

# Assessment of Mercury Contamination in Surficial Sediments of Newark Bay

by

**Alexander F. Gregory**

**Advisor: Professor Nickolas J. Themelis**

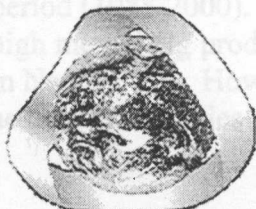
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**Department of Earth and Environmental Engineering  
(Henry Krumb School of Mines)**

**Fu Foundation School of Engineering and Applied Science  
Columbia University**

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**EARTH ENGINEERING  
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**Columbia University**

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## **EXECUTIVE SUMMARY**

This study of mercury contamination in Newark Bay sediments was initiated from a broader study of mercury sources and material balance in the New York-New Jersey Harbor, conducted for the New York Academy of Sciences' Harbor Consortium by Themelis and Gregory (2001). The author of this report concluded that a more in-depth study should be conducted on a smaller area within the Harbor where mercury contamination has been historically significant. This conclusion was also based on results from a recent study by Gregory and Gorokovich (2001), where geographic information systems (GIS) technology was used to visualize the high Hg concentrations in Newark Bay surficial sediments from 1988 to 2000. As a result, it was determined that this study should include a discussion of a) health risks associated with mercury exposure originating in aquatic environments, b) sediment and water quality characteristics that influence mercury methylation, c) source of Hg contamination to Newark Bay, and d) assessment of mercury contamination of Newark Bay sediments.

Newark Bay was chosen as the study area because it has historically contained some of the most anthropogenically enriched Hg sediments compared to the rest of the NY/NJ Harbor. Furthermore, most Hg-related industries in the Hudson-Raritan (HRB) were historically concentrated within the Newark Bay vicinity. Municipal wastewater treatment plants (WWTP) were the next largest point source contributors of mercury to Newark Bay. Tributary flow from the Hackensack and Passaic Rivers and tidal flow from the Arthur Kill and Kill Van Kull transported these plant effluent discharges into Newark Bay. However, NJ DEP reported significant reductions in WWTP emissions between 1987 and 1998. These reductions are most likely attributed to the phasing out of mercury in industrial applications, and possibly improved Hg recovery techniques by enzymatic reduction of soluble divalent mercury ( $\text{Hg}^{2+}$ ) to insoluble elemental mercury ( $\text{Hg}^0$ ) by mercury resistant bacteria.

The sediment analysis using geographic information systems (GIS) demonstrated that Newark Bay surficial sediments had high mercury concentrations relative to the rest of the Harbor over a twelve-year period (1988-2000). This method of analysis was useful in identifying sites of potentially high methyl Hg production based on the presentation of Hg and total organic carbon data in Newark Bay. However, it was not capable of modeling Hg methylation given the data deficiencies and technical limitations. Surficial

sediments were chosen as the medium of analysis because the most intense biogeochemical activity occurs at the surface layer where deposited metals participate in a variety of processes including sulfate reduction, which is the principal means of mercury methylation in estuarine sediments.

In summary, the state of mercury contamination within the Newark Bay sediments is not clearly understood. Based on the findings from this investigation, it is recommended that future studies of mercury contamination in surficial sediments in Newark Bay fill in existing data gaps by means of additional sampling. Future studies should also sample and analyze for the sulfate and sulfide content, which are necessary for estimating the mercury methylation and sulfate reducing rates. It is recommended that sampling be conducted on a long-term periodic basis taking into account both vertical (sediment cores) and horizontal sediment distributions. Establishing better trends is essential for determining whether remediation is necessary and also the form of remediation (natural, dredging, or chemical/biological).

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THE MINAMATA MERCURY DISASTER (Analysis, Remediation, and Recommendations) By Alexander F. Gregory, Solid and Hazardous Waste Management, Department of Earth and Environmental Engineering, (Henry Krumb School of Mines), Spring 2001, (Revised Fall 2001)

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Alexander F. Gregory  
November, 2001

## INTRODUCTION

The objective of this study was to assess the state of mercury contamination in surficial sediment of Newark Bay. Mercury is a concern because of its toxicity to humans and aquatic life in the methyl form (i.e.  $\text{CH}_3\text{Hg}^+$ ). The surface sediments are a concern because most biogeochemical activity, which is responsible for Hg methylation occurs at the sediment-water interface.

This work was initiated from a broader study of mercury sources and material balance in the New York-New Jersey Harbor, which was conducted for the New York Academy of Sciences' Harbor Consortium by Themelis and Gregory (2001). The NYAS report mainly focused on past and present Hg air emissions, and mercury flows into the NY/NJ Harbor. From this NYAS report, it was determined that future study areas in the Harbor should be focus to smaller sections of the Harbor to where exceptionally high Hg levels prevail. Furthermore, it was concluded that this current study should focus on the surface sediments where Hg methylation is most prevalent.

This report is divided into five sections. Section 1 examines the ecological and human health risks due to methylmercury formation in the aquatic environment. Section 2 discusses the effects of sediment and water quality on the formation of MeHg. Section 3 describes the sources of mercury to Newark Bay. In Section 4, a quantitative assessment of mercury in surficial sediments and sediment core data of Newark Bay was conducted using geographic information systems as a means of data presentation. The data used in this analysis came from a variety of sources including NYC DEP (1991a and 1993), Long *et al.* (1995), EPA (1998), and NYS DEC (2001). Conclusions and recommendations are summarized in Section 5. In the Appendix, a case study of mercury contamination in Minamata Bay, Japan is presented. The objective is to show alternative ways in which sediment mercury contamination has been assessed and to introduce remediation techniques: a) natural remediation, b) dredging, and c) chemical and microbial treatment.



## 1. ECOLOGICAL AND HUMAN HEALTH RISKS ASSOCIATED WITH MERCURY EXPOSURE AQUATIC ENVIRONMENTS

The mercury compound of principal concern is methyl mercury (Chemical formula:  $\text{CH}_3\text{Hg}^+$ , also referred to as MeHg). This form of mercury can bioconcentrate from the environmental matrix to biota tissue and it can biomagnify between successive trophic levels, resulting in neurologically adverse effects in humans mainly from the consumption of MeHg-contaminated fish. Within the last 50 years two major MeHg epidemics were recorded in Iraq and Japan resulting from the consumption of foodstocks with very high concentrations of MeHg, with death tolls recorded in the hundreds for each. However, in North America the scenario is much different with the population being much more susceptible to chronic low dose MeHg exposure. Bearing this in mind, EPA has developed a Reference Dose (RfD) of  $0.1\text{-}\mu\text{g}/\text{kg}/\text{d}$  for MeHg (EPA, 1997a), which is an estimate of daily exposure to the human population that is likely to be without an appreciable risk of deleterious effects during a lifetime.

This section addresses the a) the effects of methyl mercury on aquatic ecology, b) the mechanisms of methyl mercury exposure and uptake in humans, and c) The effects of methyl mercury on human health, including a discussion on human health concerns in the Newark Bay region and methyl mercury toxicity guidelines. Stern (*et al.* 1996) estimated that 21% of women of childbearing age in New Jersey are at risk to adverse affected associated with fish consumption. However, it is still unclear how many fish bioconcentrate MeHg in Newark Bay and how many of these that may be consumed by the public. Therefore, it is recommended that future studies identify the commercial species of fish prevalent in Newark Bay, quantify the number of commercial fish exposed to MeHg, and quantify the number of MeHg-contaminated commercial fish from the Newark Bay region that are likely to be consumed.

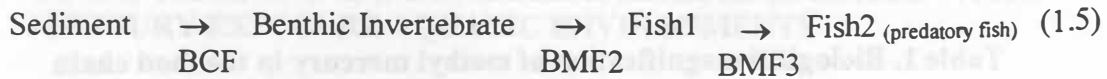
### 1.1 The effects of methyl mercury on aquatic ecology

Methyl mercury compounds have no known normal metabolic function. Their presence in living organisms, including man, is considered to be contamination from environmental sources. However, the biosynthesis of MeHg and MeHg diffusion into cells is still possible under the right conditions in the environment. Biosynthesis is determined by the type of microbial community in addition to the available concentrations of soluble mercuric ion species and methyl- $\text{B}_{12}$  compounds (Wood *et al.* 1968). Bioaccumulation into tissues of higher organisms is most likely controlled by diffusion (NRC, 1978).

Low-level exposure of methyl mercury, under certain circumstances, is associated with reduced growth and photosynthesis in phytoplankton and deformities in plants and animals. In most aquatic systems, organisms are constantly exposed to very low levels of MeHg. This still can be a major concern since MeHg can be absorbed and magnified at each trophic level of the food chain, which ultimately threatens human health. Hamilton (1971) concluded that predators had an average MeHg concentration that was almost 15 times greater than algae eaters (Table 1). Furthermore, studies have shown that only MeHg biomagnifies through successive trophic levels, with virtually all



for the benthic<sup>b</sup> food chain:



$$[\text{MeHg}]_{\text{Fish2}} = [\text{MeHg}]_{\text{sediment}} * \text{BCF} * \text{BMF1} * \text{BMF2} \quad (1.6)$$

$$\text{BCF} = [\text{MeHg}]_{\text{invertebrate}} / [\text{MeHg}]_{\text{sediment}} \quad (1.7)$$

$$\text{BMF} = [\text{MeHg}]_{\text{predator}} / [\text{MeHg}]_{\text{pray}} \quad (1.8)$$

Benoit (2001) has also demonstrated that MeHg bioaccumulation is greater in the benthic (e.g. sediment originated) food chain versus the pelagic food (e.g. water-column originated) chain for lowest level fish (fish 1). However, this estimate depends on the values of the assumed parameters  $[\text{MeHg}]_{\text{sed}}$ ,  $[\text{MeHg}]_{\text{water}}$ ,  $\text{BCF}_{\text{benthic}}$ ,  $\text{BCF}_{\text{water}}$ ,  $\text{BMF}$ , as shown by the following equation.

$$\frac{[\text{MeHg}]_{\text{Fish1}}_{\text{benthic}}}{[\text{MeHg}]_{\text{Fish1}}_{\text{pelagic}}} = \frac{[\text{MeHg}]_{\text{sed}}}{[\text{MeHg}]_{\text{water}}} * \frac{\text{BCF}_{\text{benthic}}}{(\text{BCF}_{\text{water}} * \text{BMF})} \quad (1.9)$$

$$= (5884 / 0.02) * 10^{1.5} / (10^{5.5} * 5) = 5.9$$

for:

Typical water column concentration = 0.02 ng/L (Mason and Sullivan, 1997)

Estimated wet sediment concentration = 5884 ng/L (Mason and Sullivan, 1997)

$\log \text{BCF}_{\text{benthic}} = 1.5$  between sediment and amphipods (i.e.  $\text{BCF}_{\text{benthic}} = 10^{1.5}$ ) (Mason and Sullivan, 1997)

$\log \text{BCF}_{\text{water}} = 5.5$  for phytoplankton (i.e.  $\text{BCF}_{\text{water}} = 10^{5.5}$ ) (Paterson *et al.* 1998; Watras *et al.* 1998; Watras and Bloom 1992; Bloom *et al.* 1991)

Typical BMF range between trophic levels = 3 – 7 (Watras *et al.* 1998; Mason and Sullivan, 1997; Becker and Bigham, 1995; Watras and Bloom, 1992)

## 1.2 The mechanisms of methyl mercury exposure and uptake in humans

Fish consumption is the major source of methyl mercury exposure to humans. Exposure is a function of the fish consumption rate, the type of fish consumed, the physical characteristics of the consuming population group, and the chemical interaction of MeHg in the body. National Research Council (NRC) (2000) developed a rate entry equation to quantify the amount of MeHg that enters the bloodstream:

<sup>b</sup> In the benthic food chain, MeHg bioconcentration primarily occurs via uptake into sediment-dwelling invertebrates.

$$I = D \times W \times A \times F \quad (1.10)$$

where:

I = rate of MeHg entry into the blood ( $\mu\text{g}/\text{d}$ )

D = ingested dose (microgram per kilogram of body weight per day)

W = body weight (kg)

A = fraction of MeHg that is absorbed

F = fraction of absorbed MeHg that is distributed to the blood

In humans, MeHg is readily absorbed through the gastrointestinal tract and readily enters the adult and fetal brain, where it accumulates and is slowly converted to inorganic mercury. The demethylation of MeHg into  $\text{Hg}^{2+}$  and its intrinsic toxicity are the cause of adverse health effects once it has entered the body. However, the mechanism that is responsible for these effects is unknown, nor it is understood how exposure to other forms of mercury affects methyl mercury toxicity (NRC, 2000). At the same time, much progress has been made on determining many of the toxicological characteristics of MeHg as indicated in Table 2. For example, garlic, selenium, and zinc have been cited as potential antagonists to MeHg poisoning. Previous studies also provide evidence that vitamin C (Yamini *et al.* 1984) and vitamin E (Chang *et al.* 1978) may modify MeHg toxicity. In the case of selenium, it appears that it antagonizes the metabolic effects of mercury (Fimreite 1979). It is hypothesized that protective effects of selenium are either due to an antioxidative or due to the formation of a biologically inactive compound (Hansen 1988).

### 1.3 The effects of methyl mercury on human health

Two major methyl mercury epidemics have occurred in the twentieth century. The first major case occurred in Japan, with more than 700 cases of MeHg poisoning by 1974 due to fish consumption contaminated by mercury waste discharges from the Chisso Chemical Corporation into Minamata Bay (Tsubaki 1971; WHO 1976b; Tsubaki and Irukayama 1977). Individuals exhibited paraesthesia<sup>c</sup>, ataxia<sup>d</sup>, sensory disturbances, tremors, hearing impairment, and difficulty in walking (Harada, 1995; NRC, 2000). The median total mercury level in fish was estimated to be  $11 \mu\text{g}/\text{g}$  (Berglund *et al.* 1971).

The largest outbreak of methyl mercury poisoning ever recorded occurred in Iraq during the winter of 1971-1972 as a result of consumption of homemade bread prepared from seed wheat treated with a methyl mercury fungicide. Over 6000 children and adults were admitted to hospitals with 459 reported deaths (Bakir *et al.* 1973; WHO 1976a). Patients exhibited a range of symptoms including paraesthesia, ataxia, dysarthria<sup>e</sup>, loss of hearing, and death.

In North America, chronic low-dose prenatal MeHg exposure from maternal consumption of fish is the most likely concern. These low doses have been associated with more subtle end points of neurotoxicity in children. The effects include poor

<sup>c</sup> Paraesthesia: loss of sensation at the extremities of the hands and feet in areas around the mouth

<sup>d</sup> Ataxia: loss of coordination

<sup>e</sup> Dysarthria: slurred speech

performance on neurobehavioral tests (particularly on tests of attention), fine-motor function, language, visual-spatial abilities, and verbal memory (NRC, 2000). There is also evidence that MeHg can have adverse effects on the cardiovascular system. In addition, some studies have shown an association between MeHg and cancer. However, it is inconclusive that MeHg is a carcinogen (NRC, 2000). Ultimately, neurological disturbances are the best-documented and the most widely accepted concern.

**Table 2. Toxicological characteristics of methyl mercury (NRC, 2000; WHO 1976b)**

<b>Toxicological characteristics</b>	<b>Description</b>
Average reference values	Blood: 8- $\mu\text{g/L}$ , hair: 2- $\mu\text{g/L}$ , urine: 4- $\mu\text{g/L}$ . These values indicate the total Hg in biological materials commonly used to indicate human exposure.
Biological monitoring:	Hair, blood, cord blood
<u>Toxicokinetics</u>	
<i>Absorption</i>	
Inhalation:	MeHg vapors absorbed
Oral:	Approx. 95% MeHg in fish readily absorbed in GI track
Dermal:	3-5% applied MeHg dose in guinea pigs absorbed in 5 hr
<i>Distribution</i>	<ul style="list-style-type: none"> <li>• 1-10% absorbed MeHg oral dose distributed to blood; 90% of blood MeHg in red blood cells (RBCs)</li> <li>• 50-day blood half-life (50% found in liver; 10% in head)</li> <li>• Readily crosses blood-brain and placental barriers</li> </ul>
<i>Biotransformation</i>	<ul style="list-style-type: none"> <li>• MeHg slowly demethylates to mercuric Hg (<math>\text{Hg}^{2+}</math>)</li> <li>• Tissue demethylation sites: tissue macrophages, intestinal flora, fetal liver</li> <li>• Mechanisms of demethylation unknown</li> </ul>
<i>Excretion</i>	<ul style="list-style-type: none"> <li>• Daily excretion: 1% of body burden</li> <li>• Major excretory route: bile and feces (90% excreted in feces as <math>\text{Hg}^{2+}</math>; 10% excreted in urine as <math>\text{Hg}^{2+}</math>)</li> <li>• MeHg is 16% of Hg in breast milk</li> </ul>
<i>Half-life elimination</i>	70-80 days, whole body (function of species, dose, sex, and animal strain)
<u>Toxicodynamics</u>	
<i>Critical target organ</i>	Adult and fetal brain
<i>Causes of toxicity</i>	<ul style="list-style-type: none"> <li>• Demethylation of MeHg to <math>\text{Hg}^{2+}</math></li> <li>• Intrinsic toxicity of MeHg</li> </ul>
<i>Latency period (no toxic signs during this period)</i>	<ul style="list-style-type: none"> <li>• Iraq epidemic: weeks to months</li> <li>• Japan epidemic: more than a year</li> </ul>
<i>Potential antagonists</i>	Garlic, selenium, and zinc



### 1.3.1 Human health concerns in the Newark Bay region

The EPA has estimated that 7% of all women within the U.S. exceed the RfD. Furthermore, food consumption surveys in New Jersey estimate that 21% of women of childbearing age exceed the current RfD (Stern *et al.* 1996). There is also reason to believe that over 60,000 newborns annually could be subject to risk for adverse neurodevelopmental effects from MeHg in utero exposure, based on consumption data and current population and fertility rates (NRC 2000).

### 1.3.2 Methyl mercury toxicity guidelines

In the U.S., both the Food and Drug Administration (FDA) and the EPA are responsible for the regulation of mercury. The FDA is responsible for ensuring that Hg concentrations do not exceed agency-defined levels in commercially sold fish and seafood. The EPA is responsible for monitoring Hg concentrations in environment and regulating industrial releases to the air and surface water. The Agency for Toxic Substances and Disease Registry evaluates the potential human exposure to MeHg and investigates the reported health effects, although it is not a regulatory agency. International bodies such as the World Health Organization (WHO) have also evaluated the exposure and effects of MeHg, and recommended fish consumption guidelines. However, these agencies each use different means to assess toxicant exposure. Unique agency guidelines are due to different risk-assessment methods, data sets, uncertainty factors, and different agency mandates.

The EPA has developed a reference dose (RfD)<sup>f</sup> for human consumption of methyl mercury. The RfD is also based on data that indicates the “critical dose”, which is generally the most subtle indicator of an adverse effect (EPA, 1997a). The RfD for methyl mercury was calculated as 0.1 µg/kg-day (with uncertainty factor of 10) and based on the data analysis of the 1971-1972 Iraq incident (EPA, 1997a; NRC, 2000). Comparison to 7 other MeHg intake guidelines, the RfD is relatively conservative compared to the FDA’s recommendation of 0.5 µg/kg-day (Friberg *et al.* 1971), but not as low as Washington States’ tolerable daily intake (TDI) range of 0.035-0.08 µg/kg/d (Grandjean *et al.* 1997). However, the RfD<sup>g</sup> has been criticized because it is based on the Iraqi data where MeHg exposures were not comparable to low-level, chronic exposures seen in the North American population (NRC, 2000).

