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Transport and Fate of Heavy Metals in Onondaga Lake, New York

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Lakes in the immediate vicinity of population centers provide extremely valuable resources for recreation. Industrialization, however, generally accompanies urbanization, and urban lakes particularly may be affected by pollutants of a wide variety, including toxic heavy metals, from cultural sources within the watershed. Onondaga Lake (Figure 1) typifies this situation. Located at the northwest edge of the city of Syracuse, New York, for many years the lake has been the recipient of heavy metal inputs from the city, its suburbs, and approximately 140 industries which are located in its drainage basin (MURPHY 1978). Owing to broadly-supported efforts aimed at improving water quality in Onondaga Lake during the past decade, the concentration of nutrients and some heavy metals has decreased in the lake during that period (EFFLER et al. 1981; MURPHY 1978). Few quantitative data exist, however, concerning the fate of metals which enter Onondaga Lake or of the mechanisms which have permitted the observed reductions in concentration to occur. The sediments, nonetheless, are known to contain extremely high levels of several heavy metals compared to other lakes (EFFLER et al. 1980; RAND et al. 1977), which suggests that the transport to and permanent storage in the sediments may be important.

In general the fate of heavy metals in aquatic systems depends on partitioning between soluble and settleable solid phases and may be influenced by various interactions which include coagulation, adsorption, precipitation, coprecipitation, complexation, and biotic uptake (BURRELL 1974). These factors, in turn, are known to be affected by environmental conditions, such as: pH, redox potential, metal concentrations, ionic strength, bioaccumulation, and type and concentration of complexing ligands (LECKIE & JAMES 1974). Superimposed on the aforementioned phenomena are kinetic factors which govern reaction rates, particle sedimentation, and hydrodynamics. With full appreciation of this multidimensional web of interactions, the present investigation was undertaken to develop a simple, nonsteady-state, deterministic model for prediction of the behavior of the metals Zn, Ni, and Cr in Onondaga Lake over a growing season.

MODEL DEVELOPMENT

The model for Zn, Ni, and Cr in Onondaga Lake was developed in three stages. First, important physical transport characteristics

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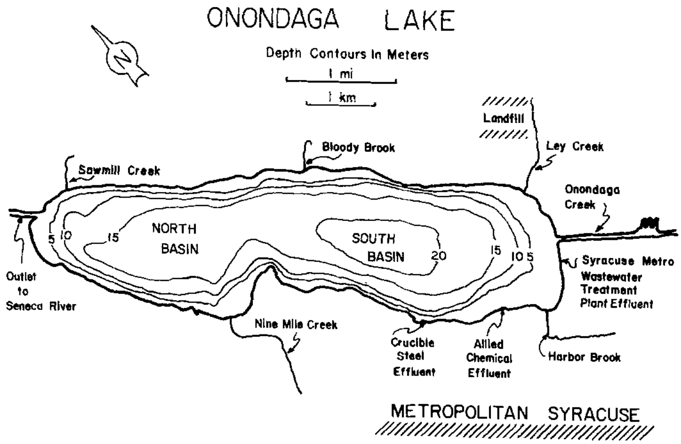

Figure 1. Onondaga Lake and vicinity (after STERNS & WHELER 1977)

of the lake were described mathematically to include morphometric characteristics, point and non-point inputs, advective and dispersive fluxes, and outputs. Second, the transport model was calibrated for the period of study by a time-dependent mass balance on chloride ion, which was assumed conservative. Chloride was especially useful for calibration of the transport model because concentrations of this ion characteristically are high in Onondaga Lake ($\geq$ 1000 mgCl/L) and cyclically variable on an annual basis due to seasonal differences in hydraulic and chloride ion loadings to the lake (MURPHY 1978). The calibrated transport model then formed the basis for prediction of in-lake concentrations of the metals Zn, Ni, and Cr from data on their concentrations in lake sources. The transport model was modified, however, to include an apparent sedimentation term to account for losses in the lake due to non-conservative behavior when it was applied to the metals.

