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MODELING CONTAMINANT BEHAVIOR IN LAKE SUPERIOR:
A COMPARISON OF PCBs, PBDES, AND MERCURY

By

MARK D. ROWE

A THESIS

Submitted in partial fulfillment of the requirements

for the degree of

MASTER OF SCIENCE IN ENVIRONMENTAL ENGINEERING

MICHIGAN TECHNOLOGICAL UNIVERSITY
2009

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This thesis, " Modeling Contaminant Behavior in Lake Superior: A Comparison of PCBs, PBDEs, and Mercury", is hereby approved in partial fulfillment of the requirements for the Degree of MASTER OF SCIENCE IN ENVIRONMENTAL ENGINEERING.

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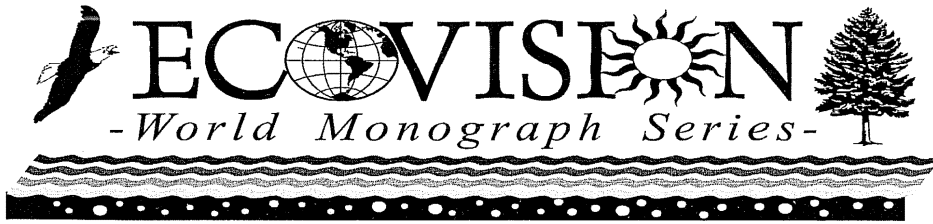
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Foreword

The entire content of this thesis was accepted for publication as a chapter in the book State of Lake Superior: Health, Integrity & Management*, which is in press at the time of this writing. The manuscript was peer-reviewed and accepted for publication by Aquatic Ecosystem Health and Management Society (AEHMS). The right to publish the work in a thesis was retained by the authors, as described in paragraph 4 of the original copyright transfer agreement. The agreement is reproduced in its entirety on the following page of this thesis, and Dr. M. Munawar, president of AEHMS, was notified of our intent to use the manuscript in a thesis, as required by the copyright transfer agreement. Dr. Noel Urban independently contributed the portions of this work related to mercury. The remainder of the content and writing is my contribution, under the guidance of my advisor, Dr. Judith Perlinger, and Dr. Urban.

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Abstract

A mass-balance model for Lake Superior was applied to polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), and mercury to determine the major routes of entry and the major mechanisms of loss from this ecosystem as well as the time required for each contaminant class to approach steady state. A two-box model (water column, surface sediments) incorporating seasonally adjusted environmental parameters was used. Both numerical (forward Euler) and analytical solutions were employed and compared. For validation, the model was compared with current and historical concentrations and fluxes in the lake and sediments. Results for PCBs were similar to prior work showing that air-water exchange is the most rapid input and loss process. The model indicates that mercury behaves similarly to a moderately-chlorinated PCB, with air-water exchange being a relatively rapid input and loss process. Modeled accumulation fluxes of PBDEs in sediments agreed with measured values reported in the literature. Wet deposition rates were about three times greater than dry particulate deposition rates for PBDEs. Gas deposition was an important process for tri- and tetra-BDEs (BDEs 28 and 47), but not for higher-brominated BDEs. Sediment burial was the dominant loss mechanism for most of the PBDE congeners while volatilization was still significant for tri- and tetra-BDEs. Because volatilization is a relatively rapid loss process for both mercury and the most abundant PCBs (tri- through penta-), the model predicts that similar times (from 2 - 10 yr) are required for the compounds to approach steady state in the lake. The model predicts that if inputs of Hg(II) to the lake decrease in the future then concentrations of mercury in the lake will decrease at a rate similar to the historical decline in PCB concentrations following the ban on production and most uses in the U.S. In contrast, PBDEs are likely to respond more slowly if atmospheric concentrations are reduced in the future because loss by volatilization is a much slower process for PBDEs, leading to lesser overall loss rates for PBDEs in comparison to PCBs and mercury. Uncertainties in the chemical degradation rates and partitioning constants of PBDEs are the largest source of uncertainty in the modeled times to steady-state for this class of chemicals. The modeled organic PBT loading rates are sensitive to uncertainties in scavenging efficiencies by rain and snow, dry deposition velocity, watershed runoff concentrations, and uncertainties in air-water exchange such as the effect of atmospheric stability.

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Abbreviations and Symbols

PBT	persistent, bioaccumulative, and toxic chemical
PCB	polychlorinated biphenyl
PBDE	polybrominated diphenyl ether
Hg(II)	oxidized mercury
Hg(0)	zero-valent mercury
C_w	total PBT concentration in the water (dissolved plus sorbed fractions)
C_a	total atmospheric PBT concentration (particle-bound plus gas fractions)
J_i, J_s	sum of all external input PBT mass flows into the lake and sediment boxes, respectively
k_{11}, k_{22}	sum of all first-order rate constants describing loss or transfer from one box to the other as a function of the concentration of the same box
k_{12}, k_{21}	sum of all first-order rate constants describing transfer from one box to the other as a function of the opposite box concentration
t_{ss}	time to reach 95 % of the steady state concentration
TSP	atmospheric aerosol particle mass concentration
f_{om}	mass fraction organic matter in aerosol particles
K_p	particle-gas partition coefficient
Φ	fraction of C_a sorbed to aerosol particles
K_{oa}	temperature corrected octanol-air partition coefficient
A_o	surface area of Lake Superior
V	volume of Lake Superior
J_{dry}	dry deposition PBT mass flow rate into the system
v_d	atmospheric aerosol particle dry deposition velocity
f_d	fraction of time not raining or snowing
J_{pwet}	particulate wet deposition PBT mass flow rate into the system
Q_{pr}	precipitation flow rate of water into Lake Superior
W_p	aerosol particle scavenging efficiency of precipitation
J_{dwet}	dissolved wet deposition PBT mass flow rate into the system
K_{aw}	temperature-corrected dimensionless Henry's law constant
J_{aw}	gaseous absorption PBT mass flow rate into the system
v_{aw}	air-water exchange velocity
J_{wa}	watershed PBT mass flow rate into the system
C_{wa}	concentration in the watershed discharge
f_w	fraction of C_w dissolved
DOM	dissolved organic matter
DOC	dissolved organic carbon
[DOC]	mass concentration of dissolved organic carbon in open water
TSS	total suspended solids in water column

v_{ps}	particle settling velocity in the water column
f_{doc}	fraction of C_w sorbed to DOM
f_s	fraction of C_w sorbed to suspended solids
r_{sw}	solid-water phase ratio
K_d	suspended solids-water partition coefficient
K_{doc}	DOC-water partition coefficient
m	sediment mixed layer mass per unit area
d_s	density of solids in sediment
p_s	porosity of sediment
z_{mix}	sediment mixed layer depth
v_{sd}	diffusive sediment-water exchange velocity
t_{bl}	aqueous boundary layer thickness
D_{iw}	diffusivity of the PBT in water
v_{sre}	sediment resuspension exchange velocity
μ	resuspension sediment mass flux density
f_{ocs}	mass fraction organic carbon in sediment solids
v_{sx}	overall sediment-water exchange velocity
f_{oc}	mass fraction organic carbon in water column suspended solids
k_{ps}	transfer rate constant for particle settling from the water column
k_{sxl}	diffusive and resuspension rate constant for PBT transfer from lake to sediment
k_{sl}	overall rate constant for PBT transfer from sediment to lake
k_{sxs}	diffusive and resuspension rate constant for PBT transfer from sediment to lake
k_{ls}	overall transfer rate constant from lake to sediment
k_{psls}	transfer rate constant for particle settling from lake to sediment
k_{sxls}	diffusive and resuspension transfer rate constant from lake to sediment
β	ratio of mass fraction organic carbon at the bottom of the sediment mixed layer to the mass fraction organic carbon of the sediment mixed layer
k_{vol}	volatilization rate constant
k_{out}	rate constant for flushing through the outlet
k_b	sediment burial rate constant

Introduction

Lake Superior is relatively remote and is impacted to a lesser extent by direct inputs of anthropogenic pollutants in comparison to the other Laurentian Great Lakes. In spite of the fact that there are few population centers and industries within the Lake Superior watershed, the lake has accumulated persistent bioaccumulative toxicants (PBTs) to an extent that has led to fish consumption advisories (USEPA, 2004a). Research over the past twenty to thirty years has shown that atmospheric deposition is the main source of several PBTs to the lake, such as PCBs (Eisenreich et al., 1981; Perlinger et al., 2004), organochlorine pesticides (Rapaport et al., 1985; Schottler and Eisenreich, 1997; Swackhamer et al., 1999), and mercury (Rolfhus et al., 2003). Concentrations of PCBs in the lake water and sediments have declined since their production and most uses were banned in the late 1970s (e.g., Jeremiason et al., 1994), but recent measurements have indicated increasing concentrations of other PBTs, such as the polybrominated diphenyl ethers (Song et al., 2004).

PBDEs are an emerging chemical class of concern in the Great Lakes (Manchester-Neesvig et al., 2001). PBDEs are added as flame retardants to many consumer products including plastic housings for electronics and polyurethane foam used in furniture. The lesser brominated PBDEs have been shown to bioaccumulate and to be transported through the atmosphere to remote locations such as the Arctic (Ikonomou et al., 2002). Existing evidence indicates that PBDEs may cause liver toxicity, thyroid toxicity, and neurodevelopmental toxicity in mammals (USEPA, 2004c). Increasing concentrations of PBDEs over time have been measured in humans and wildlife around the world (Hites, 2004).

Although relatively few measurements of PBDE concentrations in Lake Superior are available, PBDE concentrations in Lake Superior sediment, fish, and air have been reported in the literature. In the dated sediment cores reported by Song et al. (2004) the Σ PBDE concentration (11.9 ng g^{-1}) was dominated by BDE 209 (approx. 90 %) and was slightly greater than the Σ PCB concentration in surface sediments (8.3 ng g^{-1}). In the dated sediment cores, the Σ PCB had peaked around 1986 and decreased since then, while the Σ PBDE concentration was highest at the surface in most cases. In fish, Σ PBDE concentration (9.1 ng g^{-1}) was reported by Dodder et al. (2002) to be about one fifth of the Σ PCB concentration (50 ng g^{-1}). BDE 209 was not detected in the fish. Strandberg et al. reported PBDE concentrations in air at the Eagle Harbor site on the Keweenaw Peninsula of Lake Superior (Strandberg et al., 2001). Σ PCB concentrations (140 pg m^{-3}) were about twenty-five times higher than Σ PBDE concentrations (5.5 pg m^{-3}) and BDE 209 was not detected. However, Strandberg et al. reported low recoveries for BDE 209 in the analytical procedures and suggested that the reported BDE 209 concentrations be considered as estimates. More recently, Hoh and Hites reported atmospheric concentrations of PBDEs at five sites ranging from urban to rural areas in central North America

including the Sleeping Bear Dunes site, a rural location on the eastern shore of Northern Lake Michigan (Hoh and Hites, 2005). BDE 209 was a relatively abundant congener in all samples, and was associated with the particulate phase. In spite of the fact that BDE 209 has not been detected to date in air samples near Lake Superior, it seems likely that particle-bound atmospheric deposition may be the source of the high BDE 209 concentrations in Lake Superior sediment reported by Song et al. (2004). Because few measurements of PBDEs have yet been made in Lake Superior and regulations are pending, an assessment of the behavior of this class of chemicals is timely.

In this chapter we compare and contrast three chemical classes of contaminants found in Lake Superior (PCBs, PBDEs, and mercury) in order to highlight the differences and similarities in their behavior. This comparison summarizes what we do and do not yet know about the processing of these contaminants within large lakes, and also yields insights as to what may be expected in the near future. Although it is unusual to include an inorganic chemical (Hg) that undergoes oxidation-reduction transformation reactions under environmental conditions in a discussion with organic contaminants, we believe that useful insights may be gained from the comparison because the volatility of elemental mercury is in the same range as that of the organic PBTs discussed here. These three contaminant groups have one major feature in common: the balance between atmospheric deposition and volatilization is a critical factor controlling the fate of each contaminant class within large lakes. Much of the research on and modeling of mercury focuses on rates of methylation and demethylation (e.g., Regnell et al., 1997; Hintelmann et al., 2002) because it is only methylated mercury that bioaccumulates. However, to assess impacts of pending regulations, it will be necessary to understand the factors controlling the total inventory of Hg in lakes.

Mass balance models can be used to understand the major input and loss processes to and from a system. This information can direct monitoring efforts toward the most important processes. Models can also be used to estimate how long it may take impacted resources to recover without regulatory actions, or to assess whether regulatory actions are likely to be effective. Lake Superior has been the subject of previous mass balance modeling efforts (e.g., Schottler and Eisenreich, 1997; Swackhamer et al., 1999), in particular for PCBs (e.g., Eisenreich, 1987; Jeremiason et al., 1994). In this chapter, a mass balance model framework that has been used previously to model PCBs in Lake Superior (described in, Schwarzenbach et al., 2003) is applied to PBDEs and mercury. In the case of mercury, estimates of input rates are available in the literature. For PBDEs, such estimates are not available, so the lake system model was extended to include estimation of atmospheric deposition fluxes based on atmospheric concentrations. The results provide a means of comparing the environmental behavior of these classes of PBTs in addition to giving a qualitative estimate of how quickly or slowly concentrations in the lake might respond to future changes in atmospheric concentrations.

