



# Methylmercury complexes: Selection of thermodynamic properties and application to the modelling of a column experiment

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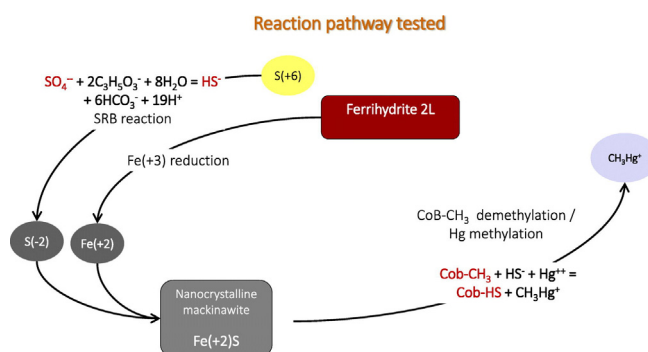
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## HIGHLIGHTS

- Reactive transport modelling of methylmercury production
- Comparison with experiment results
- Selection for the thermodynamic properties of methylmercury complexes.
- Verification of methylation rates obtained from previous studies

## GRAPHICAL ABSTRACT



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## ABSTRACT

Complexation with methyl groups produces the most toxic form of mercury, especially because of its capacity to bioconcentrate in living tissues. Understanding and integrating methylation and demethylation processes is of the utmost interest in providing geochemical models relevant for environmental assessment. In a first step, we investigated methylation at equilibrium, by selecting the thermodynamic properties of different complexes that form in the chemical system Hg-SO<sub>3</sub>-S-Cl-C-H<sub>2</sub>O. The selection included temperature dependencies of the equilibrium constants when available. We also considered adsorption and desorption reactions of both methylated and non-methylated mercury onto mineral surfaces. Then we assessed the kinetics of methylation by comparing a dedicated column experiment with the results of a geochemical model, including testing different methylation and demethylation kinetic rate laws. The column system was a simple medium: silicic sand and iron hydroxides spiked with a mercury nitrate solution. The modelling of methylmercury production with two different rate laws from the literature is bracketing the experimental results. Dissolved mercury, iron and sulfate concentrations were also correctly reproduced. The internal evolution of the column was also correctly modeled, including the precipitation of mackinawite (FeS) and the evolution of dissolved iron. The results validate the conceptual model and underline the capacity of geochemical models to reproduce some processes driven by bacterial activity.

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## 1. Introduction

Mercury (Hg) is among the most toxic elements, and has many natural sources. Human activity, especially mining and the burning of coal, has increased the mobilization of mercury into the environment. For about 200 years, anthropogenic emissions have been greater than

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natural emissions (UNEP, 2013). Mercury occurs in various chemical forms. Most atmospheric Hg is gaseous elemental mercury ( $\text{Hg}^0$ ). In surface water and soils it occurs as elemental mercury (droplets of liquid mercury) and as Hg(II) complexes (Kim et al., 2003; Ullrich et al., 2001). Hg-containing minerals, such as cinnabar and metacinnabar (two polymorphs of HgS) and montroydite ( $\text{HgO}$ ), can control its solubility (Kim et al., 2003). Much human exposure to mercury is through the consumption of fish and other marine foods, since mercury is mainly introduced into the food chain as methylmercury (MeHg). In soils, the presence of MeHg results from a balance between different competing processes (Skylberg, 2012): methylation and demethylation (Cossa et al., 2014) reactions, formation of aqueous complexes (Jay et al., 2000) and gaseous species and adsorption/desorption reactions onto inorganic and organic substrates (Kaplan et al., 2002). The balance between those different mechanisms determines bioaccumulation and MeHg transportation.

From the late 1990's, researchers have begun to use geochemical modelling to assess metal cycling and redox biogeochemistry in the environment (Wang and Van Cappellen, 1996). Concerning mercury, Bessinger et al. (2012) have proposed a comprehensive model to reproduce mercury and arsenic speciation in sediment caps and how it changes over time, including MeHg. Leterme et al. (2014) also developed geochemical modelling of a conceptual soil, to assess the relative proportion of mercury released in the atmosphere or transported through the soil column or trapped, either onto mineral surfaces or as minerals precipitated along the profile.

