



Project Summary

Physico-Chemical Model of Toxic Substances in the Great Lakes

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A physico-chemical model of the fate of toxic substances in the Great Lakes is constructed from mass balance principles and incorporates principal mechanisms of particulate sorption-desorption, sediment-water and atmosphere-water interactions, and chemical and biochemical decay. Calibration of the toxic model is through comparison to plutonium-239 data collected in the 1970's using a 23-year time variable calculation and indicates that in general, the sediments are interactive with the water column in the Great Lakes through resuspension and/or horizontal transport. Fifty percent response times of ^{239}Pu following a cessation of load extend beyond 10 years with sediment resuspension.

The calibrated model was applied to polychlorinated biphenyl (PCB) using a high and low estimate of contemporary external load and with and without volatilization. The results of the application using a 20-year calculation indicate that a load level ranging from 640 to 1390 kg/yr with volatilization (at an exchange rate of 0.1 m/d) appears to be representative of observed surface sediment data for the open lake waters. Fifty percent response times for PCB following cessation of load and including volatilization varied from less than 5 years to 10-20 years for the other lakes without volatilization. Comparison of these response times to decline of concentrations of PCB in Lake Michigan indicates that at least for that lake volatilization is occurring at an exchange rate of about 0.1 m/d.

Calculation using a solids-dependent partition coefficient for PCB indicate that the total and dissolved PCB concen-

tration in the water column and sediment PCB concentration are affected to less than an order of magnitude. Interstitial PCB concentration however increases by about two orders of magnitude over the case with a solids-independent partition coefficient. Higher exposure concentrations to benthic organisms may then result with a potential route of PCBs to the top predators in the food chain.

Calibration of the model to data on benzo(a) pyrene confirms that on a lake-wide scale the principal external source in the atmosphere and for the larger lakes such as Michigan the response time of the lake to external loads is about 6-10 years while for Lake Erie response time is about 2 years.

Application of the model is cadmium in the lakes, using a solids-dependent partition coefficient, indicates that the lakes do not reach equilibrium over a 100-year period. For constant partitioning, cadmium concentrations reach steady state in about 10-25 years. An estimate of the preceding 50-year average cadmium input ranges from 200-600 g Cd/km²-yr for the upper lakes to 2000-10,000 g Cd/km²-yr for Lake Erie. Calculated high concentrations of cadmium in interstitial water (e.g. 10 $\mu\text{g}/\ell$) indicate the importance of measuring interstitial cadmium concentrations.

This Project Summary was developed by EPA's Environmental Research Laboratory, Duluth, MN, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

There is an intense contemporary interest in the impact of toxic substances on legitimate water uses in the Great Lakes. Chemicals such as the PCBs and mirex in Lakes Michigan and Ontario, have resulted in the curtailment of recreational fishing activities. Furthermore, there is a growing concern for the effect of the presence of potentially toxic chemicals on the public health of the Great Lakes basin population. Because of these concerns, a variety of questions are raised regarding the possible recovery times of the Great Lakes following the reduction or elimination of external inputs. In addition, interest in the fate of new chemicals that may be discharged to the lakes indicates a need to develop a modeling framework that can provide a basis for projecting the fate of such chemicals in the water and sediment of Great Lakes.

This report presents the results of the development and calibration of a physico-chemical model for the Great Lakes. The report begins with the basic theory of the model, the associated model equations and useful simplifications of the model. A steady state version of the model is then applied to a two-dimensional representation of Saginaw Bay PCB distribution. Plutonium-239 is used as a calibrating variable for the Great Lakes time variable model. Further application is then made to the PCBs in the Lake system and the importance of solids dependent partition coefficient and resulting sediment diffusion is then explored. Finally, application of the model is also made to benzo(a) pyrene and cadmium in the Great Lakes.

