

# THE BEHAVIOR OF MERCURY IN THE SOIL WITH SPECIAL EMPHASIS ON COMPLEXATION AND ADSORPTION PROCESSES - A REVIEW OF THE LITERATURE

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**ABSTRACT.** The behavior of Hg in the soil is mainly controlled by adsorption and desorption processes depending on complexation, the most important ligands in solution being  $\text{OH}^-$ ,  $\text{Cl}^-$ , and organic anions. Since the solubility of  $\text{HgCl}_2$  and  $\text{Hg}(\text{OH})_2$  is rather high, the affinity of Hg to these ligands leads to an increased mobility. This is especially true for  $\text{HgCl}_2$ , whereas the hydrolysis of  $\text{Hg}^{2+}$  may result in the specific adsorption of Hg on mineral colloids. The high affinity of Hg to S explains the strong binding of Hg to soil organic matter and also the stability of  $\text{HgS}$ . Further precipitation products than  $\text{HgS}$  are unlikely to occur, since the activity of  $\text{Hg}^{2+}$  remains too low to exceed the solubility product of any other defined Hg compound. It is mainly the physical fractioning of soil organic matter (dissolved vs adsorbed) that determines the behavior and distribution of Hg in soils.

## 1. Introduction

The presence of ligands and metal ions in aqueous solutions often results in the formation of metal complexes. This association may alter their adsorptive behavior, since complexation can modify the characteristics of the metal ion such as solubility, charge, size and stereochemical configuration (Elliott and Huang, 1979). This is especially true for Hg which has a strong tendency to build complexes with  $\text{Cl}^-$ ,  $\text{OH}^-$ ,  $\text{S}^{2-}$  and S-containing functional groups of organic ligands. The purpose of this study is to provide a comprehensive review of the literature concerning the adsorption of Hg at the solid/solution interface, with primary emphasis on the role of complexation and chemical speciation in the adsorption process. The behavior of organomercurials such as  $\text{CH}_3\text{Hg}^+$  and also the volatilization of Hg from the soil will not be discussed in this paper.

## 2. Speciation of Soluble Hg in the Soil Environment

### 2.1. RELEVANT CHEMICAL PROPERTIES OF HG

Together with the elements Cd and Zn, Hg belongs to the group IIB of the periodic table. Mercury is only slightly soluble in water ( $6 \cdot 10^{-5} \text{ g L}^{-1}$ ;  $25^\circ\text{C}$ ), liquid and rather volatile ( $1.22 \cdot 10^{-3} \text{ mm}$ ;  $20^\circ\text{C}$ ) at normal temperatures. Being a "class B" metal (Pearson classification) Hg tends to associate with soft bases like S ( $\text{S}^{2-}$ ,  $\text{SH}^-$ ), I and organic S, P and N (Stumm and Morgan, 1981). As a result of coordination selectivity Hg prefers  $\text{NH}_3$  to  $\text{H}_2\text{O}$ ,  $\text{CN}^-$  to  $\text{OH}^-$ ,  $\text{Cl}^-$  and  $\text{F}^-$ , S-donors to O-donors as a ligand. The stability constants for the most important inorganic and organic Hg complexes have already been tabulated elsewhere (Sillen and Martell, 1971; Gilmour, 1971; Frimmel et al., 1976; 1980). It is not so much electrostatic but covalent interactions which are of prior importance in respect to binding mechanisms.

### 2.2. STABILITY OF HG-COMPOUNDS

**2.2.1. Redox Stability.** Under the usual conditions of temperature and pressure that occur in the soil environment, Hg may be present in three oxidation states. The most reduced is the metal  $\text{Hg}^0$ , the other two forms are ionic. It is the mercurous ion  $\text{Hg}_2^{2+}$ , where the average valence of mercury is +1 and, in oxidizing conditions especially at low pH, the mercuric ion,  $\text{Hg}^{2+}$ . The mercurous ion is not stable under environmental conditions since it dismutates into  $\text{Hg}^0$  and  $\text{Hg}^{2+}$ . The main features of the aqueous inorganic chemistry of Hg are clearly indicated by the diagram of Figure 1.

