

## A Modeling Strategy for Planning the Virtual Elimination of Persistent Toxic Chemicals from the Great Lakes: An Illustration of Four Contaminants in Lake Ontario

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**ABSTRACT.** A systematic seven-step process is proposed as a strategy for planning "virtual elimination" of persistent toxic contaminants in the Great Lakes. The strategy involves (i) estimating loadings, (ii) gathering prevailing concentration data, (iii) obtaining physical-chemical property data for the chemicals of interest, (iv) obtaining data concerning conditions in the lake, (v) applying a relatively simple steady-state mass balance model incorporating an appropriate treatment of variability and uncertainty to reconcile the range of estimated concentrations with the range of monitoring data, (vi) identifying reasonable targets for loading reductions, and finally (vii) applying the model in dynamic form to estimate how future concentrations will respond to suggested loading reductions thus providing a set of targets for virtual elimination. The uncertainties in these estimates are quantified to convey an impression of their perceived accuracy. The strategy is illustrated for four contaminants (polychlorinated biphenyls, benzo(b)fluoranthene, arsenic, and lead) in Lake Ontario.

**INDEX WORDS:** Model, toxicants, Lake Ontario, loading reductions.

### INTRODUCTION

There is continuing concern among the public, government, and scientific communities in Canada and the United States about the presence of toxic chemicals in the Great Lakes and their effects on human and ecosystem health. A convincing cause-effect relationship has been demonstrated between levels of bioaccumulative toxic chemicals in the lake and reproductive problems in native species of fish-eating birds (Government of Canada 1991, National Wildlife Federation 1994, Bowerman *et al.* 1993). There is concern about the impacts of these substances on human health especially among populations who consume large quantities of fish (Darvill *et al.* 1995). Advisories have been issued for many Lake Ontario locations, with a general recommendation to women of childbearing age and

children to limit fish consumption from Lake Ontario (OMEE 1995).

The linked biotic (fish) and abiotic (water and sediment) components of the ecosystem can only be restored to a condition in which there are no human or ecological health concerns by reducing inputs of toxic persistent chemicals to the Great Lakes and allowing natural degradation and advection processes to reduce concentrations. The International Joint Commission has advocated the virtual elimination of persistent toxic and bioaccumulative chemicals by adopting a policy of zero discharge within an ecosystem approach. After considerable progress in the 1970s the recent rate of reduction in contaminant concentrations has been disappointing, despite continued statements of intent to improve environmental quality (Governments of the United States of America and Canada 1997).

Several problems contribute to the lack of an effective strategy for the virtual elimination of these

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substances, resulting in slow progress by governments toward emission reduction policies. The number of chemicals of concern is large. There are numerous industrial, municipal, and domestic sources of each toxic chemical. Many jurisdictions and government departments are involved. Many of the chemicals have uncertain physical-chemical properties and lack comprehensive monitoring and discharge data. It is also necessary to consider atmospheric deposition to the Great Lakes from sources outside of the basin (Eisenreich and Strachan 1992, Hoff *et al.* 1996).

Mass balance models of chemical fate are capable of addressing many of these problems and have been used in the past to provide guidance for environmental regulation within the Great Lakes, notably during the large scale Green Bay PCB mass balance study (Depinto 1994). The approach described here illustrates that a relatively low cost screening level model with clearly communicated uncertainties can provide a viable framework for development of strategies to reduce levels of toxic substances in the lakes. Here a strategy for planning virtual elimination of chemicals of concern is proposed and it is illustrated by application to four chemicals in Lake Ontario, namely total polychlorinated biphenyls (PCBs), benzo(b)fluoranthene (BBF), arsenic, and lead. These chemicals have been found in Lake Ontario and/or the Niagara River at levels that exceed established criteria (Lake Ontario Toxics Committee 1989). It is hoped that the present approach may serve as a template for other chemicals and in other lakes and thus contribute to an economically feasible and expeditious process of virtual elimination. The approach is regarded as consistent with the Ninth Biennial Report of the International Joint Commission (1998), which recommends:

"Governments support the development and application of models to assist in the testing, evaluation and implementation of ecosystem indicators, monitoring strategies and management strategies for water quality, contaminants, fisheries and other ecosystem issues."

There is a view that the potential for adverse effects on ecosystem and human health is such that strategies for virtual elimination of chemicals should focus on broad based controls of chemical manufacture and use throughout the Great Lakes basin, rather than on estimating emissions and subsequent modeling efforts. This view is particularly advo-

cated by one of the authors, Ms. Shirley Thompson. In large part this paper is based on loading estimates and modeling described in Thompson (1993), to which the reader is referred for fuller details.

## METHOD

The strategy as applied to Lake Ontario has seven steps, outlined in Table 1. The overall intent is to use estimated loading data as input into a model to determine if concentrations derived from the model are consistent with measured ambient concentrations in various compartments. An uncertainty analysis is performed using Monte Carlo

**TABLE 1. Seven step strategy for virtual elimination of toxic contaminants in Lake Ontario.**

Step Number	Task
1	Estimate all annual loadings to the lake for each chemical.
2	Gather available information on current and recent chemical concentrations in compartments of the lake ecosystem including water, sediment, atmosphere, and biota.
3	Gather appropriate physical-chemical data for the chemical of interest at the relevant temperature range.
4	Gather data on the prevailing physical conditions in the lake, that affect chemical fate.
5	Apply a simple steady-state or pseudo-steady-state mass balance model, incorporating an appropriate treatment of uncertainty and variability, and attempt to reconcile model predictions with observations. Adjust the parameters if necessary to give an acceptable fit. If retrospective loading and concentration data are available (possibly in the form of a sediment chronology) calibrate the model in dynamic form.
6	Identify reasonable targets for loading reductions, considering, for example, a 15 to 30 year time frame with a variety of intensities of effort.
7	Run the mass balance model in unsteady-state or dynamic form, again considering model uncertainty and variability, for the scenarios identified in step 6 and present the findings in summary form in the hope that the scenarios of loading reductions and the resulting reduction in contaminant levels may be accepted for implementation.

techniques to quantify variability and uncertainty, enabling a comparison to be made of the range of modeled concentrations with the range of available monitoring data. If agreement is satisfactory, the model can be considered to be a reliable descriptor of chemical fate in the lake, and is further applied in its unsteady-state form to predict future concentrations in water and sediment that will result from proposed reduction strategies. A Monte Carlo analysis is again applied at this stage to provide estimates of uncertainty in modeled future concentrations. If agreement between the steady state model and available monitoring data is unsatisfactory, the unsteady-state predictions from the model should not be used to justify remedial actions. In that case, examination of possible errors in the input data to the model, the model itself, or in the monitoring data is necessary to determine the cause of the inconsistency, since clearly there exists an inadequate understanding of sources and/or fate.

A key component of this strategy is the mass balance model which is used in Steps 5 and 7. The model selected in this case was the Rate Constant Model of Mackay *et al.* (1994) although other models could be used. Indeed, there is merit in using several models independently to minimize the risk of mistakes in the parameter values selected, in the equations used, or in the method of solution.

