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Mercury Migration into Ground Water, A Literature Study

by
W. H. Carlton
Westinghouse Savannah River Company
Savannah River Site
Aiken, South Carolina 29808
J. L Carden
Westinghouse Savannah River Company
SC USA

R. Kury
Westinghouse Savannah River Company
SC USA

G. G. Eichholz
Westinghouse Savannah River Company
SC USA

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MERCURY MIGRATION INTO GROUND WATER, A LITERATURE STUDY

by

J.L. Carden, Jr., R. Kury and G.G. Eichholz

E. I. du Pont de Nemours & Company
Savannah River Laboratory
Aiken, South Carolina 29808

MERCURY MIGRATION INTO GROUND WATER

A LITERATURE STUDY

Prepared for the Savannah River Laboratory

Topical Report - Project E26-602

by

Dr. John L. Carden, Jr.

Mr. Robert Kury

Dr. Geoffrey G. Eichholz

Nuclear Engineering and Health Physics Program

School of Mechanical Engineering

Georgia Institute of Technology

Atlanta, Georgia

Submitted: May 8, 1984

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Introduction

A board review of the technical literature dealing with mercury migration in soil was performed. The approach followed was to identify relevant articles by searching bibliographic data bases, obtaining the promising articles and searching these articles for any additional relevant citations.

The bibliographic search was initiated with an on-line search of Chemical Abstracts and Energy Research Abstracts. The search algorithm used was mercury and other delimiters such as soil, sediment, clay and kaolinite. "Mercury and soil and vaporization" was also used as was "mercury and soil and migration." An in-depth manual search of Energy Research Abstracts was performed for the period 1976 through 1983.

Additional citations, covering the period 1976 through 1983, dealing with the so-called cold vapor atomic absorption technique for mercury determination were obtained from Atomic Absorption Newsletter which publishes a comprehensive bibliography twice annually. Physics Abstracts was searched for developments in instrumental neutron activation analysis for mercury determination.

As articles were obtained their bibliographies were searched for other citations of interest. A number of additional earlier articles were identified by this method. Finally, a list of authors was compiled and Chemical Abstracts was searched for additional contibutions by these authors.

The citations identified during the literature search and copies of the articles were compiled. An organizational algorithm was sought which would allow easy access to specific papers relating to questions associated with the environmental impact of buried mercury. Since "Dispersion Study of Buried Elemental Mercury," by Orebaugh and Hale is the most thorough study of the Savannah River Plant site, it was decided to organize the literature identified in the search around the major pathways and technical questions raised in that report. An obvious advantage of this approach is that it facilitates the evaluation of the central assumptions and conclusions of the Orebaugh and Hale report relative to the current technical data base.

Eight Categories were chosen into which to organize the literature. These categories include:

1. Chemical states of mercury under environmental conditions
2. Diffusion of mercury vapor through soil
3. Solubility and stability of mercury in environmental waters
4. Transport of mercury on colloids
5. Models for mercury migration through the environment
6. Analytical techniques
7. Retention of mercury by soil components
8. Formation of organomercurials.

Each paper was reviewed and a summary of information from the paper relevant to the Orebaugh and Hale report or other issues related to the land burial of mercury was prepared. These summaries are organized into the 3 categories listed above. Some of the summaries contain figures or tables taken from the article. The figure or table numbers used in the summaries are the numbers used in the article itself. A brief statement of important points associated with each category prefaces the summary of articles in that category. Reports written about the Savannah River Plant low level waste burial ground, including Orebaugh and Hale, are not summarized in this literature survey because they represent the work of the group for whom the survey was prepared.

Conclusions

A primary justification for undertaking this study was to determine if any credible evidence existed in the literature which cast doubt on the model, developed by Orebaugh and Hale, for ground water contamination from buried mercury at the low level waste burial facility at the Savannah River Plant (SRP). Our literature survey did not uncover any information that we recognize as casting serious doubt on the projections of mercury migration into ground water or any other major aspect of the Orebaugh and Hale report. A number of issues were identified which do require further study to improve the reliability of projections of environmental impact from the near surface burial of metallic mercury. This section identifies those issues the present reviewers consider the most pressing.

Little information appears in the literature concerning the contamination of ground water by metallic mercury or mercury in any chemical form. This is perhaps the case because ground water contamination by mercury has not been identified as a serious problem, not even in areas where natural sources of mercury exist. Information is available concerning the capacity of clays to absorb mercury and on the ability of various solutions to transport dissolved mercury through soil components. This data base is not sufficiently developed, however, to allow a reliable prediction of the rate of migration for a particular site. Column experiments using a soil model for the SRL site and an appropriate leachate model are required to improve the estimates of mercury migration from the site. These column experiments need to reflect the variability that likely exists in the SRP burial ground and address such variables as the following:

1. The potential role of bacteria in determining the chemical state of the mercury present in the ground water. Bacteria have been

reported to oxidize mercury metal to Hg^{2+}, reduce Hg^{2+} to Hg^0, convert Hg^{2+} to methylated forms and to demethylate mercury. Column experiments must be designed which will determine the role of bacteria in the SRL burial ground. This will require attention to the dissolved oxygen concentration in the soil solution and the bacterial population present.

2. The presence of anions what form complexes with mercury has a profound effect on the tendency of soil components to sorb mercury. Column experiments utilizing an appropriate trench water model (perhaps more than one would be necessary) would significantly add to the reliability of the migration model.
3. The solubility of Hg^0 is orders of magnitude higher in some organic solvents than in water. The model trench water must take into account the presence, if any, of organic solvents. A study of the solubility of mercury in water saturated with any solvents commonly present may also be in order to establish an upper limit on this migration mechanism.
4. The interactions between Hg^0 and soil colloids have not been studied. Because of its potential importance in the SRP burial ground, Hg^0 uptake by soil colloids requires investigation.

The effect of the buried mercury on local ground water is routinely monitored at the SRP. The technique used for this monitoring program is the so-called cold vapor atomic absorption technique. While this technique is the most widely used today, no information could be found on the effect of soil colloids on the accuracy of the method. Mercuric complexes are known to adsorb strongly to such colloids; thus it seems important to establish that the reduction and sparging technique used to partition any mercury present in the solution under analysis into the gas phase for detection removes all of the mercury present on colloids. This issue must be addressed to establish the reliability of the analytical method upon which the ground water quality monitoring program at SRP depends.

Category 1.. Chemical states of mercury under environmental conditions

Eh-pH diagrams have been reported for the system Hg - Cl^- - SO_4^{2-}. The important organomercurials dimethylmercury and methylmercuric chloride are not thermodynamically stable within the Eh-pH space of these diagrams, but the kinetics of their dissociation may be sufficiently slow to give them a fairly long half-life in natural waters. Adsorption capacities and rates of adsorption have been determined for mercury compounds on a number of clays and sand. Bacteria are believed to play an important role in the environmental transformations of mercury leading to organomercurials and the free metal. The complex aqueous chemistry of mercury is discussed. The free Hg^{2+} ion is unlikely to exist in environmental waters to any extent. The chloro or hydroxyl complexes will predominate.

1. Chemical States of Mercury Under Environmental Conditions

1.1 Hem, J.D. "Chemical Behavior of Mercury in Aqueous Media". In Mercury and the Environment. U.S. Geological Survey Prof. Paper No. 713, 19-24, 1970.

1.2 Reimers, R.S.; Krenkel, P.A. "Kinetics of Mercury Adsorption and Desorption in Sediments". J. of Water Pollut. Con. Fed. 46, 352-365, 1974.

1.3 Kothny, E.L. "The Three-Phase Equilibrium of Mercury in Nature". In Trace Elements in the Environment, A.C.S. No. 123 (ed. Kothny, E.) Reinhold, New York, 48-79, 1973.

1.4 Gavis, J.; Ferguson, J.F. "The Cycling of Mercury Through the Environment". Water Res. 6, 989-1008, 1972.

1.5 Jensen, S.; Jernelov, A. "Behavior of Mercury in the Environment". In Mercury Contamination of Man and his Environment. IAEA, Vienna. STI/DOC/10/137, 43-47, 1972.

1.6 Hahne, H.C.H.; Kroontje, W. "Significance of pH and Chloride Concentration on Behavior of Heavy Metal Pollutants: Mercury (II), Cadmium (II), Zinc (II), and Lead (II)". J. Environ. Qual. 2, 444-450, 1973.

1.7 Newton, D.W.; Ellis, R. Jr.; Paulsen, G.M. "Effect of pH and Complex Formation on Mercury (II) Adsorption by Bentonite". J. Environ. Qual. 5, 251-254, 1976.

1.8 Gilmour, J.T. "Inorganic Complexes of Divalent Mercury in Natural Water Systems". Environ. Lett. 2, 143-152, 1971.

1.9 Fagerstrom, T.; Jernelov, A. "Some Aspects of the Quantitative Ecology of Mercury". Water Res. 6, 1193-1202, 1972.

1.10 Fleischer, M., "Summary of the Literature on the Inorganic Geochemistry of Mercury". In Mercury and the Environment. U.S. Geological Survey Prof. Paper No. 713, 6-13, 1970.

1.1

Hem has looked at the stable forms of mercury in water under various environmental conditions. As is commonly done, the stable forms are plotted as a function of oxidation potential and pH in a stability-field or Eh-pH diagram. Figure 4 shows the Eh-pH diagram for mercury compounds in water containing 36 ppm chloride and 96 ppm sulfate ions. Figure 5 shows the stable soluble compounds in the same water system. Tables are included which contain the thermodynamic data required to solve the equation systems involved. The point is made that if 33.5 kcal is taken as the standard free energy of formation of dimethylmercury, no region exists on Figure 4 in which this compound would be the most stable form. The methylmercury ion was not considered in the construction of Figure 4 because no free energy estimate was available. The rate at which equilibrium is attained can be sufficiently slow to allow an unstable compound to play an important role in the environmental chemistry of an element.

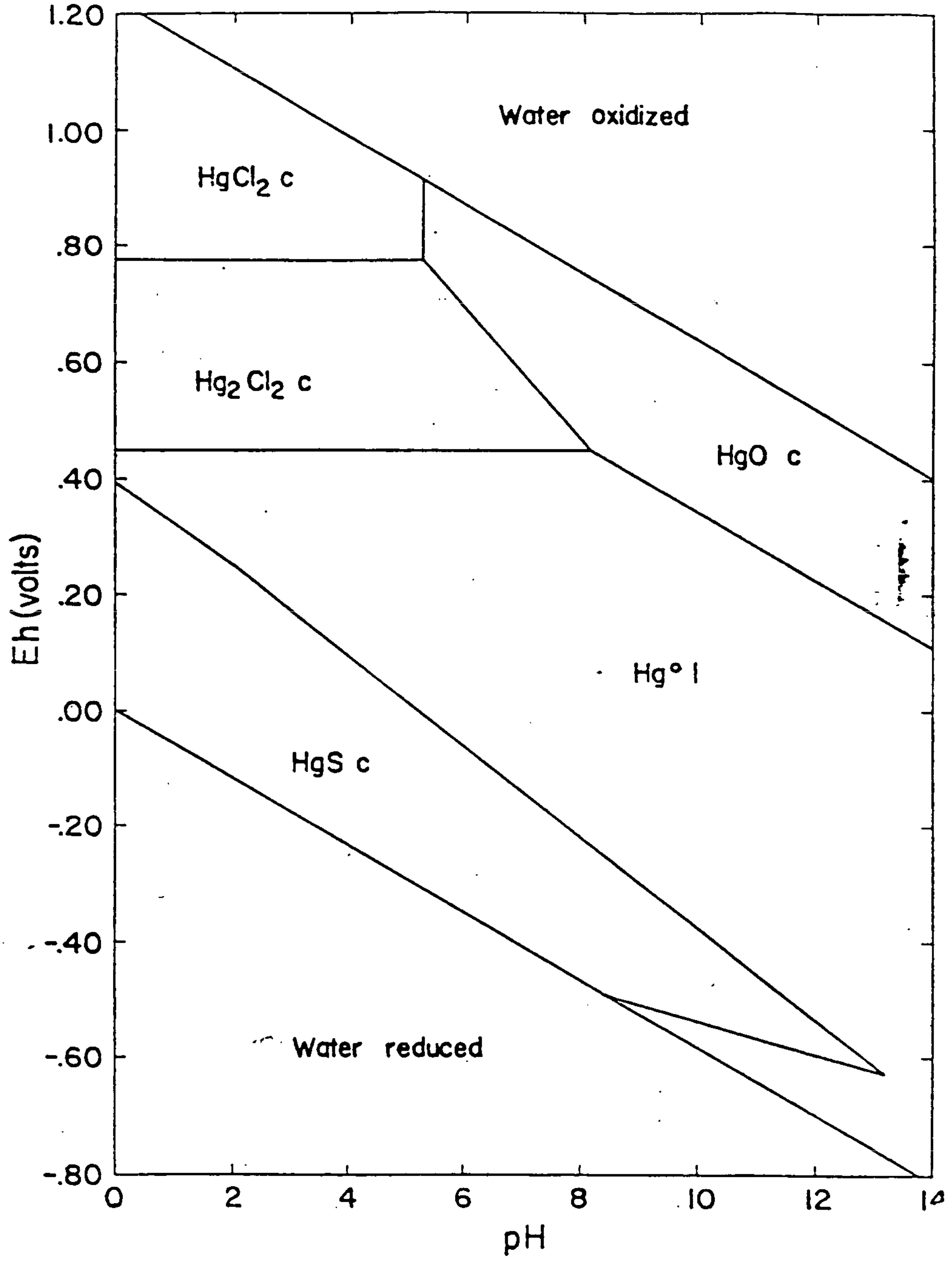

FIGURE 4.—Fields of stability for solid (c) and liquid (l) mercury species at 25°C and 1 atmosphere pressure. System includes water containing 36 ppm Cl^-, total sulfur 96 ppm as SO_4^{-2}.

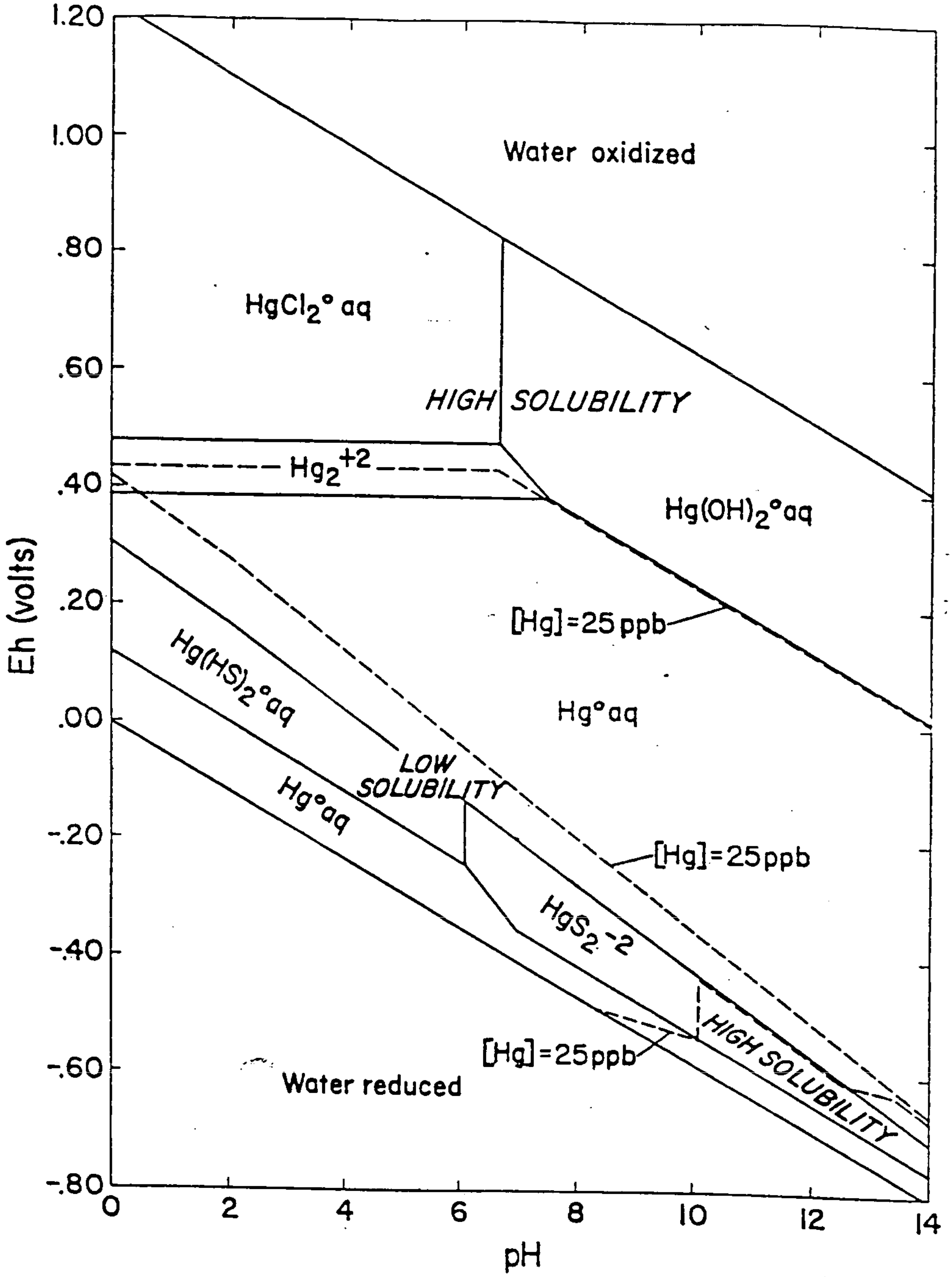

FIGURE 5.—Fields of stability for aqueous mercury species at 25°C and 1 atmosphere pressure. System includes water containing 36 ppm Cl⁻, total sulfur 96 ppm as sulfate. Dashed line indicates approximate solubility of mercury in this system.

1.2

Reimers and Krenkel studied the adsorption capacity and the kinetics of adsorption of methylmercuric chloride and mercuric chloride on sand, three clays and a synthetic organic sediment. Figure 7 shows the capacity of the three clays, illite, montmorillonite and kaolinite, in a solution containing 1 ppm Hg and varying levels of chloride. As indicated in Figure 8 the capacity of sand is approximately an order of magnitude lower than those of the clays studied. Figures 10 and 11 show the observed capacities at various pH values as a function of chloride ion concentration. The maximum adsorption rates (in micrograms of mercury per gram of material per minute) observed from a solution containing 1 ppm of mercuric chloride were as follows: illite = 65.3, montmorillonite = 35.7 and kaolinite = 9.7, fine sand = 2.9, medium sand = 1.7 and coarse sand = 1.6. Figures 13 and 14 shows the Freundlich isotherms observed for clays and sands under the conditions indicated.

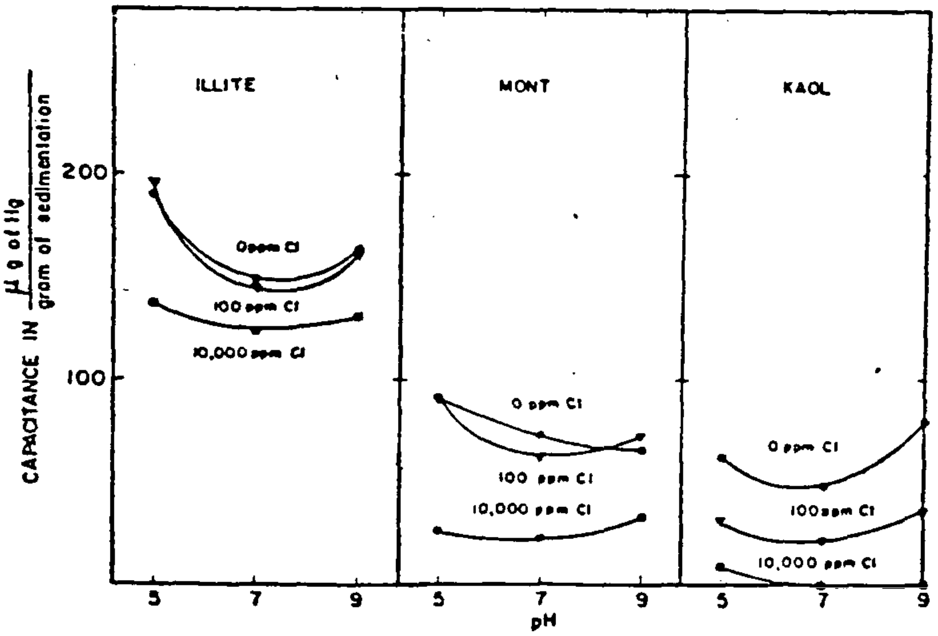

FIGURE 7.—Capacity of clays for inorganic mercury at 25°C and 1 ppm mercury.

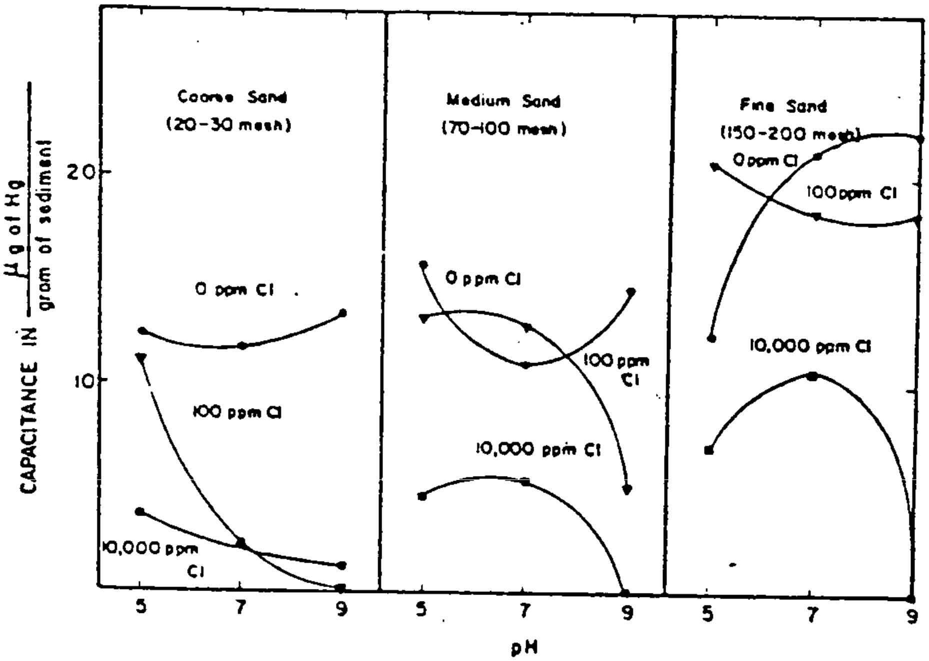

FIGURE 8.—Capacity of sand for inorganic mercuric chloride at 25°C and 1 ppm mercury.

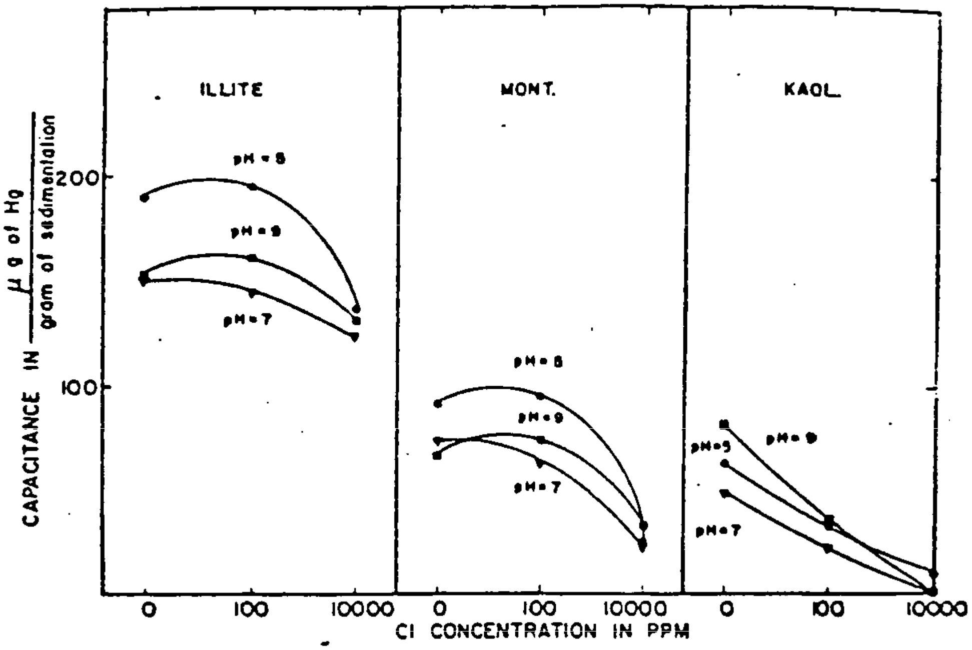

FIGURE 10.—Capacity of clay for inorganic mercury at 25°C and 1 ppm mercury.

