

A STUDY OF MERCURY RELEASE FROM LAKE SEDIMENT

(Report to Task 8 - upon Effects of Dredging
and Disposal of Dredged Materials in the
Great Lakes

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INTRODUCTION

Despite considerable concern about the fate of mercury compounds which may be made available to lacustrine ecosystems as a result of dredging practices, little information is available about what happens to methylmercury present in sediments. A laboratory experiment¹⁾ in Sweden showed that methylation of mercury was accelerated when sediment with mercury was shaken with water under aerobic conditions and that dimethylmercury may be rapidly formed when mercury-contaminated sediments are exposed to air. However, slightly different results for mercury methylation have been reported.²⁾³⁾⁴⁾ It can be said that many factors are involved in mercury methylation and the mechanisms seem to be very complex in the environment.

At C.C.I.W., experiments were undertaken to try to clarify the above problems and to assess the effects of dredging activities. The following study topics were chosen:

- 1) A brief study of the concentration of methylmercury in the Great Lakes' sediments where total mercury content has been reported to be high⁵⁾.
- 2) A study of the volatilisation of mercury compounds present and artificially added to sediment.
- 3) A study of the effects of air exposure upon mercury in sediment.
- 4) A study of the release of methylmercury from sediment subjected to mixing with water.

Chemicals used

Background levels of mercury in all chemicals used were checked and reagent blank was subtracted in each case.

Analytical procedures

Mercury in air - Mercury was collected in a cleaning solution (40 ml H₂O saturation with K₂Cr₂O₇ at 60°C, dissolved in 1 litre conc. H₂SO₄) by passing air through it with a peristaltic pump. All mercury compounds, including very volatile dimethylmercury, are rapidly oxidised and retained in the solution. Other oxidising reagents tested, such as potassium permanganate and ceric sulfate solution, were not satisfactory for the oxidation of dimethylmercury. The detection limit was found to be 0.01 µg per 1 ml of the solution, using a flameless atomic absorption technique. One disadvantage noted in the use of this cleaning solution is its interference in the reduction of mercury compounds when more than 1 ml of the solution is used.

Methylmercury in sediment - 20 ml, 2N-HCl was added to 10 g of freeze-dried sediment in a 60 ml separatory funnel. After the gases evolved from the sediment were evacuated to air, 0.1 g of CuCl was added. The sample was then shaken twice with two 20 ml benzene for 10 min. The benzene phase (40 ml) was pipetted into a 60 ml separatory funnel, washed with 10 ml H₂O and followed by shaking four times with 4 ml, 0.5% l-cysteine solution for 10 min. The l-cysteine solution (16 ml), after the addition of 4 ml 10N-HCl, was shaken three times with 3 ml benzene for 10 min.

The benzene phase (9 ml) was adjusted to 10 ml with benzene in a volumetric flask and the methylmercuric chloride was analyzed using a gas chromatograph equipped with a Ni⁶³ electron capture detector. The recovery was 95% for standard addition experiments. The precision of five replicate samples was $\pm 5\%$. The sensitivity was 1.5 ppb, using 10 g of sediment. Gas chromatograph conditions have been reported elsewhere⁷⁾.

Methylmercury in water - Gas chromatographic technique after extraction by organic solvent was applied with a slight modification^{7) 13)}. The recovery was 90% for standard addition experiments and the sensitivity was 0.25 ppb when 30 ml water was used.

Sediment sampling - shipek grab or clamshell grab was used.

Results and discussion

1) Methylmercury in sediment:- Methylmercury is formed biologically in the natural environment and is the most toxic form to living organisms. For this reason, it is desirable to focus on methylmercury contamination in the environment. Table 1 shows the methylmercury and total mercury concentration in selected Great Lakes' sediments. Even though few data are available, the percentage methylmercury of total mercury appears high in Lake St. Clair sediments, with no direct correlation to total mercury (Table 1). In recent reports^{8) 9)}, the methylmercury content in estuarine sediments, which are not heavily polluted, is less than 0.7% of

total mercury but about 0.35% in a river sediment, known to be heavily polluted with mercury. It is considered that the Great Lakes' sediments contain high percentages of methylmercury which may be correlated with observations of high mercury concentrations in certain fish species¹⁰⁾. Methylmercury in the Great Lakes water, however, has been reported to be below detection limit⁷⁾. In Minamata Bay in Japan, a recent survey shows that total mercury in the sediment is 14-586 ppm, and methylmercury in the top layer of the sediment is 3 ppb; the mercury content of the fish, however, is about 0.5 ppm¹¹⁾. This is less than reported for Canadian lake fish¹⁰⁾.

