EPA-R2-72-077
October 1972

Environmental Protection Technology Series

Control of Mercury Contamination in Freshwater Sediments

Office of Research and Monitoring
U.S. Environmental Protection Agency
Washington, D.C. 20460

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CONTROL OF MERCURY CONTAMINATION IN FRESHWATER SEDIMENTS

By

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Project 16080 GWU

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Prepared for
OFFICE OF RESEARCH AND MONITORING
U.S. ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

For sale by the Superintendent of Documents, U.S. Government Printing Office
Washington, D.C., 20402 - Price $2

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ABSTRACT

Methods for controlling the release of mercury from sediments have been developed, and the effects of dredging on the redistribution of mercury have been evaluated. A program of laboratory studies was conducted concurrently with a field survey where the extent of mercury contamination at a typical site was evaluated.

Laboratory studies consisted of both partitioning and aquarium experiments using artificially contaminated sediments as well as sediments from the polluted field site. Inorganic sulfides and long-chain alkyl thiols with suitable modifications were found to be the most effective binding agents. A number of factors were identified which affect the decision to decontaminate a polluted sediment or to remove the material by dredging. If the material is to be dredged, precautions must be taken when land disposal methods are used. The field survey consisted of determining both the horizontal and vertical extent of the mercury contamination as well as pertinent hydraulic parameters.

From results of the laboratory and field work, a pilot field project is described whereby techniques for controlling mercury contamination can be evaluated at a site where the field conditions have been fully established.

This report was submitted in fulfillment of Project Number 16080 GWU, Contract 68-01-0060, under the sponsorship of the Office of Research and Monitoring, Environmental Protection Agency.

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SECTION I

CONCLUSIONS

1. The behavior and mobility of mercury in natural water and soil systems are governed mainly by the strong binding of the mercuric ion to sediments, suspended particles, and soils. The binding capacity of solids is conveniently measured by the partition coefficient, which may be defined as the equilibrium ratio of mercury concentration in solution to that in the solid. The lower the value of this ratio, the more effective is the mercury-binding action.

2. The mercury-binding capacity of natural sediments varies widely and increases with the content of organic matter. A highly organic peaty sediment may give a partition coefficient on the order of 10^{-8}, which is about the limit measurable by present analytical methods. The partition coefficient of a sandy sediment may be around 10^{-3} and of a pure kaolin or silica sediment from 0.1 to 1.0.

3. When natural sediments are oxidized (as by mixing with oxygen-rich water or exposure of dredge spoil to air), the mercury-binding capacity is decreased. The capacity is also decreased by the presence of salt in concentrations similar to that of sea water.

4. The binding capacity of a given sediment for methylmercuric ion is several orders of magnitude less than for the mercuric ion. Since more than 99% of the mercury in most natural sediments is in the mercuric form, however, the main problem is to bind the inorganic mercury in a form which is resistant to methylation.

5. The mercury-binding capacity of sediments may be increased by the addition of sulfur compounds, such as long-chain alkyl thiols, inorganic sulfides, or natural proteins. Of these, the long-chain alkyl thiols most nearly meet all the requirements for useful and practical mercury-complexing agents. These thiols are capable of producing partition coefficients on the order of 10^{-8}, which is comparable to the best natural organic sediments we have measured. The thiols are also useful in binding methylmercuric ion.

6. The long-chain alkyl thiols can readily be applied to bottom sediments or to dredge spoils by the use of appropriate surface-active agents. The sediments so treated are less readily affected by oxidation than are the natural sediments or sediments treated with inorganic sulfides. The effectiveness of the thiols in preventing mercury uptake by fish and their lack of toxicity to the fish have been confirmed by aquarium experiments.

7. The major drawback of the thiols is that they may impart an objectionable odor or taste to the water. We believe that this objection can be overcome by the proper choice of materials and by chemical modification of the thiol group in such a way that its reactivity toward mercury is retained. The modified thiols will probably also be useful for complexing other heavy metals.

8. Plastic films (e.g., of polyethylene) do not appear to provide an effective barrier against methylmercuric ion. In conjunction with chemical sealants, however, films may be useful for retarding oxidation of the complexing agent and retaining it in place.

9. The uptake of mercury by goldfish in aquariums with contaminated sediments is less than that of fish in a natural environment with comparable sediments. The observed difference may be due to short time of exposure, to greater variability of the natural environment, or to greater uptake through the food chain. Large-scale tests will be needed to evaluate any dredging or sealing technique.

10. Mechanical dredging of mercury-contaminated sediments may increase local concentrations of waterborne mercury from less than 1 ppb to values on the order of 0.1 to 1.0 ppm. Of this increase, less than 1% is in the form of water-soluble mercury. The remaining 99% represents mercury bound to particulate matter, which will be redistributed by settling. The sediment so redistributed will be readily ingested by bottom-feeding fish. On the basis of laboratory experiments, we estimate that the amount of mercury resuspended in the water may be on the order of 10% of that removed with the dredge spoil. Hydraulic dredging may reduce the amount of material resuspended but will result in a higher percentage of water in the spoil. The mercury concentrations in the runoff water will probably require some reduction.

11. Mercury-contaminated dredge spoil placed on a landfill may release mercury due to oxidation and leaching. Release of mercury may be prevented by proper landfill design to prevent percolation and infiltration of oxygen-rich water, and by adding long-chain alkyl thiols to the spoil as it is put into place.

12. If corrective action is contemplated at a mercury-contaminated site, mercury concentrations in both the horizontal and vertical distributions should be mapped and the basic hydraulic parameters, such as velocity and flow volume, determined. This action is necessary in order to plan a dredging operation which will either

result in the removal of all mercury-contaminated sediment or will provide quantitative information on the amount of mercury to be complexed if the contamination is to be treated instream.

13. When dredging of a mercury-contaminated site is required by navigational considerations, provisions should be made prior to the operation for adequate land disposal.

SECTION II

RECOMMENDATIONS

1. The site survey conducted in Phase II at the Framingham Reservoir in Ashland should be extended over a longer period of time to account for seasonal variations in water concentration and in mercury input. The contribution of mercury from the adjacent landfill should be assessed and monitored over a meaningful period of time. If possible, mercury balances should be made in the reservoir system to determine how its mercury content is changing with time.

2. Analytical studies should be undertaken to determine the specific form of soluble organic compound believed to be present in the waters of the Ashland test site. Special attention should be given to the possible presence of mercurated anthraquinone derivatives.

3. A large-scale test should be conducted at the Framingham Reservoir in Ashland to determine the effectiveness of dredging and sealing methods under field conditions. The natural environment should be simulated as closely as possible with respect to the food chain, seasonal variations of mercury concentration, and time of exposure. The redistribution of mercury during dredging operations should be measured.

4. The leaching of contaminated dredge spoil from land disposal areas should be monitored and the effect of added complexing agents measured.

5. A laboratory program should be undertaken for the development of chemically modified thiols which will be free of the objectionable taste and odor of most of the presently available materials. This should involve the synthesis of new organic sulfur compounds and laboratory screening for effectiveness as mercury-binding agents. The effect of these thiols and similar complexing agents on the rate of methylation in naturally contaminated sediments should be investigated.

6. A laboratory program to determine the binding action of saltwater sediments should be undertaken. The effects of oil pollution and of salt concentration should be measured.

SECTION III

INTRODUCTION

Scope and Purpose

The mercury contamination of some fish in fresh waters of the United States has been well documented since 1970. In many cases, the source of mercury has been found to be industrial discharges of various mercuric compounds which have accumulated in the sediments. There have also been cases where the specific source is unknown but may be the result of a general fallout of mercury from the air. The release of mercury from the burning of fossil fuels has recently been documented and is a possible source, both through direct fallout and runoff.

The specific purpose of the JBF mercury program has been to develop and evaluate both physical and chemical methods of binding the mercury in the sediments to prevent its release to the overlying water. We have also investigated the feasibility of removing mercury-contaminated sediments by dredging and have evaluated in the laboratory the possible effects of dredging. Realizing that laboratory methods may not always be a true indication of what may happen in the field, we have in addition conducted a field investigation of mercury-contaminated sites. One of these sites was selected for extensive testing, including vertical and horizontal mapping of mercury concentrations, hydraulic parameters, and other water quality indicators. Sediments from this site have also been used in the laboratory evaluation of physical and chemical binding techniques. As part of the field investigation, a test plan has been prepared for a pilot-scale field evaluation of various binding techniques and an evaluation of the effects of dredging.

Approach

The program thus far has been divided into two concurrent phases, one being a laboratory investigation and evaluation of binding and dredging techniques, the second being a survey of mercury-contaminated sites and the conduct of an extensive mapping survey at one of the sites. A third phase, the conduct of a field pilot project, has not yet been performed, although a test plan for this phase has been proposed as part of Phase II.

In preparing our laboratory and field investigations, we have been guided by a set of decision sequences which define the mercury contamination problem and show how various actions are related. When a mercury pollution problem is suspected, it becomes necessary to identify the nature and magnitude of the problem and to decide on an appropriate course of action. The steps involved in arriving at such a decision are outlined in Figures 1, 2, and 3.

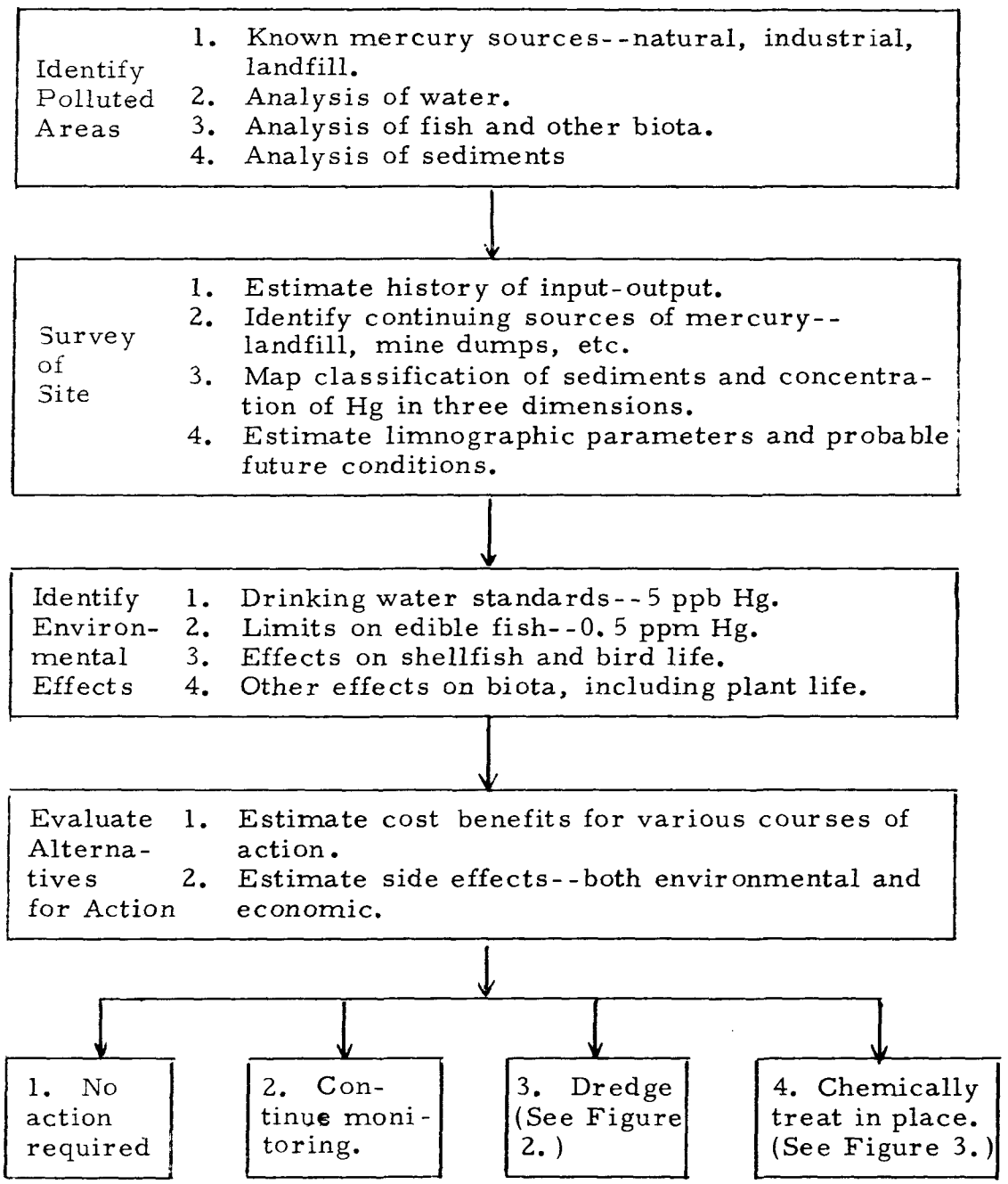


Figure 1. Decision Sequences for Control of Mercury-Polluted Water Bodies

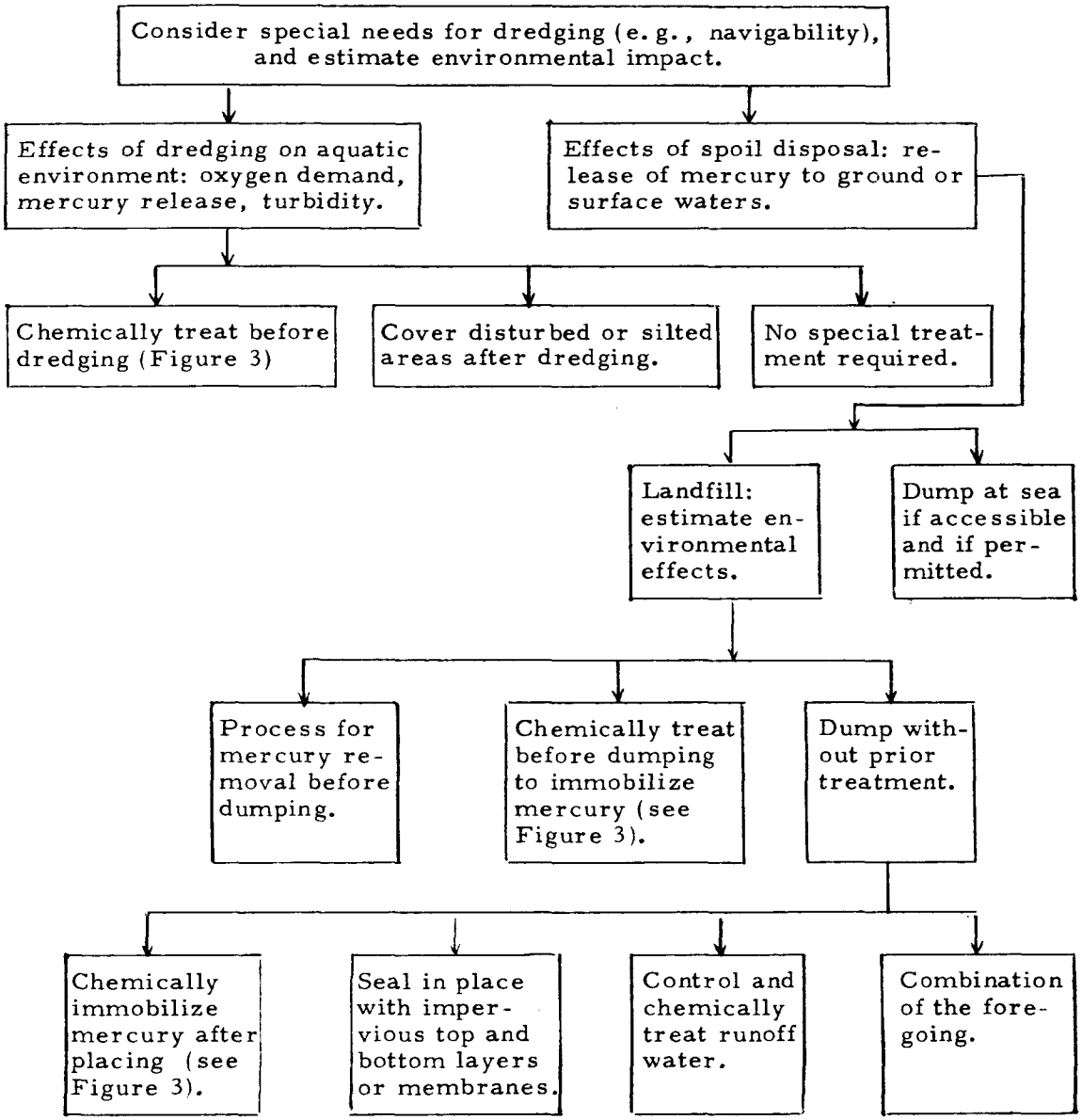


Figure 2. Decision Sequences for Dredging and Treatment of Mercury-Contaminated Sediments.

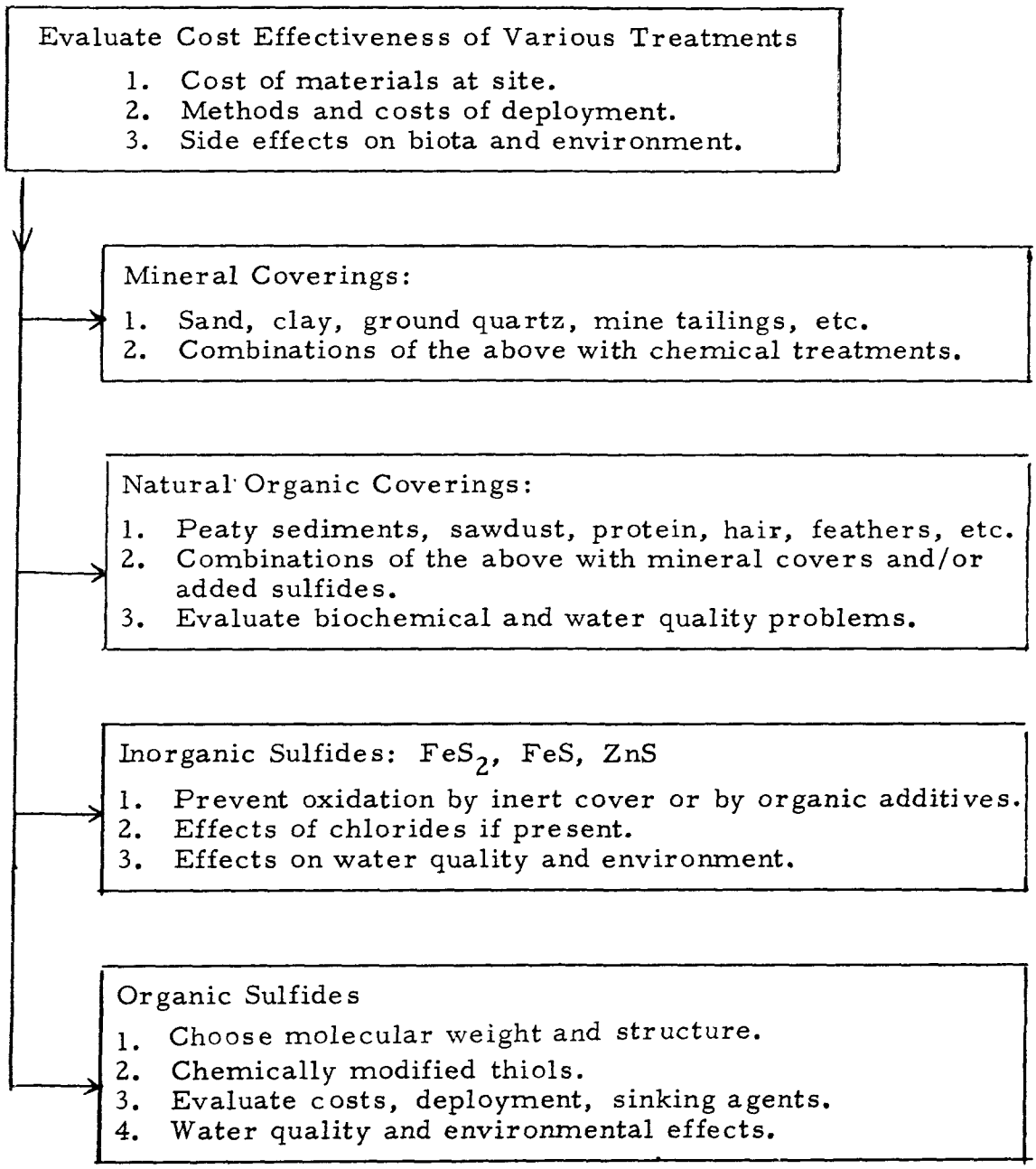


Figure 3. Decision Sequences for Sealing or Treating Sediments in Place

Referring to Figure 1, we begin with the assumption that a polluted area has been identified and confirmed by analysis. For this purpose, the analysis of mercury in predatory fish and organic sediments is most useful, since they concentrate mercury entering the water. We also assume that the sources of mercury have been stopped as far as possible. Even after the discharge of mercury has ostensibly been checked, it is still possible for mercury to enter the system from such sources as landfills, mine tailing dumps, and sediments in tributary streams.

A site survey should then be performed and should include a study of the distribution in depth of mercury in various classes of sediment. The hydraulic parameters should be defined sufficiently to permit an estimate of the future conditions in the water and sediments if the system is left to itself.

The environmental effects of the mercury should also be considered, including not only established standards for water quality and edible fish and shellfish, but also such additional effects as those on bird life and other biota, including plant life.

With this background we can evaluate the cost benefits of various courses of action and make an estimate of the probable side effects, including both environmental and economic considerations. The major alternatives appear to be: (1) take no action; (2) continue monitoring for future predictive information; (3) dredge; and (4) chemically treat the sediments in place. These last two alternatives are considered in Figures 2 and 3, respectively.

Figure 2 shows some of the decision sequences involved in dredging a contaminated site. In some cases the navigability of the waters will be the overriding consideration, and it will be necessary to dredge to maintain water depth.

If dredging is decided upon, it will be necessary to consider the effects of disturbance and possible mercury release on the water and on the biota. An alternative here is to chemically treat the sediments before dredging to minimize mercury release. After dredging, the undisturbed and/or silted areas may be further treated with chemicals or sealants to minimize the effects of freshly exposed mercury.

The handling and disposal of the contaminated dredge spoil present an especially severe set of problems. It may be necessary to impound or treat the runoff water before returning it to the source. If the spoil can be dumped at sea, a considerable economic advantage may be expected. Feasibility will depend on location and on regulations governing disposal at sea. Recent observations indicate that biological activity is reduced by a factor of 10 to 100 in the ocean depths [1], and it can be inferred that biological methylation and oxidation will probably be minimal. Transportation of the spoil to deep water, however, would increase the costs.

If the spoil is to be disposed of in a landfill, the question of mercury release becomes crucial. Our work indicates that mercury is best kept in insoluble form under anoxic conditions. In a landfill, unless the cover material is impervious and well drained, oxidizing conditions will eventually prevail as oxygenated surface waters percolate through. Mercury may then be released in soluble form in the leachate. Careful design of the landfill can prevent this.

One alternative solution would be to remove the mercury from the spoil before dumping. The low concentration of mercury (typically a few hundred parts per million) and the colloidal character of the spoil make this alternative unattractive.

A second alternative is to treat the spoil with chemicals before dumping, in order to immobilize the mercury. This affords a convenient opportunity to secure good mixing with the treating agents. The various types of chemical treatment are listed in Figure 3.

A third alternative is to dump the spoil without treatment and to try to contain the mercury by proper design of the landfill. This might involve chemical treatment of selected areas, sealing with impervious layers, control and treatment of runoff waters, or a combination of these. Containment of mercury will be easier in arid regions than in areas of high rainfall.

The types of chemical treatment involved in sealing mercury in place are shown in Figure 3. Cost-effectiveness considerations include cost of materials delivered at site, methods and cost of deployment, and possible side effects on aquatic biota and water quality.

At present we have considered four types of treatment, which can be used alone or in combination. The first alternative is to cover the sediment with mineral coverings, such as sand, clay, or other fine mineral material. Although these materials have little mercury-binding capacity in themselves, they can prevent disturbance of organic sediments and aid in maintaining anoxic conditions. If the contaminated sediments to be covered contain enough sulfide, the mercury will be adequately immobilized.

In cases where little or no natural organic matter is present, it may be desirable to add such materials in the form of natural peaty sediments or proteinaceous materials. Because of their low density, the organic coverings are easily disturbed and slow to settle. It may prove necessary to cover them with a denser material.

Among the inorganic sulfides which may be considered as mercury-binding agents are pyrite (FeS_2), ferrous sulfide (FeS), and sphalerite or zinc sulfide (ZnS). Pyrite is a cheap by-product of ore-dressing operations, but our experiments indicate that it is less effective than FeS or ZnS.

The organic thiols, in the form of high-molecular-weight alkyl mercaptans, are among the most effective mercury-binding materials we have observed. The thiols of interest are oily liquids which float on water. For these reasons we have given careful consideration to methods deployment of these materials. One promising method is to absorb them on hydrophobic oil-sinking agents, of which a large variety are known.

Another possibility is to chemically modify the thiols in order to temporarily inactivate the sulfhydryl group, thus making the odor less offensive. In the presence of mercury, the thiol will be regenerated and will bind the mercury. Preliminary investigations along this line have produced encouraging results.

An attractive feature of the thiols is that they are potentially effective in very low dose rates. We estimate that about 200 ppm of thiol in the sediment will be sufficient to bind 100 ppm of mercury. Thus it will usually be possible to effectively bind the mercury at levels of thiol treatment which will not exceed EPA guidelines for oil-polluted sediments. If the thiol is used as a barrier layer, even less may be required. In any case, the effects of these materials on the environment and on water quality must be carefully evaluated.

The decision processes discussed above show that many of the possible cures to a mercury problem involve either binding the mercury in place by chemical or physical means or removing it by dredging. Each of these actions has been shown to have some other consequence which must also be evaluated. We have considered these relationships in the design of our laboratory and field program.

SECTION IV

SEALING OR CHEMICALLY BINDING MERCURY IN PLACE

This section presents a discussion and comparison of various physical and chemical means of immobilizing mercury at the bottom of contaminated water bodies. Since no method of treatment can produce perfect immobilization, a realistic objective will be to reduce the rate of mercury release to values which will not appreciably affect the biota in the overlying or downstream waters.

Many sediments in the natural states are found to bind mercury very strongly. For this reason, it is necessary that any method of treatment be highly effective in order to reduce the natural rate of mercury release. This section covers first the requirements for effective mercury-binding agents suitable for application on a large scale. This is followed by a discussion of laboratory experiments designed to evaluate various materials in terms of these requirements. Finally, the cost of several materials for a typical application is estimated.

Criteria for Evaluating Mercury-Complexing Agents

The following list is proposed as covering the main requirements for mercury-complexing agents to be distributed in contaminated waters:

1. The equilibrium constant for the formation of the mercury complex should be as high as possible.

2. The resulting mercury complex should be extremely insoluble in water.

3. The complex should be stable toward oxidation, reduction, hydrolysis, biological action, and the presence of dissolved salts such as chlorides.

4. The rate of reaction with mercury at very low concentrations should be reasonably high. Preferably the reaction should proceed substantially to completion in a few days or weeks.

5. The material used should not adversely affect the quality of the water or the bottom sediment for its intended uses. This includes effects on fish and bottom biota in areas where such considerations are important.

6. The material should be readily convertible into a dense, granular form that will sink quickly and will not readily be dispersed into the water.

7. The cost of the material, in place at the bottom of the water and per unit of mercury complexed, should be as low as possible.

The first four of the above requirements were evaluated by measuring the partition coefficients for mercury between water and various treated sediments. The practical application of mercury-binding agents and their possible side effects on biota were studied by means of aquarium experiments with goldfish.

Measurement of Partition Coefficients

Although it is known that the transport of mercury in natural water systems is sharply limited by its strong absorption on soils and sediments, little quantitative data on the absorption has heretofore been available [2]. Such data is needed to predict and control the movement of mercury in water and soil systems as well as to evaluate the effects of mercury-complexing agents. A useful and quantitative measure of mercury absorption is provided by the partition coefficient, which, for purposes of this report, is defined as the equilibrium ratio of mercury concentration in solution to the concentration in the solid. The lower the numerical value of this ratio, the more effective is the mercury-binding action of the solid.

The partition coefficients of mercuric chloride and of methylmercuric chloride have been measured for a variety of natural sediments and minerals with and without mercury-complexing additives. Details of this work are given in Appendix A; the main results and conclusions are discussed below. Some typical data for mercuric chloride are shown in Table 1.

Runs A-16 and B-4 were made with fresh Acton sand and fresh Acton peat, respectively. The mercury-binding action of the sand is relatively low, while that of the peat is one of the best we have measured. The effectiveness of the peat may be due to the presence of sulfides and to the highly reducing conditions in the organic sediment.

Runs A-36 and B-18 show the results obtained when the same materials were aged in air for five to eight weeks before testing. In both cases, the binding capacity is diminished, probably because of oxidation. This result indicates that mercury-containing dredge spoils may release mercury if they are placed on a landfill where they can become permeated with oxygen-rich surface waters.

Runs C-1 and C-7 were made with Georgia kaolin. The addition of $CaCO_3$ to raise the pH in the latter run made some improvement, but the binding capacity is low in both cases.

Table 1

Some Representative Distribution Data for Mercuric Chloride at 24-25°C

Run No.	Time (days)	Description	Mercury Conc. (ppm)		$K = \frac{[Hg^{++}]_{H_2O}}{[Hg^{++}]_{sed.}}$	pH	Dissolved Oxygen (ppm)
			Dry Sediment	Water			
A-16	7	Fresh Acton sand	412	0.52	1.3×10^{-3}	6.2	---
A-36	7	Aged Acton sand	258	10.0	0.037	5.7	6.5
B-4	7	Fresh Acton peat	1430	<0.00002	$< 1.4 \times 10^{-8}$	5.2	0.0
B-18	7	Aged Acton peat	1335	0.0031	2.32×10^{-6}	4.8	0.6
C-1	8	Clay (Georgia kaolin)	82	40.1	0.49	5.2	5.0
C-7	7	Clay plus 5% $CaCO_3$	314	11.5	0.037	7.4	7.5
S-1	7	Ground silica, about 240 mesh	33	51.5	1.56	6.8	6.0
C-5	7	Clay plus 3% coarse pyrite	193	31.8	0.165	5.0	10.0
C-13	7	Clay plus 5% milled pyrite (-325 mesh)	300	0.0025	8.3×10^{-6}	4.5	7.1
C-25	7	Clay plus 1% FeS (fired pyr.)	321	0.154	4.8×10^{-4}	5.0	9.5
C-19	7	Clay plus 1% ppt. FeS	378	0.168	4.5×10^{-4}	4.3	4.0
C-51	7	Clay plus 5% ppt. ZnS	300	0.00053	1.77×10^{-6}	5.1	7.0
C-27	7	Clay plus 1% n-dodecyl mercpt. + 5% $CaCO_3$	1000	0.00002	2.0×10^{-8}	6.8	11.5
C-28	7	Same as C-27 + 3.5% NaCl	300	0.00006	2.0 x 10-7	7.2	8.5
C-2	7	Ppt. FeS + 3.5% NaCl	86	26	0.30	4.5	---
B-11	7	Fresh Acton peat + 3.5% NaCl	800	0.004	5.0×10^{-6}	4.8	0.0
CF-6	7	Chickn. feathrs.	1780	0.140	7.87×10^{-5}	6.5	0.9

The use of ground silica to cover mercury-contaminated sediments in pond bottoms has been proposed. Run S-1 shows, however, that this material has practically no binding capacity.

Because of the low natural mercury-binding ability of kaolin, we have used this material as a substrate for testing a number of additives. Run C-5 shows the effect of adding 3% of coarse (84% over 200 mesh) pyrite to kaolin. Only a slight improvement over straight kaolin (run C-1) is observed. Since mercuric sulfide is known to have a low solubility, it appears that very little reaction has taken place in seven days and that the reaction is probably kinetically limited.

A number of experiments were made in the attempt to increase the reaction rate of pyrite. One of the easiest and most effective methods was to mechanically mill the pyrite to a very fine powder (100% through 325 mesh). This produces a major improvement in partition coefficient, as shown by run C-63.

Another way of modifying pyrite is to heat it in the absence of air to a temperature above about 700 °C, when one atom of sulfur is lost, according to the reaction:

$$FeS_2 \longrightarrow FeS + S$$

A sample of calcined pyrite was made by this method which was estimated by weight loss to be about 35% converted to FeS. Run C-25 shows that this treatment produces some improvement over coarse pyrite but not as much as fine grinding.

The effect of particle size on the reactivity of FeS is shown by run C-19, in which the FeS was precipitated in situ by reaction of $FeSO_4$ with CaS. This material is somewhat less active than fired pyrite, even in the presence of somewhat less dissolved oxygen. If the oxygen is reduced to 1 ppm, however, this material is greatly improved (Appendix A, Table A-4).

Run C-51 shows that precipitated ZnS (laboratory reagent) is somewhat more effective than milled pyrite or precipitated FeS.

The solubility of mercuric sulfide in near-neutral solutions is controlled by its hydrolysis according to the equation:

$$HgS + 2H_2O \longrightarrow Hg^{++} + 2OH^- + H_2S$$

Since H_2S is very slightly ionized, the concentration of Hg^{++} in the presence of HgS is greater than its solubility product ($10^{-53.5}$) would indicate. Hydrogen sulfide is both soluble and reactive and is therefore readily lost from the reactive zone by diffusion and oxidation. In this manner, the hydrolysis of HgS can progress until an appreciable concentration of mercuric ion is reached.

As an alternative to the inorganic sulfides, we considered the long-chain alkyl thiols. These thiols form insoluble mercury compounds according to the reaction:

$$Hg^{++} + 2RSH \longrightarrow Hg(SR)_2 + 2H^+$$

Like H_2S, the thiols are very weak acids, and their mercury compounds are subject to hydrolysis. Unlike H_2S, however, the long-chain thiols are highly insoluble in water and tend to remain in the reaction zone, where they continue to be effective in preventing progressive hydrolysis.

Several long-chain alkyl thiols (mercaptans) are commercially available. Normal dodecyl mercaptan was chosen for most of this work because its cost is moderate and its odor is relatively low. Run C-27 shows the effect of 1% n-dodecyl mercaptan buffered with calcium carbonate. This is better than the inorganic sulfides by almost two orders of magnitude and is almost as effective as the Acton peat.

An important feature of mercury-complexing agents in some environments is their ability to function in the presence of salt or brackish water. Run C-28 shows that the effectiveness of the mercaptan decreases by about a factor of 10 in the presence of 3.5% NaCl. Under the same conditions, the precipitated FeS is five orders of magnitude less effective, and the Acton peat is two orders of magnitude less effective, as shown by runs C-21 and B-11. The mercaptan is by far the best material we have found for use in a saltwater environment.

Another approach to the bonding of mercury is the use of natural proteinaceous materials, such as wool, which has been studied by Friedman et al. [3]. Run CF-6 shows the results of reacting mercuric chloride solution with chicken feathers, which are a cheaper source of protein than wool. The distribution ratio obtained agrees well with the data of for wool but is not as good as the data for sulfides or mercaptans. As will be shown in a later section, the low capacity of feathers renders them uneconomic in comparison with the sulfides or mercaptans.

Table 2 gives the results of a variety of runs made with methylmercuric chloride. The materials which gave the best results with $HgCl_2$ generally yield the best results with CH_3HgCl, but the distribution ratios are less favorable by several orders of magnitude. Fortunately, the methylmercury content of most contaminated sediments is less than 1% of the total mercury (see below for example). The main problem, therefore, appears to be to immobilize the inorganic mercury. To do so effectively, it is desirable to bind the inorganic mercury in a form which will not be appreciably methylated. We recommend that the effect of thiols and similar complexing agents on the rate of methylation of mercury be investigated.