Methods

Site and system description

Lake Superior is the largest freshwater lake in the world by surface area ($8.21 \times 10^{10} \text{ m}^2$). The lake volume ($1.22 \times 10^{13} \text{ m}^3$) nearly equals the sum of the volumes of the other four Laurentian Great Lakes. The water flow into the lake from precipitation of $2,071 \text{ m}^3 \text{ s}^{-1}$ (average 1948 – 1999, Lenters, 2004) is approximately equal to the flow from watershed runoff of $1,620 \text{ m}^3 \text{ s}^{-1}$ (average 1948 – 1999 including the Long Lac diversion, Lenters, 2004) underscoring the importance of atmospheric deposition to the lake. The only outlet from the lake is the St. Mary's River at $2,239 \text{ m}^3 \text{ s}^{-1}$ (average flow 1949 – 1999, Lenters, 2004) giving a mean water residence time of 173 yr. Water and air temperatures are much lower than $25 \text{ }^\circ\text{C}$, and show substantial seasonal variation, as shown in Table 1. The annual mean water temperature is $3.6 \text{ }^\circ\text{C}$ (Croley et al., 2001). Wind speeds also vary seasonally with higher winds in the colder months. Parameters needed to describe the processes within the lake are given in Table 2. The oligotrophic nature of Lake Superior along with low water temperatures leads to low biological productivity (NPP of $50\text{-}100 \text{ g C m}^{-2} \text{ yr}^{-1}$, Urban et al., 2005), which is reflected in the relatively low suspended solids concentration and sediment accumulation rate indicated in Table 2.

Model overview

The overall framework of the model is a coupled two-box (water column, surface sediments) system with an atmospheric deposition component added for PCBs and PBDEs (Fig. 1). Equilibrium partitioning is assumed between particulate and gas phases in the air and between dissolved, particle-bound, and colloidal or dissolved organic matter (DOM)-bound in the water (the colloidal phase is omitted for Hg), and between solids and pore water in the sediment. Rates that are considered include transfer velocities across the air-water and sediment-water interfaces, and rates of precipitation, particle settling, aerosol deposition, watershed runoff, flushing through the outlet, and sediment accumulation. Chemical and biological degradation or transformation rates are included in some scenarios.

Lake Superior is dimictic, and the simplifying assumption that the water column is well mixed is reasonable only for model time periods of several years or more. The relatively short period of summer stratification (July – November, Bennett, 1978; Assel, 1986), and the low level of biological activity act to minimize differences in process rates in the epilimnion and hypolimnion. Transport of PBTs in the sediment layer is limited; mixing in surface sediments may occur via bioturbation, internal or wind wave-induced sediment resuspension, and diffusion in pore waters (Robbins, 1978).

The total atmospheric concentration (gas fraction plus particle-bound fraction) was selected as the independent variable to drive the model because atmospheric concentrations are available for many PBTs, whereas measurements of inputs are not available for the PBDEs.

Table 1: Monthly mean meteorological, hydrological and lake conditions for Lake Superior

Month	Over-water air temperature ^A , °C	Surface water temperature ^A , °C	Precipitation flow rate ^B , m ³ s ⁻¹	Wind speed ^C , m s ⁻¹	Percent ice coverage ^D
January	-10.7	1.9	1887	8.0	18
February	-9.2	0.5	1200	7.8	43
March	-4.3	0.5	1493	7.9	44
April	2.9	1.3	1612	6.6	12
May	8.6	2.6	2277	5.9	1
June	12.9	4.5	2512	5.3	0
July	16.1	10.1	2477	5.0	0
August	16.7	14.7	2562	5.3	0
September	12.6	13.5	2680	6.5	0
October	7.2	9.6	2246	7.3	0
November	0.0	6.7	2115	6.8	0
December	-7.0	4.5	1815	7.7	2

^AGLERL monthly data averaged over years 1900-1999 (Croley et al., 2001)

^B(Lenters, 2004)

^C(Transportation Development Centre Canada, 1991)

^DGLERL daily data averaged monthly over years 1973-2002 (Assel, 2003)

Table 2: Lake Superior process attributes

Open water

Concentration of dissolved organic carbon in open water ^A , [DOC], kg m ⁻³	0.0014
Total suspended solids in open water ^B , TSS, kg m ⁻³	4×10 ⁻⁴
Mass fraction organic carbon in suspended solids ^B , f _{oc}	0.2
Particle settling velocity ^C , v _{ps} , m s ⁻¹	1.25×10 ⁻⁵

Air

total suspended particulate in air ^D , TSP, kg m ⁻³	2.5×10 ⁻⁸
Mass fraction organic matter in atmospheric particles ^D , f _{om}	0.2

Sediment

Total sediment accumulation flux ^E , kg m ⁻² s ⁻¹	6×10 ⁻⁹
Aqueous boundary layer thickness ^F , t _{bl} , m (assumed)	5×10 ⁻⁴
Sediment mixed layer depth ^G , z _{mix} , m	0.01
Density of solids in sediment ^F , d _s , kg m ⁻³	2500
Porosity of sediment ^H , p _s	0.9
Sediment resuspension rate ^C , μ, kg m ⁻² s ⁻¹	4×10 ⁻⁸
Preservation factor of organic carbon in mixed layer (estimated from Buckley et al. ^H), β	0.93
Mass fraction organic carbon of sediment in mixed layer ^H , f _{oc_s}	0.03

^AUrban et al. (2005), ^BFrom Eisenreich et al. 1989 in Environmental Organic Chemistry text, p.1065 (Schwarzenbach et al., 2003), ^CChai & Urban (2004), ^DHarner & Shoeib (2002), ^EBased on 85 dated sediment cores as summarized in Urban (2006a), ^GEvans et al. (1981), estimated from core data from Song et al., ^FSchwarzenbach et al. (2003, p. 1074), ^HChai (2005), ^IBuckley et al. (2004)

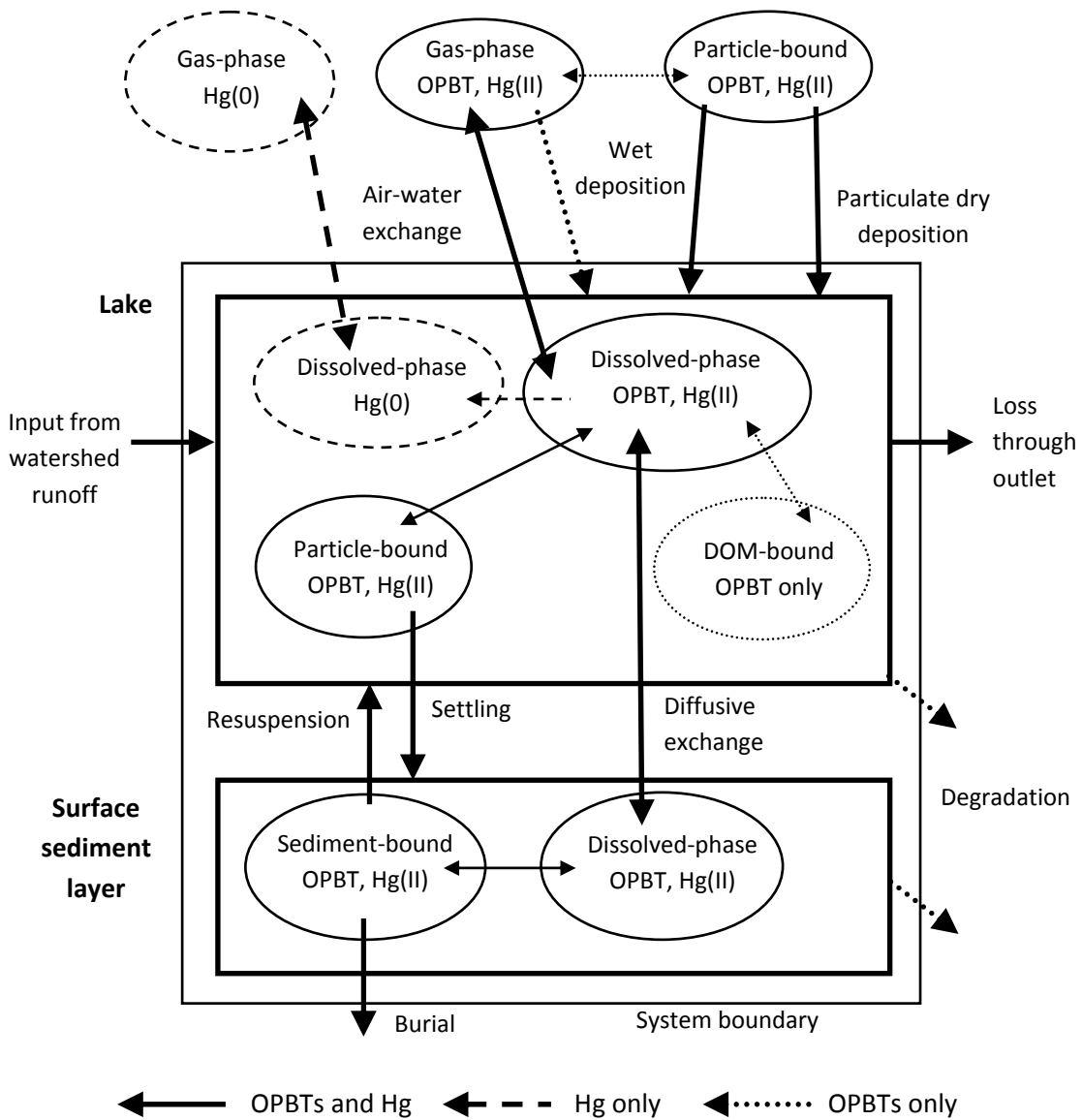


Figure 1: Schematic diagram for models of organic PBTs (OPBTs) and mercury. The models are identical except for elimination of the colloidal phase for Hg, and the addition of the transformation (reduction) from Hg(II) to Hg(0). The gas-particle partitioning and deposition of Hg was not included in this model.

Furthermore, input rates to the lake will vary depending upon environmental conditions and PBT physical-chemical properties. Thus it is of interest to include the deposition processes in the model so that the importance of different input pathways can be evaluated as a function of seasonal conditions and PBT properties.

For mercury, deposition processes were not modeled because of the greater complexity of the atmospheric chemistry of this substance. Instead, measured rates of input reported in the literature were used to drive the model. The dependent variables are the total (sum of dissolved, particulate, and colloidal) concentrations in the water column and the particle-bound concentration in the surface sediments.

To simulate historical conditions in the lake and to project future concentrations, either the analytical solutions to the differential equations (PCBs, PBDEs) or a forward Euler numerical model (PCBs, Hg) with a time step of one day were used. For PCBs and PBDEs, the independent variable is the total atmospheric concentration (C_a , particle-bound plus gas fractions). The dependent concentration variables are the total concentration in the water (C_w , dissolved plus sorbed fractions) and the concentration sorbed to solids in the sediment mixed layer (C_s). Differential equations to calculate the concentrations as a function of time in the two-box model and their solutions are described in Schwarzenbach et al. (2003)

$$dC_w/dt = J_1 - k_{11}C_w + k_{12}C_s \quad (1)$$

$$dC_s/dt = J_s + k_{21}C_w - k_{22}C_s \quad (2)$$

where J_1 and J_s are the sums of all external inputs into the lake and sediment boxes, respectively. External input into the sediment is neglected in the current model, but internal production of organic PBTs through transformation from other congeners could be included in the J_s term. The sum of atmospheric and watershed inputs are included in the J_1 term. The k terms are first-order rate constants. The k_{11} and k_{22} terms are the sums of all first-order rate constants describing loss or transfer from one box to the other as a function of the concentration of the same box. The k_{12} and k_{21} terms are the sums of all first-order rate constants describing transfer from one box to the other as a function of the opposite box concentration.

Once initial concentrations are assumed, the equations can be solved for concentrations as a function of time, taking into account the interfacial transfer velocities or steady-state concentrations as described in Schwarzenbach et al. The time to reach 95 % of the steady state concentration (t_{ss}) can also be calculated (Schwarzenbach et al., 2003).

$$t_{ss} = 6/(k_{11} + k_{22} - q) \quad (3)$$

$$q = [(k_{11}-k_{22})^2+4k_{12}k_{21}]^{1/2} \quad (4)$$

Both numerical and analytical solutions incorporated time-varying environmental conditions. For the numerical model, the average daily temperatures, wind speeds and incident radiation were fit to polynomials and process rate constants varied on a daily basis in response to environmental conditions. For the analytical solutions, first order rate constants were averaged over the year, but seasonal variation was taken into account by using monthly average values of several important variables including over-water air temperature, water surface

temperature, wind speed, precipitation rate, ice coverage, and PBT atmospheric concentration. For rate constants that consisted of a product of more than one seasonally-changing variable, a value of the rate constant was calculated for each month of the year, and monthly values were averaged to obtain an annual rate constant. In this way, covariance of seasonally-changing variables was taken into account. For comparison of the relative importance of loss processes (sinks), a standardized scenario was utilized for the three chemical classes. This scenario consisted of a 15-year simulation of the lake with initial concentrations of zero in the water column and sediments and the atmospheric concentrations (PCBs, PBDEs) or input rates (Hg) held constant at present-day values.

Process formulation

Gas-particle partitioning. Particle-gas partitioning of organic PBTs was described by Harner and Shoeib (2002) as a function of the temperature-corrected octanol-air partition coefficient, the aerosol concentration (TSP), and the fraction of organic matter (f_{om}) in the aerosol.

$$\text{Log}(K_p) = \text{log}(K_{oa}) + \text{log}(f_{om}) - 11.91 \quad (5)$$

$$\Phi = K_p \text{TSP} / (K_p \text{TSP} + 1) \quad (6)$$

where K_p is the particle-gas partition coefficient and Φ is the fraction sorbed to particles. Values of 0.2 and $10 \mu\text{g m}^{-3}$ were selected for the fraction of organic matter in the particulate phase and the total suspended particulate (TSP) concentration, respectively. An average organic matter fraction of 0.18 was found by Offenberg and Baker in measurements over southern Lake Michigan (Offenberg and Baker, 2000). Particulate concentrations measured over central Lake Superior in August 2004 were 2 - $12 \mu\text{g m}^{-3}$ (Rowe and Perlinger, 2004). The temperature-dependence of particle-gas partitioning is modeled through temperature correction of octanol-air partition coefficients (K_{oa}) based on the monthly averaged over-water air temperatures in Table 1.

