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MERCURY IN THE NATURAL ENVIRONMENT: A REVIEW OF RECENT WORK

I. R. Jonasson

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ABSTRACT

A review on mercury in the natural environment is presented to cover the literature published since the last major review which is that of James (1962). Together with the treatise by Saukov (1946) these two earlier works provide a full background on the relevant chemistry and geochemistry of mercury which is not duplicated in this report. Sections on analysis for mercury and its compounds, mercury in natural waters, aspects of pollution by mercury, mercury in soils and recent advances in the geochemistry of mercury in ores and rocks are included. A bibliography of more than three hundred published papers is included.

MERCURY IN THE NATURAL ENVIRONMENT:
A REVIEW OF RECENT WORK

GENERAL INTRODUCTION

This article on the presence of mercury in the natural environment is intended to cover the field of work since the last major review was published; i.e., that of James, 1962. His article covered specifically the geochemistry of mercury and, as he titles it, applications to geochemical prospecting. The reader is referred to James' paper for detailed discussion of the published literature up to 1961. The first treatise on mercury in the environment was published by Saukov in 1946 and is the result of an extensive compilation of data on all aspects of the subject. Together, these two review papers provide a full background on the environmental chemistry of mercury which will not be duplicated herein.

No attempt is made here to give a complete bibliography of what has appeared in the scientific literature but rather, a comprehensive selection of what are considered to be the significant contributions to current knowledge is presented.

The review is divided into sections on analysis for mercury and compounds, mercury in natural waters, aspects of pollution by mercury, and advances in the geochemistry of mercury in soils, ores and rocks.

Some references appearing in the bibliography by title are not referred to directly in the text but are included for further reading.

SECTION A

ANALYSIS FOR MERCURY

The methods of analysis for mercury are many and various. The past ten years has seen considerable development and refinement of existing techniques, such as colorimetric dithizone tests, as well as the appearance of a number of new ones. Atomic absorption spectroscopy has played a major role in many of them.

i. Classical Methods

The classical methods involving dithizone continue to be useful. An interesting study on extraction procedures for mercury in vegetation (Ward and McHugh, 1964) is available; various organometallics in water samples, such as ethylmercuric chloride and diethylmercury, were determined colorimetrically (Zamyslova *et al.*, 1968; Palalau, 1969) after permanganate oxidation and extraction into organic solvents.

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ii. Atomic Absorption Techniques

Conventional atomic absorption methods are generally favoured over colorimetric and extraction techniques. Hingle *et al.* (1967) investigated the effects of flame conditions, complexing agents, acidity, reductants and the valence state of mercury on the sensitivity of direct atomic absorption analysis. They concluded that factors which favoured generation and retention of mercury (0) in solution enhanced the signal detected from absorption of the 2537Å emission-line radiation.

More commonly reported however are methods combining extraction of mercury as dithizonate (Pyrih and Bisque, 1969) or tetraiodomercury (II) ion (Tindall, 1967) into such solvents as methyl iso-butyl ketone and aspiration of the concentrate into the flame of an atomic absorption spectrometer. The main advantage is that sensitivity of detection may be increased about two orders of magnitude and therefore allow concentrations of around 50 ppb to be determined (ppb$\equiv$1:10^9).

iii. Cold Vapour Atomic Absorption-Reduction-Aeration Methods

The methods finding most usage are aimed at overcoming lack of sensitivity suffered by conventional atomic absorption techniques and which arise because of losses of radiation-absorbing ground-state atomic mercury by excitation within the flame. Kimura and Miller (1962) adapted an existing method for the reduction of acid digested mercury samples of soil and vegetable material by tin (II) ions to concentrate mercury in a form suitable for dithizone analysis. On reduction the mercury (0) solution is flushed with a stream of air which carries mercury vapour to a trap. If however, the vapour is taken directly to a cell in the light path of an atomic absorption spectrometer then it may be detected and measured directly. This method is now widely used and is described as cold vapour atomic absorption spectrometry. One of the earliest reported uses of this reduction-aeration method is by Poluektov *et al.* (1963) where they described a sensitivity of 0.5 ppb and discussed the effects of various mineral and carboxylic acids, solvents and many cations. The prime interfering materials are selenium, tellurium, gold and platinum ions. Hatch and Ott (1968) described a similar process but with some modifications. Igoshin and Bogusevich (1968) applied the technique to determining mercury in natural water samples using a second preconcentration step involving collection of mercury on cadmium sulphide pads where the sensitivity claimed was 0.02 ppb. The method used by the Geological Survey of Canada for soils, rocks, ores and vegetable matter is such a reduction-aeration method and uses a constant volume pumping system to recirculate the mercury vapour. Sensitivity for this system (1g sample) is 5 ppb with reproducibility within ±5 per cent. Lindstedt (1970) determines mercury in biological matter by the same method. The reduction-aeration process has been coupled with other concentration techniques to further enhance sensitivity of analysis. Dall 'Aglio (1966, 1968) aerates mercury from solution onto gold covered quartz chips which are then removed for spectrographic analysis. This approach was devised to treat water samples with mercury concentrations greater than 0.02 ppb.

iv. Direct Reading Atomic Absorption Meters

Perhaps the most useful methods are those which allow direct, rapid sampling of mercury when it is present in quite low concentrations as in the atmosphere. A variety of instrumentation has been described to treat mercury in B and C horizon soils and in rocks where typical mercury concentrations may be as low as 10 ppb. The sample is heated rapidly to decompose constituent mercury compounds and the elemental vapour is passed into an atomic absorption apparatus where mercury concentrations are read directly (James and Webb, 1964; Kuznetsov *et al.*, 1965; Barringer, 1964, 1966; Hawkes and Williston, 1962; Williston, 1968; Ling, 1968). The principal shortcoming of direct reading instruments is that they are not so efficient in determining mercury accurately when organic or sulphide content of the sample is high such as is the case with humic material, vegetation or some sulphide ores. Principal interferences seem to be from organic-vapour pyrolysis products and sulphur dioxide. One piece of equipment (Barringer, 1970) is so sensitive as to allow direct monitoring of atmospheric mercury levels which are of the order of one nanogram per cubic metre. Its design also renders it free of organic interferences.

v. Preconcentration using Cadmium Sulphide and Metals

Atomic absorption analysis for mercury vapour has been the end process for a number of other published methods. The mercury content may be concentrated onto a metal by displacement reactions and then driven by heating into a cold vapour atomic absorption cell (copper wire - Brandenberger and Bader, 1967; silver screens - Hinkle and Learned, 1969; copper wire - Barakso and Tarnocai, 1970). Of relevance to the analysis of stream water samples is the work of Sutter *et al.* (1970) who measured the kinetics of autodeposition of mercury onto zinc and copper metals.

Mercury may also be concentrated onto cadmium sulphide by metathesis and the sulphide impregnated pad is heated to liberate mercury vapour in concentrated form (Monkman *et al.*, 1956; Schachter, 1966; Pappas and Rosenberg, 1966; Christie *et al.*, 1967). These techniques are best suited for natural water analysis but may also be applied to soils, air and biological materials after appropriate chemical treatments. Nanogram quantities are easily measured.

Yet another variation on atomic absorption analysis makes use of noble metals to trap mercury liberated from soils, air, soil-air and rocks. Ores and humic soils may be treated if a series of noble metal traps are used to separate the mercury from the contaminating "smokes".

The most commonly used metal is gold wire or foil (Vaughn and McCarthy, 1964; Azzaria, 1966; Azzaria and Webber, 1969; McCarthy *et al.*, 1969; Friedrich and Kulms, 1969) or gold on quartz (Vaughn, 1967); but platinum (Thilliez, 1968) and silver (McCarthy *et al.*, 1969) have also been used. All of the above methods use metal to trap mercury and then release it by heating with induction furnaces. Williston (1962, 1968), James and Webb (1964) changed the procedure slightly by measuring gas contents absorption before and after mercury was removed by gold wire.

