Mercury in Fluvial Bed Sediments Subsequent to Contamination

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ABSTRACT / Once inputs of mercury-bearing effluents to a fluvial system are stopped, levels of contamination will decline slowly to background values. Crystalline mercury phases will dissolve in response to lowered aqueous mercury concentrations, and aqueous $Hg(OH)_2$ will desorb from ferric hydroxide grain coatings as the coatings age to more ordered phases. In the Ottawa River, mercury concentrations in bed sediments are declining by about 50 percent annually.

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Introduction

Over the past few years much attention has been paid to the occurrence of mercury in the environment. Presently, there exists a basic understanding of the aqueous chemistry of mercury and a realization that man's use or misuse of mercury can cause grave deterioration of the viable environment. His ecological conscience piqued, man now endeavors to control, in the large part, the discharge of abnormal and intolerable quantities of mercury to inland and oceanic waters, and to the atmosphere. However, some damage has already been done. Serious mercury contaminations exist or are suspected to exist in the water bodies adjacent to many of the world's largest population concentrations. Because a potentially large number of people may be affected by these mercury contaminations, the nature of mercury in the aqueous environment subsequent to contamination must be defined.

Ottawa River Programme

A joint undertaking of the University of Ottawa and the National Research Council of Canada Laboratories, the Ottawa River Programme is an investigation of many parameters governing the occurrence of various persistent chemicals in a natural river system. One part of the project is the examination of mercury in the bed sediments of a 6 km study section of the Ottawa River at Ottawa, Canada (Fig. 1). The section was chosen for study because it typifies many eastern Canadian rivers with respect to the industry and settlement along its shores, and because until 1971 mercury was discharged to the section as a component of pulp mill effluent. Hart (1972) estimated that bed sediments of the study reach contained 97 percent of the mercury in the system, thus the importance of bed sediments to the eco-system is evident.

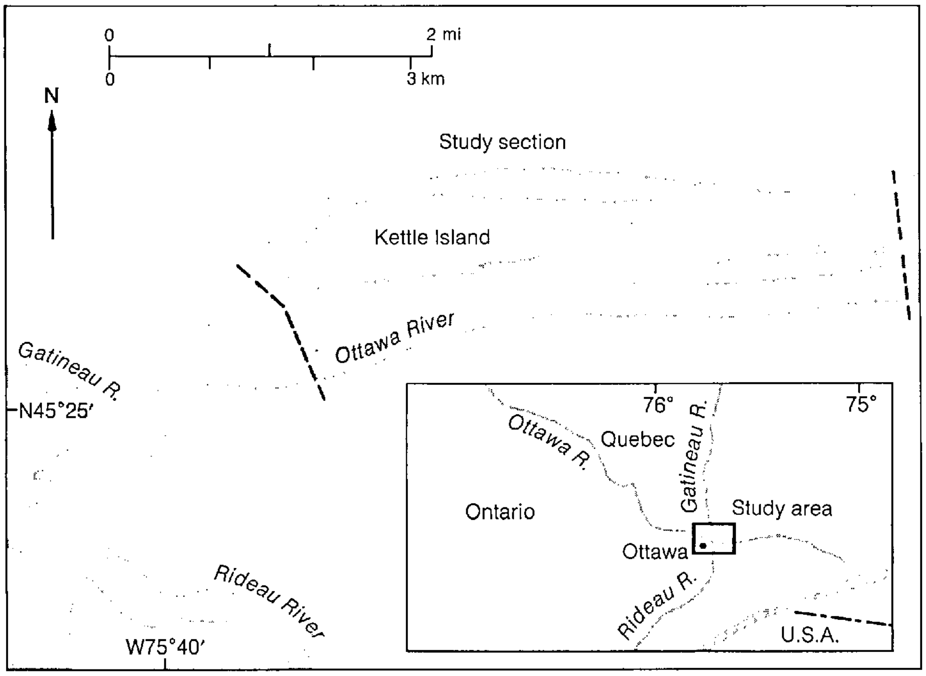


Figure 1. Study section of the Ottawa River Programme, Ottawa, Canada.

