

# Predicting Mercury Impacts to Groundwater from Coal Ash

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Mercury is a hazardous air pollutant and one of the trace elements that is not normally present in groundwater. The US EPA Clean Air Mercury Rule of 2005 established a new mercury emissions level. To date, fly ash is the most economically feasible sorbent injected into flue gas to control mercury emissions from electric power utility boilers and medical and hazardous waste incinerators. However, no significant research has been conducted to show the maximum probable concentration of mercury in groundwater leachates from fly ash monofills. Mercury, transferred from coal into air phase, onto fly ash, and later to leachate, undergoes several transformations that change its speciation. This paper shows aqueous mercury precipitation reactions, mass law, speciation and a mathematical algorithm that can be used to predict its initial aqueous concentrations. The algorithm can be used for mercury plume delineation in the vadose zone of an unconfined inorganic aquifer.



#### **1. Introduction**

Mercury is a hazardous air pollutant that circulates around the globe with an atmospheric residence time of a year before depositing back to the earth. In 1999, mercury emissions from electric power generation sources, as estimated by the United States Environmental Protection Agency (USEPA), were 48 metric ton/yr, constituting the largest atmospheric anthropogenic source of mercury in the US. A new Maximum Achievable Control Technology standard for mercury to control emissions from electric power generation sources under the Clean Air Mercury Rule was issued in March 2005.

Controlling mercury emissions from coal-fired power plants and options that may be used to effectively and economically control these emissions have been a subject of intense legislative and regulatory debates. A reduction in mercury emissions is directly associated with mercury capture by injected sorbents such as activated carbon and its concentration into coal combustion fly ash. Fly ash is utilized by different industries including the construction industry that uses fly ash in Portland cement, concrete products, road bases, structural fills, retaining walls, etc. Large amounts of mercury-laden fly ash have accumulated in various monofills and landfills throughout the country.

An extensive research has been done on enhancing mercury removal from flue gas using sorbent injection technologies and their economic aspects. Despite that fly ash now contains more mercury than ever before, very little or no scientific research has focused on predicting groundwater mercury concentrations if fly ash mercury leaches into underlying aquifers.



#### 2. Aquatic Mercury Background

Depending on the physical, chemical and biological aquifer characteristics, mercury (II) plumes in groundwater can travel long distances before reaching surface waters. In lakes, reservoirs and stream with high concentration of suspended solids, mercury (II) can be easily adsorbed by suspended matter and deposited. Then, it can be released from sediment back to the aqueous phase, taken up by aquatic biota, be lost to the atmosphere, or be transported with sediment to another location.

Many of the chemical and biological processes that control mercury (II) methylation and bioaccumulation are not completely understood. Yet, a better understanding of mercury (II) transport mechanism in different environments is necessary to better define its maximum plume concentrations and, therefore, probable extent of contamination.

In a saturated aquifer zone consisting predominantly of inorganic soils, aqueous transport is the primary mode of mercury (II) release. Vapor transport mechanism is negligible due to low Henry's constants for dominant mercury species usually encountered in normal vadose zone environment. For example, the Henry's constant for HgCl<sub>2</sub> is only  $7.1 \cdot 10^{-10}$  atm-m<sup>3</sup>/mole (Keating et al., 1997). Sorption of mercury (II) vapor was observed to increase almost linearly as soil moisture content increases from 2 to 20 %, but a further decrease in moisture content rapidly decreases mercury (II) vapor sorption and is negligible due to limited soil pore volume in saturated aquifer zone (Fang and Arch, 1981).

Mercury methylation requires the presence of a suitable methyl donor molecule. In natural aquatic environments, such as rivers, lakes, reservoirs, estuaries and oceans, a large variety of potential donor molecules are present, most of which are biologically synthesized, i.e. inert.



Methylcobalamin is thought to be the only natural methylating agent capable of transferring methyl group as carbanions (Reimers et al., 1975). Sulfate reducing bacteria have been identified as the principal methylators of inorganic mercury (II) in anaerobic sediments (Compeau and Bartha, 1985). Methylation by sulfate-reducing bacteria with production of monomethyl mercury (MMHg) takes place mainly in anoxic waters and sediments such as those present in wetland mud and benthic sediments (Berman and Bartha, 1986; Bloom, 1989, Bouton, 1990; Callister and Winfrey, 1986; Choi and Bartha, 1994; Compeau and Bartha, 1984; Craig and Moreton, 1985; Gagnon, 1996; Jackson,1988; Korthals and Winfrey, 1987; Matilainen, 1991; Newton, 1976; Olson and Cooper, 1974; Ridley, 1977; Rudd, 1983; Wren, 1995) and there is little methylation of inorganic mercury (II) in soils (Van Faasen,1973). Warm temperatures generally enhance mercury (II) methylation due to increased microbial activity (Matilainen and Verta, 1995; Matilainen et al., 1991), while the vast majority of natural aquifer systems are characterized by low temperatures and consistent redox levels.

