TECHNICAL

Performances of Assessment Models for Estimating the Transfer of Mercury in a Lake Ecosystem

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(Received July 5, 1990)

(Accepted March 11, 1991)

The performances of assessment models for estimating the transfer and bioaccumulation of mercury in a lake ecosystem were tested by being applied to a test scenario proposed in an international cooperative study named BIOMOVs. Two kinds of models have been developed to estimate mercury concentration in fish. One uses a bioaccumulation factor approach which is applied to an ecosystem in equilibrium, whereas the other is a dynamic model in which both the change of the concentration in water and the metabolism in fish are taken into account. For this scenario, the former was not adequate but the latter could predict more accurately because the concentrations were not in equilibrium. The limitations of applications were suggested for the two models employed here. It would be important in the present case to take into account that equilibrium was not attained in the ecosystem and the metabolism of mercury in the fish was very slow.

KEY WORDS: biospheric transfer model, model performance, lake ecosystem, mercury concentration, bioaccumulation factor approach, dynamic model, equilibrium condition

I INTRODUCTION

1. Background

An international cooperative study named BIOMOVs^{1,2)} (BIOspheric MOdel Validation Study) has been carried out from 1985 under the auspices of the Swedish National Institute of Radiation Protection, SSI, to test models designed for calculating the transfer and bioaccumulation of radionuclides and other trace substances in the biosphere.

The three main objectives of BIOMOVs are:
to test the accuracy of predictions of environmental assessment models for selected contaminants and exposure scenarios;
to explain differences in model predictions

due to structural deficiencies, invalid assumptions, and/or differences in selected input data; and

to recommend priorities for future research for improvement of the accuracy of model predictions.

BIOMOVs involves two different approaches to fulfilling the objectives:

Approach A, involving the formulation of test scenarios based on suitable data and a comparison of model predictions against these independent data sets; and

Approach B, involving the comparison of model predictions and associated estimates of uncertainty for specific test scenarios selected on the basis of assessment priorities in the case that such independent data sets are not available.

BIOMOVs is concerned with terrestrial and aquatic pathways of importance to the assessment of exposure for critical groups and human populations.

Several test scenarios were proposed for each approach. A scenario for a release of mercury

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Fig. 1 Geographical features of Wabigoon River and Clay Lake.

into a river, which is called Scenario A1, was provided as one of test scenarios included in Approach A. This was the scenario for which participants were requested to predict mercury concentrations in freshwater fish following chronic releases into rivers located in three different sites.

The Japan Atomic Energy Research Institute, JAERI, participated in this scenario in order to test the performances of assessment models for estimating the transfer and bioaccumulation of trace elements in aquatic ecosystems. This paper describes models and parameter values employed in the predictions and discusses the results of a comparison between the predictions and measurements concerning one of three sites.

2. Scenario description

Scenario A1 was provided to test the performances of models for predicting the behavior of mercury in freshwater ecosystems. Although three different sites in the United States and Canada were selected for this scenario, this paper deals with the typical case for which two models applied here yielded quite distinctive predictions. This site is a river system known as Wabigoon River and Clay Lake³⁾ at Dryden, Ontario in eastern Canada. A detailed description of the scenario follows.

As shown in Fig. 1, a mercury cell chloralkali plant was situated on Wabigoon River below a dam of Wabigoon Lake, approximately 90 km

Table 1 Total mercury concentrations in water and sediment taken from Clay Lake in 1979 and 1980

Site	Water (ng/l)		Sediment (mg/kg)
	Mean	Range	0-5 cm depth
Inflow to lake	29	17-46	2.4
Eastern side of lake	25	10-46	3.0
Western side of lake	16	7.5-22	—
Outflow from lake	19	12-26	2.8

above Clay Lake. Eagle River joins Wabigoon River about 45 km below the plant site. Wabigoon River has a mean annual flow of 44.5 m³/s and a drainage area of approximately 6,800 km².

During the operation of the plant from 1962 to 1969, about ten metric tons of mercury were released into Wabigoon River. It was found that fish taken from Clay Lake had mercury concentrations of up to 10 mg/kg. Approximately 85% of the mercury in the edible portion of the fish was in the form of methylmercury. In 1970, measures were taken to reduce the release of mercury from the plant, and in 1975 the mercury cells were dismantled. In 1971, levels of mercury in northern pike and walleye were 9.1 and 8.7 mg/kg, respectively. After the mercury cells were dismantled, these fish were found to have mercury

Table 2 Mean water quality parameters measured at Clay Lake in 1979 and 1980.

Site	Temp ^{a)} (°C)	Cond ^{b)} (μmhos/cm)	SS ^{c)} (mg/l)	Cl (mg/l)	SO ₄ (mg/l)	BOD ^{d)} (mg/l)	pH
Lake inflow	12	126	2.7	11	10	1.8	7.2
Lake outflow	11	125	2.7	9.8	9.7	1.2	7.2

a) Temperature, b) Conductivity, c) Suspended solids, d) Biochemical oxygen demand.