### STEP 1: ESTIMATING LOADINGS

Loadings are estimated from monitoring and flow data as discussed previously by Thompson (1992). These loadings to Lake Ontario were estimated by combining monitoring data from several sources including: atmospheric deposition (Eisenreich and Strachan 1992, and more recently Hoff *et al.* 1996), the Niagara River (Kuntz 1990), as well as other tributaries (Harangozo 1991), and almost 150 land-based Canadian sources including 27 industries (MOE 1990–1992, and Brown 1992), 31 wastewater treatment plants (Canviro Consultants 1988, 1989, 1990; B. Leclair, Ontario Ministry of the Environment, personal communication 1992; Poulton and Beak 1991; ZENON 1989; and MOE 1991), spills, bypasses, combined sewer overflows, runoff (Schroeter and Associates 1992) and backwash from water filtration plants (Beak Consultants Ltd. and Paul Theil Associates Ltd. 1991). However, for many sources, including 17 direct discharging industries from Canada and all American point and non-point sources, no monitoring data were avail-

**TABLE 2. Estimated non-atmospheric loadings to Lake Ontario (kg/year).**

Source	Arsenic	BBF	Lead	PCBs
Industry	1,204	166	16,400	8
Spills	—	8	—	—
Niagara River	137,000	570	228,000	465
Tributaries	5,000	—	—	—
Urban Runoff	2,660	—	146,000	166
Combined Sewer Overflow (CSO)	250	—	8,000	8
Sewage Treatment Plants (STP)	11,400	—	50,000	30
STP By Passes	60	8	240	—
Filtration Plants	900	—	720	—
Total	158,500	752	449,000	677

able. As a result loading estimates to Lake Ontario would likely be underestimated.

To include U.S. contributions, Canadian estimates for land sources were simply doubled based on the observation that populations and levels of industrial activity on both sides of the lake are similar. Although the U.S. side of Lake Ontario is slightly less populated than the Canadian side this correction may compensate for missing Canadian data. The assumption is only a first approximation, but should not introduce much error because the major source of the contaminants considered here is the Niagara River.

Tables 2 and 3 give the estimated land-based and atmospheric loadings. Table 3 relies heavily on the recent data reported by Hoff *et al.* (1996). The absorption rates were calculated by the model from reported air concentration. Volatilization is not included at this stage, thus the absorption figure is that of gross absorption, not the net of absorption less volatilization. Similarly, inputs from sediments are not included at this stage, but are calculated by the model. The three main sources of contaminants to the lake are the atmosphere, land-based sources around the shoreline, and the Niagara River (which includes inputs from the Buffalo/Niagara Falls region and all atmospheric input and point sources further upstream). For arsenic the proportions are Niagara River 88%, atmosphere 2%, land-based 10%, with a total of 162,000 kg/year. For lead the

**TABLE 3. Estimated atmospheric loadings (kg/year) to Lake Ontario and average concentrations.**

Pathway	Arsenic	BBF	Lead	PCBs
Wet deposition	3,000 <sup>a</sup>	58.4 <sup>b</sup>	41,000 <sup>a</sup>	58.0 <sup>a</sup>
Dry deposition	580	0	4,000	5.7
Absorption <sup>c</sup>	0	0.3	0	38.9
Net deposition	3,580	58.7	45,600	102.6
Air concentration (ng/m <sup>3</sup> )	0.48 <sup>a</sup>	0.03 <sup>b</sup>	3.7 <sup>a</sup>	0.18 <sup>a</sup>

<sup>a</sup>Hoff *et al.* 1996<sup>b</sup>Eisenreich and Strachan 1992<sup>c</sup>Estimated by the model

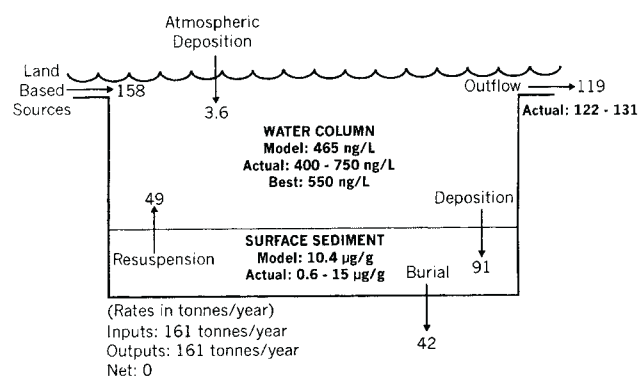
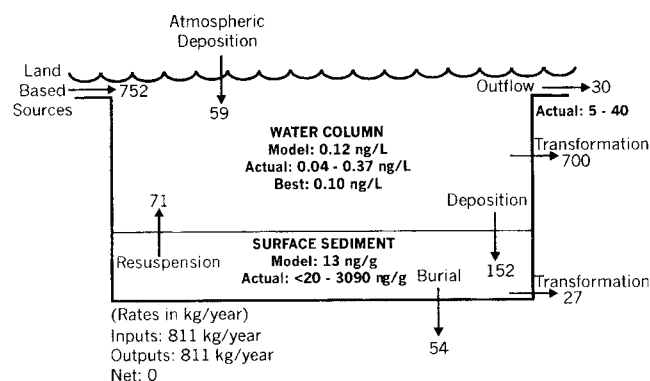
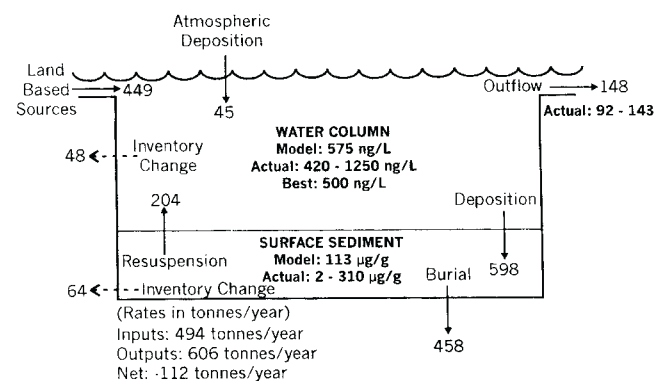
corresponding figures are 46%, 9%, and 45% with a total of 495,000 kg/year. For PCBs the percentages are 60%, 13%, and 27% totaling 780 kg/year. For BBF the contributions are 70%, 7%, and 23% totaling 811 kg/year.

It is difficult to assign error limits to these estimates. Unfortunately, in order to account for all loadings, data for inflow concentrations from the Niagara River which have been subject to rigorous quality assurance protocols must be added to suspect and fragmentary data on point and non-point sources around the lake. Given the dominance of the Niagara River inputs which depend for their accuracy on annual averages of monitored concentrations, it is believed that the total loadings are unlikely to be in error by more than a factor of two. This error estimate is later incorporated in the Monte Carlo uncertainty analysis.

## STEP 2: AMBIENT CONCENTRATIONS

Ambient concentration ranges for air, water, and sediment compartments were obtained from the following sources:

- water and suspended sediment data from Kuntz (1990), Biberhofer (1991), Tarandus Associates Ltd. (1992), L'Italien and Hedley (1993), and Rossmann and Barres (1988);
- sediment data from Mudroch and Mudroch (1992), Jaagumagi and Persaud (1992), and Persaud, *et al.* (1992);
- air data from Hoff *et al.* (1996) and Eisenreich and Strachan (1992).