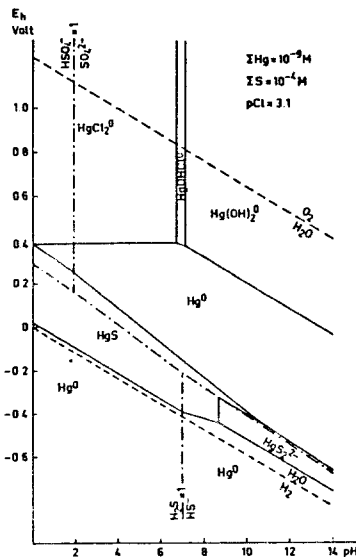


Figure 1. Inorganic Hg species as a function of pH and redox potential (from Andersson 1979)

Under naturally occurring conditions of Eh and pH the solubility of Hg is mainly determined by  $\text{Hg}(\text{OH})_2$ ,  $\text{Hg}^0$  and  $\text{HgS}$ . Over much of the area of moderately oxidizing conditions above pH 5 the predominant Hg species in solution is undissociated  $\text{Hg}^0$ . The solubility of elemental Hg is nearly constant over the whole area where the liquid metal is stable, and is relatively low, about  $56 \text{ ng g}^{-1}$  (Cranston and Buckley, 1972). Mildly reducing conditions can cause the Hg to be precipitated as the sulfide. This compound has an extremely low solubility ( $0.002 \text{ ng g}^{-1}$ ). Very strongly reducing conditions, however, may increase the solubility somewhat by converting the mercuric ion to free metal or by occurrence of the stable  $\text{HgS}_2^{2-}$  at high pH (Wollast *et al.*, 1975). High solubilities of Hg occur only in very well oxygenated environments (350 to 400 mV) which are expected to occur normally in terrestrial soils. This is mainly a result of the strong tendency of Hg(II) to associate with hydroxyl- and chloride ions.

**2.2.2. Complex Stability.** The formation of Hg(II)-complexes which are of importance in natural systems is discussed by Gilmour (1971). His calculations reveal that the values of the stability constants are highest for  $\text{Cl}^-$ ,  $\text{OH}^-$ ,  $\text{NH}_3$ , and several orders of magnitude lower for  $\text{F}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_3^-$ . The latter ligands may be excluded from further considerations because they would only be significant under unnaturally high concentrations. The insolubility of HgS compounds coupled with low  $K_n$  values for sulfides removes this group of ligands from further consideration. Ammonia hydrolyzes to ammonium ion in aqueous solutions which may then be removed from solution by specific adsorption on certain clay minerals. Only at a high pH ( $> \text{pH } 9$ ) and under conditions of  $\text{NH}_3$  formation or addition concentrations of free  $\text{NH}_3$  would approach  $10^{-5} \text{ M}$ . Since these conditions are rather extreme and under normal circumstances only trace concentrations of  $\text{NH}_3$  are found, the stability product will be small and so excluded from further discussion of soil systems. Unlike the other ligands,  $\text{Cl}^-$  and  $\text{OH}^-$  are of sufficiently high concentrations and large stability constants to dominate most natural systems. Hahne and Kroontje (1973a) calculated the relative abundance of Hg species dependent on the concentration of chloride and hydroxyl ions (pH). Hg(II) was calculated to hydrolyze in the pH range of 2 to 6, with the final species being the soluble  $\text{Hg}(\text{OH})_2$  at about pH 6. Precipitation of  $\text{Hg}(\text{OH})_2$  occurs only if the concentration of Hg(II) exceeds  $107 \text{ } \mu\text{g g}^{-1}$ , the intrinsic solubility of  $\text{Hg}(\text{OH})_2$  being  $5.37 \cdot 10^{-4} \text{ M}$ . Thus, at normal pH conditions in soils, the distribution of Hg(II) will be dependent on the solubility of  $\text{Hg}(\text{OH})_2$ .

