

Sources and remediation for mercury contamination in aquatic systems—a literature review

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“Capsule”: *This comprehensive review examines sources of mercury contamination in aquatic systems, and also considers remediation methods.*

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 and dredging are two possible remedial approaches to mercury contamination in aquatic systems, and natural attenuation is a passive decontamination alternative. 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, is a possible and very economical choice for less contaminated sites. Proper risk assessment is necessary to evaluate the effectiveness of remedial and passive decontamination methods as well as their potential adverse environmental effects. Modeling tools have a bright future in the remediation and passive decontamination of mercury contamination in aquatic systems. Existing mercury transport and transformation models were reviewed and compared.

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1. Introduction

Mercury is a hazardous environmental contaminant. In Japan, 2252 people have been affected and 1043 have died due to Minamata Disease for the past two decades, 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, 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

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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 were 1913 metric tons in 1995 (Pacyna and Pacyna, 2002). This value is slightly lower than the estimated value of 2217 from 1990 to 1995 (Pirrone et al., 1996). The amount of mercury emitted into the atmosphere through natural and re-emitted sources was estimated to be between 1500 and 2500 metric tons per year in the late 20th century (Nriagu, 1989; Nriagu, 1990).

Mercury is persistent in the environment. For this reason, effective remedial methods need to be applied 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 passive decontamination method if there are no serious adverse environmental effects on the aquatic systems. However, proper risk assessment is necessary before the selection of the best remediation or passive decontamination strategy, in order to examine other implications and avoid any additional remedy-associated adverse environmental effects.

Using modeling tools to simulate mercury transport and transformation in the environment and direct the implementation of remediation or passive decontamination for mercury-contaminated sites is a critical component of such 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.

The first part of the paper has examined sources of mercury contamination in aquatic systems in detail. This will help the readers to understand where the mercury contamination comes from, and also will help the decision-makers to decide possible source control options. Clean-up of mercury-contaminated systems is a complex problem, and needs to be further studied. The second part of the paper has summarized important information about remediation and passive decontamination for mercury-contaminated systems.

2. 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 (Nriagu, 1989; Lindqvist et al., 1991; Nriagu, 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.

The anthropogenic emission sources of mercury mostly result from: (1) solid waste incineration (municipal and medical wastes), (2) coal and oil combustion, (3) pyrometallurgical processes (iron, lead, and zinc), and (4) production of mercury and gold (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.

2.1. 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 to 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.

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, the total amount of mercury deposited in summer is 5–8 times higher than the value reported in winter (Guentzel et al., 2001). A 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 3–24 times higher than pre-industrial flux (Swain et al., 1992; 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 pre-industrial value, which was $0.37 \text{ ng cm}^{-2} \text{ yr}^{-1}$. Other researchers suggest that the current global industrial value may be even more than 4 times the pre-industrial value (Heyvaert et al., 2000; Bindler, 2003). In Sweden, it is estimated that modern deposition flux is at least 10 times higher than the pre-industrial flux (Bindler, 2003). Research performed in the southwestern United States suggests that modern flux is 24 times higher than pre-industrial deposition rate (Heyvaert et al., 2000).

2.2. 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 extensive human deforestation, surface runoff in the Amazon area in Brazil brings about $200\text{--}4600 \mu\text{g/m}^2/\text{yr}$ 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 1400 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

Table 1
Atmospheric deposition flux around the world

Location	Flux ($\mu\text{g m}^{-2} \text{ yr}^{-1}$)	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	740.9	Tan et al. (2000)
Sweden	5–30	Bindler (2003)

^aAccounts for 12% of total global anthropogenic mercury emissions.

cycle. An experiment in Germany suggests a 43 ± 5 ng/m²/h emission rate of mercury from mercury contaminated soil (Wallschläger 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, and (4) natural degradation of ferrallitic soils due to podzolization (the process by which the soil is becoming acidic). 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 km² (Dam Kofoed, 1983). The sludge-amended soil in Tennessee contains 7.3 µg/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).

2.3. 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).