The publications of McCarthy *et al.* (1969) and Hawkes and Williston (1962) include data on mercury levels in soil-air. Williston's method measured mercury in core holes at a metre depth while McCarthy measured mercury content of transpired soil-air at the surface.

vi. Catalytic Methods

Mercury vapour may also be detected by its catalytic effect on the rate of certain chemical reactions. Hinkle *et al.* (1965) reported an analytical procedure sensitive to 30 ppb which made use of the catalysis of reaction between nitrosobenzene and hexacyanoiron (II) ions where mercury concentration is proportional to colour intensity of the product of reaction after a fixed time interval.

vii. Vacuum U.V. Atomic Absorption

An interesting aspect of atomic absorption analysis for mercury utilizes resonance lines within the vacuum ultravoilet region of the mercury spectrum (L'vov and Khartsyzov, 1969). While the method gives nanogram sensitivity for mercury, iodine, sulphur and phosphorus, it does not yet appear to have any practical applications for exploration geochemistry.

viii. Neutron Activation Analysis

This method has been used extensively for mercury determinations in ores (Starchik *et al.*, 1968), waters and soils (Schutz and Turekian, 1965; Westermark and Sjöstrand, 1960), and biological materials (Kawakami, 1968; Kosta and Byrne, 1969; Sjöstrand, 1964). The methods are quite precise and sensitive (1 nanogram) but are slow compared with atomic absorption methods already described.

ix. Spark Source Mass Spectrometry

Mercury has been determined by spark source mass spectrometry (Tong *et al.*, 1969) which is a sensitive method of analysis. The main difficulty of the method lies in preparation of the sample for sparking. The process is time consuming. Perhaps the main advantage is that other elements may be determined simultaneously. The method may prove to be useful for the more difficult (analytically) elements such as platinum when nanogram sensitivity may be required.

x. Emission Spectrographic Analysis

This is used extensively by Russian geochemists. An excellent review of methods used in the USSR for mercury assay is available (Aidin'yan, 1964). Dall'Aglio (1966) analyzes water samples by means of a combined reduction-aeration-spectrographic method which measures mercury trapped on gold-covered quartz. He has recently extended the method to determine soil mercury contents (Dall'Aglio, 1970). Sensitivity is of the order of one nanogram. *See* also Feges and Podobnik (1969); Titov and Belobrov (1970).

xi. Reflectance Emission Spectrography

Palalau (1968) has published an unusual method based on changes of reflectance properties of a copper (I) iodide surface when mercury vapour reacts on it. The colour change varies as a function of mercury concentration and is measured in a re-emission spectrometer. The method is suitable for atmospheric sampling of low mercury concentrations.

xii. X-ray Fluorescence and Atomic Fluorescence Spectroscopy

X.R.F. methods have been in use for some time (Olson and Shell, 1960) but are not as sensitive as other spectroscopic methods. A.F.S. is a relatively new tool but has been used for mercury with good sensitivity (Vitkun *et al.*, 1970). It may find more use as instrumentation is improved.

xiii. Analysis of Organomercury Compounds: Chromatographic Methods

Because of the intense interest in mercury as a pollutant, considerable attention has been given to devising means of determining specific mercury compounds which may be present in air, soils, sludges and natural waters. It is well established (OIKOS Symposium, 1966) that alkylmercury compounds are considerably more toxic than elemental or inorganic mercury so methods to determine the former group based on gas-liquid chromatography (g.l.c.) and thin layer chromatography (t.l.c.) are well established. Westöö (1966) uses a combined g.l.c.-t.l.c. method for methylmercury compounds. Kitamura *et al.* (1966) used gas chromatography to separate and determine a range of organomercury compounds. Jensen and Jernelöv (1969) used a combined g.l.c.-mass spectrometer to determine methylmercury halides and could detect 50 picograms of mercury. Irukayama (1966) used paper chromatography to separate and analyze for a wide range of organomercury compounds present in sludges, shellfish and water. Johnson and Vickers (1970) studied organomercury compounds and their formulations by t.l.c. Bark *et al.* (1966) measured R_f values for an extensive series of toxicologically important metal ions, including mercury, by reversed phase t.l.c. on pure cellulose. All of these chromatographic methods are very sensitive.

xiv. Sample Treatment

Of more general interest and of relevance to all of the above mentioned techniques is a paper by Koksoy *et al.* (1967) which discusses the effects of predrying and storage of samples on mercury content and also discusses the effects of sample particle size on the measured mercury content after heating. Aidin'yan *et al.* (1969) also noted cross-contamination by mercury in stored rock samples and recorded the changes over five years.

xv. Summary

The literature dealing with the various methods available for the analysis of mercury and its compounds has been reviewed. It would seem that reduction-aeration methods are the most generally applicable and are therefore widely used in many fields of research. However the greatest sensitivity for mercury detection comes from specific instrumentation designed exclusively for that purpose. Atmospheric concentrations of mercury may be read directly in this way.

SECTION B

MERCURY IN NATURAL WATERS

i. Introduction

The importance of the hydrogeochemistry of mercury as a basis for exploration techniques for heavy metal orebodies is apparent from the increased interest in the earth sciences literature. Nor is interest in mercury in natural waters confined to mineral exploration. The rise of mercury as a pollutant revealed a considerable gap in fundamental knowledge of the chemistry, in a most general sense, of trace elements, including mercury, which move into and from water systems.

ii. General Aspects of Hydrogeochemistry

The roles complex ions play in the transfer of elements in the supergene zone has long been recognized (Shcherbina, 1956) and detailed studies of the behaviour of metal ions in aqueous media are published. The work of

Krauskopf (1956) on trace elements in seawater and the various works of Ahrens (1966 and references therein) on physico-chemical properties of metal ions and their simple complexes, are cases in point.

Attention has also been given to a most important aspect of metal ion chemistry, viz, that of naturally occurring chelates and their functions as sequesterers for both major and minor elements. An extensive review by Saxby (1969) covers all aspects of co-ordination geochemistry and the organometallic chemistry of the geochemical cycle. He includes discussion and reference to metals associated with carbonaceous and biological materials; porphyrins in sediments; amino acids; heterocyclics of oxygen, nitrogen and sulphur; humic and long chain organic acids. The work of Evans (1964) who investigated the dissolution of sulphide minerals of Zn, Mn, Ni, Fe, Cu and carbonates of Pb, Fe, Ca and Mn by aminoacids is of particular interest as well.

General information is also available on relationships between dissolved and suspended substances in river systems. The studies of Konovalov, Ivanova, Kolesnikova (1967) indicate the distributions of V, Mn, Co, Ni, Cu, Zn, Mo, Ag, Sn, Pb and Bi in both waters and suspensions of rivers of the European USSR as functions of the solution chemistry of these elements and of the physiographic conditions of river basins. In Canada, Levinson (1970) has recently presented similar data for uranium, boron and some base metals for the rivers in the Mackenzie drainage basin.

iii. Hydrogeochemistry of Mercury

Kraynov *et al.* (1966) give details of a more specific study of the mode of migration of certain trace elements (Zn, Cu, Hg, Li, Rb, Cs, As, Ge) in carbonate spring waters. Factors studied include effects of temperature, pH and redox potential of the systems. The authors conclude that Zn, Cu and Hg are supplied by sulphide orebodies. Waters were analyzed for carbonate, sulphate, chloride ions and attempts were made to correlate measured levels with concentrations of metal ions found. In particular, the levels of mercury were found to increase with increasing bicarbonate concentration whereas decreases in Cu and Zn concentrations were observed under similar conditions. Typically high mercury levels derived from a mercury mineralization are 10-80 ppb. These are to be compared with values of 0.02-0.07 ppb for what is considered to be normal groundwater (Wiklander, 1969; Stock and Cucuel, 1934).