**FIG. 1. Steady-state mass balance diagram for arsenic in Lake Ontario.****FIG. 2. Steady-state mass balance diagram for BBF in Lake Ontario.****FIG. 3. Pseudo-steady-state mass balance diagram for lead in Lake Ontario.**

Attempts were made to achieve temporal agreement between observed environmental concentration data and emissions estimates, which were made for 1992. The ranges of concentrations found in water and sediments are shown in Figures 1 through 4 and Table 6. For water, average lake concentra-



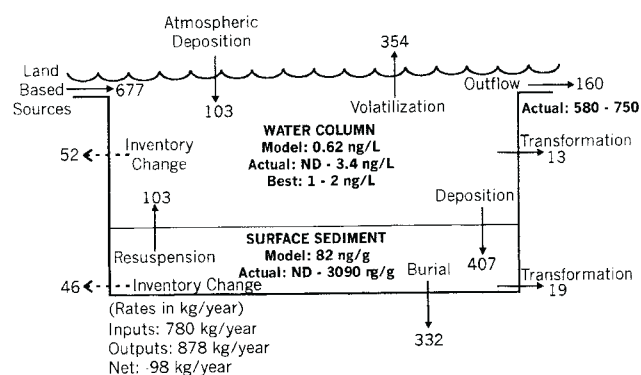


FIG. 4. Pseudo-steady-state mass balance diagram for PCBs in Lake Ontario.

tions were estimated on an area basis. Because sediment data were mainly obtained from Areas of Concern which have elevated contaminant concentrations it was judged impossible to deduce meaningful average lake-wide concentrations. For the purposes of this study a screening level agreement between observed and modeled sediment concentrations was sought. As is discussed later, a more rigorous assessment of past and present sediment concentrations would be required as a foundation for a more complex and reliable lake model.

### STEP 3: PHYSICAL-CHEMICAL PROPERTIES

Properties of the contaminants, shown in Table 4, were selected from Mackay *et al.* (1992a and b), and Diamond (1990). Some of the input parameters

are combined properties of the contaminant and the lake, and may be sensitive to long-term changes in limnology. For example, the fraction of chemical dissolved in the water column is a function of the partition coefficient of the chemical and the suspended solids concentration in the water column. If the suspended solids concentration changes (perhaps due to nutrient loading reductions or zebra mussel infestation), this fraction could change. Uncertainty in future physical conditions within the lake will thus contribute to overall model uncertainty.

### STEP 4: PREVAILING ENVIRONMENTAL CONDITIONS IN LAKE

The prevailing dimensions and conditions in the lake were determined previously by Mackay *et al.* (1994).

### STEP 5: APPLICATION OF THE MODEL FOR THE FOUR CHEMICALS

The Rate Constant Model consists of two connected parts: a lake model and a food chain model. The lake model computes the rates of the following processes: evaporation from water to air; outflow from the lake; transformation to other chemical species in water and in sediment; transfer from water to sediment and sediment to water and burial to deep, inaccessible sediments. Each of these processes is described within the model by a first order rate constant. The integrated bioaccumulation model treats uptake from water and food and loss

TABLE 4. Physical-chemical properties and partition coefficients applied to the rate constant model.

Property	Arsenic	BBF	Lead	PCBs
Fraction on depositing particles in water	0.15	0.9999	0.8	0.5
Fraction dissolved in water column	0.85	0.0001	0.2	0.5
Fraction dissolved in sediment	0.09	$4.5 \times 10^{-5}$	$5.3 \times 10^{-4}$	$1.9 \times 10^{-4}$
Fraction sorbed in atmosphere	1	0.94	1	0.05
Scavenging ratio of aerosols	180,000	200,000	180,000	100,000
Volatilization mass transfer coefficient: air side (m/h)	1	1	1	1
Volatilization mass transfer coefficient: water side (m/h)	0.01	0.01	0.01	0.01
Air-water partition coefficient	0.00001	0.00144	0.00001	0.005
Octanol-water partition coefficient	0	3,720,000	0	3,980,000
Sediment-water diffusion mass transfer coefficient (m/h)	$2.3 \times 10^{-6}$	0.00132	0.0001	0.0001
Half life in water (h)	$\infty$	1700	$\infty$	500,000
Half life in sediment (h)	$\infty$	55000	$\infty$	500,000

TABLE 5. Rate constants (1/yr) for four contaminants in Lake Ontario.

Rate Constant	Arsenic	BBF	Lead	PCBs	Confidence Factor
Evaporation from water	$8.69 \times 10^{-4}$	$1.29 \times 10^{-5}$	$2.04 \times 10^{-4}$	0.341	2
Outflow from lake	0.154	0.154	0.154	0.154	1.05
Transformation in water	0	3.57	0	$1.21 \times 10^{-2}$	3
Water to sediment transport	0.117	0.778	0.623	0.392	2
Sediment to water transport	0.227	0.287	$9.64 \times 10^{-2}$	$6.70 \times 10^{-2}$	2
Transformation in sediment	0	0.110	0	$1.21 \times 10^{-2}$	3
Burial from sediment	0.197	0.217	0.217	0.217	2
Total rate constant from water	0.271	4.50	0.778	0.899	—
Total rate constant from sediment	0.424	0.614	0.313	0.296	—
Water to sediment deposition	0.117	0.778	0.622	0.389	—
Water to sediment diffusion	$1.20 \times 10^{-4}$	$8.10 \times 10^{-6}$	$1.23 \times 10^{-3}$	$3.07 \times 10^{-3}$	—
Sediment resuspension to water	$4.57 \times 10^{-2}$	$5.02 \times 10^{-2}$	$5.02 \times 10^{-2}$	$5.02 \times 10^{-2}$	—
Sediment to water diffusion	0.181	0.237	$4.62 \times 10^{-2}$	$1.68 \times 10^{-2}$	—

by egestion, respiration, growth dilution and metabolism, for six populations of organisms. This study is principally concerned with the response of water and sediment concentrations to loading reduction strategies, and thus the bioaccumulation model was not applied. The Rate Constant Model has evolved from a fugacity based model of chemical dynamics in Lake Ontario (Mackay 1989), and has been previously shown to be a useful descriptor of PCB fate in the lake when applied in either steady-state or unsteady-state form (Mackay 1989, Mackay *et al.* 1994).

The model was used to calculate concentrations in Lake Ontario for sediment and water by applying the loadings data obtained from Step 1 along with properties of the lake and of the four chemicals. Contaminant fluxes for each process in the lake model are illustrated for the four contaminants in Figures 1-4.

The rate constants determined by the model are listed in Table 5. Rate constants for transformation in water and sediment are calculated from assumed degradation half-lives in these media. Evaporation from water, sediment burial, and sediment-water transfer rate constants are combined properties of the chemical and the lake. The rate constant for outflow depends on the residence time of water in Lake Ontario, and is independent of properties of the contaminant.

The magnitude of the rate constants indicates the relative importance of the removal and transfer processes. The key removal rate processes differ between the chemicals: for lead and arsenic the key processes are deposition to sediment and outflow to the St. Lawrence River, for PCBs they are evapora-

tion and deposition to sediments, for BBF, transformation in water.

To test the validity of the model, predicted concentrations were compared with monitoring data for sediment, whole lake, and outflow water. As shown in Figures 1 through 4 and Table 6 the water and sediment concentrations obtained from the loading estimates were within the ranges observed in monitoring studies. Figures 1 through 4 describe the steady-state (or pseudo-steady-state) mass balance of each contaminant in Lake Ontario. If there is no change in current contaminant loading rates or in the physical properties of the lake the model predicts these concentrations will not change.

The key test of validity is the comparison of the concentrations generated by the model with monitoring data. Table 6 permits this comparison on two bases. First the average or typical observed concentration can be compared with the model estimate. Agreement is generally within a factor of 3, which is regarded as satisfactory at this stage. A more meaningful comparison is of the range in monitored concentrations with a range of estimated concentrations, taking into account uncertainties in the model parameters.

