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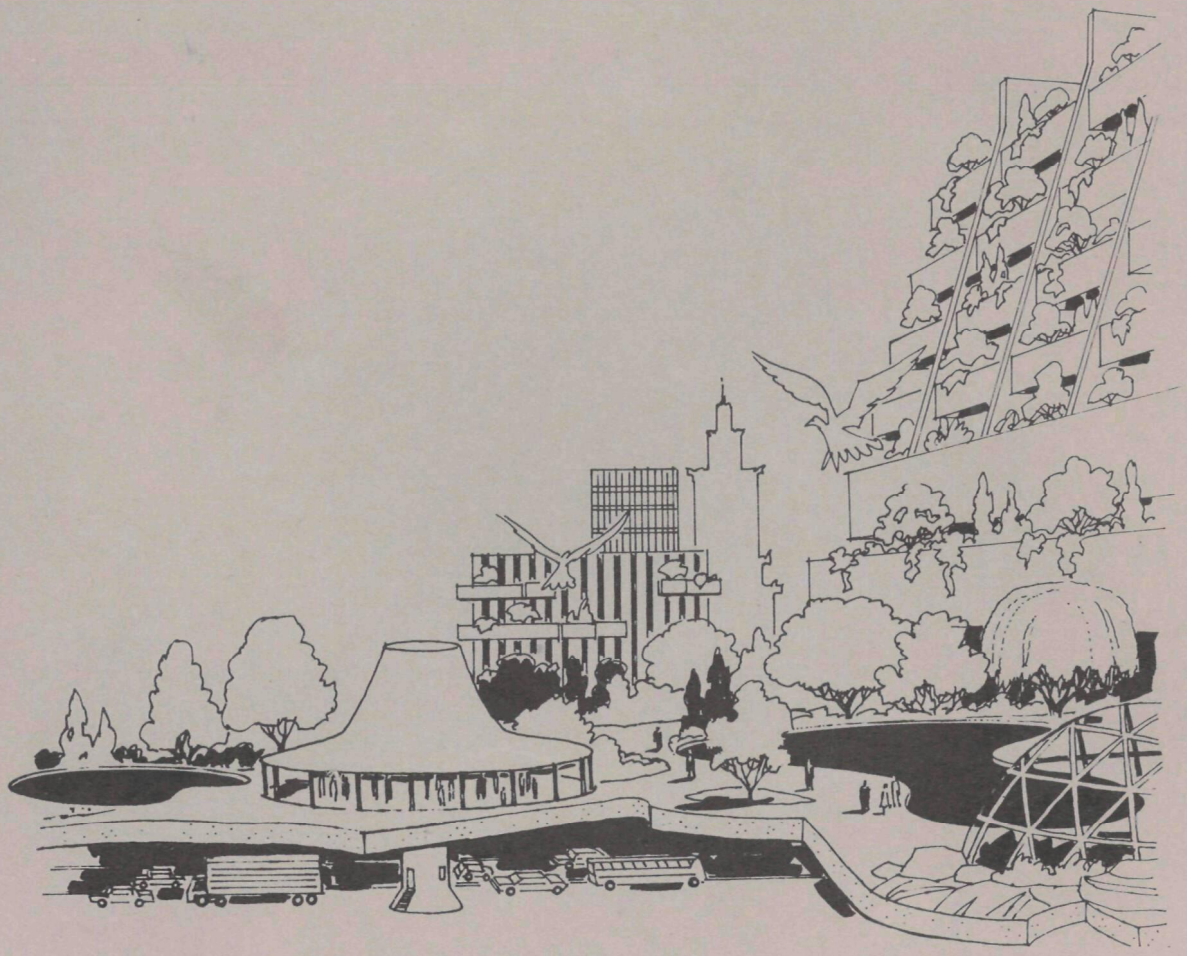
SAND AND GRAVEL OVERLAY FOR CONTROL OF MERCURY IN SEDIMENTS



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SAND AND GRAVEL OVERLAY FOR CONTROL OF MERCURY IN SEDIMENTS

by

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ABSTRACT

The release of toxic mercurials by mercury-enriched river sediments was examined in the laboratory. These tests indicated that about 1 μg of methylmercury was released per m^2 per day. The release of such toxic mercurials could be prevented by a layer of sand, 6 cm in thickness, applied over the mercury-enriched sediments. Layers of fine or coarse gravel (6 cm deep) were as effective as sand. Thinner layers of sand, 1.5 and 3 cm in thickness, appeared to be unsatisfactory. The cost of applying 3-inch layers of sand or gravel over contaminated river sediments is estimated to be about $3000 to $4000 per acre.

The formation of methylmercury occurred in sediments with low and high organic content, in sediments with low and high cation exchange capacity, and in aerobic and anaerobic sediments.

A convenient indicator of the potential toxicity of a contaminated sediment is the presence of metallic mercury. The slow release of metallic mercury occurred in aerobic sediments, but the release was much faster in anaerobic sediments. Using ascorbate as an artificial electron donor, metallic mercury could be released at high rates from aerobic sediments as well. Ascorbate appeared to be a helpful indicator of the presence of divalent biologically accessible mercury.

Although the laboratory investigations proved the soundness of the sand blanket approach, its practical and economic feasibility must be determined in a combined field and laboratory analysis program.

This report is submitted in fulfillment of Project 16080 HVA, Contract #68-01-0089, under the sponsorship of the Office of Research and Monitoring, Environmental Protection Agency.

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SECTION I

CONCLUSIONS

Laboratory simulation studies dealing with the release of toxic mercury from river sediments enriched with mercuric chloride showed that:

1. Approximately 1 μg of methylmercury is released per m^2 of sediment per day.

2. Sand applied to a thickness of 6 cm will prevent the release of this mercury during a 4-week laboratory incubation. Thinner layers of sand were unsatisfactory under the experimental conditions.

3. Other aggregates, such as fine and coarse gravel, applied to the same thicknesss were as effective as sand.

4. A field application would cost about $3000-$4000 per acre.

5. Ionic mercury introduced into a normal aerobic sediment to a concentration of about 200 ppm or less is rapidly complexed with sediment entities or converted to mercuric sulfide. The complexed form might give rise to a slow release of metallic mercury.

6. Significant quantities of metallic mercury might be released if relatively small quantities of ionic mercury are introduced into an anaerobic sediment.

7. Ascorbate might be used to identify sediments containing biologically accessible mercury deposits.

SECTION II

RECOMMENDATIONS

As a result of this research, it is recommended that:

1. A field feasibility study be conducted in an area known to release substantial amounts of toxic mercury (e.g., Detroit River).

2. The chemical and physical nature of the sediments be defined in sufficient detail to allow a projection from the test area to another contaminated area.

3. Caged bioaccumulators (e.g., carp, pike, or catfish) be used, prior to and after the preventive sand or gravel overburdens are applied so that their effectiveness can be determined.

4. Laboratory simulation tests be initiated to determine the long-term ($>$ 1 year) effectiveness of the abatement procedures.

5. The nature of mercury present in sediments be defined in much greater detail and that the broader environmental hazard of the contaminated sediments be determined.

6. The fate of mercuric sulfide and the complexed mercuric ions in an aerobic environment be determined.

SECTION III

INTRODUCTION

Following the discovery in Sweden during the late sixties of high levels of mercury in fish and seed-eating birds, fish from suspected waters in Canada and the United States were examined for mercury contamination. The findings led to the banning of fishing at many sites (Lake St. Clair, Ontario; Lake Erie, Detroit River) (1). Mercury levels in fish of 5 mg/kg and more were observed--a level well in excess of the proposed practical limit of 0.05 mg Hg/kg for food (2).

Detailed studies by Westoo (3) showed that mercury in fish, and probably in other biological systems as well (4), occurs predominantly as methylmercury, a mercurial which was used as a fungicide in agriculture (seed dressing) and industry (pulp preservation). Although contamination in many cases was clearly related to the use of this fungicide, other organic and inorganic compounds were implicated. Findings suggested that the toxic products were formed from less toxic mercury compounds.

Over the years, industrial and other activities resulted in the release of inorganic and organic mercurials in the aquatic environment. Here, these compounds are easily absorbed by surfaces of organic particulate matter, clays, silt particles, planktonic organisms, and hydrated ferric oxides. Consequently, mercury compounds tend to accumulate in the sediments of lakes and rivers, where the relatively harmless mercurials can be transformed into highly toxic and soluble methylmercury or into the harmless and insoluble mercuric sulfides (8).

Little is known concerning the biochemical and chemical processes associated with mercury in these sediments. Intuitively, it is assumed that mild anaerobic conditions would promote the formation of insoluble sulfide. Strong anaerobic environments would be undesirable because these would promote the activity of methanogenic bacteria and, from the work of Wood et al (5) and Jensen et al (6), this activity could enhance methylation processes. Strong aerobic sediment conditions also would be undesirable, because sulfides would be oxidized to sulfates, allowing the methylation of the inorganic mercury. Methylation of mercury also may proceed by a non-enzymatic process involving vitamin B_{12} (7). This means that waters with high bacterial counts and those affected by sewage discharges may promote these undesirable conversion processes.

Although much remains to be learned concerning the magnitude of these processes, it appears that the release of toxic mercurials from contaminated sediments depends on biological processes occurring in these sediments. In order to control the exchange of mercury between the

sediments and the overlying water, the biological processes occurring in the contaminated sediments must be controlled.

Clearly, in order to design efficient control methods, detailed knowledge is needed concerning environmental conditions that enhance the formation of mercuric sulfides and stimulate the release of toxic mercury. Much of this knowledge is lacking, but programs are suggested (8) to test the effectiveness of various control procedures. Proposed field methods aim at (a) increasing the pH of the water-sediment interface, (b) introducing materials with strong absorptive capacities, and (c) reducing available oxygen and thereby promoting the development of hydrogen sulfide and formation of insoluble mercuric sulfides.

The effect of an overburden of sand or gravel on the release of toxic mercurials from contaminated sediments is examined in this report. This overburden would reduce the availability of oxygen and thus promote the conversion of mercury to mercuric sulfide. Natural sedimentation could further bury the contaminated sediments reducing even more the danger of exposure and subsequent release in the water. This abatement procedure appears economically and ecologically appealing.

The sand overburden required to control the release of toxic mercury from mercury-enriched sediments was investigated, and the effectiveness of sand and fine and coarse gravel was compared. The cost involved in a field application was estimated, and some preliminary experiments were conducted to assess the immediate fate of inorganic mercury added to aerobic and anaerobic sediments.

SECTION IV

MATERIALS AND METHODS

Inorganic mercury was determined according to the flameless atomic absorption technique (FAAS) described by Hatch and Ott (9) employing the procedure and reagents described by Perkin-Elmer Corp. (10) and Kolb (11), respectively. The mercury vapor was measured at 253.7 nm. The arrangement used is illustrated in Figure 1. To measure various concentration ranges, quartz-windowed absorption cells having a light path of 1.25, 2.50, or 20 cm were used. Figures 2, 3, and 4 show the relationship between absorbancy and mercury concentration and the concentration ranges for which the three cells were employed. Calibration curves were prepared using a stock solution containing 0.1354 g of mercuric chloride ($HgCl_2$) dissolved in 1N H_2SO_4. To prepare standard curves, the stock solution was diluted to the required values. Resolution of 0.01 µg of Hg was obtained with the 20-cm cell. With 0.1 µg of Hg, a precision of about $\pm$3% was obtained.

