lakes to the Atlantic Ocean. To a lesser extent, two of Canada's other major rivers, the Fraser flowing to the Pacific Ocean and the Mackenzie flowing to the Arctic Ocean, have also been the subject of specific toxic organic chemical transport investigations. This paper overviews some of the results obtained over the last decade as they relate to two aspects of contamination of large rivers by toxic organic chemicals: 1) forms and 2) degree, of long-range transport.

In terms of number and load of toxic organic chemicals, the St. Lawrence River all along its course, is the most contaminated of the three rivers discussed here. The Fraser River is far less contaminated at least above its estuary and the Mackenzie River is relatively pristine. In rivers with low suspended solids, much of the total load of persistent toxic organic chemicals is transported in the operationally defined "dissolved" phase rather than "particulate" phase. Greater than 50% of the total load of toxic organic chemicals may be transported in the particulate phase of rivers with higher suspended sediments loads. In the St. Lawrence River a considerable proportion of the total PCB load is transported in particulates which can only be collected by supercentrifuges. "Long range" transport of relatively persistent toxic organic chemicals occurs in all of these rivers. In both the St. Lawrence River for mirex and the Fraser River for chloroguaiacols, these chemicals are still readily detectable in the water column over 600 km or more from their point of input. It is thus clear from the St. Lawrence and Fraser River examples that once relatively persistent toxic organic chemicals of industrial, agricultural or urban origin are introduced into even very large and long rivers, the distance of transport revealed by recently developed sophisticated sampling and analytical techniques can be seen to be quite great. The Mackenzie River example revealed that due to their long range atmospheric transport and deposition, persistent toxic organic chemicals of anthropogenic origin can be detected even in so-called pristine rivers in remote locations. Such distances of transport introduces chemicals from distant upstream sources first to estuaries and then to nearshore oceanic zones.

Contamination et transport à longue portée des substances organiques toxiques dans le fleuve Saint-Laurent, et les rivières Fraser et Mackenzie[1].

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Perspective de gestion

Plusieurs grands cours d'eau du Canada sont contaminés par des substances organiques toxiques, de par leurs aires de décharge et de drainage. Pour des raisons socio-économiques, la plupart des travaux de recherche sur le transport et le devenir des substances organiques toxiques portent sur les cours d'eau à forte décharge reliant les Grands Lacs au fleuve Saint-Laurent, qui débouche dans l'océan Atlantique. A un degré moindre, deux des rivières principales du Canada, la rivière Fraser qui se jete dans l'océan Pacifique et la rivière Mackenzie qui se déverse dans l'océan Arctique ont aussi fait l'objet d'études axées spécialement sur le transport des substances organiques toxiques. Cette étude offre une synthèse des résultats obtenus lors de la dernière décennie portant sur deux aspects de la contamination des grands cours d'eaux par des substances organiques toxiques: 1) modes et 2) degré, de transport à longue portée.

En fonction du nombre et de la charge de contaminants organiques toxiques, le fleuve Saint-Laurent, tout au long de son cours, est le plus contaminé des trois cours d'eau faisant l'objet de cette étude. La rivière Fraser est bien moins contaminée, du moins au-dessus de son estuaire et la rivière Mackenzie est relativement pure. Dans les rivières à faible charge en matières en suspension, la majeure partie de la charge totale de substances organiques toxiques persitantes est transportée dans ce qui est opérationnellement défini comme la phase "dissoute" plutôt que dans la phase "particulaire". Plus de 50 % de la charge totale de substances organiques toxiques est transportée dans la phase particulaire des cours d'eau à charge élevée en matières en suspension. Dans le fleuve Saint-Laurent, une fraction considérable des BPC est transportée par les particules pouvant être uniquement recueillis à l'aide d'ultracentrifugeuses. Le transport à "longue portée" des substances organiques toxiques relativement persistantes se produit dans tous ces cours d'eau. Dans le fleuve Saint-Laurent le mirex, et dans la rivière Fraser les chloroguaiacols sont aisément décelables à plus de 600 kilomètres de la source d'apport. Il est donc évident à partir de ces

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[1] Cet article fait l'objet d'une invitation de présentation au symposium "Gestion Environnementale des Eaux continentales", faisant partie du "Quatrième Entretien de Centre Jacques Cartier", Arles, France, 1990.

deux exemples, qu'une fois introduit dans un cours d'eau, aussi long et large soit-il, les substances organiques toxiques d'origine industrielle sont transportées à des distances très importantes; ce fait a été révélé grâce aux nouvelles techniques d'échantillonnage et d'analyse plus perfectionnées. L'exemple de la rivière Mackenzie révèle que grâce à leur transport atmosphérique et leur déposition à longue portée, les substances organiques toxiques persistantes d'origine anthropogène peuvent être décelées même dans des cours d'eau géographiquement isolés et considérés pures. De telles distances de transport acheminent les substances chimiques à partir de sources lointaines situées en amont, d'abord aux estuaires et ensuite jusqu'aux zones océaniques rapprochées.