Chlorides, like  $\text{H}^+$  and  $\text{OH}^-$ -ions, occur in all natural soil and water systems and may be regarded as one of the most mobile and persistent complexing agents for Hg. High  $\text{Cl}^-$  concentrations in soil solution can be expected in saline and saline-sodic soils but also as a result of anthropogenic activities, eg. fertilization or usage of road deicing salts (Feick *et al.*, 1972). Chlorides complex with Hg(II) at  $\text{Cl}^-$  concentrations above  $10^{-9} \text{ M}$  ( $35 \cdot 10^6 \text{ } \mu\text{g g}^{-1}$ );  $\text{HgCl}_2$  forms above  $10^{-7.5} \text{ M}$  ( $1.1 \cdot 10^{-3} \text{ } \mu\text{g g}^{-1}$ ), peaking at about  $10^{-4} \text{ M}$  ( $\approx 3.5 \text{ } \mu\text{g g}^{-1} \text{ Cl}^-$ ) and the anionic  $\text{HgCl}_3^-$  and  $\text{HgCl}_4^{2-}$  form above  $10^{-2} \text{ M}$  ( $350 \text{ } \mu\text{g g}^{-1}$ ) (Figure 2). Hahne and Kroontje (1973b) further predicted that at pH 4 and 5,  $\text{Cl}^-$  concentrations of 3.5 and 14 ppm, respectively, are sufficient for all Hg(II) to be in the  $\text{HgCl}_2$  form. At higher pH values, mobilization resulting from the forming of  $\text{HgCl}_2$  complexes is possible depending on the prevailing  $\text{Cl}^-$  and Hg(II) concen-

trations. The  $\text{Cl}^-$  concentration necessary for partial or complete mobilization of  $\text{Hg(II)}$  increases with increasing pH-values, resulting from the competition of  $\text{OH}^-$  with  $\text{Cl}^-$ .

*Annotation.* Equilibrium calculations should only be regarded as a more or less accurate approximation to the actual speciation. This is mainly because of the deviation of natural systems from thermodynamic equilibrium. Another difficulty is the limited knowledge of the species composition of natural systems, especially with regard to natural organic substances and other colloidal particulates and also their interactions with the Hg species.

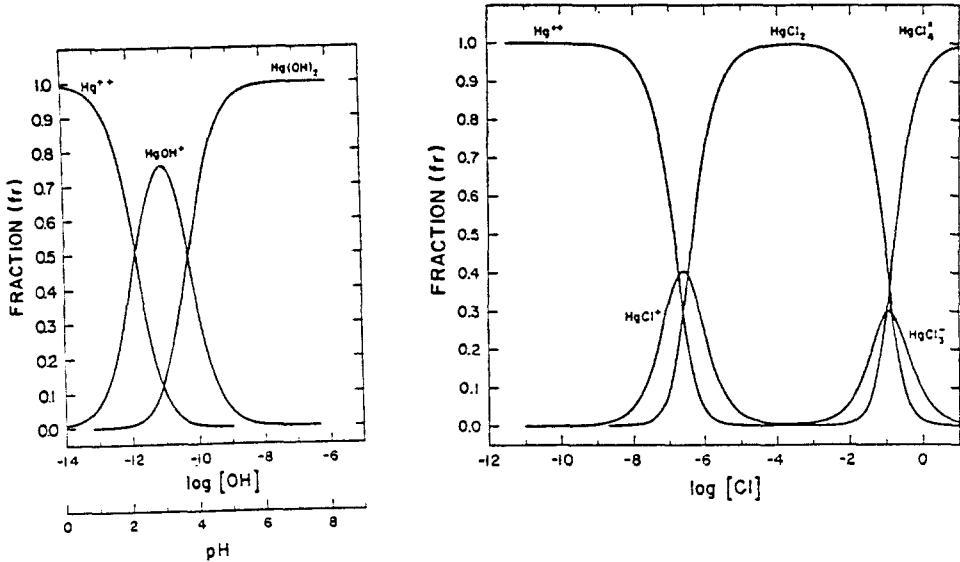


Figure 2. Predicted speciation of Hg as influenced by pH and chloride ions (from Hahne and Kroontje 1973a)

### 3. Binding of Hg in the Soil

As any other metal Hg may occur in the soil in various forms. Those are (i) dissolved (free ion or soluble complex), (ii) nonspecifically adsorbed (binding mainly due to electrostatic forces), (iii) specifically adsorbed (strong binding due to covalent or coordinative forces) (iv) chelated (bound to organic substances) and (v) precipitated (as sulfide, carbonate, hydroxide, phosphate etc.). The soluble forms of Hg in the soil environment were already discussed in Section 2. Since it is strongly bound to soil constituents, normally only trace concentrations of Hg are found in the soil solution. This is also true for conditions that do not allow precipitation of a sparingly soluble compound. Since the dominant species of  $\text{Hg(II)}$  in solution are uncharged complexes, the mechanism for sorption on the solid phase is not ion exchange but rather stable insoluble inorganic and organic complex formation.