Metallic mercury vapor, present or formed in sediments was determined with a flow-through system developed for this purpose (Figure 5). To transport metallic mercury through the measuring cell, air or N_2 was used as a carrier gas; this gas was introduced into the sediment through the fritted disk of medium porosity. A gas flow of 100 to 150 cc was commonly used for 100 ml of a watery sediment containing some 30 g dry weight of material. This allowed continuous monitoring of evolved metallic mercury.

Organic mercury in fish or in sediment was determined, where possible, by flameless atomic absorption spectroscopy (FAAS) after conversion into inorganic mercury by acid digestion (Figure 1). Digestion was carried out in 30-ml Kjeldahl flasks containing a 2-ml mixture of concentrated H_2SO_4 and HNO_3, to which $KMnO_4$ was added. Routinely, digestion was complete after 20 to 30 min at about 100C. Using methylmercuric chloride (CH_3HgCl) and $HgCl_2$ as test compounds, recoveries of 85% to 100% were observed. Lower digestion temperatures (50C to 70C) gave incomplete recovery with CH_3HgCl (12). This result was attributed to incomplete digestion. Since methylmercury is the dominant form of mercury reported in fish (13) and because its C-Hg bond is relatively strong, digestion procedures developed for methylmercury would apply to other mercurials as well. Thin layer chromatography and two types of resin (13, 28) were used to separate inorganic mercury from organic mercurials.

Reagents: Mercury compounds were obtained from the K and K Company, New York. Organic mercurials contained 2 to 5% of inorganic mercury,

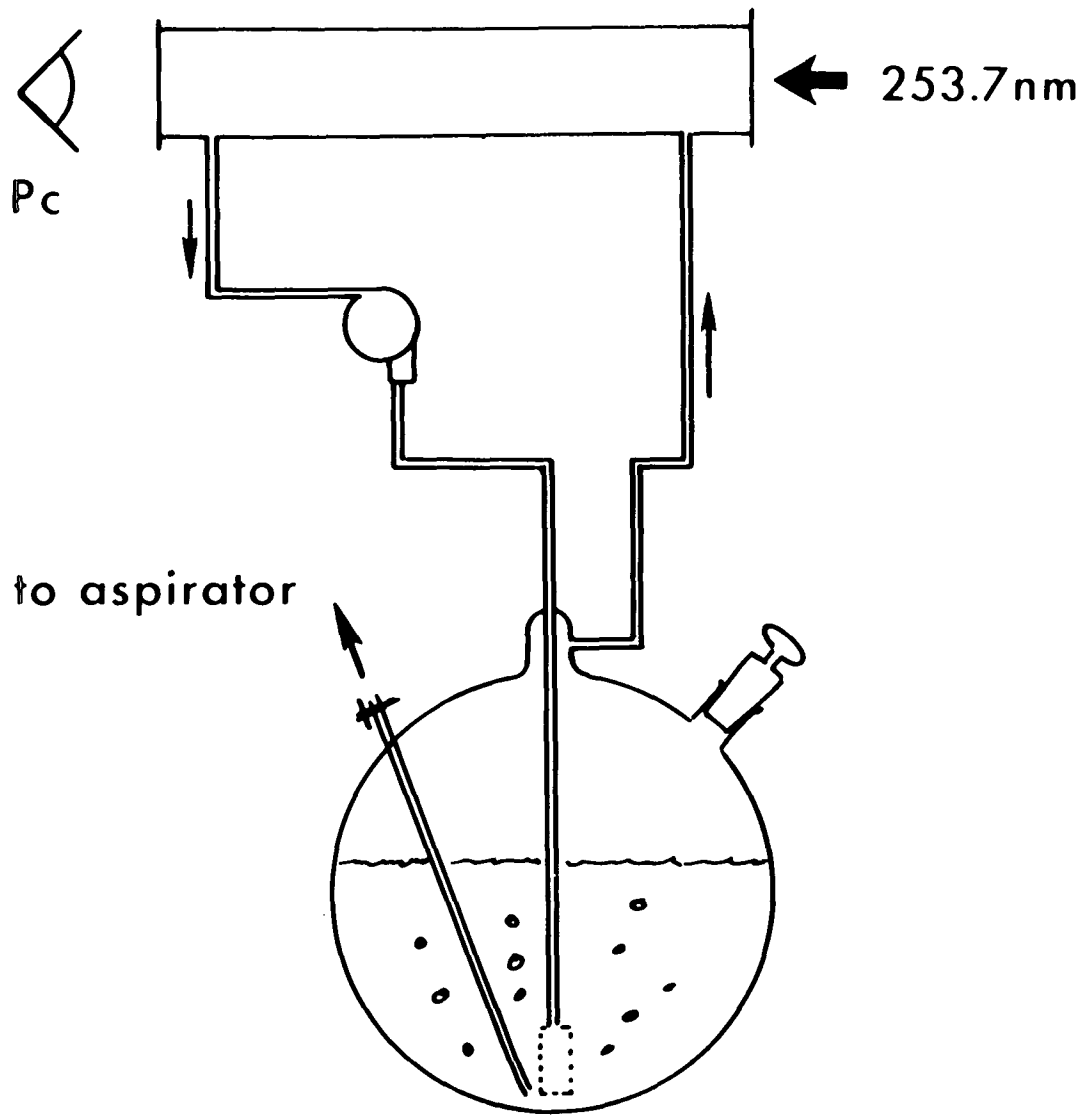

Figure 1. Schematic of closed system used for mercury analysis.

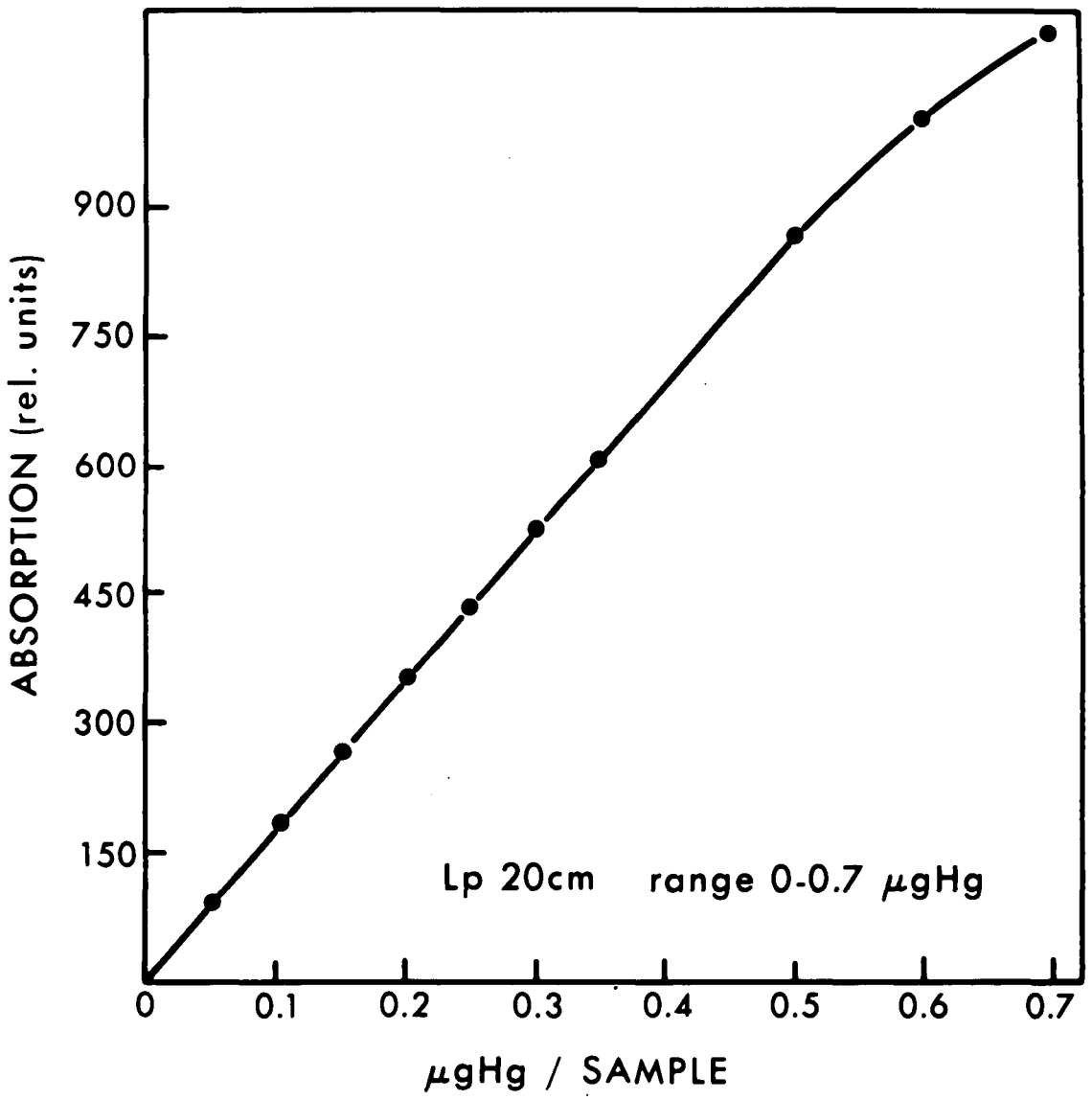

Figure 2. Calibration curve for absorption at 253.7 nm for mercury concentrations between 0 and 0.7 μg/sample.