ABSTRACT

Many of Canada's largest rivers in terms of discharge and drainage basin area, are contaminated by toxic organic chemicals. For economic-population reasons, most of the toxic organic chemical transport and fate research on large rivers has been conducted in the Great Lakes drainage basin, namely on the high discharge "rivers" which connect the Great Lakes and the St. Lawrence River which drains the lakes to the Atlantic Ocean. To a lesser extent, two of Canada's other major rivers, the Fraser River flowing to the Pacific Ocean and the Mackenzie flowing to the Arctic Ocean, have also been the subject of specific toxic organic chemical transport investigations. This paper overviews some of the results obtained over the last decade as they relate to two aspects of contamination of large rivers by toxic organic chemicals: 1) forms and 2) degree, of long-range transport. Specific chemicals are used as examples in specific river systems: PCBs, lindane and mirex in the Niagara-St. Lawrence; chlorinated guaiacols in the Fraser; and PAHs in the Mackenzie Rivers respectively.

KEY WORDS

Partitioning, particulate, dissolved, long-range transport, PCBs, mirex, chlorinated phenolics, PAHs.

INTRODUCTION

In 1988, the first major conference devoted exclusively to the fate and effects of toxic chemicals in large rivers and their estuaries was held in Quebec City in Canada. The fifty eight papers published showed that many of the world's largest rivers are already contaminated by a variety of toxic organic chemicals and that these chemicals were being introduced into estuarine and coastal zones of most of the world's oceans (Allan et al., 1990) . Globally, data from North America and from western Europe is more extensive than from other parts of the world, partly because toxic organic chemical pollution is perceived as a problem for industrialized nations, whereas more traditional water pollution issues are focused on in developing nations. Information on toxic organic chemical contamination of some of the world's best known rivers in North America - the St. Lawrence, the Hudson, the James, the Mississippi, the San Joaquin area - and in Europe - the Rhine, the Elbe and the Seine is relatively extensive.

In Canada, the study of toxic organic chemical transport mechanisms and fate in large rivers began seriously around 1980 with the investigation of the loads of such contaminants from the Niagara River to Lake Ontario. These studies involved the development of large volume sampler-extractors (McCrea and Fischer, 1985) which could allow detection of extremely low concentrations of toxic organic chemicals in the "dissolved" phase. This operationally defined phase was the content of the elutriate from a high speed centrifuge. The material collected in the centrifuge was considered the "particulate" fraction, also operationally defined. These large volume water extractors and high speed centrifuges were used to study the Niagara River and its plume into Lake Ontario and later in the 1980's, applied to the other main connecting channels or large rivers between Lakes Huron and Erie, namely the St. Clair and Detroit Rivers. At about the same time, research began in the mid-1980's into the sources and fate of toxic organic chemicals in the St. Lawrence River, draining the Great Lakes to the Atlantic Ocean.

While it was clear that the toxic organic chemical issue in the Great Lakes connecting rivers and in the St. Lawrence River were the highest priority in Canada because of international agreements with the U.S.A. and because of the large number of Canadians drawing their drinking water from this system, there are other major river systems in Canada contaminated by toxic organic chemicals. Research on the transport and fate in the Fraser River of British Columbia of toxic organic chemicals originating from the pulp and paper industry, began in the mid to late 1980's (Carey and Murthy, 1989). A less ambitious study, but one of greater logistical difficulty, was mounted

in the late 1980's on the Mackenzie River draining to the Arctic Ocean. In this case, the toxic organic chemicals in question were polyaromatic hydrocarbons possible from oil industry sources. Results from this sub-Arctic work also have also now been published (Carey et al., 1990).

The above is by no means an exhaustive list of all the research and monitoring carried out for toxic organic chemicals in rivers in Canada. While the most extensive and comprehensive research has been carried out in the St. Lawrence River and upstream with emphasis on agrochemicals and chemicals from the petrochemical industry, the Fraser River provided an example of toxic organic chemical contamination from a different source, the pulp and paper industry, as did the Mackenzie River. This overview deals only with these three river-lake systems because 1) they constitute the largest river basins draining respectively to the Atlantic, Pacific, and Arctic Oceans, which constitute Canada's three coastlines (Figure 1); and 2) the St. Lawrence, Fraser and Mackenzie Rivers are amongst the world's largest rivers in terms of discharge. The purpose of this paper is to briefly overview some of the results on toxic organic chemical transport mode in these rivers by focusing on two main themes: 1) forms,and 2) distance, of long-range transport of toxic organic chemicals in these three rivers.