A schematic representation of and the differential equations for the Onondaga Lake model are shown in Figure 2 and Table 1. Lake morphometry and thermal stratification formed the basis for model segmentation. The vertical exchange coefficient (K in Table 1) was estimated initially from the correlation presented by SNODGRASS & O'MELIA (1975) between vertical dispersive flux and mean lake depth. The transfer coefficient selected by this method was found to underestimate vertical dispersion during calibration of the model against the chloride data. Thus the coefficient was adjusted as required to effect a good calibration: 0.55 m/d to the end of June and 0.28 m/d thereafter. The decrease in the coefficient with the advance of the season coincided with thickening of the thermocline during the period. Values for the apparent metal sedimentation coefficients were selected by calibration against measured inlake metal concentrations. The equations in Table 1 were solved using a fourth-order Runge-Kutta

Table 1. Mass balance equations for Onondaga Lake, written for north basin

Epilimnion

$$V_{ne} \frac{d\,M_{ne}}{dt} = \Sigma\, Q_i M_j - \Sigma\, Q_o M_{ne} + Q_a (M_{se} - M_{ne}) + KA_n (M_{nh} - M_{ne})$$

$$- G_{ne} A_n M_{ne}$$

Hypolimnion

$$V_{nh} \frac{d\,M_{nh}}{dt} = \Sigma\, Q_i M_j - \Sigma\, Q_o M_{nh} + Q_s (M_{sh} - M_{nh}) + KA_n (M_{ne} - M_{nh})$$

$$- G_{nh} A_n M_{nh} + G_{ne} A_n M_{ne}$$

where:
- V = volume of lake sediment (L^3)
- M = concentration of heavy metal (ML^{-3})
- Q = flow rate (L^3T^{-1})
- A = area of thermocline (L^2)
- K = vertical exchange coefficient (LT^{-1})
- G = apparent sedimentation coefficient (LT^{-1})
- t = time

And subscripts: s,n,e, and h signify south and north basin, epilimnion and hypolimnion, respectively;

i,o,j, and a specify inputs, outputs, source, and advective flows.

Table 2. Morphometry of Onondaga Lake

Quantity	North Basin	South Basin	Total
Volume (m^3)	5.25×10^7	8.83×10^7	14.08×10^7
Surface Area (m^2)	3.86×10^6	7.84×10^6	11.7×10^6
Mean Depth (m)	13.6	11.3	12.0
Maximum Depth (m)	19.0	20.5	20.5
Shoreline (m)	-	-	1.79×10^7
Watershed (m^2)	-	-	6.0×10^8
Residence Time (d)			50-150

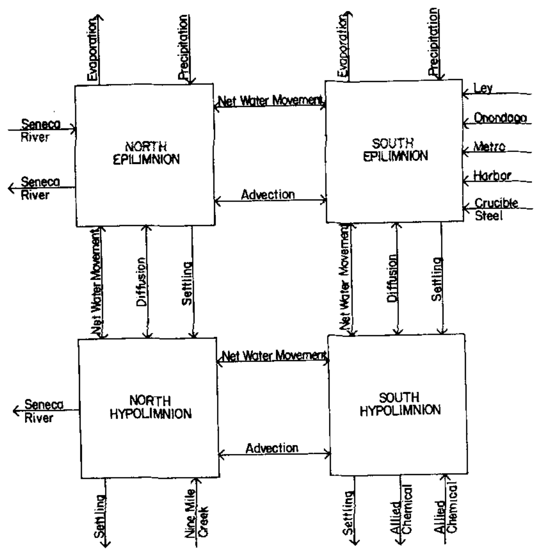

Figure 2. Schematic of Onondaga Lake; sources and sinks shown for each segment used in model

solution with a one day time-step. The model, programmed in BASIC, and a more complete description of its features are available elsewhere (SEGER 1980).

