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An assessment of thermodynamic reaction constants for simulating aqueous environmental monomethylmercury speciation

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ABSTRACT

Monomethylmercury (CH_3Hg^+) is both the most ecologically significant and the least well characterized species of mercury in environmental settings. Our understanding of the environmental speciation behavior of this compound is limited both as the result of lesser available laboratory data (when compared to inorganic mercury) as well as the uncertainties associated with our understanding of the properties of environmental ligands. A careful examination and synthesis of data reported in the technical literature led to the following findings: (1) a 25°C, zero ionic strength bicarbonate ion complexation constant estimate is remarkably close to an earlier reported value at 0.4 M: $\text{CH}_3\text{Hg}^+ + \text{HCO}_3^- \rightleftharpoons \text{CH}_3\text{HgHCO}_3$, $\log_{10}K = 2.6 (\pm 0.22, 1 \text{ SD})$, (2) three 25°C zero ionic strength reaction constants reported by DeRobertis *et al.* (1998) were confirmed to within $\sim \pm 0.1 \log_{10}K$ units: $\text{CH}_3\text{Hg}^+ + \text{OH}^- \rightleftharpoons \text{CH}_3\text{HgOH}$, $\log_{10}K = 9.47$; $2\text{CH}_3\text{Hg}^+ + \text{H}_2\text{O} \rightleftharpoons (\text{CH}_3\text{Hg})_2\text{OH}^+ + \text{H}^+$, $\log_{10}K = -2.15$; $\text{CH}_3\text{Hg}^+ + \text{Cl}^- \rightleftharpoons \text{CH}_3\text{HgCl}$, $\log_{10}K = 5.45$, (3) "best estimate" literature complexation constants corrected to zero ionic strength include: $\text{CH}_3\text{Hg}^+ + \text{F}^- \rightleftharpoons \text{CH}_3\text{HgF}$, $\log_{10}K = 1.75$ (20°C corr. Schwartzbach and Schellenberg, 1965); $\text{CH}_3\text{Hg}^+ + \text{Br}^- \rightleftharpoons \text{CH}_3\text{HgBr}$, $\log_{10}K = 6.87$ (20°C corr. Schwartzbach and Schellenberg, 1965); $\text{CH}_3\text{Hg}^+ + \text{I}^- \rightleftharpoons \text{CH}_3\text{HgI}$, $\log_{10}K = 8.85$ (20°C corr. Schwartzbach and Schellenberg, 1965); and $\text{CH}_3\text{Hg}^+ + \text{SO}_4^{2-} \rightleftharpoons \text{CH}_3\text{HgSO}_4^-$, $\log_{10}K = 2.64$ (25°C, DeRobertis *et al.*, 1998), (4) literature reported values for simulating monomethylmercury complexation with the carbonate ion may be too low: $\text{CH}_3\text{Hg}^+ + \text{CO}_3^{2-} \rightleftharpoons \text{CH}_3\text{HgCO}_3^-$, $\log_{10}K = 6.1$ (Rabenstein *et al.*, 1976; Erni, 1981), and (5) "best estimate" constants for simulating methyl mercury complexation with reduced environmental sulfur species include: $\text{CH}_3\text{Hg}^+ + \text{S}^{2-} \rightleftharpoons \text{CH}_3\text{HgS}^-$, $\log_{10}K = 21.1$; $\text{CH}_3\text{Hg}^+ + \text{SH}^- \rightleftharpoons \text{CH}_3\text{HgSH}$, $\log_{10}K = 14.5$ ($\text{H}^+ + \text{SH}^- \rightleftharpoons \text{H}_2\text{S}$, $\log_{10}K = 6.88$; Dyrssen and Wedborg, 1991); $\text{CH}_3\text{Hg}^+ + \text{RS}^- \rightleftharpoons \text{CH}_3\text{HgSR}$, $\log_{10}K = 16.5$ ($\text{H}^+ + \text{RS}^- \rightleftharpoons \text{RSH}$, $\log_{10}K = 9.96$; Qian *et al.*, 2002); and $\text{CH}_3\text{Hg}^+ + \text{CH}_3\text{HgS}^{1-} \rightleftharpoons (\text{CH}_3\text{Hg})_2\text{S}$, $\log_{10}K = 16.32$ (Schwartzbach and Schellenberg, 1965; Rabenstein *et al.*, 1978; and Erni, 1981).

Keywords: monomethylmercury, speciation, complexation, sulfhydryl, hydroxyl

INTRODUCTION

Mercury has been identified as the predominant contaminant of concern in fish consumption advisories in 48 states and one territory within the United States of America (U.S. EPA, 2004). Similar concerns about the element have been raised at the global scale and result from fish tissue mercury residues in excess of guideline values (United Nations, 2002).

Global concern about mercury in the biosphere has its roots in enhanced historical anthropogenic atmospheric emissions of the element. Generally speaking, combustion of coal and high mercury content products in incinerators leads to the atmospheric emission of gaseous mercury vapor which in turn is entrained and transported with global air masses. Subsequent deposition of atmospheric mercury onto terrestrial and aquatic surfaces can

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then lead to contamination of erstwhile pristine ecosystems.

In contrast to many other metal contaminants of environmental concern, mercury exists in a suite of naturally occurring species and oxidation states: (a) elemental mercury (Hg^0), the predominant gaseous species in the atmosphere, (b) divalent mercury (Hg^{2+}), the major oxidation state of mercury in aqueous systems, and (c) a variety of alkyl mercuric species including monomethylmercury (CH_3Hg^+), the problematic species largely responsible for fish consumption advisories, and dimethyl mercury (CH_3HgCH_3), a compound more generally observed in marine systems.

Each species of mercury may display its own unique environmental transport, bioavailability, toxicity, and biomagnification behavior. Because ionic species of mercury react with environmental inorganic and organic ligands to form various complexes, the above mentioned list of mercury compounds may only be a small subset of all possible environmental species. In addition, given that many of these species may be present at such low concentrations that they are experimentally undetectable and/or unstable when subjected to chemical separation procedures, the presence of some species may only be inferred from our knowledge of the chemical properties of each compound.

Extensive carefully screened databases of reaction constants useful for describing the environmental speciation of inorganic mercury with inorganic ligands are already in existence (Sillen and Martell, 1964, 1971; Lindsay, 1979; Rai *et al.*, 1986; Sadiq, 1992; Martell *et al.*, 1998, 2003). This work focuses on assessing the accuracy of the thermodynamic reaction constant database of the much less well characterized monomethyl compound.

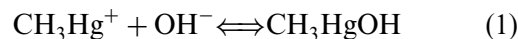
In seeking to assess the available literature, an effort was made to comply with the admonition against constructing a *Handbook of Unstable, Exotic and Nonexistent Compounds* (Grauer, 1997). On a more positive note, an effort was made to specify why one constant is selected over another (Meinrath *et al.*, 2000) and to follow the general guidelines established by Smith and Martell (1995).

METHODS

Thermodynamics of aqueous complex formation

When metal cations such as monomethylmercury (CH_3Hg^+) undergo a complexation reaction with

an environmental ligand such as the hydroxide ion (OH^-), the reaction is generally represented by an expression of the following form:



A stoichiometric reaction constant (K) describing this reaction is given by a concentration quotient:

$$K = \frac{[\text{CH}_3\text{HgOH}]}{[\text{CH}_3\text{Hg}^+][\text{OH}^-]} \quad (2)$$

where the species in brackets designate the concentrations of the product and reacting species.