Dall'Aglio (1967, 1968, 1970) used mercury analysis of natural water samples in Tuscany to help locate cinnabar deposits. In this region normal groundwater levels were 0.01-0.05 ppb Hg whereas waters from mineralized areas contained ~2 ppb Hg. Chernyayev *et al.* (1965) reported mercury levels in saline waters (0.1 g/l halide) of 3-10 ppb in background areas of the Orsk region, South Urals but up to 1,600 ppb for waters around a copper sulphide deposit. Various other trace elements such as Fe, Cu, Zn, Pb were greatly enhanced in concentration for waters near to the oxidized zone of the deposit.

Very saline waters such as those near the Permian salt deposits of the Donbas region (USSR) which contain as much as 3 g/l iodide and 200 g/l chloride do not carry much mercury (Karasik *et al.*, 1965). The mercury content decreases with increasing chloride and suggests that anionic complexes such as $[HgCl_4^{=}]$ are not so important as transporters of mercury as perhaps is $[HgCl_2]$. On the other hand the mercury content in weaker brines (1-3 g/l) is directly dependent on bicarbonate ion content (up to 400 mg/l) and also on the iodide concentration, perhaps due to $[HgI_4^{=}]$. The mercury contents found were around 10 ppb for these waters and <0.1 ppb for strong brine waters.

Bayev (1968) showed that the mercury content of stream waters intersecting dispersion aureoles from a mercury deposit (northwest Caucasus) ranged from 1-3 ppb. He noted the stream sediment contents varied according to the type of sediment (limestone, clay, etc.) and measured seasonal variations of stream-water Hg contents. Concentrations were lowest in summer and highest in winter when subsurface flow replenished the streams whereas background levels did not change seasonally. The hydrogeochemical anomalies were usually accompanied by increased sulphate and chloride ion concentrations.

The movement of mercury in the waters of hot springs may be governed by any of the aforementioned ionic factors but transport by sulphide ion (bis-sulphidomercury (II) ion) and bicarbonate ion is probably most important according to Dickson and Tunell (1968) who analyzed waters and deposits of five hot springs in the western United States. Their findings are supported by the data of Nepeina and Peshchevitskii (1968) who observed the dissolution of metacinnabar in various sulphide media.

Benes (1969) used 203-Hg to study the colloidal behaviour of trace mercury (6-200 ppb) in weak nitrate and chloride solutions over a wide range of pH (0 to 13). In solutions of pH 0 to 2 containing trace chloride, mercury exists mainly as molecular $[HgCl_2]$ and the solutions are stable with time. At pH 2 to 4 $[HgClOH]$ predominates and is strongly adsorbed onto dust particles or the container walls. The pseudocolloidal particles so formed may be either positively or negatively charged. Beyond pH 7 molecular $[Hg(OH)_2]$ predominates and is also strongly adsorbed onto surfaces such as glass or polyethylene (Benes and Rajman, 1969). However, it may be desorbed by strong acids but only if the solution is fresh. It is worth noting that Benes' data suggest methods for storing water samples which are to be analyzed for mercury. Solutions must be acidified immediately on collection or the mercury must be complexed in some other way; e.g., e.d.t.a. solutions at pH 4.5, to take advantage of the ability of mercury (II) to form very strong chelate complexes (Ahrens, 1966). Water solutions (pH 5 to 8) containing less than 500 ppb Hg tend to lose mercury to the walls of the storage container, be it glass or polyethylene, to the extent of about 70% after 5-10 days.

Shimomura *et al.* (1969) labelled mercury (II) solutions with 203-Hg and noted a slow disappearance of activity, the rate of which increased with increasing pH. The loss was reduced by addition of complexing ions such as iodide and cyanide and oxidants such as hypochlorite and permanganate; and promoted by addition of reductants like tin (II). These findings were interpreted by assuming that mercury was lost from solution as elemental mercury. Since caustic soda was used to change pH it was considered that impurity of metallic mercury in that reagent was responsible for this process. The mechanism probably goes via the rapid electron exchange reaction:

$$^{*}Hg(II) + Hg(0) \rightleftharpoons 2\,Hg(I) \qquad \text{(Sykes, 1966)}$$

when radioactive *Hg(0) will appear in solution.

The relevance of this work to the hydrogeochemistry of mercury and the formation of mercury aureoles around orebodies is worth mentioning. Saukov and Aidin'yan (1940) studied the processes by which cinnabar is oxidized and concluded that iron (III) charged waters (derived from pyrite) slowly oxidized sulphide ion to sulphate thereby freeing mercury (II) into solution. This process may be taken a step further: the presence of iron (II) ion as a reduction product opens up the possibility that it can react thus:

$$Hg(II) + Fe(II) \rightarrow Hg(I) + Fe(III)$$

and

$$2Hg(I) \rightarrow Hg(0) + Hg(II)$$

The net result of oxidation of cinnabar by ferric ions is in fact a partial reduction of mercury (II) to metallic mercury which can then diffuse out of the system to the surface. It can be seen that the process is regenerative to some extent since iron (III) reappears in solution. The rate of the overall process will depend on solution pH and nature and concentration of anions present such as chloride and these factors may in part determine the extent and intensity of the mercury anomaly subsequently measured at the surface.

Cinnabar may also be oxidized and the mercury (II) ions rendered mobile by the corrosive action of chlorine charged waters upon it. When acidic saline waters leach psilomelane deposits, chloride is oxidized by manganese (IV) to chlorine gas (Bol'shakov, 1969).

iv. Adsorption Processes

It is quite apparent that adsorption processes and surface reactions are of prime importance when the problems of the mechanisms of aquo-mercury ion migration are considered. The selected articles from the earth sciences literature already reviewed touch on these points briefly but the subject will be covered more fully in the section on mercury in soils.

However, mention should be made here of three papers which are relevant to the present discussion. Shimomura *et al.* (1969) measured the extent of adsorption of mercury (II) ions on iron (III) hydroxide both freshly precipitated and aged and observed the effects of pH and halide concentration on the processes. Since iron oxide colloids and suspensions are major constituents of natural waters and soils, the findings are of some interest. Mercury (II) is adsorbed into the oxide surfaces from solutions of relatively high pH (7, 8) (when hydroxomercury ions are present) but the formation of anionic complexes such as $[HgCl_4^{=}]$, $[HgBr_4^{=}]$ and $[HgI_4^{=}]$ inhibit the adsorption. The results indicate that mercury may be removed from solution either by cationic adsorption or coprecipitation-adsorption onto iron oxide surfaces. The implications of this study are that mercury will probably be very tightly bound to and perhaps concentrated by sediments containing high concentrations of metal oxides such as Fe(III) or Mn(IV) and therefore rendered immobile as the oxide surface ages and sinters. It may then be dispersed by stream water, especially during spring runoff, as suspended matter; cf., Dall'Aglio (1970).

The irreversible adsorption of mercury by sulphide surfaces is particularly important in concentrating mercury around sulphide deposits percolated by groundwater or into sulphide-containing soils and bog. Use has been made of the affinity of mercury for cadmium sulphide surfaces as a concentration stage prior to mercury analysis of stream water. The adsorption of mercury onto other metal sulphide surfaces is critically discussed by Phillips and Kraus (1963, 1965). The affinity of mercury for sulphur adsorption sites is also reflected by the presence of mercury in humic matter which contains organic bound sulphur either as chelates or organosulphur complexes.