Table 3 Mercury concentrations in the axial muscle of northern pike and walleye collected from Clay Lake in 1971 and 1976.

Species	Year	Mercury (mg/kg)	Length (cm)		Weight (g)	
		Mean	Mean	Range	Mean	Range
Northern pike	1971	9.09	50.8	36.0-62.0	974	312-1870
	1976	5.84	65.0	50.1-86.2	1793	879-4423
Walleye	1971	8.71	42.6	33.0-50.0	1064	454-1850
	1976	7.83	49.8	40.8-59.4	1283	482-2013

Fig. 2 Transfer of mercury in a lake ecosystem.

concentrations of 5.8 and 7.8 mg/kg, respectively.

The concentrations of mercury in water and sediment taken from Clay Lake in 1979 and 1980 are provided in **Table 1**, and mean water quality parameters are listed in **Table 2**. Total mercury concentrations in the axial muscle of northern pike and walleye collected from Clay Lake in 1971 and 1976 are presented in **Table 3**.

Participants were requested to predict mercury concentrations in the edible tissue of northern pike and walleye taken from Clay Lake in 1979 and 1980, using the above information on the site description and the measured data. They were also requested to estimate the uncertainty associated with the predictions for the scenario.

II MODEL DESCRIPTIONS

The transfer of mercury in a lake ecosystem is schematically represented in **Fig. 2**. Lake water is contaminated by the inflow of contaminated river water and the process of desorption from contaminated sediment. There are two components of mercury in lake water: mercury dissolved in water and that adsorbed on suspended solids. Equilibrium is attained between the two components. Mercury is removed from water by outflow from the lake and by the process of sedimentation of suspended solids onto sediment. Mercury in water is taken up by fish via their gills and skin, and also via food chains. Mercury adsorbed on suspended solids is not transferred

to the fish body.

Two kinds of models, the JAERI-I and JAERI-II models, have been developed to estimate the mercury concentrations in a lake ecosystem. JAERI-I uses a bioaccumulation factor approach that is applied to an ecosystem in equilibrium, whereas JAERI-II is a dynamic model in which both the change of the concentration in water and the metabolism in fish are taken into account. At first, JAERI-I was applied to this scenario, assuming that the mercury concentrations were in equilibrium. Later, however, it was learned that equilibrium had not been attained in the ecosystem because only a few years had passed since the mercury release had ceased. Also the metabolism of mercury in fish was discovered to be very slow, though the high concentration of mercury in water in the past had decreased rapidly. Therefore, the JAERI-II model was then applied to the scenario. Both models are explained below in detail.

1. The JAERI-I model

The change of mercury inventory in water with time can be mathematically expressed by the following differential equation:

$$\frac{dY}{dt} = Q + p \cdot X - (f + d) \cdot Y \quad (1)$$

where Y : mercury inventory in lake water (kg), X : mercury inventory in sediment (kg), Q : mercury inflow rate into lake (kg/y), p : transfer rate for desorption (y^{-1}), f : removal rate for outflow from lake (y^{-1}), and d : removal rate for sedimentation (y^{-1}).

The mercury inventory in sediment is considered to be constant since the inventory is large enough compared with the loss rate from sediment. The mercury inventory in water can be described by the following equation when the system reaches equilibrium:

$$Y = \frac{Q + p \cdot X}{f + d} \quad (2)$$

The concentration of mercury dissolved in water is then calculated by using a distribution coefficient approach:

$$W = \frac{\bar{Y}}{1 + K_d \cdot SS} \quad (3)$$

where W : concentration of mercury dissolved in lake water (kg/l), $\bar{Y}$: total mercury concentration in lake water (kg/l), K_d : distribution coefficient (l/kg), and SS : suspended solids in lake water (kg/l).

The transfer rate, p , was estimated by a model^(4,5) using a mass transfer coefficient and a retardation

factor. The removal rate, f , was derived from the renewal of lake water. The removal rate, d , was obtained by a particle scavenging model⁽⁶⁾ which described the loss of mercury dissolved in water by adsorption on suspended solids settling down to the bottom of lake. The transfer or removal rates, p , f , and d , can be calculated by the following equations:

$$p = \frac{K_L}{T \cdot \{\phi + 10^{-3} \cdot (1 - \phi) \cdot \rho \cdot K_d\}} \quad (4)$$

$$f = \frac{I_w}{10^3 \cdot D \cdot S}, \text{ and} \quad (5)$$

$$d = \frac{K_d \cdot R}{10^3 \cdot D \cdot (1 + K_d \cdot SS)} \quad (6)$$

where K_L : mass transfer coefficient (m/y), T : thickness of sediment exchange zone (m), ϕ : sediment porosity, ρ : density of sediment (kg/m³), I_w : water inflow into lake (l/y), D : mean depth of lake (m), S : area of lake (m²), and R : sedimentation rate (kg/m²/y).

