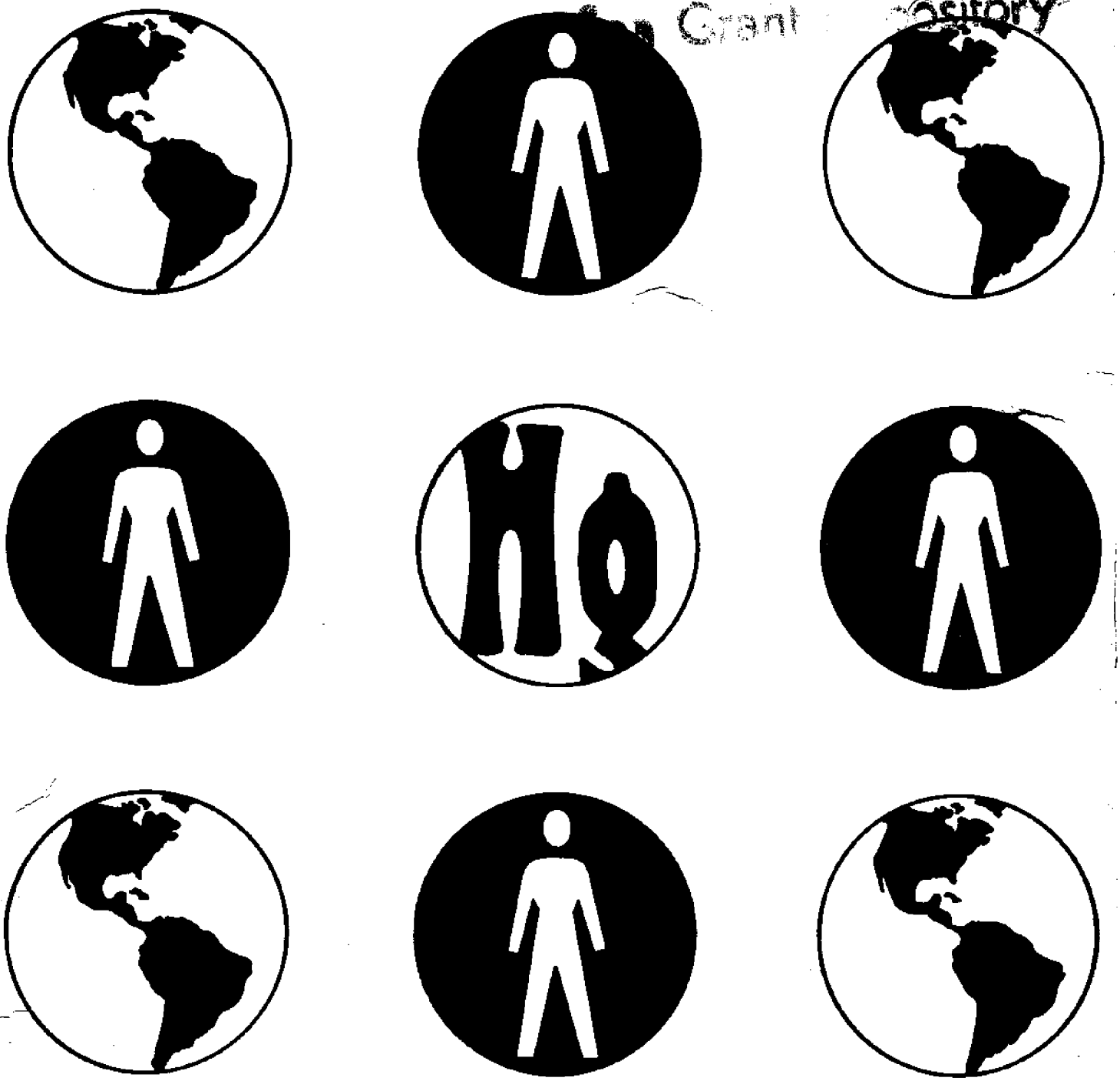
Mercury in the Environment

Frederick K. Lepple



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MERCURY IN THE ENVIRONMENT

A Global Review Including Recent Studies in the Delaware Bay Region

by

Frederick K. Lepple

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Abstract

The first section of this two-part report reviews basic properties of mercury and its compounds as related to their effect on various facets of the environment. Among the topics discussed are the chemical forms and hazards of mercury, incidents of mercury contamination, governmental standards and tolerance limits, levels of mercury in the atmosphere, biosphere, lithosphere and hydrosphere, and the flux through each segment. The reality of the "mercury problem" globally and locally is evaluated. A comprehensive review of the accepted methods of analyses for mercury and its compounds is also presented. The second section reports on recent studies of mercury levels in the Delaware Bay region and compares the concentrations found in the waters and sediments to values from other areas.

INTRODUCTION

The toxic quality of metallic mercury and its compounds has long been recognized. In the past few decades however, due to the industrial and agricultural uses of mercury and the resulting mobilization, situations have arisen in which mercury has become an environmental hazard. Although at present the majority of the world's population has not been directly affected by these events, more attention must be tendered to the social implications of present use practices and to more effective means of recycling. In perspective, the "mercury problem" should carry a warning, for as stated by Senator William S. Prouty in a report to the Environmental Subcommittee of the U. S. Senate: "What we have learned about mercury recently indicates that what we see and know about pollution is not as frightening perhaps as the unknown and unseen."

The first section of this two-part report will attempt to review briefly what is presently known about the mercury cycle in nature: the forms and relative toxicity of mercury, tolerance limits, incidents of contamination, global concentration levels and the flux of mercury through the atmosphere, biosphere, hydrosphere and lithosphere. Analytical methodology of mercury compounds is also summarized, and recommendations for further research to cover gaps in our knowledge are presented. The second section deals with mercury measurements in the Delaware Bay region and assesses the significance of these preliminary results.

PART I

A GLOBAL REVIEW

Forms and Hazards of Mercury

In nature, the principal forms of mercury are the ore cinnabar (HgS), mercury vapor (Hg°), mercurous and mercuric ions (Hg^{+} and Hg^{2+}, chiefly complexed with chloride ions), and organic compounds such as methylmercuric chloride, dimethylmercury, and phenylmercuric chloride. It has become clear that methylmercury and other alkylmercury compounds, through their propensity for the nervous system, long retention time in the body, and their effect on developing tissue pose the most serious problems (Östlund, 1969). Dimethylmercury, which is fat-soluble and nonionizable, is taken up by fatty tissues and rapidly eliminated via exhalation. Relative toxicity of alkylmercurials sharply diminishes when the carbon chain exceeds three carbon atoms.

Some of the general clinical symptoms of mercury poisoning are numbness in the extremities with possible paralysis, constriction of visual field, impaired hearing and/or speech and impaired muscular coordination. Extreme cases can result in coma followed by death.

Up to the middle of the twentieth century, most cases of mercury poisoning were the result of occupational hazards, notably those people working in laboratories and in the hat-felt industry. Subsequently, intoxication at various levels of the food web has become more acute.

From 1953 to 1960, methylmercury poisoning due to ingestion of contaminated fish occurred in a village near Minamata Bay, Japan. At least 121 cases were reported including 46 fatalities. Included were 23 cases of a cerebral palsy-like disease affecting infants who had not consumed contaminated fish. Brain damage had been largely accomplished by the time the diagnoses were made and although the administration of chelating agents increased the rate of excretion of mercury, it proved to be clinically ineffective. In 1960, the cause of this disease was discovered to be mercury dumped into the bay by manufacturing plants using mercury catalysts in the preparation of vinyl chloride and acetaldehyde, two chemicals widely used in the plastics industry. Typical waste from these plants contained up to 20 ppm (parts per million) mercury.

A similar incident occurred in Niigata, Japan in 1964 and 1965, where 47 cases of poisoning resulted in 6 deaths from the consumption of fish and shellfish containing approximately 5 ppm mercury. It is of interest to note that the Japanese are the world's heaviest consumers of fish: 62 lb/capita/year -- more than 5 times the figure for the United States.

Human consumption of grain treated with mercurials for seed purposes has led to outbreaks of poisoning in Guatemala, Iran and Pakistan, in which more than 450 persons were affected (Ordonez, et al., 1966; Jalili and Abbasi, 1961; Haq, 1963). In 1969, seven persons in a New Mexico family consumed pork from animals which had been fed seed coated with an organic mercurial called Panogen. The pork

contained 28 ppm of mercury while the grain contained 32 ppm (Likosky, et al., 1970). Three of the children became delirious, blind and eventually comatose. The illness had the appearance of an acute lethal encephalitis - a syndrome similar to "Minamata disease."

Research has shown (Tsubaki, et al., 1967; Kutsuna, 1968) that the human fetus acquires higher concentrations of mercury than the mother-to-be and thus the child may exhibit symptoms of mercury poisoning even though none are apparent in the mother. Ramel (1967) and Skerfving, et al., (1970) have reported on the possibility of genetic and teratogenic effects of methylmercury.

Standards and Tolerance Limits

At present, no official standard for mercury in air exists in the U. S. As a result of industrial studies, the American Conference of Governmental and Industrial Hygienists has recommended threshold limit values of 10 µg (microgram) for alkylmercurials and 50 $\mu g/m^3$ for all other forms of mercury (A.C.G.I.H., 1970). For drinking water, the limit of 5 ppb (parts per billion) is considered by the U. S. Bureau of Hygiene "to contain a reasonable safety factor for the protection of human health in consideration of degree of exposure, routes of entry, metabolic rate and excretion rate of the heavy metal."

The U. S. Food and Drug Administration (FDA) has fixed 0.5 ppm as the legal maximum concentration of mercury in food. The FDA arrived at its figure arbitrarily and conservatively. The calculation is based on toxological studies and on observed levels of mercury accumulated in tissues of victims. Evidence suggests that health

can be affected if the concentration in the blood is above 200 ppb. A safety factor of 10 reduces this to 20 ppb. To ensure that such concentrations are never attained, food containing over 0.5 ppm (500 ppb) is declared "unsafe."

To examine certain high consumption foods, the FDA conducted a nationwide "Mercury in Foods Survey." Included in this survey were flour, nonfat dry milk, sugar, whole egg, fluid whole milk, ground beef, beef liver, shrimp, chicken breast and potatoes. No mercury concentrations above the sensitivity of the method (± 0.02 ppm) was detected in any of the commodities except the shrimp. Of the 34 shrimp samples, four were above 0.02 ppm; the highest value was 0.05 ppm.

A standard of 0.5 ppm may be stricter than necessary: Sweden and Japan have set limits twice as high as ours - 1.0 ppm. Besides the chemical form in which mercury is ingested, its effect also depends on the total amount taken in a particular time period as well as on the concentration in a particular portion. Thus, it is difficult to set down any strict maximum level which is general enough for all consumers.

