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A COMPARISON OF TWO MERCURY ENVIRONMENTAL FATE AND TRANSPORT MODELS IN EVALUATING INCINERATOR EMISSIONS

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ABSTRACT

Human health and ecological risk assessments for waste incinerators often show that exposure to mercury from fish ingestion contributes significantly to the risk results. One of the most important elements in the analysis of mercury in incinerator risk assessments is the fate and transport modeling of mercury in waterbodies. The U.S. Environmental Protection Agency (USEPA) provides mercury modeling algorithms for waste incinerator risk assessments in its 1998 *Human Health Risk Assessment Protocol for Hazardous Waste Combustion Facilities (Risk Assessment Protocol).* These algorithms, however, do not reflect the more refined USEPA mercury model referred to as IEM-2M, a model that has been applied by USEPA in the *Mercury Report to Congress (MRTC)* as well as the *Utility Report to Congress*. The IEM-2M model better addresses the complexities of the chemistry, environmental fate, and transport of combustion source mercury emissions in both watershed and waterbody environments. This paper describes the application of the IEM-2M model to a waste incinerator risk assessment. The IEM-2M model was used to calculate mercury concentrations in fish associated with mercury emissions from an incinerator’s stack. The IEM-2M model is described and input parameter requirements and model outputs are presented. A comparison of results for the two models shows that concentrations in water calculated using IEM-2M were four times lower for divalent mercury and more than 10 times lower for methyl mercury than those calculated using USEPA's *Risk Assessment Protocol*. The benthic sediment concentrations of divalent and methyl mercury were 1.5 times lower and 10 times higher, respectively, using IEM-2M compared to the *Risk Assessment Protocol*. The mercury fish tissue concentration, and associated fish ingestion risk, calculated according to the *MRTC* using IEM-2M model results was more than 100 times lower than that calculated using the methods presented in the *Risk Assessment Protocol*.

INTRODUCTION

Human health risk assessments for waste incinerators often show that potential exposure to mercury via fish ingestion contributes significantly to the risk results. Mercury exposure via fish ingestion has often been found to be a significant contributor to total risks, accounting for more than 90% of the total non-cancer hazard index for the fish ingestion exposure pathway (1,2,3). If the mercury risk assessment results exceed regulatory target risk levels, these results can have significant ramifications for an incineration facility’s permit conditions.

Mercury fish ingestion risk assessment results are affected by a variety of factors, including toxicological data, bioavailability, emission source characteristics, and human behavior patterns. However, one of the most important elements in the chain of analyses employed in risk assessments is the fate and transport modeling of mercury in waterbodies. Mercury-related risks due to ingestion of fish by humans or birds are directly linked to modeled fish tissue concentrations which, in turn, are determined by modeled concentrations in a waterbody. The behavior of mercury in waterbodies is, however, chemically complex and the ability of mathematical models to accurately predict this behavior is limited. Nonetheless, incinerator risk assessments that include the fish ingestion exposure pathway must mathematically model the fate and transport of mercury from its emission source to a waterbody containing fish.

The USEPA (4) provides mercury modeling algorithms for incinerator risk assessments in its 1998 *Risk Assessment Protocol.* These algorithms incorporate default assumptions regarding mercury behavior. For example, the *Risk Assessment Protocol* assumes, without accounting for site-specific conditions, that 98% of the mercury present in soil is in divalent form with 2% present as methyl mercury. The *Risk Assessment Protocol* also arbitrarily assumes that 85% of the mercury in a waterbody is present as divalent mercury with the remaining 15% present as methyl mercury. Although the *Protocol* acknowledges that there are many processes affecting methylation, it does not explicitly take these into account.