Using the above equations, Eq.(3) can be rewritten as follows:

$$W = \frac{1}{I_w \cdot (1 + K_d \cdot SS) + S \cdot K_d \cdot R} \times \left[Q + \frac{K_L \cdot \rho \cdot S \cdot \bar{X}}{\phi + 10^{-3} \cdot (1 - \phi) \cdot \rho \cdot K_d} \right] \quad (7)$$

where $\bar{X}$: mercury concentration in sediment (kg/l).

Mercury concentration in freshwater fish is obtained by using a bioaccumulation factor approach as shown below, in which equilibrium is attained between the concentration in water and that in fish:

$$F = CF \cdot W \quad (8)$$

where F : mercury concentration in fish (kg/kg), and CF : bioaccumulation factor (l/kg).

Among the parameters employed in the JAERI-I model, the values of Q , SS , I_w , and $\bar{X}$ are apparently given in the scenario description. The value of S was roughly estimated from Fig. 1. The values of K_d , K_L , ϕ , ρ , R , and CF must be provided by the modeler.

2. The JAERI-II model

It was assumed that the mercury concentration in water was in equilibrium at the time that the mercury release ceased and that the concentration exponentially decreased thereafter. The mercury concentration in the water can be presented by the following function:

$$W = W_0 \cdot \exp(-k \cdot t) \quad (9)$$

where W_0 : equilibrium concentration of mercury dissolved in lake water at the time that the mercury release ceased (kg/l), k : rate of decrease in mercury concentration in lake water (y^{-1}), and t : time after the release ceased (y).

The following differential equation is used to estimate the mercury concentration in freshwater fish:

$$\frac{dF}{dt} = q \cdot W - \lambda \cdot F \quad (10)$$

where q : rate of uptake of mercury from lake water by fish (l/kg/y), and λ : excretion rate from fish due to metabolism (y^{-1}).

When the mercury concentrations reach equilibrium between fish and the surrounding water, the following relationship can be obtained:

$$\frac{F_0}{W_0} = \frac{q}{\lambda} = CF \quad (11)$$

where F_0 : equilibrium concentration of mercury in fish at the time that the mercury release ceased (kg/kg).

Using the above equations, Eq.(10) can be solved as follows:

$$F = \frac{\lambda \cdot F_0}{\lambda - k} [\exp(-k \cdot t) - \exp(-\lambda \cdot t)] + F_0 \cdot \exp(-\lambda \cdot t). \quad (12)$$

The value of F_0 was determined from the measured data on the mercury concentrations in fish collected in 1976. The mercury concentrations in fish were calculated for the time 3.5 years after the release ceased for comparison with those observed in 1979 and 1980. The values of k and λ must be prepared by the modeler. The value of W_0 needs also to be provided in order to estimate the value of k .

III PARAMETER VALUES AND UNCERTAINTY ANALYSIS

1. Parameter values employed in predictions

Among the parameters employed in the two models, the values of the following parameters have to be prepared by the modeler: K_d , K_L , ϕ , ρ , R and CF for the JAERI-I model, and W_0 , k and λ for the JAERI-II model.

The parameter values employed in the predictions, shown in Table 4, were estimated as follows.

A great part of the mercury detected in fish was found to be in the form of methylmercury though mercury released from the plant was entirely in the inorganic form. Methylation of mercury rarely takes place in organisms but

Table 4 Parameter values employed in predictions.

Model	Parameter	Value
JAERI-I	K_d	2×10^5 (l/kg)
	K_L	5.3 (m/y)
	ϕ	0.9
	ρ	2.5×10^3 (kg/m ³)
	R	0.2 (kg/m ² /y)
	CF	1×10^4 (l/kg)
JAERI-II	W_0	50 (μ g/l)
	k	2.4 (y^{-1})
	λ	0.35 (y^{-1})

mainly in bacteria in sediment.⁷⁻¹⁰⁾ Therefore, it was understood that mercury released in the inorganic form was changed to methylmercury in sediment and only then accumulated in the fish body. The values of CF were surveyed for the bioaccumulation of methylmercury in freshwater fish. Figure 3 presents the relationship between mercury concentrations in water and the CF values collected.⁸⁻¹³⁾ It is obvious that the logarithmic value of CF decreases linearly with the increase in the logarithmic value of the concentration in water. The concentration dependence of the CF value needs to be taken into account, while the value is likely to be independent of the species of fish.