A thermodynamic reaction constant is represented by:

$$K_{\text{thermo}} = \frac{\gamma_{\text{CH}_3\text{HgOH}}[\text{CH}_3\text{HgOH}]}{\gamma_{\text{CH}_3\text{Hg}^+}[\text{CH}_3\text{Hg}^+]\gamma_{\text{OH}^-}[\text{OH}^-]} \quad (3)$$

where the subscripted $\gamma_{\text{CH}_3\text{HgOH}, \text{CH}_3\text{Hg}^+, \text{OH}^-}$ terms designate the activity coefficients of the reacting species. These terms are representative of nonideal energies and correct the concentrations to thermodynamic activities (where $a_X = \gamma_X^*[\text{X}^Z]$).

Equation (1) can be represented in alternate form:



the corresponding thermodynamic reaction constant is then:

$$K_{\text{thermo}} = \frac{\gamma_{\text{CH}_3\text{HgOH}}[\text{CH}_3\text{HgOH}]\gamma_{\text{H}^+}[\text{H}^+]}{\gamma_{\text{CH}_3\text{Hg}^+}[\text{CH}_3\text{Hg}^+]\gamma_{\text{H}_2\text{O}}[\text{H}_2\text{O}]} \quad (5)$$

Although equations (3) and (5) generally represent the same type of reaction, they differ in reaction stoichiometry and the constants will differ in numerical value.

The thermodynamic standard state Gibb's free energy of a reaction can be related to its thermodynamic reaction constant by the following expression:

$$\Delta G^\circ = -RT^* \ln(K_{\text{thermo}}) \quad (6)$$

where R is the ideal gas constant and T represents the absolute temperature.

If one has thermodynamic reaction constants for at least two temperatures (K_{T_1} and K_{T_2} at temperatures T_1 and T_2 respectively), then one also can estimate

the standard state enthalpy (ΔH°) using the Van't Hoff equation:

$$\ln\left(\frac{K_{T1}}{K_{T2}}\right) = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (7)$$

This analysis is predicated on the assumption that the standard state enthalpy is invariant over the temperature range of interest. Given knowledge of both ΔG° and ΔH° , one can estimate the standard state entropy (ΔS°) using the traditional thermodynamic relationship:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (8)$$

or:

$$\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T \quad (9)$$

At this point, procedures exist for calculating standard state Gibbs free energies, enthalpies and entropies provided that one has reliable estimates of thermodynamic reaction constants at more than one temperature.

Estimation of activity coefficients

Most chemical measurements estimate quantities in terms of chemical concentrations. However, from the previous discussion, chemical activities are required to estimate thermodynamic reaction constants. A critical issue from the perspective of the present work is the ability to estimate activity coefficients for the reacting species.

Although accurate activity coefficient algorithms applicable to higher ionic strength solutions are available (*e.g.*, Bromley, Pitzer, Specific Ion Interaction Theory, *etc.*), the ion specific input parameters required for these algorithms are not. Hence, the more generic, low ionic strength Davies extension procedure (Davies, 1962) implemented in the MINTEQA2 geochemical speciation model (Allison *et al.*, 1991) was used in this work.

The Davies expression implemented in MINTEQA2 is given below:

$$\log(\gamma_i) = \frac{A \cdot z_i^2}{(1 + I^{1/2})} - 0.24 \cdot I \quad (10)$$

where γ_i is the activity coefficient of species *i*, *A* is the Debye-Huckel parameter (~ 0.509 at room temperature; Pytkowicz, 1983), z_i is the valence of

ion *i*, and *I* is the ionic strength of the aqueous medium:

$$I = \frac{1}{2} \sum (c_i \cdot z_i^2) \quad (11)$$

Given that some environmental monomethylmercury species are neutrally charged, the Helgeson procedure implemented in MINTEQA2 also was utilized for the purpose of assessing the effects of “salts” on neutral species activity coefficients:

$$\log(\gamma_o) = 0.1 \cdot I \quad (12)$$

Lastly, the MINTEQA2 procedure for estimating the activity of water also is available:

$$a_{H_2O} = 1 - 0.017 \sum c_i \quad (13)$$

where the activity of water (a_{H_2O}) equals $\gamma_{H_2O} \cdot [H_2O]$. By convention the activity of a pure liquid equals one.

Figure 1 compares mean ion activity coefficient data from Robinson and Stokes (1959) with results obtained from MINTEQA2 simulations including use of the Davies equation (Loux and Washington, 2002). This figure illustrates that, depending on the requisite data quality objectives, errors from the Davies implementation in MINTEQA2 may be significant at ionic strengths in excess of 0.1 M (Butler, 1964; Butler and Cogley, 1998).

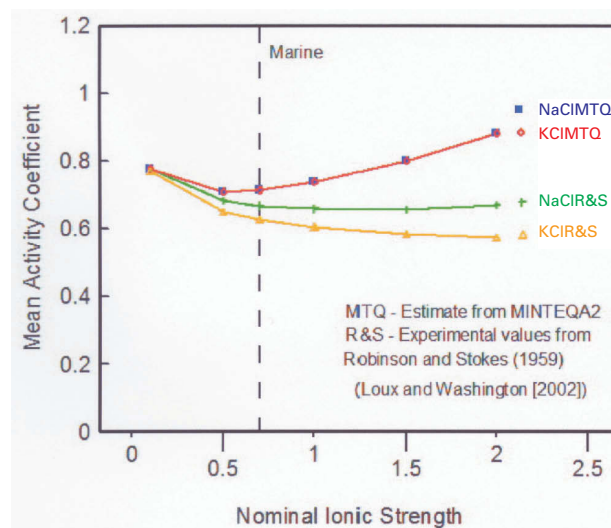


Figure 1 Comparison of MINTEQA2-generated mean ion activity coefficients with experimental values reported by Robinson and Stokes (1959). Loux and Washington (2002).

RESULTS

Table 1 depicts literature reported formation constants for monomethylmercury with the hydroxide ion. Note that these reactions suggest that monomethylmercury hydroxyl species can exist as monomers, dimers and trimers. To the authors knowledge, DeRobertis *et al.* (1998) are the only authors who reported formation constants extrapolated to an ionic strength of 0.0 M (*i.e.*, where the activity coefficients equal one). DeRobertis *et al.*

(1998) also report 25°C, 0.1 M thermodynamic data (using the stoichiometry in equation [4]):

$$\Delta G^{\circ} = 25.7 \pm 0.2 \text{ kJ/mole}$$

$$\Delta H^{\circ} = 20.5 \pm 0.5 \text{ kJ/mole}$$

$$T\Delta S^{\circ} = -5.2 \pm 0.6 \text{ kJ/mole}$$

Table 1 Equilibrium constants for CH_3Hg^+ reactions with the hydroxide ion and/or water