Particulate dry deposition. Dry deposition of organic PBTs associated with particles was estimated as described by Eisenreich and Strachan (1992) then multiplied by the area of Lake

Superior (A_o) and divided by the volume of the lake (V) to give an input per unit volume of lake water.

$$J_{dry} = C_a \Phi v_d f_d A_o / V \quad (7)$$

The dry deposition input flow (J_{dry}) is a function of the total atmospheric concentration (C_a), the particulate dry deposition velocity (v_d), the fraction of time not raining or snowing (f_d), and other terms defined previously. A value of 0.9 for the fraction of time not raining or snowing was utilized (Eisenreich and Strachan, 1992). The particulate dry deposition velocity is a parameter that is difficult to measure or estimate because it depends on the particle size distribution, turbulence at the surface, and properties of the surface onto which the particles deposit.

Various estimated values of v_d have been proposed. Particle size distributions were measured over Lake Superior in August, 2004 (Rowe and Perlinger, 2004). Particle deposition models developed by Noll et al. (2001) and Hummelshøj (1992) were applied to these particle size distributions, resulting in estimated deposition velocities ranging from 0.001 to 0.01 $m\ s^{-1}$ over the central lake. Swackhamer et al. (1988) estimated v_d based on a mass balance for PCBs in Siskiwit Lake, located on Isle Royale in Lake Superior. By measuring wet deposition and sediment burial for hepta and octa-CBs, Swackhamer et al. estimated the PCB v_d at Siskiwit Lake by attributing the residual in the mass balance to dry deposition, giving a value of 0.0016 +/- 0.0013 $m\ s^{-1}$. Air-water exchange was neglected in the mass balance for hepta and octa-CBs, which were not detected in their gas phase measurements. The estimate from Swackhamer et al. is unique because it was derived from the environmental conditions over Lake Superior, and did not require the use of artificial collection surfaces, deposition velocity models, or assumptions regarding particle size distribution. However, in their final mass balance, Swackhamer et al. reported a net volatilization flux for some octa-CBs. If volatilization was significant for hepta and octa-CBs, the deposition velocity may have been higher than the value estimated by neglecting air-water exchange. Franz et al. (1998) measured dry deposition fluxes of PCBs, PAH, metals, and TSP using a smooth collection plate around and over Lake Michigan. They found v_d for PCBs in Chicago of 0.044 to 0.072 $m\ s^{-1}$, which they felt were reasonable for particles greater than 10 μm diameter. They were not able to calculate v_d for PCBs at the over-lake and rural Sleeping Bear Dunes locations because particulate PCB concentrations were below detection limits, but PCB dry deposition flux at those locations was 32 and 15% of the value measured in Chicago. Franz et al. recommended a v_d of 0.005 to 0.020 $m\ s^{-1}$ for modeling purposes. Franz et al. stressed the strong dependence of deposition velocity on coarse particle concentration and that the coarse particle concentration decreases rapidly with distance from the source region. Because the measurements of Franz et al. were predominantly from Chicago and Southern Lake Michigan, close to source regions, the low end of their proposed range would most likely be appropriate for Lake Superior.

In the model, a deposition velocity of 0.002 m s^{-1} was selected to be consistent with prior work in the Great Lakes (Eisenreich and Strachan, 1992), and because it fell within the range of deposition velocities estimated by Swackhamer et al. (1988) for Siskiwit Lake, and from the particle size distributions measured over central Lake Superior (Rowe and Perlinger, 2004). Additional calculations were made to determine the effect of using a larger v_d similar to the value proposed by Franz et al. (1998). These calculations are presented in the section comparing model results to measurements.

For Hg, dry deposition to Lake Superior is 0.5 to $5 \mu\text{g m}^{-2} \text{ yr}^{-1}$ (Cohen et al., 2004; Seigneur et al., 2004), and contributes $10 - 50 \%$ of total atmospheric deposition at 5 to $10 \mu\text{g m}^{-2} \text{ yr}^{-1}$ (Rolfhus et al., 2003; Cohen et al., 2004; Seigneur et al., 2004); a value of $1.4 \mu\text{g m}^{-2} \text{ yr}^{-1}$ was used.

Particulate wet deposition. Particulate wet deposition (J_{pwet}) of organic PBTs was estimated as described by Swackhamer and Eisenreich (1991).

$$J_{\text{pwet}} = W_p Q_{\text{pr}} C_a \Phi / V \quad (8)$$

where Q_{pr} is the precipitation flow rate into Lake Superior, and W_p is a particle scavenging efficiency. Monthly average precipitation flow rates (Lenters, 2004) are given in Table 1. Swackhamer and Eisenreich (1991) gave values for particulate scavenging efficiency of rain ranging from $10^4 - 10^5$; a value of 5×10^4 was selected for the model.

The particulate scavenging efficiency of snow is greater than that of rain. Measurements at Eagle Harbor on Lake Superior have shown that snow is, on average, 6.2 times more efficient at scavenging pesticides from the atmosphere than rain (Carlson et al., 2004). Franz and Eisenreich (1998) reported that snow was an order of magnitude more efficient than rain at scavenging particulate PCBs and PAHs. In the model, particulate scavenging by snow was taken into account by increasing the particulate scavenging efficiency of precipitation by a factor of ten during the four months when average air temperatures were less than zero Celsius (Table 1).

Gas phase scavenging by precipitation. Dissolved wet deposition (J_{dwet}) of organic PBTs was estimated according to Swackhamer and Eisenreich (1991)

$$J_{\text{dwet}} = Q_{\text{pr}} C_a (1 - \Phi) / V / K_{\text{aw}} \quad (9)$$

where K_{aw} is the air-temperature-corrected dimensionless Henry's law constant. Falling rain droplets are assumed to rapidly reach equilibrium through air-water exchange. Franz and Eisenreich (1998) found that the dissolved concentration of PCBs in rain and snow was within a

factor of two in either direction of the concentration in equilibrium with the gas phase, and that gas phase scavenging was relatively unimportant compared to particulate scavenging. No distinction is made between gas phase scavenging of snow and rain in the model. For Hg, gas phase and particulate scavenging by precipitation are not distinguished; a total wet deposition flux of $7.6 \mu\text{g m}^{-2} \text{yr}^{-1}$, the average wet deposition flux measured at Brule River, WI for the period 1995-2004 (NADP, 2005), was used.

Gas deposition. The air water exchange input of organic PBTs by gas deposition (J_{aw}) is estimated as described by Schwarzenbach et al. (2003)

$$J_{aw} = v_{aw}C_a(1 - \Phi)A_o/K_{aw} / V \quad (10)$$

where v_{aw} is the air-water exchange velocity and K_{aw} is adjusted for the monthly water surface temperature given in Table 1. The air-water exchange velocity was estimated from the simplified mass transfer coefficient equations for a two-film model as presented by Galarneau et al. (2000). Monthly average over-water wind speeds at 10-m height for Lake Superior were obtained from Transport Development Center Canada, and are presented in Table 1. The lake surface area available for air-water exchange was reduced by the percentages of ice coverage for each month shown in Table 1.

Use of an annual frequency distribution of one-hour-averaged wind speeds in place of monthly averaged wind speeds was considered to be of relatively small benefit because the overall exchange velocity of these hydrophobic compounds is mainly a function of the air-side transfer velocity, a first-order function of wind speed in the parameterization presented by Galarneau et al. (2000). For example, using the frequency distribution of one-hour averaged wind speeds in place of an annual average wind speed resulted in a 15 % increase in the water-side exchange velocity and no increase in the air-side exchange velocity, which corresponds to increases in the overall exchange velocity of 11 % and 4 % for triCB and tetraBDE, respectively.

Watershed input. Input from the watershed is estimated as shown in Equation 11. Input from the watershed (J_{wa}) is a function of the concentration in the watershed discharge (C_{wa}), the watershed discharge into the lake, and the lake volume.

$$J_{wa} = Q_{wa}C_{wa}/V \quad (11)$$

PBT concentrations in the watershed discharge are not known for PBDEs. For the purpose of the model, the watershed discharge concentration was assumed to be equal to the precipitation concentration (dissolved plus particulate). For Hg, a watershed input of 280 kg yr^{-1} was used (Rolfhus et al., 2003).

Internal processes. Partitioning to particulate matter and DOM in the water column has an important influence on the model outcome for hydrophobic compounds. Only the dissolved fraction is available for air-water exchange, while only the particle-bound fraction is removed by settling. Partitioning to DOM is a particularly important process in Lake Superior because the suspended particulate matter concentration is low and DOM concentration is high compared to many surface waters. The fraction bound to DOM is not available for removal by air-water exchange or by particle settling. Three-phase partitioning as described by Schwarzenbach et al. (2003) was incorporated into the model for organic PBTs.

$$f_w = 1/(1 + r_{sw}K_d + K_{doc}[DOC]) \quad (12)$$

$$f_{doc} = (K_{doc}[DOC])/(1 + r_{sw}K_d + K_{doc}[DOC]) \quad (13)$$

$$f_s = (r_{sw}K_d)/(1 + r_{sw}K_d + K_{doc}[DOC]) \quad (14)$$

$$K_d = f_{oc}K_{oc} \quad (15)$$

where f_w is the fraction dissolved, f_{doc} is the fraction sorbed to DOM, f_s is the fraction sorbed to suspended solids, r_{sw} is the solid-water phase ratio, $r_{sw} = \text{TSS}$ in the water column, K_d is the suspended solids-water partition coefficient, K_{doc} is the DOC-water partition coefficient. Additional symbols are defined in Table 2.

Partitioning in the water column is slightly different for Hg than for organic PBTs. Oxidized mercury (Hg(II)) does partition among dissolved, particulate and colloidal phases as do hydrophobic organic contaminants, but thermodynamic data are not available to describe accurately the partitioning. Partition coefficients reported in the literature for Hg(II) (e.g., Mason and Sullivan, 1997; Rolfhus et al., 2003) are not based on the dissolved phase (Hg^{2+}), but on the total (dissolved plus organic and inorganic complexes) of Hg(II). Only a few measurements of binding constants with natural organic matter have been measured (e.g., Lamborg et al., 2003). Because rate constants for reduction of organically-complexed Hg(II) are not available, the state of the science would seem to ignore the speciation of Hg(II) except for the partitioning between particles and all other phases in the water column. This same approach has been used in most models of Hg cycling to date (e.g., Hudson et al., 1994; Diamond, 1999; Kotnik et al., 2002). For Hg(II), partition coefficients of $10^{5.9} \text{ l kg}^{-1}$ for the water column and $10^{3.5} \text{ l kg}^{-1}$ for the sediments were used based on measurements in Lake Superior (Rolfhus et al., 2003).

Partition coefficients describing partitioning of PCBs and PBDEs to particulate and colloidal organic carbon (K_{oc} and K_{doc}) are estimated from K_{ow} using empirical relationships from Seth et al. (1999) and Burkhard (2000), respectively.

$$K_{oc} = 0.35K_{ow} \quad \pm \text{factor of 2.5} \quad (16)$$

$$K_{doc} = 0.06K_{ow} \quad \pm \text{factor of 20} \quad (17)$$

These relations were selected from the many in the literature because they were based on recent comprehensive and critical reviews of all available measurements. Equation 16 was derived from data for a variety of hydrophobic compounds, while Equation 17 was derived exclusively from partitioning measurements for PCBs. The octanol-water partition coefficient, K_{ow} , was adjusted for the annual mean water temperature of 3.6 °C.

Partitioning between solids and sediment pore water in the sediment surface layer is estimated using Equations 12 and 14, neglecting sorption to DOM in sediment pore water. Sorption to DOM is negligible in the sediment because of the high solids content. The solids-water partition coefficient in the sediment is estimated using Equations 15 and 16 with the fraction organic carbon of the sediment given in Table 2 and K_{ow} adjusted for the average annual water temperature of 3.6 °C.

Parameterization of sediment-water exchange was modeled after Schwarzenbach et al. (2003). Terms not defined below or in previous equations can be found in Table 2.

Sediment mixed layer mass per unit area (m)

$$m = z_{mix}(1-p_s)d_s \quad (18)$$

Diffusive sediment-water exchange velocity (v_{sd})

$$v_{sd} = D_{iw}/t_{bl} \quad (19)$$

where D_{iw} is the diffusivity of the compound in water.

Sediment resuspension exchange velocity (v_{sre})

$$v_{sre} = K_{ds}\mu \quad (20)$$

where K_{ds} is calculated with Equation 15, using f_{ocs} .

Overall sediment-water exchange velocity (v_{sx})

$$v_{sx} = f_w(v_{sd} + v_{sre}) \quad (21)$$

In the model, the reduced organic carbon content in sediment solids compared to suspended solids in the lake (f_{ocs} versus f_{oc}) leads to recycling of PBTs after they are initially

deposited by sedimentation. The burial rate takes into account the further reduction in organic carbon content of the sediment with increasing depth owing to decomposition over time (Equation 31).

The parameters described above were combined into first-order rate constants describing sediment-water exchange, sediment burial, and volatilization to the atmosphere that were incorporated into the analytical solutions to equations 1 and 2.

