

Review: evaporation of mercury from soils. An integration and synthesis of current knowledge

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Abstract Understanding the mechanisms of mercury evaporation from soil to the atmosphere is necessary for tracing the fate of mercury in the biological environment and for assessing potential health effects and the impact of anthropogenic mercury emissions on the environment. In this article an integrating overview of the current knowledge of the mechanisms of mercury evaporation is presented. Abiological and biological formation of Hg(0) and/or (CH₃)₂Hg in the uppermost soil layers are the rate limiting processes of mercury evaporation from soils in background areas; the evaporation rate in background areas is probably strongly influenced by deposited airborne mercury. The evaporation rate limiting factors in mercury enriched mineralized areas with large fractions of total mercury being volatile mercury species (relative to background soil in the non-mineralized vicinity) meteorological variations and the transport characteristics of soils for volatile mercury species. Mercury evaporation rates from background soils are usually $0.2 \mu\text{g} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ and significantly smaller than from mercury-enriched mineralized areas.

Key words Evaporation · Volatilization · Soil · Mineralized area · Atmosphere · Deposition

Introduction

Anthropogenic mercury emission into atmosphere and atmospheric deposition have increased significantly since pre-industrial times, especially in the northern hemisphere (Galloway and others 1982; Johansson 1984; Lindqvist and others 1984; Slemr and Langer 1992; Swain and others 1992). Current estimates for anthropogenic mercury emission range from about 50 to 75% of the total annual mercury emission to the atmosphere; recent modell-

ing suggests that the present atmospheric mercury burden has increased by a factor of three during the last 100 years (Fitzgerald 1995). Mercury present in the environment may up-concentrate to levels toxic for biological systems. For instance, the increase of the mercury pool of freshwater systems is an important factor causing a significant increase of the mercury content in fish, where bio-concentration factors (relative to the water) up to 10⁷ were reported (Watras and others 1994). Mercury concentrations in fish from a large number of freshwater lakes, including waters remote from local sources of pollution, have been found to exceed guidelines for human consumption in Canada, the north-central and northeast United States, Sweden and Finland (OMOE 1981; Håkanson 1984; Helwig and Heiskary 1985; Håkanson and others 1988; Lathrop and others 1989; OMOE and OMNR 1989).

For tracing the fate of the mercury emitted into the environment, as well as for estimating the future development of the mercury burden of our environment and for predicting the toxic consequences, it is important to investigate the global and regional mercury fluxes. This includes quantification of the mercury which is already or potentially biologically available in the ecosystem (e.g. sorbed to soils or sediments), the mercury which is released from geological sources (e.g. ore deposits and geothermal sources) and the mercury which is released by anthropogenic activity. A major question is the importance of anthropogenic mercury relative to the mercury content in pristine environment. The answer to this question is crucial for understanding the effects of human activity and for implementing a policy of restricted use and release of mercury.

One pathway of the mercury flux in the environment is the evaporation from soils. Estimations of the quantitative significance of evaporation relative to other pathways, including emission from the bottom of the oceans, from geothermal or tectonically active areas and anthropogenic activities, are very uncertain. Too little is known about the amounts and species of mercury evaporating from soil and the factors causing and affecting this process. This article presents an integrated model of mercury evaporation from soils based upon a thorough discussion of the literature. Only processes, which are directly involved in mercury evaporation from soil, are discussed in detail, whereas general processes of gas-transport in the soil and the atmosphere are only marginally mentioned.

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Sources of evaporating mercury

Mercury evaporating from soil is likely to derive from three different sources/pools of mercury in soil:

1. **The airborne mercury pool.** This soil pool includes airborne Hg(II) and Hg(0), recently deposited on the soil surface by dry and wet deposition, including litter-fall and airborne Hg(0) recently sorbed to the soil surface from air (by gravitational settling and brownian motion). This mercury is undergoing chemical, physical and microbiological processes of transformation into oxidation states and compounds stable in the soil environment and re-distribution to sorption positions according to the affinity of the soil components. Mercury becomes strongly sorbed to humic compounds and/or it may be firmly sorbed to and occluded in soil minerals, making it relatively unavailable to abiotic and biotic processes. The speciation of wet and dry deposited airborne mercury is still under discussion. Most of the wet and dry deposited mercury is inorganic Hg(II) possibly in form of HgCl_2 and with the major fraction associated with particles (Pacyna and Ottar 1989; Iverfeldt 1991a, 1991b; Lindqvist and others 1991; Munthe 1993; Driscoll and others 1994; Keeler and others 1995). Usually less than 5% of the total deposited mercury (wet + dry) (Munthe 1993; Hultberg and others 1994) are reported to be in the form of monomethyl mercury. Most of the atmospheric mercury (>95%) is Hg(0). An unknown amount of unspecified mercury [probably mainly Hg(0)] is actively sorbed from atmosphere to soil surface, most likely contributing significantly to the total deposition of mercury (e.g. Steiness and Andersson 1991). Some of the deposited and sorbed airborne mercury [esp. Hg(0) and CH_3Hg^+] may be re-emitted according to their volatility or co-distilled with the evaporation of soil water. The rest becomes incorporated into the soil mercury pool.
2. **The geogenic mercury pool.** This soil pool includes geogenic Hg(II), Hg(I) and Hg(0) which were recently released from ore deposits and bedrock mostly by oxidation and weathering, or which originate from geothermal sources (Tunell 1964; Jonasson 1970; Jonasson and Boyle 1971, 1972; Khayretdinov 1971; Lindsay 1979; Chengliang and others 1989). As to airborne mercury, geogenic mercury undergoes a process of incorporation into the soil matrix. A steady mercury input from geological sources to soil may form according to the sorption efficiency of the soil components and rates of plant uptake, leaching and evaporation into atmosphere. In discussing mercury evaporation from soils, mineralized, geothermal or seismically active areas or areas of deep geological structures with dominance of geogenic mercury and their subsequent high fraction of volatile mercury species, have to be distinguished from background areas with their larger fraction of airborne and non-volatile mercury species.
3. **The soil mercury pool.** This soil pool includes airborne and geogenic mercury which are incorporated

into the soil matrix. This pool shows only slow transformation or turnover (e.g. translocation with soil water or volatilization) dependent on factors such as the climatic conditions.

It is likely that different abiotic and biotic processes dominate formation of volatile mercury species during the various phases of incorporation into the soil as well as when the relative inert state is reached. For instance, during transformation abiotic reduction may be very effective since Hg^{2+} is readily available to reductants.

Areas with geogenic mercury anomalies and background areas

Enhanced crustal degassing of mercury, mercury anomalies in soil, soil air and bedrock and sometimes even in the lower atmosphere can be found in the following zones of the earth:

1. Zones of high crustal heat flow (geothermal zones, including volcanoes). For more information refer to U.S. Government Printing Office (1970), Cox and Cuff (1980); Varekamp and Buseck (1983, 1984b, 1986), Priest and others (1983), Klusmann and Landress (1979).
2. Zones of mineralization, especially where the deposits are exposed to weathering.

Elevated mercury contents are typically associated with base metal sulphides and precious metal deposits (e.g. Au, Pb, Zn, Cu) and some other elements such as As and Sb. Mercury was also reported associated with non-ore deposits such as oil and gas (White 1981; Ozerova 1982; Fursov 1983; Xie and Zheng 1983; Xie and Yang 1989). The measurement of the total mercury content of soil and sometimes soil gas is a common surveying technique in geochemical exploration to locate buried ore deposits (McCarthy and others 1969b; McCarthy 1972; McNerney and Buseck 1973; Wallner 1977).

The most mercury-containing deposits and mercury deposits found to date were formed during the late mesozoic until tertiary epoches (about 1×10^6 until 150×10^6 years ago; Odd Nielsen, personal communication). The largest mercury enrichments and the highest rates of mercury degassing are usually found within the mercuriferous belt (Fig. 1), where most of the principal mercury deposits and mercury prospects are found. The global distribution of the mercuriferous zones is controlled by crustal heat flow and tectonic instability and is often marked by the presence of geothermal activity (Jonasson and Boyle 1972; Stepanov and Vild'yayev 1984). In mineralized areas, the mercury concentration of soil often increases to several thousands or even tens of thousands $\mu\text{g} \cdot \text{kg}^{-1}$ (e.g. Warren and others 1966; Friedrich and Kulms 1969; U.S. Government Printing Office 1970; Ferrara and others 1991a).

3. Zones of deep geological structures of elevated crustal permeability, acting as conduits for Hg(0) vapor from deep within the crust (e.g. rift zones and regional faults and fractures in the bedrock). Relative to faults and fractures, rift zones are considerably less abundant in the continental crust, but the processes of mercury degassing from deep within the earth crust are probably the same

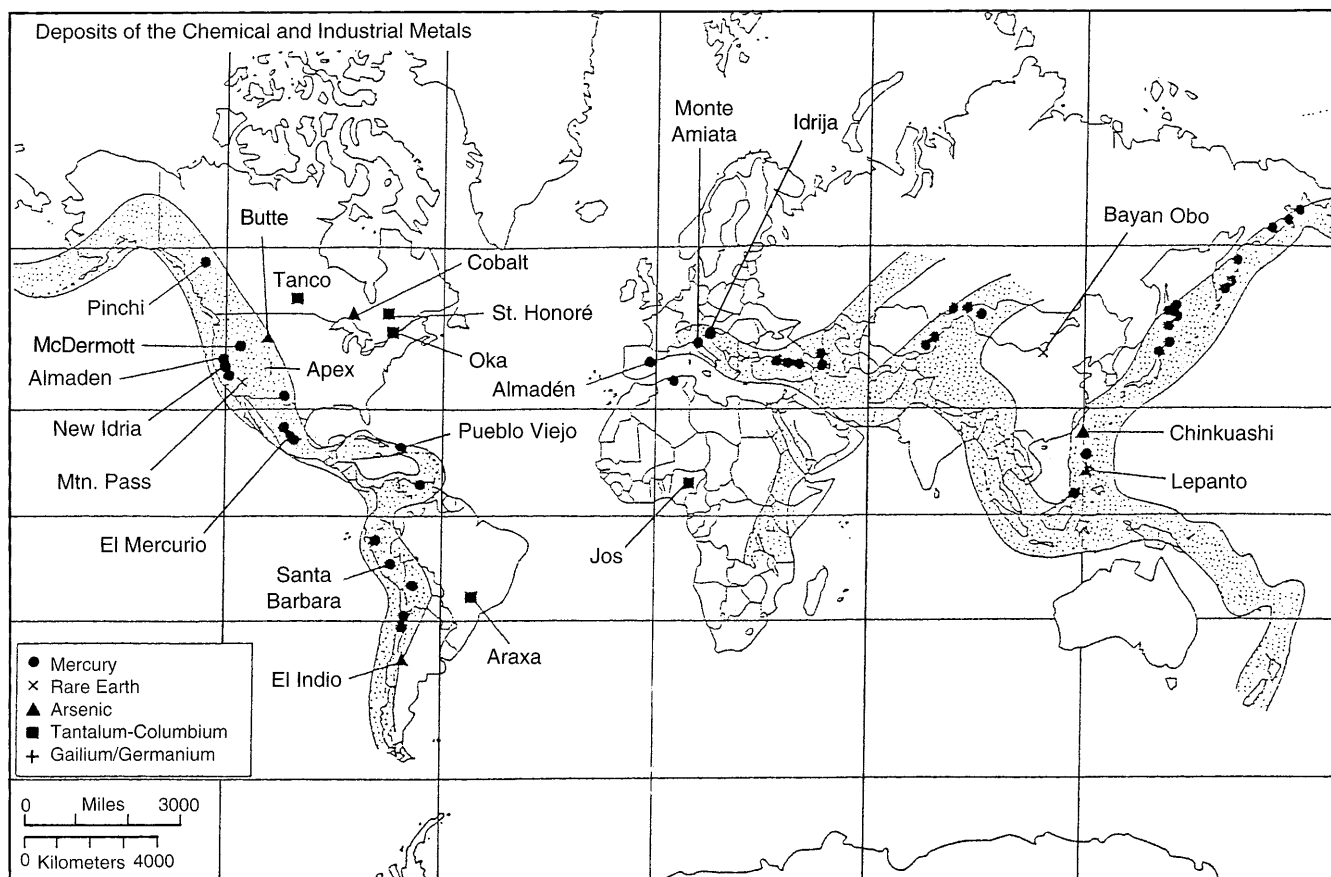


Fig. 1

Location of important metal deposits and the distribution of deep focus earthquakes along subduction zones, showing the close correlation between mercury deposits and these zones (from Kesler 1994)

as for faults and fractures. Fault-related mercury anomalies tend to be restricted in areal extent, with diameters ranging from 10 to 150 m (Kovalevskii 1983, 1986). Rasmussen (1993) reported elevated mercury concentrations (2–12 times background) from soils within 100 m from faults. The strong retention of mercury in soil is one of the factors restricting lateral mobility in soil. Not all faults and fractures are still active conduits for Hg(0) vapor due to depletion of mercury in the adjacent bedrock during recent times.

Faults and fractures can be hidden by glacial drift. If the drift, consists of clay or silt with low permeability, upward movement of mercury will be impeded; formation of mercury anomalies in soils over glacial drift of sandy till or sand is more likely.

4. Zones of seismic activity, where various tectonic processes, accompanied by mechanical stress in the rocks (e.g. pressure, tension, structure change, crushing), use some of their energy in extracting free Hg(0) vapor from rocks (e.g. Stepanov and Vild'yayev 1984; Varshal and others 1985). Strongly increased mercury concentrations (up to 100 fold) in ground water (Jin and others 1989), spring water (Zhu and You 1989) and soil air (Varshal

and others 1985; Azzaria and K-Seguin 1990) were reported for a time before, during and after seismic activity. Average Hg(0) emission rates in seismic zones exceed background crustal degassing rates 10–100 times, a phenomenon researched as tool to predict earthquakes (Varshal and others 1985; Jin and others 1989; Zhu and You 1989; Azzaria and K.-Seguin 1990). Varekamp and Waibel (1987) associated elevated mercury concentrations in a Californian lake sediment with mercury release during seismic events. Azzaria (1992) found that soils associated with a seismically active fault zone contained about four times more mercury than soils from a non-active fault zone.

The four types of zones are often associated with each other. For instance, all economic mercury deposits outside the plate margins are situated in fault zones (Jonasson and Boyle 1972). Mineralogical occurrences of mercury originate from past geothermal and tectonic activity (e.g. fossil hydrothermal systems; see Varekamp and Buseck 1983). However, fault related mercury anomalies in soil can also be found in non-mineralized and non-geothermal areas (Brooks and Berger 1978; Rasmussen 1993). Increased mercury degassing through faults or fractures may also occur during seismic and aseismic (movement of crustal blocks along fault surfaces without earthquake activity) sliding. According to Slunga (1990) most fault sliding is aseismic. This type of movement can be detected by geodetic measurements. In Sweden's Precambrian Shield, aseismic sliding is estimated to be 20 000

times more extensive than seismic sliding (Slunga 1990). The rates of vapor formation are dependent on the intensities and scales of the processes leading to the formation of the four zones, as well as on the mercury concentrations in ores and rocks. Therefore, for instance not all deposits containing elevated amounts of mercury are accompanied by substantial vapor aureoles in bedrock and/or soils (Stepanov and Vild'yayev 1984; Azzaria and Aftabi 1991). On the global scale, tectonic and geothermal activities are most intense along plate boundaries, especially the Circum-Pacific belt and Mediterranean-Asiatic belt, where the world's major mercury deposits are located (Fig. 1; Jonasson and Boyle 1972). Tectonic and geothermal processes in plate interiors, such as the Precambrian Shield, are much less intense than at plate boundaries. Hence, earthquakes in plate interiors tend to occur along pre-existing zones of weakness in the crust (e.g. fault and fracture zones and other tectonic boundaries; Sykes 1980). Zones of mercury enrichment in the Shield regions of Canada are therefore smaller and more subtle than in younger, tectonically active coastal regions. Generally there must be some kind of permeability (e.g. faults, permeable rock or till, contact zones) to provide a migration pathway for abyssal mercury to reach the surface environment.

Elevated mercury concentrations in soils associated with these four zones may be within the ranges of mercury concentrations usually found in background areas. Generally, background mercury concentrations of soil vary widely from place to place, depending on the local tectonic and geothermal setting. If total mercury contents are significantly higher in samples collected near a geological feature than further away, and all other influences are equal, it is probable that the geological feature is the source of the mercury anomaly. For instance, in a geothermal zone in China soil mercury concentrations less than $60 \mu\text{g Hg} \cdot \text{kg}^{-2-1}$ soil were defined as background concentration and higher concentrations as anomalous (Zhu and others 1986), whereas in a mineralized area in Germany mercury concentrations as high as $1800 \mu\text{g Hg} \cdot \text{kg}^{-2-1}$ soil were found, clearly exceeding the background concentrations ($< 200 \mu\text{g Hg} \cdot \text{kg}^{-2-1}$) in the unmineralized vicinity (Krömer and others 1981). Due to mercury losses from soil parent bedrock during weathering, the mercury concentrations of bedrock may have to be determined from drill core samples (Rasmussen 1993; Stepanov and Vild'dyayev 1984). In this article the term "non-background area" denotes areas of elevated mercury degassing from the earth crust and/or elevated soil mercury concentrations related to geothermal activity, mineralization, seismic activity or deep geological structures; the term will not include areas contaminated with airborne mercury or contaminated by human activity in other ways.