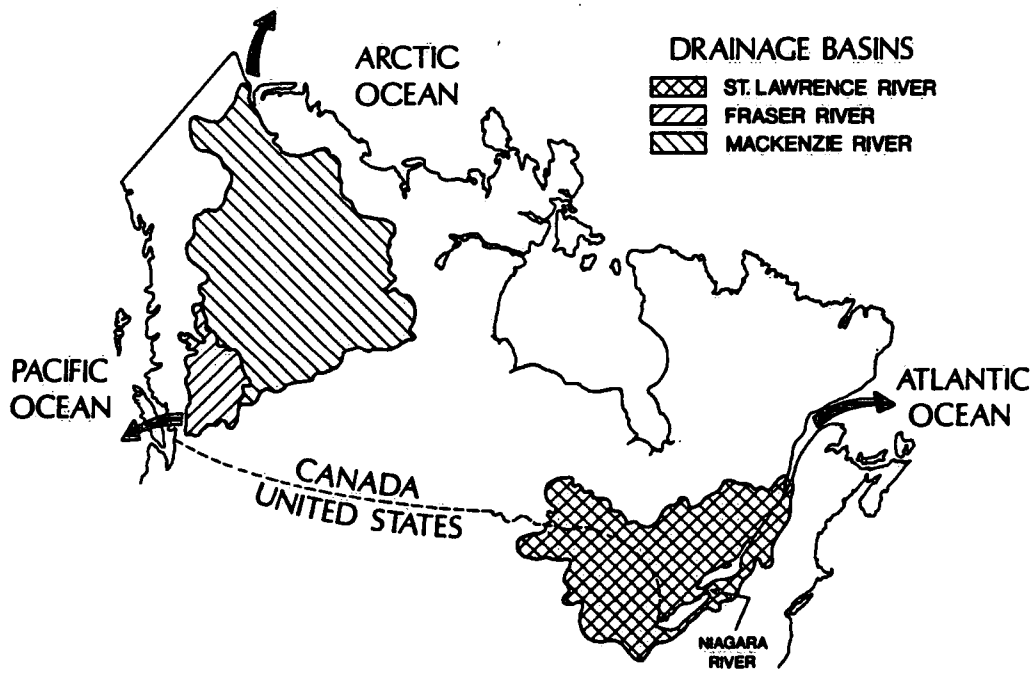

Figure 1. Drainage basins of the St. Lawrence, Fraser and Mackenzie Rivers in Canada

PARTITIONING OF TOXIC ORGANIC CHEMICALS

The Niagara River Example

The Niagara River has a discharge of some 6,000 m^3/sec. The concentrations of toxic organic chemicals in the river are extremely low (in the ppt range) but their total load transported into Lake Ontario is considerable given the flow. The distributions of PCBs and BHC in the operationally defined aqueous and particulate phases of the river water (McCrea et al., 1985) are shown in Figure 2.