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<sup>f</sup> The RfD is defined as an estimate (with uncertainty spanning perhaps an order of magnitude) of daily exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime (EPA, 1997).

<sup>g</sup> The NRC has concluded that the Iraqi study no longer be used for estimating RfDs due to the number of uncertainties associated with this data set, the NRC believes that the EPA RfD of 0.1 µg/kg per day is a scientifically justifiable level for the protection of public health. Furthermore, the Faroe Island study is believed to be more appropriate of future determination of an acceptable RfD (NRC, 2000).

## 2. EFFECTS OF SEDIMENT AND WATER QUALITY ON MERCURY METHYLATION IN ESTUARINE SEDIMENTS

### 2.1 Introduction to mercury methylation

Metals such as mercury that form alkyl compounds (i.e. methyl mercury) are a major concern because these compounds are volatile and can bioaccumulate. Ultimately, MeHg (ie.  $\text{CH}_3\text{Hg}^+$ ) is poisonous to the central nervous system in high concentrations. MeHg exists as an aquo complex ( $\text{CH}_3 - \text{Hg} - \text{OH}_2^+$ ) in solution, with covalent bonds between Hg and O (Stumm and Morgan, 1981). The toxicological properties of MeHg are characterized by the fact that it is a stable complex that is formed very quickly. Furthermore, MeHg is not readily decomposed, kinetically speaking, as shown by Reaction 1 and its Log K value of 50 in Table 3.

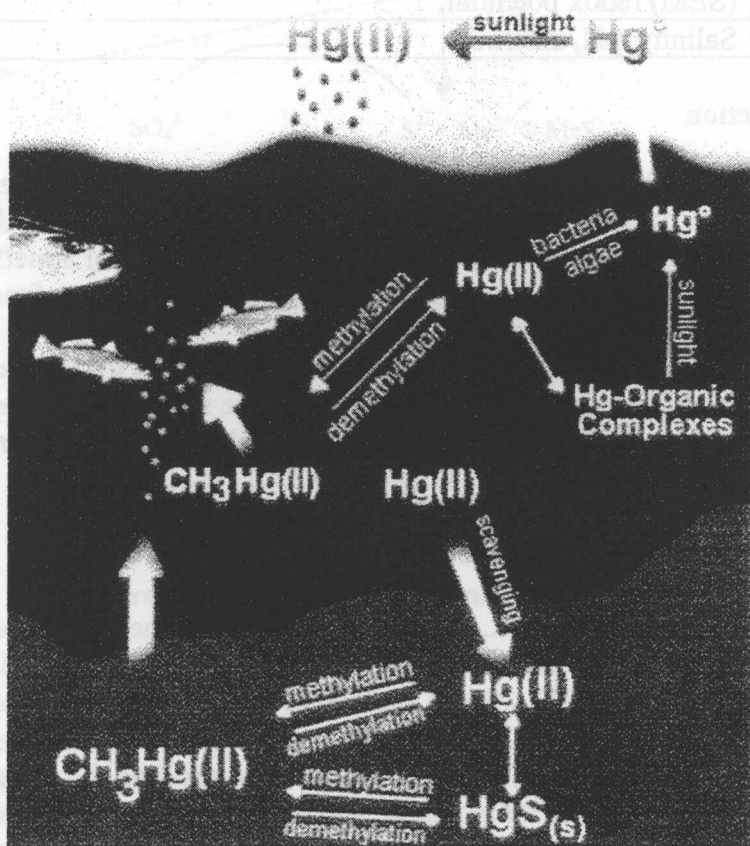
**Table 3. Stability of methymercury and its complexes (Stumm and Morgan, 1981)**

Reaction	Log K
(1) $\text{Hg}^{2+} + \text{CH}_3^- = \text{CH}_3\text{Hg}^+$	~ 50
(2) $\text{CH}_4(\text{aq}) = \text{CH}_3^- + \text{H}^+$	~ -47
(3) $\text{Hg}^{2+} + \text{CH}_4(\text{aq}) = \text{CH}_3\text{Hg}^+ + \text{H}^+$	~ 3
(4) $\text{CH}_3\text{Hg}^+ + \text{CH}_3^- = (\text{CH}_3)_2\text{Hg}$	~ 37
(5) $\text{CH}_4(\text{aq}) + \text{HgCl}_2 = \text{CH}_3\text{HgCl} + \text{H}^+ + \text{Cl}^-$	-5.2
(6) $\text{CH}_3\text{Hg}^+ + \text{Cl}^- = \text{CH}_3\text{HgCl}$	5.25
(7) $\text{CH}_3\text{Hg}^+ + \text{H}_2\text{O} = \text{CH}_3\text{HgOH} + \text{H}^+$	-4.63
(8) $\text{CH}_3\text{Hg}^+ + \text{CO}_3^{2-} = \text{CH}_3\text{HgCO}_3^-$	6.1
(9) $\text{CH}_3\text{Hg}^+ + \text{SO}_4^{2-} = \text{CH}_3\text{HgSO}_4^-$	0.94
(10) $\text{CH}_3\text{Hg}^+ + \text{S}^{2-} = \text{CH}_3\text{HgS}^-$	21.02
(11) $\text{CH}_3\text{Hg}^+ + \text{CH}_3\text{HgOH} = (\text{CH}_3\text{Hg})_2\text{OH}$	6.1
(12) $\text{CH}_3\text{Hg}^+ + \text{CH}_3\text{HgS}^- = (\text{CH}_3\text{Hg})_2\text{S}$	16.34
(13) $\text{HgS}(\text{s}) + \text{CH}_4 = \text{CH}_3\text{HgS}^- + \text{H}^+$	~ -26

The mercury cycle in aquatic systems is very complex due to the fact that thermodynamically predictable interactions between solution complexes of inorganic mercury (Hg(II)) and organo-Hg compounds, such as methyl mercury, do not exist. Through experimental work, it has been determined that MeHg is primarily produced by the reaction between bacteria and Hg(II). Kinetics control the partitioning between the organic and inorganic phases via production (i.e. methylation) and destruction (i.e. demethylation). However, methylation is more kinetically favorable as noted before.

In Figure 1, the major features of the mercury cycle are shown. Mercury enters the aquatic ecosystem primarily through the process of wet deposition of Hg(II). In the water, Hg(II) can be reduced to  $\text{Hg}^0$ , converted to Hg-organic complexes, or methylated into MeHg. Inorganic mercury also scavenges onto suspended particles and settles via sedimentation. According to Allen (1995), the most intense biogeochemical activity of any sediment is concentrated within the surface layer in which a deposited metal participates in a variety of processes, including microbial reactions, redox

transformations, adsorption-desorption exchanges, and the precipitation and dissolution of minerals. In Figure 1, Hg(II) in the sediment layer can precipitate to form sulfide complexes or methylate into MeHg.



**Figure 1. Mercury cycle in the aquatic environment**  
<http://loer.tamug.tamu.edu/Research/Mercury/mercury.htm>

The remainder of Section 2 discusses the conditions within the sediment and water column that could effect mercury methylation in Newark Bay surficial sediments. Sediment characteristics are introduced in Section 2.2 and water column characteristics are introduced in Section 2.5 as shown below in Table 4 in the order of appearance.

**Table 4. Sediment and water column characteristics**

Medium	Characteristic
Sediment	Sulfate reduction, organic matter, oxygen content, sulfide content, acid volatile sulfides (AVS) and simultaneously extracted metals (SEM) redox potential,
Water column	Salinity, pH, alkalinity

## 2.2 Sulfate reduction

Sulfate reducing bacteria (SRB) are the principal methylators of mercury in estuarine sediments (Compeau and Bartha, 1985; Gilmour *et al.* 1984). SRB methyl mercury (MeHg) production occurs via enzyme-mediated transfer of a methyl group from B-12 (Vonk and Sijpesteinjn, 1973), where microbial populations are a function of the extent of eutrophication (DeSimone *et al.* 1973).

King *et al.* (2001) recently developed a qualitative model for the mercury methylation rate (MMR), suggesting that MMR in aquatic sediments can be estimated if the sulfate reduction rate (SSR) and the concentration of bioavailable Hg are known. Benoit (2001) adapted this model from King *et al.* (2001) as shown below.

$$\text{MMR} = f \times \text{SSR} \times [\text{Hg}]_{\text{bioavailable}} \quad (2.1)$$

where:  $f$  = rate constant =  $\text{MMR}/\text{SSR}$ , was empirically determined in pure-culture assays using several sulfate-reducer strains (King *et al.* 2001). The MMR/SSR ratio in pure cultures ranged from  $0.28\text{-}26 \times 10^{-6}$  with an average of  $7.2 \times 10^{-6}$  from experimental work by King *et al.* (2001).

According to Benoit (2001), the main variables controlling the sulfate reduction rate are the sulfate concentration, temperature, and organic matter as shown below. Mercury bioavailability is proportional to the total Hg concentration and inversely proportional to sulfide content, which Benoit *et al.* (1999) demonstrated through a pore water speciation model that made it possible to estimate a bioavailability factor that can be applied to the total Hg concentration in sediments.

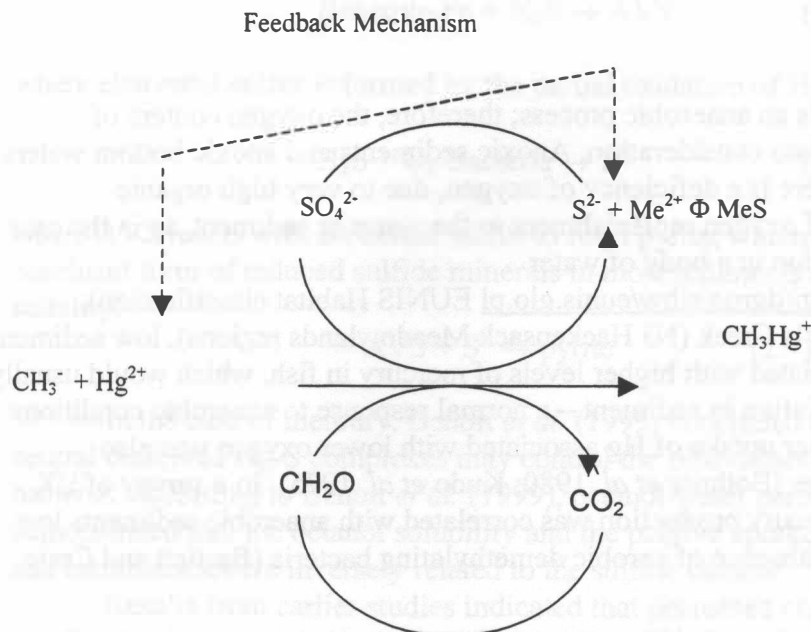
$$\text{SSR} = F([\text{Sulfate}], [\text{OM}], T) \quad (2.2)$$

$$[\text{Hg}]_{\text{Bioavailable}} = F([\text{Hg}_T], 1/[\text{sulfide}]) \quad (2.3)$$

Anid (2001) provided a model (Figure 2) that qualitatively illustrates the importance of sulfate reducing bacteria, divalent mercury, and organic matter in mercury methyl formation, which strongly supports the model adapted by Benoit *et al.* (2001) from King *et al.* (2001) as previously discussed. In the Anid model (2.2), both sulfate ( $\text{SO}_4^{2-}$ ) and organic matter ( $\text{CH}_2\text{O}$ ) react with the methyl group ( $\text{CH}_3$ ) and divalent mercury ( $\text{Hg}^{2+}$ ) to produce methyl mercury ( $\text{CH}_3\text{Hg}^+$ ).

According to this model, carbon dioxide ( $\text{CO}_2$ ) is produced as a byproduct of methyl mercury formation in the reaction with organic matter. Sulfide and the mercury sulfide complex are formed as a byproduct resulting from the reaction between sulfate, organic matter, the methyl group, and the divalent Hg cation. The model illustrates the

importance of a feedback mechanism where sulfide indirectly contributes to methylation via sulfate production.



**Figure 2. Methyl mercury formation (Anid, 2001)**

where:

$\text{CH}_3^-$  = methyl group

$\text{Hg}^{2+}$  = divalent mercury

$\text{CH}_3\text{Hg}^+$  = methyl mercury

$\text{Me}^{2+}$  = divalent metal ion (generic)

$\text{CH}_2\text{O}$  = organic matter (generic) (dissolved or particulate)

### 2.2.1 Organic matter (OM)

Organic matter is typically measured as total organic carbon (TOC) and consists of a large number of components including macroscopic particles, colloids, dissolved macromolecules, and specific compounds. The average TOC content was  $2.3 \pm 0.6\%$  of the total for surficial sediments in Newark Bay compared to an average of  $1.9 \pm 0.3\%$  for the NY/NJ Harbor (EPA, 1998). In Section 4, TOC sample concentrations in surficial sediments are shown using GIS (Figure 13).

Studies by Kelly *et al.* (1997) and Benoit *et al.* (1998) indicate that organic matter may stimulate bacterial activity that is capable of Hg methylation, thus supporting the sulfate reduction rate model discussed above in Section 2.2. In a much earlier study, Olsen and Cooper (1976) determined that high OM contents favored methylation in San Francisco Bay sediments. These results are consistent with those of Cossa *et al.* (1988) who concluded that deposition of Hg could occur by the scavenging of dissolved mercury in the water column onto organic particles. Benoit *et al.* (1998) also demonstrated that scavenging might be salinity-driven since the ratio of Hg to organic matter was shown to



be inversely related to salinity, in a study of the Patuxent River estuary study. However, Benoit *et al.* (1998) concluded that there was no linear trend between organic matter content and MeHg concentrations.

### 2.2.2 Oxygen content

Sulfate reduction is an anaerobic process; therefore, the oxygen content of sediments must be taken into consideration. Anoxic sediments and anoxic bottom waters commonly exist where there is a deficiency of oxygen, due to very high organic productivity, and a lack of oxygen replenishment to the water or sediment, as in the case of stagnation or stratification in a body of water

(<http://mrw.wallonie.be/cgi/dgrne/sibw/eunis.glo.pl> EUNIS Habitat classification).

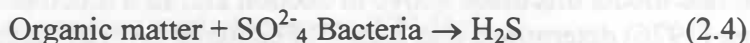
In a study of Berry's Creek (NJ Hackensack Meadowlands regions), low sediment oxygen content was associated with higher levels of mercury in fish, which would usually be attributed to Hg methylation in sediment – a normal response to anaerobic conditions (Weis *et al.* 1986). A higher uptake of Hg associated with lower oxygen was also supported by earlier studies (Bothner *et al.* 1980; Kudo *et al.* 1975). In a survey of UK estuaries, high methyl mercury production was correlated with anaerobic sediments low in sulfide content and the absence of aerobic demethylating bacteria (Bartlett and Craig, 1981).

### 2.3 Sulfide content

There has been growing experimental evidence that interactions between toxic metals and authigenic<sup>h</sup> sulfide minerals in anoxic sediments play a role in controlling bioavailability of such metals. Many transition metals form highly insoluble sulfide minerals and have been observed to adsorb and coprecipitate with commonly formed authigenic iron sulfide minerals. This process leads to the formation of sedimentary sulfide minerals and with the destruction of organic and inorganic components of sediments with which potentially bioavailable fractions of toxic metals are strongly associated. For example, DiToro *et al.* (1990) observed that there was no toxicity of cadmium to amphipods when the molar concentration of Cd was less than that of reduced sulfur.

For reference purposes, the four major processes resulting in the formation of sedimentary sulfide minerals are listed below, as specified from previous investigations (Rickard, 1969; Berner, 1970; Sweeney and Kaplan, 1973), discussed by Allen (1995) in a summary of sulfide chemistry in anoxic sediments:

when sulfides are produced from the bacterially-mediated oxidation of organic matter by sulfate reduction:



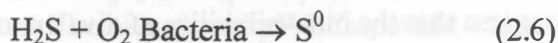
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<sup>h</sup> Pertaining to minerals or materials that grow in place with a rock, rather than having been transported and deposited.

where upon hydrochloric leaching of sediment dissolves iron minerals and H<sub>2</sub>S is generated. This kind of reaction is operationally grouped as “acid volatile sulfides” (AVS):



where elemental sulfur is formed by the partial oxidation of H<sub>2</sub>S by bacteria:



where AVS reacts with elemental sulfur to form pyrite, which is considered to be the dominant form of reduced sulfide minerals in most sediments due to thermodynamic stability:



In the case of mercury, Benoit *et al.* (1999) concluded that the passive uptake of neutral dissolved Hg-S complexes may control the bioavailability of Hg to methylating bacteria. According to Benoit *et al.* (1999), octanol-water partitioning of inorganic Hg demonstrated that the octanol solubility and the passive uptake of Hg across hydrophobic cell membranes were inversely related to the sulfide content.

Results from earlier studies indicated that decreased concentrations of mercury in the dissolved state were due to the precipitation of HgS<sub>(s)</sub>. (Compeau and Bartha, 1985; Choi and Bartha, 1994; Compeau and Bartha, 1983; Compeau and Bartha, 1987; Winfrey and Rudd, 1990; Blum and Bartha, 1980). In effect, sulfide formation complicates the methylation process by binding to both Hg<sup>2+</sup> and CH<sub>3</sub>Hg<sup>2+</sup>.

In a study of the Lower Hudson Estuary, Gilmour and Capone (1987) concluded that Hg methylation was inversely related to the sediment sulfide concentration. Finally, Craig and Moreton (1983) estimated that the maximum MeHg production rate occurred at a sediment sulfide concentration of 1.8 mg/g in a specific case study of the estuarine River Carron, UK.

### 2.3.1 The relationship between acid volatile sulfides and simultaneously extracted metals

Studies suggest that when the difference between the molar concentrations of simultaneously extracted metals (SEM) and metals in the acid volatile form (AVS) is less than 0 (ie. (SEM – AVS < 0), sulfides should be bound to all metals in theory, with none being bioavailable (NOAA, 1995 Hansen *et al.* 1996). However, if SEM – AVS > 0, then the sulfide binding capacity is exceeded, resulting in an increased potential for toxicological effects (Hansen *et al.* 1996).

Di Toro *et al.* (1992) defined SEM as the metal extracted by the AVS analytical method (not the total metal in the sediments). The best estimate of potentially bioavailable metal concentrations for comparison to AVS. SEM includes the divalent metals cadmium (Cd), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb), and zinc (Zn). Jorgensen (1977) defined AVS as a useful parameter because it represents the availability of metals, which varies by season and sediment depth in response to sulfur cycles, that

are related to temperature and productivity (Di Toro *et al.* 1990; Di Toro *et al.* 1992; EPA, 1998).

The EPA (1998) used the SEM-AVS technique in a Harbor-wide study of surficial sediments sampled during the summer of 1993 and 1994. The difference between SEM and AVS was greater than zero (i.e.  $SEM - AVS > 0$ ) for 36% of all the samples, with 54% of the Lower Harbor samples having a difference greater than zero. This contrasts with data from Newark Bay, where only 12% of all samples were greater than zero; this would suggest that the bioavailability of divalent metals is small relative to the rest of the Harbor, based on the previous discussion from Di Toro *et al.* (1992). Furthermore, Hg was not present in any of the simultaneous extractions. In the 20 SEM samples within Newark Bay, zinc exhibited the highest SEM, with lead being the second highest for 60% of the samples and copper the third highest for the remaining 40%.

## 2.4 Redox potential

Redox (oxidation – reduction) reactions play a major role in many of the reactions occurring in natural waters. The behavior of compounds containing carbon, nitrogen, sulfur, iron, and manganese in natural waters are largely influenced by redox reactions. The redox reaction consists of two parts (or half-reactions), that is the oxidation reaction (i.e. substance loses electrons) and the reduction reaction (i.e. substance gains electrons). Redox reactions must include both parts since free electrons cannot exist in solution and must also be conserved (Snoeyink V.L. and Jenkins, D., 1980).