Further measurements have been made on a sediment from Framingham Reservoir No. 2 in Ashland, Massachusetts, which is believed to have

Table 2

Some Representative Distribution Data for Methylmercuric Chloride at 24-25°C

Run No.	Time (days)	Description	Mercury Conc. (ppm) Dry Sediment	Mercury Conc. (ppm) Water	$K = \frac{[Hg^{++}]_{H_2O}}{[Hg^{++}]_{sed.}}$	pH	Dissolved Oxygen (ppm)
B-20	7	Fresh Acton peat	1470	1.0	6.8×10^{-4}	5.2	0.2
B-14	7	Fresh Acton peat	2630	2.76	1.05×10^{-3}	5.1	0.4
B-15	7	Aged Acton peat	2860	6.5	2.27×10^{-3}	5.3	0.4
C-32	7	Kaolin clay	382	470	1.23	5.1	---
C-33	7	Kaolin clay	842	1665	1.98	5.0	---
C-60	7	Clay plus 5% ZnS	300	0.45	1.5×10^{-3}	5.4	9.0
C-62	7	Clay plus 1% n-dodecyl mercaptan, plus 5% $CaCO_3$	300	0.24	8.0×10^{-4}	7.6	9.1
C-64	7	Clay plus 5% pyrite (-325 mesh)	300	37.5	.125	4.1	2.8

been contaminated with mercury by discharges from a dye-manufacturing plant. One sample of this sediment contained about 100 ppm of total mercury and 0.428 ppm of methylmercury. The partition coefficient for total mercury in this sediment is about 2.7×10^{-5}.

Recent experiments indicate that a major part (on the order of 80%) of the mercury in this sediment may be organically bound, although less than 1% is in the methylated form. We now believe that much of the mercury in this sediment may be in the form of mercurated anthraquinone derivatives, which are a probable by-product of the dye manufacturing process.

We recommend that Phase III of this program include analytical studies aimed at identifying the specific forms of mercury present in the sediment and in brackish-water sediments frem the vicinity of a dye plant in Dighton, Massachusetts. Such information will be needed to study the binding of mercury in these sediments and to evaluate the results of the pilot-scale experiments. The problem of identifying these chemical species is further discussed in Appendix E, which covers work on analytical methods.

Aquarium Studies

The aquarium studies were intended to supplement the results of the distribution experiments under conditions more closely approximating field conditions. The behavior of mercury in an actual water body will be governed not only by equilibrium conditions but by rates of diffusion and reaction and by flows of mercury and of natural mercury-complexing materials through the system.

The aquarium experiments may also serve to screen out materials which are toxic to fish. Procedures and results are summarized below and discussed in detail in Appendix B.

The experiments were conducted in five-gallon glass aquariums, eight inches by 14 inches by 10 inches deep. A one- or two-inch layer of sediment containing $HgCl_2$ or CH_3HgCl plus any required mercury-binding agents was added and allowed to stand about a week. A cover layer was then added, and the aquarium was carefully filled with water.

The aquarium was allowed to stand one or two days before the fish were added. The experiment was started by adding three or four (depending on size) goldfish about two inches long. The aquariums were aerated with bubblers during the tests.

The fish were fed about every other day with a commercial fish food containing about 20% protein. Our analysis showed negligible amounts of mercury in the food.

After nine day's exposure, the fish were killed, gutted, and the heads and tails removed. The remaining portion was then analyzed for mercury. New fish were then added to the tank, exposed for about 30 days, and analyzed in the same way. Some runs were made with different periods of exposure, as noted in Appendix B. The water was periodically analyzed for soluble mercury while the fish were being exposed. The effectiveness of mercury binding by the sediment was judged by the mercury uptake of the fish and by the concentration of soluble mercury in the water.

In all the cases the dissolved-mercury concentration decreased markedly with time, and the uptake of mercury by the fish was usually less during the second period of 30 days than in the first exposure of nine days. The loss of mercury from the water was approximately equal to the uptake by the fish

The data obtained for various sediments and additives is summarized in Table 3.

The Acton peat was the best natural mercury-binding sediment found, as might be expected from the low value of the partition coefficient. With 185 ppm of Hg in the sediment, the fish took up only about 1/2 ppm during the 30-day exposure (run C). This appeared to be due mainly to ingestion of the sediment by the fish. When the Acton peat was covered with 1/2 inch of sand, the fish lost mercury during both the nine-day and 30-day exposures (run D).

The Acton sand showed low mercury-binding capacity (runs A and S), and the fish took up mercury rapidly. One inch of clean sand cover (run B) lowered the concentration of mercury in the water and produced a loss from the fish during the 30-day test. Runs E and F showed that 1/2 inch of Georgia kaolin or of 240-mesh silica were relatively ineffective as covers. These materials were readily stirred up by the fish, and both tanks were turbid for the duration of the test.

Run G shows the effect of a thin layer of precipitated zinc sulfide. Although the fish lost mercury during the first nine days, there was a larger gain in the 30-day test. This may have been due to the oxidation of sulfides by long contact with aerated water.

Runs I, K, and L show that milled pyrite, fired FeS-ZnS mixture, and fired FeS were less effective than ZnS.

The effect of the long-chain alkyl mercaptans is shown by runs H, J, and V. Although the concentrations of mercury in the water are not particularly low, the uptake by the fish is generally less than with the inorganic sulfides. Run V showed low mercury levels in the water after the first run of 21 days. Time did not permit a second run to be made in this aquarium.

Table 3. Summary of Aquarium Data

Run No.[a]	Bottom Sediment	Hg Content		Cover Layer	Hg Concentration in Water (ppm)			Mercury Uptake by Fish (ppm, wet basis)		Remarks
		ppm	Added as		Initial	9 Days	Final	First Set of Fish (9 days)	Second Set of Fish (9 days)	
C	Acton peat	185	$HgCl_2$	None	.0004	.00037	.000056	+0.144	+0.47	Sediment ingested by fish.
D	Acton peat	100	$HgCl_2$	1/2" clean sand	---	.000077	.000055 (18 days)	-0.155	-0.48	Sand cover prevented ingestion.
A	Acton sand	100	$HgCl_2$	None	.048	.0049	.0002	+29.9	+1.98	
S	Acton sand	100	$HgCl_2$	None	0.18	---	---	+6.0 (2 days)	---	All fish died in 2 days.
B	Acton sand	100	$HgCl_2$	1" clean sand	.00055	.00025	.00012	+1.72	+0.064	
E	Acton sand	100	$HgCl_2$	1/2" Ga. kaolin	.032	---	.0003	+13.96	+0.42	
F	Acton sand	100	$HgCl_2$	1/2" 240-mesh silica	.074	---	.0008	+10.83	+1.30	
G	Acton sand	100	$HgCl_2$	.015 lb/ft^2 ZnS	.0018 (3 days)	---	.0008 (28 dys)	-0.06	+3.41 (19 days)	
I	Acton sand	100	$HgCl_2$	.0291 lb/ft^2 milled pyrite	.0407	.0096	.0075	+1.81	+5.78	
K	Acton sand	100	$HgCl_2$	.015 lb/ft^2 ZnS-FeS	.0204	.0063	.0049	+11.7	+14.4	
L	Acton sand	100	$HgCl_2$	.015 lb/ft^2 FeS	.078	.0076	.0008	+16.3	+20.2	
H	Acton sand	100	$HgCl_2$	.0051 lb/ft^2 (b) MTM on carrier	.0035	.001	.0036 (23 dys)	+0.53	+0.83 (19 days)	

Table 3 (continued)

Run No.[a]	Bottom Sediment	Hg Content		Cover Layer	Hg Concentration in Water (ppm)			Mercury Uptake by Fish (ppm, wet basis)		Remarks
		ppm	Added as		Initial	9 Days	Final	First Set of Fish (9 days)	Second Set of Fish (9 days)	
J	Acton sand	100	$HgCl_2$	.0247 lb/ft^2 NDM on sand[b]	.0045	.0035	.001	+0.78	+0.83	
V	Acton sand + NDM, $CaCO_3$	100	$HgCl_2$	None	.0016	.00045 (21 days)	---	0.90 (21 days)	---	1st exposure was 21 days.
N	Acton sand	30	CH_3HgCl	None	4.6	4.0	2.9	+16.7 (4 hrs)	---	All fish died in 4 hours.
M	Acton sand	30	CH_3HgCl	.0247 lb/ft^2 NDM on sand	.048	.035	.024	+11.1	+12.7	
R	Acton sand	30	CH_3HgCl	Polyethylene film, .001" thck	0.45	---	---	+6.0 (6 hrs)	---	All fish died in 6 hours.
T	Acton sand	30	CH_3HgCl	Polyeth. film over milled pyrite .0291 lb/ft^2	.046	.012 (10 days)	.002	+7.0 (10 days)	+2.0	
U	Acton sand	30	CH_3HgCl	Polyeth. film over NDM on sand, .0247 lb/ft^2	.021	.010 (10 days)	.003	+3.8 (10 days)	+1.4	
Q	Ashland 12/71	100.5	(c)	None	.0009[d]	.0003	.0003	+0.18	-0.05	

NOTES:
(a) See Appendix B for more detail on these runs.
(b) MTM = mixed tertiary mercaptans
NDM = normal dodecyl mercaptan
(c) Contaminated sediment, no additional mercury added.
(d) These analyses may be somewhat low; we later found that much of the Hg is organically bound.

Runs N through U were made with 30 ppm of methylmercuric chloride in Acton sand. This level is considerably higher than found in any natural sediment of which we are aware, but the data afford rapid comparison of various materials.

Run N was made with no cover, and the fish all died within four hours. The use of 0.0247 lb/ft^2 of n-dodecyl mercaptan (run M) lowered the initial concentration of mercury in the water about 100 fold. The fish survived both the nine-day and the 30-day tests, although the uptake of mercury was large.

A cover of 1-mil polyethylene film (run R) sealed at the edges with a little clean sand was less effective than the mercaptan; all the fish died within six hours.

The bests results with methylmercury were obtained with polyethylene film over milled pyrite or n-dodecyl mercaptan, as shown in runs T and U.

Run Q shows the results obtained with a contaminated sediment from the Framingham reservoir in Ashland, Massachusetts. This sediment probably contains both inorganic and organically bound mercury in the form of mercurated anthraquinone derivatives. During the 30-day run with this sediment, the fish lost mercury, although fish caught in the reservoir itself have analyzed from 0.5 to over 7.0 ppm of mercury. This indicates that the aquarium test does not adequately duplicate the conditions in the reservoir. The difference may be due to the reservoir fish ingesting sediment over long periods of time or to other mercury-contaminated food. There is also a continuing and variable mercury input to the reservoir from a landfill upstream, which may contribute to the problem.

In terms of the requirements for practical mercury-complexing agents, the aquarium results indicate that both the inorganic sulfides and the long-chain thiols are capable of markedly reducing the concentration of water-soluble mercury. The thiols are generally more effective than the inorganic sulfides, although neither has produced results equivalent to Acton peat in these short-term tests. Neither class of material showed any toxic effect on the fish in these tests. The toxicology of the thiols is further discussed in Appendix D.

The thiols, especially the mixed tertiary mercaptan, impart an objectionable odor and taste to the water. We believe this problem may be overcome by carefully selecting the type and purity of the thiol used. In addition, the odor may be eliminated by temporary chemical masking of the thiol group in such a way that its reactivity toward mercury is not impaired. We recommend that this approach be further investigated.

Under recent guidelines issued to regional representatives by the En-Environmental Protection Agency in February, 1971, a concentration

of up to 1500 ppm of oily material is permitted in a dredge sediment before it is classified as "polluted with organic matter." If 1000 ppm of a mercaptan was added to an otherwise oil-free and unpolluted sediment, the resulting mixture would be well within EPA guidelines, and the mercaptan would have the theoretical capacity to bind about 500 ppm of mercury.

The inorganic sulfides are most effective when they are in finely divided form, such as milled pyrite (-325 mesh) or as precipitated ZnS. In this form the sulfides do not sink rapidly, and they are readily dispersed into the water. It is not clear how these problems can be overcome while still maintaining the required degree of reactivity.

The alkyl thiols, being liquid at ordinary temperatures, can readily be coated onto sand by means of cationic surface-active agents. In this form they sink rapidly and are not readily redispersed or released from the treated sand. Thus, the thiols appear to be preferable to the inorganic sulfides from the standpoint of deployment.

Cost of Materials

The final requirement for a useful mercury-binding agent is that its cost should be moderate. In this section we discuss some preliminary estimates of the cost of materials for a typical situation. No attempt is made to estimate heavily site-dependent costs, such as for dredging or for moving large amounts of sand or earth cover. For purposes of these estimates, we consider four typical classes of mercury-binding materials:

1. Natural organic soils
2. Inorganic sulfides
3. Long-chain alkyl thiols
4. Natural proteins

As a basis for these estimates, we will consider the upper basin of the Framingham Reservoir, which is estimated (see Section VI) to contain about 250 lbs of mercury in seven acres of bottom, or an average of 36 lbs per acre. We assume that we wish to lower the mercury content of the water in the upper basin to a level which will permit raising edible fish. Since the maximum level of mercury permitted by the Food and Drug Administration is 0.5 ppm, and the fish, in general, will concentrate mercury by a factor of about 3000, the maximum permissible concentration in the water is taken as 0.167 ppb. No mercury input from upstream is assumed, and the mercury content of the water column is considered negligible. The mercury will be considered as mercuric ion, although recent work with sediments in this reservoir indicates that this is probably not the actual case.

Natural Organic Soils

The Acton peat will be considered as a typical organic soil (44.3% loss on ignition--see Appendix A). If we take a partition coefficient of 5.3×10^{-7} for this material (run B-5, Table A-1), we obtain a figure of 315 ppm of mercury in the peat in equilibrium with 0.167 ppb in the water. At this level it will require 1.14×10^{5} lbs of dry peat per acre to bind the 36 lbs of mercury. At an estimated moisture content of 79%, this is equivalent to 270 short tons of wet peat per acre. At a wet density of 65 lbs/ft^3, this is equivalent to a layer 2.3 in. thick. The above figure represents a worse case, since it takes no account of the absorptive capacity of the layer of organic sediment already existing in the upper basin.

This layer of peat should be covered with a layer of sand to prevent resuspension of the peat in the water and to prevent ingestion by fish, as well as to maintain anoxic conditions in the bottom. If we use 1/2 in. of a material similar to Acton sand (wet density about 130 lbs/ft^3), we will require 118 short tons per acre.

The cost of these covering materials will depend heavily on their availability at the site and on the means used for deployment. If the reservoir could be drained, the cover could probably be spread with road-grading equipment. Otherwise it would have to be dropped into the water. This latter operation would be much more difficult to control. In view of these factors, no detailed estimate of costs will be attempted. Because of the large tonnages of materials involved, however, the cost is expected to be high.

Inorganic Sulfides

For estimating purposes, we consider the case of precipitated ferrous sulfide, FeS. Run C-20 (Appendix A, Table A-4) gives data for FeS formed in situ by reaction of CaS and $FeSO_4 \cdot 7H_2O$ in the presence of clay. The concentration of Hg in the water was less than 0.2 ppb, and we assume it meets the requirement of 0.167 ppb. The amount of FeS present in this experiment is estimated to be 0.316 g, and this has removed 0.0378 g of mercury from solution. The experimental ratio of FeS/Hg is, therefore, 8.36 lbs per lb, or about a 19-fold excess over the theoretical. There is, therefore, reason to expect that this ratio may be improved with further work, but we will use this conservative figure for the present estimate. Thirty-six pounds of mercury will require 300 lbs of ferrous sulfide.

The cost of sufficiently reactive ferrous sulfide has not been adequately explored at present, but, if we assume a reasonable figure on the order of $1/lb, the cost of $300 should be relatively minor as compared to the cost of moving 270 tons of peat. If milled pyrite could be used in place

of ferrous sulfide (run C-82, Table A-4), a cost of $200 per ton, or about 10¢ per pound, might reasonably be projected. This would reduce the material cost to about $30 per acre.

The data of runs C-20 and C-82 were obtained under anoxic conditions, and it is anticipated that any sulfide will have to be covered to prevent oxication. The cost of 118 tons of covering sand will, therefore, be the same as in the case of the Acton peat. Some economies might be achieved if the reservoir could be drained and the sulfide harrowed or plowed into the bottom sediments. For the Framingham Reservoir this would seem to be a relatively low-cost operation as compared with trying to place and cover the sulfide under water.

Long-Chain Alkyl Thiols

The data obtained on the organic thiols as mercaptans (Tables A-6 and A-9) show that these materials are easily capable of reducing the concentration of dissolved mercury to levels below 0.167 ppb, even in the presence of dissolved oxygen and of much chloride. Aquarium experiments to date show no toxic effect on goldfish, and a review of the literature indicates that, because of their extreme insolubility, no toxic effects are to be expected (see Appendix D). Under anaerobic conditions no biological degradation is anticipated.

A major drawback of the thiols is their objectionable odor, which may be imparted to the overlying water. We believe that this problem may be overcome by using certain chemically modified compounds, in which the thiol group is temporarily masked but is available for reaction with mercury under appropriate conditions. Some of these masked thiols have very little or no objectionable odor.

A second drawback of the thiols (and the modified thiols) is that they are oily liquids with a density less than that of water. In order to distribute them at the bottom of the water, they must, therefore, be absorbed on porous or oleophilic materials, which will carry them to the bottom. A number of oil-sinking agents have been developed for treating oil spills and should be readily adaptable for this purpose. In particular, long-chain amines have been developed for rendering wet sand oleophilic. It should, therefore, be possible to dredge sandy bottom sediments from a water body, treat them on a barge with amines and thiol derivatives, and return them to the water. By this means, the transportation of large tonnages of material will be avoided. Alternatively, if a reservoir could be drained, the surface-active and complexing agents might be plowed or harrowed into the bottom sediments.

It is not yet clear whether a cover will be needed in the case of the modified thiols. Although a cover is probably desirable, the bottom in many cases may be sufficiently anoxic to prevent excessive biodegradation.

If we consider the results of run C-26 (Table A-6), we note that 0.844 g (1 ml) of n-dodecyl mercaptan has complexed 0.100 g of mercury, leaving 0.150 ppb in solution. This is a ratio of 8.44 lb of thiol per pound of mercury complexed, or slightly more than a fourfold excess over the theoretical. Even better results could be obtained by the addition of small amounts of calcium carbonate. The quoted price of n-dodecyl mercaptan is about $.80/lb in drum lots. Other mercaptans are available in volume at prices as low as about $.30/lb. No prices are available on modified thiols. Taking the higher value of $.80/lb for n-dodecyl mercaptan, we arrive at a cost of $244 per acre for the 306 lbs of n-dodecyl mercaptan required for 36 lbs of mercury. This cost would be reduced to about $100 if a thiol at $.30/lb could be used.

Further assuming that we emplace a mixture containing 5% of mercaptan and 0.1% of surface-active amine on wet sand, we will require a little over three tons of sand per acre and six lbs of surface-active agent. At $.40/lb the cost of the latter will be negligible.

Natural Proteins

The absorption of mercury by wool has been studied by Friedman and Waiss [3], who find that mercuric chloride approximately follows a Freundlich isotherm, given by the equation:

$$\log x \cong 0.33 \log C + 1.94$$

where x is the mercury absorbed by the wool in mg per gram, and C is the concentration of mercury in the water in grams per liter. We have made some preliminary experiments with the absorption of $HgCl_2$ by chicken feathers and find that the results agree well with those obtained for wool by Friedman and Waiss. Since chicken feathers are a cheap by-product (estimated cost $.04/lb), we will base the present cost estimates on the use of feathers but will use the distribution data for wool.

From the equation of Friedman and Waiss, we estimate that feathers in equilibrium with water containing 0.167 ppb of Hg^{++} will contain about 500 ppm of mercury. This is a ratio of 2000 lbs of feathers per lb of Hg, or 36 short tons of feathers to complex 36 lbs of mercury. At $.04/lb of dry feathers, the cost of material will be $2,880 to cover an acre of bottom. If the dry feathers are compressed to a density of 5 lbs/ft^3, this will be equivalent to a layer of feathers 4-1/4 in. thick over the area of the upper basin. Collection, transportation, and emplacement of such a large quantity of low-density material will certainly be difficult and costly. As in the case of the Acton peat, about 825 tons of sand will be required to provide a cover 1/2 in. thick.

The use of such a large quantity of proteinaceous organic matter in a small area will almost certainly have an adverse effect on the taste and

odor of the water. In addition, biodegradation of the feather protein may release soluble mercury back into the water. If the feathers are treated with a reducing agent to convert the disulfide linkages into thiol groups, the absorptive capacity may be increased by a factor of about two. The costs for such treatment have not been worked out. By destroying the natural cross-linking of the feather keratin, however, the reducing treatment may render the complexed mercury still more soluble and increase the dangers of its release into the water column.

Other agricultural by-products, such as walnut expeller meal, may be an order of magnitude more effective than wool, but large tonnages would still be required.

In summary, we find that highly active mercury-binding agents such as organic thiols or inorganic sulfides are likely to provide greater overall economy than natural materials such as peat or proteinaceous substances. The principal saving is in reducing the need to transport and emplace large tonnages of material.

If the thiols can be used without a cover layer of sand, they will be more economical than the sulfides.

SECTION V

DREDGING OF MERCURY-CONTAMINATED SEDIMENTS

The preceding section of this report indicates that chemical treatment of mercury in place is potentially less costly than physically covering the sediments with large tonnages of cover materials. For the same reason, chemical treatment, where applicable, will probably be much less costly than dredging. There will be some situations, however, where dredging of mercury-contaminated sediments will be required to maintain navigable water depths.

We have also found that in many cases mercury will be found in localized areas which may be relatively shallow. The material can be easily removed by dredging once the extent of mercury contamination is defined. This situation occurs quite often near an outfall, where a sludgelike material accumulates along the banks of a brook or river.

Dredging presents two main problems of environmental impact: dispersal of mercury throughout the water column and disposal of contaminated spoil.

During the course of this project we have gathered data pertinent to the analysis of these environmental effects, especially with regard to dispersal of mercury in the water column. Details of this laboratory work are given in Appendix C. The decisions involved in dredging and spoil disposal are discussed in Section III.

Experiments in aquariums with simulated mechanical dredging have indicated that the amount of mercury dispersed in the water column is on the order of 2-10% of that removed. With 100 ppm of mercury (as $HgCl_2$) in the sediment, total mercury concentrations in the water on the order of 1 ppm were observed after dredging.

The dissolved mercury fraction increased from fifteen- to thirtyfold after dredging. The highest value observed was 5.6 ppb, which exceeds the permissible standard for drinking water. In this case, however, the amount of mercury in solution was less than 1% of the total waterborne mercury. This indicates that the major redistribution of mercury will take place in the form of suspended particles. Measurements of sedimentation rates and their application to the prediction of mercury redistribution are discussed in Appendix C.

Since the bulk of the mercury is in the suspended form rather than in solution, it may be concluded that treatment of the bottom with mercury-complexing agents before dredging will have little effect on the total waterborne mercury. A more effective method of controlling the dispersal of mercury lies in the possible use of vertical cloth or screenlike

barriers in the water to limit the travel of fine silt. The results obtained with such barriers by the Florida Department of Transportation have recently been described by Hutt [4]. Suitable barriers might also tend to limit the zone of oxygen depletion in the water, which is caused by the dredging of reduced sediments that become a localized source of high oxygen demand.

In some cases a more effective way to prevent redistribution of mercury is to use a suction dredge in place of a mechanical dredge. Suction dredging has been successfully used for several years in a demonstration project for the restoration of Lake Trummen in southern Sweden [5]. A cutter head is required for roots and consolidated sediments, but the cutter is not necessary for recent sediments which have not yet consolidated.

A major drawback of suction dredging is the problem of spoil handling, since the spoil contains a high percentage of water. At Lake Trummen, the spoil and water are pumped ashore to two settling ponds, which are filled alternately. The overflow from the ponds is clarified with aluminum sulfate, resettled, and returned to the lake. Such facilities for spoil handling are not available in many cases.

In some isolated cases, such as the Framingham Reservoir, mercury contamination may occur in impounded areas where water level is controlled both for flood control and water resource purposes. In these cases, it may be possible to lower the water level and expose much of the contaminated sediment. This material could then be removed with conventional earth removal equipment rather than the more expensive dredging systems.

Regardless of the method used to remove the contaminated sediment, disposal of the spoil will present a potential hazard. Sediments containing more than 1 ppm of mercury are classed as "polluted with heavy metals" under EPA guidelines of February, 1971. Such sediments may be disposed of only in the ocean at depths greater than 100 fathoms or on land disposal sites.

For purposes of this report, we are concerned with how contaminated sediments can be disposed of in a landfill without risking potential release of the mercury to air or groundwater or back to the water from which it was removed. The decisions involved are shown in Figure 2.

Partitioning experiments (Appendix A) have shown that mercury is firmly bound to organic sediments and is only partially removed by such powerful complexing agents as cysteine hydrochloride. Further, these sediments are colloidal in nature and difficult to separate from the interstitial water. For these reasons, we do not consider it feasible to remove mercury from the sediment before dumping.

When placed on a landfill, contaminated sediment can lose mercury to the water which runs off or percolates through it. Our partitioning experiments indicate that more mercury tends to be released as the sediment becomes oxidized. Mercury release can be prevented by complexing it in an insoluble form. Either the inorganic sulfides or the long-chain thiols appear suitable for this purpose. As discussed in Section IV, the thiols are somewhat more effective than the sulfides, especially under oxidizing conditions. The conversion of mercury to sulfide has been found to reduce the rate of methylation [6], and it is probable that the thiols may have a similar effect.

It appears advantageous to allow the treating agent to mix with the dredge spoil as it is being moved to a landfill site. Inorganic sulfides can be added as dry powder or as a slurry in water. The thiols can be emulsified in water with the aid of a cationic agent for easy mixing with the spoil. Alternatively, they can be coated on sand which is mixed with the contaminated material.

In some cases it may be more advantageous to apply the treating agents to the spoil after it has been drained and placed on the landfill. The solid treating agents can be plowed or harrowed into the surface, or the emulsion can be sprayed on. In any event, it will be advantageous to provide a well sealed landfill to minimize oxidation and prevent leaching by oxygenated surface waters.

In summary, we can now enumerate a number of actions that should be taken when it is known that the dredge spoil material will contain an excessive concentration of mercury.

First, the extent of the mercury contamination, both horizontally and vertically, should be surveyed. In some cases the contamination can be localized to a small area, with a consequent decrease in handling effort. If the vertical concentration is known, the vertical cut can be planned so that all of the contamination is removed. If it is not possible to remove all of the material, it may be necessary to add a binding material in order to prevent release of mercury to the water from the freshly exposed sediment surface.

The amount of turbidity which results from the dredging should then be estimated. If the sediment contains organic or other natural mercury-binding material, one could expect that some mercury would be released with the turbidity and that there would be both an increase of total mercury in the water column and a redistribution in the sediment. Methods of controlling this turbidity, such as the screening material discussed above, can then be investigated.

The disposal of the spoil material should be planned in advance. If a diked disposal area of landfill is to be used, the overflow and drainage patterns should be checked. If it appears that mercury could be released in the overflow, the spoil material should be treated to bind the mercury.

A decision should then be made as to whether or not the spoils area should be covered, preferably with an impervious fill material. If there is little possibility of leakage to groundwater and if the overflow will not contain much mercury (this might be true if the spoils contain a high percentage of organic material), then it might not be necessary to add a binding agent. However, it might be desirable to cover the area with an impervious seal to prevent volatilization of mercury to the atmosphere and to prevent the penetration of oxygen-rich surface water.

If the dredge spoil is relatively free of contaminants other than mercury, it may be possible to dispose of the material at an approved open-water disposal site if the mercury can be effectively bound. A binding agent in this case should be resistant to oxidation, reduction, hydrolysis, biological action, and dissolved salts, such as chlorides. The binding agent would be mixed with the spoil material en route to the disposal area. A relaxation of the present EPA guidelines would be required.

SECTION VI

FIELD STUDIES

The field studies constituted Phase II of the program and commenced approximately three months after the start of Phase I. The primary purpose of the field investigation was to gain familiarity with site conditions which might influence the effectiveness of physical and chemical binding techniques and dredging operations to remove the contaminated sediment. A second purpose was to obtain sufficient field data at a selected site to design a field project for testing the binding and dredging techniques investigated during Phase I.

The field investigations were divided into two parts, the first being a survey of the regional offices of EPA to obtain data on known mercury-polluted sites.

The information was then compiled and reviewed in order to select one site for an intensive on-site survey. A summary of site information received is given in Table 4. A number of the sites were ruled out for on-site investigations because the environment involved salt water and our laboratory program was limited to the control of mercury in fresh-water environments. In order to hold travel costs to a reasonable level, we also sought a New England area site, if a suitable one could be found.

Three mercury-contaminated areas were reported in New England. The sites were located near Orrington, Maine, on the Penobscot River; near North Dighton, Massachusetts, on the Taunton River; and at Ashland, Massachusetts, near the Sudbury River and Framingham Reservoir No. 2. The Penobscot River and Taunton River sites involved brackish water and, except for a preliminary reconnaissance, were not considered further. The third site in Ashland, Massachusetts was selected.

Ashland, Massachusetts Site Description

The site selected for intensive investigation during Phase II was the Framingham Reservoir No. 2 located in Ashland and Framingham, Massachusetts. The source of mercury to the reservoir has been the Nyanza Chemical Corporation, located approximately 1 mile away in Ashland. Until mid-1970, mercury was discharged to a swampy area near the company, and thence to a small brook which joined the Sudbury River about one-half mile from the company site. The reservoir is formed by impounding the Sudbury River in the Town of Framingham. A general layout showing Nyanza, the brook, the Sudbury River, and the reservoir system is shown in Figures 4 and 5.

Direct releases of mercury to the swamp were discontinued by Nyanza in June, 1970, however, a large quantity of mercury has been found in

Table 4

Summary of Site Data

Site Location	Type of Site	Other Pollution Problems at Site	Hydraulic Conditions--Flow, Seasonal Effects, etc.	Extent of Total Hg in Sediments and Water	Depth of Water at Site
Whitewood Creek, South Dakota	Stream, Hg from mine waste	Cyanide, Arsenic Silt	Average discharge = 25 cfs Maximum " = 100 cfs Minimum " = 18 cfs	In water, 2-8 ppb with normal runoff. In bottom sediment, <1 ppm. In Homestake mining effluent, < 57 ppb.	1 foot
Belle Fourche River, South Dakota	River, Hg from mine waste	Cyanide, Arsenic, Silt	Average discharge = 245 cfs Maximum " = 1500 cfs Minimum " = 0	In water, <16.5 ppb. In bottom sediment, <1.0 ppm.	3 feet
Berry's Crk., New Jersey	Stream, tributary of Hackensack River	Industrial area, other pollution not identified	Not reported	In sediment, 8475 ppm at Ventron outfall, 7440 ppm 100 yards downstream.	Shallow and tidal
Arthur Kill River, New Jersey	River, small creek feeds river from GAF plant	BOD, Color, Silt	Waste effluent from GAF 10-14 million gallons per day (mgd).	In sludge at mouth of creek, 254 ppm.	Shallow in vicinity of sludge deposits
North Fork, Holston River Saltville, Virginia	River, discharge Olin Mathieson Corp.	Calcium chloride	Not reported	Concentration in sediment not known. Mercury discharge prior to August 1970 in excess of 0.58 lb/day.	Not reported
Savannah River, Augusta, Georgia	River, discharge from Olin Mathieson Corp.	High coliforms (25,000 per 100 ml)	Plant flow, 1-3 mgd.	Concentration in sediment not known. Mercury discharge prior to May 1970, 12.9 lb/day.	12 feet

Table 4 (continued)

Site Location	Type of Site	Other Pollution Problems at Site	Hydraulic Conditions--Flow, Seasonal Effects, etc.	Extent of Total Hg in Sediments and Water	Depth of Water at Site
Brunswick Estuary, Brunswick, Georgia	Tidal estuary, discharge from Allied Chem. Corp	High BOD, sludge from pulp and paper mill 1/4 mi. south of Allied outfall	Plant flow, 6-8 mgd	Concentration in sediment not known. Mercury discharge not reported.	3-10 feet Tidal variation
French Broad River, Asheville, North Carolina	River, discharge from sewage treatment plant, includes some mercury	None reported	Treatment plant discharge, 0.2 mgd	Not reported	Not reported
Cold Creek, Alabama	Creek, tributary of Mobile Rivr. Mercury from Stauffer Chemical Corp.	Other chemicals	Flow from chlor-alkali plant 40 gpm.	Discharged 0.15 lbs Hg per day prior to July 1970. Now apparently reduced to 0.07 lb per day.	Cold Creek, 1-2 feet; Mobile River, 5-40 feet.
Tombigbee River, McIntosh, Alabama	Settling basin, discharge to river from Olin Corp.	BOD discharge from Geigy Chemical Co.	Variable	Mercury discharge has been reduced to 0.12 lbs per day.	Settling basin outlet, 2-10 feet; river, 20 feet.
Lower Tenn. River, Muscle Shoals, Alabama	River, discharge from Diamond Shamrock Corp.	Swamp drainage	Variable	Discharged ~ 8.0 lbs per day prior to May 1970. Reduced to ~3.0 lbs per day after July 1970.	6-8 inches at discharge point

Table 4 (continued)

Site Location	Type of Site	Other Pollution Problems at Site	Hydraulic Conditions--Flow, Seasonal Effects, etc.	Extent of Total Hg in Sediments and Water	Depth of Water at Site
Penobscot River, Orrington, Maine	River, discharge from Sobin Chem. Corp.	High BOD in river	Tidal	Mercury discharge reduced to ~0.2 lbs per day. Sediment concentrations near discharge up to 200 ppm.	1-5 feet
Androscoggin River, Rumford, Maine	River, discharge from Oxford Paper Co.	High BOD	Not reported	Mercury concentrations in sediment up to 20 ppm. Location has been shifting in pockets downstream. Plant closed on August 15, 1970.	Variable
Taunton River, Dighton, Mass.	River, discharge from ICI, Inc. Settling lagoon	Dye waste, other heavy metals	Flow from ICI to lagoon, 8 mgd.	Mercury in sediment of upper lagoon, 120-820 ppm; lower lagoon, 10-70 ppm; in mouth of lagoon at river, 10-15 ppm.	
Sudbury River, Ashland, Mass.	Brook, discharging to Sudbury Rvr. Swamp dr. from Nyanza Chem.Corp.	Dye waste, Color	River flow, 0-200 mgd depending on season. Flow controlled at dam. Discharge at brook influenced by runoff after heavy rain.	Sediment in brook had up to 1000 ppm. Concentration in sediments of Sudbury River and Framingham Reservoir 5-160 ppm. Levels in water up to 5 ppb.	Less than 1 foot in brook; 0.5 to 4 feet in river; 4-25 feet in reservoir
Detroit River, Wyandotte, Michigan	River, discharge from Wyandotte Chemical Corp.	Not reported	Major river	Mercury discharge reduced to 0.2-0.5 lbs per day from over 10 lbs per day prior to July 1970. Concentrations in sediment 5-85 ppm within one mile downstream.	1-5 feet near shore

