Transport and fate of persistent toxic organic chemicals in aquatic ecosystems: the Niagara River to St Lawrence River Estuary example

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Abstract The transport and fate of persistent toxic organic chemicals in fresh-water ecosystems are controlled by many properties of the aquatic ecosystems themselves and of the specific chemicals. Predictions of the fate of specific chemicals can, to some extent, be modelled from chemical properties and laboratory tests, but in real aquatic ecosystems, accurate predictions of eventual sinks, trends and concentrations in biota and response to remedial measures are site specific. This paper discusses the media involved in the aquatic transport of persistent toxic organic chemicals and the role of aquatic ecosystem media in the eventual fate of the chemicals. Specific examples are drawn from the last decade of research on the Niagara River to the St Lawrence River Estuary system.

INTRODUCTION

Detection of persistent toxic organic chemical (PTOC) contamination in the Great Lakes began in the early 1960s with pesticides such as DDT and dieldrin, followed in the 1970s by other organochlorine pesticides and industrial organic chemicals such as PCBs. The insecticide mirex was then discovered in 1974 in fish in the Bay of Quinte; chlorinated dioxins were detected in herring gull eggs from colonies in Saginaw Bay in 1979; and toxaphene was detected in fish from Lake Superior in 1982. Subsequent sampling has shown that many of these PTOCs can be detected in various media throughout the entire Great Lakes-St Lawrence River ecosystem. The available information on PTOC contamination of the Niagara River to St Lawrence Estuary system although far from complete, may be greater than exists for any other fresh-water system in the world. Recently, a special volume of the journal Science of the Total Environment (Allan et al., 1990) contained several papers on the transport and fate of toxic chemicals in the St Lawrence River and Estuary and a major review was completed on Toxic Chemicals in the Great Lakes and Associated Effects (Allan et al., 1991). The special volume and review together encompass much of the research and monitoring results on transport and fate of toxic chemicals in this major river-lake estuary ecosystem.

TRANSPORT OF PERSISTENT TOXIC ORGANIC CHEMICALS

The waterways of the Niagara River to the St Lawrence River Estuary system (Fig. 1)
PTOC = PERSISTENT TOXIC ORGANIC CHEMICAL

Fig. 1 Schematic of the main components of the Niagara River to St Lawrence River Estuary system and their primary role in PTOC transport and fate.

are made up of four types of units. The first comprises the high discharge (6000-13 000 m$^3$ s$^{-1}$), rapid flow rivers, namely the Niagara and St Lawrence. Second are the shallow, short residence time (days to weeks), riverine lakes, namely St Francois, St Louis and St Pierre. Third is the deep, long residence time (10 years), Lake Ontario. Lastly, there is the fresh-water/salt-water St Lawrence Estuary.

The rivers are essentially PTOC transport systems on a grand scale. The riverine lakes provide only temporary storage or sinks even for contaminants associated with sediments because these are eventually resuspended and moved on downstream. The major sinks where long-term effects become evident are Lake Ontario and the St Lawrence Estuary. These sites are also where sediment associated contaminants can be permanently removed by deep burial in bottom sediments. Even so, some of the PTOCs transported still pass out of the system to the Gulf of St Lawrence and beyond.

Water (dissolved) and sediment (particulate-bound) analyses are a requirement to determine the transport media of PTOCs. However, reliable, quantitative data for dissolved PTOCs are still scarce. For the last decade, large volumes of water (200 up to 1000 l) have been extracted to detect these dissolved concentrations in the low ppt and ppq ranges and often continuous extraction systems are now employed. The presently detected dissolved concentrations of PTOCs in water are often an order of magnitude or more beneath former detection limits. Concentrations of PTOCs in whole water, and especially for the dissolved phase, can be highly variable in space and time and must still be viewed with caution because they are often still near our limits of analytical detection. Alternatively, most concentrations for PTOCs in suspended particulates and bottom sediments are considered reliable. Sectioned, radiodated lake
bottom sediment cores have been of great value in revealing long-term historical trends in inputs of PTOCs to the system.

