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Mercury Pollution in Natural Waters

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ABSTRACT

The focus of this thesis is to 1) investigate the sources of mercury pollution in aquatic systems, 2) compare various remedial techniques for mercury contamination in aquatic systems, and 3) use a modeling tool to simulate the transport and transformation of mercury in a lake system, coupled with remediation techniques.

Mercury is a well-known environmental pollutant. It can bioaccumulate through food chains and reach its highest level in fish. Mercury in fish is detrimental to various human organs, and it is especially dangerous to the brain development of the human embryo and fetus. Thus, an extensive study of mercury pollution in aquatic systems is of great importance.

This thesis consists of two parts. Part I provides a literature review on various sources of mercury pollution in aquatic systems and the role of three remedial technologies to remediate mercury pollution: dredging, capping, and natural attenuation. Part II deals with a case study of mercury pollution in which a modeling tool (Water Quality Analysis Simulation Program 6.0) has been applied to simulate the transport and transformation of mercury in Onondaga Lake, New York.

Result from this thesis shows that the most important anthropogenic sources of mercury pollution in aquatic systems are: atmospheric deposition, erosion, urban discharges, agricultural materials, mining, combustion and industrial discharges. For a specific site, some of these sources may play more important roles than others. Dredging, capping, and natural attenuation are three remedial techniques investigated in this thesis. Based on field and laboratory studies, capping can be an economical and effective method for mercury remediation. Though expensive, dredging is very effective for heavily polluted systems. However, sediment resuspension, due to dredging, needs to be carefully considered. Natural attenuation is less effective, but more environmentally friendly and economical.

Modeling tools to simulate mercury transport and transformation are promising. In this study, mercury concentrations and distributions in Onondaga Lake, N.Y., were predicted quite well by WASP 6.0. Considering no reduction of mercury loading in this lake system, capping and dredging are more effective remedial methods than natural attenuation for this lake.

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CHAPTER I

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Title: **Sources and Remediation for Mercury Contamination in Aquatic Systems - A Literature Review**

1.1 Abstract

Sources of mercury contamination in aquatic systems were studied in a comprehensive literature review. The results show that the most important anthropogenic sources of mercury pollution in aquatic systems are: (1) atmospheric deposition, (2) erosion, (3) urban discharges, (4) agricultural materials, (5) mining, and (6) combustion and industrial discharges. Capping, dredging, and natural attenuation are three possible remedial approaches to mercury contamination in aquatic systems. Capping seems to be an economical and effective remedial approach to mercury-contaminated aquatic systems. Dredging is an expensive remedial approach. However, for heavily polluted systems, dredging may be more effective. Natural attenuation, involving little or no cost, may be applied to less contaminated sites. Proper risk assessment is necessary to evaluate the effectiveness of remedial methods and their potential adverse environmental effects. Modeling tools have a bright future in the remediation of mercury contamination in aquatic systems. Existing mercury transport and transformation models were reviewed and compared.

Keywords: Mercury; Aquatic Systems; Remedial; Sources; Contamination; Sediment; Capping; Dredging; Natural Attenuation; Modeling.

1.2 Introduction

Mercury is a hazardous environmental contaminant. In Japan, in the 1970s thousands of people were affected and even died because of Minamata Disease, caused by elevated mercury pollution from a chemical plant (Kudo and Miyahara, 1991). Toxicology studies also proved that mercury, especially methyl mercury (MeHg), is very toxic to the human embryo and fetus (Bakir et al., 1973; Amin-Zaki et al., 1976; Harada et al., 1995). MeHg is the most toxic form of mercury. In aquatic systems, bioaccumulation through food chain may cause high levels of mercury contamination in fish from even very low concentrations of MeHg in water.

In aquatic systems, mercury exists in elemental, inorganic, and organic forms. Elemental mercury (Hg^0) is the only metal in liquid form at room temperature. It has high volatility and relatively low water solubility (Lindqvist and Rodlhe, 1985). Aqueous inorganic mercury has two valences, +1 and +2. Mercury with valence +2 is more widely spread in the environment (Loux, 1998). In most mercury studies, HgII is used as a substitute for inorganic mercury. HgII consists of both Hg^{2+} free ions and Hg^{2+} complexes. Chloride, hydroxide, sulfide, dissolved organic matter (DOM), and other chemicals are found in Hg^{2+} complexes (Morel et al., 1998). Aqueous organic mercury may be placed in two categories: (1) covalently-bonded organomercurials, such as MeHg and dimethyl mercury (dimethyl mercury being less important than MeHg in mercury transport and transformation), and (2) mercuric complexes with organic matter, such as humic substances (Gill and Bruland, 1990). Mercury can either be dissolved or remain in a particulate state in aquatic systems. It is believed that suspended organic matter plays an important role in whether mercury is dissolved or remains in a particulate state (Meili, 1997).

In the Mercury Study Report to Congress (USEPA, 1997), sources of mercury emissions were placed in three categories: natural, anthropogenic, and re-emitted sources. Mercury re-emission is the remobilization of settled mercury. The estimated global anthropogenic mercury emissions are 1,913 metric tons in 1995 (Pacyna and Pacyna, 2002). This value is slightly lower than that from 1990 to 1995 (Pacyna and Pacyna, 2002). The amount of mercury emitted into the atmosphere through natural and re-emitted sources was estimated to be between 1,500 and 2,500 metric tons per year in the late 20th century (Nariagu, 1989; Nariagu, 1990).

Mercury is persistent in the environment. Effective remedial methods need to be taken to lower mercury levels in heavily mercury-polluted aquatic systems. Capping and dredging are two widely used active remedial solutions for contaminated sediment in aquatic systems. Dredging is the process used to recover reasonable water circulation and remove benthic sediment (Barbosa and Soares de Almeida, 2001). Capping, especially *in-situ* capping, is the process of placing a layer of proper isolating materials (*e.g.*, sand) between the layer of contaminated sediment and overlying water (Palermo, 1998). Natural attenuation is the mitigation of contamination by naturally occurring processes (Khan and Husain, 2002). It is an economical and passive remedial method if there are no serious adverse environmental effects on the aquatic systems. No matter what kinds of remedial solutions are applied, proper risk assessment is necessary before remediation, in order to evaluate and prevent the potential adverse effects on the environment.

Using modeling tools to simulate mercury transport and transformation in the environment and direct the implementation of remedial solutions for mercury-contaminated sites is a critical component of such remedial strategies. However, modeling for mercury transport and transformation in aquatic systems is a complex problem, because many processes need to be considered, such as hydrodynamic and sediment processes, mercury transport and chemical reactions and transformations.

1.3 Sources of Contamination

Natural and re-emitted mercury emissions into the atmosphere are very important factors in the mercury cycle. The major naturally occurring mercury emission processes include: (1) degassing from mercury mineral deposits, (2) degassing from mercury contaminated aquatic and terrestrial systems (through reduction of Hg^{2+} to Hg^{0}), (3) volcanic emissions, and (4) forest fires (Nariagu, 1989; Lindqvist et al., 1991; Nariagu, 1994; Camargo, 2002). The mediterranean region has significant amounts of mercury mineral deposits (Bailey et al., 1973). The natural emissions of mercury were estimated to be 110 metric tons per year in that region (Pirrone et al., 2001). It is suggested that 590-930 metric tons of mercury are emitted annually from biomass burning (*e.g.*, forest fires) all over the world (Brunke et al., 2001). One important characteristic of natural and re-emitted mercury emissions is their nonpoint and wide range distributions, compared to those from anthropogenic sources. Therefore, it is difficult to estimate the emission amount accurately and apply efficient control methods.

Mercury emissions from anthropogenic sources were estimated to be 1,913 metric tons worldwide in 1995 (Pacyna and Pacyna, 2002). This estimate is slightly lower than the estimation value of 2,217 metric tons for 1990 (Pirrone et al., 1996). However, it is important to note that the estimate for 1995 does not include mercury release from gold production (Pacyna and Pacyna, 2002). The anthropogenic emission sources of mercury result from: (1) solid waste incineration (municipal and medical wastes), (2) coal and oil combustion, (3) pyrometallurgical processes (iron, lead, and zinc), (4) production of mercury and gold, and (5) other sources (Pirrone et al., 1996; Pai et al., 2000). Among these sources, coal combustion, and solid waste incineration account for more than half of the total global emissions (Pirrone et al., 1996). In the 1995 estimate of worldwide emissions, about half of the total emissions were from Asia (mostly from China, India, North and South Korea) (Pacyna and Pacyna, 2002).

In our study, the sources of mercury contamination in aquatic systems are placed in six categories: (1) atmospheric deposition, (2) erosion sources, (3) urban discharges, (4) agricultural sources, (5) mining discharges, and (6) combustion/industrial discharges.

1.3.1 Atmospheric Deposition

Mercury exists in the atmosphere in gaseous, particulate, and aqueous (*i.e.*, attached to water droplets) forms, but atmospheric mercury is mostly gaseous (Schroeder et al., 1991). About 80% of total mercury (Hg_T) in the atmosphere is in Hg^0 gaseous form (Lindqvist and Rodlhe, 1985). Due to its high volatility, Hg^0 could remain in the atmosphere for more than one year (Lindqvist and Rodlhe, 1985; Slemr and Langer, 1992), which makes long-range atmospheric transport of Hg^0 a major environmental concern. Although gaseous mercury is the predominant form in the atmosphere, particulate phase mercury can have a significant impact on atmospheric mercury deposition (Keeler et al., 1995).

Oxidation processes (*e.g.*, photochemical reactions) transform Hg^0 into HgII in the atmosphere. It is believed that these processes take place mostly at the interface of aerosols and atmospheric water droplets (Lindqvist and Rodlhe, 1985). Compared to Hg^0, HgII in the atmosphere tends to precipitate faster into surface terrestrial and aquatic systems (Venkataraman, 2000).

Studies performed throughout the world strongly support the theory that atmospheric deposition is an important (sometimes even the predominant) source of mercury contamination in aquatic systems (Hermanson, 1993; Locotte et al., 1995; Hermanson, 1998; Tan et al., 2000; Dominguez et al., 2001; Guentzel et al., 2001; Lacerda et al., 2002; Landis et al., 2002; Bindler, 2003). Some measurements and estimates of atmospheric mercury deposition are listed in Table 1:

Table 1. Atmospheric Deposition Flux around the World

Location	Flux (:g m^{-2} yr^{-1})	References
Global Average	15.8	Mason et al. (1994)
Canadian Arctic	18	Hermanson (1998)
Florida, USA	21.5	Guentzel et al. (2001)
Guizhou, China[a]	937	Tan et al. (2000)
Sweden	5-30	Bindler (2003)

[a] Accounts for 12% of total global anthropogenic mercury emissions.

Concentrations of mercury in the atmosphere and flux of mercury deposition vary with the seasons (Mason et al., 2000; Guentzel et al., 2001). In Florida, mercury concentrations in rainfall double or triple in summer, compared with the rest of the year (Guentzel et al., 2001). Because of the Florida summer increase in rainfall, the total mercury deposition flux there is 5 to 8 times higher than its drier season value (Guentzel et al., 2001). The study performed in Maryland also suggests that atmospheric mercury deposition is greatest in summer and least in winter (Mason et al., 2000).