2) The volatilisation of mercury compounds present and artificially added to sediment:-

(i) In order to test whether or not dimethylmercury is rapidly formed in sediment exposed to air, sediment (methylmercury concentration, 6 ppb and total Hg, 3 ppm) was placed and sealed in a glass container as soon as the sample was taken from the lake bottom (5 miles north of the Niagara River mouth). The mercury concentration of air inside the container was analyzed and found to be below detection limit (0.01 μg). The weight of the sediment was at least 3 kg (dry weight basis), therefore, methylmercury and total mercury present was estimated to be 18 μg and 9 mg respectively. Mercury released by rapid air exposure was calculated to be less than 0.12 μg (less than 1% of the mercury present). It was concluded that dimethylmercury was not rapidly formed under such conditions.

(ii) Several mercury compounds (CH_3HgCH_3 , CH_3HgCl and Hg) were mixed individually with wet sediment and kept in glass containers. Air was passed through the sediment by a peristaltic pump and trapped in a cleaning solution. Air flow was checked by a flowmeter (see Fig. 1). The cleaning solution in the absorption chamber was replaced with fresh solution, every week, to prevent further dilution by water vapour. The mercury concentration in the cleaning solution was analyzed and all blank values were subtracted. Results are shown in Tables 2, 3 and 4. As shown in Table 2, dimethylmercury volatilizes very rapidly from sediment. Volatilization of metallic mercury and methylmercuric chloride in Tables 3 and 4 is very limited and not significant. It can be said that dimethylmercury was the most volatile form of mercury in the sediments.

3) The effects of air exposure upon mercury in sediment:- Sediment was homogenized with a mechanical mixer and was then left outside for 2,4,5 and 9 months in open containers. The concentration of residual mercury in the sediment samples is shown in Table 5. A major portion of mercury does not seem to have been lost during this exposure to air (E-1, location 1 and E-2) although the mercury values in E-1, location 2 fluctuated. Organically rich sediment which may be mercury-rich in contaminated areas may have been suspended and flushed out by rain (E-1, location 2).

4) The release of methylmercury from sediment subjected to mixing with water:- Methylmercury in sediment seems to be poorly

extracted by organic solvent¹²⁾ and is strongly bound to large molecules such as polysulphides^{8) 13)}. Sulfide forms of inorganic mercury are insoluble in water but methylmercury is soluble with the presence of small molecules of sulfides^{13) 14)}. Here, Lake St. Clair wet sediment prepared with various concentrations of methylmercuric chloride was shaken with lake water by means of a mechanical shaker for 3 hours. The well-mixed suspension was centrifuged at 1400 r.p.m. for 30 min. The water layer was collected by decantation and analyzed for methylmercury. As shown in Table 6, a methylmercury release to water was observed when methylmercury concentration in the sediment was increased to 0.37 ppm. For concentrations of mercury in sediment of less than 0.37 ppm, methylmercury in water was undetectable and larger quantities of sediment and water would have to be used to investigate this range. This study was done with Lake St. Clair sediment only. The extent of methylmercury release to water appears to be dependent upon a number of factors which are not yet fully understood. In addition, it was confirmed that methylmercuric chloride added to the sediments was not converted to volatile mercury (dimethylmercury) during these shaking experiments. It is likely, therefore, that the methylmercuric chloride which is not released to water is bound to the sediments.

CONCLUSION

The following statements can be made as a result of these studies:

1) Methylmercury concentration in sediment is high in the Great Lakes and may be related to mercury content in fish.

2) Rapid formation of dimethylmercury in sediment during exposure to air was not observed from mercury contaminated lake sediment taken from 5 miles north from Niagara River mouth. Dimethylmercury is most responsible for mercury volatilization from sediment (metallic and monomethylmercury volatilization is insignificant).

3) A major portion of the mercury remained in the sediment after exposure to air for at least several months.

4) Some portion of the methylmercury in sediment is released to water under mixing conditions. Further experiments are needed to understand this.

Comment

Some portion of the methylmercuric chloride added also volatilizes and conversion to dimethylmercury seems to have taken place when a large quantity of methylmercuric chloride was added, or under certain pH conditions without sediment (Table 7). However, the major portion of the methylmercuric chloride artificially added and the methylmercury biologically formed will exist as complex forms with polysulfides in sediment and will be stabilized (volatilization and release to water is lowered; a freeze-drying procedure was used for sediment sample preparations

for methylmercury analysis without loss of methylmercury). Dimethylmercury formed will not be retained in sediment because of its nonionic character and high vapour pressure (50 mm Hg at 20.5°C)¹⁵).