Dall'Aglio (1970) measured the rate of uptake by alluvium of 203-Hg (ion) tracer in natural waters. He found that mercury is rapidly adsorbed over one hour and that the process is more probably dependent on the nature of the surface rather than on the type of mineral involved. Furthermore, his studies showed that there was no real correlation between mercury and any of the major stream-water constituents and suggest that its geochemical mobility is rather limited as a result of its rapid adsorption by alluvia. He concluded that the use of stream sediments for mercury prospecting provides a more valuable exploration tool than direct measurement of stream-water content.

v. Summary

Current trends in the hydrogeochemistry of mercury have been discussed. There is general agreement that mercury travels in water as aquo, hydroxo, halido, or bicarbonato complexes and also as adsorbed ions on particulate or colloidal materials. Stream sediment sampling is probably a useful method for exploration, particularly for cinnabar deposits.

SECTION C

MERCURY AS A POLLUTANT

i. Introduction

The current interest (1970) in the increasing problems and dangers of mercury pollution of natural waters suggests the need for a reassessment of all available information on the water chemistry of mercury. As with previous sections of this review the literature covered and quoted is considered to be representative and is not an attempt to give a complete coverage of known facts. It will, however, include aspects of geoexploration, industrial pollution, agricultural pollution, mining pollution as well as data on consequent biological hazards and control measures.

ii. Sources of Pollution: Industrial

Although mercury and its compounds have long been known to be toxic, it had not been generally recognized that hazards could arise from disposal of trace quantities of mercury. It was generally considered by industry that levels around 1 ppm were tolerable and these concentrations could readily be controlled.

The disaster of Minamata Bay, Japan, in the early fifties when some 41 people died of acute poisoning after eating mercury contaminated fish and shellfish caught in those waters, was the first instance of industrial mercury pollution. As one result, much has been written on the subject (e.g., Lofroth, 1969). One of the most comprehensive articles is that by Irukayama (1966) in which he describes the origins of the pollution, the nature of the mercury compounds involved and the slow processes leading to their detection. Up to the time of the Minamata accident what was known of the water chemistry of mercury was readily available in review form (Gmelin's Handbuch der Anorganischen Chemie, No. 34, 1960).

The trouble at Minamata Bay was found to be due to the direct discharge of methylmercuric chloride in sludge from factories producing vinylchloride and acetaldehyde where inorganic mercury compounds were used as catalysts in the production processes. Isolation of organomercury compounds from discharged waste water and shellfish (up to 85 ppm) proved the point. The muds on the bottom of Minamata Bay contained around 700 ppm mercury of which about 100 ppm was steam volatile and subsequently proved to be held as organometallics. The residual material was considered to be sulphides and inorganic mercury compounds. Once the causes of mercury poisoning were determined and suitable treatment of mercury wastes installed at the factories the levels of mercury in the shellfish dropped from 85 ppm to 10 ppm over a two year period and has remained constant for 5 years since. The mercury content of the muds remains virtually unchanged but in 1965 inorganic mercury was not considered to constitute an immediate hazard. A second outbreak of Minamata disease in Japan was reported in 1965 (Jun Ui, 1969) and once again was found to be due to acetaldehyde plants on the local rivers. Analysis of human hair by the method of Kitamura (1966) using a g.l.c.-t.l.c. technique showed a distinct correlation of mercury levels found in the long hair of the local women (up to 160 ppm) and the quantity of fish eaten. He was also able to show when the peak of mercury pollution was reached in the area by estimating rate of hair growth (mercury is present as an organo-compound bound to the sulphur of protein material of hair) and noting mercury contents of different sections of hair from the women.

In 1966 a symposium was held in Stockholm on the problems of mercury in the environment. Sweden has had a history of mercury contamination of its natural waters so this symposium aired all of the current knowledge of mercury in agriculture, industry, living organisms; mercury toxicity and current research in Sweden (to 1966) (ref. OIKOS Symposium, 1966). Potential sources of mercury pollution in Sweden are given by Henriques (1969), in which he lists some industries which use mercury in some form; e.g., sintering plants, iron and steel works, cement works, ceramics and glass industry, lime plants and slag wool industry. Recently, it has been established that chloralkali chemical plants and paper pulp works are major contributors to mercury pollution in Canada. (*See* newspaper reports in "The Ottawa Citizen" April 1-24, 1970 and article in Science News, 1970.) The same industries had also been labelled as pollution sources in Sweden (Tejning, 1967). Chloralkali plants use mercury electrodes in the production of caustic soda and chlorine from brine and discharge in this case consists of inorganic mercury. Balla and Kalman (1969) used 203-Hg tracer to detect sources of mercury leakage from these electrolysis cells and conclude that most of it escapes as vapour or droplets in the hydrogen gas evolved from the cells. The high mercury content (~200 ppb) of commercial chlorine bleach solutions also reflects these losses. Paper pulp plants use phenylmercuric acetate (PMA) as a slimicide and as a preservative in newspaper. It has proved possible to replace PMA by other slimicides free of mercury but in some countries (OIKOS Symposium, 1966) it is still used as a preservative. In Sweden an estimated 0.5 tons/year is added to the atmosphere from the burning of newspapers and paper products.

Pollution Sources: Agricultural

Agricultural sources may also contribute to mercury levels in the aquatic environment as well as directly to mercury levels in food. Mercury in agriculture is usually restricted to organomercury compounds used as antifungicides for seed treatment or plant disease control. Cereal crops such as wheat, rye, barley, oats and rice (OIKOS Symposium, 1966, p. 16; Furutani and Osajima, 1965; Kim and Silverman, 1968; Pappas and Rosenberg, 1966; Epps, 1966; Aomine and Inoue, 1967, 1969). Mercury fungicides also find use in controlling pests ravaging sugarbeet crops, apples, pears and some vegetable crops (Furutani and Osajima, 1965; OIKOS Symposium, 1966; Tong *et al.*, 1969). Among the principal fungicides used are phenylmercuric acetate and methylmercuric dicyandiamide. Compounds such as trichloromethylphenyl mercury have been developed for use as herbitoxic defoliants and prove to be very deadly (Braxton, Jr. and Lajiness, 1970).

Pollution Sources: Mining

Little information is available as to sources of pollution of natural waters within the mining industry. However, Dall'Aglio (1970) attributes some very high stream-water mercury contents (as high as 100 ppb) to mining activities around some cinnabar deposits of Tuscany. In this situation dump material and tailings probably are the sources of contamination according to Dall'Aglio.

One might expect that similar contamination of lakes and streams could arise in British Columbia where a number of cinnabar deposits are being worked. The sources of mercury from mining activities are not necessarily confined to mercury deposits. It has been shown (Sears, 1970; Sangster and Jonasson, 1970) that base metal deposits around the Great Lakes drainage basin contain as much as several hundred ppm mercury within the sphalerite and galena ores. This latter investigation by the Geological Survey of Canada of trace mercury contents of sulphide ores in Canadian mines is continuing and will cover all types of deposits. Whereas one might not generally expect extensive leaching of buried deposits by groundwater to the degree where possible contamination of streams becomes significant, the possibility becomes more probable in the case of discarded tailings dumped into lakes and streams. In this context areas such as Noranda, Kirkland Lake, Cobalt, Sudbury and Thunder Bay may already be contributing significant quantities of mercury to lakes and streams. So little research has been done along these lines that one can only speculate. It is intriguing to note that Swedish authorities such as Tejning (1967) have not even considered mercury from mineral sources as a potential polluter even in quite isolated areas where there is no associated industry, no significant drainage into lakes. Rather they tend to explain high mercury levels in fish in terms of atmospheric sources of pollution in some instances without any real foundations for that conclusion.

