Mercury in the Aquatic Environment

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ABSTRACT

The incidences of recent contamination of water bodies, both natural and man-made, by mercury has been rising. Mercury concentrations exceeding the regulatory guidelines have been reported for lakes with no apparent source of mercury. Apollo Lakes, in Lancaster, California, is one such body. It is the intent of this paper to focus on the Apollo Lakes to develop a mathematical model describing the transport of mercury in the system. To help formulate the model, a literature review was conducted to synthesize the findings relating to the transport of mercury in aquatic systems. Topics investigated included the factors affecting methylation of mercury and the accumulation of mercury by fish. Furthermore, this paper gives an overall review of the interactions of mercury in the aquatic environment.

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INTRODUCTION

In past decades the effect of heavy metals in the aquatic environment has attracted the attention of the scientific community. This interest can be attributed to two reasons. First, fish-kills, ecological alterations and human intoxication have focalized the issue. Second, the increasing awareness of environmental interrelationships involved in life processes have broadened the scope of research.

While the behavior of some heavy metals has been relatively predictable under certain conditions, others remain enigmatic. Of this latter group, the metal mercury is particularly interesting, and is the focus of this paper.

Mercury has some exceptional properties. Notable are its existence as a liquid-metal at ordinary room temperature and its high vapor pressure. The inability to understand the element in an aquatic system is due to the latter property. The loss of mercury to the atmosphere makes quantitative determinations difficult and these determinations are further complicated by the minute quantities of mercury, usually expressed as parts per million or billion (ppm or ppb), existing in the aquatic environment.

As like all heavy metals, mercury is toxic to biota. The degree of toxicity is dependent on the type of organism involved, the form of mercury compound and the environmental conditions.

The majority of elemental or metallic mercury poisoning cases are the the result of mercury vapor inhalation. Alkylmercury forms are the most toxic. Methylmercury derivatives, part of the alkyl family, are the dominant forms found in aquatic life. Methylmercury derivatives are characterized by the methyl radical, CH^+.

Numerous analytic techniques are described in the literature to measure the mercury content in samples of fish, water and sediment. One problem associated with analysis is sample preparation because the high vapor pressure can volatilize substantial quantities of mercury prior to analysis. Another problem is the different mercury compounds in the sample. Inorganic and organic mercury determinations require different analytical techniques since organic methyl compounds are generally more complexed and volatile. Seldom is there only one mercury compound. Flameless atomic absorption spectrophotometry, neutron activation analysis, and gas chromatography are a few of the popular techniques used in analysis today. Radiated mercury, ^{203}Hg or ^{197}Hg, are frequently used as tracers to monitor volatile and extraction losses during analysis and are also used in fish uptake studies. Difficulty in quantitative determinations has made some experimental results not reproducible (National Research Council, 1978).

The quantitative determinations of mercury are important in tracing the transport and transformation processes through the aquatic environment. The processes are complex and without data,

modelling is impossible.

Industrial waste effluent and agricultural runoff are the two largest contributors of mercury compounds to surface waters. The compounds usually deposit close to the outfall or are carried further downstream on suspended particulate matter. It was previously thought only the organic mercury compounds were accumulated by fishes. However, recent evidence supports the theory that microorganisms in sediments are able to methylate mercury from the inorganic form. This discovery means inorganic mercury can augment the quantity of the more toxic methyl form in the natural water since all forms of mercury have the potential of becoming methyl complexes.

The methylated form is accumulated by fish. The bioaccumulation results from the amount ingested being greater than the amount excreted. If mercury is not removed from the water, the accumulation occurs until death.

Although the source of mercury in humans is through the food, the path by which mercury reaches the fish is not as distinct. There are three possible paths for methylmercury accumulation by fishes: 1) through the food ingested, 2) directly from water through respiration and 3) ingested inorganic mercury forms which become methylated within the fish. All three theories have supporting evidence. Most probably the path of methylmercury accumulation in fishes is a combination of all. If the path of uptake could be ascertained, then it may be possible to devise systems to decrease or halt the production of methylmercury

without effects to the environment.

Quantitative mercury transport cycles through the water system have been proposed. But thus far, no quantitative model has been suggested.

Portions of the descriptive models have been experimentally quantified. However, the various experimental designs have naturally produced varying and sometimes conflicting results. No single factor plays a more important role in determining the outcome of an experiment than environmental influence. Therefore experimental results are certainly not transferrable under differing conditions. The confusion created by the proliferation of experimental results does not help to quantify or identify mercury transport paths.

Reaction rates of the transformation and uptake processes are particularly interesting since the rate-limiting steps could be identified. Thus far, reaction rates have also been determined on empirical basis and have helped in understanding the cycling of mercury in the aquatic system.

It becomes evident that a quantitative model is necessary to monitor the transport of mercury. A set of ordinary differential equations describing the transport of mercury through a lake system are presented in this paper. The mass balance technique is employed to derive the equations. Inorganic and organic mercury forms are treated separately. Although several assumptions and simplifications are used in the formulation, the

model can be expanded to meet more sophisticated criteria. The model has not been tested nor verified but it does present a new perception on mercury contamination in aquatic systems.

LITERATURE REVIEW

Mercury

In its natural form, mercury occurs in three oxidation states. The elemental state, Hg^0, is also referred to as the metallic state. Mercurous, Hg_2^{+2}, and mercuric, Hg^{+2}, mercury are the remaining (I) and (II) oxidation states, respectively. The electron distribution for elemental mercury is 2,18,32,18,2 (see Table 1 for mercury characteristics). The electron configuration of $4f^{14}5d^{10}6s^2$, with corresponding first three ionization potentials of 10.43, 18.65 and 34.4 eV, indicate the limitation to the oxidation (II) state. The formation of lattice structures are insufficient for stability in oxidation (III) state (Levason and McAuliffe, 1977).

The ionic state is a function of environmental conditions: pH, temperature and the presence of complexing agents. Hem (1970) diagrammed the presence of mercury compounds as functions of pH and redox potential for water containing 36 ppm Cl^- and total sulfur of 96 ppm as SO_2^{-2} (see Figure 1).

Mercury is the only metal existing as a liquid at room temperatures. The vapor pressure of mercury is high at room temperatures (see Figure 2) increasing the possibility of errors in analysis through volatilization losses. Potential vapor

TABLE 1: Mercury Characteristics

Atomic number:	80
Atomic weight:	200.6
Density in water:	13.534 g/ml
Solubility in water:	20-30 ug/l
Boiling point at 1 atm.:	357°C
Distribution of electrons:	2,8,18,32,18,2
Vapor absorption maximum:	2536.52 A
^{197}Hg half-life:	65 hours
^{203}Hg half-life:	48 days

From Burrows and Shin (1973) and Levason and McAuliffe (1977)

poisoning situations are also possible.

Characteristics of mercury are suitable for a number of different analytic techniques. Mercury has a vapor absorption line at 2536.52 A for atomic absorption analyses and emission spectrum analyses are conducted at 4358.35 A and 2536.52 A. Radioactive half-life of ^{197}Hg and ^{203}Hg are used the activated neutron analysis (Burrows and Shin, 1973).

The equilibrium constant for the reaction $Hg_2^{+2} \rightleftharpoons Hg^0 + Hg^{+2}$ is 1.15×10^{-2}. Although the reaction favors the mercurous ion formation, any slight disproportionation disrupts the stability of the reaction. Hg^{+2} forms with numerous reagents, driving the reaction toward the right, decreasing $[Hg_2^{+2}]$ and increasing $[Hg^0]$. In succeeding sections the importance of the mercuric and elemental oxidation states in relation to methylation schemes will be presented.

The decrease in $[Hg_2^{+2}]$ initially lead researchers to assume

FIGURE 1: Hg Concentration as a Function of pH and Redox Potential

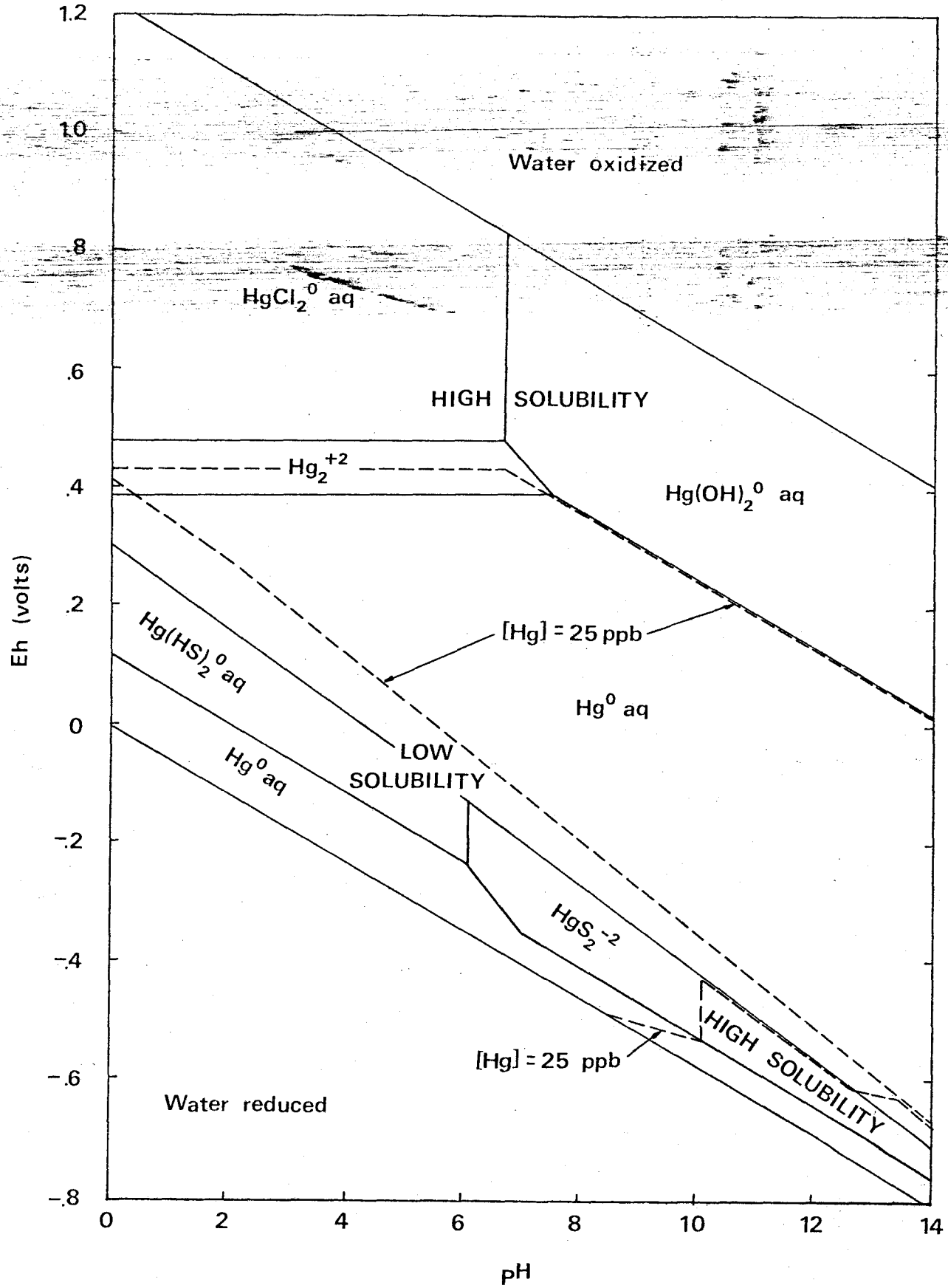
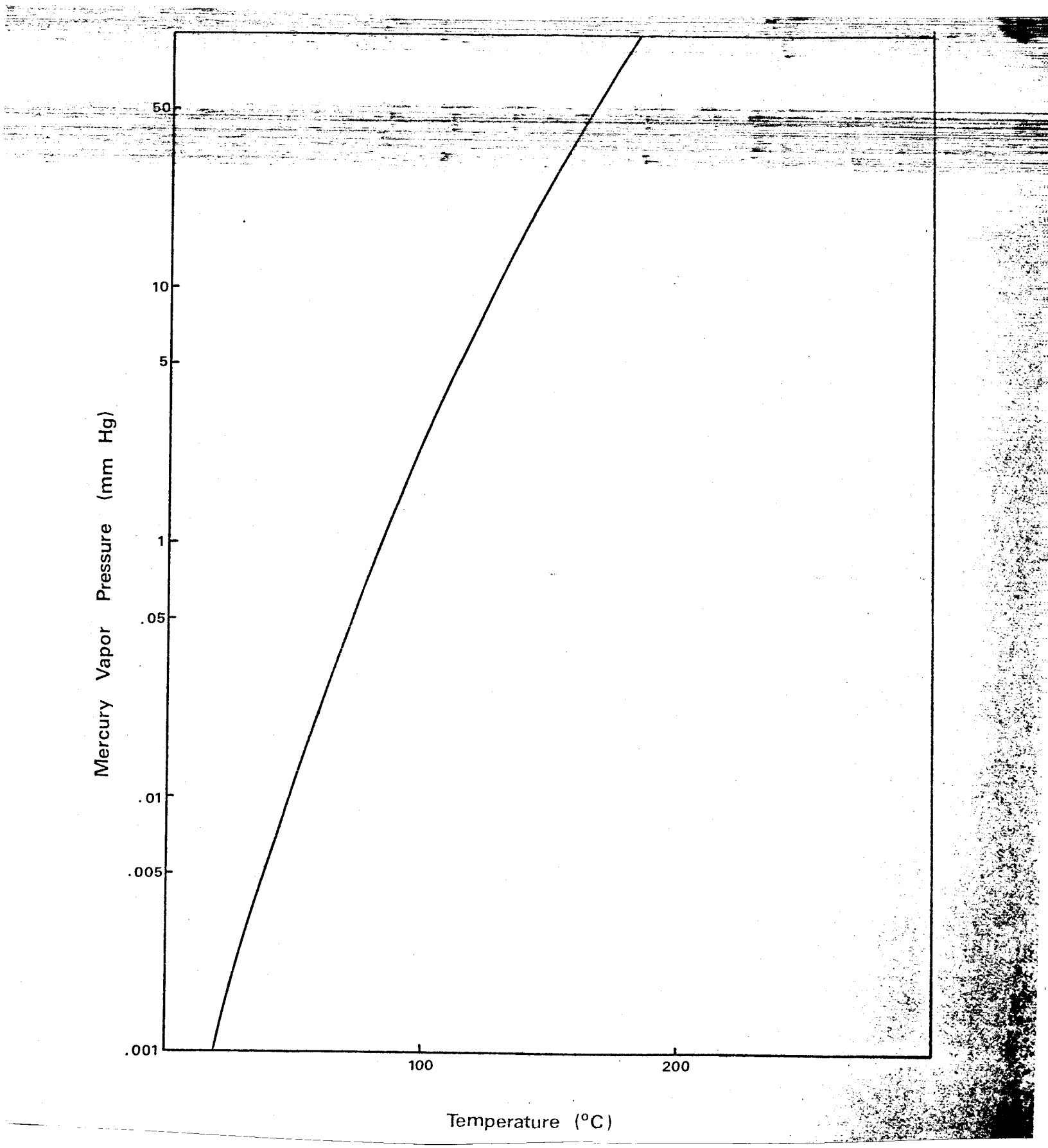


FIGURE 2: Mercury Vapor Pressure Curve



the mercurous ion did not complex with other elements. Evidence of complexing, presented in 1959 by Anderegg, showed complexing with phenanthroline in aqueous nitric acid solution. Research has produced more complexes although there is no evidence of isolated mercury (I) oxide, sulfide, hydroxide or peroxide (Levason and McAuliffe, 1977). Instead, the mercury compounds form (Burrows and Shin, 1973):

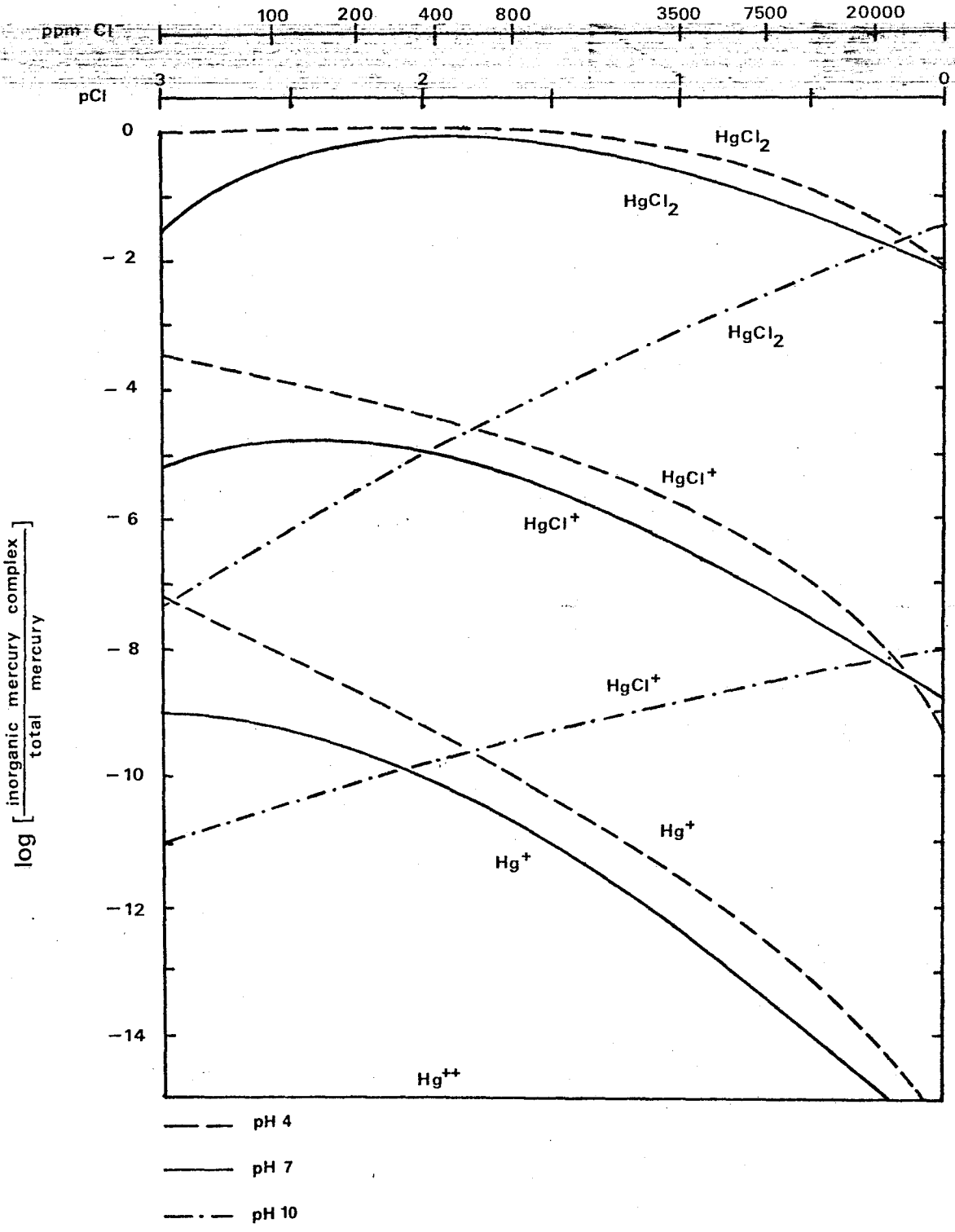
$$Hg_2^{+2} + S^{-2} \rightarrow HgS + Hg^0$$

$$Hg_2^{+2} + 2OH^- \rightarrow HgO + Hg^0 + H_2O$$

The mercuric ion forms many stable complexes with ligands by formation of covalent rather than ionic bonds. Covalent bonding of mercury (II) with halides results in low boiling points and high solubility in organic solvents relative to water, compared with true salts (Burrows and Shin, 1973; Wojtalik, 1971). The readiness in which Hg (II) forms complexes indicates the probability of small concentrations of Hg^{+2} in aqueous solutions. Burrows and Shin (1972) did extensive work in determining relative mercury compound concentrations at various pH when HgCl was dissolved in water (see Figure 3).

Although mercury (I) combines with other elements, organomercury (I) compounds have not been isolated. Both binuclear and mononuclear organomercury (I) species have been postulated as reactions prior to the formation of organomercury (II) complexes. Theoretical assumptions of the degradation of the organometallic mercurous forms are (Bloodworth, 1977):

FIGURE 3: Relative Mercury Concentrations



$[RHgHgR] \rightleftharpoons R_2Hg + Hg$ binuclear species

$[RHg] \rightleftharpoons R\cdot + Hg$ mononuclear species

In the reaction

$$RHgX + RHgX \rightleftharpoons R_2Hg + HgX_2$$

the organomercury (II) salts can be transformed into organic mercury complexes in the symmetrization process (Bloodworth, 1977). The equilibrium favors the left reaction but is driven to the right by the removal of mercury (II) salts.

From the toxicology view, there are three classes of organomercurials:

1) Arylmercury compounds. The arylmercurials encompass all mercury derivatives of aromatic hydrocarbons. The arylmercurials family, in which phenylmercuric acetate is the most recognized, has low toxicity.