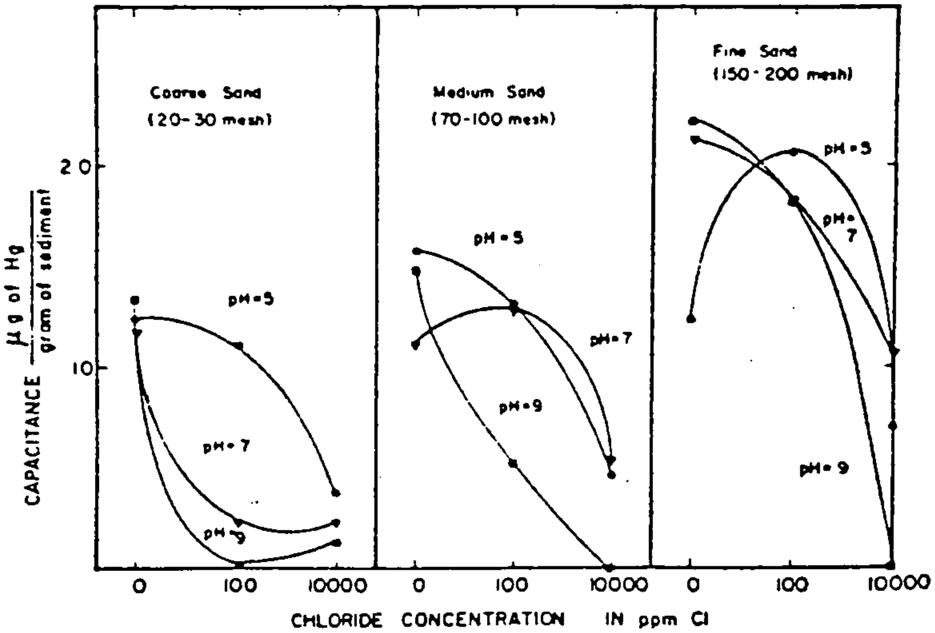

FIGURE 11.—Capacity of sand for inorganic mercuric chloride at 25°C and 1 ppm mercury.

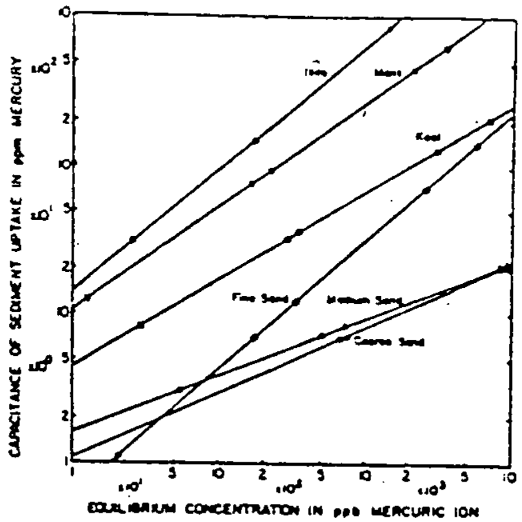

FIGURE 13.—Freundlich isotherms of clays and sands for the adsorption of $HgCl_2$ at pH 7, 0 ppm Cl^-, and 25°C.

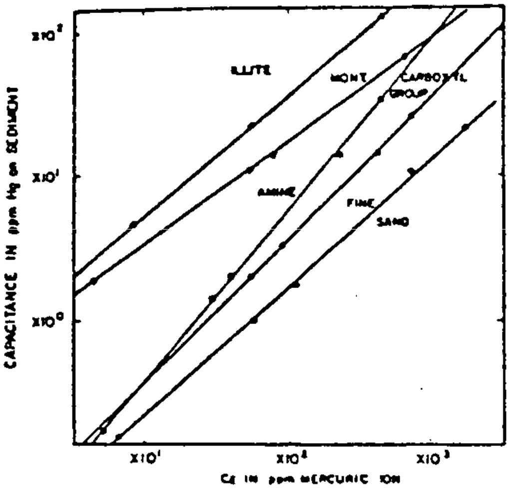

FIGURE 14.—Freundlich isotherms of clays, organics, and sands for the adsorption of $HgCl_2$ at pH 7, 0 ppm Cl^-, and 25°C.

1.3

See 5.3

1.4

See 5.4

1.5

Jensen and Jernelov discuss conversions between environmentally important forms of mercury. Pseudomonas bacteria are reported to be able to rapidly reduce Hg^{2+} to Hg^0. The extent to which this occurs in nature is not known. The importance of complexing agents in the oxidation of Hg^0 to Hg^{2+} is discussed and a relation is given for calculating the required oxidation potential in a solution containing complexing agents. The stability of various organomercurials is discussed. A number of bacteria are identified which are capable of methylation of mercury.

1.6

Hahne and Kroontje postulate the relative abundance of hydroxyl and chloride complexes under varying conditions of pH and Cl^- concentrations for the ions Hg^{2+}, Cd^{2+}, Zn^{2+} and Pb^{2+}. The equilibrium relations and basic data required for the calculations are given. Their results for mercury are shown in Figures 3 & 7. Interestingly, chloride complexation ($HgCl^+$) becomes important at very low chloride concentrations (10^{-9} M).

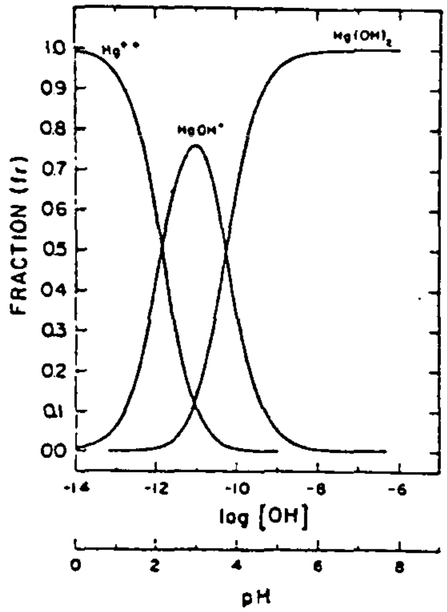

Fig. 3—Distribution of molecular and ionic species of divalent Hg at different pH values.

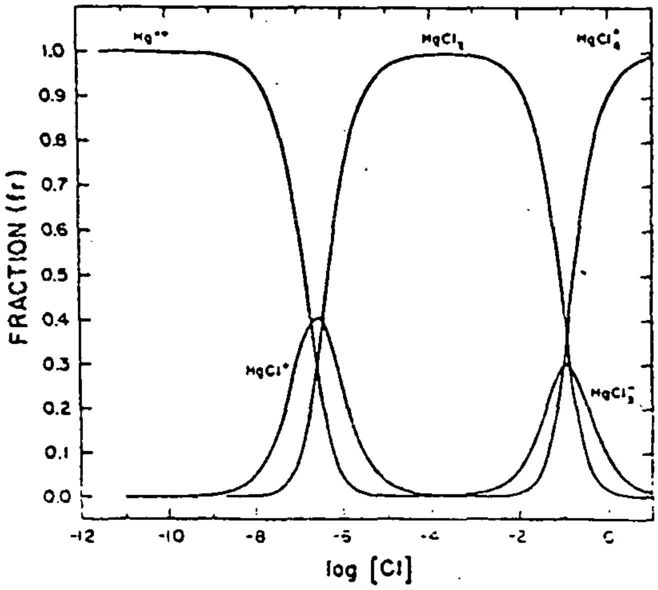

Fig. 7—Distribution of molecular and ionic species of divalent Hg at different chloride concentrations.

1.7

Newton, Ellis and Paulsen report the adsorption capacity of bentonite for Hg^{2+} in the presence of various complexing agents over a range of pH values. Table 1 gives the Hg^{2+} complexes postulated at the chloride ion and pH values tabulated. Figures 1, 2 and 3 show the observed percentage of mercury adsorbed by a bentonite suspension containing 8 mg of clay per ml at various concentrations of complexing agents over a range of pH values. Table 2 gives the quantities of mercury adsorbed under the conditions listed and Table 3 provides observations on the ease with which adsorbed mercury was removed from bentonite. The data clearly indicate Hg^{2+} adsorption onto this particular clay is near its maximum at approximately neutral pH and at low concentrations of complexing agents. This paper contains an extensive literature review of the chemistry of mercury in natural waters.

Table 1—Theoretical decimal fractions of Hg(II) complexes as functions of pH and chloride concentrations

$CaCl_2$ concentration (M)	pH	Complex $HgCl_4^{2-}$	 $HgCl_3^-$	 $HgCl_2$	 HgClOH	 $Hg(OH)_2$
10^{-1}	4	0.38	0.36	0.26	-	-
	5	0.38	0.36	0.26	-	-
	6	0.38	0.36	0.26	-	-
	7	0.38	0.36	0.26	-	-
	8	0.37	0.36	0.25	0.02	<0.01
10^{-2}	4	0.01	0.12	0.86	-	-
	5	0.01	0.12	0.86	<0.01	-
	6	0.01	0.12	0.86	0.01	-
	7	0.01	0.12	0.81	0.06	0.01
	8	<0.01	0.05	0.38	0.26	0.30
10^{-3}	4	-	0.01	0.98	<0.01	-
	5	-	0.01	0.98	0.01	-
	6	-	0.01	0.92	0.06	0.01
	7	-	0.01	0.40	0.27	0.32
	8	-	-	0.01	0.08	0.91
10^{-4}	4	-	<0.01	0.99	0.01	-
	5	-	<0.01	0.93	0.06	0.01
	6	-	<0.01	0.41	0.28	0.32
	7	-	-	-	0.06	0.91
	8	-	-	-	0.01	0.99
10^{-5}	4	-	-	0.92	0.06	0.01
	5	-	-	0.40	0.27	0.32
	6	-	-	0.01	0.08	0.91
	7	-	-	-	0.01	0.99
	8	-	-	-	<0.01	>0.99
0 ($10^{-2}M$ $Ca(NO_3)_2$)	4	-	-	-	-	0.98
	5	-	-	-	-	0.998
	6	-	-	-	-	1.0
	7	-	-	-	-	1.0
	8	-	-	-	-	1.0

Table 2—Adsorption (and loss) of Hg(II) by bentonite in 0.01*M* $Ca(NO_3)_2$ and $CaCl_2$ systems at high pH values (Initial Hg(II) concentration = 10[illegible]*M*)

0.01*M* $Ca(NO_3)_2$ pH	 $A_{relative}$†	 K_{Hg}	 Apparent ads.‡	 Actual ads.§	0.01*M* $CaCl_2$ pH	 $A_{relative}$†	 K_{Hg}	 Apparent ads.‡	 Actual ads.§
			%	μm/g				%	μm/g
6.7	-	408.1	44.9	0.225	6.6	0.930	30.0	5.7	0.0265
7.3	-	214.1	30.0	0.150	6.9	0.917	28.9	5.5	0.0252
7.9	0.921	179.0	26.4	0.122	7.2	-	29.2	5.5	0.0275
8.9	0.942	119.1	19.2	0.090	8.1	0.878	58.5	10.5	0.0461
10.2	0.860	140.8	22.0	0.095	8.9	0.862	141.4	22.0	0.0948
10.7	0.822	156.0	23.8	0.098	10.5	0.807	164.4	24.7	0.0997
11.0	0.700	162.9	24.6	0.086	10.9	0.665	224.0	30.9	0.1027

† A measure of Hg(II) loss, ^{203}Hg total activity at 1 day relative to initial total activity, values >0.950 not given.
‡ Not corrected for Hg loss.
§ Corrected for Hg loss.

Table 3—Desorption of Hg from bentonite (original adsorption in bentonite –0.01*M* $Ca(NO_3)_2$ system†)

Desorbing solution	% Hg(II) remaining on clay after successive washings‡ 1	 2	 3
0.01*M* $Ca(NO_3)_2$	87.7	81.4	75.4
0.01*M* $CaCl_2$	52.3	43.1	39.3
0.01*M* NaCl	53.0	43.5	-
0.01*M* KCl	52.7	43.6	-
0.01*N* HNO_3	69.1	53.9	48.4
0.01*N* HCl	35.6	26.1	23.2
0.01*N* H_2SO_4	58.9	46.7	-
0.01*N* HOA_c	81.0	68.5	-
H_2O	96.8	-	-

† Initial Hg concentration = 10[illegible]*M*, 52.8% adsorption at pH 4.6 in 1 day.
‡ Clay (20 mg) suspended in 5 ml desorbing solution for 1 hour, then centrifuged.

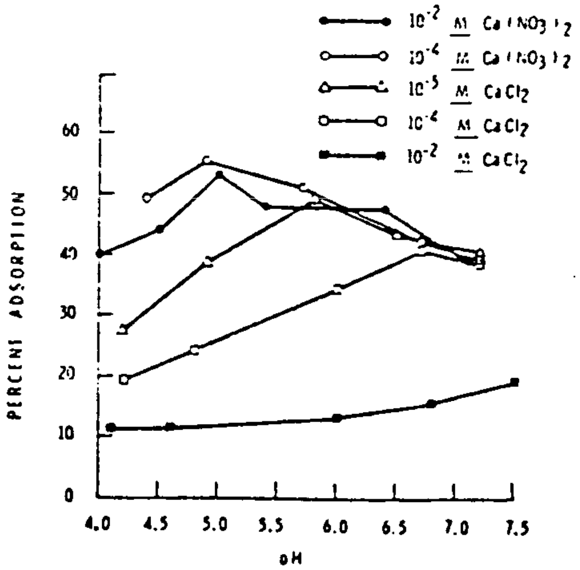

Fig. 1—Effect of varying $Ca(NO_3)_2$ and $CaCl_2$ concentrations on adsorption of Hg by bentonite as function of pH (initial Hg concentration = $10^{-7}M$).

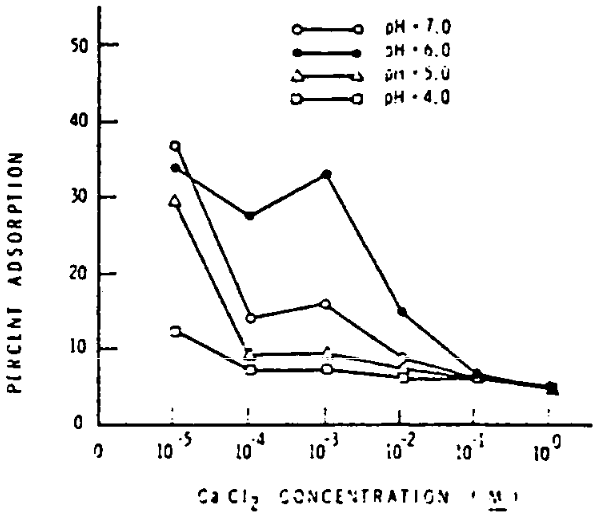

Fig. 2—Adsorption of Hg by bentonite as function of $CaCl_2$ concentration (initial Hg concentration = $10^{-7}M$).

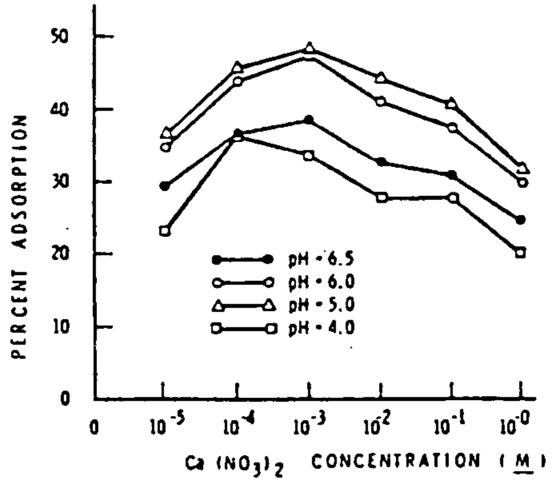

Fig. 3—Adsorption of Hg by bentonite as function of $Ca(NO_3)_2$ concentration (initial Hg concentration = $10^{-7}M$).

1.8

Gilmour presents equations which describe the nature and behavior of inorganic complexes of divalent mercury in water solutions containing common ionic species. Table 1 contains a number of these equilibria and the associated equilibrium constants. Table 2 contains the anticipated concentration ranges of these ligands in natural water systems. Calculations based on these ranges indicate that the uncharged complexes $Hg(Cl)_2$, $HgClOH$ and $Hg(OH)_2$ should be formed as indicated in Table 3. Figure 1 shows how the equilibrium concentration of each of these complexes is affected by chloride ion concentration and pH.

TABLE 1

Complex Equilibria with Hg(II) in Aqueous Systems

Equilibrium	log K_n	Ref.
$Hg^{++} + Cl^{-} = HgCl^{+}$	7.33,7.36	5,4
$Hg^{++} + 2Cl^{-} = HgCl_2$	14.15,14.16	5,4
$Hg^{++} + 3Cl^{-} = HgCl_3^{-}$	15.15,15.01	5,4
$Hg^{++} + 4Cl^{-} = HgCl_4^{=}$	15.81,15.72	5,4
$Hg^{++} + Cl^{-} + OH^{-} = HgClOH$	18.87,18.25,18.28	12,4 12,4 6,4
$Hg^{++} + OH^{-} = HgOH^{+}$	10.53,10.92	1,4
$Hg^{++} + 2OH^{-} = Hg(OH)_2$	21.89,22.64	1,4
$Hg^{++} + F^{-} = HgF^{+}$	1.56	14
$Hg^{++} + NH_3 = HgNH_3^{++}$	8.80	3
$Hg^{++} + 2NH_3 = Hg(NH_3)_2^{++}$	17.50	3
$Hg^{++} + 3NH_3 = Hg(NH_3)_3^{++}$	18.50	3
$Hg^{++} + 4NH_3 = Hg(NH_3)_4^{++}$	19.28	3
$Hg^{++} + CN^{-} = HgCN^{+}$	18.44	4
$Hg^{++} + 2CN^{-} = Hg(CN)_2$	34.5,35.36	10,4
$Hg^{++} + 3CN^{-} = Hg(CN)_3^{-}$	38.7,39.19	10,4
$Hg^{++} + 4CN^{-} = Hg(CN)_4^{=}$	41.0,41.95	10,4
$Hg^{++} + CN^{-} + OH^{-} = HgCNOH$	29.43	11
$Hg^{++} + 2SCN^{-} = Hg(SCN)_2$	17.26,18.37	16,17
$Hg^{++} + 3SCN^{-} = Hg(SCN)_3^{-}$	19.97	16
$Hg^{++} + 4SCN^{-} = Hg(SCN)_4^{=}$	21.69	16
$Hg^{++} + SCN + Cl^{-} = HgClSCN$	16.98	17
$Hg^{++} + SO_4^{=} = HgSO_4$	2.60	13
$Hg^{++} + NO_3^{-} = HgNO_3^{+}$	0.16	14
$HgS_{(s)} + S^{=} = HgS_2^{=}$	0.48	2
$HgS_{(s)} + 2HS^{-} = HgS(HS)_2^{=}$	-3.60	2
$HgS_{(s)} + 2H_2S = HgS(H_2S)_2$	-4.31	2
$HgS_{(s)} + HS^{-} + H_2S = Hg(HS)_3^{-}$	-3.59	2

TABLE 3

Calculation of Mercury(II) Complexes from 4 Wisconsin Rivers

Location	Cl^- (ppm)	pH	Decimal fraction of: $HgCl_2$	$HgClOH$	$Hg(OH)_2$
Mississippi River	6.6	8.0	< 0.01	0.08	0.92
Wisconsin River	6.2	7.6	< 0.01	0.17	0.83
Milwaukee River	26.2	8.1	< 0.01	0.22	0.78
Fox River	13.9	7.5	0.02	0.35	0.63

TABLE 2

Possible Concentration Range of Inorganic Ligands Which Complex Hg(II) in Natural Water Systems

Ligand	M (moles/l)
Cl^-	10^{-5} to 10^{-2}
OH^-	10^{-10} to 10^{-5}
F^-	trace to 10^{-4}
NH_3	trace to 10^{-5}
CN^-	trace to 10^{-5}
SCN^-	trace to 10^{-6}
$SO_4^{=}$	10^{-6} to 10^{-4}
NO_3^-	10^{-6} to 10^{-3}

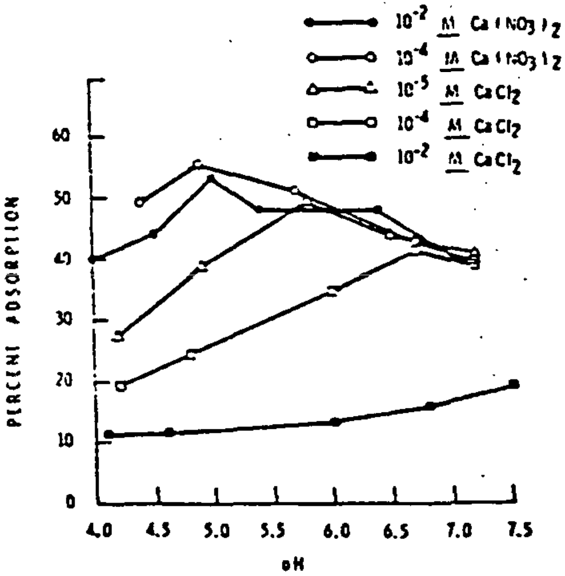

Fig. 1—Effect of varying $Ca(NO_3)_2$ and $CaCl_2$ concentrations on adsorption of Hg by bentonite as function of pH (initial Hg concentration = 10[illegible]M).

1.9

See 5.5

1.10

Fleischer gives a review of the literature through 1970 on the occurrences and distribution of mercury in the environment. An annotated bibliography is provided. More recent data are presented in some of the papers in Category 5.

Category 2. Diffusion of mercury vapor through soil.

Mercury vapor is strongly adsorbed by some clays, and the adsorption equilibria can be represented by Freundlich isotherms. Saturation is relatively slow and desorption into the gas phase is difficult. Soil bacteria appear to play a significant role in the volatilization of mercury from soil, presumably by converting oxidized forms or organomercurials into metallic mercury, which is lost by vaporization. An increasing soil moisture level is observed to reduce dramatically the rate of mercury vapor diffusion through soil columns. Mercury compounds other than the metallic vapor are observed in the atmosphere. The amount of mercury in the atmosphere above a given location is found to vary with soil surface temperature and barometric pressure. Mercury concentrations in soil around natural sources of the element diminish rapidly with distance from the source. No data on ground water around such deposits were found although many such areas have been inhabited by humans for millennia. Coal-fired power plants are observed to emit 99 percent of the mercury initially present in the coal consumed; thus producing wide-spread mercury distribution in the environment.

2. Diffusion of Mercury Vapor Through Soil.

2.1 Fang, S.C. "Sorption and Transformation of Mercury Vapor by Dry Soil". Environ. Sci. Technol. 12, 285-288, 1978.

2.2 Trost, P.B.; Bisque, R.E. "Distribution of Mercury in Residual Soils". R. Hartung and B.D. Dinman, (eds.) In Environmental Mercury Contamination. Ann Arbor Science, Ann Arbor, Mich., 178-196, 1972.

2.3 Rogers, R.D.; McFarlane, J. C. "Factors Influencing the Volatilization of Mercury from Soil". J. Environ. Qual. 8, 255-260, 1979.

2.4 Lindberg S.E.; Turner R.R. "Mercury Emissions from Chlorine-Production Solid Waste Deposits". Nature 268, 133-136, 1977.

2.5 Poelstra, P.; Frissel, M.J.; Van der Klugt, N.; Tap, W. "Behaviour of Mercury Compounds in Soils: Accumulation and Evaporation". Symposium on Comparative Studies of Food and Environmental Contamination. IAEA, Vienna, 281-291, 1973.

2.6 Lindberg, S.E.; Jackson, D.R.; Huckabee J.W.; Jansen S.A.; Levin, M.J.; Lund, J.R. "Atmospheric Emission and Plant Uptake of Mercury from Agricultural Soils Near the Almaden Mercury Mine". J. Environ. Qual. 8, 572-578, 1979.

2.7 Lindberg, S. E. "Mercury Partitioning in a Power Plant Plume and its Influence on Atmospheric Removal Mechanisms". Atmos. Envir. 14, 227-231, 1980.

2.8 Fang, S.C. "Studies on the Sorption of Elemental Mercury Vapor by Soils". Arch. Environ. Contam. Toxicol. 10, 193-201, 1981.

2.9 Johnson, D. L.; Braman, R. S. "Distribution of Atmospheric Mercury Species Near Ground". Environ. Sci. Technol. 8, 1003-1009, 1974.

2.10 McCarthy, J.H.; Meuschke, J.L.; Ficklin, W. H. ; Learned, R.E. "Mercury in the Atmosphere". In Mercury and the Environment. U.S. Geological Survey Prof. Paper No. 713, 37-39, 1970.