Reaction	$\log_{10}(K)$	Reference/conditions
$\text{CH}_3\text{Hg}^+ + \text{OH}^- \rightleftharpoons \text{CH}_3\text{HgOH}$	9.18	(Alderighi <i>et al.</i> , 2003; 0.15 M NaClO_4 ; 25°C)
$\text{CH}_3\text{Hg}^+ + \text{OH}^- \rightleftharpoons \text{CH}_3\text{HgOH}$	9.37	(Schwarzenbach and Schellenberg, 1965; 0.1 M; 20°C)
$\text{CH}_3\text{Hg}^+ + \text{OH}^- \rightleftharpoons \text{CH}_3\text{HgOH}$	9.30 9.51	(Libich and Rabenstein, 1973; cited in preceding)
$\text{CH}_3\text{Hg}^+ + \text{OH}^- \rightleftharpoons \text{CH}_3\text{HgOH}$	9.32	(Zanella <i>et al.</i> , 1968; 20°C, $I = 0.1 \text{ M KNO}_3$)
$\text{CH}_3\text{Hg}^+ + \text{OH}^- \rightleftharpoons \text{CH}_3\text{HgOH}$	9.00	(Zanella <i>et al.</i> , 1968; 25°C, $I = 0.1 \text{ M KNO}_3$)
$\text{CH}_3\text{Hg}^+ + \text{OH}^- \rightleftharpoons \text{CH}_3\text{HgOH}$	9.51	(Waugh <i>et al.</i> , 1955; 25°C)
$\text{CH}_3\text{Hg}^+ + \text{OH}^- \rightleftharpoons \text{CH}_3\text{HgOH}$	9.37	(Waugh <i>et al.</i> , 1955; 35°C)
$\text{CH}_3\text{Hg}^+ + \text{OH}^- \rightleftharpoons \text{CH}_3\text{HgOH}$	9.37	(Rabenstein <i>et al.</i> , 1975, 1978)
$2\text{CH}_3\text{Hg}^+ + \text{OH}^- \rightleftharpoons (\text{CH}_3\text{Hg})_2\text{OH}^+$	11.74	(Baes and Mesmer, 1976; 0.1 M KNO_3 , 20°C)
$\text{CH}_3\text{Hg}^+ + \text{CH}_3\text{HgOH} \rightleftharpoons (\text{CH}_3\text{Hg})_2\text{OH}^+$	2.32	(Alderrighi <i>et al.</i> , 2003; 0.15 M NaClO_4 , 25°C)
$\text{CH}_3\text{Hg}^+ + \text{CH}_3\text{HgOH} \rightleftharpoons (\text{CH}_3\text{Hg})_2\text{OH}^+$	2.37	(Libich and Rabenstein, 1973)
$\text{CH}_3\text{Hg}^+ + \text{CH}_3\text{HgOH} \rightleftharpoons (\text{CH}_3\text{Hg})_2\text{OH}^+$	2.37	(Schwarzenbach and Schellenberg, 1965; 0.1 M, 20°C)
$2\text{CH}_3\text{Hg}^+ + \text{H}_2\text{O} \rightleftharpoons (\text{CH}_3\text{Hg})_2\text{OH}^+ + \text{H}^+$	-2.15	(DeRobertis <i>et al.</i> , 1998)
$\text{CH}_3\text{HgOH} + (\text{CH}_3\text{Hg})_2\text{OH}^+ \rightleftharpoons (\text{CH}_3\text{Hg})_3\text{O}^+ + \text{H}_2\text{O}$	-3.7	(Rabenstein <i>et al.</i> , 1975, 1978)
$\text{CH}_3\text{Hg}^+ + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{HgOH} + \text{H}^+$	-4.40	(Ingman and Liam, 1974; ± 0.07 , 3 sd)
$\text{CH}_3\text{Hg}^+ + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{HgOH} + \text{H}^+$	-4.59	(Tobias, 1978)
$\text{CH}_3\text{Hg}^+ + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{HgOH} + \text{H}^+$	-4.63	(Erni, 1996)
$\text{CH}_3\text{Hg}^+ + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{HgOH} + \text{H}^+$	-4.528	(DeRobertis <i>et al.</i> , 1998; 0.0 M, 25°C)

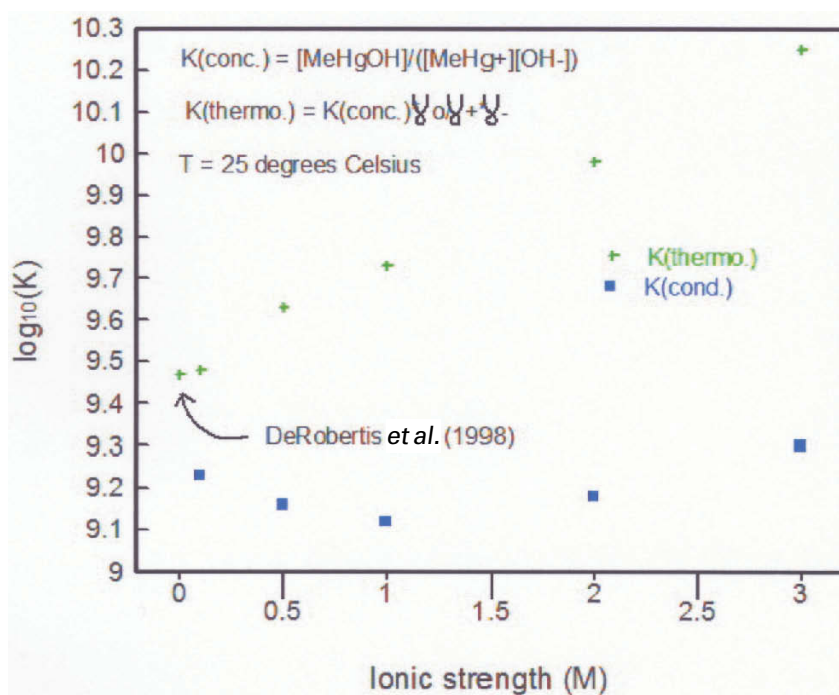


Figure 2 Comparison of concentration-based and estimated thermodynamic hydrolysis constants as a function of ionic strength. Confirmation within 0.1 units of the DeRobertis *et al.* (1998) zero ionic strength value is observed.

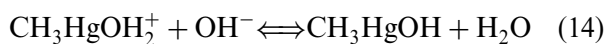
These values contrast with equivalent 25°C 0.15 M NaClO₄ values reported by Alderighi *et al.* (2003) using the stoichiometry given in equation (1):

$$\Delta H^\circ = 35.8 \pm 2 \text{ kJ/mole}$$

$$\Delta S^\circ = 57.8 \pm 8 \text{ J/(mole}^\circ\text{K)}$$

Inspection of Table 1 suggests that the hydrolysis constants using the stoichiometry in equation (1) may vary by up to 0.51 log units; this translates into a factor of uncertainty of ~ 3.2 . Those constants reported in terms of equation (4) may vary by 0.23 log units (or an uncertainty factor of 1.7). In principle one can convert between these two values provided that one has knowledge of both the activity of water and the ionization constant of water ($\sim 10^{-14}$) at the temperature of interest.

A final point to be gleaned from Table 1 is that earlier hydrolysis constants are sometimes formulated within the context of the following equation:



(Rabenstein *et al.*, 1975; Schwartzbach and Schellenberg, 1965). The numerical constant describing this formulation will equal that of equa-

tion (1) if the activity of water is assumed to remain constant at 1. Alternatively, Alderighi *et al.* (2003; and references cited therein) maintain that specification of the CH₃Hg⁺ ion is, in fact, a less rigorous convention representing the hydrated CH₃HgOH₂⁺ species.