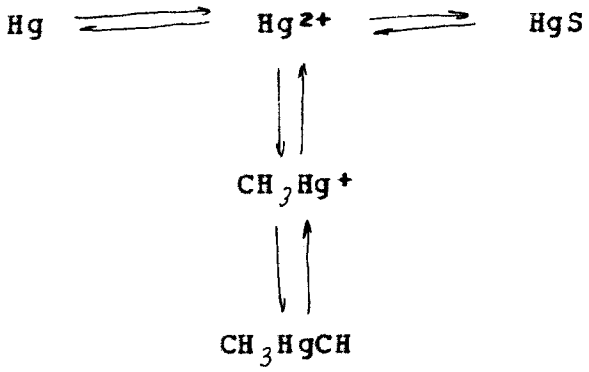
2) Alkylmercury compounds. The alkylmercurials can enter the body by absorption through the skin, inhalation, or through ingestion. Having a high affinity for lipid tissues, they are easily complexed and are most toxic of mercurial forms.

3) Alkoxyalkylmercury compounds. These compounds are chemically related to mercurial diuretics. Little is known about the toxicity except that it is much less toxic than the alkylmercurials (Falchuk, et al., 1977).

The compounds of interest in this study are the alkylmercury methylmercury derivatives. These are characterized by monomethylmercury derivatives of the form CH_3HgX or dimethylmercury derivatives of the form CH_3HgCH. The methylmercury cation, CH_3Hg^+, is not usually found in aqueous

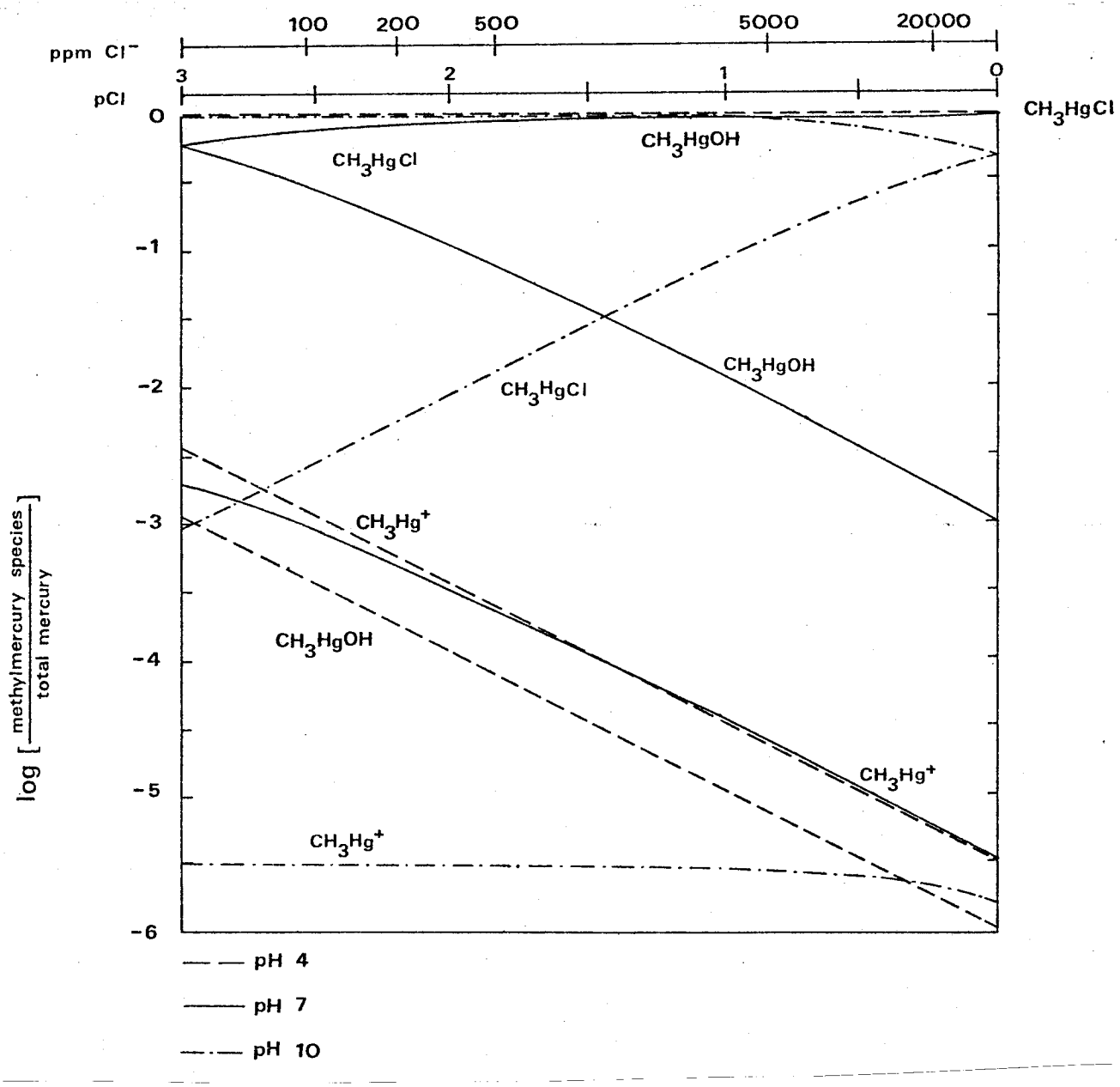
solutions because, like the mercuric ion, it tends to bind with numerous compounds. Figure 4, adapted from Burrows and Shin (1973) work on methylmercury species versus chloride ion concentration in water shows this theory.

The compilation of information regarding mercury species in water is best described by a modification of Jensen and Jernelov's (1972) representation:



HgS is stable in anaerobic solution, Ksp = 10^{-53}, and dissociates into divalent ions in aerobic solution. The mercuric ion released by the dissociation is available for further binding or reduction. $Hg^{0} \rightleftharpoons Hg^{+2}$ is mostly a function of the redox potential and pH although the bacteria genus Pseudomonas is able to reduce the mercuric ion to metallic mercury. As will be shown in the next sections, all forms of mercury are available for decomposition to Hg^{+2} by biological activity. Dimethylmercury is favored by high pH and decomposes in low pH and ultraviolet light

FIGURE 4: Methylmercury Species Versus Chloride Ion Concentration



(Jensen and Jernelov, 1972).

Quantitative Analytical Techniques

Mercury volatility and the minute quantities present in samples are the major obstacles in accurate analysis. In addition to losses due to vaporization, errors accumulate in every step of the analysis through 1) operator and machine errors, 2) use of contaminated reagents containing trace amounts of mercury and 3) mercury leaking through or adsorbing onto the container walls (National Research Council (NRC), 1978). Accumulated errors affect the reliability of experimental results because any error, when trace quantities are involved, is greatly magnified.

Mercury analytic techniques, categorized a either total mercury or organic mercury analyses, require separation and concentration of the mercury prior to the actual determination. This is especially necessary for organic mercury samples. Organic mercury analyses are difficult to perform because the strong binding of mercury to organics require more complex separation techniques.

Numerous quantitative analytical techniques are available to determine mercury concentrations in the environment. Smith (1972) has separated the different techniques for mercury compounds in Table 2. Brief descriptions are given below for the

techniques commonly used in analyses.

TABLE 2: Classification of Analytical Methods

Elemental, Total and Inorganic Analysis	Organic Mercury Compounds
Activation Analysis	Alkyl
Atomic Absorption and Flourescence	Non-Alkyl
Chromatographic Analysis	
Colorimetric	
Electrometric	
Gravimetric	
Micrometric	
Radiometric	
Spectrographic	
Titrimetric	
X-Ray	

From Smith (1972)

Pretreatment. In the field, it is often impossible to perform an analysis of the mercury content of a substance immediately after sampling. The sample must be stored until an analysis can be made. Experimental results have shown severe volatilization losses of mercury from polyethylene, polyvinyl chloride and soft glass may be avoided by acidification to about pH 0.5. Without acid pretreatment, a 26 ug Hg/l solution in polyethylene containers had the lowest mercury half-life of about 1.5 days, whereas with acid treatment little mercury loss (2%) was detected after 15 days. Acid pretreatment and a preservative solution of potassium permanganate were not enough to prevent mercury loss in

solutions of 0.1 -10.0 ug Hg/l in polyethylene and glass containers. If, however, 0.01% dichromate ion replaced the permanganate, the mercury solutions were stable up to five months (National Research Council, 1978).

Concentration and separation, which essentially produces the same results, are generally required before an analysis is performed. Concentration is the removal of the matrix from the metal and separation is the removal of the metal from the matrix (National Research Council, 1978). Either process results in an increase in the quantity of metal available for analysis. Techniques to extract mercury include evaporation, extraction into organic solvents, precipitation, reduction to elemental mercury or amalgamation.

Evaporation, a popular separation technique, is performed by application of heat to the sample. However, losses are easily incurred through unsealed connections in the volatilization apparatus. This method is undesirable for small mercury content determinations.

Solvent extraction is based on the different solubilities of compounds in solution. Benzene or toluene is mixed in aqueous solution and are allowed to separate. The organic phase containing the metal is withdrawn and analyzed. The extraction process may be done repeatedly with fresh solvent to insure complete extraction of the metal (National Research Council, 1978).

By variation of pH and addition of complexing agents, most metals can be extracted from solution samples as chelates. Dithizone is usually used as the organic chelating agent to form organomercury chelates. Metals, other than mercury, are also extracted in this process. These metals can be removed from the sample with metal-specific separation techniques. An advantage of dithizone is that colorimetric analysis can be performed on the chelates at an absorption level of about 490 nm in chloroform (Lindstedt and Skerfving, 1972).

Ashing, a separation process, is usually performed by digestion of the solution with oxidizing substances. The most common digestion solution is potassium permanganate in sulfuric acid solution. Other digestion mixtures include nitric acid, perchloric acid, hydrogen peroxide and bromine. Incomplete ashing produces erroneously low results whereas mercury in the reagents tend to erroneously high results. Blanks and standards are required to correct and detect errors (Smith, 1972).

The amalgamation technique is based on the observation that traces of mercury are immediately soluble on gold or silver. Gold and silver meshes are used to aggregate mercury particles from air samples. For a solvent extraction, a silver wire has been used with a 100 ml sample solution with 10 ml HCl in a closed flask. After overnight agitation, the wire was removed, washed with distilled water and heated to vaporize the mercury which was collected and analyzed (Lamm and Ruzicka, 1972).

Cold Vapor Atomic Absorption and Flameless Atomic Absorption. Cold vapor atomic absorption and flameless atomic absorption analyses are simlar in technique, differing only in the method used to vaporize the isolated mercury. Both start with mercury that has been removed from the sample matrix by one of the separation-concentration techniques. In cold vapor technique, the isolated mercury is placed in solution, reduced to elemental mercury and removed by aeration. The flameless technique employs heating to vaporize the isolated mercury (Smith, 1972).

The mercury vapor is collected in an absorption cell. Radiation at 253.7 nm from a hollow cathode mercury discharge lamp is absorbed by the mercury atoms. The mercury concentration of the sample is determined from comparison with a standard absorbance curve (National Research Council, 1978).

The atomic absorption method is used for total mercury analysis. It cannot be used for inorganic or organic mercury species analysis without separation before introduction into the absorbance cell.

The advantages of this method include 1) rapid analysis, 2) suitability for all pretreatment techniques, 3) can detect low concentrations and 4) equipment is relatively inexpensive (National Research Council, 1978).

Gravimetric Analysis. In gravimetric analysis, the sample is digested with a reducing solution to convert all the mercury into

elemental mercury. Heat is applied to vaporize the mercury which is collected by amalgamation on the metal screen. The difference in weight of the screen before and after amalgamation determines the mercury content in the sample (National Research Council, 1978). This method is good for large quantities of mercury since the accuracy is only as good as the balance.

Colorimetric Analysis. One of the oldest methods to determine mercury concentrations in samples is the colorimetric analysis. The orange mercury dithizone chelates formed by dithizone extraction in chloroform have a maximum absorbance at 490 nm. The accuracy of this method is generally ± 0.01 ppm (D'Itri, 1972a). Complete digestion of the sample is required for an accurate result. Errors occurring in this type of analysis arise because of incomplete digestion and interference from other metals which form similar-colored chelates (Lamm and Ruzicka, 1972).

Another dithizone method is useful in organic mercury determinations. Organic mercury compounds are extracted with benzene from the acidified homogenate sample and re-extracted with sodium sulfate solution. After oxidation with acid permanganate and the addition of urea and ethylene-diaminetetraacetic acid (EDTA), the mercury concentration is determined by titrimetric method using dithizone. This method is capable of differentiating between organic and inorganic mercury compounds in the sample (D'Itri, 1972a).

Neutron Activation Analysis. Neutron activation analysis involves isotope exchange between radioactive mercury. Samples are sealed in a quartz or polyethylene vials before irradiation with neutrons to convert ^{196}Hg to ^{197}Hg or ^{203}Hg. The gamma radiation emitted by radioactive ^{197}Hg isotopes of half-life of 65 hours, is measured by spectrophotometry. The mercury concentration is determined from a known standard scale (National Research Council, 1978).

Two types of analyses may be performed by this method. One method is the non-destructive analysis where the intact sample is irradiated. Pre-treatment of the sample is unnecessary. The other method is the destructive analysis technique performed by different chemical procedures to separate the constituents of the sample prior to irradiation. Detection of smaller concentrations and a higher degree of specificity are advantages of this method over the non-destructive analysis (Lindstedt and Skerfving, 1972; National Research Council, 1978).

The neutron activation analysis is probably the most sensitive and reliable of all techniques when determining trace amounts of mercury in biological samples (D'Itri, 1972a; Smith, 1972). Another advantage is the small amount of operator time required for analysis. Disadvantages of this technique are the high cost of equipment, requires highly trained personnel (D'Itri, 1972a) and the inability to distinguish between the chemical state of mercury in the sample (National Research Council, 1978).

Gas Chromatography. Since the necessity for quantitative organic mercury compound differentiation arose, there has not been much improvement nor have superior techniques been devised other than gas chromatography or thin-liquid chromatography. These determinations preserve the different organic structures of mercury compounds which differs from inorganic-organic determinations that preserve only the gross quality of the compounds.

Gas chromatography and thin-liquid chromatography actually refer to separation-extraction techniques. The separation technique is specific for the organic mercury compound of interest. Mercury is extracted into an organic solvent which is injected into an outlet to be vaporized. The collected gases are passed through a chromatographic column and are analyzed by electron capture detector (National Research Council, 1978).

One method of dimethylmercury concentration determination is extraction with toluene after the addition of cysteine-borate buffer at pH 8.2 to stabilize dimethylmercury in the sample (Hartung, 1972). Other separation techniques used involve dithizone.

Regulatory Limits

Health regulations regarding toxic substances are generally made with the welfare of man as the objective. The regulations

usually do not protect the health of animals but are dictated to guarantee that man suffers no adverse effects by the consumption of contaminated foods. Therefore the emphasis in this section will be placed on mercury's effect on man rather than the effect on plant or fish life.

Mercury has no known beneficial function in the sustainment of life for any organism (National Research Council, 1978). Its presence in man has proved to be detrimental to the point of being fatal. Mercury contamination is the result of accumulation through respiration, absorption through the epidermis, or from the ingestion of contaminated food.

The degree of toxicity is dependent on the length of exposure and the type of mercury compound. Methylmercury poisoning, which produces irreversible neurological damage, is usually transmitted to man through the food chain. However, inorganic mercury poisoning, whose symptoms can be reversed if recognized in time, is transmitted by non-food contact. Felt hatters and mercury miners became intoxicated when mercury was absorbed through the skin or through the respiratory tract as the vapor was inhaled (D'Itri and D'Itri, 1977).

The gastrointestinal absorption of methylmercury is about 100% complete. Therefore any quantity of methylmercury introduced via that route is assimilated into the body. 80% of inhaled vapor (mostly inorganic form) is retained while absorption of inorganic mercury from foods is about 7% of the total ingested amounts (WHO, 1976).

The kidneys in man show the highest concentration of mercury with the level in liver being second highest. Elimination of mercury is slow, the biological half-life in man is about 70 days (WHO, 1976). Fortunately most of the mercury accumulated is eventually eliminated from the body. The organic mercury compounds are more stable in the body than inorganic compounds and thus are eliminated at a slower rate.

Regulatory limits set by health agencies for mercury consumption are based on the total amount of mercury man can accumulate without harmful effects by the amount of food consumed and the mercury concentration of the food. Swedish authorities set 20 ng Hg/g as the maximum allowable level of methylmercury in whole human blood. The World Health Organization set the maximum allowable weekly intake of total mercury for a 70 kg man to be 0.3 mg Hg with no more than 0.2 mg Hg as methylmercury (National Research Council, 1978; WHO, 1976).

The United States recommended guideline for mercury concentration is a maximum allowable dietary intake of 0.3 mg Hg/70 kg man/day. A factor of safety of 10 is incorporated to insure the lowest whole blood concentration of methylmercury associated with toxic symptoms at 0.2 ppm Hg is not reached (National Academy of Science (NAS), 1973).

The U.S. Food and Drug Administration recommended the maximum limit in fishes to be 0.5 ug/g (NAS, 1973). Other countries' recommendations are listed in Table 3. The Japanese recommendation is lower than the others because of the higher

average per capita consumption of fish and other shellfish.

TABLE 3: Maximum Allowable Mercury Concentrations in Fish*

Canada	0.5 ug Hg/g
Japan	0.4 ug Hg/g
Sweden	1.0 ug Hg/g

*Modified from the National Research Council (1978)

Most of the guidelines are based on total mercury concentration rather than the more toxic methylmercury concentration. The rationale behind that choice is that most mercury forms are capable of becoming methylated in the body (WHO, 1976), that most of the mercury in fish is in the methylated form, and that total mercury determinations are easier to make.

Other guidelines recommended by the National Academy of Sciences (1973) for natural waters are listed below:

Public water supply systems:	<2.0 ug Hg/l
Constitutes a marine hazard:	>0.1 ug Hg/l
Freshwater fish and predatory organisms:	<0.5 ug Hg/l
Unfiltered water at any time or place:	<0.2 ug Hg/l
Average total Hg in unfiltered water:	<0.05 ug Hg/l

The 2 ug Hg/l in water supplies is based on a 2 l/day per capita consumption of water which amounts to an intake of 4 ug Hg/day.

The Environmental Protection Agency (US EPA, 1976) has also recommended guidelines which are similar to the earlier National Academy of Sciences criteria. The mercury concentrations acceptable in water are:

Domestic water supply:	2.0 ug Hg/l
Freshwater aquatic life and wildlife:	0.05 ug Hg/l
Marine life:	0.1 ug Hg/l

Background Concentrations

The determination of background concentrations in the environment serves two purposes. Background concentrations are required to compare and calculate the degree of pollution and they are also used as possible indicators of mercury transport. Global mercury cycles have been postulated on the basis of total mercury in each pool of accumulation (National Research Council, 1978).

However, background concentrations are difficult to determine since mercury is an ubiquitous substance. It occurs in almost all life forms and in rock material. A water body is generally considered to be representative of pre-man or background levels when no source of mercury input is detectable. The atmospheric background, sediment and soil concentrations are usually taken as

Table XVIII (Background and After Stocking),

Mercury Levels Size and Weight of Catfish by Lake

Background				After Stocking			
Present Study				Lake Buzz Aldrin:			
Date	Wet Wt. (g)	Length (in.)	Hg conc. (µg/g)	Date	Wet Wt. (g)	Length (in.)	Hg conc.(µg/g)
10/21/80	922.0	17.00	0.10	6/ 3/81-9/ 8/81	212.5	12.00	0.06
	702.0	17.00	0.11 (0.09)		212.5	12.00	0.06
	862.5	16.00	0.11 (0.11)		123.0	9.50	0.04
				6/80 F,10/80-	893.2	17.50	0.07
				9/8/81	1136.0	20.00	0.06 (0.06)
					620.7	16.00	0.04
					640.8	16.00	0.08
					770.5	17.50	0.09 (0.08)
				Lake Mike Collins:			
				6/11/80-10/14/80	822.0	17.00	0.09
				6/11/80- 9/23/80	1178.2	19.00	0.15
					1182.7	18.00	0.14
County Engineer Records							
6/ 6/78	784.25	14.72	0.20	9/19/78	1023.0	17.19	0.20

the overall global concentrations. Presented in Table 4 are "background" estimates of mercury in the environment.

TABLE 4: Background Mercury Concentrations

Atmoshere		
Remote oceanic areas	0.7 ng Hg/m^3	NRC (1978)
Urban areas	10.0 ng Hg/m^3	NRC (1978)
Soils and Sediments		
Global concentration	80-100 ppb Hg	Fleischer (1970)
Global freshwater and oceanic sediments	300 ppb Hg	Garvis and Ferguson (1972)
Natural Waters		
Freshwater average	0.02-0.06 ug Hg/l	NRC (1978)
Ocean average	0.03 ug Hg/l	NRC (1978)
Rainfall	0.20 ug Hg/l	USGS (1970)

Atmospheric Mercury Concentrations. The atmosphere is believed to be a major medium of mercury transport on a global scale. Mercury particulates are transported on the winds as well as mercury vapor which is almost entirely in the elemental form (National Research Council, 1978). Although the average levels in the atmosphere are fairly low, the total mercury content in the atmosphere is estimated to be 17 x 10^8 g which represents a substantial amount of mercury available for transport.

The concentration of mercury in the atmosphere at any given location is dependent on the surrounding environment. Coal-fired power plants, industries and sludge containing high mercury content incinerated at a sewage treatment plant have been

connected with elevated mercury concentrations in the surrounding and downwind atmosphere as well as soil samples (Cooper, et al., 1975; D'Itri, 1972b). As much as a tenfold increase in mercury concentrations was observed in soil samples downwind of the St. Clair River -- Lake St. Clair -- Detroit River industrial complex due to air bourne transport (Klein, 1972).