Many researchers link accelerated rates of MMHg production to low pH, low salinity, and the presence of decomposable organic matter in reducing environments. It appears that the combined effect of MMHg production and degradation leads to a state of equilibrium with a near constant concentrations of MMHg in sediments, that rarely exceeds 1 to 1.5 % of total mercury (II) concentration (Beijer and Jernelöv, 1979; Pak and Bartha, 1998). Kelly et al. (1995) found that total mercury (II) concentration is, generally, not useful in predicting MMHg concentrations.



#### 3. The Role of Hydroxyl Groups in Metal Adsorption

The potential for heterogeneous precipitation on soil particle surfaces is always present in aqueous systems due to the presence of OH<sup>-</sup> (hydroxyl) ion. Hydroxyl results from dissolution of soil particles and as a product of metal hydrolysis. The magnitude of the latter is a function of the solubility product. Most of the negative pH-dependent charges associated with hydroxyl (OH<sup>-</sup>) groups are located on the edges and surfaces of clays (Mitchell and Soga, 2005). Hydroxyl groups are attached to silica, iron and aluminum in inorganic soils and to carbonate groups in humus (Sparks, 1999). Under moderately acidic conditions, there is little or no charge on the surfaces. As pH increases, hydrogen dissociates from the colloid hydroxyl group and negative charges result as shown in Eq. (1) and (2):

$$= Al - OH + OH^{-} \leftrightarrow = Al - O^{-} + H_2O \tag{1}$$

$$-CO - OH + OH^{-} \leftrightarrow = CO - O^{-} + H_2O \tag{2}$$

The reactions above are reversible. When pH increases, more OH<sup>-</sup> ions are available to force the reactions to the right, and the negative charge on the particles increases. When pH reduces, reactions go back to the left and the negative surface charge reduces as well. A pH increase results in an increase in the dissolution rate of metal ligands and favors an increase in hydroxyl concentration on soil particle surfaces since the number of free active sites to which metal hydroxides can attach increases (Morel and Hering, 1993). In organic soils with normally acidic pH, ionization of organic matter containing COOH<sup>-</sup> and phenolic OH<sup>-</sup> groups occurs as follows:

$$ROH + OH^{-} = RO^{-} + H_2O \tag{3}$$



For mercury, the amount of free metal  $Hg^{2+}$  in solution is negligible compared to total complexed  $Hg_T$  (at pH 7 [ $Hg^{2+}$ ] = 10<sup>-8</sup> [ $Hg_T$ ]), and is dominated by pH dependency on  $Hg_T$  adsorption process. The calculations below show that aqueous mercury (II) concentration is heavily influenced by soil pH.

The expression for equilibrium constant is  $K_{sp} = [Hg^{2+}][OH^{-}]^{2} = 10^{-25.4} M.$ At pH 7,  $[OH^{-}]^{2} = 10^{-14}$  and the concentration of free ion is  $[Hg^{2+}] = 10^{-11.4} M.$ Since the molecular weight of  $[Hg^{2+}] = 201 \text{ g/M}, [Hg^{2+}] = 0.8 \text{ ng/L}.$ In a similar manner, it can be shown that at pH 3 and pH 5.3  $[Hg^{2+}]$  is 80 mg/L and 2 µg/L, respectively. At pH 5.3 and lower, the theoretical  $[Hg^{2+}]$  exceeds the US EPA Maximum Contaminant Level (MCL) of 2 ppb (2 µg/L).

Hg<sup>2+</sup> speciation defines the degree of its bioavailability and toxicity to biota. Natural waters frequently contain several metal competing ligands such as Cl<sup>-</sup>, S<sup>2-</sup>, and OH<sup>-</sup> that form complexes with dissolved metals (Morel and Hering, 1993). Concentrations of metal ligands can be found from equilibrium reactions. They depend on the type and concentrations of most common dissolved ligands such as chlorides and, to a lesser degree, sulfates. Chlorides present in most natural soil and water systems and is one of the most mobile and potent metal complexing agents. HgCl<sup>+</sup>, HgCl<sub>2</sub>, and HgOHCl heavily contribute to mercury (II) acute toxicity (Farrell, 1993). Mercuric chloride, HgCl<sub>2</sub>, is one of the most bioavailable mercury (II) species in oxic waters (Barkay, 1997; Laporte, 1997; Mason et al., 1995; Mason et al., 1996; Morel et al, 1998), while sulfide HgS, bisulfide Hg(SH)<sub>2</sub>, and polysulfide HgS<sub>n</sub> complexes are important for bacterial uptake in anoxic waters (Benoit et al, 1999; Hudson et al., 1994; Jay et al, 2000).