### 3.1. SPECIFIC ADSORPTION OF Hg ON MINERAL SURFACES

The specific adsorption of heavy metals on mineral surfaces may be explained by the concept of surface complexation (Leckie, 1986; Bourg, 1987; Schindler and Stumm, 1988). It is based upon the idea that reactions between dissolved substances and functional groups of solid surfaces follow the mathematical formalisms of coordination chemistry; thus adsorption to the solid surface may be described in the same way as equilibrium calculations (e.g. complexation) in solution. The concept of surface complexation provides mechanisms for adsorption of ions as well as (uncharged) molecules. The assumption that processes diminishing the activity of a free ion (like complexation in solution) should necessarily reduce ion adsorption to the solid surface has therefore to be revised. It is suggested that the adsorption of heavy metal ions is not governed primarily by the "free" metal, but by the much stronger adsorbed hydroxo, sulfato, carbonato or other metal complex species. This phenomenon is best illustrated and documented in relation to metal ion hydrolysis. We find a pH-dependent adsorption of hydrolyzable metal ions on various oxide and hydroxide surfaces, where the order of adsorption with increasing pH corresponds to the order of increasing  $p^*K$  for the first hydrolysis product of the metal ion (Figure 3). Correspondingly, Lockwood and Chen (1973) found a sharp increase of Hg-adsorption on hydrous  $MnO_2$  between pH 2.5 and 3, the explanation being the formation of the hydroxide complex in this pH range. Clearly, such adsorption is non-coulombic, since for a negatively charged surface a divalent cation should be electrostatically preferred over corresponding hydroxo complexes of a lower or no positive charge. Accordingly, some type of specific interaction with the surface must be invoked. Thus it had been suggested that the hydroxo complexes are the active species in the adsorption process. Several qualitative explanations for these findings are summarized by Elliott and Huang (1979).

The association of the  $Hg^{2+}$  ion with inorganic ligands exerts a considerable influence on the adsorption behavior of Hg. The important role of hydroxo ligands in adsorption of Hg is emphasized by adsorption experiments where chloride is added in concentrations sufficiently large to form Hg-chloro-complexes. Most experimental evidence suggests that the presence of chloride reduces the extent of adsorption (Lockwood and Chen, 1973; Forbes *et al.*, 1974; Reimers and Krenkel, 1974; Hogg *et al.*, 1978; Kinniburgh and Jackson, 1978; Randle and Hartmann, 1987). This is consistent with the data of Leckie and James (1974, quoted in Elliott and Huang, 1979) presented in Figure 4. With increasing chloride concentration, the adsorption edge shifted to higher pH values or, in other words, adsorption decreased with increasing pH. Chloride, as a typical tracer, does not undergo any specific interaction and therefore has no influence on surface properties *per se*. If at all, it is only weakly bound by physical adsorption.

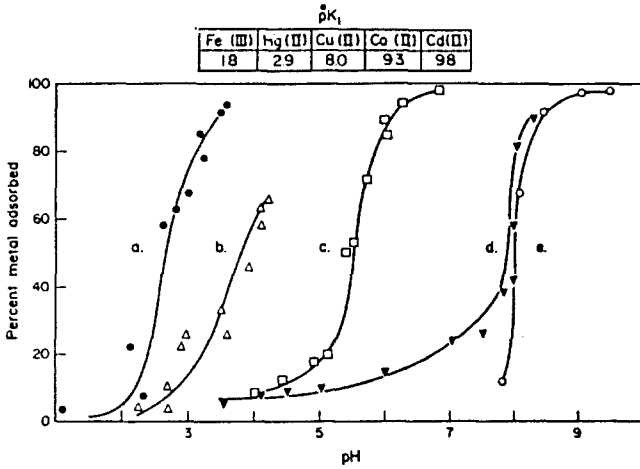


Figure 3. The pH-dependent adsorption of hydrolyzable metal ions on various oxide and hydroxide surfaces. The order of adsorption with increasing pH corresponds to the order of increasing  $p^*K$  values for the first hydrolysis product of the metal ion. (a) Fe(III) on  $\text{SiO}_2$ , (b) Hg(II) on  $\text{SiO}_2$ , Cu on  $\text{Fe}(\text{OH})_3$ , (d) Co(II) on  $\text{TiO}_2$ , (e) Cd(II) on  $\text{SiO}_2$ , (from Elliott and Huang, 1979).