Example 1 - PCBs transport

The Niagara River has a discharge of some 6000 m$^3$ s$^{-1}$ into Lake Ontario. Concentrations of "dissolved" (the fraction not removed by high speed centrifugation) PTOCs are in the ppt or ppq range. However, the total load transported into Lake Ontario can be considerable given the high discharge. Chemicals such as lindane which have low partitioning coefficients are transported primarily in the dissolved phase. Although toxic organic chemicals with high partitioning coefficients such as the higher chlorinated PCBs 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$^{-1}$) (McCrea et al., 1985).

The St Lawrence River drains the Great Lakes to the Atlantic Ocean. At its source in Lake Ontario, the flow is some 7700 m$^3$ s$^{-1}$ and rises to 12 700 m$^3$ s$^{-1}$ at its mouth at Quebec City. A given water mass traverses the river in five to seven days. Concentrations of suspended solids rise from some 1 mg l$^{-1}$ at the river source to some 10 mg l$^{-1}$ at Quebec City, at the upper end of the St Lawrence Estuary. Water samples have been collected between Lake Ontario and the estuary and processed by high speed centrifuge followed by large volume extraction of the effluent to determine changes in the fraction of the PTOC load transported in the operationally defined particulate and dissolved phases (Kaiser et al., 1990). PCB concentrations in the suspended solids decreased downstream from around 1000 ppb to 200 ppb. However, because there is a ten times increase in suspended solids, the PCB load is actually doubled due to input from various sources along the river. A further refinement of the particulate versus dissolved split was the removal from the high speed centrifuge effluent of the colloids normally incorporated into the operationally defined dissolved phase (Comba et al., 1990). The concentration of PCBs in these super centrifuged fine particles (Fig. 2) was one to two orders of magnitude higher than in the particulates normally extracted by only high speed centrifuges. The PCBs introduced to the river at its source are mainly in the dissolved phase as are those introduced along its course but they generally become more fractionated into or onto the particulate phase during passage downstream.

Example 2 - mirex transport

The insecticide and flame retardant, mirex, was first discovered at the eastern end of Lake Ontario (Kaiser, 1974). The main input of the chemical to Lake Ontario was from a source along the Niagara River. By the late 1980s, extension of sampling programs down the St Lawrence had revealed that this PTOC had been transported in the water column as far as the St Lawrence Estuary and beyond. Although the concentration of mirex in suspended particulates declines downstream, the chemical was still detectable some 1000 km downstream of the major site near Niagara Falls of its original introduction to this river-lake estuary 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 which translates to a flux of some 1 to 2 kg of mirex/year. Most recently, Kaiser et al. (1990) used improved extraction procedures to detect mirex in the operationally dissolved phase at many sites down the river. The highest value was 13 pp quadrillion. The dispersal of this highly hydrophobic chemical from the Niagara River to the St Lawrence Estuary is clear evidence of the long-range aquatic dispersion of PTOCs on a scale which only now can be quantified. Further evidence of this long-range aquatic transport comes from comparison of the mirex distribution in bottom sediment cores from Lake Ontario and the Laurentian Trough in the lower St Lawrence Estuary (Figs 1 and 3).

FATE OF PERSISTENT TOXIC ORGANIC CHEMICALS

The fate of PTOCs in aquatic ecosystems is complex and involves many processes including dilution, sorption/desorption, volatilization, burial and degradation by chemical and biological processes. The fate of PTOCs in the system is not only governed by the physicochemical characteristics of the chemicals, i.e., solubility, volatility, hydrophobicity, degree of partitioning (into or onto sediment and other particulates), lipophilicity, and resistance to degradation (by hydrolytic, photochemical, and biochemical routes) but also by factors and by processes related to the characteristics of the receiving water bodies, namely suspended particulate concentrations and type, sedimentation rates, trophic level, and food webs.
In large lakes such as Lake Ontario, three critical limnological factors which interact to affect the fate of PTOCs are (1) suspended particulate concentrations, (2) water residence time; and (3) trophic state, which are interlinked in complex and site specific ways. For example, a high inorganic sediment load combined with a high trophic state could lead to high sediment-water partitioning, followed by rapid sedimentation and burial of PTOCs. The critical processes which control the fate of PTOCs in water bodies are those which operate across the major interfaces between main ecosystem components of air, water, sediment, and biotic material. Better quantification of the role of these interfaces on the movement of PTOCs leads to a better ability to understand, model, and predict the aquatic fate of PTOCs. The following discussion focuses on these interfaces as they affect PTOC fate. A more extensive discussion is to be found in Allan (1989a).