The significance of geogenic versus deposited airborne mercury in mercury evaporation from soil

Generally, Hg(II), Hg(I) and Hg(0) are released from bedrock and transported to soil and atmosphere with pelli-

cular water, thermal water or as mercury vapour, rising along fissures in the bedrock and in the porous volume of sediments. On geological time-scales it can be translocated with tectonic movement (Friedrich and Kulms 1969; Jonasson and Boyle 1972; McNerney and Buseck 1973). In non-background areas the processes of mercury release from geological sources and mercury transport are considerably more intense than in background areas and in non-geothermally active areas, and significant fractions of total mercury that are migrating into soil are in form of Hg(0) (Hawkes and Williston 1962; Dvornikov and others 1963; Karasik and Bol'shakov 1965; Fursov and others 1968; McCarthy and others 1969a, 1969b; Jonasson 1970; Varekamp and Buseck 1984a; Chengliang and others 1989). According to Ryall (1979) and Kovalevskii (1986) mercury degasses largely as Hg(0) vapor from the earth crust. Hg(0) is also often formed during the weathering of deposits according to the ambient pH/ E_h conditions (McNerney and Buseck 1973) and/or the presence of reductants (e.g. Fe(II)) (Jonasson and Boyle 1972; Wilson and Weber 1979). Due to removal of Hg^{2+} from solution by strong complexation to soil organic matter some of the Hg(0) will be re-oxidized and Hg(I) will disproportionate to Hg(II) and Hg(0). However, in non-background areas high amounts of Hg(0) are likely to be found in soil due to the high rates of degassing from geological sources (Jonasson 1970; U.S. Government Printing Office 1970; Jonasson and Boyle 1972; Klusmann and Landress 1979; Varekamp and Buseck 1984a; Azzaria and Aftabi 1991; Sidle 1993). This can cause a strong rise in the mercury concentration of the atmosphere above ground from $1-4 \text{ ng Hg} \cdot \text{m}^{-3}$ up to tens of thousands $\text{ng Hg} \cdot \text{m}^{-3}$ (U.S. Printing Office 1970; Lindberg and others 1979; Krömer 1981; Ferrara and others 1991b; Munthe 1993). Therefore, in non-background areas degassing from crustal bedrock can be the dominant origin of mercury evaporating from soil. In background areas and areas not contaminated by human activity the rates of mercury degassing from bedrock are usually considerably lower. During the last geological epochs (late mesozoic until tertiary epochs) mercury was lost by erosion (e.g. Plouffe 1995) and by degassing from bedrock formed more than 150×10^6 years ago (Odd Nielsen, personal communication). Therefore, mercury concentrations of soil parent bedrock in these areas are usually very low (usually $< 50 \mu\text{g} \cdot \text{kg}^{-1}$) and the mercury content of the upper soil horizons is usually swamped by atmospheric mercury deposition, including input with plant debris (Jonasson and Boyle 1970, 1972; U.S. Government Printing Office 1970; Andersson 1979; Steinnes 1995); in uncontaminated background soils the mercury concentrations are usually $< 500 \mu\text{g} \cdot \text{kg}^{-1}$ (e.g. Steinnes 1995). For the following reasons it can be expected that a major fraction of the total mercury content of the upper soil layers containing organic matter, originates from atmospheric mercury deposition in background areas: (1) Mineral matter, which could contain mercury is very scarce in the humus horizons of forest soils. (2) In forest soils, probably more than 70% of the total mercury deposition

on the soil surface is retained in the humic-rich upper soil layer (e.g. Aastrup and others 1991; Driscoll and others 1994; Schlüter and others 1995b; Schlüter 1995a). A similar fraction is probably retained in the topsoil even if there is no organic layer (Semu and others 1985; Wimmer and Haunold 1973; Wimmer 1974; Hogg and others 1978; Blinov 1982). Accordingly, the mercury content in soil profiles is usually highest in the topsoil (Andersson 1979; Schlüter 1993; Grigal and others 1994). (3) Root barriers against mercury uptake from soil (Stewart and others 1975; Rauter 1976; Beauford and others 1977; Fathi and Lorenz 1980; Fukuzaki and others 1986; Godbold and Hüttermann 1988) and barriers against mercury transport from roots to above ground parts in higher/vascular plants (Ross and Stewart 1962; Gilmour and Miller 1973; Beauford and others 1977; Lindberg and others 1979) are likely to prevent a significant redistribution of mercury from deeper soil layers to the upper organic layer. Accordingly, mercury concentrations in vegetation (per dry weight) of background areas were found to be below the concentrations of the respective substrate soil even when the mercury content is related to the content of organic matter (Lindberg and others 1979; Tamura and others 1985; Bargagli and others 1986; Kovalevskii 1986; Padberg 1991; Rasmussen 1993). However, considerable bio-concentration of mercury in vegetation was sometimes reported from mineralized areas or geothermal active areas (Siegel and others 1975, 1987; Lindberg and others 1979; Warren and others 1983; Kovalevskii 1986). Furthermore, the mercury concentrations of the uppermost background soil layers are usually significantly higher than the soil parent bedrock (Andersson 1979; Schlüter 1993; Steinnes 1995). Redistribution of mercury in soil by burrowing and tunnelling organisms (e.g. earthworms) is assumed insignificant in most soils and is not considered in the present discussion. For instance, only weak bio-concentration has been reported in earthworms (Cocking and King 1994).

Accordingly, redistribution of soil mercury by vegetation is usually negligible and anthropogenic immissions may have a large impact on the upper organic rich soil layer, as is displayed by the calculation of Lindqvist and others (1991), showing that more than 80% of the total mercury in the humus layer of forest soils in south Sweden originate from anthropogenic emission. Literature data reporting low concentrations of monomethyl mercury in vegetation indicate that there is no or only negligible transfer of monomethyl mercury from soils into roots and higher parts of the plants nor do plants produce significantly additional monomethyl mercury compared to the atmospheric input (Lee and Iverfeldt 1991; Stoeppler and others 1993; Schlüter and Gäth 1999). Therefore, the soil content of monomethyl mercury is probably either due to atmospheric deposition or formation in soil. Data on the monomethyl mercury content in soils are very scarce but it seems to make up less than 2% of total mercury in soil (Van Faassen 1975; May and others 1985; Padberg 1991; Munthe 1993; Lee and others 1995). Therefore, if mercury evaporation is originating from the

upper soil layers recently deposited, airborne mercury and airborne mercury incorporated into the soil matrix, are probably the main sources in background areas. Based on field measurements of mercury evaporation from a Scandinavian podzol soil Xiao and others (1991) determined an average evaporation rate of $0.30 \text{ ng} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ for a period with temperatures about 10°C , not discriminating between mercury evaporation from soil and mercury degassing from bedrock. Schlüter and others (1995c) modelled the average mercury evaporation from a similar soil type based on their measurements of mercury evaporation from undisturbed soil columns treated with radioactive mercury tracer. The modelled evaporation rate was identical with the value of Xiao and others (1991). Since the result of Schlüter and others (1995c) did not account for the contribution of mercury degassing from bedrock, the field measurements of evaporating mercury of Xiao and others (1991) can be explained with mercury evaporation originating predominantly from deposited airborne mercury. However, to date the relative importance of the three mercury pools distinguished in this section for the evaporation flux from soil is still under discussion. In the following sections, data are presented showing that evaporation rates from mercury enriched soils of non-background areas or soils contaminated with volatile mercury species [$\text{Hg}(0)$ and $(\text{CH}_3)_2\text{Hg}$], are considerably higher than from background areas (Table 1). Therefore, degassing of $\text{Hg}(0)$ from geological sources is likely to dominate mercury evaporation from soils of mineralized areas, whereas formation of volatile mercury species from soil mercury and airborne mercury may be dominant in background areas.

The soil horizon being the dominant origin of evaporating mercury

In areas where mercury evaporation from soil is primarily originating from the soil-mercury pool, the maximum depth of the soil layers significantly contributing to the evaporation flux depend on: (1) the qualitative and quantitative distribution of mercury in the soil profile, (2) the places of formation of volatile mercury species, (3) the physical migration of the mercury species within the soil and (4) the physical and chemical sorption of mercury vapour (including all mercury species).

It is likely that most mercury is evaporating from soil layers where the highest mercury concentrations are found under conditions favoring the formation of volatile $\text{Hg}(0)$, di- and/or monomethyl mercury (see sec. 4), and where only little sorption loss to the overlying soil will occur. Therefore, the $\text{O}_{(f)}$ - and $\text{O}_{(h)}$ -horizons of forest soils and the uppermost organic rich A-horizon of soils without organic horizon can be expected to be the dominating site. In these horizons, the mercury concentrations of inorganic $\text{Hg}(\text{II})$ and CH_3Hg^+ can be found together

Table 1

Literature data of mercury concentration in air and mercury evaporation from soils. a) Schlüter and others 1995b, 1995c; b) Xiao and others 1991; c) Cannon and Dudas 1982; d) Andren

and Nriagu 1979; e) Johnson and Braman 1974; f) Schroeder and others 1989; g) Lindberg and others 1979; h) McCarthy and others 1970; i) Munthe 1993; j) Kim and others 1993; k) Lindberg and others 1994; l) Kim and others 1994

Soil type	Vegetation	Soil/Air Temperature (°C)	Hg content and Hg treatment	Mid-point of sampling period (h)	Evaporation flux (g·m ⁻² ·h ⁻¹)	Hg _{air} above soil (g·m ⁻³)	Author
Podzol (this experiment)	Coniferous forest	-/4-6	1843 μg·m ⁻² [= 120 μg Hg (HgCl ₂)]	90	0.13-0.20	0.063-0.096	a)
"	"	"	"	840	0.026-0.048	0.013-0.023	"
"	"	"	"	2302	0.0091-0.026	0.0044-0.013	"
"	"	"	"	90-3600	0.00356-0.201	0.0050-0.0964	"
"	"	"	15361 μg·m ⁻² [= 1000 μg Hg (HgCl ₂)]	90	1.78-3.85	0.86-1.86	"
"	"	"	"	840	0.077-0.27	0.037-0.13	"
"	"	"	"	2302	0.056-0.11	0.027-0.054	"
"	"	"	"	90-3600	0.0351-3.88	0.0168-1.86	"
Podzol (this experiment)	Coniferous forest	-/4-6	1843 μg·m ⁻² [= 6144 μg Hg (CH ₃ HgCl)]	90	0.014-0.018	0.0066-0.0088	a)
"	"	"	"	1631-2302	0.41-0.51	0.23-0.25	"
"	"	"	"	2984	0.23-0.41	0.11-0.20	"
"	"	"	"	90-3600	0.013-0.51	0.0066-0.25	"
"	"	"	15361 μg·m ⁻² [= 1000 μg Hg (CH ₃ HgCl)]	90	0.019-0.031	0.0092-0.019	"
"	"	"	"	1282-1631	1.96-4.22	0.95-2.03	"
"	"	"	"	2984	0.74-1.43	0.36-0.69	"
"	"	"	"	90-3600	0.019-4.25	0.0092-2.03	"
Podzol	Coniferous forest	-5 to 13/ -10 to 20	Background area	-	0-0.0014	0.0021-0.0037	b)
"	"	10/-	"	-	0.3E-3 (= mean)		"
Orthic Gray Luvisols and Chernozem	Deciduous forest	No data	Background area		0.067-0.18		c)
∅ evaporation U.S.	No data	No data	Mineralized and non-min. areas		0.015		d)
No data	No data	No data	"		5.8E-5-0.42		"
No data	Patches of lawn	No data	2000 μg·m ⁻² (HgCl ₂)	48		0.038	e)
No data	Patches of lawn	No data	Not treated			0.0065	"
No data	No data	No data	Background area			0.0042-0.34	"
No data	Coniferous forest	10/19	Background area		1E-4-1.2E-3		f)
No data	Deciduous forest	10/15	"		1.4E-3		"
No data	Open field	-/15-18	"		0.9E-3-1.4E-3		"
No data	Bare soil	-/10	1 km from cinnabar mine		ca. 0.05	0.02	g)
"	"	-/25	"		0.32-0.34	0.13	"
"	"	-/35	"		ca. 0.6	0.25	"
"	Grass planted soil	-/25	"		0.07-0.09	0.13	"
"	Bare soil	-/10	15 km from cinnabar mine		ca. 0.05	0.004	"
"	"	-/25	"		0.12-0.14	0.03	"
"	"	-/35	"		ca. 0.6	0.22	"
No data	No data	No data	Non-mineralized areas			3E-3-9E-3	h)
"	"	"	Hg-mineralized areas			0.128-20	"
"	"	"	Mineralized areas			0.068-1.5	"
Usual air concentrations	No data	No data	Background areas			1E-3-4E-3	i)
Floodplain soil	Deciduous forest	5-18/-	contaminated 50-200 μg.g ⁻¹		0.015-0.16, ∅ 44E-3		j)
Floodplain soil column	Deciduous forest	28/-	contaminated 48 μg.g ⁻¹		0.84-1.47, ∅ 1.08		"
No data	"	5-18/-	Not contaminated ^a 0.5 μg.g ⁻¹		0-0.006		"
No data, soil column	"	28/-	Not contaminated 0.5 μg.g ⁻¹		0.001-0.037, ∅ 0.016		"
Floodplain soil	Deciduous forest	7-24/-	contaminated 50-200 μg.g ⁻¹		0.010-0.2, ∅ 0.086		k)
No data	Deciduous forest	14-36/-	Not contaminated 0.5 μg.g ⁻¹		0-0.029, ∅ 7.6E-3		l)
"	Deciduous forest	12-18/-	Not contaminated 0.5 μg.g ⁻¹		0.0008-0.02, ∅ 7.1E-3		"

^a Not contaminated means that the soil Hg concentrations are within the range of common background concentration and not elevated by mineralization, geothermal or human activities

with high microbial activity and the abundance of reductants such as organic matter (Trost and Bisque 1972; Låg and Steinnes 1978; Andersson 1979; Aichberger and Hoffer 1989; Padberg 1991).

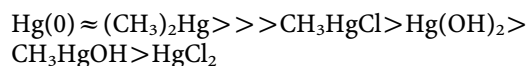
Solute and vaporous, volatile and non-volatile mercury species migrate by diffusion in and mass-transport with soil water as well as in and with soil air. Diffusion depends on the character of the medium, the size and the molecular weight of the diffusing species and the temperature. Diffusion is the most probable mechanism for slow transport of gases over short distances, particularly below the water table (Rose and others 1979). Mass transport is the only mechanism that can account for rapid migration over considerable distances. According to Ozerova (1962) mercury vapour migrates up to 2000 m through fissures in bedrock in mineralized areas. The effective diameter of the Hg(0) atom is 0.3 nm, which allows it to migrate even through ultra-thin fissures (Fursov 1990). Hg(0) has a high vapor pressure and at <200 °C it is 60000 times more volatile than for instance cadmium and zinc (Ryall 1979). Therefore, Hg(0) and probably also di- and monomethyl mercury can evaporate through soil and even hundreds of meters of bedrock or glacial overburden, which makes Hg(0) a useful indicator in geochemical exploration (e.g. Hawkes and Williston 1962; Ryall 1979; Kovalevskii 1986; Chengliang and others 1989; Fursov 1990). During migration of Hg(0) towards the atmosphere, some of the mercury may be re-adsorbed to soil. The relative amount sorbed in non-background areas is probably much smaller than in non-contaminated background areas due to a saturation of sorption sites. Re-adsorption is favored by high content of organic matter and depends quantitatively on the type of the organic matter (Trost and Bisque 1972; Fang 1978, 1981). Therefore, organic rich, upper soil horizons in non-background areas are usually more strongly enriched with mercury than mineral soil horizons containing little organic matter (Koksoy and Bradshaw 1969; Trost and Bisque 1970; Wallner 1977; Krömer 1981). Many clay minerals sorb Hg(0) vapour but to a considerably smaller degree than organic matter (Trost and Bisque 1972; Wallner 1977; Fang 1978). Also some metal oxides such as MnO₂ (Saukov 1946) were shown to possess a high capacity for sorption of Hg(0) vapour. The sorption of Hg(0) vapour increases also with an increasing accessible surface (Trost and Bisque 1972).

Desorption of sorbed Hg(0) depends on the characteristics and size of the surface area of the soil components, the amount of sorbed mercury and the presence of ambient conditions favoring desorption (e.g. Wallner 1977). After being sorbed to soil, Hg(0) can be re-oxidized abiotically or biotically (Holm and Cox 1975; Fang 1978, 1981; Landa 1978c). Due to the high binding strength of Hg²⁺ to organic matter, the oxidation of Hg(0) to Hg(II) proceeds already at redox-potentials lower than the redox-potential of the relevant half-reaction suggests (Jernelöv 1969). Therefore, Hg(II) being reduced in deeper soil layers or Hg(0) evaporating from geological sources, is likely to be re-oxidized in higher layers in background

areas, making the uppermost soil layer dominating the mercury evaporation from soil. Furthermore, the sorption loss of evaporating mercury will be small due to the short distance to the soil surface. Consistent with this Cannon and Dudas (1982) found that mercury evaporation measured above the O_(l)-horizon of a deciduous forest soil was not significantly different from the underlying O_(e)- and O_(h)-horizons. Due to the small sorptive surface of the litter components it is likely that mercury-sorption sites are more or less saturated with deposited atmospheric mercury. Therefore, it can be expected that mercury evaporating from the O_(e)-soil horizon will not be bound to a major extent to the litter or, if so, volatile mercury will be released from litter to atmosphere with a short time delay, not affecting the total mercury evaporation from soil.