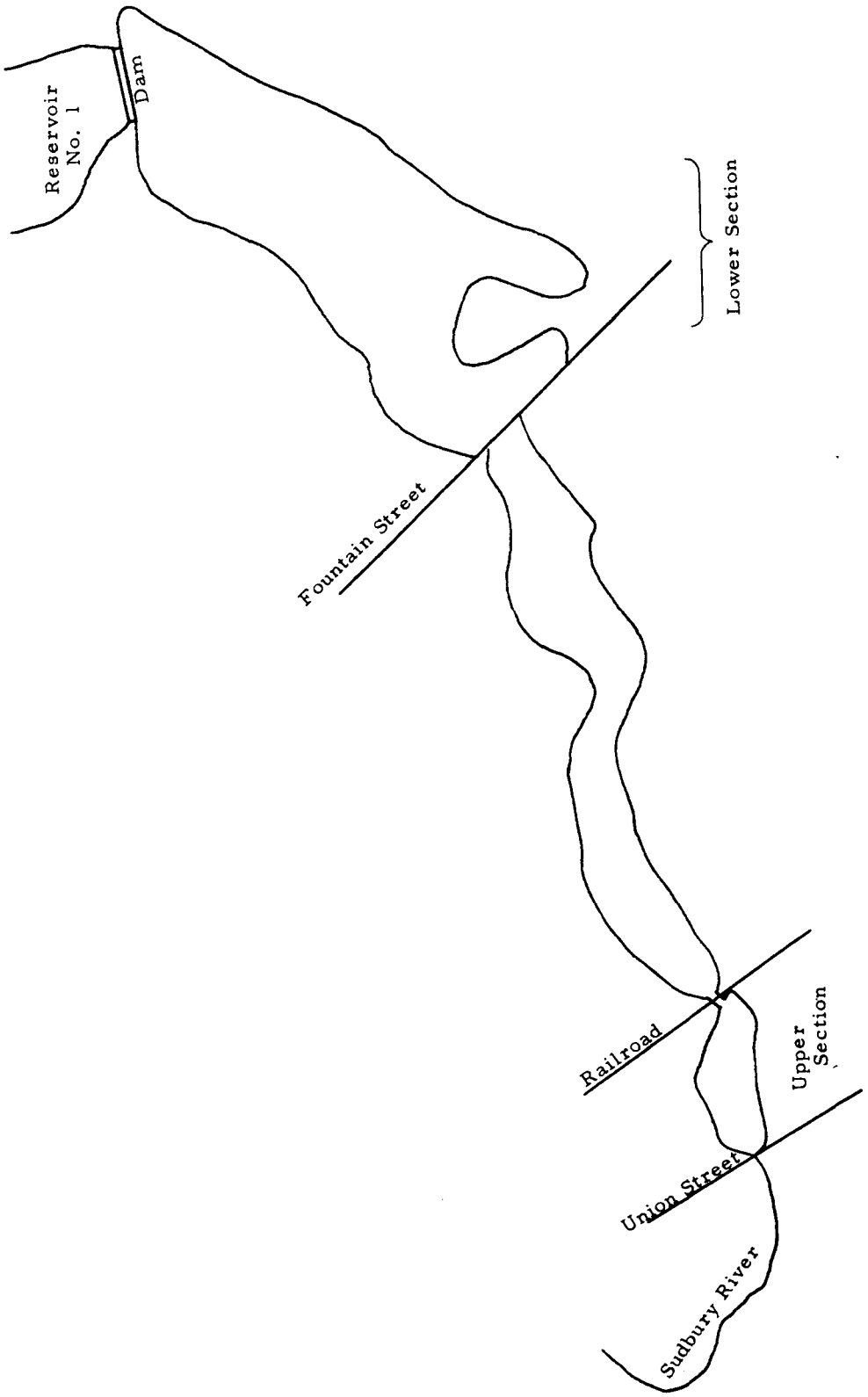


Figure 4. Plan View--Framingham Reservoir No. 2

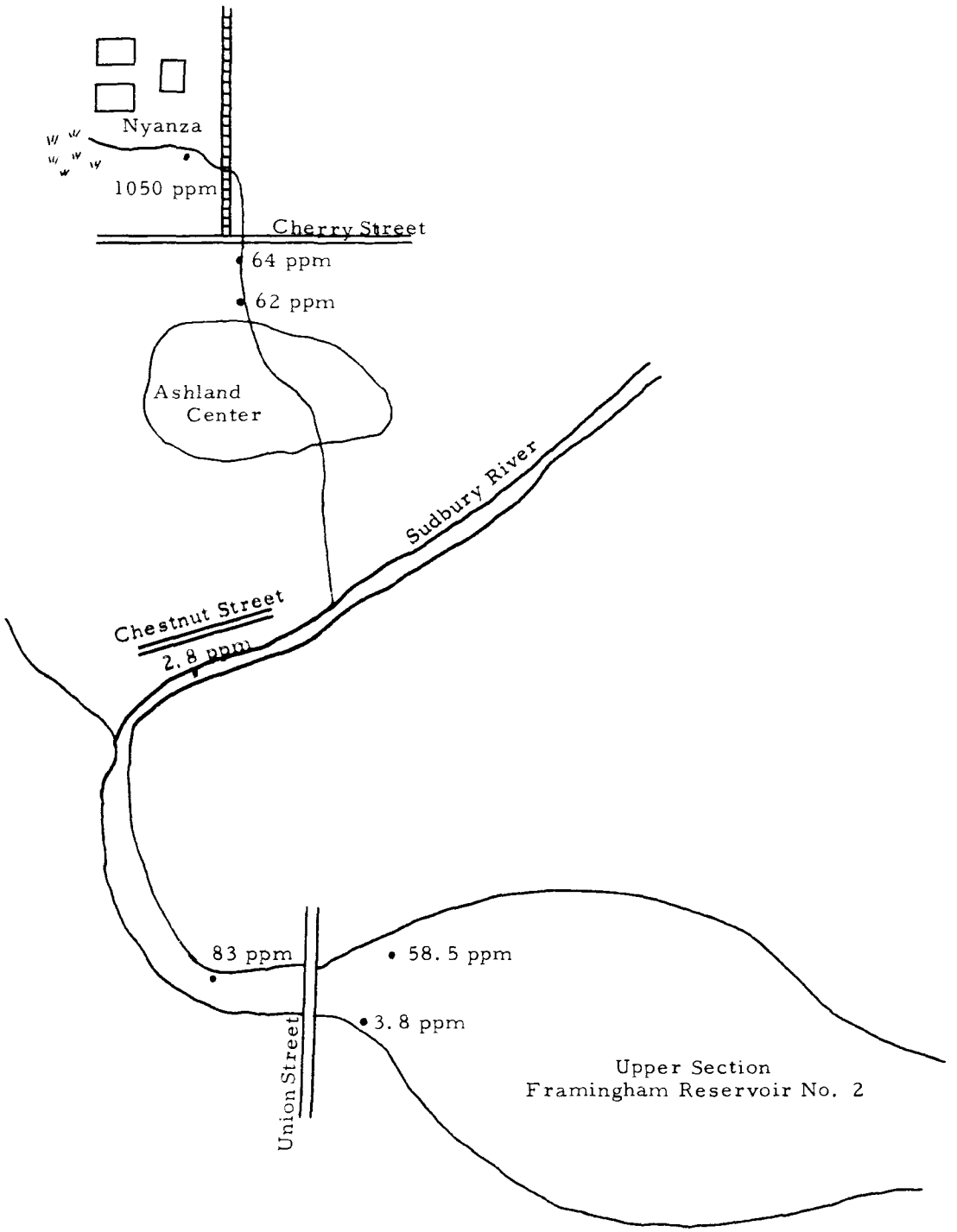


Figure 5. Plan View Showing Nyanza Chemical Corporation Relative to Sudbury River and Framingham Reservoir No. 2

the swamp sediments. Sampling in the brook has indicated that mercury is being released in runoff water from the swamp.

Process Description--Nyanza Chemical Corporation

Nyanza is located at the end of Magunco Road in the Town of Ashland. Mercury is used by the company as a catalyst in the production of anthraquinone compounds, which are used primarily for polyester dyeing. In the process of producing the anthraquinone dyes, approximately 37 lbs of mercury has been added per production batch, with a total of 2400 lbs purchased and consumed in 1970. The amount of mercury used per batch has recently been reduced to about 25 lbs. Nyanza is now employing other measures to remove mercury from the process wastes [7].

In the present production process, mercury, sulfuric acid, and anthraquinone compound are added to a reactor vessel, heated, and stirred. Benzoic acid is added, and the mixture is heated for about three hours. The mixture is then sulfonated by additional heating.

After 24 hours, the contents of the reactor vessel are blown to a water tank, where sodium chloride is added, and the contents are boiled for 24 hours. The mixture at this point is soluble in water. Up to now the mercury has been complexed with the sulfonated anthraquinone, and this step breaks the complex. After boiling, sodium sulfide and carbon black are added. This addition is made in order to remove the mercury at this point as a mercuric sulfide. Until 1970 the mercury was carried through the process with no apparent removal.

The entire mixture is pumped to a filter press, where the liquor is drawn off and pumped back to the reactor vessel. The mercuric sulfide scraped from the presses is stored in drums. Nyanza is presently investigating methods for recovering the mercury from the mercuric sulfide. The mercury concentration in the sulfide cake is about 7000 mg/kg on a dry-weight basis.

At the reactor vessel salt is added to the liquor to precipitate the disulfoanthraquinone. The liquor at this point contains approximately 5 to 15 ppm of mercury. The mixture is then pumped to a filter press, where the liquor is drawn off and pumped to the plant's sewer system. The disulfoanthraquinone is scraped from the filter press and removed for additional processing.

The liquid waste in the sewer system is blended with other liquid wastes from the plant and is treated with either lime or sulfuric acid for pH control. The treated waste is then discharged to a series of four settling basins, with a detention time of approximately 12 hours. After settling, the waste is discharged to the Ashland town sewer system and eventually through the MDC system to the Nut Island treatment plant in Boston Harbor.

Mercury Disposal Prior to June, 1970

Prior to June, 1970, the mercury followed the liquor to the settling basins, receiving only lime treatment for sulfate removal. A small part of the mercury probably settled with the calcium sulfate. The sludge at the bottom of the lagoon was periodically removed and disposed of in a landfill site on the Nyanza property. The liquor was discharged from the settling basin to a small brook which runs through a swampy area near the Nyanza plant.

The brook has been traced from Nyanza through the Town of Ashland to where it joins the Sudbury River. Sediments from the brook bed have been analyzed and show high concentrations of mercury. From measurements in the area around Nyanza it appears that the swampy area has very high concentrations of mercury and that some mercury continues to enter the brook in the drainage water from the swamp.

An accurate accounting has not been made of how much mercury was bought and consumed by Nyanza prior to 1970. If the amount was close to the 2400 lbs consumed in 1970 and if operation had been carried out for even a 10-year period, one would have to assume that up to 24,000 lbs of mercury was deposited in the brook or removed in the sludge to be deposited in a landfill site. Measurements made in the reservoir system indicate that a significant amount of mercury has reached the reservoir.

Reservoir Description

Several large reservoirs are operated by the Boston Area Metropolitan District Commission in the Framingham, Massachusetts region. Reservoir No. 2, encompassing approximately 130 acres, is formed by impounding the Sudbury River in Framingham. Mercury contamination of the sediments has been found in all parts of the reservoir and in Reservoir No. 1 on the other side of the impoundment dam from Reservoir No. 2.

The reservoirs in this area are not presently used for water supply, although they do constitute part of the long-range water supply plan for the Boston area. Water flow in this particular drainage basin is markedly seasonal, varying from a high monthly average of over 250 million gallons per day from March to April, down to 5 to 10 million gallons per day from August through October.

A plan view of Reservoir No. 2 is shown in Figure 4. At the southern end of the reservoir in the Town of Ashland is a small section isolated between a railroad bridge and the Union Street bridge. Mercury levels in the sediments from this section have been found to be as high as 164 ppm (dry-weight basis). Water depth in this seven-acre section

is 4-7 feet. The water current depends on the flow volume and may be less than 0.1 knot from August through September and up to 2 knots in the early spring. In this section of the reservoir, which is approximately 750 feet long by 325 feet wide at the maximum points, the velocity profile is greatest under the Union Street bridge, with a large area of relatively quiescent water on the near left bank area and on the far right bank. The sediment sampling program has shown that these are also the areas of highest mercury concentration. The land area surrounding this section is owned by the Metropolitan District Commission.

Extent of Mercury Contamination

In order to determine the extent of mercury contamination in the reservoir, and also in the area between the reservoir and Nyanza, a field sampling program was designed and executed. Initially, a series of grab samples were taken, commencing in the swamp area near Nyanza property, progressing down the brook through Ashland to the Sudbury River and finally to the reservoir. The grab samples were analyzed for total mercury, and, using the results, a plan was developed for taking sediment cores in the areas of high mercury concentration.

Core samples were taken with 2-foot-long by 1.5-inch-diameter plastic tubes, which were quick-frozen after sampling. Before analyzing, the cores were cut into 2-inch sections and each section was analyzed for total mercury and percentage of moisture in the sample. Knowledge of the sampling location and the vertical section position permitted mapping of the mercury concentrations in both the horizontal and vertical planes. From this data a series of contour maps for the 7-acre section was developed. Each map shows the horizontal distribution of mercury within a 2-inch vertical section. Sufficient data were available for mappings of the 0-2, 2-4, 4-6, and 6-8 inch sections. Several 18-inch cores were also examined to determine the depth of mercury penetration. The contour mappings are presented in Figures 6, 7, 8, and 9. Results of the mercury analyses on grab samples and cores are tabulated in Appendix F.

In addition to the sediment samples analyzed for total mercury, several samples were also analyzed for methylmercury. The methylmercury fraction of the total is on the order of 0.4% (see Appendix A). In addition to the sediment analyses, a number of water samples were taken. Levels of dissolved mercury in the reservoir water are generally lower than the 5 ppb standard for drinking water supplies, although there appear to be seasonal excursions above the limit. As a result of analyzing the water samples in two different ways, we believe that over 50% of the total mercury found in the water is in the form of a soluble organic compound. This possibility is discussed in more detail in Appendix A.

Water samples taken closer to the source of mercury generally have higher concentrations of both total and dissolved mercury than do samples

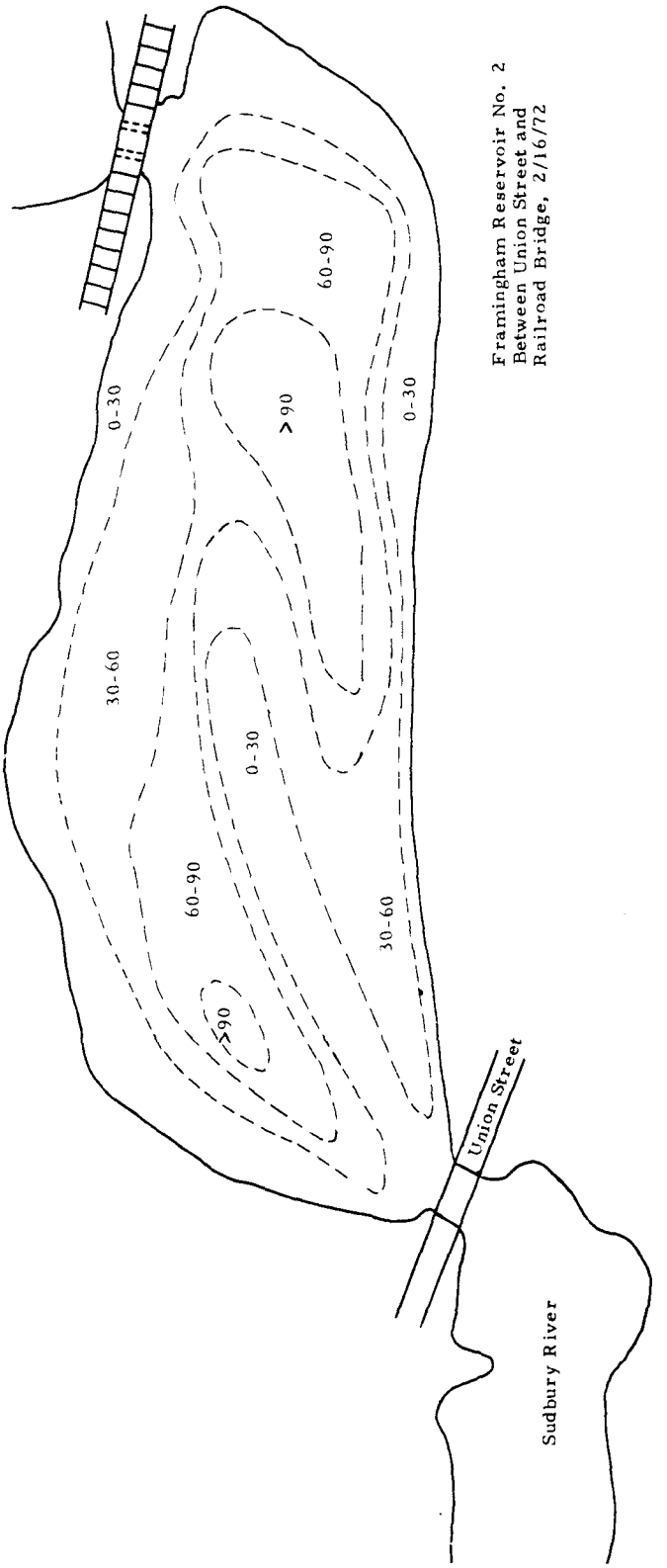


Figure 6. Mercury Contour Mappings (in ppm), 0-2 Inches, Ashland Test Site

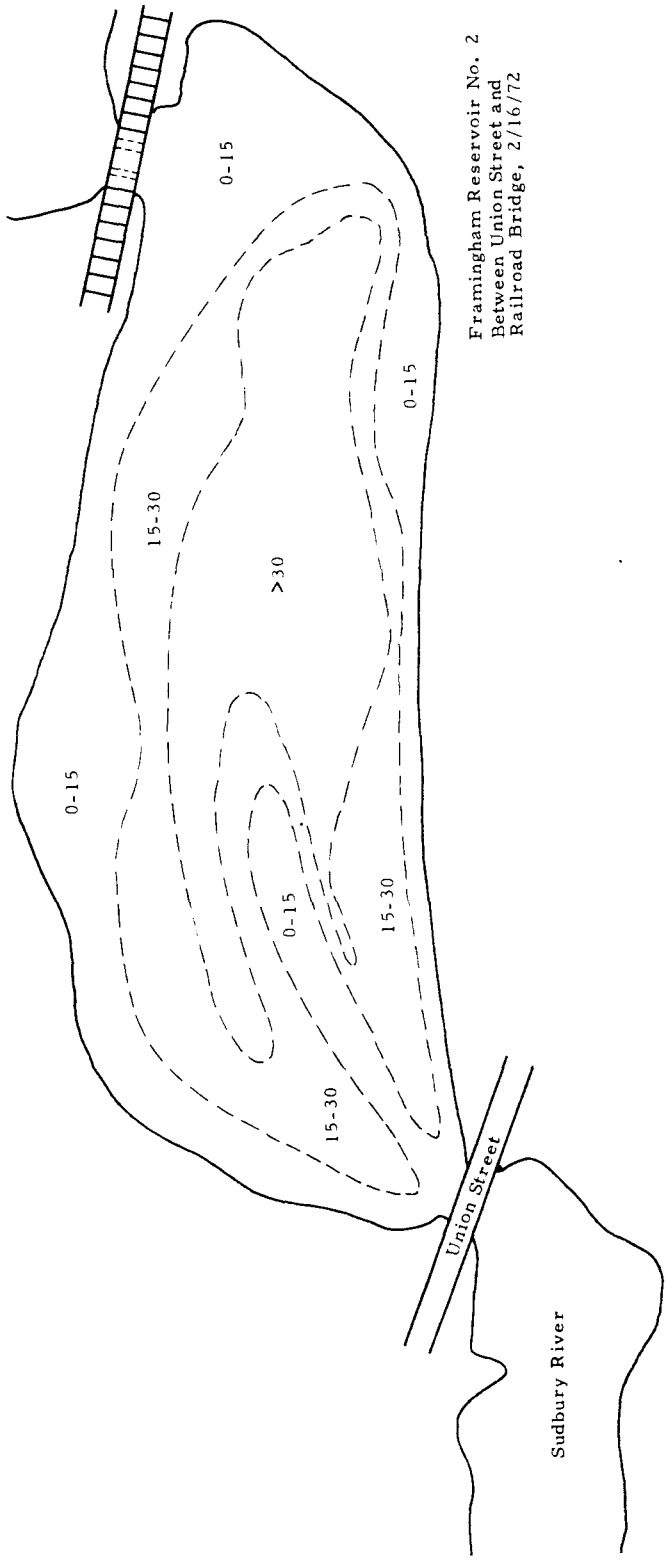


Figure 7. Mercury Contour Mappings (in ppm), 2-4 Inches, Ashland Test Site

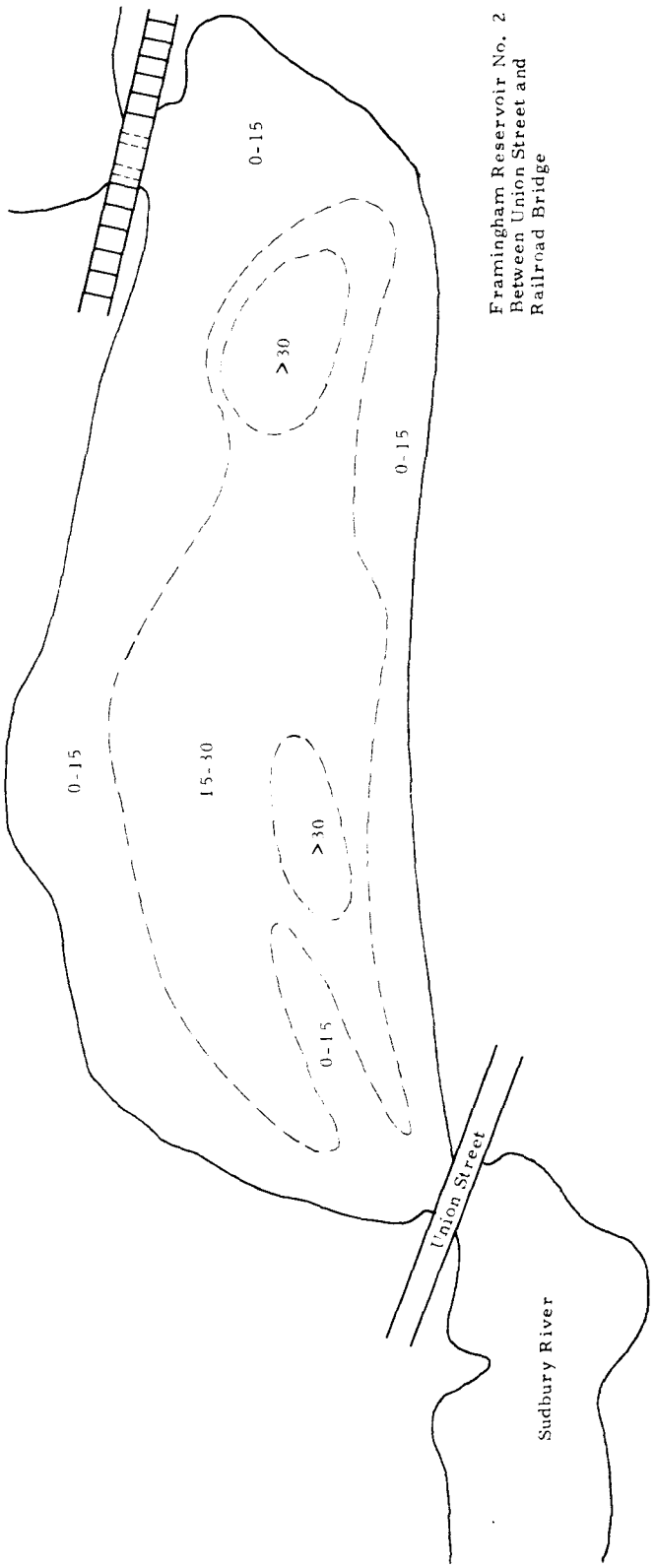


Figure 8. Mercury Contour Mappings (in ppm), 4-6 Inches, Ashland Test Site

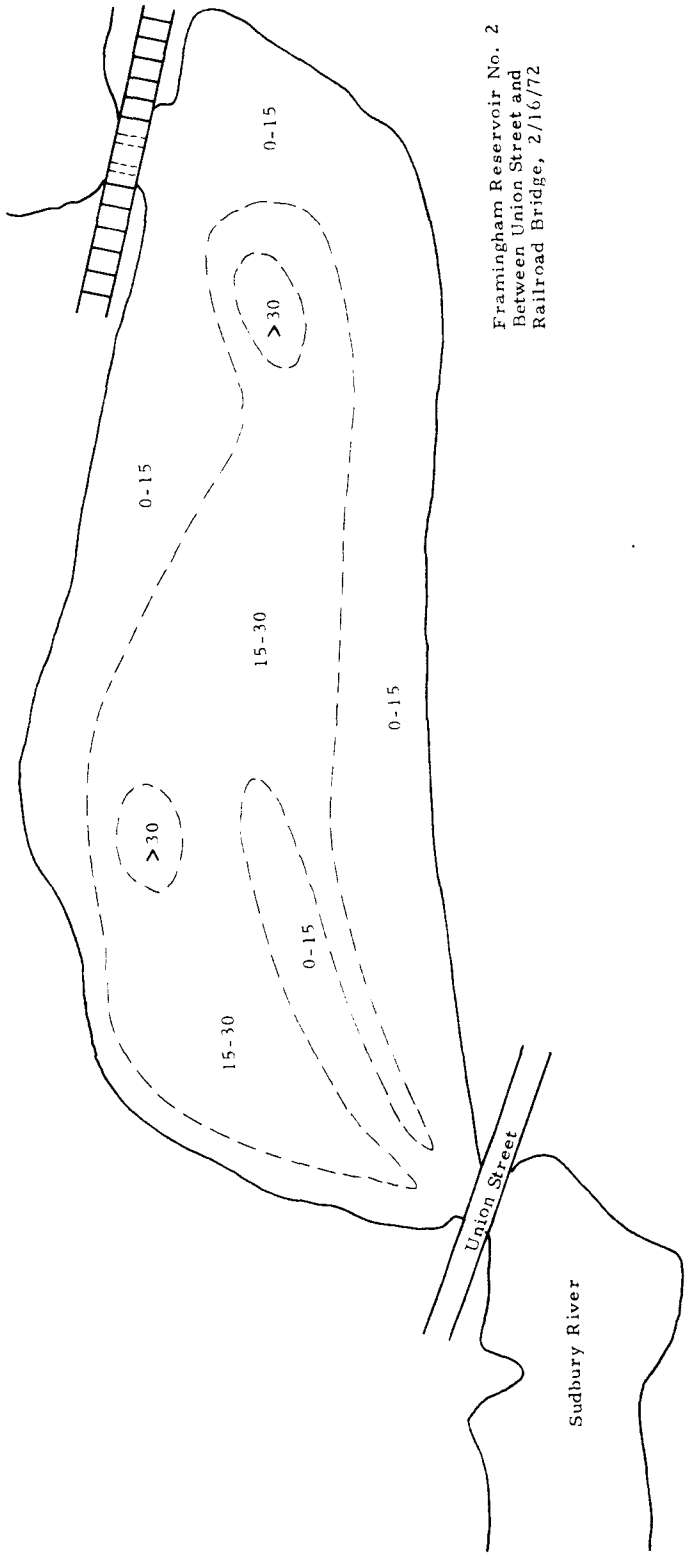


Figure 9. Mercury Contour Mappings (in ppm), 6-8 Inches, Ashland Test Site

taken in the Sudbury River and the reservoir. When runoff is high in the spring season, mercury levels in the brook appear to increase, probably because of increased erosion and leaching in the swamp and brook sediments. Levels in the reservoir tend to decrease after a heavy runoff period, probably because of the increased dilution from the river.

The results of the water analyses are given in Table F-3 of Appendix F. In order to determine whether or not aquatic life in the reservoir was affected by the mercury concentration in the sediment, we requested through the Massachusetts Division of Water Pollution Control that fish samples be taken from the reservoir by the Massachusetts Division of Fish and Game. The results of the first set of analyses are given in Appendix F. In this sampling all fish analyzed had mercury concentrations in excess of 1 ppm.

A later sampling of largemouth bass indicated that fish of this species in excess of 12 inches in length would probably have greater than 6 ppm concentrations of mercury in their tissue. Although water levels of mercury were uniformly low, the fish were accumulating relatively high levels. This latter work was performed by Mr. Thomas Palermo of the Massachusetts Division of Fisheries and Game.

Discussion

From the contour maps it is possible to determine the approximate quantity of mercury in the upper 7-acre section of the reservoir. From grab sample analyses in the remainder of the 130-acre reservoir it is also possible in a much less precise manner to estimate the quantity of mercury in the entire reservoir system.

We have determined the density of the sediment in the upper two inches of the 7-acre section to be about 78.5 lbs per ft^3. The bottom area in that section is 305,000 ft^2. The average Hg concentration on a wet-weight basis is about 20 ppm. From this data we have determined that there is about 80 lbs of Hg in the top two inches. For the two-to-four-inch layer we have estimated a density of about 90 lbs per ft^3 and an average Hg content of about 15 ppm. This gives a result of about 70 lbs of Hg. In the four-to-six-inch layer the sediment density is about 100 lbs per ft^3 and the Hg concentration approximately 8 ppm, giving a mercury content of 40 lbs. Further calculations for the six-to-eight-, eight-to-ten-, and 10-to-12-inch layers give an approximate total quantity of 250 lbs in the 7-acre section.

Grab samples in the remaining 125 acres have indicated that the mercury concentrations in the zero-to-two-inch layer range between nine and 80 ppm by dry weight. Although we have not performed core sampling in this portion of the reservoir, we can estimate on the basis of samples in the upper layer that the overall mercury concentration in this area

is on the order of one-half that in the upper 7-acre section. On this basis, the total quantity of mercury in the 125-acre lower section would be about 2250 lbs and about 2500 lbs in the total 132 acres.

Although we do not know over how long a period Nyanza has been releasing mercury, we do know that in 1970 the company consumed 2400 lbs. If in the previous 10 years a similar annual amount was consumed, a total of 24,000 lbs could have been released to the environment. If only about 2500 lbs can be accounted for in the reservoir sediments, some may have travelled further downstream and some may still be in the swamp adjacent to the company. We have, in fact, found concentrations in this swamp of up to 3500 ppm by dry weight. No analyses of lower river sediments have yet been made.

From our measurements of the mercury concentrations in the brook between Nyanza and the Sudbury River, we have evidence that mercury is continuing to be transported to the reservoir. An examination of Table F-3 of Appendix F shows that turbid samples taken from the drainage area near the Nyanza plant have a high level of mercury associated with the particulate matter in suspension. In the clear water samples from the brook, between 20% and 50% of the total mercury has been in a dissolved form. However, our water samples do not include the sediment particles along the bottom, which by visual observation appear during heavy runoff periods to be moving almost continually downstream. We believe that this bottom shifting may be responsible for a large share of the mercury transport to the reservoir.

We have discussed in Appendix A the conclusion that much of the dissolved mercury coming from the swamp area around Nyanza is probably in the form of a soluble organic compound. Under a separate contract to the Commonwealth of Massachusetts, we are investigating in more detail the circumstances of mercury leaching from the swamp. One additional point can be made about mercury in the brook between Nyanza and the reservoir, i.e., that the dissolved levels of mercury in the water are well diluted when they reach the reservoir. The highest levels of dissolved mercury we have found in the reservoir have been between 5 and 6 ppb during our October measurements. This is a period of low flow, thus we might expect that the total quantity of mercury reaching the reservoir would be highest in the spring, when the flow volume is greater.

Although mercury concentrations in the water of the reservoir are between 1 and 6 ppb, the fish have accumulated a significant amount, as witnessed by the data presented in Table F-4. It is of note that the small bluegill have over 2 ppm of mercury. These fish are bottom feeders, and this indicates that the bluegill may be accumulating mercury from ingestion of bottom material. The high levels of mercury in the largemouth bass, which are predators, indicate that the food chain may also be responsible for increasing mercury concentrations. The contribution of the mercury in the water column to the fish is unknown at this point.

SECTION VII

PROPOSED PILOT FIELD PROGRAM

One of our tasks under Phase II has been to develop a detailed pilot field program at the surveyed site, whereby the techniques of binding and dredging investigated during Phase I could be tested under realistic conditions. The importance of testing these techniques on a pilot scale before attempting a large-scale decontamination cannot be overstated. The laboratory work using aquariums has indicated that several possible methods may be effective in controlling the release of mercury from sediments. However, we have found that it is very difficult to duplicate in the laboratory the physical and chemical conditions existing at the field site.

We believe that the validity of the laboratory results must be substantiated in the field. The proposed pilot program will allow for testing of hydraulic and mechanical dredging techniques, will provide data on treatment of dredge spoils prior to disposal in a landfill site, and will test the effectiveness of complexing agents added to the bottom sediments.

The proposed pilot program should be conducted at the Ashland, Massachusetts site, since this site has been extensively surveyed and mapped over the past year. There is good access to the site over land owned by the Boston Metropolitan District Commission. This agency, which controls the water resources of the area, is quite agreeable to the proposed task.

Test Site Description

At the southern end of Framingham Reservoir No. 2 in the Town of Ashland (see Figure 4), a small section of the reservoir is isolated between a railroad bridge and the Union Street highway bridge. Mercury levels in this section have been mapped during Phase II and are shown in Figures 6, 7, 8, and 9. The water depth in this section, which encompasses an area of 7 acres, is 4-7 feet. Water currents are low, ranging from less than 0.5 knot to about 2 knots during heavy runoff periods. The current is confined generally to a fairly well defined course, leaving several large quiescent areas near the left and right banks.

The area in which the tests would be conducted is approximately 750 feet long by 325 feet wide at the maximum points. The land area surrounding the water, except for the two bridges at either end, is owned by the Boston Metropolitan District Commission. There is good access to the water from several locations along the shore. The bottom sediment material is primarily organic detritus and fine silt to a depth of

10-12 inches, except in the area of higher water velocity extending out from the Union Street bridge, where scouring has uncovered a gravelly base material.

Test Structure

We believe the decontamination tests should be conducted with as little effect as possible on the sediments or water of the reservoir. For this reason, the tests have been designed to be performed in a wooden structure similar to a cofferdam. The components of the wooden structure can be assembled on shore, with final assembly in the water. The test box, when completed, would be a rectangular structure with no bottom and could be floated into place. When ready for testing, it would sit on the bottom, with sides extending about 18 inches above the water surface. Access catwalks can be installed and flow gates provided at both ends to control the flow of water during the tests.

Figure 10 shows a suggested type of construction. The frame would be about 20 feet long and would be assembled using 2 inch x 6 inch uprights every 2 feet. After the frame is assembled, prepainted sheets of marine plywood could be nailed to the frame on both sides with staggered seams. The finished section would be approximately 20 feet long by 7 inches in width. The ends of each section would have a full-length rubber gasket, so that sections could be bolted together and still maintain a good degree of watertight integrity. The seal is not too critical, as there would be little pressure head across the section, and there is little water current in the test areas.

As each section is needed, it can be picked up with a truck crane or rolled into the reservoir and floated to the test location. After the structure is approximately in the right position 1/4-inch sheet steel or aluminum would be bolted to one side of the section to act as a keel to penetrate into the muddy bottom of the reservoir. If needed, bricks or sandbags could be used as added ballast above the keel in order to facilitate maintaining a vertical position in the water. With the proper choice of wood, metal keel, and bricks or sandbags, each section can be made almost neutrally buoyant. After all of the required sections for a test cell (40 x 20 feet) have been floated into position, they can be bolted together and cross supports installed as necessary. The result would be a floating, bottomless box that can be towed about the reservoir as required. Once it is in position, sandbags could be piled on the upper structure, and the cell would sink into place.