Although most of the mercury is attributed to industrial gas effluents, it has been suggested the sea may be a prime contributor of atmospheric mercury (Brosett and Svedung, 1977). Others have suggested the release of mercury vapor occurs with decreasing barometric pressure with the maximum mercury volatilization occurring at greatest rate decrease (McCarthy, et al., 1970). This is a possible explaination of the daily flucuation of mercury concentration in the atmosphere.

Contrasting the figures found in Table 5 are those by Klein (1972) who reports Erikssen estimated a 20 ng Hg/m^3 average global concentration. Mercury concentrations of 10-2300 ng Hg/m^3 have been reported in cities with the concentration dependent on city and the sample location within the city (Cooper, et al., 1975).

In an attempt to find a relationship between high acidity in Swedish lakes and high mercury concentration, Brosett and Svedung (1977) did extensive work collecting mercury atmospheric data. Their research result showed a linear regression relationship for mercury concentration in the air over coastal waters correlated to surface water temperature and to air temperature with

TABLE 5: Summary of Atmospheric Mercury Levels*

	Range (ng/m^3)	Average (ng/m^3)
A. REMOTE AND RURAL AREAS		
Oceanic		
particulate	<0.005-0.06	<0.15
vapor	0.6 - 0.7	0.7
Non-mineralized terrestrial		
particulate	<0.004-1.9	0.15
vapor	1.0 -10.0	4.0
B. URBAN AREAS		
particulate	<0.01-220.0	2.4
vapor	0.5 - 50.0	7.0

*Modified from the National Research Council (1978)

regression coefficients of r = 0.96 and r = 0.97, respectively. When attempting to verify their correlation with air samples off the coast of Africa, the field data were much lower than the predicted values.

In the same article the authors report mercury concentrations as a function of altitude. Data taken on November 8, 1974 in Ringenas, Sweden shows decreasing atmospheric concentrations with increasing altitude.

ALTITUDE	CONCENTRATION
Groundlevel	6.3 ng Hg/m^3
50 m	5.0 ng Hg/m^3
150-200 m	<2.0 ng Hg/m^3

In studies done over Tampa Bay, Florida, a 10 m vertical profile revealed decreasing concentrations with increasing height (Johnson and Braman, 1974). The authors suggest the higher levels near the ground surface are due to the volatilization of

mercury from the soil.

Rainfall. Atmospheric mercury may be transported to the earth either by settling or through rainfall washout. These might be important mechanisms of mercury transport to supposedly uncontaminated waters. Swedish researchers reported rainfall returns mercury to the land at a rate of about 0.5 g Hg/acre/year (Cooper, et al., 1975).

The few estimates of rainfall mercury concentrations may be found in Table 6. Note the discrepancy between the first two and last two values of rainfall concentrations.

TABLE 6: Mercury Concentrations in Rainfall

Location	Concentration	Reference
Windermere, England	6-30 ng Hg/l	Gardner (1978)
South New England Coast	10 ± 5 ng Hg/l	Fogg and Fritzgerald (1979)
Rural United Kingdom	< 200 ng Hg/l	NRC (1978)
Oakridge, Tennessee	50-540 ng Hg/l	NRC (1978)

There has been some discrepancy whether total washout of atmospheric mercury occurs following a rainstorm. More determinations are needed to solve the controversy since evidence supports the theory that total washout occurs (McCarthy, et al., 1970; Fogg and Fritzgerald, 1979) and that it does not (Johnson and Braman, 1974).

Soils and Sediments. Global estimates for typical soil concentrations are varied since many factors influence the mercury concentrations in any one area. However, researchers seem to agree on an 80-100 ppb Hg average global soil concentration (Fleischer, 1970; Garvis and Ferguson, 1972).

Values in recorded rocks and soils vary from 10 ppb Hg to 20,000 ppb Hg (USGS, 1970), with more than 80% of those values being <1000 ppb Hg. Mercury concentrations are often dependent upon the rock/soil composition. Limestones and sandstones have concentrations averaging between 30 ppb Hg and 50 ppb Hg (Fleischer, 1970). Organic-rich shales tend to have extremely high concentrations and sands the lowest values (Potter, et al., 1975).

Some values for mercury concentration for specific areas are listed in Table 7.

TABLE 7: Mercury in the Lithosphere--Freshwater Sediments

	Soils (ug/g)	Freshwater Sediments (ug/g)
Sweden	0.01-1.0	0.034-26.5
average	0.07	0.3
England	0.01-15.0	0.01-1.03
average	0.06	---
United States	0.01-4.7	0.01-1200.
average	0.07	0.3

*modified from the National Research Council (1978)

Bed sediments also exhibit a wide range of values. Unlike soils and rocks, however, the composition plays a secondary role to the mercury load carried by the water. The mercury concentration in the water will have greater influence on the concentration in the sediment than the nature of the sediment. Mercury's tendency to adsorb onto particulate matter will be enhanced with greater mercury concentrations in the water.

The sediment composition, however, will still influence the relative magnitude of concentration. Organic sediments generally possess high mercury content because of the tight complex bonds mercury forms with organic molecules. Clay and clay-containing sediments have large surface areas which present more adsorption sites. Mercury concentrations of organic and clay-containing sediments from Wisconsin lakes and rivers are in the range of 0.05 ppm Hg to 0.155 pp Hg. Sandy sediments from the same areas have slightly lower concentrations of 0.01-0.05 ppm Hg (Konrad, 1972).

Concentration in bed sediments are also functions of the distance from the outfall source. High concentrations are reported in the vicinity of outfalls and decreasing at increasing distance downstream of the outfall (Langley, 1973; Hasselrot and Gothberg, 1974). The average bottom sediment concentration of mercury above an inactive chloralkali plant in Virginia is 0.13 ppm Hg whereas 3.1-6.4 km downstream, it averaged 19.3 ppm Hg (Turner and Lindberg, 1978). In a study of two contaminated and two uncontaminated lakes in Canada conducted by

Moore and Sutherland (1980), the contaminated lakes showed higher concentrations close to the discontinued mercury mining operation located on the banks. Giaque Lake has a concentration of >5 ppm Hg within a 200 m radius of the mine whereas the central portion of the lake has values ranging 0.004-0.290 ppm Hg. Similarly, Thompson Lake has a high value of 0.439 ppm Hg within a 1 km radius of its mine site while the average concentration beyond the radius is 0.114 ppm Hg. Uncontaminated Thistlethwaite and Hidden Lakes have sediment concentrations of 0.0028 ppm Hg and <0.010 ppm Hg, respectively.

Eutrophic Wintergreen Lake, in Michigan, with no known source of mercury input has an average soil concentration of 0.095 ppm Hg with a range of 0.056-0.9158 ppm Hg (Mathis and Kevern, 1973). Contaminated Lake Michigan with bed sediments less than 200 micron diameters average about 1.0 ppm Hg with a range of 0.35-1.8 ppm Hg (Copeland, 1972).

Natural Waters. Data are scarce on the background values of mercury in lakes and rivers. A range of 0.02-0.06 ppb Hg in freshwater and 0.03 ppb Hg in ocean waters seems to be acceptable (National Research Council, 1978). The few values, however, indicate extremely low concentrations. Giaque, Thompson, Thistlethwaite and Hidden Lakes with their contrasting sediment concentrations all have similar water concentrations of 0.2 ppb Hg (Moore and Sutherland, 1980). Man-made Lake Powell, in nine water samples, presented an average value of 0.07 ppb Hg

(Potter, et al., 1975). The mercury concentrations in Lake Windetmere, England, varied over a three month test period in 1973 (Gardner, 1978). The results are tabulated below. The low November average mercury concentration was attributed to rainfall dilution.

	September	October	November
Hg concentration range (ppb)	0.016-0.056	0.013-0.075	0.000-0.027
average (ppb)	0.029	0.037	0.012
Rainfall (mm)	78	89	154

Lindberg and Harriss (1977) have shown the effect of dredging on mecury concentrations in the water above the dredge site. Sharp increases in concentrations were immediately apparent after the distrubance, however, the peak dissolved mercury concentration in the water occurred 1-2 hours after the disturbance. The authors suggest that the mercury concentration in the water is not only a function of "pH, redox potential, total dissolved sulfides and dissolved organic concentrations," but is also a function of the length of time after the sediment is disturbed.

History

Mercury, in its long and varied history of applications, has been both a useful and harmful element to man. A brief history

of mercury applications is presented below, ending with a recap of the Minamata Bay incident.

The first recorded use of cinnabar ore came from China in about 1100 B.C. when it was used for ink pigmentation. In western civilization, the element was extracted from cinnabar by simple heating in about 4 B.C. and by about 1 B.C. it was also being used extensively as a pigment (Farrar and Williams, 1977).

Although the use of mercury in China occurred at an earlier date, the development of their knowledge of its amalgamation properties coincided with western civilization advancement in the art. With its rise in amalgamation, mercury was used in alchemy. Of course, its use in alchemy was discontinued after the 1500's. (Farrar and Williams, 1977).

Around the first century A.D., mercury was extracted and sold for gilding, used in amalgamation processes for the recovery of gold and sold as a curiosity. Its use in amalgamation made it a valuable trade commodity in about 1000's. (Farrar and Williams, 1977).

The amalgamation process was introduced in the silver mines about 1550. Ground and roasted silver ore with mercury were spread over a paved area and crushed until the amalgam separated from the debris ore by washing. The amalgam, concentrated by squeezing in cloth bags, consisted of about five parts mercury to one part silver. Thus, the final step in the silver recovery process was heating the mixture to vaporize mercury (Farrar and

Williams, 1977).

Until the late 1400's, mercury was not used extensively in the medical area. Aristotle advocated the use of mercury for treating skin disorders but advised against oral ingestion. Mercury gained its pharmaceutical importance when syphilis raged the European countries in the 1560's. (D'Itri and D'Itri, 1977).

An early treatment of syphilis began by anointing the patient's body with mercury cintment for several treatment sessions. Mercuric poisoning symptoms, such as bladder irritation, swollen gums, loose teeth, salivation and psychological disturbance, had to be endured for the "cure", along with the syphilitic symptoms. Another popular treatment involved a "steam" bath where heated mercury provided the vapor in the steam box (Farrar and Williams, 1977).

If the symptoms of syphilis were advanced, it was thought the absorption of mercury had to be rapid in order to be effective. The recommended method to absorb mercury quickly was oral ingestion, but this method had diverse effects. HgCl (corrosive sublimate) was fatal, whereas cinnabar or elemental mercury, being relatively insoluble, were ineffective. Calomel ($Hg Cl$), a relatively toxic and powerful puragative, was finally promoted as the oral counteractant to syphilis. (Farrar and Williams, 1977).

Advocates and opponents of mercury as a remedy for syphilis constantly debated the issue. Finally, in the early 1900'S, the

opponents were able to curtail the extensive use of mercury pharmaceuticals for the treatment of syphilis. The question of the effectiveness of mercury in arresting syphilis development has not been answered (Farrar and Williams, 1977).

One of the notorious uses of mercury was in the manufacturing of felt hats. Mercuric nitrate was used to soften animal hairs (carrotting process) in the felting process. The French maintained a monopoly on the carrotting process until 1685 (D'Itri and D'Itri, 1977). Thereafter, of the variety of substances tested in the carrotting process, mercury continued to be regarded as the superior carrotting agent.

In 1869, the French Academy of Medicine demonstrated the dangers of mercury in the hatting industry. It was not until 1898 they passed a law to protect the employees in the industry against mercurialism. The British also recognized the dangers of the element and instigated legislation protecting the workers. By 1921, there were virtually no new cases of mercury poisoning in England. America did not pass similar legislation until 1941 (Farrar and Williams, 1977).

A list of modern applications of mercury may be found in Table 8 (D'Itri, 1972b).

Minamata Bay. Up until the 1950's, the majority of mercury poisoning cases were the result of inorganic mercury compounds. Early symptoms of inorganic mercury poisoning include headaches,

TABLE 8: 1968 Values of US Mercury Consumption

		1000's of pounds used
1.	Electrical Apparatus Industry	1500
2.	Chloralkali Industry	1300
3.	Paint Industry	803
4.	Miscellaneous	628
5.	Industrial Control Instruments Industries	606
6.	Agriculture	260
7.	Dental Preparations	234
8.	General Laboratory Use151	
9.	Catalysts	145
10.	Paper and Pulp Industry	32
11.	Pharmaceutical and Cosmetics Industies	32
12.	Amalgamation	20

fatigue, loss of appetite, nervous anxiety, irritability, loss of concentraion and increased indecision. Many of the symptoms are reversible if the exposure to the source is halted and no irreparable damage occurs in the early stages of exposure. Mercury compounds concentrated in the liver, kidney and spleen do irreparable damage when the threshold tolerance level is exceeded. Death is usually the result of uremia (D'Itri and D'Itri, 1977).

Mass mercury poisoning had disappeared, with stricter controls and guidelines, after the felt hat mercury poisoning recognition in the early 1920's. Mercury poisoning regained prominence in the 1950's when people from the Minamata Bay (Japan) area became stricken with a mysterious ailment.

Beginning in 1953, cats on Kyushu Island exhibited nervous tremors and screamed incessantly, marking the first signs of erratic behavior in the area. By 1960, the nervous tremors were observed in other animals and the prefecture health officials

diagnosed 121 people as victims of Minamata Disease. During that period, there were 46 fatalities. Even after a twenty year period after the inital outbreak of the disease, people exhbiting the symptoms are continuously being recognized as victims of the disease. By 1973, the list had increased to 850 persons (D'Itri and D'Itri, 1977).

The causitive agent for the disease, an organo-mercurial compound, was not identified until 1959. The poison was not isolated until 1969, when crystals of a sulfur-containing methylmercuric chloride were extracted from shellfish the bay. Even when the symptoms followed the pattern of heavy metal toxicity, mercury was not immediately identified because the symptoms were unlike inorganic mercury poisoning (D'Itri, 1972a).

The symptoms of organic mercury poisoning are generally irreversible, the result of permanent brain damage. The poison attacks the central nervous system. First signs of contamination are numbness in the extremities, slurred speech, irregular gait, and concentric visual constriction. Advanced symptoms include loss of coordination, heightened emotional instability, and loss of hearing and sight. Some sensory damage and motor coordination loss are recoverable, but most of the damage is permanent (Takeuchi, 1972).

The frightening mobility of the toxin is displayed when it is transmitted to the fetus by an affected mother. In fact, the fetus appears to be the sink of the ingested mercury, acting as a buffer for the pregnant mother and reducing her toxicity. There

is also speculation that chromosomal damage occurs, however, the evidence is inconclusive (D'Itri and D'Itri, 1977).

The correlation between seafood consumption and severity of symptoms triggered officials to investigate the possibilities of heavy metal contamination of the seafood. A fishing ban 1957 coincided with reduced number of cases. Since the ban did not totally eliminate the number of cases, the search continued for the source (D'Itri, 1972a).

Further investigation showed the Shin Nihon Chisso Company was responsible for the poisoning epidemic. Between 1949-1953, they discharged an estimated 220 tons of elemental mercury into the bay along with other wastes products from the manufacturing of vinyl chloride and acetaldehyde (D'Itri and D'Itri, 1977).

An accidental side reaction converted some quantity of elemental mercury into methylmercury. Mercuric oxide dissolved in sulfuric acid was used as a catalyst in the synthesis of acetaldehyde from acetylene. Mercuric chloride was the catalyst in the reaction of acetylene with hydrogen gas, for the manufacturing of vinyl chloride. In both processes, methylmercuric chloride is a possible side reaction (Takeuchi, 1972).

Additional studies have shown the inorganic mercury compounds deposited in the bay are subject to microbial activity conversion into methylmercury derivatives. This will be shown in the next section.

The Minamata Bay incident was not an isolated case of aquatic methylmercury poisoning. The stretch from Wabigoon Lake, down the Wabigoon River to Ball Lake, Ontario, has suffered from alkylmercury poisoning from direct wastes discharges into Wabigoon River from a pulp-paper mill company (alkylmercury fungicides) and a choralkali plant (mercuric chloride) (D'Itri and D'Itri, 1977). Lake St. Clair and the St. Clair River have also had periods where the fishes in the waters had concentrations which exceeded the 0.5 ppm Hg guidelines. Again the bulk of the mercury found in the waters and fishes were from chloralkali plants (D'Itri, 1977a).

Other alkylmercury poisoning incidents have occurred because alkylmercury fungicides were used as seed dressings to preserve seed grains and alkylmercury pesticides were sprayed on crops. Flour made from treated seeds averaged mercury concentrations of about 8-9 ppm Hg was responsible for mass poisoning in Iraq in 1971-1972. In Sweden, a noticible increase in erratic bird behavior was the first sign of alkylmercury poisoning from seed grains. Wild birds and domestic livestock also consumed treated grain, thus contaminating a segment of the food chain. The Austrian and Danish governments refused to sell Swedish eggs, forcing the Swedish government to take active measures. Alkylmercury seed dressings were banned in 1966 (D'Itri and D'Itri, 1977).

Apparently the trend toward inorganic mercury poisoning is decreasing while organic mercury poisoning, with its often

disguised origins, is increasing. There has been a trade-off from the less toxic to the more toxic. The consequence of using mercury, especially alkylmercury derivatives, without increased caution in disposal, is to jeopardize the environment by creating potential outbreak sites.

METHYLATION AND DEMETHYLATION

A research goal is finding a method of decreasing methylmercury uptake by aquatic life to reduce the potential poisoning hazard of humans through consumption. The following paragraphs briefly detail methylmercury production in the aquatic environment, degradation and factors which affect both.

Methylation Schemes

Mercury can be supplied to the aquatic environment in any form of mercuric compound. Under suitable conditions all compounds can convert to methylmercury (Sommers and Floyd, 1974). In anaerobic conditions, even mercuric sulfide with an equilibrium solubility product coefficient of about 10^{-53} may become the mercury source. This previously thought inert compound is capable of becoming methylated as the water is aerated. However, the quantity of methylmercury produced is less than if HgCl were the mercury source (Fagerstrom and Jernelov, 1971). In a laboratory experiment, control fish exposed to uncontaminated sediment accumulated 2.3 ug Hg whereas fish exposed to sediment ameded with HgS accumulated 3.8 ug Hg. The highest accumulation of mercury at 7.5 ug Hg belonged to fish exposed to sediment amended with HgCl (Gillespie and Scott, 1971).

Methylation occurs only when mercury is in the +2 valence

state. The relationship between the states of mercury seems to be

$$Hg_2^{+2} \rightleftharpoons Hg^{+2} + Hg^0$$ (Wood, 1974).

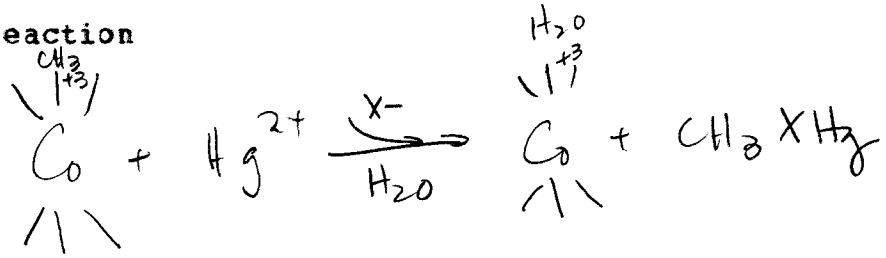
The high volatility of Hg^0 pushes the equilibrium to the right. The net result is an increased Hg^{+2} concentration. The mercuric ion may be unstable and be reduced to Hg^0 as a detoxification mechanism. The overall mercury concentration in the sediment is reduced as the volatile Hg^0 escapes into the atmosphere.

Microorganisms provide the mechanism of the methyl group transfer. Researchers have autoclaved, heated and used other sterilization techniques to verify the necessity of viable organisms for the methylation process (Jensen and Jernelov, 1969; Sommers and Floyd, 1974; Olson and Cooper, 1976; Spangler, et al., 1973).

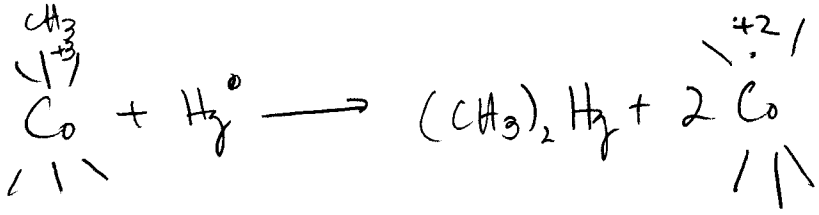
One path of methylmercury production was discovered by Landner (1971) from his work with Neurospora crassa. He showed methylation can be the result of the incorrect synthesis of methionine by a mutated mercury-resistant bacteria. This novel approach did not involve methylcobalamine (methyl B-12).

Other paths of methylation involve methylcobalamine as the alkylating agent. Methylcobalamine is a co-enzyme common to aerobic and anaerobic microbes. Any organism capable of synthesizing methylcobalamine is also a potential methylmercury producer (Wood, 1971).

Wood showed the translation of the methyl radical ion is either an enzymatic or non-enzymatic process. In the enzymatic process the reaction occurs only when the mercuric ion is present -- an anaerobic situation. The mercurous and the elemental forms inhibit the reaction and the amount of methylcobalamine present determines the reaction



The transfer of the methyl radical ion in the non-enzymatic reaction occurs under anaerobic conditions when the mercuric ion reduces to the elemental form. In this instance the determining factor for the production of monomethylmercury of dimethylmercury is the amount of Hg^0.



Three enzymes, S-adenosylmethionine, N5-methyltetrahydrofolates and methyl corrionoid derivatives provide the methyl groups for the transfer (Wood, 1974). However, only the last enzyme is effective since it transfers the CH_3^- group to Hg^{+2} as opposed to CH_3^+.