The role of the atmosphere

The air-water interface involves the atmosphere as both a source of PTOCs and waterways as a source of PTOCs to the atmosphere. Water bodies such as Lake Ontario and the St Lawrence Estuary, have large surface areas which can translate into
a large direct atmospheric input of PTOCs in vapour, wet and dry-fall-particulate phases. For specific chemicals, there remains considerable debate as to the importance of the atmospheric source relative to others because most of the data on atmospheric loads of chemicals is derived from analyses of only wet precipitation, particularly rain, for chemicals such as DDT, PCBs, toxaphene, and \( \gamma \)-BHC (Eisenreich et al., 1980). Adequate samplers necessary to measure PTOC inputs in all wet, dry and gaseous phases on a routine and event basis are only now being systematically deployed, even in the Great Lakes Basin.

The release of chemicals from water bodies to the atmosphere is a process readily accepted for those chemicals referred to as volatiles. Such volatiles are rapidly lost to the atmosphere, except in ice-covered areas during winter months. The fact that there are always measurable concentrations of volatiles such as perchloroethylene in the Niagara River to St Lawrence Estuary system, is because there are continuous industrial and municipal inputs. Other less volatile PTOCs such as the lower chlorinated PCBs and chlorinated benzenes are however also volatile and released into the atmosphere. Their contribution to the atmosphere is usually determined by difference in mass balance calculations. Using this approach, Oliver (1984a) concluded that greater than 80\% of several chlorinated benzenes, including HCB, introduced by the Niagara River to Lake Ontario, were lost from the lake by volatilization.

Because PTOCs are hydrophobic, they accumulate at water/other compartment interfaces, one of which is the atmosphere. Thus, surface microlayers on water bodies have been shown to acquire much higher concentrations of some PTOCs than are found in the underlying water (Maguire et al., 1983). The accumulation of such chemicals in microlayers may be an important step in the release of PTOCs to the atmosphere or in their bioaccumulation by certain organisms.

**The role of sediments**

The fate of PTOCs in aquatic ecosystems is highly dependent on their interaction with particulates (Allan, 1986). Sorption to suspended particulates is a key process involved in the physical transport of PTOCs and in their degree of bioavailability and eventual bioaccumulation. The relative concentrations in the particulate phase can be predicted from Fig. 4 which plots the relationship between particulate concentration, partition coefficient and the percent of chemical transported in the particulate phase. However, it should be remembered that in real aquatic ecosystems other factors such as bioaccumulation are involved in concentration of toxic chemicals in suspended "particles".