Based on the site survey, we would expect the keel plates to sink into the unconsolidated sediments. However, if this does not happen in some locations, the appropriate area can be "jetted" out, using a jet pump along the outside of the keels until the structure sinks into the bottom sediments approximately 12 inches.

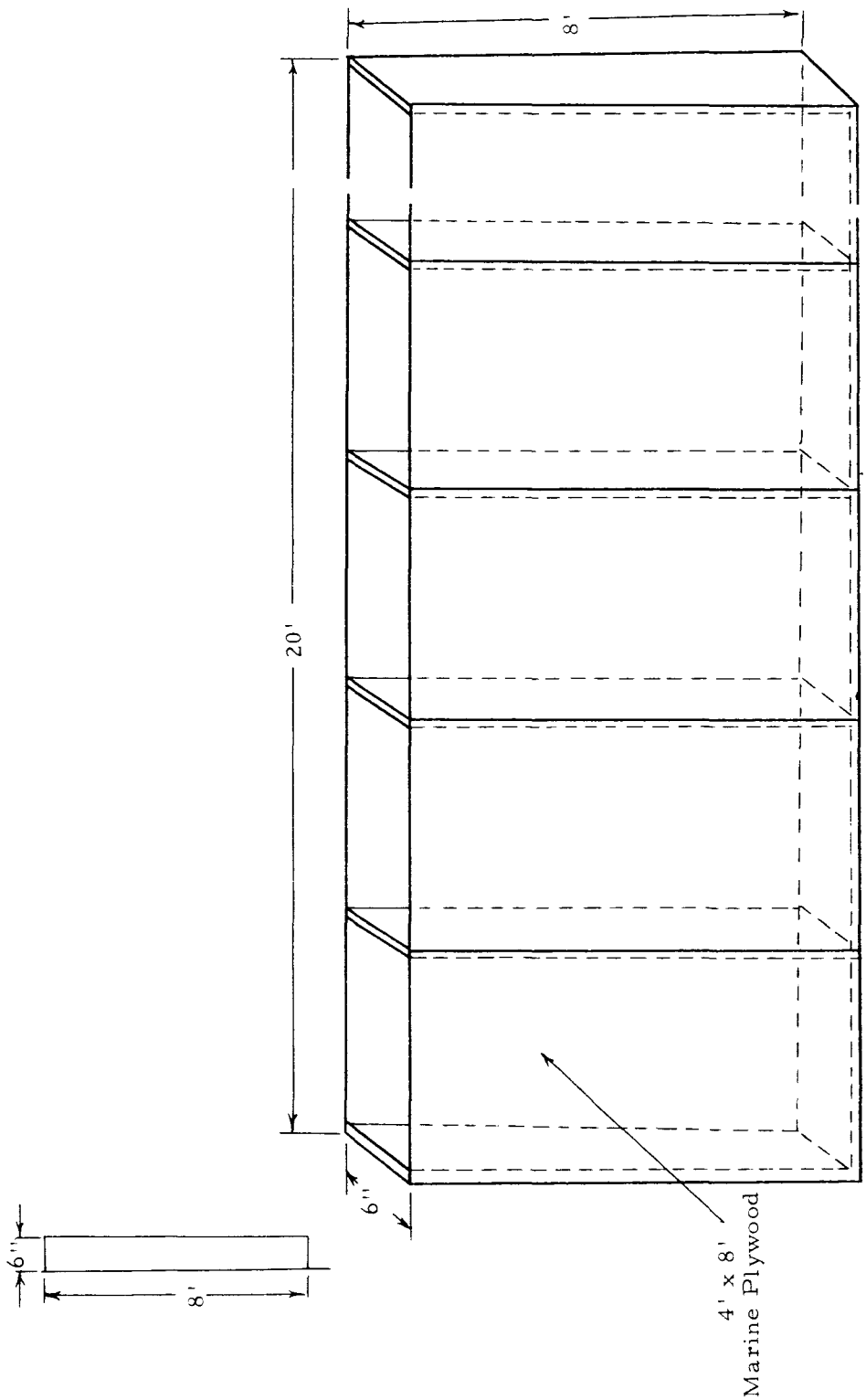


Figure 10. Suggested Frame Construction--Test Structure

An alternative assembly mode would involve the pre-assembly of a section, including keel plate and ballast, on land and then simply picking the section up with a truck crane and lowering it into place. Since the bottom drops off very quickly, the truck crane can remain on shore and, piece by piece, lower sections into place in 6 feet of water. The entire assembly can then be floated anywhere in the reservoir.

We anticipate that there may be some difficulty experienced in refloating the test structure, thus provisions should be made for installing inflatable floats to help break it loose prior to floating the structure to another location.

Dredging Tests

There are two dredging problems to consider in conducting the test program. In some cases we will want to clean the bottom area inside a test cell prior to conducting dredging simulations in an adjacent cell. This would be required in order to determine whether or not there is a noticeable effect on the clean area by adjacent dredging activities. Then there is also the problem of how to conduct the actual dredging simulation.

In most cases of dredging a polluted area, conventional dredging equipment will not be suitable. Unless dredging is required in a navigable waterway, most of the cases we have observed involved lakes, small rivers, and streams where the depth of cut would be confined to less than 2 feet. This will require equipment not normally used for dredging, such as suction trash pumps or equipment used to pump out disposal lagoons or septic tanks. In some cases it may also be possible to use specially designed dragline equipment, although this may cause excessive turbidity.

In this test program the hydraulic removal of sediments can be demonstrated using typical trash pumps of the diaphragm type. Pumps are available using electric, internal combustion, or air drive and can be rented or purchased. Rental costs for a gasoline-driven trash pump are on the order of $350 per month, including hoses. Complete units can be purchased for about $1,000.

The pump would be mounted on a flotation platform (a wooden raft with polystyrene floats), which could be positioned in different locations within the test cell. The discharge lines would be run ashore to several large storage containers. Several dredging conditions could be simulated by allowing some of the discharge to return to the test cell. The test program should include several experiments whereby the dredged material is allowed to settle in the storage containers and the supernatant treated and returned to the reservoir. The temporal behavior of mercury concentrations in the liquid would be monitored during this treat-

ment. Several effective techniques have been developed recently for the treatment of liquid streams from chlor-alkali plants, and these could be tested at this point if desired by EPA.

Tests should also be conducted on the treatment of the settled spoil material to determine the most desirable form of ultimate disposal. It may be necessary to add complexing agents to the spoil before sending it to a landfill site, or it may be possible to dispose of it in an untreated form if the landfill is designed to prevent percolation and leaching.

Tests of Mercury Bonding and Sealing Agents

In the course of our laboratory program, we have evaluated a number of materials to determine their effectiveness in decreasing the rate of release of mercury from the sediments to the water. For purposes of the pilot program, we have considered the following materials:

1. Natural sediments--organic or sandy
2. Inorganic sulfides
3. Organic thiols (mercaptans)
4. Proteinaceous materials, such as hair or feathers

Our findings have indicated that the organic and inorganic sulfides are likely to provide greater overall economy and effectiveness than the natural materials such as peat or proteinaceous substances. In some cases, two materials may be required, such as the use of a layer of sand to stabilize a complexing agent in the sediment. The details of the laboratory evaluations are discussed in Section IV above.

At the field test site we are proposing that tests be conducted on the effectiveness of materials mentioned above in reducing the rate of release of mercury to the water. We expect that the use of fish and possibly freshwater mussels will be required in these tests to indicate the effectiveness of the materials. The freshwater mussels have been used as indicators of pesticide pollution in tests conducted by the Massachusetts Division of Fish and Game, and we feel that they may also be useful as indicators of mercury and other heavy metals in the water. They can be suspended in mesh bags, both on the bottom and above, to indicate the amount of mercury taken up from the water column and from bottom sediments. We expect that tests could be conducted on the uptake rates of these organisms and a statistical base for use in the field programs could be developed. The fish would be needed to indicate if mercury continues to be concentrated through the food chain.

The test fixtures provide four 40 x 20 foot basins for the experimental program. Since the upper sediment surface (4-6 inches) is highly organic

and has a high binding capacity for mercury, one of the test fixtures will be used as a control. Indicator organisms will be added to the test basin. The control test will be run for one month with no flow through the basin. Three samples of each indicator organism will then be withdrawn and tested for mercury. The remaining organisms will then be removed and a net set added. The flow gates will be opened and for one month the basin will be open to the flowthrough of the reservoir. At the end of one month, samples of each indicator will again be taken. The flowthrough test will be run several times at different flow rates. The total reservoir flow can vary from about 5 million gallons per day in late summer to as much as 200 million gallons per day in early spring. We will also be sampling the mercury concentration in the water throughout the test period.

After the control conditions have been established, tests will be run on up to five combinations of sealing and complexing agents. An outline of the proposed plan is shown in Figure 11.

Test Procedures

Using the test structure layout shown in Figure 12, we believe the dredging tests and the sealing and binding tests can be conducted as follows. The procedures are tentative and indicate our present thinking. A final test plan should be drafted during the first two months of the program.

1. Remove by dredging the organic and underlying contaminated sand material in Section B. All removed material is to be deposited in one section of the shore container.

2. Remove by dredging only the organic material in Section A. Deposit material in section of shore container. This will be a simulated dredging operation with gates between Sections A and B open. Effects of the dredging in A will be monitored in both A and B, which is free of contaminated sediment.

3. Concurrent with step 1, control tests will be started in Section C with both inflow and outflow gates closed. The control tests have been described previously. After one month, open inflow and outflow gates in both Sections C and D, and continue control tests.

4. Concurrent with step 3, conduct first sealing and binding agent test in Section D (gates closed). After one month, the control test in Section C will require gates to be open. This will be compatible with test of the binding agent with gates open.

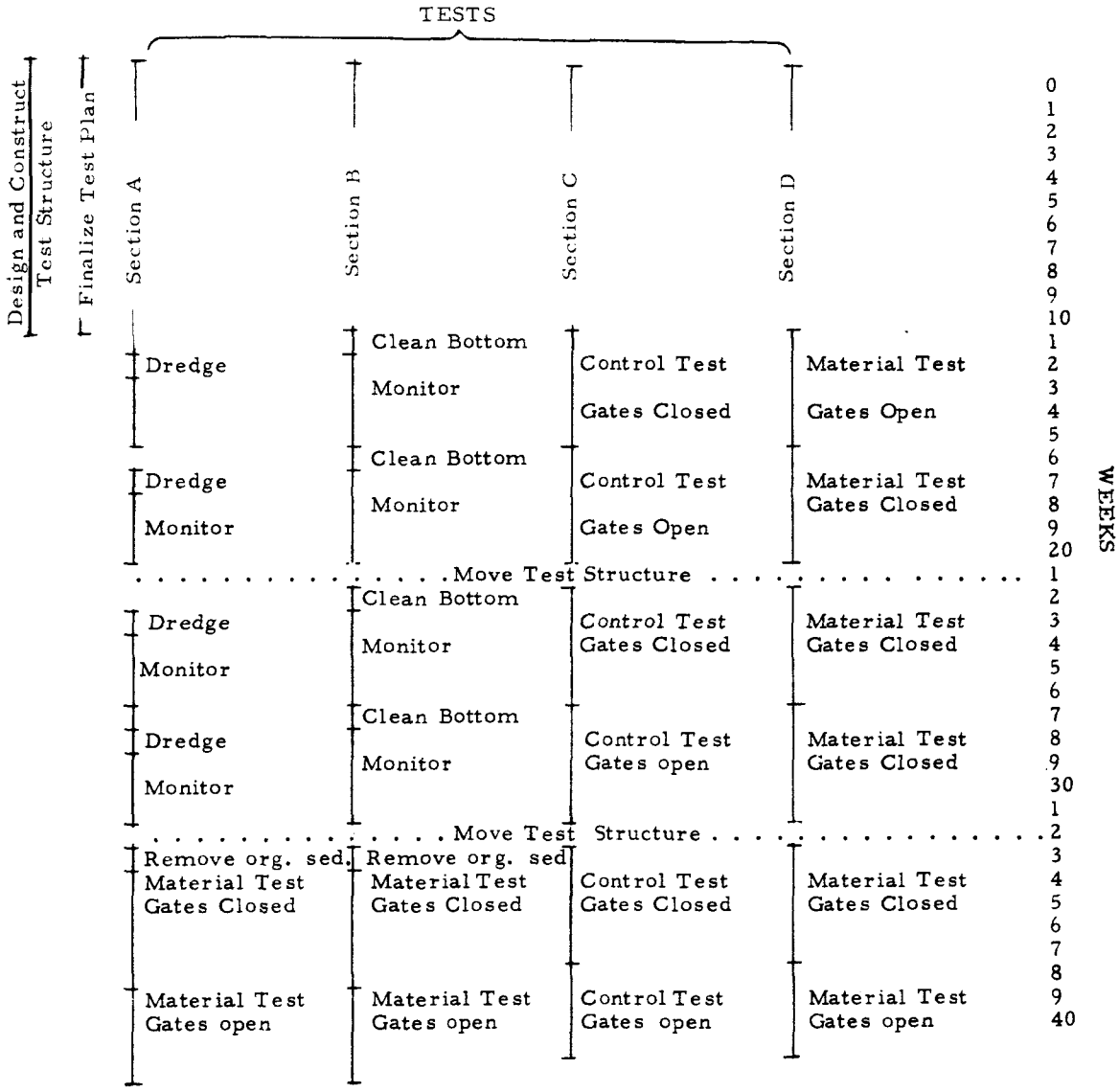


Figure 11. Field Evaluation Test Plan Outline

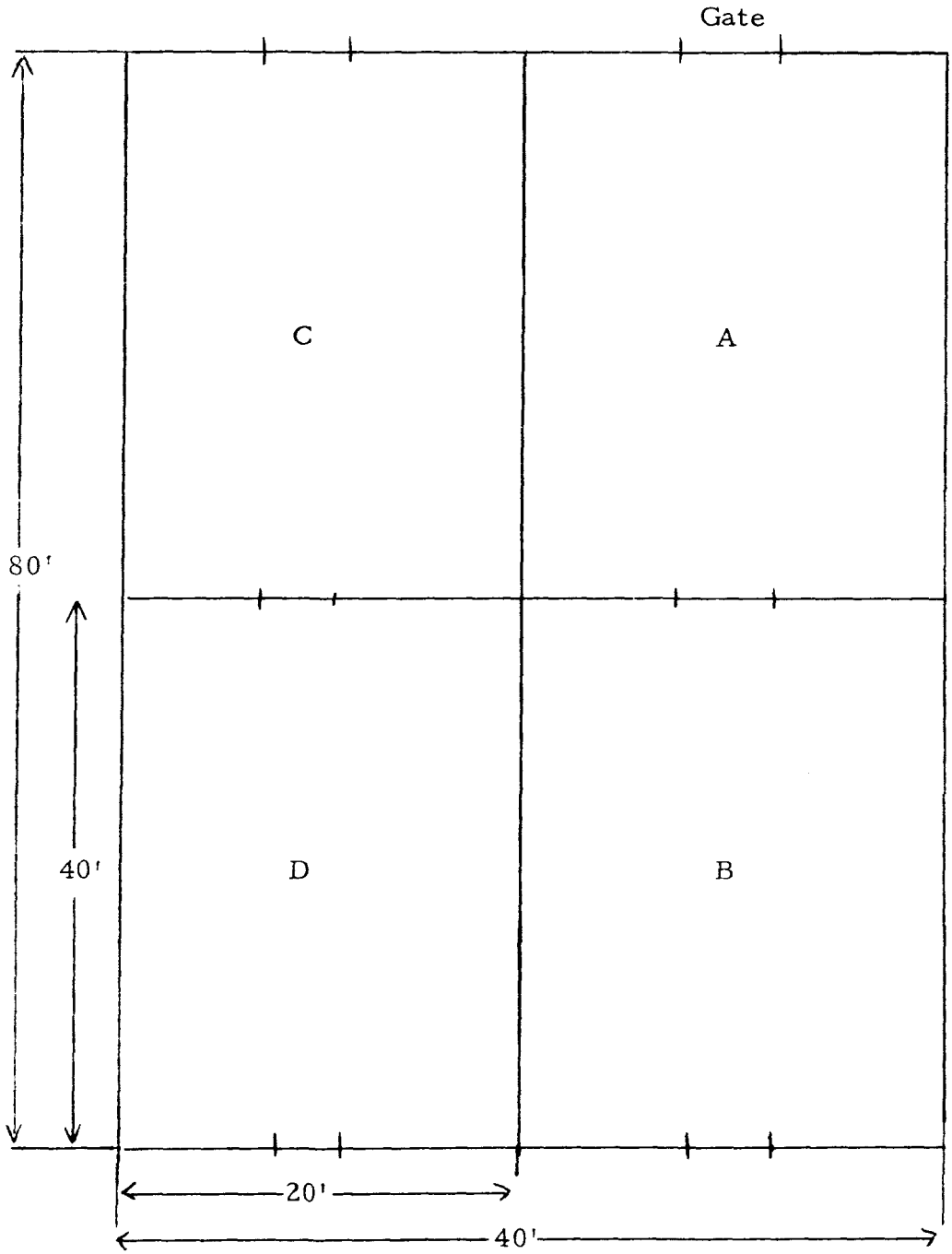


Figure 12. Test Structure Layout

5. Section A, which has had the contaminated organic material removed, can now be used for tests on the effects of dredging a sandy material. The bottom of Section B will be cleaned by skimming to insure the bottom and water column are relatively free of mercury, and then the sandy material in Section A will be removed by dredging and deposited in a section of shore container. Effects of dredging will be monitored in both Sections A and B.

6. Refloat test structure, move to new location, and repeat sequence of tests. Tests will take about two months at this location.

7. Refloat test structure and move to new location. Tests in Sections A and B will be sealing and binding tests on sandy sediment rather than dredging. The organic sediment will be removed prior to commencing the tests.

The above procedure allows for two tests of dredging organic sediments, two tests of dredging sandy sediments, and five tests of sealing and complexing agents: three on organic sediments and two on sandy sediments. The test series will require a period of about six to eight months. If additional tests are required, it may be advisable to add two additional 20 x 40 foot sections rather than extend the time period.

The following list of cover materials to be tested is suggested. The list may be augmented by EPA if desired.

1. One to two inches of clean sand over organic sediment. This material was tested and described as the "Tank D" part of the aquarium experiments (Appendix B).

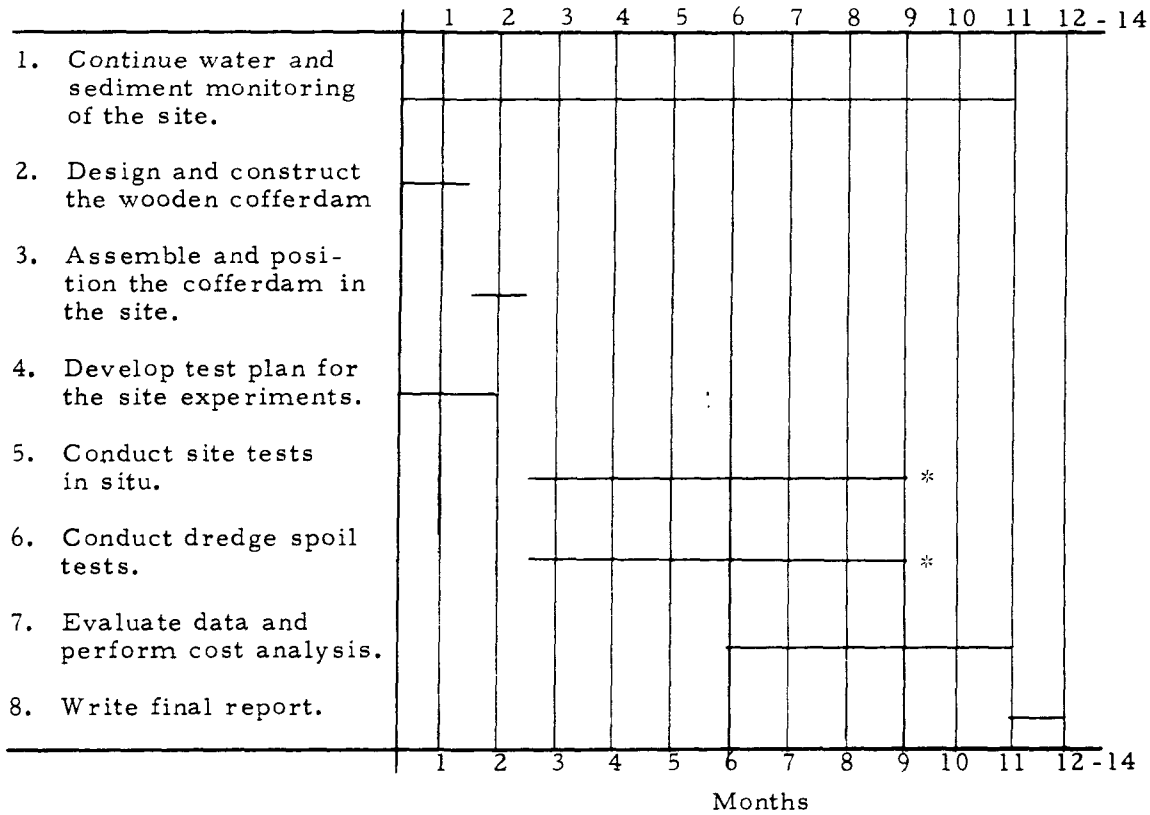
2. A cover of ferrous sulfide or milled pyrite.

3. A material consisting of a long-chain mercaptan on treated sand with and without ground limestone.

4. An organically modified mercaptan or other organic sulfur compound.

Schedule for Field Pilot Program

The field pilot program should be conducted over a 12 to 14 month period. Figure 13 shows a 12-month schedule, which would not allow for any contingencies. We suggest that two additional months should be allowed for this purpose.



*A two-month contingency is allowed at the end of these tests, if required.

Figure 13. Schedule for Field Pilot Program

Monitoring of conditions at the test site should continue throughout the field program. We have been aware of seasonal changes in the mercury levels in the water, and these should be monitored. Although a preliminary design of the cofferdam structure has been presented, this will require finalizing. A time period of 1.5 months is allowed for design and construction. The final assembling and positioning of the cofferdam will take about one month.

While the test structure is being constructed, the final test plans can be prepared; this will take about two months. The actual tests will take about six months, although the two-month contingency period would not likely be required at the end of this period. Data evaluation, cost analysis, and report writing consume the remainder of the time.

Work Summary

1. Continue monitoring mercury concentrations in the sediment and water of Framingham Reservoir No. 2. Establish three stations where bi-weekly samples will be taken over an 11-month period.

2. Design and construct a 40 x 80 foot wood test structure divided into four 20 x 40 foot sections. Each section will have an input and output gate located on the 20-foot side.

3. Assemble and position the test structure at the site.

4. Develop a final test plan for the site experiments, based on the preliminary plans in this proposal.

5. Conduct dredging, sealing, and bonding tests within the test structure.

6. Conduct tests on the binding of mercury in the dredge spoils. These tests will be conducted in a sectioned container located on shore near the test site.

7. Evaluate data from the site experiments and write final report.

SECTION VIII

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SECTION IX

ACKNOWLEDGEMENTS

The support and assistance of the Project Officer, Dr. Curtis C. Harlin, Jr., of the Robert S. Kerr Water Research Center, Environmental Protection Agency, is acknowledged with sincere thanks. In addition, the assistance of Mr. Charles Myers, of the EPA, has been greatly appreciated.

The authors also wish to acknowledge the assistance of Ms. Birgit Foley, Mr. Stephen Greene, and Mr. Thomas Hall for their patience and skill in performing both laboratory and field analytical work.

APPENDIX A

PARTITION COEFFICIENTS

The partition coefficient provides a quantitative measure of the mercury-binding capacity of sediment in the presence of overlying or percolating water. This kind of information is necessary to understand and control the movement of mercury in natural water and soil systems. For the purposes of this report, the partition coefficient will be defined as the equilibrium ratio of mercury concentration in solution to the concentration in the solid. The lower the numerical value of this ratio, the more effective is the mercury-binding action of the sediment.

In this appendix, we describe the experimental methods used for measuring the partition coefficient, the materials studied, and the results obtained both with natural sediments and with chemical additives.

Experimental Procedure

Partition coefficients were measured by placing a few hundred grams of sediment in a quart glass jar and covering it with several hundred milliliters of distilled water. A known amount of mercury was added as a standard solution of $HgCl_2$ or CH_3HgCl, together with any required additives or complexing agents. The jars were tightly covered and placed in an agitator, where they were slowly tumbled (about 10 rpm) for periods of 1 to 7 days at room temperature (24-25°C). Preliminary experiments had shown that such continuous agitation was necessary to approach equilibrium within a reasonable period of time.

Most of the runs were made with 200-300 ml of air in the sample bottle. As a result, most of these equilibrations were made with oxygen-saturated liquid (7-9 ppm of dissolved oxygen). In some runs, especially those made with highly organic sediments, enough reducing material was present to consume all the oxygen in the bottle and reduce the dissolved oxygen to a low value. Dissolved-oxygen measurements identify this situation. In other cases it was desirable to conduct the equilibration with a minimum of oxygen present. For these runs, the water used was freshly boiled and cooled to room temperature. The sample bottle was then filled to the brim with this oxygen-free water (the inclusion of 5-10 ml of air was unavoidable with the type of screw-cap we used), and the bottle was sealed. Runs made in this way are referred to as "low oxygen" in the discussion of the data.

After equilibration, dissolved oxygen and pH were measured with immersion electrodes, and the samples were roughly filtered through paper on a Buchner funnel to remove the bulk of the sediment. The filtrates were again filtered through a 0.45 micron membrane filter in order to remove fine particles and to ensure that only mercury in true solution was

measured. The final filtrates were acidified with 1 ml of HNO_3 in order to hold the mercury in solution while awaiting analysis.

The samples were analyzed for mercury with a Coleman Model 50 flameless atomic absorption analyzer, using the Hatch and Ott procedure. We found that solutions containing less than about 0.001 ppm of mercury were difficult to analyze precisely with this instrument. Most of the samples below this concentration were therefore analyzed by Jarrell-Ash, using a high-sensitivity atomic absorption apparatus with a hydrogen flame. Analyses made by this high-sensitivity method are marked with an asterisk in the following tables.

All sediment samples and all solutions containing methylmercuric chloride were refluxed with a mixture of nitric and sulfuric acids prior to analysis in order to destroy organic matter and bring the mercury into solution as Hg^{++}. Details of the analytical methods are given in Appendix E.

The accuracy of the analyses was checked by adding the total mercury found in the sediment to that in the filtrate and comparing this figure to the known amount of mercury originally added. In most cases, the mercury balance checked within $\pm$ 15%. At relatively low concentrations ($\sim$10 ppm in the sediment) a check of $\pm$ 25% was considered acceptable. If the mercury balance was outside these limits, the analysis was repeated.

The mercury content found by analysis of the wet sediments was converted to the dry basis by measuring and correcting for the moisture content. In a few cases, the analysis was also corrected by subtracting the mercury content of the solution contained in the pores of the wet solid. In all but a few runs, however, this latter correction was negligible in comparison to experimental error.

The results were expressed as the partition coefficient:

$$K = \frac{\text{ppm Hg in solution}}{\text{ppm Hg in dry solid}}$$

The values obtained in this work ranged from about 1 to about 10^{-8}. The latter value represents the limit of sensitivity of the analytical method, using the Jarrell-Ash high-sensitivity atomic absorption apparatus.

Description of Materials Used

Acton Sand

This sample was obtained from Nagog Pond, a municipal reservoir in Acton, Massachusetts. It consists largely of a siliceous sand with a minor proportion of very fine clay or silt. The material retains about

27% of water when allowed to settle and drain, and 9.3% of moisture when dewatered on a suction filter. The loss on ignition is 0.8%, which places an upper limit on the content of organic matter. A part of this loss may be due to removal of bound water from the clay fraction.

The sample has a pH of about 6.5 and contains no measurable mercury. It appears to contain some ferrous iron, as indicated by the fact that it becomes covered with a yellowish layer (probably ferric hydroxide) when a water-covered sample is allowed to stand in air.

Runs made with this sediment are identified by the prefix "A" to the run number.

Acton Peat

This material is a black, fibrous sediment obtained from a different part of Nagog Pond in the vicinity of a wooded shoreline. It is thought to consist largely of decomposed leaves from deciduous trees, and it contains 79% of water in the drained condition and 74.5% when vacuum filtered. The loss on ignition is 44.3%. It has a pH of 5.4 and a mercury content of 0.342 ppm (dry basis).

Runs made with this sediment are identified by the prefix "B" to the run number.

Georgia Kaolin

This was a commercial pure kaolin clay (Pioneer Brand, Georgia Kaolin Co., Dry Branch, Georgia), sold for use in ceramic work. The pH was about 4.6 and the loss on ignition about 16%. This loss is considered to be mainly the combined water of the clay material.

This clay was considered to be a relatively pure representative of a mineral commonly found in bottom sediments. Because of its low natural affinity for mercury, it was used mainly as a substrate for testing various chemical additives.

Runs made with this clay are identified by the prefix "C."

Ground Silica

A sample of ground silica (about 240 mesh) was obtained from Fisher Scientific Company. This material may be representative of another common constituent of sediments. In Sweden, ground silica has been proposed as a sealant for contaminated sediments.

Runs made with this material are identified by the prefix "S."

Chicken Feathers

A sample of wet chicken feathers was obtained from a local farm and stored frozen until used. Feathers are similar in composition to various animal proteins, such as wool and hair, which contain relatively large amounts of the thiol amino acid cysteine.

Runs made with these feathers are identified by the prefix "CF."

Ashland Sediment

This sediment was collected from the upper basin of Framingham Reservoir No. 2, located in Ashland, Massachusetts. The reservoir is downstream from a dye manufacturing plant which uses mercury catalysts in the production of anthraquinone sulfonic acids. Until June, 1971, the mercury-containing waste solutions from this process were discharged into a swamp and a tributary stream. Although the discharge has been stopped, the sediments in the reservoir contain mercury in amounts from 4 to over 100 ppm on the dry basis.

Two samples were used for partitioning and aquarium studies--one collected in October, 1971 and one collected in December of the same year. Both were black, highly organic, and gave evidence of chemical and industrial contamination, as shown by free oily material and colored water-extractable materials. Through the cooperation of Mr. James Longbottom of the Environmental Protection Agency, Cincinnati, we have obtained analyses of these sediments for methylmercury. The results of these and other analyses are as follows:

	October, 1971	December, 1972
Total Hg (dry basis)	31.8 ppm	100.5 ppm
Methyl Hg (dry basis)	0.125 ppm	0.428 ppm
Percentage of total Hg as methyl	0.39%	0.43%
pH	---	7.2
Moisture	---	65%
Loss on ignition	---	16%

When acidified with dilute H_2SO_4, these sediments gave off a strong odor of hydrogen sulfide. This is probably due to the presence of FeS.

Runs made with these sediments are identified by the prefix "ASH."

Climax Pyrite

This material was obtained from the Climax Molybdenum Co. and is produced as a by-product of their milling operations at Climax, Colorado. A typical analysis is as follows:

Chemical Analysis	In Percentage Weight (dry basis)
Sulfur	51.89
Iron	44.94
Insolubles	2.80
Copper	0.05
Lead	0.05
Zinc	0.23
Arsenic	0.01
Selenium	0.002
Tellurium	0.001
Phosphorus	0.006

Screen Size	Weight (percent)
Plus 35 mesh	0.1
Plus 100 mesh	38.0
Plus 200 mesh	46.0
Plus 325 mesh	12.0
Minus 325 mesh	4.0

This pyrite was shipped to us with about 8% moisture. Before use, it was washed with strong HCl, followed by acetone, and then it was dried. This treatment was intended to remove possible oxidized layers ($Fe(OH)_3$) and possible residues of flotation reagents from the surface.

Since the coarse powder as received was found to be relatively unreactive, some later runs were made with the above material, which was hand ground in a mortar. Other experiments were conducted with pyrite which had been fired in a crucible to partially decompose it to FeS. This material was also hand ground. The screen analyses of these hand-ground materials were:

Screen Size	Pyrite	Fired Pyrite
Plus 120 mesh	24.2%	6.4%
Minus 120 plus 200 mesh	32.4%	27.5%
Minus 200 mesh	43.7%	65.7%

Some later tests were made with pyrite which had been mechanically milled with alumina balls until it all passed through a 325-mesh screen.

The cost of this pyrite is $3.80 per ton at Climax, Colorado, before loading. The cost of shipping to eastern points, however, is expected

to be in the range of $70 to $100 per ton. It would therefore be advisable to locate a source of pyrite as near to the point of use as possible.

Miscellaneous Materials

Other materials used in this work were commercial products or laboratory reagent chemicals obtained from local sources.

Rate of Equilibration

The rate of equilibration was checked by agitating samples of Acton sand with various concentrations of $HgCl_2$ for periods of 1, 2, 4, and 7 days. When equilibrium is attained, the concentration of mercury in solution should no longer decrease with time. Figure A-1 shows the results obtained with a mercury concentration of 412 ppm based on the dry sediment. The concentration of mercury in solution changes rapidly for 2 days and then rather slowly up to 7 days. We have considered the 7-day point to represent substantial equilibrium, since the change after the second day is probably within the limits of analytical accuracy. In order to check this point, we performed a reverse experiment in which a mercury-saturated sediment was equilibrated with pure water. If equilibrium is being attained, the concentration of mercury in solution should reach the same level in this experiment as in the previous experiment. The point marked "x" in Figure A-1 shows that after 11 days the reverse equilibration attained only about 40% of the concentration of the 7-day point. Again, this observation must be tempered by considerations of analytical accuracy. It appears, however, that the true equilibrium is reached very slowly in this case and lies between 0.2 and 0.5 ppm of Hg^{++} in solution. The slow approach to equilibrium is in agreement with the results of Malcolm and Kennedy [2], who find that ion-exchange equilibria in coarse sediments may take several weeks to reach substantial completion.

Some results obtained at lower concentrations of mercury are shown in Figure A-2. At 137 ppm of mercury, the results are similar to those at 412 ppm, except that the 7-day point is somewhat higher than the 2-day point. (The 4-day points on these samples were rejected because of procedural problems.) The difference, however, is comparable to analytical error.

At 41.2 ppm, the equilibrium appears to have been reached by the first day, and the readings increase regularly thereafter. The increase, however, is again comparable to analytical error.

The two reverse equilibration runs at 11 days (points marked with "R" on Figure A-2), show an increase in mercury concentration. We subsequently found that this sediment is very sensitive to aging in the presence of air. When aged, the sediment loses a part of its mercury-binding capacity, probably due to the oxidation of sulfides contained in

Figure A-1. Approach to Equilibrium for a Sandy Clay with Continuous Agitation

Figure A-2. Approach to Equilibrium for a Sandy Clay with Continuous Agitation

the freshly dug sediment. The rise in mercury concentration at 11 days is probably due to oxidation of the sediment by prolonged agitation with air-saturated solution.

Similar experiments with Acton peat and with Georgia kaolin indicated that equilibrium was rapidly attained and was substantially complete in 7 days. This period of time was therefore adopted as a standard length of run for all materials.

There is some evidence, however, that a 7-day run does not produce equilibrium in all cases. In the case of coarse pyrite, the concentration appears to be limited by reaction rate rather than by equilibrium. This question is further discussed below.