Other Evidence of Mercury Contamination

Organisms other than man are also threatened by indiscriminate use of mercury compounds. Fish and shellfish are noted for their ability to concentrate heavy metals and most species are able to tolerate mercury levels that are hazardous to humans if eaten. In Minamata Bay after two years of effluent treatment for the removal of mercury, the levels in shellfish dropped from 85 to 10 ppm (dry weight

basis). The evidence indicates that mercury exists in fish mainly as the highly toxic methylmercury (Westöö and Rydalv, 1969).

Various factors which influence the accumulation of mercury in the food chain and the proportion between methyl- and total mercury are the trophic level in the marine environment (Johnels, et al., 1967; Ui, 1967) and perhaps temperature (Westöö and Rydalv, 1969; Ui and Kitamura, 1969). Persistence in the body is one factor of much importance in determining population effects. Mammals vary widely in persistence of methylmercury: the half-life may be as little as 3-7 days as in mice to estimates of 70-74 days in humans (Tejning, 1967).

The first word that mercurials used as fungicides on seed might be an environmental risk came out of Sweden at about the same time that the residents of Minamata Bay began to come down with the then mysterious "Minamata disease." Swedish ornithologists observed a decrease in the population of seed-eating and predatory birds. Further study revealed that the feathers of museum avian specimens contained fairly constant, low levels of mercury up to 1940. Specimens taken since 1940 showed levels 10 to 20 times higher. It was shortly after 1940 that methylmercury and ethylmercury were introduced as seed dressings.

In contrast to land feeders, fish-eating birds in Sweden showed a relatively constant increase in mercury content of their feathers throughout the 1900's, suggesting that in Sweden, at least, mercury water pollution has increased at a rate proportional to general in-

dustrialization. In February 1966, alkylmercury compounds were banned from general use in Sweden and bird populations have responded favorably, according to recent reports (Chem. Eng. News, 1971).

While the Japanese experience makes the New Mexico incident seem avoidable, it is especially tragic since a parallel situation involving Panogen was reported two years earlier. Several pigs on a New York farm, fed wheat grain that had been coated with Panogen, exhibited the symptoms of Minamata disease for 3-5 days before dying in a coma. Necropsy failed to support the original diagnosis of hog cholera but suggested mercurial poisoning which toxilogical tests later confirmed. Slowly coming to light are similar incidents in which farm animals and household pets have shown deleterious responses to environmental hazards in advance of any such cases involving humans (Mulvihill, 1972). Because of their place in man's ecology, these animals may well be the best sentries for environmental toxins and teratogens.

Other organisms lower on the evolutionary scale can also be used to detect abnormal concentrations of mercury or other pollutants. Especially sensitive in this respect for the aquatic habitat are scavenger types such as catfish or carp.

Sources of Mercury and Their Control

According to a recent international report (Nelson, et al., 1971), sources of mercury in industrial and agricultural countries can be divided into the following categories: (1) chlor-alkali plants, (2) industrial processes involving the use of mercurial

catalysts, (3) slimicides, used primarily in the paper-pulp industry, (4) seed treatment, (5) burning of fossil fuels, (6) natural occurrence from geological formations and (7) miscellaneous sources such as mercury-containing lamps, switches, relays and thermometers; laboratory and dental refuse; and refining or redistillation processes. The United States appears to be the world's largest consumer of mercury - the recorded figure for 1968 was 2.6×10^9 gm. World consumption of mercury has increased markedly since World War II through expansion of the chlor-alkali industry and also use in electrical applications. It has been estimated that the chlor-alkali plants using mercury cathodes lose from 100 to 200 grams of mercury per 1000 kilograms of chlorine produced.

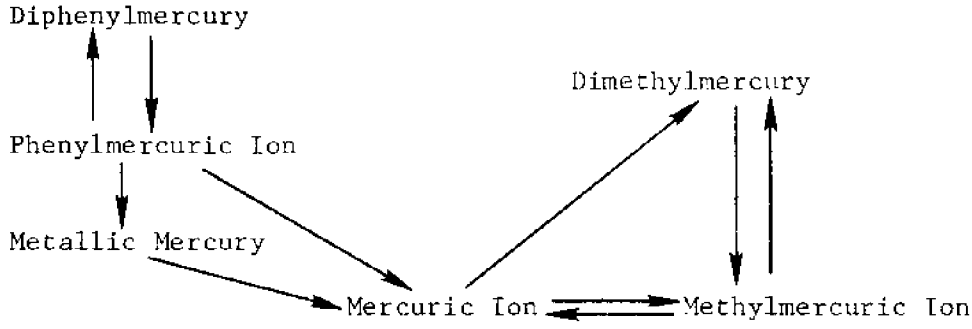
Except for the natural occurrences of mercury, all of the sources listed above can be rather easily controlled either by replacement or by reclamation. Some suggestions are given by Nelson, et al., (1971) and Wallace, et al., (1971). Natural sources of mercury might be isolated by blanketing with layers of relatively inert minerals (Jernelöv, 1970 and Langley, 1971).

Interconversion of Mercury Compounds

Previously, it was believed that all methyl- and other alkyl-mercury compounds found in the environment were man-made either directly in the laboratory or in industrial processes or indirectly as the chemical result of mixing and reacting with other products in effluents. Jensen and Jernelöv (1969) have shown mercury to be methylated in both aquarium and natural sediments, and Wood, et al.,

(1968) have demonstrated an enzymatic conversion by extracts of methanogenic bacteria. Both groups found monomethyl - and dimethyl-mercury as initial products with high mercury concentrations favoring the monomethyl form (Wood, et al., 1968) and high pH favoring the dimethyl form (Larsson, 1970). Dimethylmercury decomposes to the monomethyl form at low pH. The monomethyl mercury is directly accumulated by organisms in the water while the dimethyl form is reported to leave the aqueous phase and enter the atmosphere.

All forms of mercury appear to be capable of conversion to methylmercury either directly or indirectly (See diagram below from Jernelöv, 1969):



Although the methylation process can occur anaerobically, the rate of methylation is reduced under these conditions (Miettinen, 1970). As noted by Werner (1967) and Jernelöv (1968b), the oxygen content of the sediment-water system is very important since oxygen deficiency often leads to the production of hydrogen sulfide which can then combine with inorganic mercuric ions to precipitate the highly insoluble mercuric sulfide.

When mercury is discharged into a river or lake, neither organic

nor inorganic mercury are taken up appreciably by aquatic plants but there can be considerable surface adsorption on submerged plants (Hannerz, 1968). Adsorption on particulate matter and in sediments is extensive and much of the mercury can be immobilized in this way. Although the concentration of mercury in natural waters could in part be controlled by the precipitation of HgS locally in reducing environments, Krauskopf (1956) does not consider this process to be generally significant.

Environmental Levels of Mercury

A simplified schematic of the various inputs and sinks of mercury is presented below (from Nelson, et al., 1971):

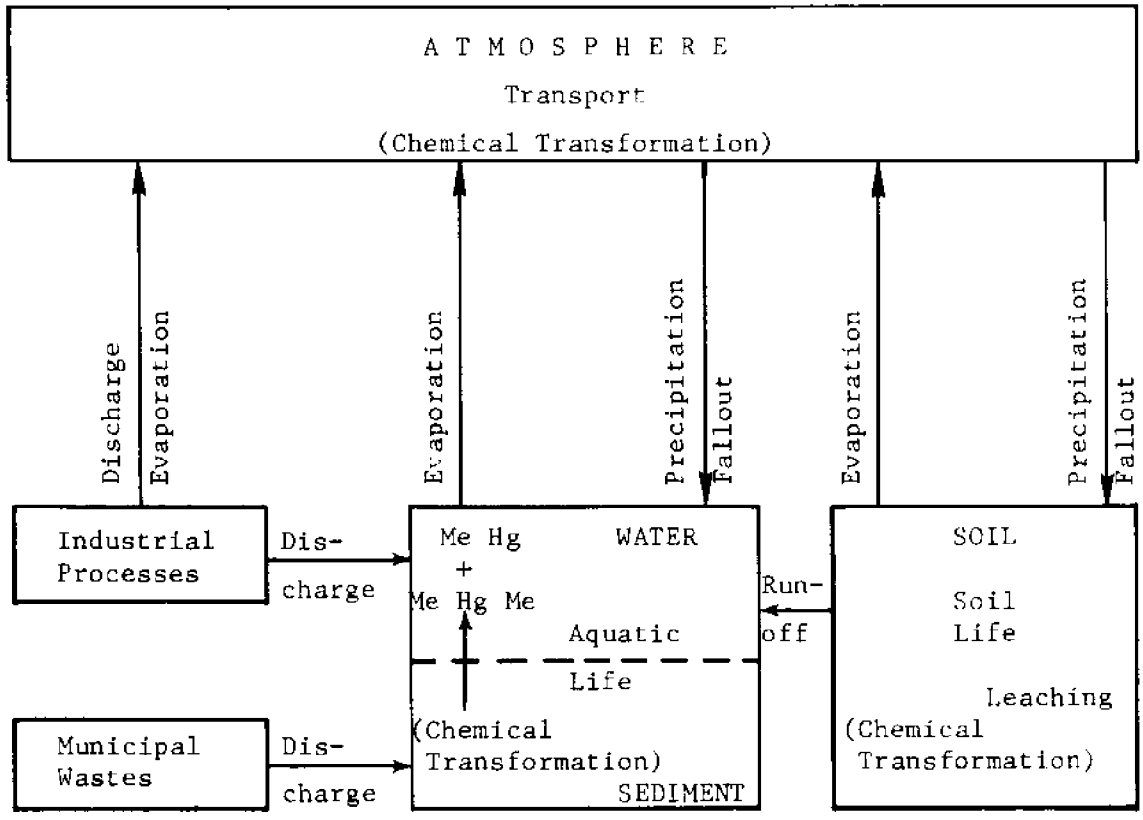


Table 1 lists some estimates of background levels of mercury from uncontaminated sources. The following subsections will briefly discuss mercury levels in the atmosphere, hydrosphere, lithosphere and biosphere. For more detailed accounts and extensive data, the reader is referred to the reports of Nelson, et al., (1971) and Wallace, et al., (1971).

a) Atmosphere

Comparatively little is known about the levels and variations of mercury in the air. Early studies done in Germany (Stock and Cucuel, 1934) yielded an average value of 0.02 $\mu g/m^3$ of total mercury in air. Measurements in the United States (Cholak, 1952) have been reported for particulate mercury which range from 0.03 to 0.21 $\mu g/m^3$. In a two-year study in the San Francisco Bay area, Williston (1968) noted seasonal trends ranging from 0.002 to 0.050 $\mu g/m^3$ in summer and from 0.001 to 0.025 $\mu g/m^3$ in winter. The higher summer levels are attributed to the temperature effect on the volatilization of mercury from ground sources. Williston also found evidence of a direct correlation with smog: 2 to 3 fold increase in atmospheric mercury levels on smoggy days as compared to normal conditions.