2.1

Fang determined the vapor-phase mercury adsorption by the solid materials listed in Table 1. Two grams of each of these materials was used in the experiments. Table 2 shows the amount of vapor adsorbed as a function of the vapor concentration. Figure 1 illustrates that the data can be represented by the Freundlich isotherm equation. Table 1 contains the experimental constants required to apply this relationship to the materials studied. Experiments were performed to determine the time dependence of the adsorption process and to determine the saturation capacity of the materials for mercury vapor. These experiments were carried out for 17 days and saturation was not reached for any of the materials. Figure 2 shows the interesting results of this series of experiments. Note that illite rapidly adsorbed mercury while montmorillonite absorbed very little vapor. Unfortunately, kaolinite was not included in this experiment. It was noted that mercury was not removed from the 5 soils listed in Table 3 after vacuum desiccation or heating to 110° C. Mercury is tightly bound to these soils, but the exact bonding involved could not be determined. Plant uptake was studied, and it was observed that the mercury content of the leaves and seeds was highly correlated with the soil Hg^{2+} content and not with the soil total mercury content.

Table I. Sorption of ^{203}Mercury Vapor by Five Montana Soils, Clay Minerals, and Others

Soils, minerals, and others	pH	Organic matter, %	Clay content, %	^{203}Hg vapor sorbed, μg[a]
Arvada[b]	8.1	2.7	40	0.018
Campspass[b]	6.6	11.5	25	0.077
Heldt[b]	8.3	2.9	25	0.076
Bainville[b]	7.5	3.2	29	0.072
Terry[b]	8.3	1.6	12	0.015
Sand				0.002
Kaolinite[b]				0.004
Bentonite[b]				0.021
Illite #35[c]				0.308
Montmorillonite #25[c]				0.008
Metabentonite #38[c]				0.059
Cellulose powder				0.004
Dry straw				0.011
Humic acid, technical				0.170
Peat[b]				0.148
Charcoal				2.943

[a] Sorption was carried out for 24 h in an atmosphere containing 75.9 μg ^{203}Hg vapor/m^3. [b] Kindly provided by the Soil Department, Oregon State University. Surface soil samples (0–20 cm depth) collected from uncultivated sites in southeastern Montana. [c] Purchased from Ward's Natural Science Establishment, Inc.

Table II. Uptake of ^{203}Hg Elemental Mercury Vapor by Dry Soils and Clay Minerals at Various Vapor Concentrations

Adsorbants	Hg^0 vapor concentration, μg/m^3				Adsorption characteristics	
	85.16, μg/2 g[a]	135.88, μg/2 g	185.19, μg/2 g	208.67, μg/2 g	n	k
Arvada	0.016	0.026	0.057	0.080	1.79	4.89×10^{-6}
Campspass	0.045	0.084	0.152	0.191	1.60	3.52×10^{-5}
Heldt	0.037	0.065	0.126	0.147	1.56	3.40×10^{-5}
Bainville	0.052	0.094	0.183	0.217	1.63	3.54×10^{-5}
Terry	0.016	0.028	0.054	0.062	1.56	1.50×10^{-5}
Illite #35	0.383	0.607	0.692	0.948	0.91	6.71×10^{-3}
Kaolinite	0.005	0.011	0.028	0.020	1.74	2.28×10^{-6}
Bentonite	0.017	0.035	0.079	0.105	2.07	1.56×10^{-6}

[a] Two-gram sample was exposed for 24 h in an atmosphere containing various ^{203}Hg vapor concentrations.

Table III. Total and Mercuric Mercury Content of Five Montana Soils Before and After Cultivation

Soils	Total ^{203}Hg content, μg		Mercuric mercury			
			Before		After	
	Before	After	μg	%	μg	%
Arvada	8.25	8.08	1.66	20.1	0.44	5.4
Campspass	20.03	22.21	0.42	2.1	0.99	4.5
Heldt	19.80	21.75	4.44	22.4	3.78	17.4
Bainville	40.05	36.70	4.04	10.1	3.78	10.3
Terry	7.20	4.56	1.97	27.4	0.41	8.9

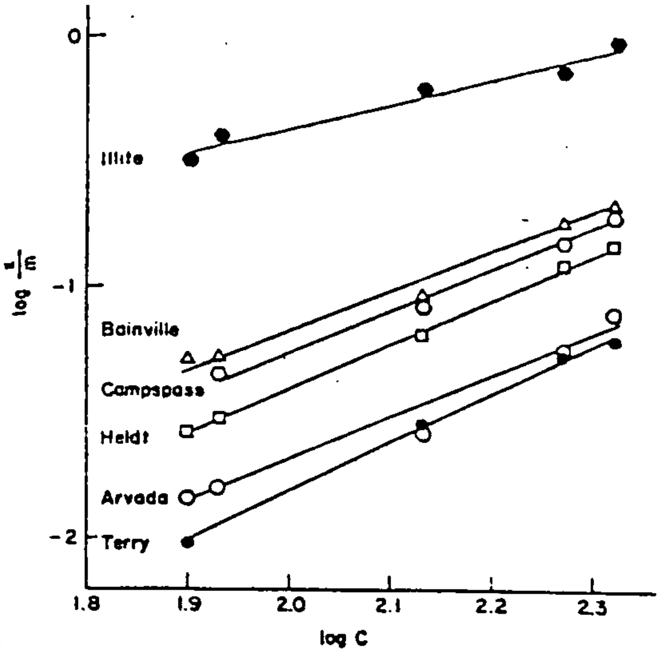

Figure 1. Freundlich's plots of metallic mercury vapor sorption by dry soils and illite

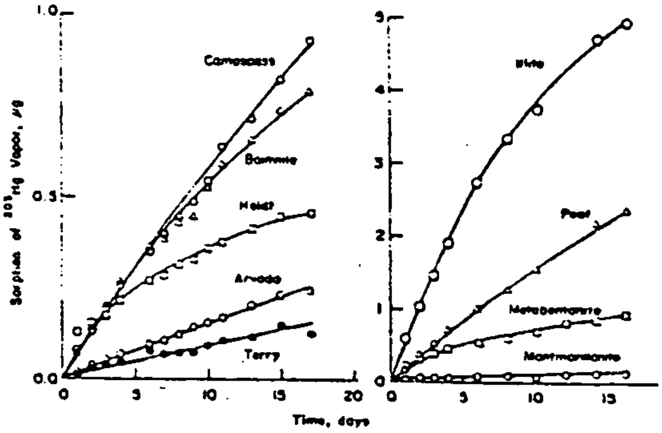

Figure 2. Accumulative sorption of metallic mercury vapor by dry soils and clay minerals

$^{203}Hg^0$ vapor concentration: 79.2 μg/m^3. Weight of soil or clay mineral sample: 2 g

2.2

See 7.10

2.3

Rogers and McFarlane studied mercury loss by vaporization and by extraction with an ammonium nitrate solution from a variety of soils amended with Hg^{2+}. An initial rapid loss of mercury was observed, followed by a more gradual decrease in the soil mercury content. Sterilized soil had a much lower rate of mercury volatilization and inoculation of sterile soil containing mercury increased the evaporation rate. This work supports the contention that a number of common soil bacteria are capable of rapidly reducing Hg^{2+} to the metallic form. Volatilization from a clay soil was observed to proceed at a much lower rate and the role of bacterial reduction was less clear.

2.4

Lindberg and Turner investigated mercury losses from an abandoned waste impoundment associated with an inactive chloralkali plant. The impoundment has a surface area of approximately 44 ha and an average mercury concentration of 150 micrograms of mercury per gram of residue. The estimated annual loss of mercury to the atmosphere is 36 kg and that to surface water is 38 kg. Unfortunately, no attempt was made to study the effect of this site on ground water. The site is a homogeneous source of known surface area making it valuable for ground water contamination modeling.

2.5

Poelstra et al. looked at the location of mercury in natural soils and at the water-borne migration of three forms of mercury (the metal, mercuric chloride and methylmercuric chloride) through soils in column experiments. Figures 3 through 5 illustrate that mercury was not displaced through the column to a significant extent.

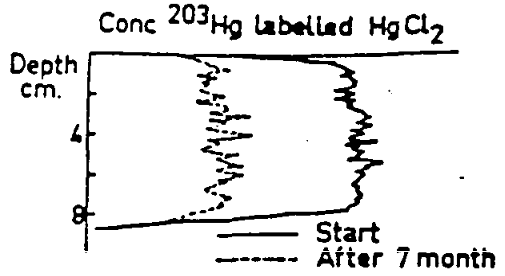

FIG. 3. Result of leaching experiments in a column with ^{203}Hg-labelled $HgCl_2$.

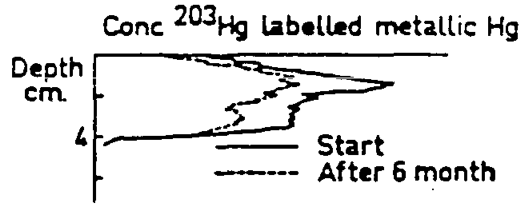

FIG. 4. Result of leaching experiments in a column with ^{203}Hg-labelled metallic Hg.

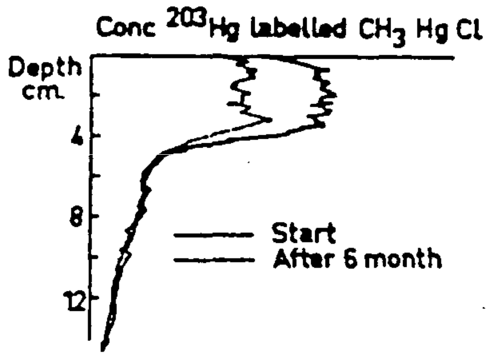

FIG. 5. Result of leaching experiments in a column with ^{203}Hg-labelled CH_3HgCl.

2.6

Lindberg et al. determined mercury emission to the atmosphere and the uptake of mercury by plants in the vicinity of the mercury mines near Almaden, Spain. As indicated in Figure 1, the concentration of mercury at the soil surface decreased rapidly with increasing distance from the mine. Plant uptake experiments indicated that mercury vapor was absorbed by plant leaves. In the plant species studied, it was found that approximately 75% of the mercury taken up by the plant resided in the above-ground portions. Mercury emission rates from soil were found to depend on soil temperature. It is postulated that soil mercury species are reduced to Hg^0 in the soil zone and then lost by evaporation.

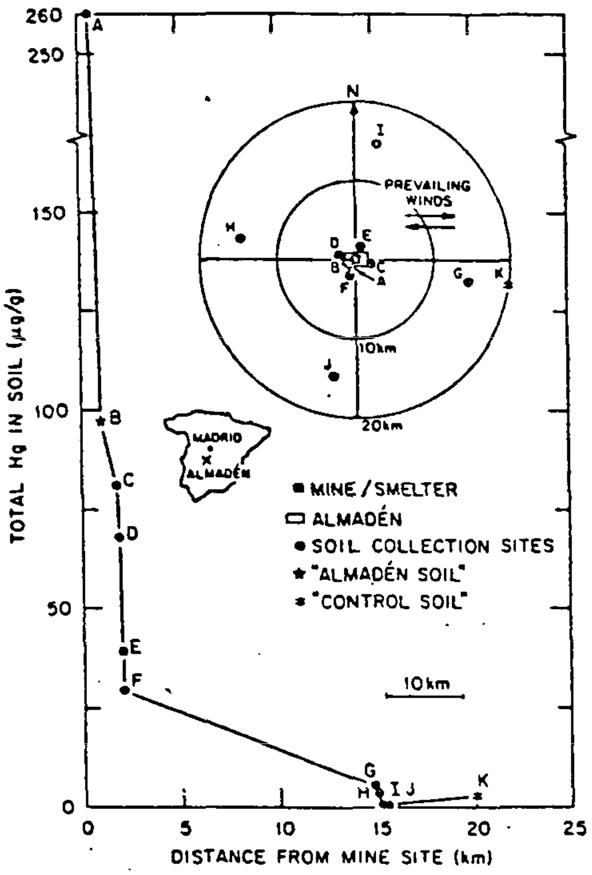

Fig. 1—Study area and concentrations of total Hg in surface soils near the Almadén cinnabar mine.

2.7

Lindberg looked at the emission of mercury from a coal-fired power plant. He found that less than 1% of the mercury contained in the coal feed is retained in the plant. Of the 99% plus emitted, approximately 7% is associated with ash and 92% is in the vapor phase. Vapor emission is conducive to wide-spread distribution of the mercury rather than local deposition. Precipitation scavenging appears to be the major atmospheric loss mechanism.

2.8

Fang evaluated the tendency of a number of soils to adsorb mercury vapor over a range of soil moisture levels. Table 1 characterizes the soils studied and Figure 1 shows the amount of mercury vapor adsorbed by each. Maximum adsorption was observed at a moisture content corresponding to soil saturation. Mercury vapor diffusion experiments were carried out with dry and essentially saturated soils. Figure 3 shows mercury penetration into columns of all of the soils studied. Figure 4 shows the effect of time on the amount of mercury present along the length of a column. While the amount of mercury present at a given depth increases with time, the diffusion rate remains constant. Figure 5 illustrates the dramatic effect of soil moisture on vapor diffusion through soil. As observed by Orebaugh and Hale, moisture greatly reduced diffusion through soil. Fang suggests a relationship to describe mercury vapor diffusion through soil. The relationship and constants resulting from this study are given in Table 3.

Table 1. Chemical and physical properties of selected eastern Montana soils

Soil sample	pH	Organic matter %	Sand %	Silt %	Clay %	Cation exchange capacity meq 100g	Water holding capacity 1/3 bar %	saturation %
Arvada	8.1	2.7	35	25	40	22.2	31	54
Campspass	6.6	11.5	19	56	25	25.5	33	80
Heldt	8.3	2.9	27	48	25	11.4	21	52
Bainville	7.5	3.9	29	42	29	15.8	21	45
Terry	8.3	1.6	74	14	12	8.4	10	37

Table 3. Sorption characteristics and diffusivity coefficient for mercury vapor of five Montana surface soils as measured in soil column study
(Mercury vapor concentration = 1 μg/m^3; the mercury vapor diffusion profile is expressed in the form of $y = ae^{-bx}$)

Soil	Moisture content %	Exposure time day	a	b	Correlation coefficient r
Arvada	air dry	1	0.413	0.097	0.95
Campspass	air dry	1	1.219	0.260	0.99
Heldt	air dry	1	0.774	0.109	0.99
Bainville	air dry	1	0.934	0.263	0.99
Terry	air dry	1	0.409	0.160	0.96
Campspass	air dry	1	1.382	0.205	0.99
Campspass	air dry	3	3.348	0.168	0.99
Campspass	air dry	5	4.181	0.212	0.97
Campspass	20	1	16.738	0.675	0.96

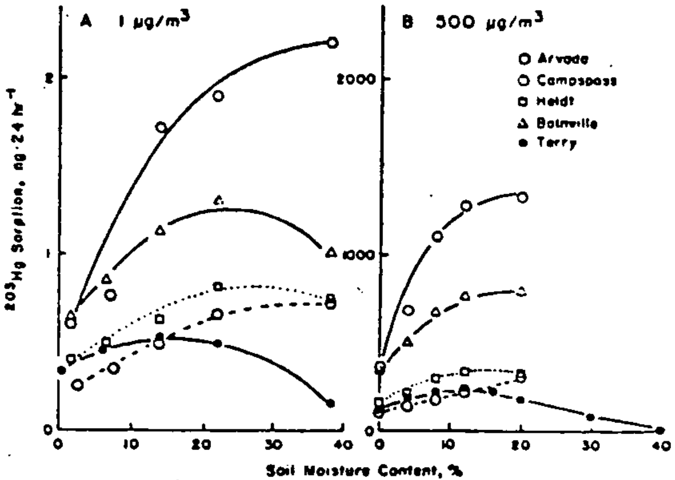

Fig. 1. Influence of soil moisture content on the sorption of ^{203}Hg elemental mercury vapor. Soils exposed for 24 hr of air containing 1 μg or 500 μg per m^3 mercury. O, Arvada: O Campspass: □ Heldt; △ Bainville: and ● Terry

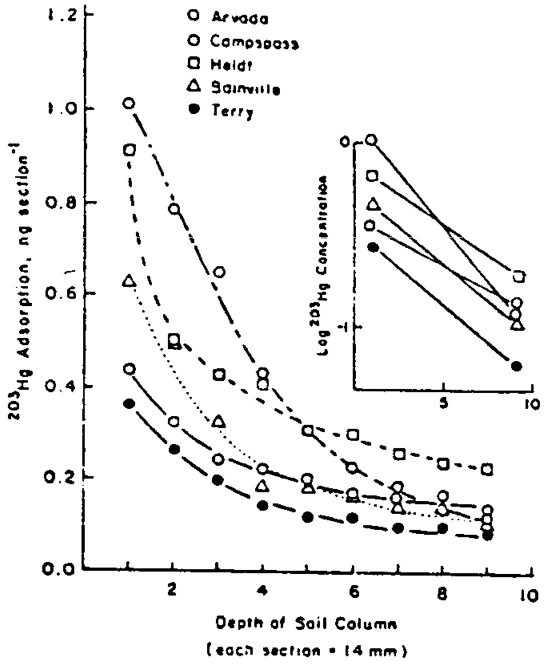

Fig. 3. Penetration of ^{203}Hg mercury vapor in dry soil columns. Exposure time 24 hr

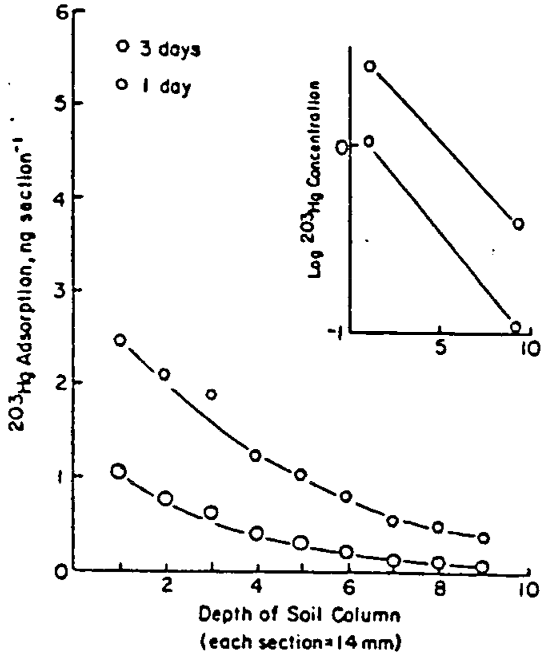

Fig. 4. Penetration of ^{203}Hg mercury vapor in dry soil column in relation to the time of exposure

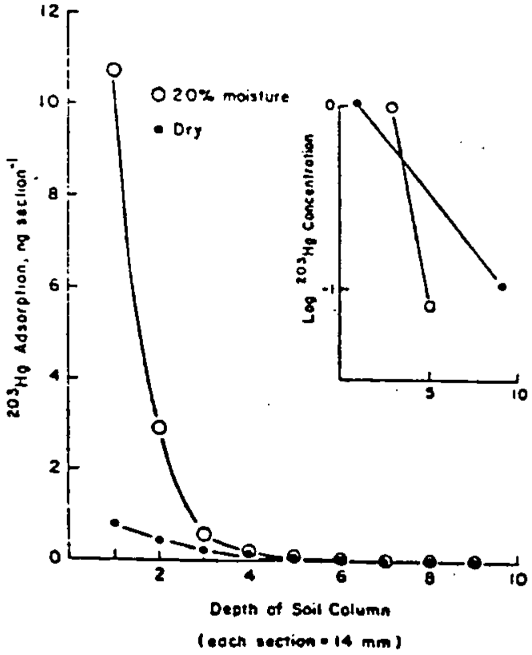

Fig. 5. Comparison of ^{203}mercury vapor penetration of dry and moist soil columns

Johnson and Braman determined the mercury compounds present in the air in the Tampa Bay area. As indicated in Table 2, they found significant quantities of compounds other than elemental mercury vapor.

Table II. Mean Values of Day and Night Mercury Species Concentration[a] and Percentages of Total Mercury at Station 1 for Period September 24–26, 1973

	On particulate	Hg^{2+}	$HgCH_3^+$		$Hg(CH_3)_2$		
Time	Hg_p	Hg(II) type	MMC type	Hg^0	DMM	Σ Hg	No. of values
Day	0.27 (6%)	0.86 (19%)	0.63 (14%)	2.57 (60%)	0.05 (1%)	4.48	19
Night	0.17 (2%)	1.58[b] (19%)	1.56 (19%)	5.03[b] (60%)	0.06 (<1%)	8.40	13

[a] ng/m³. [b] Excluding the values for the sample 0000–0200 hr September 26.

2.10

McCarthy et al. found evidence in the literature that the mercury content of the atmosphere above a give area depends on the temperature of the soil and changes in barometric pressure. The dependence on atmospheric pressure seems to be a result of "soil breathing," with the maximum atmospheric concentrations being observed at the maximum rate of decrease in atmospheric pressure.

Category 3. Solubility and Stability of Mercury in Environmental Waters

Information is available on the solubility of mercury metal in very pure water and on the complexes formed by mercury in various solutions. Eh-pH diagrams are discussed in Category 1. Mercury has been reported to adsorb strongly onto colloidal iron oxide and manganese dioxide particles substantially increasing the total amount of suspended mercury above the solubility of mercury in water. A number of soil components (clays, humics, etc.) have been reported to strongly absorb and retain mercury. An important observation is the high solubility of mercury in some organic solvents relative to its solubility in water. This raises the possibility of a higher mercury flux in percolating water contaminated with an organic solvent.

Many of the papers in this category deal with observations of mercury loss from solution. These papers are not entirely consistent, but they do indicate a strong tendency for mercury in water to be transformed from the plus two oxidation state to the metal or a complex which is then removed from the solution.

3. Solubility and Stability of Mercury in Environmental Waters.

3.1 Onat, E., "Solubility Studies of Metallic Mercury in Pure Water at Various Temperatures". J. Inorg. Nucl. Chem. 36, 2029-2032, 1974.

3.2 Toribara, T.Y.; Shields, C. P.; Koval, L. "Behavior of Dilute Solutions of Mercury". Talanta 17, 1025-1028, 1970.

3.3 Feldman, C. "Preservation of Dilute Mercury Solutions". Anal. Chem. 46, 99-102, 1974.

3.4 Yamazaki, S.; Dokiya, Y.; Fuwa, K. "Problems of Mercury Determination in Water Samples". NBS Spec. Publ. 464, 233-235, 1977.

3.5 Weiss, H.V.; Shipman, W. H.; Guttman, M. A. "Effective Storage of Dilute Solutions in Polyethylene". Anal. Chim. Acta 81, 211-217, 1976.

3.6 Lo. J.M.; Wai, C.M. "Mercury Loss from Water during Storage: Mechanism and Prevention". Anal. Chem. 47, 1869-1870, 1975.

3.7 Mahan, K.; Mahan, S. "Mercury Retention in Untreated Water Samples of the Parts-Per-Billion Level". Anal. Chem. 49, 662-664, 1977.

3.8 Newton, D.W.; Ellis, R. Jr. "Loss of Mercury (II) from Solution". J. Environ. Qual. 3, 20-23, 1974.

3.9 Jenne, E.A.; Avotins, P. "The Time Stability of Dissolved Mercury in Water Samples - 1. Literature Reviews". J. Environ. Qual. 4, 427-431, 1975.

3.10 Avotins, P.; Jenne, E.A. "The Time Stability of Dissolved Mercury in Water Samples - II. Chemical Stabilization". J. Environ. Qual. 4, 515-519, 1975.

3.11 Jensen, S.; Jernelov, A. "Behavior of Mercury in the Environment". In Mercury Contamination of Man and His Environment. IAEA, Vienna, STI/DOC/10/137, 43-47, 1972.

3.12 Carden, J. L. "A Close Look at the interactions Between the Dilute Solutions of Mercury and Borosilicate Glass Surfaces, Especially as They Relate to the Stability of Dilute Mercury Standard Solutions". 4th Joint Conference on Sensing of Environmental Pollutants. 117-120, 1978.

3.13 Benes, P. "On the State of Mercury Traces in Aqueous Solutions". J. Inorg. Nucl. Chem. 31, 1923-1928, 1969.

3.14 Jenne, E.A. "Atmospheric and Fluvial Transport of Mercury". In Man and His Environment. Geological Survey Prof. Paper No. 713, 40-45, 1970.

3.15 Trost, P.B.; Bisque, R.E., "Distribution of Mercury in Residual Soils". R. Hartung and B.D. Dinman, (eds.) In Environmental Mercury Contamination. Ann Arbor Science, Ann Arbor, Mich., 178-196, 1972.

3.16 Klusman, R.W.; et al. "Toxic Heavy Metals in Ground Water of a Portion of the Front Range Mineral Belt". PB-256-212, Colorado State. Univ., 1976.