Bartlett and Craig (1981) surveyed sediments of the Mersey and Clyde Estuaries, UK, for correlations between total mercury ( $Hg_T$ ), MeHg, organic carbon, particle size, and sulfide. They concluded that MeHg is only present in these estuarine sediments with negative redox potentials. The maximum MeHg production was predicted at a redox potential of -100 to 0 mV. In intertidal New Jersey mudflats, Compeau and Bartha (1984) determined that the highest methylation rate and the equilibrium MeHg concentration occurred at a low redox potential of -220 mV, which also corresponded to a low salinity of 0.4‰; however, this affect may be due to low sulfide content as opposed to salinity.

## 2.5 Salinity

Salinity is a measure of the total quantity of dissolved solids in water, in parts per thousand (ppt), when all organic matter has been completely oxidized, all carbonates have been converted to oxides, and bromide and iodide to chloride. (<http://mrw.wallonie.be/cgi/dgrne/sibw/eunis.glo.pl> EUNIS Habitat classification).

In estuaries, salinity increases in the seaward direction. In a biological and hydrographical characterization of Newark Bay (<http://www.sh.nmfs.gov/NEWRKbay.htm>), the average salinity ranged from 15 to 25 parts per thousand from May 1993 to April 1994, with deviations as low as 5 parts per thousand during the late spring and summer months.

According to measurements by Gilmour and Capone (1987), Hg methylation in the Lower Hudson Estuary was inversely related to salinity, with the highest methylation rates occurring in nearly freshwater sediments at salinity concentrations in the range of one part per thousand. Additional studies by Blum and Bartha (1980) and Bartlett and

Craig (1981) also support this inverse relationship between MeHg methylation and the salinity gradient.

## 2.6 pH

The pH is defined as the negative logarithm of the hydrogen ion concentration in a water body. Pure water has a pH of 7 (pH < 7 indicates an acidic solution and pH > 7 indicates a basic solution) The measure of pH is important not only because of the dissolved ion concentration, but also because the toxicity of many pollutants increases with changes in pH. Dissolution of metal ions can occur in acidic waters. Negative effects usually occur in combination with temperature, dissolved oxygen, prior acclimatization of organisms, and the ion content in the surface water. Acidic precipitation may have toxic effects on aquatic biota. Low pHs have been known to favor the mobilization and the release of many metals from sediments (MacFarlane and Livingston, 1983; Gilmour and Henry, E.A., 1991; Whinfrey and Rudd, 1990). In fresh waters, acid deposition may influence microbiological and biogeochemical changes that could lead to increased levels of methyl mercury (Gilmour and Henry, 1991). The New Jersey surface water quality criterion is: pH > 6.5 and < 8.5 (NJWSA, 2001). Average pH in Newark Bay was  $7.32 \pm 0.13$  (EPA, 1998).

## 2.7 Alkalinity

Alkalinity is not a specific polluting substance, but is a good measure of the capacity of water to neutralize hydrogen ions. It is expressed in terms of the equivalent amount of calcium carbonate (Ciemniecki, 2001). Municipal and industrial wastewater loadings typically increase the natural levels of alkalinity. Decreased levels of alkalinity can increase the toxicity of metals (NJWSA, 2001). Also, it has been proposed that low alkalinity is correlated with methyl mercury accumulation (Wiener, J.G. and P.M. Stokes, 1990)

### 3. SOURCES OF MERCURY TO NEWARK BAY

The metropolitan region surrounding Newark Bay has been one of the largest manufacturing and industrial centers in the eastern United States since the early 1800s (Mytelka *et al.* 1973; Whipple *et al.* 1976; Wilber and Hunter, 1979; Rod *et al.* 1989). These activities have resulted in pollution from municipal and industrial wastewater, stormwater runoff, accidental spills, direct dumping of wastes, and atmospheric deposition (Olsen *et al.* 1984; HydroQual, 1991). Furthermore, some of the world's largest mercury industries have operated in the Newark Bay vicinity for nearly a century (Ayres and Ayres, 1999), contributing to the anthropogenic levels of Hg in Newark Bay sediment as reported by Suszkowski (1978), Meyerson (1981), NYC DEP (1991 and 1993), Long *et al.* (1995), and EPA (1998).

In a comprehensive study of pollution and contamination in Newark Bay, Crawford *et al.* (1995) summarized the major sources of mercury. These sources included discharges from municipal wastewater treatment plants (WWTPs), combined sewer overflows (CSOs), stormwater (SW) runoff, and tributary flow. In addition, Crawford *et al.* (1995) estimated that two WWTPs in particular, Passaic Valley Sewer Commission (PVSC) and Middlesex County Sewer Authority (MCSA) were major sources of Hg. These sources are summarized in Table 5 and are further discussed in this section.

**Table 5. Sources of mercury to Newark Bay (Crawford *et al.* 1995)**

Source	Hg discharge rate (kg/day)	Hg discharge rate (kg/yr)
Municipal wastewater treatment plants <sup>i</sup>	0.72	263
Passaic Valley Sewer Commission <sup>j</sup>	2.0	730
Middlesex County Sewer Authority <sup>j</sup>	0.29	106
Combined sewer overflows	0.62	226
Stormwater runoff	0.40	146
Tributary flow <sup>k</sup>	0.42	153
<b>Total</b>	<b>4.45</b>	<b>1624</b>

<sup>i</sup> Includes discharges to the Arthur Kill, Kill Van Kull, and Hackensack Rivers up to 1989.

<sup>j</sup> PVSC discharges directly to NY Upper Bay; MCSA discharges to the mouth of the Raritan River. Crawford *et al.* (1995) assumed that Newark Bay received Hg effluent discharges from both via tidal transport.

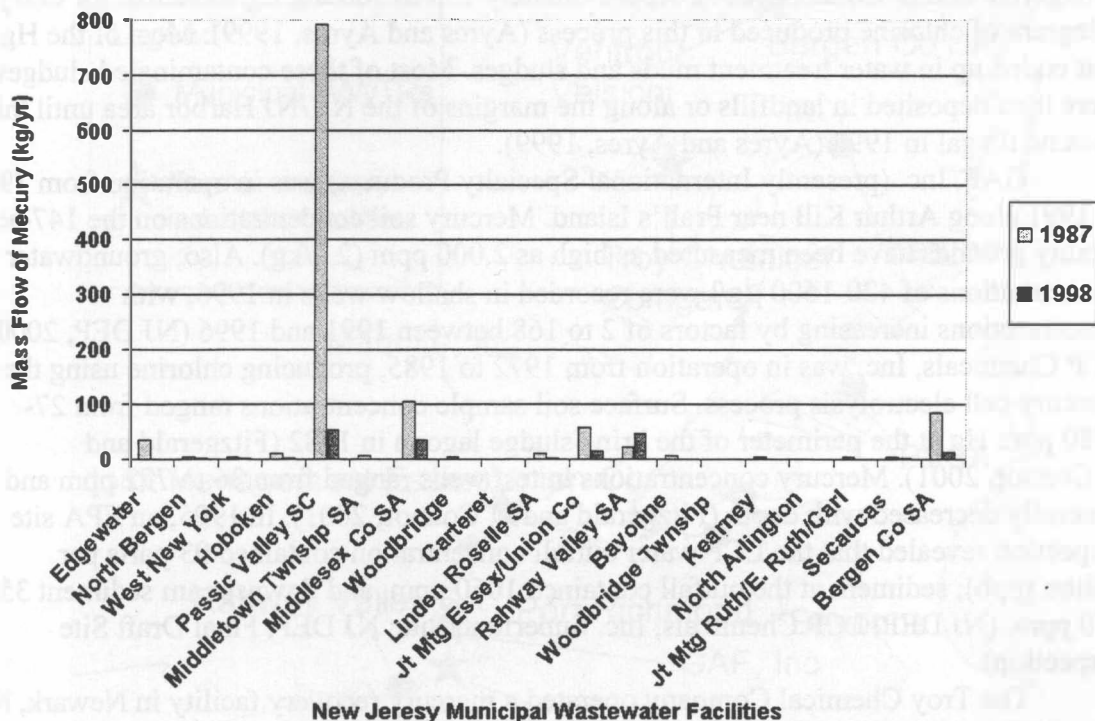
<sup>k</sup> Tributary flow was based on USGS gauging and water quality stations for Hackensack and Passaic River and reflects all other discharges /inputs to those tributaries.

#### 3.1 Municipal wastewater discharges

Crawford *et al.* (1995) estimated that 263 kg/yr of mercury entered Newark Bay from municipal wastewater treatment plants (WWTP), with an additional 730 kg/yr from Passaic Valley Sewer Authority (PVSA) and 106 kg/yr from Middlesex County Sewer Authority (MCSA) for a total WWTP contribution of 1099 kg/yr.

More recent results by Themelis and Gregory (2001) (Figure 3) show the reduction in mercury effluent discharges from New Jersey municipal wastewater facilities. Between 1987 and 1998, Hg contributions from PVSC decreased from

approximately 800 kg/yr to 50 kg/yr and MCSA contributions decreased from approximately 100 kg/yr to 40 kg/yr (HydroQual, 1991; NJ DEP, 2001). The 1987 estimates for both of these WWTPs are relatively close to those made by Crawford *et al.* (1995) (730 kg/yr for PVSC and 106 kg/yr for MCSA). The location of both these facilities, and others within the vicinity of Newark Bay are shown in Figure 4 at the end of Section 3.2.1.



**Figure 3. Reduction in mercury content of New Jersey municipal wastewater treatment plants (HydroQual, 1991; NJ DEP, 2001)**

High mercury loads from municipal wastewater have historically been attributed to the large number of industries discharging to municipal treatment plants. As of 1992, an estimated 380 industrial users discharged wastes to the Passaic Valley Sewer Commission (PVSC) facility (PVSC, 1992). It has also been estimated that industries in Northern New Jersey discharged 94% of their chemical wastes (on a weight basis) to municipal facilities, discharging only 6% directly to surface waters (NJ DEPE, 1986b).

The significant mercury reduction from municipal facilities is most likely attributed to the phasing out of necessary industrial uses and also improved wastewater treatment techniques. Improvements may have included Hg recovery techniques such as the enzymatic reduction of soluble divalent mercury ( $Hg^{2+}$ ) to insoluble elemental mercury ( $Hg^0$ ) by mercury resistant bacteria (Wagner-Dobler *et al.* 2000).



## 3.2 Industrial wastewater discharges

### 3.2.1 Historic industrial sites

Some of the world's largest mercury industrial facilities were located within the Newark Bay area. Mercury cell chlor-alkali plants were built by GAF, Inc. in Linden, NJ, by Maquite, Inc. in Elizabeth, NJ, and by LCP Chemicals just south of the GAF facility (Fitzgerald and O'Connor, 2001). Approximately 150 to 300 mg Hg were lost for every kilogram of chlorine produced in this process (Ayres and Ayres, 1999). Most of the Hg lost ended up in water treatment muds and sludges. Most of these contaminated sludges were then deposited in landfills or along the margins of the NY/NJ Harbor area until this became illegal in 1992 (Ayres and Ayres, 1999).

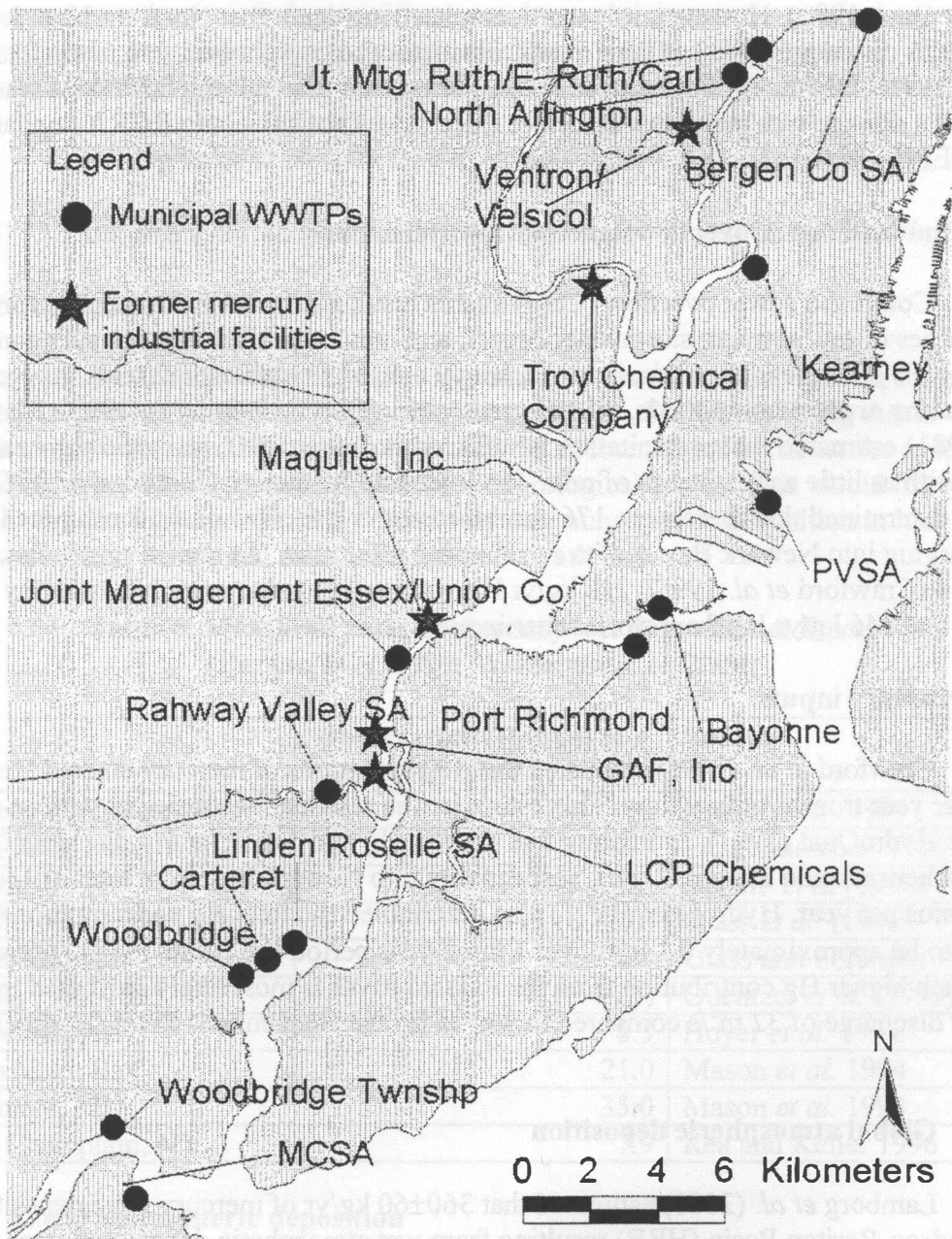
GAF, Inc. (presently International Specialty Products) was in operation from 1919 to 1991 along Arthur Kill near Prall's Island. Mercury soil concentrations on the 147-acre facility grounds have been measured as high as 2,000 ppm (2 g/kg). Also, groundwater concentrations of 420-1600 µg/l were recorded in shallow wells in 1996, with concentrations increasing by factors of 2 to 168 between 1991 and 1996 (NJ DEP, 2000). LCP Chemicals, Inc. was in operation from 1972 to 1985, producing chlorine using the mercury cell electrolysis process. Surface soil sample concentrations ranged from 27-1580 ppm Hg at the perimeter of the brine sludge lagoon in 1982 (Fitzgerald and O'Connor, 2001). Mercury concentrations in test wells ranged from 36 to 772 ppm and generally decreased with depth (Fitzgerald and O'Connor, 2001). In 1995, an EPA site inspection revealed that the LCP water outfall concentration contained 93 parts per billion (ppb); sediment at the outfall contained 1060 ppm, and downstream sediment 350-470 ppm. (NJ DEP, LCP Chemicals, Inc. Superfund Site; NJ DEP, Final Draft Site Inspection).

The Troy Chemical Company operated a mercury recovery facility in Newark, NJ from 1974 to 1980. The Troy site was drained by the artificial Pierson's Creek, which discharged untreated wastewater from initial inception in 1965 to 1982 (Fitzgerald and O'Connor, 2001). PVSC analyzed liquid waste at the Troy facility from January to May 1979 and concluded that the company was discharging approximately 150 kilograms of Hg per day to the PVSC sewage system. Continuous discharges and spills of Hg were indicated by high on-site sediment concentrations from 11,000 ppm to more than 22,000 ppm (Troy Chemical Company, Inc., undated).

Ventron/Velsicol operated a chemical processing plant from 1929 to 1974 within the Hackensack Meadowlands. The plant manufactured various mercury products including red and yellow oxide of mercury, phenyl mercuric acetate, and also reclaimed Hg from amalgams, batteries, and impure Hg (EPA, 2000). Various Hg-containing materials were dumped in a 19-acre site near Berry's Creek after 1960, much being intertidal filled land (Z. Kelman, 2001). Mercury soil concentrations up to 600 feet outside the boundary ranged from 2 to 550 ppm. It is estimated that 160 tons or more Hg were dumped on this site (URS Corporation, 1975).

Figure 4 shows the relative location of historic mercury industrial sites (i.e. GAF, Inc; LCP Chemicals; Maquite, Inc.; Troy Chemical Company; Ventron/Velsicol) and municipal wastewater treatment plants (WWTPs) in the Newark Bay Vicinity. The location of these industrial sites was based on data from Fitzgerald and O'Connor (2001),

with an estimated margin of error of two to four kilometers in the placement on Figure 4. The location of WWTPs was based on data from HydroQual (1991), with an estimated margin of error of less than one in the placement on Figure 4.



**Figure 4. Location of municipal wastewater treatment plants and former mercury industrial facilities in the Newark Bay vicinity**

### 3.2.2 Current industrial wastewater discharges

By 1989, no direct discharges of Hg were reported for any of 400 industrial facilities with permits to discharge directly into the New York/New Jersey Harbor (HydroQual, 1991). However, it is worth emphasizing again that Northern New Jersey industries discharged 94% of their chemical wastes (i.e. weight basis) to municipal facilities (NJ DEPE, 1986b) because it considered then than mixing hazardous waste with domestic sewage was more cost-effective since it was not subject to RCRA regulations (NJ DEPE, 1986a).

### 3.3 Combined sewer overflows and stormwater inputs

Combined sewer overflow (CSO) events result from heavy rainfall and consist of discharges of raw sewage, stormwater runoff, and industrial effluents that may contain high levels of suspended solids, bacteria, heavy metals, floatables, nutrients, oxygen-demanding organic compounds, oil and grease, etc. (CMC, 1992; EPA, 1992). Mytelka *et al.* (1981) estimated that precipitation is sufficient to cause CSO events 56 days each year, with as little as 0.1 inches of rain. The Interstate Sanitation Commission (ISC, 1988) determined that there were 176 combined sewer overflow outfalls estimated to be discharging into Newark Bay and its surrounding tributaries. As shown previously in Table 4 (Crawford *et al.* 1995), 226 kg/yr Hg were estimated to enter Newark Bay from CSOs and 146 kg/yr Hg from stormwater inputs.

### 3.4 Tributary inputs

Crawford *et al.* (1995) estimated that 153 kilograms of mercury entered Newark Bay per year from tributary flow. This estimate was reasonably consistent with an earlier one by HydroQual (1991), estimating that 4 kg/yr Hg and 142 kg/yr Hg discharged from the Hackensack and Passaic Rivers, respectively into Newark Bay for a total of 146 kilograms per year. HydroQual (1991) also determined the total Hg concentration in both rivers to be approximately 0.1 µg/l over a three-year period (i.e. 1986-1989). Therefore, the much higher Hg contribution from the Passaic River is most likely attributed to its higher discharge of 32 m<sup>3</sup>/s compared to 3 m<sup>3</sup>/s for the Hackensack River (HydroQual, 1991).

