Roles of Dissolved Organic Matter in Aqueous Speciation of Hg(II) and CH_3Hg^+ in East Fork Poplar Creek (EFPC), Oak Ridge, Tennessee

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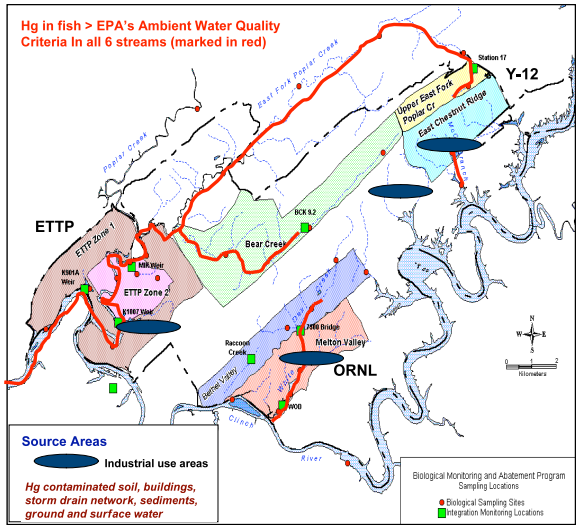
Abstract

The aqueous speciation of mercury [Hg(II)] and methylmercury (CH_3Hg^+) in contaminated East Fork Poplar Creek (EFPC) at Oak Ridge, Tennessee, is not well understood despite recognition of the important roles played by dissolved organic matter (DOM) in controlling the cycling, transport and bioavailability of Hg in the system. We determined Hg species distributions in the EFPC based on the water chemistry and a selected database of reaction constants of Hg(II) and CH_3Hg^+ with various organic and inorganic ligands, using the "PHREEQC" geochemical speciation computer code. Results show that DOM affects both Hg(II) and CH_3Hg^+ speciation by forming strong Hg(II)-DOM and CH_3Hg-DOM complexes through reactive sulfur groups or thiol-like functional groups in EFPC surface waters under conditions of pH ≈ 7.5 – 8.1 and DOM ≈ 3 mg/L. The neutral complexes of $Hg(OH)_2$ and Hg(OH)Cl, and CH_3HgCl and CH_3HgOH were found to be of secondary importance in EFPC surface water. The competitive effects of co-existing metal ions (i.e., Ca^{2+}, Mg^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, Fe^{3+} and UO_2^{2+}) on the Hg(II)-DOM and CH_3Hg-DOM complexation in the EFPC surface water were evaluated using analogous model organic compounds (i.e., cysteine and glutathione) in the lack of reliable binding constants of these metal ions with thiol-like functional groups in DOM. Results show that only Zn^{2+} (present at relatively high concentrations in EFPC) competes with Hg(II) for the binding sites (thiol) in DOM and therefore contributes to the decreased distribution of Hg(II)-DOM. The effects of other metal ions on the distribution of Hg(II)-DOM and CH_3Hg-DOM complexes are estimated to be minimal.

1. Site Description and Mercury Contamination on the Oak Ridge Reservation (ORR)



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2. Material and Methods

2.1. EFPC Surface Water Sampling and Analysis

Table 1. Chemical composition of EFPC surface waters (2007 - 2008)