Experimental Results and Discussion

Theoretical considerations

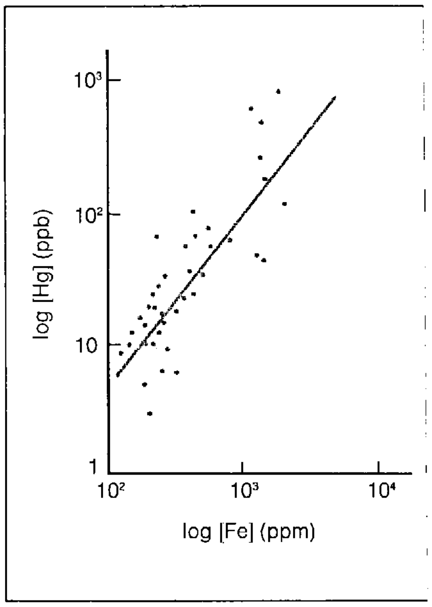
The predominant solute species likely to occur in the well-aerated Ottawa River environment, as predicted by equilibrium calculations (Hem 1970), are aqueous Hg° and the highly soluble Hg_2^{2+} and $Hg(OH)_2^\circ$. One would not expect dissolved free mercury to enter directly into equilibrium reactions with the solid Hg phases present in a river environment, because free mercury is relatively volatile and will be a lost to the atmosphere whenever the water/atmosphere interface is encountered, and because dissolved free mercury is strongly taken up by organic solvents, which maintain Hg in a highly soluble state. The Hg_2^{2+} ion likewise will be strongly complexed with soluble organic acids, but will also adsorb to colloidal- and clay-suspended particulates, and in these forms, may or may not interact with the bed sediment compartment, depending largely on flow conditions. Jenne (1968) pointed out that ion-exchange processes of clays are probably unimportant where ubiquitous ferric hydroxides are present. Dissolved Hg-organic complex stabilities are not yet understood. However, stable Hg-organic complexes will preclude the reaction of Hg bound thus with other phases, and the metastable complexes, such as those derived from pulp processing effluents, would likely break down to the stable inorganic phases mentioned previously. Hence, the aqueous form most likely to react with the solid Hg species in a fresh-water, well oxidizing environment is the hydroxide, $Hg(OH)_2^\circ(aq)$.

Hg–Fe relationships in bed sediments

Fig. 2 shows the strong relationship between fresh $Fe(OH)_3$ grain coatings and leachable Hg in the Ottawa River bed sediments. An equally strong relationship was observed between $Fe(OH)_3$ and associated leachable Mn. These correlations are in accord with earlier studies; ferric hydroxide particulates and grain coatings have been noted to provide many surface areas for the adsorption of "trace element" species (Krauskopf 1956, Jenne 1968). Precipitating ferric hydroxides tend to take down adsorbed $Hg(OH)_2$ and hydrated MnO_2 concurrently, as well as a number of other dissolved metal species. Because the concentration of ferric hydroxide coatings is largely determined by sediment surface areas, adsorbed Hg concentrations will also be related to surface areas. Fig. 3 suggests this relationship, where mean ϕ grain size ($\phi = -\log_2$ Diameter [mm]), which reflects surface area, is well correlated with leached Hg concentrations. A similar relationship was found to occur in the Ems River sediments by deGroot and others (1971).

Considering the above, the initial association between Hg compounds and the bed sediments can be understood.

Figure 2. Fresh ferric hydroxide (Fe) *vs* leachable Hg concentrations from bed sediment grain coatings. The relationship is significant at the 1% level.