Theory

Suspended Solids Model

Since many chemicals, such as PCBs, sorb to suspended particulate matter, the first step in the development of the overall model is the mass balance of suspended solids. In this work, a single class of solids is considered and is intended to incorporate inorganic solids and organic particulates. The solids are considered at steady state in the water column and sediment. The model does not directly include horizontal transport of the bed sediment. At steady state, the water column solids for a completely mixed lake is given by

$$m = \frac{W_{Ma}}{q + w_n} \quad (1)$$

where m is solids concentration (mg/ℓ), W_{Ma} is the areal loading rate of solids ($\text{g}/\text{m}^2\text{-yr}$), q is the ratio of lake flow $Q(\text{m}^3/\text{s})$ to volume $V(\text{m}^3)$ (m/yr), and w_n is the net loss of solids from the water column (m/yr) given by

$$w_n = \frac{w_a w_s}{w_{rs} + w_s} \quad (2)$$

where w_a is the settling velocity (m/yr), w_{rs} is the resuspension velocity (cm/yr) which parametrizes sediment/water interactions, and w_s is the net effective sedimentation velocity (m/yr), given by

$$w_s = \frac{w_n M}{\rho_s (1 - \Phi)} \quad (3)$$

for ρ_s as the density of the solids (g/cm^3) and Φ the porosity of the sediment. All of the above relationships apply in principle to a multi-dimensional model where additional terms for dispersion and advection must be included. The model incorporates these terms.

Toxic Substances Model

The theoretical construct for the physical-chemical fate of a toxic substance in the Great Lakes includes the following features:

1. sorption-desorption mechanism of the chemical with the suspended particulates in the water column and sediment,
2. loss of the chemical due to mechanisms such as biodegradation, volatilization, chemical and biochemical reactions, and photolysis,
3. transport of the toxicant due to advective flow transport, dispersion and mixing,
4. settling and resuspension of particulates and diffusive exchange between sediment and water column, and
5. direct inclusion of external inputs that may be subject to environmental control.

Although the computational framework is multi-dimensional, the basic equations can be readily seen for a single completely mixed lake, where the mass balance for the total toxicant is given by

$$V \frac{dc_T}{dt} = W_T - Q c_T - w_a f_p c_T + w_{rs} f_{ps} c_{Ts} + K_L A (f_{ds} c_{Ts} / \Phi_s - f_d c_T / \Phi) - K_V c_T + k_l A (c_g / H_e - f_d c_T / \Phi) \quad (4)$$

This equation is derived on the assumption that all sorption-desorption kinetics are "fast," linear and reversible. In Equation (4), the subscript "s" indicates the sediment, the total toxicant is c_T ($\mu\text{g}/\ell$ (bulk)) given by

$$c_T = c_p + c_d \quad (5)$$

where c_d is the porosity corrected dissolved concentration ($\mu\text{g}/\ell$ (bulk)) and c_p is the particulate form of the toxicant ($\mu\text{g}/\ell$ (bulk)) and is given by

$$c_p = r m \quad (6)$$

for r as the toxicant sorbed to the solids ($\mu\text{g}/\text{g}(d)$; $\text{g}(d)$ = grams dry weight).

Also in Equation (4), W_T is the external input of the chemical (kg/yr), A is the surface (sediment) area (km^2), K_L is the sediment water diffusive transfer coefficient (m/d), k_l is the volatilization transfer coef-

ficient (m/d), c_g is the toxicant concentration in the atmosphere overlying the water (ng/m^3), H_e is the Henry's constant, i.e., the partitioning between the gaseous and aqueous phase, K is an overall loss rate (d^{-1}) given by

$$K = K_d f_d + K_p f_p \quad (7)$$

and f_d and f_p are the fraction of the total in the dissolved and particulate forms respectively and are determined from

$$f_d = (1 - \pi' M)^{-1} \quad (8a)$$

$$f_p = \frac{\pi' M}{1 + \pi' M} \quad (8b)$$

In these latter equations, π' is the porosity corrected partition coefficient (ℓ/kg) given by

$$\pi' = r / c_d \quad (9)$$

The equation for the total toxicant in the surface sediment segment is

$$V_s \frac{dc_{Ts}}{dt} = w_a A f_p c_T - w_{rs} A f_{ps} c_{Ts} + K_L A (f_d c_T / \Phi - f_{ds} c_{Ts} / \Phi_s) - w_s A c_{Ts} - K_s V_s c_{Ts} \quad (10)$$

where

$$K_s = K_{ds} f_{ds} + K_{ps} f_{ps} \quad (11)$$

Similar equations are written for sediment segments below the surface sediment layer.

The report explores these equations and also the simplifying case of the steady state condition where basic relationships between external chemical loading and resulting chemical concentrations in the lake can be derived as a basis for allocation of chemical loading.