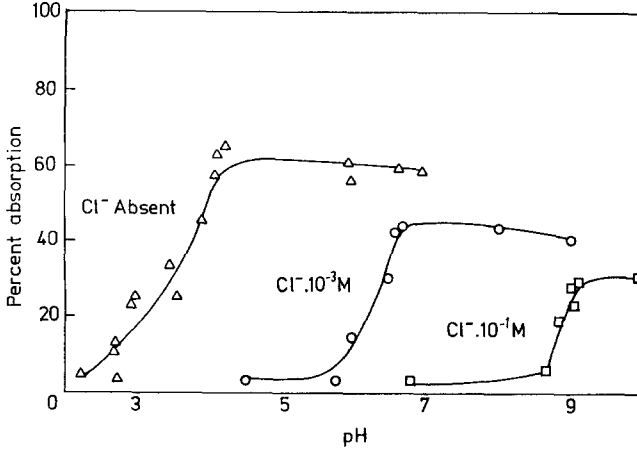


Figure 4. The adsorption of Hg(II) on silica as a function of solution pH and chloride concentration. For a given pH, increasing  $\text{Cl}^-$  concentration reduces Hg(II) uptake (from Leckie and James, 1974).

Newton *et al.* (1976) studied the influence of  $\text{Cl}^-$  on the adsorption behavior of Hg(II) on bentonite and observed maximum adsorption at solution conditions under which the  $\text{HgClOH}^0$  species was dominant. The presence of the hydroxo ligand causes a strong affinity of the complex to the surface. However, the presence of the hydroxo group does not guarantee substantial uptake. If the metal-OH bond is strongly covalent (as it is the case with  $\text{HgOH}^+$ ), the complex ions will be unable to share their hydroxo ligands with the surface. This atypical behavior of the mercuric ion in forming Hg(II)-ligand bonds with a considerable degree of covalent character was also shown by Forbes *et al.* (1974). A comparison of the specific adsorption of Hg(II) with that of other heavy metal cations (divalent Cu, Pb, Zn, Cd) shows that each of the latter elements was extensively adsorbed onto goethite at pH values less than its  $p^*K_1$  value. However, even between pH 4.1 and 5.9, which exceeds  $p^*K_1$  (= 3.70) and  $p^*K_2$  (= 2.60) for the mercuric ion, only ca. 20 % of the Hg(II) in the system was adsorbed although it would be almost completely in the  $\text{Hg(OH)}_2$  form. The relatively small adsorption of Hg(II) compared to other heavy metals is believed to be due to the greater covalency of the  $\text{HgOH}^+$  bond which minimises the stability of bonds between the oxide surface and the bridging hydroxyl groups. This suggests that adsorption inhibition in the presence of  $\text{Cl}^-$  results from complex formation, with the resulting halide complex exhibiting a lower affinity for the surface. The inability of  $\text{HgCl}_2^0$  to adsorb, and therefore for chloride to act as a bridging ligand, is consistent with the absence of measurable specific adsorption of free chloride ions on goethite. The ability of chloride to inhibit metal adsorption and to act as an effective desorbing agent is greater for metals such as Hg(II) which form stable chloride complexes, than for metals such as Cu(II) which are only weakly bound to  $\text{Cl}^-$  in aqueous solution.

### 3.2. SPECIFIC ADSORPTION OF HG BY ORGANIC SUBSTANCES

Mercury exhibits a great affinity for organic matter in soils, peats, and sediments. The "class B" character of the chalcophil element becomes evident in the very strong affinity to S-containing functional groups which are frequently found in organic molecules. It explains the accumulation of Hg in organic-rich, upper soil horizons and the predominance of organic Hg-binding even in mineral soil horizons (Dudas and Pawluk, 1976; Gotoh and Koga, 1977). Furthermore, processes as chelating, ionic exchange, inner and outer sphere complex formation, adsorption, and coprecipitation are likely to occur (Schnitzer and Kerndorff, 1981). Which type of interaction predominates will mainly depend on the properties of the humic substance and the pH of the system. About 1/3 of the total binding capacity of the soil humus is used for cation exchange processes, about 2/3 of available binding sites serve for metal complexation. Thus the "organic associated" fraction (extracted with  $\text{NaHCO}_3$ ) accounted  $\approx$  200 times more Hg than the "cation exchangeable" fraction of a contaminated soil near the Almadén mercury mine (Lindberg *et al.* 1979). Fulvic acid exerted a stronger affinity for Hg than did a strong cation-exchange resin (Lindberg *et al.* 1975). The importance of the interaction between Hg and thio-ligands may be established by the very high stability constants, the Hg-cystein complex being of primary importance. Stability constants of the fulvate complex were high enough to prevent displacing of

Hg by Cu(II) which is known to form the most stable complexes with natural organic ligands of all the cations of the Irving series.