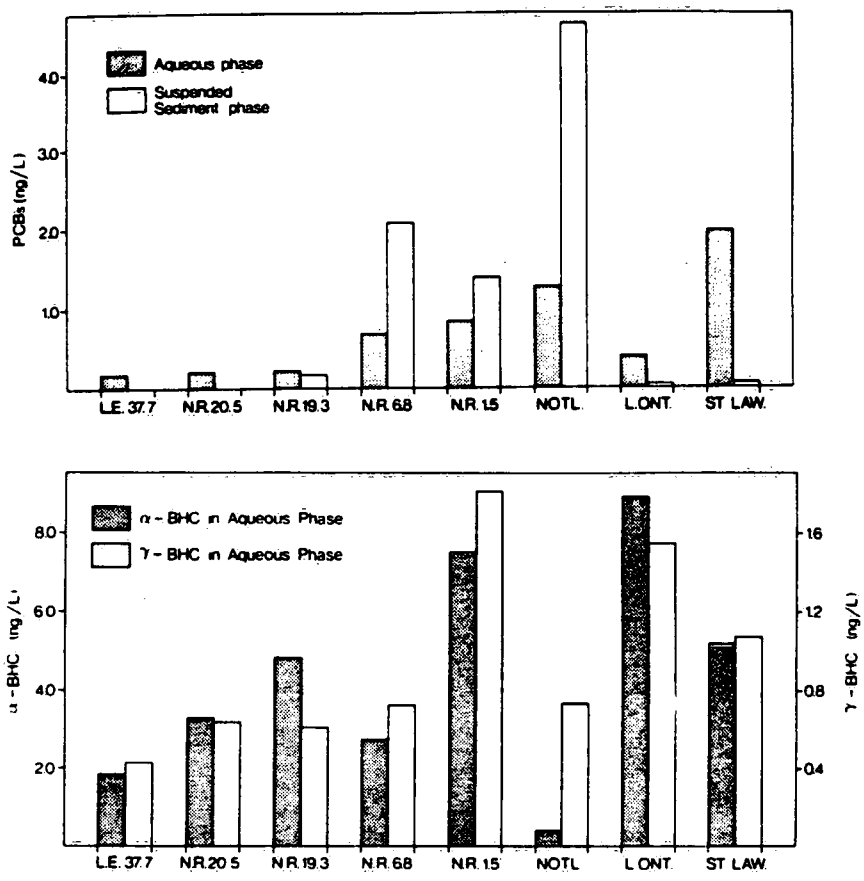

Figure 2. PCBs and BHC Distributions in the Aqueous and Particulate Phase of the Niagara River. (LE = Lake Erie; NR = Niagara River; NOTL = Niagara-on-the Lake; L.ONT. = Lake Ontario; ST. LAW. = St. Lawrence River.)

Chemicals such as lindane which have low partitioning coefficients are transported primarily in the "dissolved" phase. Although toxic organic chemicals with high sediment partitioning coefficients are concentrated in the suspended solids phase (ppb range), much of the load of such chemicals is still transported in the operationally defined "dissolved" phase because of the low suspended solids concentrations in the Niagara River (1 to 10 mg/L). The relative concentrations in these phases can theoretically be predicted from Figure 3 (Allan, 1986) which plots the relationship between suspended solids concentration, partition coefficient and percent of the toxic organic chemicals transported in the dissolved phase. However, in nature, other factors such as bioaccumulation are involved in concentration of toxic chemicals in "particles".

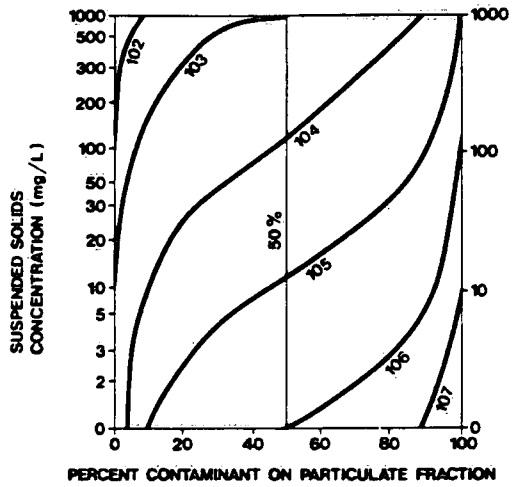

Figure 3. Theoretical Partitioning of Toxic organic Chemicals in Rivers with Different Suspended Sediment Concentrations.

The St. Lawrence River Example

At its source in Lake Ontario, the flow of the St. Lawrence River is some 7,700 m^3/sec, rising to 12,700 m^3/sec its mouth. By discharge, it is Canada's largest river. A given water mass traverses the river in five to seven days. Concentrations of suspended solids rise from some 1 mg/L at the river source to some 10 mg/L at the upper end of the St. Lawrence estuary.

Whole water samples collected between Lake Ontario and the estuary were processed by high speed centrifuge and large volume extraction of the effluent. This allowed a comparison of the changes in the fraction of the toxic organic chemical load transported in the operationally defined "particulate" and "dissolved" phases (Figure 4). PCB concentrations in the suspended solids decreased downstream from 1,000 ppb to around 200 ppb (very rough estimates of "mean" values) (Kaiser et al., 1990). However, with a ten times increase in suspended solids, the PCB load doubled due to input from various sources along the river. A further refinement was the removal from the effluent of the "coarser particulates" normally incorporated into the operationally defined dissolved phase (Figure 5)(Comba et al.,

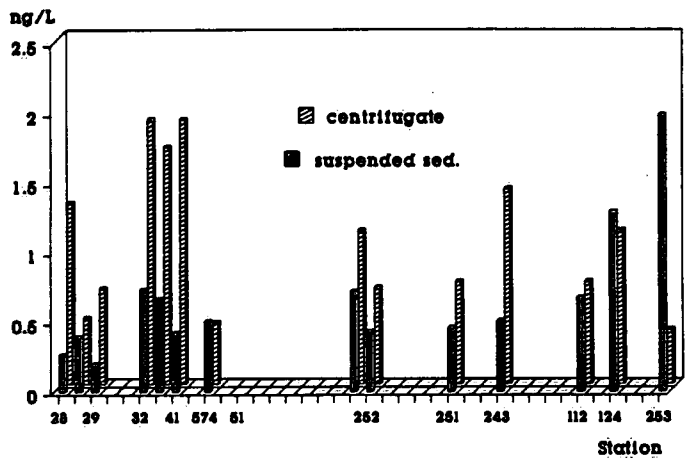

Figure 4. PCBs Partitioning in the St. Lawrence River. (Kaiser et al., 1990)

1989). The concentration of PCBs in these fine particulates was one to two orders of magnitude higher than in the particulates normally extracted by centrifuges. This fractionation shows that PCBs introduced at the river source are mainly in the "dissolved" phase as are those introduced along its course but that they become more fractionated into particulate phase as they move downstream. This, of course, is a gross generalization with many local variations.