Figure 2 displays both the estimates of the concentration-based and thermodynamic formation constants in Table 1 as a function of ionic strength. The thermodynamic constants were derived from the concentration based constants using the Davies and neutral activity coefficient expressions discussed earlier. The near equality between the DeRobertis *et al.* (1998) estimate ($\log_{10}K = 9.47$) and the thermodynamic estimate near zero ionic strength ($\log_{10}K = 9.48$) provides independent confirmation of the value reported by DeRobertis *et al.* (1998).

Table 2 lists literature-reported estimates of formation constants between CH₃Hg⁺ and halide ions. Clearly there are more data available for the chloride ion. A variation of 0.55 log units in the chloride ion constant translates into an uncertainty of a factor of 3.5.

Figure 3, analogous to Figure 2, compares concentration-based and thermodynamic estimates of the reaction constants between monomethylmercury and the chloride ion as a function of ionic strength (data obtained from Table 2). These findings (corrected

Table 2 Equilibrium constants for CH_3Hg^+ reactions with halide ions

Reaction	$\log_{10}(\text{K})$	Reference/conditions
$\text{CH}_3\text{Hg}^+ + \text{Cl}^- \rightleftharpoons \text{CH}_3\text{HgCl}$	5.21	(Alderighi <i>et al.</i> , 2003; $I = 0.15 \text{ M NaClO}_4$, 25°C)
$\text{CH}_3\text{Hg}^+ + \text{Cl}^- \rightleftharpoons \text{CH}_3\text{HgCl}$	5.46	(Waugh <i>et al.</i> , 1955; 25°C)
$\text{CH}_3\text{Hg}^+ + \text{Cl}^- \rightleftharpoons \text{CH}_3\text{HgCl}$	4.90	(Zanella <i>et al.</i> , 1968; $I = 0.1 \text{ M KNO}_3$, 25°C)
$\text{CH}_3\text{Hg}^+ + \text{Cl}^- \rightleftharpoons \text{CH}_3\text{HgCl}$	4.90	(Baes and Mesmer, 1976)
$\text{CH}_3\text{Hg}^+ + \text{Cl}^- \rightleftharpoons \text{CH}_3\text{HgCl}$	5.25	(Rabenstein <i>et al.</i> , 1978 and Tobias, 1978)
$\text{CH}_3\text{Hg}^+ + \text{Cl}^- \rightleftharpoons \text{CH}_3\text{HgCl}$	5.25	(Schwarzenbach and Schellenberg, 1965; 0.1 M , 20°C)
$\text{CH}_3\text{Hg}^+ + \text{Cl}^- \rightleftharpoons \text{CH}_3\text{HgCl}$	5.25	(Erni, 1996)
$\text{CH}_3\text{Hg}^+ + \text{Cl}^- \rightleftharpoons \text{CH}_3\text{HgCl}$	5.45	(DeRobertis <i>et al.</i> , 1998; $I = 0.0$, 25°C)
$\text{CH}_3\text{HgCl} + \text{H}^+ + \text{Cl}^- \rightleftharpoons \text{CH}_4 + \text{HgCl}_2$	~ 5.2	(Erni, 1996)
$\text{CH}_3\text{Hg}^+ + \text{F}^- \rightleftharpoons \text{CH}_3\text{HgF}$	1.5	(Tobias, 1978)
$\text{CH}_3\text{Hg}^+ + \text{F}^- \rightleftharpoons \text{CH}_3\text{HgF}$	1.5	(Schwarzenbach and Schellenberg, 1965; 0.1 M , 20°C)
$\text{CH}_3\text{Hg}^+ + \text{Br}^- \rightleftharpoons \text{CH}_3\text{HgBr}$	6.49	(Alderighi <i>et al.</i> , 2003; 0.15 M NaClO_4 , 25°C)
$\text{CH}_3\text{Hg}^+ + \text{Br}^- \rightleftharpoons \text{CH}_3\text{HgBr}$	6.70	(Waugh <i>et al.</i> , 1955; 25°C)
$\text{CH}_3\text{Hg}^+ + \text{Br}^- \rightleftharpoons \text{CH}_3\text{HgBr}$	5.98	(Zanella <i>et al.</i> , 1968; 25°C , $I = 0.1 \text{ M KNO}_3$)
$\text{CH}_3\text{Hg}^+ + \text{Br}^- \rightleftharpoons \text{CH}_3\text{HgBr}$	6.62	(Tobias, 1978)
$\text{CH}_3\text{Hg}^+ + \text{Br}^- \rightleftharpoons \text{CH}_3\text{HgBr}$	6.62	(Schwarzenbach and Schellenberg, 1965; 0.1 M , 20°C)
$\text{CH}_3\text{Hg}^+ + \text{I}^- \rightleftharpoons \text{CH}_3\text{HgI}$	8.61	(Alderighi <i>et al.</i> , 2003; 0.15 M NaClO_4 , 25°C)
$\text{CH}_3\text{Hg}^+ + \text{I}^- \rightleftharpoons \text{CH}_3\text{HgI}$	8.70	(Waugh <i>et al.</i> , 1955; 25°C)
$\text{CH}_3\text{Hg}^+ + \text{I}^- \rightleftharpoons \text{CH}_3\text{HgI}$	7.70	(Zanella <i>et al.</i> , 1968; $I = 0.1 \text{ M KNO}_3$, 25°C)
$\text{CH}_3\text{Hg}^+ + \text{I}^- \rightleftharpoons \text{CH}_3\text{HgI}$	8.60	(Tobias, 1978)
$\text{CH}_3\text{Hg}^+ + \text{I}^- \rightleftharpoons \text{CH}_3\text{HgI}$	8.60	(Schwarzenbach and Schellenberg, 1965; 0.1 M , 20°C)

$\log_{10}\text{K} = 5.48$ at $I = 0.1 \text{ M}$) also present independent confirmation of the estimate reported by DeRobertis *et al.* (1998); $\log_{10}\text{K} = 5.45$).

Table 3 illustrates reported constants between CH_3Hg^+ and oxidized species of the Group VIA elements. Sulfur is present in a variety of oxidation states in environmental sedimentary pore waters. Selenite and selenate also may be present in significant quantities in aquatic systems in arid environments.

Table 4 details literature-reported reaction constants between CH_3Hg^+ and carbonate, bicarbonate, carboxyl and phosphate ions. Carbonate and

bicarbonate ions are ubiquitous in environmental aquatic systems. Carboxyl groups are believed to comprise the majority of ionizable sites present on natural organic matter in aquatic systems. Phosphate is not typically a major ligand in aqueous environmental chemistry. The identical constants in Table 4 describing acetate ion complexation with CH_3Hg^+ may represent an instance of double reporting of the same value.