Eriksson (unpublished) estimates that the atmospheric mercury burden in the air column located above 1 hectare is 2000 mg/hectare. This level would project to a global atmospheric burden of approximately 80,000 metric tons or nearly 8 times the total estimated annual worldwide use of mercury. Although the observed levels of atmospheric mercury are still orders of magnitude below the

Table 1

Estimates of Background Levels of Mercury in Samples Not Known to be Contaminated. Compiled from Various Sources

(after Klein, 1972a)

Sample	Concentration (ppb)
Air	0.002
River and ground water	0.05
Sea water	0.1
Rain water	0.15
Raw sewage	2
Crustal rocks	50
Soils and sediments	50
Coal	200
Fish	100
Man	100

threshold values of 0.1 mg/m^3 for inorganic vapor and 0.01 mg/m^3 for organic mercury compounds, the lack of sufficient baseline data and the question of biological consequences of the transport of airborne mercury, point out the need for much additional research in this area.

b) Oceans and Rivers

The average concentration of mercury in the oceans is usually quoted as being 0.03 µg/1 (approx. 0.03 ppb - Goldberg, 1963), although Hosohara (1961) has reported deep water concentrations as high as 0.27 µg Hg/1. During the outbreak in Minamata Bay, values from 1 to 10 µg/1 were measured. Recent measurements by Leatherland, et al., (1971) in the Northeast Atlantic Ocean yielded concentrations between 0.013 and 0.018 µg/1 for 4 surface samples; concentrations in 3 deep water samples were closely similar but 2 other deep samples showed markedly lower levels. None of the above samples were filtered.

Weiss, et al. (1972) found mercury levels between 0.022 and 0.173 ppb at 2 stations in the Eastern Pacific Ocean. At the first station, which was farther out to sea, concentrations ranged from 0.012 to 0.027 ppb mercury with the average at 0.019 ppb. The concentrations at the second station (60 km from shore) ranged from 0.022 to 0.173 ppb. They attribute the difference to the possibility of varying particle content (unfiltered samples) although temperature and salinity data indicate that the samples analyzed at each of the two stations were from the same water mass.

Mercury concentrations in coastal marine environments have been studied by Klein and Goldberg (1970), Smith, Nicholson and Moore (1971)

and Burton and Leatherland (1971). Smith, et al. (1971), in a study of the tidal Thames River, differentiated between the total and dissolved mercury fractions. They found that 82 - 97% of the mercury was associated with particulate matter. Total mercury levels ranged from 0.045 to 2.85 ppb. Burton and Leatherland (1971) examined mercury concentrations in the English Channel (avg. 0.02 µg/l) and in nearby rivers (avg. 0.01 µg/l). In the La Have River, Nova Scotia, dissolved mercury levels ranging from 0.04 to 0.10 µg/l have been reported (Cranston and Buckley, 1972).

c) Sediments, Soil and Coal

Some estimates of the amount of mercury potentially available in a natural system were provided by the detailed survey of McCulloch, et al. (1971) who determined mercury levels in the surface sediments of the San Francisco Bay estuary. Concentration values from 199 samples ranged from 0.02 to 2 ppm, with the average near 0.3 ppm (compared to the average concentration of mercury in the earth's crust reported as 0.07 ppm - Vinogradov, 1959). McCulloch, et al., calculate a total of 113 tons of stored mercury based on an average sediment concentration of 0.25 ppm Hg for a 30 cm layer over the 1130 square kilometers of the estuary. Incidentally, the Environmental Protection Agency has set limits on the allowable concentration of pollutants in dredge spoils. For mercury, the limit is 1 ppm -- dredge spoil containing higher concentrations must be disposed of on land.

Klein (1972b) measured mercury in soils over an 800-square kilometer area of Michigan which incompassed residential, agricultural and

industrial sections including an airport. In 70 residential soil samples, the mean mercury level was 0.10 ppm with a standard deviation of 0.10 ppm. Agricultural soil samples (n = 91) yielded concentrations of 0.11 ± 0.09 ppm, while samples from industrial regions (n = 86) contained 0.14 ± 0.10 ppm mercury. Seven samples in the airport region had the highest levels: 0.33 ± 0.18 ppm. Analyses for other metals (Ag, Ca, Cd, Co, Cr, Cu, Fe and Zn) also indicated higher levels around the airport.

Reported concentrations of mercury in coals range from 0.012 ppm (Bertine and Goldberg, 1971) to 33 ppm (Joensuu, 1971) with an average value of nearly 1 ppm for certain American coals. Billings and Matson (1972) showed that mercury liberated during coal combustion can be discharged either as a vapor in the flue gas or retained in the furnace ash. About 90% by weight of the mercury released from a furnace fired with pulverized coal appears to be in the vapor phase and 10% remains with the furnace residual ash. They found an average mercury content of 0.2 ppm in the coal supplied to a power plant over 3 consecutive 24 hour composite sampling periods.

d) Biosphere

Numerous analyses for mercury (some reported as methylmercury) in various species of North American fish are listed by Bligh, 1970, 1971a, 1971b; Armstrong and Uthe, 1971 and Pillay, et al., 1971. Representative values of mercury levels in Atlantic coastal fish and the aquatic food chain are given in Tables 2 and 3. For comparison, contaminated fish and shellfish found dead at Minamata contained 9 to 24 ppm mercury (Löfroth, 1969).

Table 2

Mercury Levels in Atlantic Coast Fish

(from Bligh, 1971a)

SPECIES	AVG. PPM Hg
Cod	0.02-0.23
Clam	0.02-0.11
Crab	0.06-0.15
Flounder	0.07-0.17
Haddock	0.07-0.10
Herring	0.02-0.09
Herring Meal	0.02-0.14
Lobster	0.08-0.20
Oyster	0.02-0.14
Swordfish	0.82-1.00
Tuna	0.33-0.86

Table 3

Mercury in the Aquatic Food Chain

(from Bligh, 1971a)

	Number of Samples	Range of Values	Arithmetic Mean	More Numerous Organisms
Algae Eaters	39	0.01-0.18	0.05	Zooplankton; Snails; Mayfly nymphs
Zooplankton Eaters	9	0.01-0.07	0.04	Insect Larvae; Minnows
Omnivores	9	0.14-1.16	0.45	Insect Larvae and Adults; Scuds
Detritus Eaters	12	0.13-0.89	0.54	Worms; Clams; Insect Larvae
Predators	25	0.01-5.82	0.73	Insect Larvae and Adults; Frogs

In 5 specimens of the mollusc Mercenaria mercenaria collected on the southern coast of Britain (Burton and Leatherland, 1971) the levels of mercury in whole organisms without shell, ranged from 0.18 to 0.57 ppm by weight. Equivalent wet weight was 0.03 to 0.12 ppm. Values reported for various molluscs including Mercenaria which were collected on both coasts of North America (Klein and Goldberg, 1970 and Craig, 1967) are in a higher but overlapping dry weight range of 0.4 to 21 ppm mercury.

Smith (1972) analyzed 10 unwashed samples of tree and shrub tissues collected in New Haven, Connecticut. The mercury content of 6 of these samples slightly exceeded 0.5 ppm (dry weight) a level which has been suggested as the general background concentration in unmineralized areas (Shacklette, 1970). The highest value found was 1.10 ± 0.12 ppm.

Flux of Mercury in the Environment

According to Weiss, et al. (1971), the mercury content in snows deposited on the Greenland glacier indicates that substantial quantities are being mobilized over large expanses of the earth by the activities of man. They have found that the mercury, presumably removed from the atmosphere in precipitation, ranges from 35 to 75 ng/kg of water (0.035 to 0.075 ppb) during the period 800 B.C. to 1952 and from 87 to 230 ng/kg of water between 1952 and 1965. Lead analyses on the same samples also show a large increase in the concentrations of this metal in the permanent snowfield. The lead increase temporally coincides with the introduction of tetraethyl

lead to gasolines.

An examination of the environmental mercury fluxes (Table 4) suggests that the mercury burden of the atmosphere arises from the degassing of the earth's crust. There are conflicting arguments concerning the magnitude of some of the estimates in Table 4 -- see Dickson, 1972 and Patterson, et al., 1972). The implication here is that man's impact must be through an enhancement of this degassing process (e.g., agriculture, mining, construction, etc.). Gavis and Ferguson (1972) have recently estimated that as a result of human activities, about 500,000 tons of mercury have been released from the lithosphere during this century. Although this amount is about ten times that released by weathering, they show that man's contribution is but a minute fraction of the total mercury released by natural processes through the ages. Since little of the mercury that has reached the oceans has remained in solution, it is evident that the oceans have consistently been able to maintain mercury levels low enough to permit life. Gavis and Ferguson have considered the additional burden of mercury mobilized by man coupled with the natural inflow from weathering and they conclude that man has not polluted the oceans as a whole, nor is he in danger of polluting them in the near future. If this evaluation is correct, why then have we experienced environmental problems caused by mercury contamination? The reason primarily stems from the diverse and complex pathways which mercury and its compounds may travel before they attain either sufficiently high dilution, isolation, or effective removal

Table 4

Environmental Mercury Fluxes

(from Weiss, et al., 1971)

NATURAL FLOWS	Flux in Grams/Year
Continents to atmosphere	
Basis of precipitation with rain*	8.4×10^{10}
Basis of atmospheric content	4.4×10^{11}
Basis of content in Greenland Glacier	2.5×10^{10}
River transport to oceans	3.8×10^{9}
FLOWS INVOLVING MAN	
World production (1968)	8.8×10^{9}
Entry to atmosphere from fossil fuel combustion	1.6×10^{9}
Entry to atmosphere during cement manufacture	$1. \times 10^{8}$
Losses in industrial and agricultural usage	$4. \times 10^{9}$

*Average concentration of 0.2 ppb mercury according to U.S. Geological Survey

from interactions with the biosphere.

Disasters such as the Japanese and Swedish incidents are isolated cases in which a relatively concentrated mercury input was cycled over a small area. Ideally, if this input could have been uniformly diluted in the oceans, the problem would not have arisen. However, many elements and compounds resist man's attempts at dispersion: inorganic metals from coastal effluents are readily scavenged by particulate matter in the water column and/or by reaction with the sediment (Krauskopf, 1956; Goldberg, et al., 1971); organic compounds which generally exhibit low solubility in water are often found in greatest concentration in slicks at the air/sea interface (Seba and Corcoran, 1969; Szekielda, et al., 1972). It is at these interfaces that uptake into the biosphere is most likely.