3.17 Turner, R.R.; Lindberg S.E. "Behavior and Transport of Mercury in River-Reservoir System Downstream of an Inactive Chloroalkali Plant". Environ. Sci. Technol. 12, 918-923, 1978.

3.18 Poelstra, P.; Frissel, M.J.; Van der Klugt, N.; Tap, W. "Behaviour of Mercury Compounds in Soils: Accumulation and Evaporation". Symposium on Comparative Studies of Food and Environmental Contamination. IAEA, Austria, 281-291, 1973.

3.19 Reichardt, H.H.; Bonhoeffer, K.F. "Adsorption-sspektren von Gelostem Quecksilber". Zeitschrift fur Elektrochemie, 36, 753, 1930.

3.1

Onat has provided a careful determination of the solubility of metallic mercury in very pure water. Interestingly the technique he used is a colorimetric method quite different from the cold vapor method commonly used today. Table 1 gives his solubility data. Figure 3 demonstrates the results can be represented by the Clausius-Clapeyron equation which can, therefore, be used to extrapolate to solubilities beyond the experimental temperature range.

Table 1. Solubility of metallic mercury in water and the comparison of the results obtained from the reference curve and Beer's equation

Temperature (°C)	Number of determinations	Concentration of soluble mercury g-atom l*	 g-atom l†	 mg 100 ml*	Average deviation from mean mg 100 ml	 %
25	5	3.05×10^{-7}	3.09×10^{-7}	0.0061	0.0002	3.3
40	4	5.12×10^{-7}	5.19×10^{-7}	0.0104	0.0002	1.9
50	3	7.43×10^{-7}	7.47×10^{-7}	0.0150	0.0006	4.0
60	3	10.78×10^{-7}	10.87×10^{-7}	0.0216	0.0006	3.0
70	4	13.33×10^{-7}	13.37×10^{-7}	0.0267	0.0008	3.0
80	4	16.37×10^{-7}	16.40×10^{-7}	0.0328	0.0002	0.6

$S = 0.004$ (overall).

$tS/\sqrt{N} = 0.00013$ (95 per cent confidence level).

* Obtained from the reference curve constructed with a slope of 2.815×10^{-5}, absorbance concentration, mole l.

† Calculated from Beer's equation $c = A/ab$.

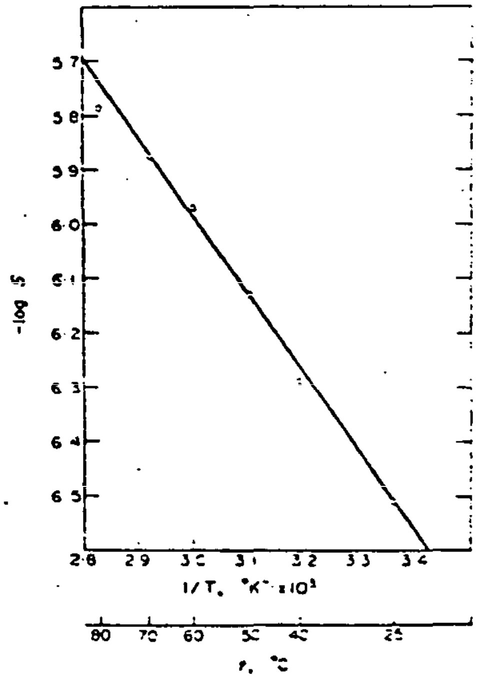

Fig. 3. The solubility curve of mercury in water. The negative logarithm of the molar solubility plotted against the reciprocal of the absolute temperature.

3.2

Toribara, Shields and Koval studied the redistribution of 203-Hg between a number of solutions as well as metallic mercury. The presence of Hg^{2+} appeared to be a requirement for tracer uptake by a solution.

3.3

Feldman investigated mercury loss from dilute solutions containing a variety of compounds expected to improve the stability of the Hg^{2+} in solution. Glass and polyethylene containers were used. Solutions containing 0.1 mg of Hg^{2+} per ml were found to be stable in glass if the solution contained 5% HNO_3 and 0.01% $(Cr_2O_7)^{2-}$. Stable here means the mercury stayed in solution in a form which could be detected by the analytical technique being used; cold vapor atomic absorption. Solutions containing 0.05% H_2SO_4 and 0.01% $KMnO_4$ were observed to lose mercury at a substantial rate. It is hypothesized this was due to scavenging of mercury by hydrated manganese dioxide produced as a result of oxidation of compounds present in solution.

Yamazaki, Dokiya and Fuwa investigated the loss of mercury from a variety of water types as shown in Figures 1 and 2. The compound added to the various solutions for study is not specified, but it seems most reasonable to assume it contained 203-Hg^{2+}. For distilled water contained in polyethylene, 40% of the activity was found distributed uniformly over the container walls. For pond water, more of the activity was found at the bottom of the container indicating sorption followed by settling. For sea water, 60% of the mercury vaporized.

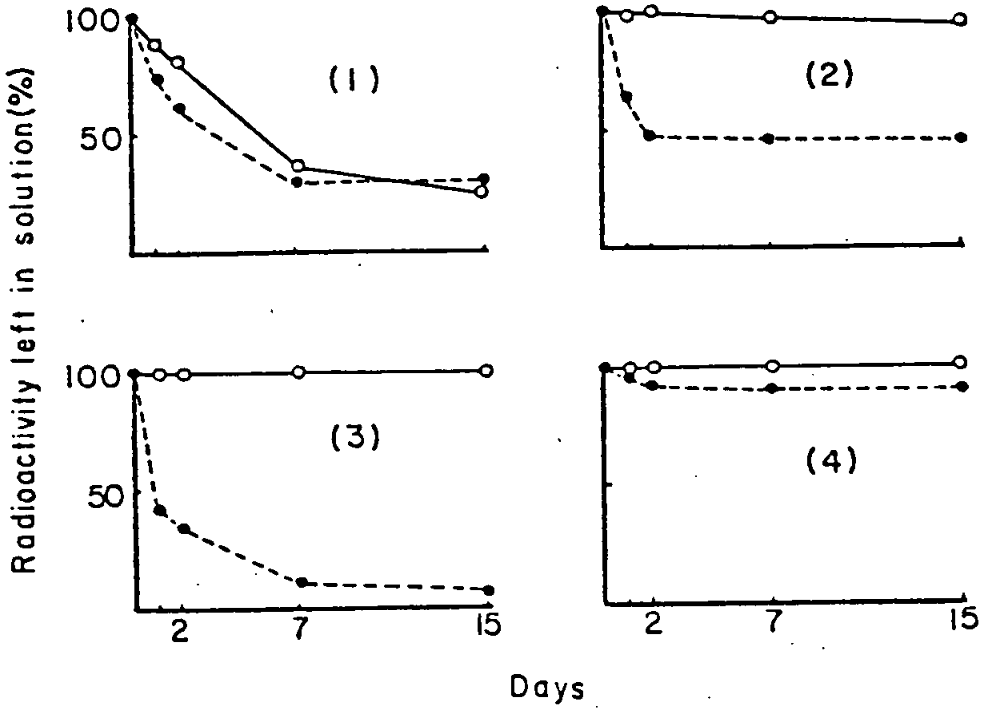

Figure 1. Behavior of ^{203}Hg(●---●) and ^{65}Zn(O——O) (1 - 5 ppb) added to (1) pond water, (2) sea water, (3) distilled water and (4) artificial sea water. 100 ml polyethylene containers were used.

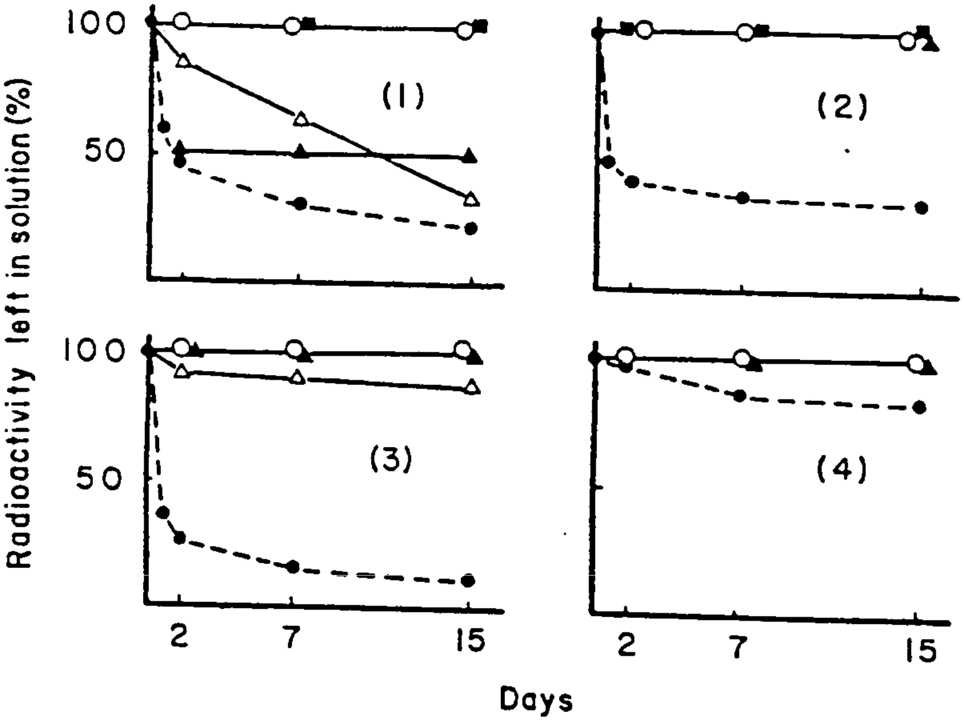

Figure 2. Effect of preservatives on the loss of ^{203}Hg(1 ppb) (1) pond water, (2) sea water, (3) distilled water and (4) artificial sea water. (●) no preservatives, (Δ) 1 mM cysteine, (■) 1 mM cysteine + 0.1N HCl, (▲) 10 ppb Au, and (O) 10 ppb Au + 0.1N HNO_3.

3.5

Weiss, Shipman and Guttman looked at methods for preventing the loss of mercury from various types of water. They found that a hot leach using 16 $MHNO_3$ as a pretreatment for polyethylene containers prior to adding the mercury solution was effective in preventing mercury loss. They postulate this result indicates the presence of agents either on the surface or incorporated into the surface which are involved in the loss mechanism. These agents reduce the Hg^{2+} in solution to mercury metal which then diffuses into or through the polyethylene. Cysteine, at the level of 10 mg/liter, was found to be effective in preventing mercury loss.

3.6

Lo and Wai investigated the stability of mercury in solution in polyethylene bottles using 203-Hg^{2+} tracer. They observed that adding enough HNO_3 to lower the pH to 0.5 effectively prevented adsorption of the tracer onto the bottle walls. It was also observed that a strong oxidizing agent, $K_2Cr_2O_7$ at 0.05% or Au^{3+} at .2 ppm, was required to prevent the reduction of Hg^{2+} to Hg metal with subsequent loss. Combining the nitric acid with one of the oxidizing agents effectively eliminated loss from solution. The study clearly indicated two loss mechanisms; adsorption onto the container surface and reduction in solution followed by loss by volatilization.

3.7

Mahan and Mahan investigated the effect of rinsing polyethylene containers with natural water low in mercury prior to introducing the same natural water containing environmental levels of mercury. This treatment seemed to reduce the rate of mercury loss as indicated in Figures 1 to 5.

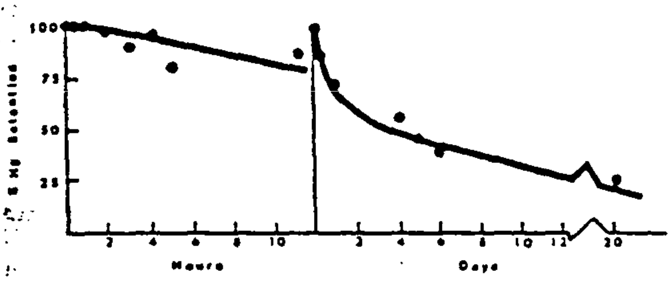

Figure 1. Plots of percent retention vs. time for an unagitated 1.0 ppb Hg solution made up with Arkansas River water and contained in a polyethylene vessel previously rinsed and soaked with river water

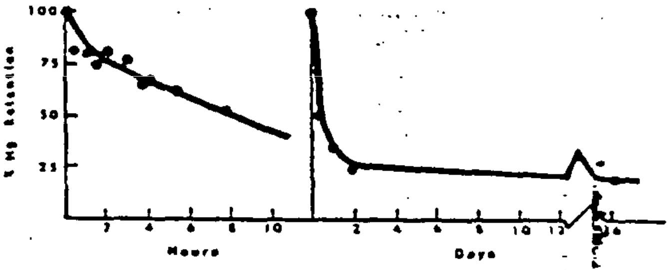

Figure 4. Plots of percent retention vs. time for an unagitated 1.0 ppb Hg solution made up with deionized distilled water and contained in a freshly cleaned polyethylene vessel

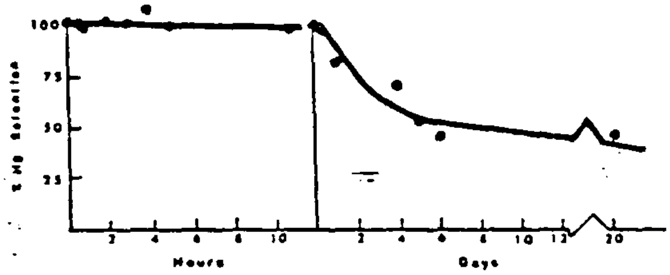

Figure 2. Plots of percent retention vs. time for an agitated 1.0 ppb Hg solution made up with Arkansas River water and contained in a polyethylene vessel previously rinsed and soaked with river water

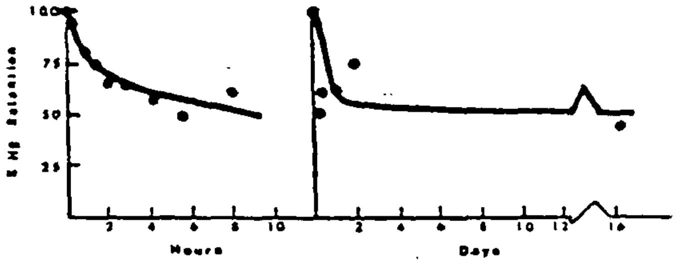

Figure 5. Plots of percent retention vs. time for an agitated 1.0 ppb Hg solution made up with deionized distilled water and contained in a freshly cleaned polyethylene container

Figure 3. Plots of percent retention vs. time for an agitated 1.0 ppb Hg solution made up with Arkansas River water and contained in a freshly cleaned polyethylene vessel

3.8

Newton and Ellis studied, among other things, the loss of mercury, presumably by volatilization, from solutions containing bentonite. At an initial concentration of 203-Hg^{2+} of 10^{-8} M most of the mercury was lost in the first day. At 10^{-6} molar approximately half of the mercury was lost the first day. Loss of the mercury in solution was more rapid than loss of the mercury adsorbed onto the clay.

3.9

Jenne and Avotins reviewed the literature on mercury stability in solution. There is a particularly interesting section on biological effects. Spangler et al. for instance speculated that the failure to find methylmercury in sediments is due to the presence of bacteria capable of degrading it to metallic mercury.

3.10

Avotins and Jenne carried out a series of experiments which demonstrated the role of certain bacteria in the conversion of Hg^{2+} to Hg^0 with subsequent loss by volatilization, adsorption onto the container walls, or absorption by microbial products followed by settling. Figure 1 illustrates their results.

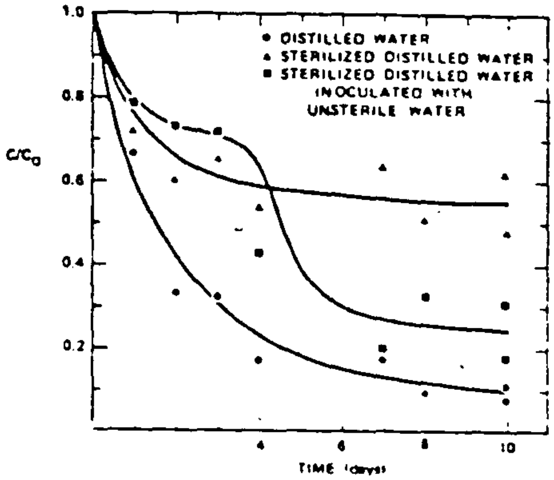

Fig. 1—Effect of biological population on loss of mercury (C/C_0 = ratio of observed to starting ^{203}Hg activity; C_0 = 1.65 μg/liter Hg; alternate test vessels were sampled each day).

3.11

See 1.5

3.12

Carden prepared solutions containing 10 ppb of Hg^{2+} and observed the concentration of Hg^0 in the solutions as the total mercury concentration decreased. See Figure 3.

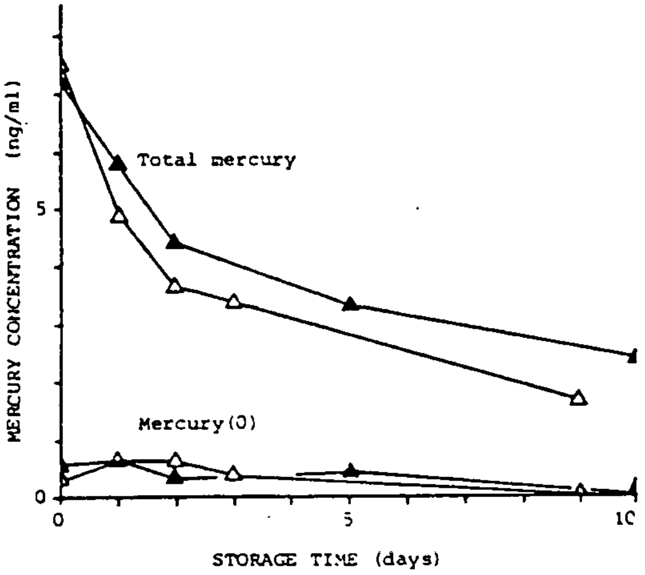

Fig.3. Total mercury and Hg(0) concentrations in solutions containing 0.05%(w/v) $K_2Cr_2O_7$ at pH=4.6.

3.13

Benes starting with dilute solutions containing Hg^{2+} attempted to determine the compounds present, their states of aggregation and particle size distribution and their mobility. The interpretation of the results is as follows: dilute solutions containing Cl^- in the pH range 0 to 2 will contain $HgCl_2$. This compound is not strongly adsorbed by suspended solids or the container surface. In the pH range 2 - 4, a mixed compound, HgClOH, is formed. At the high end of this pH range, a mercury containing solid is formed which can be centrifuged out. This solid is not $Hg(OH)_2$ or HgO because the solubility of these compounds is too high. The particulate is believed to be a pseudocolloid of mercury adsorbed onto solution particulates. In the pH range 4 - 12, $Hg(OH)_2$ is believed to predominate in solution and a decrease in centrifugable mercury is observed. Above pH 12 the centrifugable mercury increases perhaps due to increased particle loading in solution from contaminated base used to adjust the pH.

3.14

Jenne reviewed the literature on mercury migration in solution through 1970. Some relevant observations follow. Mercury forms stable complexes with a number of organic materials found in natural waters including proteins containing sulfhydryl groups and humic acids. The quantity of mercury associated with suspended particulates may be greater than the quantity in solution in natural waters. Microcrystalline iron $Fe_2O_3 \cdot nH_2O$ at 30,000 ppb will absorb 90 to 95% of mercury present in a solution with an initial concentration of 200 ppb. Montmorillonite is one tenth as effective in removing mercury from solution. The most likely sites for mercury adsorption on clays are the microcrystals of iron oxide present and the manganese oxide coatings. The compounds most likely sorbed by clays include $HgCl_3^-$, $HgCl_4^{2-}$, Hg_2Cl_2 and $HgCl_2$. While the capacity of clays for mercury is low, the element is difficult to displace once adsorbed. Mercury at trace concentrations was rapidly sorbed by microcrystalline oxides, peat moss and soils. Only a small fraction of the mercury was removed by tap water or 0.5 NaCl.

3.15

Trost and Bisque studied the distribution of mercury in soils. They determined the solubility of HgS, HgO and Hg_2Cl_2 in distilled water and a solution containing 850 ppm humic acid. The results are presented in Tables 30 and 31. Table 32 shows the amount of Hg^{2+} adsorbed by a 2 gram sample of each of the soils listed. Figure 23 shows the effect of humic acids in solution on the amount of Hg^{2+} adsorbed by illite. Figure 24 shows the effect on adsorption by montmorillonite. The exchange capacities observed were 9.5 meq Hg^{2+}/100g of montmorillonite and 7.50 for illite. Table 35 gives the sorption capacities of various soils for mercury vapor at two temperatures.

Table 30

Increase in HgS Solubility by the Presence of Humic Acid Solutions (HA) After 90 Days

Sample	*pH*	*E_h (mv)*	*Hg (pbb)*
HA + HgS	5.0	+185	450.0
	6.0	+155	48.0
	7.0	+145	10.0
Distilled H_2O + HgS	5.0	+150	15.0
	6.0	+140	0.0
	7.0	+130	0.0

Table 31

Solubilities of Mercury Compounds in Humic Acid Solutions (HA) and in Demineralized Water (H_2O) After 60 Days

Sample	*Solubility in HA (ppm)*	*Solubility in H_2O*	*Solubility in Handbook (ppm)*
HgO	200	68.0	52.0
Hg_2Cl_2	12.5	2.50	2.0

Table 32

Mercuric Ion Sorption on Humic-rich vs. Clay-rich Samples at pH 6.0

Sample	Hg^{++} *sorbed* γ
Peat	1000
Pine Mull	750
Kaolinite (API #4)	100
Illite (Beaver Bend)	350
Montmorillonite (Wards #26)	300

Table 35

Sorption of Mercury Vapor on Humic-Rich and Clay-Rich Samples

Sample	Hg° *sorbed after 5 days at 30 ± 0.5° C (in ppm)*	Hg° *sorbed after 5 days at 35 ± 0.5° C (in ppm)*
Peat	24.0	1050
Pine Mull	20.0	226
Illite	4.5	not determined
Montmorillonite	1.0	116
Kaolinite	0.8	6.8
Activated Charcoal	135.0	not determined
Ground Glass	<0.1	not determined
NaCl	<0.1	not determined

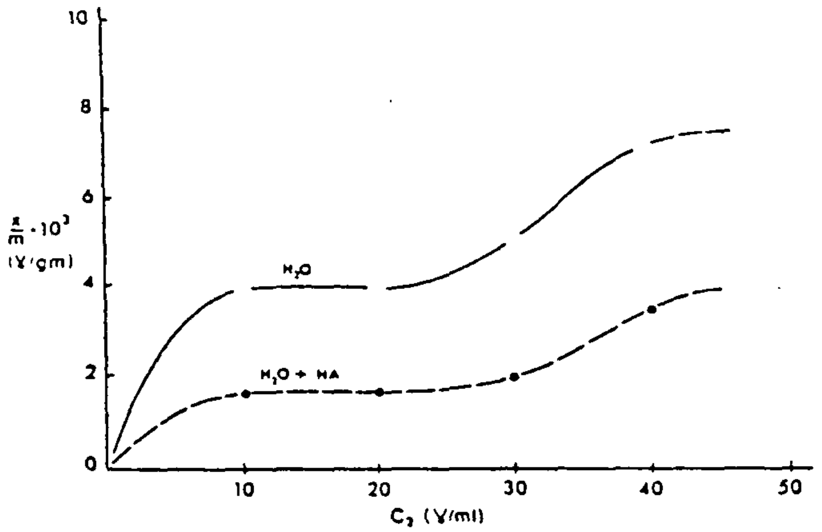

Figure 23: Adsorption Isotherm of Hg^{++} on Illite at pH 6.0. The adsorption isotherms display a decrease in mercuric ion sorption from aqueous solution by 100 mesh illite in the presence of aqueous humic acid (100 ppm C).

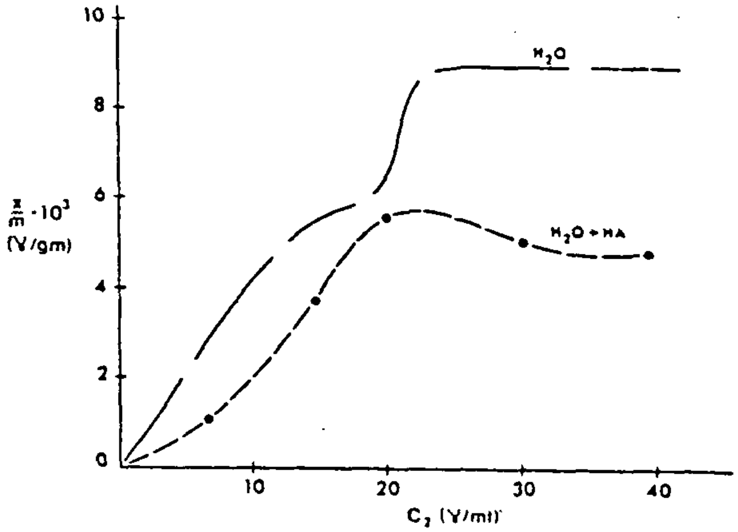

Figure 24: Adsorption Isotherm of Hg^{++} on Montmorillonite at pH 6.0. The adsorption isotherms display a decrease in mercuric ion sorption from aqueous solution by 100 mesh montmorillonite in the presence of aqueous humic acid (100 ppm C).