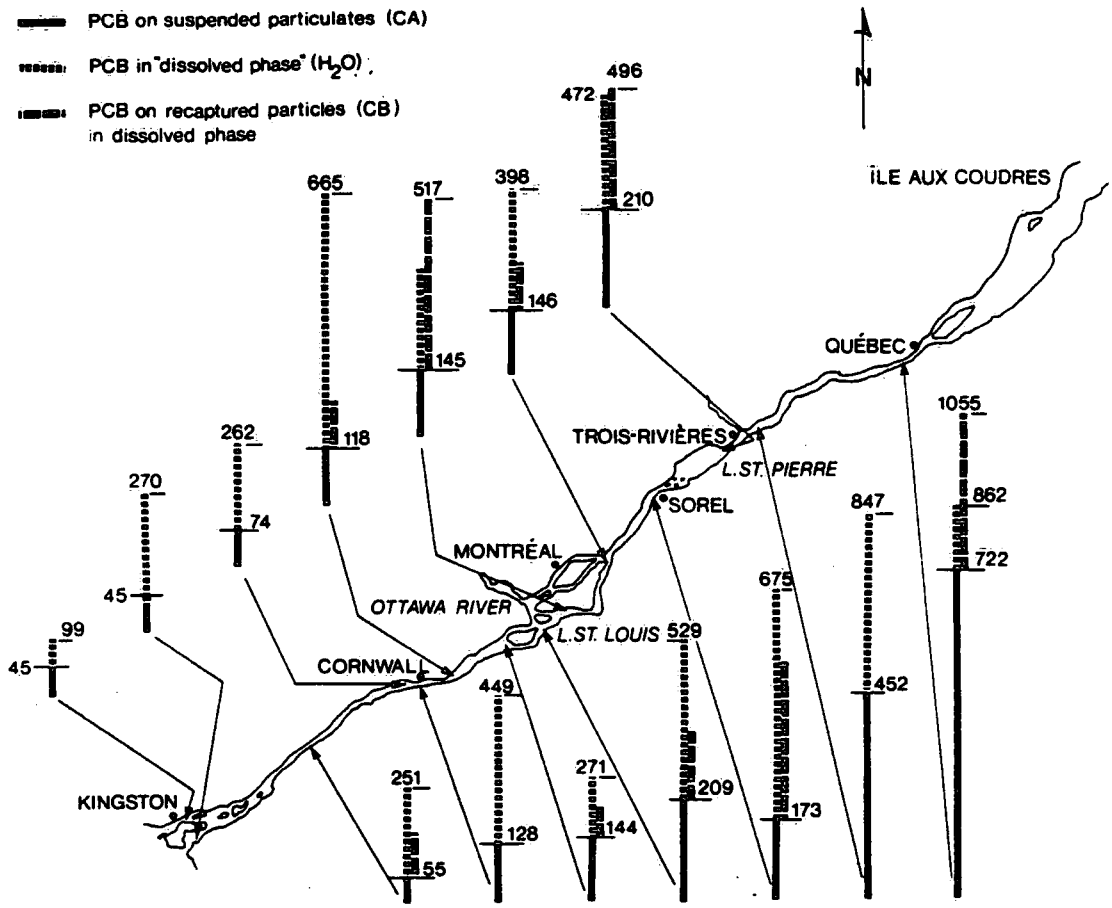

Figure 5. "Colloidally" Transported PCBs in the St. Lawrence River (Comba et al., 1989)

LONG-RANGE TRANSPORT OF TOXIC ORGANIC CHEMICALS

Mirex in the Niagara and St. Lawrence River Systems

The insecticide and flame retardant, Mirex, was first discovered at the eastern end of Lake Ontario in 1974 (Kaiser, 1974). Subsequent sampling in the late 1970's when new sampling and analytical techniques allowed lower detection limits, has now revealed that this toxic organic chemical has been transported in the water column to the St. Lawrence estuary. Although the concentration of mirex in suspended particulates declines downstream, it is still

detectable some 600 to 1,000 km downstream from the sites of its original introduction to this river-lake system. The concentrations of mirex in suspended solids at the source of the St. Lawrence are around 5 ppb and decrease to some 1 ppb near Quebec City (Figure 6). This concentration translates to a flux of some 1 to 2 kg of mirex/year. Kaiser et al. (1990) also detected mirex in the centrifugate, the operationally "dissolved" phase, at many of their