Atmospheric mercury deposition is a complex problem. Different factors, which are site-specific, may influence the transport and transformation of this metal in the atmosphere. Plants absorb atmospheric mercury through their foliage. Then mercury is passed into terrestrial systems and watersheds by litterfall. Forested watersheds can have atmospheric mercury deposition flux twice as high as unforested watersheds (Kolka et al., 1999). Wind is an important factor in atmospheric mercury transport. In the 1990s, the atmosphere in Changchun, China, was significantly polluted by wind-driven soil particles. Approximately 24% of atmospheric particulate mercury was from these wind-driven particles (Fang et al., 2001). Moisture content also has a significant influence on atmospheric mercury transport and transformation (Lindqvist and Rodlhe, 1985). High moisture content may increase the oxidation of Hg^0 substantially (Lindqvist and Rodlhe, 1985). As a result, atmospheric mercury quickly settles into terrestrial or aquatic systems.

Industrial activities have increased atmospheric mercury levels quite significantly since the start of the industrial period. Researchers throughout the world have found that modern deposition flux is 3 to 24 times higher than preindustrial flux (Swain et al., 1993; Hermanson, 1998; Heyvaert et al., 2000; Bindler, 2003). It is estimated by Fitzgerald et al. (1998) that the current global industrial atmospheric deposition rate is about 4 times higher than the preindustrial value, which was 0.37 ng cm^{-2} yr^{-1}. Other researchers suggest that the current global industrial value may be even more than 4 times the preindustrial value (Heyvaert et al., 2000; Bindler, 2003). In Sweden, it is estimated that modern deposition flux is at least 10 times higher than the preindustrial flux (Bindler, 2003). Research performed in the southwestern United States suggests that modern flux is 24 times higher than preindustrial deposition rate (Heyvaert et al., 2000).

1.3.2 Erosion Sources

Erosion of mercury contaminated soil is a very important source of mercury contamination in aquatic systems. Surface runoff from rain or snow brings the contaminated soil together with mercury already in the soil into adjacent water systems. Furthermore, human activities, such as tillage and logging, make soil subject to erosion. Thus, surface runoff can carry large amounts of contaminated soil into nearby aquatic systems. For example, due to serious human deforestation, surface runoff in the amazon area in Brazil brings about 200-4600 :g/m^2/yr of mercury from soil into nearby aquatic systems (Roulet et al., 1999).

Large amounts of particulate mercury in aquatic systems are released from river bed and bank erosion. In the St. Lawrence River in Canada, about 1.4 kmol mercury is released from the erosion of river beds and banks each year. This erosion is the major source of particulate mercury contamination in this Canadian river (Quémerais et al., 1999). Flooding also brings significant amounts of mercury into aquatic systems. A devastating flood, carrying about 1,400 kg of mercury into the Lahontan Reservoir, occurred in Nevada in 1997 (Carroll and Warwick, 2001). It should be noted that gaseous mercury can be emitted from contaminated soil and then enter, or re-enter, the atmospheric mercury cycle. An experiment in Germany suggests a 43±5 ng/m^2/hr emission rate of mercury from mercury contaminated soil (Wallschlager et al., 2002). It is also very possible that surface soil mercury may leak into underground waters.

The cause of mercury contamination in surface soil may be due to: (1) deposition of atmospheric mercury, (2) agricultural activities, (3) usage of sludge-amended soil, (4) natural degradation of ferrallitic soils due to podzolization, and (5) other reasons. The deposition of atmospheric mercury was presented in the previous section, and the agricultural sources will be discussed in the following section. Municipal sewage sludge is widely recycled to amend soil. In the early 1980s, soil, amended by municipal sewage sludge, was used each year in the United States and Europe to cover areas greater than 6.2×10^3 km^2 (Dam Kofoed, 1983). The sludge-amended soil in Tennessee contains 7.3 :g/g of mercury (Carpi, 1997a). Moreover, natural mercury forms complexes with iron oxyhydroxides during the pedogenetic processes, and this mercury may be released after the iron oxyhydroxides decompose (De Oliveira et al., 2001).

It is estimated that approximately 95% of anthropogenic mercury emitted into the environment is finally deposited in land areas (USEPA, 1997). Depending on the geochemistry and soil composition, different reactions may take place after mercury enters the land areas. Generally, mercury tends to associate with organic chemicals (such as humic substances) and inorganic iron oxyhydroxides in the soil (Kerndorf and Schnitzer, 1980; De Oliveira et al., 2001).

1.3.3 Urban Sources

Human activities may break the natural mercury cycle, and significantly increase the release of mercury into the environment. The Tapajós, one major tributary of the Amazon River, suffers elevated mercury concentrations in the water, the benthic sediment, and fish (Roulet et al., 2000). Road construction, domestic sewage discharge, mining, agricultural, and other activities began increasing in that area in the 1960s. These activities are believed to be responsible for the current mercury contamination problem (Kohlhepp, 1984). Mercury concentration in the sediment supports this hypothesis, because the mercury accumulation rate suddenly rose after the 1960s, when these human activities increased in that region (Roulet et al., 2000).

Vegetation can effectively reduce erosion. Tillage, logging, deforestation, and other activities cause loss of vegetation and greater soil erosion. These activities play an important role in the mercury cycle, because mercury contaminated soil is carried into the nearby aquatic systems more easily by surface runoff. For example, 20% of the forest area in eastern amazon was lost in three years from intensive deforestation (Aula et al., 1995), thereby increasing surface runoff and mercury soil erosion.

Discharge of domestic sewage into aquatic systems without proper treatment also increases aqueous mercury concentrations. Research conducted in the Canadian arctic region shows that mercury levels in Annak Lake and Imitavik Lake were almost the same before domestic sewage was discharged into one of them. Two decades later, mercury concentration in Annak Lake receiving sewage discharge was 15 times higher than that in Imitavik Lake receiving no sewage discharge (Hermanson, 1998).

1.3.4 Agricultural Sources

Pesticides and fungicides with mercury content were widely used in agriculture for a long time. This resulted in high concentrations of mercury in intensively cultivated soil. Estimated by Smart (1968), 2100 metric tons of mercury were used in agriculture in the 1960s throughout the world, with 1600 metric tons used in Japan alone. Due to their toxic properties, these pesticides and fungicides have been banned in many countries. As an example, these chemicals were banned in the United States in the 1970s.

Although use of pesticides and fungicides containing mercury is restricted now, they have already been widely distributed in many countries. Because of the strong persistence of mercury in the environment, mercury released long ago may still lead to serious contamination problems. In Mississippi, an agricultural region cultivated long ago shows elevated concentrations of mercury in soil, sediment, water, and fish samples (Knight and Cooper, 1996; Cooper and Gillespie Jr, 2001). The topsoil in a sample watershed measured 55.10 :g/kg of mercury. This topsoil is probably the major source of mercury contamination in that area (Cooper and Gillespie Jr, 2001).

1.3.5 Mining Sources

Mining activities have emitted historically significant amounts of mercury into the environment. The important mining sources include gold, silver, mercury, and lead mines. Small-scale gold mining is the most recent noticeable source of mercury emissions from mining activities.

From the 1980s through the early 1990s, small-scale gold mining was very popular in the amazon region of Brazil. The amalgamation method was generally used in these mines, which resulted in a significant release of mercury vapors into the atmosphere. Furthermore, in the amalgamation process, mercury remains in the processing water (Nariagu, 1993; Lacerda, 1997). Thus, discharging the processing water further increases mercury contamination in the environment. Many research studies suggest that the amazon region has a serious mercury contamination problem caused by these small-scale gold mining activities (Martinelli et al., 1988; Delacerda et al., 1989; Lacerda et al., 1991; Branches et al., 1993).

Drainage from mercury mines is also an environmental concern. Field studies suggest that mercury mine drainage contains high concentrations of inorganic mercury, MeHg, and sulfate. Elevated concentrations of sulfate (around 1000 mg/l) in mercury mine drainage favor the growth of sulfate reducing bacteria (SRB), which are mediators of mercury methylation (Rytuba, 2000). Thus, it is believed that mercury mine drainage has a high methylation rate (Rytuba, 2000).

In addition to gold and mercury mining activities, silver mining processes also emitted a large quantity of mercury into the environment. In South America, silver mining activities released approximately 400 metric tons of mercury into the environment each year from the late 16th century through the early 20th century (Aula et al., 1995).

Pribram, a Czech Republic town close to Prague, is historically active in lead mining and smelting. Throughout this town, samples of topsoil averaged about 0.36 :g/g of mercury, which was approximately 7 times higher than the background concentration (Rieuwerts and Farago, 1996). In the vicinity of the smelter and the center of the mining area, mercury concentrations were about 2 :g/g, which was almost 40 times higher than the background concentration (Rieuwerts and Farago, 1996).

Because of the persistence of mercury in the environment, historical mercury emitted from mining sources is still a serious environmental concern to surrounding areas. In Nevada, Hg_T concentration in a creek was 40-60 times higher than that in surrounding areas (Lyons et al., 1998). Because other sources of mercury contamination were insignificant, it is suggested that historical gold and silver mining activities dating back to the 19th century are responsible for the mercury contamination problem (Lyons et al., 1998). In Oregon, most mining activities began and ended before World War II. Mercury contamination in the downstream sediment of an inactive gold mine is still 2-20 times higher than that in the surrounding areas (Hygelund et al., 2001).

Mercury mining was active in southwestern Alaska from the 1900s until 1970 (Gray et al., 2000). Recent Hg_T concentrations in stream sediment averaged over 1000 :g/g, which is 1000 times higher than the background mercury level (Gray et al., 2000).

Based on these studies, it is believed that old inactive mines, some of which are over 100 years old, still pose an environmental threat to adjacent aquatic systems. Therefore, proper waste management is necessary.

1.3.6 Combustion and Industrial Sources

Combustion and industrial sources are important sources of mercury emission into the environment. In the United States, it is estimated that about 97% of total anthropogenic mercury emissions come from combustion and industrial sources (USEPA, 1997). Important combustion fuels include coal, waste, and oil. Major combustion devices include utility combustors, waste incinerators, industrial boilers, and residential combustors (USEPA, 1997). Mercury from combustion sources usually first enters the atmosphere. Then some of it settles in nearby water or land. The rest remains in the atmosphere and becomes part of the regional or global atmospheric mercury cycle.

On the global scale, Asia (especially China and India) accounts for about 50% of total anthropogenic mercury emissions (Pacyna and Pacyna, 2002). Combustion of coal as an energy source is the major source of mercury emissions in Asia (Want et al., 2000; Pacyna and Pacyna, 2002). In China, coal contains an average of 0.22 mg/kg of mercury, of which approximately 70% is emitted into the environment during combustion (Wang et al., 2000). It is also noteworthy that coal combustion comprises almost 50% (79 metric tons annually) of total anthropogenic mercury emissions (158 metric tons annually) in the United States (USEPA, 1997).

In municipal waste, mercury comes from the disposal of mercury-containing products, such as batteries, fluorescent bulbs, and paints (Carpi, 1997b). The efficiency of removing mercury by municipal waste incineration is generally quite low, from 30-45% (Chang et al., 2000). It is estimated that, in the United States, the release of 43 metric tons of mercury from municipal waste incineration is about 30% of the total mercury emissions per year (USEPA, 1997).