Demethylation

Demethylation is the dissociation of the methyl radical group from the mercuric ion. The decomposition of dimethylmercury in water takes the form of

$$CH_3HgCH_3 + H^+ \xrightarrow{H_2O} CH_3Hg^+ + CH_4$$

The production of methane gas usually accompanies the demethylation process (Wolfe, et al., 1973; Spangler, et al., 1973). Dimethylmercury decomposition is a function of the dimethylmercury concentration. The rate at which decomposition occurs is

$$d(DMM)/dt = k(DMM)\ (H^+)$$ (Wolfe, et al., 1973)

Chemical pathway for the desymmetrization of dimethylmercury is

$$CH_3HgCH_3 + Hg^{+2} \xrightarrow{H_2O} 2CH_3Hg^+$$

$$Hg^{+2} = Hg^{+2} + HgOH + Hg(OH)_2$$

and the decomposition follows

$$d(DMM)/dt = kobs(DMM)\ (Hg^{+2}).$$

k tends to increase as pH decrease confirming the decomposition is enhanced in acidic waters.

Demethylation, like methylation, is performed by a number of organisms. Methane gas and either Hg^{+2} or Hg^0 are by-products of demethylation and many organisms which are able to demethylate are also facultative anaerobic demethylators (Spangler, et al., 1973). Furthermore, anaerobic conditions favor the complete reduction of Hg^{+2} formed by demethylation so that demethylation

can be considered a detoxification mechanism. The demethylating bacteria were similar to the Pseudomonas genus.

Large amounts of methylcobalamine are produced by methane-producing bacteria. The production of methylcobalamine stabilizes the methylation-demethylation reactions. Although methane bacteria may be involved in the methylation process, pure cultures of methane bacteria have not produced methylmercury (Holm and Cox, 1974). On the strength of Spangler's work alone, perhaps only the methane bacteria seem to be involved in the methylation process and in fact do not promote methylation but rather demethylation. The relationship between the methylating activity and demethylating activity remains unclear.

FACTORS AFFECTING METHYLATION

As discussed previously, microbiological activity is necessary for methylation. Furthermore, microbial growth and activity have been positively correlated with increased methylmercury production. Thus many of the factors which affect methylation-demethylation rates are identical to those which inhibit or promote microbial growth. The following sections provide some insight of the effect of changing conditions.

Amount and Type of Microorganisms Present

The growth of mercury-resistant bacteria has an important role in the methylation process. An increase in the population of these bacteria corresponded to a decrease in methylmercury concentration in the medium (Billen, et al., 1974). Bacteria pre-innoculated with methylmercury compounds to increase their tolerance level, degraded methylmercury in shorter periods of time. Another result showed the population of the bacteria was proportional to the mercury concentration in the medium.

A few microbial growth studies were conducted by supplementing the medium with glucose and other organic sources. Glucose added to bed sediments promoted the largest production of methylmercury and the most degradation of methylmercury. The order of carbon sources promoting microbial growth was (Sommers and Floyd, 1974):

Glucose > Acetate > Methanol > Ethanol

Calcium acetate, used in conjunction with HgCl to promote methylation resulted in higher production over that of the control (Holm and Cox, 1974).

Another example of the effect of microbial growth was an observation from the experiment which monitored the rate of methylation with downstream distance from a chloralkali plant in Canada (Langley, 1973). Peak methylmercury production of 4.83 ng Hg/cm^2 occurred about 12.9 km (8 miles) downstream of the outfall. The higher microbial activity found at that location as compared with other sample sites was the cause of the peak production.

Mechanisms of microbial resistance include a) sulfide-producing Desulfovibrio desulfuricans which enhance the mercurial tolerance of P. aeruginosa, b) production of organic substances which bind or chelate heavy metals, and c) intracellular organic substances which serve to increase tolerance (Gadd and Griffiths, 1977-'78).

Resistance to mercurials can be transmitted by gene transfer as shown from A. aerogenes to E. coli (Gadd and Griffiths, 1977-'78). Metal tolerance by bacteria could occur at faster rates than if bacteria mutated by natural selection.

Microorganisms posses two limits of methylmercury production (Shin and Krenkel, 1976). The lower limit activates methylmercury production (detoxification mechanism) and the upper

limit defines the toxic build-up of methylmercury in the water inhibiting production. Shin and Krenkel cite Jensen and Jernelov's (1969) work where 0.1 mg/l HgCl and 100 mg/l HgCl concentrations approximated the lower and upper limits, respectively.

Amount and Type of Mercury Compound

A reasonable deduction is that higher methylation occurs with greater concentrations of mercury. That has proven to be true. In fact, increased methylation coincides with higher quantities of mercury, whatever the form (Holm and Cox, 1974). An example of this was shown in an experiment using San Francisco Bay sediments treated with 100 ug/g and 10 ug/g HgCl which were kept in both anaerobic and aerobic conditions. The higher mercury concentrations in the sediment produced more methylmercury in both conditions with anaerobic production being greater (Olson and Cooper, 1976). The different sediments tested showed the organic content was also associated with the methylation rate. Olson and Cooper do not believe anaerobic conditions are more conducive to methylation; instead, they feel that aerobic conditions may be more conducive to demethylation thereby misrepresenting the methylmercury production as being deceptively small.

One disagreement with the mercury concentration versus the quantity available comes from Shin and Krenkel (1976), who feel

the concentration of mercury is unrelated to methylmercury production. Mercury concentrations of 0.45 mg/l and 8.95 mg/l Hg produced 96.1 ng Hg and 88.5 ng Hg as methylmercury respectively, in bed sediment.

There exists limiting mercury concentrations over which microorganisms and other life forms cannot survive (Wojtalik, 1971). One limiting mercury concentration was 500 ug Hg/l (Billen, et al., 1974). A mercury concentration of 500 ppm Hg^{+2} in the sediment hade a toxic effect on the methylating organisms, which resulted in decreased methylmercury production (Fagerstrom and Jernelov, 1971). Using fishes as indicator organisms for methylmercury production with inorganic mercury as the mercury source showed low-level (9 ppm Hg) sediments had higher methylmercury productions than high-level (120 ppm Hg) sediment (Gillespie, 1972).

If HgS were used as the mercury source, the ratio of methylmercury produced by HgS as compared with Hg^{+2} as the source in aerated condition is 1:1/1000 (Jernelov, 1972a). The oxidation of HgS is the rate-determining step in HgS transformation to methylmercury.

pH

The redox potential is affected by the pH. Noted earlier, it is necessary for mercury to be in the mercuric state prior to

methylation. Hence the redox potential will determine if oxidation is possible. Jernelov (1972) developed the following equation to determine the necessary redox potential, G, for oxidation:

$$G = 350 + 30\log ((Hg^{+2})/a)$$

where a represents an estimate of the binding strength between Hg^{+2} and the available complex-forming substances.

Experimental results indicate lower pH results in higher accumulation of mercury in fishes (Kleinert, 1972; Konrad, 1972; Jernelov, 1972).

The general observation which can be made regarding pH and the state of the metallic cation is that (Gadd and Griffith, 1977-'78):

pH < 7.0 - metals usually exist as free ionic cations;
pH > 7.0 - metals usually exist as insoluble hydroxides or oxides.

At alkaline pH, the dominant mercury compound found is usually dimethylmercury. As the pH is lowered to acidity, the dimethylmercury degrades to monomethylmercury (Sommers and Floyd, 1974).

A minor result of experiments identifying mercury transport routes in the atmosphere done by Brosset and Svedung (1977) was that acid lakes were more susceptible to accumulating air-borne mercury than alkaline lakes. They theorized a lake with pH 4.0

would accumulate approximately four times more methylmercury than an identical lake with pH 7.0.

Related to the above is the discussion about the effect of lake conditions on methylating activity. Oligotrophic lakes generally have low pH. Jernelov, et al. (1975) proposed fishes in oligotrophic lakes accumulate more mercury than fishes in eutrophic lakes because oligotrophic lakes produce more methylmercury.

Supporting evidence comes from work done at Pigeon River Forest on Section Four Lake (oligotrophic) and Hemlock Lake (eutrophic) (D'Itri, et al., 1971). Fishes from Section Four Lake averaged mercury concentrations of 0.17 ppm Hg while fishes from Hemlock Lake averaged 0.07 ppm Hg. Contributing to the lower mercury accumulation by the fishes in Hemlock Lake, although it is generally alkaline, were the occasional anaerobic conditions and the high concentrations of particulate-detritus material which provided supplemental sites for chelating and complexing.

Twelve species of fish from Lake Paijanne, Finland, were analyzed for total mercury content over a four-year period (Hattula, et al., 1978). The highest mercury concentrations were found in the fishes corresponding to the areas where the lake was the least eutrophicated.

Temperature

The effect of temperature on methylation was studied by Sommers and Floyd (1974). They observed increased temperatures corresponded with increased methylation and demethylation rates. The theory is the higher temperatures speeds the metabolic activity of the microorganisms.

In an experiment using sediments with mercury concentrations of 250 mg Hg of either HgCl or CH_3HgCl at 4°C, they found a continuous increase of methylmercury production over the duration of the experiment. At 25°C, the sediments showed an increase of production for only the first 14 days. However the amount of Hg^{+2} converted to methylmercury was greater at the higher temperature. Perhaps the upper limit of methylating activity was reached after 14 days. Demethylation studies showed a 10% increase in demethylation at 25°C compared with that at 4°C. A continuous demethylation rate was reached after 14 days, and thereby stabilized, hinting either of the cessation of the demethylating activity or the equilibrium condition of methylating-demethylating activities.

Temperature effects on methylation was one of the variable tested in extensive experimental work by Shin and Krenkel (1976). They also observed increased methylation rates with increased temperature (see Table 9). The high jump at 35°C is explained by decreased demethylation and increased methylation.
The high jump at 35°C is explained by decreased demethylation and

TABLE 9: Summary of Results from Shin and Krenkel (1976)

	Highest production (ng Hg)	Corresponding rate (ng Hg/wk/g sediment)
Temperature		
35°C	640	32
25°C	109	4.4
15°C	59.9	2.4
5°C	48.7	1.9
Organics		
8 mg/l BOD	591	19.7
80 mg/l BOD	911	36.4
800 mg/l BOD	717	23.9
Chloride Ion Concentration		
200 mg/l Cl^-	835	33.4
1000 mg/l Cl^-	487	16.2
5000 mg/l Cl^-	202	6.7
20000 mg/l Cl^-	54.3	1.8
pH		
3.8	23.7	0.9
7.1	109	4.4
9.7	96.2	3.2
Hg concentration		
0.7 mg/l Hg	92.4	2.4
6.96 mg/l Hg	109	4.4
69.6 mg/l Hg	233	9.3

Standard conditions: T=25°C
6.96 mg/l Hg as ($HgCl$)
5 g soil
pH 7.1
0 mg/l BOD, 0 mg/l Cl^-

increased methylation.

Depth of Methylating Activity

The two reports published relating the depth of the mercury-enriched sediment and the amount of methylmercury in the overlying water have contradicting conclusions.

The first report by Jernelov (1970) showed, using fish as the indicator of methylmercury production in the sediment, methylation occurs only at the surface of the water-sediment interface. However, in the presence of dense macrofauna populations of Tubificidea and Anodanta, the mercury-rich sediment was effective up to the depth of 2 cm and 9 cm, respectively.

Four cylinders placed in water tanks were used in an experiment done by Olson and Cooper (1974). Each cylinder contained a layer of HgCl amended sediment at concentrations of 10 ppm Hg or 100 ppm Hg placed at different depths. The shallow depth was defined to have the enriched layer in the upper 1.27 cm of the cylinder while the deep zone referred to treated sediment in the lower 6.35 cm of the cylinder. Untreated sediment occupied the remaining voids. Methylation occurred even in the deep zone. In fact, the amount of mercury released from the deep zone into ther water was higher than the amount of methylmercury released by the shallow zone. The authors provided possible explanations:

1) more methylation occurs under anaerobic conditions,
2) there is a greater loss of methylmercury at shallow depths, or
3) there is a faster rate of demethylation at shallow depths.

The explanation probably lies in a combination of the above since each by itself has been experimentally verified by others as enhancing the methylation process.

Since the results of the two experiments are contradictory, the depth effect of uncontaminated sediment over contaminated sediment is unresolved. The different sediment types used by the researchers may account for the discrepancy in the findings. Olson and Cooper used sediment from the estuarine San Francisco Bay area whereas Jernelov used sediment from a eutrophic lake. Eutrophic lakes, as seen earlier, do not promote methylating activity, attributing to the low methylating activity of that sediment.

Sediment

Organic material in the sediment affects the methylating ability of the microorganisms since it is thought to be a complexing agent providing adsorption sites to bind mercury and prevent methylation or transportation (D'Itri, et al., 1971). Higher mercury concentrations are expected in sediments containing high organic content. Rock debris from Lake Powell, Arizona confirmed the assumption (Potter, et al., 1975). Wisconsin river and lake sediments also confirm the above with background concentrations in sandy sediments averaging 0.01-0.05 ppm Hg and organic-clayey sediments averaging 0.05.-0.15 ppm Hg (Konrad, 1972).

Low mercury concentrations in waters overlying high organic content is another effect of the complexing action. More methylmercury has been detected in waters over coarse sand as

compared with sediments containing silt-wood chip mixtures or pure wood chips (Akagi, et al., 1979).

Organic material seems to enhance adsorption but particle size plays a larger role in adsorption capacity of the sediment when viewed on a unit mass basis. Small particles have large surface areas (especially clays) per unit mass. The amount of mercury adsorbed per unit mass of sediment is thus a function of the amount and type of clay particles (Sommers and Floyd, 1975). Sommers and Floyd found the adsorption of phenylmercury acetate and phenylmercury ion was greater on montmorillonite clays than allophane or kaolinite clays. However the reverse was true if HgCl was the mercury compound. The adsorbed organic mercury compounds did not leach from montmorillonite as much as it did from the other sediments, indicating different adsorption mechanisms were involved in the process.

Support comes from work on Ottawa River sediments (Townsend, et al., 1974). Radioactive mercury was added to three sediment types: sand, wood chips (high organic content sediment) and fines (mixture of clays, silt and fine wood fibers) to achieve four concentrations. The resulting relative adsorption capacities are shown in Table 10. The fines and wood chips exhibited high ion exchange capacities, leading the authors to believe adsorption capacity was linked to the ion exchange of the sediment.

Another study involving kaolinite, mica and organic material showed them as major adsorbents of mercury (Bonner and Bustmante,

TABLE 10: Relative Mercury Adsorption Capacities

	0.1 ppm	10 ppm	100 ppm	1000 ppm
Sand	1.0	1.0	1.0	1.0
Wood chips	43.0	71.0	13.9	1.9
Fines	99.0	114.0	58.3	31.4

1976). Kaolinite and muscovinite adsorbed more mercury than montmorillonite and vermilite. The former sediments had ion exchange capacities of 0.1 meq/g compared to the latter with 1.0 meq/g. This contradicts the findings of Townsend, et al.

Although the mechanism of adsorption is still unidentified, the adsorption process had been fitted to both the Freundlich (Reimers and Krenkel, 1974) and Langmuir (Ramamoorthy and Rust, 1978) isotherms. The choice of isotherm lies with the type of sediment and the data. The Freundlich isotherm was fitted to the pure clays of illite, montmorillonite and kaolinite and sands. The Langmuir isotherm was fitted to the Ottawa River sediment.

Other Factors

Other conditions tested comes from the work of Shin and Krenkel (1976). Effects of temperature, organic load, chloride ion concentration, pH and mercury concentration were investigated. Each variable was changed from standard conditions to get the isolated effect. A summary of results is found in Table 9.

McMullen (1973) correlated mercury in the sediment with organic carbon, COD, organic nitrogen and sulfur. His results are shown in Table 11.

TABLE 11: Correlation of Total Mercury in the Sediment

Total Hg(y) vs.	Equation	Correlation
X = Organic Carbon	Y = -3.39 + 0.93X	r = 0.82
X = COD	Y = -4.10 + 0.35X	r = 0.82
X = Organic Nitrogen	Y = 0.76 + 4.09X	r = 0.72
X = Sulfur	Y = 7.66 + 32.7X	r = 0.60

TABLE 12: Summary of the Factors Affecting Methylation

Factor	Effect
Type of Microorganism	Most microorganisms are capable of methylating mercury.
Amount of Mercury	Microorganisms possess tolerance limits of mercury concentrations above which they cannot function. High mercury concentrations generally correspond to higher methylmercury concentrations.
Type of Mercury Compound	Organic mercury compounds are more easily transformed to methylmercury derivatives than inorganic mercury compounds.
pH	Dimethylmercury compounds dominate at high pH. Monomethylmercury compounds dominate at low pH.
Temperature	Elevated temperatures increase microbial activity thereby increasing methylmercury concentration in the surrounding environment.
Depth of Mercury-rich Sediment	Results are inconclusive.
Sediment	Waters above sediment containing high organic content usually have low mercury concentrations. However, the sediment itself will have high mercury concentration. Sediment containing particles with large surface area to volume ratios have high mercury concentrations.

FISHES

This final step of the mercury cycle explores the uptake of methylmercury by fishes which links contamination to man.

Average values of total mercury concentration in fishes are listed in Table 13. One should note even fishes in uncontaminated water exhibit level approaching the 0.5 ppm Hg guideline.

Fish metabolic rate appears to be the major factor determining the uptake by fishes. Related to the metabolic rate are the respiration rate, the dietary assimilation factor and the waste elimination rate. Hence the environmental factors affecting uptake are those influencing the fish metabolic rate.

Temperature

Temperature probably has the most effect on the metabolic rate. At lower water temperatures the suppression of the metabolic rate reduces the uptake of mercury from the water. A one-year *in situ* experiment on the south Saskatchewan River examined the uptake of mercury by caged Rainbow Trout (*Salmo gairdneri*) (Uthe, *et al.*, 1973). Fish stocked prior to winter showed no accumulation of mercury. In summer, the fish accumulated mercury and in fall, the accumulation decreased. The higher temperatures also stimulate microbial activity which

TABLE 13: Mercury Concentrations in Fishes

Location	Species	Total Mercury n	Total Mercury ppm	Comments	Reference
Section Four Lake	Rainbow	59	0.17	Oligotrophic	D'Itri, et al. (1971)
Hemlock Lake	Trout	100	0.07	Eutrophic	
St. Clair River below Sarnia, Ontario	Walleye		2.4		Bails (1972)
	Yellow Perch		0.8		
Middle of Lake St. Clair	Walleye		3.0		
	Yellow Perch		2.2		
Near outlet of Lake St. Clair	Walleye		2.5		
	Yellow Perch		0.6		
Anchor Bay	Walleye		2.4		
	Yellow Perch		---		
Off of Monroe, MI	Walleye		1.0		
	Yellow Perch		0.2		
Various locations in Wisconsin			0.19	range: 0.01-0.60 ppm	Kleinert (1972)
Chippewa, Flambeau and Wisconsin Rivers			0.80	0.06-4.62	
Fox & Menominee Rivers			0.38		
Rock & Fox Rivers, IL			0.22		
Swedish waters	Pike		1.2	Uncontaminated	Jernelov (1972b)
	Swedish Whitefish		0.6		
	Pike		5.8	Contaminated	
	Swedish Whitefish		3.1		
Wintergreen Lake, Michigan	LM Bass	14	0.49		Mathis & Kevern (1973)
	Yellow Perch	14	0.124		
	Yellow Bullhead	6	0.085		
	Hybrid Sunfish	8	0.255		
	Lake Chubsucker	5	0.038		

TABLE 13: Mercury Concentrations in Fishes (Continued)

Location	Species	Total Mercury n	Total Mercury ppm	Comments	Reference
Lake St. Clair	Pumpkinseed	22		range: 0.97-2.4	Bishop & Neary (1974)
	Bluegill	36		0.49-2.80	
	Perch	65		0.10-3.20	
	Northern Pike	69		1.60-8.95	
	Bowfin	16		0.47-7.60	
	B. Crappie	36		0.64-3.30	
	LM Bass	14		1.07-3.87	
	N. Redhorse	28		0.07-5.00	
	Channel Cat	11		0.99-3.55	
	Yellow Bullhead	27		0.52-4.00	
	Yellow Walleye	97		0.29-4.50	
	Freshwater Drum	22		0.11-1.68	
	White Bass	27		0.38-3.58	
	Muskie	13		0.92-20.4	
	Rock Bass	63		0.16-4.21	
	Carp	30		0.25-2.70	
Lake Paijanne (Sweden)	Whitefish	21	0.42		Hattula, et al. (1978)
	Vendance	100	0.42	Methylmercury	
	Smelt	76	0.63	n ppm	
	Pike	315	1.07	64 1.07	
	Bream	261	0.34	19 0.22	
	Crucian Carp	6	0.27		
	Ide	8	0.35		
	Roach	297	0.50	27 0.51	
	Burbot	121	1.51		
	Pikeperch	27	1.09		
	Perch	506	0.63	47 0.75	
Cedar Lake (IL)	Bass		0.48	0.32 58% of total	Cox, et al. (1979)
	Crappies		0.59	mercury was	
	Bluegills		0.20	CH_3HgCl	

TABLE 13: Mercury Concentrations in Fishes (Continued)

Location	Species	Total Mercury n	ppm	Comments			Reference
				1971	1972	1976	
Ball Lake, Ontario	Walleye			1.99	2.71	1.39	Armstrong & Scott (1979)
	Pike			5.05	5.72	1.80	
	Whitefish			--	0.62	0.42	
Giauque Lake	Lake Trout		3.79	Known source of mercury contamination: Mine operation			Moore & Sutherland
	Northern Pike		1.79				
	Round Whitefish		1.22				
Thompson Lake	Northern Pike		1.69	"			
	Round Whitefish		0.20				
Thistletwaite Lake	Lake Trout		0.17	Unknown source of mercury contamination			
	Northern Pike		0.42				
	Round Whitefish		0.37				
Hidden Lake	Northern Pike		0.49	"			
	Round Whitefish		0.20				
Lake Oahe		225		Range: 0.02-1.05 ppm 0.5 ppm 13% 0.35-0.49 ppm 14%			Walter, et al. (1973)

produces more mercury to the water.