The USEPA has developed a more refined mercury model referred to as IEM-2M. The IEM-2M model better addresses the complexities of the environmental fate and transport of combustion source mercury emissions in both watershed and waterbody environments. This model has been applied by USEPA in the *Mercury Report to Congress* (5,6,7) as well as the *Utility Report to Congress* (8). Although the *Risk Assessment Protocol* allows the use of more refined or alternative models, with Agency approval, we are aware of no incinerator risk assessments that have not relied on the default algorithms for mercury modeling in the *Risk Assessment Protocol* with the exception of two assessments performed by CPF Associates. The IEM-2M model offers an acceptable alternative to the default methods in the *Risk Assessment Protocol* because the model was not only developed by USEPA but also was used in important large-scale studies sponsored by USEPA

IEM-2M MODEL DESCRIPTION

USEPA developed the IEM-2M model for combustion source emissions in order to address important mercury fate and transport behaviors in a more detailed manner than previously developed Agency models (5, 9). The inputs to the IEM-2M model, and the modeling algorithms, are described in detail in Volume III of USEPA's *MRTC* (5) and the *Utility Report to Congress* (8). Although the IEM-2M model was originally developed for a lake system, it has been applied by USEPA for both lake and river systems. USEPA has noted that the model results are more reliable for steady environments, such as lakes, than unsteady environments, such as streams (5).

The IEM-2M model simulates mercury fate and transport using mass balance equations that describe watershed soils and a waterbody. It models three chemical species of mercury - elemental, divalent and methyl and, unlike the *Risk Assessment Protocol*, includes specific transformation rates affecting mercury compounds in soil, water and sediments. For example, the mass balance equations for soil are applied to three interacting components, the gas, aqueous and solid phases. Within these phases, each mercury compound is linked by a set of chemical transformation reactions including oxidation, reduction, methylation and demethylation. The mercury species are also subject to transport processes including leaching and runoff of dissolved mercury, erosion of particulate mercury and volatilization of gas phase mercury.

At the core of the IEM-2M model are nine differential equations describing the mass balance of each mercury species in the watershed surficial soil layer, in the water column, and in the waterbody's surficial benthic sediments. Transformation and transport processes are taken into account in the mass balance equations.

The IEM-2M model calculates the environmental fate of mercury based on the total loading of each mercury species to the watershed and the waterbody. The loadings considered for the watershed include wet and dry deposition in addition to vapor phase diffusion to watershed soils. The loadings considered for the waterbody include direct wet and dry deposition, runoff from the watershed into the waterbody, soil erosion from the watershed into the waterbody, and vapor phase diffusion into the waterbody.

The model also addresses several mercury sinks in the watershed and waterbody. Mercury sinks include vertical downward leaching from watershed soils, burial in lake sediments, volatilization of mercury from watershed soil and the water column, and advection of mercury out of the waterbody.

IEM-2M MODEL APPLICATION

The IEM-2M model was applied to a freshwater river known to be used for fishing located approximately five miles from an incineration facility. The model was applied in a series of steps (see Figure 1) in which information was shared between an Excel$^{®}$ spreadsheet and Scientific Workplace$^{®}$, a software program designed to perform computerized algebra and calculus functions (10). Scientific Workplace$^{®}$ was used to solve the model's differential equations using a fourth order Runge-Kutta technique and verified using an analytical solution. In previous analyses, the operation of the differential equations was verified by comparison with input and output data reported in a sample calculation presented in USEPA (11). All other calculations were performed using Excel$^{®}$.

Compile Input Data

The inputs used in this analysis were obtained either from site-specific data or directly from default values provided in the *MRTC* (5). Site-specific data included waterbody and watershed dimensions, water flow rate and current velocity, and total suspended solids concentration. Inputs obtained from the *MRTC* included chemical-specific parameters (e.g., Henry's law constants, diffusivities, partition coefficients) and default values for variables that could not readily be measured (solids settling velocities in water,