A version of the model was developed in which the total loadings and the rate constants were varied within prescribed ranges and these variations were propagated through the model to give a variation in the output concentrations. The technique used was to assign 95% "confidence factors" to all rate constants on the basis of judgement as to likely uncertainty and year-to-year variation. A confidence factor of 3 implies that 95% of all possible values lie between 1/3 and 3 times the mean value. This

TABLE 6. Observed and modeled contaminant concentrations in Lake Ontario.

Species	Water Concentration (ng/L)				Sediment Concentration (ng/g)		
	Observed range	"Best estimate" of lake wide mean	Model 95% confidence interval	Median model prediction	Observed range	Model 95% confidence interval	Median model prediction
Arsenic	400-750	550	220-990	465	600-15,000	3,700-29,500	10,400
BBF	0.048-3.42	0.10	0.04-0.37	0.12	< 20-3,090	3.5-50	13
Lead	420-1,250	500	230-1,500	575	2,000-850,000	41,000-310,000	113,000
PCBs	ND-3.4	1-2	0.28-1.38	0.62	ND-3,090	30-240	82

ND = Not Detected

assignment is necessarily subjective since no actual measurements, or their distributions, are available for these rate constants.

It was assumed that each rate constant and the total loading were lognormally distributed, with confidence factors shown in Table 5. For example, the 95% confidence factor of 3 corresponds to 2 standard deviations. The natural logarithm of the central value was allowed to vary with a standard deviation of 0.55 (a factor of 1.7) and thus with a 95% or two standard deviation limit of 1.10 or a factor of 3. The assigned standard deviations are thus  $0.5 \ln(Cf)$  where  $Cf$  is the confidence factor. For the Monte Carlo uncertainty analysis, the model was run for 1,000 trials and the input distribution and output concentrations in water and sediment stored. Output confidence factors were found to be reproducible within  $\pm 5\%$  using 1,000 discrete Monte Carlo events. The means, standard deviations, and confidence factors were then deduced for the output quantities, again on a lognormal basis.

The resulting 95% confidence intervals in water and sediment concentration are shown in Table 6. Because the model calculates sediment concentrations from loadings to water, confidence factors (and thus, 95% confidence intervals) for sediment are always larger than those for water. It is apparent that the ranges in monitoring data and in model estimates overlap, therefore the model is judged to give a satisfactory representation of the fate of these chemicals. It is possible that there is a fortuitous cancellation of errors, but as the model is applied to a larger number of chemicals this is less likely to be the case.

An advantage of this approach is that if the range of estimated concentrations is judged to be too large, i.e., the results are too uncertain, the sources of uncertainty can be quantified and appropriate research implemented to reduce the uncertainty. For

example, by varying individual rate constants it is apparent that the evaporation rate of PCBs is a major source of uncertainty, as are the reaction rate constants of BBF and the water-sediment exchange and sediment burial rate constants for arsenic and lead.

Although the model is steady-state in nature it does contain rate constants describing the current inventory change in water and sediment, thus it can treat unsteady-state situations, albeit in a simplistic manner. For PCBs and lead, loadings to the lake are currently in a slow decline as a result of a combination of regulatory measures and voluntary emission reduction programs. For these contaminants, current loading reductions were represented in the model by 5 and 3 percent per year inventory reductions in water and sediment, respectively. This simple treatment will fail when the system is rapidly adjusting to a new steady-state as a result of marked changes in input rate and slow changes in sediment concentrations from previously higher values. Fortunately the model will be most reliable for persistent chemicals for which such changes will be slow, and these are generally the substances of primary environmental concern.

It must be emphasized that the model does not treat seasonal variations since conditions are annually averaged. However, this does not invalidate the approach because the rate constants are essentially the ratio of the annual flux attributable to a process (kg/year) to the average quantity of chemical present in the water or sediment (kg) during that year. In many cases there is an incentive to develop a model incorporating seasonal variation as has been done for Lake Superior by Hornbuckle *et al.* (1994). Prior to implementing management strategies there is merit in applying several comparable screening level models, and if warranted, developing more complex predictive models. Indeed, the

approach suggested here can be viewed as a first step in the justification of more rigorous modeling efforts which treat the lake in greater spatial and temporal detail.

### STEP 6: STRATEGIES TO REDUCE LOADINGS

Since Table 2 identified the Niagara River, upstream Great Lakes, and industrial sources discharging to wastewater treatment plants as the major sources of the four chemicals of concern, possible emissions from these sources were further identified. A variety of publications were consulted to determine products and industrial sectors known to emit these chemicals (Voldner and Smith 1991, Socha 1992, Thompson 1991). From the emitting industrial sectors, contaminated products, and direct discharges which were identified, a list of targets to reduce emissions was then compiled as shown in Table 7. Modifying processes and banning certain products and raw materials of these sources within the Great Lakes basin would result in significant reductions of 5, 10, and 15% per year over 15 to 30 years.

Loading reductions of this magnitude are consistent with the approach to virtual elimination outlined in the Great Lakes Binational Strategy (Governments of the United States of America and Canada 1997), which challenges the U.S. and Canada to achieve reduction of PCBs in use and storage by 19% per year over 12 years. Specific government actions including regulatory changes and incentive programs which could accelerate the pace of virtual elimination efforts for PCBs have been outlined (U.S. EPA 1998). In Canada, timelines for the virtual elimination of anthropogenic emissions of hydrocarbons such as BBF and benzo(a)pyrene have been called for under the Canada-Ontario Agreement respecting the Great Lakes Basin Ecosystem (Governments of Canada and Ontario 1994). Given these precedents, reductions of between 5 and 15% per year appear to be reasonable and attainable targets based on economic and technical constraints.

A potential stumbling block in achieving emission reductions is the perception that non-point sources such as tributary loadings and the atmosphere are "non-targetable." Given the potential of persistent toxic chemicals to migrate long distances and between environmental media, any virtual elimination strategy will require continental or global scale efforts.

The three reduction strategies were applied to the unsteady-state model. The "modest reduction scenario" reduces loadings by 5% per year from atmosphere and land sources (i.e., if on 1 January 1998 the loading was 100 kg/year, on 1 January 1999 it would be 95 kg/year, then 90 a year later, 86 another year later, etc.). The "moderate reduction scenario" reduces total loadings to the lake by 10% from the previous year (from 100 to 90, 81, 73, etc.). The "aggressive reduction scenario" reduces loadings by 15% per year.

### STEP 7: MODELING THE EFFECTS OF LOADING REDUCTIONS

The model was run in unsteady-state form to predict future concentrations according to the three reduction scenarios corresponding to selected decreases in loadings each year, over a 15 year period.

The time responses of concentrations to changes in loadings are presented in Figures 5 to 8. The water and sediment contaminant levels decrease at similar rates, with sediment recovery lagging slightly behind improvements in water quality. Generally, over the 15 years, concentration decreases are by:

- 2 to 5% per year for the modest strategy;
- 4 to 9% per year for the moderate strategy; and,
- 6 to 14% per year for the aggressive strategy.

It should be noted that arsenic levels decrease more slowly than the other contaminants considered here because its relatively high water solubility and lack of volatilization make outflow the most important loss mechanism. Concentrations of BBF decrease rapidly due to relatively rapid degradation in water.