The predominant inorganic aquatic mercury species available for methylation in confined and unconfined aquifers are:

Hg<sup>2+</sup>, HgCl<sup>+</sup>, HgCl<sub>2</sub>, HgCl<sub>3</sub><sup>-</sup>, HgCl<sub>4</sub><sup>2-</sup>, HgOHCl, HgOH<sup>-</sup>, Hg(OH)<sub>2</sub>, Hg(OH)<sub>3</sub><sup>-</sup>, HgS, HgS<sub>2</sub><sup>2-</sup>, HgOHS<sup>-</sup> (Morel and Hering, 1993; Baldi et al, 1993a; Baldi et al, 1993b, Brookins, 1988; Gilmour, 1971; Hahne and Kroontje, 1973; Lockwood and Chen, 1973; Stotzky and Babich, 1980).

Groundwater Hg plumes, that eventually converge to various water bodies, may also include CH<sub>3</sub>HgOH, CH<sub>3</sub>Hg<sup>+</sup> and CH<sub>3</sub>HgCl (Stumm and Morgan, 1996), CH<sub>3</sub>HgS<sup>-</sup> (Dyrssen and Wedborg, 1991), Hg complexes with thiol (-RSH) groups (Gavis and Fergusson, 1972), SO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>2-</sup>, NH<sub>3</sub> (Pflughoeft-Hassett et al., 1991), and I<sup>-</sup>, F<sup>-</sup>, and Br<sup>-</sup>. Depending on the watershed chemical and biological characteristics, the list of ligands can be even broader.

A combined effect of multiple surface water ligands on the mercury (II) soil adsorption mechanism is yet to be evaluated, which is not one of the goals of this paper. More research is needed to define mercury adsorption rates for all possible surface waters mercury species. For example, the presence of  $SO_4^{2-}$  decreased  $Hg^{2+}$  retention by gibbsite Al(OH)<sub>3</sub> by forming  $Hg(OH)_2SO_4^{2-}$ , and the presence of  $PO_4^{2-}$  increased retention by gibbsite due to formation of a phosphate bridge [=AlOPO\_3Hg(OH)\_2^{2-}] (Sarkar, 1999).



## 4. Hg<sup>2+</sup> Sorption on Soil Aluminosilicates

Equilibrium reactions describing the formation of inorganic Hg complexes with chloride and sulfide are as follows:

$$Hg^{2+} + Cl^{-} \Leftrightarrow HgCl^{+} \tag{4}$$

$$Hg^{2+} + 2Cl^{-} \Leftrightarrow HgCl_{2} \tag{5}$$

$$Hg^{2+} + 3Cl^{-} \Leftrightarrow HgCl_{3}^{-} \tag{6}$$

$$Hg^{2+} + 4Cl^{-} \Leftrightarrow HgCl_{4}^{2-} \tag{7}$$

$$Hg^{2+} + Cl^{-} + H_2O \Leftrightarrow HgClOH^{0} + H^{+}$$
(8)

$$Hg^{2+} + H_2 O \Leftrightarrow HgOH^- + H^+$$
(9)

$$Hg^{2+} + 2H_2O \Leftrightarrow 2Hg(OH)_2^0 + 2H^+$$
(10)

$$Hg^{2+} + 3H_2O \Leftrightarrow 2Hg(OH)_3^- + 3H^+ \tag{11}$$

$$Hg^{2+} + S^{2-} \Leftrightarrow HgS \tag{12}$$

$$Hg^{2+} + 2S^{2-} \Leftrightarrow HgS_2^{2-} \tag{13}$$

$$Hg^{2+} + S^{2-} + H_2O \Leftrightarrow HgSOH^- + H^+$$
(14)

Sorption of Hg<sup>2+</sup> has been studied extensively and observed to occur on aluminosilicate clays and metal oxides (Kinniburgh and Jackson, 1978; Lockwood and Chen, 1973; Morel and Hering, 1993; Reimers and Krenkel, 1974; Stumm, 1992; Stumm and Morgan, 1996; Walcarius et al., 1999). A study of mercury adsorption on silica, goethite, and pyrite as a function of pH and chloride concentration using an electrochemical method confirmed a hypothesis that the extent of Hg adsorption is heavily dependent on Hg hydrolysis and concentration of mercury species



containing hydroxyl ligands (Walcarius et al., 1999). Only soluble Hg<sup>2+</sup> species with hydroxyl groups such as HgOH<sup>+</sup>, Hg(OH)<sub>2</sub>, and HgOHCl are adsorbed. Mercury chloride and mercury sulfide were not adsorbed. The aqueous mercury adsorption mechanism entails a condensation reaction between surface hydroxyl groups of soil material and mercury hydroxyl groups.