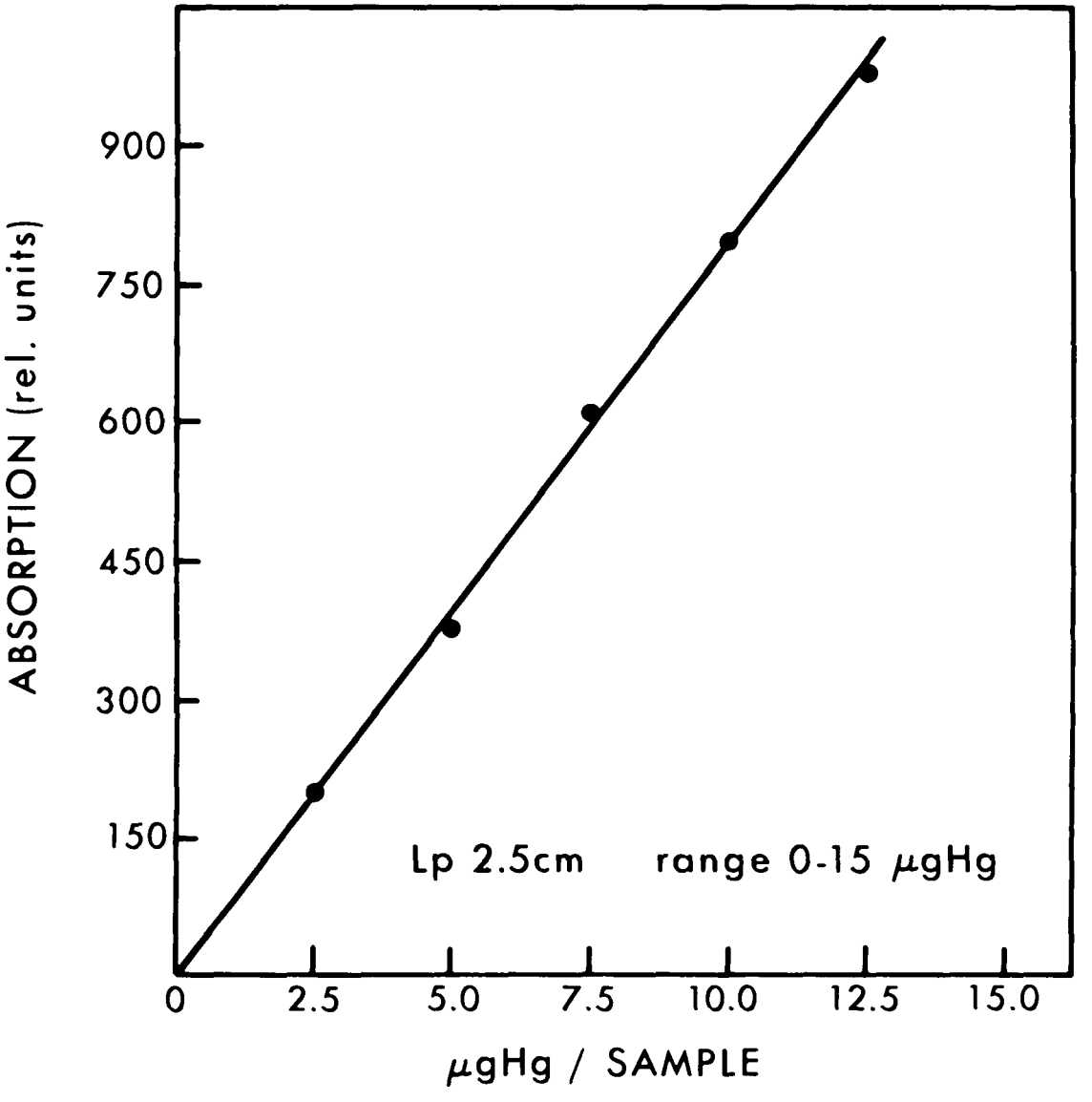

Figure 3. Calibration curve for absorption at 253.7 nm for mercury concentrations between 0 and 15 μg/sample.

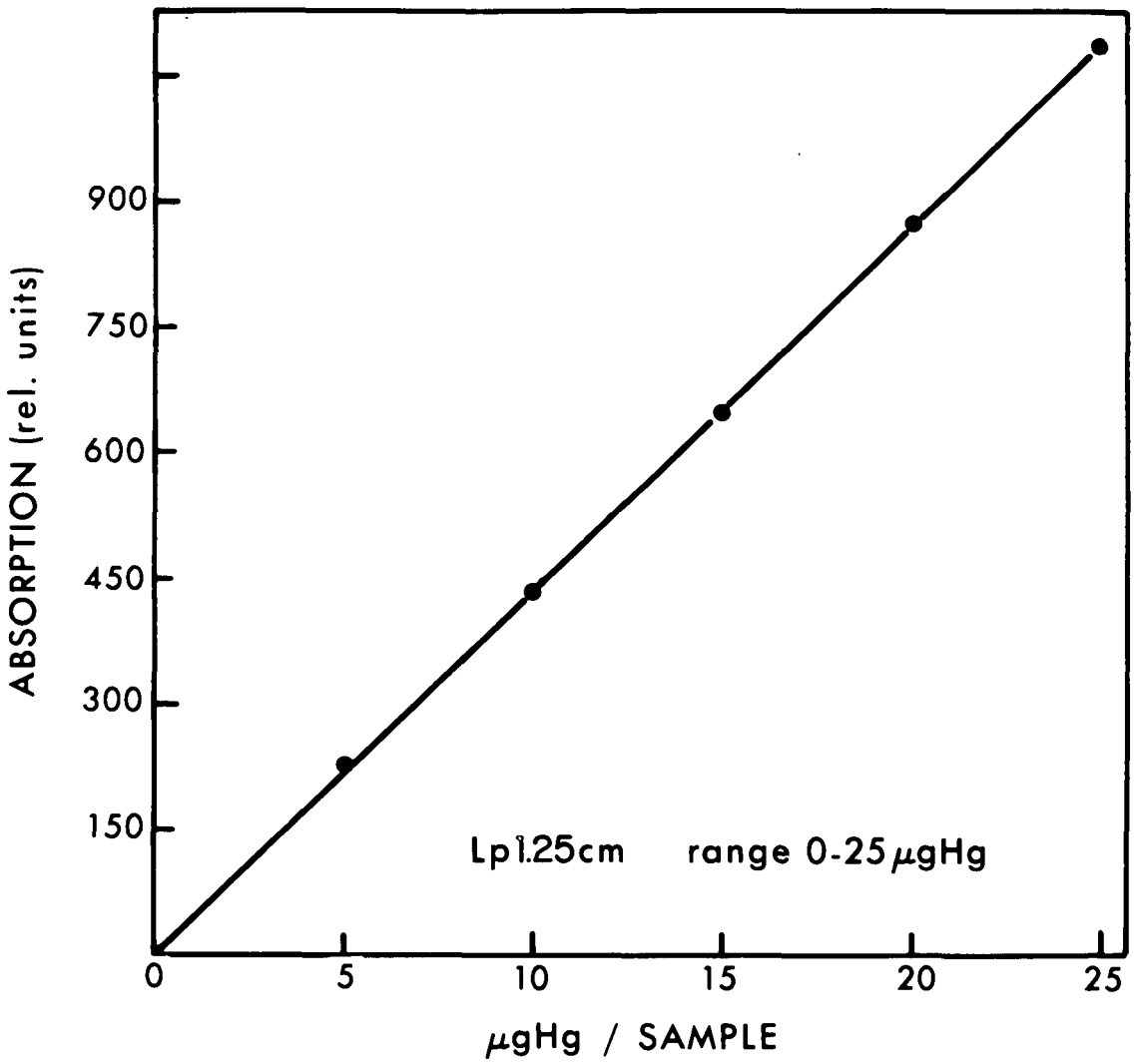

Figure 4. Calibration curve for absorption at 253.7 nm for mercury concentrations between 0 and 25 μg/sample.

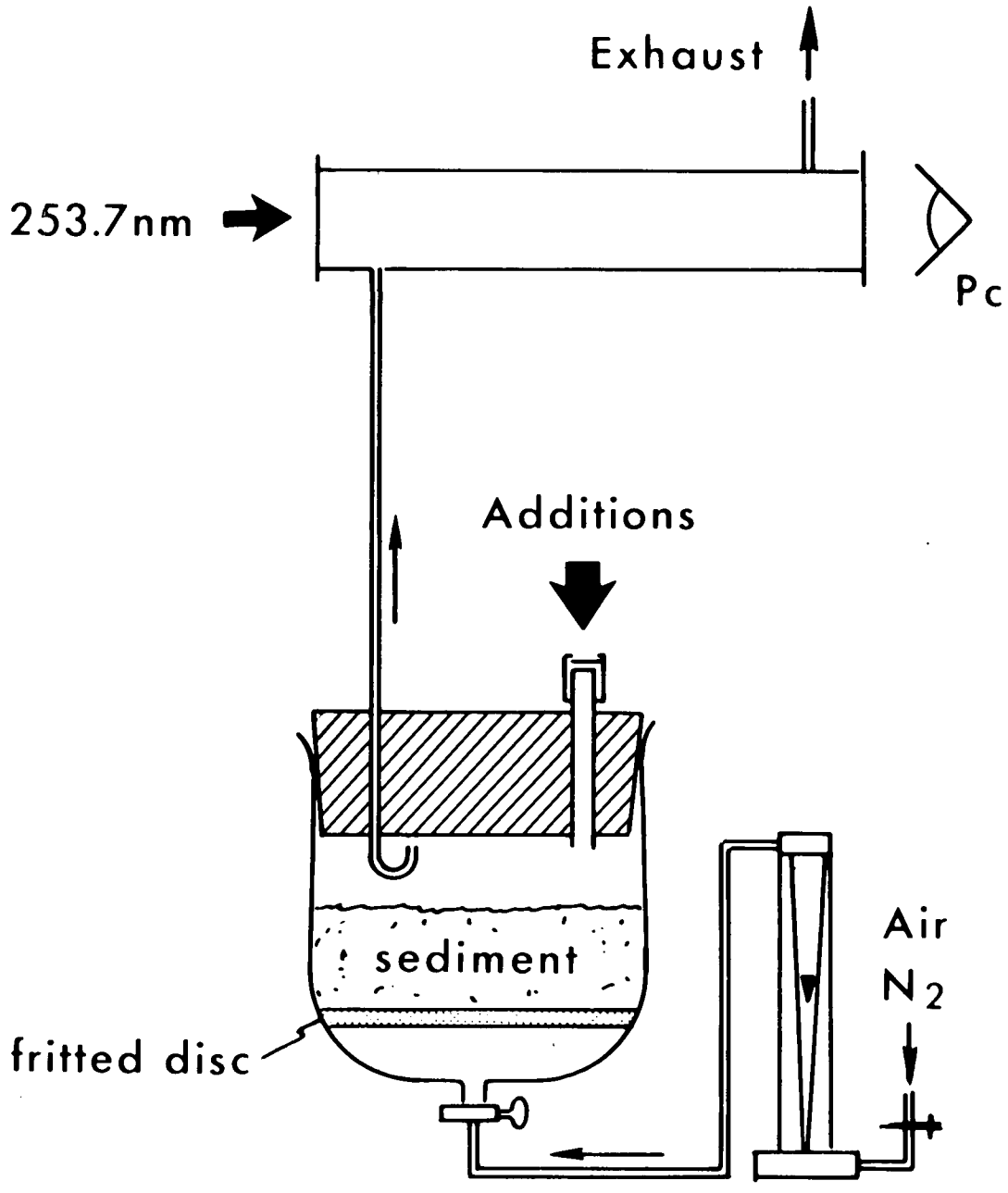

Figure 5. Schematic of flow-through system used to measure mercury vapor released directly from sediments.

as indicated by thin layer chromatography and NMR spectroscopy. Dithizone was Baker's analyzed; diphenyl thiocarbazone was Fisher's certified; and tetrahydroxy-p-benzoquinone was an Eastman Kodak Company product. Bismethylmercuric sulfide, $(CH_3Hg)_2S$, was prepared according to a procedure of Dadii et al (14) from methylmercuric bromide and sodium sulfide in ethanol. Male guppies were used as accumulators of organic mercurials. As will be seen later, guppies almost quantitatively removed organic mercurials of interest from the water, but they did not accumulate inorganic mercury compounds, even when such compounds were present at relatively high concentration. Mercury observed in fish is assimilated as organic compounds.