MATERIALS AND METHODS

Morphometric data on Onondaga Lake (Table 2) were obtained by planimetry of a bathymetric map given by STERNS & WHELER (1977). Onondaga Lake, its tributaries, and outlet were sampled weekly during the period May to September, 1978. Continuous flow data for the tributaries were obtained from the USGS (Ithaca, NY) while instantaneous outlet flow measurements were taken at least weekly and occasionally for extended periods to characterize its bi-directional flow characteristics (see below). Water samples were analyzed for total concentrations of Zn, Ni, and Cr by flameless atomic absorbance spectroscopy (Perkin-Elmer Model 603) after preliminary nitric acid digestion (EPA 1976) and for chloride concentrations by mercuric nitrate titration (APHA 1971). Temperature profiles during the period showed movement of the thermocline from an initial depth of 6 m to a final depth of 10 m during the study period.

RESULTS AND DISCUSSION

The accuracy of the transport model in predicting concentrations of conservative chloride from inputs to the lake is illustrated in Figure 3. The calibrated model revealed several unusual characteristics of physical transport in Onondaga Lake: (1)

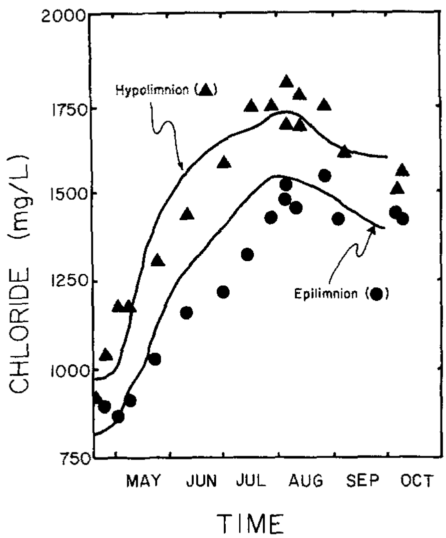

Fig. 3 Average Measured Cl^- compared to model predictions (solid lines)

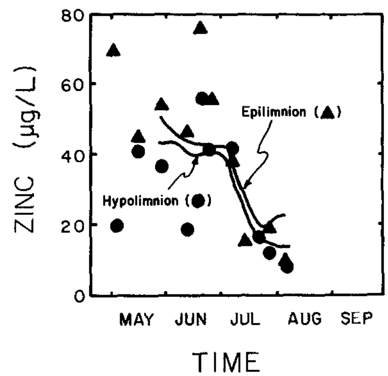

Fig. 4 Average measured Zn compared to model predictions (solid lines)

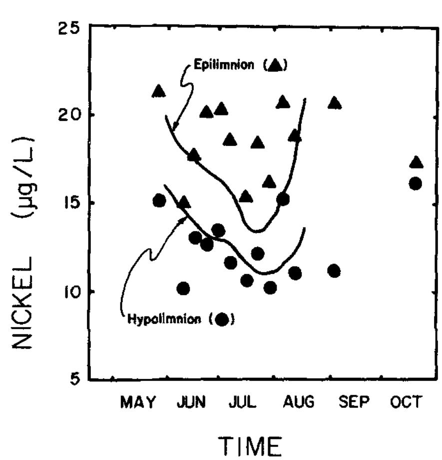

Fig. 5 Average measured Ni compared to model predictions (solid lines)

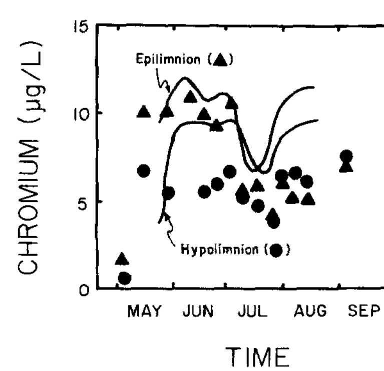

Fig. 6 Average measured Cr compared to model predictions (solid lines)

flow at the lake outlet may be unidirectional in either direction, in or out, or may be bidirectional with water flowing in both directions simultaneously; (2) during periods of bidirectional flow water leaves Onondaga Lake from the hypolimnion of the north basin while water from the Seneca River enters the north basin epilimnion; (3) elevated chloride levels in Nine Mile Creek result in water of sufficient density that the tributary enters the hypolimnion of the north basin; (4) approximately 10% of the flow from Nine Mile Creek short-circuits to the outlet without mixing in the north basin; (5) horizontally, the lake is well-mixed; and, (6) the effect of thermocline migration on vertical dispersion was of minor importance to in-lake transport during the study period.