Sorption and dissolution in aqueous solutions can be presented in the following manner:

Sorption sites + Reactants(
$$H^+$$
,  $OH^-$ , ligands)  $\rightarrow$  Surface species (15)

Surface sites 
$$\rightarrow$$
 detachment of metal species  $\rightarrow$  Metal(aq) (16)

Since most soils consist of aluminosilicates, the condensation reactions of mercury hydroxides on soil particles can be described as floows:

$$(\equiv SiOH) + HgOH^{+} \Leftrightarrow (\equiv SiO - Hg^{+}) + H_{2}O$$
(17)

$$(\equiv SiOH) + Hg(OH)_2 \Leftrightarrow (\equiv SiO - Hg - OH) + H_2O$$
(18)

$$(\equiv SiOH) + HgOHCl \iff (\equiv SiO - Hg - Cl) + H_2O$$
(19)

$$(\equiv SiOH) + HgOHS^{-} \Leftrightarrow (\equiv SiO - Hg - S^{-}) + H_2O$$
<sup>(20)</sup>

$$(\equiv SiOH) + Hg(OH)_{3}^{-} \Leftrightarrow (\equiv SiO - Hg - O^{-}) + 2H_{2}O$$
<sup>(21)</sup>

$$(=AlOH) + HgOH^{+} \Leftrightarrow (=AlO - Hg^{+}) + H_{2}O$$
<sup>(22)</sup>

$$(=AlOH) + Hg(OH)_2 \Leftrightarrow (=AlO - Hg - OH) + H_2O$$
<sup>(23)</sup>

$$(=AlOH) + HgOHCl \iff (=AlO - Hg - Cl) + H_2O$$
(24)

$$(= AlOH) + HgOHS^{-} \Leftrightarrow (= AlO - Hg - S^{-}) + H_2O$$
<sup>(25)</sup>

$$(=AlOH) + Hg(OH)_3^- \Leftrightarrow (=AlO - Hg - O^-) + 2H_2O$$
<sup>(26)</sup>

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In an ideal gibbsite sheet, two-thirds of the octahedral positions are filled with aluminum. In an ideal silica sheet, silicon occupies all tetrahedral spaces. In some clays, the tetrahedral or octahedral spaces can be replaced by magnesium and ferrous iron (Mitchell and Soga, 2005). Reactions 17-26 represent a non-electrostatic mercury (II) adsorption model which can be used to define Hg retardation for the purpose of mercury (II) plume delineation. Electrostatic models can be used to predict concentration of aqueous Hg<sup>2+</sup> which practically does not exist in its free form as, for example, Al<sup>3+</sup>, Ca<sup>2+</sup>, or Mg<sup>2+</sup>. In an electrostatic model, soil cation exchange capacity (CEC) can be used to define the extent of free Hg retardation. CEC is the first step in a groundwater mercury retardation process.

CEC for free Hg<sup>2+</sup> ion is as follows (Sparks, 1999):

$$CEC(meq/kg) \approx 10^{-5} \cdot \left(\frac{2c\varepsilon RT}{\pi}\right)^{0.5} \cdot \left(\sinh\frac{zF\psi}{2RT} + \sinh 1.15z(pH_0 - pH)\right)$$
(27)

where c - electrolyte concentration, mol

- $\epsilon$  medium dielectric constant,  $C^2/Jm$
- R universal gas constant, 8.314 J/°K mol
- T absolute temperature, °K
- z-valence of potential determining ion
- F Faraday constant, 96,485 J/V mol
- $\psi$  surface potential, V
- $pH_0 hydrogen$  ion activity when surface potential  $\psi_0 = \psi$
- pH soil hydrogen ion activity.



#### 5. Mass Law for Mercury (II) Species

This part is an example of metal-soil partition coefficient derivation based on mercury (II). The coefficient defines the ratio of concentrations of mercury (II) adsorbed onto soil to that remaining in aqueous solution.

Consider the following metal complex formation reactions with ligands A<sup>-</sup> and B<sup>-</sup>:

$$M^{2+} + mA^{-} = MA_{m}^{(m-2)-} \qquad \beta_{m}$$
(28)

$$M^{2+} + nB^{-} = MB_{n}^{(n-2)-} \qquad \beta_{n}$$
<sup>(29)</sup>

where  $\beta_m$  and  $\beta_n$  are the complex formation constants with ligands  $A^-$  and  $B^-$ , respectively.

