

Literature study concerning mercury and arsenic
distribution in petroleum and geothermal
systems

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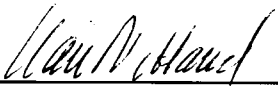
To develop a bibliography relevant to understanding the origin of Hg and As in petroleum by doing literature searches and by personal communications at a production geochemistry conference.

Key-words:

Mercury, arsenic, natural gas, condensate, petroleum

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Summary

Mercury and arsenic are known to be present in many natural gas and oil reservoirs. Their presence has both technological and environmental consequences. Oil companies are applying methods of removing these metals from their products. However, the understanding of the geological and geochemical factors that give rise to high levels of these toxic metals needs to be improved. Knowledge of these factors would benefit exploration and production efforts.

Very costly and lengthy shutdowns have occurred in cases such as those at Skikda, Algeria, and Pecos Slope, New Mexico due to mercury and arsenic respectively. The occurrence of mercury in coal used as fuel in hydrothermal power plants has been the subject of recent investigations related to environmental concerns. In the USA alone, it is estimated that 170 tons of mercury are introduced into the atmosphere each year.

In this study, special emphasis has been placed on the literature which casts light on the geological, geochemical and geomicrobial factors that affect the presence of Hg and As in petroleum.

The primary supply of metals for ore mineralisation are linked to the mechanisms of seafloor spreading (plate tectonics) and igneous provinces (rising mantle plumes/volcanism). These events bring the chalcophilic elements (Cu, Zn, As, Hg etc.) along with S from the interior of the earth.

Volcanic activity could introduce material rich in mercury into the petroleum source rock. The high levels of Hg in the gas produced from the Rotliegend Sandstone in North Germany (700 to 4400 $\mu\text{g}/\text{m}^3$) are believed to be due to the underlying Volcanite. Sulphide mineralisation of fractures related to tectonic plate subduction could provide detrital material rich in Hg to new basins where petroleum source rocks are being formed. The example of California cinnabar mineralisation is referred to herein. Hydrothermal activity below sedimentary basins or the intrusion of basalt into shale were also seen to be potential sources of Hg and As.

Much attention was given in this study to the geomicrobiology literature. Microbes are known to be involved in processing of the organic matter where petroleum source rocks are formed. It is noteworthy that the As and Hg species found in natural gas and condensates are also the species formed when microorganisms attempt to detoxify the sedimentary environment containing minerals of these metals.

1 Introduction

Mercury is found in trace concentrations in all natural gas and in the air we breathe. However, it was not until 1973, that the petroleum industry recognised the serious operational problems caused by mercury. At this time, a catastrophic failure occurred at the Skikda LNG Plant in Algeria. This resulted from mercury corrosion in four spiral wound aluminium heat exchangers. The failure resulted in 14 months of plant downtime (Bingham 1989).

Brazed aluminium plate fin heat exchangers are the predominant choice for cryogenic service. Aluminium is used because of its brazeability, excellent mechanical properties at cold temperatures, and superior heat transfer characteristics. Mercury corrosion is experienced with other metals as well eg. copper alloys (Lund 1996).

After the Skikda failure, a review of the Groningen field in Holland determined similar corrosion attacks within the gas gathering system. Mercury, with concentrations ranging from $0.001 \mu\text{g}/\text{m}^3$ to as high as $180 \mu\text{g}/\text{m}^3$, was the cause of the Groningen problem.

Since this time, knowledge of the mechanism behind mercury corrosion, techniques for analysis of mercury and methods for removal of mercury have increased substantially. However, not much data showing the variation of mercury in petroleum from different parts of the world has as yet been made public. The geological and geochemical factors that give rise to the occurrence of mercury are presently not understood. This literature survey is a first step in trying to get some understanding of this relationship.

Mercury contamination in the environment due to the burning of coal in hydrothermal power plants has led to research using advanced techniques such as EXAFS and XANES in order to understand the nature of mercury in coals (Gaffney 1997). Blanchard and Roberson 1997, state that using a typical $200 \text{ ng}/\text{g}$ mercury concentration in coal, the potential exists for 170 tons of mercury to be introduced into the environment each year in the USA alone.

It appears that the six month shutdown of 600 natural gas wells in Chaves County, Southeast New Mexico, USA, played a large role in making the oil industry aware of the occurrence of arsenic in petroleum (Slaton 1989). Concern and interest for arsenic is related more to the health and environmental hazard aspect. Information and data on arsenic is even more sparse than that on mercury.

2 The Origin Of Mercury and arsenic in sedimentary organic matter

2.1 Hydrothermal origin of metal sulfides

The theory of plate tectonics suggests that continents are continually in motion. As seen in Figure 1, large scale convection of the upper mantle drives plates across the surface



Figure 1. Cross section of the interior of the earth taken from Siever 1983.

of the earth and causes continents to drift (Siever 1983). This theory tidily accounts for the slow, steady volcanic activity that occurs at mid-ocean ridges (where new ocean

crust is born) and near subduction zones (where old, dense sections of the ocean floor sink back into the earth's hot interior). It can however not explain the abrupt outbursts necessary to create large igneous provinces. Coffin and Eldholm 1993, summarise the presently held view that deep rooted, narrow plumes of warmer than average material rise episodically through the mantle. See Figure 2. When it reaches the base of the lithosphere, a plume decompresses and partially melts, producing an upwelling of magma and a long-lasting locus of volcanic activity known as a hot spot. Some of the magma may erupt as a tremendous flood of lava. Unlike the slow, steady drifting of continents and the spreading of the mid-ocean ridges, the surfacing of mantle plumes takes place in an erratic and episodic manner.

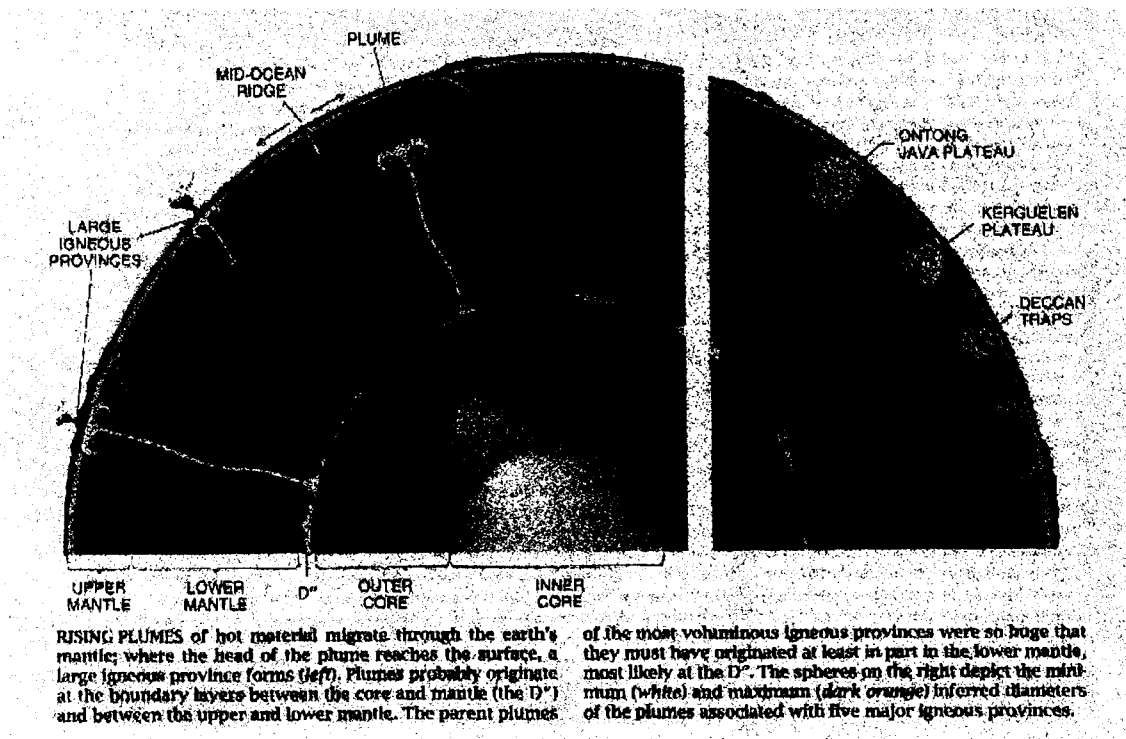


Figure 2. Illustrating how the igneous provinces are formed. This process also brings siderophilic elements and sulfur from where they are trapped in the interior of the earth. Taken from Coffin and Eldholm 1993.

The primary supply of metals for ore mineralization on the earth is linked to these two mechanisms of sea floor spreading (plate tectonics) and igneous provinces (rising mantle plumes). The chalcophilic, or sulfur-loving metals such as copper, zinc, arsenic, mercury, along with volatile elements such as chlorine and sulfur are believed to be trapped deep within the interior of the earth between the siderophilic core and the mantle (Brimhall 1991). Occasionally, these ore elements ascend toward the surface where they become minable metals.

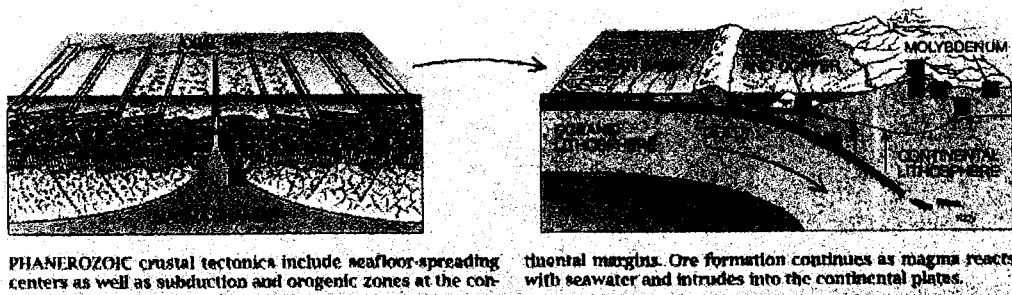


Figure 3. Illustrating two of the main mechanisms of ore formation, namely, where plates are created or subducted.

An example of the Phanerozoic supracrustal era of ore deposition is shown in Figure 3. Large convection engines divided the lithosphere into vast mobile plates. Most depositions of ores occurs at the margins of these plates, at the points where they are created or deformed and consumed. This is shown schematically in Figure 3.