Cember, et al. (1978) showed the mercury body burden of fishes was a function of both water temperature and mercury concentration. The equation of uptake was

$$y(t) = A + t/(B + Ct)$$

where $y(t)$ = mercury concentration in fish after t hours,
A = initial mercury concentration in fish,
B, C = dependent on concentration and temperature (see Figures 5 and 6)

Bioconcentration factors calculated in this experiment were related only to temperature.

$$C(T) = C(9)(\exp(0.066(T-9))) \qquad \text{for } 9^{\circ}C<T<33^{\circ}C$$

where $C(T)$ = bioconcentration factor at temperature T.

The waste elimination rate is reduced with temperature (Burrows, 1973; Bonner and Bustamante, 1976). The biological half-time of methylmercury for fish in waters at 0.5-4.0°C was 1.5 times that at 16-19°C, indicating the lower temperatures inhibit elimination rates (Ruohtula and Miettinen, 1975). Body clearance rates of non-growing fishes and fishes kept at cold (6-8°C) water were lower than normal (DeFreitas, et al., 1974). Large fish have slower clearance rates than smaller fish. The clearance rates are linked to the metabolic rate.

HgCl and phenylmercuric acetate were administered to Rainbow Trout (MacLeod and Pessah, 1973). The 96 HR TLm, defined as the mercury concentration which 50% of the fish survive after 96

FIGURE 5: Estimation of Parameter B

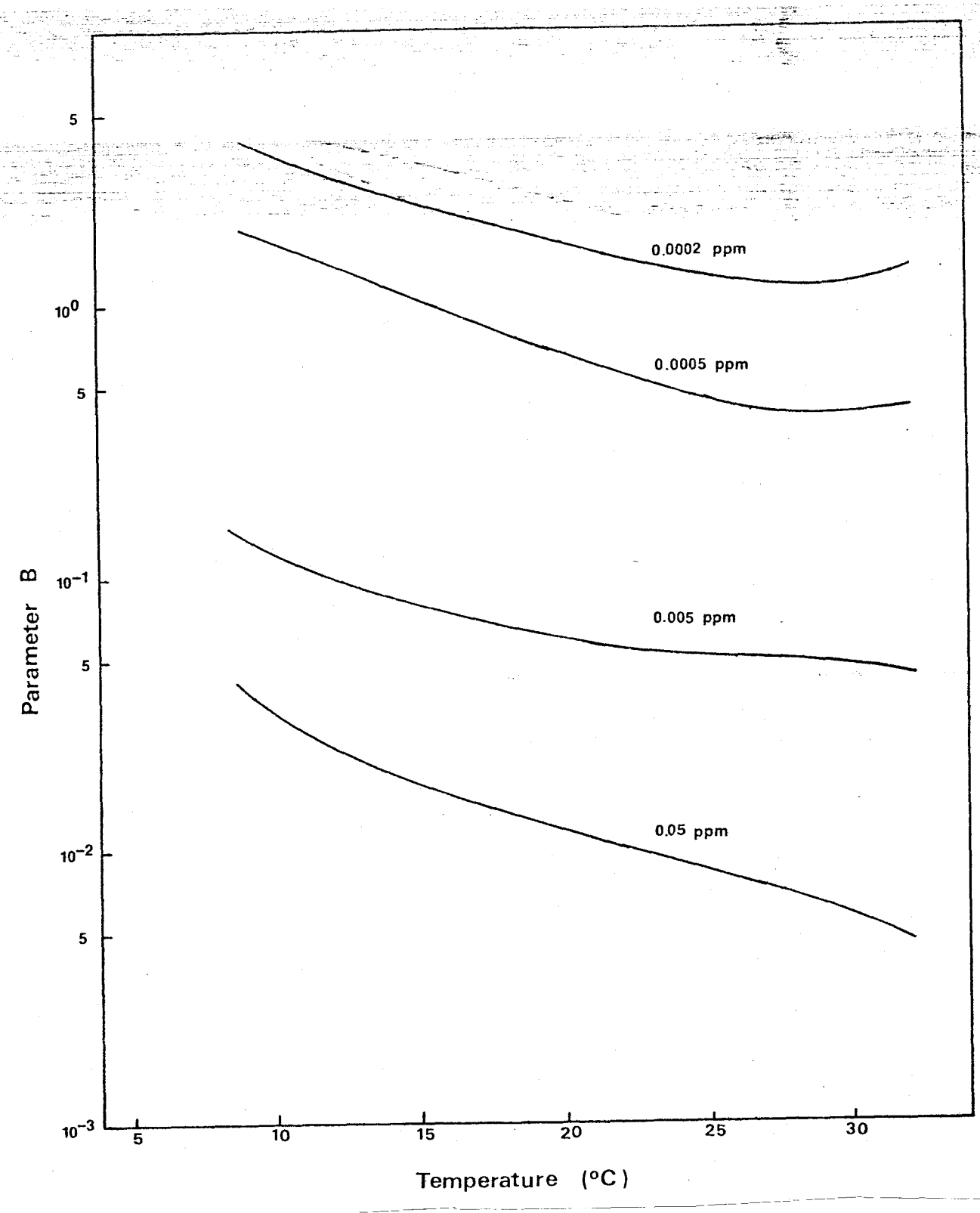
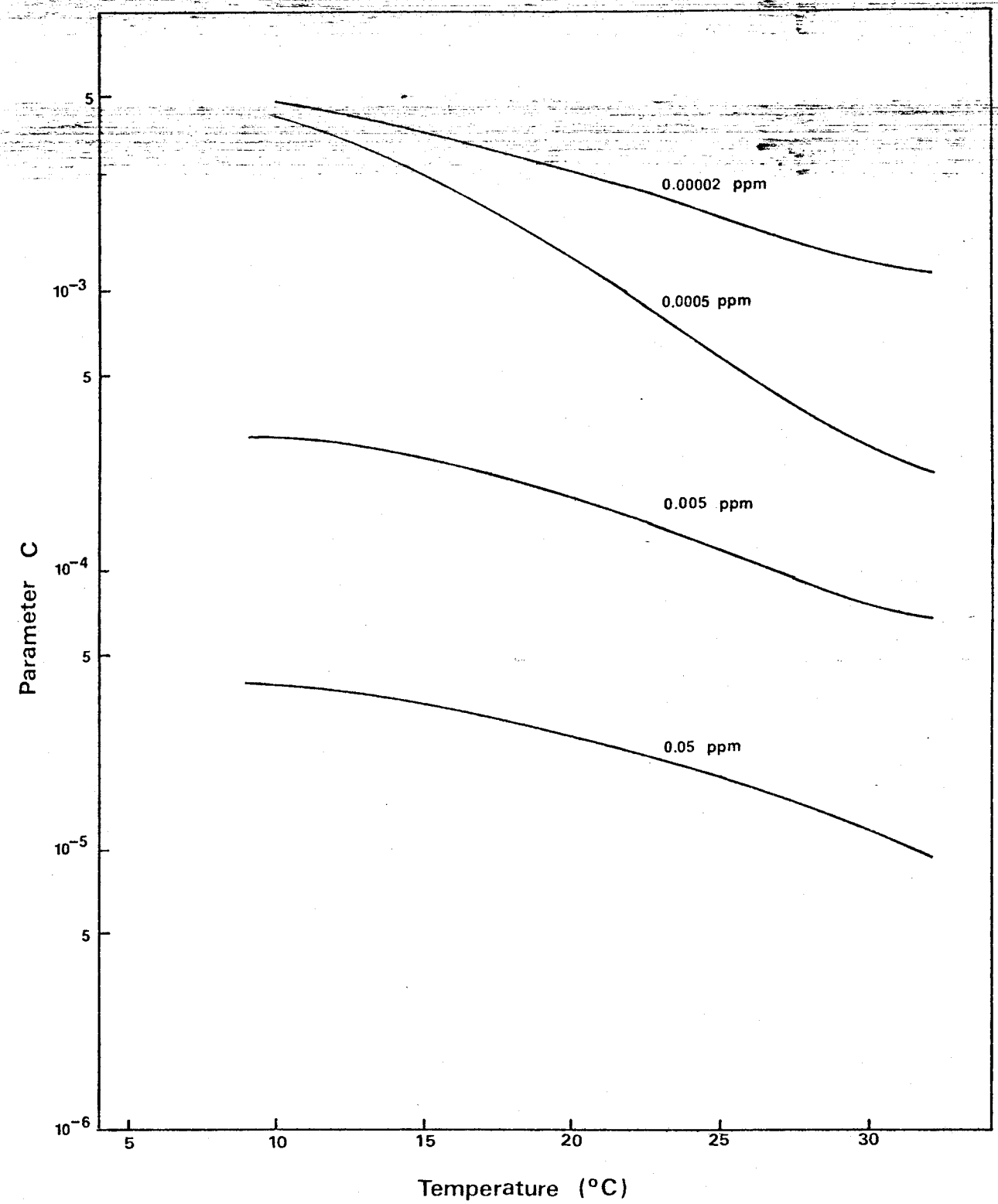


FIGURE 6: Estimation of Parameter C



hours, at various temperatures are given in Table 14.

TABLE 14: 96 Hr TLm for Rainbow Trout

	5°C	10°C	20°C
96 hr TLm (mg Hg/l)	0.4	0.28	0.22
Bioconcentration factors for water concentration 0.1 mg Hg/l	4	10	22

High bioconcentration factors occurred with low mercury concentrations in the waters, implying fish are better able to assimilate low concentrations of mercury rather than high concentrations.

MacLeod and Pessah made the following conclusions about their study:

1) the higher temperatures increase the toxicity of $HgCl_2$,

2) temperature has a greater effect on modifying the toxicity levels when the mercury concentration in the water are higher, and

3) temperature changes have a greater effect on toxicity when the water temperatures are low.

Trends of Mercury Uptake and Correlation Studies

Organic mercury compounds are more easily assimilated in the body than inorganic forms. (MacLeod and Pessah, 1973; Gillespie and Scott, 1971). Higher organic accumulations explain the

greater toxicity of the methylated forms. CH HgCl is approximately 7 times more toxic than HgCl when exposed to Rainbow Trout fingerlings for 24 hours (Wobeser, 1975a). The affinity of organic compounds results in the rejection and elimination of inorganic forms by the body (Burrows, 1973). Rejected inorganic forms are not reaccumulated by the fish.

High sub-lethal mercury concentrations in the water tend to produce higher fish flesh concentrations (McKone, et al., 1971; Taimi, 1973; Burrows, 1973).

Fishes exposed to contaminated waters, then removed to uncontaminated waters reduced their mercury burden (Burrows and Krenkel, 1973). Clay Lake fishes transferred to Heming Lake in November 1970 exhibited marked decreases in mercury burden in the next year (Lockhart, et al., 1972) (see Table 15).

TABLE 15: Percentage of Hg Body Burden Remaining After Transfer

	n	recapture Hg/original Hg
January 1971	9	105%
April 1971	18	83%
July 1971	17	82%
October 1971	5	71%

After the source of mercury contamination is removed from lakes, the fishes generally show decreased contamination levels. Armstrong and Scott (1979) noted decreased mercury contamination

in fishes from Ball Lake after the chloralkali plant, discharging wastes into the Wabigoon River, reduced mercury output to 3% of pre-1970 levels and halted mercury discharge in October 1975. Substantial decreases were noted in just 6 years. Jernelov, et al. (1975) predicted a 10-15 year lag period before decreases in mercury sources would be reflected in the top predatory fish. Even temporary contamination of lakes with mercury run the hazard of being contaminated for extended periods of time (Moore and Sutherland, 1980; Ruohtula and Miettinen, 1975). Pike transferred from Lake Kyrksjon to Lake Tovsattertjarn showed no change in the body burden after a year (Hasselrot and Gothberg, 1974).

In goldfish, 79.3% of the body burden is found in the mucus formed around the gills (McKone, et al., 1971). The mercuric ion may be accumulated and excreted from the mucus. Burrows (1973) discovered 16-45% of the mercury activity in bluegills can be removed by the scraping of the slime coat and 25% removed by rinsing the fish in uncontaminated water.

The initial loss of methylmercury may be high -- up to 40% by removing the mucus. The biological half-life was about 38.5 days for the first few days. Thereafter, the elimination slowed to the biological half-life of 130 days (Burrows, 1973).

Fish species will, to some extent, indicate relative mercury concentrations between fish. In total mercury studies done on Lake Oahe, South Dakota, Northern Pike had the highest average mercury concentration of the 22 species examined (Walter, et al.,

1973). Walleyes also exhibited high mercury concentrations. These observations are again reflected in Table 13. On the other end, catfish seemed to concentrate less mercury than other species (Koirtyohann, et al., 1974). The low accumulation was related to catfish having no scales and a lower respiration rate (Taimi, 1973).

Correlation studies are conducted in an attempt to related mercury concentration to easier-to-measure physical characteristics, i.e., length and weight. However, since uptake is largely dependent on the environment, each water body would have unique correlations. The best correlations are done on single species in a specified lake and correlated to weight. Correlation studies are listed in Table 16.

Methylmercury/Total Mercury Controversy

Methylmercury is more toxic than the inorganic forms. Yet, almost all guidelines addressing acceptable mercury concentrations in fishes for consumption are stated as total mercury rather than methylmercury. Justifying the use of the total mercury guidelines was the belief most of the mercury in fishes was in the methylated form. Table 17 shows the results of methylmercury as a percentage of the total mercury in fishes.

The table depicts two sides of the controversy. On one side the results indicate methylmercury concentrations are represented

TABLE 16: Correlation Studies of Mercury in Fishes

Species	Total Mercury Concentration Correlated to:	Correlation Coefficient	Comments	Reference
Rainbow Trout	length & length/weight	0.25	Smaller fish with large surface area of gills to body weight ratio had higher accumulation of mercury.	D'Itri, et al. (1971)
Largemouth Bass	weight	0.591	Y = 0.411 + 0.0791X Y = ppm Hg, X = kg	Koirtyohann, et al. (1974)
Pike	weight	0.75	n = 22, Lake Dellen	Hasselrot & Gothberg (1974)
	weight	0.84	n = 43, Lake Kyrksjon	
--	age & length	--	n = 225, no correlation	Walter, et al. (1973)
	Axial Muscle Mercury Correlated to:			
Pike	weight	0.90	n = 26, Lake Asjon	Hasselrot & Gothberg (1974)
--	weight	0.82	Y = 0.205 + 0.00025X	Mathis & Kevern (1973)
	length	0.90	Y = -0.5745 + 0.0265 X	
	Methylmercury/Total Mercury Correlated to:			
--	length	-0.064		Bishop & Neary (1974)
Perch	age	0.032		
Yellow Pike	age	0.061		

by total mercury. On the other, it supports the movement calling for "methylmercury" to replace the "total mercury" phrase in the guidelines. Although total mercury analyses are numerous, easily performed and have a high degree of accuracy, the impetus for methylmercury in the standards lies in economics. The 0.5 ppm Hg as methylmercury guideline could be met by a greater number of fishes. The impact on commercial fishing areas could be tremendous considering the incident at Ball Lake, Ontario when contaminated fishes closed the fishing season and many resorts surrounding the lake went out of business (D'Itri and Di'Itri, 1977).

Westoo (1973) disputed the findings of Bache, et al. (1971). Westoo cited the use of whole fish analysis produced the low results of 31-43% methylmercury as total mercury for the one-year-old Lake Trout. Perhaps the results cannot be compared since different species of test fish and analytical techniques were used by the researchers. Bache, et al. had a methylmercury recovery factor of 55% while Westoo, using gas chromatography for methylmercury analysis, achieved 79% recovery; with partition coefficient correction, a 98% recovery. Westoo maintains fish age has no effect on methylmercury/total mercury ratios, whereas Bache, et al. found them to be positively correlated.

Paths of Mercury Transport to Fishes

TABLE 17: Methylmercury as a Percentage of Total Mercury in Fish

Average Percentage	Range	Comments	Reference
98.7			Hattula, et al. (1978)
93.0	81-98	Salmon flesh from Morrumsan River	Westöö (1973)
	26-67	Pike flesh and viscera from Lake Vanern	
88.9	82-96	16 species tested	Bishop & Neary (1974)
	88-115	Pike, n=7	Phillips & Gregory (1979)
	80-124	Carp, n=3	
58		Largemouth Bass	Cox, et al. (1979)
50		Guppies, artifically contaminated sediment	Gillespie (1972)
	31-43	Lake trout, one-year old, whole fish analysis	Bache, et al. (1971)
	37-101	Lake trout, two- to twelve-years old, whole fish analysis	

The main mercury transport paths are the food and water vectors. But the relative importance of each vector in the transport process is still undetermined. The amount of mercury accumulated has been related to the fish species, trophic level and metabolic rates.

A factor in the uptake process is the trophic level of the species (Jernelov, et al., 1975; Wobeser, 1975b). Bottom dwelling organisms concentrate more mercury from the water, whereas higher-level trophic organisms accumulate more methylmercury from food (Jernelov and Lann, 1971). Pikes accumulated 60% of the mercury body burden from food as opposed to 25% in bottom feeders.

Predatory fishes usually have higher mercury concentrations than lower trophic level fishes (Potter, et al., 1975). Supporting trophic level experiments include:

Dragonfly Damselfly Nymphs	Water Bugs	Tadpoles	Mosquito Fish	Beetles
Lake Chubsucker	Yellow Bullhead	Yellow Perch	Hybrid Sunfish	Largemouth Bass

Low --> Methylmercury Concentration --> High
Trophic Level

From Holm and Cox (1974) and Mathis and Kevern (1973).

It appears bottom fauna and organisms accumulate methylmercury directly from the water, then it is bioconcentrated up the

trophic pyramid. Hasselrot and Gothberg (1974) believe after the mercury in the water is removed by bottom dwellers, the fish-to-fish transport of mercury becomes important.

Predatory fishes retain 10-15% of the mercury in the food consumed (Jernelov and Lann, 1971). Phillips and Gregory (1979) reached a similar conclusion of dietary assimilation using Northern Pike fed Young-Of-The-Year Carp. Their experiment revealed fishes in laboratory setting did not accumulate mercury in the same fashion as fishes in the natural environment. Laboratory uptake amounts may be significantly different from the uptake in the natural environment.

Other researchers feel the food vector is secondary to the water vector (Armstrong and Scott, 1979). Decreased methylmercury concentrations in the water was responsible for the drop in mercury concentration in fishes.

A concentration factor (CF) is defined as

$$CF = \frac{\text{Specific activity of higher trophic organisms}}{\text{Specific activity of lower trophic organisms}}$$

Concentration factors helped to determine uptake routes using radioactive inorganic and organic mercury compounds. The uptake process was

$$\text{Bacteria} \xrightarrow[CF > 1]{1} \text{Larva} \xrightarrow[CF < 1]{2} \text{Guppies} \xrightarrow[CF < 1]{3} \text{Cichlids}$$

The importance of bioconcentration through the food chain (route

1) is implied where CF > 1.0. CF < 1.0, routes 2 and 3, implied mercury compounds are not transferred through the trophic level (Hamdy and Prabhu, 1979).

Transfer coefficients also revealed the water vector to be as important as the food vector (DeFreitas, et al., 1974).

The longer life span of predatory fishes may explain their high mercury burdens. The longer lives allow for greater accumulation and assimilation of mercury, regardless of the uptake route (DeFreitas, et al., 1974). Reversely, short lives and rapid growth of lower organisms (growth dilution) induce low concentrations.

Rainbow Trout which adsorbed methylmercury through the gill membranes excreted mercury at a faster rate than those given methylmercury orally or by injection (Ruohtula and Miettinen, 1975). Although the water vector may dominate, this finding implies the high excretion rate falsely suggests low uptake, resulting in a misconception.

Some speculate that the bulk of methylmercury is not transferred by the water or food vectors. Some researchers feel Hg^{+2} is the mercury form carried through the water and accumulated by fishes. Once in the fish an undefined methylation reaction commences. Under experimental conditions, pure cultures of E. coli, Pseudomonas fluorescens, Pseudomonas aeruginosa, Citrobacter, Bacillius megaterium and Bacillius subtillis were able to oxidize Hg^{0} to Hg^{+2} (Holm and Cox, 1974). No methylation

occurred of the mercuric ion produced because the methyl radical ion was not present. This confirms the possibility of Hg^{+2} transport through the water.

Methylation of the mercury already in the fish has also been demonstrated. Liver homogenate of various tuna fishes were amended with HgCl . The results showed the yellow-fin tuna and albacore had high activities in the formation of methylmercury (Imura, et al., 1972). If CH_3HgCl reacted chemically with $^{203}HgCl$ without liver homogenate, no methylmercury was formed. However, another study showed only fish exposed to CH_3HgCl accumulated CH HgCl (Uthe, et al., 1973), so that methylmercury contamination comes from the surroundings and fishes do not internally produce methylmercury.

Another possible vector of transport is the suspended matter in the water (Armstrong and Scott, 1979). Equilibrium values of mercury concentrations in fish were 0.2 ppm Hg in a system with fish in contact with bed sediment while the concentration dropped to 0.02 ppm Hg when fish had no contact with the sediment (Kudo and Mortimer, 1979). The water concentration for both systems ranged 0.002-0.005 ppm Hg. Dissolved mercury adsorbed on suspended particles was also the suspected route of leakage from holding ponds of an inactive chloralkali plant into an adjacent river (Turner and Lindberg, 1978).