Column preparation: Columns were prepared following the procedure described by Jernelov (15) and as shown in Figure 6. For all experiments reported here, the mercury-rich sediment was prepared by adding 16 mg Hg (as $HgCl_2$) to 160 ml of watery sediment (the amount of Hg-enriched sediment used in each cylinder). This Hg-enriched sediment was spread on a 10-cm sediment, relatively free of mercury, in a 10-cm diameter column. The enriched layer contained about 200 µg of Hg/g of dry sediment and was about 1 cm in thickness. Subsequently, sand or coarse or fine gravel was spread over the enriched layers to the required thickness, and tap water was added for a total volume of about 4 liters. The depth of water layer was approximately 12 cm. Six guppies were added to the control and to each experimental series. The columns were placed in an environmental chamber, which was kept at 20C and subjected to 12-hr light/dark intervals. Illumination was provided by fluorescent and incandescent light sources. The light intensity was approximately 0.3 mW cm^{-2} (400 to 700 nm). The sand used for these experiments was obtained from a local distributor and fractionated by a standard sieve procedure before use. The -30 +70 fraction (particle sizes between 210 and 595 microns) was used for all experiments. The fine gravel ranged from 3/16 to 1/4 inch in particle size. The size distribution was between 3/4 and 1 inch for the coarse gravel.

Sediments: The sediments used for the experiments described in this report were obtained from the fresh water section of the Patapsco River in Maryland. Two sediment "types" were used. One sediment (collected near Baltimore, Maryland, and referred to as Sediment I) was relatively rich in sulfur as determined according to the methods of Vogel (16) and Carius (17). Both methods suggested a sulfur content of about 1% in dry sediment. The cation exchange capacity (CEC) of this sediment was about 10 milli-equivalents (me) per 100 g of sediment as determined by the method of Toth and Ott (18). The organic content of Sediment I was approximately 7%. This was determined by weight loss at 500C for 2 hr. The difference in weight before and after ignition was taken as

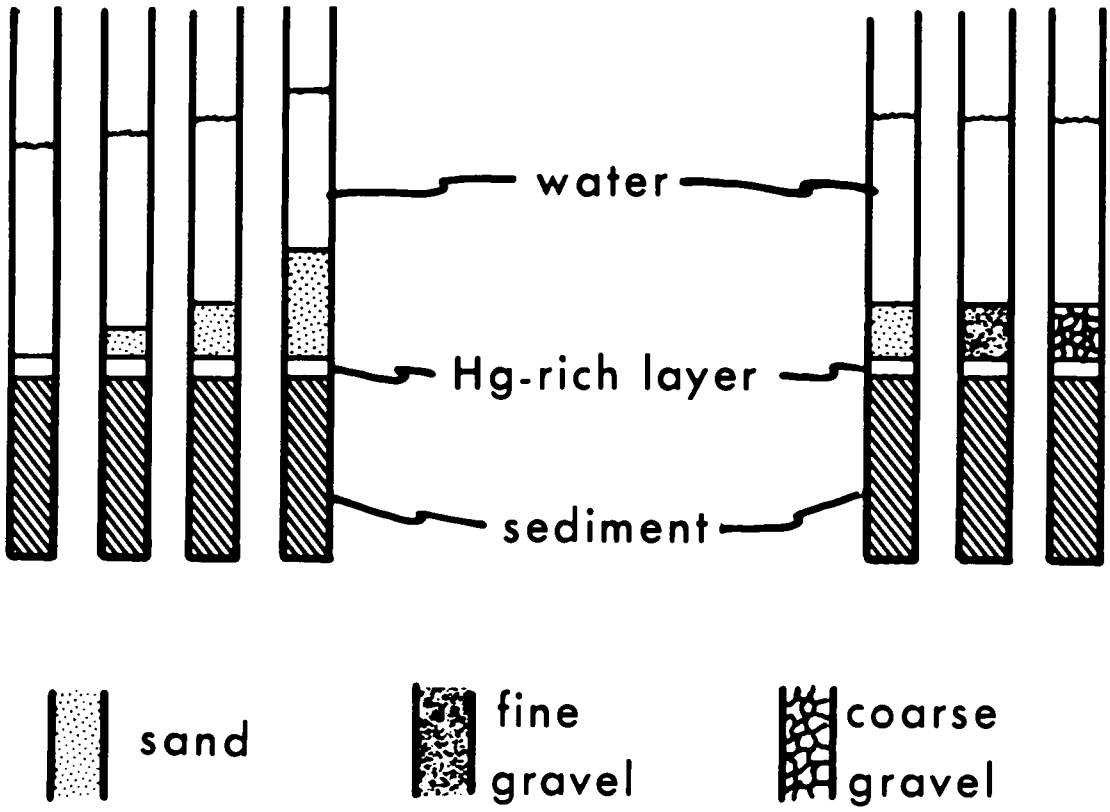

Figure 6. Schematic of laboratory incubation procedure.

the organic fraction and expressed as a percentage of the total weight. Similar measurements were made on Sediment II, obtained from the Patapsco River near Frederick, Maryland. The organic content of Sediment II was about 10%, and the CEC was 19 me per 100 g of dry sediment.

Organic and inorganic Hg in sediment: To determine inorganic Hg in sediment, an aliquot of known weight (~ 1 g) was mixed with 2 ml of concentrated acid (H_2SO_4 + HNO_3) with $KMnO_4$ added and kept at room temperature for 30 min. Subsequently, the sample was made up to 5 ml, centrifuged at 5000 g, and the Hg content of the supernatant was analyzed. To determine the total Hg content of a sediment, a similar procedure was followed, except that the mixture was digested for 20 min at 100C (19, 20). The organic content was taken as the difference between the total Hg content of the sediment and the inorganic fraction.

SECTION V

RESULTS AND DISCUSSION

Retention of mercurials by sediments: It is to be expected that both $HgCl_2$ and CH_3HgCl will, to a given extent, form complexes with sediment entities. The extent to which this occurs depends on the affinity of both salts for binding sites. We assumed that the binding ability of a sediment is reflected by the cation exchange capacity and organic content (21).

An assessment of the ability of sediments to retain inorganic mercury was made by mixing 1 mg of Hg as $HgCl_2$ with a sediment slurry containing 10 g (dry weight) of Sediment I in about 40 ml volume. After a 2-hr incubation period at room temperature, the liquid fraction was removed by vacuum filtration (Whatman 41), and the Hg content of the leachate was determined. Subsequently, the solid fraction was mixed with diluted HCl, to a final concentration of about 1N. After 2 hr of incubation, the leachate was removed, and the mercury content was determined in the acid leachate. The mercury content of the solid fraction also was measured. The observed results, recorded in Table 1, show that a large majority of the added inorganic mercury was retained by the solid sediment fraction.

Table 1

Distribution of Hg between solid and liquid phase in 10 g (dry weight) of sediment mixed with 1000 µg of Hg as $HgCl_2$.

Fraction	µgHg	% Total
Liquid (H_2O)	< 10	< 1
Liquid (1N HCl)	< 50	< 5
Solid	800	90
% Recovery		90-95

Similar measurements were made with CH_3HgCl. The results, recorded in Table 2, show that methylmercury is not as readily absorbed as inorganic mercury. For example, whereas water and acid extraction removed only insignificant quantities of inorganic mercury from the

absorbing complex, about two-thirds of the organic mercury was removed by this procedure. The non-ionic nature of methylmercury might be responsible for the difference in behavior. Thus, once formed in the sediment layers, methylmercury could be released to the overlying water.

Table 2

Distribution of Hg between solid and liquid phase in 10 g (dry weight) of sediment mixed with 200 μg of Hg as CH_3HgCl.

Fraction	μgHg	% Total
Liquid (H_2O)	58	29
Liquid (HCl)	80	40
Solid	50	25
% Recovery		94

Retention of inorganic mercury in the sediment also could occur through its conversion to a sulfide (HgS). In contrast, the release of methylmercury would be enhanced by complexing with sulfur. As will be discussed later, the formation of bismethylmercuric sulfide, $(CH_3Hg)_2S$, an organic mercurial which is even more toxic than methylmercury, is likely to occur under such conditions. Because of its non-polar nature, the release of this compound would occur more readily than methylmercury. A third organic mercurial that is readily released from sediments is the volatile dimethylmercury (CH_3HgCH_3), which, according to Wood and co-workers (5), is formed under alkaline conditions.

The nearly complete absorption of Hg^{++} to the solid fraction is not surprising, considering the affinity of the divalent ions for absorption sites and the fact that the amounts used are small (about 0.112 me/100 g sediment) relative to the cation exchange capacity of this sediment (10 me/100 g).

Apparently, methylmercury is less readily absorbed on the solid sediment fraction. The relatively low binding capacity of methylmercury is indicative of the monovalent bond and the non-ionic nature of the salt. Our results indicate that the interstitial liquid and the solid fraction of the sediment should be sampled to determine the extent of the methylation process.

Uptake of organic and inorganic mercury by guppies: To determine whether the mercury present in guppies is of an organic or inorganic origin, measurements were made of the extent and the rate of Hg uptake by male guppies exposed to known quantities of either organic or inorganic mercury.

In these experiments, usually 8 to 10 guppies were incubated at about 20C in 100 ml aged aquarium water spiked with about 25 μg Hg as CH_3HgCl, $(CH_3Hg)_2S$, or $HgCl_2$. At given time intervals, guppies were removed from the incubator and analyzed for Hg content by the procedures described earlier. Results of a typical series are presented in Figure 7.

A rapid increase in the Hg content was observed in guppies exposed to methylmercury and bismethylmercuric sulfide. Guppies exposed to the inorganic mercury also showed increased Hg content, but the total amounts retained were much less and did not increase significantly with time.

At initial mercury concentrations of 25 μg of methylmercury per 100 ml of water, about 1 μg of Hg accumulated per guppy (average weight was 100 mg). Occasionally, values of 2 to 3 μg per fish were observed. At the lower values, most guppies survived.

Mercury concentrations of 50 μg of methylmercury per 100 ml volume also were tested; but, at these levels, most of the animals died within a 2-hr exposure.

To test whether guppies quantitatively remove methylmercury from the medium, 7 guppies were exposed to 16.5 μg Hg (as CH_3HgCl) in 100 ml water. After 77 hr the animals and the medium were analyzed for Hg, and only 0.1 μg Hg was found in the medium, and a total of 12.5 μg of Hg was found in the animals, indicating a recovery of about 75%.

The concentration of methylated mercurials used in the above experiments is high relative to values most likely to be encountered in contaminated environments. A more realistic approach would use less than one-hundredth of that concentration and exposure times of weeks or months. To simulate a natural situation more realistically and to obtain some estimate of the lower threshold level at which guppies accumulate organic mercurials, the rate of accumulation was determined as a function of mercury concentration. To this end, guppies were exposed to concentrations of methylmercury varying between 3 μg to 15 μg per liter. After 36 hr of exposure, the animals were sacrificed and analyzed. The results, illustrated in Figure 8, show a near-linear relationship between mercury accumulation by the guppies and the mercury content of the liquid.