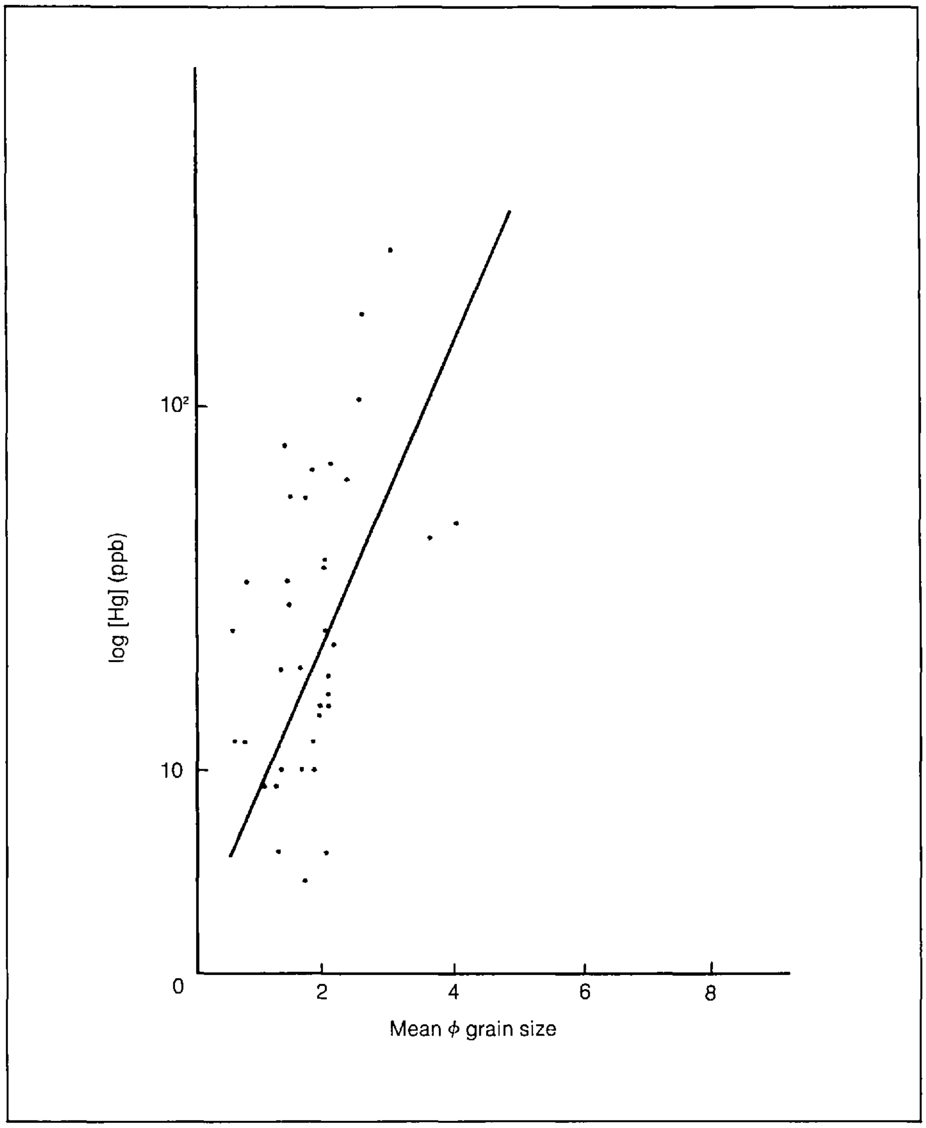


Figure 3. Leachable Hg concentration *vs* bed sediment grain size. The relationship is significant at the 1% confidence level.

Aqueous Hg species, largely $Hg(OH)_2$, become components of the bed sediment by virtue of adsorption to ferric hydroxide grain coatings. With sufficient time, and with the continuation of suitable oxidation-reduction conditions, crystalline HgO or HgS will develop. However, the total of the solid phases would necessarily be small, because they would be affected by equilibrium reactions with the highly soluble $Hg(OH)_{2(aq)}$ and $Hg_2{}^{2+}{}_{(aq)}$ phases.