Reactions (28) and (29) can be presented as the following mass balance equations (Morel and Hering, 1993):

$$TOTM = [M^{2+}] + [MA_m^{(m-2)-}] + [MB_n^{(n-2)-}] + \dots$$
(30)

$$TOTM = [M^{2+}](1 + \beta_m [A^-]^m + \beta_n [B^-]^n + ...)$$
(31)

In surface waters, inorganic ligands are normally in excess of trace metals that they bind and ion activity  $\gamma$  is required as follows:

$$TOTM = [\gamma_m M^{2+}](1 + \beta_m [\gamma_a A^-]^m + \beta_n [\gamma_b B^-]^n + ...)$$
(32)

This is not the case for groundwater which is normally extremely dilute. Based on the Debye-Hückel equation, for very dilute solutions of  $Hg^{2+}$ , sulfur and chlorine ions and moderate pH



ranges, the activity coefficients for  $Hg^{2+}$ ,  $Cl^-$ ,  $S^{2+}$ , and  $OH^-$  are around 1.0. A simplified mass law for dilute inorganic aqueous  $Hg^{2+}$  species can be written in the following manner:

$$Hg_{T} = Hg^{2+} \begin{pmatrix} 1 + \beta_{1}[Cl^{-}] + \beta_{2}[Cl^{-}]^{2} + \beta_{3}[Cl^{-}]^{3} + \beta_{4}[Cl^{-}]^{4} + \beta_{5}[OHCl^{2-}] + \beta_{6}[OH^{-}] \\ + \beta_{7}[OH^{-}]^{2} + \beta_{8}[OH^{-}]^{3} + \beta_{9}[S^{2-}] + \beta_{10}[S^{2-}]^{2} + \beta_{11}[OHS^{3-}] \end{pmatrix} (33)$$

Most references show formation constant values at 25°C. The van't Hoff expression will be used to obtain the formation constants at 15°C (Sawyer et al., 1994) as the average groundwater temperature in Houston, TX:

$$\ln \frac{K_{(T_2)}}{K_{(T_1)}} = -\frac{\Delta H^0}{R} \left( \frac{T_1 - T_2}{T_1 \cdot T_2} \right)$$
(34)

where  $T_1$  and  $T_2$  – initial and final temperatures, respectively, K

R – Universal Gas Constant, 8.314 J/K mol

 $\Delta H^0$  – standard enthalpy of formation at 25°C, kJ/mol.

Table 1 lists standard enthalpies of formation at 25°C and the stability (formation) constants at 25°C and 15°C obtained using Eq. (34). The last column indicates if these values are cited in MINTEQA2 User's Manual (USEPA, 1991).

Hg	$\Delta H^0{}_{\rm f}$	-log	-log	MINTEQA2 <sup>(4)</sup>
species	(kJ/mol) <sup>(1)</sup>	$K_{\rm f298K}{}^{(2)}$	$K_{\rm f288K}{}^{(3)}$	
Hg <sup>2+</sup>	171.1	6.6	6.8	Yes
$HgCl^+$	-18.8	7.2	7.4	Yes
HgCl <sub>2</sub>	-224.3	14.0	16.0	Yes
HgCl <sub>3</sub> <sup>-</sup>	-388.7	15.1	17.1	Yes
HgCl <sub>4</sub> <sup>2-</sup>	-554.0	15.4	20.5	Yes
HgClOH	-222.17	18.1	20.2	Yes



HgOH <sup>+</sup>	-84.5	10.6	11.4	Yes			
Hg(OH) <sub>2</sub>	-355.2	21.8	25.1	No			
Hg(OH) <sub>3</sub> <sup>-</sup>	-474.42	20.9	25.3	Yes			
HgS	-58.2	7.9	8.4	No			
$HgS_2^{2-}$	-81.76	14.3	15.1	Yes			
HgSOH <sup>3-</sup>	-163.74	18.5	20.0	No			
<ol> <li>Ref. (Lide, 2005-2006; Lindsay, 1979; Morel &amp; Hering, 1993; Rosenberg &amp; Epstein, 1990; Sawyer et al., 1994; Sparks, 1999; Speight, 2005; Wagman et al., 1982)</li> <li>Ref. (Morel &amp; Hering, 1993)</li> <li>Formation constants at 15°C, Eq. (34)</li> <li>Ref. (USEPA, 1991)</li> </ol>							

Table 1. Formation constants for  $Hg^{2+}$  species at 25°C and 15°C.