However, at these points of subduction, one also finds an accumulation of organic matter. This is illustrated in Figure 4. Volcanic activity in this figure could supply Hg together with the ash settling out in the basin where organic matter is deposited.

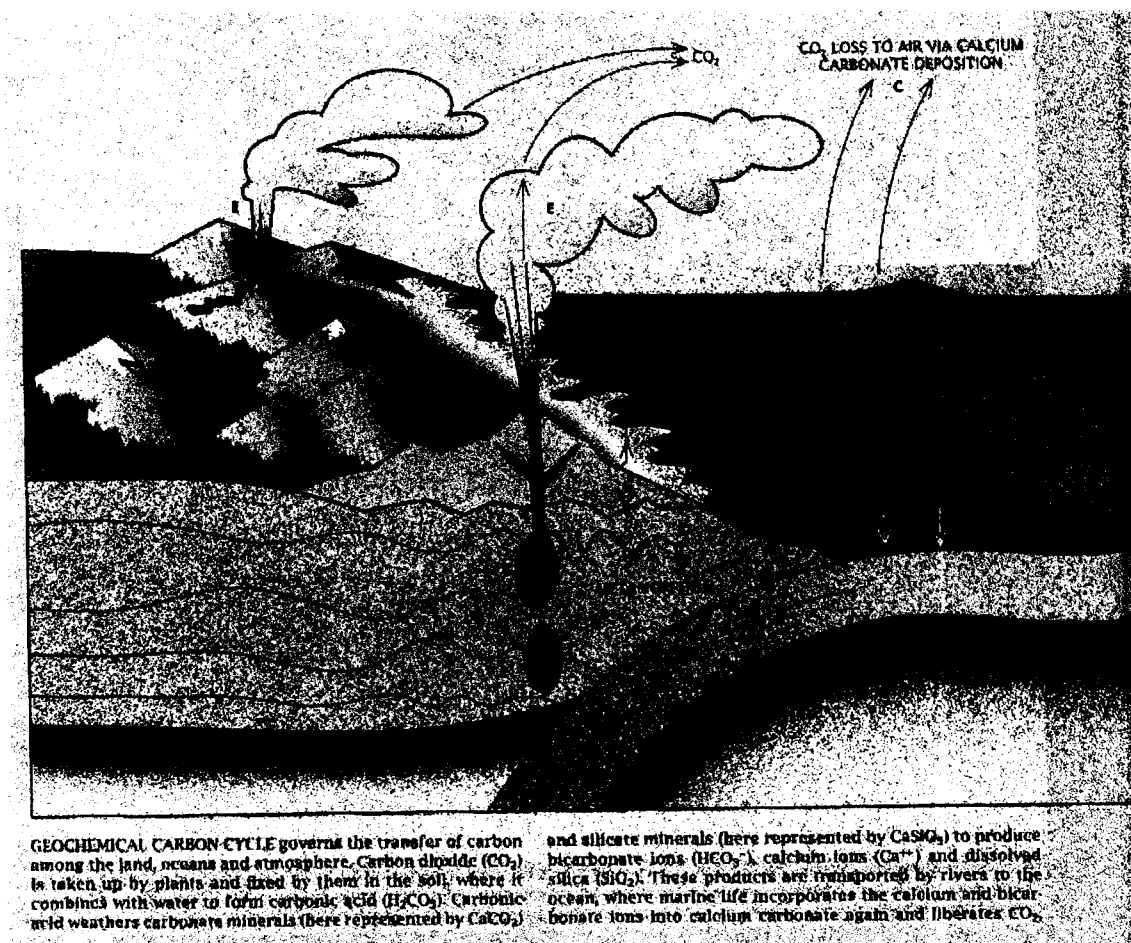
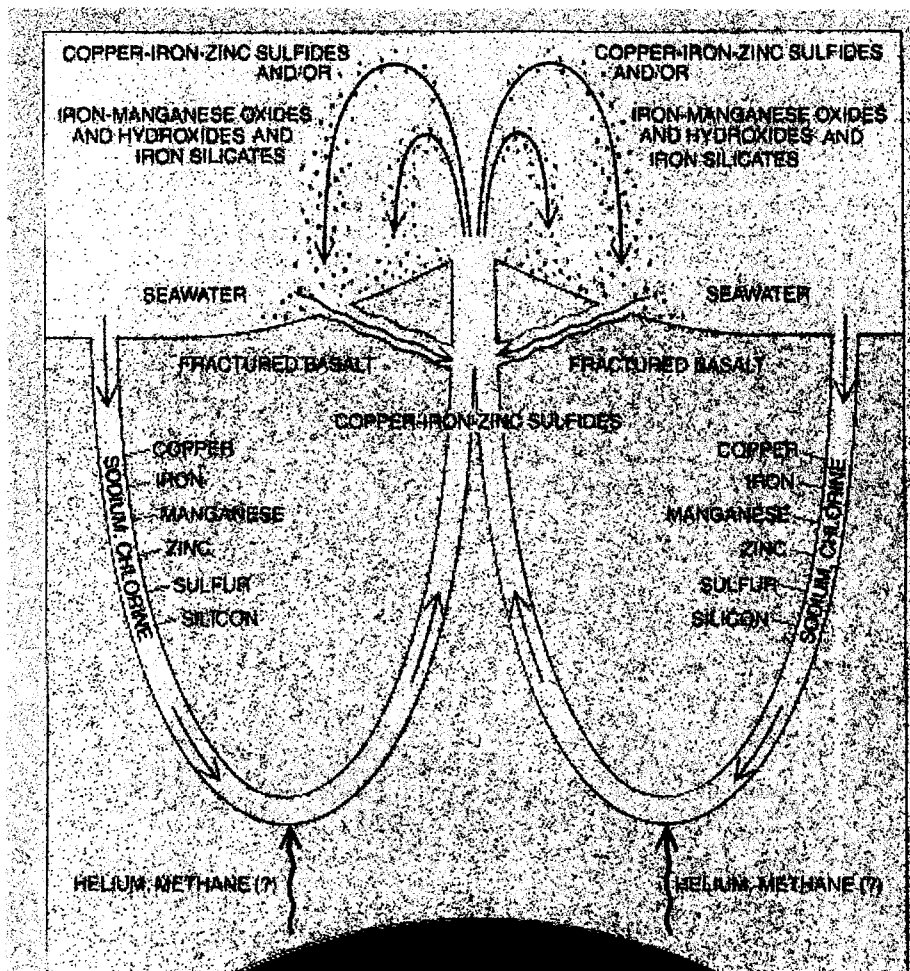


Figure 4. Illustration of the interplay between the formation of sedimentary basins where organic matter is deposited and the occurrence of volcanic events which could supply ash rich in mercury and arsenic.

Taken from Brimhall 1991.

Recent work on the mineral deposits from sea-floor hot springs has made geologists aware of the prominent role of hydrothermal convective systems at the seafloor-spreading centres in generating much of the world's ore minerals. This process is illustrated in Figure 5. The most prevalent mineral of mercury is cinnabar (HgS). It is found in highest concentrations in volcanically active zones, such as the circum-Pacific volcanic belt, the East Pacific Rise, and the Mid-Atlantic Ridge (Ehrlich 1995). Rona 1986 gives an indication of mineral deposits formed by seafloor hot springs in Figure 6. He mentions that fluids derived from magma and mantle are Sb, As, Hg and Se. These metals are transported as complexes of chlorine to where they are deposited as polymetallic sulfides.



MINERALIZATION PROCESS is shown in a cross-sectional view of two symmetrical hydrothermal convective circulation systems at a sea-floor spreading center. Seawater penetrates downward to a depth of several kilometers through fractured crust containing various metals. Heat from an underlying magma chamber causes the water to expand and to rise convectively. The heated water dissolves a number of elements, including metals, from the rock and takes a few elements. Additional metals may come from the magma chamber and the underlying mantle, along with helium and possibly methane gas. In "leaky" systems fresh seawater penetrates downward and mixes with the upwelling hot, metal-rich solutions, triggering the precipitation of metals as sulfides in the crust; metals remaining in solution are deposited on the sea floor from hot springs. In "tight" systems the solutions discharge directly into hot springs that deposit sulfides on the sea floor. The diagram is schematic.

Figure 5. The mineralization process deduced from studies of mineralisation at sea floor spreading centres. Taken from Rona 1986.

Ehrlich 1996 states that most metal sulfides of commercial interest are of igneous origin. Current theory explaining their formation invokes plate tectonics. It has and is playing a central role in their formation. The process as illustrated in Figure 3 where hydrothermally enriched mineralised regions move out from spreading centres to a point of subduction is thought to be the cause of the porphyry copper ore and mercury close to the California coast. After subduction, the following successive steps take place: (a).Remelting of the subducted oceanic crust, (b).The rising of the resultant magma, (c).Release of water with fracturing of incipient rock and the formation of hydrothermal solution containing hydrogen sulfide during progressive partial cooling of the magma, and finally; (d).reformation of copper and other metal sulfides such as cinnobar by crystallization of the cooling magma and/or from reaction of H₂S in the hydrothermal solution with metal constituents in the cooled magma in the fractured rock (Strahler 1977, Bonatti 1978, Tittley 1981, Ehrlich 1996).

The red squares in Figure 7 show the positions of the mercury mines in the San Francisco Bay area. These mercury mines are associated with the faulting which in turn is due to plate subduction. The west coast of North America (California and Mexico) would be a good area to study the finer details of the association of hydrocarbons and the presence of Hg. This could be pursued in the next phase of this study. Further study should examine specific sedimentary basins where there is an association of Hg and As with the occurrence of fossil fuels (coal, gas and oil).