Discussion of Results

Acton Sediments

Partition coefficients measured for Acton sand and Acton peat are summarized in Table A-1. The first five runs of this table show that the partition coefficient increases from around 4×10^{-4} at the lower concentrations to 1.3×10^{-3} at 412 ppm in the dry sediment. The increase in value with concentration shows that several different absorption mechanisms are active in this complex mixture, and the stronger binding sites are the first to become saturated.

Run A-42 was made with low oxygen and shows little difference from run A-20.

Further work with this sediment showed that its mercury-binding capacity is diminished on storage, as shown by run A-36 with sand which had been stored in an open tub in the laboratory for 5 weeks after digging. The effect is even more marked if the aged sand is allowed to become completely dry, as shown in runs A-37 through A-39. In these runs, also, there is an increase in partition coefficient with increasing mercury concentration.

Further experiment showed that, when the fresh sand was acidified with dilute H_2SO_4, a distinct odor of H_2 was given off. This was probably due to the decomposition of a trace of FeS, since the sample had already been observed to contain considerable iron. When the dry sand was acidified, however, no trace of H_2S was detectable. This indicates that the FeS had been lost on standing, probably by oxidation to an iron sulfate. This loss of FeS would account for the loss of mercury-binding ability in the aged or dried sand.

Following these experiments, all sediment samples were stored in closed barrels and covered with several inches of water in order to retard oxidation as much as possible.

Table A-1

Partition Coefficients for Acton Sediments with Mercuric Chloride at 24-25°C

Run No.	Time (days)	Description	Mercury Conc. (ppm) Dry Sediment	Mercury Conc. (ppm) Water	$K = \frac{[Hg^{++}]_{H_2O}}{[Hg^{++}]_{sed.}}$	pH	Dissolved Oxygen (ppm)
A-25	6	Acton sand (fresh)	13.7	.0052	3.8×10^{-4}	6.6	4
A-27	6	Acton sand (fresh)	13.7	.004	2.9×10^{-4}	6.6	5
A-24	7	Acton sand (fresh)	41.2	.024	5.8×10^{-4}	6.6	3
A-20	7	Acton sand (fresh)	137	.048	3.5×10^{-4}	6.6	---
A-16	7	Acton sand (fresh)	412	0.52	1.3×10^{-3}	6.2	---
A-42	6	Fresh sand low O_2	137	.045	3.3×10^{-4}	6.2	0.0
A-36	7	Aged sand (5 weeks)	258	10.0	.037	5.7	6.5
A-37	7	Aged and dried sand	244	33.8	0.14	6.0	5
A-38	7	Aged and dried sand	100	0.42	.042	6.2	4
A-39	7	Aged and dried sand	30	.046	.014	6.4	3.5
B-3	4	Acton peat (fresh)	1430	<.0002*	$< 1.4 \times 10^{-7}$	4.9	0.0
B-4	7	Acton peat (fresh)	1430	<.00002*	$< 1.4 \times 10^{-8}$	5.2	0.0
B-5	7	Acton peat (fresh)	476	<.0002*	$< 5.3 \times 10^{-7}$	5.3	0.0
B-6	7	Acton peat (fresh)	2670	.0044*	1.65×10^{-6}	5.1	0.0
B-7	4	Acton peat (fresh)	2670	.074	2.8×10^{-5}	4.8	1.0
B-8	2	Acton peat (fresh)	2670	.062	2.3×10^{-5}	5.0	1.0

Table A-1 (continued)

Run No.	Time (days)	Description	Mercury Conc. (ppm)		$K = \frac{[Hg^{++}]_{H_2O}}{[Hg^{++}]_{sed.}}$	pH	Dissolved Oxygen (ppm)
			Dry Sediment	Water			
B-9	7	Acton peat (fresh)	8000	.192	2.4×10^{-5}	4.7	0.0
B-10	7	Acton peat (fresh) low O_2	2670	.0258	9.7×10^{-6}	5.1	0.0
B-18	7	Acton peat Aged 2 months	1335	.0031	2.3×10^{-6}	4.8	0.6
B-21	7	Fresh peat, 3 g cysteine HCl	1320	8.8	6.7×10^{-3}	4.1	0.6
B-22	7	Fresh peat 3 g thiourea	1365	.044	3.2×10^{-5}	5.4	0.4
B-23	7	Fresh peat 3 g $Na_2S_2O_3$	890	.09	1.0×10^{-4}	5.8	0.5

*High-sensitivity analyses by Jarrell-Ash Division.

Runs B-3 through B-5 were made with Acton peat at mercury levels up to 1430 ppm. In no case was any mercury detectable in the filtrates, although the detection limit for run B-4 (as reported by Jarrell-Ash) was .00002 ppm. These results lead to a partition coefficient of less than 1.4×10^{-8} for this run. In the case of run B-3, a low value was reached in only 4 days, indicating that this sediment approaches equilibrium even more rapidly than the Acton sand.

Runs B-6 through B-9 indicate that the partition coefficient increases as the mercury content is raised to 8000 ppm. This again indicates that this sediment contains several types of binding sites.

It is interesting to note that, although no special precautions were taken to exclude air, little or no dissolved oxygen was found in the overlying liquid in the above runs. We attribute this to the chemical oxygen demand of this highly reduced sediment. The oxygen is probably consumed by reduced iron species, such as $Fe(OH)_2$ and FeS. This question is further discussed in Appendix C, where it is shown that the dissolved oxygen can be reduced to low values by this sediment within 10 or 15 minutes.

Run B-10, with low oxygen, was substantially equivalent to runs B-6 and B-7 made in the presence of 2-300 ml or air. This indicates that a considerable amount of oxygen can be consumed by this sediment without impairing its mercury-binding capacity. When a sample of this peat was aged in air for two months. however, the partition coefficient increased by about two orders of magnitude, as shown by run B-18. If such a sediment were dredged up and placed in a landfill, we would expect mercury to be released as the spoil became permeated with oxygen-rich surface waters.

Further experiments showed that the Acton peat gave off a strong odor of H_2S when acidified with dilute H_2SO_4, indicating an even higher FeS content than the sandy sediment from the same site. The presence of iron was confirmed by precipitating $Fe(OH)_3$ from the acid extract. The excellent mercury-binding capacity of this sediment is probably due to its sulfide content, together with the anoxic conditions maintained by its high biochemical oxygen demand.

The ferrous sulfide in these sediment probably originates from the biochemical reduction of sulfate ions in the presence of iron by the organic materials. This conclusion is in agreement with the results of Tuttle et al. [8], who have found that acid mine drainage (essentially ferric sulfate) can be reduced to FeS by heterotrophic bacteria with sawdust as the only nutrient. This natural scavenging mechanism may provide a powerful tool for the control of mercury in contaminated waters.

We were unsuccessful in obtaining quantitative analyses for sulfur as sulfide in the Acton sediments, but such an analysis is obviously of

major importance in assessing the natural binding capacity of sediments. Sulfide analyses should be obtained as a part of any large-scale operation.

Runs B-21 through B-23 of Table A-1 show the results of adding water-soluble mercury-complexing agents to contaminated Acton peat. The object of these experiments was to bring the mercury into solution so that is could be removed from the sediment. These results relate to the problem of trying to decontaminate dredge spoil before damping.

Of the additives tries, cysteine hydrochloride (run B-21) was the most effective in solubilizing mercury. Even in this case, however, over 99% of the mercury would be bound to the sediment in equilibrium with an equal weight of water. Thiourea and sodium thiosulfate were even less effective. The colloidal nature of these peaty sediments is such that they are not readily amenable to washing with water. These results indicate that it is probably not practical to remove mercury from spoil by this method, even if cysteine or similar complexing agents were available in sufficient quantities.

Kaolin Clay and Silica

Results of these materials are shown in Table A-2. Runs C-1 through C-14 were made with straight clay containing no additives. The mercury analyses on the sediment were corrected where necessary for the mercury contained in the pore water of the moist filter cake. The results show that the Hg concentration in the clay increases with liquid concentrations up to a value of 80 or 90 ppm. This maximum value is reached at a liquid concentration of 1 to 6 ppm, and further increase of the liquid concentration to about 166 ppm produces no further increase in the sediment concentration. This kind of result would be expected if the clay had a limited ion-exchange capacity which become saturated at these relatively low concentrations of mercury.

The decreasing values of $\underline{K}$ at liquid concentrations of 1 ppm and below indicate that a variety of types of binding site are active and that the binding may become very effective at low concentrations of mercury in the solid.

Run C-7 shows the effect of controlling the pH by addition of $CaCO_3$. A marked improvement over straight clay is found.

Runs S-1 and S-2 show that the ground silica (240 mesh) has even less mercury-binding ability than the kaolin. This binding capacity is probably due mainly to surface adsorption.

Ashland Sediments

Our first measurements of the partition coefficients of these sediments were based on mercury analyses of the filtrates made by the usual

Table A-2

Partition Coefficients for Minerals and Sediment from Ashland, Mass. at 24-25°C

Run No.	Time (days)	Description	Mercury Conc. (ppm)		$K = \frac{[Hg^{++}]_{H_2O}}{[Hg^{++}]_{sed.}}$	pH	Dissolved Oxygen (ppm)
			Dry Sediment	Water			
C-1	8	Georgia kaolin	82	40.1	0.49	5.2	5.0
C-2	4	Georgia kaolin	83	166.4	2.0	5.2	6.0
C-3	4	Georgia kaolin	88	38.8	0.44	5.2	5.0
C-4	7	Georgia kaolin	31.6	1.08	0.034	5.1	10.0
C-13	6	Georgia kaolin	90	6.2	0.069	5.2	---
C-14	6	Georgia kaolin	10	0.0175	1.8×10^{-2}	5.4	---
C-7	7	5 g $CaCO_3$	314	11.5	0.037	7.4	7.5
S-1	7	Silica, 240 mesh	33	49	1.5	6.8	6.0
S-2	7	Silica, 240 mesh	29.6	31.6	1.1	7.4	8.0
ASH-1A	7	Ashland sed. October	31.8	0.0016	5.0×10^{-5}	6.4	0.5
ASH-1B	7	Ashland sed. October '71	31.8	0.0016	5.0×10^{-5}	6.4	0.5
ASH-2A	7	Ashland sed. December '71	102.5	0.0028	2.7×10^{-5}	6.3	1.9
ASH-2B	7	Ashland sed. December '71	98.5	0.0028	2.6×10^{-5}	6.3	1.9

room-temperature oxidation with permanganate. We subsequently found that, if these filtrates were digested with nitric-sulfuric acids under reflux, the measured mercury content was increased by a factor of 5 to 10. This result indicates that most of the mercury was organically bound, yet less than 1/2% of the total mercury in these samples was in the methylated form.

We therefore postulated that most of the mercury in these sediments was in the form of mercurated anthraquinone sulfonic acids or similar derivatives. Such mercurated species are a probable by-product of the mercury-catalyzed alpha-sulfonation of anthraquinone. In order to check this hypothesis, we dissolved 5 g of the sodium salt of commercial 1-anthraquinone sulfonic acid in 250 ml of boiling water and allowed the bulk of the dissolved salt to crystallize out. The mother liquor was considered to simulate the by-products of the commercial sulfonation operation. It was found to contain 7.5 ppm of mercury when analyzed by reflux digestion, but only 1.5 ppm or 20% of the total when analyzed by room-temperature digestion. This result is consistent with the hypothesis that most of the mercury in the Ashland sediments is organically bound to anthraquinone derivatives.

As a result of this finding, we have revised some of our earlier work with the Ashland sediments. The last four runs of Table A-2 show some revised values of the distribution coefficient. It should be noted that these values of 2 to 5 x 10^{-5} are not directly comparable to coefficients measured with $HgCl_2$, since the Ashland sediments contain different species of mercury compounds.

The distribution coefficient of this material after aging is further discussed below in Apendix C under treatment of dredge spoil.

Natural and Fired Pyrite

The results obtained with Climax pyrite are summarized in Table A-3. Runs C-5 and C-6 show the results of adding 3% of pyrite (as received, except for washing and drying) to Georgia kaolin.

Comparison with runs C-1 and C-2 of Table A-2 shows that the amount of mercury bound to the solid is about doubled but that the concentrations in solution are still much higher than would be expected from the formation of mercuric sulfide. It therefore appears that the reaction of the pyrite is very slow and is probably limited by insufficient surface area. Alternatively, the reaction may be limited by a layer of highly insoluble ferric hydroxide on the surface of the pyrite particles.

Runs C-37 through C-55 were designed to test these hypotheses. For these runs the pyrite was hand-ground to reduce its particle size (see section on materials), and various iron complexing agents were

Table A-3

Partition Coefficients for Pyrite Additives with Mercuric Chloride at 24-25°C

Run No.	Time (days)	(a) Description	Mercury Conc. (ppm) Dry Sediment	Mercury Conc. (ppm) Water	$K = \frac{[Hg^{++}]_{H_2O}}{[Hg^{++}]_{sed.}}$	pH	Dissolved Oxygen (ppm)
C-5	7	3 g pyrite, as received	193	31.8	0.16	5.0	10.0
C-6	7	3 g pyrite, as received	176	20.8	0.12	5.1	9.0
C-37	7	5 g ground pyrite, 10 ml acetic acid	300	.003	1.0×10^{-5}	3.4	2.0
C-38	7	Same as C-37 + 0.6 g BHA (b)	300	.044	1.5×10^{-4}	3.4	---
C-39	7	Same as C-37 + 0.85 g $KF \cdot 2H_2O$	173	24.2	0.14	4.0	---
C-40	7	Same as C-37 + 0.5 g oxalic acid	171	24.5	0.14	3.0	---
C-45	7	Same as C-37 + 10.0 g oxalic acid	210	17.1	0.08	2.4	---
C-46	7	Same as C-37 + 15.8 g $KF \cdot 2H_2O$	236	12.2	0.05	5.8	---
C-55	7	5 g ground pyrite, low O_2, 200 ml sawdust ext.	300	0.78	2.6×10^{-3}	4.6	6.2
C-56 A	7	Same as C-55 + 5 g Na_2SO_3	59	46.4	0.79	7.9	0.8
C-63	7	5 g milled pyrite -325 mesh	300	.0025*	8.3×10^{-6}	4.5	7.1
C-82	7	Same as C-63 5 g $CaCO_3$, 5 g Fe, low O_2	299	<.00004*	$<1.3 \times 10^{-7}$	7.0	1.1

Table A-3 (continued)

Run No.	Time (days)	(a) Description	Mercury Conc. (ppm) Dry Sediment	Mercury Conc. (ppm) Water	$K = \frac{[Hg^{++}]_{H_2O}}{[Hg^{++}]_{sed.}}$	pH	Dissolved Oxygen (ppm)
C-10	7	5 g fired pyrite	377	0.21	5.6×10^{-4}	5.4	4.0
C-25	7	5 g fired pyrite	321	.154	4.8×10^{-4}	5.0	9.5
C-41	7	5 g ground, fired pyrite, 10 ml acetic acid	300	.0006	2.0×10^{-6}	3.5	---
C-42	7	Same as C-41 + 0.6 g BHA (b)	300	.0005	1.7×10^{-6}	3.3	---
C-43	7	Same as C-41 + 0.85 g $KF \cdot 2H_2O$	300	0.09	3.0×10^{-4}	3.8	---
C-44	7	Same as C-41 + 0.5 g oxalic acid	210	16.9	0.08	2.4	---
C-56	7	5 g ground, fired pyrite; low O_2, 200 ml sawdust ext.	300	.027	9.0×10^{-5}	4.6	2.6

*High-sensitivity analysis.

(a) All runs made with 100 grams oven-dried Georgia kaolin.

(b) BHA = Benzohydroxamic acid

added in order to try to dissolve any layer of $Fe(OH)_3$. The best runs of this series were runs C-37 and C-58 with and without the addition of acetic acid. The acid appears to produce a slight improvement, but neither run gives the low values of soluble mercury expected from a sulfide. The remaining runs of this series show that the three iron-complexing agents, benzohydroxamic acid, potassium fluoride, and oxalic acid, have a deleterious rather than a beneficial effect.

Run C-55 was intended to be low in oxygen, but the oxygen concentration of 6.2 ppm shows some air was inadvertently dissolved. This run also contained 200 ml of the liquid extract from decomposing sawdust, in the hope that this would simulate the bioreducing action of natural organic sediments. Not only was this attempt unsuccessful, but the extract appears to have solubilized some mercury.

To test the possibility that the reaction may be inhibited by a surface layer of free sulfur, run 56A was made with the addition of 5 grams of sodium sulfite. This reagent is known to dissolve elemental sulfur to form sodium thiosulfate. The concentration of mercury in solution, however, was increased by this treatment.

The best results with pyrite were obtained by mechanically milling the material to -325 mesh, as shown in runs C-63 and C-82. The use of $CaCO_3$ and low-oxygen conditions in run C-82 gave a slight improvement. In neither of these runs, however, is the mercury concentration reduced to a value comparable to the Acton peat.

Since pyrite is structurally a disulfide (i.e., it contains the $S_2^=$ ion) rather than a simple sulfide, we considered that a simple iron sulfide (FeS) should be evaluated. One way of obtaining this material is to heat pyrite in the absence of air to a temperature in excess of about 700°C, when one atom of sulfur is lost, according to the equation:

$$FeS_2 \rightarrow FeS + S$$

A sample of calcined pyrite was prepared by this method and, according to weight loss measurements, it was about 35% converted to FeS.

Runs C-10 and C-25, made with this material, show a considerable improvement over straight pyrite, but the mercury in solution is still much higher than expected from theoretical considerations. Some of the observed improvement may be due to increase of surface area during firing.

Runs C-41 through C-44 were made with hand-ground (see section on materials), fired pyrite in combination with various iron-complexing agents. Benzohydroxamic acid (run C-42) appears to produce a slight improvement over straight acetic acid, but the difference is probably within experimental error. None of these materials is significantly better than the -325 mesh pyrite.

Run C-56 shows a deleterious action of the sawdust extract, similar to that found in run C-55.

Other Inorganic Sulfides

Further results with various inorganic sulfides are shown in Table A-4. The effect of adding 5 grams of calcium sulfide to Acton sand is shown by run A-33. The high concentration of mercury in solution is probably due to the formation of soluble $HgS_2^=$ or similar species at the high pH produced by this excess of sulfide. If the excess of sulfide is reduced, as in run C-11, a considerable improvement is effected. Still better results ($K < 1.6 \times 10^{-7}$) were obtained by restricting the supply of oxygen. The actual concentration of oxygen could not be measured because of interference by sulfide. The addition of acetic acid (run C-31) also produces an improvement over run C-11, possibly by preventing formation of $HgS_2^=$.

A very finely divided form of FeS can be prepared in situ by reaction of CaS with $FeSO_4$. Run C-19 is comparable to runs C-10 and C-25 of Table A-3, which were made with fired pyrite. Runs C-20 and C-58 show that an improvement of two or three orders of magnitude is achieved by restricting the oxygen. Run C-58 contained 200 ml of the liquid extract from a decomposing sawdust slurry which had been inoculated with Acton peat. It was hoped that this would simulate the biochemical reducing effect of the peat. The small residual oxygen shows that this was not completely effective.

Run C-51 shows the results obtained with zinc sulfide (precipitated laboratory reagent). This material is comparable to ground pyrite. Run C-54 contained 200 ml of sawdust extract and the oxygen was restricted. The lack of improvement over run C-51 may be due to some mercury-solubilizing effect of the sawdust extract (compare run C-55, Table A-3).

Run C-52 was made with free sulfur in the form of reagent-grade flowers of sulfur (sublimed). No appreciable mercury-binding action is observed (compare run C-1, Table A-2).

In seeking ways to improve the utilization of pyrite, we heated a sample with an equimolar amount of powdered electrolytic iron. The reaction:

$$FeS_2 + Fe \rightarrow 2FeS$$

took place smoothly at a low red heat. After cooling, the product was easily disintegrated into a coarse powder.

A similar reaction was carried out using an equimolar quantity of zinc dust in place of iron. The reaction:

Table A-4

Partition Coefficients for Various Inorganic Sulfide Additions with $HgCl_2$ at 24-25°C

Run No.	Time (days)	(a) Description	Mercury Conc. (ppm) Dry Sediment	Mercury Conc. (ppm) Water	$K = \frac{[Hg^{++}]_{H_2O}}{[Hg^{++}]_{sed.}}$	pH	Dissolved Oxygen (ppm)
A-33	6	Acton sand 5 g CaS	412	10.1	.024	9.0	---
C-11	7	.180 g CaS	1260	.248	2.0×10^{-4}	8.4	---
C-12	7	.180 g CaS low O_2	1260	<.0002*	$<1.6 \times 10^{-7}$	8.4	---
C-31	7	.110 g CaS, 25 ml acetic acid	300	.001	2.2×10^{-6}	3.4	---
C-19	7	.11 g CaS, 1.0 g $FeSO_4 \cdot 7H_2O$	378	1.68	4.5×10^{-4}	4.3	4.0
C-20	7	Same as C-19 low O_2	378	<.0002*	$<5.3 \times 10^{-7}$	4.5	1.0
C-58	7	Same as C-20 200 ml sawdust ext.	300	.0092*	3.0×10^{-5}	5.9	0.6
C-51	7	5 g pptd. ZnS	300	.00053*	1.8×10^{-6}	5.1	7.0
C-59	7	Same as C-51 low O_2, 200 ml sawdust ext.	300	.0013*	4.0×10^{-6}	5.2	0.6
C-52	7	5 g flowers of sulfur	79	32.5	0.41	5.4	8.2
C-69	7	5 g fired FeS	268	.0175	6.5×10^{-5}	5.6	5.2
C-70	7	5 g fired FeS	101	.0125	1.2×10^{-4}	5.8	5.3
C-71	7	5 g fired FeS · ZnS	263	.0152	5.8×10^{-5}	6.2	4.2
C-72	7	5 g fired FeS · ZnS	85	.0007	8.2×10^{-6}	6.8	4.6

*High-sensitivity analysis.

(a) All runs prefixed with "C" were made with 100 grams oven-dried Georgia kaolin.

$$FeS_2 + Zn \rightarrow FeS + ZnS$$

was not violent but was somewhat more energetic than in the previous case. The product may be considered approximately equivalent to natural sphalerite (a natural ZnS, some of which contains much iron). No fine grinding was performed on either of these materials.

Runs C-69 through C-72 show that these two materials offer no appreciable advantage over milled pyrite as far as the partition coefficient is concerned. They are, however, less finely divided than the milled pyrite and would therefore have less tendency to become resuspended in the water column. If they could be made economically and utilized efficiently, they might compete with milled pyrite.

Miscellaneous Additives

Results obtained with various additives to kaolin clay and with chicken feathers are shown in Table A-5.

Run C-22 was made with calcium carbonate and ferrous sulfate, which at this pH is oxidized in situ to $Fe(OH)_3$. An improvement over straight clay of about 100-fold is found.

In runs C-23 and C-50 the $Fe(OH)_3$ was formed by reaction of calcium carbonate with ferric sulfate. In this case the precipitation involves no oxidation but only hydrolysis of the ferric salt. Run C-23 contained insufficient $CaCO_3$, as evidenced by the pH of 2.9. At this hydrogen ion concentration the absorption of mercury is poor. Run C-20 contained more $CaCO_3$ and had a pH of 6.6. The distribution ratio is considerably higher than in the case of run C-22, where the $Fe(OH)_3$ was formed by oxidation. In all these cases the binding of mercury by $Fe(OH)_3$ is much less effective than the binding by sulfides.

Runs C-48 and C-49 were intended to learn if sawdust has an appreciable reducing effect under these experimental conditions. These experiments were prompted by literature reports that ferric sulfate in acid mine drainage could be biologically reduced to FeS in the presence of sawdust. The sawdust used in these experiments was inoculated with turbid water from the Acton sediments in the hope of introducing suitable bacteria. At the end of a week, however, run C-48 still contained 5 ppm of dissolved oxygen, indicating no appreciable biochemical oxygen demand. Run C-49, with ferric sulfate, also showed no evidence of biochemical reduction. It appears likely that the duration of these runs was too short to produce appreciable biochemical reduction. Bacterial action may also have been inhibited by the high concentrations of mercury in solution in these runs.

Sodium thiosulfate has occasionally been used as a precipitant for mercury. When heated, the solutions deposit HgS. Run C-57, however, shows that this reaction is not effective at room temperature within 7 days. In fact, the thiosulfate appears to have a solubilizing

Table A-5

Partition Coefficients for Miscellaneous Materials with $HgCl_2$ at 24-25°C

Run No.	Time (days)	(a) Description	Mercury Conc. (ppm) Dry Sediment	Water	$K = \frac{[Hg^{++}]_{H_2O}}{[Hg^{++}]_{sed.}}$	pH	Dissolved Oxygen (ppm)
C-22	7	1 g $CaCO_2$ 2.1 g $FeSO_4$	321	0.91	2.8×10^{-3}	6.5	3.0
C-23	7	1 g $CaCO_3$, 3 g $Fe_2(SO_4)_3 \cdot nH_2O$	12.8	57	4.4	2.9	5.0
C-50	7	5 g $CaCO_3$, 3 g $Fe_2(SO_4)_3 \cdot nH_2O$	251	9.5	0.04	6.6	5.0
C-48	7	200 g sawdust	300	4.9	0.016	5.0	5.0
C-49	7	22 g sawdust, 3g. $Fe_2(SO_4)_3 \cdot nH_2O$	172	26.5	0.15	2.8	---
C-57	7	5 g $Na_2SO_4 \cdot 5H_2O$	59	46.4	0.79	7.9	0.8
C-83	7	5 g Dowex A-1	135	0.022	1.7×10^{-4}	6.9	4.4
C-84	7	5 g Dowex 1x8	87	0.008	9.3×10^{-5}	7.2	4.6
CF-1	1	5 ml HNO_3	1630	0.68	4.17×10^{-4}	< 2.0	---
CF-2	1	5 g $CaCO_3$	1360	0.55	4.04×10^{-4}	7.0	---
CF-3	1	No addition	1380	0.43	3.12×10^{-4}	6.4	---
CF-4	7	No addition	1785	0.062	3.48×10^{-5}	6.2	1.9
CF-5	3	No addition	1780	0.245	1.38×10^{-4}	6.2	0.7
CF-6	7	No addition	1780	0.140	7.87×10^{-5}	6.5	0.9
CF-7	7	No addition	1780	0.164	9.2×10^{-5}	6.6	0.5
CF-8	1	No addition	1680	2.9	1.73×10^{-3}	---	---

(a) Runs prefixed with "C" made with 100 grams dry clay; Runs prefixed with "CF" made with 14 grams of chicken feathers (dry basis).

effect on the mercury, probably by formation of a soluble thiosulfate complex.

Runs C-83 and C-84 were made to test the mercury-binding capacity of two commercial ion-exchange resins. Dowex A-1 is a chelating resin consisting of a styrene-divinyl benzene matrix to which are attached iminodiacetate groups. Dowex 1x8 is a strongly basic anion-exchange resin which may function by attaching $HgCl_4^=$ or similar anionic species. The results show that neither resin is as effective as the sulfides with inorganic mercury. The cost of these resins (about \$400 per ft^3 for A-1 and \$60 to \$80 per ft^3 for 1x8) will probably be too high for expendable use on a large scale. One cubic foot of these resins weighs about 50 lb.

The remaining runs of Table A-5 show the results obtained by exposing chicken feathers to mercuric chloride solutions under various conditions. Similar work with wool, which is chemically similar to feathers, has been reported by M. Friedman et al. [3]. Runs CF-1 through CF-3 show that pH has little effect on the sorption of mercury by feathers. The remaining runs, equilibrated for various times, show show the best ratios obtained at 7 days. It is possible that some small improvement would result from longer equilibration times. The distribution ratio of 3.48×10^{-5} obtained in run CF-4 agrees well with the results of Friedman et al. for wool.

It should be noted that the feathers produced a turbid solution containing much colloidal matter, which was difficult to remove on a membrane filter. In practice, this colloid would probably become suspended in the water and would increase its total mercury content.

Long-Chain Alkyl Thiols

Table A-6 summarizes the partition data we have obtained with long-chain alkyl thiols (mercaptans).

Run C-7 is a control run made with calcium carbonate only and gives a partition coefficient of .037. The addition of n-dodecyl mercaptan with calcium carbonate lowers the partition coefficient to the order of 10^{-8}, as shown by runs C-15, C-16, and C-27. The observed concentrations of dissolved mercury are on the order of .00002 ppm (.02 ppb), which equals the best results obtained with Acton peat. As shown by run C-27, these low mercury concentrations are obtained even in the presence of 11.5 ppm of dissolved oxygen. The molecular weight of n-dodecyl mercaptan is around 202. Therefore, about 2 pounds of mercaptan will theoretically be required to complex 1 pound of mercury in the form of the mercaptide, $Hg(SC_{12}H_{25})_2$.

Runs C-24 and C-26 show that, in the absence of the calcium carbonate buffer, the partition coefficients are higher. Run C-24 appears to be somewhat out of line and is probably in error. Run C-26 shows that even in the absence of $CaCO_3$ the concentration of mercury in solution

Table A-6

Partition Coefficients for Long-Chain Alkyl Thiols with $HgCl_2$ at 24-25°C

Run No.	Time (days)	(a) Description	Mercury Conc. (ppm) Dry Sediment	Mercury Conc. (ppm) Water	$K = \frac{[Hg^{++}]_{H_2O}}{[Hg^{++}]_{sed.}}$	pH	Dissolved Oxygen (ppm)
C-7	7	5 g $CaCO_3$	314	11.5	.037	7.4	7.5
C-15	7	1 g $CaCO_3$, 1 ml NDM (b)	378	.00003*	7.9×10^{-8}	7.5	---
C-16	7	Same as C-15 low O_2	378	<.00002*	$< 5.3 \times 10^{-8}$	7.7	3.0
C-24	7	1 ml NDM	321	.05	1.6×10^{-4}	5.1	10.0
C-26	7	1 ml NDM	1000	.00015*	1.5×10^{-7}	4.4	12.0
C-27	7	5 g $CaCO_3$, 1 ml NDM	1000	.00002*	2.0×10^{-8}	6.8	11.5
C-53	7	1 ml NDM, aged 36 days	300	.0154	5.2×10^{-5}	5.0	15.0
A-47	7	Sand + Armac T 1 ml NDM	307	.0005	1.6×10^{-6}	6.4	7.6
A-48	7	Same as A-47	108	<.00004*	3.7×10^{-7}	6.2	6.1
A-57	7	Same as A-47 fresh batch	112	<.00004*	3.6×10^{-7}	8.5	4.9
A-58	7	Same as A-57 + 5 g $CaCO_3$	125	<.00004*	$< 3.2 \times 10^{-7}$	7.2	5.0
A-59	7	Same as A-57 + 5 g Fe, low O_2	93	.0016	1.7×10^{-5}	7.3	1.1
A-60	7	Same as A-48 + 5 g Fe, low O_2	93	.012	1.3×10^{-4}	6.8	1.2
A-61	7	Same as A-60 old batch NDM	92	.0094	1.0×10^{-4}	6.9	1.1
C-17	7	1 g $CaCO_3$, 1 ml MTM (b)	378	<.00002*	$< 5.3 \times 10^{-8}$	7.6	---
C-18	8	1 g $CaCO_3$, 1 ml THM (b)	378	<.00002*	$< 5.3 \times 10^{-8}$	7.6	5.0

Table A-6 (continued)

Run No.	Time (days)	(a) Description	Mercury Conc. (ppm) Dry Sediment	Mercury Conc. (ppm) Water	$K = \frac{[Hg^{++}]_{H_2O}}{[Hg^{++}]_{sed.}}$	pH	Dissolved Oxygen (ppm)
C-65	7	1 ml DDD (4)	300	6.2	.017	5.4	6.2
C-66	7	1 ml DDD 5 g Zn dust	300	.0114	3.8×10^{-5}	5.4	0.8
C-67	7	1 ml DDD 5 g Fe powder	300	.0254	8.5×10^{-5}	7.6	0.8
C-68	7	1 ml DDD 100 ml saw-dust ext.	300	3.8	.013	6.0	6.4

*High-sensitivity analysis

(a) All runs prefixed with "C" made with 100 grams dry kaolin.

(b) NDM = n-dodecyl mercaptan
MTM = mixed tertiary mercaptans
THM = t-hexadecyl mercaptan
DDD = di-t-dodecyl disulfide

is reduced to well below 1 ppb with 1000 ppm in the solid.

Run C-53 was made with 1 ml of n-dodecyl mercaptan, which had been added to 100 grams of dry clay and aged in air for about 2 months. During this time the mixture lost most of its odor, and it was thought that the mercaptan was oxidized to a disulfide by the reaction

$$2RSH + 1/2\ O_2 \longrightarrow RSSR + H_2O$$

Surprisingly, this preparation retained a substantial effectiveness as a mercury scavenger, as shown by the partition coefficient of 5.2×10^{-5}. It is probable that the mercaptan was not completely oxidized during this period and that the loss of odor was due to selective oxidation of some volatile impurity.

Since the long-chain thiols are oily liquids which float on water, it is necessary to combine them with some denser material in order to deploy them at the bottom of the water. As a sinking agent we chose Acton sand, which was treated with a cationic surface-active agent to render it preferentially wettable by oil. A number of suitable fatty amines and their derivatives are commercially available for this purpose, and we used Armac-T, which is described as a tallowamine acetate and is made by Armour Industrial Chemical Co. These cationic agents have the advantage that they will displace water from the surface of the wet sand, thus avoiding the need to dry it before applying the mercaptan. Since the Armac-T functioned satisfactorily, we made no search for an optimum cationic agent.

We made a mixture of 550 g of wet sand, 1/2 g of Armac-T (about 1/10% on the dry sand), and 50 ml of n-dodecyl mercaptan with enough water to permit stirring. After mixing, the mercaptan was found to be well absorbed and to be held by the sand even after long periods of submersion in water. Ten grams of this mixture was equivalent to about one ml of pure mercaptan.

Runs A-47 through A-61 were made with the above mixture, which was added to fresh Acton sand in amounts sufficient to give 1 ml of mercaptan to 2-300 grams of sand. Runs A-47, A-48, and A-57 show that the mercaptan is highly effective when applied in this way, although the partition coefficients are not quite as low as those previously obtained with clay. Run A-58, with $CaCO_3$, produced a mercury concentration in solution of less than 0.04 ppb, which is in the range of our best previous results.

Runs A-59 through A-61 were made with low oxygen and with 5 g of powdered iron added to provide additional reducing action. Although the dissolved oxygen was reduced to about 1 ppm in these runs, the partition coefficients are less favorable than those obtained in the presence of oxygen. These results are unexpected, and we are not yet able to offer an explanation.

Run C-17 was made with a mixed tertiary mercaptan (MTM) which had an average molecular weight of 212 and an average of 13.3 carbon atoms in the chain. In addition to having the thiol group in a tertiary carbon atom, this material probably has a more-or-less branched hydrocarbon chain. Its biodegradability may therefore be less than that of a straight-chain primary mercaptan. The partition coefficient of $<5.3 \times 10^{-8}$ is substantially equal to that of n-dodecyl mercaptan.

Run C-18 shows that equally good results were obtained with tertiary hexadecyl mercaptan (THM), which probably has a structure similar to MTM but a molecular weight of 258. These results indicate that the effectiveness of the long-chain mercaptans is relatively independent of the structural details of the alkyl group.