Transfer rate constants from lake to sediment (K_{11})

Transfer rate constant for particle settling (k_{ps})

$$k_{ps} = f_p v_{ps} A_0 / V \quad (22)$$

Diffusive and resuspension transfer from lake to sediment (k_{sxl})

$$k_{sxl} = v_{sx} A_0 / V \quad (23)$$

Transfer rate constants from sediment to lake (K_{12})

Diffusive and resuspension transfer from sediment to lake (k_{sl})

$$k_{sl} = k_{sxl} / f_w / K_{ds} \quad (24)$$

Transfer rate constants from sediment to lake (K_{22})

Diffusive and resuspension transfer from sediment to lake (k_{sxs})

$$k_{sxs} = v_{sx} / m / f_s / K_{ds} \quad (25)$$

Transfer rate constants from lake to sediment (K_{21})

Overall transfer rate constant from lake to sediment (k_{ls})

$$k_{ls} = k_{psls} + k_{sxls} \quad (26)$$

Transfer rate constant for particle settling from lake to sediment (k_{psls})

$$k_{psls} = v_{ps} f_s / m \quad (27)$$

Diffusive and resuspension transfer rate constant from lake to sediment (k_{sxls})

$$k_{sxls} = v_{sx} / m \quad (28)$$

Loss rate constants (Schwarzenbach et al., 2003)

$$k_{vol} = v_{aw} f_w A_0 / V \quad (29)$$

$$k_{out} = Q_{out} / V \quad (30)$$

$$k_b = \beta v_{ps} r_{sw} / m \quad (31)$$

where β is the ratio of organic carbon content at the bottom of the sediment mixed layer to the organic carbon content of the sediment in the mixed layer.

Contaminant information

Physical-chemical properties. The physical-chemical properties selected for use in the model are given in Table 3. Beyer et al. (2002) compiled available measurements of properties for PCBs and derived a set of internally consistent properties, taking into account reported measurement uncertainties. Wania and Dugani (2003) used the same approach to derive a set of internally consistent properties for PBDEs. The selected values are plotted in Figure 2. The octanol-water partitioning behavior of PCBs and PBDEs does not differ greatly, but PBDEs are much less volatile than PCBs, resulting in PBDEs favoring water over air and octanol over air relative to PCBs. Air-water partition coefficients estimated from bond contributions as described in Schwarzenbach et al. (2003) are reasonably close to the values from Wania and Dugani derived from measured properties (Fig. 2). Properties for decaBDE 209 were not reported and were extrapolated from the properties of lesser-brominated congeners, as shown in Figure 2.

Enthalpies of phase transfer are needed to adjust the partitioning coefficients to temperatures other than 25 °C. Enthalpies of phase transfer were included in the properties database for PCBs derived by Beyer et al. (2002). Measured enthalpies for octanol-air partitioning of PBDEs were available from Harner and Shoeib (2002), and enthalpies for air-water partitioning were reported by Cetin et al. (2005). Measured enthalpies for octanol-water partitioning of PBDEs were not available, so typical values for PCBs were assumed, as indicated in Table 3. Enthalpies for Hg transformations were reported in or were calculated from literature data (Table 3).

Degradation rates. Chemical and biological degradation rates may have an overriding influence on environmental fate for some compounds in lakes, while for other compounds degradation rates may be insignificant. Prior estimates of mass balances for PCBs in Lake Superior and in Siskiwit Lake (on Isle Royale) have considered degradation rates of PCBs to be negligible (Swackhamer et al., 1988; Jeremiason et al., 1994). Relatively rapid photodecomposition of PBDEs has been documented in laboratory studies; however, degradation rates have been shown to be matrix-dependent and the degradation products include lesser-brominated congeners and other brominated compounds (Hua et al., 2003; Bezares-Cruz et al., 2004; Eriksson et al., 2004; Soderstrom et al., 2004). Many degradation steps would be required to completely mineralize PBDEs. Stepwise reductive dehalogenation of PBDEs to lesser-brominated congeners has been observed in the laboratory in the presence of zero-valent iron and at slower rates in the presence of environmentally-relevant sulfide

Table 3: Physical-chemical properties of PBTs at 25 °C used in the model.

Congeners:	--	--	33	52	101	180	28	47	99	153	209
Compound	Hg(0)	Hg(II)	triCB ^C	tetraCB ^C	pentaCB ^C	heptaCB ^C	triBDE	tetraBDE	pentaBDE	hexaBDE	decaBDE
log K _{oa}			7.98	8.14	9.00	10.23	9.41 ^A	10.44 ^A	11.26 ^A	11.89 ^A	15.21
ΔH _{oa} (KJ mol ⁻¹)			-75.62	-86	-79.77	-82.41	-84 ^A	-92 ^A	-100 ^A	-108 ^A	-141
log K _{ow}		5.9 ^F , 3.5 ^F	5.71	5.82	6.35	7.19	5.80 ^B	6.39 ^B	6.76 ^B	7.08 ^B	8.71
ΔH _{ow} (KJ mol ⁻¹)			-20	-37.56	-8.81	-8.27	-20	-20	-20	-20	-20
log K _{aw}	-0.43 ^D	-13.8 ^G	-1.81	-1.82	-1.97	-2.05	-3.11 ^B	-3.35 ^B	-3.67 ^B	-3.86 ^B	-5.02
ΔH _{aw} (KJ mol ⁻¹)	29.7 ^E		55.62	48.44	70.96	74.14	59.2 ^H	58.4 ^H	70.8 ^H	62.1 ^H	63.2 ^H
Molecular mass (g mol ⁻¹)	200.6		258	292	326	395	407	486	565	643	959
Le Bas molar volume (cm ³ mol ⁻¹)			247	268	289	331	266	289	312	335	429

^ALog K_{oa} and ΔH_{oa} for PBDEs, Harner & Shoeib (2002) (properties for decaBDE were extrapolated)

^BLog K_{ow}, ΔH_{ow}, log K_{aw}, PBDEs, Wania & Dugani (2003) (The ΔH_{ow} values are typical for PCBs. PBDE data were not available. Properties for decaBDE were extrapolated)

^CPCB properties; Beyer et al. (2002)

^D(Malcolm and Keeler, 2002)

^ECalculated from literature data (Hudson et al. 1994; Poissant et al. 2000; Kotnik et al. 2002; Malcolm and Keeler 2002; Lamborg et al. 2003)

^FDistribution coefficients (l kg⁻¹) for water column and sediments calculated from data of Rolffhus et al. (2003)

^GValue for HgO from Seigneur et al. (2004)

^HCetin et al. (2005)

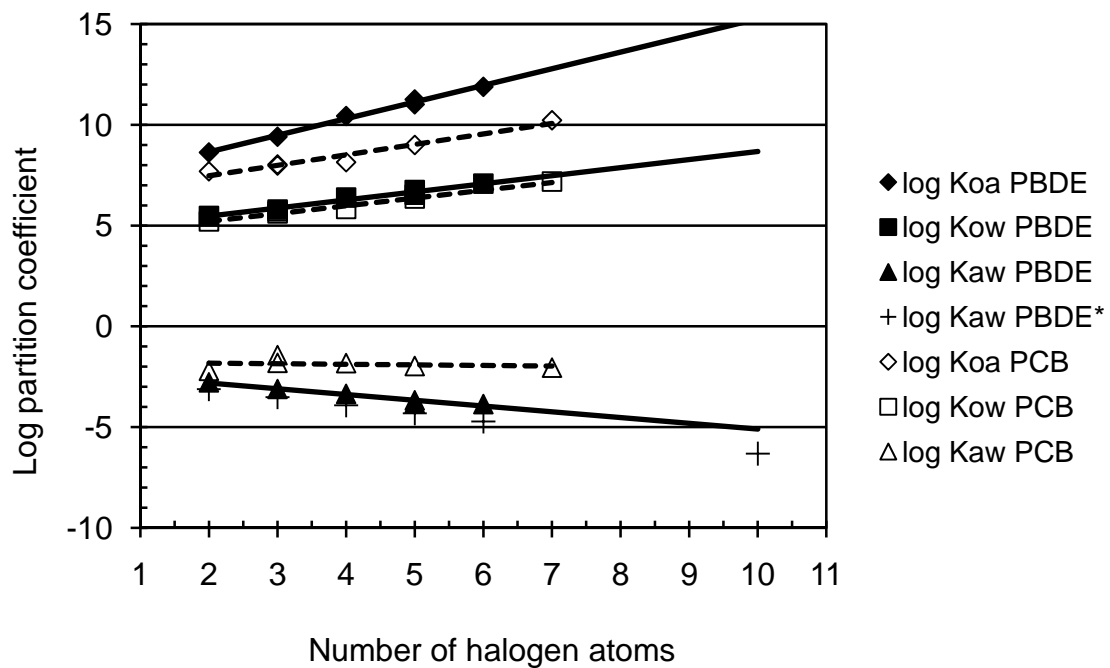


Figure 2: Log partitioning coefficients for PCBs (Beyer et al., 2002) and PBDEs (Wania and Dugani, 2003). *Air-water partition coefficients for PBDEs estimated from bond contributions as described in Schwarzenbach et al. (2003)

minerals. After 14 days in the presence of zero-valent iron, iron sulfide, and sodium sulfide, 94, 2, and 33 %, respectively, of BDE 209 was transformed to lesser brominated congeners (Keum and Li, 2005). If degradation of PBDEs does occur at appreciable rates in the environment, it may serve to transform decaBDE 209 to lesser-brominated congeners that are more susceptible to bioaccumulation and long-range transport in the atmosphere. Actual degradation rates in the environment would likely be slower than in laboratory studies as a result of sorption to organic materials and lower temperatures. Empirical evidence exists to indicate that PBDEs are sufficiently persistent in the environment to be transported to remote areas, such as the Arctic, and to accumulate in biota (Hites, 2004).

Measured overall degradation rates of PBDEs in the environment are not available at this time, but degradation rates estimated from chemical structure and properties using software packages have been published. Gouin et al. (2004) reviewed chemical degradation rate estimation methods and concluded that the popular software package EPIWIN predicts more rapid degradation than what is observed in the environment for highly persistent chemicals such as PCBs. The EPIWIN software package uses the BIOWIN program to estimate aerobic, aqueous biodegradation rates. The USEPA PBT Profiler uses the BIOWIN survey module to estimate ultimate degradation rates in water and sediments (USEPA, 2004b). The aerobic degradation rate given by BIOWIN is reduced by a factor of nine in PBT Profiler to account for assumed anaerobic conditions in sediments. Degradation by hydroxyl radical in the air is not included in our model because this would influence the gas-phase concentration, which is a user input to the model. The set of high and low half-lives from estimates reported in the literature were used to calculate high and low degradation rate constants for use in the model (Table 4). Degradation mechanisms other than biological degradation were not explicitly included in the estimates, however the high and low rate estimates cover a wide enough range to account for some contribution from other mechanisms.

For mercury, several transformations are well known. Although the methylation and demethylation reactions are of prime importance in regulating the concentration of methyl mercury, the species that is bioaccumulated and responsible for fish advisories, these reactions generally are slow and involve only a small fraction of the total mercury. For instance, in Lake Superior methyl mercury accounts for only about 1.4 % of the total mercury in the lake (Rolfhus et al., 2003). For our stated goal of modeling total mercury inventories in the lake, it is not necessary to include the methylation and demethylation reactions. Similarly, although some oxidation of Hg(0) to Hg(II) may occur, the rate is generally considered to be very low except in the presence of high chloride concentrations (Amyot et al., 1997a; Kotnik et al., 2002; Vette et al., 2002) and this reaction was also omitted from our model. The major reaction of interest is the reduction of Hg(II) to Hg(0) as this rate controls the ratio of Hg(II) to Hg(0) in a lake and thus the availability of Hg(0) for volatilization. Reduction of Hg(II) was modeled as having three components: an abiotic photoreduction mediated by UV light (Amyot et al., 1997b) with an

Table 4: Degradation rate constants (s^{-1}) used in the model, selected from high and low estimates reported in the literature.

Congeners:	28	101	180	28	47	99	153	209
Compound:	triCB	pentaCB	heptaCB	triBDE	tetraBDE	pentaBDE	hexaBDE	decaBDE
water, high	2.7E-07	2.7E-07	6.7E-08	9.6E-08	2.7E-08	2.7E-08	2.2E-08	2.2E-08
water, low	9.6E-09	3.1E-09	1.8E-09	3.2E-08	3.2E-09	3.2E-09	2.7E-09	2.7E-09
sediment, high	6.7E-08	6.7E-08	1.7E-08	9.6E-09	6.7E-09	6.7E-09	6.7E-09	6.7E-09
sediment, low	1.8E-09	1.8E-09	5.7E-10	3.2E-09	2.5E-09	2.5E-09	2.5E-09	2.5E-09

Sources of estimated half-lives:

- Gouin et al. (2004) (EPIWIN); PCB water and sediment
- Cousins & Palm (2003) (EPIWIN); PCB and PBDE water and sediment
- USEPA PBT profiler (USEPA, 2004b); PCB and PBDE water and sediment
- Wania & Daly (2002), PCB water and sediment
- Gouin & Harner (2003) (BIOWIN); PBDE water and sediment
- Palm et al. (2002) (EPIWIN); PBDE water and sediment

Half lives reported in the literature were used to calculate rate constants as follows: Degradation rate constant (s^{-1}) = $0.693 / (\text{half life, hr}) / (3600 \text{ s hr}^{-1}) / 2$. The factor of two is to account for lower temperatures, 25 °C half-lives increase by approximately a factor of two at 10 °C (Wania and Daly 2002).

attenuation of 0.9 m^{-1} (S. Green, Michigan Technological University, Houghton, MI, pers. comm.), a biological component largely confined to the epilimnion (Mason et al., 1993; Vette et al., 2002), and an abiotic reaction occurring in the dark throughout the water column. The first two reactions were modeled similarly using expressions from Chapra (1997) for light dependent reactions; maximum reaction rate constants of $8 \% \text{ d}^{-1}$ and $2 \% \text{ d}^{-1}$ were used based on studies in Lake Michigan (Vette et al., 2002). A rate constant of $0.15 \% \text{ d}^{-1}$ for the dark reaction yielded a ratio of Hg(II) to Hg(0) of 3.5, similar to that observed in Lake Superior (Rolfhus et al., 2003).