Declining Hg concentrations

Prior to 1971, unnaturally high concentrations of Hg were probably present in all compartments of the Ottawa River study section due to contamination by pulp mill effluent (no data is available on Hg levels before that time). Shortly after the use of phynol-mercuric compounds as a slimicide agent in pulp processing was discontinued, Oliver and Kinrade (1972) reported bed sediment Hg levels in the study section to be as high as 1,990 ppb in the summer of 1971. Corresponding Hg analyses on samples taken in the summers of 1972 and 1973 (as part of the Ottawa River Programme) showed that Hg concentrations were decreasing. Three locations sampled by Oliver and Kinrade were resampled for the Ottawa River Project approximately two years later. Oliver and Kinrade's 1971 samples 5-2, 6-1, and 6-2 are compared to samples BS206, BS208, and BS209, collected in 1973 (Table 1). Samples 5-2 (BS206) and 6-2 (BS209) were taken from mid-channel in the secondary channel north of Kettle Island. Sample 6-1 (BS208) was taken near the north shore of the same channel. Assuming the decline of Hg concentrations to be exponential, and assuming, for the sake of comparison, a background Hg concentration everywhere equal to zero, the half-life, $t_{1/2}$, of Hg at each of the locations is calculated. For mid-channel

Table 1 Comparison of Hg Concentration Data

Oliver and Kinrade (1972)		1973 Ottawa River Project		$t_{1/2}$ (year)
Sample no.	Concentration (ppb)	Sample no.	Concentration (ppb)	
6-1	1990	BS 208	600	1.15
6-2	250	BS 209	62	.99
5-2	90	BS 206	16	.85

samples (5-2 and 6-2) the half-life rates of decrease are slightly less than one year. The marginal sample (6-1) has a half-life slightly greater than one year.

In addition, corresponding Ottawa River Project samples from 1972 and 1973 were compared. Replicate samples were taken at eleven sites. The average 1972 Hg concentration of 310 ppb declined to an average of 128 ppb in one year. The half-life for this decrease is 0.78 year. The rates of decline of Hg concentrations in the two channels are thus in close agreement. Unfortunately, the calculations are rather approximate, owing to the difficulties and uncertainties involved in obtaining replicate samples at the same localities from year to year, and the small number of north channel samples taken by Oliver and Kinrade (their study was regional, covering several miles of the Ottawa River and its tributaries).

Mechanical *vs* chemical removal of Hg

The decrease of Hg in bed sediment is probably due to at least two types of processes, (1) the transport of unnaturally contaminated grains out of the system, those grains being replaced by "background-contaminated" grains from above the pulp mills formerly contributing Hg to the section, and (2) the chemical desorption of Hg associated with ferric hydroxides, and the dissolution of crystalline forms of Hg. It is notable that the uptake (methylation) of Hg from bed sediments by benthic organisms is not a significant factor in the study reach, as there is only a very low biomass (Hart 1972). Bed sediment and hydraulics studies (Waslenchuk, in press) show that the north channel sediments are being transported at a rate of about 1/20 to 1/50 of the rate of main channel sediments. Assuming that the calculated rates of decrease in Hg in the north and main channels are accurate, it is clear that the transport of contaminated grains out of the system does not entirely explain the decrease. The samples in Table 1 are listed in order of increasing measured sediment transport rate. The 11 main channel samples are in a more energetic environment than the north channel samples, and so would appear at the bottom of the list. Evidently the sediment transport process does affect the rate of Hg decline in the system. However, sediment transport rates range over five times an order of magnitude, whereas half-lives range over only about 25 percent. Chemical desorption and equilibrium reactions are therefore indicated to be important mechanisms in the readjustment of Hg concentrations after unnatural contamination has ceased. Laboratory tests on artificially contaminated Ottawa River sediments (Kudo 1974) showed chemical mechanisms to remove adsorbed Hg at a half-life (rate) of 0.82 year, a figure that is reasonably consistent with the decrease rates determined in field studies.

Chemical removal

There are two aspects to the chemical removal of Hg from the bed sediment compartment. First, in response to lower concentrations of Hg compounds in the water column subsequent to cessation of effluent input, crystalling HgO and HgS will dissolve to aqueous species, by reactions such as:

$$HgO_{(c)} + H_2O = Hg(OH)_{2(aq)} \qquad (1)$$

and

$$HgS_{(c)} = Hg_2^{2+} + 2S^{=}$$

These reactions will proceed until a new equilibrium is reached between the crystalline and natural aqueous species, at "background" levels.