The simple relationship of partition coefficient measured as an equilibrium constant between the concentration of a PTOC in the particulate phase and the concentration in solution is complicated by several factors. At a given particulate concentration, the concentration of the chemical in solution controls the amount sorbed but only at relatively low sediment concentrations. There is an inverse relationship between the concentration of absorbing solids and the partition coefficient. Other controlling factors are particulate type, especially organic content of the particles. Suspended particulates in many aquatic systems are highly organic and actually made up of living or dead phytoplankton and bacteria. Removal of these particles by centrifugation results in a dark organic paste, which by virtue of bioaccumulation can contain unexpectedly high
concentrations of PTOCs relative to theoretical predictions. Other suspended particulates, especially resuspended lake or river bottom sediments, are made up primarily of inorganic material and have an organic carbon content of only some 3% or less. However, some of this organic content can be in the form of thin organic coatings on the mineral substrates. In fact, partitioning of PTOCs onto aquatic particulates may not be so much of a sorption process as one of exclusion from water and solubilization of the chemical into an organic (lipid-like) surface layer on the particles. Time is also a factor because some 60% of total sorption is usually complete in a few minutes. There are, however, two phases to sorption: the rapid component completed in a very short time period, and a slower component that may continue for longer in real aquatic ecosystems where exposure times can be very long. When sediment contaminants are desorbed, it is usually only the rapid component that becomes quickly bioavailable. However, with time in real aquatic ecosystems, the slower component could eventually be released. Clearly, most of these factors which affect the partitioning of PTOCs onto particulates (suspended solids/sediments) and thus their transport and fate in aquatic ecosystems are site related. Although laboratory tests and models may provide some basic insight to help predict aquatic fate, the true fate of PTOCs is often quite site specific.

The most important role played by sediments in the fate of PTOCs in aquatic ecosystems is permanent removal by burial (Allan, 1986). For many PTOCs by far the largest remaining mass not transported downstream, volatilized/or degraded, is in bottom sediments. Bottom sediments of lakes and impoundments are often major sinks and sites of eventual burial of PTOCs. Distribution patterns of PTOCs in lake bottom sediments provide clues to sites of maximum loadings and permit analyses of long-
term input trends. For example, Lake Ontario sediment maps of concentrations of some PTOCs such as mirex reveal the Niagara River to be a major source (Thomas, 1983). Alternatively, for other PTOCs such as PCBs, the distribution patterns are more complex and, although the Niagara River is a major source, other sources, such as the atmosphere, are involved. The areas of highest concentrations reflect these sources and in-lake processes of sediment focusing.

Lake sediment cores can be analyzed to determine changes in historical inputs of PTOCs and to find out the rate at which these chemicals are buried (Durham & Oliver, 1983). Sediment cores from the Niagara Basin of Lake Ontario at a site where sedimentation rates are high, close to the mouth of the Niagara River, have depth distributions for several PTOCs, such as mirex, PCBs, total chlorobenzenes and octachlorostyrene which reveal maximum inputs to have occurred in the 1960s and early 1970s (Durham & Oliver, 1983).

The role of biota

Productivity in water bodies is primarily a result of nutrient levels and has a strong influence on three major processes affecting PTOC fate: (1) sedimentation, (2) degradation, and (3) bioaccumulation. The role of phosphorus and nitrogen in primary productivity and the role of these nutrients in setting lake and river trophic levels is important because it in turn can influence such processes as PTOC burial by increased (or decreased) sedimentation rates; degradation rates of chemicals by biological processes; and bioavailability and bioaccumulation. PTOC fate is also affected by the relative importance of bottom-up (eutrophication), but also by top-down (fish stocking) control.

The effect of nutrients on increasing phytoplankton and zooplankton population densities is well established. In turn, this leads to greater seston concentrations and increased sedimentation rates. Accumulation and/or sorption of PTOCs into these organisms, both when alive and dead, is rapid. In the Niagara River, the concentrations of some PTOCs in suspended particulates at the inflow to Lake Ontario were often much higher than at the source of the river at Fort Erie (Fox et al., 1983). In this case, the larger size fractions were made up primarily of zooplankton which had either bioaccumulated or sorbed the PTOCs during the short travel time (<24 h) of the river between the two locations.