It is important to emphasize that the rate of concentration decay in sediments is very sensitive to the assumed sediment mixed layer depth. This depth varies with location, being greater in near-shore regions with higher resuspension rates. Obviously a more accurate estimation of the rate of concentration decay in sediment requires a more detailed model with greater horizontal segmentation and including vertical segmentation in the sediment. Such models will require extensive site specific data including dated sediment core concentration profiles and studies of sediment-water exchange rates.

Propagation of errors through the unsteady-state



TABLE 7. Sources to target for emission reductions.

Sources Identified from Monitoring Data	Sources	
	Industrial	Consumer Product
<b>A</b> 4 Great Lakes (79%) <b>R</b> Niagara River (10%) <b>S</b> Tributary—Moir R. (3%) <b>E</b> (Deloro mining site runoff) <b>N</b> STPs (4%)—(Mississauga <b>I</b> Lakeview (3%)) <b>C</b> Atmospheric (3%) Industry (0.4%)— (Dofasco & Stelco (0.3%), Petroleum)	Processing of iron and steel, copper/nickel and gold account for approximately 54, 40 and 3%, respectively of releases in Ontario. Any industry using significant quantities of fossil fuels, particularly coal (e.g., electrical power generators), emits significant quantities. Although lead/zinc production emissions account for 9% of loadings Canadian-wide their sources are mainly in other provinces. Also, glass-making emits arsenic.	70% of arsenic used in the U.S. is attributable to pesticide manufacture and thus is released during pesticide use. Fuel combustion, particularly coal but also oil, releases significant amounts of arsenic.
<b>P</b> 4 Great Lakes (12%) <b>A</b> Niagara River (79%) <b>H</b> Industry iron & steel (14%) <b>s</b> —(Dofasco (9%) & Stelco (5%)) Spills from Dofasco (1.5%)	Production of coke in iron and steel production, aluminum reduction (i.e., manufacture of charcoal and carbon black) and the catalytic cracking of petroleum account for 60, 25 and 4% respectively of estimated annual emission of BaP in Canada. Fuel combustion from stationary sources releases 2% of emissions. Agricultural and prescribed burning is reported to emit 6% of American BaP emissions, compared to 3% from wildfire.	Produced by residential combustion of wood in woodstoves/fireplaces and fossil fuels, particularly when combustion is inefficient. Wear of tires (carbon black is a reinforcing agent for synthetic rubber) is estimated to account for 5% of BaP emissions. High levels in car exhaust, using gasoline and diesel fuel. Two-cycle engines (i.e., operation on an oil/gas mix) produce more PAHs than do 4-cycle engines. PAHs are the main constituent of coal tar, coal tar pitches, creosote, petroleum pitch and asphalt. Use of asphalt for roads results in runoff containing PAHs.
<b>L</b> 4 Great Lakes (59%) <b>E</b> Urban runoff (19%) <b>A</b> Atmospheric (12%) <b>D</b> STPs (7%)—(Toronto, Hamilton, and Mississauga) Industry (2%)—(Dofasco (1%) Stelco (0.5%)) Metal casting (0.6%)— General Motors (0.4%), Canada Pipe (0.1%)	Significant sources of lead are: iron and steel production (30% of total emitted); copper/nickel production (24%); ferrous foundries (20%); waste oil incineration (6%); metal fabricating industries (4%); milling and concentrating lead-bearing ores (4%); aircraft fuel use (4%); and municipal refuse incineration (2%).	Lead is released from the use/disposal of many products including ammunition, automobiles, babbitt and bearing alloys, brass and bronze, electrical cable sheathing, enamels, glassware, inks, radiation shields, lubricants, paints and pigments, piping, solder, fertilizer, storage batteries, and tank linings. Lead exists as a trace component in coal and fuel oil. After phasing out lead in gasoline in 1987 estimates of emissions from gasoline powered vehicles in Ontario in the early 1990s range from very small to more than 30%.
<b>P</b> 4 Great Lakes (25%) <b>C</b> Niagara River (45%) <b>B</b> Urban runoff (17%) <b>s</b> Atmospheric (9%) Industry-Petro (1%)	PCBs are mostly found in electrical equipment (i.e., transformers account for 92% of total, capacitors 7%, electromagnets 0.2% and others 0.5%). PCBs are also in mechanical equipment (0.1%) (i.e., hydraulic equipment, heat transfer equipment and vacuum equipment).	PCBs are released from the use/disposal of a number of products: lamp ballasts; many consumer products (consumer electronics, refrigerators, washing machines, and air conditioners); contaminated mineral oils; and chemicals containing PCB contamination.

STP - Sewage Treatment Plant

BaP - Benzo(a)pyrene

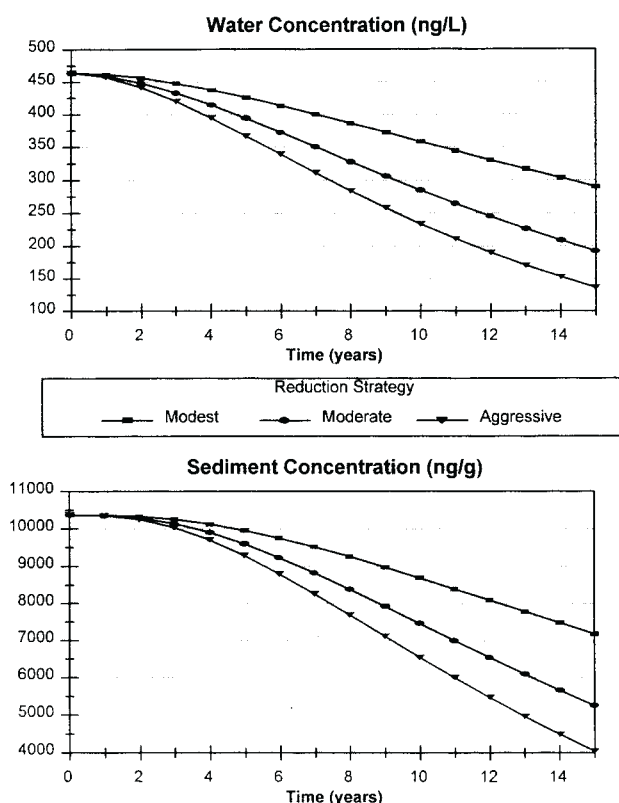


FIG. 5. Arsenic concentrations in water and sediment with decreasing inputs to Lake Ontario.

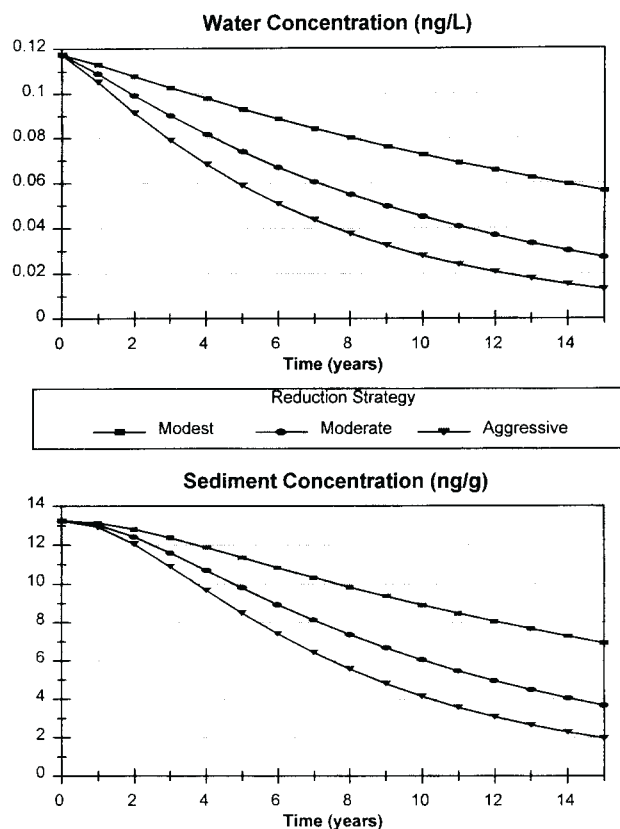


FIG. 6. BBF concentrations in water and sediment with decreasing inputs to Lake Ontario.

model was examined using Monte Carlo methods similar to those applied to the steady-state model. Because forcing functions are applied to loading estimates to represent the various emission reduction strategies, only the seven rate constants were varied during the unsteady-state uncertainty analysis. The deduced confidence factors thus represent uncertainty in the load-concentration relationship defined by the model.