The mercury species evaporating from soil

It is widely accepted that mercury evaporating from soil in non-background and background areas is predominantly in form of Hg(0) vapour and/or dimethyl mercury vapour, probably with minor contributions of monomethyl mercury and soluble Hg(II)-salt (Hitchcock and Zimmermann 1957; Kimura and Miller 1964; Frear and Dills 1967; Alberts and others 1974; Johnson and Braman 1974; Schlüter 1995b). Some of the volatile and non-volatile mercury species may evaporate from soil by co-distillation with evaporating water. The volatility of the evaporating species is differing considerably, with elemental mercury and dimethyl mercury being by far the most volatile compounds. In Table 2 some important air/water-distribution constants are listed, indicating the sequence of volatility:



Hg(0) and (CH₃)₂Hg are the only two mercury species classified as “volatile”, since their solvation in water is entirely due to London forces. The other mercury species are classified as “non-volatile”, with at least 500 times lower air/water-distribution constants than the volatile species (Iverfeldt 1984, Iverfeldt and Lindquist 1984).

Formation, and turnover of Hg(0) in soil and its evaporation from soil

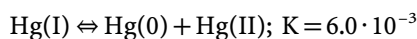
Abiotic reduction of Hg(II) to Hg(0) in soil
Abiotic reduction according to the E_h/pH conditions of the soil: Mercury migrates into soil as Hg(0) degassing from geological sources, or as Hg(I) and Hg(II) transported with the groundwater rising from geological sources or as the result of tectonic movement (Jonasson and Boyle 1972). Mercury in all the oxidation states is also released during weathering of soil parent rock (Tun-

Table 2

Experimentally determined distribution constants for important soil Hg compounds. a) Sanemasa 1975; b) Talmi and Mesmer 1975; c) Iverfeldt and Lindqvist 1982; d) Iverfeldt and Lindqvist 1980; e) Iverfeldt and Persson 1985

Compound	$K_d = [\text{HgX}(\text{g})]/[\text{HgX}(\text{aq.})]$ (g HgX · m ⁻³ air/g HgX · m ⁻³ aq.)	Temperature (°C)	Reference	Cl ionic strength
Hg ⁰	0.29	20	a	0
(CH ₃) ₂ Hg	0.31	25	b	0
(CH ₃) ₂ Hg	0.15	0	b	0
CH ₃ HgCl	1.9×10^{-5}	25	c	0.7
CH ₃ HgCl	1.6×10^{-5}	15	c	1.0
CH ₃ HgCl	0.9×10^{-5}	10	c	0.2×10^{-3}
Hg(OH) ₂	3.2×10^{-6}	25	d	0.2×10^{-3}
Hg(OH) ₂	1.6×10^{-6}	10	d	0.2×10^{-3}
CH ₃ HgOH	10^{-7}		e	
HgCl ₂	2.9×10^{-8}	25	d	0.2×10^{-3}
HgCl ₂	1.2×10^{-8}	10	d	0.2×10^{-3}

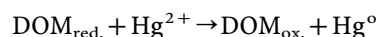
ell 1964; McNerney and Buseck 1973) and sediments during soil formation and from atmospheric deposition. Hg(I) is likely to disproportionate completely to Hg²⁺ and Hg(0), since Hg²⁺ is strongly sorbed to soil components (e.g. Andersson 1979; Schlüter 1993):



The E_h/pH conditions and the presence of strong mercury sorbents in most soils (especially organic matter) make Hg(II) the predominant mercury species in most soils (Andersson 1970, 1979; Jernelöv 1969; Schlüter 1995b). Hg(0) may occur as a large fraction of mercury in soils in mineralized areas with a significant flux of Hg(0) from geological sources.

Abiotic reduction of Hg(II) mediated by humic acids (HA), fulvic acids (FA) and other reductants: Hg(I) and Hg(II) can be reduced by reductants such as Fe²⁺ or organic material, for instance in groundwater (Jonasson 1970; Jonasson and Boyle 1972; Wilson and Weber 1979). HA and FA extracted from pond sediments and soils were found to mediate reduction of dissolved inorganic Hg(II) in aqueous solution (Strohal and Huljev 1971; Alberts and others 1974; Miller and others 1974, 1975; Miller 1975; Skogerboe and Wilson 1981). Alberts and others (1974) explained this with a reaction of Hg²⁺ with free radical electrons. HA and FA are known to contain a free radical component (Schnitzer and Khan 1972; Chen and others 1977; Senesi and Schnitzer 1977), which is partially or fully responsible for the reducing power of humic material (Wilson and Weber 1977). Alberts and others (1974) hypothesized that HA can act as catalyst or mediator in the reaction with electrons being delivered from other sources or by consumption of the radical groups. Frear and Dills (1967), Blinov (1982) and Wimmer (1974) reported mercury evaporation from soils treated with Hg²⁺ to increase with increasing soil moisture up to a certain degree. Wimmer (1974) reported mercury evaporation rates from various Hg²⁺ treated soils to decrease with increasing content of humic matter. These findings indicate that it is not solely the soil content of humic

matter but the quantity of dissolved organic matter (DOM), specifically DOM-mercury complexes, that affects the mercury evaporation rate. Hence, increasing soil moisture is accompanied by an increasing amount of DOM-Hg complexes, followed by an increasing evaporation rate. Consistent with this, Allard and Arsenie (1991) found indications that FA had to be complexed with Hg²⁺ to mediate the reduction to Hg(0). Generally, the content of mercury in soil solution and soil extracts is well known to be highly correlated with the content of DOM (Lodenius and others 1983; Lindqvist and others 1991; Johansson and Iverfeldt 1994; Schlüter 1995a). Consistent with this, Schlüter and others (1995b) explained the measured mercury evaporation from a podzolised forest soil to be mainly dependent on the concentrations of Hg²⁺ and DOM, expressed as:



Since they did not find any effect of the amount of Hg²⁺ applied to the soil surface on the fraction of mercury evaporating per hour, they concluded that the content of DOM in the organic soil layer was in excess compared to the content of Hg²⁺; consequently, they expressed the rate of this pseudo-first order reaction as:

$$\text{Reduction rate} \approx k \cdot [\text{DOM}]^0 \cdot [\text{Hg}^{2+}]^1$$

with $[\text{DOM}] \gg \gg [\text{Hg}^{2+}]$ and k = soil specific reduction constant.

Consistent with this, Miller and others (1974) found that HA mediated the reduction of Hg²⁺ independent of the HA/Hg weight ratio over a wide range of 400:1 to 5:1. At higher ratios (>1000:1) the evaporation almost halted, probably due to effective mercury binding and immobilization of ionic Hg²⁺ and/or Hg(0), whereas at lower ratios (<0.5:1) the evaporation rapidly decreased, probably due to consumption of the reductive potential. Also Blinov (1982) found that Mercury evaporation increased linearly with the amended amount of inorganic Hg(II) added to arable soddy podzolic sandy clay loam soil up to 12–14 mg · kg⁻¹. Concerning the soil specific reduction

constant, Skogerboe and Wilson (1981) found indications that FA is a better reducing agent than HA due to a higher reduction potential. It has also been shown, that the free radical concentration of organic matter increases with an increase in molecular weight of colloidal particles and degree of humification (Kleist and Mücke 1966; Retcofsky and others 1968; Riffaldi and Schnitzer 1972), which mediated Hg^{2+} reduction (e.g. Alberts and others 1974). Since HA and FA can also reduce other metal ions than Hg^{2+} (Kleist and Mücke 1966), the mercury reducing capacity may also depend on the concentrations and species of other metals in the soil.

Several authors have reported a rapid initial release of $\text{Hg}(0)$ from an aquatic solution containing HA or FA and Hg^{2+} , followed by a strong decline towards a low level steady state evaporation over a period of time ranging from 30 h to 3–4 days (Alberts and others 1974; Miller and others 1974; Skogerboe and Wilson 1981; Allard and Arsenie 1991). The authors attributed this decline to consumption of the reducing factor, effectively binding and immobilizing the mercury as ionic Hg^{2+} and/or $\text{Hg}(0)$. However, in contrast humic acids seem to possess a high reduction potential. Alberts and others (1974) found a significant decrease of free radicals in HA only after addition of $2000 \text{ mg} \cdot \text{kg}^{-1}$ inorganic Hg^{2+} , indicating that the observed decrease of the evaporation rate at smaller mercury additions was not due to a consumption of the reduction potential. Schlüter and others (1995b, 1995c) measured rapidly decreasing evaporation rates during the first 33 days after surficial Hg^{2+} treatment of podzolised forest soil columns, followed by a slow decrease, approaching asymptotically a zero evaporation rate during the remaining 130 days. They explained this with Hg^{2+} leaching from the zone of evaporation and with an increasing fraction of the applied Hg being strongly sorbed to the soil, and therefore not available to DOM, which carries the reductive factor; consumption of the reductive factor or decreasing reduction potential of this factor was ruled out since the evaporative mercury loss relative to the applied amount did not decrease with the applied amount. In accordance with these results, other scientists have reported a slow Hg^{2+} sorption to HA and FA, lasting from several days to a few weeks, implying the participation of sorption processes other than physical sorption (Strohal and Huljev 1971; Xu and Allard 1991). Also other authors have found that mercury evaporation from different soils containing at least 0.9% organic carbon treated with Hg^{2+} declines from maximum to minimum levels over 15 days (Frear and Dills 1967; Johnson and Braman 1974; Landa 1978b; Rogers 1979; Rogers and McFarlane 1979). Schlüter and others (1995b) demonstrated that the rapid decline of mercury evaporation can be explained with an abiotic reduction of Hg^{2+} rather than a biotic mediated process, due to the lack of features typical for microbiological detoxification (e.g. lag-phase, culmination of the evaporation rate, concentration effect on the fraction of evaporating mercury). It is likely that abiotic reduction of Hg^{2+} often dominates mercury evaporation from soils in background ar-

reas if soil conditions are unfavorable for biotic reduction or if the soil concentrations of biologically available mercury are too low to induce biotic reduction.

The reduction of Hg^{2+} by interaction with DOM may primarily originate from atmospheric mercury deposition for two reasons: (1) The fraction of airborne mercury from the total mercury content of the upper soil layer is often dominating. (2) The data presented in this article indicate that the availability for an interaction with reductive acting DOM of recently deposited atmospheric Hg^{2+} is probably higher than the Hg^{2+} which has been incorporated into the soil matrix and become relatively unavailable to abiotic or even biotic reduction during recent months or years.

Therefore, mercury evaporation from soil may originate from airborne mercury and the deposition rate may influence the evaporation rate. Furthermore, it seems reasonable that abiotic reduction also depends on the rates of mercury immobilization and mainly microbiologically mediated remobilization.

Biotic reduction of Hg(II) to $\text{Hg}(0)$ in soil

Biotic mediated mercury evaporation comprises the ability of mercury resistant soil microorganisms to detoxify their environment by transformation of inorganic and organic Hg(II) to volatile mercury species, which subsequently evaporate into the atmosphere quickly (Vaituzis and others 1975). Studies on population dynamics of microorganisms suggest that inorganic and organic mercury species in the natural environment can modify the composition of the bacterial community by favoring organisms able to transform them (Wollast and others 1975). When transforming mercury compounds, microorganisms are either able to utilize the pollutant (organo mercury) for their energy and carbon requirements or they modify the mercury species enzymatically (inorganic and organo mercury) without using it as a nutritional source (Billen and others 1974). The resistance to mercuric mercury and organo mercurials is due to enzymes that are encoded by *mer* genes (Silver 1981; Barkay and Turner 1989) and induced by these chemicals. Various bacteria strains are shown to mediate Hg^{2+} reduction to $\text{Hg}(0)$ by the mercury reductase enzyme which is encoded by the *merA* gene. Induction of biotic mercury reduction requires certain concentrations of bioavailable mercury. For instance, Hansen and others (1984) and Murray and Kidby (1972) reported a lag-phase in bacterial growth of a Hg^{2+} resistant strain of *Escherichia coli* and *Saccharomyces cerevisiae*, reducing Hg^{2+} to $\text{Hg}(0)$ (see also Summers and Silver 1978). Barkay and Pritchard (1988) reported a lag-phase in $\text{Hg}(0)$ evaporation after estuarine microbial cultures were treated with Hg^{2+} . The concentration levels of Hg^{2+} , necessary to induce microbial reduction in soils of low mercury sorptivity, such as a sand soil, is probably in the range of several to several hundred $\text{mg Hg} \cdot \text{kg}^{-1}$ (Van Faassen 1973). In soils with high content of organic matter or clay, the effective mercury levels are expected to be considerably higher due to the strong and bio-unavailable sorption (Van Faassen 1973; Martin 1988).

Rogers (1979) and Rogers and McFarlane (1979) observed an initial increase of mercury evaporation after application of Hg^{2+} to a sandy soil poor in organic matter, to reach the maximum after about 25 h. This curve shape with an initial lag-phase and a cumulation of mercury evaporation can be explained with a biotic reduction of Hg^{2+} to $\text{Hg}(0)$.

Due to the following observations mercury evaporation from soils amended with mercury is often assumed to be a microbially mediated process, where Hg^{2+} is reduced to $\text{Hg}(0)$.

Autoclavation reduced the mercury evaporation from soils amended to $1 \text{ mg Hg} \cdot \text{kg}^{-1}$ compared to non-sterile soils, independent of the content of organic matter (0.5–7% C_{org}) (Landa 1978b; Rogers and McFarlane 1979). However, tests were not performed to check if the mercury reducing enzymes of the killed microorganisms were inhibited by the autoclavation. Furthermore, the effect of the stringent autoclavation on the reduction potential of HA and FA was not investigated by the authors nor did I find any other literature data dealing with this. An indication that autoclavation reduces the mercury reducing potential of organic matter is the data presented by Rogers and McFarlane (1979). They found that the mercury evaporation from an organic rich clay soil (3.4% C_{org}) amended with Hg^{2+} to $1 \text{ mg Hg} \cdot \text{kg}^{-1}$ followed an exponential curve profile more typical for abiotic reduction than for the biotic reduction suggested by them.

When they performed the same experiment with an autoclaved soil, the curve shape was the same but the evaporation occurred on a strongly reduced level (Fig. 2).

Glucose treatment sometimes increases mercury evaporation from various soils treated with Hg^{2+} (Landa 1978b). However, HA and FA are formed from soil organic substances under intensive participation of microorganisms. Hence, increasing microbial activity by addition of nutrients may also effect formation and quality of the reductive potential of HA and FA. Furthermore, it has been

shown that reducing agents, such as glucose and yeast extract in the growth media of micro-biological culture experiments promote the abiotic reduction of Hg^{2+} (Gillespie 1972).

Reinoculation of autoclaved soils with fresh soil (5% of the initial soil weight) caused mercury evaporation to increase for a short period of time (Rogers and McFarlane 1979). However, this may as well be explained by micro-biological formation of humic substance containing reductive potential and concomitant liberation of some sorbed Hg^{2+} by turnover of organic matter, making it available for reduction to $\text{Hg}(0)$. Reduction may also be explained by abiotic reduction by the inoculation soil. Increasing soil temperature increased the mercury evaporation from Hg^{2+} treated soils (Landa 1978a). However, this may also be due to acceleration of an abiotic reduction process, as well as an increase in the vapour pressure of the formed volatile mercury.

To date, microbial culture experiments give the only definite proof for soil microorganisms (such as bacteria, yeasts and chlorella algae cells) being able to mediate Hg^{2+} reduction (Magos and others 1964; Komura and Izaki 1971; Brunner and Bott 1974; Schottel and others 1974; Ben-Bassat and Mayer 1975). No in-situ proof has been found in the literature, showing that $\text{Hg}(\text{II})$ reduction and evaporation of $\text{Hg}(0)$ from soil is dominated by microbial activity.

Therefore, to date it cannot be said, to what extent microbially mediated Hg^{2+} reduction occurs in soils under various conditions. However, the literature data suggest that the reduction of Hg^{2+} to $\text{Hg}(0)$ with subsequent evaporation from soil to atmosphere may be a combined abiotic and biotic process, with a possible dominance of either of these two being dependent on soil characteristics like pH, E_h , quality and quantity of mercury sorbents such as organic matter and clay, soil moisture, and concentration and species of mercury. It also seems plausible that abiotic Hg^{2+} reduction is dominating in soils of high organic matter content, in which the reduction potential of the soil organics is likely to be dependent on microbial activity and on the soil characteristics affecting the quality and quantity of HA and FA formed. Consistent with this, mercury evaporation from a sandy soil poor in organic matter (<0.5% C_{org}) and amended to $1 \text{ mg Hg} \cdot \text{kg}^{-1}$ with soluble inorganic $\text{Hg}(\text{II})$ salt followed a curve shape typical for biotic mediated evaporation (Rogers 1979; Rogers and McFarlane 1979). However, when the sandy soil was sterilized before mercury treatment, evaporation showed a rapid initial decrease of mercury evaporation (Rogers and McFarlane 1979), typical for an abiotic mediated evaporation (Fig. 3). After reinoculation with non-sterile soil the evaporation rate culminated after a lag-phase, typical for a biotic mediated evaporation. Although the two authors suggested a solely microbially mediated evaporation process, the previous discussion in this paper suggests that the evaporation behaviour from this soil is better explained with a biotic process being swamped by the abiotic evaporation process.