TABLE 18: Generalizations Regarding Mercury Accumulation By Fish

1. High water temperatures increase mercury uptake in fish.

2. Organic mercury compounds are more easily assimilated by fish than inorganic mercury compounds.

3. Fish show decreased mercury concentrations when removed from contaminated waters.

4. Fish species may determine relative mercury concentrations.

5. Fish age and length do not appear to be correlated with the level of mercury contamination.
Fish weight, however, seems to have high positive correlation to the level of mercury contamination.

6. The major form of mercury in fish seems to be methylmercury derivatives.

7. The vector whereby mercury is transmitted to the fish is still not understood.
Although it is almost certain that food and water are the major vectors of transport, the evidence is still inconclusive to which vector is more important.

THE MODEL

The history of methylmercury contamination in the aquatic environment can be traced to the Minamata Bay disaster in the 1950's. Since then, more cases have been documented in the literature. On the growing list, of interest is the Apollo County Park in Lancaster, California, which has slightly elevated mercury concentrations in the water with no apparent mercury source. The intent of this section is to develop a model that traces and identifies the transport paths of mercury in the aquatic system with Apollo County Park as the site of

investigation.

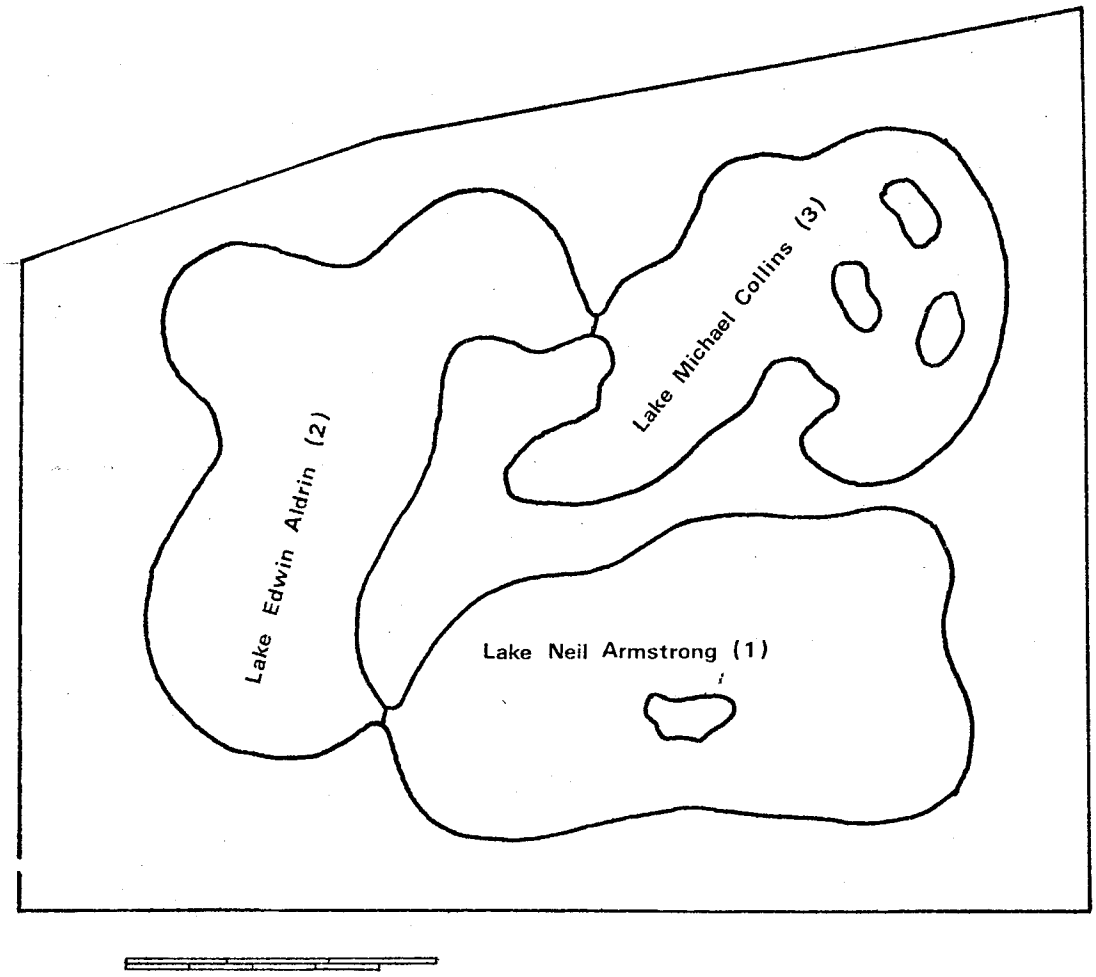
Apollo County Park

Prior to construction of the Apollo County Park, in Antelope Valley, the land was nearly devoid of vegetation. High elemental boron and salts concentrations in the soil in addition to the underlying layer of impermeable clay were unfavorable to plant life. The scant rainfall, 15-20 cm/year, did not enhance the condition.

The 56-acre park (see Figure 7 and Table 19) was designed as an aquatic recreational facility utilizing reclaimed wastewater and fresh water to fill three connecting man-made lakes: Lake Neil Armstrong (Lake 1), Lake Edwin Aldrin (Lake 2), and Lake Michael Collins (Lake 3). In addition to the aesthetic value, the lakes support sport fishing and recreational boating activities.

In March 1971 the lakes were stocked with 20 Channel Catfish, 50 Red-Ear Sunfish and 100 Largemouth Black Bass. 100 small Rainbow Trout were added in December 1971. In March 1973, an analysis of the stocked fishes for heavy metal contamination revealed one specimen of Rainbow Trout had a 2 mg/kg Hg concentration. Since that quantity exceeds the recommended guideline of 0.5 mg/kg, more analyses on mercury contamination were conducted (see Table 20). Subsequent analyses revealed

FIGURE 7: Apollo County Park



APOLLO COUNTY PARK

TABLE 19: Apollo County Park

Land area:	56 acres
Lake surface area:	26 acres
Total Lake volume:	306585 m^3
Lake 1:	128690 m^3
Lake 2:	102195 m^3
Lake 3:	76700 m^3
Inflow:	1900 m^3/day
Average redox potential:	-850 millivolts
Nominal average detention time of water:	162 days
Average evaporation rate:	2.49 m/yr
Mean values:	
TDS:	912 mg/l
Alkalinity:	148 mg/l
pH:	8.4
Turbidity:	9-33 JTU

Rainbow Trout and Largemouth Bass had higher concentrations than the other species.

The obvious source of mercury would be the lake inflow, but that was discounted because of insignificant concentrations, so other sources were investigated. The most probable source of mercury contamination is from the sediment in the lake. Table 21 shows the mercury concentration of the soil outside of the lake is much higher than the mercury concentration of the sediment in the lake. This finding is consistent with the theory that calls for a slow diffusion of mercury in the soil to mercury in the water. The accumulationof mercury by fishes provides the mechanism whereby all the mercury in the system would eventually be eliminated. The average mercury concentration for sediments in the lake was 0.254 mg/kg, outside the park the natural soil mercury concentration was 0.657 mg/kg.

TABLE 20: Mercury Analysis of Fishes in Apollo Lakes

Fish	Date tested	Total Months in Lakes	Mercury Concentration
Rainbow Trout			
1	3/28/73	15	2.0 ppm
1	5/25/73	18	2.28
1	5/25/73	18	1.92
1	5/25/73	18	2.66
1	5/25/73	18	3.17
1	5/25/73	18	1.92
1	4/09/74	28	2.9
Channel Catfish			
1(a)	5/04/73	2 minutes*	0.32
4(a)	5/25/73	3 minutes	0.25 average
10(a)	5/25/73	3 minutes	0.46 average
1	4/09/74	36	1.4
1(a)	4/09/74	13 minutes	0.9
Red-ear Sunfish			
1	4/09/74	36	1.0
1(b)	4/09/74	24*	0.4
Largemouth Black Bass			
1	5/08/73	25	2.95
1(b)	5/25/73	18*	3.0
1	5/25/73	26	0.88
1	4/09/74	36	2.0
1(b)	4/09/74	24*	3.5
1(b)	4/09/74	12*	0.9

(a) indicates fish born in lakes or plant of 3/1/73
(b) indicates fish born in lakes
* indicates an approximation

Another possible source is the wind depoits over the water. The wind can easily pick up mercury-containing particles in the natural soil outside of the park and deposit them on the water surface. The high redox potential of the water is sufficient for oxidation to the mercuric state.

The feeding habits of the fishes partially determined their mercury concentrations. Bass fingerlings fed mainly on Daphnia, the zooplankton with the highest population for an average

TABLE 21: Mercury Concentrations in the Soil and Lake Water

Location	Sample	Mercury Content (ppm)
Outside of park	soil	0.240
	soil	0.880
	soil	0.851
Inside of park	soil	0.100
	soil	0.391
	soil	0.252
Lake 1	sediment	0.531
Lake 1	sediment	0.212
Lake 2	sediment	0.101
Lake 3	surface sed.	0.197
	middle sed.	0.343
	deep sed.	0.143
Lake 1	water	<0.001 mg/l
Lake 2	water	<0.001 mg/l
Lake 3	water	<0.001 mg/l
Lancaster Water Reclamation Plant	effluent	0.3 ug/l

more space.

concentration of 1.38 mg/kg, which accounts for their higher mercury concentration. Catfish, as shown in the previous sections, having different metabolic rates and feeding habits, accumulate less mercury than other species.

The findings of high mercury contamination in the fishes forced the closure of the proposed fishing season. The level of mercury in the lakes is confined to the 30.48 cm sediment depth overlying the 10 mil thick polyethylene lake lining. Eventually, it is expected that the level of mercury in the fishes will decrease because of the removal of fishes (and mercury) from the lakes, and that fishing will be unrestricted.

The interim guideline suggested for controlled fishing until the long-term mercury level is reduced was that Rainbow Trout be

stocked in the lakes. The Rainbow Trout selection was based on 1) easy availability from hatcheries, 2) do not reproduce, 3) provide a good test fish, 4) are easily caught and 5) survive in the water as long as the water temperature does not exceed 26°C. The intent was that the fish would not be in the lake long enough to accumulate extensive amounts of mercury.

Methylmercury Concentration

Before addressing the quality models, the discrepancy of methylmercury concentrations in the environment must be investigated.

The transport theories of mercury eventually reach the quagmire where the high quantities of methylmercury in the aquatic life must be explained by the low quantities found in the environment. This puzzle has been partially solved by research but still is not fully explained. Presented below are brief descriptions of methylmercury concentrations in the environment and the possible explanations for its scarcity.

The atmosphere is assumed to be a source of methylmercury since methylated forms are volatile. Methylmercury and dimethylmercury presumably diffuse through the water into the atmosphere after formation in the sediment. The results of mercury species distribution above the Hillsborough Bay area in Florida are shown in Table 22 (Johnson and Braman, 1974). These

results indicate that the atmospheric load of mercury is approximately 20% in the methylated form. As seen, highly volatile dimethylmercury is a very small percentage of the total. Of 33 consecutive two-hour sampling, only 9 samples contained trace amounts of dimethylmercury for an average concentration of 0.4 ng Hg/m^3 (Johnson and Braman, 1974).

TABLE 22: Average Concentration of Mercury Species

(Above Hillsborough Bay)

Particulate Mercury	4% of Total Hg
Mercury (II)-type compounds	25%
Methylmercury (II)-type compounds	21%
Elemental mercury vapor	49%
Dimethylmercury	1%

One theory for the low dimethylmercury concentration may be attributed to the decomposition of dimethylmercury in ultraviolet light (Wood, 1974).

$$CH_3HgCH_3 \longrightarrow Hg + (CH_3)_2$$

The methyl ion can acquire two hydrogen atoms to form methane gas or combine to form ethane. However the results of laboratory experiments repudiate this theory to claim photochemical decomposition or degradation of dimethylmercury or methylmercury does not occur (Wolfe, et al., 1973).

One might expect rainfall washout to contribute to

methylmercury being transported back to earth; however, initial results suggest otherwise (Johnson and Braman, 1974).

The methylmercury concentration in sediments are also low. The sediments receiving the mercuric ion or elemental mercury showed <1% of the total mercury to be in the methylated form (Holm and Cox, 1974). The Sambre River bottom sediments which had mercury concentrations up to 70 mg Hg/g had no detectable methylmercury content (Billen, et al., 1974). The Seine River sediment showed no methylmercury and the sediment from The Albegua, Fiora and Paglia Rivers averaged methylmercury concentration was 0.03 ppm Hg. That represents 0.03% of the total mercury concentration (Batti, et al., 1975).

Investigation into the Lake St. Clair area revealed one explanation for the low methylated compounds in the sediment. Laboratory results show methylmercury is degraded to methane, elemental mercury or the mercuric ion (Spangler, et al., 1973). Of 207 microorganisms cultured, 30 proved to be aerobic demethylators and of that group, 22 were facultative anaerobes. Only one of the facultative anaerobes was not able to demethylate methylated compounds.

Under acidic conditions dimethylmercury transforms to methylmercury (Wood, 1971).

$$CH_3HgCH_3 \longrightarrow CH_3Hg^+ + CH_4$$

The reaction usually acquires a hydrogen atom when in water to produce the methyl ion and methane gas (Wolfe, et al., 1973).

One theory for the high accumulation of methylmercury in fish and the low quantity in the water is a one-way transport model of methylmercury transfer. This transport is best written

$$CH_3Hg^+ \text{ (in sediment)} \longrightarrow CH_3Hg^+ \text{ (in water)} \longrightarrow CH_3Hg^+ \text{ (in fish)}$$

The fish constantly accumulate methlymercury from the water pushing the reaction to the right. An experiment designed to test this effect was done by Akagi, et al., (1979). The methylmercury content in the water column was the same regardless of whether the systems contained fish. However the system containing fish produced ten times more methylmercury than the other. The rate of methylmercury production seemed to be governed by the rate of removal from the water.

Another hypothesis resolving the water-fish discrepancy is that plant life may accumulate substantial portions of methylmercury from the water. In less than three weeks with water concentrations of 10 ppb Hg, the plant, Elodea densa, accumulated the mercury to the extent of 1000 ppm (Mortimer and Kudo, 1974). The results of that experiment also show the sediment systems containing plants accumulated more mercury than those without any plants.

Qualitative Model

The previous sections should have provided some insight into the transformation and transport processes of mercury in the

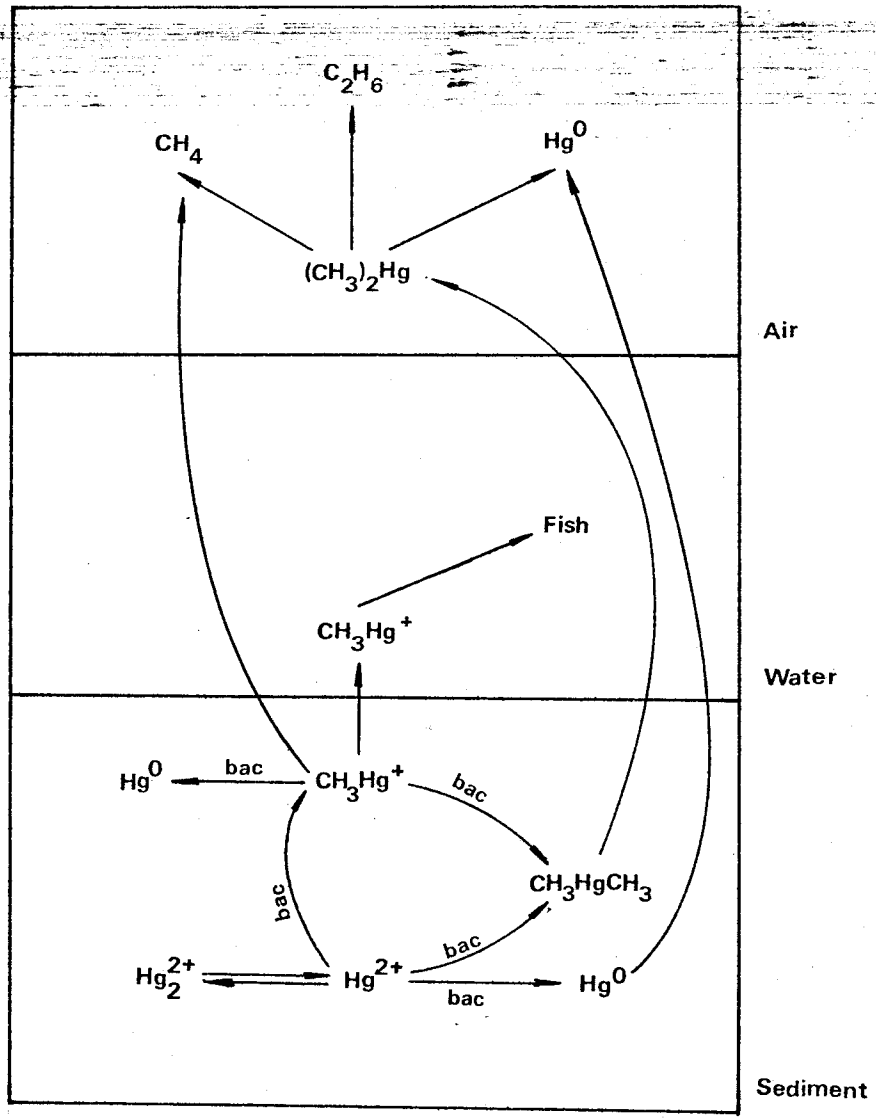
aquatic environment. Segments of the processes were examined individually because of the complex interactions resulting from environmental conditions. The integration of these components resulted in a model of the mercury cycle.

The qualitative model best describing the transport-transformation processes was developed by Wood (1971) (See Figure 8). Experimental results of the preceeding sections verify every transformation and flow pattern. This representation is based on the water-transport principle of mercury accumulation in fishes.

A simplistic qualitative model which preserves the essence of the Wood model is depicted in Figure 9. The simplistic model differs from Wood's model because no differentiation is made between the different inorganic mercury compounds present in the system. All species are included under the lumped-parameter heading of "Inorganic Mercury". Organic mercury compounds are similarly handled and are encompassed under the "Organic Mercury" label.

The simplified model is used in this paper. The justification for the lumped parameters is that most of the mercury found in the system is of one inorganic species of one organic species. The previous sections have shown the scarcity of methylmercury in the aquatic environment and that generally, the mercury found in the fish flesh is of the organic (alkyl) form.

FIGURE 8: Wood's Qualitative Model



Quantitative Model

The deterministic model presented is described by a set of ordinary differential equations. The material balance equation is applied to the paths of interest identified in Figure 9. Balances on the water, sediment and biota account for the mercury in the system. It also serves to identify the source and sinks of mercury in the system as well as project time-variant concentrations. The eight equations describing the system and parameter identifications follow on the next pages.