Activities of hydroxyl ion and proton are related as follows:

$$[OH]^{-} = 10^{pH-14} \tag{35}$$

Substituting the values of stability constants at 15°C from Table 1 into Eq. (33) gives the

following expression for simplified mercury mass law:

$$Hg_{T} = Hg^{2+} \cdot \begin{pmatrix} 1 + 10^{7.4} [Cl^{-}] + 10^{16} [Cl^{-}]^{2} + 10^{17.1} [Cl^{-}]^{3} + 10^{20.5} [Cl^{-}]^{4} + 10^{20.2} [OHCl^{2-}] \\ + 10^{11.4} \cdot 10^{pH-14} + 10^{25.1} \cdot 10^{2(pH-14)} + 10^{25.3} \cdot 10^{3(pH-14)} + 10^{8.4} [S^{2-}] \\ + 10^{15.1} [S^{2-}]^{2} + 10^{20} [OHS^{3-}] \end{pmatrix}$$
(36)

where  $\beta = 10^{-\log K}$ <sub>f</sub>

$$[OHCl^{2^{-}}] = \begin{cases} [OH^{-}] & if \quad 10^{pH-14} \le [Cl^{-}] \\ [Cl^{-}] & if \quad 10^{pH-14} > [Cl^{-}] \end{cases}$$
(37)

$$[OHS^{3-}] = \begin{cases} [OH^{-}] & if \quad 10^{pH-14} \le [S^{2-}] \\ [S^{2-}] & if \quad 10^{pH-14} > [S^{2-}] \end{cases}$$
(38)

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Equations (37) and (38) can be programmed using any engineering software. To simplify further

derivations, let

$$\lambda = \begin{pmatrix} 1+10^{7.4}[Cl^{-}]+10^{16}[Cl^{-}]^{2}+10^{17.1}[Cl^{-}]^{3}+10^{20.5}[Cl^{-}]^{4}+10^{20.2}[OHCl^{2-}] \\ +10^{11.4}\cdot10^{pH-14}+10^{25.1}\cdot10^{2(pH-14)}+10^{25.3}\cdot10^{3(pH-14)}+10^{8.4}[S^{2-}] \\ +10^{15.1}[S^{2-}]^{2}+10^{20}[OHS^{3-}] \end{pmatrix}$$
(39)

Then, Eq. (33) can be written as

$$Hg_{\rm T} = \lambda \cdot Hg^{2+} \tag{40}$$

Therefore, the following expression for  $Hg^{2+}$  is also true:

$$\log[Hg^{2+}] = \log\frac{[Hg_T]}{[\lambda]} \tag{41}$$

Molar concentrations for the rest of mercury species can be found in the same manner using Eq.(36). For small [Cl<sup>-</sup>], for example, [HgCl<sup>-</sup>] can be defined as:

$$\log[HgCl^{-}] = \log \frac{10^{7.4} \cdot [Cl^{-}][Hg_{T}]}{[\lambda]}$$
(42) If

pH and total mercury, chloride and sulfur concentrations are known, Eq. (42) can be solved. To graphically show concentration distribution between the mercury species provided by Eq. (36), assume the following boundary conditions:

$$Hg_T = 10^{-5} M$$
;  $S^{2-} = 10^{-4} M$ ;  $Cl^- = 10^{-3} M$ .

Figure 1 below shows molar concentrations of dominant inorganic aquatic mercury species as function of pH.





Fig.1. Eq. (36) - Aquatic mercury speciation when  $Hg_T = 10^{-5}$  M,  $S^{2-} = 10^{-4}$  M,  $Cl^- = 10^{-3}$  M. Equation (36) predicts aqueous mercury speciation for inorganic soils of vadose zone. It indicates a strong dependency on pH and Cl<sup>-</sup> and S<sup>2-</sup> concentrations. In aqueous solutions having Cl<sup>-</sup> concentrations of  $10^{-6}$  to  $10^{-5}$  M, the major species such as  $HgCl^+$  and  $HgOH^+$  are positively charged. Higher Cl<sup>-</sup> concentrations result in higher  $HgCl_2$ . Higher pH values result in higher concentration of hydroxyl-containing Hg(II) species  $HgOH^+$  and  $Hg(OH)_2$ . For the boundary



conditions given in Fig. 1, hydroxyl species dominate Hg-Cl and Hg-S complexes at pH 9 and above. HgOHCl and HgOHS<sup>-</sup> are transitional complexes between acidic and alkaline media and vice versa. In the absence of sulfide, the speciation of inorganic Hg in freshwaters is dominated by three uncharged complexes,  $HgCl_2$ ,  $Hg(OH)_2$  and HgOHCl. In seawater (3% salinity) containing more than 0.5 M Cl<sup>-</sup>, Hg exists primarily as  $HgCl_3^-$  and  $HgCl_4^{2-}$ .