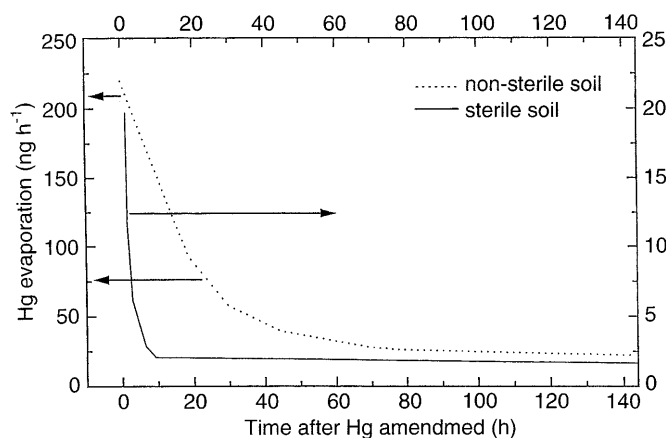


Fig. 2

Mercury evaporation from sterile and non-sterile clay soil amended to $1 \text{ mg Hg} \cdot \text{kg}^{-1}$ [as $\text{Hg}(\text{NO}_3)_2$] at 0 h. The graph is prepared after data from Rogers and McFarlane (1979)

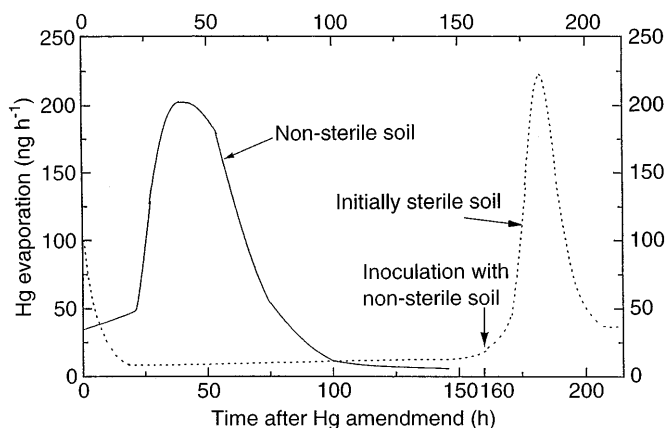


Fig. 3

Mercury evaporation from sandy soil amended to $1 \text{ mg Hg} \cdot \text{kg}^{-1}$ [as $\text{Hg}(\text{NO}_3)_2$] at 0 h. The dotted line depicts the data for a sterile soil that was inoculated 160 hours after mercury amendment. The solid line depicts the data for a non-sterile soil. (The figure is based on data from Rogers and McFarlane 1979)

These literature data indicate that biological mediated evaporation is favored in soils of common mercury content ($< 1 \text{ mg Hg} \cdot \text{kg}^{-1}$) and poor in organic matter (e.g. $< 1\% C_{\text{org.}}$), whereas higher contents of organic matter rather favor abiotic mediated evaporation. It is likely that a decreasing amount of mercury is available to microorganisms with increasing soil content of organic matter, which increases the mercury concentration necessary to induce formation of reductive acting enzymes. This is consistent with the data of Rogers and McFarlane (1979), showing that evaporation from a Hg^{2+} ($1 \text{ mg Hg} \cdot \text{kg}^{-1}$) treated sandy soil poor in organic matter ($0.5\% C_{\text{org.}}$) and clay ($3.5\% \text{ clay}$) decreased with the decreasing fraction of NH_4NO_3 extractable mercury, whereas no such relationship was found for a clay soil with $3.4\% C_{\text{org.}}$ and $34\% \text{ clay}$. Although the authors suggest a solely microbially mediated evaporation, the curve shape of the clay soil rather indicates an abiotic process, whereas the shape of the sandy soil displays a shape typical for biotic mediated processes. Furthermore, during the first six days (period of significant mercury evaporation) of the experiment with mercury amendment 43% of the applied mercury were lost from the sandy soil and only 20% from the clay soil. This may also indicate that the microbial potential to cause mercury evaporation is much higher than the potential of abiotic processes.

Formation, turnover and evaporation of mono- and dimethyl mercury

Organic mercury compounds, deposited from atmosphere or formed in soil, are not thermodynamically stable in natural environments. However, for some species physico-chemical and biological transformation processes are slow enough to enable occurrence of concentration levels that are of environmental concern. Thus, monomethyl mercury is only slowly physico-chemically degraded in

water (Baughman and others 1973; Burrows and Krenkel 1974; Benes and Havlik 1979), making it the only non-volatile organo-mercury compound, known to occur naturally in the soil environment (e.g. Lexmond and others 1976). Besides formation of monomethyl mercury in soil by abiotic (Rogers 1976, 1977; Nagase and others 1982; Klein and others 1983; Lee and others 1985; Weber and others 1985) and biotic methylation of Hg^{2+} (Tonomura and others 1972; Spangler and others 1973a; Vonk and Sijpestein 1973; Van Faassen 1975; Compeau and Bartha 1984), atmospheric deposition of monomethyl mercury is another important source (Padberg 1991; Munthe 1993; Hultberg and others 1995). Generally, the concentration of monomethyl mercury in soil is lower than 2% of the total Hg concentration (e.g. May and others 1985; DiGiulio and Ryan 1987; Revis and others 1989; Padberg 1991; Lee and others 1995; Van Faassen 1975). From predominance calculations by Baughmann and others (1973), Krenkel and Goldwater (1974) and Wollast and others (1975) it can be concluded that CH_3HgCl and CH_3HgOH are the predominant defined monomethyl mercury compounds in the soil solutions of significant volatility. However, the content of defined organo-mercury compounds in soil is generally assumed to be very small due to the high affinities of CH_3Hg^+ to solute and solid organic matter (Baughman and others 1973; Reimers and Krenkel 1974a, 1974b; Martin 1988), decreasing the volatility of monomethyl mercury. For instance more than 95–99% of the total content of monomethyl mercury can be expected sorbed to the immobile organic soil matrix of a podzolised forest soil (Schlüter 1995b). Formation and existence of $(\text{CH}_3)_2\text{Hg}$ in soil as well as evaporation from soil are very uncertain. Some authors state that it can be formed abiotically (Jensen and Jernelöv 1972; Baughman and others 1973; Cross and Jenkins 1975; Craig 1986) or biotically (Imura and others 1971; Cross 1973; Beijer and Jernelöv 1979) and that it may be stable in a natural environment with neutral to alkaline pH (Fagerström and Jernelöv 1972; Jensen and Jernelöv 1972). Other scientists point to the rapid and complete disproportionation reaction of $(\text{CH}_3)_2\text{Hg}$ with Hg^{2+} to form $2 \text{ CH}_3\text{Hg}^+$ (Cross 1973).

Theoretically, the formation of $(\text{CH}_3)_2\text{Hg}$ from Hg^{2+} or CH_3Hg^+ may be a microbial detoxification reaction due to the high volatility of $(\text{CH}_3)_2\text{Hg}$. However, no experimental data have been found clearly indicating the distinct formation or detection of $(\text{CH}_3)_2\text{Hg}$ in non-contaminated natural soil or water environment. Wallschläger and others (1995) positively identified considerable amounts of $(\text{CH}_3)_2\text{Hg}$ and $\text{Hg}(0)$ purged by nitrogen from a mercury contaminated floodplain soil. Stoeppler and others (1993) reported having found indications for the presence of about equal amounts of mono- and dimethyl mercury in forest and grassland soil. Also the existence of $(\text{CH}_3)_2\text{Hg}$ in atmosphere is still under discussion (Munthe 1993) and no literature describing $(\text{CH}_3)_2\text{Hg}$ deposition have been found. However, Johnson and Braman (1974) found by operational definition that most of the mercury evaporating from a patch of lawn treated

with Hg^{2+} were in form of $\text{Hg}(0)$, some CH_3Hg^+ and very little $(\text{CH}_3)_2\text{Hg}$. Rogers (1975) used the same sampling system as Johnson and Braman (1974) and claimed that dimethyl mercury dominated evaporation from soil treated with inorganic $\text{Hg}(\text{II})$, followed by $\text{Hg}(0)$, CH_3Hg^+ and inorganic $\text{Hg}(\text{II})$. However, no test of the separation effectivity and efficiency was presented nor has further literature been found confirming these findings. Furthermore, Johnson and Braman (1974) detected by the same technique considerable fractions of the total atmospheric mercury (1 m above ground) to be in form of $\text{Hg}(0)$ (49%), CH_3Hg^+ (21%), inorganic $\text{Hg}(\text{II})$ (25%) and some dimethyl mercury (1%). The values of monomethyl mercury and may be also of dimethyl mercury are unrealistic high (e.g. Munthe 1993), which questions the results obtained by the used separation technique. Dimethyl mercury decomposes rapidly photolytically (probably in the order of hours or days) in the atmosphere to $\text{Hg}(0)$ or non-volatile mercury species and methyl radicals, which in turn react to methane (Baughman and others 1973; Niki and others 1983; Lindqvist and Rodhe 1985; Iverfeldt and Lindqvist 1986; Munthe 1993). This process makes it difficult to determine if dimethyl mercury is possibly one of the evaporating mercury species. $\text{Hg}(0)$ is shown to be an important species of mercury evaporation from soil, however, the relative importance of $(\text{CH}_3)_2\text{Hg}$ is still unclear. Even though only small amounts of CH_3Hg^+ are found in the soil as a result of methylation and demethylation processes (e.g. Schlüter 1993), the gross formation of CH_3Hg^+ may be considerably higher, followed by an additional demethylation or dimethylation process. However, as to date no data on the gross methylation rate in soil are available.

Transformation of CH_3Hg^+ to volatile mercury species
A large number of bacterial strains isolated from sediments and soils were reported to break down monomethyl mercury to CH_4 and $\text{Hg}(0)$ (Tonomura and others 1968, 1972; Furukawa and others 1969; Spangler and others 1973a; Billen and others 1974; Lexmond and others 1976). CH_3Hg , $(\text{CH}_3)_2\text{Hg}$ and other organo-mercurials are transformed by an organomercurial lyase enzyme, which is encoded by the *merB* gene, to CH_4 and Hg^{2+} (Billen and others 1974; Schottel 1978; Barkay and Turner 1989; Baldi and others 1991). The formed Hg^{2+} can be micro-biologically reduced to $\text{Hg}(0)$ as described in section 4.1. (Summers and Sugarman 1974; Summers and Silver 1978; Baldi and others 1991). Abiotic degradation of monomethyl mercury by photolysis and acidolysis are unlikely to occur to major extent in soil (e.g. Baughmann and others 1973; Cross 1973). Demethylation of monomethyl mercury acting as the methylator for other metal ions (Jewett and Brinckman 1974) is also possible. Studying the evaporation of mercury from monomethyl mercury treated podzolised forest soils, Schlüter and others (1995b) found strong indications that monomethyl mercury is micro-biologically converted to more volatile $\text{Hg}(0)$ and/or $(\text{CH}_3)_2\text{Hg}$ and that these two mercury species dominate mercury evaporation resulting from trans-

formation of CH_3Hg^+ . This was based on the observation that the mercury evaporation rate increased rapidly after a lag-phase until a maximum was reached; then the evaporation rate decreased again (Fig. 4). Furthermore, the fraction of monomethyl mercury lost by evaporation of mercury increased with increasing monomethyl mercury treatment, which is typical for micro-biological processes dependent on sociological adaptation. Billen and others (1974) demonstrated such a sociological adaptation on a bacteria culture treated with CH_3Hg^+ , in which decomposition increased simultaneously with an increase in the number of monomethyl mercury resistant bacteria, able to mineralize this compound after a lag-phase. They also found resistant bacteria to mineralize CH_3Hg^+ more intensively in culture at higher concentrations of this compound. A lag-phase in transformation of CH_3Hg^+ to $\text{Hg}(0)$ by a mixed inoculum from sediment was reported by Spangler and others (1973b).

The resulting mercury evaporation from monomethyl mercury treated soil was also considerably higher than for soil treated with the same amount of mercury in form of soluble inorganic salt, indicating that the biological mechanisms of mercury evaporation can be more important than abiotic ones (Schlüter and others 1995b). This result is consistent with considerably higher evaporative mercury losses being reported from soils treated with CH_3Hg^+ than for soils treated with inorganic mercury (Hogg and others 1978; Landa 1979). In contrast to micro-biologically mediated reduction of Hg^{2+} , which may not become effective in soil of strong and efficient mercury sorption, monomethyl mercury related mercury evaporation may generally be dominated by a micro-biological process. Since methyl mercury is 50–100 times more toxic than inorganic mercury (Summers and Silver 1978; Silver 1981) and less strongly and less efficient sorbed to soil (e.g. Reimers and Krenkel 1974a; Martin 1988; Padberg 1991; Schlüter and others 1995a, 1995b), it

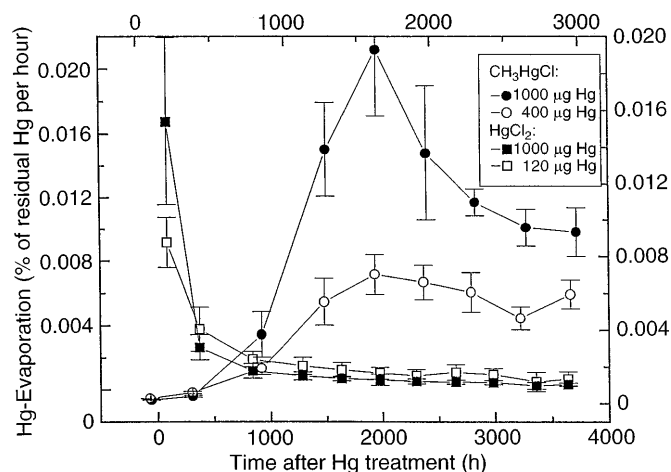


Fig. 4

Hg evaporation from CH_3HgCl and HgCl_2 treated soil columns. Each graph depicts the calculated arithmetic means of Hg evaporation from four replicate soil columns, each. Also depicted are the standard deviations of the population means

may be more available to microorganisms than inorganic mercury. Microbiological conversion of monomethyl mercury may already occur at a concentration less than $1 \text{ mg} \cdot \text{kg}^{-1}$ (e.g. Van Faassen 1973). Landa (1979) measured the mercury loss from various soils (0.9–6.7% wt. Corg.) treated with $1 \text{ mg Hg} \cdot \text{kg}^{-1}$ (as CH_3HgCl) over 60 days; the loss of CH_3Hg^+ increased with a decreasing content of organic matter, probably causing an increasing content of biologically available CH_3Hg^+ . Unfortunately, the authors presented their evaporation data in a form, not allowing for the interpretation of the development of the evaporation rate with time after CH_3Hg^+ treatment. Also Rogers (1976) found more monomethyl mercury in a sterilized Hg^{2+} treated soil compared to a non-sterile soil, indicating a micro-biological breakdown of monomethyl mercury at natural mercury concentrations. Since in all these experiments the CH_3Hg^+ concentrations were raised up to tenthousand times of the concentrations in background soil, and since the fraction of CH_3Hg^+ lost by mercury evaporation is dependent on the applied amount of CH_3Hg^+ (Schlüter and others 1995b), the quantitative evaporative loss of mercury due to CH_3Hg^+ formation in soil cannot be assessed to date.

Evaporation of defined inorganic Hg(II) salts from soil

Predominance calculations suggest that HgCl_2 , HgOHCl and $\text{Hg}(\text{OH})_2$ are the predominant dissolved defined inorganic Hg(II) species in soil solution (e.g. Andersson 1970; Hahne and Kroontje 1973; Schlüter 1993, 1995a). However, due to the high sorption affinity of mercury to different soil components, including dissolved organic matter (e.g. Andersson 1970, 1979; Schlüter 1993), only a minor fraction of the total mercury content of uncontaminated soils of background areas will be in a defined inorganic Hg(II) species and able to evaporate. It is likely that in the upper organic rich soil layer the content of dissolved inorganic Hg(II) is considerably less than 1% of the total mercury content (e.g. Andersson 1970, 1979; Schlüter 1995b). For this reason and due to the low volatility of these defined inorganic mercury species (Table 1) it is very unlikely that they contribute significantly to the overall mercury evaporation, even when considering some co-distillation with evaporating water. This is also consistent with the calculations of those mercury species which can dominate mercury evaporation from Hg^{2+} or CH_3Hg^+ treated soil (Schlüter and others 1995b).

Factors influencing the mercury evaporation rate from soil

A large fraction of the total mercury content in soil in non-background areas is highly volatile Hg(0). Hence, the mercury evaporation rate from these soils, as well as from soils contaminated with volatile mercury, is probably mainly dependent on the factors ruling the transport

of mercury vapour in soil and the release of mercury vapours from the soil to the atmosphere. The mercury evaporation from background soils and soils contaminated with inorganic Hg(II) is in addition dependent on the reaction kinetics of the processes producing Hg(0) and/or $(\text{CH}_3)_2\text{Hg}$.