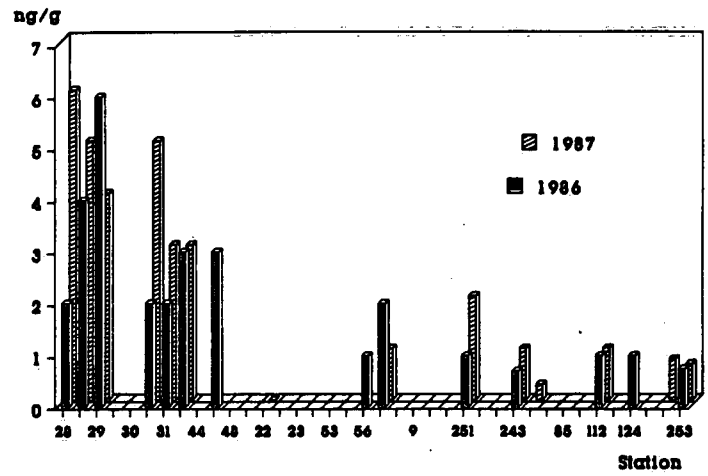

Figure 6 Mirex in suspended solids of the St. Lawrence River (Kaiser et al., 1990)

sampling stations on the river. The highest value was 13 pp quadrillion. The dispersal of this highly hydrophobic chemical throughout the Lake Ontario and St. Lawrence River system is clear evidence of the potential long-range dispersion of toxic organic chemicals on a scale which only now can be quantified by analyses of abiotic water column media.

Chloroquaiacols in the Fraser River

The Fraser River of British Columbia has a mean annual discharge of 2,700 m^3/sec, a length of 1,253 km and a drainage basin of 230,400 km (Table 1). The river enters the ocean via its estuary, at Vancouver. The river is contaminated throughout much of its length with chlorinated phenolics originating from the pulp and paper

industry (Carey and Murthy, 1988). Analyses for chlorophenolics in the upper estuary revealed the presence of chlorinated quaiacols at the inland end of the estuary. Because the pulp and paper mills which introduce these chemicals to the river are located up to 600 km upstream from the estuary, this meant that these relatively persistent toxic organic chemicals were being transported down the Fraser River for this distance. The importance of the quaiacols to the total chlorinated phenolic load in the estuary was greater during high river discharge conditions (Figure 7).

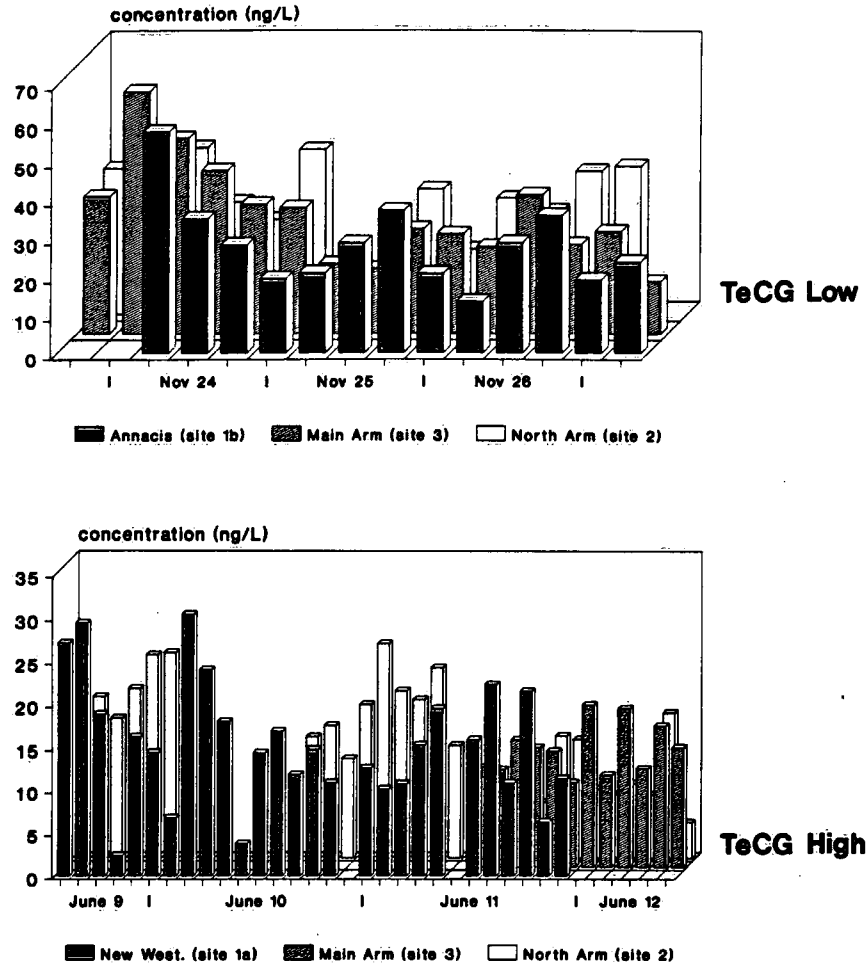

Figure 7. Chloroguaiacols in the Fraser River in low and high flow conditions (Carey and Murthy, 1988)