FIGURE 9: Simplistic Qualitative Model

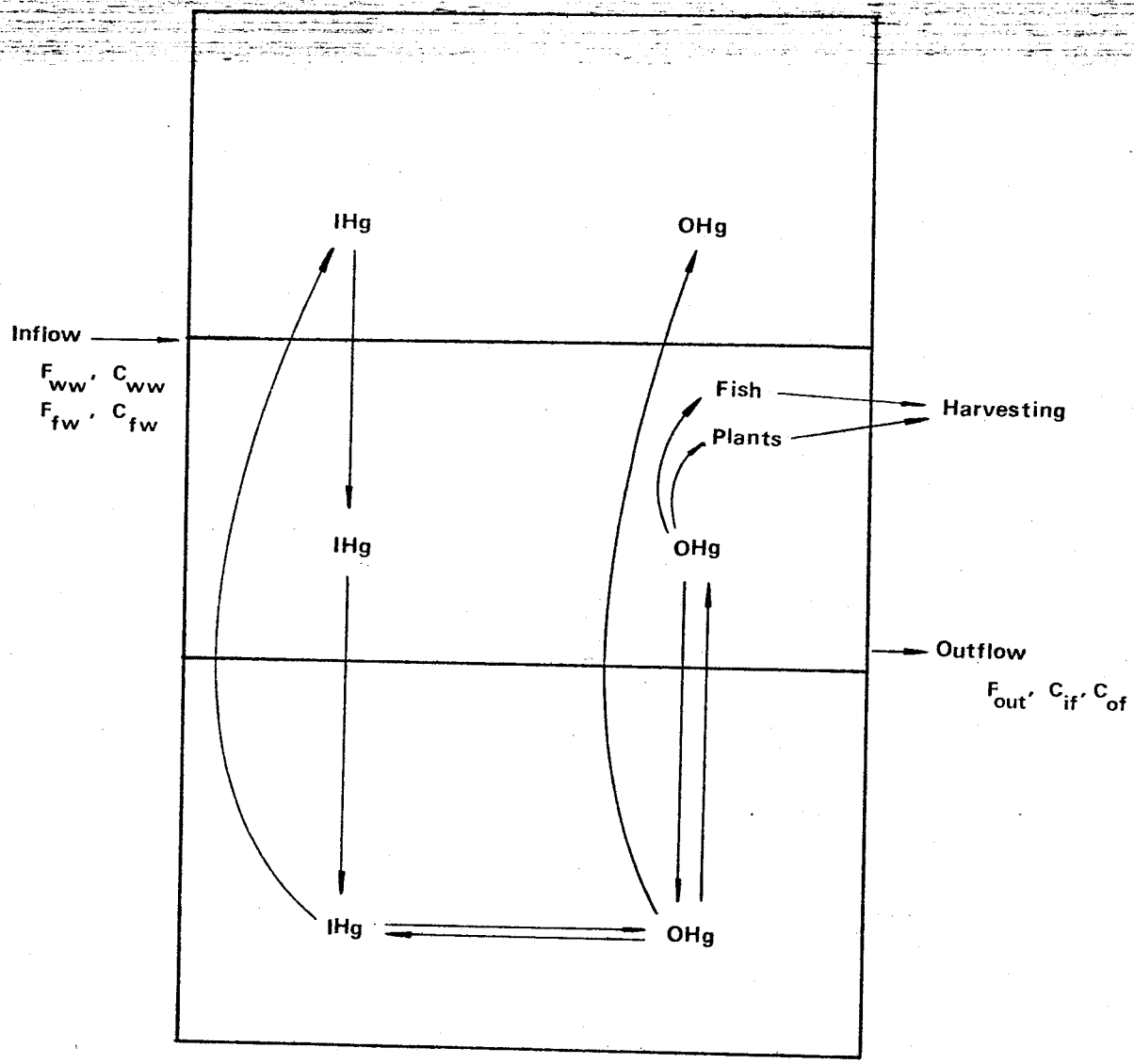


TABLE 23: Mass Balance Equations

In - Out = Reaction + Accumulation

Fluid	IHg:	$\frac{dC_{IF}}{dt} = \frac{1}{V_F}(F_{WW}C_{WW} + F_{FW}C_{FW} + K_{FR}A - F_OC_{IF} - M_SK_{AIS})$
	OHg:	$\frac{dC_{OF}}{dt} = \frac{1}{V_F}(M_S(K_{DOF} - K_{ADOS}) - F_OC_{OF} - M_FK_{UF} - M_PK_{UP})$
Sediment	IHg:	$\frac{dC_{IS}}{dt} = K_{AIS} - C_{IS}\alpha_1K_{VI} - C_{IS}\alpha_2K_M$
	OHg:	$\frac{dC_{OS}}{dt} = K_{AOS} + \frac{D_1M_P}{M_S} - C_{OS}(K_{VO}\beta_1 + K_{DOF} + \beta_2K_D)$
Fish	Mass:	$\frac{dM_F}{dt} = M_{FI} - M_{FO} - K_GM_F(\frac{S_F}{K_{SF} + S_F})$
	OHg:	$\frac{dC_F}{dt} = \frac{1}{M_F}(M_{FI}C_{FI} - M_{FO}C_{FO} - M_FK_{UF}C_F)$
Plants	Mass:	$\frac{dM_P}{dt} = -F_OM_P(\frac{1}{V_F}) - K_{GP}M_P(\frac{S_P}{K_{SP} + S_P}) - D_1M_P$
	OHg:	$\frac{dC_P}{dt} = \frac{1}{M_P}(-F_OM_PC_P(\frac{1}{V_F}) - M_PK_{UP}C_P)$

TABLE 24: Definition of Terms

Concentrations

C_{WW}: Concentration of IHg in wastewater flow

C_{FW}: Concentration of IHg in freshwater flow

C_{IF}: Concentration of IHg in lake

C_{OF}: Concentration of OHg in lake

C_{IS}: Concentration of IHg in sediment

C_{OS}: Concentration of OHg in sediment

C_{FI}: Concentration of OHg in fish at input

C_{FO}: Concentration of OHg in fish at output

C_{P} : Concentration of OHg in plants in water and output

C_{F} : Concentration of OHg in fish

Masses

M_{S} : Mass of sediment

M_{F} : Mass of fish

M_{P} : Mass of plants

M_{FI}: Mass of fish inputed per period of time

M_{FO}: Mass of fish harvested per period of time

Flows

F_{WW}: Flow of wastewater into lake

F_{FW}: Flow of freshwater into lake

F_{O} : Flow of water out of lake

TABLE 24: Definition of Terms (Continued)

Rates

K_{FR} : Fallout rate of IHg from the atmosphere per time

K_{AIS} : Rate of adsorption of IHg from fluid to sediment

$$= \frac{\text{mass of solute adsorbed}}{\text{unit mass of adsorbent}} \text{ per time}$$

K_{DOF} : Rate of desorption of OHg from sediment to fluid

$$= \frac{\text{mass of solute desorbed}}{\text{unit mass of adsorbent}} \text{ per time}$$

K_{AOS} : Rate of adsorption of OHg from fluid to sediment

$$= \frac{\text{mass of OHg adsorbed}}{\text{unit mass of sediment}} \text{ per time}$$

K_{UF} : Rate of uptake of OHg from fluid by fish

$$= \frac{\text{mass of OHg accumulated}}{\text{unit mass of fish}} \text{ per time}$$

K_{UP} : Rate of uptake of OHg from fluid by plants

$$= \frac{\text{mass of OHg adsorbed}}{\text{unit mass of plants}} \text{ per time}$$

K_{VI} : Rate at which volatilization occurs for IHg

K_{M} : Rate at which methylation occurs: IHg $\xrightarrow{bac}$ OHg

K_{VO} : Rate at which volatilization occurs for OHg

K_{D} : Rate at which demethylation occurs for OHg

K_{G} : Maximum growth rate of fish

K_{GP} : Maximum growth rate of plants

Miscellaneous

A : Surface area of the lake

α_1 : Percent of IHg in sediment which is volatilized

α_2 : Percent of IHg that is converted to OHg

TABLE 24: Definition of Terms (Continued)

β_1 : Percent of OHg in sediment that is volatilized

β_2 : Percent of OHg in sediment that is converted to IHg

S_F : Concentration of growth limiting substrates in water for fish

K_{SF} : Substrate concentration at half the maximum growth rate for fish

S_P : Concentration of growth limiting substrates in water for plants

K_{SP} : Substrate concentration at half the maximum growth rate for plants

D_1 : Decomposition term for plants

$$= \frac{\text{percent of plant mass decomposing}}{\text{unit time}}$$

Assumptions

The model has many assumptions that arise to simplify the complex nature of the cycle and the difficulty in determining parameter values.

The following assumptions are made.

1) Environmental conditions remain constant in time and space. This allows predictability of the fish metabolic rate and microbial activity in the system. The variations of pH, alkalinity and nutrients are small in these two dimensions. Temperature does vary and plays an important role in the mercury cycle. The routes can be expressed as a function of temperature in a more sophisticated model.

2) Water is implicitly assumed to be the vector of transport. This allows the direct calculation of uptake by the metabolic rate of fishes rather than the complex water and food assimilation theory of mercury accumulation. If a single non-predatory fish is used in this model, the assumption is perfectly valid. However, if other species are included so that a food chain develops, the assumption is no longer valid and other equations must be added to describe this dimension.

3) The system is completely aerobic. This assumption is made because the depth of sediment overlying the polyethylene lining is about one foot.

4) Methylmercury derivative comprise the bulk of the organic mercury load.

5) Only organic mercury is accumulated by biota. The high methylmercury/total mercury ratio justifies this assumption. The mercury entering the lake system is inorganic. Industry is the prime consumer of mercury and the by-products would probably be inorganic.

7) Organic and inorganic volatile mercury compounds are released from the sediment, travel through the water, and escape into the atmosphere.

8) Single species of fish and plant life are in the lake at any one time. More species of either may be included with the addition of pertinent growth parameters and mass equations.

9) The growth of plants and fish are expected to follow the monod growth pattern.

10) The fishes do not decompose in the lake. The fishes in the lakes have short residence times of about five days when sport fishing is allowed. The plants are floating algae, the decomposition term is included but not quantified.

Advantages and Disadvantages

The strength of this type of mathematical model is its inherent expansivity. Additional parameters lead to the development of a sophisticated model which better approximates the real situation.

For example, the constant reaction rates may be replaced with time-variant rates. In fact, all parameters can be expressed as a function of time. Parameter variation modifications are more realistic than constant values since they depend largely on the environment. Temperature appears to be the major influence on kinetics, therefore the parameters may be expressed as a function of temperature (daily or seasonal) fluctuations of the system.

Material balances applied to discrete mercury forms would also better approximate the actual system. Instead of lumped parameters, the mercury species could be discretized to the different methylmercury compounds and the common inorganic compounds. This change results in the ability to follow the

intricate mercury transformation process, i.e., a representation much like Figure 8.

The entire lake system may also be divided into sub-systems, where each represents an area of different characteristics. This fits perfectly for the Apollo Lakes system. Each lake can be represented by a unique set of material balances since there is no interaction except for flow. The flow variable provides the link that binds the separate sub-systems together. This represents a special case where the lakes are basically independent of each other, however, the concept may be applied to a single lake. The geometry of the lake may permit the discretization of the lake if the flow is such that some parts of the lake are stagnant. Waters are not expected to provide significant quantities of mercury because of the resulting equilibrium condition. Thus the criteria for separation is the aerobic-anaerobic division.

The net effect of all modifications is the elimination of some assumptions that inhibit the crude model in favor of more sophistication and reliability.

The main disadvantage of this model is the heavy reliance placed on the reaction rates which virtually predetermines the outcome. The parameter values must be representative of the physical process which they describe. Usually determined in the laboratory conditions, replicating the actual conditions, these parameters are still difficult to calibrate. The literature search has produced a small quantity of information on rates (see

Table 25). → insert blank page for Table 25

Bisogni and Lawrence (1975) have done research on the kinetics of mercury methylation in anaerobic and aerobic aquatic environments in the laboratory. The following equation they developed describes the production rate of mono- and dimethylmercury in a complete mix system.

$$\log (NSMR) = n(\log(G(B*Hg))$$

where NSMR = Net Specific Methylation Rate,
G = coefficient of microbial growth rate which is related to the production rate of enzymes and methyl group transfer,
B = free[Hg^{2+}] ions/[total inorganic mercury], coefficient of biochemical availability of inorganic mercury for methylation,
Hg = concentration of all forms of mercury,
n = psuedo-order of reaction

The experiments have shown the rate of methylation is higher in the aerobic than anaerobic system. Futhermore, in the aerobic environment, the average value of the psuedo-order was .28, whereas the average value of n in the anaerobic system was 0.15.

One group of researchers have mathematically modelled the uptake of mercury by fish. Fagerstrom, et al. (1974), used Northern Pike (Esox lucius) in a controlled environment to formulate their model which is based on body weight, rate of growth and mercury body burden. Simultaneous solution of two differential equations, a linear equation, and an exponential equation models the uptake of mercury by the pike.

TABLE 25: Reaction Rates

Methylation Rates

Average Temperature	Rate ($ng/cm^2/week$)	Comments	Reference
60^oF	0.14-3.59	Pickwick Reservoir Sediment	McMullen (1973)
70^oF	0.11-0.64	Uptake by Guppies	
5 ng Hg/g sediment/day		Production over 28 days	Holm & Cox (1974)

Adsorption-Desorption Rates

	Inorganic Mercury	Organic Mercury
Mercaptans	84.2	116.8
Illite	65.3	24.4
Montmorillonite	35.7	16.8
Amines	10.5	
Kaolinite	9.7	
Carboxyl	7.3	
Fine Sand	2.9	
Medium Sand	1.7	
Coarse Sand	1.6	

Reimers & Krenkel (1974)

Comments

Measurements in ug Hg/g sediment/minute
Desorption of inorganic mercury is almost negliable for clays, organics and sand, except for high chloride concentrations at pH 7 for illite and sands at high chloride concentrations.
Desorption/adsorption ratio for sand is 1/10; for clays is 1/100.
Desorption of organic mercury follow in the order of:
Fine Sands Illite Montmorillonite Mercaptans

TABLE 25: Reaction Rates (Continuted)

Uptake Rate for Fishes

Body Weight	Uptake Rate (ug/hr/fish)	Comments	Reference
2 g	0.78×10^{-3}	Minnows kept at 15-16°C	DeFreitas, et al. (1974)
10 g	2.67×10^{-3}		
100 g	15.5×10^{-3}		
500 g	36.0×10^{-3}		
1000 g	58.5×10^{-3}		

Species	Reaction Rate (1/time)	Comments	Reference
Guppies	0.0279	$C_t = C_o e^{kt}$	Taimi (1973)
Minnow	0.0596	C_t = Concentration at time t	
Catfish	0.0123	C_o = Initial Concentration	
Bluegill	0.0179	k = Reaction Rate	

Fallout Rate

0.5 g Hg/acre/year		Swedish findings	Cooper, et al. (1975

While the model in this paper has the advantage of expansivity, the new parametersalso gave the duplicity of adding more uncertainty the model. As noted earlier, the mercury analysis is difficult to perform because of its volatile nature. Each parameter that must be calibrated adds a certain amount of error to the model. The summation of erros may render the model useless. It is practical, therefore, to perform a least-error analysis to find the optimum number of parameters introducible into the model.

Computer Solution

The desired results of the model are obtained by the solution of the differential equations. The simultaneous solution, although manually obtainable, is slow and tedious. The ideal tool to generate a solution is the computer program "Computer Systems Modelling Program (CSMP)". This canned program solves the differential equations, allow the flexibility of programming and can generate output in a variety of modes.

Briefly, the program consists of three main sections labelled INITIAL, DYNAMIC, and TERMINAL. The INITIAL section contains the constant-value parameters and the initial conditions. The DYNAMIC section is the body of the program. The input into this section is similar to a regular Fortran program with the exception that the computer sorts the equations if not otherwise specified. The differential equations are listed in this section

as well as any other pertinent equations. The TERMINAL section stipulates the mode of output and the time of interest. In this section, it is possible to request repeated runs resulting from changes in the parameter values listed in the INITIAL section to determine system response. The mode of output requested can be either tabulated printout and/or graphical solution.

The programming follows the Fortran language except that it has its own specified functions and solution techniques. A more detailed description of CSMP may be found in James, et al., (1977).

The choice of CSMP clearly lies in its versatility displayed in the TERMINAL section. One run can simulate many conditions including shock loadings. This feature allows for the introduction of impulse functions and monitors the ability of the system to adapt and acclimate itself to sharp changes in the environmental conditions. This application to the toxic substances is invaluable.

CONCLUSION

The existence of mercury in the aquatic environment was probed after elevated concentrations were found in fishes from the Apollo Lakes. The source of mercury is unknown, therefore a study into the methylation and transportation processes was instigated.

The investigation of the methylation process showed the microorganisms present in the sediment were probably responsible for the methylation of inorganic mercury. All forms of mercury are subject to methylation by bacteria.

Of all the environmental factors, temperature appears to be dominate since it affects the metabolism rate of the microorganisms and fishes. Temperature and methylating activity increase positively.

The transportation process is still not understood. The importance of the food vector through bioconcentration up the food chain, or the water vector through adsorption of mercury on suspended material, is not well-quantified or distinguished because of contradictory published data. The water vector, however, seems to dominate in species at the lower end of the food chain where accumulation is via respiration and adsorption. The food vector appears to be dominant in the species higher on the food chain and accumulation occurs from the bioconcentration of contaminated food.

In spite of the uncertainty of which is the dominant vector, a model describing the system was formulated. With the assumption the water vector is dominant, a set of material balances on inorganic mercury, organic mercury, fish mass, fish mercury concentration, plant mass and plant mercury concentration resulted in a set of ordinary differential equations describing the transport of mercury. The equations provide a crude model to monitor the mercury transport and identify mercury sources and sinks.

The assumptions which inhibit the model may be discarded when the model is expanded. Yet, this model advantage of expansivity is directly related to the disadvantage of calibrating the additional parameters introduced in the expansion process. The optimum number of parameters introduced subject to an error analysis is needed to resolve the dilemma. The model provides an initial basis from which to construct more sophisticated models.

The ultimate goal of the modelling process is to monitor mercury compounds in the aquatic environment and its uptake by aquatic like. Ideally, the model would be expressed in terms of environmental parameters: temperature, pH, BOD, amount and type of microorganisms, sediment type, etc. The model is then described as completely as possible in general physical terms, and thus is more applicable to all systems rather than the area-specific model.

At this time, the modelling of mercury is obstructed by the lack of reproducible experimental data. The volatile nature of

mercury can lead to experiment designs where some mercury is unaccountable, and the numerous analytic techniques used in quantifying mercury inhibit the comprehensive understanding of the transport and transformation processes. Much of the information derived from literature searches can only truly be taken in a qualitative sense since quantitative values are suspect without verification or standardization of analytic techniques. The difficulty lies in discerning the "acceptable" values. Only when the physical-chemical-biological processes of mercury are understood and better analytic techniques for organic mercury compounds are developed will there be advancement in modelling.

RECOMMENDATIONS

Further research in the area of mercury uptake by fish and comprehensive methylation studies are needed to fully understand the transformations of mercury in the aquatic environment. The following recommendations are suggested for future study.

1) A primary objective should be quantifying reaction rates. The literature review has shown continuing work in this area is needed. Research results similar to those presented by Taimi (1973), Bisogni and Lawrence (1975), Shin and Krenkel (1973), Fagerstrom, et al. (1974), etc., are essential if any type of modelling of mercury is to be successful.

2) Laboratory research is needed to verify the mathematical model presented in this paper. To accomplish this, it is suggested that a controlled environment be used to the inflow and outflow material can be carefully analyzed for mercury compounds. One scheme is to enclose an aquarium tank which has sterilized sediment innoculated with bacteria and nutrients. The addition of mercury compound (perhaps $HgCl$) into either the sediment or water in known amounts constitutes the mercury source.

   To reduce the number of parameters, only one species of fish is added to the aquarium. It is further suggested that 100 tagged goldfish be entered in the first week. Every week, ten fish would be removed for mercury analysis and ten newly

tagged fish would be added to the aquarium. At the end of ten weeks, there would be uptake data for the goldfish; thereafter, steady-state data is generated since the oldest fish would be removed for analysis at the end of every week.

Mercury in the inflow and outflow of the water in the tank would be monitored periodically to check the accumulation or production of methylmercury in the sediment. The air surrounding the tank would be analyzed to determine mercury volatility. In similar vein, the sediment should be periodically analyzed for bacterial population and mercury content.

The final result will be a better guess about the values and importance of unquantified parameters and the ability to use the mathematical model presented in this paper.

3) Better analytical techniques for organic mercury compounds differentiation need to be developed. This work is vital to the modelling process because accurate mercury concentrations need to be obtained with a high degree of reproducibility.

4) Finally, it is recommended that work in mercury research be more coordinated. Experimental results need to be verified. Currently, there are some laboratory results which contradict earlier findings. These need to be resolved. Perhaps one of the problems in this area is related to the numerous techniques now used to analyze mercury. Since no established acceptable technique for mercuryis available, researchers use

whichever technique they feel is best. This leeds to inconsistent results and in the extreme case, the results cannot even be compared because of the different analytical techniques employed.

REFERENCES

Akagi, H., D.C. Mortimer, and D.R. Miller, "Mercury Methylation and Partition in Aquatic Systems," Bulletin of Environmental Contamination and Toxicology, Vol. 23, No. 3, October 1979, pp. 372-376.

Armstrong, F.A.J., and D.P. Scott, "Decrease in Mercury Content of Fishes in Ball Lake, Ontario, Since Imposition of Controls on Mercury Discharges," Journal of the Fisheries Research Board of Canada, Vol. 36, No. 6, June 1979, pp. 670-672.

Bache, C.A., W.H. Gutenmann, and D.J. Lisk, "Residues of Total Mercury and Methylmercuric Salts in Lake Trout as a Function of Age," Science, Vol. 172, May 28, 1971, pp. 951-952.

Bails, J.D., "Mercury in Fish in the Great Lakes," in Environmental Mercury Contamination, R. Hartung and D.B. Dimann, Ed., Ann Arbor Science Pub., Inc., Michigan, 1972, pp. 31-37.

Batti, R., R. Magnaval and E. Lanzola, "Methylmercury in River Sediments," Chemosphere, Vol. 4, No. 1, January 1975, pp. 13-14.

Billen, G., C. Joiris, and R. Wollast, "A Bacterial MethylmercuryMineralizing Activity in River Sediments," Water Research, Vol. 8, No. 4, April 1974, pp. 219-225.

Bishop, J.N., and B.P. Neary, "The Form of Mercury in Freshwater Fish," in Proceedings of the International Conference on Transport of Persistent Chemicals in Aquatic Systems, Ottawa, Canada, May 1-3, 1974, National Research Council of Canada, pp. III 25-29.

Bisogni, J. and A.W. Lawrence, "Kinetics of Mercury Methylation in Aerobic and Ananerobic Aquatic Environments," Journal of the Water Pollution Control Federation, Vol. 47, No. 1., January 1975, pp. 135-152.

Bloodworth, A.J., "The Organic Chemistry of Mercury," in The Chemistry of Mercury, C.A. McAuliffe, ed., MacMillan Press of Canada, Canada, 1977, pp. 139-258.

Bonner, W.P., and R.B. Bustamante, "Behavior of Mercury in Suspended Solids and Bottom Sediments," Water Resources Research Center Report No. 50, University of Tennesse, July 26, 1976, 118 pgs.

Brandt, H.T. and R.E. Kuhns, "Final Report: Apollo County Park, Waste Water Reclamation Project for Antelope Valley Area," Los Angeles County Engineer, Sanitation Division Report, January 1975, 230 pgs. Brosset, C., and I. Svedung,

"Preliminary Study of the Possibility of a Relationship Between High Acidity in Lakes and High Mercury Content in Their Fish Populations," NTIS No. IVL-B-378, June 1977, 31 pgs.

Burrows, W.D., "Elimination of Methylmercury by Fish" in "Mechanisms of Mercury Transformation in Bottom Sediments, Part II, Final Report," by P.A. Krenkel, W.D. Burrows, E.B. Shin, K.I. Taimi, and E.D. McMullen, Vanderbilt University, Environmental and Water Resources Engineering, Technical Report No. 32, October 1973, pp. 134-172.