Results and Discussion

Comparison of model predictions to measurements

An attempt was made to verify the model for each compound class by comparison with literature data. For validation of the PCB modeling, we use data reported by Jeremiason et al. (1994). These authors constructed a mass balance for PCBs in Lake Superior based on measurements of PCB concentrations in air, water, sediment, and precipitation. Decreasing PCB concentrations in the water column between 1980 and 1992 indicated a loss of 26,500 kg had occurred, compared to an accumulation in the sediments of 4,900 kg since 1930 based on dated sediment cores. The authors concluded that sediment burial could not account for the loss of PCBs from the lake, and that volatilization likely accounted for the difference. A detailed mass balance was constructed for the year 1986 in which volatilization was used to close the mass balance.

The same initial atmospheric, aqueous, and sediment concentrations used by Jeremiason et al. were used as initial concentrations in our model, and the model output is compared to the detailed 1986 mass balance results in Figure 3. The mass balance estimate of Jeremiason et al. was for the total PCB concentration, while the model requires input of properties that vary over a wide range for specific congeners. To represent the behavior of total PCBs in the model, the properties of the four tetra CBs listed in the properties compilation of Beyer et al. (2002) were averaged to represent the aggregate or average physical-chemical properties of all (total) PCBs. TetraCB was selected as the representative homolog group by calculating the concentration-weighted mean PCB homolog from the congener-specific concentrations reported by Baker and Eisenreich (1990) for Lake Superior water in August of 1986. In both the mass balance and in the model, the watershed input was estimated by assuming that the PCB concentration in watershed discharge was equal to the concentration in precipitation.

The model prediction of total PCB inputs is nearly identical to the estimate of Jeremiason et al. within a factor of 0.99, and estimates of pathways for PCB entry to the lake agree with the Jeremiason et al. estimates within factors of 0.79 to 1.2. The total loss rate of PCBs from Lake Superior predicted by the model was higher than the estimate of Jeremiason et al. by a factor of 2.5. This higher loss rate resulted in a reduction of dissolved plus DOM-bound

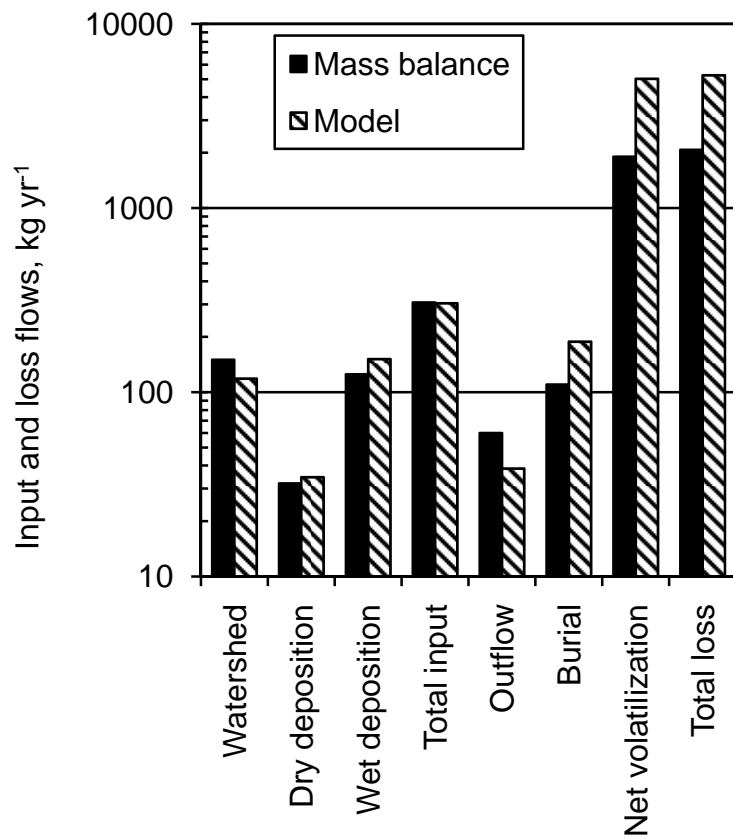


Figure 3: Comparison of model results to a 1986 empirical mass balance for PCBs in Lake Superior by Jeremiason et al. (1994).

PCB concentration from 0.80 to 0.38 ng l⁻¹ over one year. In comparison, the rate of decrease reported by Jeremiason et al., based on concentration measurements from 1980 to 1992, would have reduced PCB concentration from 0.8 to 0.65 ng l⁻¹ over one year. The model predictions of loss flows by outflow, burial, and volatilization differed from the estimates of Jeremiason et al. by factors of 0.64, 1.7, and 2.6, respectively (Fig. 3). Discrepancies in burial rates may be caused by uncertainties in partitioning coefficients, settling velocities, and other sedimentation parameters. In particular, a higher value of K_{doc} would decrease loss rates to both sediment burial and volatilization, bringing model loss rates closer to those of Jeremiason et al. This is discussed further in the section on sensitivity of model results to input variables. Overestimation of air-water exchange may be caused by atmospheric stability over the lake during the spring and summer months, which would inhibit air-water exchange (Honrath et al., 1997) and is not taken into account in the model.

A quantitative model validation for PBDEs in Lake Superior is difficult because few measurements are available, and there are no measurements of aqueous concentration in the lake. Historical PBDE atmospheric concentrations are not available prior to 1998 (Hites, 2004). However, a comparison can be made using measured PBDE atmospheric (Strandberg et al., 2001) and sediment (Song et al., 2004) concentrations. PBDE commercial production began in the 1970s and PBDE concentrations were first detected in archived Great Lakes bird eggs from the 1970s (Hites, 2004). Therefore, PBDE concentrations in air, sediments and water were set equal to zero for 1970, and then concentrations in air were modeled as increasing linearly to the values reported by Strandberg et al. for 2000. The model was run for thirty years and the predicted sediment accumulation rates for PBDEs 47 and 99 were compared with those measured by Song et al. In the comparison, the total PBDE fluxes reported by Song et al. were divided by three because PBDEs 47 and 99 each accounted for approximately one third of the total PBDE (not including 209) value reported by Song et al. (2004); results of the comparison are shown in Figure 4.

The predicted fluxes are within the range of accumulation rates reported by Song et al. for four sediment cores, but the modeled accumulation rates appear to increase at a greater rate over time than the sediment core measurements, leading to a higher value at the surface. The dissolved plus DOM-bound and particle-bound water column concentrations at the end of the model period were 0.014 and 0.001 ng l⁻¹ of BDE 47 and 0.009 and 0.001 ng l⁻¹ of BDE 99. Few measurements of surface water PBDE concentrations are available for comparison. Surface water total PBDE concentration for Lake Michigan was measured as 0.031 ng l⁻¹ in 1997 and 0.158 ng l⁻¹ in 1999 (reported in, Hale et al., 2003). In the San Francisco Estuary, concentrations of 0.016 to 0.180 ng l⁻¹ for BDE 47 and 0.012 to 0.091 ng l⁻¹ for BDE 99 were reported, with concentrations in some samples falling below reporting limits (Oros et al., 2005). The modeled water column concentrations are near the low end of the reported measurements for North

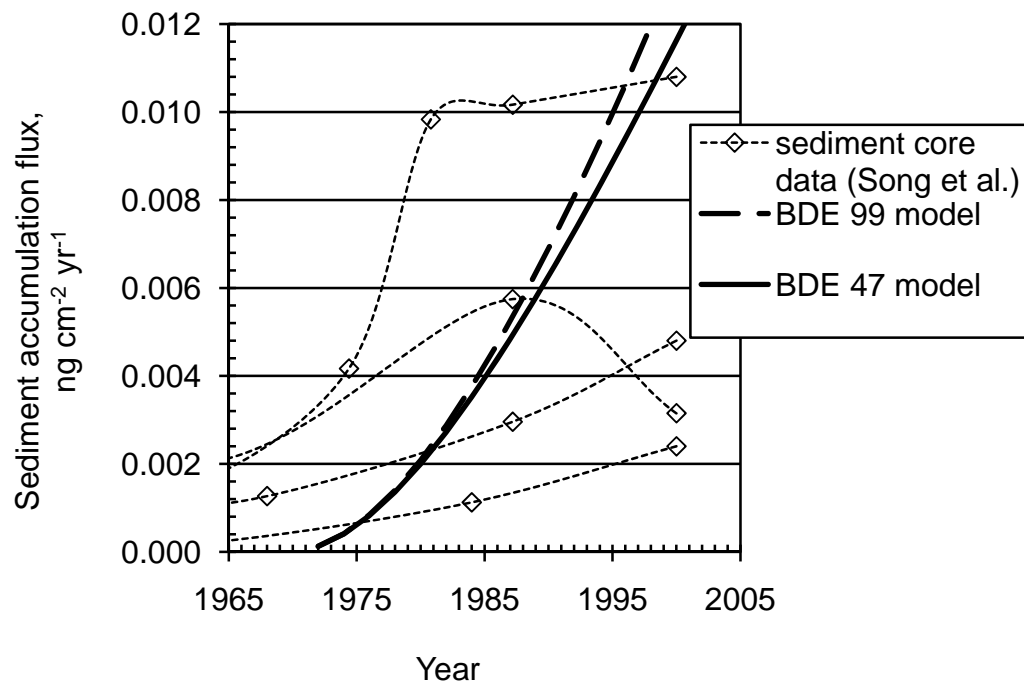


Figure 4: Comparison of the model sediment accumulation flux for BDEs 47 and 99 to sediment accumulation fluxes from sediment core measurements. Atmospheric concentrations were assumed to start at zero in 1970 and increase linearly to values measured by Strandberg et al. (2001) in 2000. Sediment accumulation fluxes measured from four dated sediment cores are plotted for comparison (Song et al., 2004). Sediment accumulation fluxes reported by Song et al. were divided by three because BDEs 47 and 99 each accounted for approximately one third of the Σ PBDE (not including 209) reported by Song et al.

American surface waters, which is consistent with the greater distance of Lake Superior from population centers in comparison to Lake Michigan or the San Francisco Estuary.

While there is reasonable agreement between modeled PBDE concentrations and the few available measurements, there is uncertainty in many of the parameters in the model. The modeled PBDE loading rate is sensitive to uncertainties in particulate scavenging efficiencies by precipitation and to the dry deposition velocity. Chemical degradation was not included in this simulation, and could act to reduce the rate of PBDE accumulation. Uncertainties in partitioning coefficients, settling velocities, and other sedimentation variables also influence the sediment accumulation rate estimate, as mentioned above for PCBs.

The influence of uncertainty in the particulate dry deposition velocity (v_d) was evaluated by re-calculating the above comparisons of model results to measurements with v_d increased by a factor of three (0.006 m s^{-1} versus 0.002 m s^{-1}). This increase resulted in a v_d at the low end of the range proposed by Franz et al. (1998), which may be appropriate for a region that is removed from populated areas. In the model scenario for PCBs, a three-fold increase in v_d reduced the net loss of PCBs by 1% over the simulation period. In the model scenario for PBDEs, a three-fold increase in v_d increased the net storage of BDE 47 by 20% and of BDE 99 by 37%. With the three-fold increase in v_d the dry deposition input flow became equal to the wet deposition input flow for PBDEs, given the selected value of the particle scavenging efficiency of precipitation and rates of precipitation over Lake Superior. The sensitivity of the PCB mass balance to v_d is small because of the overriding influence of air-water exchange, but the PBDE mass balance is much more sensitive to v_d .

For mercury, validation of the model was attempted by simulating the historical increase in mercury loadings to the lake. Regional studies have shown that atmospheric deposition of mercury increased by a factor of 3.7 over a 130 year period (2.2 % per year, Engstrom et al., 1994). A model simulation was run in which both atmospheric deposition and tributary inputs increased at 2.2 \% yr^{-1} from pre-industrial rates of $3.7 \text{ } \mu\text{g m}^{-2} \text{ yr}^{-1}$ (Engstrom et al., 1994) and 83 kg yr^{-1} (calculated as the present day rate divided by 3.7), respectively. This simulation ignores the significant inputs of Hg to Lake Superior from mining activities (Kerfoot et al., 2002); sediment and pore water profiles indicate that Hg from mine residues in the lake is mobilized and biologically available (Matty and Long, 1995; Urban et al., 2006b).

Concentrations predicted at the end of the 130-year simulation are not sensitive to the initial concentrations. The predicted sediment-phase concentration is sensitive to the partition coefficient (K_D) used for the sediments. Use of $10^{3.5} \text{ l kg}^{-1}$, the value reported for total mercury in Lake Superior sediments (Rolfhus et al., 2003) causes a large underestimation of mercury concentrations in the sediments (7 ng g^{-1} predicted vs. $26\text{-}209 \text{ ng g}^{-1}$ observed) and a corresponding overestimation of the total mercury concentration in the water (183 pg l^{-1} predicted vs. 88 pg l^{-1} measured). It is likely that some of the mercury measured in the pore waters is in reduced form and that the partition coefficient for Hg(II) is, therefore, underestimated. Use of the same partition coefficient for the sediments and water column ($10^{5.9} \text{ l kg}^{-1}$) leads to predicted sediment-phase concentration of 42 ng g^{-1} and a predicted

concentration of 93 pg l⁻¹ in the water column, values in better agreement with those measured. On the other hand, use of this K_D value leads to a prediction that 58 % of Hg losses occur by volatilization with 41 % buried. The mass balance presented by Rolfhus et al. (2003) indicates that 70 % of losses are via volatilization and 27 % are through burial. This distribution of losses can be achieved with a sediment partition coefficient of 10^{4.5} l kg⁻¹, but then sediment-phase concentrations (28 ng g⁻¹) are underestimated and water column concentrations are again overestimated (129 pg l⁻¹). The model accurately predicts the distribution between Hg(0) and Hg(II) (the calibration was performed for a 15-year simulation).