PAHs in the Mackenzie River

Like the St. Lawrence to the Atlantic and the Fraser to the Pacific, the Mackenzie is the river with the largest drainage basin (Figure 1) (1.7 million km^2) and discharge to Canada's third coastline, the Arctic Ocean. The Mackenzie River is pristine in comparison to the St. Lawrence and even in comparison to the Fraser

SAMPLE SITE	M1	M2	M3	M4	M5	M6	M7
naphthalene	0.199	0.071	0.021	0.04	0.067	0.145	0.185
fluorene	0.053	0.035			0.024	0.059	0.043
phenanthrene	0.037						
fluoranthene						0.01	0.011
benzo(b)fluoranthene						0.01	
benzo(k)fluoranthene	0.097	0.067	0.019	0.022	0.035	0.077	0.034
dibenzo(a,h)anthracene	0.032	0.023	0.012	0.014	0.021	0.023	0.016
indeno(1,2,3,c,d)pyrene						0.036	
benzo(g,h,i)perylene						0.031	
total PAHs	0.418	0.196	0.052	0.076	0.147	0.391	0.289
suspended solids	0.022	0.106	0.576	0.672	0.576	0.312	0.344

[1]M1 is the closest site to Great Slave Lake, just upstream of the Liard River. M6 is just upstream of the Mackenzie delta. M2 to M5 are evenly spaced intermediate sites. M7 is in the delta.

Table 1. PAHs Present in Suspended Sediments of the Mackenzie River under high flow Conditions in 1986 (Carey et al., 1990)

River. However, the river is not entirely free from man's influence. The study referred to here took place on the Mackenzie River proper, between Great Slave Lake, the river's source, and its delta. The aim

was to resolve whether the oil extraction and processing facilities at Norman Wells in the Northwest Territories were responsible for pollution of the river with PAHs (polyaromatic hydrocarbons). Using the time of travel approach, a series of eight sampling sites were visited at widely spaced intervals along the river. The distance covered was some 1,250 km. Suspended suspended concentrations in the river during low flow vary from about 40 mg/L upstream of Norman Wells to about 135 mg/L downstream closer to the delta (Carey et al., 1990). Suspended solids concentrations during the high flow period were over 800 mg/L.

In low flow conditions, low levels of PAHs from petroleum related sources could be detected but these sources were likely natural in origin, for example from oil seeps. Under high flow conditions (Table 1), the PAHs were dominated by those normally associated with combustion. The combustion sources were hypothesized to be due to runoff of snow contaminated with PAHs deposited after long-range atmospheric transport of the chemicals. This hypothesis implies that other toxic organic chemicals of atmospheric origin may also be transferred by runoff to the Mackenzie River and transported downstream. Such chemicals as HCB, lindane, and DDT and its metabolites have been detected at very low concentrations in the bottom sediments of Great Slave Lake (Mudroch et al., 1990), the source of the Mackenzie River.

CONCLUSIONS

Collectively, the large rivers of Canada have been more intensively studied as to their concentration of toxic organic chemicals than the rivers of most countries with the possible exceptions of the United States and some countries in western Europe. The reasons for this have been 1) the recent focus for the past ten years on contamination from industry, agriculture and urban sources of the Great Lakes-St. Lawrence River system; and 2) concern on a National scale with contamination of rivers from the general resource based agricultural, pulp and paper, and oil industries of Canada. In terms of number and load of toxic organic chemicals, the St. Lawrence River all along its course, is the most contaminated of the three rivers discussed here. The Fraser River is far less contaminated at least above its estuary and the Mackenzie River is relatively pristine.

Conclusions as to form of transport of toxic organic chemicals in Canadian rivers is biased because of the very low suspended solids content of the St. Clair, Detroit, Niagara and St. Lawrence rivers of the Great Lakes-St. Lawrence system where most studies have taken place. In these rivers, much of the total load of persistent toxic organic chemicals is transported in the operationally defined "dissolved" phase rather than "particulate" phase. With high partition coefficients and fractions greater than 50% of the total load may be transported in the particulate phase of rivers with higher suspended sediments loads.

Conclusions as to the "real" form of transport are also confounded by the "operational" definition of particulates. For example, in the St. Lawrence River a considerable proportion of the total PCB load was transported in particulates which can only be collected by supercentrifuges rather than by the normal high speed centrifuges used to remove the operationally normally defined "particulate" fraction. However, irrespective of transport mode, the total amount of toxic organic chemicals transported will be bioavailable or potentially so, for example by injestion by biota. A possible exception to this may be fine particulates of combustion origin such as those containing PAHs, dioxins, or furans, for example from municipal incinerators.