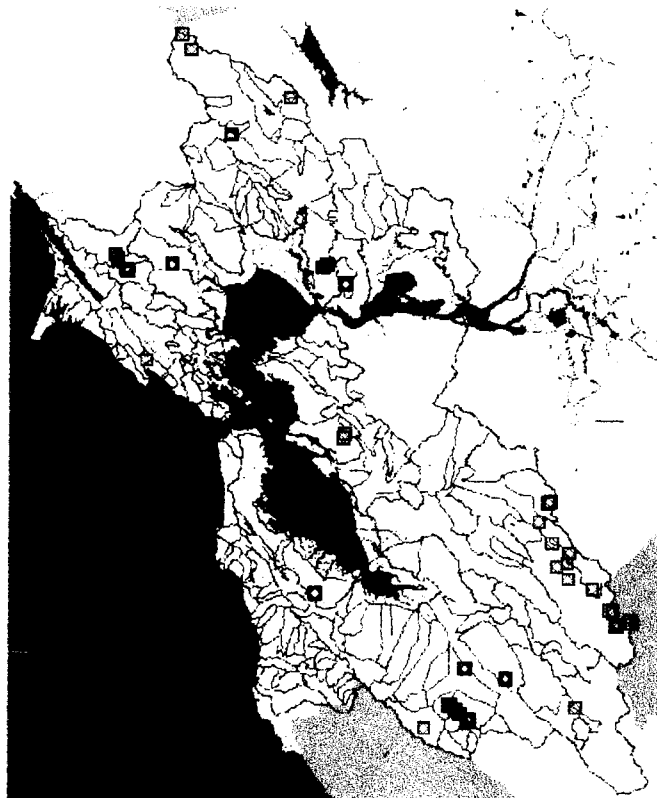
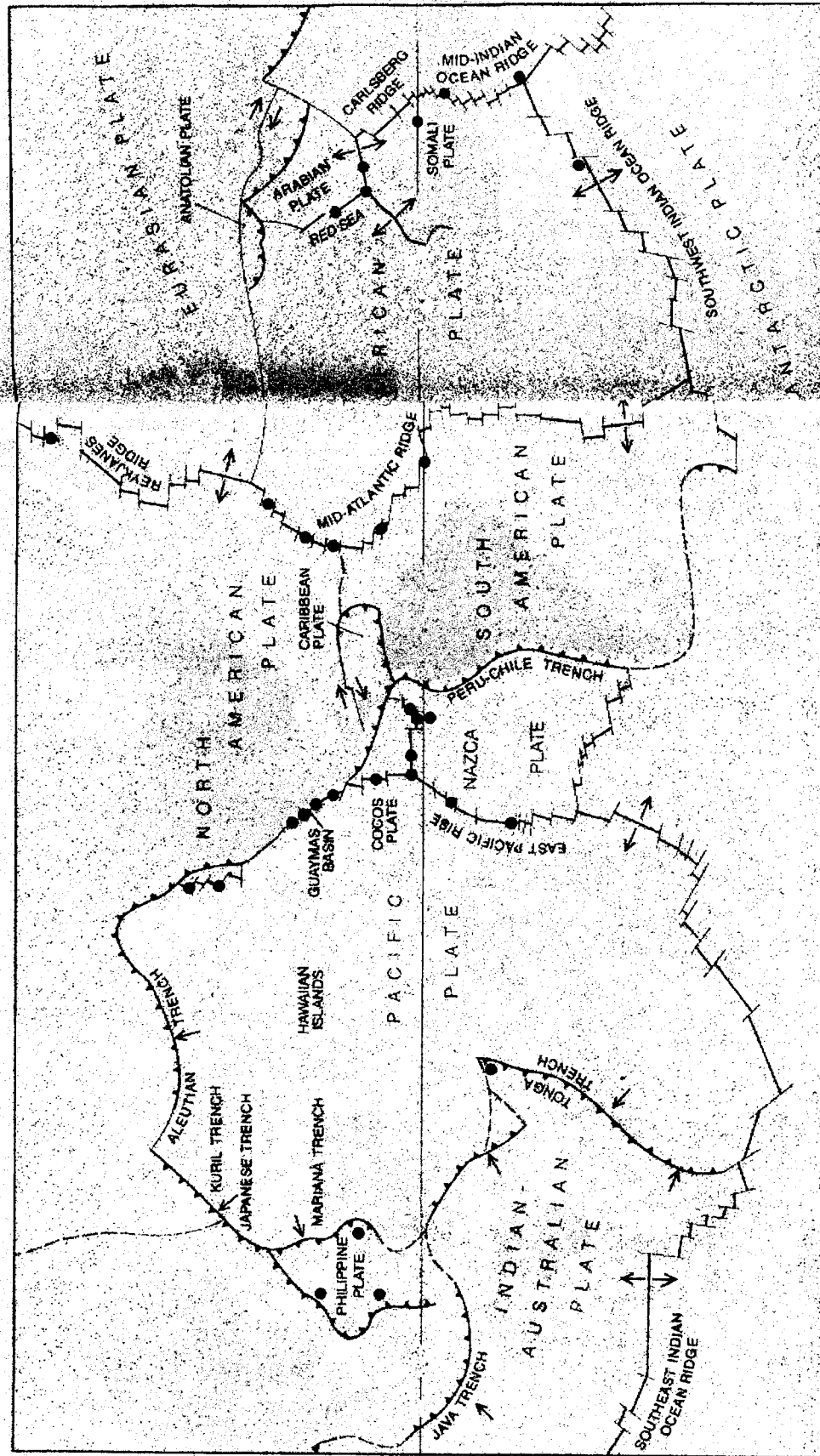


Figure 7. There are 20 mercury mine sites in the San Francisco Bay area which are associated with faults. The faults in turn are related to the plate tectonic subduction in this area. From <http://regis.berkeley.edu/analysis.html>, 1998.



MINERAL DEPOSITS formed by sea-floor hot springs are identified by the colored circles on this map. The conditions necessary for the formation of such a deposit are seawater as an ore-forming fluid, fractured volcanic rock or sediment as a permeable medium and a source of metals, and a magma chamber as a source of heat. Favorable conditions occur at sites along the boundaries of the plates that make up the lithosphere (the earth's rigid outer shell) and in volcanic regions within plates, as in the Hawaiian Islands.

Figure 6. Map showing the plate tectonic spreading centres and mineral deposits.

2.2 Possible ways of enriching mercury and arsenic in sedimentary basins where fossil fuels are formed.

From the preceding discussion, we can suggest the following geological situations which could possibly have provided increased levels of Hg to sedimentary basins:

2.2.1 Volcanic activity

Volcanic activity as illustrated in Figure 4 could result in the introduction of relatively high levels of Hg into organic matter being deposited in a basin. Zettlitzer et al. 1997, mentions that the “mercury source” of the gas produced from the Rotliegend sandstone in Northern Germany is the underlying Volcanite - of volcanic origin.

2.2.2 Sulfide mineralisation of fractures during tectonic plate subduction

Sulfide mineralisation of fractures due to tectonic plate subduction is illustrated in Figure 3 and Figure 7. In the case of Figure 7, it is quite feasible that the many Hg mineralised fractures of San Francisco Bay would supply Hg enriched detrital material to the basin where hydrocarbons were formed.

2.2.3 Hydrothermal activity below a sedimentary basin

Hydrothermal activity directly below a basin could introduce sulfides of Hg and As. This is exemplified for the case of the Red Sea in Figure 8 (Taken from Rona 1986).

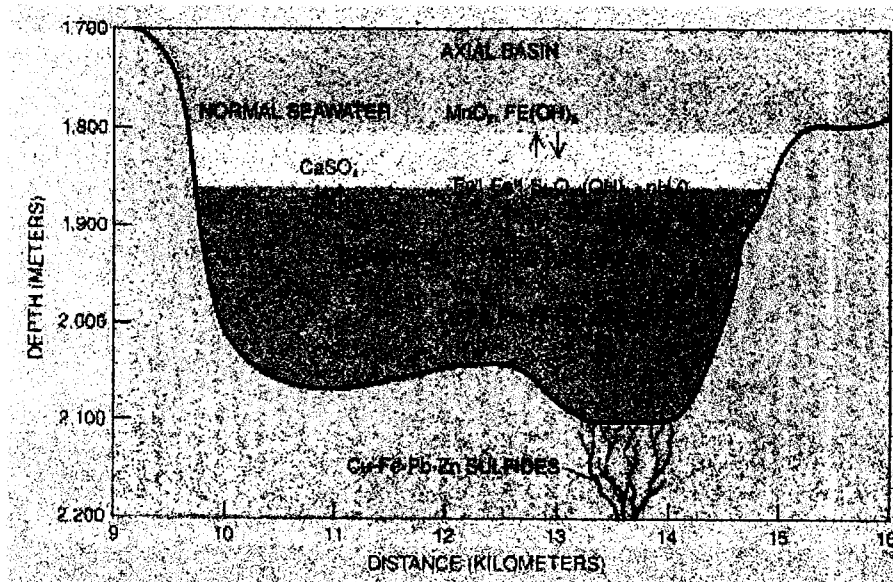


Figure 8. The Red Sea mineralization typifies a setting where hydrothermal activity below a basin occurs.

2.2.4 Intrusion of basalt into petroleum source rocks

An example of a situation where basalt intrusion occurred into a shale is shown in Figure 9 (Taken from Edmond and Van Damm 1983). In a Besshi deposit, a massive sulfide ore body lies in the midst of sediment, usually shale. one example of this is the Guamas Basin in the middle of the Gulf of California where the East Pacific Rise is penetrating into the continental plate. River sediments from Mexico have supplied sediment to a depth of several hundred meters.

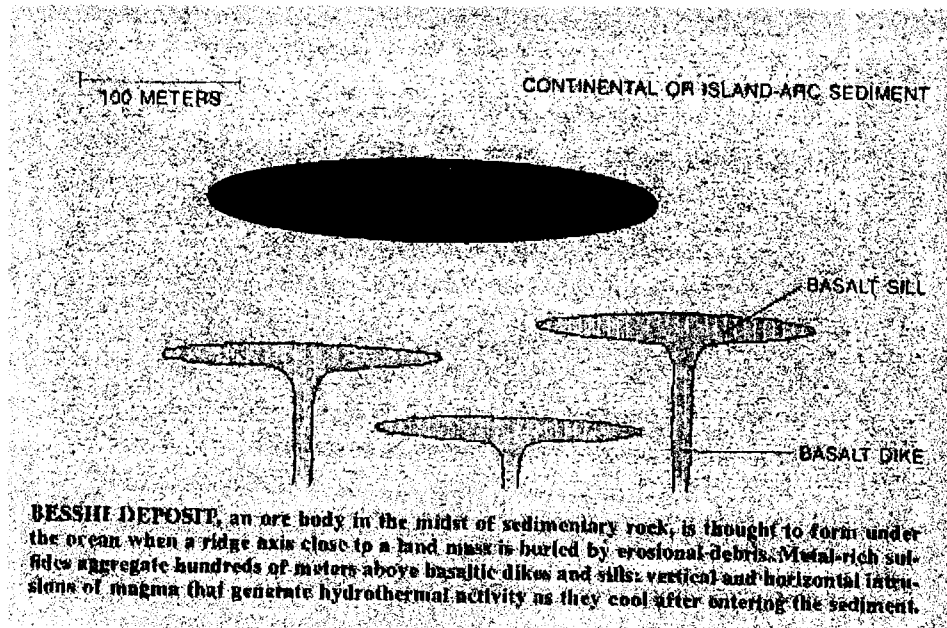


Figure 9. Schematic illustration of a Besshi deposit. Taken from Edmond and Van Damm 1983.