### 3.5 Global atmospheric deposition

Lamborg *et al.* (2000) estimated that 360±60 kg/yr of mercury were deposited to the Hudson-Raritan Basin (HRB) resulting from wet atmospheric deposition<sup>1</sup> from global sources. For a surface area of 42,000 km<sup>2</sup> for the HRB, this corresponds to a Hg flux of 8.57±1.43 g/yr-km<sup>2</sup>, which is within range of other recent U.S. Hg flux measurements shown in Table 6. From this flux estimate, 25±4 kg/yr would be deposited in the Hackensack-Passaic Basin with a negligible amount deposited into Newark Bay alone as shown in the calculations below:

<sup>1</sup> EPA (1997a) defined wet deposition as the mass transfer of dissolved gaseous or suspended particulate mercury species from the atmosphere to the earth's surface by precipitation.

Hg input to Hackensack-Passaic Basin from atmospheric deposition =

$$(2910 \text{ km}^2) \times (8.57 \pm 1.43 \text{ g/yr-km}^2) \times (1 \text{ kg} / 1000 \text{ g}) = 25 \pm 4 \text{ kg/yr}$$

where: Surface area of the Hackensack-Passaic Basin = 2910 km<sup>2</sup> (Simpson *et al.* 1975; Suszkowski, 1978) and

Hg input to Newark Bay from atmospheric deposition =

$$(17.15 \text{ km}^2) \times (8.57 \pm 1.43 \text{ g/yr-km}^2) \times (1 \text{ kg} / 1000 \text{ g}) = 0.15 \pm 0.02 \text{ kg/yr} \approx 0 \text{ kg/yr}$$

where: Surface area of Newark Bay = 17.15 km<sup>2</sup>

Compared to the Hg input of 1624 kg/yr estimated by Crawford *et al.* (1995), Hg inputs resulting from wet atmospheric deposition are negligible. Furthermore, Hg that is deposited into watershed basins will eventually be accounted for in tributaries as it is transported there via surface runoff due to meteorological events. This would likely explain why Crawford *et al.* (1995) did not include atmospheric deposition in his summary of Hg sources and mass loadings to Newark Bay.

**Table 6. Measured rates of mercury wet depositional fluxes (Bergan *et al.* 1999; Weinstein *et al.* 2000)**

USA	Observation (Range) in g Hg/ km <sup>2</sup> / yr	Source
N. New York State 1993	10	Burke <i>et al.</i> (1995)
Little Rock Lake, WI	8.7	Fitzgerald <i>et al.</i> 1991
Wisconsin	9 (5 – 13)	Benoit <i>et al.</i> (1994)
NE Minnesota 1988-1989	15 (6 – 20)	Glass <i>et al.</i> (1991)
Upper Midwest	7.4	Glass and Sorensen 1999
Florida 1992-1993	(15 – 23)	Guentzel <i>et al.</i> (1995)
Lake Michigan	8.3	Hoyer <i>et al.</i> 1995
Chesapeake Bay	21.0	Mason <i>et al.</i> 1994
Baltimore, MD	35.0	Mason <i>et al.</i> 1994
Lake Champlain, NY	7.9	Rea and Keller 1996

### 3.6 Local atmospheric deposition

In the Newark Bay area, local industrial activities emit Hg into the atmosphere, which can end up in aquatic sediment via wet deposition and sedimentation. Themelis and Gregory (2001) made an estimate of Hg emissions from New York and New Jersey combustion sources in a report to the New York Academy of Sciences. Hg emissions from a) fossil fuel combustion, b) iron and steel production, c) waste-to-energy plants, d) sewage sludge incinerators, and e) medical waste incinerators from that report are summarized below in Table 7.

**Table 7. Summary of mercury emissions from combustion sources in New York and New Jersey for 1999-2000 (Themelis and Gregory, 2001)**

Combustion source	Mercury emission in the HRB (kg/yr)
Fossil fuel combustion	873
Iron and steel production	644
Waste-to-energy plants	140
Sewage sludge incinerators	152
Medical waste incinerators	0.91 (Negligible)
<b>Total</b>	<b>1809</b>

EPA (1997a) assumed that 40% of mercury from combustion sources is of the reactive gaseous form, which readily deposits locally, and assumed that the remaining 60% enters the global cycle in the elemental form ( $Hg^0$ ). Furthermore, Bergan *et al.* (1999) estimated the oxidation period of  $Hg^0$  to  $Hg^{2+}$  ranges from 0.5 to 1.5 years, however Lindberg *et al.* (1992) and Xiao *et al.* (1991) concluded that dry deposition of  $Hg^0$  may occur when the surface air concentration of  $Hg^0$  is high. Based on EPA (1997a) assumptions, Themelis and Gregory (2001) estimated that 724 kg/yr Hg is deposited to the HRB from local combustion sources as shown in the calculations below:

Mercury deposition to the HRB from local combustion sources =

$$(1809 \text{ kg/yr}) \times (0.40) = 724 \text{ kg/yr}$$

Of this amount deposited to the HRB, a negligible amount would be accounted for in the deposition to Newark Bay as shown in the calculations below:

Mercury deposition to Newark Bay from local combustion sources =

$$(724 \text{ kg/yr}) \times (17.15 \text{ km}^2 / 42,000 \text{ km}^2) = 0.29 \text{ kg/yr}$$

where: Area of HRB equals 42,000  $\text{km}^2$  and Newark Bay area equals 17.15  $\text{km}^2$  as previously noted.



## 4. ASSESSMENT OF MERCURY CONTAMINATION IN SURFICIAL SEDIMENTS OF NEWARK BAY

### 4.1 General description of Newark Bay

Newark Bay is an enclosed estuarine<sup>m</sup> body of water located in the heavily industrialized New York-New Jersey metro area with a water volume of approximately 0.11 km<sup>3</sup>:

$$\text{Water volume} = (\text{surface water area}) \times (\text{average depth}) \quad (4.1)$$

where: Surface water area = 17.15 km<sup>2</sup>, determined by area approximation of a Newark Bay map projected with ESRI ArcView 3.2 GIS software; average depth = 6.7 m (EPA, 1998)

The main tributaries to Newark Bay are the Hackensack and Passaic Rivers as shown in Figure 5. HydroQual (1991) measured the average discharge for the Hackensack River (3 m<sup>3</sup>/s) and the Passaic River (32 m<sup>3</sup>/s). Olsen *et al.* (1984) estimated the drainage basin for each river to be 525 km<sup>2</sup> and 2,400 km<sup>2</sup>, respectively. The net flow through Newark Bay is southward toward the Arthur Kill and Kill Van Kull. However, there are significant diurnal tidal fluxes into Newark Bay and its tributaries that have the potential to transport contaminants from other places within the NY/NJ Harbor to the Bay (Olsen *et al.* 1984; HydroQual, 1991). These tidal influences have been measured as far north as 35 and 27 kilometers up the Hackensack and Passaic Rivers, respectively (Suszkowski, 1978).

### 4.2 Characterization of Newark Bay sediments

Sediment formation occurs at the bottom of water bodies by the deposition of particles in the water column, which originate from either soil and other suspended matter carried by inflowing water from direct discharges (DiToro, 2001). Otherwise, these particles are formed within the water itself as a result of the growth, metabolism, and death of plants and animals (DiToro, 2001). Suszkowski (1978) determined that the majority of Newark Bay sediments have historically been composed of fine-grained particles and that the leading contributor of these smaller sized particles was the Passaic River. This is consistent with findings by Olsen *et al.* (1984) and Meyerson (1988) whom estimated that 70% of fine-grained sediments entering the NY/NJ Harbor were riverborne, 20% were of marine origin, and 10% were discharged from wastewater treatment plants (WWTPs).

Fine-grained sediments make up the silt-clay fraction of sediments. A standard classification system is shown below in Table 8 to describe the size (i.e. diameter) distribution of sediments (Salomons and Forstner, 1984), where it was seen that fine-grained sediments are on the order of a factor three smaller than sand. Fine-grained particles generally deposit in deeper regions (DiToro, 2001). In contrast, sand-sized particles generally deposit in more shallow regions (DiToro, 2001).

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<sup>m</sup> An estuary is a partially enclosed body of water defined by an area where freshwater flows intermix with saltwater. Estuaries act as cleansers, filtering out upstream pollutants, nutrients, and sediments as water flows through fresh and salt marshes. (National Estuarine Research Reserves).



Table 2. Summary of mercury concentration in sediments of Newark Bay

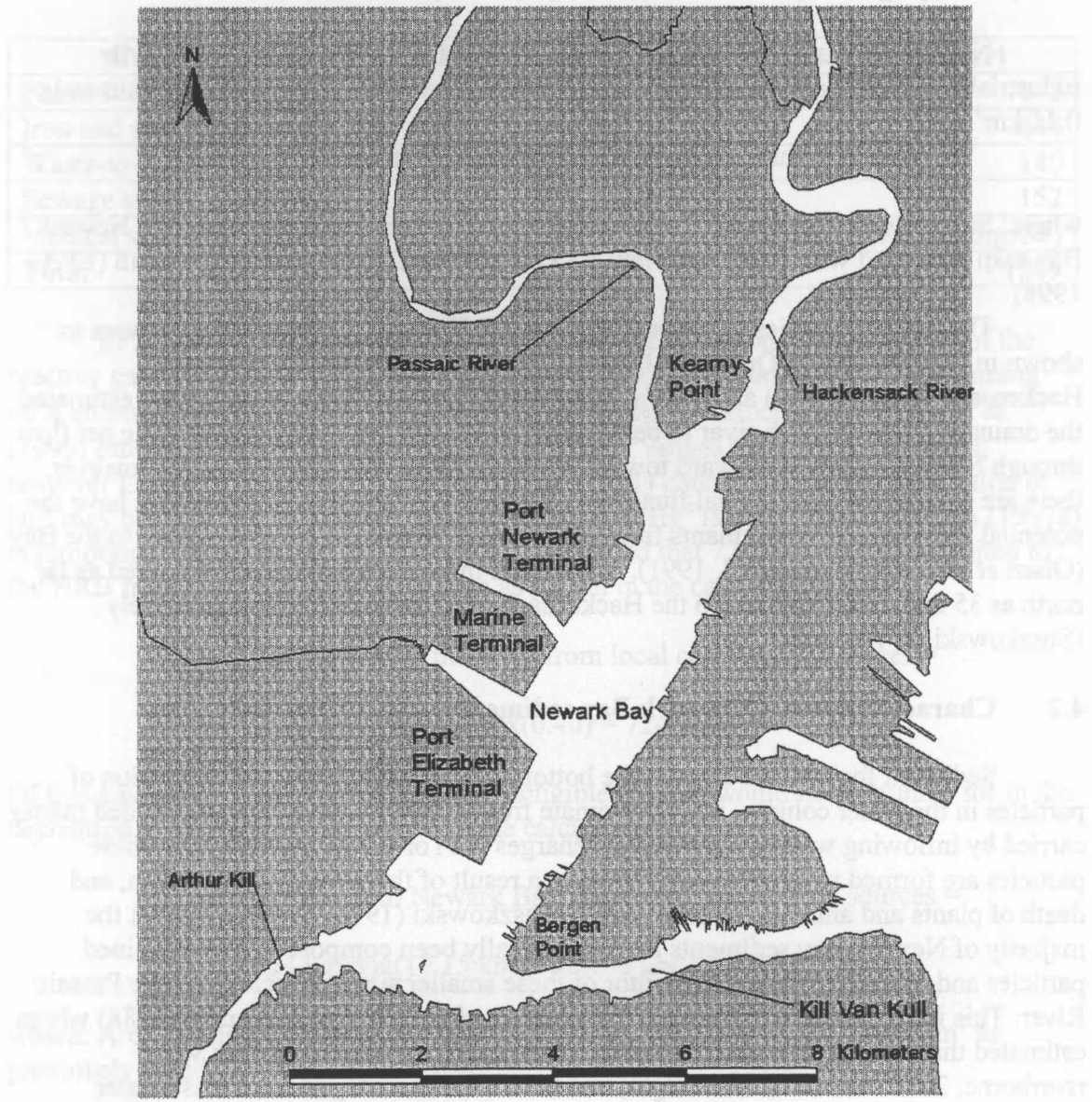


Figure 5. Newark Bay

**Table 8. Standard classification of sediment size distribution (Salomons and Forstner, 1984)**

Clay	Silt	Sand	Gravel
< 2 $\mu\text{m}$	2 – 60 $\mu\text{m}$	60-1000 $\mu\text{m}$	> 1000 $\mu\text{m}$

Please note that the terms “clay”, “silt”, etc., refer to “clay-sized” and “silt-sized” particles, and not actual pure clay or silt particles.

Olsen *et al.* (1984) reported that on average 0.17 million metric tons of fine-grained sediments accumulated annually in Newark Bay. The rate at which sediment accumulates is the sedimentation rate  $J_{ss}$  ( $\text{g}/\text{cm}^2\text{-yr}$ ), where the annual increase in sediment depth ( $\omega$ ) is measured in  $\text{cm}/\text{yr}$ . In Table 9, the range of the annual increase in sediment depth is shown for various aquatic locations. Olsen *et al.* (1984) estimated the annual increase of fine-grained sediments to be 9  $\text{cm}/\text{yr}$  in dredged areas of the NY/NJ Harbor, which is within the range of  $\omega$  for river deltas (i.e. 1-10  $\text{cm}$ ) as shown in Table 8.

$$\text{where: } J_{ss} = \rho_s (1-\phi)\omega \quad (4.2)$$

$$\rho_s = \text{density of solids (g}/\text{cm}^3) \quad (4.3)$$

$$\phi = \text{porosity} = (\text{volume of water})/(\text{volume of water} + \text{volume of solids}) = (\rho_s - \rho_B)/(\rho_s - \rho_w) \quad (4.4)$$

Typical values of  $\phi = 0.7\text{-}0.9$  in top few centimeters of sediment (Bernier 1980; Robbins and Edginton, 1975)

$$\text{where: } \rho_B = \text{wet bulk density (i.e. weight of a known volume)} \quad (4.5)$$

$$\rho_w = \text{density of water} = 1 \text{ g}/\text{m}^3 \quad (4.6)$$

$$\omega = \text{annual increase in sediment depth (cm}/\text{yr)} \quad (4.7)$$

**Table 9. Range of the annual increase in sediment depth for various aquatic locations (DiToro, 2001)**

Location	$\omega$ (cm/yr)
River deltas	1-10
Lakes and estuaries	0.1-1.0
Oceans	0.001-0.01

At least nine dredging projects have been recorded by USACE in 1999 (<http://www.nan.usace.army.mil/business/buslinks/navig/>). Based on this data, between 2.8  $\text{km}^2$  and 5.7  $\text{km}^2$  (i.e. 16.3% to 33.2% of Newark Bay) of channels were surveyed for dredging in 1999 as shown in Table 10. The dredging area estimate was calculated from channel lengths and widths specified by USACE. Figure 6 shows the Federal shipping channels within the NY/NJ Harbor. Using the estimate for dredged area in Newark Bay

(i.e. 2.8 km<sup>2</sup> and 5.7 km<sup>2</sup>) and the annual mass deposition rate of 0.17 million metric tons fine-grained sediment (Olsen *et al.* 1984), a sedimentation rate  $J_{ss}$  of 3 to 6.1 g/cm<sup>2</sup>-yr was approximated as shown below:

$$\text{Sedimentation rate } J_{ss} = (0.17 \times 10^6 \text{ tons}) \times (10^6 \text{ g} / 1 \text{ ton}) \times (1 / 2.8 \text{ to } 5.7 \text{ km}^2) \times (1 \text{ km}^2 / 10^6 \text{ m}^2) \times (1 \text{ m}^2 / 10^4 \text{ m}^2) = 3 \text{ to } 6.1 \text{ g/cm}^2\text{-yr}$$

**Table 10. Authorized dredging projects in Newark Bay for 1999**  
(<http://www.nan.usace.army.mil/business/buslinks/navig/>)

Name of channel	Date of survey	Authorized project			
		Width (max/min) (ft)	Length (mi)	Area (max/min) (mi <sup>2</sup> )	Depth (ft)
South Elizabeth Channel	4/30/99	1000/290	0.7	0.13/0.04	40
Port Elizabeth Pierhead Channel	4/30/99	290	1.1	0.06	40
Port Newark Pierhead Channel	4/30/99	300	0.78	0.04	40
Newark Bay Main Channel – South Reach	3/30/99	1000/1750	1.0	0.19/0.33	40
Newark Bay Main Channel – Middle Reach	3/30/99	500/1750	2.1	0.2/0.7	40
Newark Bay Main Channel – North Reach	3/30/99	500/900	1.6	0.15/0.27	35
Elizabeth Channel	3/30/99	500/1350	1.49	0.14/0.38	40
Port Newark Branch Channel	3/30/99	400/1050	1.6	0.12/0.32	40
Bergen Point widening at the right turn into Newark Bay	5/26/99	800	0.25	0.04	40
<b>Estimated of area in Newark Bay dredged = 1.1 to 2.2 mi<sup>2</sup> (= 2.8 to 5.7 km<sup>2</sup>)</b>					

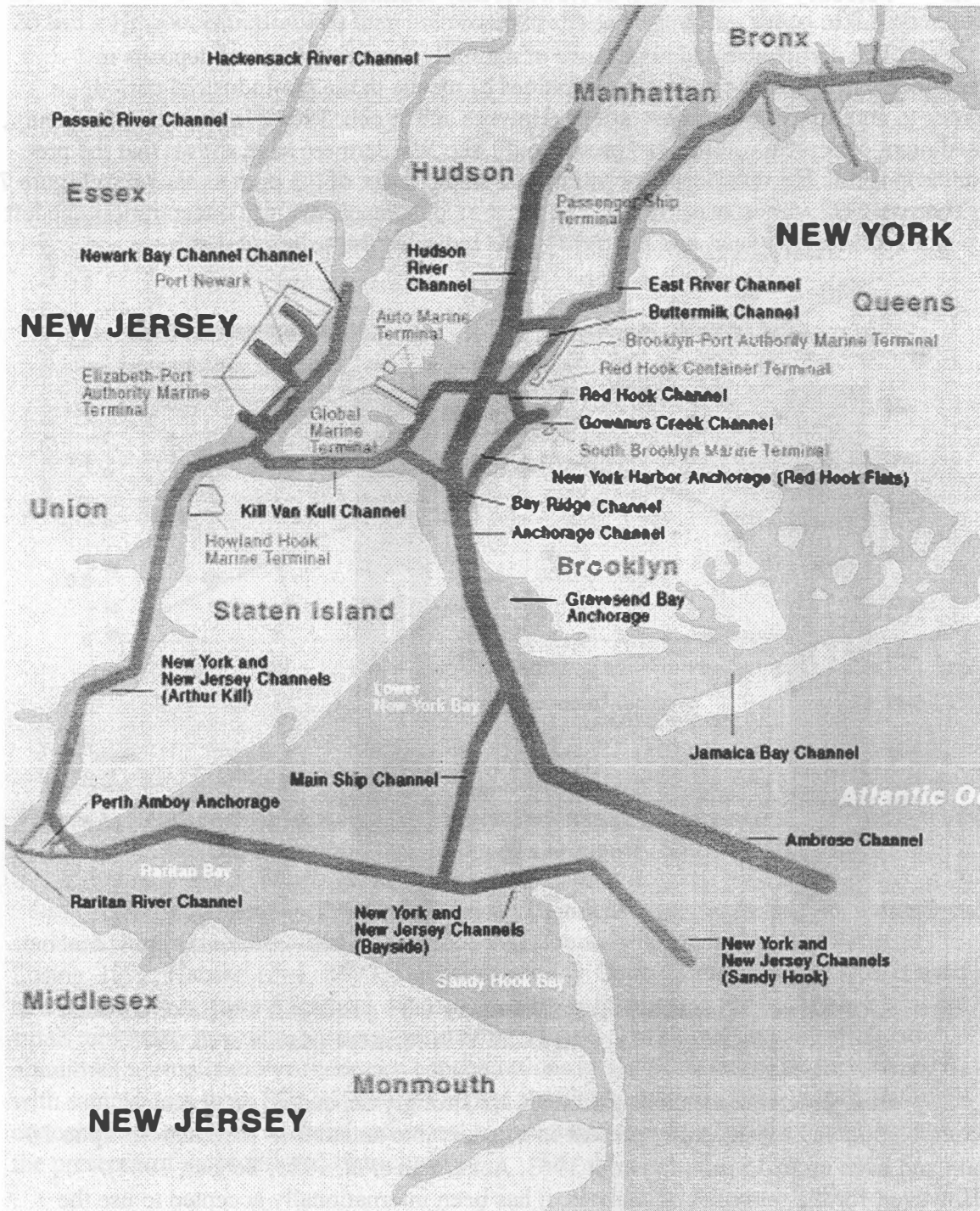


Figure 6. Shipping channel network in the NY/NJ Harbor  
<http://www.nan.usace.army.mil/images/map4.jpg>

### 4.3 Mercury accumulation in Newark Bay sediments

The occurrence and abundance of naturally occurring mineral deposits in sediments is reflected by the concentrations of metals in the pre-industrial period, i.e. prior to anthropogenic concentrations (Hawkes and Webb, 1962). In the case of mercury, sediment core profiles of Lake Ontario and Lake Windermere have shown that the pre-anthropogenic Hg sediment concentration is in the range of 0.3 ppm as shown in Figure 7 (Thomas 1972; Aston *et al.* 1973). The top x-axis indicates the Hg concentration, the left y-axis indicates the year, and the right y-axis indicates the sediment depth.