Model Calibration

The time scale of the model is considered to be long term, i.e., year to year. The physical segmentation of the model considers the Lakes to be completely mixed with the exception of Lake Erie (Figure 1). This Lake is divided into three basins; west, central, and east to reflect varying regions of solids deposition and water column solids concentrations. In addition, Saginaw Bay is included as a separate embayment from Lake Huron to represent a more local region interacting with a large lake. Three sediment segments of 2 cm each in depth are included under each of the lakes or region of lake. This results in a model with eight water column segments and 24 sediment segments totaling 32 segments.

The calibration procedure was as follows: (a) From a review of data on fine grain solids loading to the Lakes, net depositional flux of solids, and water column suspended solids concentrations, Equation (1) was used to provide first estimates of w_n , the net loss

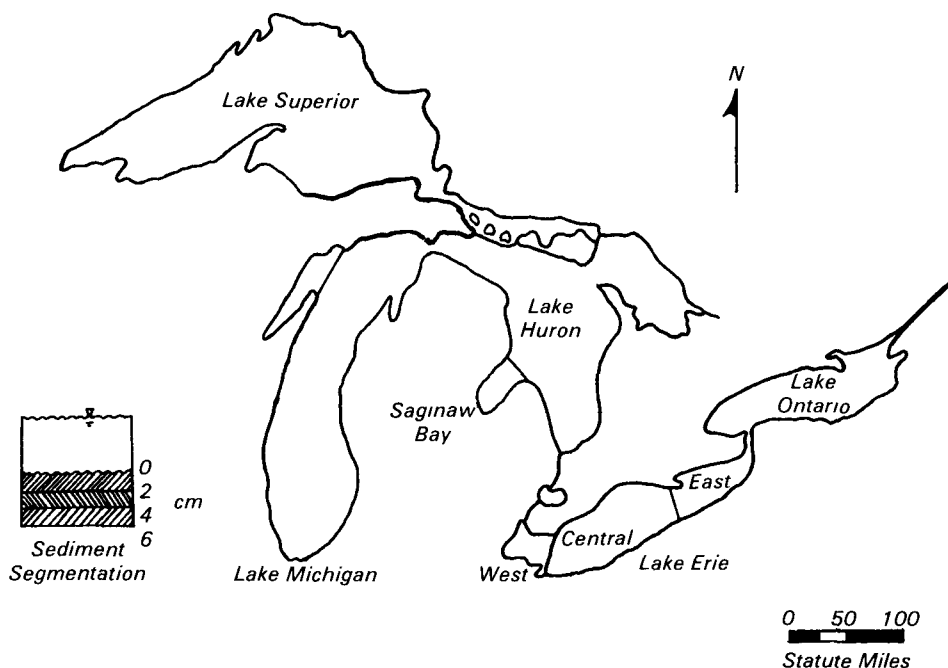


Figure 1. Great Lakes and Saginaw Bay and sediment segmentation used in model.

rate of solids from the water column. From assigned porosity in the surface sediment layer, particle density and net flux of solids to the sediment, the net sedimentation rate is computed from Equation (3); (b) With the estimate of the net loss of solids, w_n , a range of particle settling velocities were assigned and the resuspension velocity necessary to maintain the solids balance was computed from Equation (2) as

$$w_{rs} = w_s \left(\frac{w_a}{w_n} - 1 \right) \quad (12)$$

(c) Since there are an infinite number of combinations of settling and resuspension velocities that will result in the same solids balance, the time variable plutonium-239 model was numerically solved to provide the tracer calibration. All decay mechanisms and sediment diffusion were assumed to be zero and a sensitivity analysis using three values of plutonium solids partitioning was conducted.

Figure 2 shows the results of the plutonium calibration under different conditions on particulate settling (for $w_a = w_{net}$, resuspension is zero). The calibration is not favorable for the case of no resuspension and is improved by including the resuspension parameter. No significant difference was noted between 2.5 and 5 m/d. Additional sensitivity analysis discussed in the full report supported the conclusion that some interaction of the sediment with the water column is occurring in the Lake system.