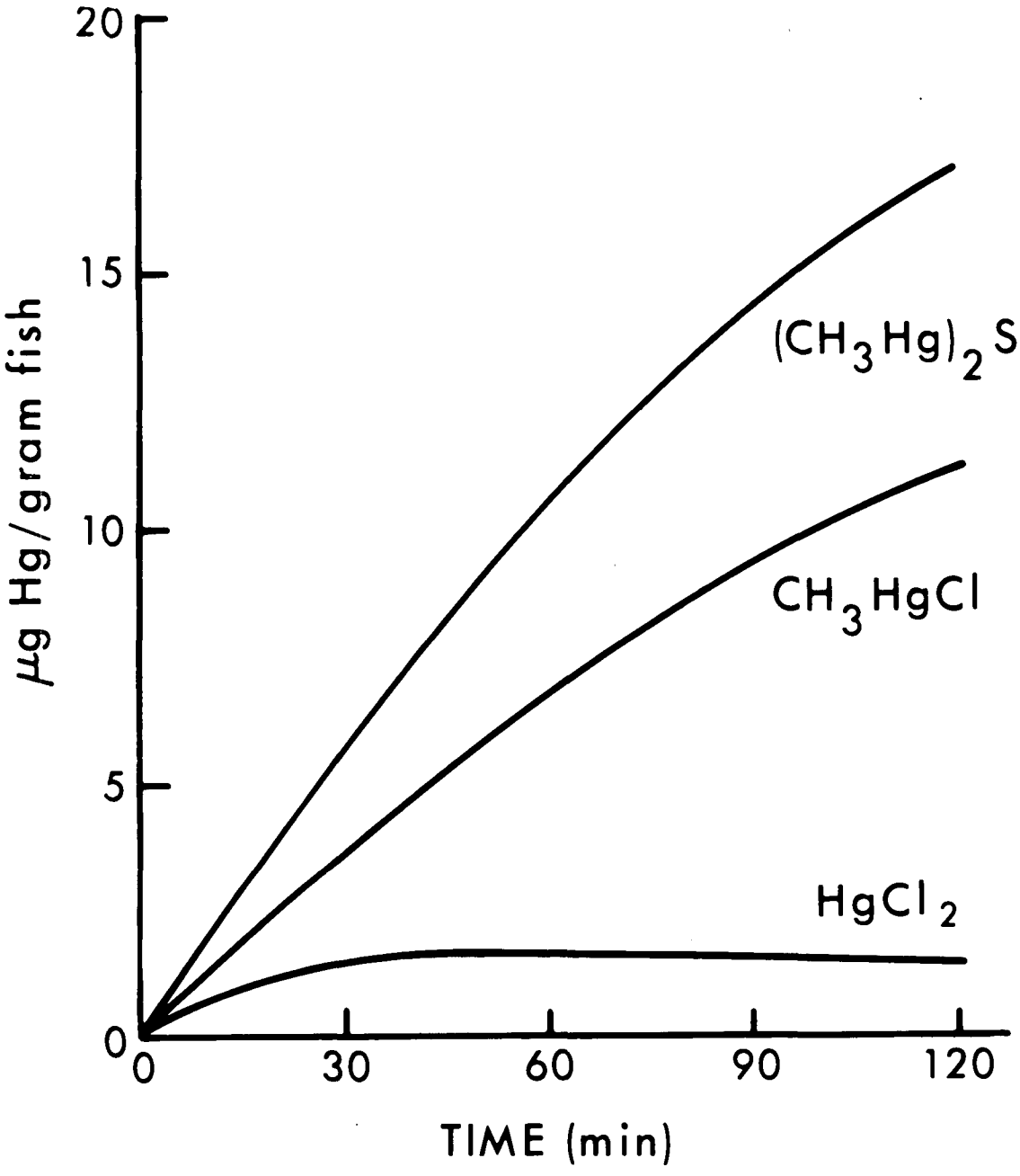

Figure 7. Time course of mercury assimilation by guppies.

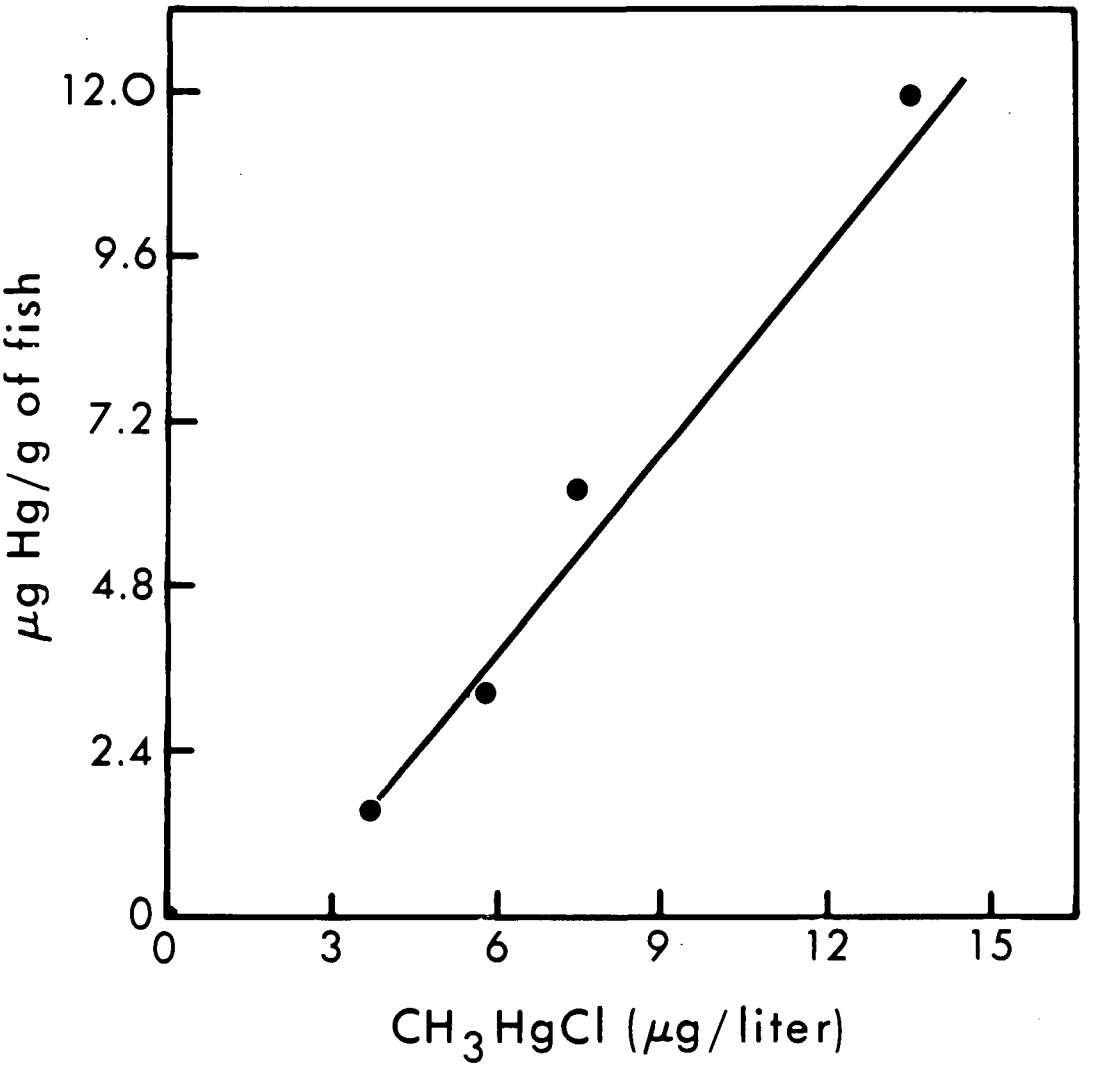

Figure 8. Methylmercury uptake by guppies as a function of concentration.

These findings suggest that guppies will tolerate prolonged exposure to relatively low concentrations of methylmercury and that they are capable of concentrating organic mercurials even if present at reasonably low concentrations. At the lower limit used in the above experiments, a concentration factor of about 1000 was calculated, estimating a guppy's volume at 0.3 ml. On the basis of these results, the investigators are confident that the methylmercury formed in the laboratory simulations (described in the following sections) is accumulated by the fish.

Effect of sand on the release of organic mercury: The objective of this series of experiments was to determine the extent of organic and inorganic mercury release from mercury-enriched sediments covered by layers of sand of varying thickness. The procedure is based on Swedish observations (22) that mercury-rich layers become inactive rapidly when covered with 2 to 10 cm of mercury-poor sediment. To evaluate the efficacy of this "burying procedure," a laboratory simulation was carried out using sediments enriched with mercuric chloride (200 μg of Hg/g of dry sediment) and covered with layers of sand 0, 1.5, 3, and 6 cm in thickness. (The stratification is illustrated in Figure 6.) Incubators were supplied with at least 6 guppies each, and, after a 4-week incubation, the mercury content was determined in the fish, in the overlying water, in the enriched sediment layers, in the sand, and in the sediments beneath the enriched layers. It was assumed that this type of analysis would provide some indication of the extent of the mercury's vertical transport through the sediment and sand layers.

The data on mercury accumulation by guppies are recorded in Tables 3 and 4. On the basis of the observed data, it is apparent that the formation of methylmercury is low in those incubators supplied with a sand cover of 6 cm over the mercury-enriched layer. Although the mercury accumulation by fish varied widely with sand covers of 1.5 and 3 cm, it appears that this overburden is only partially effective in controlling the release of methylmercury.

Experiments reported in Tables 3 and 4 were conducted with Sediment I and Sediment II differing in organic content (7% vs 10%) and cation exchange capacity (10 me vs 19 me). Considering prevailing experimental conditions and the obtained results, it appears that these sediment parameters have little effect on the release of toxic mercurials.

In all incubators with 1.5 cm of sand, and in a few with 3 cm, a build-up of black material on top of the sand layers was observed. This material was due to the activity of sludge worms (Tubificidae) present in large quantities of Sediment I (obtained 2 miles below a sewage outfall). The mercury content of the worms' rejects was measured; as expected, this

content was quite similar to that in the mercury-enriched layer of the experimental series. In the control series, no mercury was detected. Although a similar build-up was not observed in incubators with 6 cm of sand, the results suggest that in areas where the sludge fauna carries on its function actively, additional coverage might be required. Besides the conveyance of mercury by sludge worms, vertical transfer apparently was limited, since only small amounts of mercury were detected in the sand and sediment above and below the enriched layer. (See Table 5.) Sediment II, collected far from sewage outfalls, did not exhibit this sludge worm activity. Therefore, a shallower sand overburden would control the release from a sediment typified by Sediment II.

Table 3

Effect of sand overburden on the mercury content (μg) of surviving guppies incubated for 3 weeks using Sediment I enriched with $HgCl_2$.

	Sand Overburden			
Additions	0 cm	1.5 cm	3 cm	6 cm
None (Control)	0.3	0.2	0.2	0.2
$HgCl_2$ Enriched	No survivors	2.5	2.5	0.5
$HgCl_2$ Enriched	3.5	3.3	1.0	0.4

Note: Due to animal mortality, only a few fish were available for analyses at the end of the 3-week incubation. Results reported here are based on the analysis of 2 fish and are expressed as μg Hg/g fish.

Table 4

Effect of sand overburden on the mercury content (μg) of surviving guppies incubated for 4 weeks using Sediment II enriched with $HgCl_2$.