2.2.5 Long distance atmospheric transport

Fitzgerald et al. 1998 reviewed the case for atmospheric Hg contamination in remote areas. Improvements in analytical methods, sampling techniques, and experimental design over the past decade has provided more reliable data on Hg. The authors state that the quality of the Hg data obtained after mid-1980's has improved dramatically and is less plagued with blank and analytical problems compared to previous work. This has led to less ambiguous conclusions regarding the relative influence of anthropogenic and natural Hg fluxes.

These above mentioned authors emphasize that global tectonic theory probably provides a useful framework for evaluating natural Hg fluxes. A broad and geochemically consistent data base indicates that, over large regions of the globe, human-related emissions and depositions during the past century have increased relative to natural sources (Lindqvist 1991, Porcella et al. 1995, Watras and Huckabee 1994). Moreover, the signal is evident in remote regions. Lake sediments, bogs and soils are indicators of airborne Hg pollution.

The above mentioned experience regarding airborne Hg makes it quite feasible to imagine that during active times, large geothermal fluxes from ocean ridges could have been transported to sedimentary basins.

2.3 From ore minerals to the mercury and arsenic species in petroleum

2.3.1 Introduction

Bacterial activity and low-temperature chemical reactions are thought to produce kerogen, metal organic complexes and hydrocarbons (Diagenesis up to 50 C). The stage during which increasing temperature causes kerogen to thermally decompose to bitumen and bitumen to oil, condensate and gas, is called Catagenesis and occurs between 50 C and 200 C. (Hunt 1996, Tissot and Welte 1984).

Bacteria and fungi are involved in the conversion of both As and Hg to the organometallic species found in petroleum. (Ehrlich 1996) The literature which is perceived to cast some light on the relationship between ore minerals and the As and Hg species in petroleum, will be summarised herewith.

2.3.2 Geomicrobial interaction with arsenic

2.3.2.1 *Distribution of arsenic in the earth's crust*

Although As is generally toxic to life, some microorganisms exist which can metabolise forms of this element. In some cases they can use them as energy sources, in others as electron acceptors, and in still others they metabolise them to detoxify them.

Arsenic is widely distributed in the crust of the Earth, but at low concentration (Caparella 1972). It rarely occurs in elemental form. It is usually combined with sulfur, as in orpiment (As_2S_3) or realgar (AsS); as As_2Se_3 or As_2Te_3 ; or as sulfosalts, as in eragite (Cu_3AsS_4) or arsenoryrite (FeAsS). It is also found as arsenides of heavy metals such as iron (loellingite, FeAs_2), copper (domegkite, Cu_3As), nickel (nicolite, NiAs), and cobalt (Co_2As). Sometimes the element occurs in the form of arsenite minerals (arsenolite or clauderite, As_2O_3) or in the form of arsenate minerals (erythrite, $\text{Co}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$; scorodite, $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$; olivenite, $\text{Cu}_2(\text{AsO}_4)(\text{OH})$).

Arsenopyrite (FeAsS) is the most common and widespread mineral form of arsenic; orpiment and realgar are also fairly common. The ultimate source of arsenic on the Earth's surface is igneous activity. On weathering of arsenic-containing rocks, which may contain 1.8 ppm of the element, the As is distributed through the upper lithosphere and hydrosphere.

Arsenic concentration in soil may range from 0.1 to more than 1000 ppm. The average concentration in seawater is given as 3.7 $\mu\text{g}/\text{liter}$ (ppb) and in fresh water as 0.5 $\mu\text{g}/\text{liter}$. In air, arsenic may be found in the concentration range of 1.5 - 53 ng/m^3 (Bowen 1979). Some living organisms may concentrate As manyfold to accumulate As 200 - 3000 times in excess of its concentration in their growth medium (Lunde 1973). Man may artificially raise the arsenic concentration in soil and water through the introduction of sodium arsenite (Na_2AsO_3) or cacodylic acid ($(\text{CH}_3)_2\text{AsO} \cdot \text{OH}$) as herbicide. The valence states in which arsenic is usually encountered in nature include -3, 0, +2, +3, and +5.

2.3.2.2 Toxicity

Arsenic compounds are toxic to most living organisms. Arsenite (AsO_3^{2-} or AsO_2^-) has been shown to inhibit dehydrogenases such as pyruvate, alpha-ketoglutarate, and dihydrolipoate dehydrogenases (Mahler and Cordes 1966). Arsenate uncouples oxidative phosphorylation; i.e., it inhibits ATP synthesis by chemiosmosis (Da Costa 1972).

2.3.2.3 Microbial oxidation and reduction of arsenic-containing minerals

Arsenic combinations with Fe, Cu, and S such as orpiment and arsenopyrite are oxidised by bacteria (Silverman and Lundgren 1959, Ehrlich 1963, Ehrlich 1964, Carlson et al. 1992, Groudeva et al. 1986, Ngubane and Baecker 1990). The ability of *T. ferrooxidans* and other acidophilic, iron-oxidising bacteria to oxidise arsenopyrite is beginning to be industrially exploited in beneficiation of precious metal-containing, sulfidic ores (Olson 1994). Some bacteria, fungi and algae are able to reduce arsenic compounds (Challenger et al. 1933, Challenger 1951, Cheng and Focht 1979, McBride and Wolfe 1971) to produce trimethyl arsine.

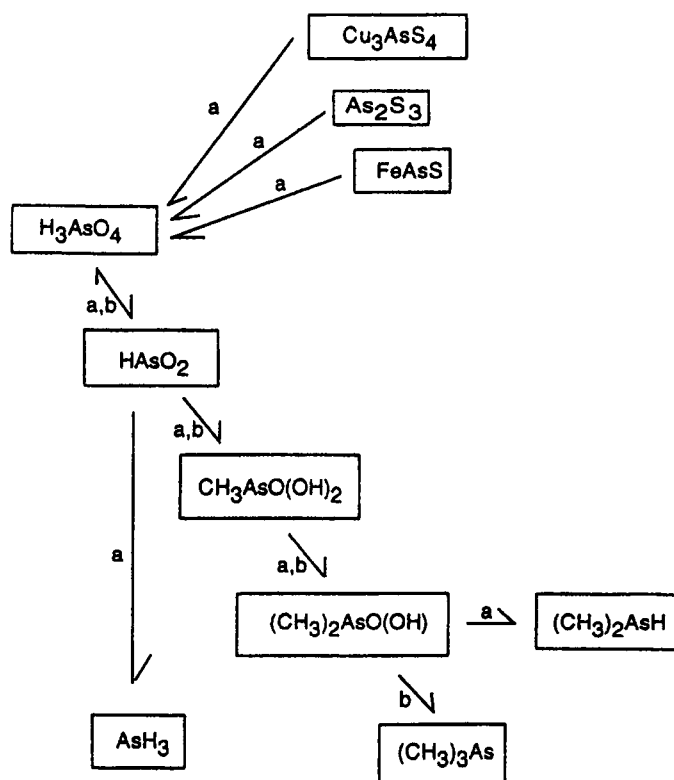


Figure 10. Summary of possible microbial interactions with arsenic compounds: (a) performed by bacteria, (b) performed by fungi. Taken from Ehrlich 1996.

Observations of microbial reduction of arsenic compounds in seawater (Johnson 1972) and in soils (Cheng and Focht 1979) have been reported. Figure 10 summarises those reactions involving arsenic compounds that are catalysed by microorganisms. The oxidation of methylated arsine, although not indicated in the diagram, has been suggested by Cheng and Focht 1979. The As cycle in natural waters has been discussed by Ferguson and Gavis 1972. In marine waters the cycle has been examined by Andreae 1979 and by Scudlark and Johnson 1982.

2.3.2.4 Summary

Although arsenic compounds are toxic to most forms of life, some microbes metabolise them. Arsenite and arsenate have been shown to be reduced by certain bacteria and fungi. When reducing the As to the -3 oxidation state, the bacteria produce arsine and/or dimethyl arsine, whereas the fungi produce trimethyl arsine. All of these arsines are volatile.

The manner in which this type of bacterial activity is related to petroleum generation, expulsion and production will be further examined in the study that will follow this survey. According to Block-Bolten and Glowacki 1989, As occurs in petroleum in the form of arsine. This study has shown that the stage and conditions under which microorganisms generate arsine and how it is incorporated and enriched in natural gas and oil needs further study.

2.3.3 Geomicrobial interaction with mercury

2.3.3.1 Distribution of mercury in the earth's crust

The concentration of mercury in the Earth's crust has been reported as 0.08 ppm (Jonasson 1970). Its concentration in fresh waters may range from 0.01 to 10 ppb, although concentrations as high as 1600 ppb have been measured in waters in contact with copper deposits in the southern Urals (Jonasson 1970). The maximum permissible level in potable waters in the United States has been set at 5 ppb. The average concentration of Hg in sea water has been reported at 0.2 - 2 ng/l (Fitzgerald et al. 1998).