Table 5 describes formation constants between CH_3Hg^+ and a variety of reduced species commonly found in anoxic aquatic systems. Aqueous environmental sulfide ions are typically

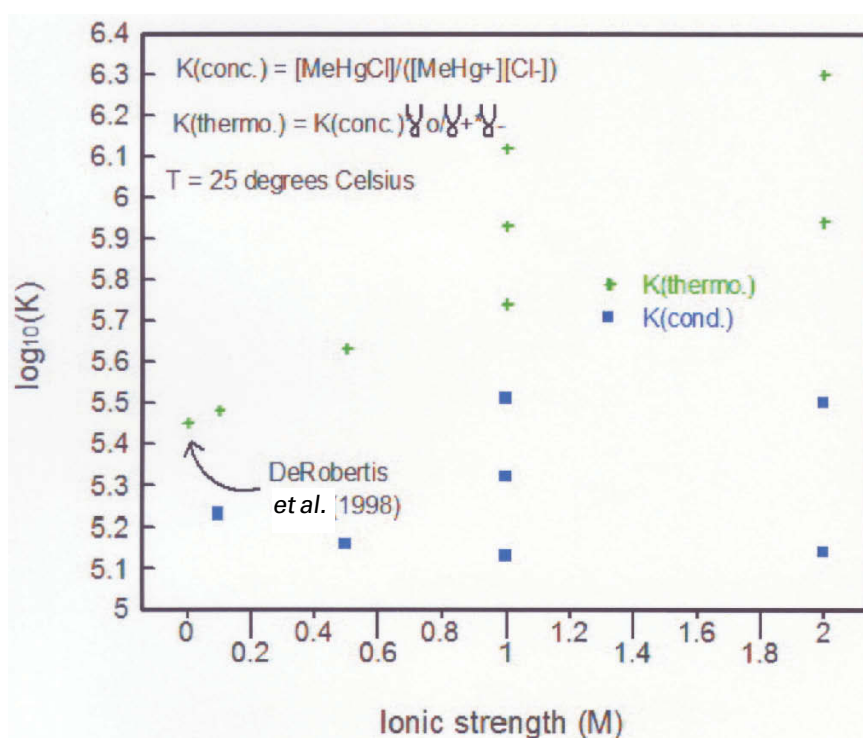


Figure 3 Comparison of concentration-based and estimated thermodynamic monomethylmercury/chloride ion complexation constants as a function of ionic strength. Confirmation within approximately 0.1 units of the DeRobertis *et al.* (1998) zero ionic strength value is observed.

generated *via* microbial reduction of sulfate. The constants between CH_3Hg^+ and sulfide ions are problematic in the sense that considerable variation exists in estimates of the second pK_a of H_2S .

The foremost current hypothesis is that the majority of CH_3Hg^+ present at “background”

concentrations in environmental aquatic systems is generally sequestered by thiol groups (RS^-) present in natural organic matter. The one log unit variation in the reported constants between pure compound laboratory values and those observed with natural organic carbon is rather remarkable given the varia-

Table 3 Equilibrium constants for CH_3Hg^+ reactions with group VIa anions

Reaction	$\log_{10}(\text{K})$	Reference/conditions
$\text{CH}_3\text{Hg}^+ + \text{SO}_3^{2-} \rightleftharpoons \text{CH}_3\text{HgSO}_3^-$	8.11	(Schwarzenbach and Schellenberg, 1965; 0.1 M, 20°C)
$\text{CH}_3\text{Hg}^+ + \text{SO}_3^{2-} \rightleftharpoons \text{CH}_3\text{HgSO}_3^-$	7.96	(Rabenstein <i>et al.</i> , 1976, 1978)
$\text{CH}_3\text{Hg}^+ + \text{SO}_4^{2-} \rightleftharpoons \text{CH}_3\text{HgSO}_4^-$	0.94	(Rabenstein <i>et al.</i> , 1976, 1978)
$\text{CH}_3\text{Hg}^+ + \text{SO}_4^{2-} \rightleftharpoons \text{CH}_3\text{HgSO}_4^-$	0.94	(Erni, 1996)
$\text{CH}_3\text{Hg}^+ + \text{SO}_4^{2-} \rightleftharpoons \text{CH}_3\text{HgSO}_4^-$	2.64	(DeRobertis <i>et al.</i> , 1998; 0.0 M, 25°C)
$\text{CH}_3\text{Hg}^+ + \text{S}_2\text{O}_3^{2-} \rightleftharpoons \text{CH}_3\text{HgS}_2\text{O}_3^-$	10.90	(Schwarzenbach and Schellenberg, 1965; 0.1 M, 20°C)
$\text{CH}_3\text{Hg}^+ + \text{S}_2\text{O}_3^{2-} \rightleftharpoons \text{CH}_3\text{HgS}_2\text{O}_3^-$	11.05	(Rabenstein <i>et al.</i> , 1978)
$\text{CH}_3\text{Hg}^+ + \text{SeO}_3^{2-} \rightleftharpoons \text{CH}_3\text{HgSeO}_3^-$	6.46	(Rabenstein <i>et al.</i> , 1976, 1978)
$\text{CH}_3\text{Hg}^+ + \text{HSeO}_3^- \rightleftharpoons \text{CH}_3\text{HgHSeO}_3$	2.70	(Rabenstein <i>et al.</i> , 1976)
$\text{CH}_3\text{Hg}^+ + \text{SeO}_4^{2-} \rightleftharpoons \text{CH}_3\text{HgSeO}_4^-$	1.12	(Rabenstein <i>et al.</i> , 1976, 1978)
$\text{CH}_3\text{Hg}^+ + \text{SCN}^- \rightleftharpoons \text{CH}_3\text{HgSCN}$	6.05	(Rabenstein <i>et al.</i> , 1976)
$\text{CH}_3\text{Hg}^+ + \text{SeCN}^- \rightleftharpoons \text{CH}_3\text{HgSeCN}$	6.79	(Rabenstein <i>et al.</i> , 1976)

Table 4 Equilibrium constants for CH₃Hg⁺ reactions with carbonate, carboxyl and phosphate ions

Reaction	log ₁₀ (K)	Reference/conditions
CH ₃ Hg ⁺ + CO ₃ ²⁻ ⇌ CH ₃ HgCO ₃ ⁻	6.1	(Rabenstein <i>et al.</i> , 1976)
CH ₃ Hg ⁺ + CO ₃ ²⁻ ⇌ CH ₃ HgCO ₃ ⁻	6.1	(Erni, 1996)
CH ₃ Hg ⁺ + HCOO ⁻ ⇌ CH ₃ HgOOCH	2.67	(Libich and Rabenstein, 1973; 0.4 M, 25°C)
CH ₃ Hg ⁺ + CH ₃ COO ⁻ ⇌ CH ₃ HgOOCCH ₃	4.54	(Alderighi <i>et al.</i> , 2003; 0.15 M NaClO ₄ , 25°C)
CH ₃ Hg ⁺ + CH ₃ COO ⁻ ⇌ CH ₃ HgOOCCH ₃	3.18	(Libich and Rabenstein, 1973; 0.4 M, 25°C)
CH ₃ Hg ⁺ + CH ₃ COO ⁻ ⇌ CH ₃ HgOOCCH ₃	3.18	(Rabenstein <i>et al.</i> , 1978; 0.4 M, 25°C)
CH ₃ Hg ⁺ + CH ₃ CH ₂ COO ⁻ ⇌ CH ₃ HgOOCCH ₂ CH ₃	3.39	(Libich and Rabenstein, 1973; 0.4 M, 25°C)
CH ₃ Hg ⁺ + H ₂ PO ₄ ⁻ ⇌ CH ₃ HgHPO ₄ ⁻ + H ⁺	-1.74	(Ingman and Liam, 1974; ± 0.03, 3 SD)

Table 5 Equilibrium constants for CH₃Hg⁺ reactions with reduced sulfur, carbon and nitrogen species