Additions	Sand Overburden 0 cm		1.5 cm		3 cm		6 cm	
None	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.2
(Control)	0.2	-	0.1	-	0.2	-	0.2	-
$HgCl_2$	5.0	3.5	5.6	2.6	1.0	0.8	0.3	0.3
Enriched	2.1	2.5	2.1	0.4	0.5	0.2	0.1	0.2
$HgCl_2$	4.3	3.3	0.3	0.3	0.3	0.3	0.6	0.4
Enriched	4.9	3.8	1.8	0.8	0.2	0.1	0.2	0.1

Note: Each value indicates an individual animal and is expressed in μg of Hg/g of fish.

Table 5

Mercury content of sand and sediment above and below Hg-enriched layer.

	Sand 0 cm	1.5 cm	3 cm	6 cm
Sand (μg Hg/g sand)	-	0.5	0.2	0
Sediment (5 cm beneath enriched layer) (μg Hg/g sediment)	0.4	0.7	0.1	1.5

Note: For details, see Table 3.

The pH of the liquid phase also was measured and analyzed for mercury content. Although the initial pH value of the water in all incubators was slightly acidic (6.7 to 6.9), alkaline values were observed in all incubators at the end of the 3-week incubation. Considering the algal growth observed in most incubators, the rise in pH might be due to a significant decline in the carbon dioxide content of the water.

As recorded in Table 6, algal concentrations of incubators supplied with 0 and 1.5 cm of sand were relatively high in comparison to values observed with 3 and 6 cm of sand. However, these values might be misleading since, in the latter cases, algal growth along the walls was significant, and representative sampling was virtually impossible. Although no attempts were made to determine the specific distribution, it appeared from the color that blue-green algae were predominant in incubators with 3 and 6 cm; green varieties appeared to dominate in incubators supplied with 0 and 1.5 cm of sand. It is not known whether sand constituents or differences in the rate of nutrient release from the sediment is the principal cause of the phenomenon.

Table 6

Mercury content of the liquid phase at the end of a 3-week incubation using Sediment I.

	Sand			
	0 cm	1.5 cm	3 cm	6 cm
Total Hg (μg/liter)	5	10	4	1
Total Hg Filtrate (μg/liter)	.4	.4	.5	.4
Suspended algae (mg/liter)	13	23	4	4

Note: 0.45 micron (Millipore) filter was used.
The algal content was derived from chlorophyll estimation. To determine this content, an 80% acetone extract was prepared and read at 663 nm. To convert chlorophyll concentration to algal concentration, a content of 2% dry weight was assumed.

Significant quantities of mercury were observed in the water (see Table 6). This "suspended" mercury apparently was present on or in the algal cells, since it could be removed almost completely from the liquid phase by filtration over 0.45 micron filters (Millipore). As shown in Table 6, at least 90% of the mercury remained on the filter. This fraction was found to be inorganic in nature.

Comparison of sand and fine and coarse gravel: A layer of sand 6 cm in thickness controlled the release of organic mercury to the overlying water. To examine the usefulness of other aggregates, the effectiveness of fine gravel (5 to 6 mm) and coarse gravel (18 to 25 mm) was compared with sand. (This type of coarse gravel is used routinely in the preparation of "popcorn" concrete. Popcorn concrete was not tested because it was felt that the addition of cement would significantly increase the pH and thus invalidate the comparison with other aggregates.) In this comparison, 6-cm layers of the two grades of gravel were used instead of sand (see Figure 6). This series employed two experimental (+Hg) and one control (-Hg) incubator. Incubation time was 3 weeks.

The results, recorded in Table 7, revealed that coarse and fine gravel are as effective as sand in controlling the release of toxic mercury. In laboratory experiments, the use of gravel required less precaution than for sand, but it remains to be seen whether this also holds true for field application.

Table 7

Effect of a 6-cm overburden of sand or gravel on the mercury content (μg) of surviving guppies incubated for 3 weeks in the presence of Sediment II enriched with $HgCl_2$

Aggregate	Sand	Fine gravel	Coarse gravel
Size distribution (mm)	0.2 to 0.6	5 to 6	19 to 25
No Hg added (Control)	0.1 0.2	0.2 0.3	0.2 0.3
$HgCl_2$ Enriched	0.2 0.2	0.3 0.2	0.3 0.3
	0.2 0.2	0.2 0.2	0.3 0.3
	0.2 0.2	0.2 0.2	0.3 0.3

Note: Content is based on values of individual animals and expressed in μg Hg/g fish.

To demonstrate and summarize the effect of a 6-cm sand or gravel overburden on mercury abatement, all data observed in the presence of a 6-cm cover (irrespective of sediment type and the nature of the cover material) and in the absence of a cover were pooled separately and compared to the pooled control values. Results, illustrated in Figure 9, show that a 6-cm cover surpresses the release of toxic mercurials from contaminated sediments. Comparisons of the calculated means and the standard deviations indicate the soundness of the observed data.

Effect of anaerobioses on release of toxic mercury: Wood and co-workers (5) reported that anaerobically incubated extracts of methanogenic bacteria stimulate the conversion of inorganic mercury into methylmercury. If a similar conversion occurs in sediments, one would expect the production of methylmercury to be relatively high under strictly anaerobic conditions. This aspect was examined by comparing methylmercury formation in an anaerobic sediment (argon equilibrated) to an aerobic sediment (air equilibrated). Containers similar in design to those used for aerobic experiments were fitted with male and female ground joints and used as anaerobic incubators.

After a one-month incubation, the liquid phases were removed from both series, filtered over Whatman #40 filter paper, adjusted to pH 6.5 with HCl, and flushed with air to remove volatile gases (H_2S, CH_4) and to raise the level of dissolved oxygen. Subsequently, eight guppies were added to the liquid, and the mercury content of the guppies was determined after two and five days of exposure. To obtain a rough estimate of the residual organic mercury in the sediment, part of the enriched layer was removed from the incubators and extracted with 1N HCl. It was assumed that acid extraction would remove the loosely bound toxic mercurials. After neutralization with NaOH, guppies were added to the extract, incubated for a day, and, subsequently, analyzed as usual.

The results, recorded in Table 8, showed that the concentration of toxic mercury (i.e., guppy assimilable) is higher in the anaerobic incubator than in the aerobic incubator. Considering the residual mercury content of the sediment (as analyzed in the 1N HCl extract), it appears that the toxic mercury is released to the liquid phase under anaerobic conditions, but it is retained, at least in part, under aerobic conditions.

The investigators cannot offer a reasonable explanation for the observed difference. Conceivably, the organic fraction constitutes a significant part of the ion exchange capacity of this sediment, and anaerobiosis could have adversely affected its capability to retain ions. From these qualitative results one would conclude that aerobic and anaerobic

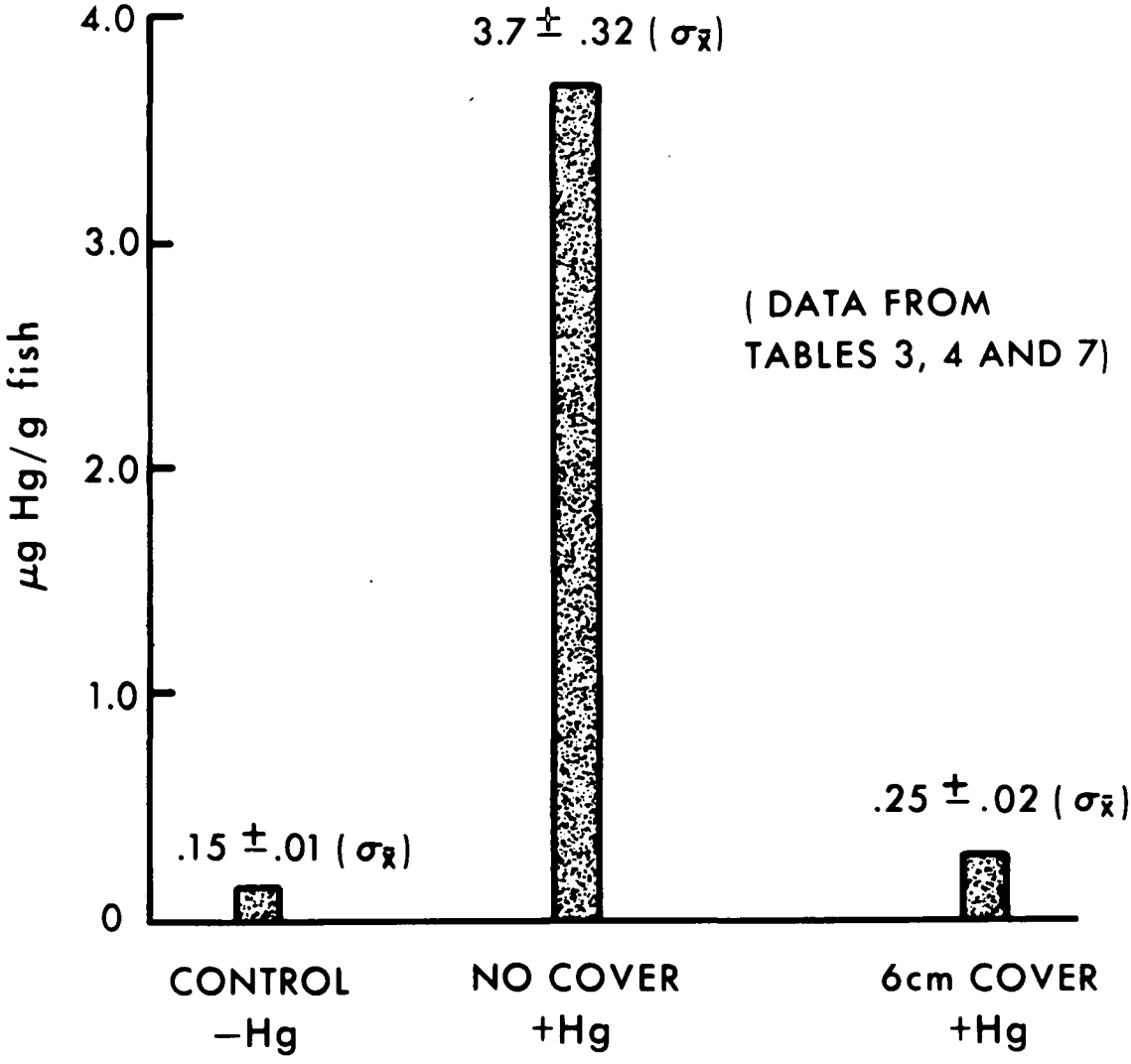

Figure 9. Effect of protective cover 6 cm in depth on mercury accumulation by guppies.

conditions stimulate the formation of toxic mercury to about the same extent, but that strong anaerobic conditions enhance the release of toxic mercury from the sediment.

Table 8

Estimate of mercury content (μg) in the liquid phases and acid extracts of mercury-enriched sediments incubated aerobically or anaerobically.

	Aerobically incubated	Anaerobically incubated
Water phase	0.2 to 0.3	5 to 6
Acid extract	1.4 to 1.8	0.5 to 0.6

Note: Values represent the content of mercury per incubator (4 liters) and are rough estimates only.