Anions	Conc. range (mol/L)	Average conc. (mol/L)	Co-existing metals	Conc. range (mol/L)	Average conc. (mol/L)
HCO_3^-	2.0×10^{-3} – 2.1×10^{-3}	2.0×10^{-3}	Ca^{2+}	7.7×10^{-4} – 1.1×10^{-3}	9.0×10^{-4}
Cl^-	2.2×10^{-4} – 6.5×10^{-3}	3.1×10^{-4}	Mg^{2+}	4.5×10^{-4} – 4.8×10^{-4}	4.6×10^{-4}
SO_4^{2-}	3.0×10^{-2} – 4.1×10^{-2}	3.4×10^{-4}	Na^+	7.7×10^{-4}- 1.1×10^{-3}	9.0×10^{-4}
F^-	3.0×10^{-4} – 7.0×10^{-4}	5.0×10^{-4}	K^+	5.0×10^{-5} –9.0×10^{-5}	6.0×10^{-5}
NO_3^-	1.0×10^{-4} – 2.8×10^{-2}	1.3×10^{-4}	Li^+	7.0×10^{-7} – 1.0×10^{-6}	9.0×10^{-7}
PO_4^{3-}	2.5×10^{-6} – 1.2×10^{-5}	5.0×10^{-6}	Zn^{2+}	1.6×10^{-7} – 2.6×10^{-7}	2.1×10^{-7}
pH, DOC, dissolved Hg(II) and CH_3Hg^+			Cu^{2+}	1.2×10^{-8} – 2.8×10^{-8}	2.2×10^{-8}
pH	7.5 – 8.2 with most pH = 7.8		Ni^{2+}	4.6×10^{-9} – 1.6×10^{-8}	9.5×10^{-9}
DOC	≈15 ppm		Cd^{2+}	5.2×10^{-8} – 1.3×10^{-9}	8.7×10^{-10}
Humics	≈1.5 ppm		Pb^{2+}	6.1×10^{-10} – 1.3×10^{-9}	5.2×10^{-10}
Hg (II)	≈ 6×10^{-11} – 4.0×10^{-9} mol/L		UO_2^{2+}	1.7×10^{-8} –2.2×10^{-8}	2.0×10^{-8}
CH_3Hg^+	≈ 1 $\times10^{-12}$ – 5.0×10^{-12} mol/L		Fe^{3+}	2.6×10^{-8} – 2.8×10^{-8}	2.7×10^{-8}

2.2. Selected Geochemical Thermodynamic Data

Table 2. Selected reaction constants of Hg(II) and CH_3Hg^+ with inorganic ligands

Reaction	Log β	Reaction	Log β
$Hg^{2+} + H_2O = HgOH^+ + H^+$	-3.40[a]	$Hg^{2+} + HPO_4^{2-} = HgHPO_4$	8.8[a]
$Hg^{2+} + 2\,H_2O = Hg(OH)_2 + 2\,H^+$	-5.98[a]	$Hg^{2+} + HPO_4^{2-} = HgPO_4^- + H^+$	3.25[a]
$Hg^{2+} + 3\,H_2O = Hg(OH)_3^- + 3\,H^+$	-21.1[a]	$Hg^{2+} + SO_4^{2-} = HgSO_4$	1.4[a]
$Hg^{2+} + Cl^- = HgCl^+$	7.31[a]	$Hg^{2+} + 2\,SO_4^{2-} = Hg(SO_4)_2^{2-}$	2.4[a]
$Hg^{2+} + 2\,Cl^- = HgCl_2$	14.00[a]	$Hg^{2+} + F^- = HgF^+$	1.57[b]
$Hg^{2+} + 3\,Cl^- = HgCl_3^-$	14.925[a]		
$Hg^{2+} + 4\,Cl^- = HgCl_4^{2-}$	15.535[a]	$CH_3Hg^+ + H_2O = CH_3HgOH + H^+$	-4.53[b]
$Hg^{2+} + Cl^- + H_2O = HgOHCl + H^+$	4.27[b]	$2\,CH_3Hg^+ + H_2O = (CH_3Hg)_2OH^+ + H^+$	-2.11[b]
$Hg^{2+} + H_2O + CO_3 = HgCO_3 + 2\,H^+$	-6.68[a]	$CH_3Hg^+ + Cl^- = CH_3HgCl$	5.39[b]
$Hg^{2+} + H_2O + HCO_3^- = Hg(OH)CO_3^- + 2\,H^+$	-5.00[a]	$CH_3Hg^+ + F^- = CH_3HgF$	1.71[b]
$Hg^{2+} + H_2O + CO_2 = HgHCO_3^+ + H^+$	-2.35[a]	$CH_3Hg^+ + SO_4^{2-} = CH_3HgSO_4^-$	1.37[b]
$Hg^{2+} + H_2O + CO_2 = HgHCO_3^+ + H^+$	-3.40[a]	$CH_3Hg^+ + HPO_4^{2-} = CH_3HgHPO_4$	5.4 [b]