It is also highly probable that lake areas overlying mineralization, clay sediments or black shales which can be quite high in mercury content, up to 2 ppm (Saukov, 1946), may also contain considerable mercury in their waters. There are extensive black shale deposits in Canada which are known to contain around 1 ppm mercury (Cameron, unpubl.). An interesting paper by Warren and Delavault (1969), who measured mercury contents of some British soils, records a suggestion that there may be a possible link between high mercury content and high rates of cancer and multiple sclerosis. The mercury is thought to be of geological origin.

The next section of this review concerns biological conversions of inorganic mercury to lethal organometallic mercury and will make the point that trace quantities of mercury, no matter what the source, are potentially hazardous and cannot be ignored.

There is a great need for fundamental information concerning the migration processes by which trace elements, including mercury, move from their origins and into natural waters. Such studies would involve detailed studies of redox reactions within groundwater, soils horizons and surface waters; and on related heterogeneous interactions between these media.

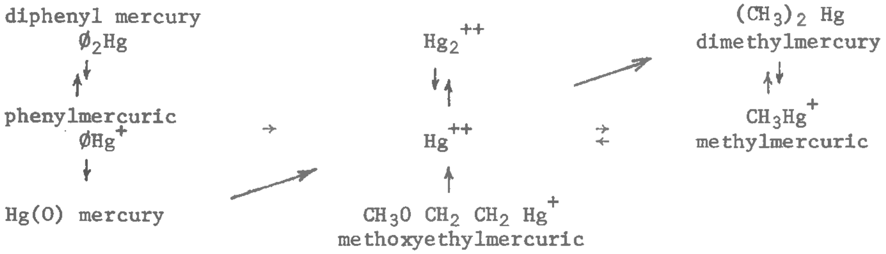
iii. Inter-relations between Inorganic Mercury and Organomercury Compounds

So far, the discussion of pollution aspects of mercury in natural waters has centred on effects resulting from introduction of organomercury compounds directly into water systems although mention has been made of introduction via mining and some industrial sources of inorganic mercury into natural waters. The latter sources were considered to be far less dangerous than the former (OIKOS Symposium, 1966; Irukayama, 1966) until recently when it was discovered that inorganic mercury compounds (e.g. mercury (II) ions) could be easily transformed into methyl- and dimethylmercury by bacterial action within bottom sludges where total mercury contained can be as high as 29 ppm (Andersson, 1967) as in Sweden or up to 700 ppm as in Minamata Bay.

The extensive work of Jernelöv (1968, 1969) in Sweden has shown that mercury is methylated by bacteria in sludge and mud under anaerobic conditions which may prevail in such media; but more recently Wood *et al.* (1968) and Wood (1970) have demonstrated that inorganic mercury may be converted to methylmercury and dimethylmercury either by the action of a methanogenic bacterium or by a purely nonenzymatic process involving reaction between mercury (II) ions and alkylcobalamins. This work has already been reviewed (Wood, 1970) from the viewpoint of pollution. It follows that mercury coming into natural water systems from any weak source may contribute significantly to the measured mercury contents of fish which can concentrate the subsequently produced methylmercury compounds by factors of up to 3,000 within their tissue.

In Sweden in particular, there has been extensive investigation of the methylmercury content of fish (Norén and Westöö, 1967; Westöö, 1967; Tejning, 1967; Johnels *et al.*, 1967). Thus waters relatively free of nutrients (sewage) with levels of 0.2 ppb in mercury could well give rise to contaminated fish containing 600 ppb mercury - a figure above what is currently considered to be the "safe" limit. The U.S. Bureau of Water Hygiene is currently considering a level of 5 ppb for drinking water. It should be recalled that Dall'Aglio (1970) showed that mercury in waters near cinnabar deposits could contain 2 ppb mercury. In more polluted waters subject to waste discharge, the bacterial mechanism would serve to compound the problems of mercury contamination by methylmercury compounds.

Jernelöv, in his series of papers, has proposed a mechanism for the hydrochemical behaviour of mercury in aquatic ecosystems. It may be summarized thus:



Full details are presented in Jernelöv's published work.

If mercury enters the water system as mercury (II) ions then it may undergo any of the conversions shown. Phenylmercuric (acetate) and methoxyethylmercuric (acetate) are typical of the pesticides used in seed treatment. There are many others (OIKOS Symposium, 1966, p. 21) and all degrade ultimately to mercury metal (Kimura and Miller, 1964) or to methylmercuric forms according to the redox and pH conditions of the environment. It is of interest to point out that dimethylmercury which Wood *et al.* (1968) considered to be the active mercury pollutant form rather than methylmercuric ion, is a volatile liquid (boiling point 96°C) and could be lost into the atmosphere from soil or water. The scheme presented is therefore very simplified. Most mercury compounds will degrade to mercury metal under the action of sunlight whether in soil or water surfaces or in the atmosphere. The chemistry of the photolysis of dimethylmercury is well documented (Wolf and Walker, 1968) and refs. therein; Gomer and Noyes, Jr., 1949). The significance of these processes is apparent when one considers that anomalous mercury found in the atmosphere may well indicate a lake or swamp source or a soil mercury anomaly.

In concluding this section on mercury as a pollutant it is reasonable to point out that other metals hitherto considered innocuous as trace elements (antimony, tellurium, selenium, bismuth, lead, arsenic, cadmium and thallium) may also prove to be dangerous polluters (Nozaki, 1966) if they too can undergo similar concentration and methylation processes leading to their enhanced accumulation in living tissue (Andersson, 1967). There is some evidence that arsenate (McBride and Wolfe, 1969) can be methylated under similar conditions as is mercury in soil or sediment to give alkylarsines (Bowen, 1966). Work is also in progress on methylation of selenium and tellurium (McBride and Wolfe, 1970). Instances of arsenic pollution in Canadian waters at Yellowknife, N.W.T. and Deloro, Ontario are well documented. Lake-bottom sediments have been shown to contain over 400 ppm arsenic in the latter case. Little is known of the extent to which oily tissue of fish can accumulate dangerous alkylarsines which may form in such systems.

iv. Control Measures

Among the control measures discussed by Jernelöv are removal of bottom sludges by pumping and dredging, treatment of the waters with various silicate precipitants and covering the lake or river bottom with enough sediments to seal in the mercury containing sludges. Unfortunately pumping and dredging operations are very expensive. They were applied in Minamata Bay where 16 million cubic metres of bottom sediment were dumped onto the shore.

Precipitation with aluminium sulphate is being tested in some Swedish lakes. Results are as yet unknown. Passage of water through ion exchange resins has also been tried in an attempt to remove mercury from waste waters (Itaya, 1969).

A Japanese article gives information on treating mercury-polluted water with ionizing radiation but this too is very expensive (and not very successful) and would probably kill off everything else in the system as a side effect (Sunada, 1969).

The main problem with mercury is that it continuously recycles from mud to water and fish so this cycle must be broken in some way. Jernelöv considers that self-purification of water systems will take such a long time that methods must be devised to hasten the processes. Wood shares this opinion.

v. Summary

Aspects of industrial, agricultural and mining pollution by mercury in waters, soils and atmosphere in terms of its inorganic and organometallic chemistry have been discussed with some emphasis on recent studies regarding chemical and biochemical interconversions which occur in nature. Corrective measures for such pollution have been reviewed. To date results have not been encouraging.

SECTION D

MERCURY IN SOILS

i. Introduction

The presence of mercury in soils covering buried sulphide orebodies is well known and much use is made of its presence by exploration geologists in their search for such deposits.

The geochemistry of mercury in the surficial environment was first presented in detail by Saukov (1946) and later extended by other Russian workers such as Ozerova and Aidin'yan (1966) who discussed mercury in the sedimentary process (*see* also Saukov *et al.*, 1962). Other review articles have since been published on the same subject; the most notable of these being that of James (1962) who covers the field over the intervening fifteen years.