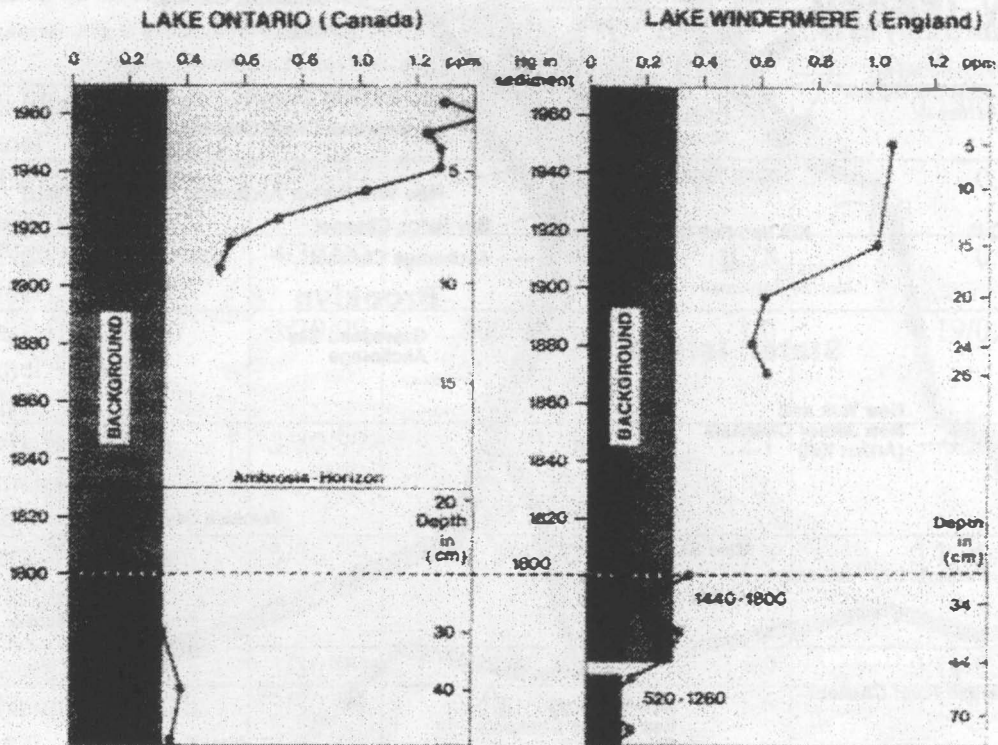
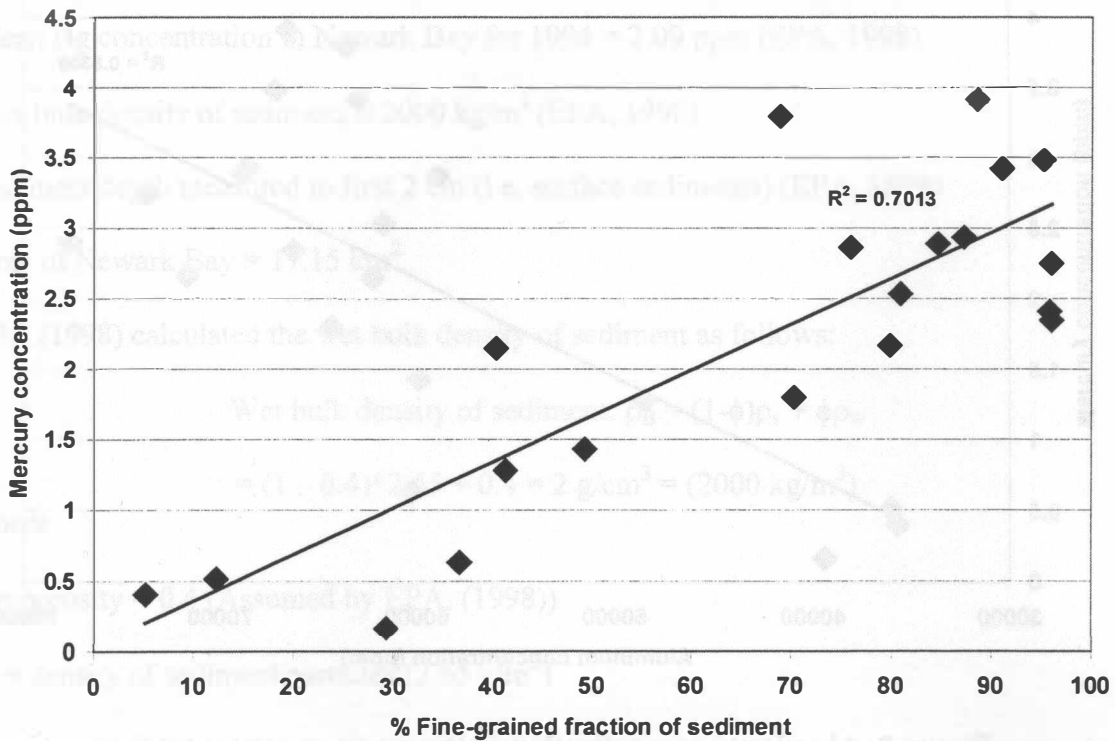


Figure 7. Mercury in sedimentary core profiles from Lake Ontario (Thomas 1972) and Lake Windermere (Aston *et al.* 1973)

Heavy metal contents in sediments are strongly dependent on granular composition and are generally present in considerable amounts in the fractions up to 20  $\mu\text{m}$  and even up to 35  $\mu\text{m}$  (de Groot 1963; Ackerman *et al.* 1983; Schoer, 1984). However, for the purposes of analysis, it has been internationally accepted to use the fraction  $< 63 \mu\text{m}$  (i.e. silt and clay-sized particles) because of the amounts of heavy metals and improved efficiency in the sieving procedure (Allen, 1995). In addition, Allen (1995) noted the importance of fine-grained sediments due to the fact the benthic biota generally take their food from this fraction of sediments. Figure 8 shows a plot of Hg surficial sediment concentration versus the fraction of fine-grained sediments for samples taken in Newark Bay (EPA, 1998). The results would indicate that Hg concentration is a



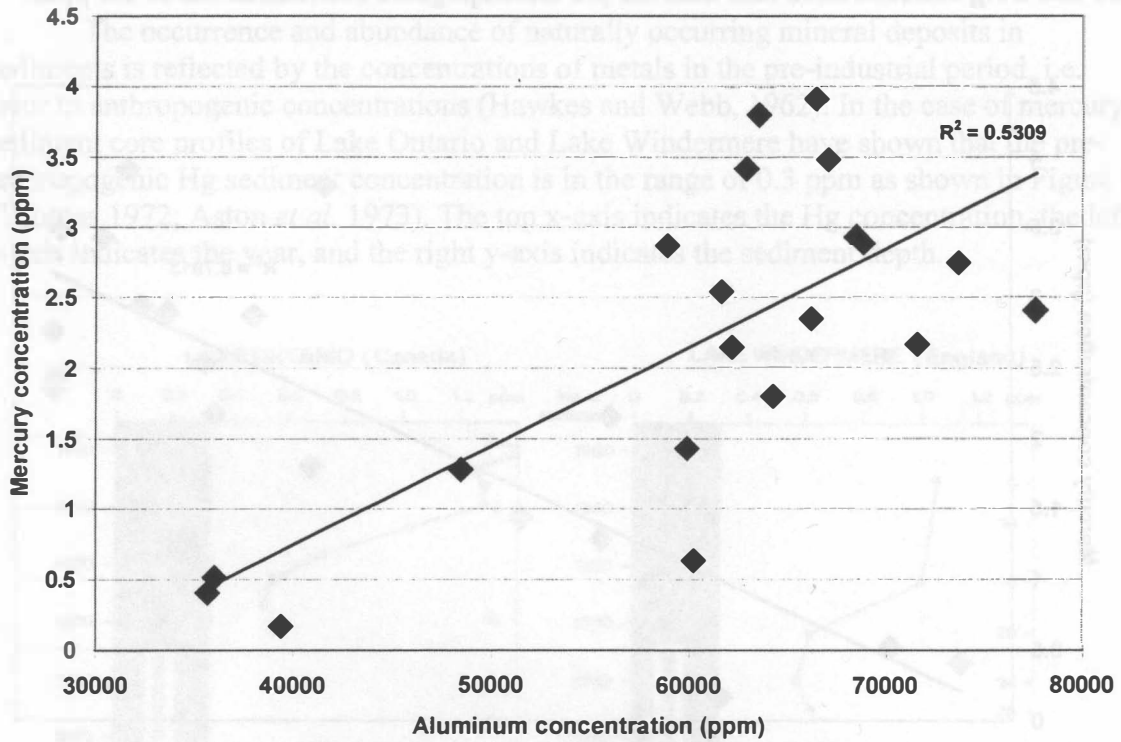
function of the fine-grained fraction of sediments. Furthermore, only one sample out of 20 had a Hg concentration less than the pre-anthropogenic concentrations of 0.3 ppm.



**Figure 8. Relationship between the surficial sediment concentration of mercury and the fine-grained fraction of sediments (EPA, 1998)**

Anthropogenic enrichment of various chemical compounds can be assessed with standard aluminum-normalization techniques (Luoma, 1990; Schropp *et al.* 1990; Loring, 1991; Hanson *et al.* 1993; Daskalakis and O'Connor, 1995). Aluminum is used as a conservative tracer of crustal deposition, since anthropogenic contributions of it are small relative to its presence in natural sediment pools. Figure 9 shows the application of aluminum normalization of mercury concentrations in surficial sediments of Newark Bay with sample data from EPA (1998). At higher aluminum concentration ranges, the concentration of Hg in surficial sediments shows more variation, which would indicate the presence of anthropogenic enrichment.





**Figure 9. Aluminum normalization of the mercury concentration in surficial sediments of Newark Bay (EPA, 1998)**

#### 4.3.1 Surficial sediment analysis

In an EPA-Region-2 (1998) sediment quality study of the NY/NJ Harbor system, a total of 2000 kg mercury were estimated to be present in the first 4 cm of Newark Bay surficial sediments, based on samples taken in 1993 and 1994. However, this study determined the surface area of Newark Bay to be 32 km<sup>2</sup> (i.e. twice the area of 17.15 km<sup>2</sup> estimated in this report). This is because EPA (1998) also included Arthur Kill, Kill Van Kull, and a portion of the Passaic River as part of the Newark Bay study area, resulting in a greater volume of surface sediments. The equation below shows how the Hg mass in surface sediments was calculated by EPA (1998):

$$\begin{aligned}
 & (\text{Mean mercury concentration}) \times (\text{Wet bulk density of sediment}) \times \\
 & (\text{Sediment depth of the mean mercury concentration}) \times (\text{Newark Bay surface area}) = \\
 & \text{Mass of mercury in surficial sediments for a specified depth} \quad (4.8)
 \end{aligned}$$

where:

Mean Hg concentration in Newark Bay for 1993 = 2.28 ppm (EPA, 1998)

Mean Hg concentration in Newark Bay for 1994 = 2.09 ppm (EPA, 1998)

Wet bulk density of sediment  $\cong$  2000 kg/m<sup>3</sup> (EPA, 1998)

Sediment depth measured to first 2 cm (i.e. surface sediments) (EPA, 1998)

Area of Newark Bay = 17.15 km<sup>2</sup>

EPA (1998) calculated the wet bulk density of sediment as follows:

$$\begin{aligned}\text{Wet bulk density of sediment: } \rho_B &= (1-\phi)\rho_s + \phi\rho_w \\ &= (1 - 0.4)*2.65 + 0.4 = 2 \text{ g/cm}^3 = (2000 \text{ kg/m}^3)\end{aligned}$$

where:

$\phi$  = porosity = 0.4 (Assumed by EPA, (1998))

$\rho_s$  = density of sediment particles (2.65 g/m<sup>3</sup>)

$\rho_w$  = density of water (1 g/cm<sup>3</sup>)

However, typical porosity values for the top few centimeters are in the order of 0.7 to 0.9 versus 0.4 to 0.7 at greater depths as already indicated (Berner, 1980; Robbins and Edgington, 1975). Therefore, assuming 0.8 as a more realistic porosity value for surficial sediments, the wet bulk density would be equal to:

$$\begin{aligned}\rho_B &= (1-\phi)\rho_s + \phi\rho_w \\ &= (1 - 0.8)x(2.65 \text{ g/cm}^3) + (0.8)x(1 \text{ g/cm}^3) = 1.33 \text{ g/cm}^3 = (1330 \text{ kg/m}^3)\end{aligned}$$

which is more appropriate for sediments that are primarily composed of water.

Therefore with an adjusted Newark Bay area of 17.15 km<sup>2</sup> and a wet bulk density of 1330 kg/m<sup>3</sup>, the mercury mass in Newark Bay surficial sediments for 1993 and 1994 at a depth of 2 cm for each year equals:

$$\begin{aligned}(2.28 \text{ } \mu\text{g/kg} + 2.09 \text{ } \mu\text{g/kg}) \times (1 \text{ kg} / 10^6 \text{ } \mu\text{g}) \times (1330 \text{ kg/m}^3) \times (2 \text{ cm}) \times (1 \text{ m} / 100 \text{ cm}) \times \\ (17.15 \text{ km}^2) \times (10^6 \text{ m}^2 / 1 \text{ km}^2) = 1993 \text{ kg } (\cong 2000 \text{ kg}).\end{aligned}$$

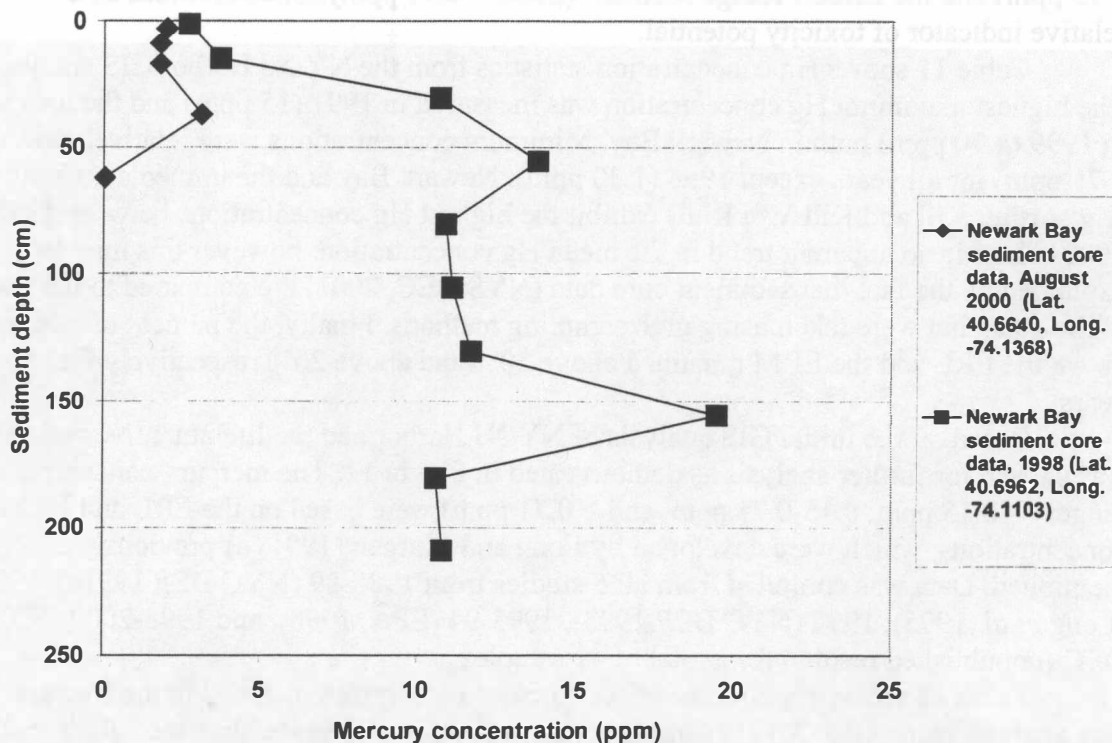
This revised estimate is roughly the same as EPA's (1998). However, EPA (1998) included Arthur Kill, Kill Van Kull, and a portion of the Passaic River in their surface

area estimate of Newark Bay. Secondly, EPA (1998) also made a very conservative assumption of the surficial sediment porosity (i.e.  $\phi = 0.4$ ) resulting in a wet bulk density that may have been uncharacteristically high (i.e.  $2000 \text{ kg/m}^3$  vs.  $1330 \text{ kg/m}^3$ ). Furthermore, EPA (1998) estimated the mass of Hg in surficial sediment using the average Hg concentration for the entire Harbor sample population (i.e.  $0.79 \text{ ppm Hg}$  for 1993 and  $0.70 \text{ ppm Hg}$  for 1994) versus the average Hg concentration for Newark Bay (i.e.  $2.28 \text{ ppm Hg}$  for 1993 and  $2.09 \text{ ppm Hg}$  for 1994) as was done in this report.

#### 4.3.2 Sediment core analysis

In 1998 and 2000, the New York State Department of Environmental Conservation (NYS DEC, 2001) took sediment cores from Newark Bay and measured the mercury concentrations. The 1998 core was taken at a location 2.5 km south of Kearny Point along the eastern shore of Newark Bay. The 2000 core was taken approximately 1 km south of the 1998 core, also along the eastern shore. The interpretations of these results are shown in Figures 10. NYS DEC (2001) estimated the average Hg concentration of the sediment cores at specified depth intervals. In Figure 10, the average Hg concentrations are plotted versus the average depth determined from the specified core depth intervals.