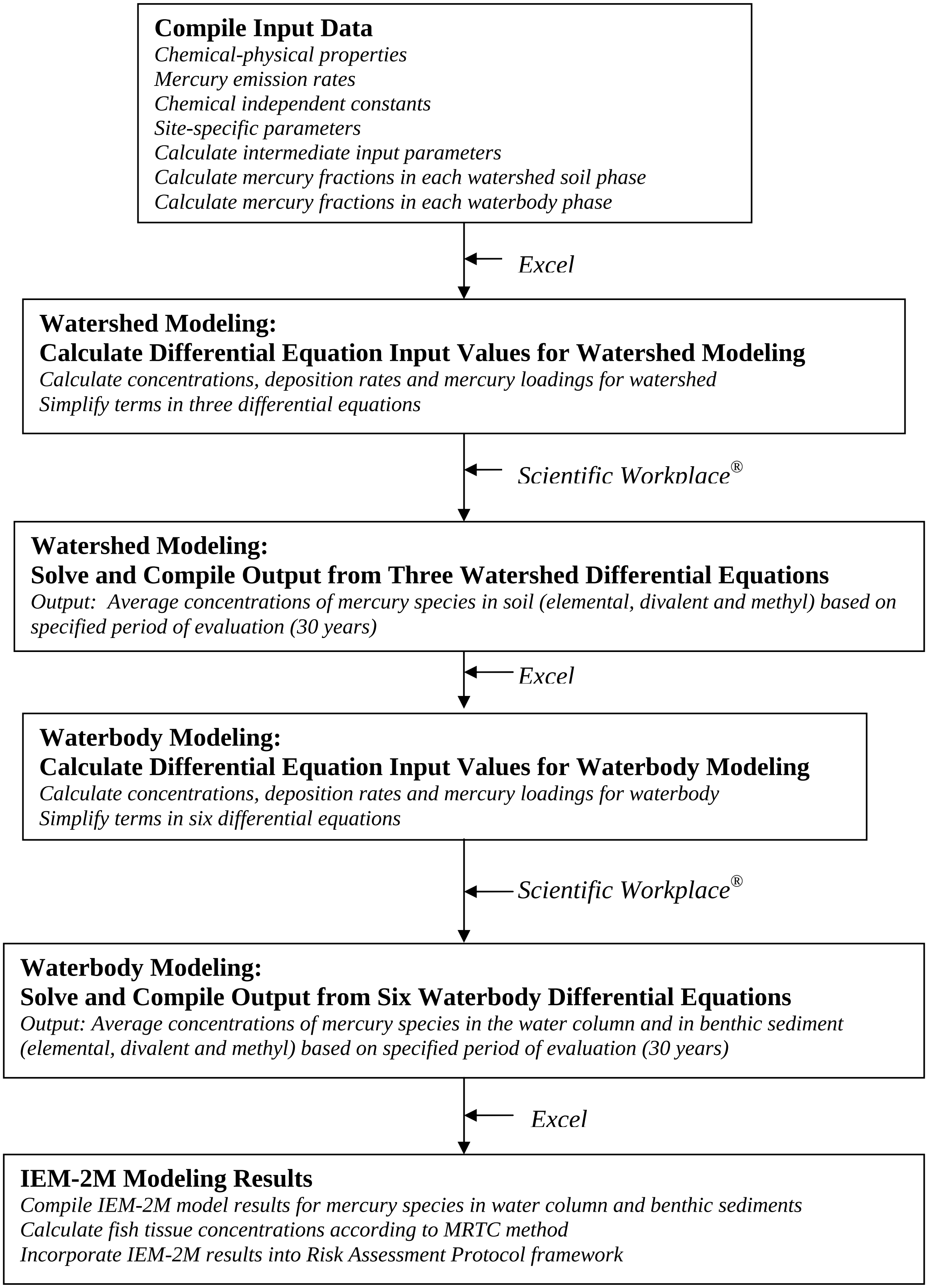

Figure I. Flow Chart For IEM-2M Modeling

mineralization rate for upper benthic solids, particle enrichment ratio). A number of intermediate parameters necessary for the IEM-2M model are also calculated using *MRTC* modeling algorithms and the input data, such as the fractions of each mercury species present in gas, water and solid phases in watershed soils and the waterbody, and rate constants for each mercury species (soil volatilization, runoff, leaching, erosion and water volatilization).