Distributions (gas, particulate, dissolved, sorbed). The predicted partitioning of specific congeners of PCBs and PBDEs between particulate and gas phases varies seasonally with air temperature. Tri-CB is almost entirely in the gas phase throughout the year. On the other extreme, deca-BDE is entirely bound to particles throughout the year. Compounds with intermediate levels of halogenation span a wide range of partitioning behavior and show substantial seasonal variation. Arnout et al. (2004) found reasonable agreement between the partitioning model of Harner and Shoeib (2002) given in Equation 5, and particle-gas partitioning of PBDEs measured over the Baltic Sea.

Partitioning in the water column is a more complex process than partitioning between particulate- and gas-phases because of a third compartment in the water column, colloidal organic matter, and large ranges of uncertainty in partition coefficients. The predicted partitioning behavior in the water column is shown in Figure 5. The PBDEs have a greater tendency to partition to the particulate and colloidal organic matter than the PCBs, but the difference is not as great as in the case of particle-gas partitioning. Mercury(II) is predicted to partition to particles more strongly than a penta-CB, and it has the additional complication of being reduced to Hg(0); the ratio of Hg(II) to Hg(0) is controlled largely by the rate of reduction but is also influenced by the rates of loss of Hg(II) (burial) and Hg(0) (volatilization) from the water column.

Seth et al. (1999) and Burkhard (2000) reported large ranges of uncertainty in their correlations of K_{oc} and K_{doc} to K_{ow} given in Equations 16 and 17; these are shown by the dashed lines in Figure 6. The data from which the correlations were derived showed a great deal of variability, probably as a result of variation in the sorptive properties of suspended particles and natural organic matter in addition to measurement uncertainties. It may take weeks or months for suspended particles to reach sorptive equilibrium with large, hydrophobic compounds; the long time required may account for some of the variability in partitioning measurements (Seth et al., 1999). Measurements of PCB partitioning to suspended particles in Lake Superior exhibited scatter over more than an order of magnitude and no relation with K_{ow} (Baker et al., 1991). The range of K_{ow} and the range of scatter for K_{oc} values for PCBs measured by Baker et al. are indicated by the shaded box in Figure 6. Biomagnification in phytoplankton and zooplankton was suggested as a mechanism of enrichment in settling particles rather than equilibrium partitioning (Baker et al., 1991).

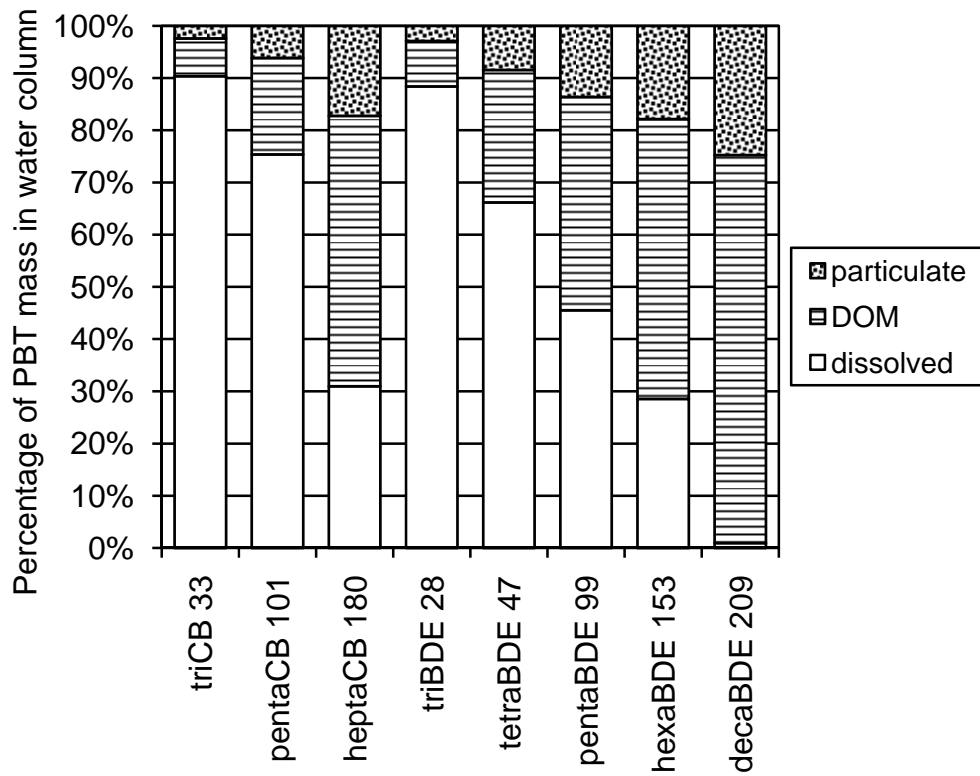


Figure 5: Water column partitioning between the dissolved, particle-bound, and dissolved organic matter (DOM)-bound predicted by the model.

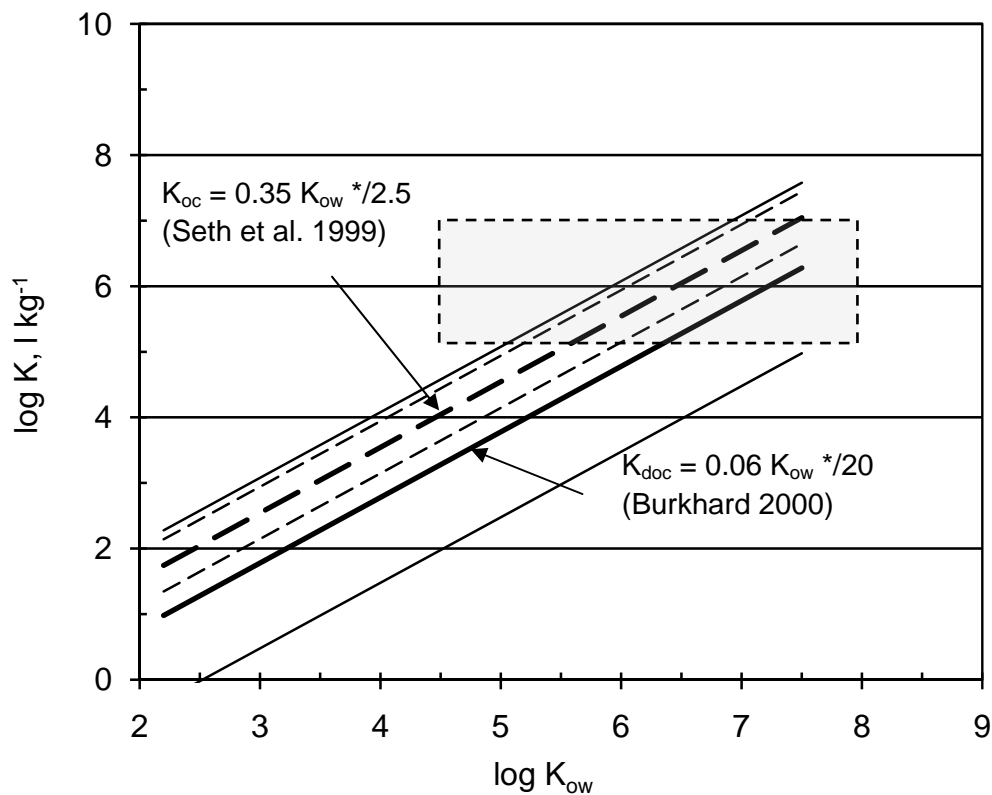


Figure 6: Correlations used to estimate partitioning to dissolved organic carbon and particulate organic carbon in the model. Uncertainty factors are given with the equations and represented by the narrow lines. The shaded box indicates the range of K_{oc} values measured by Baker et al. (1991) for PCBs in Lake Superior.

On the other hand, Baker et al. did find a strong dependence of the recycling ratio (defined as the sedimentation flux divided by the burial flux) at the sediment-water interface on hydrophobicity. The recycling ratio is plotted as a function of K_{ow} in Figure 7 for measurements by Baker et al. (1991) and predictions of the model. In the present model, the recycling ratio is determined largely by the ratio of fraction organic carbon in settling particles (0.2, Table 2) to the fraction organic carbon of solids in the sediment mixed layer (0.03, Table 2), which results in a recycling ratio of approximately six (0.2/0.03) for all compounds, as shown in Figure 7. The modeled recycling ratio is also weakly influenced by the diffusive sediment-water exchange. In contrast, Baker et al.'s measured values range from 50 for highly chlorinated PCBs to 4000 for less chlorinated congeners. The actual mechanism of recycling of organic PBTs at the sediment-water interface is not well understood. An equilibrium partitioning model may not fully describe the mechanisms of enrichment on settling particles and recycling at the sediment-water interface. However, the combined effect of the discrepancies between model and observation shown in Figures 6 and 7 result in a model that does predict increasingly efficient removal by burial in the sediments with increasing hydrophobicity, as is observed in measurements from sediment cores. Therefore, even if the details of the mechanisms by which enrichment and burial occur are not fully described by the model, the model results do reflect the increasing importance of sediment burial as a loss mechanism with increasing hydrophobicity.

Relative importance of input and loss processes. Prediction of the relative importance of input and loss processes is a useful outcome of a mass balance model in that monitoring and research efforts can be directed toward the most influential processes. Model predictions of the relative magnitudes of input and loss processes shown in Figures 8 and 9 are applicable to the chosen scenario but do provide a useful comparison of the contaminant classes. The scenario to which Figures 8 and 9 apply involves a gaseous concentration of 10 pg m^{-3} as input for each PCB and PBDE congener, initial aqueous and sediment-phase concentrations of zero, and a model run time of 15 years. For Hg, watershed and atmospheric deposition rates (rather than the atmospheric concentration) were fixed at current rates (Rolfhus et al., 2003). This scenario was selected rather than steady-state conditions, because some compounds require such a long time to reach steady state that it would never occur. For the first comparison (Figures 8 and 9) air-water exchange processes of deposition and volatilization are considered separately.

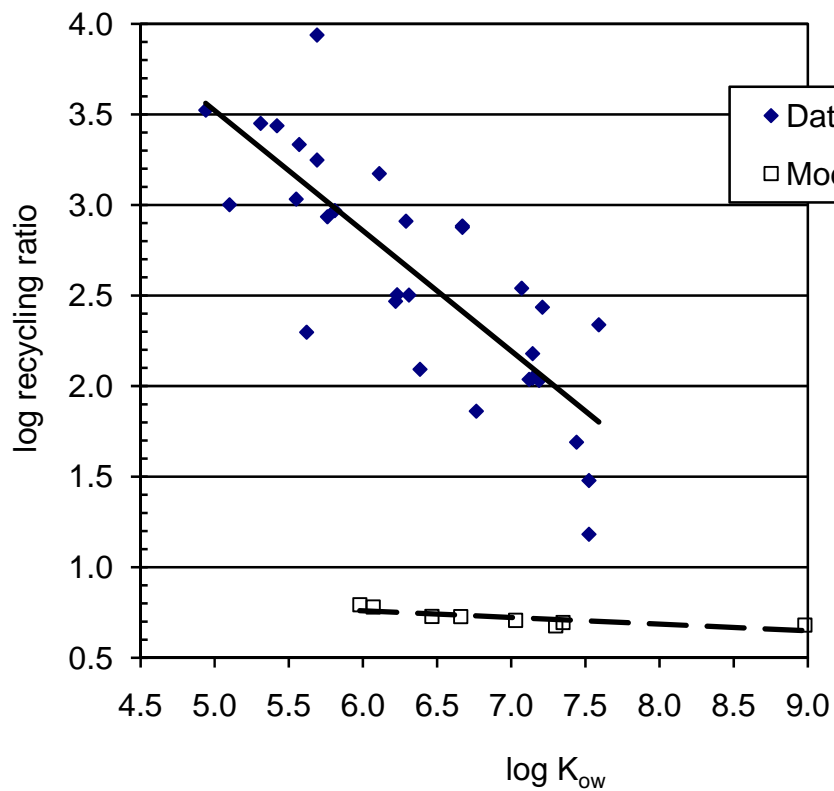


Figure 7: Recycling ratio for PCBs in Lake Superior as a function of $\log K_{ow}$, calculated from data in Baker et al. (1991). Recycling ratio is the settling flux divided by the sediment accumulation flux. Recycling ratios from the model are shown for comparison. The model was run with zero initial concentrations for 15 years with atmospheric concentrations of $10 \text{ } \mu\text{g m}^{-3}$ for each congener.