Results of various studies suggest that inorganic colloids contribute more to the adsorption of organomercurials (which are not considered in this review), whereas inorganic Hg-compounds are more strongly and to a greater amount bound to soil organic matter (Aomine and Inoue, 1967; Inoue and Aomine, 1969; Farrah and Pickering, 1978; Semu *et al.*, 1987). Results furthermore indicated that organic components were even more relevant in Hg adsorption at higher Hg concentrations. This is due to a larger adsorption capacity of organic matter as compared with mineral colloids (Brümmer, 1986). Even upon equilibrating with 100 mg Hg L<sup>-1</sup> its adsorption sites were not yet saturated. The adsorption capacity of various clay minerals and organic substances were examined in laboratory experiments (Trost and Bisque, 1970). The humus rich materials revealed a by far higher adsorption capacity than pure clays. These results were verified by Fang (1978) and Landa (1978). It is not only the amount but also the quality of organic matter that decides about the sorption capacity for Hg. This becomes evident by comparing Hg-adsorption of soils with identical mineralogy and humus content but varying vegetation cover ( $\approx$  humus quality) (Semu *et al.*, 1987). Ramamoorthy and Rust (1976) showed that sorption maximum was correlated to surface area > organic content > cation exchange capacity (CEC) > grain size whereas the bonding constant correlated in the order organic content > grain size > CEC > surface area.

The effect of soil reaction has impressively been shown by Andersson (1979). As can be seen from Figure 5, the only effective sorbent for inorganic Hg in acid soils (pH < 4.5 to 5) is the organic material, whereas in neutral soils iron oxides and clay minerals become much more effective. The implications for natural soils will be that under acidic conditions prevailing for example in podzolic soils, organic matter can be expected to dominate the sorption of Hg. In neutral soil types iron oxides and clay minerals may be dominating. In soil horizons low in organic matter, the mobility of Hg will increase with decreasing pH, thus making translocations within the profile or out it increasingly probable.

The strong affinity of Hg to functional groups of soil organic matter refers to bulk particulate organic matter as well as dissolved organic ligands. As a consequence the mechanisms regulating the partition of organic matter between aqueous and solid phases should play a dominant role in the control of the concentrations and thus on the transport of those metals which are strongly complexed (both as solution complexation and adsorption) by organic matter (Bourg and Schindler, 1985).

*3.2.1. Solubility of metal-organic complexes.* We do not know much about the solubility of metal-organic complexes in water and how solubility is affected by ligand concentration, metal ion concentration, metal:ligand ratio, and pH. This is also true for Hg-organic complexes, especially when natural organic ligands are considered. Since the stability of metal-organic complexes decreases with decreasing pH, the amount of metal immobilization is strongly dependent on the complex stability, only very stable complexes being able to exist at low pH. Due to the effects of competition the influence of pH becomes less important with increasing ligand concentration.



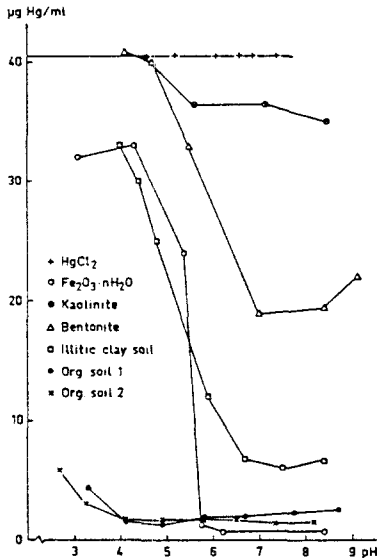


Figure 5. Retention of Hg by soils and soil components as influenced by pH (from Andersson, 1979).