Mercury can exist in nature as Hg metal or as Hg compounds. The metal is liquid at ambient temperature and has a significant vapour pressure (1.2×10^{-3} mm Hg at 20 C) and a heat of vaporisation of $14.7 \text{ cal mol}^{-1}$ at 25 C (Vostal 1972). The most prevalent mineral of Hg is cinnabar (HgS). It is found in highest concentrations in volcanically active zones, such as the circum-Pacific volcanic belt, the East Pacific Rise, and the Mid-Atlantic Ridge (Ehrlich 1996). The occurrence of Hg metal is rarer. In water, inorganic Hg may exist as aquo, hydroxo, halido, and bicarbonate complexes of Hg ion, but the Hg ion may also be adsorbed to particulate or colloidal materials in suspension (Jonasson 1970). In soil, inorganic Hg may exist in the form of elemental Hg vapour that may be adsorbed to soil matter, at least in part. It can also exist as mercuric humate complexes at pH 3 - 6 or as $\text{Hg}(\text{OH})^+$ and $\text{Hg}(\text{OH})_2$ in the pH range 7.5 - 8.0. The latter two species may be adsorbed to soil particles. Mercury in soil and water may also exist as methyl mercury ($(\text{CH}_3)\text{Hg}^+$) which may be adsorbed by negatively charged particles such as clays.

2.3.3.2 Toxicity (Anthropogenic mercury)

The extent of Hg toxicity for human beings and other animals became apparent only in recent times as a consequence of environmental pollution by Hg compounds. The toxicity manifests itself by major physical impairments and death due to intake of the compounds in food and water. Incidents of Hg poisoning in Japan (Minamata disease),

Iraq, Pakistan, Guatemala, and the United States drew special attention to the problem. In some of these cases, food made from seed grain treated with Hg compounds to inhibit fungal damage before planting was consumed. The seed grain had not been intended for food use. In other cases, food such as meat became tainted because the animals yielding the meat drank water that had become polluted by Hg compounds or they had eaten Hg - tainted feed. The local Hg level may be affected by human activity.

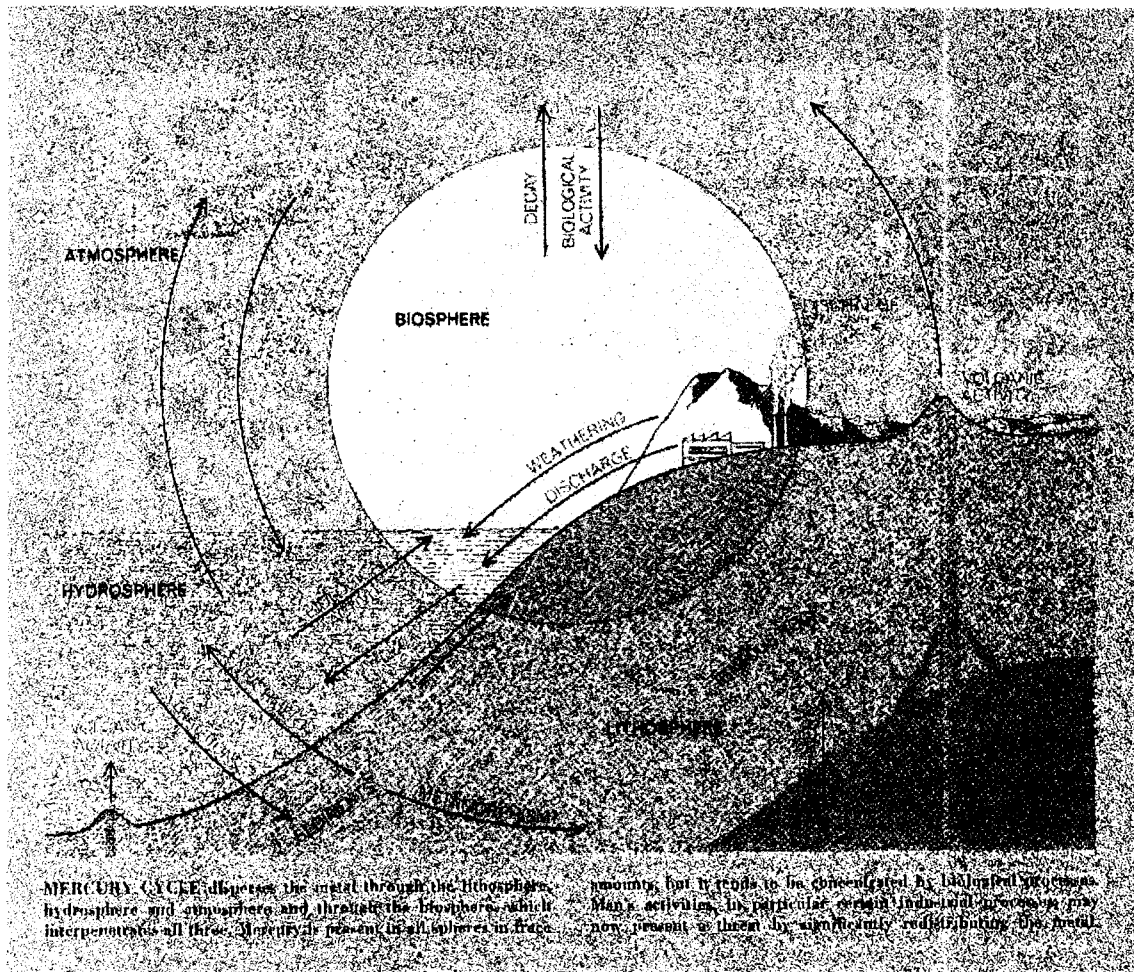


Figure 11. Illustration of the mercury cycle in our industrial age. Taken from Goldwater 1971.

Some industrial operations, such as the synthesis of certain chemicals like vinyl chloride and acetaldehyde, which employ inorganic Hg compounds as catalysts, or the electrolytic production of chlorine gas and caustic soda, which employs Hg electrodes, or the manufacture of paper pulp, which makes use of phenyl mercuric acetate as a slimicide, may pollute the environment (Jonasson 1970). In agriculture, organic compounds used as fungicides to prevent fungal attack of seed may pollute the soil. In mining, the exposure of Hg ore deposits and other deposits in which Hg is only a trace component leads to weathering and resultant solubilization and spread of some of the Hg into the environment.

As Jonasson 1970, has pointed out, inorganic Hg compounds were considered less toxic in the past than organic hg compounds. However, since the discovery that inorganic Hg compounds can be converted into organic ones (e.g. methyl mercury), this is no longer considered to be true. Living tissue has a high affinity for methylmercury ($(\text{CH}_3)\text{Hg}^+$).

Fish have been found to concentrate it up to 3000 times over the concentration found in water. This is because the methylmercury is fat as well as water soluble and is more readily taken up by living cells than mercuric ion. Owing to its lipid solubility, nervous tissue, especially the brain, has a high affinity for methylmercury. It is also bound by inert matter, especially negatively charged particles such as clays.

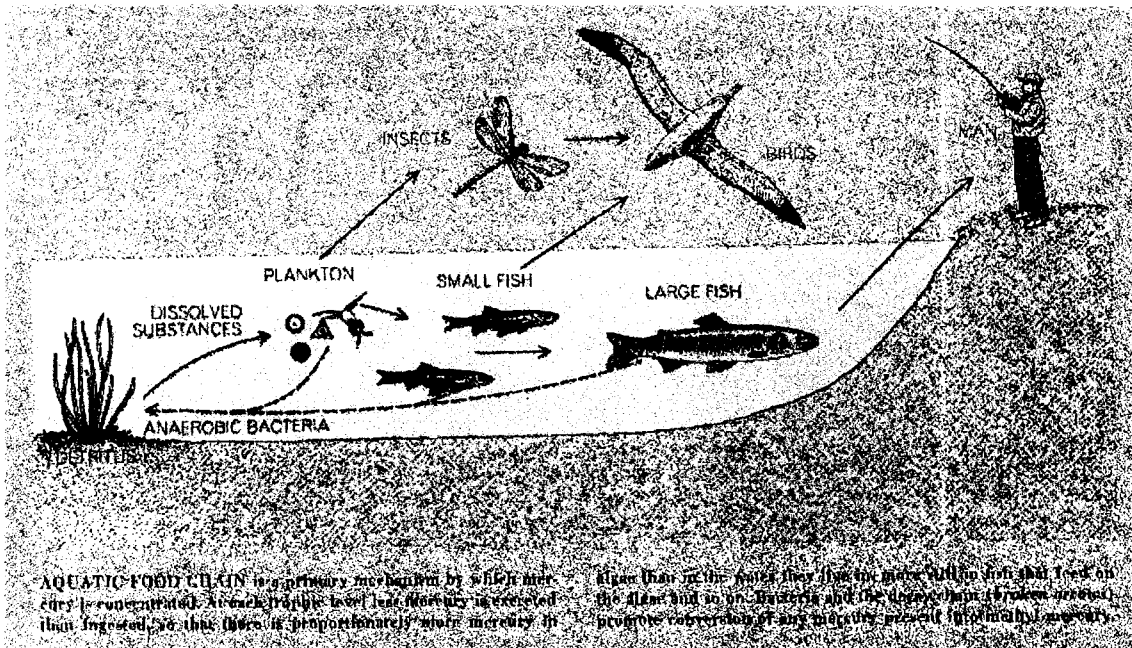


Figure 12. Illustration of the sources of toxicity to man from a polluted environment (Goldwater 1971).

Dimethylmercury ((CH₃)₂Hg) is volatile. It can thus enter the atmosphere from soil or water phases. The ultraviolet component of sunlight can, however, dissociate dimethylmercury into volatile elemental Hg, methane and ethane.

The alkyl mercurials attack the brain cells, which are susceptible to injury from this form of Hg. The **chemical basis for this toxicity in man** seems to be **mercury's strong affinity for sulfur, particularly for the sulfhydryl groups (S-H) in proteins** (for which As and Pb have similar affinity). Bound to proteins in a cell membrane, the Hg may alter the distribution of ions, change electric potentials and thus interfere with the movement of fluid across the membrane. There are also indications that the binding of Hg to proteins disturbs the normal operation of structures such as mitochondria and lysosomes within the cell. Alkyl Hg appears to be especially dangerous because the Hg is firmly bonded to a carbon atom, so that the molecule is not broken down and may maintain its destructive action for weeks or months. In this respect it differs from the inorganic and phenyl (aryl) mercurials, and that may explain why it produces **permanent injury to brain tissue**, whereas the injury caused by inorganic and aryl mercurials is almost invariably reversible (Goldwater 1971).