Figure 9 shows time trends in model confidence factor for water and sediment concentration of PCBs for each of the three reduction scenarios, and is representative of results for the four contaminants. Confidence factors for the modest reduction strategy do not show a significant increase with time, indicating the 5% per year reduction in loadings does not significantly disturb the initial, pseudo-steady-state conditions. Uncertainty in model predictions increases with time and with more aggressive reduction strategies, although at long times, Cf asymptotically approaches a maximum value.

A useful regulatory question that can be addressed by the Monte Carlo version of the un-

steady-state model is: how long will it take for water and sediment to reach benchmark concentrations below current levels? For example, a benchmark on the path to virtual elimination could be reduction of levels in water and sediment to one tenth current concentrations. The Monte Carlo version of the unsteady-state Rate Constant Model allows for estimation of the time required to reach this benchmark using each of the three loading reduction strategies. Because model parameters vary, the times are expressed by a probability function. Figure 10 shows the estimated times to reach the one tenth current concentration benchmark in water and sediment under each scenario. The times were fitted to a Gaussian distribution to represent the probability that the benchmark concentration will be reached during a given year. The peak of the distribution represents the most likely year the benchmark will be reached. All four data sets are shown on the same scale to highlight differences in model uncertainties among the contaminants. The contaminants are arranged from the most rapid response time (BBF) to the slowest (arsenic). Differences in

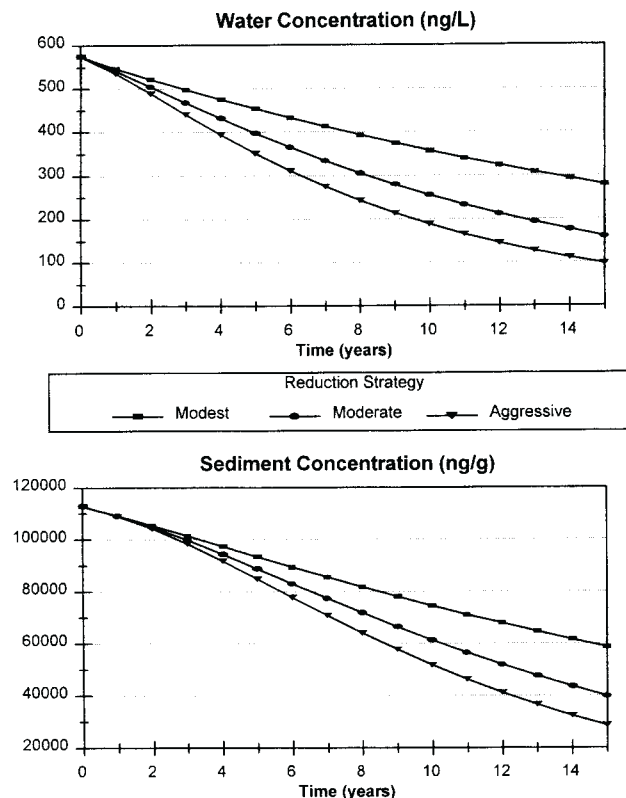


FIG. 7. Lead concentrations in water and sediment with decreasing inputs to Lake Ontario.

response times between chemicals are most pronounced for the aggressive reduction scenario, while all contaminants are most likely to reach the benchmark at approximately the same time (~47 years) under the modest strategy. This again illustrates that the modest reduction strategy does not significantly disturb pseudo-steady-state conditions within the lake, as emissions reach one tenth current levels after 46 years under this scenario. In contrast, under the aggressive reduction strategy, emissions will reach one tenth current levels in 15 years, but arsenic concentrations in water are not likely to reach the benchmark until 22 years after loading reductions are implemented. Sediment recovery lags behind water under the aggressive strategy, but differences are damped out as the pace of loading reduction is reduced.

### DISCUSSION

The mass balance model clearly demonstrates how concentrations in the lake respond to changes in loadings to the lake. It provides a valuable frame-

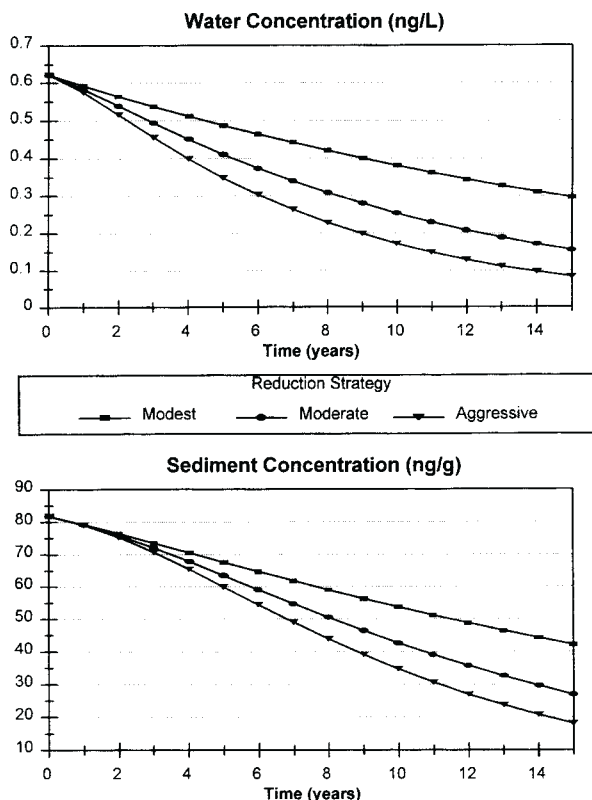


FIG. 8. Total PCB concentrations in water and sediment with decreasing inputs to Lake Ontario.

work and decision support system to encourage rational regulation. By combining chemical properties, lake properties, chemical concentrations and loadings the model is able to provide a complete, consistent picture of chemical fate. The model yields a "snapshot" of contamination status at one moment in time and can also be used to estimate future conditions in the lake. For example, after 5 years, according to the aggressive strategy, conditions are predicted to have improved such that:

- arsenic could be reduced from 630 ng/L to 435 ng/L in water and from 15  $\mu\text{g/g}$  to 12  $\mu\text{g/g}$  in sediment;
- BBF could be reduced from 0.12 ng/L to 0.06 ng/L in water and from 14 ng/g to 9 ng/g in sediment;
- lead could be reduced from 575 ng/L to 350 ng/L in water and from 110  $\mu\text{g/g}$  to 85  $\mu\text{g/g}$  in sediment; and,
- PCBs could be reduced from 0.60 ng/L to 0.35 ng/L in water and from 80 ng/g to 60 ng/g in sediment.