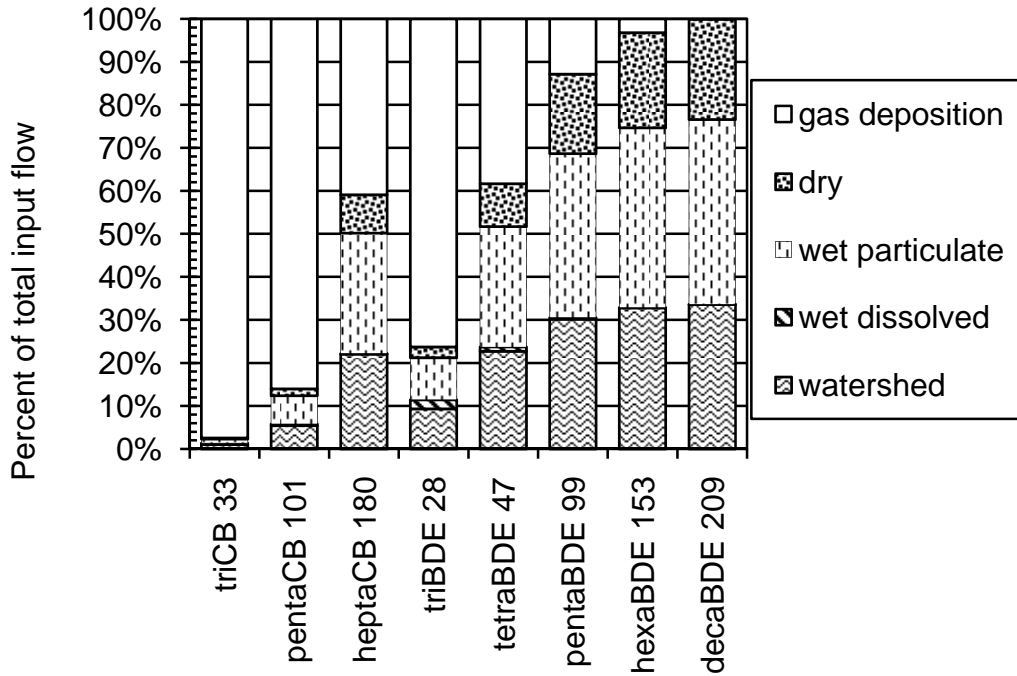


Figure 8: Relative importance of input processes to Lake Superior for PCBs and PBDEs. The model was run with zero initial concentrations for 15 years with atmospheric concentrations of 10 pg m^{-3} for each congener.

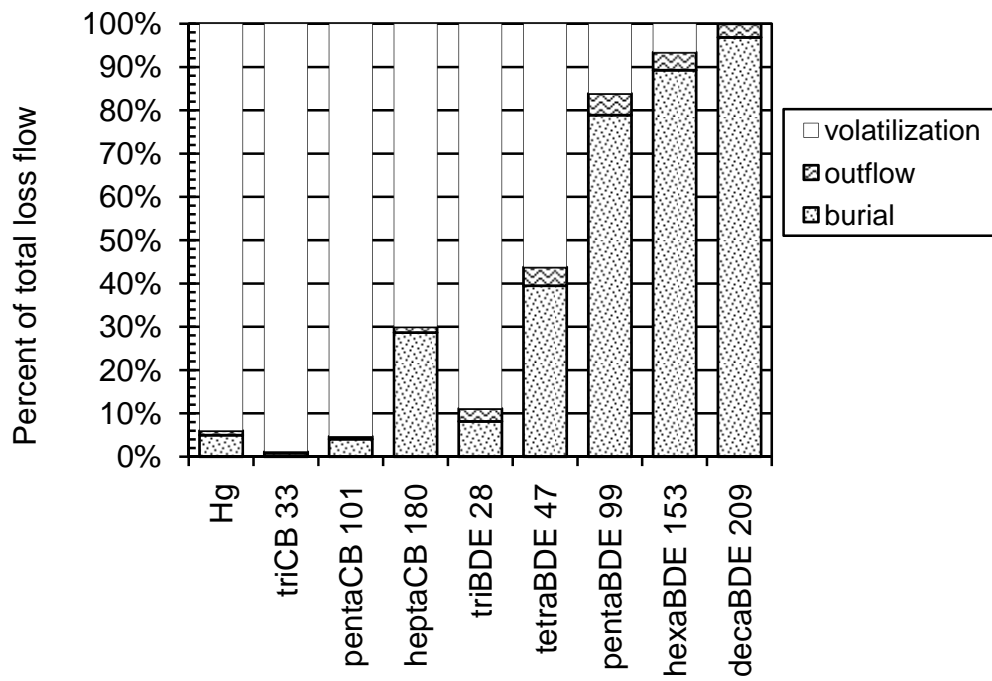


Figure 9: Relative importance of loss processes to Lake Superior for Hg, PCBs and PBDEs. The model was run with zero initial concentrations for 15 years with atmospheric concentrations of 10 pg m^{-3} for each congener.

Mercury and PCBs are much more susceptible to air-water exchange than are PBDEs (Figs. 8 and 9). This difference in behavior amongst compound classes results directly from differences in Henry's law constants (Table 3); the dimensionless Henry's law constants for elemental mercury (0.37, Malcolm and Keeler, 2002) and PCBs (~0.01) are one to four orders of magnitude higher than those of the PBDEs. Thus if fugacities of Hg(0) or PCBs are much higher in air than in water, gas deposition may be a major mechanism for entry into the lake, and conversely when the fugacity in air is low relative to water, volatilization may be the dominant mechanism for loss from the lake. For all but the tri- and tetra- BDEs, gas exchange is unlikely to be a major pathway. It should be noted that the volatility of elemental mercury (i.e., high Henry's law constant) is tempered by the rate of reduction of Hg(II); hence the relative importance of burial and volatilization as loss mechanisms as well as the concentration of Hg in the water column in different lakes will be regulated largely by the factors that regulate the reduction of Hg(II) and re-oxidation of Hg(0) (depth of photic zone, biological productivity, chloride concentration).

Loss by burial is likely to be more important for PBDEs than for either mercury or PCBs (Figure 9). It is important to realize that this difference is driven by differences in Henry's law constants, not by differences in the strength of partitioning between water and solids. Values of $\log K_{ow}$ are similar for PCBs (from 5.7 – 7.2) and PBDEs (from 5.8 – 8.7). The distribution coefficient for Hg(II) ($10^{5.9} \text{ l kg}^{-1}$) (Malcolm and Keeler, 2002) when normalized for the fraction organic matter in suspended solids yields a value for $\log K_{oc}$ (6.2) comparable to those of the more chlorinated PCBs and less brominated DEs. Thus the tendency of all compound classes to sorb to particles or to be taken up by organisms is roughly comparable. It is because volatilization competes with sorption and particle burial for mercury and PCBs but not for PBDEs that burial is more important for PBDEs than for the other compound classes.

The focus on relative magnitudes of pathways above can obscure differences in absolute magnitudes of pathways (Fig. 10). In comparing actual magnitudes of processes, it is not meaningful to depict gas deposition and volatilization separately as they are components of the single process of air-water exchange. Figure 10 also compares compound classes under the same scenario described above rather than predictions of current process rates. Note that the mercury flows in Figure 10 are divided by ten to put them on the same scale as the organic PBTs. The uncertainties or lack of data concerning historical atmospheric concentrations (PCBs, PBDEs) or input rates (Hg) compromise the utility of predicting current process rates. Under the scenario represented in Figure 10, mercury, tri- and penta-CB are near steady state, while the other PBTs have not yet reached steady state. Because the scenario used initial concentrations of zero, the fugacity in the air was initially higher than that of the water and net deposition occurred for compounds susceptible to air-water exchange. As steady state was approached, these compounds transitioned to net volatilization, and volatilization grew to balance the flow into the lake from wet and dry deposition that was not accounted for by burial and outflow. In Figure 10, PBDE 28 is the only PBDE that has transitioned to net volatilization. For triCB, the flows are small because there is little wet and dry deposition and no fugacity difference

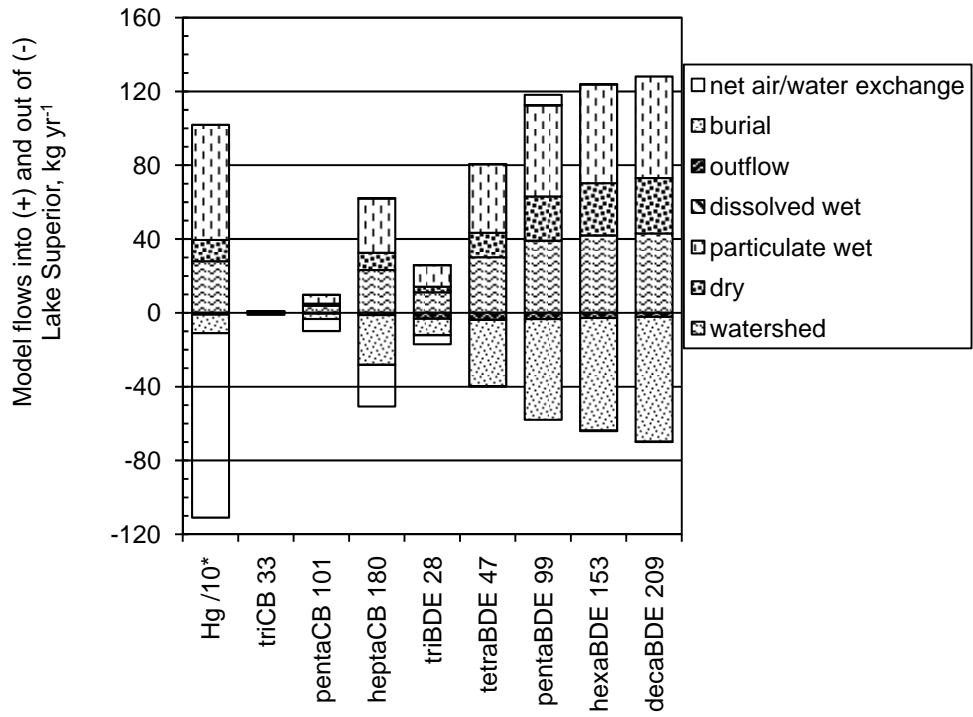


Figure 10: Flows into and out of Lake Superior. The model was run with zero initial concentrations for 15 years with atmospheric concentrations of 10 pg m^{-3} for each congener. *Mercury flows were divided by 10 to match the scale of the organic PBTs.

between air and water to drive air-water exchange. The larger flows for the more hydrophobic compounds result from higher loadings through wet and dry particulate deposition and higher steady-state concentrations that lead to higher loss flows through burial and outflow. Similarly, for mercury the high flows result from high atmospheric concentrations and efficient scavenging of Hg(II) by particles and precipitation.

Time to steady state. The time to steady state indicates how quickly concentrations of PBTs may decrease if loading rates are decreased in the future. A compound with a long time to steady state tends to accumulate relatively high concentrations in the system, and concentrations respond slowly to changes in loading because of the low loss rate from the system. The time to steady state is calculated using Equations 3 and 4, which are functions only of the overall loss rate constants, not of input rates.

The majority of PCB mass in air and water consists of tri- through penta-CBs, which are predicted to have times to steady state of a few to several years, as shown in Figure 11. Mercury is predicted to have a time to steady state that is similar to a mid-range PCB. Therefore, one would expect that if atmospheric loadings decreased over a period of years, concentrations of Hg and PCBs in the lake system would, with only a slight lag, follow the trend in atmospheric loading. Since production and use of PCBs ceased in the late 1970s, decreasing PCB concentrations have been observed in Lake Superior water and sediment. Aqueous concentrations of PCBs exhibited decreases as early as 1980 and have decreased at a rate of 20 % per year (Jeremiason et al., 1994), and dated sediment cores indicate a maximum PCB concentration around 1986 (Song et al., 2004). The response of PCB concentrations to reduced loading within a few to several years is consistent with the times to steady state for PCBs shown in Figure 11. Although the large sediment reservoir slows lake recovery, the dynamic exchange between sediments and water column (Baker et al., 1991) still allows the system to respond to decreased inputs within a decade. Similarly, if atmospheric emissions of mercury are reduced through regulations and if these reductions in emissions result in a subsequent decrease in inputs to the lake (cf. Cohen et al., 2004; Seigneur et al., 2004), a relatively rapid decrease in inventories in the water column should be observed. Although sediments are an important locus for mercury methylation, the model predicts that total mercury concentrations in the surface sediments also would decline rapidly in response to decreased atmospheric deposition. The model predicts times to steady state for PBDEs on the order of several decades. Thus PBDE concentrations are unlikely to respond as quickly to reductions in loading as do concentrations of PCBs and Hg.

Similarities in physical chemical properties between PBDEs and toxaphene suggest that PBDEs may persist in Lake Superior longer than PCBs, assuming that degradation rates in the lake are not significantly higher for PBDEs. Toxaphene is a persistent organochlorine pesticide that was used in North America through the 1980s and is present in Lake Superior at concentrations higher than in the other Laurentian Great Lakes (Perlinger et al., 2004).

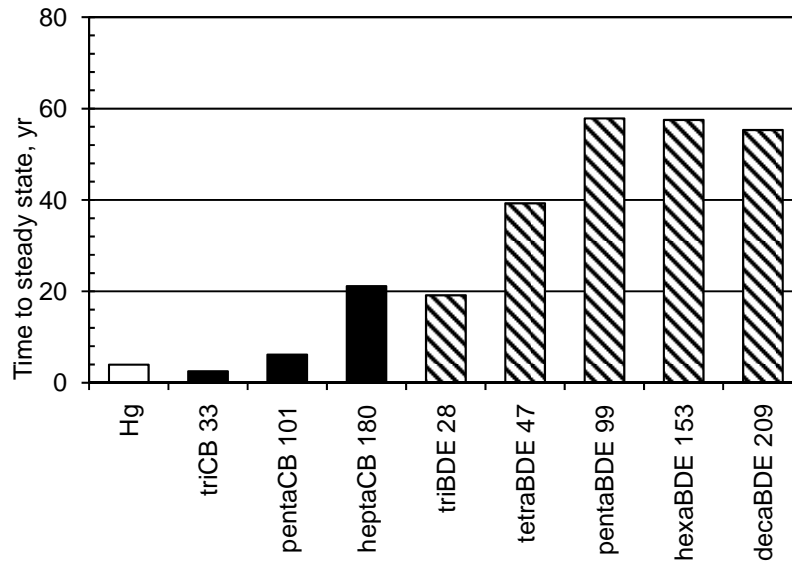


Figure 11: Time to steady state of Hg, PCBs, and PBDEs in the Lake Superior system, neglecting degradation. The model was run with zero initial concentrations for 15 years with atmospheric concentrations of 10 pg m^{-3} for each congener.