[a] from Powell et al., 2005; [b] from Martell et al (2001) and recalculated using Davis equation to ionic strength (I) = 0

Table 3. Selected interaction constants of Hg(II) and CH_3Hg^+ with Thiols (-RS) in NOM

NOM	Reaction	log K	pH	I (M)	Method
HA & peat	$Hg^{2+} + 2RS^- = RS\text{-}Hg\text{-}SR$,	38.2 - 40.4	3 - 5	~0.5	CLE-SEM (Hhwaja et al., 2006)
DOM isolates	$Hg^{2+} + RS^- + RX^- = RS\text{-}Hg\text{-}XR$	28.7 ± 0.1	4-7	0.1	EDLE (Haitzer et al., 2003)
SOM	$Hg^{2+} + RS^- + RO^- = RS\text{-}Hg\text{-}OR$	31.6 - 32.2	3 - 3.4	~ 0.6	CLE-SEM (Skyllberg et al., 2000)
DOM	$Hg^{2+} + RS^- = RS\text{-}Hg^+$	29.9 – 33.5	7.4 –7.8	na	CLE-SPE (Black et al., 2007)
DOM	$Hg^{2+} + RS^- = RS\text{-}Hg^+$	26.1 – 29.2	7.0– 9.8	0.6	CLE-SSE (Han & Gill, 2005)
DOM	$Hg^{2+} + RS^-$ = RS-Hg	21 – 24	7.5	na	Red. Hg (Lamborg et al., 2003)
DOM isolate	$Hg^{2+} + RS^- = RS\text{-}Hg^+$	28.5	7.0	0.1	EDLE (Haitzer et al., 2002)
Peats & DOM	$Hg^{2+} + RS^- = RS\text{-}Hg^+$	25.8 – 27.2	6.0	0.01	SEM (Drexel et al., 2002)
DOM	$Hg^{2+} + RS^- = RS\text{-}Hg^+$	20.6 – 22.4	4 - 6	0.06	CLE-SSM (Benoit et al., 2001)
SOM & DOM	$CH_3Hg^+ + RS^- = RS\text{-}CH_3Hg$,	15.6 – 17.1	2 – 5.1	0.25	CLE (Karlsson & Skyllberg, 2003)
SOM	$CH_3Hg^+ + RS^- = RS\text{-}CH_3Hg$,	16.3 – 16.7	3 – 4.3	0.01	SEC (Qian et al., 2002)
HA	$CH_3Hg^+ + RS^- = RS\text{-}CH_3Hg$,	10.39–14.96	5 - 9	0.001	EDLE (Amirbahman et al., 2002)
HA & FA	$CH_3Hg^+ + RS^- = RS\text{-}CH_3Hg$	12.15–14.48	6.5	0.0001	EDLE (Hintelmann et al., 1995)

NOM = Natural organic matter, SOM = soil organic matter, DOM = dissolved organic matter, HA = Humic acid, FA = Fulvic acid, RS^- = reduced sulfur groups (thiols) in NOM, RX^- = functional groups (X=O/N/S) in NOM, CLE = Competitive ligand exchange, SPE = Solid phase extraction, EDLG = Equilibrium dialysis ligand exchange, SSE = Solvent-Solvent extraction; SEM = Sorption equilibrium modeling, SEC = Sorption equilibrium calculation, na = not available.