3.16

Klusman looked at the concentrations of a number of metals in the ground water around the Front Range Mineral Belt in Colorado. Mercury is one of the elements found in the mineralization in this area. No difference could be detected in the mercury content of groundwater from highly mineralized areas and that from nonmineralized areas. This was not the case for some other elements such as Cu, Zn and Fe.

3.17

Turner and Lindberg, as a followup to 2.4, studied the fate of mercury seeping out of two abandoned waste ponds formerly associated with a chloralkali plant. These ponds have a surface area of 44 ha. The mercury content of the first meter of one of the settling ponds was about 200 micrograms/gram while that of the second meter of soil was about 50. The total mercury content of one of the ponds is estimated at 90,000 kg. The exact chemical nature of the waste is not known, but it is believed to be at least partially elemental mercury. Extraction of surface soil from one of the ponds with rain water at pH = 3.8 removed less than 2% of the total mercury present. Again no studies of the impact of these sources on ground water were performed.

3.18

See 2.5

3.19

Reichardt and Bonhoeffer found the solubility of mercury in hexane to be 6.5 mg/liter at 65° C.

Category 4. Transport of mercury on colloids

Mercuric complexes have been observed to bind to iron and manganese oxides; potential soil colloids. Binding apparently occurs at surface hydroxyl groups and is favored over a broad pH range. The binding of mercury to clay has been found to be a strong function of the type of clay, the solution pH and the presence of complexing ions.

4. Transport of Mercury on Colloids

4.1 Eichholz, G.G.; Wahlig, B.G.; Powell, G.F.; and Craft, T. F. "Subsurface Migration of Radioactive Waste Materials by Particulate Transport". Nucl. Technol. 58,511-520, 1982.

4.2 Kinniburgh, D. G.; Jackson, M.L. "Adsorption of Mercury (II) by Iron Hydrous Oxide Gel". Soil Sci. Soc. Am. J. 42, 45-47, 1978.

4.3 Lockwood, R.A.; Chen, K.Y. "Adsorption of Mercury (II) by Hydrous Mangenese Oxides". Env. Sci. Technol 7, 1028-1034, 1973.

4.4 Benes, P. "On the State of Mercury Traces in Aqueous Solutions". J. Inorg. Nucl. Chem. 31, 1923-1928, 1969.

4.1

Eichholz, Wahlig, Powell and Craft investigated the role of suspended particulate in the migration of radionuclides through various naturally occurring solids. The solids studied included sand, basalt, limestone and shale. Prior to the study the solids were passed through a 40 - 50 mesh sieve and packed into columns. Cationic nuclides were found to adsorb onto the clay (kaoline) used as the mobile particulate. For nuclides which adsorbed, this was found to be a significant migration pathway.

4.2

Kinniburgh and Jackson studied the adsorption of Hg^{2+} by an iron hydrous oxide gel suspension. They considered the role of Cl^- and OH^- ligands in the adsorption process and concluded that HgClOH and $HgCl_2$ are not strongly adsorbed. They postulate Hg^{2+} ions are coordinated with two surface - OH groups forming a stable $Hg(OH)_2$ like surface complex. Table 1 shows the extent of adsorption at two pH values and Figure 2 shows the extent of adsorption as a function of pH.

Table 1—Adsorption of mercury(II) by freshly prepared iron gel in the presence and absence of chloride.†

Treatment	Final pH	% Hg(II) adsorbed	Distribution ratio, D§
Fe gel – Hg(II)	4.50	91.5	10.8
	5.95	99.77	430
Fe gel – Hg(II) – NaCl‡	4.50	68	2.13
	5.95	99.59	240
Fe gel – Hg(II) – $CaCl_2$‡	4.50	70	2.33
	5.95	99.56	227

† Initial concentration, 2.5 × $10^{-4}M$ Hg(II) and 0.093M Fe gel. Background electrolyte 1M $NaNO_3$ in all cases.
‡ 10.0 × $10^{-4}M$ NaCl and 5.0 × $10^{-4}M$ $CaCl_2$, respectively.
§ D = (% Hg(II) adsorbed/100 − % Hg(II) adsorbed).

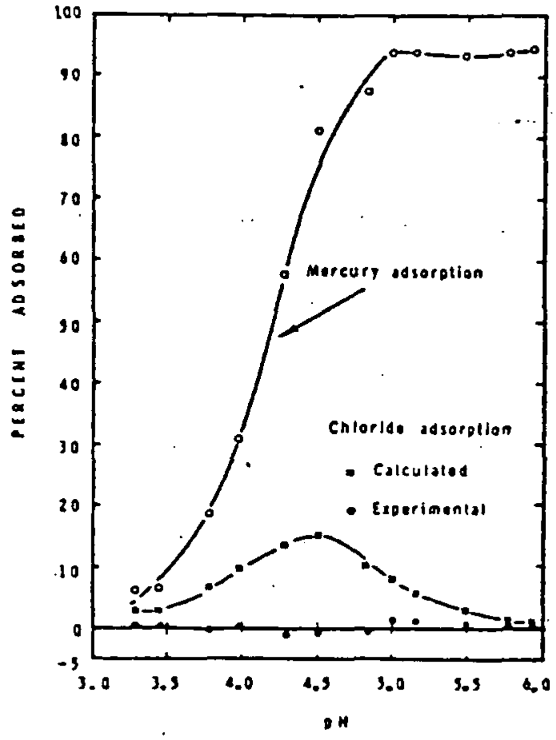

Fig. 2—Hg(II) and Cl adsorption by Fe gel (0.001M in Fe), as a function of final pH, from a solution containing 1 × $10^{-4}M$ Hg, 4 × $10^{-4}M$ Cl, and 1M $NaNO_3$. The experimental chloride adsorption is compared with that calculated on the assumption that the adsorption of all mercury complexes is proportional to their initial concentration in solution.

4.3

Lockwood and Chen observed that mercury is strongly adsorbed by hydrous manganese dioxide. Adsorption increased with increasing pH and decreased with increasing chloride ion concentration. Mercury appeared complexed at the solid surface by - OH groups. The adsorption data was fitted to a Freundlich isotherm.

4.4

See 3.13

5. Models for Mercury Migration Through the Environment

5.1 Lassiter, R.R.; Malanchuk, J.L. "A Model Evaluation of the Relative Importance of Factors Influencing the Environmental Behavior of Mercury". Mercury Cycling Symposium on Environmental Chemistry and Cycling Processes. (Conf-760429), 182-195, 1978.

5.2 Rae, J.E.; Aston, S.R. "The Role of Suspended Solids in Estuarine Geochemistry of Mercury". Water Res. 16, 647-654, 1982.

5.3 Kothny, E.L.; In E. Kothny (ed.) "The Three-Phase Equilibrium of Mercury in Nature". In Trace Elements in the Environment, A.C.S. No. 123, Reinhold, New York, 48-79, 1973.

5.4 Gavis, J.; Ferguson, J.F. "The Cycling of Mercury Through the Environment". Water Res. 6,989-1008, 1972.

5.5 Fagerstrom, T.; Jernelov, A. "Some Aspects of the Quantitative Ecology of Mercury". Water Res. 6, 1193-1202, 1972.

5.6 Frades, J.P.; Hildebrand, S.G.; Huckabee, J.W.; Murias, B. S.; Diaz, F. S.; Wilson, R.H. "A Study of the Environmental Cycling of Mercury". Nature and Res. 13,14-18, 1977.

5.7 Bernard, S.R.; Purdue, P. "Metabolic Models for Methyl and Inorganic Mercury". Health Physics 46, 695-699, 1984.

5.8 U.S. Geological Survey. "Mercury in the Environment". In Mercury and the Environment. U.S. Geological Survey Prof. Paper 713, 1-5, 1970.

5.9 Shacklette, H.T. "Mercury Content of Plants". In Mercury and the Environment. U.S. Geological Survey Prof. Paper 713, 35-36, 1970.

5.10 U.S. Geological Survey". "Tables". In Mercury and the Environment. U.S. Geological Survey Prof. Paper 713, 53-67, 1970.

Category 5. Models for mercury migration through the environment

The models identified do not deal with the migration of mercury through soil into ground water. They do, however, raise a number of interesting points. Data on the migration of mercury from concentrated natural sources are available as are data on major sources derived from human activity. These papers provide a reference for considering the mercury problem. The global ecology of mercury is complex as indicated by the models reviewed. The role of complexing agents and methylation on Eh-pH diagrams is discussed. The importance of organic constituents in silt in retaining mercury is discussed.

5.1

Lassiter and Malanchuk developed a detailed numerical model of mercury partitioning in a stream ecosystem. Figure 1 shows a schematic of the elements of the model. This model might be modified to predict mercury migration from a burial trench.

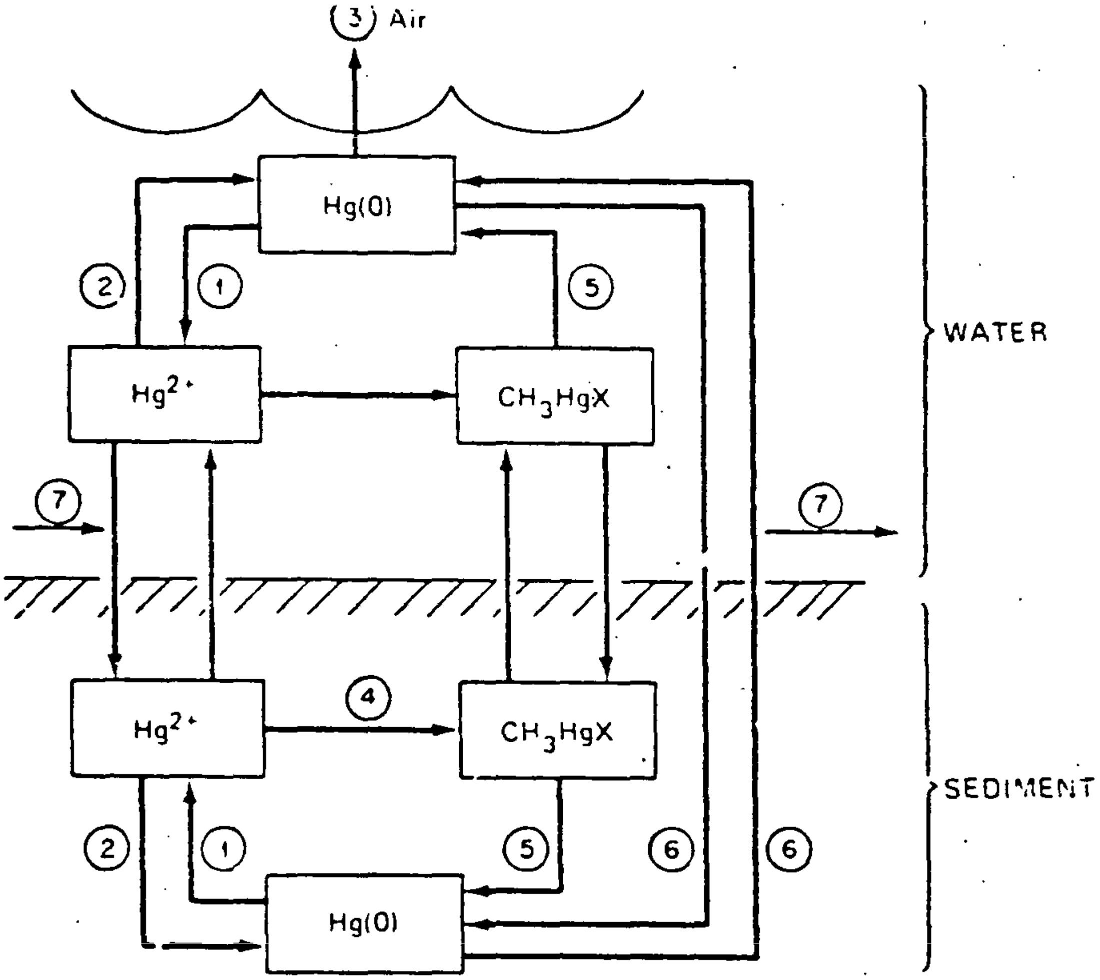

Fig. 1 Schematic representation of the components, transformations, exchanges, and transport pathways represented in the model. Oxidation, 1; reduction, 2; volatilization, 3; methylation, 4; demethylation, 5; sediment—water exchange, 6; flow dispersion, 7.

5.2

Rae and Aston studied mercury in water and suspended solids at 8 stations along the Wyre Estuary. They found total mercury was strongly correlated with the amount of particulate present and that the mercury actually in solution represented a negligible fraction of the total mercury budget. A high correlation was also found between the total organic carbon content of the suspended particulates and the total mercury present. Increased salinity was found to not materially affect the amount of mercury present on particulate further confirming the theory that the mercury is associated with the organics present and is not retained by an ion exchange process.

5.3

Kothny discusses the cycling of mercury in the global environment. His model looks at the major environmental components (water, air and soil) and the mercury transfer relationships within and between them. Figure 1 shows the global model presented. The movement of mercury in soil and the solution of mercury vapor by percolating water are not discussed. Table 5 provides data on mercury levels in several soils. Well aerated soils from the American plains which have not been exposed to artificial mercury sources are typically found to contain 0.07 μg/g of mercury. It was observed that on several well drained and aerated soils of pH 6 - 7, the ratio of mercury in runoff water to the amount of mercury in the A_1 soil horizon was equal to 6×10^{-4} indicating a substantial retention of mercury by surface soil.

Oxidation of mercury deposits (cinnabar) leads to the formation of both mercury vapor and inorganic mercurials. The inorganics are observed to be retained by clays and hydroxides to travel relatively short distances from the source. The vapor can be pumped by barometric pressure changes leading to broader distribution.

Figure 6 shows the mercury content of plants grown in environments containing varying amounts of mercury. The plant samples were dried prior to analysis thus losses may have occurred. Information about the chemical forms of mercury in these various environments is discussed. It appears that complexed forms of mercury are not readily assimilated by plants, but mercury vapor is rapidly assimilated by some species such as the coniferae.

The final section of the paper presents an interesting discussion of the global mercury budget with comments about possible past and future states.

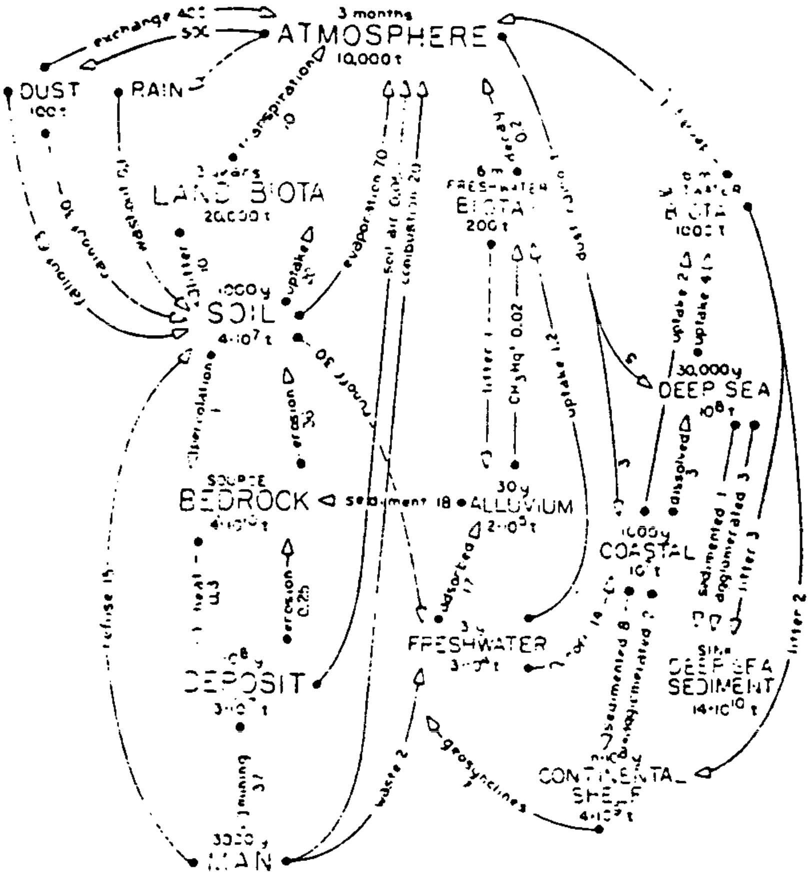

Figure 1. The cycle of mercury in nature. Dots represent sources and arrowpoints are the sink for each route. Numbers on the routes are tons per day. Residence time in years (y) and months (m) are above each entity. Immobilized tonnage (metric, t) is indicated below each entity.

Table V. Mercury in Soils[a]

Material	*Content, μg Hg/g*
Uplifted oceanic sediments (*1, 47*)	0.1 to 1
Franciscan sediments, Calif.[b]	0.2 to 0.5
Ultrabasic outcrops, Calif.[b]	0.02 to 0.1
Alluvial sediments, Calif.[b]	0.02 to 0.25
Weathered lava, Berkeley Hills, Calif.[b]	0.08 to 0.22
Other igneous rocks, Calif.[b]	0.03 to 1
Soils derived from igneous rocks (*47*), mean	0.07
Soils derived from continental sediments (*32*)	0.07
Coal, shale, petroleum (*1, 24*)	0.01 to 10
Quartz monzonite, Sierra Nevada, Calif.[b]	0.17
Lenses of biotite, derived from above[b]	0.8

[a] On a dry basis.
[b] Author's data by method from Ref. *17*. All values reported are from areas not related to mineralization.

5.4

Gavis and Ferguson reviewed mercury cycles in the aquatic environment. Table 1 contains mercury concentrations that have been observed in bodies of water around the world.

The authors offer the observation that the state in which mercury occurs depends on the redox potential and pH of its environment and upon the nature of the anions and complexing agents present. They go on to state that some important natural complexing agents such as those containing sulfhydryl groups should not effect the Eh-pH diagrams developed for these systems because the complexing agents themselves are not stable in water. It is obvious that such complexing agents do play a predominant role in the aquatic chemistry of mercury in surfce water presumably due to the slow degredation rates of the complexing agents.

Figure 1 shows an Eh-pH diagram for the insoluble mercury phases in equilibrium with a solution containing 1 mmole each of chloride and total sulfur. Figure 2 shows the soluble compounds and their approximate concentrations in the same solution. Note that the predominant soluble burial ground species should be Hg^0, as predicted by Orebaugh and Hale. An observation of importance here is the higher solubility of Hg^0 in some organics such as hexane relative to water. Organic contamination of the ground water could, therefore, increase the mercury migration rate.

The authors comment that, while thermodynamic data are not available to demonstrate it, methylmercuric chloride and dimethylmercury should be unstable in naturally occurring waters. Their presence in bodies of water is due to kinetic barriers to decomposition. A study of the kinetics of their decomposition in ground water would provide a basis for evaluating the potential for migration of these organomercurials in slow moving aquifers.

It is estimated that 10^{10} metric tons of rock are weathered each year. The mean mercury content is estimated at approximately 80 µg/kg, thus approximately 800 tons of mercury are released from rock into the environment each year. Most of this mercury moves through surface water systems. Terrestrial plants do not appear to concentrate mercury, but plants grown in mercury-rich soils show correspondingly higher concentrations of mercury. Mercury deposits (HgS and Hg^0) occur in a number of regions including Almaden, Spain; Tuscany, Italy and in California. Some hot springs and sediments near these deposits are particularly rich in mercury. Mercury transport away from these deposits apparently has little or no deleterious effect on the local environment.

The natural release of mercury to the environment by rock weathering versus the release of mercury as a result of human activities is discussed. Weathering has been estimated to release 800 tons of mercury per year and Table 2 gives mercury production rates for major human activities. It is estimated that approximately one third of the mercury produced from minerals (Table 2) is lost to the environment thus in 1970 approximately 8,100 tons of mercury were released to the global environment as a result of human activity; 10 times the amount from weathering. It is interesting to note that more than half of the "artificially" released mercury resulted from the combustion of fossil fuels! Coal conservatively contains 1 mg/kg mercury and the same value is given for oil.

TABLE 1. MERCURY IN NATURAL WATERS—SELECTED WORLD-WIDE REPORTED CONCENTRATIONS

Source and location	Mercury ($\mu g\ l^{-1}$)
Sea Water, near Helgoland	0.03
Sea water, Ramapo deep, Pacific Ocean	0.15–0.27
Sea waters, off USSR	0.7–2.0
River water, European USSR	0.4–2.8
River water, Armenia	1–3
Saale River, Germany	0.035–0.145
River water, Italy	0.01–0.05
River water, near mercury deposits, Italy	up to 136
Colorado River, Arizona	< 0.1
Ohio River, Illinois	0.1
Mississippi River, Kentucky	< 0.1
Kansas River, Topeka, Kansas	3.5
Missouri River, Montana	< 0.1
Missouri River, St. Louis, Mo.	2.8
Hudson River, New York	0.1
Lake Champlain, New York	< 0.1
Maumee River, Antwerp, Ohio	6.0
Delaware River, New York	< 0.1

TABLE 2. WORLD MERCURY PRODUCTION, 1900–1970

Decade	Mercury produced from minerals (metric tons × 10^3)	Mercury released from fossil fuels (metric tons × 10^3)	
		Coal and lignite	Petroleum
1900–1909	34.3	9.3	0.3
1910–1919	37.6	12.5	0.6
1920–1929	37.8	13.8	1.5
1930–1939	35.9	13.6	2.3
1940–1949	61.5	16.6	3.6
1950–1959	65.0	21.4	7.7
1960–1969	78.5	26.9	14.7
1970 (year)	10.0 (est.)	3.0 (est.)	1.8 (est.)
Totals	361	117	33
Grand total		511 × 10^3 tons	
Mercury from weathering at 800 tons yr^{-1}		57 × 10^3 tons	

10,000

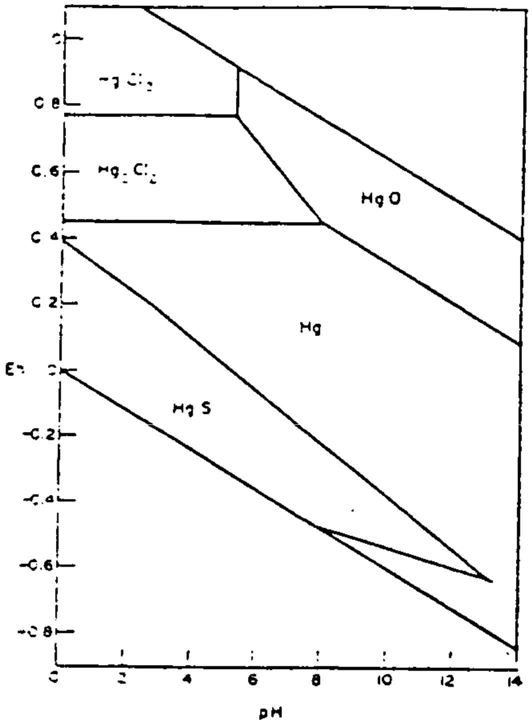

FIG. 1. The Eh-pH diagram for Hg, showing solid phases in equilibrium with water and the atmosphere at 25°C with 10^{-3} mol l^{-1} each of chloride and total sulfur.

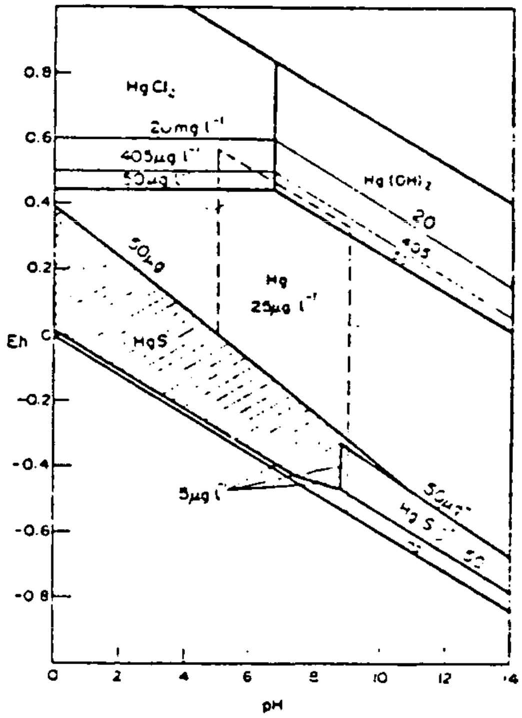

FIG. 2. The Eh-pH diagram for Hg, showing predominant species in solution for concentrations of total Hg greater than 5 µg l^{-1} in equilibrium with water and the atmosphere at 25°C with 10^{-3} mol l^{-1} each of chloride and total sulfur.