Extreme nutrient inputs to aquatic systems result in organic rich bottom sediments in which biota such as oligochaete worms predominate. Such biota can naturally accumulate high levels of certain PTOCs relative to the sediments (Oliver, 1984b) and can also introduce shifts in isomer ratios between the sediments and their predators. Such burrowing worms also contribute to recycling of sedimented PTOCs by bioturbation of surface sediment layers to depths which can represent several years of sedimentation. Degradation rates of PTOCs may also be influenced by trophic state. Increased nutrient loads increase productivity which in turn increases food sources for bacteria and fungi. At higher trophic levels, bacteria and fungi become more abundant and both types of organisms are well known laboratory degraders of many PTOCs. Because of the many variables involved this process has been mainly quantified by laboratory tests using cyclone fermenter systems to measure both aerobic and anaerobic degradation rates for specific chemicals.
Given equal loadings of PTOCs to an aquatic ecosystem, the eventual concentrations found in biota appears to bear an inverse relationship to the trophic status of the particular water body. The reasons can be many but may include the length of the food chain involved or the degree to which a greater total biological (lipid) mass can dilute the same chemical load. More productive lakes have higher seston concentrations and are often shallower and have more organic rich resuspended bottom sediments. Thus, the particulates in suspension have a greater ability to sorb PTOCs, consequently buffering or diluting concentrations.

Concentrations of specific chemicals in all trophic levels are required to fully understand the role of trophic state in the biological fate of PTOCs. Borgmann & Whittle (1983) determined concentrations of PCBs and DDT in various trophic level biota from Lake Ontario and found that concentrations in the netplankton were similar to those found in mysides, which only spend part of the day close to or in contact with bottom sediments and their resuspended component. Even extremely insoluble PTOCs found almost exclusively in bottom particulates can thus pass into food webs by direct uptake by benthic and planktonic organisms. Bioaccumulation of PTOCs in Lake Ontario, as in other water bodies, is influenced by trophic state and the corresponding food web in the lake. Lake trout from Lake Ontario have body burdens of PTOCs, such as mirex and dioxins, which are very highly partitioned to particulates and thus expected to be rapidly buried in bottom sediments. Although transfer of PTOCs to biota directly from suspended particulates has been demonstrated it is more likely that fish relying mainly on benthic organisms as a food source are more likely to bioaccumulate sediment-associated PTOCs. By corollary, reduction in contamination of fish species is slowest for those fish which rely on benthic organisms or their predators as major food sources. Crude mean values for three PTOCs in Lake Ontario biota are based on many diverse values but simplify a complex data base for a few selected chemicals (Table 1). The general picture of the ranges of concentrations in various organisms and media becomes evident.

Table 1 Summary and range of concentrations of organic pesticides in Lake Ontario media (ppt or ng/kg[L])* (compiled from Borgmann & Whittle, 1983; Fox et al., 1983; Strachan & Edwards, 1984; Weseloh, 1983).

<table>
<thead>
<tr>
<th></th>
<th>Total DDT</th>
<th>Mirex</th>
<th>Lindane</th>
</tr>
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<tbody>
<tr>
<td>Raw water</td>
<td>0.3-57</td>
<td>0.1</td>
<td>0.4-11</td>
</tr>
<tr>
<td>Bottom sediment</td>
<td>25 000-218 000</td>
<td>144 000</td>
<td>46 000</td>
</tr>
<tr>
<td>Benthos</td>
<td>440 000-1 088 000</td>
<td>41 000-228 000</td>
<td>NA</td>
</tr>
<tr>
<td>Suspended sediments</td>
<td>40 000</td>
<td>15 000</td>
<td>1000-12 000</td>
</tr>
<tr>
<td>Plankton</td>
<td>63 000-72 000</td>
<td>ND-12 000</td>
<td>12 000</td>
</tr>
<tr>
<td>Fishes</td>
<td>620 000-7 700 000</td>
<td>50 000-340 000</td>
<td>2000-360 000</td>
</tr>
<tr>
<td>Herring gull eggs</td>
<td>7 700 000-34 000 000</td>
<td>1 800 000-6 350 000</td>
<td>78 000</td>
</tr>
</tbody>
</table>