Burrows, W.D., and P.A. Krenkel, "Studies on Uptake and Loss of Methylmercury-203 by Bluegills (Lepomis macrochirus Raf.)," Environmental Science and Technology, Vol. 7, No. 13, December 1973, pp. 1127-1130.

Burrows, W.D., and E.B. Shin, "Chemistry of Mercury in the Environment," in "Mechanisms of Mercury Transformation in Bottom Sediments, Part II, Final Report," by P.A. Krenkel, W.D. Burrows, E.B. Shin, K.I. Taimi, and E.D. McMullen, Vanderbilt University, Environmental and Water Resources Engineering, Technical Report No. 32, October 1973, pp. 1-30.

Cember, H., E.H. Curtis and B.G. Baylock, "Mercury Bioconcentration in Fish: Temperature and Concentration Effects," Environmental Pollution, Vol. 17, No. 4, December 1978, pp. 311-319.

Cooper, H.B.H. Jr., G.D. Rawlings and R.S. Foote, "Air-Water-Land Interfaces of Mercury in Urban Atmospheres," American Institute of Chemical Engineers Symposium Series, Vol. 71, No. 145, 1975, pp. 1-9.

Copeland, R.A., "Mercury in the Lake Michigan Environment," in Environmental Mercury Contamination, R. Hartung and B.D. Dinman, ed., Ann Arbor Science Pub., Inc., Michigan, 1972, pp. 71-76.

Cox, J.A., J. Carnahan, J.D. DiNunzia, J. McCoy and J. Meister, "Source of Mercury in Fish in New Impoundments," Bulletin of Environmental Contamination and Toxicology, Vol. 23, No. 6, December 1979, pp. 779-783.

Cranston, R.E. and D.E. Buckley, "Mercury Pathways in a River Estuary," Environmental Science and Technology, Vol. 6, No. 3, March 1972, pp. 274-278.

Dean, J.A. (editor), Lange's Handbook of Chemistry, Twelfth Edition, McGraw-Hill Book Company, New York, 1979, pp. 10-12.

DeFreitas, A.S.W., S.U. Qadri and B.E. Case, "Origins and Fate of Mercury Compounds in Fish," in Proceedings of the International Conference on Transport of Persistent Chemicals

in Aquatic Systems, Ottawa, Canada, May 1-3, 1974, National Research Council of Canada, pp. III 31-36.

D'Itri, F.M., The Environmental Mercury Problem, CRC Press, Cleveland, Ohio, 1972a.

D'Itri, F.M., "Sources of Mercury in the Environment," in Environmental Mercury Contamination, R. Hartung and B.D. Dinman, ed., Ann Arbor Science Pub., Inc., Michigan, 1972b, pp. 5-25.

D'Itri, F.M., C.S. Annett and A.W. Fast, "Comparison of Mercury Levels in an Oligotrophic and an Eutrophic Lake," Marine Technology Society Journal, Vol. 5, No. 6, November-December 1971, pp. 10-14.

D'Itri, P.A. and F.M. D'Itri, Mercury Contamination: A Human Tragedy, John Wiley and Sons, New York, 1977.

Fagerstrom, T., B. Asell and A. Jernelov, "Model for Accumulation of Methyl Mercury in Northern Pike Esox lucius," Oikos, Vol. 25, No. 1, 1974, pp. 14-20.

Fagerstrom, T. and A. Jernelov, "Formation of Methyl Mercury from Pure Mercuric Sulphide in Aerobic Sediment," Water Research, Vol. 5, 1971, pp. 121-122.

Fagerstrom, T., and A. Jernelov, "Some Aspects of the Quantitative Ecology of Mercury," Water Research, Vol. 6, 1972, pp. 1193-1202.

Falchuk, K.H., L.J. Goldwater and B.L. Vallee, "The Biochemistry and Toxicology of Mercury," in The Chemistry of Mercury, C.A. McAuliffe, ed., MacMillan Press of Canada, Canada, 1977.

Farrar, W.V. and A.R. Williams, "A History of Mercury," in The Chemistry of Mercury, C.A. McAuliffe, ed., MacMillan Press of Canada, Canada, 1977, pp. 261- 283.

Fleischer, M., "Summary of the Literature on the Inorganic Chemistry of Mercury," USGS Professional Paper No. 713, US Government Printing Office, Washington, DC, 1970, pp. 6-13.

Fogg, T.R. and W.R. Fitzgerald, "Mercury in Southern New England Coastal Rains," Journal of Geophysical Research, Vol. 84, No. C11, Novemeber 20, 1979, pp. 6981-6989.

Fujita, M. and K. Hashizume, "The Accumulation of Mercury by Freshwater Planktonic Diatom," Chemosphere, Vol. 1, No. 5, September 1972, pp. 203-207.

Fujita, M. and K. Hashizume, "Status of the Uptake of Mercury from the Freshwater Diatom Synedra ulna," Water Research, Vol. 29, No. 10, October 1975, pp. 889-894.

Gadd, G.M. and A.J. Griffiths, "Microorganisms and Heavy Metal Toxicity," Microbial Ecology, Vol. 4, No. 4, 1977-1978, pp. 303-317.

Gardner, D., "Dissolved Mercury in the Lake Windermere Catchment Area," Water Research, Vol. 12, No. 8, 1978, pp. 573-575.

Garvis, J. and J.F. Ferguson, "The Cycling of Mercury Through the Environment," Water Research, Vol. 6, 1972, pp. 989-1008.

Gillespie, D.C., "Mobilization of Mercury from Sediments into Guppies (Poecilia reticulata)," Journal of the Fisheries Research Board of Canada, Vol. 29, No. 7, July 1972, pp. 1035-1041.

Gillespie, D.C. and D.P. Scott, "Mobilization of Mercuric Sulphide from Sediment into Fish under Aerobic Conditions," Journal of the Fisheries Research Board of Canada, Vol. 28, No. 11, November 1971, pp. 1807-1808.

Hamdy, M.K. and N.V. Prabhu, "Behavior of Mercury in Biosystems: III. Biotransference of Mercury Through Food Chains," Bulletin of Environmental Contamination and Toxicology, Vol. 21, No. 1/2, January 1979, pp. 170-178.

Hartung, R., "The Determination of Mono- and Dimethylmercury Compounds by Gas Chromatography," in Environmental Mercury Contamination, R. Hartung and B.D. Dinman, ed., Ann Arbor Science Pub., Inc., Michigan, 1972, pp. 157-161.

Hasselrot, T.B. and A. Gothberg, "The Ways of Transport of Mercury to Fish," in Proceedings of the International Conference on Transport of Persistent Chemicals in Aquatic Systems, Ottawa, Canada, May 1-3, 1974, National Research Council of Canada, Canada, pp. III 37-47.

Hattula, M.L., J. Sarkua, J. Janatuinen, J. Paasivirta and A. Roos, "Total Mercury and Methylmercury Contents in Fish From Lake Paijanne," Environmental Pollution, Vol. 17, No. 1, September 1978, pp. 19-29.

Hem, J.D., "Chemical Behavior of Mercury in Aqueous Media," USGS Professional Paper No. 713, US Government Printing Office, Washington, DC, 1970, pp. 19-23.

Holm, H.W., and M.F. Cox, "Mercury in Aquatic Systems: Methylation, Oxidation-Reduction and Bioaccumulation," Ecological Research Series, US EPA, EPA-660/3-74-021, August 1974, 38 pgs.

Imura, N., S.-K. Pan and T. Ukita, "Methylation of Inorganic Mercury with Liver Homogenate of Tuna Fish," Chemosphere, Vol. 1, No. 5, September 1972, pp. 197-201.

James, M.L., G.M. Smith and J.C. Wolford, Applied Numerical Methods for Digital Computation with Fortran and CSMP, second edition, Harper and Row, Pub., Inc., New York, 1977.

Jensen, S., and A. Jernelov, "Biological Methylation of Mercury in Aquatic Organisms," Nature, Vol. 223, August 16, 1969, pp. 753-754.

Jensen, S., and A. Jernelov, "Behavior of Mercury in the Environment" in Mercury Contamination in Man and His Environment, A joint undertaking by the International Labor Organization, Food and Agricultural Organization of the United Nations, The World Health Organization and the International Atomic Energy Agency, IAEA publication, Technical Series No. 137, Vienna, 1972.

Jernelov, A., "Release of Methyl Mercury from Sediments with Layers Containing Inorganic Mercury at Different Depths," Limnology and Oceanography, Vol. 15, No. 6, November 1970, pp. 958-960.

Jernelov, A., "Factors in the Transformation of Mercury to Methylmercury," in Environmental Mercury Contamination, R. Hartung and B.D. Dinman, ed., Ann Arbor Science Pub., Inc., Michigan, 1972a, pp. 167-172.

Jernelov, A., "Mercury and Food Chains," in Environmental Mercury Contamination, R. Hartung and B.D. Dinmna, ed., Ann Arbor Science Pub., Inc., Michigan, 1972b, pp. 174-177.

Jernelov, A., and H. Lann, "Mercury Accumulation in Food Chains," Oikos, Vol. 22, No. 3, 1971, pp. 403-406.

Jernelov, A., L. Lander and T. Larsson, "Swedish Perspectives on Mercury Pollution," Journal of the Water Pollution Control Federation, Vol. 47, No. 4, April 1975, pp. 810-822.

Johnels, A.G., T. Westermark, W. Berg, P.I. Persson and B. Siostrand, "Pike and Some Other Aquatic Organisms in Sweden as Indicators of Mercury Contamination in the Environment," Oikos, Vol. 18, No. 2, 1967, pp. 323-333.

Johnson, D.L., and R.S. Braman, "Distribution of Atmospheric Mercury Species Near Ground," Environmental Science and Technology, Vol. 8, No. 12, November 1974, pp. 1003-1009.

Klein, D.H., "Some Estimates of Natural Levels of Mercury in the Environment," in Environmental Mercury Contamination, R. Hartung and B.D. Dinman, ed., Ann Arbor Science Pub., Inc., Michigan, 1972, pp. 25-29.

Kleinert, S.J., "Mercury Levels in Wisconsin Fish," in Environmental Mercury Contamination, R. Hartung and B.D. Dinman, ed., Ann Arbor Science Pub., Inc., Michigan, 1972,

pp. 58-70.

Koirtyohann, S.R., R. Meers and L.K. Graham, "Mercury Levels in Fishes from Some Missouri Lakes With and Without Known Mercury Pollution," Environmental Research, Vol. 8, 1974, pp. 1-11.

Konrad, J.G., "Mercury Contents from Bottom Sediments from Wisconsin Rivers and Lakes," in Environmental Mercury Contamination, R. Hartung and B.D. Dinman, ed., Ann Arbor Science Pub., Inc., Michigan, 1972, pp. 52-58.

Krenkel, P.A., "Distribution of Mercury in Aquatic Life," in "Mechanisms of Mercury Transformation in Bottom Sediments, Part II, Final Report," by P.A. Krenkel, W.D. Burrows, E.B. Shin, K.I. Taimi, E.D. McMullen, Vanderbilt University, Environmental and Water Resources Engineering, Technical Report, No. 32, October 1973, pp.31-59.

Kudo, A., and D.C. Mortimer, "Pathways for Mercury Uptake by Fish From Bed Sediments," Environmental Pollution, Vol. 19, No. 3, July 1979, pp. 239-245.

Lamm, G.G., and J. Ruzicka, "The Determination of Traces of Mercury by Spectrophotometry, Atomic Adsorption, Radioisotope Dilution and Other Methods," in Mercury Contamination in Man and His Environment, A joint undertaking by the International Labor Orgaization, Food and Agricultural Organization of the United Nations, World Health Organization and the International Atomic Energy Agency, IAEA publication, Technical Series No. 137, Vienna, 1972.

Landner, L., "Biochemical Model for the Biological Methylation of Mercury Suggested from Methylation Studies in vivo with Neurospora crassa," Nature, Vol. 230, No. 5294, April 16, 1971, pp. 452-454.

Langley, D., "Mercury Methylation in an Aquatic Environment," Journal of the Water Pollution Control Federation, Vol. 45, January 1973, pp. 44-51.

Levason, W., and C.A. McAuliffe, "The Coordination Chemistry of Mercury," in The Chemistry of Mercury, C.A. McAuliffe, ed., MacMillan Press of Canada, Canada, 1977, pp. 49-135.

Lindberg, S., and R. Harriss, "Release of Mercury and Organics from Resuspended Near-Shore Sediments," Journal of the Water Pollution Control Federation, Vol. 49, No. 12, December 1977, pp. 2479-2487.

Lindstedt, G., and S. Skerfving, "Methods of Analysis," in Mercury in the Environment, An Epidemiological and Toxicological Appraisal, L. Friberg and J. Vostal, ed., CRC Press, 1972.

Lockhart, W.L., J.F. Uthe, A.R. Kenney and P.M. Merle, "Methylmercury in Northern Pike (Esox lucius): Distribution, Elimination, and Some Biochemical Characteristics of Contaminated Fish," Journal of the Fisheries Research Board of Canada, Vol. 29, No. 11, November 1972, pp. 1519-1523.

McCarthy, J.N. Jr., J.C. Meuschke, W.H. Ficklin and R.E. Learned, "Mercury in the Atmosphere," USGS Professional Paper No. 713, Us Government Printing Office, Washington, DC, 1970, pp. 36-39.

McKone, C.E., R.G. Young, C.A. Bache and D.J. Lisk, "Rapid Uptake of Mercuric Ion by Goldfish," Environmental Science and Technology, Vol. 5, No. 11, November 1971, pp. 1138-1139.

MacLeod, J.C., and E. Pessah, "Temperature Effects on Mercury Accumulation, Toxicity, and Metabolic Rate in Rainbow Trout (Salmo gairdneri)," Journal of the Fisheries Research Board of Canada, Vol. 30, No. 4, April 1973, pp. 485-492.

McMullen, E.D., "Methylation of Mercury in Natural Sediments," in "Mechanisms of Mercury Transformations in Bottom Sediments, Part II, Final Report," by P.A. Krenkel, W.D. Burrows, E.B. Shin, K.I. Taimi, and E.D. McMullen, Vanderbilt Universitry, Environmental and Water Resources Engineering, Technical Report No. 32, October 1973, pp. 173-220.

Mathis, B.J., and N.R. Kevern, "Distribution of Mercury, Cadium, Lead and Thallium in a Eutrophic Lake," Institute of Water Research, Michigan State University, June 1973, NTIS No. PB-221-993, 25 pgs.

Moore, J.W., and D.J. Sutherland, "Mercury Concentrations in Fish Inhabiting Two Polluted Lakes in Northern California," Water Research, Vol. 14, 1980, pp. 903-907.

Mortimer, D.C., and A. Kudo, "Interaction Between Aquatic Plants and River Bed Sediments in the Uptake of Mercury from Flowing Water," in Proceedings of the International Conference on Transport of Persistant Chemicals in Aquatic Systems, Ottawa, Canada, May 1-3, 1974, National Research Council of Canada, 1974, pg. III 11-15.

National Academy of Sciences, National Academy of Engineering, Environmental Studies Board, Committee on Water Quality, "Water Quality Criteria, 1972," US EPA Ecological Research Series, EPA-R3-73-033, March 1973.

National Research Council (NRC), An Assessment of Mercury in the Environment, Report of the Panel on Mercury, National Academy of Sciences, Washington, DC, 1978, 185 pgs.

Olson, B.H., and R.C. Cooper, "In situ Methylation of Mercury in Estuarine Sediment," Nature, Vol. 252, No. 5485, December

20/27, 1974, pp. 682-683.

Olson, B.H., and R.C. Cooper, "Comparison of Aerobic and Anaerobic Methylation of Mercuric Chloride by San Francisco Bay Sediments," Water Research, Vol. 10, No. 2, 1976, pp. 113-116.

Phillips, G.R., and R.W. Gregory, "Assimilation Efficiency of Dietary Methylmercury by Northern Pike (Esox lucius)," Journal of the Fisheries Research Board of Canada, Vol. 36, No. 12, December 1979, pp. 1516-1519.

Potter, L., D. Kidd and D. Standiford, "Mercury Levels in Lake Powell: Bioamplification of Mercury in Man-Made Desert Reservoir," Environmental Science and Technology, Vol. 9, No. 1, January 1975, pp. 41-46.

Ramamoorthy, S., and B.R. Rust, "Heavy Metal Exchange Process in Sediment-Water Systems," Environmental Geology, Vol. 2, No. 3, 1978, pp. 165-172.

Reimers, R.S., and P.A. Krenkel, "Kinetics of Mercury Adsorption in Sediments," Journal of the Water Pollution Control Federation, Vol. 46, No. 2, February 1974, pg. 352-365.

Ruohtula, M., and J.K. Miettinen, "Retention and Excretion of ^{203}Hg-Labelled Methylmercury in Rainbow Trout," Oikos, Vol. 26, No.3, 1975, pp. 385-390.

Shin, E.B., and P.A. Krenkel, "Mercury Uptake by Fish and Biomethylation Mechanisms," Journal of the Water Pollution Control Federation, Vol. 48, No. 3, March 1976, pp. 473-501.

Smith, R.G., "Methods of Analysis for Mercury and Its Compounds; A Review," in Environmental Mercury Contamination, R. Hartung and B.D. Dinman, ed., Ann Arbor Science Pub., Inc., Michigan, 1972, pp. 97-136.

Sommers, L.E., and M. Floyd, "Microbial Transformations of Mercury in Aquatic Environments," Purdue University, Water Resources Research Center Technical Report No. 54, December 1974, 80 pgs.

Spangler, W.J., J.M. Spigarelli, R.S. Rose, R.S. Flippin and H.H. Miller, "Degradation of Methylmercury by Bacteria Isolated from Environmental Samples," Applied Microbiology, Vol. 25, No. 4, April 1973, pp. 488-493.

Taimi, K.I., "Uptake of Methylmercury by Fish," in "Mechanisms of Mercury Transformation in Bottom Sediments, Part II, Final Report," by P.A. Krenkel, W.D. Burrows, E.B. Shin, K.I. Taimi, and E.D. McMullen, Vanderbilt University, Environmental and Water Resources Engineering, Technical Report No. 32, October 1973, pp. 80-134.

Takeuchi, T. "Biological Reactions and Pathological Changes in Human Beings and Animals Caused by Organic Mercury Contamination," in Environmental Mercury Contamination, R. Hartung and B.D. Dinman, ed., Ann Arbor Science Pub., Inc., Michigan, 1972, pp. 247-289.

Townsend, D.R., A. Kudo, H. Sayeed and D.R. Miller, "Mercury Transport by Bed Sediment Movements," in Proceedings of the International Conference on Transport of Persistent Chemicals in Aquatic Systems, Ottawa, Canada, May 1-3, 1974, National Research Council of Canada, Canada, pp. I 47-51.

Turner, R.R., and S.E. Lindberg, "Behavior and Transport of Mercury in River-Reservoir System Downstream of an Inactive Chloralkali Plant," Environmental Science and Technology, Vol. 12, No. 8, August 1978, pp. 918-923.

United States Environmental Protection Agency, "Quality Criteria for Water," EPA 440/9-76-023, July 1976, pp. 98-102.

United States Geological Survey, "Mercury in the Environment," USGS Professional Paper No. 713, US Government Printing Office, Washington, DC, 1970, 67 pp.

Uthe, J.F., F.M. Atton and L.M. Royer, "Uptake of Mercury by Caged Rainbow Trout (Salmo gairdneri), in the South Saskatchewan River," Journal of the Water Pollution Control Federation, Vol. 30, No. 5, May 1973, pp. 643-650.

Walker, C.M., F.C. June and H.G. Brown, "Mercury in Fish, Sediments, and Water in Lake Oahe, South Dakota," Journal of the Water Pollution Control Federation, Vol. 45, No. 10, October 1973, pp. 2203-2210.

Westoo, G., "Methylmercury as Percentage of Total Mercury in Flesh and Viscera of Salmon and Sea Trout of Various Ages," Science, Vol. 181, No. 4099, August 10, 1973, pp. 567-568.

Wobeser, G., "Acute Toxicity of Methyl Mercury Chloride and Mercuric Chloride for Rainbow Trout (Salmo gairdneri) Fry and Fingerlings," Journal of the Fisheries Research Board of Canada, Vol. 32, No. 11, November 1975a, pp. 2005-2013.

Wobeser, G., "Prolonged Oral Administration of Methyl Mercury Chloride to Rainbow Trout (Salmo gairdneri) Fingerlings," Journal of the Fisheries Research Board of Canada, Vol. 32, No. 11, November 1975b, pp. 2015-2023.

Wojtalik, T.A., "Accumulation of Mercury and Its Compounds," Journal of the Water Pollution Control Federation, Vol. 43, No. 6, June 1971, pp. 1280-1292.

Wolfe, N.L., R.G. Zepp, J.A. Gordon and G.L. Baughman, "Chemistry of Methyl-Mecurials in Aqueous Solutions," Chemosphere, Vol.

2, No. 4, May 1973, pp. 147-152.

Wood, J.M., "Environmental Pollution by Mercury" in Advances in Environmental Science and Technology, Vol. 2, J.N., Pitts and R.L. Metcalf, ed., John Wiley and Sons, Inc., New York, 1971, pp. 39-56.

Wood, J.M., "Biological Cycles for Toxic Elements in the Environment," Science, Vol. 183, No. 4129, March 15, 1974, pp. 1049-1052.

World Health Organization, "Mercury" in Environmental Health Criteria, I., Geneva, 1976, 131 pg.