For the 1998 sediment core data shown in Figure 10, the mercury concentration increased from  $2.7 \text{ ppm}$  to  $13.8 \text{ ppm}$  in the first 50 cm. The Hg concentration then decreased to  $10.9 \text{ ppm}$  at a depth of approximately 75 cm, with a peak Hg concentration of  $19.5 \text{ ppm}$  at a depth of approximately 150 cm (Figure 10). For the 2000 sediment core data shown in Figure 10, the Hg concentration was considerably less compared to 1998 core data with respect to depth, suggesting that the sediment conditions in Newark Bay are subject to very localized influences.



**Figure 10. Depth profile of mercury concentrations measured from sediment cores taken in Newark Bay in 1998 and 2000 (NYS DEC, 2001)**

#### 4.4 Visualization of surficial sediment and sediment core data using geographic information systems

Visualization of sediment data in Newark Bay was done using ESRI ArcView Geographic Information Systems (GIS) 3.2 software for analysis. Data from five studies was analyzed, including data previously presented in the discussion of surficial sediments and sediment cores (NYC DEP 1991a, 1993; Long *et al.* 1995; EPA, 1998; NYS DEC, 2001). These studies were used based on their availability and relevance to mercury contamination in Newark Bay.

In a recent study, Gregory and Gorokovich (2001) utilized GIS<sup>n</sup> for the visualization of mercury surficial sediment concentrations in the NY/NJ Harbor. A database of 370 surficial sediment mercury concentration samples was compiled from the five studies previously mentioned. This initial analysis visually demonstrated that Newark Bay, Arthur Kill, Kill Van Kull, the East River, and Western Long Island Sound contained a large distribution of samples having high Hg concentrations relative to the remainder of the NY/NJ Harbor during the 1988-2000 sample period as shown in Figure . The Hg concentration ranges in Figure 11 were based on the Effects Range Low<sup>o</sup> (ERL =

<sup>n</sup> Aronoff (1995) defines GIS in a broad sense as any manual or computer based set of procedures used to store and manipulate geographically referenced data.

<sup>o</sup> The Effects Range-Low (ERL) is defined as concentration at which biological affects begins to be seen (Long and Morgan, 1991; Long *et al.* 1995a).

0.15 ppm) and the Effects Range Median<sup>P</sup> (ERM = 0.71 ppm) concentrations, as a relative indicator of toxicity potential.

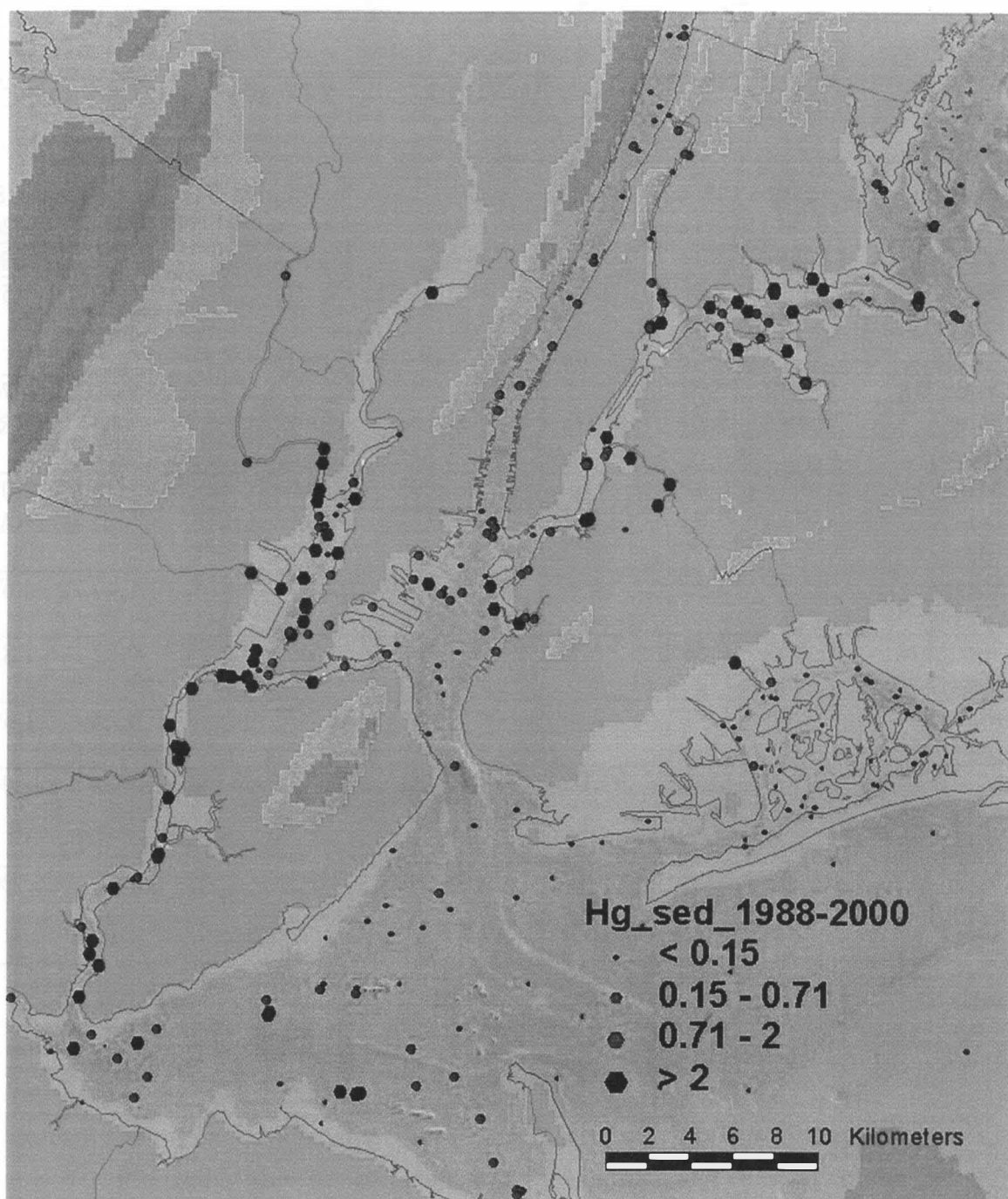
Table 11 shows Hg concentration statistics from the NY/NJ Harbor GIS analysis. The highest maximum Hg concentration was measured in 1991 (15 ppm) and the lowest in 1999 (4.70 ppm) both in Newark Bay. Minimum concentrations were relatively low (< 0.71 ppm) for all years except 1998 (1.30 ppm). Newark Bay and the immediate vicinity (e.g. Arthur Kill and Kill Van Kull) exhibit the highest Hg concentrations between 1988-2000. There is no apparent trend in the mean Hg concentration; however this may be explained by the fact that sediment core data (NYS DEC, 2001) are compared to the rest of the data, that were taken using grab sampling methods. Finally, the percent of samples above the ERL and the ERM remained above 50% and above 20% respectively for all years.

Based on the initial GIS analysis of NY/NJ Harbor and the literature, Newark Bay was chosen for further analysis as demonstrated in Figure 12. The mercury concentration ranges (< 0.15 ppm, 0.15-0.71 ppm, and > 0.71 ppm) were based on the ERL and ERM concentrations, which were developed by Long and Morgan (1991) as previously mentioned. Data was compiled from all 5 studies from 1988-89 (NYC DEP 1991a), 1991 (Long *et al.* 1995), 1992 (NYC DEP 1993), 1993-94 (EPA, 1998), and 1998-2000 (NYS DEC (unpublished results) for a total of 41 samples.

Table 12 shows Hg concentration statistics for samples included in the Newark Bay analysis using GIS. All Hg sample concentrations were greater than the ERL for all years, which is an indicator of the beginning of adverse biological effects, compared to only 50% for the entire NY/NJ Harbor. At least 50% of all Hg sample concentrations were greater than the ERM, which is a stronger indicator of the possibility of adverse biological effects, compared to only 20% for the Harbor. The maximum Hg concentration of 6.99 ppm was measured in 1992 and the lowest Hg concentration of 0.17 ppm was measured in 1994. Over this 12 year time period there was no general decrease in the maximum and minimum Hg concentration as would be expected with the improving environmental conditions of the harbor as a whole. However, the limited sample populations could explain this lack of trends.

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<sup>P</sup> The Effects Range-Median (ERM) is defined as the concentration usually associated with biological effects (Long and Morgan, 1991; Long *et al.* 1995a).



**Figure 11. Mercury surficial sediment sample locations and concentrations in the NY/NJ Harbor (1988 – 2000)**

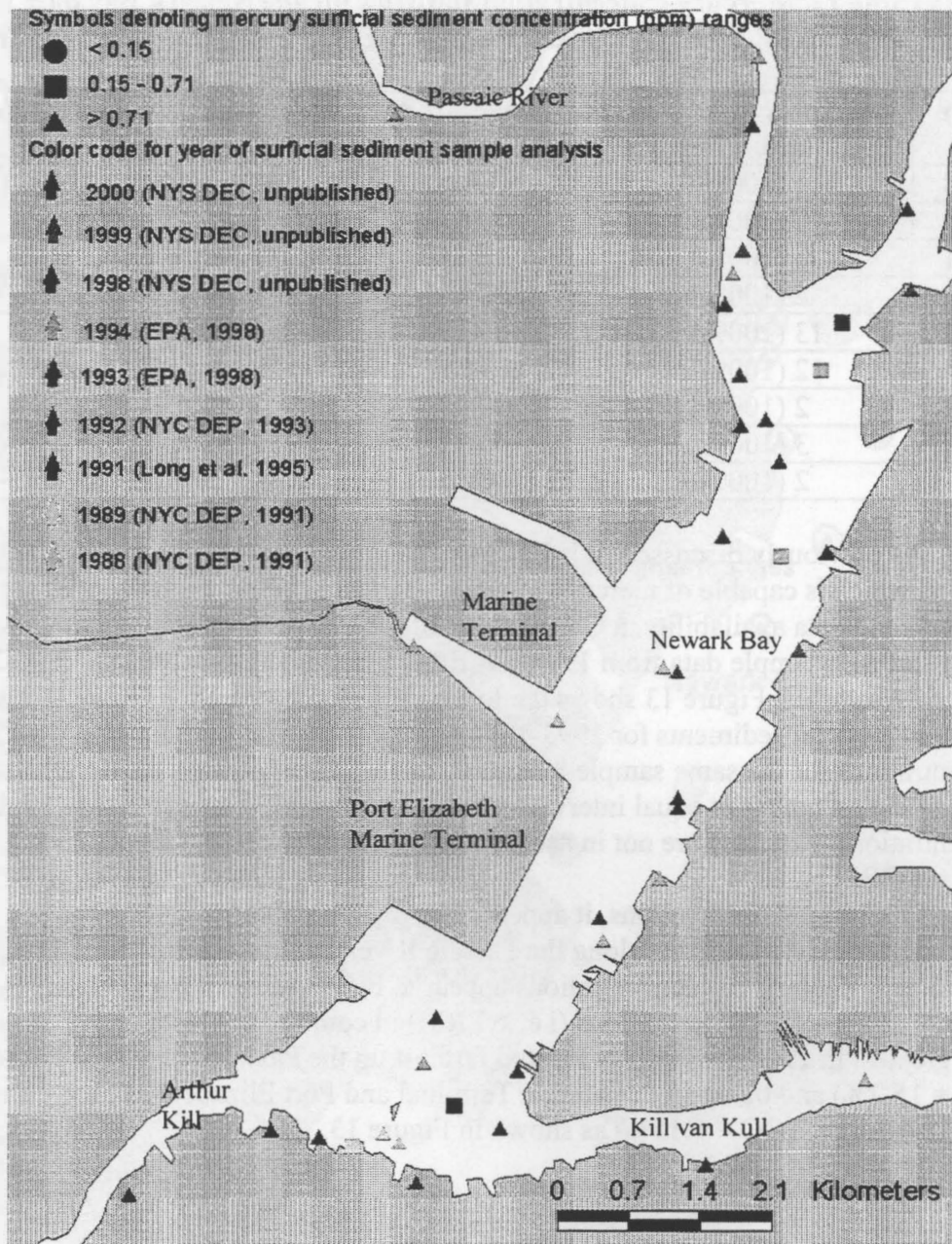


**Table 11. Mercury concentration statistics for the NY/NJ Harbor data set  
(NYC DEP, 1991 and 1993; Long *et al.* 1995; NYS DEC, 1998-2000)**

	NYC DEP, 1991		Long <i>et al.</i> 1995	NYC DEP, 1993		EPA, 1998		NYS DEC, 2001		
<b># Samples in GIS database</b>	82 (32 for 1988, 50 for 1989)		38	81		168 (84 samples taken each year)		64 (3 for 1998, 18 for 1999, 43 for 2000)		
<b>Year</b>	<b>1988</b>	<b>1989</b>	<b>1991</b>	<b>1992</b>	<b>1993</b>	<b>1994</b>	<b>1998</b>	<b>1999</b>	<b>2000</b>	
<b>Mean Hg conc. (ppm)</b>	1.91	2.29	2.29	1.17	0.79	0.70	2.10	1.58	1.79	
<b>Max. Hg conc. (ppm)</b>	12.00 (AK)	3.00 (NB)	15.00 (NB)	6.99 (KK)	5.36 (AK)	6.70 (AK)	2.70 (NB)	4.70 (HR)	5.10 (AK)	
<b>Min. Hg conc. (ppm)</b>	0.11 (HR)	0.05 (ER)	0.03 (LH)	0.03 (BA)	0.01 (BA)	0.00 (BA)	1.30 (UH)	0.03 (BA)	0.31 (ER)	
<b>Range (ppm)</b>	11.89	2.95	14.97	6.96	5.35	6.70	1.40	4.67	4.79	
<b>Variance (ppm)</b>	5.10	0.66	6.23	2.68	1.12	1.16	0.52	1.83	1.58	
<b>Std. Dev. (ppm)</b>	2.26	0.81	2.50	1.64	1.06	1.08	0.72	1.35	1.26	
<b>% Samples &gt; ERL</b>	96.9%	88%	92.1%	88.9%	67.9%	59.5%	100%	83.3%	100%	
<b>% Samples &gt; ERM</b>	71.9%	46%	81.6%	38.9%	31%	25%	100%	66.7%	86%	

Symbols in () indicate regions within the NY/NJ where Hg surface sediment concentrations were highest and lowest.

Symbol: AK – Arthur Kill, BA – Bight Apex, ER – East River, HK – Hackensack River, KK – Kill Van Kull, LH – Lower Harbor, and UH – Upper Harbor.



**Figure 12. Mercury sediment sample locations and concentrations in Newark Bay (1988 – 2000)**

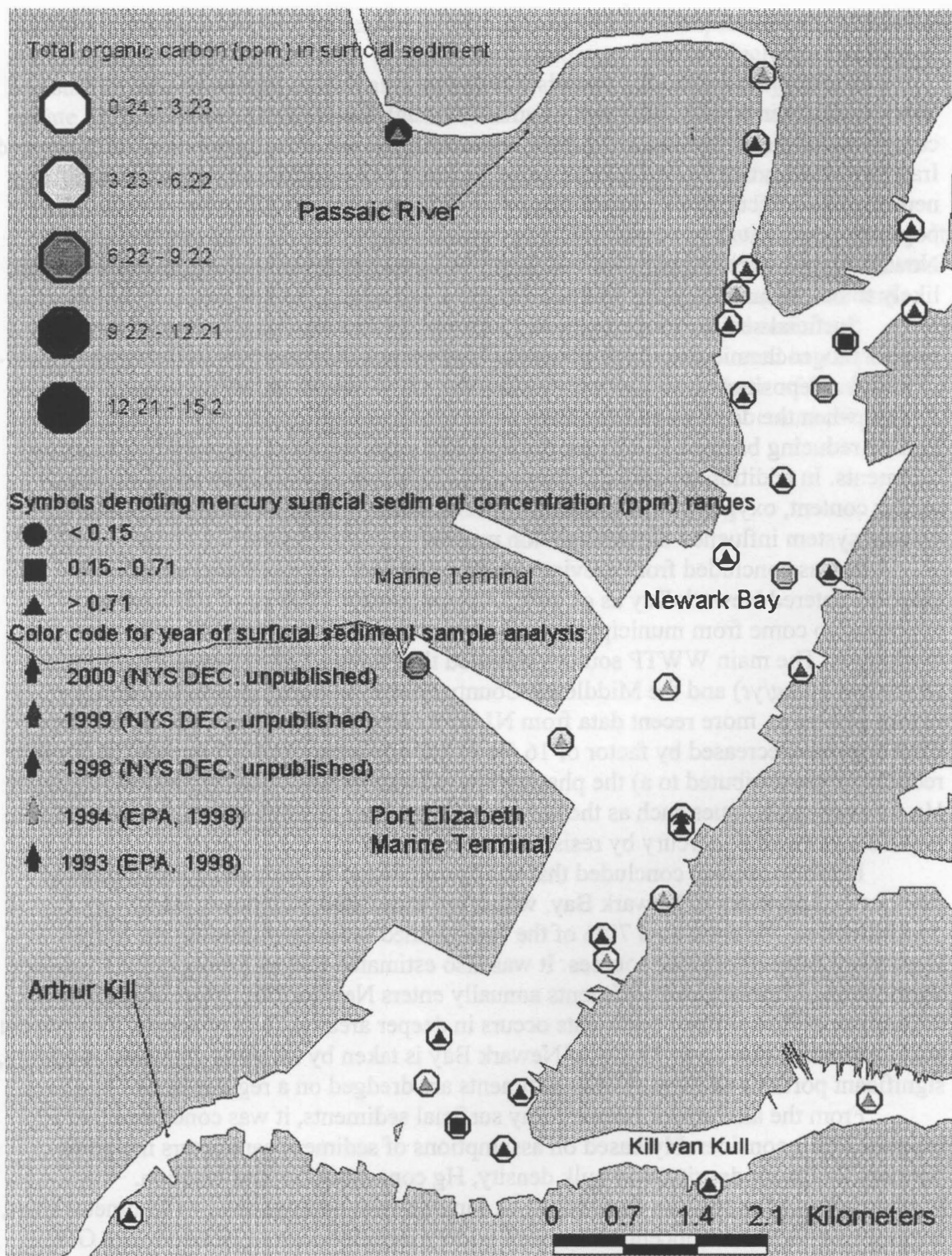
*Figure 13. Comparison of mercury and total organic carbon sediment concentrations in Newark Bay (1988-94 and 1998-2000)*

**Table 12. Mercury concentration statistics for the Newark Bay data set (NYC DEP, 1991 and 1993; Long *et al.* 1995; NYS DEC, 1998-2000)**

Year	# samples > ERL	# samples > ERM	Max. Hg (ppm)	Min. Hg (ppm)
1988	1 (100%)	1 (100%)	4.5	4.5
1989	2 (100%)	1 (50%)	3	0.22
1991	4 (100%)	4 (100%)	3.9	1.1
1992	2 (100%)	2 (100%)	6.99	1.75
1993	13 (100%)	11 (85%)	5.36	0.41
1994	12 (100%)	10 (83%)	3.42	0.17
1998	2 (100%)	2 (100%)	2.7	2.3
1999	3 (100%)	3 (100%)	2.6	1.9
2000	2 (100%)	2 (100%)	3.1	2.0

As previously discussed, it is believed that organic matter may stimulate bacterial activity, which is capable of mercury methylation. Based on an assessment of the literature and data availability, a GIS analysis of total organic carbon in sediments was conducted with sample data from 1993-94 (EPA, 1998) and 1998-2000 (NYS DEC) for a total of 32 samples. Figure 13 shows the locations and concentrations of total organic carbon in surficial sediments for 1993-1994 and 1998-2000 in combination with Hg concentrations for the same sample locations. The TOC concentrations were divided into 5 classification ranges at equal intervals strictly for showing where relatively higher concentrations exist, and are not in according with any toxicity guidelines such as the ERL and ERM.