The value of K_d in fresh water was determined from the relationship between concentrations of mercury dissolved in water and those adsorbed on suspended solids, which were given for the other site of Scenario A1.²⁾ The value of K_L was based on diffusion-related processes and the renewal time of the sediment surface layer.⁵⁾ Although the values of ϕ , ρ , and R were different from lake to lake, values obtained from a larger lake¹⁴⁾ were used here. The value of W_0 was derived from the relationship of the CF parameter shown in Fig. 3 and the mercury concentrations in fish at the time that the mercury release ceased. The value of k was determined from Eq.(9) and was assumed to be constant. The value of λ was obtained for northern pike by both laboratory and field experiments,⁸⁾ and was also used for walleye.

2. Uncertainty analysis

Uncertainty analysis was carried out by a pa-

Fig. 3 Bioaccumulation factors as a function of mercury concentration in surrounding water.

parameter perturbation technique. Extreme maximum and minimum values were selected for each of the following several parameters, which had to be provided by the modeler and were considered to be important in each model: K_d , K_L , R and CF for the JAERI-I model, and W_0 and λ for the JAERI-II model.

Since the probability distributions of the parameter values were not sufficiently known, the ranges of the values were determined by one of three subjective judgments: a factor of two for λ ; a factor of five for K_d , K_L , R and CF ; and a factor of ten for W_0 . Calculations were then undertaken by putting various sets of the extreme values into the models in order to obtain both upper and lower estimates. Correlations between the parameters were not taken into account in choosing the values. Equal weight was given to all sets of the values. The confidence interval for the results was then defined by both the two estimates.

IV RESULTS AND DISCUSSION

The mercury concentrations in northern pike and walleye calculated by the JAERI-I and the JAERI-II models are shown in Fig. 4, along with mean measured values for the fish collected from Clay Lake in 1979 and 1980. Uncertainties in

the estimation are also indicated with intervals for both the predicted values.

In the parameter perturbation technique, equal weight was given to all the possible sets of parameter values, although they were sometimes highly unlikely. The range of uncertainty produced by this technique would therefore tend to be large. The JAERI-I model yielded estimates varying within the range of more than two orders of magnitude, whereas the estimates by the JAERI-II model varied within the range of one order of magnitude. This was because the scenario description yielded more advantageous information to the JAERI-II than to the JAERI-I, that is, data were given on the concentrations observed in fish at the time that the mercury release ceased.

The central estimate by the JAERI-I model was from one to two orders of magnitude less than the measured values, although the CF value chosen for the calculation was one order of magnitude as large as that commonly used in assessment models.¹²⁾ The predictions by the JAERI-I model could not cover all the observed values but only those for northern pike. This underestimation could be explained as follows. Since the metabolism of methylmercury in such large-sized fish was very slow, the high concentration of mercury in fish, reflecting the earlier high concentration in

Fig. 4 Mercury concentrations in fish calculated by prediction models in comparison with those observed in 1979 and 1980.

water, was retained even after the concentration in water decreased rapidly.

On the other hand, the JAERI-II model showed higher consistency with the observations than did the JAERI-I model. However, the estimated values were still lower than the measured values and did not cover the levels of the concentrations measured for walleye. It might be inappropriate to apply the value of λ for northern pike to that for walleye. For this scenario, the JAERI-II model seems to be appropriate as a whole, and the predictions can be improved simply by setting another group of parameter values. However, the present model has been developed specifically for the scenario and therefore must be modified when applied to another assessment.

V CONCLUDING REMARKS

The performances of assessment models for predicting the transfer and bioaccumulation of mercury in a lake ecosystem were tested by application to the test scenario proposed in the international cooperative study BIOMOVs. Two models, the JAERI-I and the JAERI-II, have been developed to estimate the mercury concentration in fish. The JAERI-I model uses a bioaccumulation factor approach that is applied to an ecosystem in equilibrium, whereas the JAERI-II model is a dynamic model in which both the change of the concentration in water and the metabolism in fish are taken into account. For this scenario, the JAERI-I model was not ad-

equated but the JAERI-II model could predict more accurately because the concentrations were not in equilibrium after the mercury release ceased. The limitations of applications were suggested for the two models employed here.

When the transfer of a trace element in an aquatic ecosystem is predicted by an assessment model, it is important to select an appropriate model by understanding fully the characteristics of the ecosystem in advance. In the case of this scenario, it would be important to take into account that equilibrium was not attained in the ecosystem and the metabolism of methylmercury in large-sized fish was very slow.

ACKNOWLEDGEMENT: The author would like to express appreciation to all members of the Committee on the Environmental Behavior of Radionuclides, established within JAERI, for their helpful discussions and suggestions. The author also wishes to thank Mr. H. Matsuzuru and Mr. T. Homma of the Department of Environmental Safety Research, JAERI, for their valuable comments.

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