2.4. Agricultural sources

Pesticides and fungicides with mercury content were widely used in agriculture for a long period of 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 µg/kg of mercury. This topsoil is probably the major source of mercury contamination in that area (Cooper and Gillespie Jr, 2001).

2.5. 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 (Nriagu, 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 emit 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 $\mu\text{g/g}$ 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 $\mu\text{g/g}$, 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 $\mu\text{g/g}$, which is 1000 times higher than the background mercury level (Gray et al., 2000).

Based on these studies, it is believed that 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.

2.6. 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 (Wang 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 to 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).

3. Remediation and passive decontamination for mercury pollution

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 implemented to contaminated systems.

3.1. 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 the impact of 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). Thus, this capping layer can prevent the mercury that leached from the sediment from entering the overlying water. In one test, capping material adsorbed 99.9% of mercury in concentrations at 200–500 µg/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. ABS usually is a reactive geochemical barrier layer that can actively block the contaminant release from the sediment entering into the overlying water, without the hydraulic contact between the sediment and the overlying water being disturbed (Jacobs and Forstner, 1999). 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, diffusion, etc.), buried mercury 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 scour the capping layer and release mercury 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 mercury. Sediment consolidation, due to gravity, moves mercury from buried sediment into the capping layer. This sediment consolidation may be a more important factor in the transfer of mercury from buried sediment into the capping layer than molecular diffusion of mercury (Moo-Young et al., 2001). Capping materials vary in their compressibility, which affects the extent of sediment compression (Moo-Young et al., 2001). In aquatic systems, mercury is in various forms, including elemental, inorganic, or organic. Some forms may have a stronger tendency to attach to sediment than others. For example, 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 (especially on the fate of buried mercury under the capping layer) should be performed to verify and optimize this technology.

3.2. Dredging

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. 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 adverse environmental threats if they are not well planned and implemented (Nichols et al., 1990; Schultz et al., 1995; Vale et al., 1998; Van Den Berg et al., 2001). 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 (Nichols et al., 1990; Vale et al., 1998; Van Den Berg et al., 2001).

Several research studies suggest that significant amounts of settled sediment were resuspended by dredging, and elevated turbidity was observed (Nichols et al., 1990; Vale et 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).

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 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 site (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 another limitation. It has been reported that the cost of active contaminated sediment remediation, including environmental dredging, could be as high as \$1409/m³ (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.

3.3. 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 a choice for 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. Biological (e.g., microbial decomposition), physical (e.g., advection, dispersion, adsorption, settling, and evaporation), and chemical (reactions) processes are major mechanisms involved in the transformation and transport of mercury (Garbaciak et al., 1998).

Natural attenuation approach was selected for 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 volatilization.

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 to 0.5 ng/g (dry sediment) per day in a field study (Marvin-Dipasquale and Oremland, 1998). MeHg is also photodegraded 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. 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, adding ferrous ions in the presence of phlogopite particles can enhance the reduction of HgII (Charlet et al., 2002). 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 enhance the burial and separation 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).

4. Existing models to simulate mercury transport and transformation

Modeling tools are crucial for the remediation and passive decontamination 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 are 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 USEPA (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 OLM 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).

Table 2
Models simulating mercury transport and transformation

References	Models	Purpose	Site studied	Sampling media	Mercury species targeted
<i>River Systems</i>					
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 ⁰ , 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 , MeHg
<i>Lake Systems</i>					
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 (New York)	Water	Hg ⁰ , 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 ⁰ , MeHg, Hg _T
Gbondo-Tugbawa and Driscoll (1998)	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
<i>Coastal systems</i>					
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 ⁰ , 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 ⁰ , MeHg, Hg _T

^aAlso can be applied to lake systems.

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.

5. 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 industrial or municipal sources.

Remediation and passive decontamination for contaminated sediment are possible alternatives to clean-up mercury-contaminated aquatic systems. To evaluate and prevent potential adverse effects on the environment, careful risk assessment is necessary before remediation or passive decontamination. 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 a choice for 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 are needed to calibrate and validate existing models of mercury transport and transformation.

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