The second aspect of the chemical removal of Hg is the desorption of species like $Hg(OH)_2{}^{\circ}{}_{(aq)}$ from ferric hydroside grain coatings. Desorption will occur in response to the aging of the ferric hydroxide grain coatings, to which $Hg(OH)_2$ first adsorbed. In fluvial sediments, ferric hydroxides may become more crystalline with age, changing with time to goethite and possibly lepidocrocite (Langmuir and Whittemore 1971) In the process of aging, the hydroxide coatings lose their state of high surface area and thus lose their ability to hold much of the Hg, Mn, and other adsorbed species. Experiments on leaching Ottawa River bed sediments with 12 percent HCl showed that an initial rapid dissolution of Fe coatings corresponded to a rapid dissolution of adsorbed Mn (Fig. 4). A break in slope of the curve is followed by a period of less rapid dissolution of Fe, which indicates that a second phase of iron is present, probably as limonite or goethite. A corresponding break in slope occurs on the manganese leaching curve, followed by a horizontal portion, indicating that the aged form of iron has released any previously adsorbed manganese. If adsorbed Hg behaves similarily to adsorbed Mn, as is likely, then it is evident that aging of ferric hydroxide coatings does result in desorption of Hg. The same test was not done for Hg due to the difficult nature of Hg analyses. Conceivably, aging periods on the order of a month would be sufficient to cause substantial reordering of ferric hydroxide precipitates, and substantial liberation of adsorbed trace elements. The actual rate of loss of Hg from the bed sediment compartment would probably be somewhat less than the rate of liberation of Hg from aged iron hydroxide coatings, because in order for the fresh ferric hydroxide – adsorbed Hg relationship of Fig. 2 to be maintained. part of the liberated Hg must re-adsorb to fresh ferric hydroxide, or migrate to new sites on the fresh coatings.

Experimental Methods

All iron and manganese concentrations were determined on 12 percent HCl leachates by standard Atomic Absorption Spectrophotometry methods. Reproducibility of results in all cases was within 10 percent. Hg analyses were made at the NRC laboratories by flameless Atomic Absorption methods.