From a practical standpoint, it is much more efficient to control the release of potentially harmful materials than to oppose natural accumulation processes with their accompanying misfortunes. If the additional cost must be measured against profit instead of the benefit of mankind, let it be considered "back payment" for years of indiscriminate abuse of land, air and water resources.

Analytical Methodology for Mercury Compounds

Sampling and analyses of mercury in the environment and in biological samples offer extremely challenging problems. The low concentrations of mercury in these samples, together with the volatility of mercury compounds and their tendency to adsorb on surfaces and particles, only add to the difficulties associated with

the variety of matrices. The following discussions are brief reviews of several different analytical methods. Due to the large number of publications involved, this review will only attempt to cover major works.

A bibliography prepared by the U. S. Department of the Interior (1970) lists approximately 60 papers describing various analytical techniques for determining mercury using atomic absorption, colorimetry, dithizone titration, isotope exchange, neutron activation, pyrolysis and x-ray fluorescence. General reviews of the inorganic, analytical and radio-chemistry of mercury are included in the U. S. Atomic Energy Commission publication edited by Roesmer (1970). A more recent report (Nelson, et al., 1971) also covers analytical methods with recommendations for standardization of samples and units for reporting mercury values.

The two major categories for analyses are organic mercury compounds and total mercury. Although total mercury concentration values are useful for estimating potential hazards, the special toxilogical significance of organic mercurials such as methylmercury indicates a need for differentiation and quantification of the various forms of mercury. Specific knowledge of these forms can also be used to trace the source.

a) Organic Mercury Analyses

Solvent extraction and gas chromatography have proven to be effective for the characterization and quantification of organic mercury compounds. Gas chromatography can identify methyl-, ethyl-,

and phenyl-mercuric compounds. Dimethylmercury gives no response in an electron capture detector but it can be converted into a methylmercuric halide for quantification. Inorganic mercury is not measured at all by this technique.

For the determination of mercury in a wide variety of biologic materials, a sensitivity approaching 0.001 ppm in favorable cases has been reported (Westöö, 1967). The process consists of the homogenization of a 10 gram sample of fish tissue with water in a blender, addition of concentrated hydrochloric acid and extraction of the methylmercuric chloride into benzene. Interferences are eliminated by complexing with aqueous (acidic) cysteine acetate and reextracting into a small volume of benzene. After drying, an aliquot is injected into the gas chromotograph column (Carbowax 20M on chromosorb W at 180°C).

A rapid semimicro method for methylmercury residue analysis in fish by the use of gas chromatography was developed by Grift, et al. (1971). Inorganic and dimethylmercury do not interfere in the analysis of methylmercury (average recovery 99 ± 5%). This procedure was verified by thin layer chromatography.

b) Total Mercury Analyses

For determination of total mercury (organic plus inorganic) concentration in various samples, the following 3 methods have been widely used: 1) colorimetry, 2) activation analyses by neutron radiation and 3) flameless atomic absorption spectrophotometry. Application of these techniques plus other novel approaches will

be examined.

1) Colorimetry: The classical method for determining low concentrations of mercury in biological samples is the dithizone method (Nobel, 1961), which although specific is not sensitive enough. The dithizone method (Vesterberg, Bäcklund and Sjöholm, unpublished) can briefly be described as follows: wet digestion of 50 ml of sample such as urine with sulphuric acid-nitric acid mixture; final oxidation with hydrogen peroxide; reduction with hydroxylammonium chloride; extraction of lipids, etc., with chloroform; extraction of mercury from acidic solution with dithizone in chloroform and finally the measurement of the absorbance of dithizone solution at 490 nm before and after extraction of mercury by a reversion solution (iodide plus phthalate buffer at pH 3.9). Mercury content is determined from a standard curve using samples treated in the same manner.

Kothny (1969, 1970) has described a spectrophotometric method for determining mercury which is based on the reaction of mercuric ion with iodide and crystal violet. Interferences are eliminated by adding sulfite in excess of oxidants, ethylene glycol monomethyl ether, and EDTA. A single extraction step with toluene enables the determination of 0.1 µg of mercury in a 1-cm cell with a standard spectrophotometer at 605 nm. Procedures are given for air, vegetation and urine analysis.

2) Activation Analyses: Neutron activation analysis (NAA) is a highly specific and sensitive method for the determination of mercury, provided adequate precautions are taken in aliquoting,

handling, storage and pre-irradiation processing of the samples. With proper enrichment and chemical separation, the reported limit of detection is approximately 0.1 to 0.01 ng/ml, several orders of magnitude more sensitive than colorimetry techniques (FAO, 1971).

Sjöstrand (1964) simultaneously determined mercury and arsenic in biological and organic materials by NAA. Irradiating a 0.5 g sample for 2-3 days and separating the mercury by electrolytic deposition on gold foil, resulted in a sensitivity of 0.5 ppb mercury. Kim and Silverman (1965) measured mercury levels in wheat and tobacco leaf by NAA using ^{197}Hg with a simple exchange separation. In 1967, Samsahl reported a radiochemical method for the determination of arsenic, bromime, mercury, antimony and selenium in neutron-irradiated biological material. Using an anion-exchange separation system and a ^{203}Hg tracer, 96% of the mercury was recovered with a standard deviation of ± 7%.

Pillay, et al. (1971) investigated oven-drying, freeze-drying, and oxygen plasma ashing procedures for preparing biological and environmental samples prior to NAA. Their results indicate no significant loss of inorganic radioactive mercury from the fish homogenate. The freeze-drying process was also performed on a set of fish homogenates, human brain tissues, plankton/algae and sediment/silt samples previously analyzed for their mercury content by NAA without any pre-irradiation preparation. Significant loss of mercury from all the samples except sediment/silt occurred during the freeze-drying process. Since the use of radioactive tracer indicated that there was no appreciable loss of Hg^{2+} during freeze-drying, the authors attribute the

observed losses to volatile forms of mercury. Use of a low temperature asher for pretreatment demonstrated that this technique is not suitable since up to 98% of the Hg^{2+} form of mercury in fish samples was lost after 7 hours.

Based on these studies, Pillay, et al., decided to work with wet tissue weights on solid biological samples. For plankton/algae samples and sediment/silt samples, aliquots of the sample to be analyzed were taken and dried to constant weight, thereby enabling indirect estimation of dry weight. Tracer studies showed that the errors in their pretreatment and NAA procedure were less than 15% at the 0.01 ppm level and less than 5% at the 2 ppm level of mercury in biological tissues. As was demonstrated by an intercalibration involving 8 analytical methods and 28 laboratories, discrepancies reflect the "art" involved.

3) Flameless Atomic Absorption Spectrophotometry (FAAS): Ordinary atomic absorption techniques, involving atomization of the sample solution to an aerosol which is introduced into a flame, has not found much use for trace determination of mercury. The detection limit when compared with other heavy metals is unfavorable unless tedious extraction methods are used. Capitalizing on the relatively high volatility of mercury and the extremely strong light absorption of the monoatomic mercury vapor at 253.7 mn, workers have been measuring the mercury content by flameless methods introduced by Woodson (1939). In general the sensitivity is approximately 10 ng/ml, but with careful concentration the limit is 0.2 ng/ml.

Clarke and Hermance (1938) have shown that minute amounts of metals (the sulfides of which are less soluble than cadmium sulfide) are completely removed by allowing solutions of the metal ions to filter slowly through filter paper impregnated with cadmium sulfide. Ballard and Thornton (1941) used these impregnated and preignited asbestos fiber filters to remove mercury ions from solution. The mercury sulfide so obtained was heated and the vapor absorption was measured using a spectrophotometer. In a subsequent paper, Zuehlke and Ballard (1950) described a more compact and less expensive photometer for measuring mercury vapor at levels near 0.02 µg per 150 ml of solution. A correction for interfering organic substances was reported by Ballard, et al. (1954), also using a photometer. Ling (1967, 1968) has described a sensitive, simple mercury photometer using a mercury resonance lamp as a monochromatic source (253.7 nm emission line).

Kimura and Miller (1962) were the first to use the reaction between mercury (II) and tin (II) to isolate elemental mercury from its matrix. They used a concentrating aeration procedure at room temperature following digestion of samples with sulphuric acid, hydrogen peroxide and potassium permanganate.

Lindström (1959) has discussed the losses caused by evaporation of metallic mercury from extremely dilute neutral standard solutions of mercury compounds. Shimomura, et al., (1969) suggest the use of complex-forming agents such as iodide or cyanide, or oxidants in order to prevent this loss. Other workers prepare dilute standard solutions daily (in acidic medium) which also tends to reduce volatilization.

Igoshin and Bogusevich (1968) state that after storage for 6-8 days, natural water loses mercury by adsorption to the walls of the container. In an acidic solution in the presence of permanganate, there is no such loss even after boiling. Digesting the sample with higher concentrations of permanganate-sulphuric acid has also been shown to decompose organic mercurials such as methyl- and phenyl-mercury.

Omang (1971) tested the stability of a 0.1 ppm mercury standard in 1N solutions of hydrochloric acid, nitric acid and sulphuric acid as well as a sulphuric acid-potassium permanganate mixture by means of a radioactive ^{203}Hg tracer. None of the four solutions stored in open bottles changed their activity appreciably within one week of preparation.

For mercury levels in aqueous solution, the interferences mentioned by Poluektov, et al. (1964)and Lindstedt (1970), need not be taken into consideration unless industrial waste water, possibly containing high concentrations of organic solvents, noble metals or halides other than chloride, is to be analyzed.

In FAAS analyses of mercury, the equilibrated vapor is diluted with carrier gas and sensitivity is lost. It has been shown (Uthe, Armstrong and Stainton, 1970) that with one dynamic system only 7% of available mercury may be present in the cuvette at the time of measurement. Stainton (1971) devised a syringe transfer procedure which allows the mercury vapor in equilibrium with the reducing solution to be injected into the cuvette. At the 4 µg/l level, 18%

of available mercury is in the cuvette. Sensitivity is 0.2 µg/l and precision is ± 1% at the 20 µg/l level.

Another limitation in sensitivity can be caused by high blank values. Purification of reagents is necessary to reach lower detection limits. One simple method is to add a small amount of tin (II) chloride to the reagent, and to strip the elemental mercury thus formed by bubbling air through the solution. The potassium permanganate used for digestion, however, cannot be purified in this manner.