PCB Mass Balance

The range of contemporary (i.e., approximately within the past 5-10 years) external total PCB loads to the Great Lakes was estimated at a high and low load level. The estimated ranges of PCB loads incorporate three components: the atmospheric input, tributary loads and direct point source inputs from municipal and industrial sources. Rather than attempt to describe each of these components in detail and recognizing the wide variability in some of the reported data, a range of concentrations or loading rates was applied. The computations were then made at two load levels (high and low) and with and without volatilization. A constant partition coefficient of 100,000 ℓ/kg was used throughout and a volatilization exchange coefficient of 0.1 m/d was estimated.

The results of the four conditions (high and low load levels, with and without volatilization) after running the preceding calibrated model with zero initial conditions for 20 years to approximate steady state, are shown in Figures 3 and 4. Comparison to the limited water column and sediment data indicates that the upper load level without volatilization overestimates the data in the open lake waters. The effect of volatilization of PCB as indicated in Figure 3 is to reduce the steady state water column concentration by 50-70% except for Lake Erie where the reduction due to volatilization is about 30%. This reflects the higher fraction of PCB in the

particulate phase for Lake Erie due to the higher solids concentration. The inclusion of volatilization also has a significant effect on the time to reach equilibrium. For example, for Lake Michigan at the upper level of loading without volatilization, the time to equilibrium in the water column is greater than 20 years in contrast to less than 10 years when volatilization is included.

Plutonium and PCB Response Times

Simulations were made of the response of the Great Lakes system to an instantaneous elimination of the external load using the preceding model. For plutonium, the results indicated that the time to reduce the concentration by 50% is less than 5 years when resuspension is not included but increase by about an order of magnitude under resuspension is incorporated. For PCB, the effect of volatilization in the 50% response time (including resuspension) was investigated and, as an example, it was calculated that for Lake Michigan the response time varies from 15-20 years without volatilization to 1-2 years with volatilization.

Effect of Solids Dependent Partitioning and Sediment Diffusion

An evaluation was made of the sensitivity of the model to a hypothesized dependence of the partition coefficient on the solids concentration. For plutonium, the results showed that settling velocities of 2.5-5.0 m/d with or without solids-dependent partitioning provide an approximately equal representation of the observed data. For PCB, a compilation of published data indicated that the PCB partition coefficient did exhibit a marked dependence on the solids concentration at levels of less than 1 ng/ℓ to sediment solids concentrations.

Two cases of solids dependent partitioning of PCBs were therefore examined:

- a) $\pi = 73,990 M^{-435}$, and
- b) $\pi = 25,120 M^{-1.2}$ for solids $< 10 \text{ ng}/\ell$
 $\pi = 73,900 M^{-435}$ for solids $\geq 10 \text{ ng}/\ell$.

The calculations indicated that the total and dissolved water PCB concentrations are not sensitive in a significant way to the assumption on partitioning. The principal effect on the dissolved component is in Western Lake Erie where the dissolved concentration increases by a factor of three. In all other lakes, however, for practical purposes, the total and dissolved concentrations are unaffected by the partitioning assumption including the case of a constant solids-independent partition coefficient. The sur-