Watershed Modeling

The watershed modeling begins with the calculation of air concentrations and deposition rates over the watershed, as well as loading rates of each mercury species to the watershed. The different sources of loadings to the watershed that are modeled consist of direct wet and dry deposition and gaseous diffusion of divalent and elemental mercury to the watershed.

The watershed modeling component of IEM-2M then calls for the simultaneous solution of three differential equations (one for each mercury species) to calculate mercury concentrations in watershed soil. The terms in the differential equations were simplified by performing intermediate calculations, resulting in the simplified differential equations shown below:

$$dC_{s1}/dt = 1.92\text{x}10^{-6} + 9.13\text{x}10^{-3}\ (C_{s2}) - 88\ (C_{s1})$$
$$dC_{s2}/dt = 2.69\text{x}10^{-4} + 0.913\ (C_{s3}) - 0.030\ (C_{s2})$$
$$dC_{s3}/dt = 0.018(C_{s2}) - 0.92(C_{s3})$$

where:

C_{s1} = Elemental mercury concentration in watershed soil (g/m^3)
C_{s2} = Divalent mercury concentration in watershed soil (g/m^3)
C_{s3} = Methyl mercury concentration in watershed soil (g/m^3)

These differential model equations were then programmed into Scientific Workplace® and solved. The output of the watershed modeling effort produced watershed soil concentrations for the three mercury species for the specified time period evaluated (30 years for this application).

Waterbody Modeling

The waterbody modeling begins with the calculation of air concentrations and deposition rates over the river, as well as loading rates of each mercury species to the river. Five different sources of loadings to the river are modeled: direct deposition onto the waterbody, runoff from impervious surfaces, runoff from pervious surfaces, soil erosion, and gaseous diffusion to the waterbody. The watershed soil concentrations calculated above are used to calculate two of the waterbody loading rates, runoff load from pervious surfaces and soil erosion load.

The next waterbody modeling step is the simultaneous solution of six differential equations (one for each mercury species) in order to calculate mercury concentrations in the water column and sediment. Similar to the watershed modeling, intermediate calculations were performed to simplify the terms present in the six differential equations. The final series of differential equations resulting from this process are presented below:

$$dC_{wt1}/dt = 2.39\text{x}10^{-8} + 8.24\text{x}10^{-4}\,(C_{s1}) + 2.74\,(C_{wt2}) - 104\,(C_{wt1}) + 2.28\text{x}10^{-3}\,(C_{bt1})$$
$$dC_{wt2}/dt = 5.02\text{x}10^{-6} + 1.76\text{x}10^{-4}\,(C_{s2}) + 5.48\,(C_{wt3}) - 99.1\,(C_{wt2}) + 1.59\text{x}10^{-3}\,(C_{bt2})$$
$$dC_{wt3}/dt = 3.07\text{x}10^{-8} + 2.59\text{x}10^{-4}\,(C_{s3}) + 0.365\,(C_{wt2}) - 100\,(C_{wt3}) + 2.25\text{x}10^{-3}\,(C_{bt3})$$
$$dC_{bt1}/dt = 60.4\,(C_{wt1}) + 3.65\text{x}10^{-4}\,(C_{bt2}) - 0.652\,(C_{bt1})$$
$$dC_{bt2}/dt = 3.57\text{x}10^{+3}\,(C_{wt2}) + 0.73\,(C_{bt3}) - 0.635\,(C_{bt2})$$
$$dC_{bt3}/dt = 3.35\text{x}10^{+3}\,(C_{wt3}) + 0.0365\,(C_{bt2}) - 1.38\,(C_{bt3})$$

where:

C_{wt1} = Total elemental mercury concentration in water column (mg/L or g/m^3)
C_{wt2} = Total divalent mercury concentration in water column (mg/L or g/m^3)
C_{wt3} = Total methyl mercury concentration in water column (mg/L or g/m^3)
C_{bt1} = Total elemental mercury benthic layer sediment concentration (g/m^3)
C_{bt2} = Total divalent mercury benthic layer sediment concentration (g/m^3)
C_{bt2} = Total methyl mercury benthic layer sediment concentration (g/m^3)

The differential model equations were programmed into Scientific Workplace® and solved. The output of the waterbody modeling effort produced total water column concentrations as well as total benthic sediment concentrations in the river.