Various industrial sectors have been important sources of mercury emission. Historically, chemical plants were a major pollution source. Baikal polygon is a heavily industrialized region in Siberia, which suffers a serious mercury contamination problem (Yagolnizer et al., 1995). In this region before 1998, a chemical plant using mercury cathodes discharged wastewater highly polluted with mercury into adjacent aquatic systems. The maximum mercury concentration detected in the effluents was 0.05 mg/l, even after purification (Koval et al., 1999). In Europe in the 1980s, about 18% of total anthropogenic emissions into the atmosphere was from chlor-alkali plants (Pacyna and Munch, 1991). Due to stricter regulations, emissions from chlor-alkali plants have dropped significantly (Pacyna and Pacyna, 2002). In the Middle East, it is estimated that 22 metric tons of mercury were released into Haifa Bay, Israel, from a chlor-alkali plant from 1956 through the early 1990s (Krom et al., 1994). However, the technology of removing mercury in wastewater, contaminated by chlor-alkali plants, was significantly improved in 1976. As a result, mercury-contaminated wastewater discharged into the bay in 1978 was reduced to about 2% of that in 1975 (Krom et al., 1994).

Metal production and recovery sectors have emitted large amounts of mercury into the environment. In Ontario, Canada, mercury from metal recovery (such as iron, steel, lead, and zinc) is the single largest environmental contamination source. From this source alone, approximately 6.8 metric tons of mercury contaminate the environment each year (Innanen, 1998). On a larger scale, Canada emits about 24 metric tons of mercury each year from metal production and recovery sectors. This source is, by far, the most important point source of anthropogenic mercury emissions in Canada (Innanen, 1998).

All over the world, other important industrial sources of mercury emissions into the environment include the manufacture of cement, electrical apparatus, pulp and paper, thermometers, and fluorescent lamps (Beim and Grosheva, 1992; Moreira and Pivetta, 1997; USEPA, 1997).

1.4 Remedial Actions for Mercury Contamination

Mercury is persistent in the environment. Mercury emissions into the environment have been lessened in recent years. Nevertheless, historically emitted mercury, adsorbed mainly by sediment, is still a dangerous threat to aquatic organisms, animals and even humans.

Even if source control of contaminated wastewater is achievable, it may still take a very long time, perhaps centuries, for mercury-contaminated aquatic systems to reach relatively safe mercury levels in both water and surface sediment naturally (Miserocchi et al., 1993; Krom et al., 1994). It may take even longer to reduce mercury levels in deep sediment. Due to human activities or natural processes, *e.g.*, hydrodynamic flows, bioturbation, molecular diffusion, and chemical transformation, the buried mercury can be remobilized into the overlying water. This is one of the major concerns about mercury contamination.

Thus, proper environmental management procedures should be applied to lower mercury levels in mercury-contaminated water systems. Source control, contaminated sediment remediation, or their combination, are the usual options for cleaning up mercury contaminated sites. In general, four kinds of treatments of contaminated sediment are available: (1) *in-situ* containment, (2) *in-situ* treatment, (3) *ex-situ* containment, and (4) *ex-situ* treatment (Palermo, 1998). Sediment containment does not decompose the contaminants, but only separates them from the overlying water. On the other hand, sediment treatment processes involve contaminant removal or degradation.

Capping is widely used to contain sediment, whereas dredging can either contain or treat sediment, or both. Natural attenuation is contamination reduction by naturally occurring processes. In natural attenuation, no containment or treatment measures are applied to contaminated systems.

1.4.1 Capping

In-situ capping (ISC) is on site placement of proper covering material over contaminated sediment in aquatic systems. In *ex-situ* capping (ESC), contaminated sediment is dredged and relocated to another site, where one or multiple isolating layers are placed over the sediment (Palermo, 1998; Liu et al., 2001). ESC is a combination of dredging and capping. In ESC, capping is used to minimize adverse environmental effects at the disposal site after sediment is dredged at the original *in-situ* site.

Laboratory research suggests that ISC can be effective in reducing mercury contamination in aquatic systems. Experimental tests show that the capping material, composed of a mixture of sand and finer particles, can adsorb mercury and other heavy metals very well (Moo-Young et al., 2001). In one test, capping material adsorbed 99.9% of mercury in concentrations at 200-500 :g/l (Moo-Young et al., 2001). This test showed that a capping layer can be a good barrier between mercury-contaminated sediment and the overlying water. More research in this area may be needed.

ISC field studies were conducted in Hamilton Harbour, Canada, which suffered significant contamination from zinc, copper, mercury, and other metals. A cap, approximately 35 cm thick and composed mostly of sand, was placed in the system to contain polluted sediment (Azcue et al., 1998). After one year of *in-situ* capping, a field study investigated the effectiveness of ISC. Except for a few cases in some sampling cores, mercury concentrations were generally low (less than 5×10^{-6} g/kg) in the capping layer, compared with 0.43-0.96 g/kg in the original sediment (Azcue et al., 1998). It should be noted that some mercury in the capping layer may be caused by deposition from the overlying water. This result suggests that a capping layer can contain mercury in the original sediment quite well. However, future studies should be conducted to prove this hypothesis conclusively.

To decide whether a contaminated aquatic system is suitable for ISC, site characterization is the preliminary and crucial step. In general, aquatic environments with low hydrodynamic flows, such as lakes and bays, are good candidates for ISC (Thoma et al., 1993). Depending on the hydrodynamic, geotechnical conditions, and target contaminants, different capping materials are used. Sand and other fine materials are good for quiescent environments (Palermo, 1998). For erosive systems, coarser materials should be considered (Palermo, 1998). It is notable that

Jacobs and Forstner (1999) proposed the idea of using active barrier systems (ABS) with ISC. ISC with ABS adsorbs target contaminants in the sediment water. Thus, ISC with ABS prevents the release of target contaminants into the overlying water more effectively than ISC alone (Jacobs and Forstner, 1999). A good candidate for applying ISC with ABS is zeolite (Jacobs and Forstner, 1999).

The major advantages of ISC are low cost, extensive suitability to a wide range of contaminants, and low adverse environmental effects (Azcue et al., 1998; Palermo, 1998). However, ISC is not a treatment process. Therefore, long-term environmental effects, including possible remobilization of contaminated sediment, need to be carefully considered. It is suggested that regular monitoring of the capped system should be carried out.

There are two major concerns about ISC: First, for various reasons (hydrodynamic flows, bioturbation, consolidation, transformation, *etc.*), buried contaminants may pass through the capping layer and enter into the overlying water. Hydrodynamic currents caused by human activities or natural processes, such as shipping, tide, and groundwater flow, may blow up the capping layer and release the contaminants into the water. For example, laboratory experiments suggest that subaqueous groundwater flow reduces the efficiency of capping significantly (Liu et al., 2001). The movement of benthic organisms may also facilitate the remobilization of buried contaminants. Sediment consolidation, due to gravity, moves contaminants from buried sediment into the capping layer. This sediment consolidation may be a more important factor in the transfer of contaminants from buried sediment into the capping layer than molecular diffusion of contaminants (Moo-Young et al., 2001). Capping materials vary in their compressibility, which affects the extent of sediment compression (Moo-Young et al., 2001). Contaminants usually are in various forms. Some forms may have a stronger tendency to attach to sediment than others. For example, mercury can be elemental, inorganic, or organic. Inorganic mercury is more likely to attach to sediment than organic mercury. Activity of inorganic mercury deep within the sediment is generally low. However, some of this inorganic mercury can be transformed into organic mercury through possibly biological processes. Organic mercury, such as MeHg, can escape into the overlying water more easily than inorganic mercury. The second major concern is that the placing of the capping layer can cause resuspension of originally settled sediment. However, a pilot test conducted in a Canadian harbor suggests that no significant sediment was resuspended by the placement of the capping layer (Hamblin et al., 2000).

Generally speaking, capping is a promising economical method for treating mercury-contaminated aquatic systems. Further studies and tests should be performed to verify and optimize this technology.

1.4.2 Dredging

Based on their objectives, there are generally four types of dredging: (1) dredging to open up clogged channels, (2) dredging to recover water depth, (3) dredging for mining purposes, and (4) environmental dredging to remove contaminated sediments (Barbosa and Soare de Almeida, 2001). Mechanical and hydraulic dredging, and their combination, are the most commonly used dredging techniques.

Dredging appears to be an effective remedy for systems heavily polluted by mercury. Minamata Bay, Japan, contained as high as 600 mg/kg of mercury in settled sediment (Hosokawa, 1993). Dredging began in 1977 and ended in 1990. Monitoring data shows that careful implementation of dredging did not cause a significant adverse impact on the environment from sediment resuspension (Hosokawa, 1993). At most sampling points, mercury concentrations were below 5 mg/kg after dredging (Hosokawa, 1993). Compared with the initial concentrations, this dredging project was very effective. Moreover, dredging caused insignificant sediment resuspension. Samples during and after dredging showed that mercury concentrations in water and fish were below the safety requirement (Hosokawa, 1993).

However, dredging activities may cause serious environmental threats if they are not well planned and implemented. Dredging-induced sediment resuspension is a major environmental concern. Given no significant disturbance, buried heavy metals, including mercury, are strongly adsorbed by sediment and can generally be regarded as safely separated from the overlying water. However, human activities (such as dredging and shipping) and natural occurrences (such as storms and tides) can remobilize sediment-adsorbed mercury.

Several research studies suggest that significant amounts of settled sediment were resuspended by dredging, and elevated turbidity was observed (Nichols et al., 1990; Vale eta al., 1998; Van Den Berg et al., 2001). Other natural occurrences and human activities, such as tides and shipping, may increase sediment resuspension in aquatic systems undergoing dredging (Vale et al., 1998). A laboratory experiment mimicking ocean dredging discovered that about 5% of MeHg and less than 1% of Hg_T was released from contaminated sediment (Bloom and

Loasorsa, 1999). It is also noteworthy that sediment pore water, which usually contains high concentrations of mercury, can readily release mercury into the overlying water (Gilmour et al., 1992).

After comparing different dredging techniques, it is suggested that a combination of mechanical and hydraulic dredging produces the least sediment resuspension (Hauge et al., 1998). Mathematical models were developed to estimate dredging costs, efficiency, and environmental effects (Hayes et al., 2000; Blazquez et al., 2001).

Another consideration is oxidation change in buried anoxic sediment. During dredging, oxygen in overlying water can enter buried anoxic sediment and possibly oxidize and release contaminants (Vale et al., 1998). The formation of MeHg, mainly in the uppermost 10 cm of benthic sediment, is insignificant in lower sediment (Gilmour et al., 1992; Bloom et al., 1998). However, after dredging, some buried sediment is mixed with surface sediment, or water, which can produce an environment of sulfate and organic matter favoring the production of MeHg (Bloom and Loasorsa, 1999). For instance, research in England shows that water discharged from dredging sites has a high concentration of organic matter, favoring the production of MeHg (Newell et al., 1999).

Laboratory experiments suggest that increased levels of some metals, such as Fe and Cd, are found in aquatic organisms during and after dredging (Vale et al., 1998). Thus, we need to carefully consider possible mercury bioaccumulation from dredging.

On the other hand, dredging of the contaminated sediment is only a temporary solution to the problem (Barbosa and Soares de Almeida, 2001). The treatment of dredged sediment is usually very costly. Therefore, confinement (disposal followed by capping) and direct disposal are more common alternatives. The two most widely used disposal sites are land and sea water (Barbosa and Soares de Almeida, 2001).