From initial observations, it appears that higher total organic carbon concentrations were recorded along the Passaic River and various locations along the Newark Bay shore. TOC concentrations appear to be lower away from the shore. The intensity of high Hg concentrations (i.e. > ERM) in combination with high TOC appear to be greatest in 1994 for samples located farthest up the Passaic River (Hg = 1.16 ppm, TOC = 15.2%) and between the Marine Terminal and Port Elizabeth Marine Terminal (Hg = 2.41 ppm, TOC = 9.15%) as shown in Figure 13.



**Figure 13. Comparison of mercury and total organic carbon sediment concentrations in Newark Bay (1993-94 and 1998-2000)**

## 5. CONCLUSION

Mercury in the methyl form is a major health concern because it can bioaccumulate in aquatic life and in humans through the consumption of MeHg-contaminated fish. Past cases of MeHg contamination in human populations of Japan and Iraq have shown that MeHg in high concentrations can result in serious adverse neurological effects. It is recommended that future studies a) update Newark Bay fish population estimates, b) measure MeHg exposure and uptake to commercial fish in Newark Bay, and c) estimate Newark Bay MeHg-contaminated fish populations that are likely to be consumed by the public.

Surficial sediments were chosen as the medium of analysis because the most intense biogeochemical activity of any sediment is concentrated within the surface layer in which a deposited metal participates in a variety of processes. Methyl mercury is formed when the divalent mercury ion reacts with a methyl group via sulfate reduction. Sulfate reducing bacteria (SRB) are the principal methylators of mercury in estuarine sediments. In addition to sulfate reduction, the bulk mercury concentration, organic matter content, oxygen content, sulfide content, salinity, pH, and alkalinity within the aquatic system influence the methylation process.

It was concluded from previous studies that as much as 1600 kilograms of mercury entered Newark Bay as of 1991. Approximately 1100 kg of this total was estimated to come from municipal wastewater treatment plant (WWTP) effluent discharges. The main WWTP sources included the Passaic Valley Sewer Commission (PVSC) (730 kg/yr) and the Middlesex County Sewer Authority (MCSA) (106 kg/yr) plants. However, more recent data from NJ DEP (2001) indicates that the Hg effluent discharge has decreased by factor of 16 for PVSC and a factor of 2.5 for MSCA. Drastic reductions are attributed to a) the phasing out of commercially used Hg and b) improved Hg recovery techniques such as the enzymatic reduction of soluble divalent mercury into insoluble elemental mercury by resistant bacteria.

Previous studies concluded that the Passaic River is the leading contributor of fine-grained particles to Newark Bay, which are associated with heavy metal contamination. An estimated 70% of the fine-grained sediments entering the NY/NJ Harbor are from riverborne sources. It was also estimated that an average of 0.17 million metric tons of fine-grained sediments annually enters Newark Bay. More importantly, deposition of fine-grained sediments occurs in deeper areas such as channels. The present study estimated that up to 33.2% of Newark Bay is taken by shipping channels; therefore, significant portions of Newark Bay sediments are dredged on a regular basis.

From the analysis of Newark Bay surficial sediments, it was concluded that Hg estimates vary considerably based on assumptions of sediment parameters including porosity, sediment density, wet bulk density, Hg concentration, and location. Furthermore, sediment core data, based on samples take approximately 1 kilometer apart, suggest that sediment concentrations vary widely from location to location. The GIS analysis of sediment Hg and total organic carbon (TOC) concentrations visually demonstrate the existing data gaps between samples.

In summary, the state of mercury contamination and methyl mercury formation within the Newark Bay sediments is not clearly understood. To date, there has not been a study documenting the trends of methyl mercury production in Newark Bay or the



NY/NJ Harbor as a whole. The reason for this is two-fold: a) Sampling has been random and isolated to single-year events; b) Sampling parameters have not included the sulfate and sulfide concentrations, which are important in determining the methylation and sulfate reduction rates. Therefore, it is recommended that longer observation periods be implemented, taking into account the vertical (sediment cores) and horizontal sediment distributions. It is also recommended that sediment core sampling be conducted on a periodic basis to determine the trends of Hg contamination in Newark Bay sediments. Establishing better trends is essential to determining whether remediation is necessary. It is recommended that future studies of mercury contamination in Newark Bay sediments be modeled after past studies conducted in Minamata Bay, incorporating sulfate and sulfide sampling, long observation periods, and horizontal and vertical sediment distributions. In the Appendix of this study, this issue is further discussed in a report on mercury contamination in Minamata Bay, conducted for the Department of Earth and Environmental Engineering, Solid and Hazardous Waste Management course, April 2001.



## 6. References

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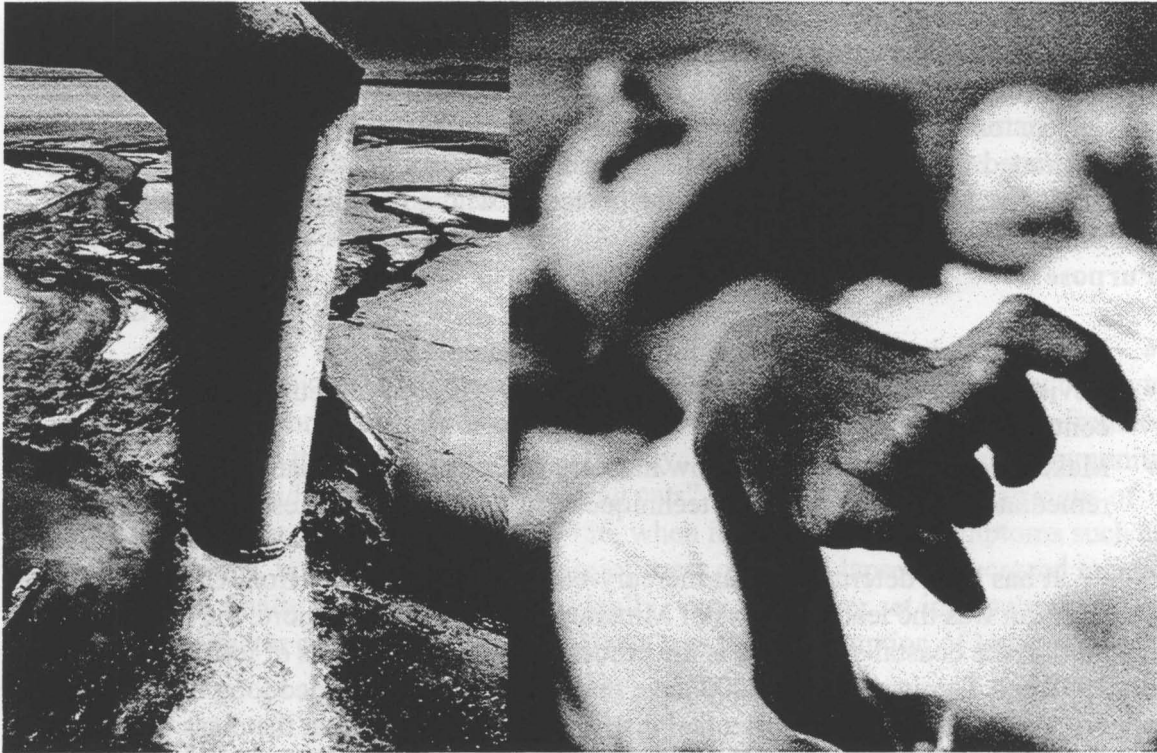
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## APPENDIX

### THE MINAMATA MERCURY DISASTER Analysis, Remediation, and Recommendations



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## Introduction

Minamata Bay, located in the southernmost end of Kumamoto Prefecture in southwestern Japan, is the site of one of the most serious cases of mercury pollution in the environment. Mercury-contaminated effluent was discharged into the Bay from 1932 to 1968 by the Chisso Chemical Corporation, which eventually resulted in Minamata Disease. Through its natural cycle, mercury methylated in the Bay sediments, accumulating in fish and shellfish, a major food staple of the local populous. This resulted in toxic central nervous system disease among the people who consumed contaminated fishery products over long periods of time. Over 2000 people have been designated as Minamata Disease patients so far, of whom roughly 900 have died.

## Purpose

- Briefly examine the causes and impacts of Minamata Disease
- Review and critically analyze literature on the subject of mercury sediment contamination
- Make recommendations as to how mercury sediment contamination can be remediated, based on previous techniques and future possibilities.

It has been determined that mercury-contaminated effluent from Chisso Chemical Corporation was the leading cause of Minamata Disease. Furthermore, the methylation of mercury in the coastal sediments is the process of concern in terms of toxicity. Kudo *et al.*, 1998 and Tomiyasu *et al.*, 2000 have respectively recommended long observation periods and both vertical & horizontal distribution analyses so that the mass balance and transport of mercury in sediments can be better assessed. Remediation has occurred by both natural (i.e. exacerbated deposition of clean sediment as a result of a 200-yr event storm) and artificial (i.e. dredging) means. Future remediation may benefit from dredging and clean sediment deposition. However, chemical leaching and microbial treatment may be applicable.

## The Causes and Impacts of Minamata Disease

### *The Chisso Chemical Corporation*

During the 1930's, Japan's chemical industry turned to organic chemical compounds derived from calcium-carbide-generated acetylene. At the time, it was known that acetylene blown over mercuric sulfate would pick up one water molecule to produce acetaldehyde.

The Chisso Chemical Corporation used mercury as a catalyst for the vinyl chloride synthesis reaction ( $\text{HgCl}_2$ ) and in the production of acetaldehyde ( $\text{HgSO}_4$ ). The total amount of mercury used in the chemical factory over four decades (1932-1968) was not available in any published documents (Kudo *et al.*, 1992). One partial record available estimated a total use of 200 tons during the 1949-53 period based on the fact that 500-1000 grams of mercury were lost for each ton of acetaldehyde produced (Nomura, 1968). In 1976, the Kumamoto prefecture proposed that 150 tons of mercury

had been deposited in the bottom of Minamata Bay. However, no basis for this estimate was provided and the amount of escaping from the Bay through tidal action was never considered.

All waste products that were the result of rapid development by Chisso in Minamata were dumped without treatment into the bay, where fishery resources were severely damaged. By natural biochemical transformation and bioaccumulation processes, fish accumulated mercury at acutely toxic levels above the legal limit of 0.4 ppm (Fujiki, 1976). Even with stringent wastewater regulations, concentrations in water at this level were generally not noticeable because techniques for wastewater analysis were not yet developed to detect these minute concentrations. Furthermore, it was not yet known at the time that inorganic mercury could be transformed into its organic counterpart through natural processes.

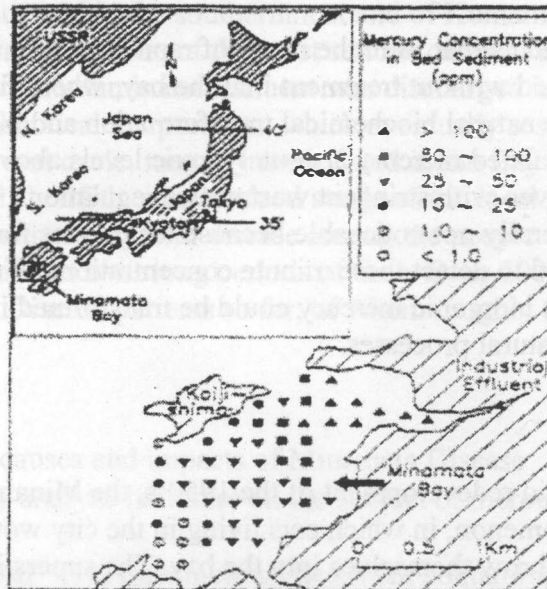
### *Minamata Disease*

During the rapid redevelopment of the 1950's, the Minamata community began to notice a strange phenomenon, in which cats living in the city would go through a frenzied dance and ultimately throw themselves into the bay. The superstitious fishing community named this "the suicide-prone group of dancing cats". Some of the first human signs of the disease were first recorded in May of 1956, when four patients had symptoms such as severe convulsions, intermittent loss of consciousness, repeated lapses into crazed mental states, and then finally permanent coma. Finally, very high fever set in, resulting in death. The one factor common among all patients was the consumption of large amounts of fish.

### **Discussion of past mercury sediment contamination studies of Minamata Bay**

In a study by Kudo *et al.* (1998), twenty-four monitoring stations were established to record mercury movement from Minamata Bay to Yatsushiro Sea during the summer months from 1975 – 1996. For the prime purposes of the study, only total mercury in the surface bed sediments from each station were sampled. At least 1 kg (wet weight) of the surface sediments to a depth of 4 cm was collected from each station by an Ekman sampler. The error associated with sample location was  $\pm 100$  m. The stations were positioned (not all stations were sampled annually) at various distances from the effluent. The so-called Kanagawa method was used to analyze for total mercury concentration; it was based on the standards of the National Research Council of Canada (NRCC) and the US National Bureau of Standards.

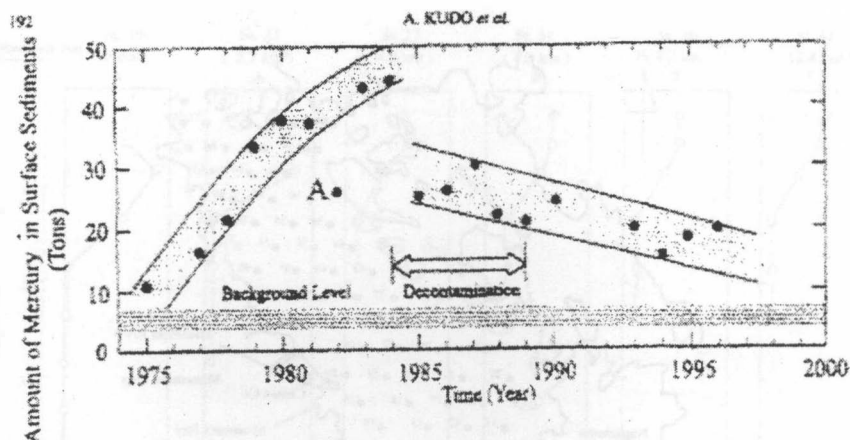
General trends show Hg sediment concentration decreasing over time and with distance from the effluent (Figure 1). Even after 16 years of analysis, several important observations could be made. Highest concentrations observed in Minamata Bay sediments were over 100 ppm. In most cases, mercury concentrations in the Yatsushiro Sea were reduced to levels considered below the acutely toxic level (concentration) in 1990.



**Figure 1. Location of Minamata Bay and mercury concentrations in 1975 (Kudo *et al.*, 1980)**

The conclusions drawn from this historic study (Kudo *et al.*, 1998) were consistent with the ones reached six years earlier (Kudo *et al.*, 1992), three of which specifically address the state of contamination in the sediments: a) A natural decontamination process should be considered to reduce the cost of artificial decontamination, b) A long observation period in a contaminated area is essential for to fully understanding the natural and artificial phenomena occurring, this in turn can help to reduce decontamination costs and restore a healthy ecosystem, and c) The Minamata Bay area will be restored by the year 2011, based on data obtained over the last 22 years.

Conclusion three is of major importance because it proposed a specific timeframe for when Hg sediment concentrations would recede to background levels of four to six parts per million. Figure 2 (Kudo *et al.*, 1998) illustrates the amounts of mercury existing in the surface sediments (4 cm) of the Yatsushiro Sea. From 1975 to 1984, there was a steady increase in the mercury mass balance in the surface sediments. In 1985, there was a significant drop in the mass balance. And thereafter, the mass balance has steadily decreased.

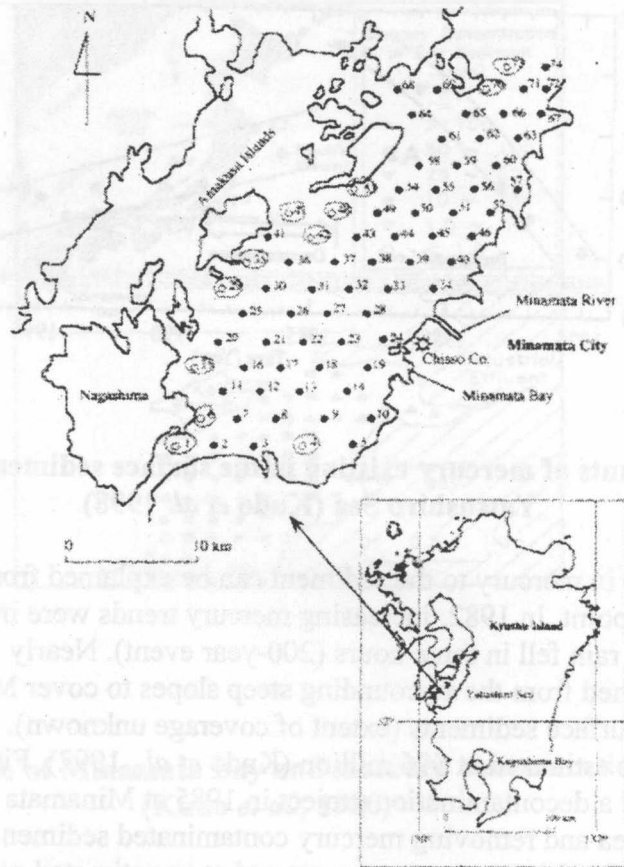


**Figure 2. Amounts of mercury existing in the surface sediments (4 cm) of the Yatsushiro Sea (Kudo *et al.* 1998)**

The decrease in mercury to the sediment can be explained from a natural and anthropogenic standpoint. In 1982, increasing mercury trends were interrupted when 400 mm (11.4 inches) of rain fell in three hours (200-year event). Nearly 1 million tons of natural soil was washed from the surrounding steep slopes to cover Minamata Bay and the Yatsushiro Sea surface sediments (extent of coverage unknown). This natural process had a clean-up effect estimated at \$96 million (Kudo *et al.*, 1992). Finally, the Japanese government initiated a decontamination project in 1985 at Minamata Bay by enclosing a heavily contained area and removing mercury contaminated sediments (> 25 ppm). As a result, 1.5 million tons of sediments were removed at an estimated cost of \$500 million, which included creating a modern harbor and 0.53 million m<sup>2</sup> (over 100 acres) of vacant lot land (Kudo *et al.*, 1998).

In a study by Tomiyasu *et al.* (2000), the spatial variations of mercury in the sediment of the Yatsushiro Sea were assessed. The most significant difference between the historic (Kudo *et al.*) and spatial variation (Tomiyasu *et al.*, 2000) studies was the vertical and horizontal distribution analysis conducted in the latter. Although the Tomiyasu study was not conducted with a long observation period, the vertical and horizontal analysis provided additional insight into characterizing the extent of contamination in Minamata Bay and the Yatsushiro Sea.