Various workers have developed methods for trace determination of mercury in geological materials by atomic absorption spectroscopy. Pyrih and Bisque (1969) combined dithizone extraction with direct AAS in the organic layer and achieved a detection limit of 0.05 ppm mercury in rock samples. Vaughn and McCarthy (1964) describe a method in which the mercury vapor produced by direct heating of the sample was measured by atomic absorption. Deposition of mercury vapor as an amalgam and subsequent release by heat followed by light absorption measurements in the gas phase have been used by Warren, et al. (1966) and Brandenberger and Bader (1967). Hatch and Ott (1968) decomposed the rock sample by treating the rock with sulphuric acid and hydrogen peroxide in unstoppered flasks, thus only acid-soluble mercury was determined and the possibility of loss by evaporation was not eliminated. In their procedure, they passed the mercury vapor released from the sample solution by stannous sulfate (closed system) directly throughout a light absorption call. Large amounts of easily reducible elements must be absent from the sample

solution.

Another FAAS method is described by Kalb (1970) for determining the concentration of mercury in the low ppb range in water and sediment samples. The analysis is free of interferences due to the use of a silver amalgamator that separates the mercury from the other volatile materials in the sample. The mercury amalgamate is subsequently heated by an induction furnace, freeing the mercury, which is carried by an air stream into the optical path of the instrument.

Bailey and Lo (1971) used the cold vapor atomic absorption technique originally described by Hatch and Ott (1968) but modified for an open system. A Technicon Auto sampler and a peristaltic pump are used to introduce the sample and reagents. The sample size required for analysis is 7 ml of solution and the coefficients of variation calculated at the 2, 4, 6 and 8 ppb levels are 7.6, 6.1, 2.3 and 1.6% respectively. This method, in which it is possible to analyze 22 samples per hour, has been satisfactorily applied to a wide variety of samples including water, coal, oil, blood, urine, hair, fish and other foodstuffs. Comparisons with manual procedures agree within ± 0.2 ppm.

Anderson, et al. (1971) used a combustion technique with the collection of nanogram quantities of mercury on a thin film of gold. The gold is then heated at 500°C and the volatilized mercury is determined using resonance absorption of the 253.7 nm wavelength line with background correction. The detection limit is 0.001 µg of mercury and total analysis time for a tissue sample, which would normally require lengthy acid digestion periods, is less than 15

minutes. Airborne elemental mercury can also be monitored using this collecting technique.

4) Other Analytical Methods: Braman (1971) presented a new method for mercury analysis which utilizes a membrane probe and a spectral emission (253.7 nm line) detector. Mercury compounds are reduced to metallic mercury, diffused into a helium carrier gas stream through a rubber diaphragm immersed in the sample solution and then passed through a dc discharge. Extraction, preconcentration and gas chromatographic separations are avoided. Limits of detection are claimed to be 10 to 20 times lower than those of FAAS with only the requirement of converting all mercury compounds into the metallic form by reduction (except those mercury compounds which initially are able to diffuse through the membrane).

An atomic fluorescense system for the determination of nanogram quantities of mercury was described by Muscat, Vickers, and Andren (1972). This system makes use of either reduction-aeration or combustion techniques for the generation of mercury vapor and a silver amalgamator for collection of mercury prior to the final measurement. The resulting fluorescence signal was recorded and the peak height was taken as a measure of the intensity of fluorescence. The amalgamator must be cooled before additional samples can be run, so that the cycle time for the entire process was approximately 9 minutes. The described method is capable of quantitative determination of mercury in samples containing as little as 0.6 mg of mercury. Results are reported for applications to water, rock, wheat flour

and natural sediment samples. The authors also point out several attractive features which make the use of such an open system advantageous when compared to the commonly used closed system approach. With the amalgamator, nearly all the mercury vapor is injected into the fluorescent cell at the same time whereas the closed system inevitably distributes the mercury vapor over a relatively large volume. Also, the open system plus the amalgamator allows the use of a carrier gas other than air. Replacement of air by argon results in approximately a 100-fold increase in the fluorescence signal. Muscat et al., demonstrated that mercury determinations of of sediment samples by three techniques (furnace atomic fluorescence, wet digestion atomic fluorescence and wet digestion atomic absorption) yield identical results within the precision of the methods.

Hadeishi and McLaughlin (1971) describe a new type of atomic absorption spectrophotometer - one that detects trace mercury in host material, based on hyperfine structure lines in a magnetic field. This device can detect mercury at levels near 0.04 ppm in approximately one minute and no chemical separation from the host material is necessary.

A commercially available chelating resin which selectively and quantitatively collects methylmercury and inorganic forms of mercury over a pH range of 1 to 9 has been reported by Law (1971). Collected mercury, plus the noble metals, are readily eluted with acidic 5 per cent solution of thiourea and the resin can be reused for several cycles. Law also discusses the selectivity, pH effects, capacity

and elution characteristics of the resin.

Field and Laboratory Studies

It is known that mercury is strongly held by bottom sediments as well as particulate matter. To explain possible binding mechanisms, Krauskopf (1956) has suggested a) correlation or sorption on hydrated ferric oxide, b) surface sorption and/or ion-exchange with naturally occurring minerals such as clays, and c) sorption and/or chemical combination with organic material. Since these mechanisms are in turn dependent upon such environmental parameters as temperature, salinity, pH, Eh, etc., it is not surprising that the mercury content in sediments varies so greatly. Feick, Horne and Yeaple (1972) have postulated that the runoff of road deicing salt may release significant amounts of mercury from contaminated freshwater sediments in addition to being a serious contaminant itself. Since chloride ion complexes strongly with mercury, and sodium and calcium ions can compete with mercury ions for exchange sites, Feick and co-workers investigated the effect of adding sodium chloride and calcium chloride to both sandy and organic-rich freshwater sediments. In all instances, the addition of either of these salts to the water in equilibrium with the sediments, released mercury to the water. Ratios of aqueous divalent mercury to divalent mercury in the sediment increased by 2 to 5 orders of magnitude. They also found that the effect increased as the mercury burden of the sediments increased. The pH changes caused by the salt addition are possible contributors to the mercury release.

Langley (1971) used fish under controlled laboratory conditions as indicators to compare mercury methylation of sediment samples from a contaminated river. Goldfish concentrated methylmercury in their bodies and the increase over background levels was measured by gas-liquid chromatography. Results showed that different locations varied in methylating capacity by a factor of 40 and that methylation did not directly relate to mercury concentration in sediments. The rate of methylation was found to be extremely low: 1 to 3 ng Hg/ cm^2/week, suggesting that a long period would be required for mercury-contaminated sediments to purge to normal background levels.

Jernelöv (1970) investigated the turnover of mercury in aquatic ecosystems by measuring the depth of the contaminated sediment layer which results in the release of biologically formed methylmercury. In his laboratory study, mercuric chloride was added to a sediment layer from a eutrophic lake with low background levels of mercury. Fish were used to accumulate methylmercury released from the sediments since Jernelöv found that gillbreathing fishes rapidly and almost quantitatively absorb this form of mercury from the water. The uptake of mercuric ion by goldfish was studied by McKone, et al. (1971). Mercury was found to initially concentrate in the external mucus secreted by the fish. The appearance of this secretion seemed to be stimulated by the addition of mercury to the water. Goldfish exposed to 1 ppm of mercuric chloride died within 4 hours, while no outward signs of toxicity were noted in concentrations of 0.25 ppm.

The concentrations of both total mercury and methylmercury

increased with age in a study of 1 to 12 year old lake trout by Bache, Gutenmann and Lisk (1971). They also found that the proportion of methylmercury to total mercury also increased with age.

Harriss, et al. (1970) exposed a species of marine diatom and several natural freshwater phytoplankton communities to various concentrations of organomercurial fungicides. Of the four mercurials studied (phenylmercuric acetate, methylmercury dicyandiamide, diphenylmercury and N-methylmercuric tetrahydromethanohexachlorophthalimide), diphenylmercury was the least toxic. At 1 ppb of the other three mercurials, a significant reduction in photosynthesis and growth was observed. At 50 ppb, essentially all inorganic carbon uptake was stopped. They noted that the toxicity of any particular mercurial compound decreases with increasing cell concentration in lake samples in a manner similar to effects of chlorinated hydrocarbons. Nuzzi (1972) found that mercury, as phenylmercuric acetate, was inhibitory to three phytoplankton species at concentrations as low as 0.06 µg/l.

Hannan and Patouillet (1971) demonstrated that mercury has a more toxic effect on the growth rates of various algae than copper, lead and cadmium, and that mercury is much more toxic to phytoplankton than DDT. Although the experiments showed that recovery from certain pollutants did take place, the cultures inhibited by mercury were less able to recover than others. Matsumura, et al. (1971) found that phenylmercuric acetate, an organomercurial widely used as a fungicide and slimicide, is metabolized quickly by soil and aquatic microorganisms. One of the major metabolic products was identified to be dimethyl-

mercury but in no cases were any methylmercury derivatives found.

Imura, et al. (1971) studied the chemical methylation of mercuric chloride with methylcobalamin (a vitamin B_{12} analog and a known methyl donor in biological systems). Methylcobalamin was incubated with various amounts of mercuric chloride in a phosphate buffer (pH 7.0) at 37°C in the dark. A silica gel thin-layer chromatograph of a benzene extract revealed that two reaction products, dimethylmercury and methylmercuric chloride were formed in different ratios depending on the molar ratio of the reactants and the reaction times. The rate of methylation reaction was estimated by quantitative gas chromatography. Their results show that highly toxic methylmercury is easily generated from inorganic mercury in the presence of methylcobalamin.

Matson, et al. (1972) found that mercuric chloride and methyl mercuric chloride inhibited the biosynthesis of lipids, especially galactolipids and chlorophylls in photosynthetically grown freshwater algae. Mercuric chloride at concentrations of 3.5 ppm gave 50% inhibition of galactolipid biosynthesis, 98% inhibition of chlorophyll synthesis in Ankistrodesmus braunii and a slightly smaller degree of inhibition in Euglena gracilis. Actually, significant inhibition of galactolipid synthesis occurred when the mercuric chloride level was below 1 ppm. In the case of methyl mercuric chloride, a 2 ppm level inhibited 98% of chlorophyll synthesis and 85% of galactolipid synthesis. The authors postulate that the greater inhibitory effect of methylmercuric chloride may be due to the fact that methylmercuric

chloride may be due to the fact that methylmercuric chloride, being somewhat less polar than mercuric chloride, may have better permeation through the membrane lipid region to get access to the target molecules, enzymes.

Fowler (1972) fed low doses of methylmercuric chloride to female rats for 12 weeks and upon excision of the kidney, he observed the extrusion of numerous cytoplasmic masses from the kidney cells. He suggests that the in vivo metabolism of methylmercury to inorganic mercury may produce this effect and account for the proteinuria found in persons occupationally exposed to organic mercury compounds.