IEM-2M Model Results

A summary of the IEM-2M model results for the river is shown in Table I. These results include watershed soil concentrations, total concentrations in the water column and total benthic sediment concentrations.

The IEM-2M model results can be incorporated into the risk assessment framework defined by the 1998 *Risk Assessment Protocol*. This requires calculating dissolved phase waterbody concentrations from the IEM-2M model results and then using these concentrations in place of the dissolved waterbody concentrations calculated according to the *Risk Assessment Protocol*. Dissolved phase waterbody concentrations can be calculated from the IEM-2M total waterbody concentrations, as shown in Table I, using a standard partitioning model presented by USEPA (12), sediment:water partition coefficients and suspended sediment concentrations.

COMPARISON OF MODEL RESULTS

This paper illustrates an application of a more refined USEPA model for mercury than is currently embodied in the 1998 *Risk Assessment Protocol*. The difference in results from

Table I. Results From Application of the IEM-2M Model for a River

Parameter	Value	Units	Basis
1. IEM-2M Model Output for a River (a)			
Concentrations in watershed soil			
$C_{s,1}$ (30) - elemental	7.10E-07	g/m^3	IEM-2M Model output
$C_{s,2}$ (30) - divalent	6.66E-03	g/m^3	IEM-2M Model output
$C_{s,3}$ (30) - methyl	1.26E-04	g/m^3	IEM-2M Model output
Total concentrations in water column			
$C_{wt,1}$ (30) - elemental	2.29E-09	mg/L	IEM-2M Model output
$C_{wt,2}$ (30) - divalent	7.03E-08	mg/L	IEM-2M Model output
$C_{wt,3}$ (30) - methyl	2.59E-09	mg/L	IEM-2M Model output
Total benthic sediment concentrations			
$C_{bt,1}$ (30) - elemental	8.76E-06	g/m^3	IEM-2M Model output
	1.17E-04	mg/kg DW	Calculated (b)
$C_{bt,2}$ (30) - divalent	4.82E-04	g/m^3	IEM-2M Model output
	6.43E-03	mg/kg DW	Calculated (b)
$C_{bt,3}$ (30) - methyl	7.57E-05	g/m^3	IEM-2M Model output
	1.01E-03	mg/kg DW	Calculated (b)
2. Calculated Dissolved Concentrations Based on IEM-2M Model Output			
Dissolved elemental mercury in water column	2.28E-09	mg/L	(Total elemental mercury water column concentration, $C_{wt,1}$) / **{** 1 + (suspended sediment:water partition coefficient for elemental Hg, K_{dw} * abiotic solids concentration in the water column, S_w * 1E-6) + (suspended biotic solids:water partition coefficient for elemental Hg, K_{Bio} * biotic solids concentration in the water column, S_{Bio} * 1E-6) **}** (5,12)
Dissolved divalent mercury in water column	5.03E-08	mg/L	(Total divalent mercury water column concentration, $C_{wt,2}$) / **{** 1 + (suspended sediment:water partition coefficient for divalent Hg, K_{dw} * abiotic solids concentration in the water column, S_w * 1E-6) + (suspended biotic solids:water partition coefficient for divalent Hg, K_{Bio} * biotic solids concentration in the water column, S_{Bio} * 1E-6) **}** (5,12)
Dissolved methyl mercury in water column	1.51E-09	mg/L	(Total methyl mercury water column concentration, $C_{wt,3}$) / **{** 1 + (suspended sediment:water partition coefficient for methyl Hg, K_{dw} * abiotic solids concentration in the water column, S_w * 1E-6) + (suspended biotic solids:water partition coefficient for methyl Hg, K_{Bio} * biotic solids concentration in the water column, S_{Bio} * 1E-6) **}** (5,12).