Soil characteristics

Soil physical characteristics

Movement of mercury vapour in soil depends on inter-crumb pore space, shape of the crumbs, porosity of the crumbs and the water content as well as depth variations of the groundwater table (Hartge 1978; Schachtschabel and others 1984). Fang (1981) found that more mercury was sorbed to the surface layers of a moist soil column than to an air dry replicate, but the Hg(0) vapour diffused deeper into the air dry soil columns. This is explained with diffusion rates decreasing with the water content of the soil pores. Fursov (1990) reported a migration rate of Hg(0) vapour through fine-grained sands of $1 \text{ cm} \cdot \text{min}^{-1}$ and through loess like loams of $0.25 \text{ cm} \cdot \text{d}^{-1}$, indicating the importance of pore size.

Sorption capacity, mercury species, mercury content in soil

Various authors have found the evaporation rate of Hg^{2+} treated soils to increase with decreasing organic matter content (Wimmer 1974; Landa 1978b; Rogers 1979; Rogers and McFarlane 1979), and with decreasing clay content (Rogers 1979; Rogers and McFarlane 1979). Accordingly, Rogers and McFarlane (1979) found mercury evaporation related to the amount of soluble and easily exchangeable fraction of the non-soluble bound mercury in a Hg^{2+} treated sandy soil; however, this relationship was not confirmed for a clay soil. Organic matter, certain clay minerals and Fe-, Mn- and Al-oxides are known to have high sorption capacities and/or affinities for inorganic Hg(II) and monomethyl mercury (Shimomura and others 1969; Lockwood and Chen 1973; Forbes and others 1974; Reimers and Krenkel 1974a; Kinniburgh and Jackson 1978; Obushkovskaya 1982). Organic matter dominates the sorption of mercury especially under acid conditions, whereas metal oxides and clay may become more important under less acid to neutral pH (Låg and Steinnes 1978; Andersson 1979; Schlüter 1995b). All these findings indicate that mercury has to be available for certain biotic and abiotic processes to mediate evaporation into the atmosphere. This also suggests that mercury evaporation reduces the mobile mercury pool in the soil available for leaching into water systems. Schlüter and others (1995b, 1995c) found from their experiment of mercury evaporation from and leaching in a podzolised forest soil, that a significant fraction of the solute mercury may evaporate from the soil.

Consistent with mercury sorption affecting mercury evaporation, the speciation of the defined inorganic mercury compounds in soil is another important factor. Rogers (1979) found the evaporation rates of Hg^{2+} treated soils

to decrease with the solubility of the applied inorganic Hg(II) species; the mercury evaporation from soils treated with soluble HgCl_2 , $\text{Hg}(\text{NO}_3)_2$ and $\text{Hg}(\text{C}_2\text{H}_3\text{O}_2)_2$ was higher than for the ones treated with less soluble HgO and much higher than for the insoluble HgS treatment. Miller and others (1974) demonstrated that the reduction of Hg^{2+} by HA stopped with formation of HgS. Also HA in excess of Hg^{2+} , reduced the mercury evaporation due to strong complexation (Miller 1975). And Allard and Arsenie (1991) demonstrated that formation of mercuric chloro-complexes at high Cl^- concentration and the complexation of FA with Eu inhibited Hg evaporation. Other authors have also reported declining mercury evaporation from aqueous solution when Hg^{2+} is complexed by chloride or EDTA, effectively decreasing the amount of Hg^{2+} available for reduction to Hg^0 (Jenne and Avotins 1975). Furthermore, higher evaporation is reported from monomethyl mercury treated soils compared with inorg. Hg(II) treated soils, and evaporation rates of the monomethyl mercury treated soils remained high for a longer period of time than for the inorg. Hg(II) treated soils (Landa 1978b; Landa 1979; Schlüter and others 1995b).

The activation energy (E_a) of mercury evaporation from soil gives also indications of the importance of the mercury species and their binding to soil. The following E_a for different types of soil were found by fitting the Arrhenius equation to the data of mercury evaporation rates at different soil temperatures:

For a mercury rich soil in a geothermal area [supposedly with a high fraction of Hg(0)]:

$$E_a = 12.8 \pm 2.5 \text{ Kcal} \cdot \text{mol}^{-1} \text{ (Siegel and Siegel 1988)}$$

For a mercury contaminated soil [predominantly HgS and only minor fraction of Hg(0)]:

$$E_a = 25.8 \pm 2.6 \text{ Kcal} \cdot \text{mol}^{-1} \text{ (Lindberg and others 1994)}$$

For a background soil [probably predominantly inorg. Hg(II) bound to soil]:

$$E_a = 17.3 \pm 7.7 \text{ Kcal} \cdot \text{mol}^{-1} \text{ (Kim and others 1994)}$$

These data indicate that mercury evaporation occurs most easily in soils rich in Hg(0), followed by soils dominated by inorg. Hg(II), which is bound to soil components and probably relatively easily available for transformation to volatile mercury species. The highest activation energy of mercury evaporation was found in soils whose mercury content is dominated by the extremely insoluble, and therefore for transformation probably relatively unavailable, HgS.

Mercury evaporation from various soils usually increases with increasing content of inorganic Hg(II) (Frear and Dills 1967; Rogers 1979; Blinov 1982; Schlüter and others 1995b) monomethyl mercury (Schlüter and others 1995b) and was reported to increase considerably stronger for a podzolised forest soil treated with monomethyl mercury than with inorganic Hg(II) (Schlüter and others 1995b). Even though all these studies involved experimental conditions more or less different from natural ones (e.g. dis-

turbance of the soil profile or amendment with high mercury concentrations relative to background concentrations), the results indicate that mercury evaporation increases with the soil mercury content, which is probably due to an increasing availability to the abiotic and biotic processes of formation of volatile mercury species.

After formation of volatile mercury species in soil, the subsequent release into the atmosphere is partially dependent on the sorption affinity of these species to the various soil components, the sorption capacity and oxidation to less volatile mercury. Data describing Hg(0) sorption to soil components and re-oxidation was already discussed, however, no data in the literature concerning $(\text{CH}_3)_2\text{Hg}$ have been found. Retention of formed volatile mercury is probably only intermediate, the sorbed species being replaced or released due to changes in the mercury affinity to the soil sorbent (e.g. transformation of the soil sorbent) or otherwise changing soil conditions. Furthermore, evaporation from Hg(0) amended soils was reported to increase with increasing Hg(0) content (Staiger and Podlesak 1983).

Soil acidity

Landa (1978a) and Rogers (1979) found that mercury evaporation from various soil types treated with Hg^{2+} increased with increasing soil pH. And Frear and Dills (1967) found indications for mercury evaporation from a Hg^{2+} treated agricultural soil being favored by adjusting the soil pH to higher values.

Schlüter and others (1995b) found that DOM mediated mercury evaporation from undisturbed HgCl_2 treated podzolised forest soils increased significantly ($P=0.013$, Power=0.924) with rain pH increasing from about 3.2 to 5.6 resulting in a slightly increased soil pH. Since humic acid and fulvic acid, extracted from pond sediments, soil or bog water, were found to increasingly mediate Hg^{2+} reduction with decreasing pH (Alberts and others 1974; Skogerboe and Wilson 1981; Allard and Arsenie 1991), Schlüter and others (1995b) explained their finding with an increasing content of reductive acting DOM in soil solution with increasing rain pH, swamping a lower reduction potential of the DOM. Several studies have shown that the content of DOM in soil solution tends to decrease with acidification due to increasing aggregation and precipitation of DOM (Overbeek 1977; Schnitzer 1978; Ritchie and Posner 1982; Hay and others 1985). In a similar experiment, Schlüter and others (1995b) treated soil with monomethyl mercury, but did not observe an effect of rain acidity on mercury evaporation and explained this with microbially mediated evaporation, not being affected by rain acidity. Landa (1979) found the mercury evaporation from soils treated with CH_3Hg^+ being highest for strongly alkaline soils and lowest for slightly acid soils, which may be due to an increase in the production of $(\text{CH}_3)_2\text{Hg}$ with increasing pH. Soil acidity is known to be an important factor determining the microbial and plant sociology of a soil site. The produced soil organics therefore can have very different potentials and capacities for the reduction of Hg^{2+} .

Soil water content and redox potential (E_h)

Landa (1978a, 1979) found that mercury evaporation from different soil samples treated with inorganic $Hg(II)$ or CH_3Hg^+ increased with increasing soil water content up to a certain level (about 1/3 bar water holding capacity) and decreased again when this level was exceeded. In air dry soils the evaporation from both mercury treatments nearly stopped and re-started after re-wetting. This is consistent with the observation that air dried HA stored for 2 years showed no loss of its radical content (Kleist and Mücke 1966) and microorganisms are known to surpass dry periods by formation of spores. Schlüter and others (1995b) irrigated undisturbed soil profiles of a well drained podzolised forest soil, treated with Hg^{2+} or CH_3Hg^+ , with different rain intensities and for different durations. The soil water content varied from extreme wetness, caused by simulation of a rain storm, to about field water holding capacity; no effect on mercury evaporation was found. This may indicate that in nature only extreme dryness may have a significant effect on evaporation from well drained soil profiles in background areas or areas contaminated with non-volatile mercury. Different soils exposed to $Hg(0)$ rich atmosphere increasingly sorbed mercury with increasing water content up to a certain water content (about 1/3 bar water holding capacity) and decreased again when this content was exceeded (Fang 1981). The same $Hg(0)$ amended soils did not release mercury into the atmosphere when they were air-dry, but did so when adjusted to 1/3 bar water content (Landa 1978c). Senesi and Schnitzer (1977) suggested from their investigation results that water-logged or poorly drained soils, where reducing conditions prevail, contain high concentrations of organic free-radicals. This may lead to an increase in abiotic reduction of Hg^{2+} to $Hg(0)$.

It can be concluded that water content influences the formation process of volatile mercury as well as the release of the volatile mercury from soil to air, causing a combined effect of soil water content on the evaporation rate from soils of background areas and soils contaminated with non-volatile $Hg(II)$ species.

For mercury enriched soils of mineralized areas and soils contaminated with volatile mercury species the effect of the water content on the release of these volatile mercury species is likely to be most important. Indications for such an effect are the measurements of mercury in soil air in a mercury rich mineralized area. McNerney and Buseck (1973) found that mercury rich soils with a high clay content in mineralized areas displayed a strong decline of the mercury content in the soil air as the amount of water increased already at low water content; soils with a low clay content showed no decline of the mercury content in soil air even at high water content. They explained this with a clogging of pore spaces. Wallner (1977) found that the mercury content of soil air in mercury enriched soils in mineralized areas increased after events with increasing precipitation volume and they ascribed this to a surficial clogging of soil pores. An increasing filling of pore space with water also reduces the

rapid migration of mercury through the soil by mass-flow of vaporous mercury together with soil air, and increases the importance of the slower diffusive transport of mercury vapour through soil water (Williston 1964; Wallner 1977). Johnson and Lindberg (1995) calculated the concentration of $Hg(0)$ in soil air at 10 cm depth as a function of soil moisture and $Hg(0)$ evaporation rate from soil, using a strongly simplified diffusion model; the $Hg(0)$ concentration in soil air increased exponentially with soil moisture due to strongly reduced diffusion rate, and the increase was stronger the higher the evaporation rate from soil was. Furthermore, a significant filling of pore space with water leads to a downward mass-transport of solute volatile and non-volatile mercury species with soil water.

As already discussed, the soil E_h , which is strongly dependent on soil water content, is another important factor influencing the abiotic formation or transformation of mercury according to thermodynamic stability. No literature data were found concerning an effect of soil E_h on the abiotical or biotical formation of volatile mercury.

Meteorological conditions

Generally it can be expected that the transport in and the release of volatile mercury species from soil to atmosphere respond stronger to variations in meteorological conditions than the processes of formation of these species. Therefore, for soils of background areas as well as for soils contaminated with non-volatile mercury species, it can be expected that the production of volatile mercury is the evaporation rate limiting process. For soils in non-background areas and soils contaminated with volatile mercury species, the meteorological conditions are probably influencing the mercury evaporation rate stronger than for soils of background areas and soils contaminated with non-volatile mercury species, due to the high content of volatile mercury [esp. $Hg(0)$] usually associated with these soils.

Barometric pressure

According to Andersson (1979), the barometric pressure varies usually 2–3%, which means that the upper 2–3% of the vertical air filled pore space of the soil column are completely emptied and refilled (ventilated). Hence, with a groundwater table or bedrock in, for instance 1 m depth, only the upper 2–3 cm of the surface layer are ventilated.

Krömer and others (1981) did not find an effect of barometric pressure on the mercury concentration of the atmosphere directly above the mercury rich soil surface in a mineralized area. However, McCarthy and others (1969a, 1969b, 1970), McNerney and Buseck (1973) found the mercury evaporation from mercury rich soils in non-background areas to increase with decreasing barometric pressure.

No literature has been found clearly indicating effects of barometric pressure on mercury evaporation from soils in background areas. In general it seems very likely that

barometric pressure has only little influence and is mostly swamped by other effects, such as temperature.

Soil and air temperature

The temperature in the upper centimeters of soil usually follows the air temperature with a short phase lag, and is 1–2 °C lower than air temperature.

Many authors found mercury evaporation to increase with temperature from various CH_3Hg^+ treated soil types (Landa 1979), from soils treated or contaminated with inorganic Hg(II) (Frear and Dills 1967; Landa 1978a; Blinov 1982; Lindberg and others 1994) and from soils in background and non-contaminated areas (Lindberg and others 1979; Xiao and others 1991; Kim and others 1994) as well as in non-background areas (McCarthy and others 1970; Lindberg and others 1979; Krömer and others 1981; Siegel and Siegel 1988). Field measurements of mercury evaporation rates displayed a seasonal and diurnal variation, with the rates being highest in summer and during the daytime and lowest during winter and the nighttime (Schroeder and others 1989; Xiao and others 1991; Kim and others 1994; Lindberg and others 1994). This is probably due to increasing vapour pressure for the different mercury compounds, especially those species that are highly volatile, such as Hg(0) and $(\text{CH}_3)_2\text{Hg}$, and a decreasing sorption by soil due to increasing thermal motion. Furthermore, when the soil air expands with increasing temperature it rises and contributes to mercury evaporation from soil. Increasing temperature also causes an increase in reaction rates and microbiological activity resulting in a more intensive formation of volatile mercury species.

The extent to which temperature affects mercury evaporation is still under discussion. Lindberg and others (1979) found that the Hg evaporation rate of a bare uncontaminated soil in a background area increased only slightly with increasing soil temperature from 10 °C (lowest measured temperature) to 15–20 °C. In this range Hg evaporation can be described satisfactorily by a linear function whereas the Hg evaporation rate increases exponentially from 15–20 °C to 35 °C. However, bare mercury rich soil in a mineralized area showed a rapid increase of evaporation with temperature already from 10 °C on. This is consistent with recent findings on the activation energy (E_a) of mercury evaporation from soil, obtained by fitting the Arrhenius equation to the data of the temperature dependent evaporation rates: Siegel and Siegel (1988) determined for a mercury rich soil [supposedly high fraction of Hg(0)] in a geothermal area an E_a close to the molar heat of vaporization of Hg(0), whereas the E_a of a background forest soil (Kim and others 1994) and of an inorganic Hg(II) [with only small fraction Hg(0)] contaminated soil (Lindberg and others 1994) were considerably higher. This indicates that other processes than the evaporation of volatile mercury species from background soils and soils contaminated with non-volatile mercury are the evaporation rate limiting factors. These data show that, independent of the temperature, mercury evaporation from soils rich in volatile mercury species is

higher than evaporation from soils in background areas or soils contaminated with non-volatile Hg(II) species. Furthermore, in summer the soil is mostly rather dry, which counteracts an increasing mercury evaporation rate due to increasing temperature by an increasing sorption strength of volatile mercury (Landa 1978a, 1978c, 1979). Khayretdinov (1971) stated that freezing of soil water may result in formation of positively charged ice, which repels Hg(0) vapor in soil into the unfrozen parts of the soil or outside the ice crystals, which also may result in a decreasing rate of atmospheric mercury sorption to soil surface; soil ice may also be negatively charged, causing Hg(0) vapor sorption to persist in winter and being more extensive than in fall and a rapid rise in mercury content in soil air during the thawing period. However, it seems that these effects are poorly understood and that hardly anything can be said about the importance for sorption of mercury in natural soil.

In diurnal and seasonal variations of mercury evaporation, factors other than daily and seasonal temperature variations may be involved, especially in soils of background areas and soils contaminated with non-volatile mercury species. Senesi and Schnitzer (1977) showed that irradiation of FA, extracted from a podzol soil, with sunlight caused an additional formation of transient radicals with short life-span. Although sun-light does not penetrate far into soil, it is possible that additional radical formation during day-time may significantly increase mercury evaporation from soils, where the abiotic reduction of Hg^{2+} in the uppermost micro-or millimeter-layer is a quantitative important process in the overall evaporation from soil.

Other meteorological factors

The following factors may also have an effect on mercury evaporation from soil, but only few literature data have been found:

Air humidity, wind speed and the turbulent mixing of air masses above the soil surface affecting the mercury exchange across the soil/atmosphere interface.