Swackhamer et al. (1999) noted that although toxaphene compounds span a range of K_{ow} values that is similar to that of PCBs, toxaphene compounds have lower Henry's law constants, reducing the rate of volatilization from the lake. The low water temperatures of Lake Superior further reduce Henry's law constant. As does toxaphene, PBDEs have K_{ow} values in the range of PCBs, but have substantially lower Henry's law constants (K_{aw} values), as shown in Figure 2.

Sensitivity of model results to uncertainty in inputs. Considerable uncertainty exists in a number of the model input variables. The sensitivity of the model results to uncertainty in the input variables must be considered before any conclusions can be reached. Time to steady state is a single number that characterizes the behavior of a particular compound in the system, therefore it was selected as a model output with which to evaluate the sensitivity of the model to uncertainty in the input values. To evaluate model sensitivity, a value of time to steady state was calculated after multiplying or dividing the input value by an uncertainty factor. The uncertainty factor was taken from the literature where available, or subjectively estimated if no published value was available.

Results of the sensitivity analysis are given in Figures 12 through 14. Note the log scale, in contrast to the linear scale of Figure 11. The results of the nominal model input values are indicated by the large diamond symbols and are the same values as are shown in Figure 11. In spite of the large number of uncertain variables influencing the sediment burial rate, the model results were relatively insensitive to many of them. Among the sedimentation variables, time to steady state was most sensitive to the dissolved organic carbon – water partition coefficient (K_{doc}) and the sediment mixed layer depth. Unfortunately, partitioning to DOM is not well quantified. We opted to use the relationship recommended by Burkhard (2000) throughout the manuscript because it is a well-documented estimate. In the comparison made in Figure 3, the relationship determining partitioning to dissolved organic carbon recommended by Burkhard of $K_{doc} = 0.06 K_{ow}$ is used. Partitioning to DOM has an important influence on all of the model loss rates because the fraction of a chemical bound to DOM is not available for air-water exchange or for removal by sedimentation. A higher value of K_{doc} would decrease the modeled rates of both burial and air-water exchange, bringing the modeled loss rates closer to the estimates of Jeremiason et al. (Figure 3). A sediment mixed layer depth of one centimeter was selected based on the sediment core data from Song et al. (2004), which indicated a mixed layer depth of one centimeter or less. On the other hand, Baker et al. (1991) suggested a mixed layer depth of two centimeters. Even this relatively small variation influences the model results because of the large sorptive capacity of the sediment.

The main variables influencing air-water exchange are the overall air-water exchange velocity (v_{aw}) and the temperature-corrected dimensionless Henry's law constant ($K_{aw}(T_w)$). The model results were sensitive to these variables except for the higher-brominated PBDEs, for which air-water exchange is of little importance. The uncertainty of air-water exchange

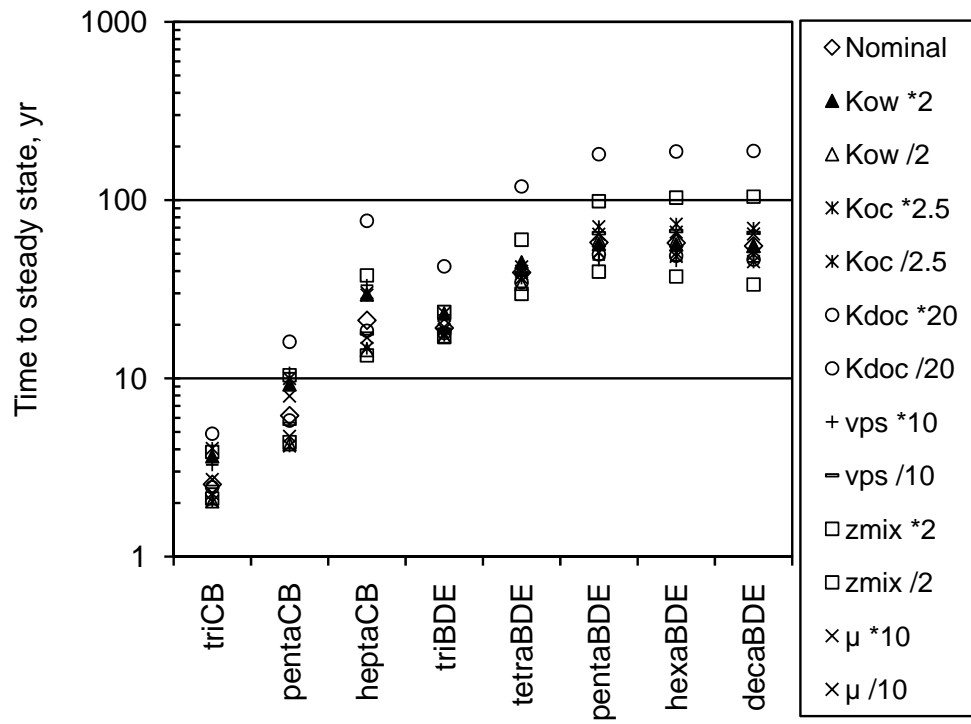


Figure 12: Influence of sedimentation variables on time to steady state, neglecting degradation. The model was run with zero initial concentrations for 15 years with atmospheric concentrations of 10 pg m^{-3} for each congener.

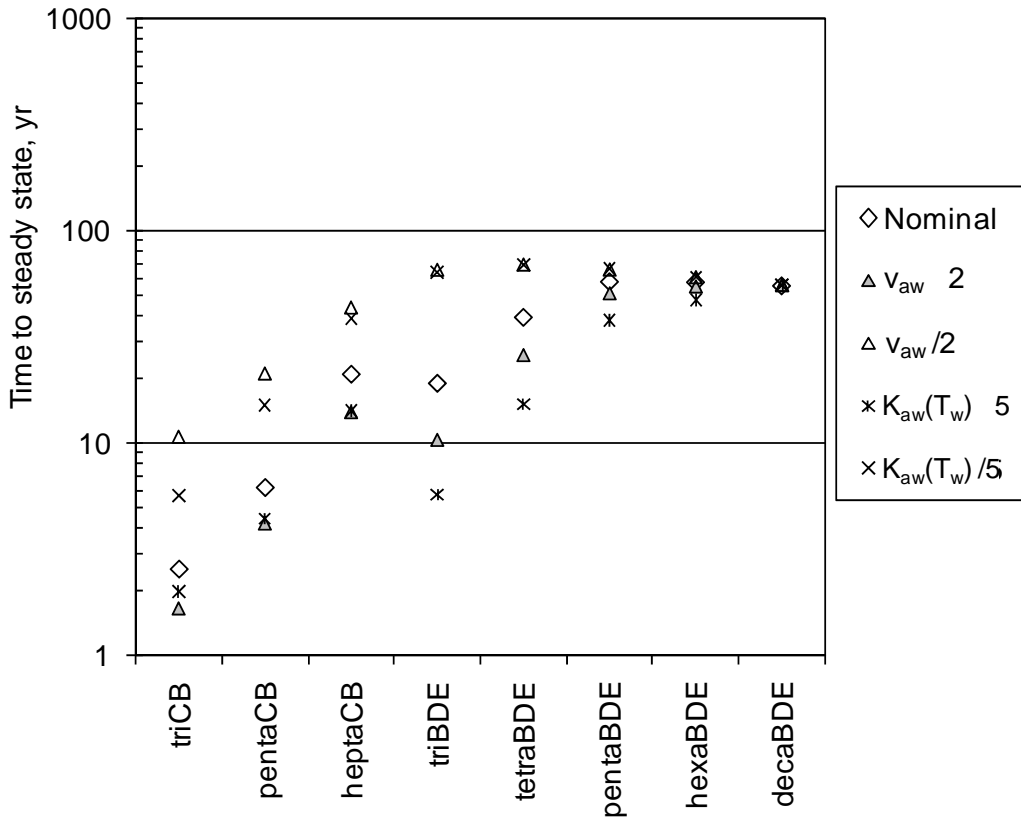


Figure 13: Influence of air-water exchange variables on time to steady state, neglecting degradation. The model was run with zero initial concentrations for 15 years with atmospheric concentrations of 10 pg m^{-3} for each congener.

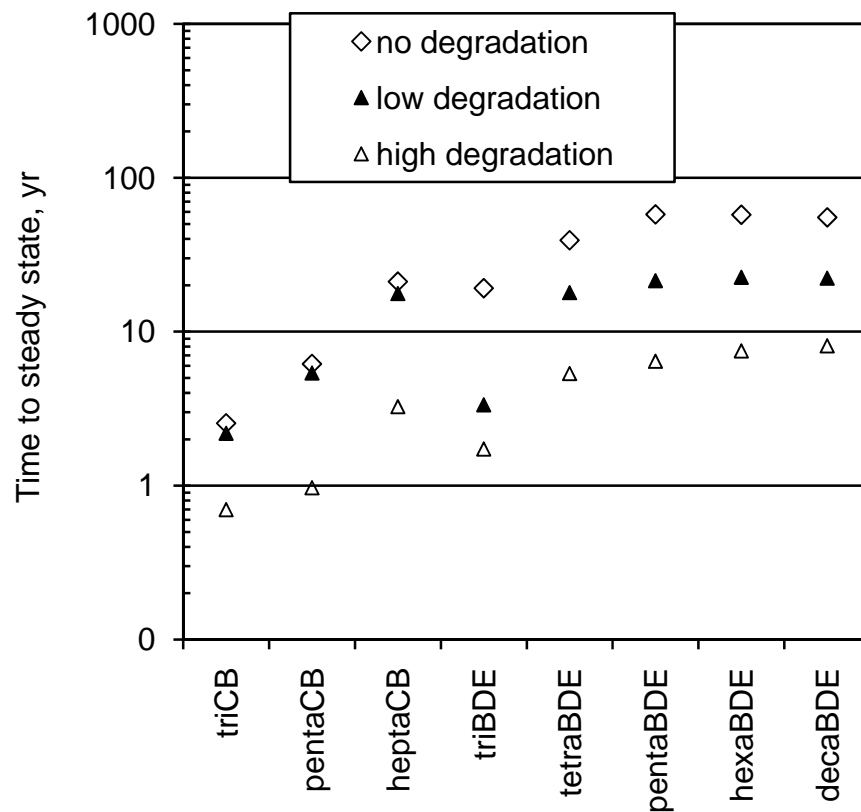


Figure 14: Influence of high and low estimates of degradation rates on the time to steady state. The model was run with zero initial concentrations for 15 years with atmospheric concentrations of 10 pg m^{-3} for each congener.

estimated using the model employed here can be estimated when direct measurements become available.

Degradation rates for PBDEs have not been measured in the environment, but estimated values were collected from the literature, as discussed previously. The model results are perhaps most sensitive to uncertainty in the degradation rates. Most mass balance estimates have assumed that degradation of PCBs in Lake Superior occurs at a negligible rate. The high range of degradation rates result in times to steady state of less than one year, which appears to be unrealistically low. The low estimates of PCB degradation rates have little influence on the model outcome, which is consistent with the assumption that PCBs degrade at negligible rates in water and sediment. Degradation rates have less influence on PCBs than on PBDEs because the loss rate of PCBs from the system by volatilization is high compared to the low estimate of degradation rates. The PBDE results show greater sensitivity even to the low estimates of degradation rates because the loss rates from the system are lower for PBDEs than for PCBs. It remains to be seen whether the estimated degradation rates for PBDEs will be observed in the environment where sorption and low temperatures may retard degradation.

Significant uncertainties exist in the model inputs, but higher times to steady state are predicted for PBDEs than for PCBs under most of the scenarios shown in Figures 12 through 14. The prediction of greater persistence of PBDEs in Lake Superior than PCBs is primarily a result of the physical chemical properties of the compounds; the lesser volatility of PBDEs reduces the rate of loss by volatilization, which is a relatively rapid loss process for PCBs. The uncertainty that seems most capable of changing the model outcome is if PBDEs in fact degrade at substantial rates in water and sediment.

Summary

A mass-balance model for Lake Superior was applied to polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), and mercury to determine the major routes of entry and the major mechanisms of loss from this ecosystem as well as the time required for each contaminant class to approach steady state. The model indicates that mercury behaves similarly to a moderately-chlorinated PCB, with air-water exchange being a relatively rapid input and loss process. Wet deposition rates were about three times greater than dry deposition rates for PBDEs. Gas deposition was an important process for tri- and tetra-BDEs (BDEs 28 and 47), but not for higher-brominated BDEs. Sediment burial was the dominant loss mechanism for most of the PBDE congeners while volatilization was still significant for tri- and tetra-BDEs. Because volatilization is a relatively rapid loss process for both mercury and the most abundant PCBs (tri- through penta-), the model predicts that similar times (from 2 - 10 yr) are required for the compounds to approach steady state in the lake. The model predicts that if inputs of Hg(II) to the lake decrease in the future then concentrations of mercury in the lake will decrease at a rate similar to the historical decline in PCB concentrations following the ban on production and most uses in the U.S. In contrast, PBDEs are likely to respond more slowly if atmospheric

concentrations are reduced in the future because loss by volatilization is a much slower process for PBDEs, leading to lesser overall loss rates for PBDEs in comparison to PCBs and mercury. Uncertainties in the chemical degradation rates and partitioning constants of PBDEs are the largest source of uncertainty in the modeled times to steady-state for this class of chemicals. The modeled organic PBT loading rates are sensitive to uncertainties in scavenging efficiencies by rain and snow, watershed runoff concentrations, and uncertainties in air-water exchange such as the effect of atmospheric stability.

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