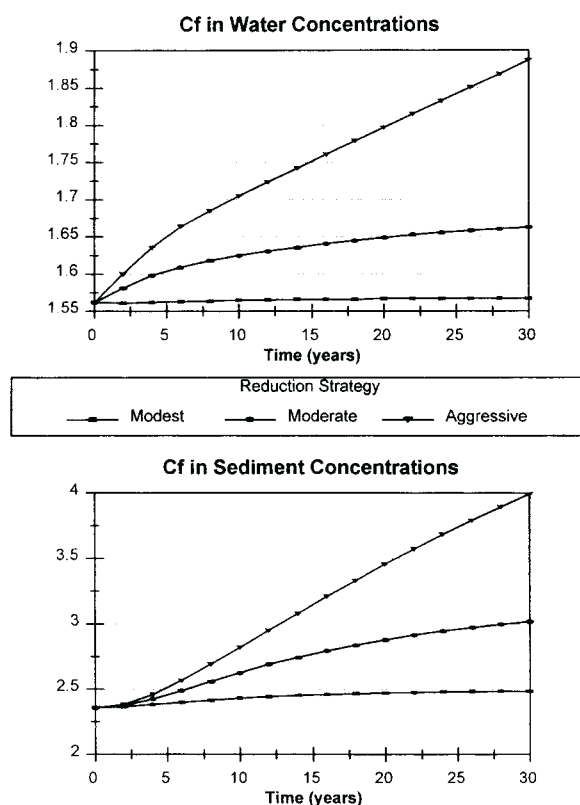


FIG. 9. Confidence factors for predicted water and sediment concentrations of PCBs.

The model is also useful in identifying the time frame required to meet standards or objectives under various reduction strategies. For example, the sediment "lowest effect level" (LEL) guidelines are exceeded for arsenic and lead. For arsenic, 1992 sediment concentrations of 15  $\mu\text{g/g}$  exceed the 5.5  $\mu\text{g/g}$  LEL (Persaud et al. 1992). To achieve the LEL will most likely require 13 to 22 years depending on the intensity of the strategy applied. For lead, 1992 sediment concentrations of 110  $\mu\text{g/g}$  exceed the 31  $\mu\text{g/g}$  LEL. To reach the LEL will most likely require 15 to 28 years depending on the strategy. For PCBs, the "no effect level" (NEL) of 0.01  $\mu\text{g/g}$  was exceeded but could likely be reached in 20 years by the aggressive reduction strategy.

As a result of this study certain priorities can be identified. There is a need for more and better documented data on loadings, especially from municipal, industrial, and tributary sources. Concentration data for contaminants in water, sediments, air, and biota are often incomplete, difficult to access, and have been obtained using different analytical meth-

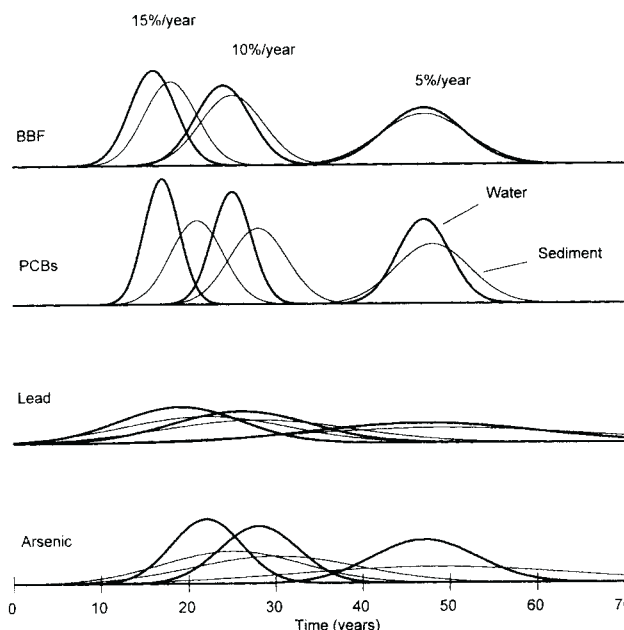


FIG. 10. Predicted time to reach 1/10 current concentrations.

ods by different agencies. Better coordination of data acquisition and processing is required. The model could be improved by horizontal and vertical segmentation of the water column and more detailed treatment of sediment and its exchange with water. Seasonal changes could be incorporated. Examination of the rate constants shows which processes are most important and should be subjected to more accurate determination. The model thus provides not only a quantitative mass balance of contaminants in the system, but it can help identify research and monitoring priorities, and direct researchers to the topics which are of greatest value in improving that mass balance.

Strategies for the entire Great Lakes basin, based on modifying processes and products of identified contaminant sources, could eventually result in "virtual elimination." Mass balance modeling offers a useful tool to monitor progress towards an uncontaminated lake containing fish which are once again safe for unlimited consumption by humans and wildlife.

## CONCLUSIONS

The strategy outlined here and illustrated for four chemicals in Lake Ontario is believed to be a logical and feasible framework for planning virtual elimination of persistent, toxic chemicals from the



Great Lakes. Clearly the remediation process can only be accomplished by a long-term commitment to reduce loadings. Regrettably there are only sparse data on existing loadings with very little published information from the U.S. side of Lake Ontario. This strategy could be readily applied to other chemicals and other lakes and would require only modest resources for implementation. It provides a rational method of identifying priorities and setting attainable targets on the road to virtual elimination. It is hoped that this planning strategy (or one like it) will be accepted and applied by the International Joint Commission and the federal, provincial, and state governments within the Great Lakes basin.

### ACKNOWLEDGMENTS

D. Mackay and M. MacLeod are grateful for financial support from NSERC, DuPont Canada Ltd., and the consortium of companies who support the Environmental Modelling Centre at Trent University. The authors thank E. Bentzen and K. Oldham for helpful criticism during the preparation of this paper. Finally, we gratefully acknowledge Tom Tseng and the late Eva Voldner, whose many contributions to the study of environmental health include pointing the way to examining sources of chemicals in terms of their uses and not only their final emissions.