Wallner (1977) found only weak indications of reduced mercury evaporation from mercury rich soil of a mineralized area with increasing air-humidity.

Kim and others (1994) and Lindberg and others (1994) demonstrated on contaminated and background soil that the mercury evaporation rate is also dependent on the mercury concentration in air above soil surface, which was influenced by wind speed and turbulent mixing and vegetation. Lindberg and others (1979) found a significant difference in the evaporation rate from bare and grass planted soil in a mercury rich mineralized area; however, no such difference in the evaporation rates was found for background soil. This may indicate that turbulent mixing of air masses above ground is of minor importance for soils of background areas and soils contaminated with non-volatile mercury species. This is consistent with the results of Xiao and others (1991), who, using a throughflow chamber for measurement, did not

find an effect of turbulent air-mixing on the mercury evaporation rates in a background area.

Soil cover including vegetation

Lindberg and others (1979) measured mercury evaporation rates from mercury rich soil in a mineralized area and from soil with background concentrations of mercury. For bare soil the mercury evaporation rates were higher than for the respective soil with grass vegetation. The authors attributed this primarily to a reduced mixing of air at the soil surface with air overlying the grass canopy. Also shading of the soil surface, decreasing the soil temperature, may contribute to the difference. Snow covering the soil surface may also affect the evaporation rate of soil. Jonasson (1973) found that mercury migrated from a mercury soil in a mineralized area into the snow cover which may indicate that some mercury can even evaporate through snow covers.

Calculated and measured evaporation rates from soils

Based on soil lysimeter experiments with Hg^{2+} treated Scandinavian Podzols, Schlüter and others (1995c) calculated that about 5.2% of total deposited atmospheric Hg can be expected to evaporate, independent of variations in atmospheric mercury deposition throughout the year. They also found that deposited atmospheric mercury will be susceptible to evaporation for about 300 days after it has been bound in the soil matrix comparable to soluble inorganic Hg(II) salt applied to the soil. Furthermore, taking the present total Hg deposition (wet + dry) of about $50 \mu\text{g} \cdot \text{m}^{-2} \cdot \text{a}^{-1}$ below coniferous forest [mainly inorganic Hg(II)] (Driscoll and others 1994) in south and southwest Sweden about $0.30 \text{ ng} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ will evaporate from soil, according to the 5.2% evaporation. Their findings are consistent with the data presented by Lindqvist and others (1991), who, based on an input/output balance and a limited number of evaporation measurements from soil, calculated the annual evaporation to be less than 5.2% of the annual Hg deposition in south-western Sweden (Gårdsjön area). The calculated Hg evaporation rate of $0.30 \text{ ng} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ of Schlüter and others (1995c) is also consistent with the range of measurements ($0\text{--}1.4 \text{ ng} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$) made in south-western Sweden and identical with the average evaporation rate for the period with a soil temperature of about 10°C (Xiao and others 1991). This accordance of the presented model data with Swedish data is probably due to the similarity of the soil characteristics.

Stepanov and Vild'yayev (1984) are often cited in literature with their calculated crustal background emission of $0.036 \text{ ng} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ (see also Varekamp and Buseck 1986). However, this value has to be considered carefully, since it is based on several assumptions and simplifications and no further literature data have been found confirm-

ing this value or reporting measurements of crustal degassing from background areas.

Further literature data of mercury evaporation from soils treated with mercury, from soils in non-background areas and from soils in background areas are listed in Table 1. The data show that mercury evaporation from mineralized areas and mercury contaminated soils is usually higher than from background areas and that the evaporation rate from background soils is usually smaller than $0.2 \mu\text{g} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$.

Summary and conclusion

1. There are strong indications that the volatile mercury species [Hg(0) and/or $(\text{CH}_3)_2\text{Hg}$] dominate mercury evaporation from soil, but little is known about the relative importance of the two species or contributions from other organic and inorganic mercury species.
2. It is likely that the uppermost organic rich soil horizons (O- and A-horizons) contain the mercury pool for formation of volatile mercury species which dominates evaporation from soil in background areas and soils contaminated with non-volatile Hg(II) species. In mercury enriched soils in non-background areas, where large fractions of total mercury are usually volatile mercury species relative to background areas, soil usually becomes a minor evaporation source compared to geological sources.
3. Mercury evaporation from soil is a combined process determined by
 - A. the net formation of volatile mercury species, which is the resultant of abiological and biological formation of dimethyl mercury and abiological and biological reduction of Hg^{2+} to Hg(0). Biological reduction of Hg^{2+} to Hg(0) is favoured in soils of high amounts of available Hg^{2+} and high microbiological activity, whereas abiological reduction is favoured in soils of high organic matter content and/or deep E_h . Microbiological reactions can cause considerably higher mercury evaporation rates than abiologically mediated evaporation. Therefore, in many soils mercury evaporation may be dominated by biological mercury evaporation.
 - B. The diffusive movement and mass-transport of volatile mercury in and with soil air and soil solution towards the soil surface. The migration of mercury species may be delayed by sorptive interactions with the soil components. Soil physical characteristics (e.g. shape, size and distribution of soil pores), soil chemical characteristics (sorption affinity of soil components for volatile mercury species) and meteorological conditions (air temperature, barometric pressure) are more or less strongly influencing the transport of volatile mercury within the soil; the hydrological conditions (e.g. variations of the level of the ground-water table) are probably also important.
 - C. The release of the volatile mercury species from the soil surface across the soil-atmosphere interface is influenced by additional meteorological factors (air hu-

midity, turbulent mixing of the overlying air, wind speed and residence time of air masses over the source area).

4. The long-term rate limiting process of mercury evaporation from soils of background areas and soils contaminated with non-volatile mercury species is probably the formation of volatile mercury species while meteorological conditions may cause short term variations. For soils of non-background areas and soils contaminated with volatile mercury species, the long-term evaporation rate is probably mainly dependent upon migration of the volatile mercury species within the soil and therefore upon the meteorological conditions. Measuring the effect of meteorological conditions upon mercury evaporation from soil in non-background areas (e.g. barometric pressure) may possibly be used to decide whether geogenic mercury is ruling the evaporation rate or being an important factor.
5. Mercury evaporating from soils in background areas is probably mostly originating from deposited airborne mercury. Whereas in non-background areas, mercury evaporation originates primarily from geological sources.
6. Mercury evaporation from soils may reduce the pool of mobile mercury in soil and hence affect the leaching of mercury from the soil into water systems.
7. Generally, mercury evaporation from soils increases with increasing water content up to a certain level (possibly 1/3 bar water content) due to enhanced formation of volatile mercury species and to the release of sorbed volatile mercury. The evaporation rate probably decreases when the threshold is exceeded, due to the reduction of pore space available for upward movement of mercury vapour with mass-flow of soil air and a beginning downward leaching of solute volatile and non-volatile mercury species.
8. Mercury evaporation rates from background soils are usually $<0.2 \mu\text{g} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ and significantly smaller than from mercury rich soils in non-background areas or mercury contaminated soils.

References

- AASTRUP M, JOHNSON J, BRINGMARK E, BRINGMARK L, IVERFELDT Å (1991) Occurrence and transport of Hg within a small catchment area. *Water Air Soil Pollut* 56:155–167
- AICHBERGERK, HOFER GF (1989) Contents of As Hg Se in agricultural soils of upper Austria. *Bodenkultur* 40:1–11
- ALBERTS JJ, SCHINDLER JE, MILLER RW, NUTTER DE (1974) Elemental mercury evolution mediated by humic acid. *Science, USA* 184:895–897
- ALLARD B, ARSENIÉ I (1991) Abiotic reduction of mercury by humic substances in aquatic system – an important process for the mercury cycle. *Water Air Soil Pollut* 56:457–464
- ANDERSSON A (1970) Some facts about the geochemistry of mercury. *Grundförbättring* 23:31–40 (in Swedish)
- ANDERSSON A (1979) Mercury in soils. In: Nriagu JO (ed) *The biogeochemistry of Hg in the environment*. Elsevier, Amsterdam, pp 79–106
- ANDREN AW, NRIAGU JO (1979) The global cycle of mercury. In: Nriagu JO (ed) *The biogeochemistry of mercury in the environment*. Elsevier, Amsterdam, pp 1–21
- AZZARIA LM (1992) Mercury in soil associated with faults, Charlevoix seismic zone, Quebec, Canada. Presented at Tenth Iraqi Geological Congress, Baghdad, Iraq, Dec 28–31, Union of Iraqi Geologist, UIG
- AZZARIA LM, AFTABI A (1991) Stepwise thermal technique for estimating mercury phases in soils and sediments. *Water Air Soil Pollut* 56:203–217
- AZZARIA LM, K.-SEGUIN M (1990) Mercury anomalies in soil-air in relation to earthquakes, Charlevoix seismic zone, Quebec, Canada. *International Colloquium on Gas Geochemistry*, 3–5 Oct, Mons, Belgium (Abstract)
- BALDI F, SEMPLICI F, FILIPPELLI M (1991) Environmental applications of mercury resistant bacteria. *Water Air Soil Pollut* 56:465–475
- BARGAGLI R, BARGHIGIANI C, MASERTI BE (1986) Mercury in vegetation of the mount Amiata area. *Chemosphere* 15:1035–1042
- BARKAY T, PRITCHARD H (1988) Adaptation of aquatic microbial communities to pollutant stress. *Microb Sci* 5:165–169
- BARKAY T, TURNER R (1989) Gene probes to predict responses of aquatic microbial communities to toxic metals. In: Vernet J-P (ed) *Proc Internat Conf on Heavy Metals in the Environment*, Geneva. CEP Consultants England, pp 57–60
- BAUGHMAN GL, GORDON JA, WOLFE NL, ZEPP RG (1973) Chemistry of organomercurials in aquatic systems. US Environmental Protection Agency, EPA-660/3-73-012
- BEAUFORD W, BARBER J, BARRINGER AR (1977) Uptake and distribution of mercury within higher plants. *Physiol Plant* 39:261–265
- BEIJER K, JERNELÖV A (1979) Methylation of mercury in aquatic environments. In: Nriagu JO (ed) *The biogeochemistry of mercury in the environment*. Elsevier, Amsterdam
- BEN-BASSAT D, MAYER AM (1975) Volatilization of mercury by algae. *Physiol Plant* 33:128–132
- BENES P, HAVLIK B (1979) Speciation of mercury in natural waters. In: Nriagu JO (ed) *The biogeochemistry of mercury in the environment*. Elsevier, Amsterdam, pp 175–202
- BILLEN G, JOIRIS C, WOLLAST R (1974) A bacterial methylmercury-mineralizing activity in river sediments. *Water Res* 8:219–225
- BLINOV BK (1982) Experimental evaluation of certain parameters of mercury migration from surface soil. *Sov Meteorol Hydrol* 5:43–49
- BROOKS RA, BERGER BR (1978) Relationship of soil-mercury values to soil type and disseminated gold mineralization, Getchell Mine area, Humboldt County Nevada. *J Geochem Explor* 9:186–104
- BRUNKER RL, BOTT TL (1974) Reduction of mercury to the elemental state by a yeast. *Appl Microbiol* 27:870–873
- BURROWS ND, KRENKEL PA (1974) Loss of methylmercury-203 from water. *Anal Chem* 11:1613–1614
- CANNONK, DUDAS MJ (1982) Seasonal pattern of gaseous mercury emanations from forested soils in Alberta. *Can J Soil Sci* 62:541–543
- CHENY, SENESI N, SCHNITZER M (1977) Information provided on humic substances by E_4/E_6 ratios. *Soil Sci Soc Am J* 41:352–358
- CHENGLIANG Z, LIYIN W, YONG D, SHENGFENG P (1989) Distribution of trace Hg and its mode of occurrence over Fankou Pb-Zn deposit, Guangdong, China. *J Geochem Explor* 33:73–83

- COCKING D, KING ML (1994) Earthworm bioaccumulation of mercury from contaminated flood plain soils. In: *Mercury Pollution Integration and Synthesis*. Lewis Publishers, Boca Raton, USA, pp 381–395
- COMPEAU G, BARTHA R (1984) Methylation and demethylation of mercury under controlled redox pH and salinity conditions. *Appl Environ Microbiol* 48:1203–1207
- COX ME, CUFF KE (1980) Rn and Hg surveys: Geothermal exploration in NE Maui Hawaii. In: *Geothermal energy for the eighties*, Annual Meet Papers pp 451–454
- CRAIG PJ (1986) Mercury. In: Bernhard M, Brinckman FE, Sadler PJ (eds) *The importance of chemical speciation in environmental processes*. Springer Verlag, Berlin Heidelberg New York, pp 447–464
- CROSS RJ (1973) Organomercurials in the environment. *Chem Indust*, 4 August 73, 719–721
- CROSS RJ, JENKINS CM (1975) Chemical studies relating to environmental organomercurials. *Environ Pollut* 8:179–184
- DI GIULIO RT, RYAN EA (1987) Mercury in soils sediments and clams from a North Carolina peatland. *Water Air Soil Pollut* 33:205–219
- DRISCOLL CT, OTTON JK, IVERFELDT Å (1994) Trace metals speciation and cycling. In: Moldan B, Cerry J (eds) *Biogeochemistry of small catchments*. J Wiley, New York
- DVORNIKOV AG, VASILEVSKAYA AE, SHEHERBAKOV V (1963) Mercury dispersion aureols in the soils of the Nagol'ny range. *Geochem Internat* 5:501–509
- FAGERSTRÖM T, JERNELÖV A (1972) Some aspects of the quantitative ecology of mercury. *Water Res* 6:1193–1202
- FANG SC (1978) Sorption and transformation of Hg vapor by dry soil. *Env Sci Technol* 12:285–288
- FANG SC (1981) Studies on the sorption of elemental Hg vapor by soils. *Arch Environ Contam Toxicol* 10:193–201
- FATHI M, LORENZ H (1980) Bindungsformen von Hg, Cd, Pb in Biotopen, Verhalten in der Nahrungskette und Vorkommen in Nahrungsmitteln. *Metabolismus in Pflanze Tier und Mensch*. ZEBs-Berichte, Dietrich Reimer Verlag, Berlin
- FERRARA R, MASERTI BE, BREDER R (1991a) Mercury in abiotic and biotic compartments of an area affected by a geochemical anomaly (Mt. Amiata, Italy). *Water Air Soil Pollut* 56:219–233
- FERRARA R, MASERTI BE, MORELLI M, EDNER H, RAGNARSON P, SVANBERG S, WALLINDER E (1991b) In: Farmer JG (ed) *Vertical Distribution of atmospheric mercury concentration over a cinnabar deposit*. Proc Int Conf on Heavy Metals in the Environment, Edinburgh 1, pp 247–250
- FITZGERALD WF (1995) Is mercury increasing in the atmosphere? The need for an atmospheric mercury network (AMNET). *Water Air Soil Pollut* 80:245–254
- FORBES E, POSNER AM, QUIRK JP (1974) The specific adsorption of inorganic Hg(II) species and Co(III) complex ions on goethite. *J Coll Inter Sci* 49:403–409
- FREAR DEH, DILLS LE, (1967) Mechanism of the insecticidal action of mercury and mercury salts. *J Econ Ent* 60:970–974
- FRIEDRICH G, KULMS M (1969) Eine Methode zur Bestimmung geringer Konzentrationen von Quecksilber in Gesteinen und Böden und ihre Anwendung bei der geochemischen Exploration von Erzlagerstätten. II. Quecksilber als Indikator bei der geochemischen Exploration. *Erzmetall* 22:214–218
- FUKUZAKI N, TAMURA R, HIRANO Y, MIZUSHIMA Y (1986) Mercury emission from a cement factory and its influence on the environment. *Atmos Environ* 20:2291–2299
- FURSOV VZ (1983) Gasmercury method for mineral deposits prospecting. Nauca, Moscow (in Russian)
- FURSOV VZ (1990) Mercury vapor surveys) technique and results. *J Geochem Explor* 38:145–155
- FURSOV VZ, VOL'FSON NB, KHVALOVSKIY AG (1968) Results of a study of mercury vapour in the Tashkent earthquake zone. *Dokl Akad Nauk SSSR* 179:208–210
- FURUKAWA K, SUZUKI T, TONOMURA K (1969) Decomposition of organic mercurial compounds by mercury-resistant bacteria. *Agric Biol Chem* 33:128–130
- GALLOWAY JN, THORNTON JD, NORTON SA, VOLCHOK HL, MCLEAN RAN (1982) Trace metals in atmospheric deposition: a review and assessment. *Atmos Environ* 16:1677–1700
- GILLESPIE DC (1972) Mobilization of mercury from sediments into Guppies. *J Fish Res Bd Can* 29:1035–1041
- GILMOUR JT, MILLER MS (1973) Fate of mercuric-mercurous chloride fungicide added to turfgrass. *J Environ Qual* 2:145–148
- GODBOLD DL, HÜTTERMANN A (1988) Inhibition of photosynthesis and transpiration in relation to mercury-induced root damage in spruce seedlings. *Physiol Plant* 74:270–275
- GRIGAL DR, NATER EA, HOMAN PS (1994) Spatial distribution patterns of mercury in an east-central Minnesota landscape. In: Watras CJ, Huckabee JW (eds) *Mercury pollution integration and synthesis*. Lewis Publ, Boca Raton
- HAHNE HCH, KROONTJE W (1973) The simultaneous effect of pH and chloride concentration upon Hg(II) as a pollutant. *Soil Sci Soc Am J* 37:838–843
- HÅKANSON L (1984) Metals in fish and sediments from the river Kolbäckån water system, Sweden. *Arch Hydrobiol* 101:373–400
- HÅKANSON L, NILSSON A, ANDERSSON T (1988) Mercury in fish in Swedish lakes. *J Environ Pollut* 49:145–162
- HANSEN CL, ZWOLINSKI MD, WILLIAMS JW, (1984) Bacterial removal of mercury from sewage. *Biotechnol Bioengineer* 26:1330–1333
- HARTGE KH (1978) *Einführung in die Bodenphysik*. Enke Verlag, Stuttgart
- HAWKES HE, WILLISTON SH (1962) Mercury vapor as a guide to lead-zinc-silver deposits. *Min Cong J* 48:30–32
- HAY GW, JAMES JH, VAN LOON GW (1985) Solubilization effects of simulated acid rain on the organic matter of forest soil; preliminary results. *Soil Sci* 139:422–430
- HELWIG DD, HEISKARY SA (1985) Fish mercury in N.E. Minnesota lakes, final report. Minnesota Pollution Control Agency MN
- HITCHCOCK AE, ZIMMERMAN PW (1957) Toxic effects of vapors of mercury and of compounds of mercury on plants. *Ann NY Acad Sci* 65:474–497
- HOGG TJ, STEWART JWB, BETTANY JR (1978) Influence of the chemical form of Hg on its adsorption and ability to leach through soils. *J Environ Qual* 7:440–445
- HOLM HW, COX MF (1975) Transformation of elemental mercury by bacteria. *Appl Microbiol* 29:491–494
- HULTBERG H, IVERFELDT Å, LEE Y-H (1994) Methylmercury input/output and accumulation in forested catchments and critical loads for lakes in southwestern Sweden. In: Watras CJ, Huckabee JW (eds) *Mercury pollution, integration and synthesis*. Lewis Publishers, Boca Raton, pp 313–322
- IMURA N, SUKEGAWA E, PAN S, NAGAO K (1971) Chemical methylation of inorganic mercury with methylcobalamin, a vitamin B12 analog. *Science* 172:148
- IVERFELDT Å (1984) Structural, thermodynamic and kinetic studies of mercury compounds; applications within the environmental mercury cycle. (PhD) University of Göteborg
- IVERFELDT Å (1991a) Occurrence and turnover of atmospheric mercury over the Nordic countries. *Water Air Soil Pollut* 56:251–265
- IVERFELDT Å (1991b) Mercury forest canopy throughfall water and its relation to atmospheric deposition. *Water Air Soil Pollut* 56:553–564