Strictly speaking, all articles concerning mercury aureoles in soils should be covered in this section but most of the published work on aureoles describes only the mere presence and concentration of mercury rather than its chemistry within the soil and therefore the discussion of mercury in soils will be restricted to those publications which bear directly upon the problems of mercury geochemistry, leaving the documentation of articles on mercury aureoles and their use in mineral exploration for later discussion within this section.

Some information on the chemistry of mercury in soils and sediments has been covered in previous sections on mercury in water where mention was made of adsorption and sediment transport processes. The accumulation of mercury in river-bottom sediments, soils and sludges was discussed from the viewpoint of pollution, but the form mercury may take in all such media is little studied excepting of course the work by Jernelöv (1968) and Irukayama (1966) on organometallics. This section will also cover work on the movement of mercury in soils, sediments, entrapped air and to and from the atmosphere.

ii. Abundance of Mercury in Soil

The abundance of mercury in the crust is considered to be about 0.08 ppm (Saukov, 1946; Vinogradov, 1959). There is little information regarding the abundance of mercury in soils but Stock and Cucuel (1934) listed mercury contents for different soil types and propose a mean value of 0.07 ppm for all soils. Their data suggest that forest soils and humus are highest in mercury compared with clay soils and sands. Goldschmidt (1954) considers that mercury accumulates in upper soil horizons being derived from forest litter. A full summary on mercury abundances in soils, rocks and vegetation is presented in James' review.

iii. Forms of Mercury in Soil: Vapour

It is quite apparent from the large number of publications on the subject that a considerable amount of mercury in soils is present as elemental vapour, probably adsorbed on soil matter. A study of mercury vapour in the Tashkent earthquake zone (after 1966) showed no measurable mercury in soil-air or atmosphere (<1 ppb) but samples of clay, sand and loam were collected at 1.5-metre depths down to 5 metres. These were degassed and the adsorbed mercury vapour collected. Highest values of about 70 ppb were collected over known faults (and unknown faults) and compared with a background of about 2 ppb (Fursov, Vol'fson and Khvalovskiy, 1968). Tectonic disturbances can give rise to mercury vapour, according to Gusev *et al.* (1969), as a result of thermomechanical disintegration of cinnabar in tectonic clays. They devised laboratory experiments to ball mill cinnabar down to 3-micron particle size. Temperatures were kept to around 40°C (not allowing for localized heating) during a run. Mercury droplets were observed at the end of each experiment. This information conflicts somewhat with that presented by Karasik and Gerasimova (1967, 1969) who reported that dry mercury ores and cinnabar continuously evolve mercury vapour in the oxidized zone by the action of natural waters and below it by evaporation. They measured much higher mercury concentrations over a temperature range 20- 227°C than predicted by thermodynamic calculations. At one stage of the procedure however, the cinnabar was crushed in a laboratory shaker for 500 hours when a significant quantity of free mercury must have been produced.

The work of Aidin'yan *et al.* (1969) and Koksoy *et al.* (1967) also demonstrates the ability of rock materials to collect and lose mercury vapour when samples of differing mercury concentration are stored together. Karasik and Bol'shakov (1965) studied aureoles of mercury over the Nikitovka ore field and were able to measure mercury concentrations in both atmosphere and soil-gas over a range 0.2 to 1.6 ng/l. It is interesting to note that the measured data was the same regardless of whether the sample was collected by auger or simply dug up from 0.5 metre depth. The inference again is that the soil-air mercury is physically adsorbed onto the soil and rock material. Both soil-air mercury and atmospheric mercury were maximal over the mercury mineralization and showed the same profile as total soil mercury (5-60 ppm). Since mercury is continuously lost from the soil to the atmosphere the total mercury content depends on renewal from below which must also be continuous. Whatever the cycle in the soil proper may be, the source of all mercury, in this case at least, is vaporous.

The previously discussed findings of Jernelöv (1968) and Wood (1970) which showed that elemental mercury was an important part of the mercury cycle in soil, river bottom sediments and water, also showed that elemental mercury could be derived from mercury (I) and (II) ions as well as from organometallic compounds (*see* also Kimura and Miller, 1964).

Trost and Bisque (1970) produced an interesting study of the relative affinities of mercury vapour and mercury (II) ions for clay and humic soils.

They concluded that different sources of mercury, viz; ionic or vaporous, could be differentiated by an analysis of relative mercury contents in humic soils horizons and clay-rich horizons from the one profile. They studied adsorption of each form of mercury on the different soil types and on various clays and formed their conclusions from these data which were, essentially, that if a high ratio of mercury-organic to mercury-clay were found then the source was vapourous. If the ratio was less than 2 then the source was ionic. For these areas in Colorado and Oregon this may well be true but as Warren *et al.* (1966) rightly point out, each soil must be treated on its merits. In the areas of British Columbia where Warren worked there is a broad mercury-bearing metallogenic province. They found that soil samples taken from horizons with either a high clay content or a high organic content carried a significantly greater quantity of mercury than did the soil profile taken as a whole. In fact they concluded, for their area, that when the B and C horizons contain appreciably more mercury than do the A horizons, mineralization is nearby. Like Goldschmidt they concluded that A horizons which are rich in mercury are so because of the accumulation of decayed plant materials. A horizons may also be rich in manganese dioxide which Saukov (1946) has shown capable of trapping mercury vapour by an adsorption-oxidation process in quantities up to 70 per cent of its own weight. Koksoy and Bradshaw (1969) mapped soil mercury profiles over mercury-antimony deposits in two locations in Turkey. They found that the mercury content of A horizons was generally greater than the C horizons particularly near mineralization in the Halikoy area where soil depths were shallow. In the Ivrindi area where mineralization is overlain by compact clays, mercury content generally increases with depth reflecting the strong adsorption of all forms of mercury by the clays.

Of the clay minerals those with the largest surface areas probably are the most efficient scavengers for mercury vapour; so montmorillonite and vermiculite would be expected to be better absorbers than say kaolinite. Base metal deposits covered by clays present one of the more difficult problems to be encountered in geochemical prospecting since very few ions can pass through to the surface to form significant dispersion aureoles.

Fedorchuk (1958) presents evidence for the presence of two different forms of native mercury deriving from different sources, both of which may find their way into the soils as the parent rocks weather. Mercury directly related to the ore may contain quantities of antimony, lead, zinc, arsenic, copper and silver, whereas supergene mercury contains only trace quantities of such metals. In the case of the hypogene mercury, carbonaceous clays are the media in which droplets of mercury are held in contents up to 76 per cent by weight.

iv. Mercury Vapour in Soil-Air and Atmosphere

Mention has already been made above of some measurements of mercury concentrations of soil-air and atmosphere (Karasik and Bol'shakov, 1965; Fursov *et al.*, 1968). Karasik and Morozov (1966) determined mercury in soil, rocks and soil-gas near mud volcanoes of the Kerch-Tamin' province and found enrichments in some areas of up to 1,000 times background. Optimum depth of sampling was 0.5 to 0.7 metre for soil-gas where mercury levels ranged from 0.1 to 1.0 ng/l. In the same localities atmospheric air contained around 0.1 ng/l in some cases.

The current interest in soil-gas mercury as an exploration tool is considerable. One of the earliest applications of the technique was by Hawkes and Williston (1962) who noted that soil-gas mercury collected 1-2 metres below the surface over the mineralized fault of the Cordero mercury mine showed a similar profile to that of total soil mercury. In this instance the mineralization was some 30 feet below the surface. Provided that the covering sediments are porous to mercury vapour the technique has wide potential in detecting hidden mineralization, particularly in desert areas.