We need to be aware that the disposal of dredged sediments poses a potential threat to the surrounding environment. For example, increased turbidity and sedimentation is usually observed at the dredge disposal sites (Nichols et al., 1990). The leakage of mercury into groundwater systems from disposal sites is another concern. In Georgia, the lower Savannah River showed elevated concentrations of some metals (including mercury) in living organisms close to an upland dredge disposal site (Winger et al., 2000). Since there are no other obvious pollution sources in that area, the contamination most likely comes from the dredge disposal (Winger et al., 2000). Contaminated dredged sediment confinement is widely used to prevent potential adverse environmental effects from dredge disposal. Adjusting pH to an optimal level is a common method to immobilize heavy metals. However, this may not be enough (Muller and Pluquet, 1998). It is noteworthy that adding materials containing iron is quite effective in immobilizing some heavy metals (Cd and Zn) in dredged sediment. To the best of our knowledge, these iron-bearing materials have not been tested on mercury contaminated sediment yet. If necessary, contaminated dredged sediment should be properly treated before disposal. Sometimes, contaminated dredged sediment can be treated and reused as building materials (Roeters, 1998). In this case, the potential health and environmental effects from these materials should be carefully considered.

The very high cost of dredging is also an economic problem. It has been reported that the cost of active contaminated sediment remediation, including environmental dredging, could be as high as \$1,409/m^3 (Cushing, 1999).

In general, dredging can be very effective in cleaning up heavily mercury-contaminated sediment. This has been the case in Japan. However, it has disadvantages and concerns that need to be carefully addressed first, such as sediment resuspension, oxidation change, disposal method, and cost.

1.4.3 Natural Attenuation

Natural attenuation means contamination decrease by naturally occurring processes (Khan and Husain, 2002). Relying on natural attenuation alone, no aggressive remedial methods would be applied, and contaminated aquatic systems would be expected to recover naturally. If no serious adverse environmental effects would occur, natural attenuation may be applied to less contaminated sites.

The advantages of natural attenuation over active remedial methods include: (1) no sediment resuspension, (2) little or no cost, and (3) no change in benthic conditions (Garbaciak et al., 1998). However, contaminated systems in natural attenuation should be regularly monitored to ensure environmental safety. Natural biological (*e.g.*, microbial decomposition), physical (*e.g.*, advection, dispersion, adsorption, settling, and evaporation), and chemical (reactions) processes are major mechanisms to reduce contamination (Garbaciak et al., 1998).

Natural attenuation was applied to some aquatic systems with inorganic or organic contamination (Kao and Prosser, 2001; Lin and Puls, 2001). Experiments and field studies demonstrate possible natural attenuation of mercury contamination by reduction, demethylation, and votalization.

Two important ways to naturally reduce HgII in surface waters are photoreduction and microbial reduction. In low mercury concentrations (low picomolar range), photoreduction is more effective than microbial reduction (Amyot et al., 1997a; Amyot et al., 1997b). In high mercury concentrations (over 50 picomole), microbial reduction is more effective (Morel et al., 1998). In deep anoxic environments, certain bacteria in the presence of humic substances are reductants of HgII (Alberts et al., 1974; Morel et al., 1998).

Microbial demethylation of MeHg was observed in contaminated sediment (Oremland et al., 1995; Marvin-Dipasquale and Oremland, 1998). SRB and methanogenic bacteria are probable agents in microbial demethylation (Oremland et al., 1995). Hg_T concentration and organic substance content are important factors in microbial demethylation (Marvin-Dipasquale et al., 2000). A demethylation rate ranged from 0.02-0.5 ng/g (dry sediment) per day in a field study (Marvin-Dipasquale and Oremland, 1998). MeHg is also photodegradated in surface waters (Sellers et al., 1996). Photodegradation of MeHg seems to be a first-order reaction with respect to MeHg concentration and sunlight intensity (Sellers et al., 1996).

In aquatic systems, Hg^0 volatilization plays an important role in the natural attenuation of mercury contamination (Amyot et al., 1997c). Hg^0 is probably the end-product of some reduction processes of MeHg and HgII (Sellers et al., 1996; Amyot et al., 1997a). Due to its high volatility,

Hg^0 produced by the reduction of MeHg and HgII rapidly evaporates into the atmosphere most of the time. This evaporation is a major natural attenuation of mercury in some aquatic systems.

In the United States, field experiments in natural attenuation of mercury-contaminated aquatic systems were performed in the state of Washington. In Whatcom Waterway at Bellingham, mercury concentration in the surface sediment was about 4.5 mg/kg in the 1960s (Garbaciak et al., 1998). After source control and natural attenuation, mercury concentration in the surface sediment was reduced to about 0.5 mg/kg (Garbaciak et al., 1998).

Enhanced natural attenuation means natural decontamination, accelerated by human influences (Garbaciak et al., 1998). For example, chemicals favoring naturally existing bacteria that decontaminate certain pollutants can be introduced into contaminated aquatic systems. Enhanced natural attenuation was applied to mercury-contaminated Eagle Harbor, in the state of Washington. A thin cap (6 cm) was placed on the contaminated sediment to accelerate the sedimentation and burial effects, because the natural sedimentation process was too slow (Garbaciak et al., 1998). Compared to thick capping, this enhanced natural attenuation method of thin capping did not change the benthic environment significantly (Garbaciak et al., 1998).

However, due to the strong persistence of mercury in the environment, it may take a long time for heavily-contaminated aquatic systems to fully recover through natural attenuation. Even if zero input of mercury could be achieved, it would still take 50 years for surface sediment mercury concentrations in Haifa Bay, Israel, to reach levels less than 0.3 ppm naturally (Krom et al., 1994).

1.5 Existing Models to Simulate Mercury Transport and Transformation

Modeling tools are crucial for the remediation of mercury contamination. Simulation of mercury transport and transformation in aquatic systems is complex, involving hydrodynamic and sediment processes and mercury transport and transformation processes.

Due to the complexity of mercury transport and transformation in aquatic systems, considerable site-specific data is needed to calibrate and validate mercury transport and transformation models. In these models, data accuracy is very important. Because of limitations in analysis accuracy, mercury data reported before the 1980s should be reviewed with caution (Braga et al., 2000). Based on the type of aquatic systems that the models can simulate, mercury transport and transformation models can be placed in three categories: (1) river systems, (2) lake systems, and (3) coastal systems. Generally speaking, modeling of mercury transport and transformation in lake systems is much easier than that in river and coastal systems. The major reason is the simplicity of hydrodynamic conditions in lake systems.

Carroll et al. (2000) developed a mercury transport and transformation model for river systems by combining RIVMOD (a hydrodynamic and sediment transport model), WASP 5 (a water quality model), and MERC 4 (a kinetic subroutine for WASP 5). RIVMOD, WASP 5, and MERC 4 were all developed by the USEPA. To simplify the program, the sediment transport routine was removed from RIVMOD (Carroll et al., 2000). WASP 5 (Water Quality Analysis Simulation Program 5) is a dynamic water quality program for various aquatic systems, such as lakes, rivers, and coastal systems (Wool et al., 2002). The latest version of WASP is 6.1. Specific subroutines can easily be combined with the WASP main model to serve certain purposes. For example, a new mercury subroutine was developed for WASP 6.1 in 2002 (USEPA, 2002). In general, the mercury transport and transformation model, developed by Carroll et al. (2000), can simulate quite accurately inorganic mercury cycling in the Carson River in Nevada. MeHg is also simulated by this model. However, the simulated model performance of MeHg is not that accurate (Carroll et al., 2000). Other mercury transport and transformation models for river systems include a mercury bioaccumulation model, developed by Schultz et al. (1995), and the IEM-2M model, developed by the U.S. EPA (1997).

For lake systems, Bale (2000) developed a 2D finite element model to describe the mercury transport and transformation in Clear Lake, California. Four mercury species are simulated by the model: HgII, MeHg, Hg^0, and nonreactive mercury. Samples from seven different sites in Clear Lake were analyzed (three for calibration and four for validation), and the modeling results were quite close to field measurements (Bale, 2000). Other mercury transport and transformation models for lake systems include the OLMM model, developed by Henry et al. (1995), the QWASI model, developed by Diamond (1999), and the RMCM model, developed by Gbondo-Tugbawa and Driscoll (1998).

According to Širca et al. (1999), it is more difficult to simulate mercury transport and transformation in coastal areas than in freshwater systems, due to complex water chemistry and hydrodynamics in coastal areas. The 2D STATRIM (STAtionary TRIeste Mercury) model is a 2D mercury transport and transformation model, developed for the Gulf of Trieste by

Širca et al. (1999). This model consists of two submodels: PCFLOW2D-HD and MIKE 21 MT. PCFLOW2D-HD is a hydrodynamic model, and MIKE 21 MT is a sediment transport model. Compared with freshwater mercury models, 2D STATRIM is not as effective. In general, this model tends to overestimate mercury concentrations. Other mercury transport and transformation models for coastal systems include the ECoS model, developed by Abreu et al. (1998), and the modified PCFLOW 3D model, developed by Rajar et al. (2000).

The number of mercury transport and transformation models in the literature is quite small. Only a few models link the modeling tool with contamination remediation and predict the remedial results in benthic sediment and overlying water. Table 2 describes some existing mercury transport and transformation models:

Table 2. Models Simulating Mercury Transport and Transformation

References	Models	Purpose	Site Studied	Sampling Media	Mercury Species Targeted
River Systems					
Carroll et al. (2000)	A combination of **RIVMOD** (a hydrodynamic and sediment transport model), **WASP 5** (a water quality model), and **MERC 4** (a kinetic subroutine for **WASP 5**)	Simulate mercury transport and transformation	Carson River (Nevada)	Suspended and benthic sediment; overlying water	HgII, Hg^{o}, MeHg, Hg_T
Schultz et al. (1995)	A mercury bioaccumulation model	Assess dredging effects on fish	Kokemaenjoki River and its estuary (Finland)	Benthic sediment; overlying water; fish	MeHg, Hg_T
USEPA (1997)	**IEM-2M** (the mercury extension of Indirect Exposure Methodology-2) [a]	Simulate mercury transport and transformation in watersheds and aquatic systems	N/A	Watershed; Water	HgII, Hg^{0}, and MeHg
Lake Systems					
Henry et al. (1995)	**OLMM** (the Onondaga Lake Mercury Model: a modified model of **MERC 4** to simulate mercury transport and transformation in Onondaga Lake)	Evaluate the effects of various source controls and decontamination methods	Onondaga Lake (NewYork)	Water	Hg^{o}, MeHg, Hg_T
Diamond (1999)	**QWASI** (the Quantitative Water Air Sediment Interaction model)	Simulate mercury transport and transformation	A hypothetical lake	Benthic sediment; overlying water	HgII, Hg^{o}, MeHg, Hg_T

Table 2. Models Simulating Mercury Transport and Transformation *(Continued)*

References	Models	Purpose	Site Studied	Sample Media	Mercury Species Targeted
Lake Systems					
DisplayText cannot spa	**RMCM** (the steady-state Regional Mercury Cycling Model simulating mercury mass balance) and **FLUX** (a mathematical model simulating mercury loading)	Determine the characteristics of mercury contamination	Onondaga Lake (New York)	Benthic sediment; overlying water; fish	MeHg, Hg_T
Bale (2000)	A mathematical model involving hydrodynamic and transformation processes	Simulate mercury transport and transformation	Clear Lake (California)	Benthic sediment; overlying water	HgII, Hg^0, MeHg, Inert Hg
Coastal Systems					
Abreu et al. (1998)	**ECoS** (the Estuarine Contaminant Simulator model)	Estimate mercury contamination	Ria de Aveiro Coastal Lagoon (Portugal)	Benthic sediment; overlying water	Hg_T
Širca et al. (1999)	**2D STATRIM** (the 2D STAtionary TRIeste gulf Mercury model with two submodels: **2D MIKE21MT,** as the sediment transport model, and **PCFLOW2D-HD**, as the hydrodynamic model)	Simulate mercury transport and transformation	The Gulf of Trieste	Benthic sediment; overlying water; plankton	HgII, Hg^o, MeHg, Hg_T
Rajar et al. (2000)	Modified **PCFLOW 3D** (a hydrodynamic model including a sediment transport module)	Model mercury transport and transformation	The Gulf of Trieste	Benthic sediment; overlying water	HgII, Hg^o, MeHg, Hg_T

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[a] Also can be applied to lake systems.