5.5

Fagerstrom and Jernelov review the transformations of mercury in an aquatic ecosystem. Figure 1 summarizes the transformations considered by the authors. The paper discusses each compound indicated on the figure and describes the environmental factors affecting its stability.

The authors discuss the effect of complex formation on the oxidation of elemental mercury. They give the potential, E, necessary for oxidation of Hg^0 to Hg^{2+} as

$$E = 850 + 30 \log \left\{ \frac{Hg^{2+} - tot}{\alpha} \right\}$$

where α is the coefficient measuring the binding strength of the complexes between divalent mercury and available complexing agents. Unfortunately, neither α or tot are precisely defined, but $\alpha > 10^{21}$ is quoted for organic sediments from lakes. The implication here is that Hg^0 can be oxidized to Hg^{2+} at a substantially reduced potential relative to that given in Orebaugh and Hale in Figure 3-2 in the presence of organic complexing agents. The relevance of this observation to the SRP burial ground is, however, quite uncertain. The complexing agents discussed here are organic materials containing sulfhydryl groups and these materials are normally observed in suspended particulate in the water column of bodies of water. If such particulates are present in the soils of the burial trenches they may enhance the conversion of Hg^0 to Hg^{2+} but they will then in turn bind the Hg^{2+} in the form of a strongly bound complex. If the > ligands involved are associated with a particulate too large to move through the soil matrix, the mercury will remain immobilized.

These authors also briefly discuss binding to kaolin and the effects of coprecipitation with iron or mangenese. A brief description of the formation of methyl and dimethyl mercury is also given.

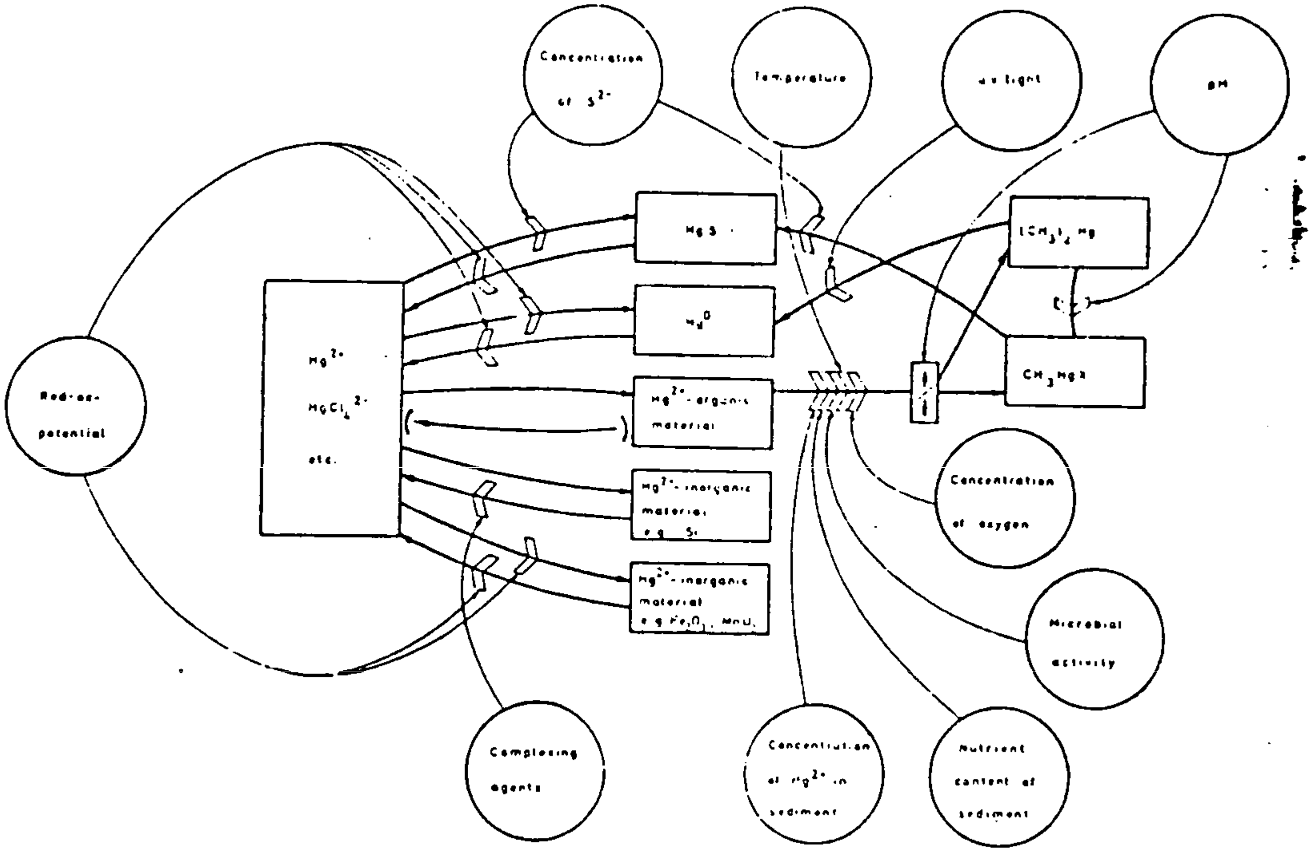

FIG. 1. Conversion of mercury compounds.

5.6

Frades et al. reported the early stages of a study of the impact of mercury around the mercury mines in Almaden, Spain. A single well defined ore body of cinnabar and quicksilver in a vertical bed of quartzite is the only naturally occurring mercury for hundreds of miles around. The ore body has been exploited more or less continuously since the Carthaginians and shows no signs of exhaustion. The mining and smelting operations are in close proximity, thus mercury is introduced into the environment from a "point" source. Despite the very long period over which mercury has been emitted as a result of human activity, there are no obvious adverse environmental or health effects. This study, which was in its early stages at publication of the article, was designed to quantitatively evaluate the mercury flux and its effects on the surrounding environment and population. ORNL was a participant in this study.

5.7

Bernard and Purdue suggest human metabolic models for both methylmercury and elemental mercury. A three-compartment model was developed for the elimination of methylmercury while a four-compartment model was required for elemental mercury.

5.8

The U.S. Geological Survey prepared a general review of mercury in the environment in response to the developing concerns of the late 1960's over artificial mercury sources. This article summarizes the natural abundance and distribution of mercury in the environment.

5.9

Shacklette reported data on mercury assimilation and translocation by plants. Plants growing in soils containing "normal" amounts of mercury contain less than 500 ppb where as plants grown in high mercury content soils contain 2 to 7 times as much. Very high concentrations have been found in plants with roots directly in contact with cinnabar.

5.10

The U.S. Geological Survey tabulated data on the mercury content of a wide variety of environmental constituents. Analytical techniques have improved significantly since most of these studies were performed.

Category 6. Analytical techniques

The analytical method in widest use remains the so called cold vapor atomic absorption technique. Instrumental neutron activation analysis is an alternative technique capable of comparable sensitivity. Investigations dealing with the possible effects of mercury adsorbing colloids on the accuracy of cold vapor results could not be located although an observation in paper 7.6 could be explained by retention of Hg on solution colloids.

6. Analytical Techniques

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6.4

Lawrence et al. describe a simple inexpensive and sensitive method for the determination of mercury. The authors report a precision of 2.9% (RSD) for 1.0 ml containing 10 ng of mercury (II). Factors involved in obtaining optimum performance include, sample mixing, flow rate, volume and depth of injection needle in the reduction vessel.

6.5

Simpson and Nickless describe a dual aeration chamber cold vapor apparatus. They claim a detection limit of 12.5 ppt for mercury at the maximum sample volume of 20 ml.

6.6

Minagawa and Takizawa describe the use of a chelating resin preconcentration for the simultaneous detection of traces of inorganic and organic mercury in fresh water. The resin contains dithiocarbamate groups which bind to mercury but not to alkali and alkaline earth metals. Mercury is eluted with a thiourea solution. The detection limit reported is 0.2 ng/l for both forms of mercury.

6.7

Goulden and Anthony show how total mercury in natural waters can be separated into three classes of mercury compounds. Changes in the reduction scheme allow for separation of inorganic mercury, arylmercury compounds and alkylmercury compounds. The authors report a detection limit of 1 ng of mercury per liter under optimum conditions. They conclude that trace metals acting as catalysts play an important role in the reduction.

6.1

Hatch and Ott outline a procedure for the determination of mercury in water by reduction-aeration. The authors report a sensitivity and accuracy for mercury determination in the range of 1 ppb.

6.2

Hawley and Ingle discuss improvements in the cold vapor atomic absorption determination of mercury. Their discussion centers around the design of a reduction vessel which enables the mercury to be concentrated in a small volume of carrier gas, thus improving sensitivity. The detection limits are reduced from 0.02 ppb to 1 ppt Hg(II). They discuss the optimization of instrumental parameters for the lowest detection limit and talk about ways to avoid loss and contamination.

6.3

Oda and Ingle discuss their development of a continuous sample introduction reduction vessel to replace the normal once through discrete sample reduction vessel. An advantage of continuous sample introduction is elimination of sample introduction and flushing cycles. The disadvantages of using this vessel are reduced sensitivity, poorer detection limits and longer analysis times.

6.8

Hutton and Preston discuss capabilities of a simple non-dispersive fluorescence spectrometer. The authors claim comparable detection limits to more complex systems. Their results are shown in Table 1.

TABLE I

COMPARISON OF DISPERSIVE AND NON-DISPERSIVE DETERMINATION OF MERCURY IN EXTRACTS FROM ESTUARINE SEDIMENTS AND SEA SHRIMPS

Sample volume = 1 ml.

Mercury concentration/$\mu g\ l^{-1}$

	Sediments		Shrimps	
	Dispersive	Non-dispersive	Dispersive	Non-dispersive
Blank	<1	<0.05	<1	<0.06
1	14	10	3	4
2	16	7	3	3
3	12	11	3	3
4	6	6	3	3
5	9	10	8	6
6	9	12	4	3
7	11	12	3	4
8	11	9	3	4
9	12	11	3	4
10	10	13	—	—

6.9

Chapman and Dale developed a simple apparatus which uses water displacement instead of an auxiliary gas stream to transfer equilibrated mercury vapor to the absorption cell. Advantages of the apparatus include elimination of window fogging and delivery to the absorption cell of undiluted sample vapor.

6.10

Sanemasa et al. investigated a direct reduction-aeration technique applied to mercury ions absorbed on an anion-exchange resin. The idea is to remove the resin bound mercury ions without an elution process. They report that the extent of recovery is affected by the shape of the bubbler, and that temperature affects the removal time. Four ml of sulfuric acid and 8 ml of Tin(II)chloride are necessary to give quantitative recoveries from the resin.

6.11

Lutze compared a variety of cold vapor methods including gas-purged partitioning, bottle aeration, syringe injected partioning and a dual bubbler apparatus. His results are shown in Table 1. Lower detection limits are possible with a preconcentration step, followed by reduction to elemental Hg vapor liberated into a small volume of gas.

TABLE I

COMPARISON OF COLD-VAPOUR GENERATION OF MERCURY METHODS

Operating conditions: hollow-cathode lamp current 3.0 mA; wavelength 253.6 nm; spectral band pass 0.5 nm; damping "B"; recorder 10 mV; chart speed 2.5 cm min^{-1}, background correction used; volume of tin(II) chloride solution 2 ml.

Method type	Mass of mercury injected/ng	Solution volume/ml	Mercury concentration/ µg l^{-1}	Scale expansion	Flow-rate/ ml min^{-1}	Mean absorbance (6 readings)	Relative standard deviation, %
Gas-purged partitioning	0	50	0.00	7 ×	1500	0.013	21
	10	50	0.20	7 ×	1500	0.053	20
	20	50	0.40	7 ×	1500	0.097	13
	50	50	1.00	7 ×	1500	0.217	3
Bottle aeration	0	50	0.00	7 ×	600	0.030	11
	10	50	0.20	7 ×	600	0.096	10
	50	50	1.00	7 ×	600	0.352	[illegible]
Syringe-injected partitioning ..	0	10	0.00	6 ×	—	0.020	13
	2	10	0.20	6 ×	—	0.036	[illegible]
	10	10	1.00	6 ×	—	0.198	3
	20	10	2.00	6 ×	—	0.385	4
Dual-bubbler	0	10	0.00	10 ×	480	0.018	30
	2	10	0.20	10 ×	480	0.101	6
	10	10	1.00	10 ×	480	0.412	4

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6.12

Matsunaga and Takahashi discuss a simplification of the method proposed by Umezaki and Iwamoto for the determination of organic mercury. The use of glutathione concentrations in the range of 1 - 5 x 10^{-4}% in 0.1 M ammonia gave extraction recoveries of 95%. Thus glutathione is a reagent for back extraction which does not interfere with the reduction of organic mercury.

6.13

Kuldvere reports that polypropylene flasks can be used in the determination of mercury without any risk of loses. Mercury(II) in solution must be analyzed immediately in the absence of permanganate to avoid loss. Upon addition of a slight excess of permanganate, no loss of mercury was observed over a two day period. The author concludes that polypropylene has a high affinity for tin(II)chloride, which if present, can cause premature reduction to mercury(0) with subsequent loss.

6.14

Gardner deals with the problem of water vapor in the syringe injection technique for mercury determination by cold-vapor atomic absorption spectrometry. The effects of passing the mercury containing vapor through a tube of magnesium perchlorate desiccant preceeding the absorption cell are shown in Table 1. The author concludes that to achieve good reproducibility the use of a drying agent should be avoided when possible.

TABLE 1

The effect of damp and fresh magnesium perchlorate, heat and no water vapour removal on the mean atomic absorption measurements of replicates from bulk samples.

Water vapour control	Sample	Standard graphs[a]	*n*	Mean absorption[b]
Used $Mg(ClO_4)_2$	A	V	27	0.201 ± 1.5
Fresh $Mg(ClO_4)_2$	A	W	22	0.232 ± 1.7
Heat cell, no $Mg(ClO_4)_2$	B	X	17	0.283 ± 0.95
No heat, no $Mg(ClO_4)_2$	C	Y	12	0.216 ± 0.69

[a] See Fig. 1. [b] Mean and relative standard deviation (%).

6.15

Stuart describes several commonly used reagents which affect peak shape in coldvapour atomic absorption spectrometry for mercury. The use of excess hydroxylammonium chloride results in a "hold-back" effect which causes a severe reduction in both peak height and peak area. Another type of interference is observed with cysteine hydrochloride which slows the rate of release of mercury from solution. Peaks are broadened as the amount of cysteine is increased. These effects are shown in Tables 1 and 2.

TABLE 1

Effect of addition of hydroxylammonium chloride on the mercury absorbance peak

Amount added (ml)[a]	**0.00**	**0.01**	**0.02**	**0.05**	**0.10**	**0.20**	**0.30**
Peak height (%)	**100**	**97**	**98**	**85**	**60**	**34**	**13**
Peak area (%)	**100**	**98**	**98**	**83**	**65**	**36**	**11**

[a] 5 g of hydroxylammonium chloride in 10 ml of water.

TABLE 2

Effect of cysteine hydrochloride (added as a 1% w/v solution) on the mercury absorbance peak

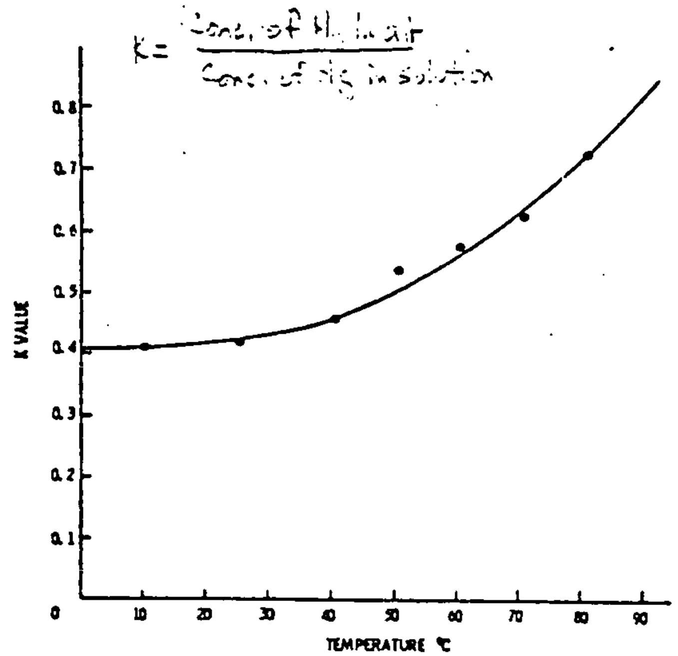
Amount added (ml)	**Peak height (%)**	**Peak area (%)**	**Peak width (s)**
0.00	100	100	41
0.02	100	100	40
0.05	94	95	42
0.10	67	104	62
0.20	36	96	104

6.16

Jirka and Carter describe an automated sampling system using the cold vapor technique. Aqueous suspensions of sediment samples are used in the system following a persulfate oxidation and stannous chloride reduction. The authors avoid the use of digestion methods because of the potential hazards from the strong oxidizing agents and high temperatures required. Their method yields one hundred percent recovery of HgS with a detection limit of 0.1 µg per liter for aqueous samples.

6.17

Koirtyohann and Khalil determined the partition coefficient of mercury between air and a dilute water solution. Their results are given in Figure 3.



$$K = \frac{\text{Conc. of Hg in air}}{\text{Conc. of Hg in solution}}$$

Figure 3. Effect of temperature on the partition constant

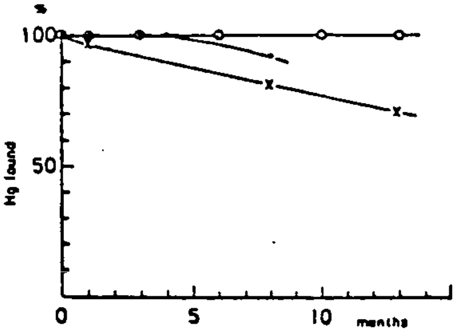
6.18

Knechtel and Fraser report a method capable of digesting large samples, up to 5 grams, for mercury analysis. The method was used on various sample types including soils. Nitric and sulfuric acids were used with V_2O_5 as a catalyst. The detection limit reported is 0.01 μg/g.

6.19

Narasaki et al. report recoveries of mercury in excess of 90% from organic material after oxidation with sulfuric acid and 50% hydrogen peroxide. The authors state that the mercury sensitivity of the cold vapor atomic absorption technique is enhanced by using a sintered-glass bubbler and magnetic stirrer instead of a nozzle bubbler.

Ambe and Suwabe developed a procedure for the preparation of standard solutions of mercury containing sodium chloride. The mercury concentration was on the order of 1 - 1,000 ppb with a stable shelf life of more than one year. The stability of the mercury depends on pH and the type of container used. These effects are shown in Figures 1 and 2. The addition of sodium chloride enhanced the stability of mercury as shown in Figure 4.



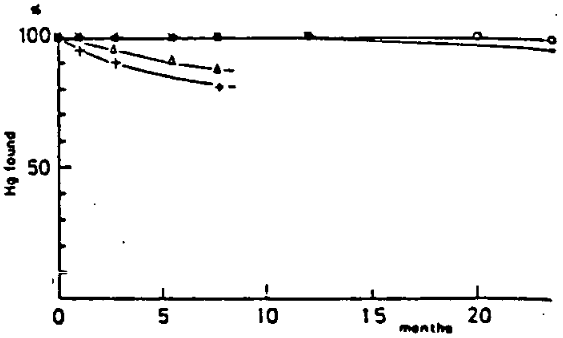
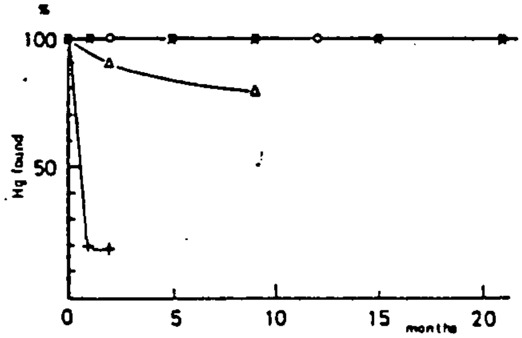


Fig. 1. Stability of mercury solution in various storage vessels. o Glass ampoule. • Glass bottle. x Polyethylene bottle.

Fig. 2. Effect of pH of the mercury solutions on stability. Glass ampoules: pH 1 (o), pH 2 (•), pH 3 (x), pH 5 (▵). Polyethylene bottle: pH 1 (+).



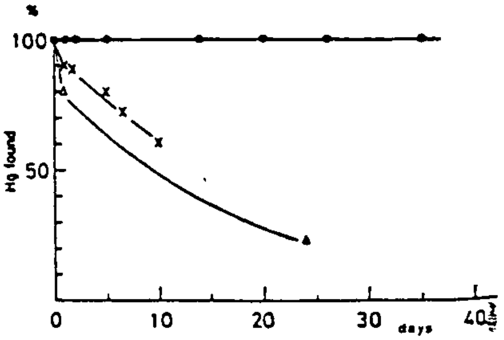


Fig. 3. Stability of mercury solutions of various concentrations at pH 1 and 3 sealed in Pyrex glass ampoules. At pH 1, 1000 p.p.b. (o), 500 p.p.b. (•), 20 p.p.b. (x), 1 p.p.b. (▵) At pH 3, 20 p.p.b. (+).

Fig. 4. Stability of mercury solutions (1 p.p.b.) containing 3.0% sodium chloride solution. 3% NaCl solution: glass ampoule (o), glass bottle (•). Aqueous solution: glass ampoule (x), glass bottle (▵).

6.21

Moody et al. used gold tetrachloride to stabilize very dilute mercury solutions. Two such solutions were prepared and certified as NBS Standard Reference Materials (SRM 1641 and 1642) with a shelf life of one year. Tables 2 and 3 give the solution concentrations obtained by the three analytical techniques used.

TABLE 2. *Comparison of certification analyses - Standard Reference Material 1641*

	Concentration (ng Hg/ml)
Certified value	1.49 ± 0.05[a]
Theoretical value	1.495
Analytical technique	
Neutron activation analysis	1.48 ± 0.02[b]
Isotope dilution spark source mass spectrometry	1.50 ± 0.02[b]
Atomic absorption	1.52 ± 0.02[b]

[a] 95 percent confidence limit.
[b] Standard deviation.

TABLE 3. *Comparison of certification analyses - Standard Reference Material 1642*

	Concentration (ng Hg/ml)
Certified value	1.18 ± 0.05[a]
Theoretical value	1.23
Analytical technique	
Neutron activation analysis	1.21 ± 0.06[b]
Isotope dilution spark source mass spectrometry	1.18 ± 0.02[b]
Atomic absorption	1.17 ± 0.03[b]

[a] 95 percent confidence limit.
[b] Standard deviation.

6.22

Gorski, Heinonen and Suschny report a round-robin laboratory comparison of results obtained on a fresh water sample and an air filter sample. Neutron activation and atomic absorption (cold vapor) were the most commonly used techniques. Little difference was observed between these techniques, and the results obtained for the fresh water sample indicated the laboratory techniques in use were adequate.

6.23

Koons and Helmke irradiated four standard soils for neutron activation analysis to determine the concentrations of various elements and to test for inhomogeneities in the samples. A coefficient of variation was calculated based on the standard deviation of the mean values for the samples. The coefficient takes into account sample loss during transfer after irradiation, geometry uncertainties, undetected variations in neutron flux, and counting statistics. The coefficient of variation was below 5% for most of the elements tested and the differences in concentrations for the elements in the different soils was for the most part very low.

6.24

Thatcher reviews the procedure for analyzing trace elements in water samples using neutron activation analysis. The author compares the results with other instrumental methods, principally atomic absorption. The standard deviations for the analysis of standard samples by NAA was 8.0 and 8.9 versus 15.9 and 18.5 percent for atomic absorption analysis.

6.25

Tatton discusses the uses of thin-layer chromatography and gas-liquid chromatography for the separation and identification of organomercury compounds.

6.26

Heinonen, Merten, and Suschny access the results of an intercomparison of mercury determinations in flour using destructive activation analysis, nondestructive activation analysis, and chemical methods. The participating laboratories reported adequate accuracy and precision for mercury in the ppm-range but reported unsatisfactory results for the ppb-range. Contamination of the samples prior to activation may have been responsible for the unsatisfactory results.

6.27

Westermark and Ljunggren discuss the procedure and major factors involved in using destructive neutron activation analysis for the determination of mercury. They review several accepted methods by different authors. These methods can be applied to a variety of sample types as shown in Table 17.