The work of Vaughn, McCarthy, Jr., and others between 1964 and 1969 has tapped this potential. They have devised a system of collection techniques to trap soil-gas mercury which has led to the mapping of mineralized veins containing gold (Cortez), mercury (Silver Cloud and Battle Mountain), and lead-zinc-silver (Coeur d'Alene). They have noted the effects of daily variations in barometric pressure, temperature and showers of rain on the soil-gas content.

At the Silver Cloud mine up to 1,300 ng mercury was collected at the surface in a two-hour period when sampling over the disseminated cinnabar deposits compared with 4-5 ng in background areas. At each locality the pattern of the mapped anomaly was similar for soil and soil-gas (both outlining the mineralization) but no direct correlation could be found for mercury contents in each medium. The authors concluded after further testing that the mercury in soil-gas was not derived from the soil but rather from below it. It should be noted that the soils tested were from B horizons. If the observations of Trost and Bisque (1970) are valid then one might expect that a significant correlation for soil-gas and humic horizon mercury would be measurable. The soil-gas mercury is transferred to the atmosphere through the A horizons so perhaps sufficient is collected to enable some kind of averaged equilibrium to be set up. McCarthy *et al.* also detected mercury in the atmosphere at levels of up to 1,000 feet above the surface and showed that optimum height for such measurements was around 200 feet. Typical atmosphere levels over two mercury mines were 10-20 times background, and over porphyry copper deposits levels were 5-10 times background.

Barringer (1964, 1966, 1970), whose instrumentation for direct measurement of atmospheric mercury has been previously described in this report, measured atmospheric levels of mercury in various provinces and territories of Canada and considered the method to have great potential in exploration and pollution studies. Unfortunately little of the work of his group has been published to date.

Weiss (1970) has devised a technique for collecting dust particles from the air by means of screens of nylon filaments. Among the many elements he analyzes for is mercury. In the vicinity of mineralization the dust particles hold higher levels of mercury than background. By sampling at less than 200 feet from aircraft anomalous areas may be outlined for further exploration. The form of mercury may be either adsorbed vapour or particulate sulphides.

v. Mercury in Soils: Nonvapour Forms

The most thorough study of mercury in soils is that of Andersson (1967). He is working on a program designed to give data on the average contents of Swedish soils in both cultivated and uncultivated areas and to determine the extent of variations from these average values. This information is vital in determining whether pollution exists and if so, its degree of severity. His research also involved a study of the absorption of mercury ions by clay and humus and losses of mercury from pot tests. The radioisotope, 203-Hg, was used in all of these experiments. Andersson obtained an average value of 60.1 ppb from 273 soil samples with a range of 4 ppb to 992 ppb. Variations are less in cultivated soils because the extremes are smoothed out. He concludes that a high humus content is needed for the mercury content to exceed 150 ppb assuming no previous pollution, say from seed dressing. Andersson lists other factors which cause variations in soil content: pH due to liming of cultivated soils; varying rates of breakdown of humic matter; and differences in hydrological and drainage conditions of the land. In certain parts of the country variations are noted which may be ascribed to geological circumstances in some cases and to atmospheric pollution from smelters in others. (See for example Johnels *et al.*, 1967). The proximity of cities where soot and smoke are discharged also has an effect on the measured levels. Andersson notes that generally over Sweden mercury is distributed in the topsoil at five to ten times the concentrations of the subsoils. He suggests the reasons for this circumstance involved vegetable decay and absorption from the atmosphere; both gaseous and from rain water.

If one considers vaporous mineral sources and remembers that alkylcobalamins may convert inorganic mercury (ions) to organometallics which may preferentially be held in humic horizons, then two more accumulative mechanisms may be added to those given by Andersson. He also finds that in some profiles the influences of groundwater may cause mercury ions to rise to the upper horizons by capillary action.

vi. Mercury (II) Ion-Humate Complexes

One of the more interesting aspects of his study concerns the distribution of mercury ions between the phases in organic matter - water and mineral matter - water systems at different pH. Mercury was added to these mixtures as 203-mercury (II) chloride. For the system organic matter-water the mobility of mercury (II) ions is heavily dependent on pH. Between pH 3-6 mercury is fixed to the humus. In acid solution the complexes presumably do not form to any great extent whereas mobility at high pH reflects the degree of dissolution of humic matter, thereby taking mercury into solution. It turns out that the amount of "dissolved" mercury is directly dependent on the amount of easily soluble humic matter. This data leads to the conclusion that all the original mercury (II) ions in the system were converted to mercury-humate complexes. The capacity of the humates for mercury (II) ions appears to be around 2.5 mg/g humus and added mercury in excess of this amount leads to the presence of free mercury (II) ions in the system. For further information on similar mercury humate systems *see* Mekhonina (1969).

vii. Mercury (II) Ions and Mineral Soils

In the case of the mineral matter-water system the maximum fixation of mercury to solids takes place at pH 7.5-8.0 which corresponds to the pH at which mercury (II) is completely converted to $[Hg(OH)_2]$ molecules from $[HgOH^+]$ ions. Adsorption of these species onto ion exchange sites of clay minerals and by hydrated oxides is the most likely mechanism.

viii. Modes of Adsorption

Mercury is more easily washed free from mineral soils than humic matter indicating perhaps that the binding mechanisms are somewhat different. Humates contain sulphur sites upon which mercury may adsorb very strongly. The affinity of mercury for sulphur adsorption sites is well known and is reflected by the presence of mercury in black shales of Precambrian age (Cameron, 1970) and ores which have obviously undergone some metamorphosis. If mercury containing shale is heated not all of the mercury comes off below 400°C. Fedorchuk (1961) reported that mercury enters pyrite in shales and heating at 450°C for eight hours does not remove it. Some of his samples retained 1 ppm of mercury. Mercury present as simple sulphides is lost quite quickly at 200-300°C (Koksoy and Bradshaw, 1969). The immediate inference is that in shales, some ores, probably bituminous coals (Kashkay and Nasibov, 1968), and humus matter some mercury is not present as simple sulphides but as covalently bonded sulpho-organometallic compounds. Further evidence of the thermal stability of such compounds is afforded by the observation by Noren and Westöö (1967) that frying or boiling fish removes no organomercury at all. Irukayama (1966) lists a number of sulphur containing complexes such as $CH_3.Hg.S.CH_3$ which are present in fish and shellfish.

ix. Adsorption of Mercury (II) Ions in Clays

Trost and Bisque (1970) noted in their study of uptake of mercury vapour and mercury (II) ions by clays and humic soil that the type of clay did not seem to influence the degree of adsorption of ions. Since they studied montmorillonite, illite and kaolinite-type clays, this must be regarded as an unusual observation considering the vast differences in relative surface areas of these clays. One may conclude that most adsorption sites, in say montmorillonite, were blocked in some way, perhaps by iron ions. The work of Aomine *et al.* (1967-69) discussed the retention of phenylmercuric ions by soils high in clays. They observed that the rate of leaching of mercury through profiles was related to clay content and type. Kimura and Miller (1964) demonstrated that slow breakdown of phenylmercuric acetate (PMA), ethylmercuric compounds and methylmercuric compounds in soils yielded mercury (II) ions and mercury vapours. PMA was comparatively stable (<20% loss) but EMA and MMA lost 30-50 per cent of the original material after 50 days. EMA disappeared mainly as mercury vapour but MMA was lost unchanged. Thus the work of Aomine *et al.* (1967-69) probably involves primarily phenylmercuric cations and discussion of the adsorptive properties of these ions is not clouded by the presence of significant mercury (II) ion. These authors studied adsorption of PMA into soils containing up to 30 per cent montmorillonite, illite, allophane or kaolinite and observed considerable differences in adsorption capacity within the various soils. The adsorption in montmorillonite soils was very high (0.5 m-mol/g) and was about twice that for allophane and about fifty times that for kaolinite. Even allowing for surface area effects the adsorption per area is still greater for montmorillonite than for the others. It was concluded that the mercury was largely held in interlayer sites as a monolayer in montmorillonite. Leaching with water removes little mercury. However allophane and kaolinite lost all of their mercury on leaching with water. Differential thermograms show that the adsorbed PM ions are lost at about 200°C from montmorillonite clays.