2.3.3.3 Microbial interactions with mercury

(1) Detoxification

Microorganisms have in recent years been shown to be intimately involved in interconversions of inorganic and organic Hg compounds. The initial discoveries of the microbial activities were those of Jensen and Jernelov 1969, who demonstrated the production of methylmercury from mercuric chloride (HgCl_2) added to lake sediment samples and incubated for several days in the laboratory. They also noted the production of dimethylmercury ($(\text{CH}_3)_2\text{Hg}$) from decomposing fish tissue, containing methylmercury or supplemented with Hg^{2+} , and incubated for several weeks.

Most microbial interactions with Hg are **detoxification** reactions. By forming volatile elemental Hg or dimethylmercury, neither of which is water soluble, the microbes ensure removal of Hg from their environment into the atmosphere. Even microbial methylmercury ($(\text{CH}_3)\text{Hg}^+$) formation may be a form of Hg detoxification, because methylmercury can be immobilized in sediment or soil by adsorption to negatively charged clay particles, which removes it as a toxicant from the microbial environment. Similarly, the precipitation of HgS by reaction of Hg^{2+} with biogenic H_2S is a type of Hg detoxification since the solubility of HgS is very low ($K_{\text{sol}} = 10^{-49}$). **Of all these detoxification mechanisms, the formation of volatile metallic Hg appears to be the predominant microbial detoxification mechanism** (Robinson and Tuovinen 1984). Baldi et al. 1987 demonstrated the presence of a significant number of Hg resistant bacteria that could reduce Hg^{2+} to Hg^0 but not methylate it at sites surrounding natural Hg deposits situated in Tuscany, Italy. Baldi et al. 1989, also isolated 37 strains of aerobic, Hg resistant bacteria from Fiora River in southern Tuscany, which receives drainage from a cinnabar mine. All 37 strains were able to reduce Hg^{2+} to Hg^0 but only three were able to degrade methylmercury. None were able to generate methylmercury.

(2) Microbial methylation of mercury

An early study of the biochemistry of microbial methylation of mercury involved the use of the cell extract of a methanogenic culture in the presence of low concentrations of Hg^{2+} , which caused formation of $(\text{CH}_3)_2\text{Hg}$ but little methane (CH_4), through preferential interaction between methylcobalamin and Hg^{2+} (Wood et al. 1986). Although the production of methylcobalamin in this instance depended on enzymatic catalysis, the production of $(\text{CH}_3)_2\text{Hg}$ from the reaction of Hg^{2+} with cobalamin did not. This nonenzymatic nature of mercury methylation by methylcobalamin was confirmed by Bertilsson and Neujahr 1971, Imura et al. 1971 and by Schrauzer et al. 1971.

Sulfate reducers such as *Desulfovibrio desulfuricans* appear to be the principal methylators of Hg in some anoxic estuarine sediments when sulfate is limiting and fermentable organic energy sources are available (Compeau and Bartha 1985). The methyl group was shown to originate from carbon-3 of the amino acid serine, which was transformed to methyl carbon via tetrahydrofolate and transferred to Hg via Co Porphyrin (methylcobalamin) (Berman et al. 1990, Choi and Bartha 1993).

The fungus *Neurospora crassa* uses a still different reaction for methylating Hg (Landner 1971). This organism first complexes Hg^{2+} ion with homocysteine or cysteine nonenzymatically, and then with the help of a methyl donor and the enzyme transmethylase, cleaves $(\text{CH}_3)\text{Hg}^+$ from this complex. Figure 13 illustrates the reaction with homocysteine.

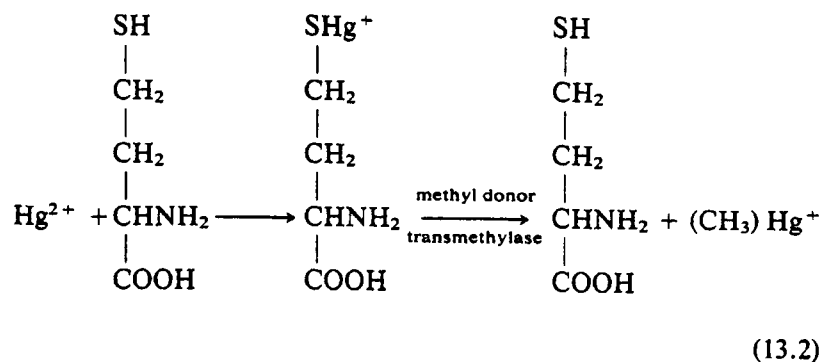


Figure 13. Complexation of Hg^{2+} with cysteine as an intermediary in the formation of $(\text{CH}_3)\text{Hg}^+$. Taken from Ehrlich 1996.

Although in the laboratory, bacterial methylation of Hg appears to be favored by anaerobic conditions, partially aerobic conditions are needed in nature. This is because under in situ anaerobic conditions, biogenic H_2S may prevail and, as a result, mercuric Hg^{2+} will exist most probably as HgS (Fagerstrom and Jernelev 1971, Vostal 1972). HgS cannot be methylated without prior conversion to a soluble Hg^{2+} salt or HgO (Yamada and Tonomura 1972). It has been shown that H_2S , which in nature is frequently of biogenic origin, can transform pre-existing methylmercury into dimethylmercury (Craig and Bartlett 1978). Figure 14 shows schematically the transformations of Hg discussed herein.

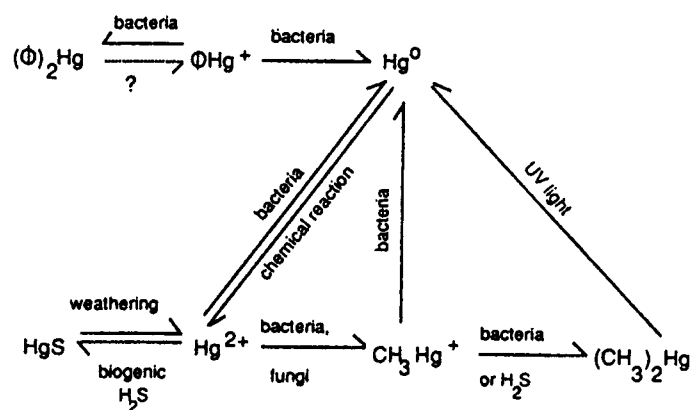


Figure 14. Mercury transformations by microbes and by chemical and physical agents. Taken from Ehrlich 1996.

Mercuric ion is reduced to volatile metallic mercury by a number of bacteria and fungi. Not all reduction of mercuric mercury observed in nature is biological (Nelson and Colwell 1975). Chemical reduction may occur as a result of interaction with humic acid (Alberts et al. 1974).

2.3.3.4 Summary (The mercury cycle)

On the basis of the interactions of microbes with Hg compounds described in the foregoing sections, it is apparent that microbes play an important role in the movement of Hg in nature, i.e., in soil, sediment, and aqueous environments. One of the main results of microbial action on Hg, whether in the form of mercuric ion or alkyl- or aryl-

mercury ions, seems to be its volatilisation as Hg^0 . Methylmercury ion may also be an intermediate in the formation of volatile dimethylmercury. Methylmercury is more toxic to susceptible forms of life than mercuric ion, owing to the greater lipid solubility combined with its positive charge of the former.

A mercury cycle is outlined in Figure 14. Mercuric sulfide of volcanic origin slowly auto-oxidises to mercuric sulfate on exposure to air and moisture and may become disseminated in soil and water through groundwater movement. Bacteria and fungi may reduce the Hg^{2+} to Hg^0 , as may humic substances. The volatile mercury (Hg^0) may be adsorbed by soil, sediment, and humic substances, or lost to the atmosphere. Some of the Hg^{2+} may also become methylated through the action of bacteria and fungi. Some of the positively charged mercuric ions, methyl mercury ions as well as phenyl mercuric ions, may be fixed by negatively charged soil and sediment particles and by humic matter and thereby become immobilised (Korthals and Winfrey 1987).

Methylation and demethylation of Hg together with Hg reduction has also been observed in estuarine sediments (Compeau and Bartha 1984), sulfate reducers being the principal agents of methylation when the supply of sulfate is limiting (Compeau and Bartha 1985).

Mercuric ion may be converted to mercuric sulfide by bacterially generated H_2S and thereby be immobilised in a sediment. Only the formation of HgS is strictly anaerobic; methylation or reduction of mercuric mercury can occur aerobically or anaerobically. Methylmercury is water - soluble and is adsorbed by sediment. To further detoxify this species, bacteria convert it to the more volatile and water - insoluble dimethylmercury. The latter species readily escapes into the atmosphere. Reduction of Hg^{2+} to Hg^0 is a more important detoxification reaction in nature than methylation. Microbes metabolising mercury are generally resistant to its toxic effects.

The mercury cycle in nature is under the influence of microorganisms. The manner and time when inorganic minerals of mercury were supplied to a sedimentary basin needs to be considered when evaluating the magnitude of the potential mercury problem for each field.

3 Published data on mercury and arsenic levels in sedimentary organic matter.

The very serious financial consequence of arsenic in gas was illustrated by the report of Slaton 1989. In the spring of 1988 production had to stop for the over 600 natural gas wells in Chaves County, Southeast New Mexico, USA. The reason was that traces of arsenic compounds were found in some parts of natural gas pipelines. Further investigation indicated the existence of arsenic in gas reservoirs. Slaton reports that the Pecos Slope gas was back on stream early in 1989 under a plan between producers and Transwestern Pipeline. The New Mexico State lost \$19 million in revenue as a result of the shutdown. Parker Gas Treating Co. of Houston supplied a system which directs gas through a scrubbing unit and then into a vertical absorbent bed. Here the arsenic is stripped with a copper-zinc absorbent.