From the data reviewed here, there is "long range" transport of relatively persistent toxic organic chemicals in these Canadian rivers. In both the St. Lawrence River for mirex and the Fraser River for chloroguaiacols, these chemicals are still readily detectable in the water column, albeit by rather sophisticated sampling and analytical techniques, over 600 km or more from their point of origin. Most rivers studied elsewhere in the world are not this long or contain several sources of the chemical so that the absolute distance of transport is difficult to resolve. Nevertheless, it is clear from the St. Lawrence and Fraser River examples that once relatively persistent toxic organic chemicals of industrial, agricultural or urban origin are introduced into even very large and long rivers, the distance of transport using present analytical techniques can be seen to be quite great. Such distances of transport introduces chemicals from distant upstream sources first to estuaries and then to nearshore oceanic zones. The Mackenzie River example reveals that due to long range atmospheric transport and deposition, persistent toxic organic chemicals of anthropogenic origin can be detected even in so-called pristine rivers in remote locations.

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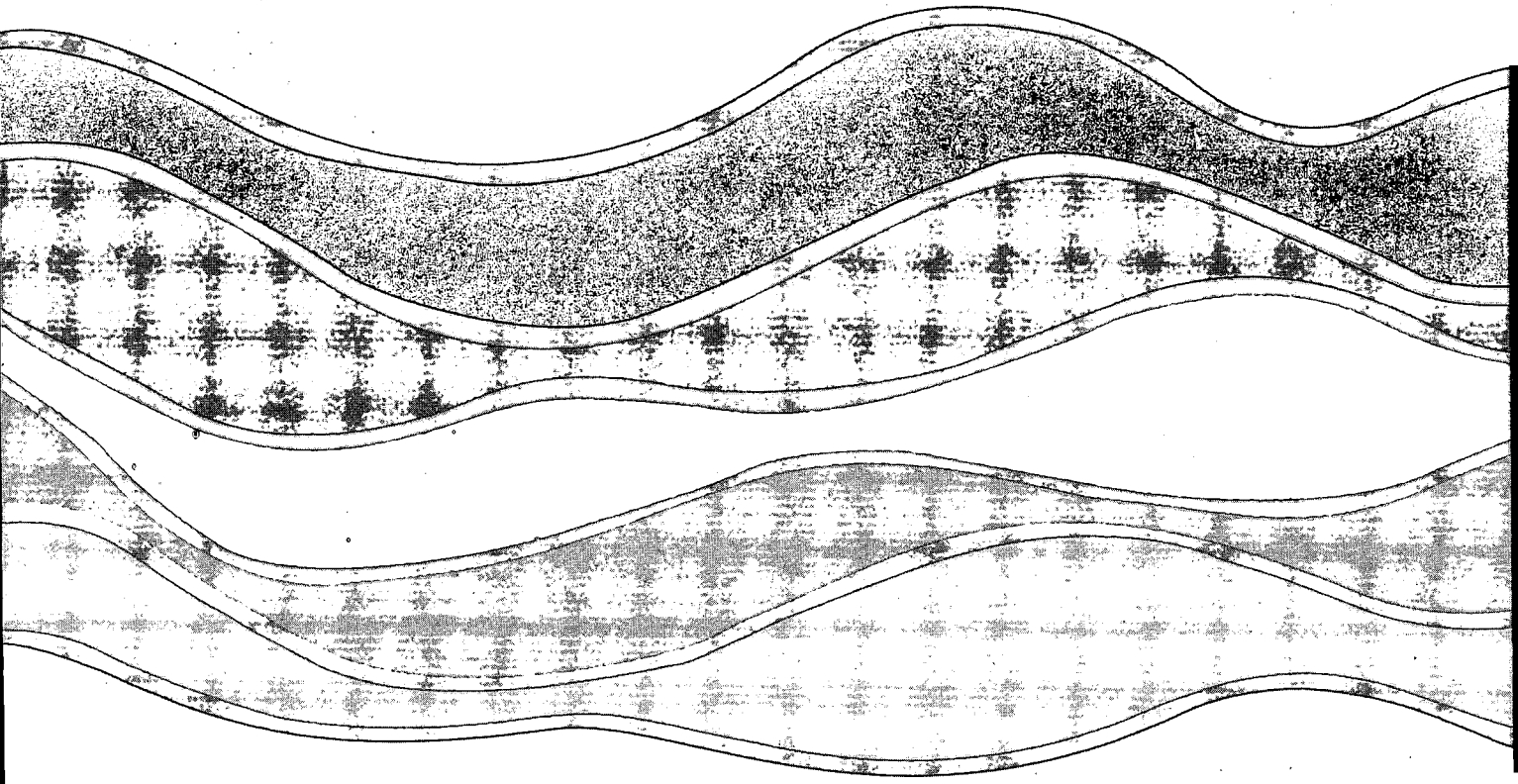

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