It may be inferred from this work that clays can play a key role in collecting and retaining mercury ions and that the type of clay is particularly important in determining what may be a background level for mercury in a soil type. One interesting feature of this work was that deferrated clays adsorbed more mercury than did untreated clays. Adsorption for each type of clay was maximal at pH 6.

The work of Benes (1969) and Benes and Rajman (1969) on adsorption of trace mercury (II) ions onto silicate surfaces, dust particles and plastic material has been discussed in a previous section. The findings are equally relevant to this discussion on the uptake of mercury ions by soil colloids.

x. Attempts to Determine Mercury Forms in Soil

The approach to this problem has been a simple one. Barren soils were loaded with mixtures of known inorganic mercury compounds which may be expected to be present in soils and the mixtures heated slowly to recorded temperatures thereby driving off all the mercury compounds successively as they decomposed. Koksoy *et al.* (1967) employed this technique with added elemental mercury, mercury (II) oxide, mercury (II) sulphide, mercury (II) chloride. Their objective was to run known mixtures and record the temperature of mercury extraction data and compare these with data from field samples. On this basis it is expected that elemental mercury would be totally lost at near 120°C but more stable species like the oxide and sulphide did not begin to decompose until 270°C and 210°C respectively. This procedure is best suited to rock samples where such compounds may well be present but in soils the spectrum of possible mercury compounds will be far wider. A multitude of alkyl and aryl mercurics of differing volatilities and decomposition temperatures would spread across the range of temperature under study. Adsorbed or occluded ions, atoms or complexes such as humates would also obscure the analysis and unless one species was suspected to predominate (say, mercury (II) chloride in areas affected by saline groundwaters) it would be very difficult to decide just which compounds were contributing to the measured mercury. The high thermal stability of Hg-S bonds in various compounds has already been referred to in this and other sections.

One other approach has been to try selective extractants on soils containing mercury. Dvornikov *et al.* (1963) assumed the presence of the same group of compounds as did Koksoy *et al.* (1967). They outlined an extraction procedure designed to separate chlorides, oxide, sulphide, metal and organics. Unfortunately the scheme was greatly over simplified and high degrees of cross-contamination were probable. An anonymous critique (1966) was subsequently published which pointed out the shortcomings of the separation scheme quite neatly. Shcherbakov *et al.* (1970) have recently published new data on mercury in coal. Preliminary studies (Jonasson, 1970 unpubl.) in the Geological Survey's laboratories involving a more sophisticated separation program for mercury in humic and soil materials, show that for humus samples about 15 per cent total mercury was lost as noncondensable volatiles from boiling water and a further 5 per cent could be trapped as steam volatiles. The remainder stayed with the solids (70 per cent after 5 hours of slow Soxhlet extraction) and with the aqueous extract (10 per cent). The total mercury content of this particular sample was around 220 ppm. It was taken from gaps in rocks overlying mineralized veins containing cinnabar. For comparison, the B horizon soil (also containing some organic matter) contained less than 10 ppm mercury.

While these results are rather sparse in information they do at least show that a high percentage of the mercury present in humus above an allegedly gaseous supply is firmly fixed to the organics. The noncondensables may well be elemental mercury and some low boiling organometallics. Various other solvents and extracts have been selected to enable specific separation of particular groups of compounds.

xi. Mercury in Snow, Ice and Permafrost

While snow, ice and permafrost can hardly be described as soils, it is of interest to consider whether mercury, which moves as a vapour (and ions) through soil, can permeate ice in the same way. There is little information in the literature to support such a contention but indications are that it will. There is one publication, that of Lehnert-Thiel and Vohryzka (1968), which discusses mercury aureoles in permafrost areas of East Greenland around a tetrahedrite-galena-sphalerite deposit. In permafrost then, mercury can move around sufficiently to produce measurable dispersion aureoles. Pitul'ko (1969) describes geochemical aureoles of lead, zinc, yttrium, copper, niobium, zirconium and some other elements around rare-metal deposits and notes that the mobility of different ions may change with depth of sample point. For example, lead is more mobile than niobium near the surface but the converse is true at depths of 0.8 m.

How mercury may behave at different depths considering the number of forms it can take is an interesting question. The problem as to how mercury aureoles in permafrost (or any other aureole) may be replenished is also intriguing, assuming of course that the mineralization does not outcrop into the active zone. Some clues may be provided as in Piguzova (1965) where the author described movement of groundwaters beneath permafrost landscape. Some other elements whose aureoles in permafrost have been mapped include copper, (Allan and Hornbrook, 1970) and molybdenum (Kovalevsky, 1969).

Boyle (1965 and refs. therein) has looked at heavy metal aureoles around lead-zinc-silver deposits at Keno Hill, Yukon Territory, which is in a region of discontinuous permafrost.

The ability of ice and snow to trap metal ions (or vapours?) is apparent from Boyle's study (Boyle, 1960) of native silver and gold occurrences in ice in the Yukon. Kolotov, Kiseleva and Rubeykin (1965) have measured trace metal contents of snow (zinc, copper and lead) 10 cm above soil and across a tin deposit. They found a distinct increase in concentration of metals immediately above the vein. An article by Karavayev *et al.* (1965) described the presence of a large number of volatile organic acids around a weathered coal deposit in permafrost. These acids would normally be lost to the atmosphere except for the cold-trap effect of the permafrost. One might presume that volatile mercury may be trapped and accumulated in like fashion. It is well known from the chemical literature that some redox reactions may occur in ice with little effect on rate by the change to a solid medium. The electron exchange reaction between iron (II) and iron (III) aquo-ions is a good example. Here, the oxidation-reduction processes go via the hydrogen bonded structure of the ice with exchange occurring over unusually long distances (100Å). The mechanism is akin to that which allows hydrogen and hydroxylions such high mobilities through aqueous solutions (Horne, 1963).

xii. Summary

The chemistry of mercury in soils, soil-air and atmosphere has been discussed with the emphasis on forms mercury may take when it is retained by soil organics and soil minerals. The possibility that mercury may be accumulated in snow and permafrost was also discussed.

SECTION E

MERCURY AUREOLES AND EXPLORATION

This section covers very briefly the literature concerning mercury dispersion aureoles and the types of mineralization sought; mercury ore deposits; trace mercury occurrences in rocks and mercury-metal associations in various types of ore deposits. Since this review is mainly concerned with mercury in the surficial environment no formal discussion is made of the above mentioned topics. The relevant literature is included in the Bibliography.

Mercury aureoles have been located around mineralization of many types and are associated with many metals. Among the metals sought using mercury dispersion aureoles are boron, nickel, copper, zinc, arsenic, selenium, strontium, molybdenum, palladium, silver, cadmium, tin, antimony, tellurium, barium, platinum, gold, mercury, thallium, lead, bismuth. The references listed contain information on all of these elements.

SECTION F

BIBLIOGRAPHY

References are listed alphabetically. The lists include all publications referred to in the text and a considerable number that are not so described but which are nevertheless considered to be pertinent contributions to this review of mercury in the natural environment. Many of the latter provide ancillary information relevant to the general chemistry of mercury, such as stability constant data, rate of reaction parameters, thermodynamic functions and adsorption mechanisms. Others provide a comprehensive selection of references published since 1961 which describe advances made in the use of trace mercury aureoles in rock, soils and orebodies as an exploration tool to aid in the search for economic mineralization.

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