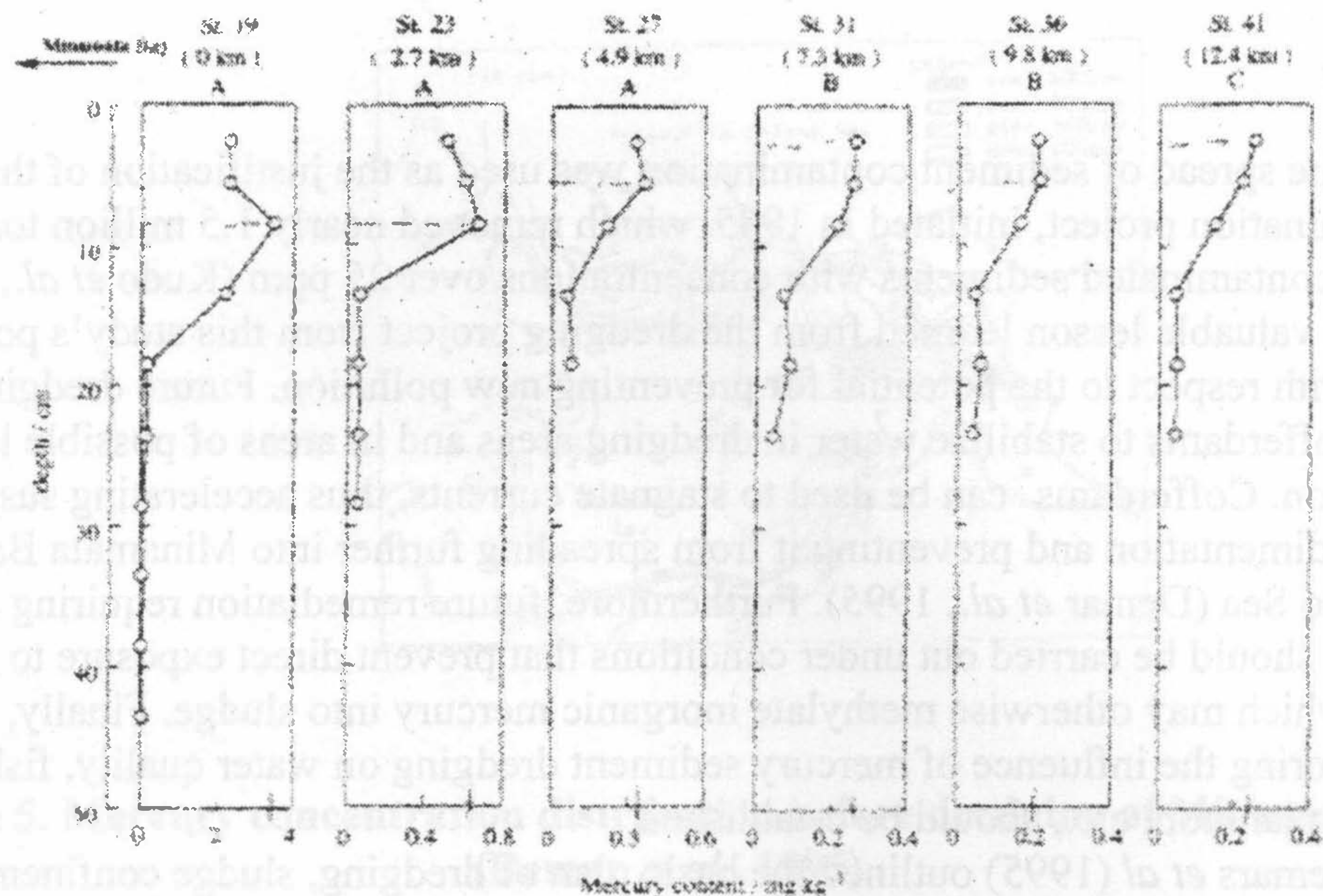
Sediments were sampled at 62 stations in the Yatsushiro Sea in March of 1996 (Figure 3). In the vertical distribution, the total amount of mercury was at a relatively uniform low concentration in the sediment cores. These low values were interpreted to represent pre-anthropogenic background concentrations, which ranged from 0.036 to 0.92 ppm (mean 0.059±0.013 ppm) for the Yatsushiro Sea. This mean value was similar to that of 0.043±0.027 ppm for the surface sediment of an unpolluted area of Kagoshima Bay, in southwestern Japan (Sakamoto, 1985). Highest concentrations for all samples ranged from 0.086 to 3.46 ppm (Tomiyasu *et al.*, 2000).



**Figure 3. Location of sediment samples taken in the Yatsushiro Sea in March 1996 (Tomiyasu *et al.* 2000)**

General trends indicate that the higher Hg sediment concentrations were obtained from stations near Minamata Bay and the Minamata River (Figure 4). Furthermore, concentrations decreased with distance from the contaminant effluent source. Finally, the inspection of the cores indicated that mercury deposition had not been fixed in sediments of Minamata Bay, but had been transported, despite 30 years since contaminated effluent had been discharged (Tomiyasu *et al.*, 2000).





**Figure 4. Vertical profiles of mercury in the sediment in order of distance from Minamata Bay (Tomiyasu *et al.*, 2000)**

The results and general trends are of significant importance for several reasons. Results from the historic study (Kudo *et al.*, 1998), are consistent in that the Hg concentration decreased with distance from the contaminant source. However, the vertical distribution analysis has made possible a more conservative estimation of pre-anthropogenic background sediment concentrations than those estimates proposed by Kudo *et al.* 1998 (0.100 – 0.200 ppm), that were higher by a factor of 2-4. Furthermore, the combination of horizontal and vertical distribution may provide more insight into the transport of mercury in the Bay vicinity as the general trends suggest. In summary, future studies would benefit from both a long observation period and a horizontal and vertical distribution analysis.

### Mercury Contamination Remediation

The previous section addressed recent studies that have assessed the state mercury sediment contamination in Minamata Bay and the Yatsushiro Sea. Two studies in particular were critically analyzed: 1) *Lessons from Minamata Mercury Pollution, Japan – After a Continuous 22 Years of Observation* (Kudo *et al.*, 1998) and 2) *Mercury contamination in the Yatsushiro Sea, south-western Japan: spatial variations of mercury in sediment* (Tomiyasu *et al.*, 2000). In this final section, recommendations will be made on three means of remediation, two of which have already been mentioned (i.e. dredging and natural deposition). An additional alternative (i.e. chemical & microbial treatment),



when applied on a large scale, may be more economically and environmentally beneficial.

### *Dredging*

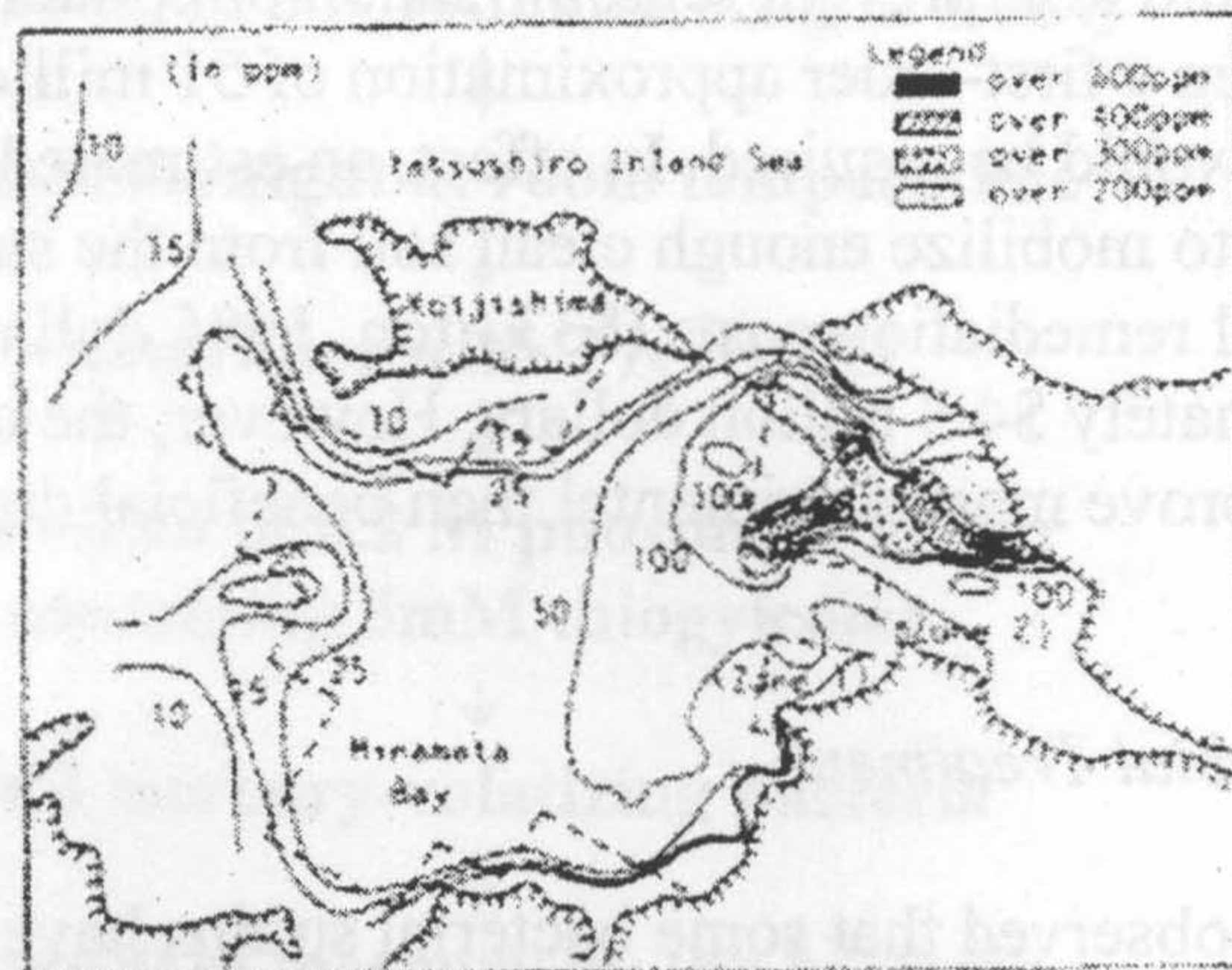
The spread of sediment contamination was used as the justification of the artificial decontamination project, initiated in 1985, which removed nearly 1.5 million tons of mercury contaminated sediments with concentrations over 25 ppm (Kudo *et al.*, 1998). The most valuable lesson learned from the dredging project from this study's point of view is with respect to the potential for preventing new pollution. Future dredging may require cofferdams to stabilize water in dredging areas and in areas of possible land reclamation. Cofferdams\* can be used to stagnate currents, thus accelerating suspended sludge sedimentation and preventing it from spreading further into Minamata Bay and the Yatsushiro Sea (Demars *et al.*, 1995). Furthermore, future remediation requiring sludge treatment should be carried out under conditions that prevent direct exposure to sunlight and air, which may otherwise methylate inorganic mercury into sludge. Finally, a system for monitoring the influence of mercury sediment dredging on water quality, fishery products, plankton, etc., should be established.

Demars *et al.* (1995) outlined the basic plan of dredging, sludge confinement, and supervision of Minamata Bay. However, no recommendations were made as to how future remediation in the Yatsushiro Sea would be addressed. The Yatsushiro Sea has a mean sediment concentration of 0.57 ppm of mercury (estimated average sediment depth = 29 cm), which is greater than the average background concentration of  $0.059 \pm 0.013$  ppm by about a factor of 10 (Tomiyasu *et al.*, 2000). Furthermore, some zones within the dredging area had Hg sediment concentrations greater than 600 ppm versus 100 ppm measured by Kudo *et al.*, 1998 (Figure 5). As shown below, if the surface sediments (4 cm) of the Yatsushiro Sea ( $636 \text{ km}^2$ ) were to be dredged, about 3.18 million tons of sediment would need to be removed, treated, and relocated.

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\* A cofferdam is a temporary or removable structure used to keep earth or water from entering the construction site.





**Figure 5. Mercury concentration distribution before dredging of Minamata Bay (Demar *et al.*, 1995)**

(Adams, O'Connor, and Weisberg 1998)

Wet bulk density,  $D = (1-p)r_s + pr_w$

Where:  $p$  = porosity (mean of 0.4 assumed)

$r_s$  = density of sediment (quartz, etc.) particles ( $2.65 \text{ g/cm}^3$ )

$r_w$  = density of water ( $1 \text{ g/cm}^3$ )

Therefore,  $D = ((1-0.4) * 2.65) + 0.4 = 2 \text{ g/cm}^3$  ( $\text{tons/m}^3$ )

or  $0.5 \text{ g/cm}^2$  in the top four centimeters of surface sediment

Therefore, sediment removed =  $(0.5 \text{ g/cm}^2) * (636 \text{ km}^2) * (10^{10} \text{ cm}^2 / \text{km}^2) * (1 \text{ ton}/10^6 \text{ g})$   
 $= 3.18 \text{ million tons}$

Assuming a unit removal cost of \$333/ton (1985 dollars), then a first order estimate for the total cost of artificial dredging project on the Yatsushiro Sea would be \$1.1 billion. In effect, the dredging option may prove to be too costly.

### *Natural Remediation*

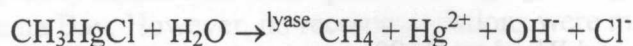
Natural remediation via transport and deposition of clean sediment is most unlikely to occur on a scale that would resolve mercury contamination in the Yatsushiro Sea. The 1982, 200-yr storm event mobilized nearly 1 million tons of clean soil from the surrounding countryside, depositing into Minamata Bay and the Yatsushiro Sea. Ignoring sediment transport behavior, a first-order approximation indicated a surface layer of only 0.08 cm thickness clean sediment (assuming soil density =  $2.0 \text{ g/cm}^3$ ) was deposited in the Yatsushiro Sea ( $= 636 \text{ km}^2 \gg 3 \text{ km}^2$  for Minamata Bay).

Neither Kudo nor Tomiyasu proposed the level of clean sediment deposition preventing remobilization of contaminants in the Yatsushiro Sea. However, 80 cm of sirasu (volcanic ash earth/soil of low specific gravity, locally produced), was sprinkled in

the form of slurry to contain the contaminated sediment in the reclamation area (Demar *et al.*, 1995). Assuming that a fraction of this (4 cm surface sediment, Kudo *et al.*, 1998) clean sediment would also prevent remobilization of contaminated sediment in the Yatsushiro Sea, then a first-order approximation of 51 million tons (i.e. 12.8 million m<sup>3</sup>) of clean sediment would be required. In effect, an estimated twenty 200-yr event storms would be required to mobilize enough clean soil from the surrounding area. In terms of equivalent artificial remediation costs (\$333/ton, 1985 dollars), then a first order estimate would be approximately \$4.3 billion dollars. However, the occurrence of this is very unlikely and may prove more detrimental than beneficial due to possible flooding and erosion.

### *Chemical & Microbial Treatment*

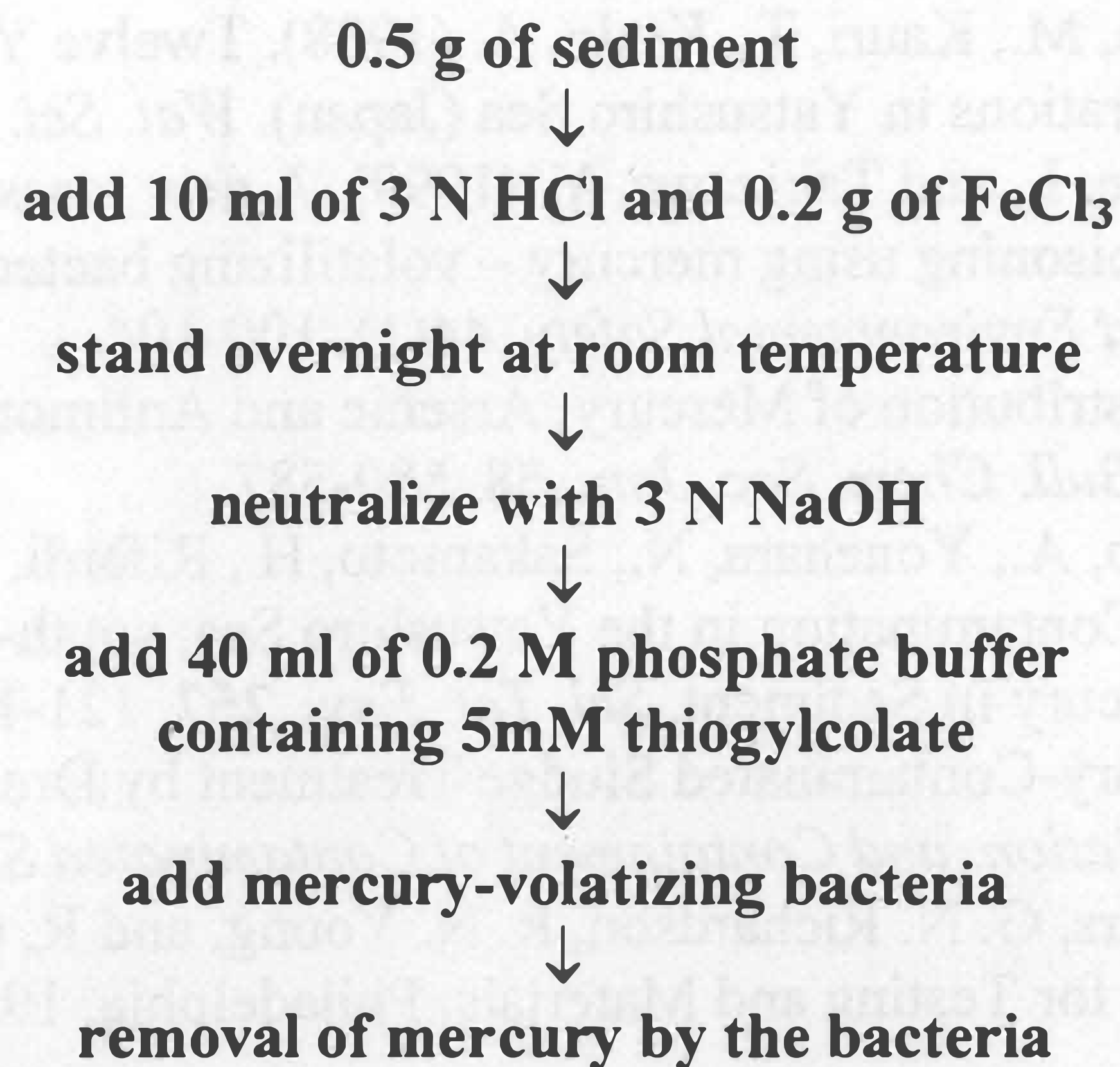
It has been observed that some bacterial strains have been found to transform mercury compounds such as mercury chloride and methylmercury chloride into volatile mercury vapor. (Clark *et al.*, 1977; Nakamura *et al.*, 1990; Summers and Silver, 1972). These bacteria can detoxify the compounds by the actions of two enzymes acting sequentially.



This characteristic was used to develop a method for the detection of methylmercury in human hair (> 50 µg/g Hg in hair considered to be the threshold level for the manifestation of Minamata Disease (ICPS, 1990)).

The Minamata Disease detection methods may one day be applied on a grand scale to remediate remaining contamination. In a more recent study by Nakamura *et al.*, 1999, a method for the removal of mercury sulfide from mercury-contaminated sediments was developed. This method consisted of chemical leaching and volatilization of mercury. Testing resulted in more than 85% of mercury in sediment being extracted with chemical leaching, while 62.9-75.1% mercury in sediments being removed from volatilization by bacteria. Methylmercury was also removed from the soil at a high efficiency (Nakamura *et al.*, 1999). The results suggest that a combination of chemical leaching and microbial treatment on a large scale could be used for the efficient removal of both organic and inorganic mercury from ocean sediments (Figure 6). With time additional information may help to determine how costs compare with traditional remediation techniques such as dredging.





**Figure 6. Procedure for the removal of mercury from the sediment (Nakamura *et al.* 1999)**

### Conclusions

- Mercury-contaminated effluent from the Chisso Chemical Corporation was the leading cause of Minamata Disease resulting in over 2000 diagnosed and 900 fatalities.
- Long observation periods and both vertical & horizontal distribution analyses should be incorporated in future sediment studies.
- In the past, dredging was the most common means of contaminated sediment remediation; in the future chemical leaching and microbial treatments may be the economically and environmentally friendly alternative of choice.

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