- IVERFELDT Å, LINDQVIST O (1980) Determination of distribution equilibria between water and air. In: Report no 415; Project Coal, Health and Environment. The Swedish State Power Board, S-16287 Vällingby, Sweden
- IVERFELDT Å, LINDQVIST O (1982) Distribution equilibrium of methyl mercury chloride between water and air *Atm Environ* 16:2917–2925
- IVERFELDT Å, LINDQVIST O (1984) The transfer of mercury at the air/water interface. *Proc. Int. symp. gas transfer at water surfaces*. Reidel Publishing, pp 533–538
- IVERFELDT Å, LINDQVIST O (1986) Atmospheric oxidation of elemental mercury by ozone in the aqueous phase. *Atmos Environ* 20:1567–1573
- IVERFELDT Å, PERSSON I (1985) The solvation thermodynamics of methylmercury(II) species derived from measurements of the heat of solution and the Henry's law constant. *Inorgan Chim Acta* 103:113–119
- JENNE EA, AVOTINS P (1975) The time stability of dissolved mercury in water samples. I: Literature review. *J Environ Qual* 4:427–431
- JENSEN S, JERNELÖV A (1972) Behavior of mercury in the environment. In: *Mercury contamination in man and his environment*. Int Atomic Energy Agency, Vienna 1972, Tech Rep Ser Nr 137
- JERNELÖV A (1969) Conversion of mercury compounds. In: Jernelöv A (ed) *Chemical Fallout*. C.C. Thomas Publ, pp 68–74
- JEWETT KL, BRINCKMAN FE (1974) Transmethylation of heavy metal ions in water. Presented before the Division of Environmental Chemistry, American Chemical Society (Los Angeles, 31 March–5 April 1974). Abstract of papers
- JIN Y, WU Z, SHEN C, WEI J, ZHU H (1989) Earthquake prediction through the observation and measurement of mercury content variation in water. *J Geochem Explor* 33:195–202
- JOHANSSON K (1984) Mercury in sediment in Swedish forest lakes. *Verh Int Verein Limnol* 22:2359–2363
- JOHANSSON K, IVERFELDT Å (1994) The relation between mercury content in soil and the transport of mercury from small catchments in Sweden. In: Watras CW, Huckabee JW (eds) *Mercury pollution, integration and synthesis*. Lewis Publ, Boca Raton, pp 323–328
- JOHNSON DL, BRAMAN RS (1974) Distribution of atmospheric mercury species near ground. *Environ Sci Technol* 8:1003–1009
- JOHNSON DW, LINDBERG SE (1995) The biogeochemical cycling of Hg in forests: alternative methods for quantifying total deposition and soil emission. *Water Air Soil Pollut* 80:1069–1077
- JONASSON IR (1970) Mercury in the natural environment: a review of recent work. *Geol Surv Can Paper* 70–57
- JONASSON IR (1973) Migration of trace metals in snow. *Nature* 241:447–448
- JONASSON IR, BOYLE RW (1971) Geochemistry of mercury. In: *Proceedings special symposium on mercury in man's environment*. Roy Soc Can Ottawa, Ontario, pp 5–21
- JONASSON IR, BOYLE RW (1972) Geochemistry of mercury and origins of natural contamination of the environment. *Can Min Metal Bull Jan*:32–39
- KARASIK MA, BOL'SHAKOV AP (1965) Mercury vapour at the Nikitovka ore field. *Dokl Akad Nauk SSSR* 161:204–206
- KEELER G, GLINSORN G, PIRRONE N (1995) Particulate mercury in the atmosphere: its significance, transport, transformation and sources. *Water Air Soil Pollut* 80:159–168
- KESLER SE (1994) *Mineral resources, economics and the environment*. MacMillan College Publ, New York
- KHAYRETDINOV IA (1971) Gas mercury aureoles. *Geochem Int* 8:412–422
- KIM K-H, LINDBERG SE, HANSON PJ, MEYERS TP, OWENS JG (1993) In: *Proceedings of the Ninth International Conference on Heavy Metals in the Environment*. 1993:328–331
- KIM K-H, LINDBERG SE, MEYERS TP (1994) Micro-meteorological measurements of mercury vapor fluxes over background forest soils in eastern Tennessee. *Atmos Environ*
- KIMURAY, MILLER VL (1964) The degradation of organomercury fungicides in soil. *J Agric Food Chem* 12:253–257
- KINNIBURGH DG, JACKSON HL (1978) Adsorption of Hg(II) by iron hydroxide gel. *Soil Sci Soc Am Proc* 42:45–47
- KLEIN S, WOGGON H, PLASS R, JEHLE D, ZYDEK G, NICKEL B (1983) Transmethylierungsreaktionen zwischen anorganischem Quecksilber und Organozinkverbindungen unter in vitro- und in vivo Bedingungen. In: Anke M (ed) *Mengen- und Spurenelemente*. Leipzig, Karl Marx Universität, pp 78–92
- KLEIST H, MÜCKE D (1966) ESR Untersuchungen von Huminsäure-Metall-Verbindungen. *Z Chem* 6:380–382
- KLUSMANN RW, LANDRESS RA (1979) Mercury in soils of the Long Valley California geothermal system. *J Volcanol Geotherm Res* 5:49–65
- KOKSOY M, BRADSHAW PMP (1969) Secondary dispersion of mercury from cinnabar and stibnite deposits, West Turkey. *Color Sch Mines Q* 64:333–336
- KOMURA I, IZAKI K (1971) Mechanism of mercuric chloride resistance in microorganisms. I. Vaporization of a mercury compound from mercuric chloride by multiple drug resistant strains of *Escherichia coli*. *J Biochem* 70:885–893
- KOVALEVSKII AL (1983) Mercury/Biogeochemical prospecting for mineral deposits. *Geolog Rudn (Geology of Ore Deposits)* 25:94–97
- KOVALEVSKII AL (1986) Mercury-biogeochemical exploration for mineral deposits. *Biogeochemistry* 2:211–220
- KRENKEL PA, GOLDWATER L (1974) Mercury: environmental considerations, Part II. In: Bond RG, Straub CP (eds) *Critical reviews in environmental control* 4 CRC-Press, Boca Raton, FL, pp 251–305
- KRÖMER E (1981) *Geochemische Untersuchungen zur Verteilung von Quecksilber und Quecksilberverbindungen in Böden und Gesteinen*. (PhD) Universität Aachen, Fakultät Bergbau und Hüttenwesen
- KRÖMER E, FRIEDRICH G, WALLNER P (1981) Mercury and Hg compounds in surface air, soil gases, soils and rocks. *J Geochem Explor* 15:51–62
- LÅG J, STEINNES E (1978) Regional distribution of Hg in humus layers of Norwegian forest soils. *Acta Agricult Scand* 28:393–396
- LANDA ER (1978a) Soil water content and temperature as factors in the volatile loss of applied mercury(II) from soils. *Soil Sci* 126:44–48
- LANDA ER (1978b) Microbial aspects of the volatile loss of applied mercury(II) from soils. *J Environ Qual* 7:84–86
- LANDA ER (1978c) The retention of metallic mercury vapor by soils. *Geochim Cosmochim Acta* 42:1407–1411
- LANDA ER (1979) The volatile loss of Hg from soils amended with methylmercury chloride. *Soil Sci* 128:9–16
- LATHROP RC, NOONAN KC, GUEUTHER PM, BRASINO TL, RASMUSSEN PW (1989) Mercury levels in walleyes from Wisconsin lakes of different water and sediment chemistry characteristics. (Tech Bull 163) Dept. of Natural Resources, Madison, Wisconsin
- LEE YH, IVERFELDT Å (1991) Measurement of methylmercury and mercury in run-off, lake and rain waters. *Water Air Soil Pollut* 56:309–321
- LEE YH, HULTBERG H, ANDERSON I (1985) Catalytic effect of various metal ions on the methylation of mercury in the presence of humic substances. *Water Air Soil Pollut* 25:391–400

- LEE YH, BORG G, IVERFELDT Å, HULTBERG H (1995) Fluxes and Turnover of methylmercury: mercury pools in forest soils. *Int. Conf. on Mercury as a Global Pollutant*, May 31–June 4 1992, Monterey. Lewis Publishers, Boca Raton, USA
- LEXMOND TM, HAAN FAM, FRISSEL MJ (1976) On the methylation of inorganic mercury and the decomposition of organo-mercury compounds—a review. *Neth J Agri Sci* 24:79–97
- LINDBERG SE, JACKSON DR, HUCKABEE JW, JANZEN SA, LEVIN MJ, LUND JR (1979) Atmospheric emission and plant uptake of mercury from agricultural soils near Almaden mercury mine. *J Environ Qual* 8:572–578
- LINDBERG SE, KIM K-H, MEYERS TP, OWENS JG (1995) A micrometeorological approach for quantifying air/surface exchange of mercury vapor: proof of principal and measurements over contaminated soils. *Environ Sci Technol* 29 (1), 126–135
- LINDQVIST O, RODHE H (1985) Atmospheric mercury – a review. *Tellus* 37 B:136–159
- LINDQVIST O, JERNELÖV A, JOHANSSON K, RODHE H (1984) Mercury in the Swedish environment, global and local sources. SNV PM 1816, Swedish Environmental Protection Agency, S-171 85, Solna, Sweden
- LINDQVIST O, JOHANSSON K, AASTRUP M, ANDERSSON A, BRINGMARK L, HOVSENIUS G, HÅKANSON L, IVERFELDT Å, MEILI M, TIMM B (1991) Mercury in the Swedish environment. Recent research on causes, consequences and corrective methods. *Water Air Soil Pollut* 56
- LINDSAY WL (1979) *Chemical equilibria in soil*. J Wiley, New York, pp 344–363
- LOCKWOOD RA, CHEN KH (1973) Adsorption of Hg(II) by hydrous manganese oxides. *Environ Sci Technol* 7:1028–1034
- LODENIUS M, SEPPÄNEN A, UUSI-RAUVA A (1983) Sorption and mobilization of Hg in peat soil. *Chemosphere* 12:1575–1581
- MAGOS L, TUFFEREY AA, CLARKSON TW (1964) Volatilization of mercury by bacteria. *Br J Ind Med* 21:294–298
- MARTIN (1988) Bioinorganic chemistry of toxicity. In: Seiler G, Sigel H (eds) *Handbook of toxicity of inorganic compounds*. Marcel Dekker Inc, New York, pp 9–25
- MAY K, AHMED R, REISINGER K, TORRES B, STOEPLER M (1985) Studies on the biochemical cycle of mercury. III. Methyl mercury contents in specimens of the environmental specimen bank and other materials. In: Lekkas TD (ed) *Int. Conf. Heavy Metal Environment*. CEP Consultants, Edinburgh, UK, pp 513–515
- MCCARTHY JH (1972) Review: Mercury vapour and other volatile components in the air as guides to ore deposits. *J Geochim Explor* 1:143–162
- MCCARTHY JH, GOTT GB, VAUGHN WW (1969a) Distribution and abundance of mercury and other trace elements in several base-and precious-metal mining districts. *New Mexico Bur Mines Miner Res Circ N* 101:99–108
- MCCARTHY JH, VAUGHN WW, LEARNED RE, MEUSCHKE JL (1969b) Mercury in soil gas and air – a potential tool in mineral exploration. *Geol Surv Circ* 609
- MCCARTHY JH, MEUSCHKE JL, FICKLIN WH, LEARNED RE (1970) Mercury in the atmosphere. *US Geol Surv Prof Pap* 713:37–39
- MCNERNEY JJ, BUSECK PR (1973) Geochemical exploration using mercury vapor. *Economic Geology* 68:1313–1320
- MILLER RW (1975) The role of humic acids in the uptake and release of mercury by freshwater sediments. *Verh Internat Verein Limnol* 19:2082–2086
- MILLER RW, SCHINDLER JE, ALBERTS JJ (1974) Mobilization of mercury from freshwater sediments by humic acid. In: *Mineral cycling in southeastern ecosystems*. AEC Symposium Series, May 1–3, Augusta, Ga, pp 445–451
- MILLER RW, SCHINDLER JE, ALBERTS JJ (1975) Mobilization of mercury from freshwater sediments by humic acid. In: *Mineral cycling in southeastern ecosystems*. AEC Symposium Series, May 1–3 1974, Augusta, Ga, pp 445–451
- MURRAY AD, KIDBY DK, (1972) Mercury distribution and transformations in growing yeast. *Abst Ann Meet Am Soc Microbiol* 98:17
- NAGASE H, OSE Y, SATO T, ISHIKAWA T (1982) Methylation of mercury by humic substances in an aquatic environment. *Sci Total Environ* 24:133–142
- NIKI H, MAKER PD, SAVAGE CM, BREITENBACH LP (1983) A long-path fourier transform study of the kinetics and mechanism for the HO-radical initiated oxidation of dimethyl mercury. *J Phys Chem* 87:4978–4981
- OBUSKHOVSKAYA TD (1982) Mercury sorption by soil minerals. *Sov Soil Sci* 14:49–55
- OMOE (1981) *Handbook of analytical methods for environmental samples*. Ontario Ministry of the Environment, Rexdale, Ontario
- OMOE, OMNR (1989) *Guide to eating Ontario sport fish*. Ontario Ministry of the Environment and Ontario Ministry of Natural Resources, Toronto, Ontario
- OVERBEEK JTG (1977) Recent developments in the understanding of colloid stability. *J Colloid Interface Sci* 58:408–422
- OZEROVA NA (1962) Primary dispersion halos of mercury. *Acad of Science, UdSSR Inst Geol of Ore Deposits, Petrography, Mineralogy and Geochemistry (IGEM) Proc* 72:135
- OZEROVA NA (1982) Regional foundations of the mercury metric method of prospecting for ore and gas and oil deposits. In: *Geochemical methods of prospecting for mineral deposits 1*. IMGRE, Moscow, pp 69–71 (in Russian)
- PACZYNA JM, OTTAR B (1989) Control and fate of atmospheric trace metals. *Kluwer, Dordrecht*, pp 303–310
- PADBERG S (1991) Quecksilber im terrestrischen Ökosystem. *Forschungszentrum Jülich, Institut für Chemie 4, FRG*
- PLOUFFE A (1995) Glacial dispersal of mercury from bedrock mineralization along Pinchi fault, north central British Columbia. *Water Air Soil Pollut* 80:1109–1112
- PRIEST GR, HADDEN RM, WOLLER NM, BRAND CB (1983) Preliminary soil-mercury survey of Newberry Volcano, Deschutes County. In: Priest GR, Vost BF, Black GL (eds) *Oregon survey of potential geothermal exploration sites at Newberry Volcano, Deschutes County, Oregon Open File Report-State of Oregon*. Dept of Geology and Mineral Industries 0–83–3, pp 45–67
- RASMUSSEN PE (1993) The environmental significance of geological sources of mercury: a precambrian shield watershed study. (PhD) University of Waterloo, Ontario, Canada
- RAUTER W (1976) Aufnahme von Quecksilber aus der Umgebungsluft durch Pflanzen und seine Speicherung in pflanzlichen Geweben. *Z Lebensm Unters-Forsch* 162:1–6
- REIMERS RS, KRENKEL PA (1974a) Kinetics of mercury adsorption and desorption in sediments. *J Water Pollut Control Fed* 46:352–365
- REIMERS RS, KRENKEL PA (1974b) Sediment sorption phenomena. In: Bond RG, Straub CP (eds) *Critical reviews in environmental control*. CRC Press, Boca Raton, FL. Vol 4, pp 265–278
- RETCOFSKY HL, STARK JM, FRIEDEL RA (1968) Electron spin resonance in American coals. *Anal Chem* 40:1699–1704
- REVIS NW, OSBORNE TR, HOLDSWORTH G, HADDEN C (1989) Distribution of mercury species in soil from a mercury-contaminated site. *Water Air Soil Pollut* 45:105–113