1.6 Conclusion

The most important anthropogenic sources of mercury pollution in aquatic systems are: (1) atmospheric deposition, (2) erosion, (3) urban discharges, (4) agricultural materials, (5) mining, and (6) combustion and industrial discharges. Depending on the specific site, some of these sources may play more important roles than others. For remote, sparsely populated areas, atmospheric mercury deposition may be the most important source. For urban areas, the most important sources may be discharges from combustion and industry, as well as from other urban sources.

Remediation methods for contaminated sediment are widely used to clean up mercury-contaminated aquatic systems. To evaluate and prevent potential adverse effects on the environment, careful risk assessment is necessary before remediation. Field and laboratory studies suggest that ISC can be an effective and economical remedial approach to mercury contamination. Dredging is an expensive remedial method. In dredging, sediment resuspension is a major environmental concern. However, for heavily polluted systems, dredging seems to be more effective. If there are no serious adverse environmental effects, natural attenuation, involving little or no cost, may be applied to less contaminated sites.

Mercury transport and transformation models are promising and necessary tools in the remediation of mercury contamination in aquatic systems. Due to the complexity of mercury transport and transformation in aquatic systems, considerable data is needed to calibrate and validate existing models of mercury transport and transformation.

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CHAPTER II

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Title: A Model Approach for Evaluating Effects of Remedial Actions on Mercury Speciation and Transport in a Lake System

2.1 Abstract

This paper provides a model approach for understanding mercury cycling in aquatic systems. The information gained is then used for evaluating three remedial actions, namely, natural attenuation, dredging, and capping. Onondaga Lake, N.Y. was used as a model aquatic system. Mercury transport and speciation in both the water column and the benthic sediment were simulated by using a Water Quality Analysis Simulation Program (WASP). Model predictions for the water column generally agreed with the measured values reported in literature for Onondaga Lake. Sensitivity analyses of the model were conducted for determining the impact of transport mechanisms and speciation mechanisms. Advection, sorption, and settling were important mechanisms of Hg transport in the water column. In the benthic sediment, settling of Hg from the water column was the most important input source of Hg. Reduction, methylation, and demethylation were important mechanisms of Hg speciation in both the water column and the benthic sediment. Assuming that Hg loading is steady, natural attenuation showed no positive impact for remediation of Hg contaminated aquatic systems as compared to dredging and capping.

Keywords: Mercury; Speciation; Transport; Modeling; WASP; Remediation.

2.2 Introduction

Mercury cycling in aquatic systems is a complex problem, and aquatic sediments are a major sink for mercury. Mercury can accumulate in the sediment from point and non-point sources, depending on a number of environmental processes, such as chemical, physical, biological, geological, and anthropogenic processes (Benoit et al., 1999; Braga et al., 2000; Hylander et al., 2000). It is believed that the associated mercury contamination in aquatic systems can be decreased by imposing effective management and monitoring strategies. Remediation strategies in this study include methods of dredging, capping, and natural attenuation. Since each remedial action can result in a change in the physical, chemical, and biological conditions of the sediment, it is expected that the speciation and transport of Hg might change as the result of implementing a remedial action. However, the effectiveness of such remediation practices have not been adequately assessed and long-term reliability have not been proven (Degetto et al., 1997).

U.S. EPA provided guidance for Hg as the recommended water quality criteria, which established water quality standard under the Clean Water Act to protect human health and aquatic life. The water quality criteria for both total Hg and methyl mercury (MeHg) are 1.4 μg/L for fresh water Criterion Maximum Concentration (CMC), 0.77 μg/L for fresh water Criterion Continuous Concentration (CCC), and 0.51 μg/L for human health effects (U.S. EPA, 2002). No target level is set for sediments.

WASP (Water Quality Analysis Simulation Program, USEPA) was developed as part of water quality analysis (Wool et al., 1996). WASP is applicable to all kinds of aquatic systems and has a submodel, which is called TOXI, for simulating the fate and transport of organic chemicals or metals. A detailed description of WASP 6.0 and the TOXI model is provided in WASP 6.0 manual which is available in the WEB (Wool et al., 1996). Carroll et al. (2000) simulated the transport and fate of mercury in the Carson Rivera, Nevada by modifying WASP5. Henry et al. (1995a) modified WASP4 incorporated with MCM (Mercury Cycling Model) for understanding the fate of Hg in Onondaga Lake, New York. These studies concluded that the modified model could accurately simulate Hg fate for the sites studied under given conditions. However, further research is desirable.

This paper describes a model approach for simulating the fate of Hg in aquatic systems by modifying WASP6.0 and presenting the model simulations as part of a remedial investigation. Furthermore, the obtained modeling results have been verified against the results obtained from the new version of WASP (WASP6.1).

2.3 Study Site

Onondaga Lake, which is located in Onondaga County, New York, next to the city of Syracuse, was selected for modeling the fate of mercury. This lake was chosen for the following reasons. 1) A lake system is generally simple when compared to other systems such as river and estuarine systems; 2) extensive studies for water quality and mercury have been done in this lake, which means several model parameters are available in literature for incorporating in the model; and 3)

Onondaga Lake represents an aquatic system that is contaminated by mercury through urban and industrial activity.

Onondaga Lake has a surface area of 12 km^2, a volume of 1.31×10^8 m^3 (a length of 7.6 km and a maximum width of 2 km), and mean and maximum depth of 12 m and 20 m, respectively. It receives runoff from a catchment estimated to cover an area of 600 to 620 km^2 (Quamrul Ahsan and Blumberg, 1999). Onondaga Lake is considered a hypereutrophic lake as evidenced by low transparency, phytoplankton blooms and depletion of DO during fall turnover. It has a rapid flushing rate (2.6 to 5.2 times/yr) (Bloom and Effler, 1990). During summer stratification, the thermocline is located at approximately 9 to 10 m below the water surface, and the hypolimnion is anoxic and sulfidic (Effler, 1995; Henry et al., 1995a). Surface water flows into the lake from seven tributaries: Onondaga Creek, Ninemile Creek, Ley Creek, Sawmill Creek, Harbor Brook, East Flume, and Bloody Brook. The first two tributaries, Nine Mile Creek and Onondaga Creek, account for about 75 % of the inflow to the lake. The third largest inflow (15 %) is the discharge from the metropolitan sewage treatment plant (METRO). The remainder of the inflow water is composed by direct rainfall and the several small brooks and streams around the lake. The lake water flows out to the Seneca River, which flows into Lake Ontario (Bloom and Effler, 1990; Effler, 1995).

Onondaga Lake is one of the principal Hg contaminated aquatic systems and a topic of intensive research for the last few decades. Historically, Onondaga Lake has received loadings from industrial wastewater (two chlor-alkali plants) and discharges from the metropolitan sewage treatment plant (Gbondo-Tugbawa and Driscoll, 1998; Henry et al., 1995a). The chlor-alkali plants were closed in 1977 and 1988 (Jacobs et al., 1995). Gbondo-Tugbawa and Driscoll (1998) provided the mass loading, percent contribution of Hg and MeHg to Onondaga Lake, and a model approach.

2.4 Modeling Approach and Procedure

Available modeling parameters such as mercury concentrations, physicochemical, biological and hydro-geological data were collected from the literature that dealt with Onondaga Lake and the remaining parameters were estimated based on the literature survey.

The WASP6.0's TOXI model is used for simulating a 6-month period, from April 1989 to October 1989, a period where field measurements are available in the literature (Bloom and Effler, 1990).

In this model, WASP 6.0 is set to calculate net flow transport across a segment interface, sediment bed volume statically, and modeling time step automatically. A brief description of the individual model parameter incorporated with WASP 6.0 follows. A summary of the input parameters used in the model is provided in the Appendix.

2.4.1 Segmentation

The targeted lake, Onondaga Lake, was conceptually divided into two segments to represent the water column and the benthic sediment. The environmental conditions and mercury transformation rates may differ in these two segments. The depth of the sediment segment was set to 0.65 m because contamination is generally limited to the upper 0.65 m of sediments with the majority of contamination localized in the upper 0.20 m (Bloom and Effler, 1990).

2.4.2 System

Three species of mercury were specified in the model; inorganic Hg (HgII, $HgCl_2$), elemental mercury (Hg^0), and methylmercury (MeHg, CH_3HgCl). Particulate matter whose diameters are larger than 0.4 :m (Babiarz et al., 2001) were specified as solids in the model. The density of solids was estimated by assuming that suspended matter is mostly composed of organic detritus in Onondaga Lake (Johnson and DosSantos, 1991) with 1.27 g/cm^3 as the density (Chapra, 1997). Mercury concentrations in the water column, which were observed by Bloom and Effler (1990), were averaged through the total volume of the lake and were used as input values for initial mercury concentrations (see Appendix). Hg^0 concentration was calculated by subtracting the amount of MeHg and HgII from total mercury (HgT). Initial total mercury concentrations for the benthic sediment was calculated by using mercury concentration observed by Henry et al. (1995b) (see Appendix). Initial Hg^0 concentration for the benthic sediment was assumed to be zero.

Solids concentration in the water column presented by Jacobs et al. (1995) was used as the initial solids concentration in the water column. In the benthic sediment, solids concentration (630 g/L) was estimated from the density (1.6 g/cm^3) and moisture content (61.7 %) of solids. The density of solids was estimated by assuming that the sediment of Onondaga Lake contains 66 % of calcium carbonate with density 2.71 g/cm^3 and 26.2 % of clastics with density 2.5 g/cm^3 based on dry weight. The moisture content of the solids is 61.7 % (Auer et al., 1996). Therefore, the density of solids was estimated to be about 1.6 g/cm^3. Dissolved fractions of MeHg (0.71) and HgII (0.85) were presented by Schetagne et al. (2000) and Poissant and Pilote (1998). Dissolved fractions of elemental mercury and the solids were assumed to be zero.

2.4.3 Modeling Parameters

2.4.3.1 Sorption

Partition coefficients of HgII and MeHg to DOC were reported by Allison and Allison (2000). The partition coefficients (L/kg) of HgII and MeHg to solids were set at $10^{4.9}$ and 10^5, respectively as reported by Allison and Allison (2000). Regarding Hg^0, the partition coefficient (3×10^4 L/kg) to solids was obtained from Mackay et al. (1995). Since only few literature studies have reported partition coefficient of Hg^0 to DOC, it was assumed that the partition coefficient of Hg^0 to DOC is the same as that of Hg^0 to solid.

2.4.3.2 Volatilization

It is believed that volatilization mainly affects Hg^0 in the mercury cycling. The volatilization rate for Hg^0 was set at 0.2 m/day (Hudson et al., 1994) as the transfer rate across the air-water interface.

2.4.3.3 Transformation

In general, mercury may change among different species (HgII, Hg^0 and MeHg), transport along the whole water body, and bioaccumulate through microbial and fish uptake. Through chemical and biological transformation, mercury can be oxidized, reduced, methylated, demethylated, or bioaccumulated.