*These values are only of the crudest nature and are not statistical means. Where only one value is given, the numbers are means, often of widely ranging values. Where a range is given, several sources of data were involved. ND = not detected; NA = not analysed.
The preferred biological sample media to detect PTOCs in Lake Ontario have been predator fish and the eggs of fish-eating herring gulls. In these media, PTOCs often in the ppm or high ppb range. PTOC concentration trends in most predatory fish from the Great Lakes have shown dramatic declines relative to concentrations ten and twenty years ago (Allan, 1989b). Concentrations of some organic pesticides such as DDT were extremely high in lake trout in the early seventies. The highest DDT concentrations in lake trout from Lake Ontario were around 4.5 ppm in 1977 and by 1985 these concentrations were reduced to about 1 ppm. The eggs of the fish-eating herring gull show similar downward trends in concentrations of PTOCs, including the DDT metabolite DDE (Bishop & Weseloh, 1990). Bioaccumulation of mirex has occurred in both Lake Ontario biota and biota in the St Lawrence Estuary. A comparison of the concentrations in biota from the two water bodies is given in Fig. 5, with the exception of Beluga whales in the St Lawrence Estuary because there are no aquatic mammals in Lake Ontario (Comba et al., 1992).

Degradation

Many PTOCs are degraded by chemical and biological processes. The latter are often the result of bacterial (Baxter, 1989) or fungal related dechlorination. The former are often related to hydrolysis; and photochemical processes which may be influenced by the presence of humic matter and other naturally occurring chemicals in water such as hydrogen peroxide. When quantifying the transport or fate of specific PTOCs, it
is important that degradation products also be determined. For example, the compound DDE is now measured rather than the parent DDT in Great Lakes media. The same applies for mirex and its photodegradation product, photo-mirex. Degradation processes and rates are also site specific in that chlorinated phenols have been found to be degraded more by biological than photochemical processes, for example, in shallow streams versus open lake waters. A review of these tropics is to be found in a companion paper in this volume (Carey, 1993).

CONCLUSIONS

General limnological information generated by earlier work can be used in conjunction with more recent contaminant-specific and problem-oriented research to refine our understanding of the transport and fate (the pathways) by which PTOCs move within aquatic ecosystems. The best way to resolve such pathways and to have confidence in future levels of exposure or predictions of rates of ecosystem recovery is by collection and analysis of multi-media samples. Interpretation of this ecosystem data provides hypotheses for further testing either by subsequent sampling; laboratory microcosm simulations; physical-chemical and toxicological testing; or by theoretical modelling based on the properties of the contaminants and specific polluted water bodies. At present, there is evidence from several studies of formerly severely contaminated aquatic ecosystems that natural decontamination for PTOCs can be surprisingly rapid (years to decades) if complete removal of point sources is achieved. Alternatively, when sources are primarily diffuse, recovery is slower. A site specific knowledge base also allows prediction of how an aquatic ecosystem will respond to any additions of new chemicals of known physical-chemical properties, degradation or bioaccumulation rates and toxicity as determined by laboratory testing.

In the Niagara River to St Lawrence Estuary ecosystem, many PTOCs have undergone order of magnitude reductions in loadings during the last two decades. Nevertheless, internal processes such as sediment resuspension and focusing and bioturbation are ways by which bottom sediment bound contaminants are recycled for long periods within the system. In fact, many hydrophobic PTOCs such as DDE and PCBs, which have to a large extent now been permanently buried in deep lake bottom sediments, continue to be bioaccumulated up to the highest trophic level aquatic biota as a result of these internal limnological recycling processes. Permanent removal of PTOCs is not, of course, confined to deep burial in lake bottom sediments. As mentioned earlier, many PTOCs are permanently removed from aquatic ecosystems by rapid flushing downstream and by volatilization or degradation.

Research into PTOC transport and fate in aquatic ecosystems should remain focused on the interfaces between the major media and on the processes which transfer chemicals between them. PTOC interactions between land, air, sediments, and biota, all need to be understood and quantified. To do so at specific sites is costly and often capital (analytical equipment) and labour (biological aspects) intensive but is the only real way of understanding and accurately predicting contaminant fate, site recovery, or response to remediation. Only on the basis of such knowledge can meaningful and realistic control actions, regulations, and remedial action plans be decided upon and implemented.
REFERENCES