- RIFFALDI R, SCHNITZER M (1972) Effects of diverse experimental conditions on ESR spectra of humic substances. *Geoderma* 8:1–10
- RITCHIE GSP, POSNER AM (1982) The effect of pH and metal binding on the transport properties of humic acids. *J Soil Sci* 33:233–247
- ROGERS RD (1975) Methylation of mercury in a terrestrial environment. In: *International Conf on Heavy Metals in the Environment*. Toronto, Canada, C218–C221
- ROGERS RD (1976) Methylation of mercury in agricultural soils. *J Environ Qual* 5:454–458
- ROGERS RD (1977) Abiological Methylation of mercury in soil. *J Environ Qual* 6:463–467
- ROGERS RD (1979) Volatility of Hg from soils amended with various Hg compounds. *Soil Sci Soc Am J* 43:289–291
- ROGERS RD, MCFARLANE (1979) Factors influencing the volatilization of Hg from soil. *J Environ Qual* 8:255–260
- ROSE AW, HAWKES HE, WEBB JS (1979) *Geochemistry in mineral exploration*. Academic Press, New York, pp 657
- ROSS RG, STEWART DKR (1962) Movement and accumulation of mercury in apple trees and soil. *Can J Plant Sci* 42:280–285
- RYALL WR (1979) Guidelines for collection, preparation and storage of geological samples for mercury analysis. (Tech Comm 67) Institute of Earth Resources, CSIRO Division of Mineralogy, Australia
- SANEMASA I (1975) The solubility of elemental mercury vapor in water. *Bul Chem Soc Jap* 48:1795–1798
- SAUKOV AA (1946) Geochemistry of mercury. (Geokhim. Rtuti.) (Mineralogo-Geokhim. Seriya Nr 17) Akad Nauk SSSR Inst Geol Nauk 78
- SCHACHTSCHABEL P, BLUME HP, HARTGE K-H, SCHWERTMANN U (1984) *Lehrbuch der Bodenkunde*. Enke Verlag, Stuttgart
- SCHLÜTER K (1993) The fate of mercury in soil. A review of current knowledge. Commission of the European Communities; *Soil Groundwater Res Rep IV*
- SCHLÜTER K (1996) Translocation of ^{203}Hg labelled HgCl_2 and CH_3HgCl in a iron humus podzol studied by radio-analytical techniques. *Z Pflanzenern Bodenkunde* 159:215–226
- SCHLÜTER K (1997) Sorption of inorganic mercury and monomethyl mercury in an iron-humus-podzol soil of southern Norway studied by batch experiments. *Environmental Geology* 30 (3/4):266–278
- SCHLÜTER K, GÄTH S (1999) Evaporation von Quecksilber aus kontaminierten Böden und deren Bedeutung für die Hg-Aufnahme von Kulturpflanzen. In: *Umweltforschungsplan des Bundesministeriums für Umwelt Naturschutz und Reaktorsicherheit*. Bodenschutz FKZ 29671005, Umweltbundesamt Berlin
- SCHLÜTER K, ALSTAD J, SEIP HM (1995a) Mercury translocation and evaporation in and from soils: I. Soil lysimeter experiments and the use of Hg-203 radiolabelled compounds. *J Soil Contam* 4 (4):327–354
- SCHLÜTER K, SEIP HM, ALSTAD J (1995b) Mercury translocation in and evaporation from soil: II. Evaporation of mercury from podzolised soil profiles treated with HgCl_2 and CH_3HgCl . *J Soil Contam* 4 (3):269–299
- SCHLÜTER K, SEIP HM, ALSTAD J (1996) Mercury translocation in and evaporation from soil: III. Quantification of evaporation of mercury from podzolised soil profiles treated with HgCl_2 . *J Soil Contam* 5 (2):121–139
- SCHNITZER M (1978) Some observations on the chemistry of humic substances. *Agrochim* 22:216–225
- SCHNITZER M, KHAN SV (1972) *Humic substances in the environment*. Dekker, New York
- SCHOTTEL JK (1978) The mercury and organomercurial detoxifying enzymes from a plasmid bearing strain of *Escherichia coli*. *J Biol Chem* 253:4341–4349
- SCHOTTEL J, MANDAL A, CLARK D, SILVER S (1974) Volatilization of mercury and organomercurials determined by inducible R-factor systems in enteric bacteria. *Nature* 251:335–337
- SCHROEDER WH, LINDQVIST O, MUNTHER J (1989) Volatilization of mercury from natural surfaces: water and soil. In: Vernet JP (ed) *Heavy metals in the environment*. CEP Consultants Edinburgh, Geneva
- SEMU E, SINGH BR, STEENBERG K, SELMER-OLSEN AR (1985) Mobility of ^{203}Hg -labeled mercuric chloride in soil columns. *Acta Agric Scand* 35:129–135
- SENESE N, SCHNITZER M (1977) Effects of pH, reaction time, chemical reduction and irradiation on ESR spectra of fulvic acid. *Soil Sci* 123:224–234
- SHIMOMURA S, NISHIKARA V, FUKUMOTO Y, TANASE Y, (1969) Adsorption of mercuric ions by ferric hydroxide. *J Hygenic Chem* 15:84–89
- SIDLE WC (1993) Naturally occurring mercury contamination in a pristine environment. *Environ Geol* 21:42–50
- SIEGEL SM, SIEGEL BZ (1988) Temperature determinants of plant-soil-air mercury relationships. *Water Air Soil Pollut* 40:443–448
- SIEGEL SM, SIEGEL BZ, PUERNER N, SPEITEL T, THORARINSSON F (1975) Water and soil biotic relations in mercury distribution. *Water Air Soil Pollut* 4:9–18
- SIEGEL SM, SIEGEL BZ, BARGHIGIANI C, ARATINI K, PENNY P, PENNY D (1987) A contribution to the environmental biology of mercury accumulation in plants. *Water Air Soil Pollut* 33:65–72
- SILVER J (1981) Mechanisms of bacterial resistances to toxic heavy metals: arsenic cadmium and mercury. In: Brinckman FE, Fish RH (eds) *Environmental speciation and monitoring needs for trace metal containing substances from energy related processes*. Natl Bureau of Standard, Washington DC (Publ Nr 618), pp 301–314
- SKOGERBOE RK, WILSON SA (1981) Reduction of ionic species by fulvic acid. *Anal Chem* 53:228–232
- SLEMR F, LANGER E (1992) Increase in global atmospheric concentrations of mercury inferred from measurements over the Atlantic Ocean. *Nature* 355:434–436
- SLUNGA RS (1990) The Baltic shield earthquakes. *Tectonophysics* 189:323–331
- SPANGLER WJ, SPIGARELLI JL, ROSE JM, MILLER HM (1973a) Methylmercury: Bacterial degradation in lake sediments. *Science* 180:192–193
- SPANGLER WJ, SPIGARELLI JL, ROSE JM, FLIPPIN RS, MILLER HH (1973b) Degradation of methylmercury by bacteria isolated from environmental samples. *Appl Microbiol* 25:488–493
- STAIGER K, PODLESAK W (1983) Studies on the fixation and release of vaporous mercury in soils. *Bodenkultur* 34:187–195
- STEINNES E (1995) Mercury. In: Alloway BJ (ed) *Heavy metals in soils*. Blackie, London and J Wiley, New York, pp 245–259
- STEINNES E, ANDERSSON M (1991) Atmospheric deposition of mercury in Norway: temporal and spatial trends. *Water Air Soil Pollut* 56:391–404
- STEPANOV II, VILD'YAYEV VM (1984) The sources of mercury vapor. *Geochem Int* 21:9–10
- STEWART JWB, BETTANY JR, RENNIE DA, HUANG PM, MCKERCHER RB (1975) Tracer-aided studies of the movement of toxic elements in soil-plant-water systems under controlled conditions. In: *Origin Fate Chem Residues Food Agric Fish Proc Rep 2 Res Co-ord Meet, Meeting Date 1973–1974*. IAEA, Vienna, Austria, pp 23–34

- STOEPLER M, PADBER S, BUROW M, MAY K (1993) Methyl mercury in terrestrial compartments. The present state of the art. *Forschungszentrum Jülich, Germany*, 28 Jul–16 Sept 1993
- STROHAL P, HULJEV D (1971) Investigation of Hg pollutant interaction with humic acids by means of radiotracers. In: *Nuclear techniques in environmental pollution*; Int Atomic Energy Agency; Proc Symp Nucl Techniques in Environ Pollut. Vienna, pp 439–446
- SUMMERS AO, SILVER S (1978) Microbial transformations of metals. *Ann Rev Microbiol* 32:637–672
- SUMMERS AO, SUGARMAN LI (1974) Cell-free mercury(II)-reducing activity in a plasmid-bearing strain of *Escherichia coli*. *J Bacteriol* 119:242–249
- SWAIN EB, ENGSTRÖM DR, BRIGHAM ME, HENNING TA, BREZONIK PL (1992) Increasing rates of atmospheric mercury deposition in midcontinental North America. *Science* 257:784–787
- SYKES LR (1980) Earthquakes and other processes within lithospheric plates and the reactivation of pre-existing zones of weakness. The continental crust and its mineral deposits. *Geol Assoc Can Spec Pap* 20:215–237
- TALMI Y, MESMER RE (1975) Studies on vaporization and halogen decomposition of methylmercury compounds rising GC with microwave detector. *Water Res* 9:547–552
- TAMURA R, FUKUZAKI N, HIRANO Y, MIZUSHIMA Y (1985) Evaluation of mercury contamination using plant leaves and humus indicators. *Chemosphere* 14:1687–1693
- TONOMURA K, MAEDA K, FUTAI F, NAKAGAMI T, YAMADA M (1968) Stimulative vaporization of phenylmercuric acetate by mercury resistant bacteria. *Nature* 217:644–646
- TONOMURA K, FURUKAWA K, YAMADA M (1972) Microbial conversion of mercury compounds. In: Matsumura F, Bores GM, Misate T (eds) *Environmental toxicology of pesticides*. Academic Press, New York, pp 115
- TROST PB, BISQUE RE (1970) Differentiation of vaporous and inorganic origin of trace Hg in soils. Abstracts 3rd Intl Geochem Symp. Toronto, Ontario
- TROST PB, BISQUE RE (1972) Distribution of Hg in residual soils. In: Hartung R (ed) *Environ mercury contamination*. Ind Conf Meeting Date 1970; Ann Arbor Publ, Ann Arbor, Mich, pp 178–196
- TUNELL G (1964) Chemical processes in the formation of mercury ores and ores of mercury and antimony. *Geochim Cosmochim Acta* 28:1019–1037
- US GOVERNMENT PRINTING OFFICE WASHINGTON (1970) Mercury in the environment. *Geol Surv Prof Pap* 713
- VAITUZIS A, NELSON JD, WAN W, COLWELL RR (1975) Effects of mercuric chloride on growth and morphology of selected strains of mercury-resistant bacteria. *Appl Microbiol* 29:275–286
- VAN FAASSEN HG (1973) Effects of mercury compounds on soil microbes. *Plant Soil* 38:485–487
- VAN FAASSEN HG (1975) Methylation of mercury compounds in soil, sediment and sewage-sludge samples. *Plant Soil* 44:505–509
- VAREKAMP JC, BUSECK PR (1983) Mercury anomalies in soils: a geochemical exploration method for geothermal areas. *Geothermics* 12:29–47
- VAREKAMP JC, BUSECK PR (1984a) The speciation of mercury in hydrothermal systems with applications to ore deposition. *Geochim Cosmochim Acta* 48:177–185
- VAREKAMP JC, BUSECK PR (1984b) Changing mercury anomalies in Long Valley, California: Indication for magma movement or seismic activity. *Geology* 12:283–286
- VAREKAMP JC, BUSECK PR (1986) Global mercury flux from volcanic and geothermal sources. *Appl Geochem* 1:65–73
- VAREKAMP JC, WAIBEL AF (1987) Natural cause for mercury pollution at Clear Lake, California, and paleotectonic inferences. *Geology* 15:1018–1021
- VARSHAL GM, SOBOLEV GA, BARSUKOV L, KOLTSOV AV, KOSTIN BI, KUDINOVA TF, STAKHEYEV YI, TRETYAKOVA SP (1985) Separation of volatile components from rocks under mechanical loading as the source of hydrogeochemical anomalies preceding earthquakes (Results of large-scale model). *Pure Appl Geophys* 122:463–477
- VONK JW, SIJPESTEIJN AK (1973) Studies on the methylation of mercuric chloride by pure cultures of bacteria and fungi. *Antonie van Leeuwenhoek* 39:505–513
- WALLNER P (1977) Quecksilber Gehalte in Böden, der Bodenluft und in der bodennahen Atmosphäre im Bereich einiger bekannter Erzvorkommen. (PhD) Fakultät Bergbau und Hüttenwesen, Universität Aachen
- WALLSCHLÄGER D, HINTELMANN H, EVANS RD, WILKEN R-D (1995) Volatilization of dimethylmercury and elemental mercury from river Elbe floodplain soils. *Water Air Soil Pollut* 80:1325–1329
- WARREN HV, DELAVAUULT RE, BARASKO J (1966) Some observations on the geochemistry of mercury as applied to prospecting. *Econ Geol* 61:1010–1028
- WARREN HV, HORSKY SJ, KRUCKEBERG A, TOWERS GHN, ARMSTRONG JE (1983) Biogeochemistry a prospecting tool in the search for mercury mineralization. *J Geochem Explor* 18:169–173
- WATRAS CJ (1994) Sources and fates of mercury and methylmercury in Wisconsin Lakes. In: Watras CJ, Huckabee JW (eds) *Mercury pollution, integration and synthesis*. Lewis Publ, Boca Raton, pp 153–177
- WEBER JH, REISINGER K, STOEPLER M (1985) Methylation of mercury(II) by fulvic acid. *Environ Technol Letters* 6:203–208
- WHITE DE (1981) In: BJ Skinner (ed) *Active geothermal systems and hydrothermal ore deposits*. *Econ Geol 75th Anniversary Volume*, pp 392–423
- WILLISTON SH (1964) The mercury halo method of exploration. *Eng Min J* 165:98–101
- WILSON SA, WEBERJH (1977) Electron spin resonance analysis of semiquinone free radicals of aquatic and soil fulvic and humic acids. *Anal Lett* 10:75–84
- WILSON SA, WEBER JH (1979) An EPR study of the reduction of vanadium(V) to vanadium(IV) by fulvic acid. *Chem Geol* 26:345–354
- WIMMER J (1974) Untersuchungen über die Wanderung und Auswaschung von Hg im Boden. *Bodenkultur* 25:369–379
- WIMMER J, HAUNOLD E (1973) Untersuchungen über den Hg Gehalt Österreichischer Böden mit Hilfe der Neutronenaktivierungsanalyse. *Bodenkultur* 24:25–30
- WOLLAST R, BILLEN G, MACKENZIE FT (1975) Behavior of mercury in natural systems and its global cycle. *Environmental Science Research*, vol 7. *Ecol Toxicol Res*, pp 145–166
- XIAO ZF, MUNTHE J, SCHROEDER WH, LINDQVIST O (1991) Vertical fluxes of volatile mercury over forest soil and lake surfaces in Sweden. *Tellus* 43B:267–279
- XIE X, YANG B (1989) Application of multiparametric geochemical methods in the search for oil in the Qinggang region near Daqing Oil Field. *J Geochem Explor* 33:203–213
- XIE X, ZHENG K (1983) Recent advances in geochemical exploration in China. *J Geochem Explor* 19:423–444
- XU H, ALLARD B (1991) Effects of a fulvic acid on the speciation and mobility of mercury in aqueous solutions. *Water Air Soil Pollut* 56:709–717
- ZHU B, YOU Z (1989) Mercury content reflection of the Lancang-Gengma aftershocks. *J Seismol Res* 12:(2), 161–162
- ZHU B, ZHANG I, ZHU L, ZHENG Y (1986) Mercury arsenic antimony bismuth and boron as geochemical indicators for geothermal areas. *J Geochem Explor* 25:379–388