TABLE XVII. METHODS FOR DESTRUCTIVE ACTIVATION ANALYSIS OF MERCURY

Reference	Principle of detection	Nuclide measured	Wet combustion	Main method of separation	Carrier yield measurement	Applied to
Hamaguchi et al.[2]	Beta counting	^{203}Hg	Yes	Precipitation as the sulphide	Yes	Marine organisms and water
Sjostrand [3]	Gamma spectrometry	^{197}Hg	Yes	Distillation and electrolysis	Yes	Virtually all sorts of samples
Kellershohn et al. [4]	Gamma spectrometry	^{203}Hg	Yes	Precipitation of Hg and distillation	Yes	Blood
Kim et al. [5]	Gamma spectrometry	^{197}Hg	Yes	Exchange with metallic Hg	No[a]	Biological samples
Kosta et al. [6]	Gamma spectrometry	^{197}Hg	No (burning in hot air and oxygen)	Evaporation and sorption on selenium	No[b]	Biological samples and water
Johansen et al. [7]	Gamma spectrometry	^{197}Hg	Yes	Sulphide precipitation at pH 8-9	No[b]	Biological and some industrial samples
Häsänen [8]	Gamma spectrometry	^{197}Hg	Yes	Desposition on Cu powder	No[b]	Biological samples

[a] Yield determined to be 90% in separate study; all samples corrected for this.

[b] Assumed to be close to 100%.

6.28

Ljunggren et al. discuss the usefulness of neutron activation analysis in measuring total mercury concentration. They point out its high sensitivity, specificity and ability to accomodate numerous types of sample materials. The detection limit for mercury is in the range of 0.1 ng per gram.

6.29

Floyd and Sommers propose a simple one-step procedure for extracting total mercury from soils and sediments. The procedure uses concentrated HNO_3 and 4N $K_2Cr_2O_7$ for digestion of soil. This method was compared with other digestion procedures and the results are shown in Table 2.

Table 2—A comparison of methods for determining total mercury in soils and sediments

Sample	Proposed procedure (HNO_3-$K_2Cr_2O_7$)	Hg obtained by method* A	B	C	D
	ng Hg/g				
		Soils			
Plainfield	79	74	59	48	-
Chalmers	89	82	63	70	95
Portageville	132	129	78	90	130
Houghton	108	100	55	58	118
Fincastle	104	102	50	45	-
		Sediments			
Big Turkey	91	81	82	72	-
Wawasee	168	157	117	129	155
Long	317	309	228	228	320
Monroe	145	145	90	85	150
Pleasant	195	187	110	102	-
Average	142.8	136.6	93.2	92.7	-

* Method A, digestion with H_2SO_4, HNO_3, $KMnO_4$, and $K_2S_2O_8$ (Iskander et al., 1972); Method B, digestion with HNO_3 (Thorpe, 1971); Method C, digestion with H_2SO_4, HNO_3, and $K_2S_2O_8$ (Melton et al., 1971); Method D, digestion with H_2SO_4, HNO_3, $K_2S_2O_8$, and $KMnO_4$ (Jacobs and Keeney, 1974).

6.30

Lag and Steinnes analyzed Norwegian forest soil for mercury by neutron activation analysis after pretreatment of the soil with (A) digestion with HNO_3/H_2SO_4 in the presence of Hg carrier in an apparatus equipped with an reflex condenser and (B) digestion with hydrofluoric acid. Table 1 compares the results obtained on 4 soil samples using these two methods. The results obtained for mercury do not show high regional variations.

TABLE I. COMPARISON OF RESULTS OBTAINED ON FOUR SAMPLES USING METHODS A AND B FOR THE DISSOLUTION STEP

Sample	Method A (ppm)	Method B (ppm)
1	0.195 0.199	0.197
2	0.188 0.208	0.228 0.208
3	0.201 0.221	0.209 0.196
4	0.231 0.204	0.204 0.213

Category 7. Retention of mercury (Hg°, ionic, organic and vapor) by soils

The literature dealing with mercury sorption by soil seems rather confused. This may be due to the complexity of the system involved. The extent and rate of sorption depends on the surface and in some cases the bulk properties of the soil components, the relative abundance of these components in the soil, the chemical environment of the mercury in solution and the bacterial activity in the soil. Despite the complexity, conditions have not been reported under which mercury in solution moves rapidly through soil.

7. Retention of Mercury (Hg, ionic, organic, vapor) by Soils

7.1 Landa, E.R. "Microbial Aspects of the Volatile Loss of Applied Hg (II) From Soils". J. Environ. Qual. 7, 84-87, 1974.

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7.13 Kudo, A.; Hart, S.J. "Uptake of Inorganic Mercury by Bed Sediments". J. Environ. Qual. 3, 273-278, 1974.

7.14 Frenet-Robin, M.; Ottmann, F. "Comparative Study of the Fixation of Inorganic Mercury on the Principal Clay Minerals and Sediments of the Loire Estuary". Estuar. and Coast. Mar. Sci. 7, 425-436, 1977.

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7.2

Landa investigates the sorption of mercury vapor by a number of soils. The mercury uptakes observed are presented in Table 2. He found that mercury volatilization from these soils proceeded to a negligible extent at temperatures up to about 100° C, but increased dramatically at higher temperatures as indicated in Figure 2. A variety of classes of extractants were used to probe the mercury retention mechanism on the soil. Interestingly sodium hydroxide was the most efficient extractant while chelating agents were ineffective. Table 3 contains the results of the extraction experiments. Landa interprets the extraction results as indicating organic binding of the mercury in the soil systems.

Table 2. Uptake of mercury by five Montana soils following 10 day exposure to air stream containing 14.3 μg Hg^0 m^3 air. Values shown are means of three replicates ± 1 standard error

SOIL	µg Hg/kg soil
Arvada	10.5 ± 1.7
Campspass	40.8 ± 1.0
Heldt	23.7 ± 2.4
Bainville	45.6 ± 2.7
Terry	9.5 ± 1.0

Table 3. Removal of sorbed mercury vapor from soils by various chemical extractants. Values shown are means of three replicates

Extractant	Soil	Hg Extracted				
		Arvada	Campspass	Heldt %	Bainville	Terry
(a) distilled water		0.1	0.2	0.4	0.2	0.4
(b) 1 N KCl		0.1	0.0	0.0	0.2	0.2
(c) 1 N CaCl$_2$		0.2	0.1	0.2	0.3	0.2
(d) 1 N HCl		71.1	15.8	1.2*	56.2	79.6
(e) 1 N NaOH		91.7	74.3	89.3	82.7	93.3
(f) 0.5 M acetylacetone		1.6	0.9	2.8	1.5	3.7
(g) 0.1 M [illegible]		1.7	3.7	6.7	3.2	1.5
(h) 0.5 N Cu [illegible]		0.6	0.3	0.0	0.2	1.2
(i) DTPA:TEA:CaCl$_2$		0.2	0.4	0.5	1.5	1.1
(j) 0.1 M cysteine		4.0	3.7	5.3	2.1	2.9
(k) benzene		9.3	5.1	11.9	14.7	12.6
(l) methanol		1.1	0.4	0.3	2.1	0.7

* 1.4 N HCl extracted 49.6%.

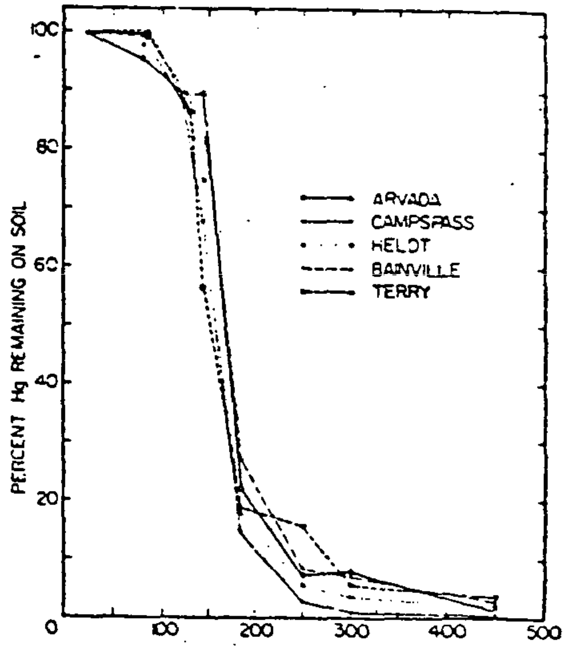


Fig. 2. Volatile loss of sorbed mercury from soils as a function of temperature.

7.3

Hannan and Thompson determined the uptake of 203-Hg^{2+} from filtered sea water by a number of sediment samples. They observed at least 95% uptake by all sediments and essentially no leaching when the sediments were equilibrated with Hg^{2+} free sea water.

7.4

Harsh and Doner studied how mercury is distributed in river wash soil containing cinnabar from mine tailings. They found that 90% of the total mercury present remained in the sulfide form. Under the oxidizing conditions of the river wash soil, mercuric sulfide would not be expected to be stable thermodynamically thus the weathering of HgS is kinetically unfavorable under the condition studied.

7.5

Farrah and Pickering found that in the presence of Cl^- ion, the order of uptake of Hg by the clays studied was illite > montmorillonite > kaolinite. Based on their study of clay uptake under varying conditions of pH and a variety of ligands, solution processes such as complexation and precipitation have a dominating influence over sorption by clay.

7.6

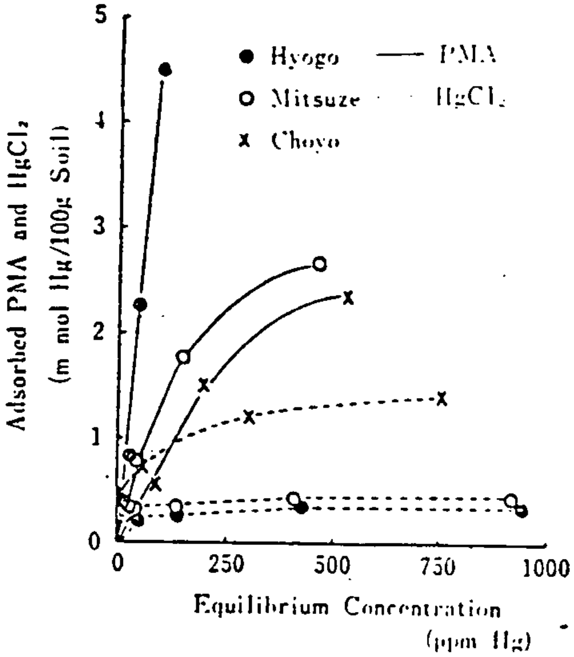
Hogg, Stewart and Bettany investigated the migration of methylmercuric chloride, phenylmercuric acetate and mercuric chloride through two soil types. Sixty cm soil columns were used in the experiments with the mercury compound mixed into the to 10 cm of soil. The columns were irrigated with sewage effluent. Table 2 lists the components of the sewage effluent. Other cations present in the sewage effluent and soils migrated through the columns, but mercury was not observed to migrate below the 20 cm level in any of the columns. Leaching of the top 10 cm of the columns with $CuCl_2$, NH_4OAc, EDTA or DTPA removed less than 0.3% of the applied mercury. Six normal HCl extracted up to 90% of the applied mercury. Since 6 N HCl is believed to dissolve soil colloids, it is postulated that mercury had been retained by adsorption onto these colloids. It was also observed that 203-Hg analysis gave slightly higher results for leaching with NH_4OAc, EDTA and DTPA than did cold vapor atomic absorption.

Table 2—Composition of sewage effluent used for irrigation.

Parameter	Value
EC, mmhos/cm	2.25
pH	8.51
	ppm
Cl^-	183
Na^+	240
K^+	19.8
Ca^{2+}	125
Mg^{2+}	93
NH_4	5.8
$(NO_3^- + NO_2^-)$	9.9
SO_4^{2-}-S	229
BO_3^{3-}-B	0.95
Zn^{2+}	0.03
Hg^{2+}	0.001
HPO_4^{2-}-P	2.9
Total P	3.8
Org. N	5.7
Inorg. C	58
Org. C	27

7.7

Aomine and Inoue determined the retention of phenylmercuric acetate and $HgCl_2$ by three soil types. Their results are shown in Figure 1. The soil types are as follows: Hyogo, montmorillonite and light clay; Mitsuzi, sandy loam and koalinite and Choyo, allophanic and light brown clay loam.



7.8

Inoue and Aomine determined the adsorption of phenylmercuric acetate on the three clay minerals shown in Figure 3. The effect of the exchangable cation is reported in Figure 2.

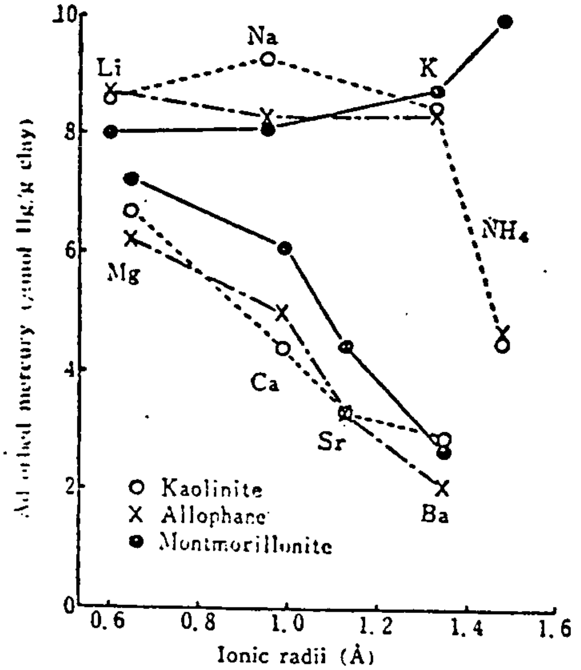


Fig. 2. Effect of exchangeable cations on the adsorption of phenylmercuric acetate by the clay minerals.

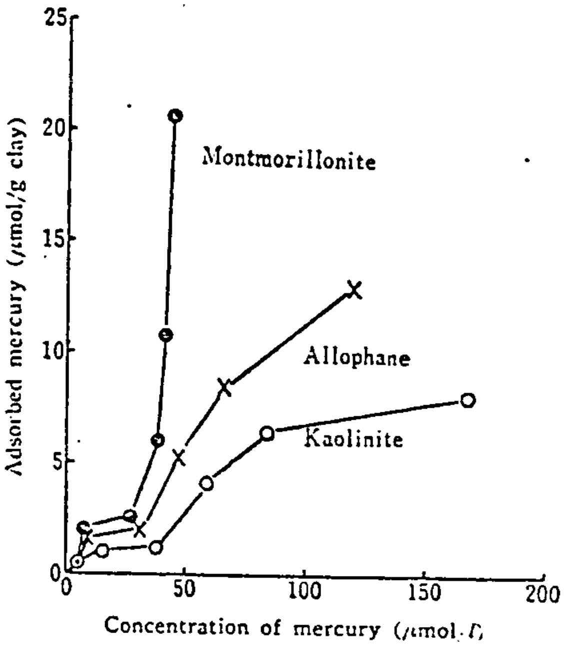


Fig. 3. Adsorption isotherms of phenylmercuric acetate on the clay minerals.

7.9

Aomine, Kawasaki and Inoue investigated mercury buildup in soils treated with phenylmercuric acetate. The level of application was not known with certainty but was believed to be in the range of 100 g to 3 kg per ha. The observed mercury levels and soil types studied are reported in Table 1. The authors attributed the low levels of mercury found in some soil types to leaching through the top horizons of soil. The tendency of mercurials to be converted to volatile forms reported after this work cast doubt on this interpretation.

RETENTION OF MERCURY BY SOILS (I)

Table 1. Mercury content, mechanical composition, and major clay minerals of soil samples

Sample	Depth cm	Mercury ppm	Sand %	Silt %	Clay %	Humus %	Clay mineral*
PADDY SOILS							
Hyogo (Saga)	0-10	0.49	36	29	30	3.7	Mt
	10-20	0.35	12	50	36	1.3	
Mitsuze (Saga)	0-25	tr	63	18	15	3.4	Kl
	25-35	tr	78	12	9	1.7	
Futsukaichi (Fukuoka)	0-15	0.34	52	26	17	5.2	Kl
	15-25	0.60	55	25	17	3.0	
	25-35	1.04	62	22	14	1.7	
Kumamoto	0-17	0.10	30	38	27	4.1	Mt
	17-27	tr	28	46	23	2.3	
Oita	0-20	0	53	24	20	3.9	Kl
	20-30	0	51	28	19	2.4	
Miyazaki	0-20	0.13	60	21	16	4.1	Chl, Ill
	20-40	0	51	25	21	4.2	
Taniyama (Kagoshima)	0-19	0.16	58	22	17	2.3	Kl
	19-50	0	63	26	7	3.4	
ORCHARD SOILS (ORANGE)							
Kyuragi-1 (Saga)	0-30	0.22	52	18	26	2.5	Kl
	30-50	0.25	59	17	22	1.1	
Kyuragi 2	0-30	0.29	59	16	22	3.7	Kl
	30-50	0.55	56	13	29	1.1	
Kumamoto-1	0-20	tr	25	27	45	2.2	Kl
	20-45	0	24	25	50	1.1	
Kumamoto-2	0-20	0.14	44	29	24	2.7	Kl
	20-40	0	44	28	26	1.6	
Miyazaki	0-20	0.10	60	21	16	3.3	Ill, Kl
	20-40	tr	59	23	17	2.5	
ORCHARD SOILS (APPLE)							
Ogawa (Nagano)	0-10	0.44	52	25	20	3.9	Mt
Aomori-1	0-60	2.20	54	18	15	13.7	Allo
	60-70	0.36	63	16	13	6.8	
Aomori-2 (control)	0-25	0	55	18	15	11.3	Allo
	25-50	0	54	21	17	7.3	

* Mt = montmorillonite, Kl = kaolin, Chl = chlorite, Ill = illite, Allo = allophane.

7.10

See 2.2

7.11

Blatter found some evidence that mercury forms interlayer structures with montmorillonite.

7.12

Niebla, Korte, Alesii and Fuller looked at $HgCl_2$ migration through 4 soil types with three eluting solutions; deionized water, simulated landfill leachate and 0.25 mm Na_2EDTA. Retention of mercury by the soils was least for the simulated leachate. The solution type was observed to have a larger effect on leaching than the soil type.

7.13

Kudo and Hart looked at the kinetics of $HgCl_2$ uptake by a variety of freshwater sediments. Figure 3 shows the time course observed for the absorption of mercury by the sediments. Uptake rates were found to depend strongly on the concentration of mercury in the water and the water velocity. Aerobic and anaerobic systems demonstrated similar kinetics.

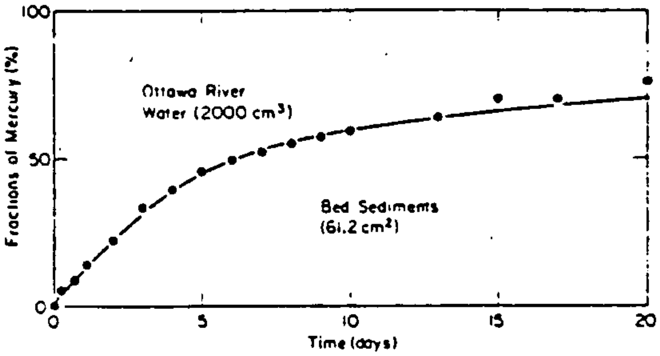


Fig. 3—Redistribution of mercury between water and bed sediments.

7.14

Frenet-Robin and Ottmann studied the adsorption of mercuric chloride by kaolinite, illite and montmorillonite. Different clay concentrations and salinity levels were used. Mercury desorption from the clays was also studied. Table 2 gives the amount of mercury adsorbed on the clays as a function of time and Figure 2 presents these data graphically. Approximately 4 hours were required to reach saturation, thus the capacity studies shown in Table 3 and Figure 3 were performed by contacting the clay/mercury solution with agitation for 4 hours. Table 4 gives the exchange capacity and the maximum rate of mercury fixation. Unfortunately this last quantity does not seem adequately defined. Figure 4 shows the capacity of the clays at two initial mercury levels as a function of salinity. The effect of turbidity is shown in Figure 5. Table 6 shows the percent of mercury desorbed from the clays. The clay suspensions used contained particles with a size range of 3.5 to .2 micrometers (80%). It is suggested that mercury is only fixed on the smallest particles and that the amount fixed is inversely proportional to the diameter of the particles.

Table 2. Fixed mercury level on clay minerals (µg g^{-1}) in terms of time at 1 g l^{-1} turbidity and 50 µg l^{-1} initial mercury concentration

		Time (h)				
Salinity (‰)	Sediments	1	2	4	6	8
0	Kaolinite	31·7	36·8	37·8	37·9	38·0
	Calcic Bentonite	28·5	37·8	42·2	43·0	42·8
	Sodic Bentonite	31·2	41·2	45·9	45·2	45·6
	Illite	30·7	37·5	40·7	40·9	40·5
20	Kaolinite	23·3	28·6	30·5	31·2	31·0
	Calcic Bentonite	39·3	45·5	48·1	48·6	48·4
	Sodic Bentonite	23·5	35·9	41·3	41·7	41·9
	Illite	23·2	31·4	35·1	36·0	35·9

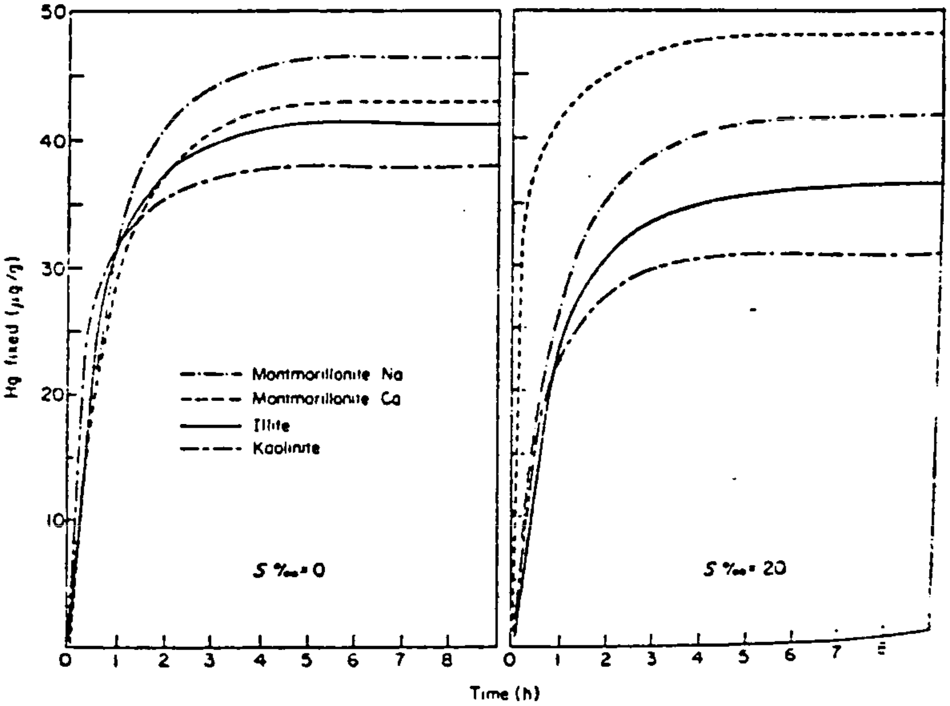


Figure 2. Fixed mercury level in the sediments in terms of (a) time in [illegible] expressed in µg/g of sediment (b) time in salt water (20‰) expressed in [illegible] sediment.

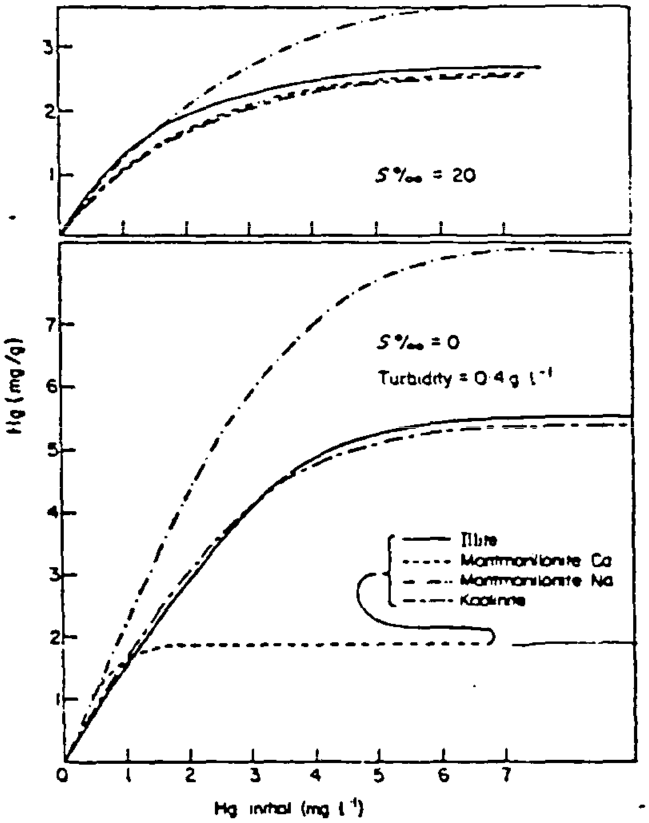


Figure 3. Mercury level in the sediments in terms of initial mercury concentration at 0·4 g l^{-1} turbidity.