In a parallel experiment, mass spectrometric analysis was used to determine the formation of methane in the anaerobic incubator. A gradual increase in the methane concentration was observed. The rate of increase appeared to follow first-order kinetics, indicative of a logarithmic cell reproduction. At the end of a one-month incubation, about 900 μmole CH_4 was formed per 100 g sediment. In the same period and calculated on an equimolar basis, approximately 0.03 μmole of methylmercury was formed. Apparently, the rate of methylmercury formation is small relative to the rate of methane formation, suggesting that both products are formed independently.

Effect of redox state on release of mercury: Results discussed thus far are concerned with transformations of mercuric chloride into organic mercurials. From a toxicological point of view, the latter are of principal concern. Transformations leading to their formation are depicted in Figure 10.

In the general scheme, other interconversions also must be considered, both in connection with abatement procedures and the translocation of mercury. Although little is known about the importance of reactions leading to the formation of mercury complexes in a sediment, intuitively one would assume that inorganic and humic entities of the sediment play

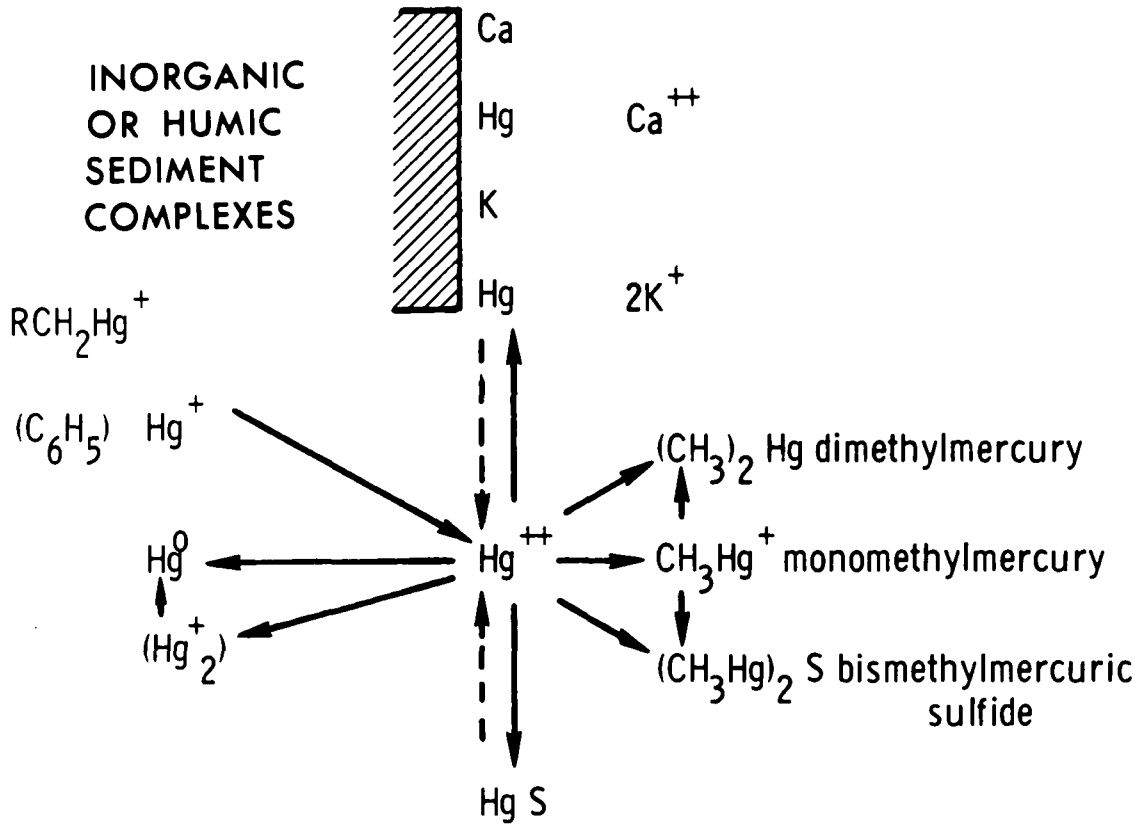

Figure 10. Transformation pathways of mercury and its derivatives in aquatic environment.

an important role in stabilizing mercury contaminated sediments. This aspect was examined previously (see Tables 1 and 2). The formation of the relatively insoluble mercuric sulfide (HgS) must be considered as another stabilizing factor. Its formation and its ultimate fate is determined, to a large extent, by the redox state of the sediment.

The measured redox state of sediments is largely a function of the microbial activity, the presence of oxygen, and the availability of degradable organic substances. Reducing conditions usually result if aeration is relatively low, and these conditions promote the formation of insoluble sulfides (25). The extent to which this occurs depends upon the availability of sulfur. If sulfur is limited and mercury is available in an ionic form (Hg^{++}), reduction to metallic mercury (Hg^{o}) will occur. Since the redox state of a sediment can be assessed by using simple sensing probes, its value assumes significance principally because it can be used in the field as a convenient indicator of the hazard posed by a mercury-laden sediment. Therefore, the investigators assessed the effect of the redox state on the release of metallic mercury by an aerobic, i.e., high-redox potential, sediment and by an anaerobic, or low-redox potential, sediment.

The high-redox potential sediment was obtained by drying material in air overnight at room temperature. Subsequently, 30 g of this material was added to 100 ml distilled water, mixed thoroughly, and transferred to the sediment chamber illustrated in Figure 5. The Eh of the prepared sediment was about 450 mV (Orion 96-78-00). Various amounts of $HgCl_2$ were added through the entrance port (see Figure 5), and the release of Hg^{o} was measured as a function of time. The results are illustrated in Figure 11.

The amount of metallic mercury evolved from an aerobic sediment was dependent on the relative amount of mercuric chloride added to it. The release pattern observed upon addition of different amounts of $HgCl_2$ to a constant amount of sediment (30 g), presented in Figure 11, also was observed when the sediment was increased and the mercury content of the liquid was held constant.

Figure 11 also shows that the rate of Hg^{o} evolution increased gradually upon addition of $HgCl_2$ until, about an hour later, a steady state value was attained. To determine the rate of Hg^{o} formation, the efflux was scrubbed by the solution of nitric acid and sulfuric acid, and the mercury content of the solution was determined by the usual procedure. It was found that approximately 1 μg of Hg^{o} was released per min by 30 g of sediment enriched with 100 mg of $HgCl_2$ and flushed with about 100 cc of air per min.

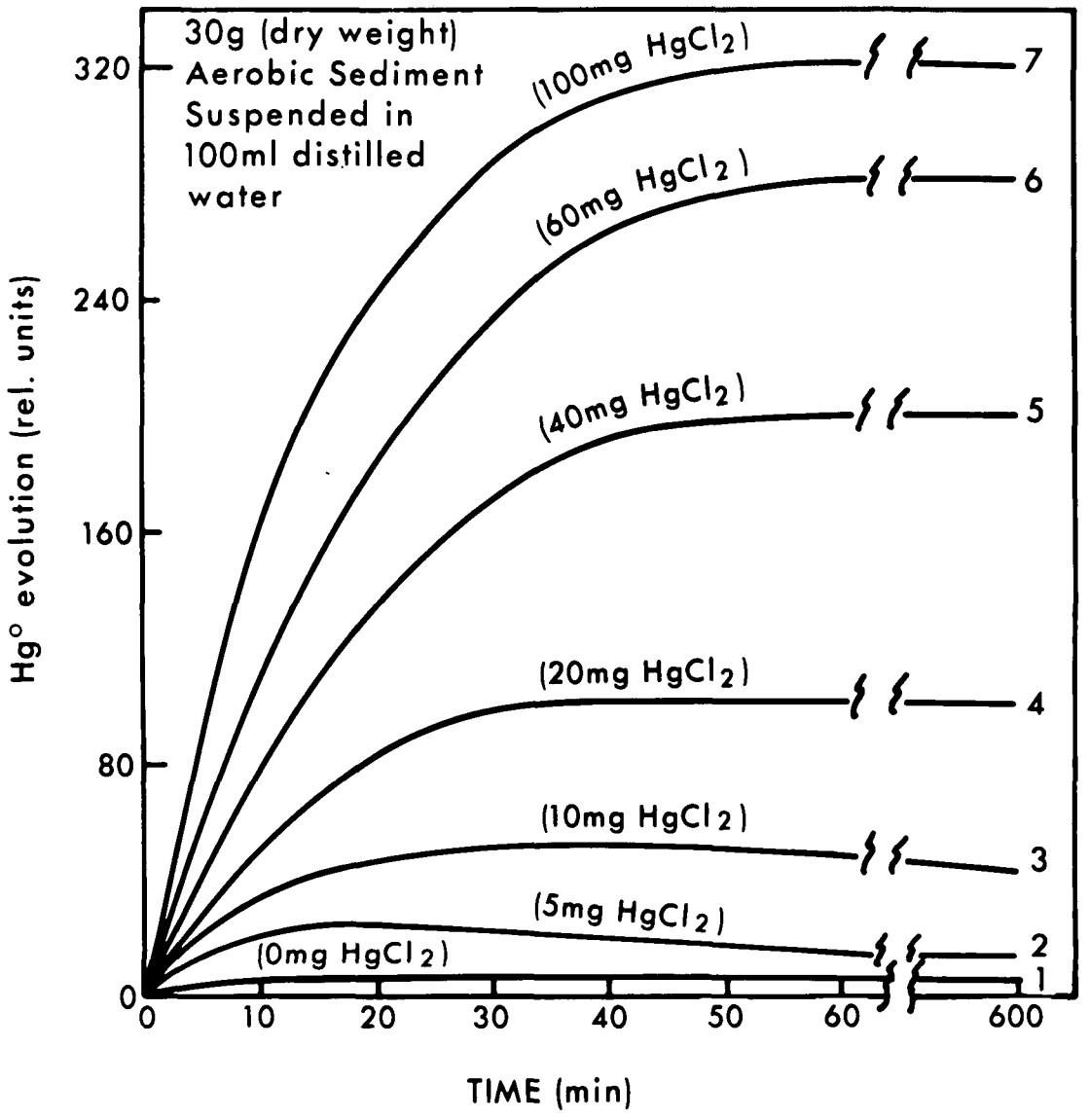

Figure 11. Rate of Hg^{o} evolution from aerobic sediments spiked with $HgCl_2$.

The release of metallic mercury from anaerobic sediments appeared to follow different kinetics. For example, the addition of 50 μg of $HgCl_2$ to an anaerobic sediment (Eh = ~ 50 mV) resulted in an immediate release of substantial amounts of metallic mercury (Figure 12, curve 1). Subsequent addition of 50 μg each increased the rate of Hg^o evolution until, after 4 additions, the rate of release became constant at about 1 μg of Hg^o per min (Figure 12, curve 4).

A comparison between the two sediments reveals other differences as well. For example, whereas Hg^o evolution was at its maximum at 200 μg of $HgCl_2$ per 30 g of anaerobic sediment, about 500 times as much $HgCl_2$ was required for the production of a similar amount of Hg^o from the aerobic sediment. Although no effect was observed if $HgCl_2$ was added to an aerobic sediment, a 200 μg dose of $HgCl_2$ added to an anaerobic sediment produced a Hg^o gush of a magnitude that was beyond the measuring range of the apparatus.