(a) Concentrations were calculated for a 30-year time period of emissions.

(b) Dry weight sediment concentrations were calculated as follows: (total benthic concentration g/m^3 / sediment density dry weight 75,000 g/m^3 from *MRTC*) * 1,000 g/kg * 1,000 mg/g .

these two modeling methods can be substantial. Table II presents the results of the IEM-2M model application for the river described in this paper alongside the results that were obtained for the same waterbody using the *Risk Assessment Protocol* algorithms. The water column concentrations for divalent mercury were roughly four times lower for IEM-2M compared to the *Risk Assessment Protocol*. The water column concentrations for methyl mercury were roughly 20-26 times lower using IEM-2M compared to the *Risk Assessment Protocol*. Benthic concentrations of divalent mercury were about two times lower using IEM-2M. Benthic concentrations of methyl mercury, in contrast, were 10 times higher using IEM-2M compared to the *Risk Assessment Protocol*.

DISCUSSION AND CONCLUSIONS

The method used to calculate fish tissue concentrations from dissolved phase waterbody concentrations differs substantially between the *MRTC* and the 1998 *Risk Assessment Protocol*. The *MRTC* (6,7) specifies that dissolved methyl mercury concentrations in the water column should be combined with methyl mercury fish tissue bioaccumulation factors (BAFs) to calculate fish tissue concentrations. The 1998 *Risk Assessment Protocol*, in contrast, specifies that the dissolved phase concentrations for methyl mercury *and* divalent mercury should be summed first and then combined with the methyl mercury BAF. Combining a methyl mercury BAF with a divalent mercury water concentration is inconsistent with common risk assessment practice. However, the justification for adding divalent and methyl mercury concentrations presumably has some link to uncertainties inherent in the static default assumptions regarding mercury transformations in the *Risk Assessment Protocol*. By using the more refined IEM-2M model to calculate species-specific mercury water column concentrations, not only are the limitations of the *Risk Assessment Protocol* mitigated but fish tissue concentrations can be more appropriately calculated solely on the basis of methyl mercury water column concentrations. This refinement can have a significant impact on incinerator risk assessment results for the fish ingestion exposure pathway. In this study, the IEM-2M model, in conjunction with *MRTC* methods, produced fish tissue concentrations, and associated fish ingestion risks, more than 100 times lower than calculated using the methods presented in the *Risk Assessment Protocol*.

Future efforts are needed to improve the feasibility and regulatory acceptability of applying more refined models in waste incinerator risk assessments, including modeling mercury in waterbodies. An important element in any future effort will be validation of the IEM-2M model in both lake and stream/river water systems. In addition, USEPA's IEM-2M model should be programmed into a readily accessible platform for use in incinerator risk assessments. Although modeling uncertainties affect the IEM-2M model, it still presents a substantial improvement over the default *Risk Assessment Protocol* methods.

Table II. Comparison of IEM-2M Model Results and
Results from USEPA's 1998 Risk Assessment Protocol for a River

Parameter	IEM-2M Model Result	1998 Risk Assessment Protocol Result
Water Column Concentrations		
Total divalent mercury concentration	7.0E-8 mg/L	2.7E-7 mg/L
Total methyl mercury concentration	2.6E-9 mg/L	5.1E-8 mg/L
Dissolved divalent mercury concentration	5.0E-8 mg/L	2.1E-7 mg/L
Dissolved methyl mercury concentration	1.5E-9 mg/L	3.9E-8 mg/L
Benthic Sediment Concentrations		
Total concentration in benthic sediments for divalent mercury	6.4E-3 mg/kg DW	1.0E-2 mg/kg DW
Total concentration in benthic sediments for methyl mercury	1.0E-3 mg/kg DW	1.2E-4 mg/kg DW

DW = dry weight.

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