Many of the commercial mercaptans, especially those with a tertiary alkyl structure, possess a penetrating odor which would interfere with their use on a large scale. One way of overcoming this objection is to oxidize the mercaptan to a disulfide (R-S-S-R). This reaction is well known in the petroleum industry as a means of sweetening sour gasolines.

We have found that commercial di-t-dodecyl disulfide (DDD) is a liquid of negligible odor, while the corresponding mercaptan has a strong and unpleasant odor. Run C-65, which contained about 1% of DDD based on the clay, gave a partition coefficient of .017, which is about a 30-fold improvement over straight clay (run C-1, Table A-2). It is possible that the reaction of DDD with mercuric ion is slow and that further improvement would have resulted from a longer contact time.

Runs C-66 and C-67 show that reducing agents (powdered Zn and Fe, respectively) decrease the partition coefficient by over 3 orders of magnitude. The partition coefficients are 3.8×10^{-5} and 8.5×10^{-5}, respectively. The effect of the metal powders is probably to slowly regenerate the mercaptan by reduction of the disulfied. Here, again, more data on reaction rates is needed.

Run C-68 was made with DDD and 100 ml of the extract of decomposing sawdust, in the hope that biochemical reduction would take place. Since the sawdust extract produced little improvement over run C-65, no appreciable biochemical reduction was observed. It is probable that bacterial action was inhibited in this case by the artificially high concentration of mercury. The possibility thus remains that the disulfides could be reduced in a natural anoxic environment, given a longer time and lower mercury concentrations.

Methylmercuric Chloride

Tables A-7 and A-8 summarize the partition coefficient data we have obtained with various sediments and additives using CH_3HgCl in place of $HgCl_2$. As expected for a monovalent ion, CH_3Hg^+ is much less

Table A-7

Partition Coefficients for Methylmercuric Chloride with Acton Sediments at 24-25°C

Run No.	Time (days)	Description	Mercury Conc. (ppm)		$K = \frac{[Hg^{++}]_{H_2O}}{[Hg^{++}]_{sed.}}$	pH	Dissolved Oxygen (ppm)
			Dry Sediment	Water			
A-43	7	Acton sand	40.5	4.6	.12	6.9	8.1
A-44	7	Acton sand	40.7	3.9	.096	6.9	7.7
A-45	7	Acton sand	11.9	1.03	.086	7.2	6.5
A-46	7	Acton sand	12.0	0.91	.076	7.1	7.6
A-49	7	Sand + Armac T, 1 ml NDM	100	8.0	.08	6.3	6.0
A-50	7	Sand + Armac T, 1 ml NDM	30	1.21	.04	6.4	5.7
A-51	7	Sand + Armac T, 1 ml NDM	19	0.65	.034	6.4	4.9
A-52	7	Sand + Armac T, 1 ml NDM (fresh)	106	6.35	.06	6.7	9.4
A-53	7	Same as A-52 + 5 g $CaCO_3$	96.5	4.25	.044	6.9	7.8
A-54	7	Same as A-53 low O_2	119	0.02	1.7×10^{-4}	7.0	1.2
A-55	7	Same as A-53 + 5 g Fe, low O_2	126	0.11	8.7×10^{-4}	7.6	1.2
A-56	7	Same as A-52 + 5 g Fe, low O_2	132	0.35	2.7×10^{-3}	8.4	1.2
A-62	7	Same as A-55 old batch NDM	111	0.10	9.0×10^{-4}	7.2	1.1
	7	Acton peat, aged 2 months	2860	6.5	2.3×10^{-3}	5.3	0.4
B-17	7	Acton peat, aged 2 months	143	0.048	3.4×10^{-4}	5.4	0.2
B-19	7	Acton peat, fresh	2630	2.76	1.0×10^{-3}	5.1	0.4
B-20	7	Acton peat, fresh	1470	1.0	6.8×10^{-4}	5.2	0.2

Table A-8

Partition Coefficients for Methylmercuric Chloride with Various Additives at 24-25 °C

Run No.	Time (days)	(a) Description	Mercury Conc. (ppm) Dry Sediment	Mercury Conc. (ppm) Water	$K = \frac{[Hg^{++}]_{H_2O}}{[Hg^{++}]_{sed.}}$	pH	Dissolved Oxygen (ppm)
C-32	7	Georgia kaolin, no additive	382	470	1.23	5.1	---
C-33	7	Georgia kaolin, no additive	842	1665	1.98	5.0	---
C-60	7	5 g ZnS	300	0.45	1.5×10^{-3}	5.4	9.0
C-61	7	5 g ZnS, low O_2, 200 ml sawdust ext.	300	0.68	2.3×10^{-3}	5.3	0.4
C-62	7	5 g $CaCO_3$ 1 ml NDM	300	0.24	8.0×10^{-4}	7.0	9.1
C-64	7	5 g milled pyrite -325 mesh	300	37.5	0.125	4.1	2.8
C-73	7	5 g FeS-ZnS	68	3.6	.054	7.2	4.6
C-74	7	5 g FeS-ZnS	35	1.96	.056	7.2	4.2
C-75	7	5 g FeS-ZnS	17	1.11	.065	6.4	3.8
C-79	7	5 g $CaCO_3$, 5 g -325 mesh pyrite	32	51.5	1.60	6.9	2.9
C-80	7	5 g -325 mesh pyrite, 5 g Fe, low O_2	162	13.6	.084	6.8	0.9
C-81	7	Same as C-80 + 5 g $CaCO_3$, low O_2	242	8.8	.036	7.0	1.2
C-86	7	5 g Dowex A-1	104	1.16	.011	6.9	7.6

(a) All runs made with 100 grams oven-dried Georgia kaolin.

strongly bound that is Hg^{++}, the partition coefficients being several orders of magnitude greater in the case of methylmercury. Comparison with the pervious tables shows that the materials which bind Hg^{++} most strongly are also the best binding agents for CH_3Hg^+. The lowest partition coefficient we have found is the value of 1.7×10^{-4} for n-dodecyl mercaptan coated on Acton sand (run A-54).

Effect of Dissolved Chlorides on the Partition Coefficient

The effect of dissolved chlorides is important to the study of mercury-sediment interactions in marine and estuarine environments and also in estimating possible effects of runoff of road deicing salts. Table A-9 gives the results of a series of runs made with various sediments and additives in the presence of NaCl and of $CaCl_2$.

Runs A-24 and A-26 show that 35 g per liter of NaCl (about the concentration of sea water) will increase the distribution ratio by almost 2 orders of magnitude. This corresponds to an increase in the concentration of dissolved mercury by a factor of about 70.

The same general type of result is shown by runs B-4 through B-14. The effect is more severe at the higher mercury concentrations and at the higher concentrations of chloride obtainable with $CaCl_2$.

Runs C-20 and C-21 give some results showing the effect of NaCl on the precipitation of mercury as a sulfide. A very large increase of solubility is produced, which is quite unexpected from the known equilibrium constants of mercury with sulfide ion and with chloride ion.

Runs C-27 through C-30 show the effect of chlorides on the trapping of mercury by n-dodecyl mercaptan. An increase of only 1 order of magnitude in dissolved mercury is observed. Run C-29 shows an increase of about 2 orders of magnitude in the presence of a very high concentration of $CaCl_2$. Run C-30 confirms the results of C-28 at a higher mercury level. With the exception of run C-29, these very high mercury removals were obtained in the presence of 8.5 to 12 ppm of dissolved oxygen.

Runs C-74 and C-78 show that 3.5% NaCl has little effect on the partition coefficient of methylmercuric chloride, probably because the CH_3Hg^+ ion is less strongly complexed by the chloride ion than is Hg^{++}.

Runs C-84 and C-85 show the effect of chloride on binding by the anion exchange resin Dowex 1x8. About a sixfold increase in partition coefficient was produced by NaCl.

Runs ASH-9A and 9B show the effect of 35 g per liter of NaCl on the partition coefficient of the Ashland sediment. It is about an order of magnitude greater in the presence of salt than in its absence (compare runs ASH-1A, 1B, 2A, and 2B of Table A-2).

Table A-9

Effect of Soluble Chlorides on Partition Coefficient at 24-25°C

Run No.	Time (days)	(a) Description	Mercury Conc. (ppm) Dry Sediment	Water	$K = \frac{[Hg^{++}]_{H_2O}}{[Hg^{++}]_{sed.}}$	pH	Dissolved Oxygen (ppm)
A-24	7	Fresh Acton sand, no salt	41.2	.024	5.8×10^{-4}	6.7	3.0
A-26	6	Same as A-24 + 35 g/l NaCl	45.4	1.70	3.8×10^{-2}	6.6	7.0
B-4	7	Acton peat no salt	1430	<.00002*	$< 1.4 \times 10^{-8}$	5.2	0.0
B-6	7	Same as C-37	2670	.0044	1.6×10^{-6}	5.1	0.0
B-11	7	Acton peat 35 g/l NaCl	800	.004*	5.0×10^{-6}	4.8	0.0
B-12	7	Same as B-11	2670	25.0	9.4×10^{-3}	4.6	0.0
B-13	7	Acton peat 165 g/l $CaCl_2$	800	1.58	1.9×10^{-3}	3.7	0.0
B-14	7	Same as B-13	1535	215	0.14	3.6	0.0
C-20	7	Low O_2, 0.11 g CaS, 1.0 g $FeSO_4 \cdot 7H_2O$	378	.0002*	5.3×10^{-7}	4.5	1.0
C-21	7	Same as C-20 + 35 g/l NaCl	86	26	0.30	4.5	---
C-27	7	5 g $CaCO_3$ 1 ml NDM (b)	1000	.00002*	2.0×10^{-8}	6.8	11.5
C-28	7	Same as C-27 + 35 g/l NaCl	300	.00006*	2.0×10^{-7}	7.2	8.5
C-29	7	Same as C-27 + 165 g/l $CaCl_2$	300	.0025*	8.3×10^{-6}	5.4	2.0
C-30	7	Same as C-27 + 35 g/l NaCl	1000	.00024*	2.4×10^{-7}	7.2	12.0
C-74	7	5 g FeS-ZnS CH_3HgCl	35	1.96	.056	7.2	4.2
C-78	7	Same as C-74 + 35 g/l NaCl	54	1.24	.023	3.4	6.2
C-84	7	5 g Dowex 1x8	87	.0081	9.3×10^{-5}	7.2	4.6

Table A-9 (continued)

Run	Time (days)	(a) Description	Mercury Conc. (ppm) Dry Sediment	Mercury Conc. (ppm) Water	$K = \frac{[Hg^{++}]_{H_2O}}{[Hg^{++}]_{sed.}}$	pH	Dissolved Oxygen (ppm)
C-85	7	Same as C-84 + 35 g/l NaCl	105	.062	5.9×10^{-4}	5.2	5.6
ASH-9A	7	Ashland, December, 1971 35 g/l NaCl	100	.017	1.7×10^{-4}	6.0	3.6
ASH-9B	7	Same as ASH-9A	100	.019	1.9×10^{-4}	6.0	3.6

*High-sensitivity analysis

(a) Runs made with $HgCl_2$ except as noted.

APPENDIX B

AQUARIUM EXPERIMENTS

This appendix gives the results of measurements of the release of mercury from contaminated sediments and its uptake by goldfish. The first section discusses some preliminary experiments, in which the rate of extraction of mercury was measured for a period of several weeks with no fish present. The following sections describe the results obtained in aquariums with goldfish. As in the partition measurements, we have chosen to work at moderate-to-high mercury levels in order to study the effects of various addition agents.

Static Extraction Experiments

The results of some static extraction experiments with three different types of sediment are shown in Table B-1. The mercury-laden sediments used in these experiments were those filtered off from the correspondingly numbered equilibrium runs. In making a static run, the bottles containing the sediment were carefully refilled with distilled water (about 600 ml) and allowed to stand quietly for a number of weeks at room temperature. Water samples were periodically withdrawn, filtered through a 0.45 micron membrane filter, and analyzed for mercury.

In the case of the clay sediments (runs C-1, C-2, and C-3), much of the original mercury was lost with the filtrate during the original equilibration run. In these cases, we have estimated the true mercury content of the sediment at the beginning of the static experiment.

Table B-1 shows the mercury concentrations in the water obtained in the original equilibrium run and at the end of one, two, and three weeks, in the static experiments. The "A" and "C" runs show a lower concentration of mercury during the static runs than at equilibrium. Runs A-30 and A-31, which contain n-dodecyl mercaptan, not only show a low initial concentration, but the mercury analysis diminishes with time.

The "B" runs (Acton black peat), however, show a higher concentration of mercury in the static experiments than during equilibrium. This appears to indicate that disturbing these sediments can release mercury, possibly by oxidation of mercuric sulfide to more soluble species. Runs B-3 and B-4 appear to indicate that mercury is reabsorbed by this sediment between 7 and 14 days. This may be due to the re-establishment of strongly reducing conditions at the bottom of the sediment layer during standing.

Table B-1

Extraction of Mercury from Sediment under Static Conditions (all runs made with $HgCl_2$)

No. (a)	Mercury Content in ppm (dry basis)	Mercury in Water (ppm)				Remarks
		Equilibrium (b)	7 days	14 days	21 days	
A-16	412	0.52	.0424	.0327	.0585	
A-20	137	.048	.0138	.0180	.036	
A-24	41.2	.024	.008	.0213	.0154	
A-30	137	.0048	.0014	.0017	.00087	Cont. n-dodecyl mercptn+$CaCO_3$
A-31	137	.0024	.0010	.00133	.0003	Same as above
A-36	258	10.0	.036	.0150	.026	Aged sediment
B-3	1430	<.0002	.00785	.0019	----	
B-4	1430	<.0002	0.154	.057	.057	
B-5	476	<.0002	nil	.0046	----	
C-1	93.5	40.1	.85	.875	.75	
C-2	207	166.4	7.4	8.9	8.0	
C-3	80.0	38.8	.78	.68	.65	

(a) Run numbers beginning with "A" denote Acton sandy sediment, "B" denotes Acton black peat, and "C" denotes kaolin clay.

(b) This column gives equilibrium concentrations obtained with the same sediment by continuous mixing for 7 days.

Procedure for Aquarium Experiments

These experiments were made in 5-gallon glass aquariums, 8 inches by 14 inches by 10 inches deep. A one- or two-inch layer of the sediment to be tested was placed in the bottom (after removing excess water), and a solution of the required amount of mercuric chloride was distributed over the sediment and stirred in. Methylmercuric chloride was added as dry solid, which was well mixed with several hundred grams of dry sand in order to facilitate uniform distribution. About 3.5 kg (dry basis) of sand was used in one tank or about half that weight of peat. The sediment was allowed to stand about a week with daily stirring in order to equilibrate the mercury. The sediment was then leveled and a layer of covering material added if required. The aquarium was filled by carefully pouring water onto a floating wooden board in order to minimize disturbance of the sediment.

The water used was from the Burlington, Massachusetts, municipal water supply. It is obtained from local wells and has a pH of 5.9 to 6.4 and a hardness of 62-149 mg/l $CaCO_3$ equivalent.

The aquarium was allowed to stand one or two days before the fish were added. The experiment was started by adding three or four goldfish about 2 inches long. The aquariums were aerated with bubblers during the test.

This fish were fed about every other day with a commercial fish food having the following reported analysis:

Crude protein--not less than 20%

Crude fat--not less than 2%

Crude fiber--not more than 5%

Ash--not more than 12%

Moisture--not more than 12%

and the following reported ingredients:

Wheat flour, meat meal, cornmeal, 2.5% steamed bone meal, 5% ground malt flour, 2% alfalfa leaf meal, fish liver oil, fish meal, 0.5% irradiated dried yeast, 0.5% salt.

Our analysis of the food showed a mercury content of 0.0405 ppm. The amount fed was not accurately measured, but it is estimated to be on the order of 0.05 g per day for each aquarium. This gives an estimated mercury input of 0.08 microgram over the 40-day duration of an experiment.

After 9 days exposure, the fish were killed, gutted, and the heads and tails removed. The remaining portion was then analyzed for mercury.

New fish were then added to the tank, exposed for 30 days, and analyzed in the same way.

It should be noted that the mercury content of the fish is reported on a wet basis in order to be comparable with the FDA guidelines on edible fish (0.5 ppm). Since the fish filets contain about 83% moisture, the reported mercury content may be multiplied by 5 to give the approximate analysis on the dry basis.

Results of Aquarium Experiments

The results of the aquarium tests with goldfish are summarized in Table B-2. Runs A and B were made with Acton sand with 100 ppm of mercury as $HgCl_2$. Tank A was uncovered and tank B was covered with 1 inch of clean sand over the mercury-contaminated sand. The initial water concentration in tank A of .048 ppm is about the equilibrium value obtained by tumbling the sand with mercury solution for 7 days. (Compare run A-20 of Table A-1.) The final value was .0002 ppm, as shown in Table B-2.

It is of interest to compare the mercury loss of the water with the mercury uptake of the fish. If we estimate that aquarium A contained 6 liters of water, then the change in concentration over the first 9 days indicates a loss of 259 micrograms of mercury. If we estimate the total weight of the whole fish to be about 8.4 grams and assume that the increase in concentration of the filets is about the same as that of the whole fish, we find a total uptake of 251 micrograms in 9 days. The close agreement of these two figures indicates that most of the mercury lost from the water was taken up by the fish. If anything, a slight amount of mercury was taken up by the sediment, but there is no evidence for a release of mercury. The 0.08 microgram of mercury added with the food is negligible in the above estimate.

For the following 30-day period we estimate that 28 micrograms of mercury was lost from the water and 17 micrograms gained by the fish. Again a slight absorption, rather than a release, of mercury is indicated.

Applying the same estimates to the first 9 days of tank B, we find a loss of 1.8 micrograms in the water and a gain of 1.45 micrograms in the fish, again a slight absorption of mercury by the sediment. The 30-day run in tank B showed a loss of mercury by both the water and the fish: 0.78 and 0.54 micrograms, respectively, or a total of 1.3 micrograms of mercury which must have been abosrbed by the sediment.

In order to explain these results, we must postulate not only that the bulk of the sediment is releasing mercury either not at all or at most very slowly and that some part of it is actively absorbing mercury. A reasonable postulate is that the excreta of the fish are taking up the mercury. If we estimate that about 3.0 g of fish food was placed

Table B-2

Summary of Aquarium Experiments

Tank No.	Bottom Sediment		Cover Layer	Total Hg in Water		Total Hg in Fish Wet Basis (about 83% Water)			Remarks
	Type	Hg (ppm)		Time (days)	ppm	Exposure (ppm)	Exposure (ppm)	Change	
A	2" Acton sand ($HgCl_2$)	100	None	0	.048				-4 fish added.
				3	.017				
				9	.0049	.176	31.1	+29.9	-After 9 days
				11					-New fish added.
				30	.00136				
				41	.00020	.24	2.22	+1.98	-After 30 days
B	2" Acton sand ($HgCl_2$)	100	1" clean sand	0	.00055				-4 fish added.
				3	.00040				
				9	.00025	.176	.348	+ 172	-After 9 days.
				11					-New fish added.
				30	.000066				
				41	.000122	.24	.176	-.064	-After 30 days.
C	2" Acton peat ($HgCl_2$)	185	None	0	.0004				-4 fish added.
				3	.0003				
				9	.00037	.176	.32	+.144	-After 9 days.
				11					-New fish added.
				30	.00020				
				41	.000056	.240	.71	+.47	-After 30 days.
D	2" Acton peat ($HgCl_2$)	100	1/2" clean sand	6	.000077				-4 fish added.
				9		.240	.085	-.155	-After 9 days.
				18	.000055				
				39		.202	.154	-.048	-After 30 days.
E	2" Acton sand ($HgCl_2$)	100	1/2" kaolin	0	.032				
				9	----	.190	14.15	+13.96	-9-day exposure, new fish added.
				24	.001				
				39	.0003	.077	.50	+ .42	-30-day exposure.

Table B-2 (continued)

Tank No.	Bottom Sediment		Cover Layer	Total Hg in Water		Total Hg in Fish Wet Basis (about 83% Water)			Remarks
	Type	Hg (ppm)		Time (days)	ppm	Exposure (ppm)	Exposure (ppm)	Change	
F	2" Acton sand ($HgCl_2$)	100	1/2" ground silica	0	.074				
				9	----	.190	11.02	+10.83	-9-day exposure, new fish added.
				24	.0061				
				39	.0008	.077	1.38	+ 1.30	-30-day exposure.
G	2" Acton sand ($HgCl_2$)	100	ZnS, 5 g = .015 lb/ft^2 on carrier	3	.0018				
				9	-----	.190	.128	- .06	-9-day exposure, new fish added.
				23	.0008				
				28	-----	.143	3.55	+ 3.41	-19-day exposure.
H	2" Acton sand ($HgCl_2$)	100	Mixed tertiary mercaptan .0051 lb/ft^2 on carrier	3	.0035				
				9	-----	.190	.724	+ .53	-9-day exposure, new fish added.
				23	.0036				
				28	-----	.143	.968	+ .83	-19-day exposure.
Ashland	1" Ashland Reservoir Sediment (Oct. '71 sample)	26	None	19	-----	.190	.330	+ .14	-19-day exposure.
				33	.0002				
				38	-----	.190	.256	+ .07	-38-day exposure.
I	2" Acton sand ($HgCl_2$)	100	Milled pyrite .0291 lb/ft^2	0	.0407				
				5	.0144				
				9	.0096	.143	1.95	+ 1.81	-9-day exposure, new fish added.
				24	.0056				
				39	.0075	.143	5.92	+ 5.78	-30-day exposure.
J	2" Acton	100	n-dodecyl mercaptan (on sand) .0247 lb/ft^2	0	.0045				
				5	.0048				
				9	.0035	.143	0.92	+ .78	-9-day exposure, new fish added.
				24	.00175				
				39	.0010	.143	0.97	+ .83	-30-day exposure.

Table B-2 (continued)

Tank No.	Bottom Sediment		Cover Layer	Total Hg in Water		Total Hg in Fish Wet Basis (about 83% Water)			Remarks
	Type	Hg (ppm)		Time (days)	ppm	Exposure (ppm)	Exposure (ppm)	Change	
K	2" Acton sand ($HgCl_2$)	100	ZnS-FeS, .015 lb/ft^2	0	.0204				
				5	.0086				
				9	.0063	.143	11.8	+11.7	-9-day exposure, new fish added.
				33	.0022				
				39	.0049	.143	14.5	+14.4	-30-day exposure.
L	2" Acton sand ($HgCl_2$)	100	FeS .015 lb/ft^2	0					
				5					
				9		.143	16.4	+16.3	-9-day exposure, new fish added.
				33					
				39		.143	20.3	+20.2	-30-day exposure
M	2" Acton sand (CH_3HgCl)	30	n-dodecyl mercaptan (on sand) .0247 lb/ft^2	0	.048				
				7	.042				
				9	.035	.143	11.2	+11.1	-9-day exposure, new fish added.
				26	.024				
				40	.024	.143	12.8	+12.7	-30-day exposure.
N	2" Acton sand (CH_3HgCl)	30	None	0	4.6	.143	16.8	+16.7	-All fish died within 4 hours.
				1	3.2				
				5	3.4				
				7	3.8				
				9	4.0				
				12	4.1				
				13	---	.143	19.1	+19.0	-All fish died within 4 hours. ZnS-FeS added after water sample
			ZnS-FeS added .015 lb/ft^2	14	2.3				
				15	2.2				
				21	2.0				
				26	2.9				
P	2" Acton peat	0	Polyethylene film	70	----	----	----	-----	-No gas bubbles formed under film in 70 days.

Table B-2 (continued)

Tank No.	Bottom Sediment		Cover Layer	Total Hg in Water		Total Hg in Fish Wet Basis (about 83% Water)			Remarks
	Type	Hg (ppm		Time (days)	ppm	Exposure (ppm)	Exposure (ppm)	Change	
Q	Ashland sediment (Dec. '71 sample)	100.5	None	0	.0009				
				6	.0007				
				9	.0003	.143	.327	+ .18	-9-day exposure, new fish added.
				27	.0005				
				30	.0003	.158	.109	- .05	-30-day exposure.
R	2" Acton sand (CH_3HgCl)	30	Polyethylene film (.001")	0	0.45	0.16	6.15	+6.0	-All fish died in 4-6 hours. Tank drained and refilled.
				6	0.33	0.21	1.7	+1.5	-All new fish died in 4-6 hours. Experiment terminated.
S	2" Acton sand (Repeat of Tank A)	100	None	0	0.18				
				1	----				-4 of 5 fish died.
				2	----	.21	9.3	+9.1	-Last fish died.
				7	.0056				-Experiment termin.
T	2" Acton sand (CH_3HgCl)	30	Polyethylene film over milled pyrite .0291 lb/ft^2	0	.046				
				7	.012				
				10	.012	.21	7.2	+7.0	-New fish added.
				25	.009				
				40	.002	.21	2.25	+2.0	-30-day exposure.
U	2" Acton sand (CH_3HgCl)	30	Polyethylene film over NDM-coated sand .0247 lb/ft^2	0	.021				
				7	.010				
				10	.010	.21	4.04	+3.8	-New fish added.
				25	.015				
				40	.003	.21	1.63	+1.4	-30-day exposure.

Table B-2 (continued)

Tank No.	Bottom Sediment		Cover Layer	Total Hg in Water		Total Hg in Fish Wet Basis (about 83% Water)			Remarks
	Type	Hg (ppm)		Time (days)	ppm	Exposure (ppm)	Exposure (ppm)	Change	
V	2" Acton sand ($HgCl_2$) Mixed with $CaCO_3$ .166 lb/ft^2 + NDM-coated sand, .0247 lb/ft^2 NDM.	112.5	None	0 19 21	.0016 .00055 .00045	.21	1.10	+ .90	-21-day exposure.

in tank A over the 41-day run and that 19 micrograms of mercury was lost during the same period, this would require a mercury concentration of 10 ppm in the total excreta, or about 50 ppm based on the protein content only. The data of Friedman et al. for wool [4] (see Appendix A) indicate that these values are consistent with very low concentrations (less than 0.01 ppb) in the water.

The salient result of these experiments appears to be that in no case were we able to observe any evidence of mercury release by the sediments after the fish were added.

The results obtained with Acton peat are shown by runs C and D. Note that tank C contained 185 ppm of mercury in the sediment (dry basis) rather than 100 as in the other cases. The initial concentration of 0.0004 ppm Hg in the water is somewhat higher than would be expected from the equilibrium experiments. (Compare run B-5, Table A-1.) This higher value may be due to the fact that the aquarium was aerated, while the equilibrium experiment was essentially anoxic. As before, the mercury concentration in the water decreased steadily with time. During the first 9 days, the water lost 0.18 micrograms of mercury, while the fish gained 1.21 micrograms. This is in contrast to the results with Acton sand, where a net loss of mercury was observed. The same type of result was observed during the 30-day run on tank C, where the water lost 1.88 micrograms, but the fish gained 3.94 micrograms. In both cases we believe that the net gain in mercury was due to ingestion of the organic bottom sediment by the fish. This position is supported by the fact that, when these fish were killed, the intestines were found to be full of black sediment. These results indicate that, in order to prevent the uptake of mercury by fish, not only must the mercury content of the water be low, but they must also be denied access to mercury-laden sediments high in organic matter.

Tank D of Table B-2 shows the result of covering the Acton peat with a layer of clean sand. The mercury content of the water was so low that some difficulty was experienced with the analysis and only two acceptable results were obtained. The initial mercury content of the water was 0.46 micrograms, while the total mercury loss by both sets of fish was 1.7 micrograms. Thus, the system shows a net loss of mercury to the sediment. This indicates that the 1/2-in. sand layer was effective in preventing ingestion of the mercury-laden peat by the fish. Another factor may be that the mercury-laden sediment was held under anoxic conditions by the cover layer of sand, and the mercury was thus prevented from being returned to solution by oxidation or by methylation.

Tanks E and F show the results of covering mercury-contaminated Acton sand with 1/2-in. of kaolin clay in 1/2 in. of ground (about 240 mesh) silica, respectively. The effect of these coverings is shown by comparison with runs A and B.

Although the results are somewhat better than those obtained with uncovered Acton sand, they are less favorable than those found with 1 inch of clean sand cover. The cost of clay or silica would probably preclude the use of a thickness much greater than 1/2 in., while at least about 1/2 in. is needed to obtain a reasonable coverage.

The finely divided nature of these materials permitted them to be easily stirred up by the fish. Both tanks, but especially the one containing kaolin, were turbid for the duration of the experiment. The use of these materials is not recommended.

Tank G was covered with a thin layer of precipitated zinc sulfide on a granular ceramic material (oil-absorbent). The mixture contained about 5% of ZnS by weight and was applied at the rate of only 0.3 lb per square foot. This formed a layer about 1/8 in. thick. Since the ZnS was not adhered to the granules, it tended to become suspended in the water and formed a turbid tank. This may have promoted intereaction of the ZnS with dissolved mercury but would be undesirable in a lrage-scale experiment. The results indicate that the ZnS was very effective during the period of the first 9 days but that the fish gained excess mercury during the second test period of 30 days. Any conclusions based on these tests must be regarded as tentative, since none of the results have been confirmed by repetition. We may postulate, however, that the precipitated HgS may have been re-oxidized to a soluble form during the prolonged exposure to aerated water.

Tank H was covered with a mixture of 100 g of a porous-ceramic oil absorbent (treated to render it oleophilic), 5 g of $CaCO_3$, and 2 ml of mixed tertiary mercaptans. This mixture was applied at the rate of about 0.3 lb per square foot, forming a layer about 1/8 in. thick. While this material was not entirely effective in preventing mercury uptake by the fish, it was more effective than a much thicker layer of clay or ground silica. Unlike the ZnS, it did not appear to lose its effectiveness during the 30-day test. We believe that, since this mercaptan was absorbed on the interior of the porous granules, it was largely inaccessible to the dissolved mercury in the water. Further experiments, in which a mercaptan is absorbed on the external surface of sand particles, are discussed below.

The run marked "Ashland" (following run H) was made with a sample of sediment obtained in October, 1971 from Framingham Reservoir No. 2 in Ashland, Mass. This sample contained about 32 ppm of mercury (dry basis) as the result of industrial pollution of a tributary stream. The very low mercury content of the water appears to be related to a high sulfide content of the sediment. No cover was used in this aquarium, and the small mercury uptake of the fish is probably due to the ingestion of the sediment by them. These results may be contrasted with the results of analyses of fish taken from the actual reservoir, most of which show over 1 ppm of mercury, with some in excess of 10 ppm. It appears that aquarium tests do not simulate the

actual environment as far as mercury is concerned. The difference may be due to uptake of mercury in the food chain, to duration of exposure, or to continuing or intermittent mercury input to the reservoir from the tributary stream.

Runs I through L were made with mercuric chloride in Acton sand to compare the effects of various mercury-complexing agents. Run I shows the effect of milled pyrite, which was applied at the rate of about 0.03 lbs per square foot of bottom area and was mixed into the sand layer to a depth of about 1/2 in. The results can be compared to run A, which is the control run for this group. Several points of difference arise from this comparison. In the first place, the concentration of dissolved mercury is higher after the first 9 days in run I than in the control run. The final value for run I (0.0075 ppm) can also be compared to the value of 0.0025 ppm obtained with a higher total mercury concentration in the distribution experiment C-63, Table A-3. On the basis of the distribution experiment, a lower concentration would have been expected in run I if equilibrium had been approached. Possibly the mercury was initially concentrated by the pyrite and then oxidized to soluble form by the aerated aquarium water.

The uptake of mercury by the fish (1.81 ppm) during the first nine days of run I appears to be less than expected from the corresponding period of the control run. During the final 30-day period, however, the uptake was greater in run I than in the control, as expected from the higher concentration of dissolved mercury.

Run J was covered with about 0.024 lb/ft^2 of n-dodecyl mercaptan. The mercaptan was applied to 100 g of sand with the aid of the surface-active agent Armac T. The mercaptan-coated sand was then stirred into the top half-inch of the mercury-containing bottom sediment.

The concentration of dissolved mercury in run J shows a considerable improvement over run I and over the initial nine days of run A. The very low values of dissolved mercury obtained in run A after 40 days suggest that this control run should be repeated (see run S below).

With respect to mercury uptake by the fish, run J shows a considerable improvement over both the control run and run I. This again illustrates the superiority of the mercaptans over the inorganic sulfides for complexing mercury.

Runs K and L made with lower dosages of pyrogenic sulfides formed by heating pyrite with powdered zinc or iron, respectively. It was hoped that these sulfides would be more reactive than pyrite, but the uptake of mercury by the fish shows that neither was highly effective. The dissolves oxygen in these runs was in the range of 7.0 to 7.4 ppm, and the pH was 7.2, which is typical for these experiments. At the end of the run the dissolved iron was 0.05 and 0.06 ppm for K and L,

respectively, and there was no yellow precipitate of ferric hydroxide in either tank. Thus, there is no evidence of excessive oxidation of these sulfides.

Runs M and N were made with 50 ppm of mercury as methylmercuric chloride in Acton sand. This concentration is much higher than any naturally occurring level of which we are aware. The values of 0.1 to 0.4 ppm previously reported for Ashland sediment are probably typical. The high values used in the aquariums, however, permit comparative data to be rapidly acquired.

Tank M was treated with about 0.025 lb/ft^2 of n-dodecyl mercaptan, while tank N was an untreated control.

The water analyses show that the treatment lowered the concentration of soluble mercury about 100-fold throughout the duration of the experiment. The fish in the treated tank survived for the full test period but picked up a considerable concentration of mercury. Under actual field concentrations the pickup would have been much less. In the control tank N, however, all the fish died within about four hours, and they picked up more mercury in this time than in 30 days in tank M.

Tank N was allowed to stand for 13 days with periodic water analyses, and a new set of fish was added. These fish again died within four hours. On the 14th day the tank was treated with 0.15 lb/ft^2 of ZnS-FeS mixture, but this did not appreciably reduce the mercury in solution, either immediately or on subsequent standing.

Tank P was covered with a polyethylene film over Acton peat. The object was to see if the peat would give off gas bubbles which would gather under the film and tend to lift it. No bubbles were observed during the 70-day test period at room temperature.

Tank Q was made with the sample of contaminated sediment from the Framingham reservoir in Ashland, Massachusetts which was collected in December, 1971. The results are quite similar to those obtained with the earlier sample (October, 1971) of Ashland sediment, as reported above. Again the uptake of mercury by the fish was small compared to the values reported for fish from the reservoir. No carp have been taken from the reservoir, but 4- to 6-in. bluegills are reported to contain from 1.5 to 3.5 ppm of mercury. Since bluegills are also a foraging fish, the data may be comparable to that for carp. The higher levels in the reservoir fish indicate that their mercury uptake is probably through the food chain rather than directly from the water.

As discussed in Appendix A, the mercury content of the Ashland sediments may be mainly bound as anthraquinone derivatives. The identity and physiological action of these substances should be

characterized in more detail. Runs R, T, and U were made to learn the effect of a plastic film cover on Acton sand with CH_3HgCl and various chemical treatments. For these runs, the polyethylene film (1 mil) was cut to fit the aquarium and laid on the surface of the sediment before the tank was filled with water. The edges of the film were weighted and sealed with a little clean sand.

Run R was made with no chemical treatment and only the plastic film. Comparison with run N (without film) shows that the concentration of mercury had been reduced by about an order of magnitude, both initially and at the end of six days. Two sets of fish were used, one at the start and one at the end of six days. Both sets of fish died within four hours and the experiment was terminated.

Tank T was treated with 0.291 lbs/ft^2 of milled pyrite, which reduced the initial mercury concentration by an order of magnitude as compared to run R. The mercury continued to fall off with time. The fish in this tank survived for both the 9-day and 30-day test periods, and the mercury gained during the first nine days was comparable to that gained in 4-6 hours in the untreated tank R.