From the above, it appears that at least two processes control the release of metallic mercury in sediments. The slow process, as seen with the aerobic sediment, could be a reflection of biological activity. Tonomura et al (26, 27) reported the "bio-conversion" of organic mercury into metallic mercury carried out by mercury-resistant microorganisms. However, it is not clear whether this conversion was active or passive in nature. In sediments, a physico-chemical process could be responsible for the conversion of Hg^{++} into metallic mercury. A slow release of electrons, due to a biological process, could lead to the reduction to Hg^o. As will be discussed later, once the divalent ion is complexed with a sediment entity or is converted into mercuric sulfide, it is much less likely to be converted into the metallic form.

The fast process observed with anaerobic sediments undoubtedly is due to a chemical reduction of $HgCl_2$ according to $Hg^{++} + 2e \longrightarrow Hg^o$. In an anaerobic sediment, a pool of various reduced entities could provide electrons for such a reduction. This point was investigated by using ascorbate as an electron donor with (a) aerobic sediment, (b) anaerobic sediment, and (c) water. In all three cases, metallic mercury was produced from $HgCl_2$ if ascorbate also was present.

In effect, a stochiometric relationship was observed between the mercury gush and ascorbate addition it $HgCl_2$ was added immediately after the addition of ascorbate. However, if $HgCl_2$ was thoroughly mixed with the aerobic sediment and ascorbate added later, no mercury gush occurred, and normal release kinetics were observed. It made no difference whether aerobic sediment or an artificial resin was used. The latter (Chelex 100) retained Hg^{++} (28) as firmly as the sediment, and

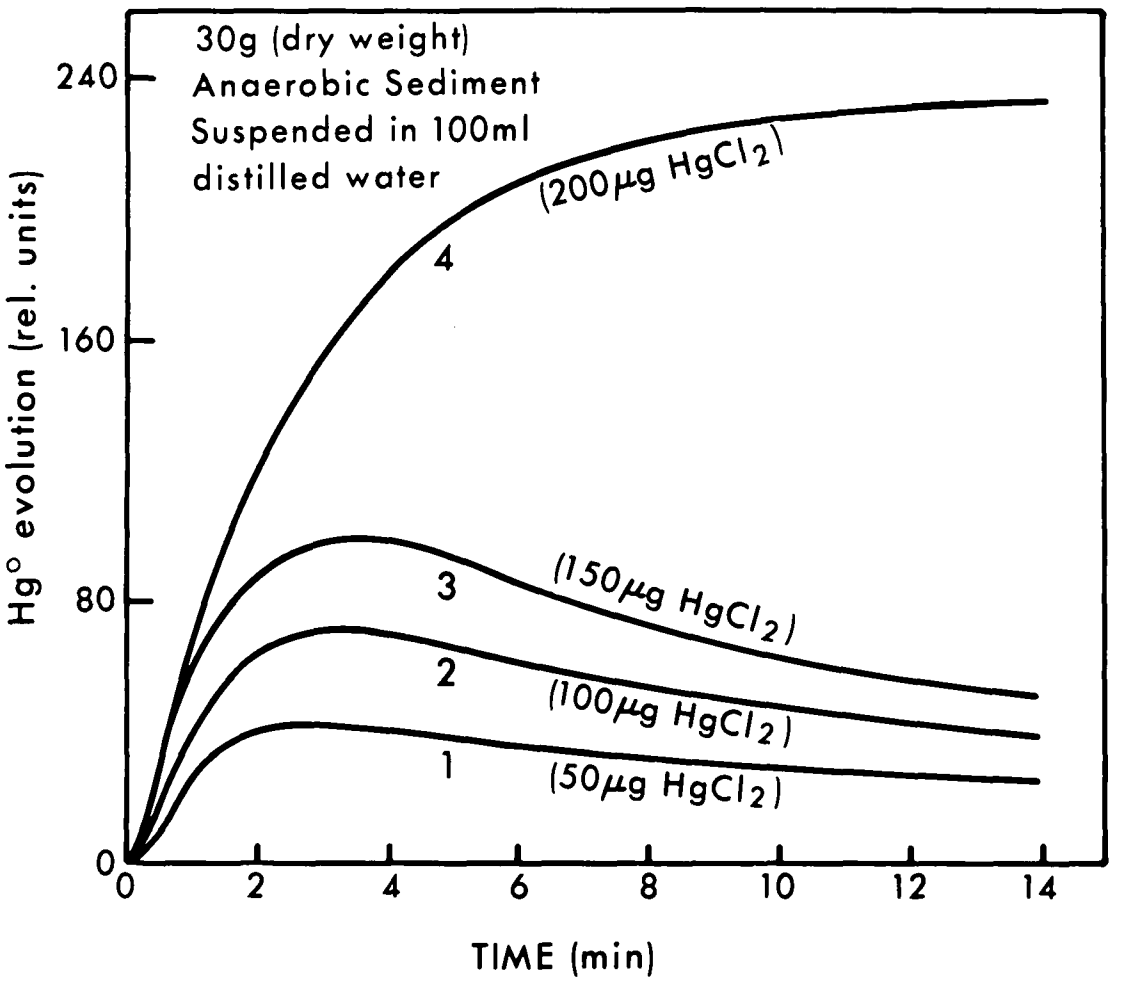

Figure 12. Rate of Hg^{o} evolution from anaerobic sediments spiked with 50 μg of $HgCl_2$.

ascorbate was unable to reduce the divalent ion and release it in the metallic form.

These observations strongly suggest that once the divalent ion is converted into the sulfide form or complexed with a sediment entity (probably most of them are organic in nature), the ion no longer is readily reduced by natural electron donors or artificial ones with a reducing potential equal to that of ascorbate. One is tempted to draw a similar conclusion for enzymatic and non-enzymatic reductions.

SECTION VI

ECONOMIC CONSIDERATIONS

In the laboratory simulation program, the use of sand and gravel was tested as a means of preventing the release of toxic mercury from mercury-enriched bottom sediments. This laboratory simulation led to the conclusion that common sand and fine or coarse gravel, applied to a thickness of about 2 to 3 inches, can virtually eliminate the release of toxic mercurials from contaminated sediments. In this section, the approximate cost of applying this abatement procedure in the field is evaluated.

Trenton Channel of the Detroit River near Wyandotte was selected as a "representative" location. The channel varies from approximately 1/8 mile to 1/4 mile in width. The landside depth is about 13 ft, the channel depth is 28 ft, and the depth on the island side is 4 ft. The area of interest is a 200-ft-wide and one-mile-long band on the Michigan side immediately below Wyandotte Chemical Company. This strip is known to be heavily contaminated with mercury (1).

These economic projections assume the use of the cheapest grade of sand selling at about $.95 a yard (approximately 1.5 ton). (Gravel is not considered separately since the cost of application appears very similar to that of sand.) Considering typical trucking, loading, and unloading charges, the price increases to $2.25 a yard in a scow at dockside. Since the overland transportation costs are significant, the possibility of a waterborne source of supply--possibly from a nearby dredging operation--was explored. The nearest large-scale sand mining operation is in Lake Erie and, although materials of various grades are shipped to the Detroit area, this source appeared not to be competitive with pit sources in Michigan--at least in the cheap, low-grade, sand market.

A number of application methods were considered, but a barge-mounted system appeared to be the most adaptable and economical. This system consists of a fixed-boom clam shell, feeding a conveyor belt that delivers the material to a swivel-type sand piler. A clam shell with a 2-1/2 to 3-yard bucket can load a conveyor at the rate of about 200 tons per hour. The swivel piler would be a 16-inch unit, handling about 200 tons per hour, allowing maximum use of the piler. A swivel piler can spread sand or other small-lump aggregate material over a 270° arc. Depending upon the speed of the barge, swivel motion, and sedimentation characteristics at the locale, a fairly even layer of material could be applied over the mercury-laden sediments.

The distribution equipment would be assembled on a small equipment barge at Wayndotte, towed to the site, and anchored there. A tug would deliver sand-filled 800- to 1000-yard-capacity scows alongside the barge-mounted equipment as a supply source. Ideally, the tug would tow enough material to the site during the early morning to allow continual operation of the spreading machinery during the daylight hours.

Table 9 presents estimates of the fixed and variable costs associated with this hypothetical case. The following assumptions were made: (a) the site is near enough to port for the tug to return empty sand scows at night and to deliver loaded ones by early morning, (b) weather conditions are ideal, (c) traffic at the site is negligible, and (d) no machinery down-time is experienced.

Table 9

Estimated fixed/variable costs of distributing sand in an area south of Wyandotte.

Fixed Costs:	
Spreading Equipment System (i.e., swivel piler, conveyor, clam shell, fixtures, hopper, etc.)	$20,000.00
Variable Costs:	
Sand, dockside, per yard	2.25
Tug boat and crew, per 12-hour day	1,900.00
Deck scow, 800- to 1000-yard capacity, per day	100.00
Equipment barge, per day	30.00
Labor, per day (2)	80.00
Equipment maintenance, per day	10.00

Based on these considerations, the cost of applying 3 inches of sand to 2-, 25-, and 50-acre areas was estimated. The results, shown in Table 10, suggest that the overall cost of application would increase linearly as a function of the size of the area treated.

Table 10

Estimate of the cost involved in the application of 3 inches of sand to 2, 25, and 50 acres of sediment contaminated with mercury.

	Number of Acres		
	2	25*	50
Fixed Costs($):	20,000	20,000	20,000
Variable Cost($):			
Sand	1,670	20,800	41,600
Tug rental	1,900	24,700	47,500
Scow rental	100	1,300	2,500
Barge	30	390	750
Labor	80	1,040	2,000
Maintenance	10	130	250
S/Total	3,790	48,360	94,600
Number of days	1	13	25
Yards of sand	740	9,250	18,500

* An area of this size is used as an example in the discussion.

The preliminary nature of this cost evaluation is recognized. Such factors as the local conditions of transportation, the actual sediment characteristics, the accessibility and topography of the site, water currents and depth, prevailing weather conditions, and the availability of labor, materials,and hardware have an impact on the cost. Such factors, which are site-dependent, could not be fully evaluated at this time.

SECTION VII

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SECTION VIII

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Mercury pollution control, methylated mercurials

27 Abstract

The release of toxic mercurials by mercury-enriched river sediments was examined in the laboratory. Tests showed a release of 1 μg of methylmercury per m^2, per day. Methylmercury occurred in sediments with low and with high organic content, in sediments with low and high cation exchange capacity, and in aerobic and anaerobic sediments. The release of toxic mercury could be prevented by a layer of sand, 6 cm in thickness, applied over the mercury-enriched sediments. Layers of fine or coarse gravel (6 cm deep) were as effective as sand. Thinner layers of sand, (1.5 and 3 cm) were unsatisfactory. The cost of applying 3-inch layers of sand or gravel was about $3000 to $4000 per acre. A slow release of metallic mercury occurred in aerobic sediments. The release was much faster in anaerobic sediments. Using ascorbate as an artificial electron donor, metallic mercury could be released at high rates from aerobic sediments as well. Ascorbate appeared to be a useful indicator of divalent and biologically accessible mercury. The laboratory investigations proved the soundness of the sand blanket approach. Its practical and economic feasibility must be determined in a combined field and laboratory analysis program.

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