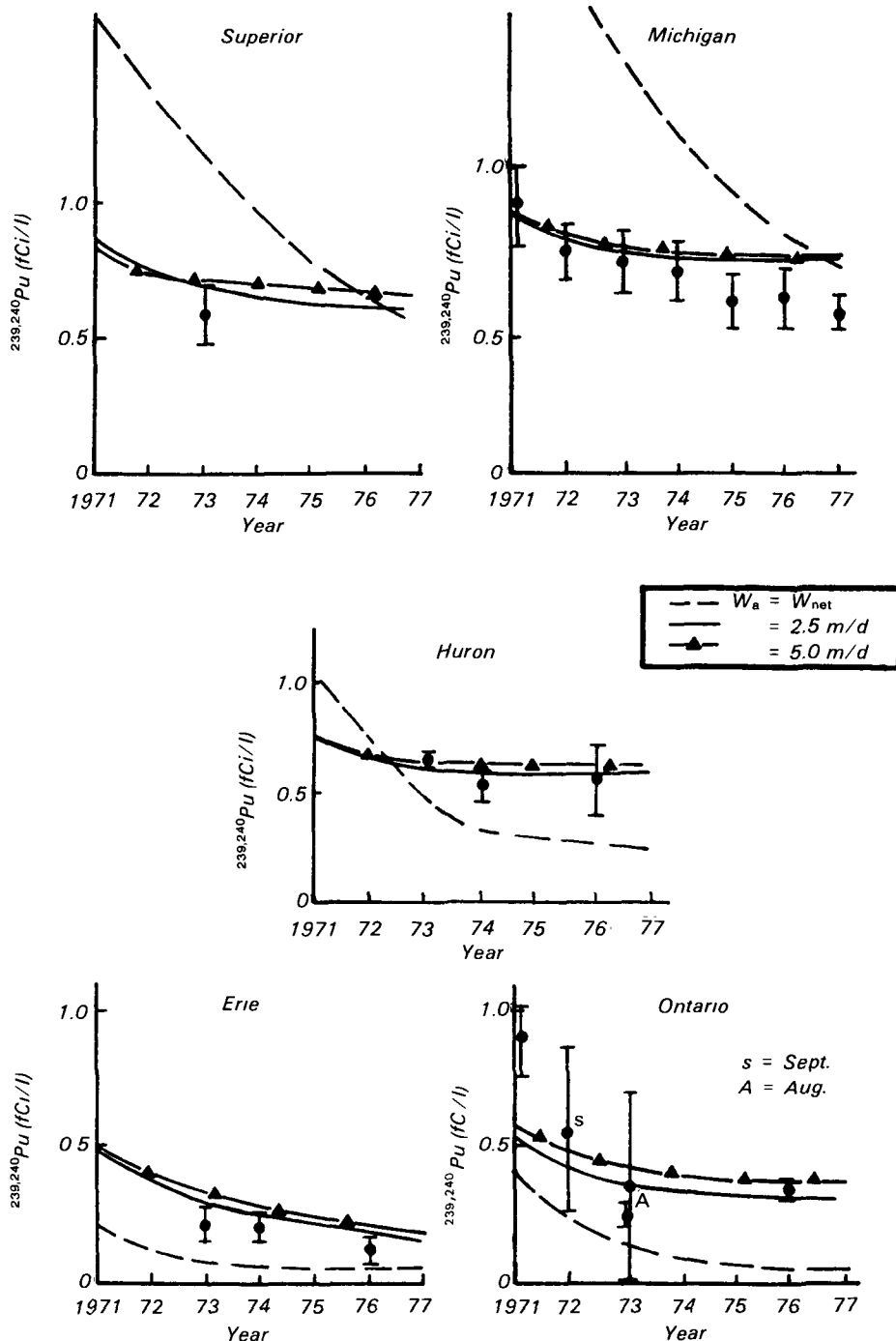


Figure 2. Comparison of calculated $^{239,240}\text{Pu}$ concentration (fCi/l) in the water column for all lakes to 1971-1977 data for three conditions of the particulate settling velocity. $\pi = 400,000 \text{ l/kg}$.

face sediment concentration was also not markedly affected (to order of magnitude) by the partitioning assumption, although a decline of about 50% is evident in the lake sediment and a decline of about 70% is calculated for the surface sediment of Saginaw Bay.

These reductions in sediment PCB particulate concentration reflect the assumed reduced partitioning at the high solids concentrations and are, therefore, subsequently reflected in the PCB concentration of the interstitial water of the surface sediment. It is in the interstitial water that the effect of the solids-dependent partitioning was most pronounced. Increases in the dissolved PCB concentration of about two orders of magnitude were calculated.

For Lake Michigan, as an example, the interstitial concentration of PCB as calculated for a constant partition coefficient is about 0.25 ng/l . For a variable partition coefficient (Relationship (b) above), the concentration increases to about 30 ng/l . Values of pore water PCB at three stations in southern Lake Michigan have been reported at levels of 159, 214, and 342 ng/l which is about one order of magnitude higher than that calculated. However, the estimate of 30 ng/l represents a lake-wide average including regions of nondeposition. One would, therefore, expect an observed lake-wide average to be less than individual core samples.

The calculation on the sensitivity of the PCB distribution in the Great Lakes to a sediment-dependent partition coefficient indicated that since the increased interstitial PCB concentration in the sediment is about two orders of magnitude higher than the overlying water dissolved PCB concentration, one would expect benthic organisms to carry a significantly higher body burden than organisms exposed solely to the water column and as a result would be a potential significant source of PCBs to top predators in the food chain.

Since the interstitial PCB component is potentially significant and since the issue of solids-dependent partitioning is of contemporary interest on constructing mass balances of PCB, it is recommended that additional sampling of pore water PCB and PCB concentration in benthic organisms be conducted in various Great Lakes regions.