Tank U was treated with 0.0247 lbs/ft^2 of n-dodecyl mercaptan under the plastic film. The results may be compared with those of run M (mercaptan with no film) and run R (film with no mercaptan). The initial mercury concentration in tank U was about half that of tank M and 1/20 that of tank R. The major part of the improvement is thus attributable to the mercaptan treatment rather than to the film. Tank U may have suffered some disturbance at about 25 days, which caused a slight increase in mercury concentration. Despite this, however, the pickup of mercury by the fish is appreciably lower than in tank M or in tank T, which was treated with milled pyrite.

Tank S was a duplicate of run A with uncovered Acton sand and $HgCl_2$. The initial mercury concentration of tank S was about four times that of tank A, and the fish survived only one or two days. The cause of this difference in behavior is not known but may be due to differences in age, organic content, or oxidation of the two sediment samples. The result indicates that in making comparisons between different treatments care should be taken that the sediments being compared are as nearly identical as possible.

Tank V was run by mixing NDM-coated sand and calcium carbonate with the entire mass of mercury-laden sand. Only one run of 21 days was made with this aquarium because of lack of time. Run V may be compared with run J, in which the NDM-coated sand was used as a cover layer only and to which no $CaCO_3$ was added. Although the mercury concentrations in the water are lower in run V than in run J, the uptake by the fish is about the same.

It is estimated that the water lost about 9.1 micrograms of mercury, while the fish gained 7.5 micrograms--a slight net loss. It is probable that, if run V had been continued with new fish, the mercury uptake would have been much less, since only about 3.8 micrograms of mercury remained in solution. A cover layer of clean sand would probably have greatly improved the performance of this tank (compare runs A and B).

APPENDIX C

DREDGING OF MERCURY-CONTAMINATED SEDIMENTS

The dredging of mercury-laden sediments presents two major problems of environmental impact: first, the dispersal of mercury throughout the water column and, second, the disposal of the contaminated spoil. This appendix gives the results of laboratory experiments aimed at providing some of the data needed to analyze these problems.

Simulated Dredging Experiments

Dredging experiments were conducted in aquariums A, B, and C after the fish had been removed and after the water had been allowed to stand for several days. Dredging was simulated by removing about a liter of bottom sediment by repeated dipping of a small spoon into the tank. Mercury content, turbidity, dissolved oxygen, and pH were measured before and after the disturbance, as shown in Table C-1. As expected, both dissolved and total mercury are increased by the dredging. In the case of the sand tanks, total mercury appears to increase with turbidity. Because of the black color of the Acton peat, the turbidity reading is high, although the actual weight of suspended material may be less than in the case of the sand.

Since the bulk of the mercury is in the suspended form rather than in solution, it may be concluded that the treatment of the bottom with mercury-complexing agents before dredging will have little effect on the total waterborne mercury.

From the volume of water in the tanks (about 11 liters), the amount of mercury resuspended in the water can be estimated as a fraction of the mercury removed. These values range from about 2 to 10 per cent, as shown in Table C-1.

Dissolved oxygen and pH were little affected by the dredging except in the case of the Acton peat, where the dissolved oxygen dropped from 7.1 ppm to 1.8 ppm in the course of a few minutes. Further experiments showed that the result could be repeated at will simply by stirring Acton peat into oxygen-rich water. We believe that the disappearance of oxygen is caused by rapid reaction with reduced iron compounds, such as $Fe(OH)_2$ or FeS, which may be contained in the sediment in finely divided form. This view is supported by the fact that we obtained a similar result by stirring a slurry of precipitated $Fe(OH)_2$ (from $FeSO_4$ and NaOH) into oxygen-rich water. In small ponds or in confined areas, this depletion of dissolved oxygen may be detrimental to biota.

Table C-2 shows the results of dredging tanks I and J, which were treated with milled pyrite and n-dodecyl mercaptan, respectively. It

Table C-1

Simulated Dredging Experiments

	Aquarium No.		
	A	B	C
Sediment	Acton sand	Acton sand	Acton peat
Hg Content (ppm)	100	100	185
Cover	None	1" Clean sand	None
Mercury Content of Water (ppm)			
Filtered (Before Dredging)	.00020	.000122	.000056
Filtered (After Dredging)	.0056	.002	.0008
Turbid (After Dredging)	0.58	1.66	.208
Total Hg Removed in Spoil (mg)	166	193	100
Total Hg Suspended in Water (mg)	6.4	18.3	2.3
Percent of Hg Suspended in Water	3.8	9.5	2.3
Turbidity (JTU)			
Before Dredging (With Fish Present)	20	15	240
Before Dredging (No Fish)	5	4	6
After Dredging (10 min.)	280	680	1050
Dissolved Oxygen (ppm)			
Before Dredging (10-15 min.)	6.0	6.9	7.1
After Dredging	5.4	5.1	1.8
10 Days After Dredging	6.9	7.3	7.0
pH Before Dredging	7.4	7.4	5.7
pH After Dredging	7.2	6.2	5.4

Table C-2

Simulated Dredging Experiments

	Aquarium No.	
	I	J
Sediment	Acton sand	Acton sand
Hg Content (ppm)	100	100
Cover	Milled pyrite .0291 lb/ft^2	Milled pyrite .0247 lb/ft^2
Before Dredging		
Total Hg (ppm)	0.17	0.15
Hg in Solution (ppm)	0.035	0.027
Turbidity (JTU)	40	27
Dissolved Oxygen (ppm)	7.0	6.6
pH	6.7	6.6
After Dredging		
15 minutes		
Total Hg (ppm)	0.785	0.948
Hg in Solution (ppm)	0.033	0.07
Turbidity (JTU)	110	80
Dissolved Oxygen (ppm)	8.4	8.5
pH	7.1	7.0
6 hours		
Total Hg (ppm)	0.445	0.65
Hg in Solution (ppm)	0.042	0.05
Turbidity (JTU)	45	30
Dissolved Oxygen (ppm)	7.4	7.6
pH	7.0	7.0
24 hours		
Total Hg (ppm)	0.170	0.181
Hg in Solution (ppm)	0.040	0.014
Turbidity (JTU)	20	20
Dissolved Oxygen (ppm)	7.2	6.0
pH	6.5	6.7

should be noted that the concentration of dissolved mercury in these tanks is higher than that shown in Table B-2 at the conclusion of the fish tests. This is because these two tanks were disturbed and a allowed to settle for a day before the simulated dredging was started.

The total mercury in the water after dredging is due mostly to suspended matter rather than to mercury in true solution. As previously suggested, the use of mercury-binding agents has made little difference in the total mercury concentration. The data at 6 hours and at 24 hours show that the initial conditions have been largely restored at the end of the latter period. This is shown graphically in Figure C-1, in which total and dissolved mercury are plotted as a function of time.

Prediction of Mercury Redistribution

As a direct consequence of physically removing sediment by mechanical means, a certain amount of benthal deposits will become dispersed in the water column. This is primarily a result of washoff and overflow as the sediment is lifted. The use of vacuum dredging techniques will significantly reduce the amount of material that becomes entrained in the water column, since most of the particulate matter, when disturbed, will be drawn by the vacuum system. From a knowledge of the length of time that the material from either type of removal operation is suspended, one can predict its redistribution by superimposing the effects of a current velocity. Previous tests have indicated that the majority of mercury becomes adsorbed to organic particles, hence, an estimate of the redistribution of mercury associated with "lost sediment" from dredging can be obtained.

Sediments may be broadly classified as noncohesive or cohesive. Noncohesive sediments consist of discrete particles whose movement depends on their physical properties, such as size, shape, density, and relative location with respect to other particles. In cohesive sediments significant forces exist between the particles, and these forces may inhibit the individual particle behavior. In the case of dredging, sediment may be initially cohesive in character, but once the bond is broken they may behave noncohesively as far as transport is concerned. It is also possible that a reverse transformation may occur; sediment initially noncohesive in nature may, through chemical or physical reactions, coalesce.

Because natural sediment is irregular in shape, settling velocities cannot be accurately predicted by the application of hydrodynamic theories such as Stokes Law, which holds for spherical particles. Hence, it was felt that, in order to get settling velocities characteristic of the Ashland sediment, a quiescent settling test should be conducted. The test apparatus basically consisted of a cylindrical container which had sampling taps at various heights (see Figure C-2).

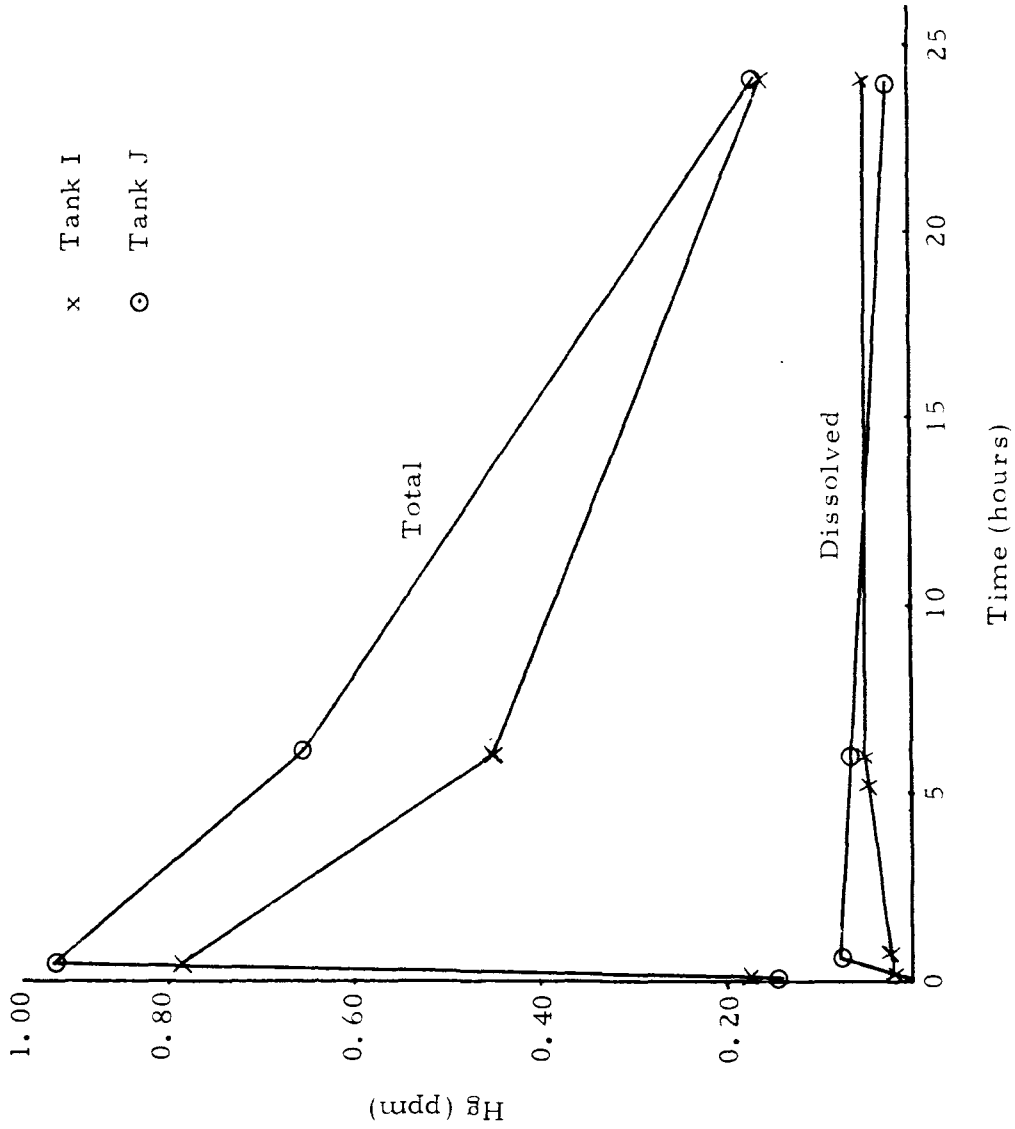

Figure C-1. Decrease of Total and Dissolved Mercury as a Function of Time After Initial Dredging Disturbance

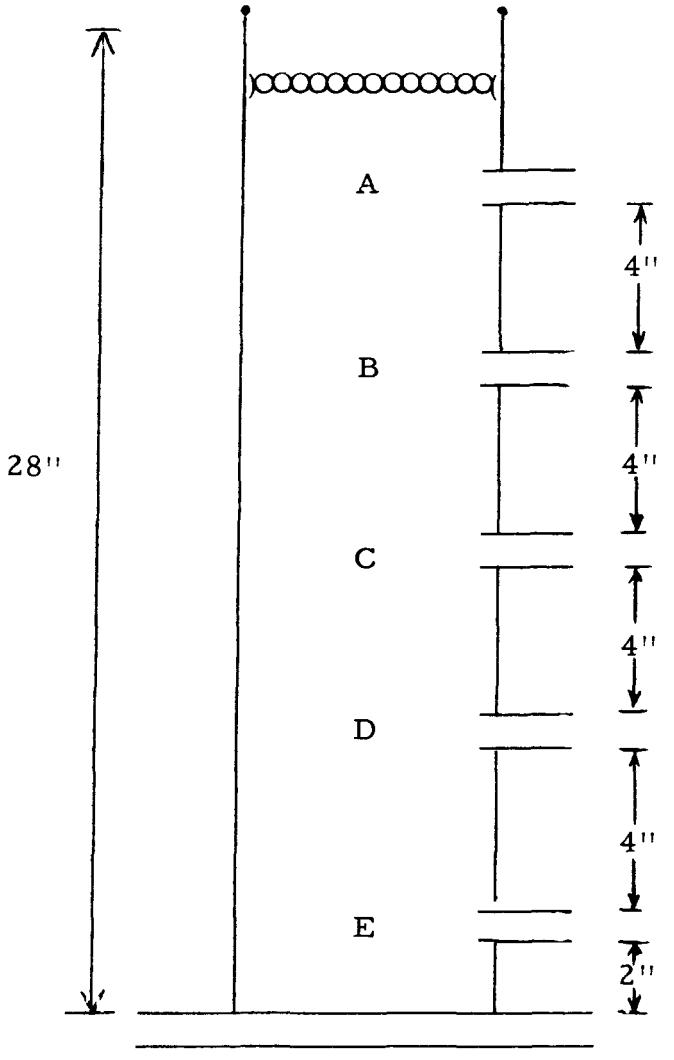

Figure C-2. Settling Chamber

The transparent cylinder was 29 in. high and 5-1/2 in. in diameter (I.D.). Five sampling positions were used, spaced 4 in. apart, with the first being 2 in. from the bottom. The mean water height was 28 in., with variations from 28-1/2 in. to 27-1/2 in. during the course of the test.

At various time intervals after the start of the test, samples were drawn from different heights, and a measure of relative amounts of suspended solids was determined by turbidity tests. The settling velocities were then determined by dividing the depth of water above the sampling point by the period of settling. Extreme care was taken to ensure uniform temperature in the water and uniform ambient temperature ($\pm$ 1/2°C). Subsequent tests were made to determine mercury level associated with turbidity reading. Turbidity values were measured in JTU and mercury concentrations in ppm.

From the test data elapsed times required for turbidity levels to drop to predetermined levels were determined. The elapsed times required to reach turbidity levels of 400, 300, 200, and 100 JTU at various heights in the settling chamber are given in Table C-3.

If the assumption is made that the same collection of particles is responsible for a given turbidity level as settling continues, the settling velocities can be estimated by dividing the traversed height by elapsed time. For example, for the 400-JTU particles, 67 minutes (73-6 = 67 minutes) was required to traverse 12 inches (18-6 = 12 inches) which results in an estimated characteristic settling velocity of

$$v_{400} = \frac{12 \text{ in.} \times \frac{1 \text{ ft.}}{12 \text{ in.}}}{67 \text{ min.} \times \frac{60 \text{ sec.}}{\text{min.}}} = 0.248 \times 10^{-3} \text{ ft/sec.}$$

Corresponding velocities associated with other particle groups are listed in Table C-4.

Figure C-3 illustrates the settling velocities for each group. From Table C-4 it can be seen that larger velocities are associated with the higher turbidity groups, with the exception of the 100 group. The 400, 300, and 200 groups appear to be made up of particles of progressively smaller dimensions (the smaller the particle, the higher the drag force and, consequently, the lower the settling velocity). For the 100 group, one would normally extrapolate that the particles would be smaller and that the velocity would be lower. However, as is clear from Table C-4, the 100 group's behavior could be the result of a system of fine particles coalescing to form larger particles after a period of time, resulting in turbidity levels of 100 JTU in the upper layer and then proceeding to settle at a velocity characteristic of the larger size. Such an occurrence would account for the long delay

Table C-3

Elapsed Time in Minutes to Reach Various Turbidity Levels

Height (in.)	400 JTU	300 JTU	200 JTU	100 JTU
18	6	21	69	270
14	8	24	81	255
10	18	36	93	280
6	73	107	172	350
2	360	---	---	---

Table C-4

Settling Velocity as a Function of Height, Turbidity, and Elapsed Time

Particle Group	Elapsed Time (min.)	Transversed Height (in.)	v (ft/sec)
400	67	12	0.248×10^{-3}
300	86	12	0.196×10^{-3}
200	103	12	0.162×10^{-3}
100	80	12	0.238×10^{-3}

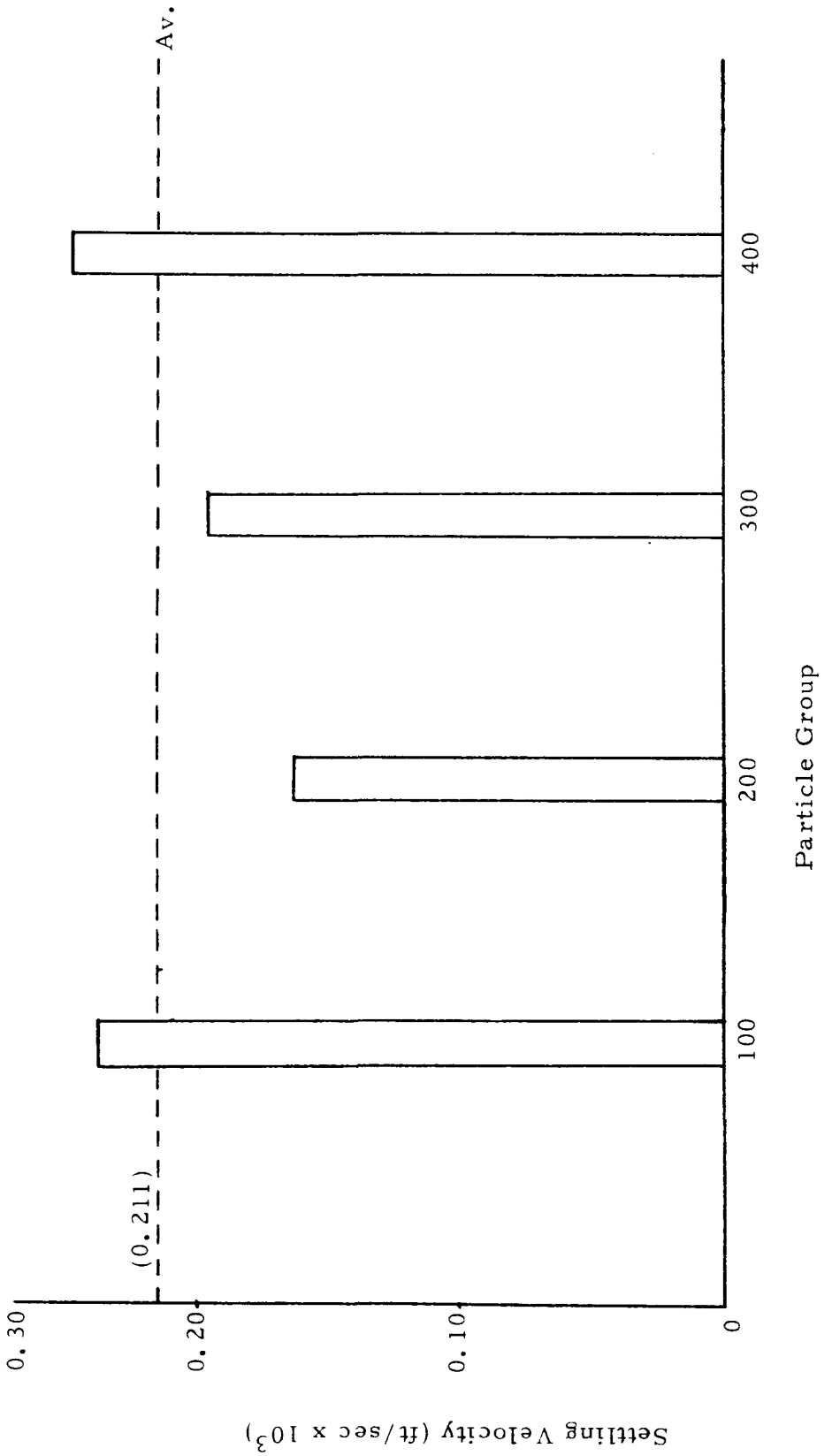

Figure C-3. Settling Velocities Characteristic of Various Particle Groups

Figure C-4. Settling Velocities vs Particle Group

time of 270 minutes at the 18-in. level (see Tables C-3 and C-4), followed by an 80-minute transit time (350-270 = 80) to reach the 6-in. level. However, to estimate transport distances of suspended particles, it is necessary to know the amount of time in suspension, which would include formation time. Hence, a more representative velocity can be obtained by using the total time from the start of the test to determine the settling velocities. Settling velocities determined on this basis are presented in Table C-5.

Figure C-4 contains the results of Table C-5, indicating higher settling velocities associated with higher-number turbidity groups.

Figure C-5 contains a plot of mercury concentration versus turbidity readings. Examination of this group shows that the majority of the adsorbed mercury is associated with turbidity levels of over 100, thus useful settling velocities will be those in the vicinity of 100 to 400 JTU.

The horizontal distance traveled by a particle group is given by

$$d = v_c t$$

$$t = \frac{h}{v_s}$$

$$t = \frac{h}{6 \times 10^{-6}} \text{ (JTU)}$$

$$d = 1.66 \times 10^{6} \frac{h v_c}{\text{(JTU)}}$$

where d = transport distance

v_c = stream current velocity (ft/sec)

h = height (ft)

v_s = settling velocity (ft/sec)

JTU = turbidity level

For a given current and height of disturbance, the redistribution of particles within a particular turbidity grouping can be predicted. In order to determine the approximate quantity of mercury deposited at a distance d from the dredging site, the time of deposition and the mercury distribution as a function of turbidity are required. For the Ashland test site, Figure C-5 shows mercury concentration versus turbidity.

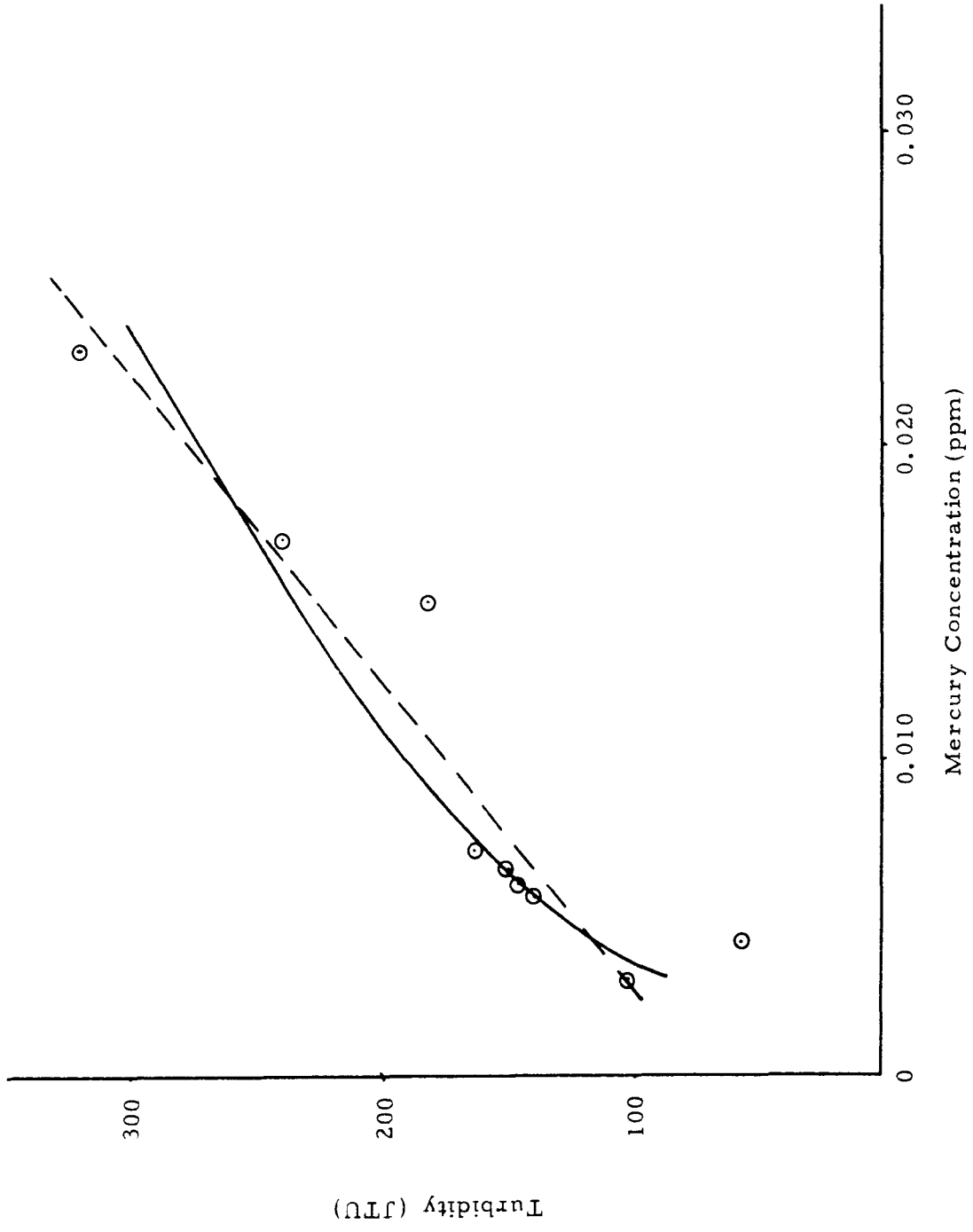

Figure C-5. Mercury Content vs Turbidity Levels

Table C-5

Settling Velocities with Revised Elapsed Time

Group	Test Time (min.)	$\bar{v}$ ft/sec
400	73	0.238
300	107	0.163
200	172	0.097
100	350	0.048

Treatment of Dredge Spoil

In the course of working with the Acton sediments (Appendix A—Table A-1) it was found that the mercury-binding capacity decreased on aging and exposure to air. This leads to the possibility that contaminated dredge spoil may release mercury if it is placed on a landfill and exposed to air and oxygen-rich surface waters.

We made several experiments in which samples of Ashland sediment were exposed to air and alternately moistened and dried for a period of two weeks. These results were inconclusive in that only a slight and variable decrease in partition coefficient was observed after the above aging treatment.

We now beliver that, because of the high organic content of the Ashland sediments, two weeks was insufficient to produce appreciable oxidation and that longer term exposures are needed. We recommend that such long-term experiments be conducted as part of Phase III of this program.

APPENDIX D

PHYSIOLOGICAL EFFECTS OF ORGANIC THIOLS

If the long-chain alkyl thiols (mercaptans) are to be used for complexing mercury on a large scale, it is necessary to make an estimate of their possible impact on the aquatic environment. It is well known that the thiol (-SH) group is an essential constituent of animal protein and that many organic thiols are physiologically active. As with other physiologically active materials, an excess may be harmful.

In this appendix we review first some of the beneficial properties and medicinal uses of thiols and related materials. Second, we review the recent literature on the toxicity of the simple alkyl thiols and estimate their probable effect on fish life.

Beneficial Properties and Medicinal Uses of Thiols and Related Substances

It has long been recognized that thiols are beneficial to cell reproduction. An early patent by Sutton [9] discusses the use of alpha thioglycerol as a cell stimulant to decrease the healing time of wounds.

Much of the recent literature deals with the use of thiols as antidotes for poisoning by heavy metals. In this review we will confine the discussion to the effects of thiols on mercury poisoning.

It is known that certain sulfides will interfere with the disinfecting action of mercuric chloride. As early as 1908, Chick [10] found that a culture of B. paratyphosus, which had apparently been killed with solutions of $HgCl_2$, could be revived within a limited period of time by exposure to solutions of hydrogen or ammonium sulfide. These sulfides are believed to act by removing the mercuric ion from its combination with the organism, through precipitation of the very insoluble mercuric sulfide.

The principle of removing mercury from combination with the organism has been widely applied in the development of antidotes for mercury poisoning in humans. Bidstrup [11] discusses the use of the dithiol BAL (2, 3-dimercaptopropanol) in the treatment of acute poisoning by mercuric chloride. The use of BAL has greatly improved the prospects for recovery in such cases.

In cases of chronic mercury poisoning, BAL is less useful, but the thiol derivative N-acetyl penicillamine has been found effective in relieving the symptoms and in increasing the elimination of mercury [12, 13]. More recently, Takahashi and Hirayama [14] have suggested the use of indigestible and unabsorbable thiol compounds to accelerate the elimination of methylmercury from animals. Reduced human hair

powder contains thiol groups originating from its cysteine content and was found effective in aiding the elimination of methylmercury from mice. Synthetic resins containing thiol groups were also suggested.

Another recent report by Ganther et al. [15] indicates that the presence of selenium in diets fed to Japanese quail is effective in decreasing the toxicity of methylmercury compounds. It is known [16] that selenium forms an even less soluble compound with mercury than does sulfur, and the authors suggest that the protective action of the selenium derivatives is probably due to its mercury-binding capacity. Thus, even an element which by itself may be highly toxic has a beneficial effect in the prevention of mercury toxicity.

Toxicity of Alkyl Thiols

The short-chain alkyl thiols are known to be toxic to fish and other biota. Methyl mercaptan, found in kraft paper mill effluents, is comparable to hydrogen sulfide in its toxic effects. Van Horn et al. [17] report that the safe concentration (no mortality in 120 hours) of methyl mercaptan for minnows is 0.5 ppm.

As the length of the hydrocarbon chain is increased, the solubility, volatility, and sulfur content of the mercaptans decrease. Shugaev [18] concludes that the toxicity of the long-chain mercaptans is more or less equal to that of the hydrocarbons of the same chain length. We have found no data on the toxicity to fish of mercaptans having more than four carbons in the alkyl group. Turnbull et al. [19] have performed experiments on the toxicity of butyl mercaptan (in the form of the sodium salt) to bluegill sunfish. Their results (calculated as free mercaptan) show that 50% of the fish will survive for 24 hours at a concentration of 20.2 ppm and 50% will survive for 48 hours at a concentration of 15 ppm. From these figures they estimate a safe concentration of 2.5 ppm or about 5 times that for methyl mercaptan.

As the length of the alkyl chain is further increased, the toxic effects of the mercaptans become limited by their rapidly decreasing solubility in water. Reid [20] points out that the solubility of the longer-chain normal mercaptans is about the same as that of the normal alkane containing one more carbon atom. The solubility in a given hydrocarbon series decreases rapidly with increasing molar volume [21]. These facts are illustrated by the data shown in Table D-1. Although no experimental solubilities are available for the higher mercaptans, their solubility may be taken as equal to that of the corresponding hydrocarbon, as shown in the adjacent column of Table D-1. The solubility of n-dodecyl mercaptan thus estimated is 0.013 ppm, which is far below the safe limit of 2.5 ppm discussed above for butyl mercaptan.

Table D-1

Some Solubilities of Normal Mercaptans and Normal Alkanes at 20-30° C

n-Alkyl Radical R	Solubility in mg/l (ppm)	
	Mercaptan (R-SH)	Alkane ($R-CH_3$)
C_6H_{11}	43	52
C_7H13	14	15
C_8H_{15}	5	6
$C_{11}H_{21}$	--	0.2
$C_{12}H_{23}$	--	0.013
$C_{17}H_{33}$	--	0.007

The solubility considerations thus indicate that no toxic effect on fish is to be expected from treating the bottom sediments with long-chain thiols. This conclusion is supported by our own aquarium experiments, in which no toxic effect was apparent with goldfish exposed for 30 days to water in contact with sediments containing either n-dodecyl or t-dodecyl mercaptan.

APPENDIX E

ANALYTICAL PROCEDURES AND METHOD DEVELOPMENT

Most of the analytical work performed on this project was concerned with the determination of total mercury in samples containing inorganic mercury or organomercury compounds or both. We also undertook, in cooperation with the Jarrell-Ash Division of Fisher Scientific Company, to establish a procedure by which methylmercury and other organomercury compounds could be separated from their naturally occurring mixtures and unambiguously identified. The method chosen was to separate the individual mercury species by gas chromatography and collect them in a specially designed microcell. The collected samples were identified by laser Raman spectroscopy. A successful microcell has been demonstrated, and Raman spectra have been obtained with sub-microgram quantities of a number or organomercury derivatives. Considerable difficulty has been experienced with the gas chromatographic separations, however, and further work on separation techniques will be required to obtain an operational system.

We are indebted to Mr. James Longbottom, of the Environmental Protection Agency, Cincinnati, Ohio, for analyzing sediments from the Framingham Reservoir for methylmercury.

Inorganic and Total Mercury Analyses

These analyses were made by the procedure of Hatch and Ott [22] using atomic absorption spectrophotometry. In preparing samples for this analysis it is important that the final solutions be freed from organic matter and that all the mercury be in inorganic form. Samples of solutions known to contain only inorganic mercury and containing only traces of organic matter were analyzed by the following procedure:

1. The sample was acidified with a solution of 2.5% HNO_3 and 2.5% H_2SO_4.
2. A few drops of 5% $KMnO_4$ solution were added and the mixture allowed to stand for a few minutes. The color of permanganate should persist on standing.
3. The excess permanganate was destroyed with hydroxylamine hydrochloride solution.
4. The mercury was reduced to the metallic state with stannous chloride.
5. A stream of air was passed through the solution to vaporize the mercury and carry it into the spectrophotometer.

All samples containing organic matter or organically bound mercury were digested prior to analysis by boiling under reflux with a mixture of $H_2SO_4 \cdot HNO_3$. Such samples include all sediments, fish, and all samples known to contain methylmercury or other organically bound mercury. The procedure is as follows:

1. The sample (1 to 5 g of solid or 10 ml of solution) was weighed or pippetted into a 250-ml boiling flask.

2. A few boiling chips, 10 ml conc. HNO_3, and 10 ml 50% H_2SO_4 were added.

3. The flask was fitted with a water-cooled reflux condenser and boiled under reflux for two hours.

4. The flasks were cooled for 15 minutes, and 5 ml of a mixture of two parts conc. HNO_3 and one part 50% H_2O_2 was added.

5. The samples were again refluxed for 45 minutes.

6. The samples were cooled and the condensers washed down with 25 ml deionized water.

7. Twenty ml of 5% $KMnO_4$ were added and the mixture allowed to stand 1/2 hour. (If the permanganate color does not persist, small amounts of $KMnO_4$ crystals are added until it does. Some samples low in organic matter require only a few drops of $KMnO_4$ solution at this point. The minimum amount required to give a permanent color should be used, since $KMnO_4$ contributes appreciably to the blank reading.