HgS formation is generally favored at low pH and low sulfide concentration. For low E<sub>h</sub>, high pH and high sulfide, HgS is present as  $HgS_2^{2-}$  and  $HgSOH^-$  (Fujiki and Tajima, 1992; Gardner, 1994). HgS was reported to be stable in flooded soils but became unstable when the soils became aerobic (Aomine and Inoue, 1967; Aomine et al., 1967, Engler and Patrick, 1975). Conditions for high sulfide typically develop in anoxic, organic-rich sediments high in sulfate, but can also occur in surface waters as a result of industrial or domestic wastewater discharges. Methylation is inhibited at high sulfide concentrations due to changes in mercury (II) speciation. Sulfatereducing bacteria are important methylators of mercury (II) in anaerobic sediments. Sulfate stimulates microbial methylation mercury (II) at low sulfate concentrations typical for freshwater. However, at high levels in reducing conditions methylation is inhibited due to sulfide formation which may be the reason why MMHg levels in sediments rarely exceed 1% of total mercury (II) concentration (Fagerström and Jernelöv, 1971; Gillespie and Scott, 1972; Yamada and Tonomura, 1972a; Yamada and Tonomura, 1972b; Yamada and Tonomura, 1972c). In estuarine and marine environments, formation of charged sulfide and chloride complexes may be the primary reason for reduced methylation activity.



### 6. Derivation of Mercury (II) Soil Partition Coefficient

The following expression defines the percent of total mercury adsorbed onto soil particle surfaces:

$$(\%)TOTHg_{(adsorbed)} = \frac{TOTHg_{(hydroxylated)}}{TOTHg_{(solution)}} \cdot 100\%$$
(43)

The ratio  $\Phi$  of mercury adsorbed to total aqueous mercury can be defined by incorporating Eq. (36) into Eq. (43) as follows:

$$\Phi = \frac{Hg^{2+} \left(10^{20.2} [OHCl^{2-}] + 10^{11.4} 10^{pH-14} + 10^{25.1} 10^{2(pH-14)} + 10^{25.3} 10^{3(pH-14)} + 10^{20} [OHS^{3-}]\right)}{Hg_T} (44)$$

Eq. (44) can be simplified to the following expression, named here mercury (II) Soil Partition Coefficient:

$$\Phi = \frac{\left(10^{20.2} \left[OHCl^{2-}\right] + 10^{11.4} \cdot 10^{pH-14} + 10^{25.1} \cdot 10^{2(pH-14)} + 10^{25.3} \cdot 10^{3(pH-14)} + 10^{20} \left[OHS^{3-}\right]\right)}{\lambda} (45)$$

where  $\lambda$  is defined by Eq. (39).



	[Cl <sup>-</sup> ] =							
pН	$[S^{2}] =$	[S <sup>2-</sup> ] =	10 <sup>-2</sup> M	10 <sup>-3</sup> M	$[S^{2-}] =$	[S <sup>2-</sup> ] =	10 <sup>-30</sup> M	[S <sup>2-</sup> ] =
s.u.	10 <sup>-3</sup> M	10 <sup>-2</sup> M	$[S^{2-}] =$	$[S^{2-}] =$	10 <sup>-4</sup> M	$10^{-1} M$	$[S^{2-}] =$	10 <sup>-5</sup> M
			10 <sup>-3</sup> M	10 <sup>-2</sup> M			10 <sup>-1</sup> M	
1	0.0002	0.0000	0.0000	0.0000	0.0222	0.0000	1.0000	0.6959
2	0.0022	0.0000	0.0000	0.0002	0.1863	0.0000	1.0000	0.9584
3	0.0221	0.0009	0.0009	0.0019	0.6961	0.0000	1.0000	0.9962
4	0.1830	0.0093	0.0094	0.1623	0.9584	0.0000	1.0000	0.9998
5	0.6910	0.0844	0.0874	0.6553	0.9962	0.0000	1.0000	1.0000
6	0.9571	0.4772	0.4881	0.9502	0.9997	0.0002	1.0000	1.0000
7	0.9962	0.9018	0.9048	0.9900	1.0000	0.0016	1.0000	1.0000
8	0.9998	0.9874	0.9901	0.9992	1.0000	0.0172	1.0000	1.0000
9	1.0000	0.9911	1.0000	1.0000	1.0000	0.1929	1.0000	1.0000
10	1.0000	0.9999	1.0000	1.0000	1.0000	0.9040	1.0000	1.0000
11	1.0000	1.0000	1.0000	1.0000	1.0000	0.9990	1.0000	1.0000
12	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
13	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
14	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000

Table 2 lists the  $\Phi$  values calculated for several Cl<sup>-</sup> and S<sup>2-</sup> molar concentrations.

Table 2. Values of  $\Phi$  for different pH, [Cl<sup>-</sup>] and [S<sup>2-</sup>].