Application of Model to Benzo(a) Pyrene and Cadmium

The physico-chemical model was further applied to two other chemicals: (a) benzo(a) pyrene, a polycyclic aromatic hydrocarbon and b) cadmium, a representative metal. Figure 5 summarizes the results for the BaP

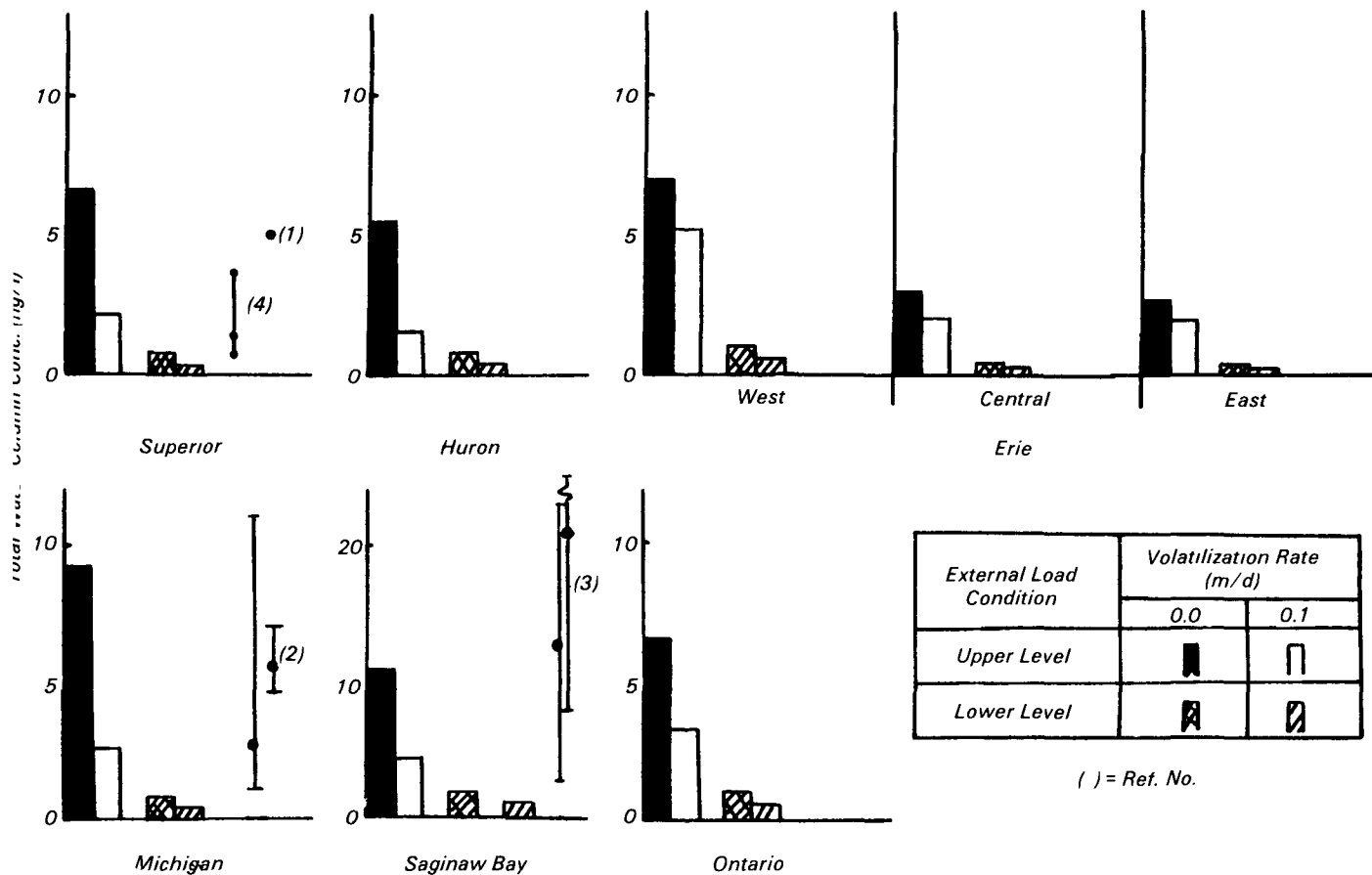


Figure 3. Calculated water column total PCB concentration (ng/l) for conditions on external load and volatilization rate.