8. The excess $KMnO_4$ is destroyed with hydroxylamine hydrochloride, and the solution is diluted to 100 ml.

9. The digested solution is analyzed as above.

Most of the samples were analyzed with a Coleman Model MAS-50 atomic absorption spectrophotometer. Some samples containing less than 1 ppb of mercury were sent to Jarrell-Ash Division for analysis with a specially equipped absorption spectrophotometer, using a hydrogen flame. The detection limit of this device is in the range of 0.02 to 0.04 ppb, and the calibration curve is stated to be linear down to this limit. Most of the samples analyzed by both instruments gave somewaht lower values with the Jarrell-Ash equipment. This may indicate some low level of interference in the flameless Coleman instrument.

Gas Chromatographic Separations

The gas chromatograph which was used for this study was a Fisher/ Victoreen Catalog No. 11-104-11, which embodied a Ni^{63} electron-capture detector and was equipped with a selection of columns, the stationary phases of which were Chromosorb W and Carbowax, as recommended in the literature for the separation of mercury compounds. However, columns with Chromosorb W alone proved satisfactory for the separation. The gas chromatograph was modified to allow for collection of fractions by splitting the effluent stream from the column in a ratio of 1:1 to the detector and to an output collector port. The effluent collector port was maintained at the column temperature, and, although the chromatograph was equipped with variable temperature programming capabilities, no use was made of this. Although gas chromatography is a technique not difficult to practice, in the course of this study it was found difficult to obtain a column with the required properties to give sharp effluent peaks. This was possibly due to the circumstance that the columns were of stainless steel, and this might have had a deleterious effect through Hg adsorption. Within the time scale of the experiment, it was not possible to investigate the potentials of glass columns. The experimental evidence, however, disclosed that the detector was not responsible for the difficulties encountered, and improvements to the column undoubtedly are the primary requirements.

An attempt was made to develop a method by which both inorganic and methylmercury could be simultaneously determined on the same gas chromatogram. We therefore tried to isolate the two forms of mercury as mercaptides and to separate and estimate both forms by gas chromatograph. In theory, the methylmercury should form a mercaptide of the type CH_3HgSR, while inorganic mercury should form $Hg(SR_2)$, where R is a hydrocarbon radical. If R is sufficiently large, there should be an appreciable difference in molecular weight between the two species. We chose dodecyl mercaptan ($C_{12}H_{25}SH$) because of its molecular weight and because its low volatility renders it relatively inoffensive to work with.

Preliminary extraction experiments were made in which 300 ml of aqueous solutions of $HgCl_2$ or CH_3HgCl, containing 100 ppm of Hg, were extracted with 1 ml (849 mg) of n-dodecyl mercaptan dissolved in 100 ml of petroleum ether. After four days of agitation, the aqueous solutions were separated and both were found to contain less than 1 ppb of Hg (Hg^{++} = 0.234 ppb and CH_3Hg^+ = 0.832 ppb), indicating substantially complete extraction of the mercury. The petroleum ether extracts were evaporated down until only the mercury-containing mercaptan remained.

These concentrates were then gas chromatographed on a 5% SE-30 column at 195°C. The initial chromatogram showed a characteristic peak at six minutes, which appeared with CH_3Hg^+ and in a mixture of

CH_3Hg^+ with Hg^{++}, but not in Hg^{++} alone. Other peaks were present, but their interpretation was less clear.

It was then found that the heater on the electron-capture detector of the chromatograph was not functioning reliably and that the detector was not operating at the desired temperature of about 220°C. When the chromatograms were repeated after the heater was repaired, however, the six-minute peak had disappeared and only minor differences were found between the two forms of mercury.

We then prepared pure samples of $Hg(SC_{12}H_{25})_2$ and of $CH_3HgSC_{12}H_{25}$ by reaction of the mercaptan with HgO or with CH_3HgOH, respectively. These materials were examined by laser Raman spectroscopy and found to produce spectra which correlated well with the various interatomic bonds assumed to be present (see Table E-1 below).

When these compounds were heated for 5 minutes at 200°C, however, extensive decomposition was found to take place. The Raman spectra were altered, with disappearance of peaks attributed to the C-Hg bond and to the Hg-S bond. Visual examination of the heated samples revealed the presence of droplets of free mercury, together with dark material which may have been HgS. A brief examination of the literature indicated that the mercury mercaptides are known to be readily decomposable by heat by at least two mechanisms:

$$Hg(SR)_2 \rightarrow Hg + R\text{-}S\text{-}S\text{-}R$$

$$Hg(SR)_2 \rightarrow HgS + R\text{-}S\text{-}R$$

By analogy with the decomposition of methylmercuric sulfide, we infer that the methylmercury mercaptide may decompose according to some reaction, such as:

$$2CH_3HgSR \rightarrow Hg(CH_3)_2 + Hg(SR)_2$$

These products may further decompose according to the reactions:

$$Hg(CH_3)_2 \rightarrow Hg + C_2H_6$$

$$Hg(SR)_2 \rightarrow Hg + R\text{-}S\text{-}S\text{-}R$$

$$Hg(SR)_2 \rightarrow HgS + R\text{-}S\text{-}R$$

Thus, except for the possible production of ethane by the methylmercury derivative, the decomposition products of the two types of mercaptide are much the same. This would account for the general similarity and for the multiple peaks obtained on the gas chromatograms. The extent of decomposition of $Hg(CH_3)_2$ at 200°C is not yet clear, but it is evident that any analytical scheme involving separation of the mercaptides at high temperatures will be subject to difficulties.

Table E-1

Characteristic Frequencies (cm^{-1}) of Some Mercury Compounds

Compound	S-H	C-S	C-Hg	S-Hg	Hg-Cl
$(CH_3)_2Hg$			515		
$(C_2H_5)_2Hg$			488		
$(C_6H_5)_2Hg$			(660)		
$(C_6H_5CH_2)_2Hg$			(445)		
CH_3HgCl			560		295
C_6H_5HgCl			662		315
$(C_{12}H_{25}S)_2Hg$		725		425, 330	
$CH_3HgSC_{12}H_{25}$		730	535	425	
$C_{12}H_{25}SH$	2580	660			
$HgCl_2$					280
HgS (red)				300	

We made a further attempt to obtain thermally stable derivatives of Hg^{++} and CH_3Hg^+ by reacting them with ortho mercapto aniline. It was hoped that the formation of chelate rings by the nitrogen atom of this ligand would confer sufficient thermal stability on the complex to permit it to be chromatographed as such. Both the Hg^{++} and the CH_3Hg^+ complex, however, were found to liberate mercury when heated for five minutes at 200°C.

It may be possible to separate the mercaptides in solution at room temperature by column or thin-layer chromatography. We recommend that these techniques be investigated. For the present program, however, we elected to try to separate methylmercury as CH_3HgCl by gas chromatography according to known methods.

The level of detection of methylmercuric chloride was found to be much higher (in excess of 1500 nanograms in benzene solution) than expected. Mud samples of known methylmercuric chloride concentration were analyzed on the gas chromatograph, but no methylmercuric chloride could be detected. The concentrations were as high as 1500 ppm Hg as CH_3HgCl (dry basis). A Raman analysis on these samples was not undertaken due to the strong Raman lines of the solvent benzene. The water solutions are known to be too weak in concentration for Raman analysis.

Solutions to the problems of the detector and the low sensitivity observed in an instrument capable of much better performance were being sought when the mercury program was terminated. It is highly probable that the solutions are quite simple ones involving an increased detector temperature and switching from a stainless-steel column to a glass column.

Design of the Microcell

Several cells were designed to permit collection of sub-microgram quantities of sample from the gas chromatograph. The filled cell could then be mounted in the sample compartment of the Raman system and aligned with the laser beam for excitation. Each successive design permitted the use of smaller quantities of collected material. The final design, shown in Figure E-1, permitted handling of samples with a volume of less than 200 nanoliters. The cell was joined to the effluent part of the gas chromatograph via a hollow septum, and the U-shaped portion was immersed in a reservoir maintained at -50°C. When the elution from the gas chromatograph was completed, the cell was transferred to another cold reservoir maintained at -190°C to freeze the sample onto the walls of the cell. Under this condition, the air and other gasses in the cell were evacuated with assurance of minimal sample losses. Subsequent to evacuation, the liquid nitrogen was transferred from the U-tube section to the microcapillary portion of the cell, and by the process of sublimation the sample was released from the walls of the U-tube and condensed and trapped in the microcapillary cell. Raman spectra were obtained from less than

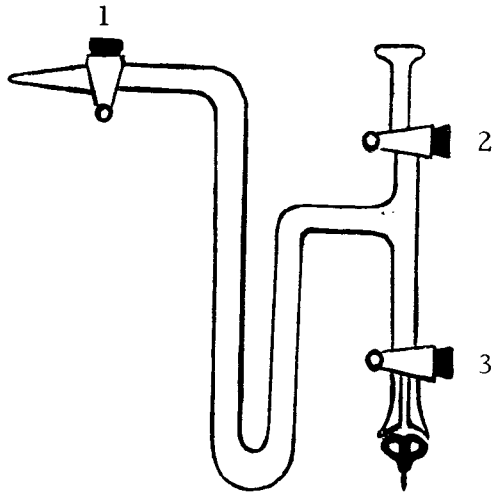

Figure E-1. Microcell for Sampling Output of Gas Chromatograph. (Capillary into which sample is distilled for Raman spectroscopy is at lower right.)

200 nanoliters of dimethylmercury and diethylmercury from an injection of 250 nanoliters of each compound into the gas chromatograph, following the above procedure.

Raman Spectroscopy of Mercury Compounds

Organomercury compounds are good candidates for analysis by Raman spectroscopy because the carbon-mercury bond produces a strong polarizability change in the molecule. This in turn leads to strong Raman scattering. Nevertheless, Raman spectroscopy is not a technique that lends itself to trace analysis, and some means of preliminary concentration and isolation of the compounds of interest is needed.

The instrument used for the present work was a Jarrell-Ash Model 25-500 Raman Spectrometer equipped with a CRL Model 52 Organ-Krypton ion laser and an f/0.95 collection lens assembly.

Raman spectra were obtained on pure samples of available organometallic compounds, using volumes of 10 microliters of the pure material. Each sample was contained in a melting-point capillary tube positioned in a focused laser beam directed onto the sample at 90° with respect to the Raman radiation imaged on the entrance slit of a 0.5-m focal length double monochromator. Typical data obtained are shown in Table E-1. For dimethylmercury, the band at 515 Δcm^{-1} is produced by the symmetrical stretch of C-Hg-C; a shift in frequency occurs for this mode of vibration in other compounds. Thus it is present at 488 Δcm^{-1} in the diethyl form and at 445 Δcm^{-1} in the dibenzyl compound.

Similarly, the characteristic frequencies due to the S-Hg and Hg-Cl bonds can be identified by comparison with HgS and $HgCl_2$, respectively.

The Raman technique should be readily adaptable to all classes of compounds. Dependent only on the ability to isolate the components, it is capable of providing a positive identification of sub-microgram quantities of material. It thus provides an excellent complement to the gas chromatograph, which can separate components but provides no positive identification. We recommend that efforts to interface the Raman spectrometer with the gas chromatograph be continued.

APPENDIX F

FIELD SURVEY SAMPLE COLLECTION

As discussed in Section VI, a field survey was performed in the Ashland, Massachusetts area. Grab sediment samples, core sediment samples, and water samples were collected in Framingham Reservoir No. 2 and in the brook and Sudbury River between Nyanza Chemical Corporation and the reservoir. The results of the analyses on these samples are presented in Tables F-1, F-2, and F-3.

Fish samples were collected by the Massachusetts Division of Fish and Game at the request of the Massachusetts Division of Water Pollution Control. The analyses were performed by the Lawrence Laboratory of the Massachusetts Department of Public Health. Results of the fish analyses are presented in Table F-4. Analyses on the largemouth bass samples were also performed by the Westboro Laboratory of the Division of Fish and Game, with results showing somewhat higher concentrations of mercury. Since most of the fish had been analyzed by the Lawrence Laboratory, their results are reported herein.

Analyses of other water-quality parameters in the Framingham watershed area were obtained from the Boston Metropolitan District Commission, as were the flow volume data. These results are reported in Tables F-5 and F-6, respectively.

Water samples were preserved in the field by the addition of 3 ml of concentrated HNO_3 per 100 ml of sample. In some cases water samples were filtered in the field through a 0.45 micron Millipore filter prior to acidification. These samples were used for determination of the dissolved-mercury fraction.

Grab samples were obtained using a small scoop at the end of an extendable pole. Samples were refrigerated in the laboratory until analysis. The core samples were obtained by forcing a 2 ft x 1.5 in. plastic coring tube into the reservoir or river bottom. Cores could be taken in water depths up to 15 feet. In the upper seven-acre section, the maximum water depth is eight feet. In some areas of the lower section, water depth reaches a maximum of about 30 feet. Core samples were frozen until analysis. The sample was retained in the plastic tube, which was then cut into two-inch sections. The thawed samples were analyzed for total mercury and per centage of moisture. Results of the core analyses in the upper two-inch sections agreed closely with the nearby grab-sample analyses.

Water samples were analyzed in two different ways. Near the end of the program, we discovered that a large fraction of the dissolved mercury in the reservoir was in the form of a soluble organic

TABLE F-1

Grab Sample Analyses--Ashland, Massachusetts Area

Sample Number	Hg (mg/kg, wet weight)	% Moisture	Hg (mg/kg, dry weight)	Location
E-1 (Sediment)	2.2	21	2.79	Chestnut Street, Sudbury River
E-2 (Sediment)	39.0	53	83.0	Union St. Bridge, Sudbury River
E-3 (Sediment)	19.9	66	58.5	Reservoir No. 2, Upper Section
E-4 (Sediment)	3.38	11	3.8	Reservoir No. 2, Upper Section
E-5 (Sediment)	12.3	38	20.0	Reservoir No. 2, Upper Section
E-6 (Sediment)	315	70	1050	Brook near Nyanza Plant
E-7 (Sediment)	4.6	50	9.25	Reservoir No. 2, Upper Section
E-8 (Sediment)	54.8	14	64.0	Cherry Street, Brook
E-12 (Sediment)	36.3	59.5	89.5	Reservoir No. 2, Lower Section
E-13 (Sediment)	15.7	27	21.5	Reservoir No. 2, Upper Section
E-14 (Sediment)	40.8	64.6	115.0	Reservoir No. 2, Upper Section
E-15 (Sediment)	13.9	42.0	24.0	Reservoir No. 2, Upper Section
E-16 (Sediment)	49.1	52.1	100.2	Reservoir No. 2, Upper Section
E-17 (Sediment)	31.7	35	48.8	Reservoir No. 2, Upper Section
E-18 (Sediment)	74.0	55	164.0	Reservoir No. 2, Upper Section

TABLE F-1 (Continued)

Sample Number	Hg (mg/kg, wet weight)	% Moisture	Hg (mg/kg, dry weight)	Location
E-19 (Sediment)	18.0	35	27.7	Reservoir No. 2, Upper Section
E-20 (Sediment)	12.5	33.7	18.9	Reservoir No. 2, Upper Section
E-21 (Sediment)	11.3	12.7	12.9	Reservoir No. 2, Upper Section
E-22 (Sediment)	18.2	51.8	37.7	Reservoir No. 2, Upper Section
E-23 (Sediment)	10.6	43	18.6	Reservoir No. 2, Lower Section
E-24 (Sediment)	30.6	62	80.5	Reservoir No. 2, Lower Section
E-25 (Sediment)	20.0	67.2	61.0	Reservoir No. 2, Lower Section
E-26 (Sediment)	14.5	62.5	38.7	Reservoir No. 2, Lower Section
E-27 (Sediment)	5.96	36.2	9.35	Reservoir No. 2, Lower Section
E-28 (Water lily)	0.556	85.3	3.78	Reservoir No. 2, Upper Section
E-29 (Sediment)	18.3	36.6	28.9	Reservoir No. 2, Upper Section
E-31 (Sediment)	7.28	38.6	11.9	Reservoir No. 2, Upper Section
E-33 (Sediment)	14.4	28.3	20.5	Reservoir No. 2, Upper Section
E-35 (Sediment)	3.30	30.0	4.7	Reservoir No. 1
E-37 (Sediment)	3.23	38.0	5.2	Reservoir No. 1
E-38 (Sediment)	2.18	20.0	2.72	Reservoir No. 1
E-39 (Sediment)	3.42	33.2	5.1	Reservoir No. 1

TABLE F-1 (Continued)

Sample Number	Hg (mg/kg, wet weight)	% Moisture	Hg (mg/kg, dry weight)	Location
E-41 (Sediment)	27.6	48.5	53.6	Reservoir No. 2, Upper Section
E-43 (Sediment)	41.4	36.4	65.1	Reservoir No. 2, Lower Section
E-44 (Sediment)	39.0	34.7	59.8	Reservoir No. 2, Lower Section
E-45 (Moss)	1.268	40.0	2.1	Cherry Street near Nyanza
E-46 (Moss)	0.246	40.0	0.41	Concord St. near unpolluted brook
E-47	582.0	83.5	3504.0	Nyanza swamp area
E-48	43.7	89.3	408.0	Brook before rr culvert (l. brnch)
E-49	64.4	44.4	116.0	Brook before rr culvert (r. brnch)
E-50	3.37	24.2	4.44	Gravel material near railroad culvert

TABLE F-2

Core-Sample Analyses--Ashland, Massachusetts Area

Sample Number	Hg (mg/kg, wet weight)	% Moisture	Hg (mg/kg, dry weight)	Location
C-1 (0-2 inches)	30.4	67.0	92	Reservoir No. 2, Upper Section
C-1 (2-4 inches)	17.7	53.0	37.6	
C-1 (4-6 inches)	8.6	33.3	12.8	
C-2 (0-2 inches)	10.6	53.0	22.6	Sudbury River
C-2 (2-4 inches)	0.81	54.0	1.76	
C-3 (0-2 inches)	20.0	75.0	80.0	Reservoir No. 2, Upper Section
C-3 (2-4 inches)	17.4	53.6	37.6	
C-3 (4-6 inches)	11.6	54.1	25.3	
C-4 (0-2 inches)	9.55	83.0	56.1	Reservoir No. 2, Upper Section
C-4 (2-4 inches)	7.21	42.2	12.5	
C-4 (4-6 inches)	10.3	34.8	15.8	
C-5 (0-2 inches)	14.9	71.0	51.4	Reservoir No. 2, Upper Section
C-5 (2-4 inches	10.2	45.5	18.7	
C-5 (4-6 inches)	8.95	55.0	19.8	
C-6 (0-2 inches)	21.9	61.0	56.1	Reservoir No. 2, Upper Section
C-6 (2-4 inches)	22.8	54.5	50.0	
C-6 (4-6 inches)	9.72	37.2	15.5	
C-6 (6-8 inches)	7.7	47.7	14.7	
C-7 (0-2 inches)	1.35	13.5	1.56	Reservoir No. 2, Upper Section
C-7 (2-4 inches)	0.49	21.0	0.62	
C-8 (0-2 inches)	14.1	42.0	24.3	Reservoir No. 2, Upper Section
C-8 (2-4 inches)	6.35	23.6	8.35	
C-8 (4-6 inches)	17.7	36.6	28.1	
C-8 (6-8 inches)	5.4	31.9	7.9	
C-8 (8-10 inches)	4.36	27.8	6.04	
C-9 (0-2 inches)	15.8	47.0	29.8	Reservoir No. 2, Upper Section
C-9 (2-4 inches)	7.75	52.5	16.3	
C-9 (4-6 inches)	7.42	37.5	11.9	
C-9 (6-8 inches)	9.50	56.5	21.8	
C-9 (8-10 inches)	9.85	57.5	23.1	
C-10 (0-2 inches)	16.3	53.7	35.2	Reservoir No. 2, Upper Section
C-10 (2-4 inches)	14.0	45.5	25.7	
C-10 (4-6 inches)	3.5	32.4	5.18	

TABLE F-2 (Continued)

Sample Number	Hg (mg/kg, wet weight)	% Moisture	Hg (mg/kg, dry weight)	Location
C-11 (0-2 inches)	17.3	72.5	63.0	Reservoir No. 2, Upper Section
C-11 (2-4 inches)	17.3	50.0	34.6	
C-11 (4-6 inches)	6.65	36.8	10.5	
C-12 (0-2 inches)	2.42	38.9	3.96	Reservoir No. 2, Upper Section
C-12 (2-4 inches)	3.2	35.6	4.95	
C-12 (4-6 inches)	0.278	32.0	0.41	
C-12 (6-8 inches)	1.51	29.0	2.13	
C-13 (0-2 inches)	16.5	76.0	68.9	Reservoir No. 2, Upper Section
C-13 (2-4 inches)	19.7	53.0	42.8	
C-13 (4-6 inches)	13.0	46.4	24.3	
C-13 (6-8 inches)	4.48	36.2	7.01	
C-14 (0-2 inches)	24.6	64.5	69.4	Reservoir No. 2, Upper Section
C-14 (2-4 inches)	7.5	32.9	11.2	
C-14 (4-6 inches)	5.4	34.0	8.17	
C-15 (0-2 inches)	13.2	53.6	28.5	Reservoir No. 2, Upper Section
	8.45	37.6	13.5	
	1.34	24.6	1.78	
	4.35	40.7	7.5	
	4.67	32.8	6.95	
	5.4	46.3	10.10	
C-17 (0-2 inches)	9.65	86.2	68.9	Reservoir No. 2, Upper Section
C-17 (2-4 inches)	14.60	48.8	28.6	
C-17 (4-6 inches)	7.01	46.1	13.0	
C-17 (6-8 inches)	9.81	69.0	31.6	
C-19 (0-2 inches)	27.2	49.6	54.5	Reservoir No. 2, Upper Section
C-19 (2-4 inches)	14.1	42.4	24.5	
C-19 (4-6 inches)	20.2	48.6	39.3	
C-19 (6-8 inches)	8.4	40.3	14.0	
C-19 (8-10 inches)	10.9	45.3	19.9	
C-21 (0-2 inches)	11.35	89.1	100.4	Reservoir No. 2, Upper Section
C-21 (2-4 inches)	9.5	52.1	19.9	
C-21 (4-6 inches)	18.7	52.7	39.5	
C-21 (6-8 inches)	6.95	43.2	12.4	
C-21 (8-10 inches)	8.39	61.0	21.5	
C-21 (10-12 inches)	2.47	37.4	3.94	
C-21 (12-14 inches)	1.63	64.0	4.52	
C-21 (14-16 inches)	3.89	69.0	12.5	

TABLE F-2 (continued)

Sample Number	Hg (mg/kg, wet weight)	% Moisture	Hg (mg/kg, dry weight)	Location
C-22 (0-2 inches)	9.25	89.5	88.0	Reservoir No. 2, Upper Section
C-22 (2-4 inches)	22.5	47.7	43.0	
C-22 (4-6 inches)	15.6	48.3	30.2	
C-22 (6-8 inches)	23.4	49.4	46.1	
C-22 (8-10 inches)	24.8	41.8	42.6	
C-22 (10-12 inches)	10.8	30.9	15.6	
C-22 (12-14 inches)	3.42	33.9	5.17	
C-22 (14-16 inches)	4.78	67.4	14.6	
C-22 (16-18 inches)	10.2	55.0	22.6	
C-22 (18-20 inches)	0.29	24.5	0.38	

TABLE F-3

Water-Sample Analyses--Ashland, Massachusetts Area

Sample Number	Date	Dissolved Hg (0.45 filter), μg/l (ppb)		Total Hg, μg/l (ppb)		Location
		Reflux	Nonreflux	Reflux	Nonreflux	
W-6	8/27/71	27.0				Brook near Nyanza (combined flow)
W-7	8/27/71	1.0				Cherry Street--brook
W-8	8/27/71	1.25				Res. No. 2--upper sectn.
W-9	10/10/71		1.9			Res. No. 2--upper sectn.
W-10	10/10/71		1.8			Res. No. 2--upper sectn.
W-11	10/10/71		0.65			Res. No. 2--lower sectn.
W-12	10/10/71		0.9			Res. No. 2--lower sectn.
W-13	10/10/71		0.5			Res. No. 2--lower sectn.
W-15	10/27/71				3.0	Brook near Nyanza (left branch)
W-20	10/27/71			440.0	380.0	Brook near Nyanza (right branch)
W-16	10/27/71	5.6	<0.2			Res. No. 2--upper sectn.
W-17	10/27/71	3.8	<0.2			Res. No. 2--upper sectn.
W-21	10/27/71	3.2	<0.2			Res. No. 2--upper sectn.
W-18	10/27/71		<0.2			Sudbury R. before Res. #2

Table F-3 (continued)

Sample Number	Date	Dissolved Hg (0.45 filter), μg/l (ppb)		Total Hg, μg/l (ppb)		Location
		Reflux	Nonreflux	Reflux	Nonreflux	
W-25	11/12/71	2.2	0.3			Res. No. 2--upper sectn.
W-26	11/12/71	3.4	0.2			Res. No. 2--upper sectn.
W-31	12/28/71				16.4	Brook near Nyanza (combined flow)
W-32	12/28/71				16.8	Brook near RR culvert
W-34	12/28/71				10.2	Cherry St. --brook
W-51	12/28/71				3.6	Brook midway between Cherry St. and town
W-42	12/28/71				3.5	Brook, police sta. culvert
W-43	12/28/71			3.4	< 0.2	Res. No. 2--upper sectn.
W-44	12/28/71				0.2	Res. No. 2--upper sectn.
W-45	12/28/71				10.2	Concord St. --brook
W-46	12/28/71				5.4	Confluence of 2 brooks
W-47	12/28/71				2.5	Brook confluence with Sudbury River
W-48	12/28/71		0.5			Brook confluence with Sudbury River
W-49	12/28/71				1.3	Sudbury R. after conflu.
W-50	12/28/71		< 0.2			Sudbury R. after conflu.

Table F-3 (continued)

Sample Number	Date	Dissolved Hg (0.45 filter) μg/l (ppb)		Total Hg μg/l (ppb)		Location
		Reflux	Nonreflux	Reflux	Nonreflux	
W-58	2/10/72			2.0		Res. No. 2--upper sectn.
W-60	2/10/72			3.8		Res. No. 2--upper sectn.
W-65	3/31/72			22.0		Brook near Nyanza (right branch)
W-66	3/31/72	15.0				Brook near Nyanza (right branch)
W-63	3/31/72			18.0	3.9	Brook near Nyanza (left branch)
W-67	3/31/72				4.4	Brook near RR culvert
W-68	3/31/72		2.7			Brook near RR culvert
W-69	3/31/72			5.6	3.7	Cherry St.--brook
W-70	3/31/72		1.4			Cherry St.--brook
W-75	3/31/72			8.6		Sudbury R. after conflu.
W-76	3/31/72	8.6				Sudbury R. after conflu.
W-77	3/31/72			4.0		Sudbury R. before Res. #2
W-78	3/31/72	4.0				Sudbury R. before Res. #2
W-81	4/12/72			2.6	0.2	Res. No. 2--upper sectn.
W-82	4/12/72	1.8	0.2			Res. No. 2--upper sectn.
W-87	4/12/72			21.0	3.0	Confluence of 2 brooks

Table F-3 (continued)

Sample Number	Date	Dissolved Hg (0.45 filter), μg/l (ppb)		Total Hg, μg/l (ppb)		Location
		Reflux	Nonreflux	Reflux	Nonreflux	
W-88	4/12/72					Confluence of 2 brooks
W-89	4/12/72				3.0	Confluence of 2 brooks
W-90	4/12/72		0.2			Confluence of 2 brooks
W-91	4/12/72				5.1	Brook near RR culvert
W-92	4/12/72		1.1			Brook near RR culvert
W-93	4/12/72			16.6		Brook near Nyanza (right branch)
W-94	4/12/72	5.6				Brook near Nyanza (right branch)
W-95	4/12/72				6.6	Brook near Nyanza (left branch)
W-96	4/12/72		3.5			Brook near Nyanza (left branch)
W-97	4/12/72				6.0	Brook near Magunco Rd.
W-98	4/12/72	9.0	3.4			Brook near Magunco Rd.
W-99	4/21/72			2.4	0.27	Sudbury R. after conflu.
W-100	4/21/72	2.4	0.2			Sudbury R. after conflu.
W-101	4/21/72				4.6	Confluence of 2 brooks
W-102	4/21/72		0.6			Confluence of 2 brooks

Table F-3 (continued)

Sample Number	Date	Dissolved Hg (0.45 filter), μg/l (ppb)		Total Hg, μg/l (ppb)		Location
		Reflux	Nonreflux	Reflux	Nonreflux	
W-103	4/21/72			12.0	4.5	Cherry St. --brook
W-104	4/21/72	6.8	1.1			Cherry St. --brook
W-105	4/21/72				4.7	Brook near RR culvert
W-106	4/21/72		0.86			Brook near RR culvert
W-107	4/21/72			83.0	39.0	Brook near Nyanza (right branch)
W-108	4/21/72	41.0	0.9			Brook near Nyanza (right branch)
W-109	4/21/72				4.7	Brook near Nyanza (left branch)
W-110	4/21/72		0.91			Brook near Nyanza (left branch)
W-111	4/21/72			9.6	4.3	Brook near Magunco Rd.
W-112	4/21/72	5.8	1.4			Brook near Magunco Rd.

Table F-4

Fish-Sample Analyses--Ashland, Massachusetts Area

Specie	Weight (lbs)	Length (in.)	Hg(mg/kg, ppm)
Largemouth Bass	3.3	17.0	7.6
Largemouth Bass	2.9	17.0	6.0
Largemouth Bass	2.7	16.0	6.0
Largemouth Bass	1.8	14.5	6.9
Largemouth Bass	0.9	12.0	4.2
Largemouth Bass	0.7	10.6	1.6
Largemouth Bass	0.2	7.8	0.64
Largemouth Bass	0.1	6.9	3.5
Smallmouth Bass	0.96	12.0	3.25
Smallmouth Bass	0.61	10.0	2.4
Smallmouth Bass	0.55	9.0	1.3
Smallmouth Bass	0.13	5.0	1.9
Bluegill	0.36	6.0	1.5
Bluegill	0.31	6.0	1.5
Bluegill	0.26	5.0	2.4
Bluegill	0.19	4.5	1.6
Bluegill	0.18	4.5	2.4
Yellow Perch	0.13	4.5	2.7
Crappie	0.36	6.5	1.45
Crappie	0.32	6.0	1.70

NOTE: Analyses made by the Massachusetts Department of Public Health, Lawrence, Mass., Laboratory.

Table F-5

Water Quality Parameters--Framingham Reservoir Watershed

Location	Date	Turbidity	Color	Chloride	Alkalinity	Hardness	pH	°F	Tryptone, G. E. Agar		Coliform Colonies
									20°, 48 hr	35°, 24 hr	100 ml, MF
Sudbury	3/23/70	1.5	65	34	7.0	28	6.6	34	120	180	1200
River,	4/21/70	4.0	80	72	7.5	33	6.8	58	320	130	25
Concord	5/18/70	1.5	90	47	9.0	26	6.5	60	1000	400	2
Street,	6/15/70	3.4	110	60	12	16	6.8	60	2200	1100	0
Ashland--	11/30/70	2.8	130	60	10	44	6.8	38	900	600	0
Before	2/1/71	2.6	55	57	9.0	38	6.2	32	800	130	60
brook frm	4/26/71	1.4	52	88	7.0	43	6.6	48	700	160	25
Nyanza	9/27/71	2.8	90	78	14	75	6.8	60	1300	900	0
joins rvr.	10/26/71	2.2	75	86	9.0	72	6.8	54	2600	1100	14
Cherry St.	3/23/70	15.0	1800-mhgny	725	44	565	6.7	44	1600	900	200
Ashland--	4/21/70	0.5	2750	2650	96	1000	8.5	44	3500	3300	1000
Below	5/18/70	0.3	3500-mhgny	2600	430	930	11.4	62	0	30	0
Nyanza on	6/15/70	0.2	5000	6900	1000	1680	11.9	70	2	1	0
brook	11/30/70	1.2	2000	850	115	200	8.4	40	1800	1200	0
	2/1/71	7.2	250	500	450	285	11.6	34	1	6	0
	4/26/71	4.5	900	300	1000	200	12.0	56	9	160	0
	9/27/71	0.2	3000	1850	180	750	9.0	60	220,000	150,000	10
	10/26/71	3.8	300	620	140	320	10.3	54	1300	3000	0
Framing-	3/23/70	1.0	75	55	8.0	34	6.7	36	60,000	1200	800
ham Res.	4/21/70	10.0	55	74	7.5	38	6.7	50	2600	420	2700
#2, Foun-	5/18/70	1.1	80 (pink)	70	9.0	35	6.9	62	30,000	18,000	800
tain St.	6/15/70	2.7	125	105	16	60	7.6	64	6000	600	50
	11/30/70	4.7	88	80		55			20,000	2700	160
	2/1/71	3.7	55		11		6.3	32	2000	160	500
	4/26/71	1.0	55		6.0		6.7	42	800	90	900
	9/27/71	2.4	36	63		62		69	7600	5000	4
	10/26/71	2.7	52		12		7.1	58	300	180	0

TABLE F-6

Average Flow Volumes, Framingham Reservoir No. 2 (1968)

Month	Flow Volume (million gallons per day)
January	44.9
February	62.5
March	266.7
April	83.5
May	51.3
June	77.6
July	39.9
August	10.9 (Some water through gates)
September	7.76 (All water through gates)
October	4.2 (No flow in 14 days)
November	28.5 (No flow in 10 days)
December	52.6

compound which we believe may be amercurated anthraquinone derivative. The particular complex was not being digested by the cold-digestion procedures normally employed on water samples. Many of the water samples were then refluxed with nitric acid and sulfuric acid, resulting in mercury levels up to 10 times higher than those obtained with the cold procedure. The reflux procedures are described in Appendix E. Results of both reflux and nonreflux analyses are reported in Table F-3. The soluble mercury fraction was determined by analyzing samples which had been passed through a 0.45 micron filter.

Beginning with sample number W-63 in Table F-3, the odd-number samples were total-mercury samples and the even-number samples were used for dissolved-mercury determination. Successive odd-even number samples are from the same location.

*U.S. GOVERNMENT PRINTING OFFICE:1972 514-149/73 1-3

SELECTED WATER RESOURCES ABSTRACTS
INPUT TRANSACTION FORM

W

Control of Mercury Contamination in Freshwater Sediments

Yeaple, D. S.; Johanson, E. E.; Feick, G.

JBF Scientific Corporation

16080 GWU

68-01-0060

Environmental Protection Agency report number EPA-R2-72-077, October 1972.

Methods for controlling the release of mercury from sediments have been developed, and the effects of dredging on the redistribution of mercury have been evaluated. A program of laboratory studies was conducted concurrently with a field survey where the extent of mercury contamination at a typical site was evaluated.

Laboratory studies consisted of both partitioning and aquarium experiments using artificially contaminated sediments as well as sediments from the polluted field site. Inorganic sulfides and long-chain alkyl thiols with suitable modifications were found to be the most effective binding agents. A number of factors were identified which affect the decision to decontaminate a polluted sediment or to remove the material by dredging. If the material is to be dredged, precautions must be taken when land disposal methods are used. The field survey consisted of determining both the horizontal and vertical extent of the mercury contamination as well as pertinent hydraulic parameters.

From results of the laboratory and field work, a pilot field project is described whereby techniques for controlling mercury contamination can be evaluated at a site where the field conditions have been fully established.

*Water Quality Control, *Metals, *Mercury, Water Pollution Treatment, Sediments

Sludge Treatment, Ultimate Disposal, Sediment Treatment, Field Surveys, Pilot Project

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