Recommendations for Further Work

1) Economic and Social Factors: There is a need for a detailed inventory of mercury flow and studies on the economic feasibility of recycling. Wallace, et al. (1971) suggest an accountability system for mercury and other persistent, toxic substances similar to the one used by the Atomic Energy Commission for fissionable materials.
2) Analytical Prodedures: Although the art of detection is well advanced, there is a major necessity for research into the technique of sampling, sample storage, and sample preparation. Rapid, non-destructive analyses for total mercury as well as improved methods for determining organomercurials are also needed.
3) Decontamination of Mercury-Polluted Regions: Several schemes have been proposed (See Wallace, et al., 1971, Table 19),

but as yet no single method combines maximum effectiveness with minimum cost and ecological damage.

4) Environmental Levels: Measurement and Control. Detailed studies are needed on mercury levels in atmosphere, hydrosphere and biosphere with the purpose of evaluating the amount and mechanism of transfer. Realistic standards have to be set.

5) Physiological Effects: More knowledge is required concerning the distribution, and mode of action of mercury in the body. Genetic, teratogenic and long-term effects of exposure should be investigated in greater detail.

6) Protective Agent Against Poisoning: Irreversible damage is now a likely result. One of the most urgent needs, therefore, is an antidote to block the action of mercurials, especially methylmercury.

Summary

The interconversion of mercury and mercury compounds to the highly toxic methylmercury form has been established. In addition to accidental poisoning from indescriminate use or discharge of mercurials, organic mercury compounds such as methylmercury tend to accumulate in many organisms in all environments. The results may be disasterous at any trophic level including man. There is no known agent capable of blocking the effects of methylmercury poisoning.

Our experiences with mercury, arsenic, cadmium, lead, pesticides and polychlorinated biphenyls (PCB) indicate a very basic lack of knowledge concerning man's position and interaction with various facets of our environment. Surgeon General Jesse L. Steinfeld, testifying before a Senate subcommittee, very succinctly stated the problem: ". . . knowledge is our primary need. Through basic research we need to know much more about levels of trace elements essential to health, levels which can be tolerated without health hazards, the pathogenesis of toxicity, interactions, and repair and defense mechanisms at the cellular, organ, and body level."

"The problem of the health effects of toxic metals is a legitimate area for concern," he summarizes. "In the final analysis there are no nonhazardous substances. There are only nonhazardous ways to use substances."

PART II

MERCURY LEVELS IN THE DELAWARE BAY REGION

Background and Research Aims

The most heavily populated areas in the world are along the coastal regions. Therefore, man's major point of contact with the ocean is in nearshore areas, especially estuaries, and it is in these areas where most solid and liquid pollutants are dumped. Estuaries are important to commercial fisheries since they serve as nursery grounds for larval and juvenile forms. It is estimated that about 65% of all the commercial fish and shellfish harvested in the United States consists of species that occupy estuarine areas during some phase of their life cycle (Lowman, et al., 1971).

The principle direct hazard to human health from marine pollution is through consuming fish or shellfish that have accumulated toxic materials. Shellfish in particular may also pick up and concentrate bacteria and viruses from sewage in estuaries and closed inshore waters. Other effects of marine pollution on man may be indirect, such as a reduction of his food supply (U. N. Conf., 1972). Among the pollutants that may affect the supply and quality of food are certain heavy metals such as mercury, lead and cadmium. Since mercury can quite unsuspectingly attain toxic concentrations in natural water systems, the experimental portion of this study was initiated in order to establish total mercury concentration levels in the Delaware estuarine system.

Field Sampling

The locations of the sampling sites are shown on Figure 1 and further described in the Legend. Stations 4 to 34 and S1 to S4 (depicted as black dots in Figures 1-3) were taken while onboard R/V Skimmer while samples from stations A to G, K and L, and river samples H, I, and J (all denoted by black dots with crosses) were collected from shore. Surface samples from Skimmer were obtained with a 10 liter polyethylene bucket. Deep samples were collected in plastic Van Dorn bottles set 1 meter above the bottom sediments. Polypropylene bottles (0.5 liter capacity) were used to collect the river and shore samples. All water samples were chemically fixed within 15 minutes of collection by the manner described in the next section.

Analytical Techniques

a) Reagents and Standards: All reagents were Coleman "Mercury-Free Reagents." Mercury standards were prepared daily from a stock solution of 1 µg/ml mercury which had been stablized in an aqueous acid permanganate solution. Deionized water obtained by passing tap water through an Illinois Water Treatment Duplex Deionizer cartridge system was used throughout in the preparation of standards and blanks. Water treated in this manner is reported by the manufacturer to have a resistivity of 15 megohm with less than 0.04 ppm solids. A working standard curve was established for each set of analyses and proved to be a linear function from 0 to 10 ppb of mercury. Checks on reagent blanks were also performed periodically and found never

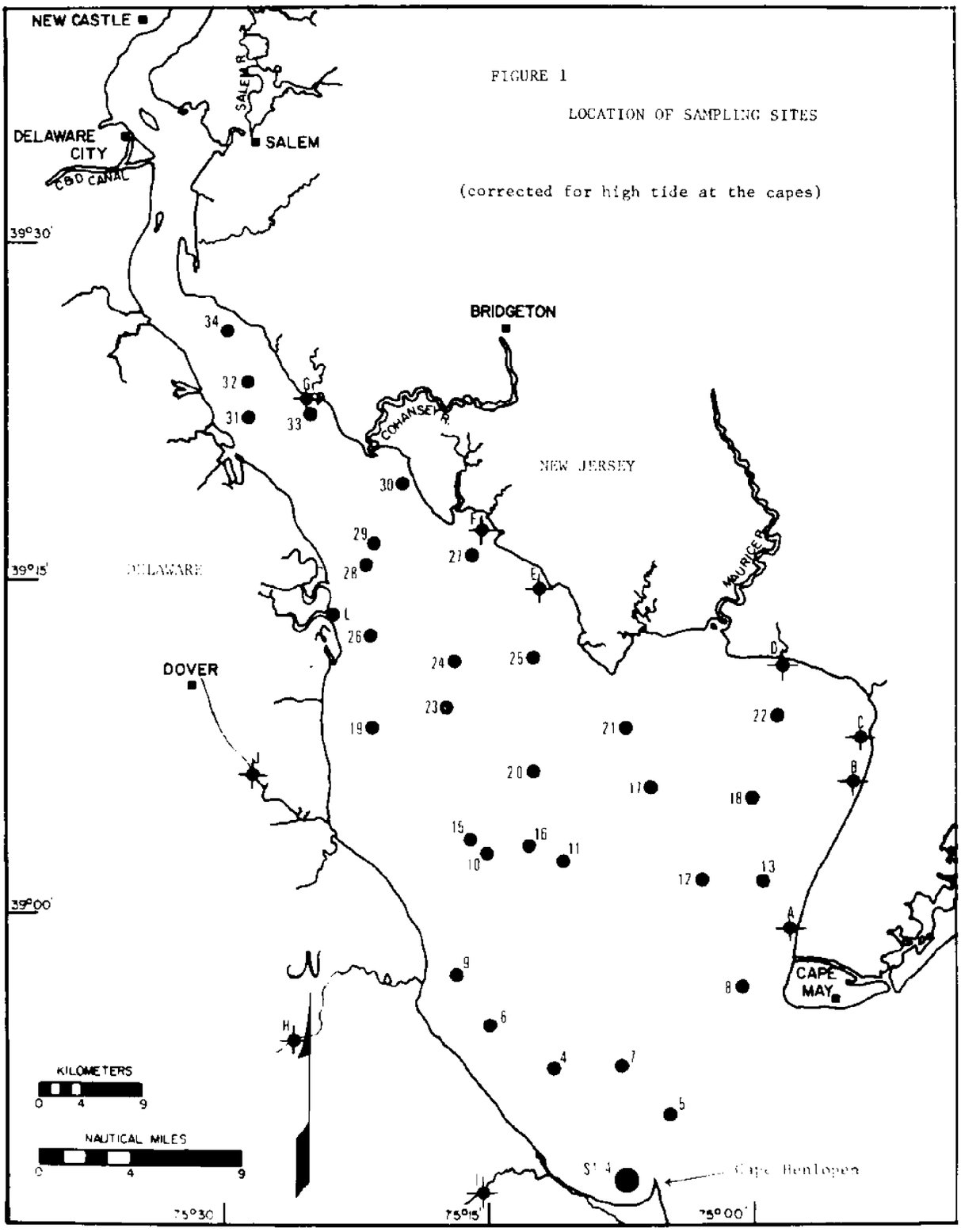


FIGURE 1

LOCATION OF SAMPLING SITES

(corrected for high tide at the capes)

to exceed 0.005 µg mercury. All values reported are corrected concentrations.

b) Sample Preparation: Water samples were prepared in duplicate by pipetting 100 ml of solution into 300 ml BOD bottles. An attempt was made to obtain a representative subsample with respect to the original amount of particulate matter present in the bucket or Van Dorn sampler. This was desirable because of the relatively high concentration of mercury associated with particulate matter. It was observed that samples taken from the same bucket but separated by a 2 to 5 minute sampling interval, could result in considerably different total mercury concentrations - some greater than 50%. However, if care was taken to maintain the particulate matter in suspension while subsampling, the reproducibility of the sampling procedure was excellent. As quickly as possible after transferring the samples to the BOD bottles, 5 ml of 4N nitric acid, 5 ml of 18N sulfuric acid and 4 drops of 5% potassium permanganate were added to oxidize the sample and stabilize the ionic mercury in solution.

c) Sample Analyses: In most cases, the samples were analyzed within 48 hours of collection, although the pretreatment described above preserves the mercury content for much longer periods (Igoshin and Bogusevich, 1968). Total mercury was measured by flameless atomic absorption with a Coleman Model MAS-50 Mercury Analyzer system. The chemistry is based on the method developed by Hatch and Ott (1968). Prior to analysis, 5 ml of hydroxylamine hydrochloride is added to each sample in order to reduce the excess permanganate.

Legend to Figure 1

JD Stations (Nos. 4-34) refer to "Jersey-Delaware Cruise" Station.

Station	Location
A	Cape May Jetty
B	Pierces Point
C	Reeds Point
D	Moors Beach
E	Fortesque
F	Nantuxent
G	Bacons Neck
H	Mispillion River
I	Broadkill River
J	St. Jones River
K	Dewey Beach (38° 38', 75° 04')
L	Port Mahon
S1	NW of Cape Henlopen (38° 52', 75° 11')
S2	" (38° 52', 75° 10')
S3	" (38° 51', 75° 09')
S4	" (38° 49', 75° 04')

Stannous chloride (5 ml of 10% solution) is then added to reduce all of the dissolved mercury to the metallic form. The mercury is vaporized and circulated by the bubbler system through an absorption cell. The 253.7 nm mercury spectral line emitted by a mercury lamp is absorbed by the vapor and the change in transmittance is detected by the phototube. Over the concentration range of 0 to 10 ppb, the limit of detection is approximately 0.01 ppb mercury.