Furthermore it has been shown that a ratio of fulvic acid:metal  $> 2$  favors the formation of watersoluble complexes, while a ratio becoming  $< 2$  leads to insoluble complexes accumulating in soils and sediments (Schnitzer and Kerndorff, 1981). On the other hand natural organic substances are subjected to coagulation and precipitation phenomena. The solubility of humic acids decrease with decreasing pH. Thus it is probable that solid metal-organic complexes can exist even at extremely acidic soil reaction. Bourg and Schindler (1985) concluded that trace metals strongly complexed with organic matter such as Hg(II) should be expected to be significantly controlled by organic matter. In solutions of approximately neutral pH (6 to 8) these metals will most likely move with dissolved organic matter, the latter preventing their precipitation as hydroxides or carbonates. In acid waters (e.g. organic C rich acid forest soils) these metals should be drawn downwards along with the transported organic matter and trapped in the horizon where these organic molecules precipitate. This is consistent with the observation that podzolic soils may contain maximum Hg-concentrations in the horizons of humus accumulation (Figure 6) (McKeague and Kloosterman, 1974; Obukhovskaya and Zyrin, 1987; Zyrin and Sadovnikoya, 1988).

*3.2.2. The influence of dissolved organic ligands on Hg-adsorption to solid surfaces.* There is a considerable amount of speculation on the role of dissolved organic ligands and its association with metals. Most studies indicate that association with dissolved organic matter can both increase and decrease the solubility of trace metals (Lindberg *et al.*, 1975). According to Vuceta (1976) the addition of dissolved organic ligands

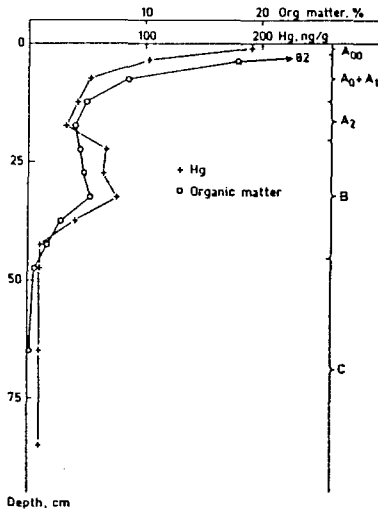


Figure 6. Distribution of Hg and organic matter in a podzolic soil (from Andersson 1979).

may generally result in (i) an inhibition of metal adsorption because of strong complex formation with the metal ion or by competing with the surface for available adsorption sites (ii) no perceptible change in the extent of adsorption if the ligand has weak complex forming ability and exhibits a lack of affinity for the solid surface or (iii) an enhanced adsorption of the ligand is capable of strong complex formation and also possesses a substantial affinity for the solid surface. One has to bear in mind that according to the concept of surface complexation not only cations or hydroxo complexes but any metal complex may be specifically adsorbed onto solid surfaces. General ideas on the influence of organic complexation and metal adsorption are comprehensively discussed by Elliott and Huang (1979) and Bourg (1988). An illustrating example for Hg is given by Trost and Bisque (1970) (Figure 7). They studied the change of adsorption on illite due to the addition of dissolved humic acid ( $100 \mu\text{g g}^{-1}$  DOC). The sorption of Hg was reduced for about 35 % by the formation of a Hg-humate complex that lowered the activity of (available)  $\text{Hg}^{2+}$ -ions. Other studies confirm the inhibition of Hg-adsorption on mineral surfaces due to the presence of humic acids, glycine, leucine, acetate, cyanide or NTA (Mekhonina, 1969; qtd. by Moraghan, 1971; MacNaughton and James 1974, Farrah and Pickering, 1978).

### 3.3. FORMATION OF NEW PRECIPITATES

It can generally be stated that the lower the content of heavy metals in the soil and the more sites there are available for high-affinity adsorption, the more likely it is that

adsorption/desorption processes will determine the concentration of the elements in solution. As far as Hg is concerned, surface complexation with solid surfaces as well as complexation processes of organic and inorganic ligands mainly determine the composition of the soil solution. The formation of a definite compound was only observed under reducing conditions and at high sulfide contents favoring the formation of HgS. With the exception of cinnabar ( $\alpha$ -HgS), solid compounds of Hg in contaminated soils have not been identified neither by direct determination nor by calculations of the saturation index. Probably the solution concentrations remains too low to allow a definite, thermodynamically stable Hg compound (e.g. carbonate, phosphate, hydroxide) to precipitate (Brümmer, 1986; Bourg 1988).