It was reported that oxidation of Hg^0 to HgII in natural water is negligible. However in natural seawater, Hg^0 may be oxidized at a first order rate of 0.1 hr^{-1} where the presence of high concentration of chloride and particle surface catalyze the oxidation of Hg^0 by oxygen (Amyot et al., 1997a). In this model, oxidation of Hg^0 was considered to be insignificant.

HgII may be reduced to Hg^0 in the water column by photoreduction in the presence of sunlight and by microbial reduction in the presence of heterotrophic bacteria, or some species of phytoplankton. In low mercury concentration (low picomolar range), photoreduction is more effective than microbial reduction (Amyot et al., 1997b; Amyot et al., 1997c; Morel et al., 1998). In high mercury concentration (over 50 picomole), microbial reduction is more effective (Morel et al., 1998). Mason et al. (1995) reported that microorganisms play a pivotal role in the biogeochemistry of mercury in the aquatic system by reducing ionic mercury with a reduction rate constant in the epilimnion of Mystic Lake, Minnesota between 0.02 and 0.04 day^{-1} primarily due to heterotrophic bacteria. The rate constants declined with depth: 0.01 day^{-1} at 9 m depth and less than 0.005 day^{-1} at 17 m depth. In this model, the reduction rate constant in the water column was set to be 0.012 day^{-1} based on the average depth of water column (12 m) with respect to biological reduction of HgII. Very few literature data are available for mercury reduction in the sediments. U.S. EPA (1997) suggested that the reduction rate constant in the lake sediment could be 10^{-6} day^{-1}.

In Onondaga Lake, net annual MeHg production in the water column was 0.60 kg MeHg in 1992. Net methylation rates increased with depth. At 3 m, 9 m, and 15 m of depth, net methylation rates were reported to be 0.003 ng≅L^{-1}≅day^{-1} (giving a rate constant of 0.0006 day^{-1}), 0.03 ng≅L^{-1}≅day^{-1} (rate constant = 0.006 day^{-1}), and 0.11 ng≅L^{-1}≅day^{-1} (rate constant = 0.055 day^{-1}), respectively (Henry et al., 1995b). Therefore, a net methylation rate constant (0.0058 day^{-1}) was calculated from the net annual production and the simulated initial concentration of MeHg. Generally, the methylation rate constant in the sediment is much higher than that in water column. In freshwater sediments, it was reported that maximum potential methylation rate constants are between 10^{-5} and 10^{-1} day^{-1} (Gilmour and Henry, 1991). A recent study reported that specific mercury methylation rate constants were 0.012 day^{-1} at Ranger Lake and 0.016 day^{-1} at Lake Vernon in Ontario, Canada (Hintelmann et al., 2000). For this model, the gross methylation rate constant in sediment was set at 0.01 day^{-1}.

Demethylation is stimulated by enzymatic or photochemical mechanisms, suggesting that MeHg is shown to be degraded by some bacteria and by light (Morel et al., 1998). In addition, it was reported that photodegradation is probably one of main degradation pathways for MeHg in water with low mercury concentration (less than 50 pM). Gilmour and Henry (1991) reported that maximum potential demethylation rate constants in the water column were between 0.001 and 0.025 day^{-1}. For this model, the water column demethylation rate constant was ignored because net methylation was considered. In the sediment, very few literature studies have reported demethylation rate constants. It was reported that the percentage of MeHg in Hg_T (% MeHg) in the sediment was lower than that of the water column (Gilmour and Henry, 1991). In a study of Ranger Lake and Lake Vernon in Ontario, Canada, demethylation rate constants in the sediment were estimated to be 0.417 day^{-1} and 0.528 day^{-1}, respectively (Hintelmann et al., 2000). For this model, values ranging between 0.001 and 5.28 day^{-1} were tested. It has been found that a rate of 0.1 day^{-1} simulated the data reasonably well.

2.4.3.4 Biouptake

Biouptake factors reflect the magnitude of a chemical partitioning between a biological medium such as plants or animals and an external medium such as air, soil or water (USEPA, 1997). In the study of mercury mass balance in Onondaga Lake (Henry et al., 1995b), net uptake by fish was estimated to be 0.20 kg/year, meaning that uptake rate constant is 0.002 day^{-1} as calculated by using the result of net uptake by fish multiplied by MeHg mass concentration in the lake. In this model, values ranging between 0.002 day^{-1} and 0.2 day^{-1} were initially tested. It has been found that a rate of a 0.02 day^{-1} simulated the reported data reasonably well.

2.4.4 Transport

2.4.4.1 Solid settling and resuspension

Time variable solids settling velocity was provided by Effler and Brooks (1997). The resuspension of bottom sediment may result in less net sedimentation. However, resuspension was considered insignificant in deep water due to the relative quiescent region in Onondaga Lake (Henry et al., 1995b). In this model, solid settling rate was considered equal to net settling rate.

2.4.4.2 Exchanges

Exchange fields may simulate all kinds of diffusion and dispersion within and between the water column and the benthic sediment. Generally, the vertical mass transport is governed by concentration gradients between surface and bottom layers and by the vertical diffusion coefficient (Owens, 1989). In this model, diffusion between the water column and the benthic sediment was simulated by using 1.0×10^{-10} m^2/s as molecular diffusion coefficient, which was reported in WASP6.0 manual (Wool et al., 1996). In the water column, vertical dispersion was observed due to spring and fall turnover (Bloom and Effler, 1990; Henry et al., 1995a). However, the vertical diffusion within the water column was not considered in this model because only one segment was defined in the water column.

2.4.5 Loading

Mass loading of HgII (0.0264 kg/d; 0.132 mol/d) and MeHg (0.85×10^{-3} kg/d; 0.004 mol/d) to Onondaga Lake was presented by Gbondo-Tugbawa and Driscoll (1998). These values include background, urban runoff, discharge of Metro and Chlor-alkali facility. Inputs of HgII and MeHg to Onondaga Lake were simulated using a Mass loading (kg/d) function in WASP6.0. The loading of solids into Onondaga Lake was simulated using boundary concentration (mg/l) function in WASP6.0 under the assumption that the loading concentration of the solid was the same as that of the system concentration (i.e. solid concentration in the lake water). During the model simulating period, i.e., the six month period, constant mass loadings were assumed due to the lack of time-specific data. Atmospheric deposition (0.006 kg/year) and groundwater flux

(0.001 kg/year) were not considered in this model due to relatively minor contributors of Hg to Onondaga Lake (Henry et al., 1995b).

2.4.6 Flow

Flow rate was estimated to be 15.23 m^3/s by averaging the annual flow rates of major tributaries into Onondaga Lake, which were reported by Quamrul Ahsan and Blumberg (1999).

2.5 Model Simulation for Possible Remedial Actions

The fate of mercury during and after possible remediation actions was simulated. Remediation strategies include dredging, capping, and natural attenuation.

2.5.1 Dredging

Dredging is the process used to remove the contaminated benthic sediments (Barbosa and de Almeida, 2001). In modeling dredging action, two segments, which are the water column and the benthic sediment, were defined. It was also defined in the model that the benthic sediment has no mercury after dredging.

During and after dredging, remobilization of buried contaminated sediments may deteriorate the water quality significantly (Kwon and Lee, 1998). Therefore, the remobilization of sediment was simulated in the model. Assuming that cutterhead suction dredging is a dredging process with a rate of 15000 m^3 of sediment per hour and sediments from the sediment-water interface up to 20 cm deep are removed during 20 working days, a removed sediment volume of 2.4×10^6 m^3 was estimated. According to Hayers et al. (2000), about 0.0035 % of the dredged sediments may be lost in the water column and produce resuspension, which suggests that 0.0035 % × 2.4×10^6 m^3 equaling 84 m^3 of the sediment is subject to resuspension. Knowing the volume of the resuspended sediment together with the HgII and MeHg concentrations in the sediment, the mass of HgII and MeHg resuspended was estimated to be 2.646 g/d and 0.0106 g/d, respectively. Due to the lack of Hg^0 data and relatively small Hg^0 concentration in sediment, the release of Hg^0 was ignored. Another consideration for dredging is the reaeration of buried sediments. Oxygen in the water column may enter the deep sediments, and possibly oxidize some contaminants (Vale et al., 1998). However, reaeration of buried sediment was not considered because of the lack of data.

2.5.2 Capping

Capping is the process of placing a layer of proper isolating materials to cover and separate the contaminated sediments from water column (Liu et al., 2001a; Palermo, 1998).

In this model, a capping layer was introduced to separate the contaminated sediment bed and the water column, giving a total of three segments, after the implementation of capping, which are the water column, the capping layer, and the benthic sediment. Sand was considered as a capping material (Hamblin et al., 2000; Hosokawa, 1993; Ravikrishna et al., 2000). Assuming that all the parameters of the capping layer were the same as those of the benthic sediment except for mercury concentration, the depth of the sand layer was set to be 0.5 m, which was believed to be a proper capping depth in some studies (Azcue et al., 1998; Talbert et al., 2001). Zero concentrations of HgII, Hg^0 and MeHg were assigned to the capping layer.

After capping, the mass transfer of mercury in the buried contaminated sediments by diffusion and advection should be considered (Liu et al., 2001b; Moo-Yound et al., 2001). Assuming that diffusion is a major process of mass transfer for buried sediments, diffusion between the original sediment bed and the capping layer was considered in this model. Consolidation, which is induced contaminant transport as a result of gravity, is important for the contaminant transport between the capping layer and the sediment (Moo-Yound et al., 2001). However, due to unavailability of field data, consolidation was not applied to this model.

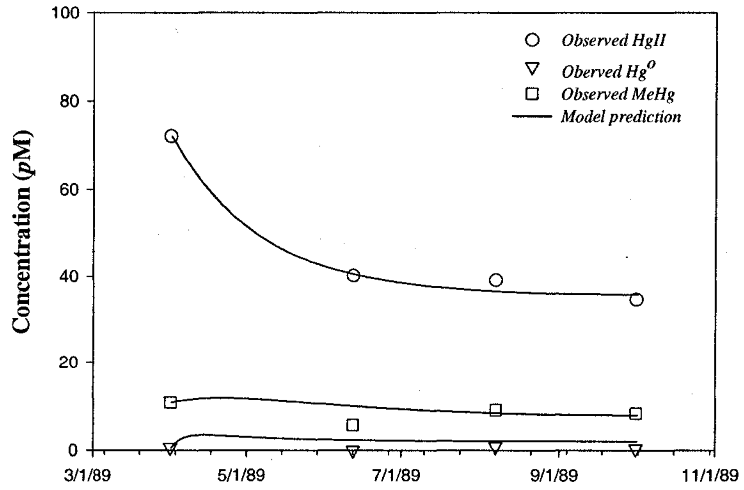
2.5.3 Natural Attenuation

Natural attenuation is the decrease of contamination due to naturally occurring processes (Khan and Husain, 2002). Assuming that Hg loading is steady for the simulation period, the simulation without any action was defined as natural attenuation in this model.

2.6 Modeling Results

In the base model (WASP 6.0) for mercury speciation and transport, the species of mercury (HgII, Hg^0, MeHg) were simulated in the water column and the benthic sediment in Onondaga Lake for a 6-month period. Figure 1 gives a comparison of model predictions and observed Hg concentrations. HgII and MeHg concentrations were predicted well while Hg^0 concentration was somewhat higher than the observed values. Although Hg^0 concentration was over-predicted, Hg_T distributions agreed with the observed field data due to the relatively low Hg^0 concentration.