Reaction	log ₁₀ (K)	Reference/conditions
CH ₃ Hg ⁺ + S ²⁻ ⇌ CH ₃ HgS ⁻	21.2	(Schwarzenbach and Schellenberg, 1965; 0.1 M, 20°C)
CH ₃ Hg ⁺ + S ²⁻ ⇌ CH ₃ HgS ⁻	21.02	(Erni, 1996)
CH ₃ Hg ⁺ + SH ⁻ ⇌ CH ₃ HgSH	14.5	(Dyrssen and Wedborg, 1991)
(H ⁺ + SH ⁻ ⇌ H ₂ S)	6.88	(Dyrssen and Wedborg, 1991)
CH ₃ Hg ⁺ + RS ⁻ ⇌ CH ₃ HgSR	16.12	(Dyrssen and Wedborg, 1991)
(H ⁺ + RS ⁻ ⇌ RSH)	9.34	(Dyrssen and Wedborg, 1991)
CH ₃ Hg ⁺ + RS ⁻ ⇌ CH ₃ HgSR	15.7	(Friedman, 1973 and Simpson, 1961; cysteine, pKa = 8.6)
CH ₃ Hg ⁺ + RS ⁻ ⇌ CH ₃ HgSR	15.9	(Friedman, 1973 and Simpson, 1961; histidine, pKa = 9.0)
CH ₃ Hg ⁺ + RS ⁻ ⇌ CH ₃ HgSR	16.3–16.7	(Qian <i>et al.</i> , 2002; nat. org. matter)
(H ⁺ + RS ⁻ ⇌ RSH)	9.96	(Qian <i>et al.</i> , 2002)
CH ₃ Hg ⁺ + RS ⁻ ⇌ CH ₃ HgSR	16.1–16.7	(Skylberg <i>et al.</i> , 2003; nat. org. matter)
(H ⁺ + RS ⁻ ⇌ RSH)	8.5, 9.5	(Skylberg <i>et al.</i> , 2003)
CH ₃ Hg ⁺ + CH ₃ HgS ⁻ ⇌ (CH ₃ Hg) ₂ S	16.3	(Schwarzenbach and Schellenberg, 1965; 0.1 M, 20°C)
CH ₃ Hg ⁺ + CH ₃ HgS ⁻ ⇌ (CH ₃ Hg) ₂ S	16.3	(Rabenstein <i>et al.</i> , 1978)
CH ₃ Hg ⁺ + CH ₃ HgS ⁻ ⇌ (CH ₃ Hg) ₂ S	16.34	(Erni, 1996)
CH ₃ Hg ⁺ + CH ₃ ⁻ ⇌ (CH ₃) ₂ Hg	~ 37	(Erni, 1996)
CH ₄ (aq) + HgCl ₂ ⇌ CH ₃ HgCl + H ⁺ + Cl ⁻	-5.2	(Erni, 1996)
Hg ²⁺ + CH ₃ ⁻ ⇌ CH ₃ Hg ⁺	~ 50	(Erni, 1996)
CH ₄ (aqu.) ⇌ CH ₃ ⁻ + H ⁺	~ -47	(Erni, 1996)
Hg ²⁺ + CH ₄ (aqu.) ⇌ CH ₃ Hg ⁺ + H ⁺	~ 3	(Erni, 1996)
HgS(s) + CH ₄ ⇌ CH ₃ HgS ⁻ + H ⁺	~ -26	(Erni, 1996)
CH ₃ HgOH + 2H ⁺ ⇌ CH ₄ + Hg ²⁺	~ 1.6	(Erni, 1996)
CH ₃ Hg ⁺ + NH ₃ ⇌ CH ₃ HgNH ₃ ⁺	7.60	(Schwarzenbach and Schellenberg, 1965; 0.1 M, 20°C)
CH ₃ Hg ⁺ + CH ₃ NH ₂ ⇌ CH ₃ HgNH ₂ CH ₃ ⁺	7.78	(Alderighi <i>et al.</i> , 2003; 0.15 M NaClO ₄ , 25°C)

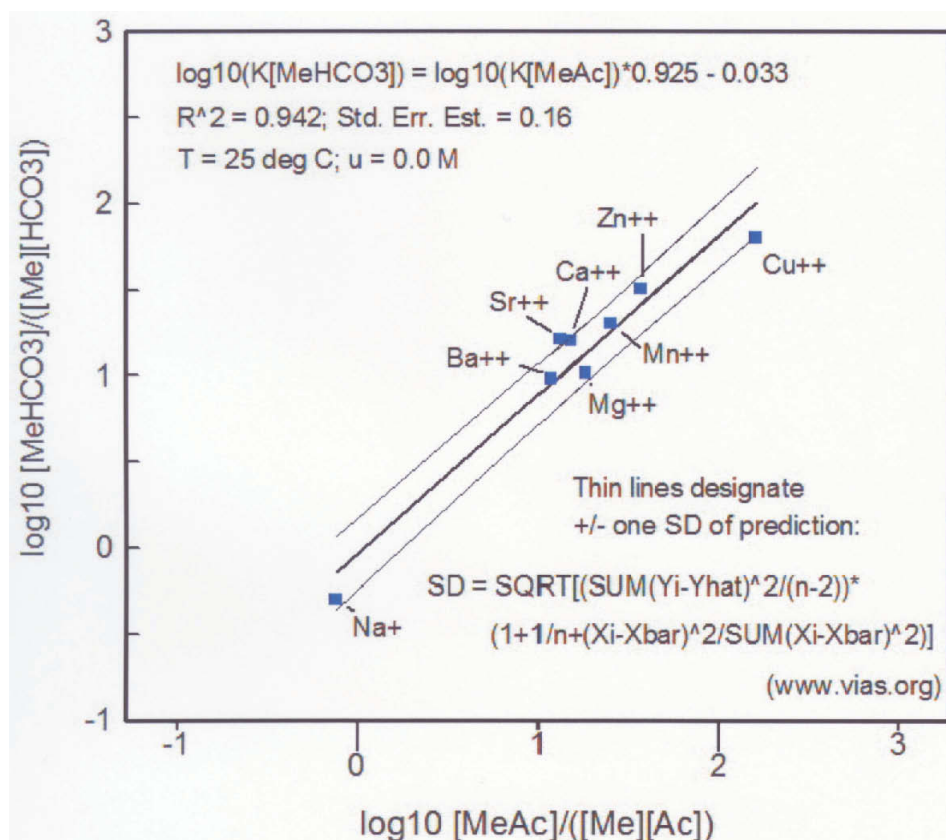


Figure 4 Regression relationship between \log_{10} complexation constants for various metals with acetate and bicarbonate ions. Data from Smith, Martell and Motekaitis (2003). $\log_{10}(K_{\text{MeHCO}_3}) = \log_{10}(K_{\text{MeAcetate}}) * 0.925 - 0.033$ ($r^2 = 0.942$; Std. error est. = 0.016).

tions among constants reported in previous tables. The range of values reported by Qian *et al.* (2002) and Karlsson and Skyllberg (2003) of 16.1 to 16.7 for reactions between CH_3Hg^+ and thiol groups may be indicative of a spectrum of thiol site energies resulting from variations in adjacent functional groups (Loux, 1998). Some of this variation also may result from differences in estimated acidity constants. Lastly, analogous to reactions with the hydroxide ion, a sulfide based monomethylmercury dimer is believed to exist in aqueous solution.