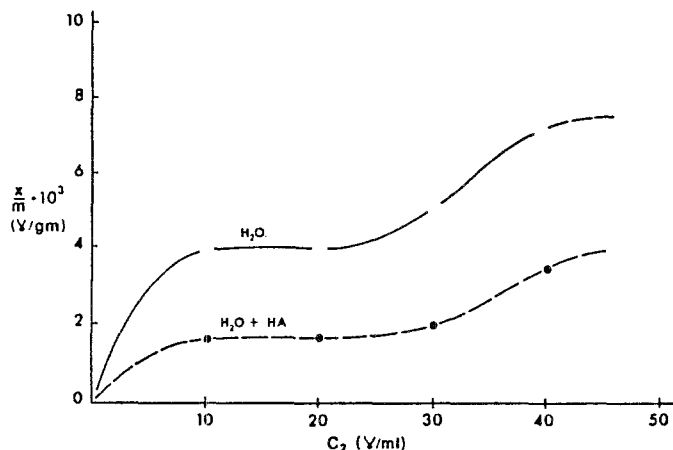


Figure 7. Adsorption isotherm of  $Hg^{2+}$  on illite at pH 6. The adsorption isotherms display a decrease in mercuric ion sorption from aqueous solution by illite in the presence of aqueous humic acid (from Trost and Bisque, 1972).

With the exception of soils with sulfidic mineralization HgS is not a major component in aerobic soils under normal circumstances. It is interesting feature that "native" cinnabar (deposited from eroded mine tailings) may primarily remain  $\alpha$ -HgS form although it was not expected to be a thermodynamically stable mineral under prevailing oxidizing conditions (Harsh and Doner, 1981). The lack of Hg sorbed to soil constituents indicate that weathering of cinnabar was slow and perhaps kinetically unfavorable in that soil.

**3.3.1. Influence of ligands on the solubility of HgS.** The general increase of the solubility of Hg due to the high intrinsic solubility of some of its complexes was already mentioned. The "intrinsic solubility" takes into account the solubility of complexes as a complete molecule in its undissociated form, whereas the solubility product of a compound is based on the ionic product. For  $Hg(OH)_2$  this results in an

increase of solubility from 0.043 ppm  $\text{Hg}^{2+}$  (calculated by solubility product) to 107 ppm  $\text{Hg(II)}$  (Hahne and Kroontje, 1973b). Generally ligands with a strong affinity to Hg that form highly soluble complexes are able to increase the solubility of Hg-compounds. The formation of chloro complexes which are extremely soluble ( $6.6 \text{ g L}^{-1}$ ) increase the solubility of sparingly soluble precipitates. At a chloride concentration of 1 M  $\text{Cl}^-$  ( $\approx 35000 \mu\text{g g}^{-1}$ ) the solubility of mercuric hydroxide and sulfide increases by a factor of  $10^5$  and  $3.6 \cdot 10^7$ , respectively. Even at a (natural occurring) chloride concentration of  $3.5 \mu\text{g g}^{-1}$ , the solubility of  $\text{Hg(OH)}_2$  and  $\text{HgS}$  increases by a factor of 55 and 408, respectively.

This effect is principally the same with the presence of soluble humic acids (Trost and Bisque, 1970). Kerndorff and Schnitzer (1980) described this reaction as  $3 \text{RCOO}^- + 2 \text{HgS} \rightarrow (\text{RCOO})_3\text{Hg}^{2+} + 2 \text{S}^{2-}$  ( $\text{RCOO}^-$  = functional group of a humic acid).

## 5. Conclusions

It is obvious that other than solubility equilibria determine the concentration of Hg in the soil solution. The most likely explanations for the observed deviations are (a) the formation of organic complexes and (b) the rapid adsorption of Hg to solid surfaces. Because of the higher Hg binding capacity of soil organic matter in relation to minerals, interactions between Hg and organic constituents are more important for the distribution of Hg in the soil. Only under very specific conditions (namely subsoil horizons very low in organic C or alkaline soils), the adsorptive behavior will be mainly controlled by its direct interaction with an inorganic surface. Regarding normal environments the distribution of Hg in the soil will be more or less subjected to the physical (dissolved vs adsorbed) fractioning of organic matter.

Generally, the strong binding results in a low availability and mobility of Hg in the soil. From many experiments it can be concluded that plant uptake (Gracey and Stewart, 1974; Käferstein *et al.*, 1979; Kloke, 1985; Cappon, 1986) and leaching (Poelstra *et al.* 1974, Frimmel *et al.* 1983) is relatively insignificant in topsoils with mixed organic and mineral components, as long as the soil material is in a flocculated state. Nevertheless under certain conditions translocations and leaching may occur where pH and  $\text{Cl}^-$  concentrations are favorable for the formation of Cl complexes (Frimmel, 1983; Behra, 1986)

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