3.1 Occurrence and removal of arsenic in petroleum.

It appears that the discovery of arsenic compounds in parts of the natural gas pipelines from the Abo Field (Enron Corp.) in South East New Mexico was responsible to alert Oil Companies and Governments of the possible danger to life posed by the presence of As in petroleum (Slaton 1989). Brief mention was made by Lund 1996, that there was some indication of a problem with arsenic in natural gas in Europe. Block-Bolten and Glowacki 1989 gave an overview of some methods of removing arsenic compounds from natural gas and accompanying water. The pyrolysis method makes use of the volatility of arsine. Pyrolysis of arsines is achieved by passing the gas over heated copper, iron, nickel or cobalt. The adsorption methods used make use of solid soda lime, copper oxide, zinc oxide, lead monoxide, copper chromite and activated carbon. In absorption methods permanganic acid or its salts, dichromic acid or its salts, nitric acid, or peroxides, are used. Block-Bolten and Glowacki conclude that

1. Natural gas with arsine content higher than 50 $\mu\text{g/l}$ (ppb) must be purified. The maximum safe concentration of arsine in air for an eight hours exposure period (Threshold Limit Value) has been set as low as 50 ppb. This can be compared with hydrogen cyanide TLV at 10000 ppb.
2. Associated water from the natural gas wells where arsine was found present a source of environmental pollution. The problem can be solved by precipitation of high stability metal arsenates.
3. Potassium permanganate absorption method appears to be optimal because it permits purifying of gas and water simultaneously; the process is simple and environmentally safe; and because maintenance costs are low.

The Institute Francais du Petrole has been active in developing methods for removing As and Hg from petroleum. An example of such a process is given in the patent by Mank et al. 1995.

3.2 Reported observations of Hg in petroleum.

Bingham 1989 gives Hg concentrations in air as ranging between 1 ng/m^3 and 10 $\mu\text{g/m}^3$ (1 ppm is approx equal to 10 000 $\mu\text{g/m}^3$). He states that natural gas typically contains Hg concentrations between 50 to 200 $\mu\text{g/m}^3$.

Bingham alludes to work which has shown that factors affecting the concentration of mercury in natural gas are amongst others:

- (1). Pipe surface adsorption.

The mercury content of natural gas is appreciably reduced due to chemisorption onto steel pipe walls. The reduction in concentration was found to be 20 - 40 times higher in uncoated walls as compared to coated pipelines. For pipelines in operation for 10 years, mercury concentration was found to be reduced by less, namely, one - tenth between inlet and outlet of the pipeline. on the other hand, for a newer pipeline, a reduction to one - hundredth the inlet mercury concentration was experienced.

(2). Condensation of mercury into the liquid phases of hydrocarbons and gas treating chemicals (glycol absorber, scrubbers).

This results from the higher solubility of mercury in higher molecular weight streams. Some concentrations of mercury in natural gas reported in the more recent literature is given by Bingham 1989 and by Mussig and Rothmann 1997. These reported concentrations are compared in Table 1. The technical solutions for removing mercury in natural gas are summarised by Mussig and Rothmann. Personal contacts have been made during the Production Geochemistry Conference. These contacts informed me that Mobil Technology Company has 20 patents on the removal of mercury in gas. Contacts have been made with individuals in companies such as ICI Katalco (U.K.) offer services to remove mercury from gas in North Sea oil fields. A treatment of Hg in the North Germany petroleum from an analytical point of view was given by Zettlitzer et al. 1997. As seen in Table 1 above, Mussig and Rothmann 1997 give the Hg concentration in gas from the Permian sandstone (Rotliegend formation) as 70 - 3500 $\mu\text{g}/\text{m}^3$. The range of concentrations reported by Zettlitzer is 700 to 4499 $\mu\text{g}/\text{m}^3$. These latter authors determined the Hg concentrations in the condensates from this area to be 3 - 6 $\mu\text{g}/\text{g}$ (ppm). Most of the Hg was in the elemental form. Of the organic mercury compounds, only methyl mercury was detected in concentrations of between 0.005 and 0.1 $\mu\text{g}/\text{g}$. Formation brines contained less than 1 $\mu\text{g}/\text{g}$ total mercury and very low concentrations of monomethyl mercury. ($<0.002\mu\text{g}/\text{g}$).

An example of a Hg problem in the USA is discussed by Lund 1996. At the Anschutz Ranch East plant in Southern Wyoming, the inlet Hg has been measured at between 8 and 24 $\mu\text{g}/\text{m}^3$. The plant has approximately 77 000mg/day of Hg removed. The plant Hg removal is performed with three parallel sulfur-impregnated carbon beds. Outlet concentrations of $<0.002\mu\text{g}/\text{m}^3$ are achieved. Several examples of piping failure and liquid metal embrittlement are given in this paper as well as practical suggestions on the best conditions for the operation of the Hg removal unit.

Another reasonably extensive discussion of a Hg problem is that of Pongsiri 1997. The author relates the Hg occurrence in Unocal Thailand's operations in the Gulf of Thailand to some volcanic fumaroles. Coal stringers with Hg content ranging from 0.02 $\mu\text{g}/\text{g}$ to 0.23 $\mu\text{g}/\text{g}$ and the 10 to 25 $\mu\text{g}/\text{m}^3$ found in the natural gas probably owe their origin to these fumaroles. The total Hg in condensate is generally 500 - 800 ng/g, whereas the Hg concentration in the produced formation water is between 30 and 800 ppb. Mercury is said to occur mainly in the elemental form. The treatment facilities are referred to in this article. Deep-well injection of mercury-contaminated solid waste is applied. Water is discharged after gravitational separation and chemical flocculation techniques have been applied to it. Most metals determined in source rock extracts were found by Olsen 1997 to be associated with the asphaltenes of the extracted organic matter. The metals which had a different association were Se and Hg which were found to be more strongly associated with the sulfur containing components. The association of Hg with S could be due to reaction with SH groups in the original organic matter as exemplified in Figure 13.

The distribution of Hg and As in products distilled from different oil shales was found by Olsen et al. 1986, to vary from shale to shale. This again suggests that amount of these

metals generated with petroleum, is dependant on the original detrital material that entered the basin where the source rock formed. This would in turn dependant on the factors mentioned in 2.2 of this report.

Table 1 . Mercury concentrations reported in natural gas.

Bingham 1989		Mussig and Rothmann 1997	
Location	$\mu\text{g}/\text{m}^3$	Location	$\mu\text{g}/\text{m}^3$
Algeria		Algeria	
wellhead	50 - 80	Sonatrach	4500
pipeline entrance	0.1 - 89	average	50 - 200
Skikda plant inlet	0.001 - 0.65		
Groningen		The Netherlands	5 - 250
wellhead	180		
to pipeline	12	Norway	0.5 - 30
North Germany		Germany	
wellhead	15 - 450, 5000	Permian	70 - 3500
South Germany			
wellhead	<0.1 - 0.3	Mid. Jurassic	2 - 6
South America	69 - 119	South America	0.01 - 120
Far East 1	3 - 20	Far East	60 - 190
Far East 2	58 - 193		
Far East 3	0.02 - 0.16		
Indonesia		Indonesia	0.1 - 300
Sumatra	200 - 300		
Africa	0.3 - 130		
Middle East	1 - 9	Iran	1 - 9
USA			
Eastern pipeline	0.019 - 0.44		
Midwest pipeline	0.001 - 0.1		0.06
North America	0.005 - 0.04	North America	0.001 - 0.05?

4 References

ALBERTS, J.J., SCHINDLER, J.E., MILLER, R.W., and NUTTER, D.E., Jr. (1974). Elemental mercury evolution mediated by humic acid. *Science* 184, 895 - 897.

4 References

- ALBERTS, J.J., SCHINDLER, J.E., MILLER, R.W., and NUTTER, D.E., Jr. (1974). Elemental mercury evolution mediated by humic acid. *Science* 184, 895 - 897.
- ANDREAE, M.O. (1979). Arsenic speciation in seawater and interstitial waters: The influence of biological-chemical interactions on the chemistry of a trace element. *Limnol. Oceanogr.*, 24, 440 - 452.
- AUDEH, C.A. (1993). Hydrogen sulphide: An effective reagent for reducing the elemental mercury content of liquid hydrocarbons. ACS, Division of Fuel Chemistry, preprints of papers presented at the 206th ACS National Meeting, Chicago, Aug 22 - 26, 38 No. 3, 787.
- BERMAN, M., CHASE, T., Jr., and BARTHA, R. (1990). Carbon flow in mercury methylation by *Desulfovibrio desulfuricans*. *Appl. Environ. Microbiol.*, 56, 298 - 300.
- BERNER, R.A., and LASAGA, A.C. (1989). Modelling the geochemical carbon cycle. *Sci. Am.*, March, 54 - 61.
- BERTILSSON, L., and NEUJAHN, H.Y. (1971). Methylation of mercury compounds by methylcobalamin. *Biochemistry* 10, 2805 - 2808.
- BINGHAM, M.D. (1989). Field detection and implications of mercury in natural gas. SPE Paper 19357, pp. 1 - 40.
- BLANCHARD, L.J., and ROBERTSON, J.D. (1997). Determination of mercury in coal using radiochemical neutron activation analysis. *Analyst*, 122, 1261 - 1264.
- BLOCK-BOLTEN, A., and GLOWACKI, K. (1989). Natural gas separation from arsenic compounds. SPE Gas Technol. Symp. (Dallas, Texas, 6/7-9/89) Proc., SPE paper No 19078, pp. 221 - 230.
- BODLE, W.W., ATTARI, A., and SERAUSKAS, R. (1980). Considerations for mercury in LNG operations. Paper presented at the Sixth International Conference on Liquefied Natural Gas.
- BONATTI, E. (1978). The origin of metal deposits in the oceanic lithosphere. *Sci. Am.*, 238, 54 - 61.
- BOWEN, H.J.M. (1979). *Environmental chemistry of the elements*. Academic Press, London.
- BRIMHALL, G. (1991). The genesis of ores. *Sci. Am.*, May, 48 - 55.
- CARAPPELLA, S.C., Jr., (1972). Arsenic: element and geochemistry, In: Fairbridge, R.W., E. *The Encyclopedia of Geochemistry and Environmental Sciences*. Encyclopedia of Earth Sciences Series IVA. Van Nostrand Reinhold, New York, pp. 31 - 42.
- CARLSON, L. LINDSTROEM, E.B., HALLBERG, K.B., TUOVINEN, O.H. (1992). Solid-phase products of bacterial oxidation of arsenic pyrite. *Appl. Environ. Microbiol.*, 58, 1046 - 1049.