### REFERENCES

- Beak Consultants Limited and Paul Theil Associates Limited. 1991. *Study of 1989 Dry Weather Discharges to the Metropolitan Toronto Waterfront*. Report submitted to Metropolitan Toronto and Region Remedial Action Plan and Ministry of the Environment.
- Biberhofer, H. 1991. Unpublished data supplied by Dr. Hans Biberhofer, National Water Research Institute, Burlington, Ontario.
- Bowerman, W.W., Kramer, V.J., and Giesy, J.P. 1993. A review of factors affecting productivity of bald eagles in the Great Lakes Region: Implications for recovery. Abstract from: Environmentally Induced Alterations in Development: A focus on Wildlife, Dec. 10-12, 1993, Racine, WI.
- Brown, P. 1992. Unpublished data provided by Ms. P. Brown, Project Engineer, Pollution Abatement, Conservation and Protection—Ontario Region, Environment Canada.
- Canviro Consultants. 1988. *Thirty Seven Municipal Water Pollution Control Plants: Pilot Monitoring Study*. Report submitted to Water Resources Branch, Ministry of the Environment (MOE).
- . 1989. *Municipal Industrial Strategy for Abatement (MISA) Preregulation Monitoring, Metal Casting Sector*. Report submitted to the Ministry of the Environment (MOE).
- . 1990. *St. Catharines Area Pollution Control Plan (SCAPCP): Urban and Industrial Discharges Study*. City of St. Catharines, St. Catharines, Ontario.
- Darvill, T.E., Lonky, J., Reihman, H., and Daly, H. 1995. The Oswego Newborn and Infant Development Project News Release. Release of Preliminary results of ongoing longitudinal study for a sample of nearly 700 newborns born at the Oswego Hospital at a workshop sponsored by the Ecology Centre at Ann Arbor, entitled "The Environmental Connection: Rising Rates of Breast Cancer, Reproductive Disorders and Children's Disease".
- Depinto, J.V. 1994. The Role of Mass Balance Modeling in Research and Management of Toxic Chemicals in the Great Lakes: The Green Bay Mass Balance Study. *Great Lakes Research Review* 1(1):1-8.
- Diamond, M. 1992. Modelling the Fate and Transport of Arsenic and Other Inorganic Chemicals in Lakes. Ph. D. dissertation, The University of Toronto, Toronto, Ontario.
- Eisenreich, S., and Strachan, W. 1992. *Estimating Atmospheric Deposition of Toxic substances to the Great Lakes: An Update (Draft)*. Great Lakes Protection Fund, Environment Canada.
- Government of Canada. 1991. *Toxic Chemicals in the Great Lakes and Associated Effects*. Minister of Supply and Services, Ottawa, Ontario, Canada.
- Governments of Canada and Ontario. 1994. *The Canada-Ontario Agreement respecting the Great Lakes Basin Ecosystem*. Available [http://www.cciw.ca/glimr/data/canada-ontario-agreement/].
- Governments of the United States of America and Canada. 1997. *The Great Lakes Binational Toxics Strategy, Canada-United States Strategy for the Virtual Elimination of Persistent Toxic Substances in the Great Lakes*. Available from [http://www.epa.gov/glnpo/p2/bnsinto.html].
- Harangozo, S. 1991. *Water Quality Data Ontario Lakes and Stream 1987, Volume XXII*. Queen's Printer for Ontario, Toronto.
- Hoff, R.M., Strachan, W.M.J., Sweet, C.W., Chan, C.H., Shackleton, M., Bidleman, T.F., Brice, K.A., Burniston, D.A., Cussion, S., Gatz, D.F., Harlin, K., and Schroeder, W.H. 1996. Atmospheric Deposition of Toxic Chemicals to the Great Lakes: A Review of Data Through 1994. *Atmospheric Environment* 30:3505-3527. **Errata:** (1997) *Atmospheric Environment* 31:1585.
- Hornbuckle, K.C., Jeremiason, J.D., Sweet, C.W., and Eisenreich, S.J. 1994. Seasonal Variations in Air-

- Water Exchange of Polychlorinated Biphenyls in Lake Superior. *Environ. Sci. Technol.* 28:1491–1501.
- International Joint Commission. 1998. *Ninth Biennial Report on Great Lakes Water Quality*. Available by request from [http://www.ijc.org]. International Joint Commission, Washington, D.C. and Ottawa, Ontario.
- Jaagumagi, R., and Persaud, D. 1992. *The In-place Pollutants Program, Volume VII: A Synthesis of the Program*. Queen's Printer for Ontario, Toronto.
- Kuntz, K. 1990. *Joint Evaluation of Upstream/Downstream Niagara River Monitoring Data for the Period April 1988 to March 1989*. The Niagara River Data Interpretation Group.
- Lake Ontario Toxics Committee. 1989. *Lake Ontario Toxics Management Plan*. Environment Canada, United States Environmental Agency, Ontario Ministry of the Environment, New York State Department of Environmental Conservation.
- L'Italien, S., and Hendley, L. 1993. *Organic Contaminants in the Great Lakes 1986–1990 (Draft)*. Inland Waters Directorate, Burlington, Ontario.
- Mackay, D. 1989. Modeling the long-term behavior of an organic contaminant in a large lake: application to PCBs in Lake Ontario. *J. Great Lakes Res.* 15 (2):283–297.
- , Shiu, W., and Ma, K.C. 1992a. *Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals. Volume I: Monoaromatic Hydrocarbons, Chlorobenzenes and PCBs*. Chelsea, Michigan: Lewis Publishers Inc.
- , Shiu, W., and Ma, K.C. 1992b. *Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals. Volume II: Polynuclear Aromatic Hydrocarbons, Polychlorinated Dioxins and Dibenzofurans*. Chelsea, Michigan: Lewis Publishers Inc.
- , Sang, S., Vlahos, P., Diamond, M., Gobas, F., and Dolan, D. 1994. A rate constant model of chemical dynamics in a lake ecosystem: PCBs in Lake Ontario. *J. Great Lakes Res.* 20 (4):625–642.
- Ministry of the Environment (MOE). 1991. *Report on the 1989 Industrial Direct Discharges in Ontario*. Queen's Printer for Ontario, Toronto.
- Ministry of the Environment (MOE). 1990–1992. Series of MISA reports on various industrial sectors Queen's Printer, Toronto.
- Mudroch, A., and Mudroch, P. 1992. Geochemical composition of the nepheloid layer in Lake Ontario. *J. Great Lakes Res.* 18(1):132–153.
- National Wildlife Federation. 1994. *Hormone Copycats*. National Wildlife Federation Publications. Ann Arbor, MI.
- Ontario Ministry of Environment and Energy (OMEE). 1995. *Guide to Eating Ontario Sport Fish 1995–1996*. Queen's Printer of Ontario, Toronto.
- Persaud, D., Jaagumagi, R., and Hayton, A. 1992. *Guidelines for the Protection and Management of Aquatic Sediment Quality in Ontario*. Queen's Printer for Ontario, Toronto.
- Poulton, D., and Beak Consultants. 1991. *Toronto Main STP MISA Pilot Site Study Component Report: Water Quality*. Report submitted to the Ministry of the Environment (MOE), Toronto.
- Rossmann, R., and Barres, J. 1988. Trace element concentrations in near-surface waters of the Great Lakes and methods of collection, storage, and analysis. *J. Great Lakes Res.* 14(2):188–204.
- Schroeter and Associates. 1992. *Loadings of Toxic Contaminants from Urban Nonpoint Sources to the Great Lakes from Ontario Communities*. Final Report submitted to the Wastewater Technology Centre, Burlington, Ontario, Ref # 91-3.
- Socha, A. 1992. *Candidate Substances List for Bans or Phase-outs*. Ontario Ministry of the Environment, Queens Printer for Ontario, Toronto.
- Tarandus Associates Limited. 1992. *The Evaluation of Water, Sediment and Benthic Invertebrates from Long-term Sensing Sites in 1990*. Ontario Ministry of the Environment (OME).
- Thompson, S. 1992. *Estimating Loadings of Eighteen Persistent Toxics to Lake Ontario*. Environment Canada Report NO: KE403-1-0203.
- . 1993. A Practical Approach to Reduce Persistent Toxic Chemicals in Lake Ontario. Masters dissertation, Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, ON.
- United States Environmental Protection Agency (U.S. EPA). 1998. *Virtual Elimination of PCBs, Draft Options Paper*. Great Lakes National Program Office, October, 1998. Available from [http://www.epa.gov:80/grtlakes/bns/pcboptions/pcb-ve.pdf].
- Voldner, E., and Smith, L. 1991. Production, Usage and Atmospheric Emissions of 14 Priority Toxic Chemicals. Report to the International Joint Commission.
- ZENON Environmental Inc. 1989. *Analysis of Influent and Effluents from Water Pollution Control Plants*. Report submitted to Metro Toronto Works Department, Water Pollution Control Division.

Submitted: 28 September 1998

Accepted: 9 July 1999

Editorial handling: R. Peter Richards