(a) Water Column



(b) Benthic Sediment

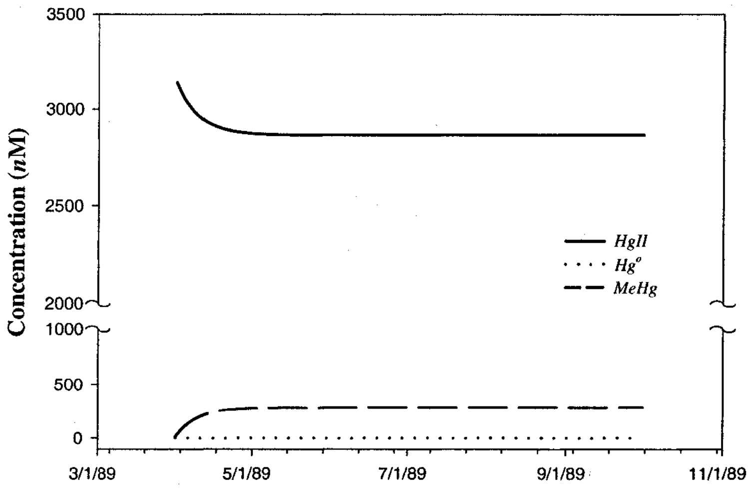


Figure 1. Comparison of Observed and Model Simulated Hg Concentration in the Water Column and Benthic Sediment (note: Observed Hg concentrations (Bloom and Effler, 1990) are mean values; In benthic sediment, no observed data are available in the literature).

2.6.1 Sensitivity Analysis

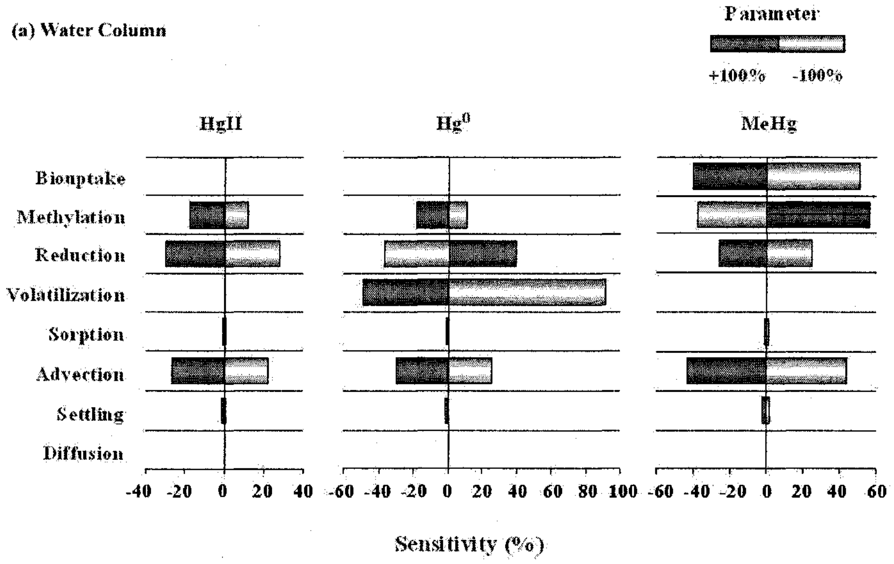
Sensitivity analysis is one way to identify the importance of various model parameters (Chapra, 1997). Sensitivity can be analyzed by using specific perturbations in the input and output variables. Therefore, the model sensitivity to a parameter change is defined as the relative change in the mercury concentration divided by the relative change in the parameter value (Lohman et al., 2000; USEPA, 1997).

$$Sensitivity\ (\%) = \frac{(C - C_B)/C_B}{(P - P_B)/P_B} \cdot 100$$

where, C_B is the calculated value of model output in the base simulation; C is the calculated value of model output after a change in parameter; P_B is the model parameter value in the base simulation; and P is the model parameter value in the sensitivity simulation.

Kinetic parameters, representing principal mechanisms for mercury speciation and transport, were major targets for the sensitivity analysis. Diffusion, settling, advection, sorption, volatilization, reduction, methylation and biouptake (by fish) are of great importance in the model. In this model, sensitivity analysis was conducted by increasing or decreasing a single model parameter by 100 %. The results are summarized in Figure 2:

(a) Water Column



(b) Benthic Sediment

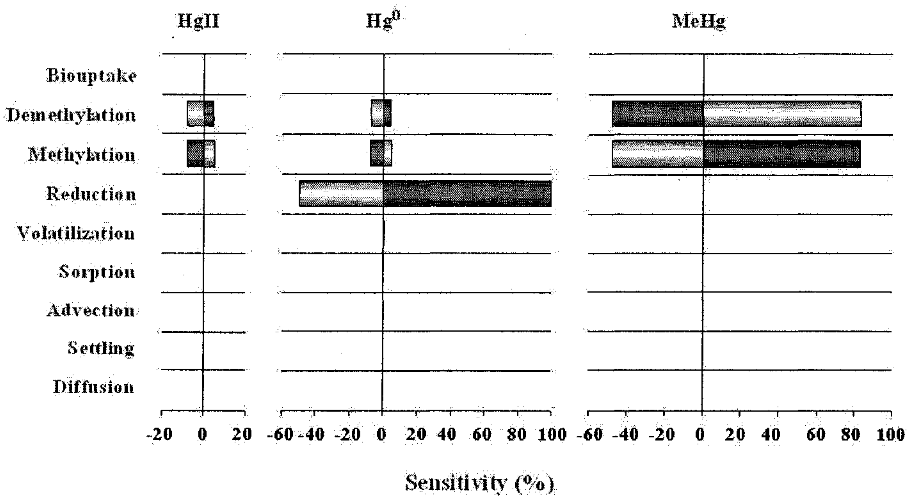


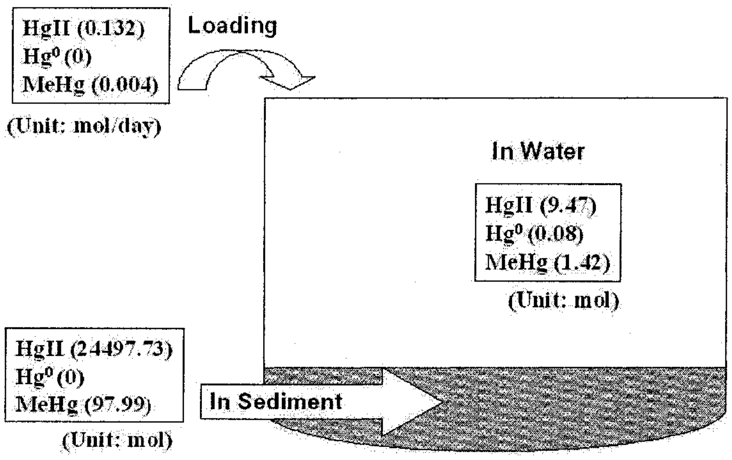
Figure 2. Model Sensitivity Analysis in (a) the Water Column and (b) the Benthic Sediment for 6-month Simulation

The mercury level depended strongly on advection, volatilization, reduction, methylation, and biouptake in the water column. Specifically, Hg^0 level was sensitive to volatilization and MeHg level was sensitive to biouptake. The magnitude of settling and sorption did not affect the mercury level in this model significantly. In the benthic sediment, mercury concentrations depended strongly on reduction, methylation, and demethylation. Both in the water column and the benthic sediment, the magnitude of diffusion did not have any effect on the mercury concentrations. The probable reason is that loading inputs were much higher than the diffusion effects. Diffusion was defined as the vertical exchange between the pore water and the water column in this model. Generally, exchange across the sediment-water interface serves as an important process in regulating water column concentration of metals in natural waters. According to a research study in Pallette Lake, Wisconsin (Hurley et al., 1994), diffusive mercury fluxes from sediments may influence mercury concentrations in the water column near sediments. However, diffusion of mercury from the sediment was apparently a minor source for mercury flux to the water column, specifically during summer stratification period (Hurley et al., 1994). Due to the lack of site-specific data and model approach, there is considerable uncertainty in this diffusion mechanism.

2.6.2 Mass Balance

Mercury mass balance was calculated for Onondaga Lake based on input values obtained from literature (see Appendix) and model output results for a 6-month simulation. The overall mass balance for mercury in Onondaga Lake is shown in Figure 3:

(a) Model Input



(b) Model Output

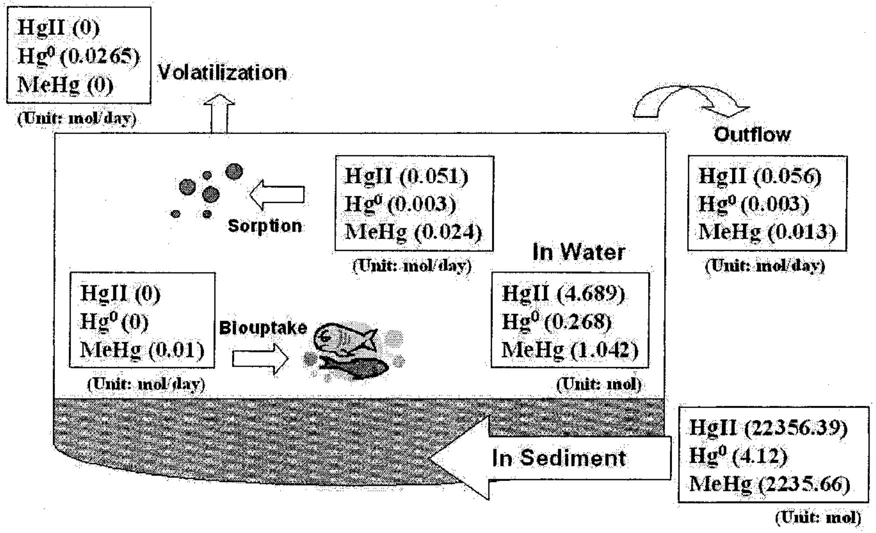
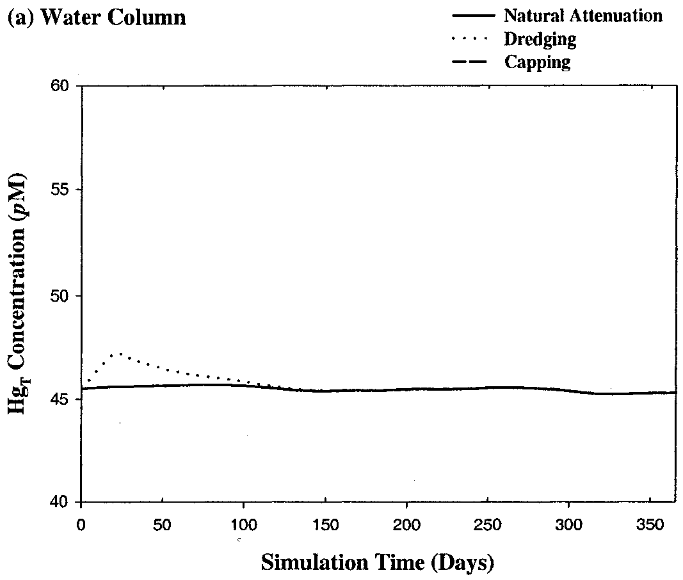


Figure 3. The Overall Hg Mass Balance for 6-month Simulation

The values provided in Figure 3 (a) are based on the values shown in the Appendix and then converted to molar concentration or molar mass. Tributary loading is a major source of mercury into the lake system, expressed by mercury loading to the lake for 6 months. Mercury mass existing in both lake water and lake sediment at the initial time was also considered as input mercury mass. Summing up the loading of Hg to the lake for the six month period (183 days) to the mercury in the water column and the sediment provides Hg_T of 24,632 mol. Figure 3 (b) represents the various model output for the lake after six month period. Output components included outflow from the lake, volatilization to air, sorption to particles, biouptake by fish for 6 months, and mercury mass existing in both lake water and lake sediment after 6 months. In this model, mercury sorbed to particulate matter may be a candidate for settling to the sediment. The majority of mercury was shown to exist in the lake sediment. Mercury mass in water was shown to transport by outflow, sorption and settling. Summing up the various forms of Hg obtained from the model for the six month period provides a value for Hg_T of 24,637 mol which is in good agreement with the above reported value for the input.