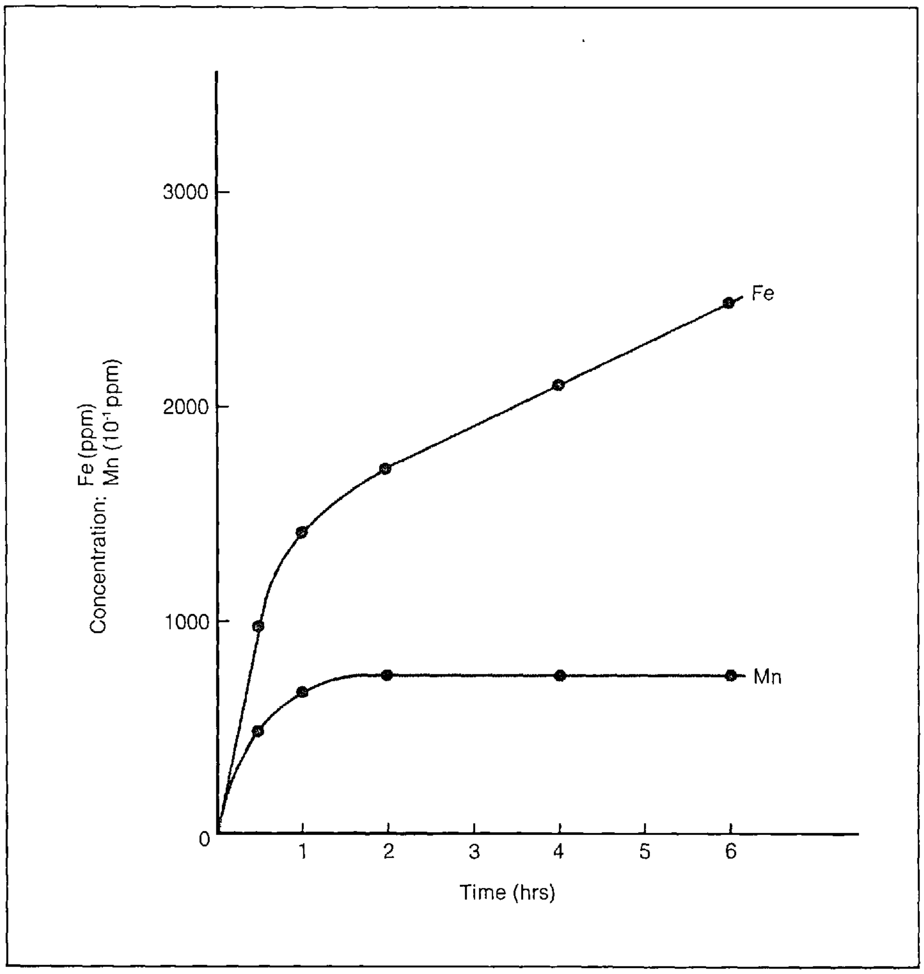


Figure 4. Fe and Mn concentrations in bed sediment grain coatings *vs* leaching time in 12% HCl.

on acid leaches of duplicate samples. Reproducibility of Hg values was on the order of 15 to 20 percent less than that of Fe and Mn. The inaccuracies arose not in the analyses themselves, but rather in obtaining representative subsamples.

For iron, the leaching procedure consisted of treating each of several homogenous five-gram sub-samples of a single sample with 100 ml of 12 percent HCl, filtering off the leachates sequentially over a period of about eight hours. The leachates were then analyzed, and the concentrations of Fe removed from the grain coatings were plotted against leaching time, as in Fig. 2. The concentration of Fe at the break in slope was taken as the "fresh ferric hydroxide" concentration. Manganese and mercury concentrations in the leachates quickly reached a maximum, around the time of the break in slope of the Fe curve. The maximum values were considered to be the "leachable" manganese and mercury concentrations.

Bedload discharge measurements were obtained by two methods, (1) tracking dune-crest migration by sonic depth sounding, and (2) direct measurement with a bedload sampler operated by a scuba diver (Waslenchuk, in press). The two methods yielded discharge rates that agreed within 15 percent.

Conclusions

In an aerated fluvial system, aqueous $Hg(OH)_2$ is associated with bed sediments by virtue of adsorption to ferric hydroxide grain coatings, and by crystalline HgO precipitates. Subsequent to the cessation of unnatural Hg inputs, the system will react to approach a new equilibrium with respect to Hg at background levels. Both mechanical and chemical mechanisms operate to reduce Hg concentrations in the bed sediments of the contaminated area, mainly by three processes:

1. The transport of unnaturally contaminated sediment grains downstream, which are replaced by grains of lower background Hg levels from upstream of the artificial Hg input.
2. In response to lower aqueous Hg concentrations in the water column, crystalline forms of Hg dissolve slowly to regain equilibrium. The products of dissolution likely will be lost to the atmosphere due to high vapor pressures, or will be kept in solution by organic complexing.
3. As a result of the aging of ferric hydroxide grain coatings, adsorbed Hg and other trace-elements will be liberated. Some of the liberated Hg will become associated with fresh ferric hydroxide precipitates in the immediate area, maintaining a strong Fe–Hg correlation. The rest will be transported downstream in solution.

The net rate of the processes above is apparently on the order of a 50 percent annual decrease in Hg. There is evidence that the net loss proceeds exponentially, in which case the half-life is 0.78 to 1.15 years. Therefore, the bed sediments of a fluvial system will slowly recover from unnatural Hg contamination. The liberated Hg will not be lost from the environment, but will, to some extent, enter the atmosphere, and, more importantly, will migrate downstream to the oceans.

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