Results and Discussion

Table 1 lists the analytical mercury determinations together with accessory sampling data (depth, date of collection, time of day, tidal stage, salinity and Secchi disc depth) when available. Water temperatures at the period of collection in January 1972 ranged from 1.9° to 6.5°C while water temperatures for the four samples taken in July 1972 averaged 21.0°C. Total mercury concentrations in the surface samples are plotted in Figure 2. Although the upper bay values are significantly smaller than those in the lower portion, no simple correlation exists between total mercury content and salinity. Mercury levels tend to decrease near the mouth of the bay and again reach a minimum value of 0.1 ppb near Dewey Beach, approximately 8 miles south of Cape Henlopen. Especially striking is the relatively high concentration (0.4 to 0.5 ppb mercury) region near the center of the bay. An expected correlation between transparency (Secchi disc measurement) and sediment load was not borne out if one assumes that total mercury content is directly related to the amount of particulate matter. Investigations in an estuarine system in Canada

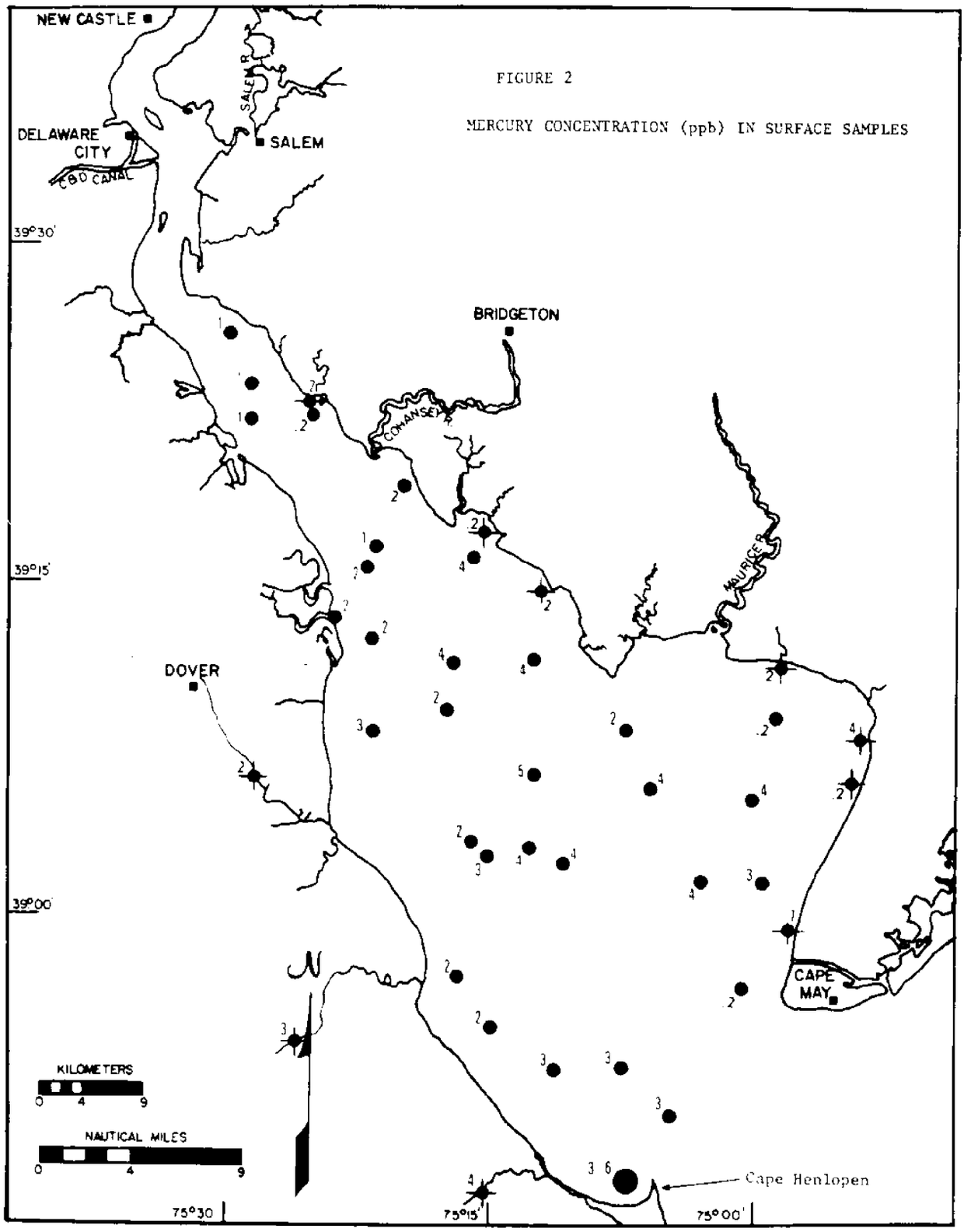


FIGURE 2

MERCURY CONCENTRATION (ppb) IN SURFACE SAMPLES

(Cranston and Buckley, 1972) have shown that the mercury content in suspended particles less than 60 μ diameter increased linearly with the log of the mean specific area of the particles. This increased adsorption effect of smaller diameter particles might explain the phenomena observed in Delaware Bay. However, neither the concentration of the suspended particulates nor the size distribution was measured in this study. Future work will attempt to determine these effects and to differentiate the total mercury concentrations in filtered and unfiltered samples from the same station.

The total mercury concentrations in deep water samples taken 1 meter from the bottom are shown in Figure 3. Including the numerical degree of uncertainty, there seems to be no significant difference between the surface and deep concentrations of total mercury. Realistically however, too little is known of the physical transport processes, sources of local pollution and the chemical properties of the bay sediments to predict vertical mercury gradients in the water column.

Other Mercury Measurements in the Delaware Bay Region

Bopp and Biggs (1972) analyzed Delaware Bay sediments near shellfish banks for contents of several trace metals including mercury. Values of the 124 surface sediment samples ranged from 0.09 ppm to 4.70 ppm with an average concentration value of 0.73 ppm mercury. Mercury levels in surface sediments of the Murderkill and St. Jones Rivers, Delaware were examined by Bopp, Lepple and Biggs (1972). For the St. Jones River, which receives sewage effluent from Dover, Delaware and in general drains a region more urbanized than the

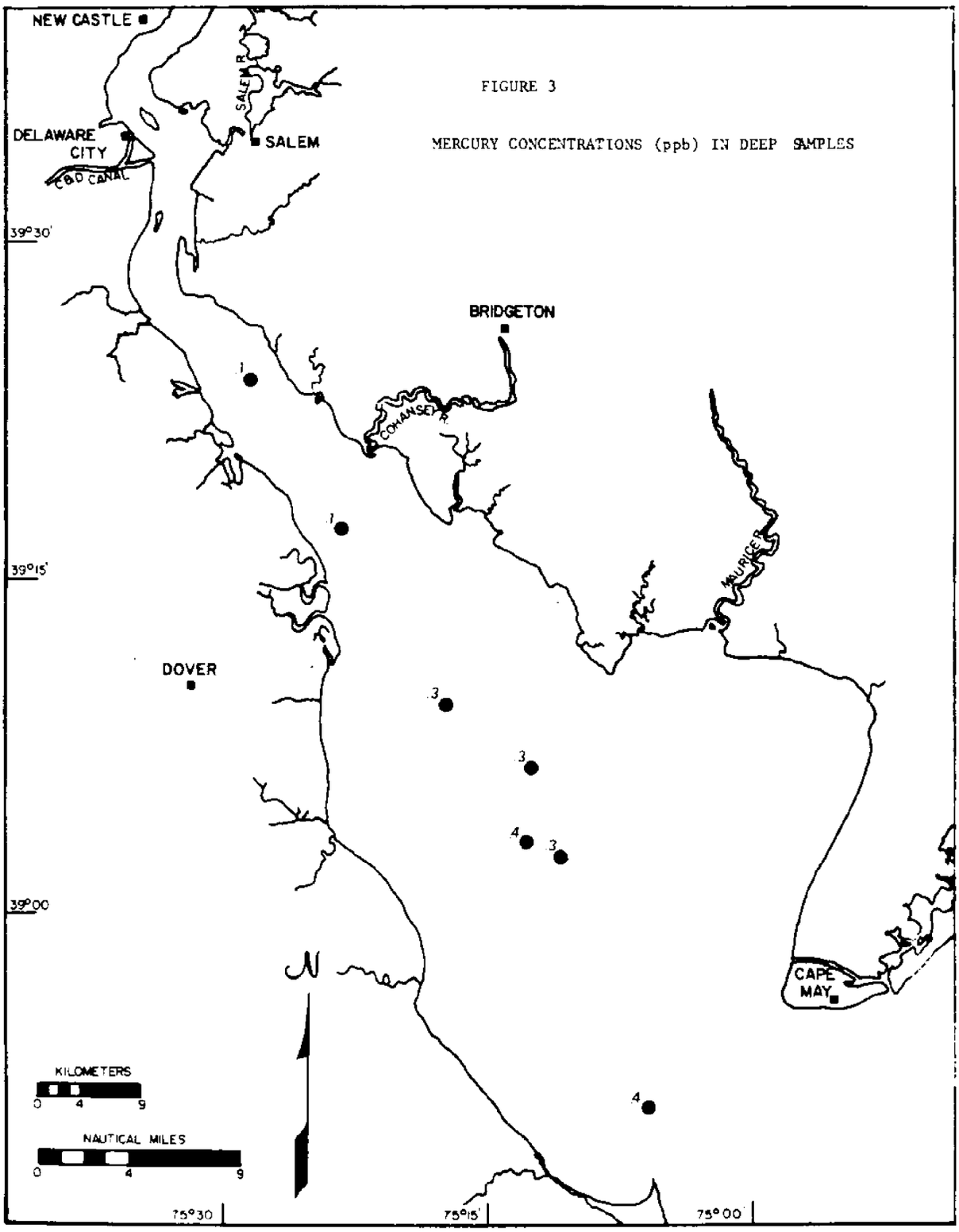


FIGURE 3

MERCURY CONCENTRATIONS (ppb) IN DEEP SAMPLES

Murderkill River, sediment levels ranged from 0.14 to 3.08 ppm mercury with an average of 0.63 ppm for 27 samples. The Murderkill River, in close proximity but as yet receiving no major industrial or municipal effluent, had sediment concentrations of mercury which ranged from 0.07 to 0.98 ppm, with an average of 0.24 ppm mercury for the 29 samples analyzed.