Although the bicarbonate ion (HCO_3^-) is ubiquitous in oxidic environmental waters, the author has found in the literature only one reaction constant suitable for describing a reaction of the type: $\text{CH}_3\text{Hg}^+ + \text{HCO}_3^- \rightleftharpoons \text{CH}_3\text{HgHCO}_3$ (Libich and Rabenstein, 1973). Figure 4 displays a least squares fit between metal acetate reaction constants listed in Martell, Smith and Motekaitis (2003) and metal bicarbonate constants listed in the same reference. Generally speaking, the formation constants for these two types of reactions are very highly correlated. If furthermore corrects the Libich

and Rabenstein (1973) acetate monomethylmercury \log_{10} reaction constant of 3.18 to zero ionic strength (using the MINTEQA2 Davies procedures), one obtains a \log_{10} value of the constant of 2.87. From the regression expression in Figure 4, one can estimate a $\log_{10}(K)$ value of 2.62 (± 0.22 [1 std. dev.]; VIAS, 2006) for the methyl mercury-bicarbonate reaction. This value compares very favorably with that reported by Libich and Rabenstein (1973; $\log_{10}K = 2.67$). An analogous preliminary analysis concerning the monomethylmercury-carbonate ion complex suggests that the literature-reported $\log_{10}K$ value of 6.1 may be too low.

CONCLUSIONS

Table 6 represents a “best estimate” set of constants selected from the information listed in Tables 2 through 6. Where possible, concentration-based constants were “corrected” to thermodynamic constants given that the temperature was known and that the aqueous medium had an ionic strength

Table 6 Monomethylmercury formation constants selected in this work; $\log_{10}K$ values in bold designate constants independently confirmed to within ± 0.1 log units. Enthalpy and entropy values derived from data published by Waugh *et al.* (1955)

Reaction	$\log_{10}K$	ΔG° kJ	ΔH° kJ	ΔS° J/ $^\circ K$	Comments
$CH_3Hg^+ + OH^- \rightleftharpoons CH_3HgOH$	9.47	-54.1	-24.6	98.9	DeRobertis <i>et al.</i> (1998) $\log_{10}K$ value ($I=0.0, 25^\circ C$); confirmed here
$2CH_3Hg^+ + H_2O \rightleftharpoons (CH_3Hg)_2OH^+ + H^+$	-2.15	12.3			DeRobertis <i>et al.</i> (1998) ($I=0.0, 25^\circ C$); independent estimate of -2.26
$CH_3Hg^+ + Cl^- \rightleftharpoons CH_3HgCl$	5.45	-31.1			DeRobertis <i>et al.</i> (1998) ($I=0.0, 20^\circ C$); confirmed here
$CH_3Hg^+ + F^- \rightleftharpoons CH_3HgF$	1.75	-9.82			(Schwarzenbach and Schellenberg, 1965; corrected to $I=0.0 (20^\circ C)$)
$CH_3Hg^+ + Br^- \rightleftharpoons CH_3HgBr$	6.87	-38.6			(Schwarzenbach and Schellenberg, 1965; corrected to $I=0.0 (20^\circ C)$)
$CH_3Hg^+ + I^- \rightleftharpoons CH_3HgI$	8.85	-49.7			(Schwarzenbach and Schellenberg, 1965; corrected to $I=0.0 (20^\circ C)$)
$CH_3Hg^+ + SO_4^{2-} \rightleftharpoons CH_3HgSO_4^-$	2.64	-15.1			DeRobertis <i>et al.</i> , 1998; (0.0 M; $25^\circ C$)
$CH_3Hg^+ + CO_3^{2-} \rightleftharpoons CH_3HgCO_3^-$	6.1				(Rabenstein <i>et al.</i> , 1976)
$CH_3Hg^+ + HCO_3^- \rightleftharpoons CH_3HgHCO_3$	2.62				Present work
$CH_3Hg^+ + S^{2-} \rightleftharpoons CH_3HgS^-$	21.11				Ave. of values from references (Schwarzenbach and Schellenberg, 1965; Ermi, 1996)
$CH_3Hg^+ + SH^- \rightleftharpoons CH_3HgSH$	14.5				(Dyrssen and Wedborg (1996))
$H^+ + SH^- \rightleftharpoons H_2S$	6.88				(Dyrssen and Wedborg (1996))
$CH_3Hg^+ + RS^- \rightleftharpoons CH_3HgSR$	16.5				(Qian <i>et al.</i> , 2002; NOM ~ average of range)
$H^+ + RS^- \rightleftharpoons RSH$	9.96				(Qian <i>et al.</i> , 2002)
$CH_3Hg^+ + CH_3HgS^{1-} \rightleftharpoons (CH_3Hg)_2S$	16.32				Average of 2 values

of ~ 0.1 M. Note that the sulfate constant in Table 6 differs by 1.7 log units from two earlier estimates.

The organic carbon thiol methyl mercury complex constant in Table 6 is set at roughly the geometric mean of the range of values observed by Qian *et al.* (2002) and Karlsson and Skyllberg (2003). Whether a geometric mean is an appropriate value is dependent on the nature of distribution of thiol site binding energies. Specifically, the geometric mean would be most appropriate if one assumes that the distribution of site binding energies is Gaussian in nature and that the standard deviation of the distribution is relatively small. Alternatively, if the distribution is very broad, then the geometric mean would be in error only by approximately a factor of 3.2.

Many of the constants in Table 6 are not corrected to zero ionic strength and many do not have corroboration. In addition, there is insufficient data to estimate zero ionic strength standard state enthalpies and entropies with most of this data. Hence, considerable experimental work remains to be completed in this area. Alternatively, one may prioritize work by scrutinizing these constants from another perspective. For example, Table 7 lists water quality values for a wetland site in the upper Devil's Lake Basin published by Sando *et al.* (2003). Sando *et al.* did not report the sulfhydryl site concentrations associated with dissolved organic carbon and hence an estimate of the concentration of this parameter was made using a RS^- /dissolved organic matter relationship published by Haitzer *et al.* (2002; 5E-9 sites/mg DOM; assuming monodentate binding with the $Hg[II]$ ion). In addition, sulfide ion concentrations were assumed to be present at the detection limit ($3.12E-8$ M).

Figure 5 illustrates the MINTEQA2 (Allison *et al.*, 1992) predicted speciation of monomethyl mercury in the Devil's Lake basin over a pH range of 4 to 10. These simulations were conducted using a recently recompiled version of the model suitable for modern versions of the WINDOWS[®] operating system, the constants in Table 6, the data in Table 7 and a sample input file developed by Loux (2005). Generally speaking, the monomethylmercury reduced sulfur complexes are predicted to exceed that of the other species by orders of magnitude. Based on these simulations, errors of even 1 log unit in the constants of the other species in Figure 5 will not likely result in significant changes in estimates of monomethylmercury speciation when relative concentration comparisons are made on a percentage basis. These simulations also suggest: (1) reduced

Table 7 Input data for MINTEQA2 monomethylmercury speciation simulations (data from Sando *et al.* (2003); wetland site in upper Devil's Lake Basin). Concentrations in units of moles/L unless otherwise designated. Sulfide ion concentration assumed to be present at the detection limit

CH ₃ Hg ⁺	1.740E-12	M	Cl ⁻	2.280E-04	M
SO ₄ ⁼	4.370E-03	M	Na + 1	6.090E-03	M
K ⁺	3.580E-04	M	Mg ⁺⁺	2.470E-03	M
Ca ⁺⁺	1.500E-03	M	RS ⁻	2.000E-07	M
DOC	19.9	mg/L	pH	8	
HS ⁻	3.12E-8	M			

sulfur complex concentrations with monomethylmercury will exceed those of the other species by at least two orders of magnitude, (2) hydroxy and sulfur monomethyl mercury dimer concentrations are expected to be very low at ambient monomethylmercury concentrations, (3) carbonate and bicarbonate monomethylmercury concentrations are expected to be very low, (4) monomethylmercury free ion and sulfate complex concentrations tend to be comparable, and (5) on a percentage basis, chloro and hydroxy monomethylmercury complex concentrations would be significant only in the absence of reactive reduced sulfur species.