2.6.3 Modeling Results for Possible Remedial Actions

To test possible remedial actions, the model was used to simulate the fate of mercury for a one year period. The predictions by the model for Hg_T level in both the water column and the benthic sediment during and after remedial actions are presented in Figure 4:



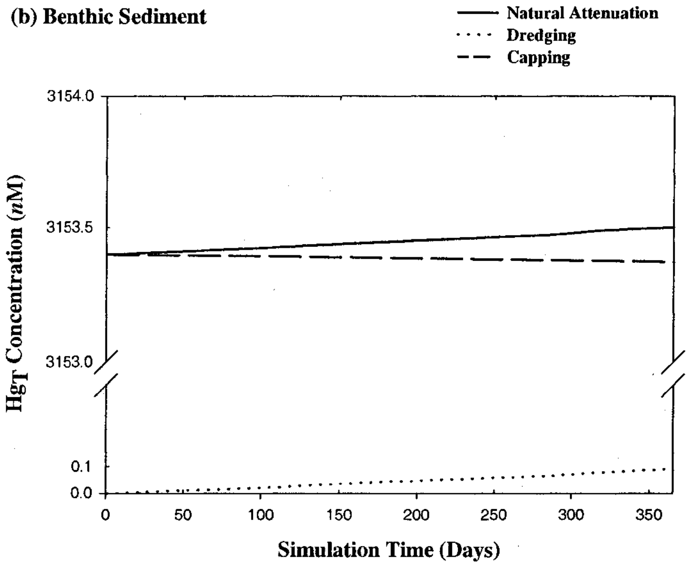


Figure 4. Model Predictions for Hg_T in (a) the Water Column and (b) the Benthic Sediment during and after Remediation (note: Capping action provides the same fluctuation in Hg level as natural attenuation action).

For the water column, capping and natural attenuation provide the same mercury concentrations during the simulation period. The possible reason is that the system had much larger mercury loading from the boundaries than the mercury flux between sediment and water column. In the benthic sediment, capping actions brought different behavior of Hg as compared with that of natural attenuation. In the case of dredging action, Hg in the water column is shown to increase suddenly during and immediately after dredging action (20 working days) due to the sediment resuspension.

In natural attenuation, Hg in the sediment increased with time. It is worthwhile to note that this model was simulated on the assumption of continuous Hg loading during the simulation period. In the case of capping, it is worth noting that increasing Hg was not observed in benthic sediment while Hg concentrations in the capping column might increase with time.

2.6.4 Validation of WASP 6.0 against WASP 6.1

The obtained modeling results from WASP 6.0 have been compared to the results obtained from the new version of WASP (WASP6.1, Wool et al., 2002). WASP 6.1, which has been developed recently to enhance water quality analysis simulation against WASP 6.0, has two submodels: the EUTRO (conventional pollutant model) and TOXI (organic chemical and metal model). WASP 6.1 also includes several enhanced kinetic submodels such as the Mercury and the Thermal and Fecal Coliform model. In WASP 6.1, the mercury model is capable of simulating three forms of mercury (Hg II, Hg^0, MeHg) with three different solids type (Wool et al., 2002). In this study, the TOXI submodel of WASP 6.0 was modified to simulate the fate of mercury. Both versions of WASP were simulated with the same input parameters values listed in the Appendix. Table 3 shows that modeling results of WASP 6.0 are relatively in agreement with that of WASP 6.1 in both of water column and benthic sediment even though minor different modeling results between the two versions of WASP are observed. Regarding the benthic sediment, the major deviation was with regards to Hg^0. However, Hg^0 exists in a relatively low concentration in the aquatic systems and hence will have very minor impact. It is worthwhile to note that the two versions of WASP have different mercury modeling functions and modeling approaches. Hence, the validation of WASP 6.0 against WASP 6.1 will provide more confirmation of the results for the benthic sediments since no measured data is available in literature.

Table 3. Comparison of Modeling Results from Different version of WASP (WASP6.0 and WASP6.1)

(a) Water Column

(Unit: ngL^{-1} as Hg)

	June 1989			August 1989			October 1989		
	WASP 6.0	WASP 6.1	Ref *	WASP 6.0	WASP 6.1	Ref *	WASP 6.0	WASP 6.1	Ref *
HgII	8.118	8.062	8.056	7.33	7.298	7.841	7.179	7.145	6.952
Hg^0	0.472	0.062	0.005	0.42	0.035	0.156	0.41	0.016	0.078
MeHg	2.046	3.288	1.134	1.695	3.288	1.828	1.595	3.19	1.671

* Bloom and Effler (1990) provides measured Hg concentration in the water column (averaged values through the total volume of the lake) from April to October 1989. The data on April are not presented because initial model input value of Hg concentration is the same as field measurements.

(b) Benthic Sediment

(Unit: ngL^{-1} as Hg)

	Initial Model Input**	June 12 1989		August 7 1989		October 24 1989	
		WASP 6.0	WASP 6.1	WASP 6.0	WASP 6.1	WASP 6.0	WASP 6.1
HgII	630000	574995	568182	574957	568141	574917	568132
Hg^0	0	42	0.02	74	0.03	122	0.04
MeHg	2520	57486	64329	57496	64365	57492	64364

** Measured Hg concentration by Henry et al. (1995b) was used as the initial Hg concentration in modeling the benthic sediment.

2.7 Conclusion

Hg concentrations and distributions in Onondaga Lake were predicted quite well by WASP 6.0 model for the observed field data reported. Advection, sorption, and settling were important mechanisms of Hg transport in the water column. In the benthic sediment, settling of Hg from the water column was the most important input source of Hg. Both in the water column and the benthic sediment, reduction, methylation, and demethylation were important mechanisms of Hg speciation. Assuming that Hg loading is steady, natural attenuation has no effect on the remediation of Hg contaminated aquatic system as compared with dredging and capping actions. Therefore, other remedial actions such as dredging and capping can be alternatives to remediation for Hg contaminated aquatic systems. However, it is expected that reduction of Hg loading may cause natural attenuation to be a good alternative to remediation for Hg contaminated aquatic systems.

Considering the complexity of Hg speciation and transport, this model simulation might have some uncertainties in the prediction of Hg cycling. The need for obtaining more field data with time for both the water column and the sediment will pave the way for developing a more rigorous model that will provide a clear remedial action picture.

2.8 Recommendations

Follow-up studies may be conducted to improve understanding of the mercury pollution problem in natural waters:

1. Simulations based on WASP may be performed under the condition that no mercury loading is present in the system. Currently, mercury loading to the system is very high, and the result is that diffusion between the benthic sediment and the water column is insignificant.

2. Under the condition that no mercury loading is present in the system, we may perform model simulations of the system for a longer time period (such as 50 years) to examine the long term effects of certain remedial techniques.

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Appendix: Input Parameters for Mercury Modeling used in WASP6.0

Parameter	Value	Reference
Lake Geohydrological Parameter		
Water Column		
Volume (m^3)	1.31×10^8	Quamrul Ahsan and Blumberg (1999)
Depth (m)	12	Quamrul Ahsan and Blumberg (1999)
Velocity (m/s)	8.84×10^{-4}	calculated by using the flowrate
Flowrate (m^3/s)	15.23	Calculated based on Quamrul Ahsan and Blumberg (1999)
Benthic Sediment		
Volume (m^3)	7.8×10^6	calculated by using the depth
Depth (m)	0.65	Bloom and Effler (1990)
Velocity (m/s)	0	Assumed
System Parameter		
Water Column		
Initial Hg Concentration (mg/L)	HgII (1.45×10^{-5})	calculated based on Bloom and Effler (1990)
	Hg^0 (1.3×10^{-7})	calculated based on Bloom and Effler (1990)
	MeHg (2.17×10^{-6})	calculated based on Bloom and Effler (1990)
Solid Concentration (mg/L)	3.98	Jacobs et al. (1995)
Hg loading (kg/d)	HgII (0.0264)	Gbondo-Tugbawa and Driscoll (1998)
	Hg^0(0)	Assumed
	MeHg (0.85×10^{-3})	Gbondo-Tugbawa and Driscoll (1998)
Solid loading (mg/L)	3.98	Assumed
DOC (mg/L)	4.3	calculated based on Wang and Driscoll (1995)
Dissolved Fraction	HgII (0.85)	Schetagne et al. (2000)
	Hg^0 (0)	Assumed
	MeHg (0.71)	Schetagne et al. (2000)
	Solid (0)	Assumed
Temperature	Time variable	Jacobs et al. (1995)
pH	Time variable	Wang and Driscoll (1995)

Appendix: Input Parameters for Mercury Modeling used in WASP6.0 (cont'd)

Parameter	Value	Reference
Benthic Sediment		
Initial Concentration (mg/L)	HgII (0.63)	calculated based on Henry et al. (1995b)
	Hg^0 (0)	Assumed
	MeHg (2.52×10^{-3})	calculated based on Henry et al. (1995b)
Solid Concentration (mg/L)	6.3×10^5	calculated by using density and moisture content
DOC (mg/L)	4.4	calculated based on Wang and Driscoll (1995)
Temperature	time variable	Jacobs et al. (1995)
pH	time variable	Wang and Driscoll (1995)
Constant Parameter		
Partition coefficient to solids (L/kg)	HgII (79344)	Allison and Allison (2000)
	Hg^0 (30000)	Mackay et al. (1995)
	MeHg (100000)	Allison and Allison (2000)
Partition coefficient to DOC (L/kg)	HgII (251188)	(Allison and Allison, 2000)
	Hg^0 (30000)	Assumed based on Mackay et al. (1995)
	MeHg (100000)	Allison and Allison (2000)
Volatilization (m/day)	Hg^0 (0.2)	Hudson et al. (1994)
Oxidation (day^{-1})	water column (0)	Assumed
	benthic sediment (0)	Assumed
Reduction (day^{-1})	water column (0.012)	calculated based on Mason et al. (1995)
	benthic sediment (10^{-6})	USEPA (1997)
Methylation (day^{-1})	water column (0.0058)	calculated based on Henry et al. (1995b), meaning net methylation rate
	benthic sediment (0.01)	estimated based on Gilmour and Henry (1991) and Hintelmann et al. (2000)
Demethylation (day^{-1})	water column (-)	net methylation considered
	benthic sediment (0.1)	estimated based on Gilmour and Henry (1991) and Hintelmann et al. (2000)

Appendix: Input Parameters for Mercury Modeling used in WASP6.0 (cont'd)

Parameter	**Value**	**Reference**
Biouptake (day^{-1})	0.02	Simulated
Solid settling velocity (m/s)	time variable	Effler and Brooks (1997)
Exchange (molecular diffusion coefficient, m^2/s)	1.0×10^{-10}	WASP6 manual