Figure 2 (based on Table 2) shows plots of mercury partition coefficient vs soil pH and 10<sup>-3</sup>M and 10<sup>-2</sup> M of chloride and sulfide, respectively. Based on Table 2, adsorption front moves toward higher pH values as sulfur and chloride concentrations increase. As previously indicated, Table 2 and Figure 2 reflect adsorption of Hg<sup>2+</sup> by clay minerals and soil materials in inorganic or slightly organic soils.





Fig. 2. Plot of  $\Phi$  vs. soil pH at (a)  $10^{-3}$ M; (b)  $10^{-2}$ M sulfide chlorine.

In the absence of ligands, sorption of  $Hg^{2+}$  by illite and kaolinite changes little with pH which indicates that sorption of free  $Hg^{2+}$  is governed by constant clay charges (Farrah and Pickering, 1978). With montmorillonite, however,  $Hg^{2+}$  sorption decreases with increasing pH showing that sorption is governed by variable charge. CEC is the sum of constant and variable charges. Sorption of mercuric chloride from aqueous solution by illite, bentonite and kaolinite drastically increases with a reduction in soil pH. The adsorption peaks in the range from pH7 to pH9 and the extent of adsorption increases in the order kaolinite < bentonite < illite (Anderson, 1979). In highly organic soils, strong binding of mercury (II) is largely associated with organic fraction of soil (Lindberg et al., 1979). In acidic soils, adsorption of mercury (II) on humus dominates but in alkaline and calcareous soils, clay mineralogy and metal oxides dominate due to formation of more particle-reactive HgOH<sup>+</sup> (Anderson, 1979; Bringmark, 1997).

Eq. (36) shows that  $Hg^{2+}$  mobility is much higher at acidic pH which fully concurs with multiple Hg studies (Beijer and Jernelöv, 1979; Duarte et al., 1991). The effect of  $Hg^{2+}$  complexation with Cl<sup>-</sup> on  $Hg^{2+}$  mobility has been described in several adsorption studies. HgCl<sub>2</sub> was reported to be 19

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poorly adsorbed by most inorganic soils (Yin et al, 1976). Addition of Cl<sup>-</sup> decreases Hg<sup>2+</sup> adsorption on a loamy sand soil at low pH but has little effect at high pH (Barrow and Cox, 1992). An instantaneous release from sediment when Cl<sup>-</sup> (> $2 \cdot 10^{-2}$  M) is added confirms strong Cl affinity for Hg (Wang et al., 1991). A drastic reduction in Hg<sup>2+</sup> adsorption by inorganic colloids occurs at Cl<sup>-</sup> concentrations of  $10^{-3}$  M or higher (Anderson, 1970a). Additionally, HgCl<sub>2</sub> salts are hardly adsorbed by soils and clays (Aomine and Inoue, 1967). Chlorides sharply reduce mercury (II) adsorption by bentonite clay especially at low pH (Newton et al., 1976). At pH6 or lower, increasing the CaCl<sub>2</sub> concentration from  $10^{-5}$  to  $10^{-4}$  M depresses adsorption and higher CaCl<sub>2</sub> levels are required to decrease adsorption at neutral pH. Similar inhibitory effect of Cl<sup>-</sup> on Hg<sup>2+</sup> adsorption was found for hydrous iron oxide gel (Kinniburgh and Jackson, 1978) and precipitated iron oxide (Lockwood and Chen, 1974).



#### 7. Summary

Coal combustion fly ash contains significant amount of leachable mercury. Leaching and aqueous transport is the primary mode of mercury release. Mercury species distribution in aquatic media is governed by sorption on soil particles. A Mass Law for dominant aquatic mercury species is presented. Mercury remaining in aqueous solution is shown as the difference between initial leachate mercury and mercury adsorbed onto soil. Groundwater mercury (II) plume retardation is presented as a two-stage process consisting of free Hg<sup>2+</sup> retardation and adsorption of hydroxylated species.

An algorithm that predicts aquatic mercury concentration is developed based on mass law for dominant aquatic mercury species. It demonstrates that in acidic and slightly acidic soils, about half of mercury in coal combustion fly ash leachate is susceptible to further transport as part of groundwater plume. The initial mercury concentration was found to exceed the US EPA Maximum Contaminant Level (MCL) of 2 ppm. Aqueous sulfide concentration was found to have no significant effect on mercury adsorption. Chloride has the most significant effect on aqueous mercury mobility. Adsorption increases at higher soil pH and reduces with an increase in chloride concentration. The algorithm is in excellent agreement with findings by multiple researchers. It offers an additional and valuable insight into groundwater mercury (II) transport.



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