- CHALLENGER, F. (1933). The formation of organo-metalloid compounds by microorganisms. Part II. Trimethylarsine and dimethylarsine. J. Chem. Soc., pp 95 - 101.
- CHALLENGER, F. (1951). Biological methylation. Adv. Enzymol., 12, 429 - 491.
- CHENG, C-N., and FOCHT, D.D. (1979). Production of arsine and methylarsines in soil and in culture. Appl. Environ. Microbiol., 38, 494 - 498.
- CHOI, S-C., and BARTHA, R. (1993). Cobalamin-mediated mercury methylation by *Desulfovibrio desulfuricans* LS. Appl. Environ. Microbiol., 59, 290 - 295.
- COFFIN, M.F., and ELDHOLM, O. (1993). Large igneous provinces. Sci. Am., 269, 26 - 33.
- COMPEAU, G., and BARTHA, R. (1984). Methylation and demethylation of mercury under controlled redox, pH, and salinity conditions. Appl. Environ. Microbiol., 48, 1203 - 1207.
- COMPEAU, G., and BARTHA, R. (1985). Sulfate - reducing bacteria: principal methylators of mercury in anoxic estuarine sediments. Appl. Environ. Microbiol., 50, 498 - 502.
- CRAIG, P.J., and BARTLETT, P.D. (1978). The role of hydrogen sulfide in environmental transport of mercury. Nature (Lond.) 275, 635 - 637.
- DA COSTA, E.W.B. (1972). Variation in the toxicity of arsenic compounds to microorganisms and the suppression of the inhibitory effects of phosphate. Appl. Microbiol., 23, 46 - 53.
- EDMOND, J. M., and VON DAMM, K. (1983). Hot springs on the ocean floor. Sci. Am., 248, 70 - 84.
- EHRlich, H.L. (1963). Bacterial action on orpiment. Econ. Geol., 58, 991 - 994.
- EHRlich, H.L. (1964). Bacterial oxidation of arsenopyrite and enargite. Econ. Geol., 59, 1306 - 1312.
- EHRlich, H.L. (1996). Geomicrobiology, 3rd Ed., Marcel Dekker, New York, 719p., ISBN 0-8247-9541-5.
- FAGERSTROM, T., and JERNELOEV, A. (1971). Formation of methyl mercury from pure mercuric sulfide in aerobic organic sediment. Water Res., 5, 121 - 122.
- FERGUSON, J.F., and GAVIS, J. (1972). A review of the arsenic cycle in natural waters. Water Res. 6, 1259 - 1274.
- FITZGERALD, W.F., ENGSTROM, D.R., MASON, R.P., and NATER, E.A. (1998). The case for atmospheric mercury contamination in remote areas. Env. Sci. & Technol., 32, 1 - 7.
- GAFFNEY, J. (1997). *Personal Communication*.
- GOLDWATER, L.J. (1971). Mercury in the environment. Sci. Am., 224, 15 - 21.

- HUNT, J.M. (1996). Petroleum geochemistry and geology. 2nd Ed., W.H. Freeman, New York, 743 pp.
- IMURA, N., SUKEGAWA, E., PAN, S-K., NAGAO, K., KIM, J-Y., KWAN, T. (1971). Chemical methylation of inorganic mercury with methyl-cobalamin, a vitamin B₁₂ analog. *Science* 172, 1248 - 1249.
- JENSEN, S., and JERNELOEV, A. (1969). Biological methylation of mercury in aquatic organisms. *Nature (Lond.)* 223, 753 - 754.
- JOHNSON, D.L. (1972). Bacterial reduction of arsenite in seawater. *Nature(Lond.)* 240, 44-45.
- JONASSON, I.P. (1970). Mercury in the natural environment: a review of recent work. *Geol. Surv. Can., Paper 70-57*, 39 pp.
- KORTHALS, E.T., and WINFREY, M. R. (1987). Seasonal and spatial variations in mercury methylation and demethylation in an oligotrophic lake. *Appl. Environ. Microbiol.*, 53, 2397 - 2404.
- LINDQVIST, O., Ed., (1991). Mercury as an environmental pollutant. In *Water, Air and Soil Pollution, Special Volume 56*, Kluwer Academic Press, Dordrecht.
- LUND, D.L. (1996). Wyoming operator solves mercury exposure problems. *Oil and Gas Journal*, May 13, 70.
- LUNDE, G. (1973). Synthesis of fat and water soluble arseno organic compounds in marine and limnetic algae. *Acta Chem. Scand.* 27, 1586 - 1594.
- MAHLER, H.R., and CORDES, E.H. (1966). *Biological chemistry*. Harper and Row, New York.
- MANK, L., BARTHEL, Y., CAMERON, C., and SARRAZIN, P. (1995). Process for the elimination of mercury and possibly arsenic from hydrocarbons. Patent No: US 5384040 950124.
- McBRIDE, B.C., and WOLFE, R.S. (1971). Biosynthesis of dimethyl arsine by *Methanobacterium*. *Biochemistry* 10, 4312 - 4317.
- MISRA, A., LAUKART, A., and LUBCKE, T. (1993). Dehydration, mercury removal and hydrocarbon dewpoint control in Söhligen Gas field, Germany. *Erdöl, Erdgas Kohle* 109 Feb. 193), 67.
- MUSSIG, S., and ROTHMANN, B.(1997). Mercury in natural gas - problems and technical solutions for its removal. SPE Paper 38 088, 1997 SPE Asia Pacific Oil and Gas Conference, Kuala Lumpur, Malaysia, 14 - 16 April.
- NELSON, J.D., and COLWELL, R.R. (1975). The ecology of mercury-resistant bacteria in Chesapeake Bay. *Microb. Ecol.*, 1, 191 - 218.
- NGUBANE, W.T., and BAECKER, A.A.W. (1990). Oxidation of gold-bearing pyrite and arsenopyrite by *Sulfolobus acidocladarius* and *Sulfolobus BC* in airlift bioreactors. *Biorecovery* 1, 255 269.
- OLSEN, K.B., EVANS, J.C., SKLAREW, D.S., GIRVIN, D.C., NELSOM, C.L., LEPEL, E.A., ROBERTSON, D.E., and SANDERS, R.W. (1986). Partitioning and chemical speciation of mercury, arsenic, and selenium during inert gas oil shale retorting.

Commonwealth Kentucky et al East Oil Shale Symposium (Lexington, KY, 11/18-20/85) Proc., pp 131 - 147.

OLSEN, S.D. (1997). Development and application of ICP-MS for the analysis of metals in sedimentary organic matter. Ph.D. thesis. University of Newcastle, Newcastle upon Tyne, U.K.

OLSON, G.J. (1994). Microbiological oxidation of gold ores and gold bio-leaching. FEMS Microbiol. Lett., 119, 1 - 6.

PHANENSTIEL, L.L., McKINLEY, C., and SORENSEN, J.S. (1976). Mercury in natural gas. Paper presented at the Am. Gas Assoc. Oper. Sect. Proc. Transm. Conf., May 3-5.

PLOUFFE, A. (1995). Glacial dispersion of mercury from bedrock mineralization along Pinchi Fault, north central British Columbia. Water, Air and Soil Pollution 80, 1109 - 1112.

PONGSIRI, N. (1997). Thailand's initiatives on mercury. SPE Asia Pacific Oil and Gas Conference, Kuala Lumpur, Malaysia, 14-16 April 1997. SPE Paper No. 38087, 99. 553 - 558.

PORCELLA, D., HUCKABEE, J.W., WHEATLEY, B., Eds., (1995). Mercury as an environmental pollutant. In Water, Air and Soil Pollution, Special Volume 80, Kluwer Academic Press, Dordrecht.

RONA, P.A. (1986). Mineral deposits from sea-floor hot springs. Sci. Am., 254, 66 - 74.

SCHRAUDZER, G.N., WEBER, J.H., BECKHAM, T.M., and HO, R.K.Y. (1971). Alkyl group transfer from cobalt to mercury: reaction of alkyl cobalamins, alkyl cobaloximes, and of related compounds with mercury acetate. Tetrahedron Lett., 3, 275 - 277.

SCUDLARK, J.R., and JOHNSON, D.L. (1982). Biological oxidation of arsenite in seawater. Estuarine, Coastal and Shelf Science 14, 693 - 706.

SIEVER, R. (1983). The dynamic earth. Sci. Am. 249(September), 30 - 39.

SILVERMAN, M.P., and LUNDGREN, D.G. (1959). Studies on the chemoautotrophic iron bacterium *Ferrobacillus ferrooxidans*. I. An improved medium and a harvesting procedure for securing high cell yields. J. Bacteriol., 77, 642 - 647.

SLATON, M. (1989). Southeast New Mexico: Ironing out arsenic-tainted wrinkle. Southwest Oil World 36(11), 14, 17.

STRAHLER, A.N. (1977). Principles of Physical Geology. Harper & Row, New York.

TISSOT, B.P., and WELTE, D.H. (1984). Petroleum formation and occurrence. 2nd Ed., Springer-Verlag, Berlin, New York, 699p.

TITLEY, S.R. (1981). Porphyry copper. Am. Scientist 69, 632 - 638.

VOSTAL, J. (1972). Transport and transformation of mercury in nature and possible routes of exposure. In Eds., L. Friberg and J. Vostal, Mercury in the Environment. An Epidemiological and Toxicological Appraisal. CRC Press, Cleveland, pp. 15 - 27.

WATRAS, C.J., and HUCKABEE, J.W. Eds., (1994). Mercury as a global pollutant: Towards integration and synthesis. Lewis Press, Boca Raton.

YAMADA, M., and TONOMURA, K. (1972). Microbial methylation of mercury in hydrogen sulfide-evolving environments. J. Ferment. Technol., 50, 901 - 909.

YAN, T.Y. Method and device for simultaneously drying and removing metallic and organic mercury from fluids. PCT Patent, International Publication Number WO 94/05392, Int. Publ. Date march 17, 1994.

ZETTLITZER, M., SCHØLER, H.F., EIDEN, R., and FALTER, R. (1997). Determination of elemental, inorganic and organic mercury in North German gas condensates and formation brines. SPE International Symposium on Oilfield Chemistry, Houston, Texas. SPE paper No 37260, pp. 509 - 516.