calculations and indicates that a more favorable (but not totally desirable) comparison to observed data is obtained at the higher BaP partition coefficient of 100,000 l/kg. On the basis of this application of the physico-chemical model to BaP in the Great Lakes, it was concluded that the estimate of the BaP partition coefficient obtained from published empirical relationships is probably low by about an order of magnitude for the Great Lakes system, and with an increased BaP partition coefficient and assuming loss due to volatilization, the physico-chemical toxic substances model of the Great Lakes approximate observed BaP water column and sediment data to order of magnitude.

The application of the model to cadmium in the Great Lakes indicated that the degree of any dependence of the cadmium partition coefficient with solids has a marked effect on time to steady state and interstitial cadmium concentration. Under a solids-dependent cadmium partition assumption, the Great Lakes, especially the upper Lakes, do not reach a steady state condition after 100

years of constant loading while under a constant partition coefficient for cadmium, the Lakes do reach an equilibrium condition varying from about 25 years for Lake Michigan to 10 years for Lake Erie. Also the concentration of cadmium in the Lakes would be expected to increase by about 60% over the next 50 years if the average cadmium loading for the preceding 50 years continues.

Based on assumed sediment cadmium concentrations for Lake Erie, it is estimated that the cadmium concentration in the water column is about an order of magnitude higher than the other Lakes. Finally, the results indicate that if loads are projected to increase, then cadmium concentrations in the Lake system may increase to levels of concern.