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TABLE 1

The concentration of methylmercury and total mercury in sediments tested
(dry weight basis)

LOCATION	Me Hg ($\mu\text{g}/\text{kg}$)	Total Hg (mg/kg) ^{(1)*}	%MeHg of total Hg
LAKE ST. CLAIR 1	18.5	2.13	0.87
2	9.1	2.3	0.40
3	13.0	-	-
PILOT ISLAND ^{(2)*} 1	6.2	0.11	0.65
2	0.2	0.11	0.18
3	8.0	2.37	0.34
PORT STANLEY (L. ERIE)	0.4	0.07	0.57
NIAGARA ON THE LAKE ^{(3)*} 1	6.0	3.9	0.15
2	7.0	2.9	0.24
HAMILTON BAY 1	0.4	0.75	0.05
2	2.4	3.89	0.06

(1)* HATCH AND OTT METHOD

(2)* DISPOSED SEDIMENTS FROM L. ST. CLAIR AND EXPOSED TO AIR FOR 1 YEAR.

(3)* 5 MILES NORTH FROM NIAGARA RIVER MOUTH.

TABLE 2

Release of dimethylmercury from sediments (μg as Hg)

No. of experiment	Dimethylmercury Added	Pumping time	Found	Recovery (%)
1	1.20	3 hr.	1.05	90
2	12.0	4 hr.	11.4	95
3	6.6	2.5 hr.	6.3	95

TABLE 3

Release of metallic mercury from sediment

Metallic mercury added	Pumping time	Recovery (%)
107 mg in 100 g wet sediment	0 day	0
	3 day	0
	20 day	0
	28 day	0.005
	32 day	0.03
	35 day	0.10
	59 day	0.33

TABLE 4
Release of methylmercuric chloride from sediment

CH ₃ HgCl added	Pumping time	air volume	Recovery (%)
1590 µg(as Hg) in 200 g wet sediment	3 day	0.97 m ³	1.3
	9 day	2.72 m ³	2.5
	16 day	5.27 m ³	2.7
		8.07 m ³	2.9
		9.95 m ³	3.0
		12.00 m ³	3.1
		14.14 m ³	3.2
		16.46 m ³	3.2
		18.90 m ³	3.2
	85 day	20.63 m ³	3.2

TABLE 5

Variation of mercury in sediments exposed to air
(PPM total Hg as dry weight basis)

Sediment homogenized			after 2 months	after 4 months	after 5 months	after 9 months
E-1	2.9	location 1	2.3	2.6	2.4	3.0
		location 2	1.0	3.0	1.7	-
E-2	1.5	location 1	1.5	1.2	-	1.2

E-1: 5 miles from Niagara River Mouth

E-2: Lake St. Clair

Location 1: Outdoor, but protected from rainfall

Location 2: Outdoor, and exposed to rainfall.

TABLE 6
Release of methylmercury to water

No.	Mehg added(μ g)	wet sediment(g)	Mehg in sediment(ppm)	Lake Water(ml)	Mehg in water after shaking(ppb)
1		14	-	30	<0.25
2	0.5	14	0.036	30	<0.25
3	1.5	14	0.107	30	<0.25
4	2.5	14	0.180	30	<0.25
5	2.5	14	0.178	40	<0.25
6	5.0	14	0.360	40	<0.25
7	7.5	14	0.535	40	0.4
8	10.0	14	0.714	40	0.6
9	18.7	50	0.374	100	0.7
10	28.1	50	0.562	100	1.1
11	15.0	40	0.375	40	<0.25
12	22.5	40	0.562	40	0.5

TABLE 7

Volatilisation test of mercury,

from methylmercuric chloride and dimethyl mercury solution.

EXP. NO.	SAMPLE	AIR VOLUME PASSED(m ³)	CLEANING SOLUTION IN 1ST. ABSORPTION CHAMBER (µg Hg/ml)	CLEANING SOLUTION IN 2ND. ABSORPTION CHAMBER (µg Hg/ml)
1	Wet sediment + MeHgCl (200g) (1590 µg as Hg)	6.02	0.21	0.02
2	Distilled water (pH=5-6) (50ml) + MeHgCl (100 µg as Hg)	0.12	0.29	not detected
3	Distilled water adjusted (pH=9) (50ml) + MeHgCl (100 µg as Hg)	0.22	-	0.06
4	Distilled water (pH=5-6) (30ml) + Saturated Dimethyl Hg (10ml)	0.011	-	more than 1 µg/ml
1	Wet sediment + MeHgCl (200g) (1590 µg as Hg)	0.167	-	0.08

NOTE: Cleaning solution diluted to twice by water vapor introduced through wet sediment was used in 1st. absorption chamber for all experiments and one in 2nd. absorption chamber was fresh in each experiment.