The calibrated transport model next was applied to loads of Zn, Ni, and Cr to the lake and recalibrated by adjusting apparent sedimentation coefficients (G in Table 3). Predicted and measured concentrations of the metals in Onondaga Lake are shown in Figures 4-6 for the period of study. As shown by these data, the model accurately predicted the magnitude of concentrations and general trend toward increasing or decreasing concentration for each metal during the simulation period; week to week variations in observed concentrations were dampened by the model.

Values for the apparent sedimentation coefficients required for calibration of the model for the three metals are given in Table 3. As seen from the values in Table, a step increase in the sedimentation coefficient at the end of June was required for simulation of Zn and Cr concentrations, but not for Ni. This requirement seemed reasonable for the following reasons. First, 75 percent of the Ni load was in a dissolved (filterable) form and in the lake Ni remained mainly dissolved, while Zn and especially Cr were predominantly particulate. Thus, Zn and Cr should have been subject to sedimentation loss as particulate matter from the water column to a greater degree than Ni. Additionally, phytoplankton loss rates from the epilimnion appeared to increase at the end of June based on trends in chlorophyll-a concentrations during the period (SEGER 1980). The latter observation, together with the fact that EFFLER et al. (1981) estimated sinking rates of phytoplankton in Onondaga Lake during the period to be about 0.4 m/d, suggests a link between algal loss and particulate metal sedimentation. That the algal settling velocities were of the same order of magnitude as those determined by calibration for the metals, lends support to this hypothesis. The apparent sedimentation coefficients required to calibrate the Onondaga Lake model for the metals were approximately an order of magnitude larger than those measured directly using sedimentation traps in the north basin (data not shown). This discrepancy appears largely due to location of the major metal sources in the south basin and elevated sedimentation losses of particulate metals in near-shore areas proximate to those sources.

Based on the results of modeling the movement of the three metals it was estimated that amounts of Zn equivalent to an average of 38% of the external load was lost to the sediments during the

Table 3. Apparent sedimentation coefficients (G, m/d) used to calibrate model for Zn, Ni, and Cr

Metal	Period	
	May-June	July-August
Zn, epilimnion	0.05	0.40
Zn, hypolimnion	0.05	0.80
Ni, epilimnion	0.05	0.05
Ni, hypolimnion	0.30	0.30
Cr, epilimnion	0.30	0.70
Cr, hypolimnion	0.50	0.90

study period. For Ni and Cr, the figure was 36% for each metal. The model calculations indicated that transport of Ni from the epilimnion to the hypolimnion prior to sedimentation was due mainly to dispersion (75% of Ni lost to sediments), which was supported by the fact that most of the Ni was soluble. Also greater vertical concentration gradients existed for Ni than for either Zn or Cr over much of the simulation period, as may be seen in Figures 4-6. Vertical transport of Zn and Cr, however, was dominated by particle settling, as 84% of the Zn and 75% of the Cr which was lost to the sediments came from epilimnetic waters by sedimentation during the study period.

Owing to the greater sedimentation rates estimated for Zn and Cr compared to Ni, and thus the greater tendency for the former two metals to occur in settleable particulate phases, the former metals may be considered to behave less conservatively than Ni. Furthermore, Cr appeared somewhat less conservative than Zn during transport through Onondaga Lake. Based, however, on the overall percentage of the total load of each metal lost to the sediments, the three metals appeared equally nonconservative.

On the basis of the data shown in Figures 4-6 it appears that the model for Onondaga Lake (Table 1) accurately simulates the transport and fate of Zn, Ni, and Cr in the lake during a typical period of stratification. Further work involving field sampling and metal analysis would be required to verify the accuracy of the model predictions and to extend the applicability of the model to other periods of the year. The model illustrates, however, the usefulness of a simplified approach to the complex factors which affect the fate of heavy metals in lakes with regard to predicting concentrations of these pollutants based on their inputs.

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