2.3. Modeling of Aqueous Speciation of Hg(II) and CH_3Hg^+

An equilibrium geochemical speciation computer code **PREEQC** (Parkhurst and Appelo, 2004) was applied to (1) calculate the distribution of various aqueous species of Hg(II) and CH_3Hg^+ in EFPC (Figure 1) based on Tables 1-3 and other relevant geochemical reactions, and (2) evaluate the effects of co-existing metals on speciation distribution of Hg(II) (Figure 2).

3. Geochemical Modeling Results

3.1. Distribution of Aqueous Hg(II) and CH_3Hg^+ Species

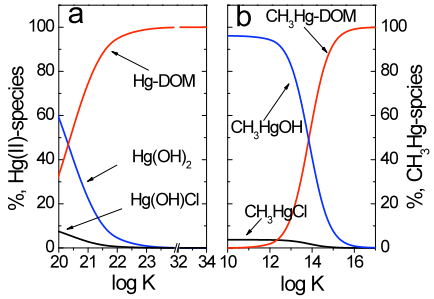
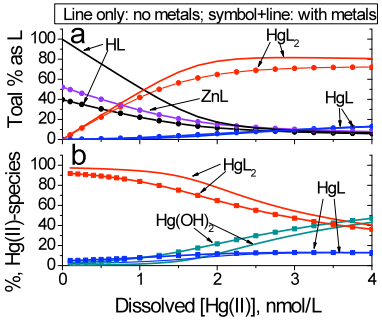


Figure1. Calculated aqueous species distribution of Hg(II) = 2.5 nmol/L (**a**), and CH_3Hg^+ = 5×10^{-12} mol/L (**b**), as a function of log K = 20 – 34 for RS-Hg(II) and log K = 10 – 17 for RS-CH_3Hg^+ at pH = 7.8 and $[RS^-]$ = 4 nmol/L (estimated from dissolved humic isolates in EFPC surface water). Hg-DOM and CH_3Hg-DOM represent 1:1 complexes of RS-Hg(II) and RS-CH_3Hg in Table 3, respectively.

3.2. Effects of Co-existing Metal Ions on Hg(II) and CH_3Hg^+ Speciation



← For most metal ions, their binding constants with thiol groups in DOM are not available in literature. Cysteine (CYS) and glutathione (GS) were selected as model organic ligands for these reactions. The formation constants (log K) of complexes (1:1 and 1:2) of metals (M) with thiols (L) in CYS and GS were selected from Martell et al (2001) and Berthon et al (1995) to mimic the competitive complexation of M with L. Results are shown in Figure 2.

Figure 2. Effects of co-existing metal ions (Table 1) on the distribution of thiol groups (L) (**a**), and Hg(II) speciation distribution (**b**) at various Hg(II) concentrations (Table 1). pH = 7.8 and total thiols concentration (L) = 4 nmol/L. (Note: additional modeling result shows no effect of co-existing metals on CH_3Hg^+ speciation)

4. Major Conclusions

- **DOM (i.e., dissolved humic substances) in EFPC surface waters plays a major role in both Hg(II) and CH3Hg+ speciation. Neutral complexes of $Hg(OH)_2$ and Hg(OH)Cl are calculated to be as secondary important species (preferred for bacterial methylation).**
- **Hg(II) methylation may be inhibited by DOM in EFPC due to the formation of strong Hg(II) complexes with thiols in DOM.**
- **Zn^{2+} presents at relatively high concentrations in EFPC and is a potential competitor for Hg(II) binding to sites (thiol) in DOM.**
- **A literature review gives a broad range of log K values (21 to 40 for Hg(II)-RS and 10 to 17 for CH_3Hg-RS complexes (Table 3)), suggesting that the quantitative characterization of reactive binding sites in DOM and their interactions with Hg(II), CH_3Hg^+, and other metal ions in environments, remain to be developed.**
- **The binding mechanisms and strength of Hg(II) and CH_3Hg+ with DOM vary from site to site and need to be determined under site-specific conditions.**