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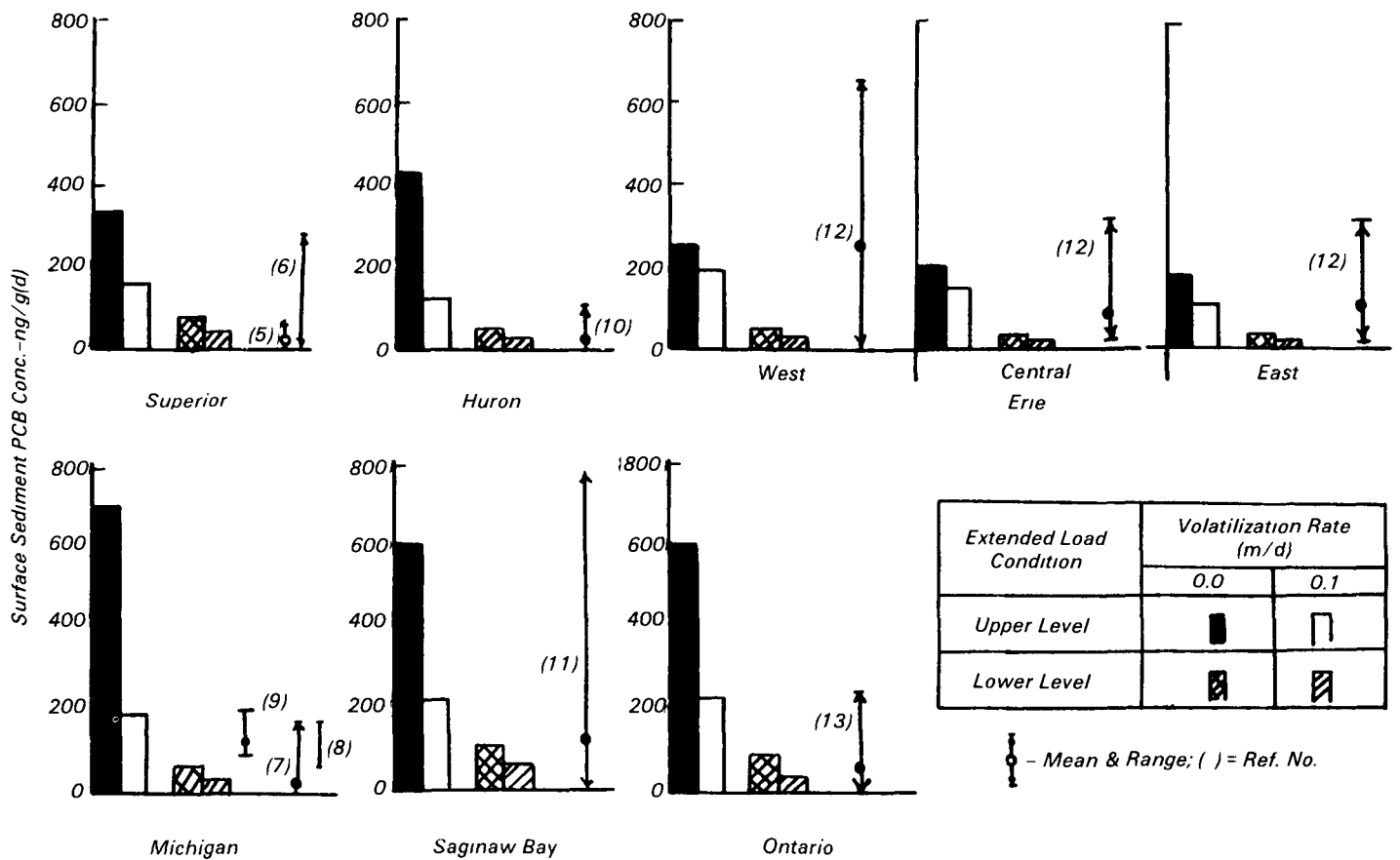
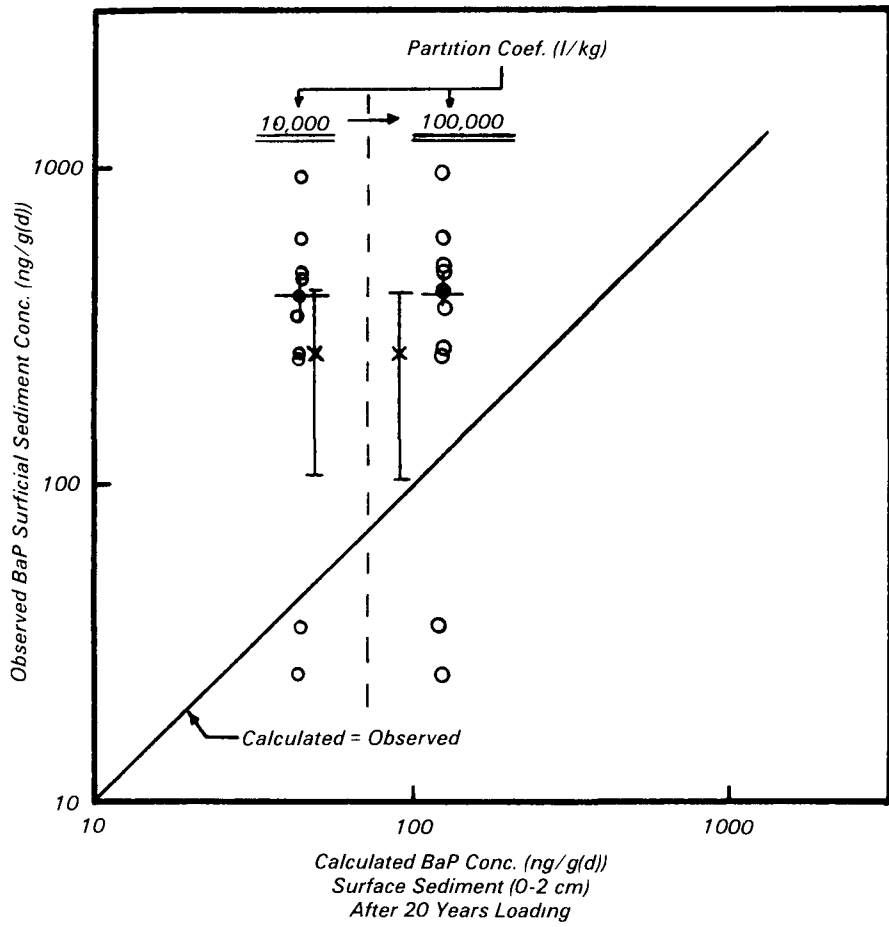


Figure 4. Calculated surface sediment PCB concentration (ng/g) for conditions on external load and volatilization rate and comparison to observed data



Key.

○ = Individual Data } Lake Michigan (14)

◆ = Mean

⊗ = Mean ± Std. Dev. } Lake Erie (14)

(n = 3)

Figure 5. Comparison between surface sediment BaP concentrations after 20 years and observed concentrations.