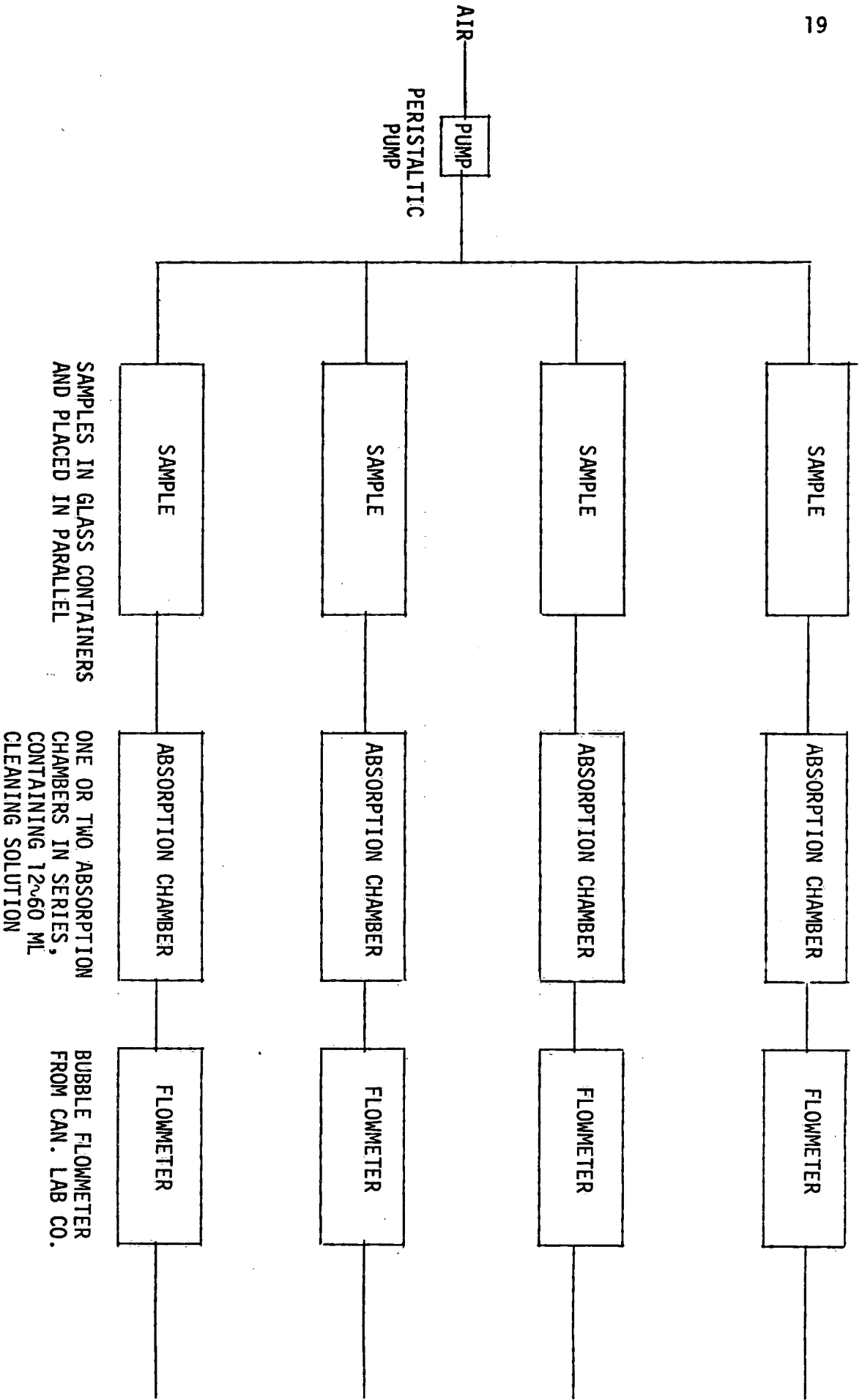


Fig. 1 SCHEME OF A SYSTEM FOR TRAPPING MERCURY VAPORS IN AIR