Table 7 summarizes some additional “estimated” constants for possible monomethylmercury reactions with carboxyl sites on natural organic carbon and with hydroxyl groups on environmental hydrous iron

and manganese oxides. These numbers may be useful for screening level investigations until experimental values become available.

DISCLAIMER

The United States Environmental Protection Agency through its Office of Research and Development funded and managed the research described here. It has been subjected to the Agency's administrative review and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use. Although this document has been through the Agency peer review process, it does not necessarily reflect official agency policy.

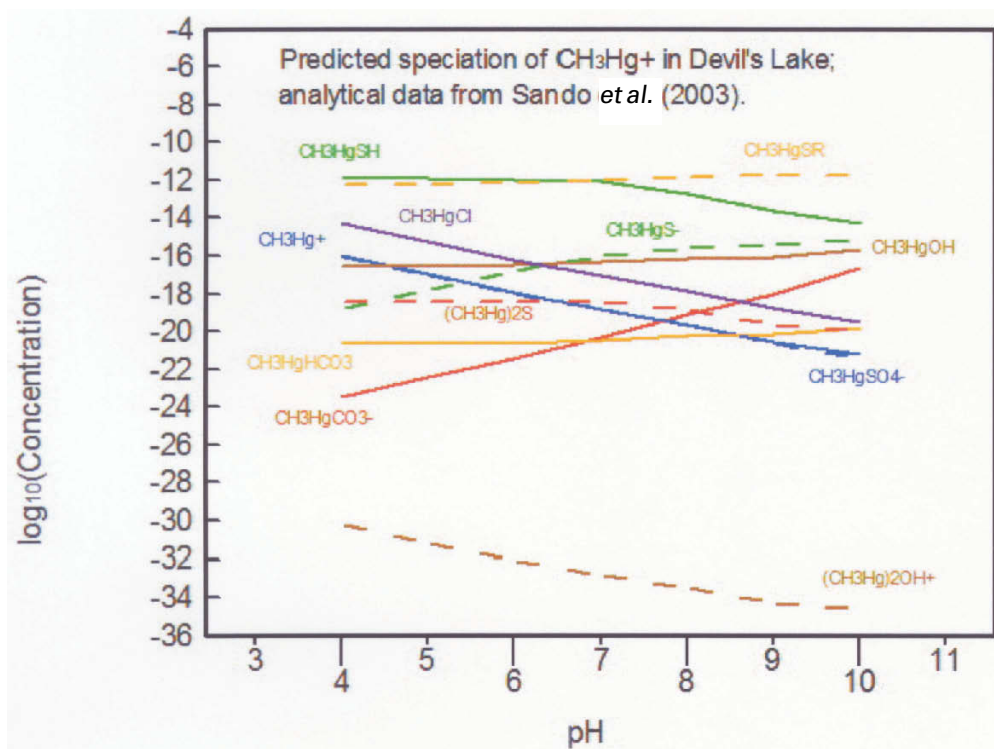
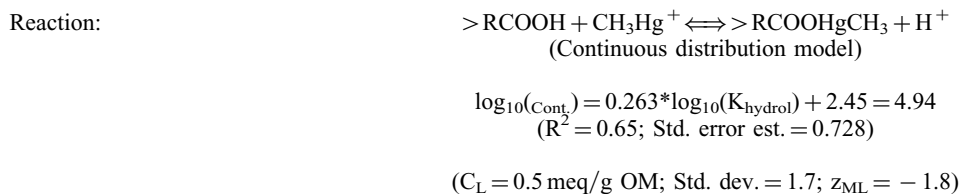
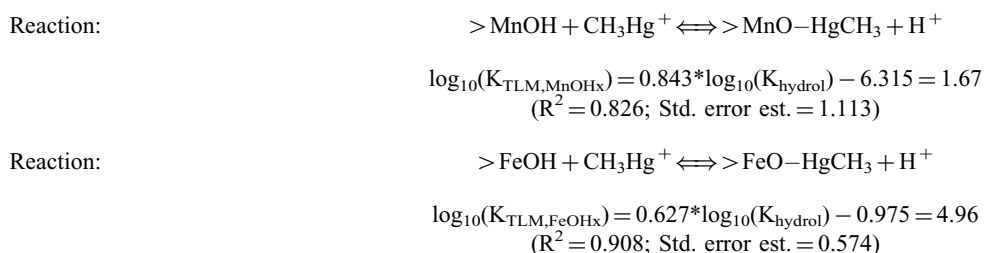


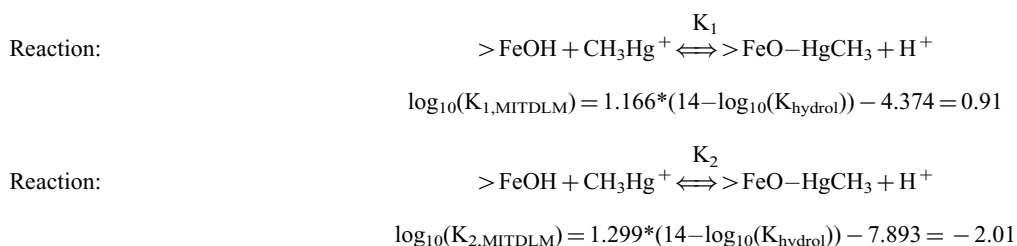
Figure 5 MINTEQA2-simulated speciation of monomethylmercury in a drainage basin in Devil's Lake. Sando *et al.* (2003) did not report RSH concentrations; therefore the estimation procedure from Haitzer *et al.* (2002) (5E-9 moles of reduced sulfur sites/mg DOM) was used instead. In addition, sulfide ion concentrations were assumed to be present at the detection limit (3.18E-8 M).

Table 8 Estimated constants for simulating methyl mercury complexation reactions with sites on hydrous iron oxide, hydrous manganese oxide and carboxyl sites on natural organic carbon (Dzombak and Morel [1990]; Susetyo *et al.* [1993]; Smith and Jenne [1991]; Loux [1998]; $K_{\text{hyd}} = [\text{CH}_3\text{HgOH}]/[\text{CH}_3\text{Hg}^+][\text{OH}^-] = 9.47$). Ionization constant for water assumed to equal 10^{-14} Carboxyl sites on natural organic carbon (data obtained from Susetyo *et al.* [1993]; Loux, [1998]):

Triple Layer Model adsorption constants (data obtained from Smith and Jenne [1991])



MIT Diffuse Layer Model (Dzombak and Morel [1990]; converted to the present notation):



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