Biggs, Miller and Otley (1972) measured dissolved mercury levels in several watersheds in Kent and Sussex Counties, Delaware. During 1971-1972 in these counties, which have little industrial activity, the levels of mercury in rainwater appeared to exhibit a seasonal trend with the highest values (>0.5 ppb) in September-October and January-February with lower values in the spring and summer. The average time-weighted concentrations were 0.4 to 0.5 ppb mercury in rainwater. The streams in the watersheds contained approximately the same average concentration and there was a general association of higher levels in rainfall with higher levels in the stream discharge.

Heavy metals are known to be concentrated in sea slicks (Duce, et al., 1972). Szekielda, et al. (1972) investigated sea foams and surface slicks collected at frontal convergence zones in Delaware Bay. In all five samples they found that mercury was enriched by at least three orders of magnitude in comparison to average bay water (reported to be approximately 0.3 ppb, this author's study). It is difficult to speculate whether transfer through the air/sea interface by atmospherically-derived mercury or whether some type of organic/ inorganic fractionation from dissolved mercury in the water column

is primarily responsible for this enrichment. Knowledge of mercury concentrations in ambient air and in airborne particulate matter is needed in this evaluation. Reliable values of mercury levels in various biota of the Delaware Bay region are also lacking.

Concerning some other possible sources of mercury to the river-bay system, the Diamond Shamrock Corporation located at Delaware City was reported (Wallace, et al., 1971) to be discharging 29.1 lb of mercury per day (July 14, 1970), which has been reduced to 3.0 lb per day as of August 21, 1970. Also affecting the mercury levels in this region are additions of commercial chlorine bleach which can contain up to 200 ppb mercury (Jonasson, 1970) and the burning of oil and coal (Joensuu, 1971) coupled with rainout of gaseous and particulate mercury.

Environmental Assessment of the Delaware Bay Region

Sufficient data exists for mercury concentrations in bottom sediments and the water column to compare this region with other areas of the country and the world. Table 6 lists various mercury levels in bottom sediments as viewed against the natural background levels of 0.05 to 0.07 ppm mercury. Possibly with the exception of the San Francisco area which may be influenced by nearby heavy metal deposits, the reported locations should have no excessive natural mercury contributions. New Haven harbor has an average mercury concentration approximately ten times higher than the "average sediment." The fact that the mercury concentrations decrease to background levels in sediment samples a few miles distant from active effluent discharges quantifies man's influence. Similar effects are

evident in the other sets of data, although the specific indications will not be repeated here. Samples from shellfish banks in Delaware Bay (Bopp and Biggs, 1972) and the St. Jones River sediments also contain an order of magnitude more mercury than uncontaminated sediment. Urbanization and industrialization again are primary factors. This is demonstrated in a comparison of mercury and other trace metal levels in the Murderkill and St. Jones Rivers (Bopp, et al., 1972).

Table 7 presents representative mercury concentrations in natural waters. Baseline values for uncontaminated waters are given in Table 1. Delaware rainwater (Biggs, et al., 1972) contains approximately three times the amount of mercury than does uncontaminated rainwater, while the three Delaware rivers examined here (Table 5) have nearly seven times more mercury than the general level of 0.05 ppb. The mercury content of the seawater near Dewey Beach, Delaware is in agreement with the value given by Klein (1972a) in Table 1. This figure (0.10 ppb) may be representative for coastal ocean water but the average for the entire ocean should be closer to 0.03 ppb. From this perspective, the waters of the Delaware region are approximately one order of magnitude more contaminated with respect to mercury than open ocean water and less than an order of magnitude below the mercury levels attained in Minamata Bay during the outbreak of mercury poisoning. This evaluation does not constitute a clean bill of health for Delaware Bay, however. The large quantities of insufficiently-treated effluents released into the bay daily warrants careful monitoring throughout the system especially for heavy metals and

halogenated hydrocarbons. Unless adequate controls are implemented, both the quality and quantity of fish and shellfish caught in the estuary will diminish.

Table 5

Total Mercury Levels in Waters of the Delaware Bay Region

Station	Mercury Concentration* Sample (ppb)	Depth (m)	Date	Time	Tidal Stage	Salinity (%)	Secchi Depth (m)
JD 4	0.27± .03	0	1/10/72	0825	Slack	25.82	0.80
JD 5	0.29± .01	0	"	1035	Ebb	24.02	2.30
JD 5	0.35± .01	47	"	"	Ebb	29.96	--
JD 6	0.17± .02	0	1/11/72	0930	--	23.63	1.00
JD 7	0.32± .07	0	1/10/72	0930	Ebb	23.26	1.80
JD 8	0.20± .03	0	"	1240	Flood	26.20	0.70
JD 9	0.21± .01	0	1/11/72	1020	--	20.76	0.80
JD 10	0.30± .00	0	1/10/72	1545	Flood	21.24	1.50
JD 11	0.35± .05	0	"	1500	Flood	23.33	1.75
JD 11	0.29± .01	14	"	"	Flood	26.16	--
JD 12	0.39± .17	0	"	1410	Ebb	21.89	0.70
JD 13	0.30± .00	0	"	1320	Ebb	21.20	0.70
JD 15	0.20± .00	0	1/11/72	1121	--	15.00	1.10
JD 16	0.26± .15	0	"	1224	--	11.14	1.50
JD 16	0.35± .05	12	"	"	--	23.15	--
JD 17	0.36± .10	0	1/12/72	1058	Ebb	19.25	1.60
JD 18	0.40± .22	0	"	1215	Slack	17.16	0.55
JD 19	0.27± .13	0	1/11/72	1554	--	15.51	0.50
JD 20	0.50± .08	0	"	1335	--	12.84	1.40
JD 20	0.33± .03	12	"	"	--	23.42	--
JD 21	0.22± .05	0	1/12/72	1430	--	18.58	1.10
JD 22	0.23± .06	0	"	1319	Flood	14.67	0.50
JD 23	0.22± .02	0	1/11/72	1442	--	10.88	0.95
JD 23	0.27± .03	6	"	"	--	21.84	--
JD 24	0.36± .10	0	1/12/72	1639	--	11.21	1.25
JD 25	0.40± .20	0	"	1525	--	15.96	1.00
JD 26	0.21± .01	0	1/19/72	0837		14.41	0.20

Table 5 (continued)

Total Mercury Levels in Waters of the Delaware Bay Region

Station	Mercury Concentration* Sample (ppb)	Depth (m)	Date	Time	Tidal Stage	Salinity (%)	Secchi Depth (m)
JD 27	0.45± .35	0	1/12/72	1615	--	12.59	1.00
JD 28	0.15± .02	0	1/19/72	0915	--	13.06	0.20
JD 29	0.11± .01	0	"	0958	--	14.61	0.70
JD 29	0.13± .01	14	"	"	--	14.61	--
JD 30	0.20± .09	0	"	1050	--	13.16	0.60
JD 31	0.11± .01	0	"	1204	--	9.63	0.30
JD 32	0.13± .01	0	"	1228	--	10.77	0.50
JD 32	0.10± .00	11	"	"	--	10.76	--
JD 33	0.15± .00	0	"	1120	--	10.12	0.25
JD 34	0.12± .00	0	"	1313	--	8.21	0.60
JD 24	0.08± .00	0	"	1209	--	14.81	0.80
A	0.67± .17	0	1/13/72	--	--	26.67	--
B	0.18± .03	0	"	--	--	19.38	--
C	0.39± .01	0	"	--	--	17.28	--
D	0.18± .03	0	"	--	--	12.73	--
E	0.16± .05	0	"	--	--	15.06	--
F	0.18± .03	0	"	--	--	12.17	--
G	0.22± .01	0	"	--	--	8.62	--
H	0.28± .03	0.1	1/21/72	0930	Ebb	0.1	--
I	0.50± .19	0.1	"	1000	Ebb	0.1	--
J	0.21± .10	0.1	"	0900	Flood	0.5	--
K	0.10	0	"	--	Flood	--	--
L	0.24± .02	0	1/12/72	0800	--	12.25	--
S1	0.60± .18	0	7/12/72	1030	--	--	--
S2	0.56± .21	0	"	1050	--	26.00	1.50
S3	0.41± .01	0	"	1303	--	27.30	1.75
S4	0.27± .01	0	"	1528	Ebb	24.35	1.75

* Average of duplicate samples ± deviation from the mean.

Table 6

Comparison of Mercury Levels in Bottom Sediments

Location	Mercury Concentration (ppm)	Remarks	
Average Concentration in Earth's Crust	0.07		(1)
Unconsolidated Soils & Sediments	0.05		(2)
San Francisco Bay	0.02 to 2.00; avg 0.30	n = 199	(3)
New Haven Harbor (Connecticut)	0 to 2.57; avg 0.78	n = 64	(4)
La Have River and Estuary (Nova Scotia)	0.09 to 1.06; avg 0.34	n = 5	(5)
Southern California Coast	0.02 to 1.00; avg 0.34	n = 6	(6)
Delaware Bay Shellfish Banks	0.09 to 4.70; avg 0.73	n = 124	(7)
Murderkill River, Delaware	0.07 to 0.98; avg 0.24	n = 29	(8)
St. Jones River, Delaware	0.14 to 3.08; avg 0.63	n = 27	(8)

n = number of samples

References: (1) Vinogradov (1959)
(2) Klein (1972a)
(3) McCulloch, et al. (1971)
(4) Applequist, et al. (1972)
(5) Cranston and Buckley (1972)
(6) Klein and Goldberg (1970)
(7) Bopp and Biggs (1972)
(8) Bopp, et al. (1972)

Table 7

Comparison of Mercury Levels in Natural Water Systems

Location	Total Mercury Concentrations (ppb)	Remarks	
Minamata Bay, Japan	1.6 to 3.6	highly polluted	(1)
N. W. Pacific Ocean	0.06 to 0.27	highest level in deep water	(2)
English Channel	0.014 to 0.021	unfiltered	(3)
Heligoland	0.03	"	(4)
N. E. Atlantic	<0.03 to 0.020	"	(5)
E. Pacific Ocean	0.022 to 0.173	"	(6)
La Have River and Estuary	0.036 to 0.380	"	(7)
Delaware Bay	0.10 to 0.70; avg 0.28	"	(8)
Atlantic Ocean	0.10	"	(8)
Delaware Basin Rivers	0.21 to 0.50; avg 0.33	"	(8)
Delaware Streams	~0.3 to 0.7; avg 0.5	filtered	(9)
Delaware Rainwater	0.4 to 0.5; avg 0.4	"	(9)
Delaware River (Port Jervis)	<0.1	4/23/70	(10)

References:
(1) Hosohara, et al. (1961)
(2) Hosohara (1961)
(3) Burton and Leatherland (1971)
(4) Stock and Cucuel (1934)
(5) Leatherland, et al. (1971)
(6) Weiss, et al. (1972)
(7) Cranston and Buckley (1972)
(8) This report, Table 5
(9) Biggs, et al. (1972)
(10) Wallace, et al. (1971)

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