TABLE 3. Mercury fixture in the sediments (µg g^{-1}) in terms of initial mercury concentration (mg l^{-1})

Salinity (‰)	Sediments Turbidity = 0·4 g l^{-1}	Initial mercury concentration (mg l^{-1})					
		0·02	0·05	0·1	0·5	1·0	5·0
0	Kaolinite	36·0	88·0	181·0	880	1 720	5 120
	Calcic bentonite	48·7	97·7	208·5	1 068	1 685	1 900
	Sodic bentonite	49·7	116·0	239·0	1 135	2 251	7 725
	Illite	32·2	90·7	188·0	815	1 595	5 275
20	Kaolinite	29·5	69·6	149·0	520	970	2 470
	Calcic bentonite	49·5	116·0	241·0	550	1 030	2 500
	Sodic bentonite	49·0	109·0	227·0	450	1 210	3 450
	Illite	27·2	71·5	133·0	675	1 275	2 625

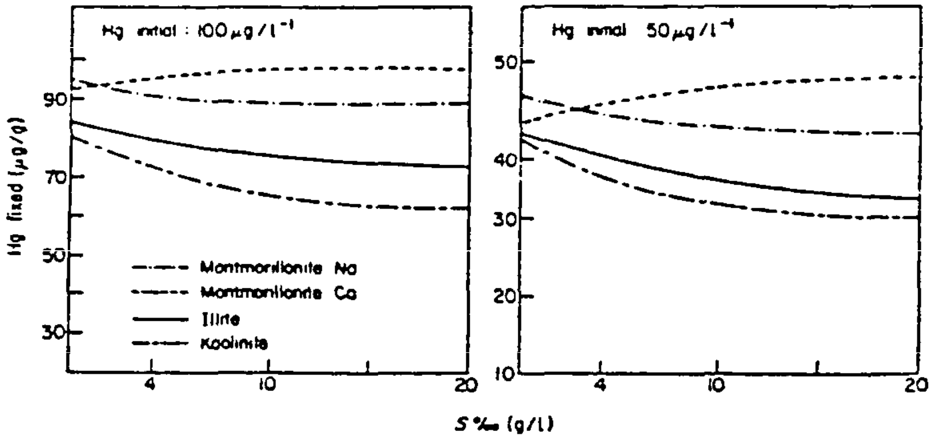


Figure 4. Fixed mercury level in the sediments in terms of salinity at 1 g l⁻¹ turbidity.

TABLE 4. Comparison of interchange capacity and maximum rate of mercury fixation

	Interchanging capacities of cations in milli-equivalent for 100 g	Maximum rate of mercury fixed mg g⁻¹	
		Freshwater	Salt water (20‰)
Montmorillonite	100 to 130	7·7	3·6
Kaolinite	20	5·4	2·5
Illite	20 to 30	5·5	2·7

TABLE 6. Proportion of mercury desorbed from different clays after 4 h agitation. Highest concentrations of mercury found for each salinity in the study area

Clay minerals	Freshwater (0)	Salt water (20 ‰)
Calcic montmorillonite	6·8%	5·4%
Sodic montmorillonite	3·5%	4·2%
Illite	10·6%	14·6%
Kaolinite	4·1%	19·6%

7.15

MacNaughton and James investigated the effects of hydrolysis and chloride complex formation on the adsorption of Hg^{2+} by silicone dioxide particles in water. They found that adsorption depended strongly on both pH and chloride ion concentration and displayed a maximum with respect to pH at the chloride ion concentrations studied. Figures 4 and 5 show their results.

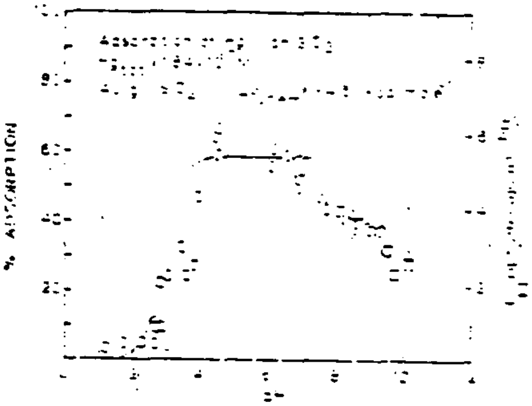


FIG. 4. The adsorption of Hg(II) from 1.84×10^{-7} mole dm^{-3} solutions by quartz as a function of pH and ionic strength. The ionic strength conditions are indicated: ○, 10^{-1} mole dm^{-3} $NaClO_4$; □, 10^{-2}; △, 2×10^{-3}; ×, 10^{-1} mole dm^{-3} $Mg(NO_3)_2$.

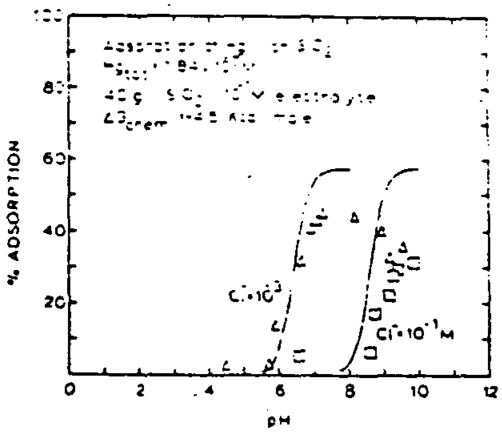


FIG. 5. The adsorption of Hg(II) from 1.84×10^{-7} mole dm^{-3} solutions by quartz as a function of pH and complexing ligand. The total ionic strength is 10^{-1} mole dm^{-3} ($NaClO_4$, NaCl) where Cl^- is: △ 10^{-3} mole dm^{-3} and □ 10^{-1} mole dm^{-3}.

Category 8. Formation of organomercurials

The action of bacteria and bacterial metabolites on mercury is complex and still under investigation. Bacteria capable of converting Hg^0 to methylated forms have not been observed, but bacteria are known which can convert Hg^0 to Hg^{2+}. Methylation of divalent mercury is well established. Bacteria capable of demethylating to Hg^0 and methane have been observed. Bacterial demethylation has been used to explain the low concentration of methylmercury in naturally occurring sediments. Bacteria have been found which reduce Hg^{2+} to Hg^0 with subsequent loss by volatilization.

8. Formation of Organomercurials

8.1 Landa, E.R. "Microbical Aspects of the Volatile Loss of Applied Mercury (II) from Soils". J. Environ. Qual. 7, 84-86, 1978.

8.2 Rogers, R.D. "Methylation of Mercury in Agricultural Soils". J. Environ. Qual. 5, 454-458, 1976.

8.3 Holm, H.W.; Cox, M.F. "Transformation of Elemental Mercury by Bacteria". Appl. Microbiol. 29, 491-494, 1975.

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8.5 Jensen, S.; Jernelov, A. "Biological Methylation of Mercury in Aquatic Organisms". Nature 223, 753-754, 1969.

8.6 Wood, J.M.; Penley, M.W.; DeSimone, R.E. "Mechanisms for Methylation of Mercury in the Environment". In Mercury Contamination of Man and His Environment. IAEA, Vienna. STI/DOC/10/137, 49-65, 1972.

8.7 Bisogni, J.J.; Lawrence, A.W., "Kinetics of Mercury Methylation in Aerobic and Anaerobic Aquatic Environments". J. Water Pollut. Con. Fed. 47, 135-152, 1975.

8.8 Spangler, W.J.; Spigarelli, J.L.; Rose, J.M.; Miller, H.M. "Methylmercury: Bacterial Degredation in Lake Sediments". Science 180, 192-193, 1973.

8.9 Bartlett, P.D.; Craig, P.J. "Total Mercury and Methyl-Mercury Levels in British Estuarine Sediments-II". Water Res. 15, 37-47, 1981.

8.1

Landa studied the loss of Hg^{2+} from the surface of five Montana soils. He found that loss rate depended on the soil type, the presence of bacteria, and the addition of bacterial nutrients. Figure 1 shows the effects of those variables on mercury loss from the five soils studied. The mercury compound volatilized from the soil was not identified but assumed to be Hg^0.

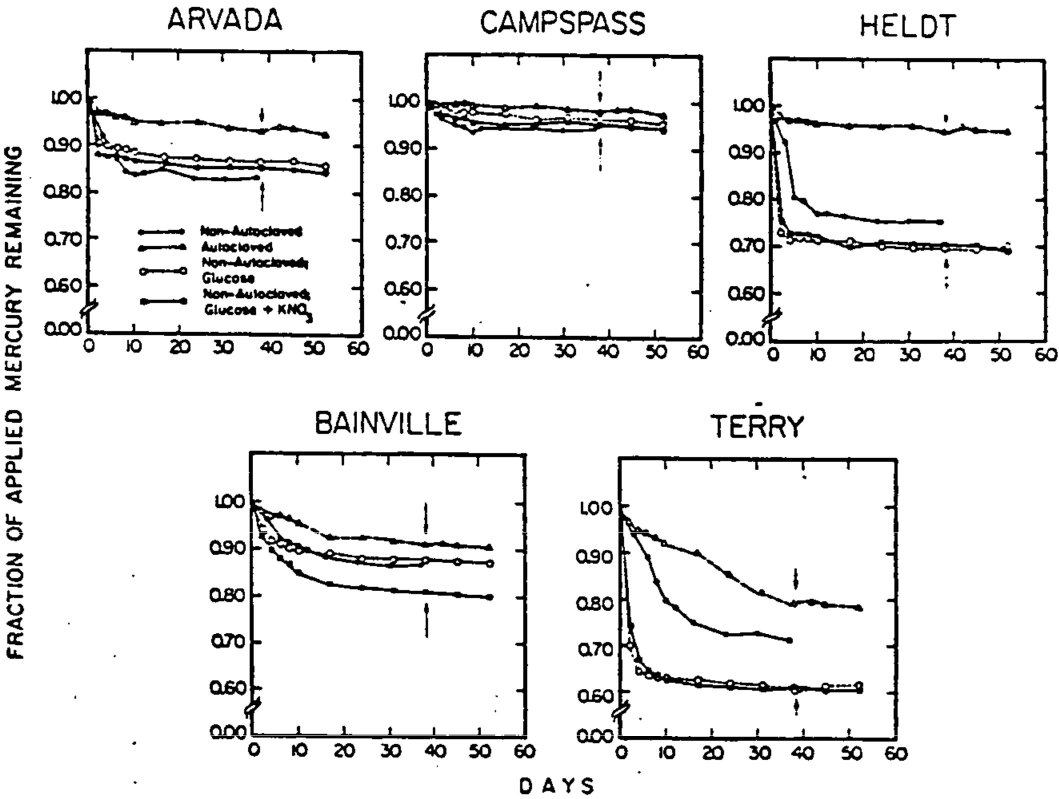

Fig. 1—Effect of autoclaving, glucose, and glucose + KNO, on Hg loss from soils. Vertical arrow at day 38 indicates initiation of irrigation with inoculum suspension or metabolic substrate solution.

8.2

Rogers observed the production of methylmercury in soil samples amended with Hg^{2+}, but the fraction of mercuric ion converted to the organic form was only about 1×10^{-5}. He suggests that methylation may be an intermediate step with a final product which is lost from the soil. Table 5 shows the effect of moisture on methylmercury production; Table 6 shows the effect of temperature and Table 7 shows the effect of the initial Hg^{2+} concentration.

Table 5—Methylmercury occurrence in soils with various moisture contents

Soil	Moisture-holding capacity	Concentration 1 week	Concentration 3 weeks
	%	ng CH_3Hg^+/50 g soil	ng CH_3Hg^+/50 g soil
Sand	25	88† ±16‡	§
	50	98 ±25	§
	75	105 ±12	§
Loam	25	223 ±14	130 ±6
	50	188 ±12	63 ±10
	75	212 ±12	54 ±0
Clay	25	306 ±35	166 ±66
	50	256 ±14	108 ±0
	75	195 ±53	51 ±22

† Mean of three replications.
‡ ± 1 standard deviation.
§ Sample lost.

Table 6—Methylmercury occurrence in soils incubated at various temperatures

Soil	Incubation temperature	Concentration 1 week	Concentration 3 weeks
	°C	ng CH_3Hg^+/50 g soil	ng CH_3Hg^+/50 g soil
Sand	4	42† ±13‡	65 ±0
	24	67 ±0	§
	36	123 ±9	109 ±15
Loam	4	65 ±10	188 ±4
	24	169 ±19	62 ±10
	36	300 ±15	46 ±0
Clay	4	128 ±39	178 ±13
	24	179 ±21	107 ±0
	36	195 ±30	36 ±0

† Mean of three replications.
‡ ± 1 standard deviation.
§ Sample lost.

Table 7—Methylmercury occurrence in soils incubated for 1 week with amendments of varying mercuric nitrate concentration

Soil	$Hg(NO_3)_2$ added	CH_3Hg^+ detected
	μg Hg/50 g soil	ng/50 g soil
Sand	5,000	29† ±3‡
	12,000	56 ±7
	25,000	98 ±25
Loam	5,000	38 ±8
	12,000	79 ±5
	25,000	188 ±12
Clay	5,000	41 ±4
	12,000	100 ±9
	25,000	256 ±14

† Mean of three replications.
‡ ± 1 standard deviation.

8.3

Holm and Cox looked at the interactions between a number of pure bacterial cultures and elemental mercury. He found that some bacteria including Bacillus subtilis oxidize essentially all of the Hg^0 added while other bacteria including Escherichia coli oxidize very little. No methylmercury was detected in any of the cultures.

8.4

Jernelov discusses the state of knowledge concerning mercury conversion prior to 1972. He indicates that many ecological systems should tend to convert any mercury present to methylmercury: a theory which does not seem to be supported by subsequent experimentation. He does discuss a lake in Sweden contaminated by a chloralkali plant which was closed 25 years earlier. At the time of writing, the contaminated sediments were buried under some decimeters of fresh sediment and the fish in the lake had relatively low mercury contents.

8.5

Jensen and Jernelov demonstrated that the amount of methylmercury in sediments increased after the addition of Hg^{2+} at concentrations up to 100 ppm. Beyond that concentration, the formation of methylmercury was depressed.

8.6

Wood, Penley and DeSimone discuss various biochemical pathways for the methylation of mercury.

8.7

Bisogni and Lawrence set up a series of steady state microbial reactors to determine the extents and rates of mercury methylation under varying conditions of Hg^{2+} input concentration, microbial growth rate and oxygenation level. Tables 1 and 2 contain the operating conditions for the aerobic and anaerobic reactors used. Table 8 contains the results for the anaerobic reactors while Table 11 contains those for the aerobic reactors. Rates are also tabulated for methylation under the conditions studied.

TABLE I.—Anaerobic Reactor Operating Characteristics

Unit Designation*	Net Specific Growth Rate (day^{-1})	Reactor Feed Solution		COD Loading Rate (g COD/l of reactor/day)	Hg Application Rate (mg Hg/l of reactor. day)
		COD (mg/l)	Hg^{2+} (mg/l)		
6A-30	1/6	6,000	0.1	1.0	0.0167
6B-30	1/6	6,000	1.0	1.0	0.167
6C-30	1/6	6,000	10.0	1.0	1.67
6D-30	1/6	6,000	100.0	1.0	16.7
12A-30	1/12	6,000	0.1	0.5	0.0083
12B-30	1/12	6,000	1.0	0.5	0.083
12C-30	1/12	6,000	10.0	0.5	0.83
12D-30	1/12	6,000	100.0	0.5	8.3
24A-30	1/24	6,000	0.1	0.25	0.0041
24B-30	1/24	6,000	1.0	0.25	0.041
24C-30	1/24	6,000	10.0	0.25	0.41
24D-30	1/24	6,000	100.0	0.25	4.1
24C-20	1/24	6,000	10.0	0.25	0.41
24C-10	1/24	6,000	10.0	0.25	0.41
6A-30S	1/6	6,000	0.1	1.0	0.0167
6B-30S	1/6	6,000	1.0	1.0	0.167
6C-30S	1/6	6,000	10.0	1.0	1.67
6D-30S	1/6	6,000	100.0	1.0	16.7

* The last two digits indicate operating temperature (°C).

TABLE II.—Aerobic Reactor Operating Characteristics

Unit Designation*	Net Specific Growth Rate (day^{-1})	Reactor Feed Solution		COD Loading Rate (g COD/l of reactor/day)	Hg Application Rate (mg Hg/l of reactor/day)
		COD (mg/l)	Hg^{2+} (mg/l)		
O6A-30	1/6	3,000	0.1	0.5	0.0167
O6B-30	1/6	3,000	1.0	0.5	0.167
O6C-30	1/6	3,000	10.0	0.5	1.67
O6D-30	1/6	3,000	100.0	0.5	16.7
O12A-30	1/12	3,000	0.1	0.25	0.0083
O12B-30	1/12	3,000	1.0	0.25	0.083
O12C-30	1/12	3,000	10.0	0.25	0.83
O12D-30	1/12	3,000	100.0	0.25	8.3
O24A-30	1/24	3,000	0.1	0.125	0.0041
O24B-30	1/24	3,000	1.0	0.125	0.041
O24C-30	1/24	3,000	10.0	0.125	0.41
O24D-30	1/24	3,000	100.0	0.125	4.1
O6C-20	1/6	3,000	10.0	0.5	1.67
O6C-10	1/6	3,000	10.0	0.5	1.67

* The last two digits indicate operating temperature (°C).

TABLE VIII.—Steady-State Distribution of Mercury Forms for Anaerobic Reactors

Unit Designation	Daily Input of Hg/l of Reactor (mg/day)	Weight Percentage Transformed to				Recovery All Forms (%)
		Hg^0 (effluent gas) (%)	$(CH_3)_2Hg$ (effluent gas) (%)	CH_3Hg^+ (reactor) (%)	Remaining in Inorganic Form (reactor) (%)	
6A-30	0.0167	71.9	0.3	5.9	14.3	92.4
6B-30	0.167	40.9	0.1	1.0	49.3	91.3
6C-30	1.67	42.5	<0.1	0.2	52.0	94.6
6D-30	16.7	48.0	<0.1	0.1	44.9	92.9
12A-30	0.0083	54.4	0.2	4.6	38.9	98.0
12B-30	0.083	8.4	<0.1	0.7	84.4	93.5
12C-30	0.83	13.7	<0.1	0.1	81.0	94.7
12D-30	8.3	16.6	<0.1	<0.1	79.8	96.4
24A-30	0.0041	52.0	<0.1	3.3	41.0	96.3
24B-30	0.041	13.9	<0.1	0.6	79.8	94.3
24C-30	0.41	17.2	<0.1	0.1	80.1	97.3
24D-30	4.1	22.8	<0.1	<0.1	72.8	95.5
6A-30S	0.0167	58.0	0.1	3.6	32.7	94.3
6B-30S	0.167	45.7	<0.1	0.4	51.0	97.1
6C-30S	1.67	47.1	<0.1	0.1	47.5	94.6
6D-30S	16.7	39.5	<0.1	<0.1	53.5	93.0
24C-20	0.41	17.0	<0.1	0.1	78.9	96.0
24C-10	0.41	23.1	<0.1	0.1	72.8	95.9

TABLE XI.—Steady-State Distribution of Mercury Forms for Aerobic Reactors

Unit Designation	Daily Input of Hg/l of Reactor (mg/day)	Weight Percentage Transformed to				Recovery All Forms (%)
		Hg^0 (effluent gas) (%)	$(CH_3)_2Hg$ (effluent gas) (%)	CH_3Hg^+ (reactor) (%)	Remaining in Inorganic Form (reactor) (%)	
0-6A-30	0.0167	71.1	0.1	7.6	1.1	79.9
0-6B-30	0.167	79.3	<0.1	1.3	2.1	82.8
0-6C-30	1.67	88.5	<0.1	0.3	1.3	90.1
0-6D-30	16.7	78.6	<0.1	0.1	0.4	79.1
0-12A-30	0.0083	72.5	0.1	10.2	1.2	84.0
0-12B-30	0.083	88.3	<0.1	1.5	2.4	92.2
0-12C-30	0.83	79.9	<0.1	0.2	1.2	81.3
0-12D-30	8.3	81.3	<0.1	<0.1	0.6	82.0
0-24A-30	0.0041	66.5	0.2	15.7	1.0	83.4
0-24B-30	0.041	72.8	<0.1	2.9	2.1	77.8
0-24C-30	0.41	95.8	<0.1	0.5	1.8	98.1
0-24D-30	4.1	83.4	<0.1	0.1	0.8	84.3
0-6C-20	1.67	81.5	<0.1	0.3	1.3	83.1
0-6C-10	1.67	84.4	<0.1	0.3	1.3	86.0

8.8

Spangler, Spigarelli, Rose and Miller found that while methylmercury was initially produced from Hg^{2+} added to a sediment loaded aerobic reactor, after a period of about two months the concentration of methylmercury in the sediment began to fall and eventually returned to near its initial level. All volatilized mercury was collected and no methylmercury was found. Further studies demonstrated that the methylmercury was reduced to Hg° and methane by bacteria.

8.9

Bartlett and Craig report a large survey of the methylmercury content in estuarine sediments. Their basic premise is that the ambient concentration of methylmercury in sediment is strongly dependent on the redox potential of the local sediment solution. They explain this dependence as being due to oxygen sensitive bacterial populations responsible for both methylation and demethylation. Methylation is primarily carried out by anaerobic bacteria and demethylation by aerobic bacteria. Some of their observations, however, require the additional postulation of anaerobic demethylators and aerobic methylators. Little evidence is provided to support this proposition. Figures 11 and 12 show an interesting observation. The methylmercury level in sediment rises rapidly after collection to a maximum in 20 to 30 days and then begins to decline.

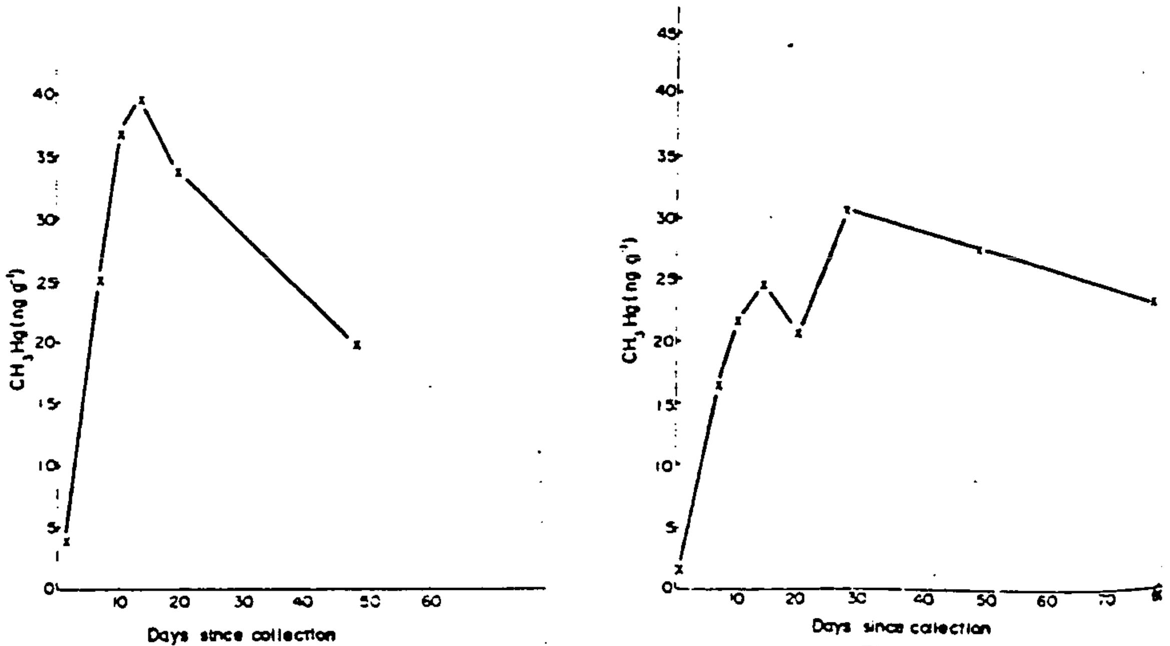

Fig. 11.

Fig. 12.

Figs 11 and 12. Time Dependence of methyl mercury levels in stored sediments (1975). Reproduced from Mence (1977) with permission.

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Name W H Carlton
Phone 53280
Position Manager, Level 4
Organization SRTC, Environ. Technology

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