Leterme et al. (2014) explained that in spite of being an important tool, geochemical modelling suffers from the lack of well characterized sites. Actually, the counterpart of being able to reproduce detailed reactive mechanisms is that those models may require an important input dataset, including site-specific parameters. Even if determined, the values may suffer from variability and heterogeneities and uncertainties of measurements or phenomena. As an alternative, we propose building a model to reproduce the results of a less complex column experiment. The model itself would include all the complexity governing MeHg fate, including methylation/demethylation reactions, the formation of aqueous complexes and gaseous species and surface complexation reactions. Johannesson and Neumann (2013) conducted a comprehensive set of measurements in groundwater along a 13 km flowpath located within a confined aquifer in southeastern Texas, USA. Their biogeochemical model was able to highlight the main mechanisms (mineral dissolution and sorption onto oxide surfaces) responsible for the speciation of total Hg. Most of them have been integrated in the present model, except for the complexation with polysulfides.

The aim of this study is to test geochemical modelling in a more controlled context like the column experiment performed by Hellal et al. (2015). The geochemical calculations on Hg fate can then be somehow

constrained or compared with respect to those experimental results. In addition, taking advantage of the analyses performed by Hellal et al. (2015), the calculations are especially focused on methylmercury fate (methylation/demethylation and transportation), allowing testing of the methylation/demethylation rates available to date in the literature (Bessinger et al., 2012; Heyes et al., 2006). Before comparing the calculations with the experimental results, we include a critical selection for MeHg complexes, consistent with the database built up by Leterme et al. (2014) for Hg-bearing species. The selection extended to surface complexation reactions and methylation/demethylation rates, following the review and case study proposed by Bessinger et al. (2012) and Cossa et al. (2014).

## 2. Selection of thermodynamic properties for methylmercury aqueous complexes

Methylmercury is a strongly toxic complex that accumulates in the muscles and various living tissues of living organisms. After Thomassin and Touze (2003), the methylation of mercury is favored in anoxic environments by the presence of sulfate-reducing bacteria and of sulfur. Generally speaking, the methylation reaction proceeds this way (:



Dimethyl products are found as both aqueous complexes (in basic solutions) and in gaseous form, currently in moderately basic waters (Stumm and Morgan, 1996). Methylation of mercury is reversible. We selected MeHg species using thermodynamic data processed according to guidelines describes by Blanc et al. (2012) and consistent with the previous selection by Leterme et al. (2014). The thermodynamic parameters associated with complexation reactions have been collected and discussed from Erni (1977), Alderighi et al. (2003), Loux (2007) and Skylberg (2012), for various chemical systems, at 25 °C. Loux (2007) are especially important, resulting from an extrapolation to infinite dilution of large experiment datasets. Alderighi et al. (2003) have measured, by calorimetry, the heat exchanged during various complexation reactions involving methylmercury. From these measurements, we were able to calculate the entropy of complexes, which are reported in Table 1. Actually, they provided  $\Delta S_r$  for reactions involving  $\text{CH}_3\text{Hg}^+$  as primary specie. In order to use these measurements, we have considered the reaction:



**Table 1**  
Selection for thermodynamic properties of MeHg-bearing species.

Specie	Equilibrium	Log <sub>10</sub> K (298.15 K)	S° (J/mol·K)	References
$\text{CH}_3^-$	$\text{CH}_{4,\text{aq}} = \text{CH}_3^- + \text{H}^+$	-46.00		(1)
$\text{CH}_3\text{Hg}^+$	$\text{CH}_{4,\text{aq}} + \text{Hg}^{++} = \text{CH}_3\text{Hg}^+ + \text{H}^+$	3.00	65.91	(1), this work
$\text{CH}_3\text{HgCl}$	$\text{CH}_3\text{Hg}^+ + \text{Cl}^- = \text{CH}_3\text{HgCl}$	5.45	142.91	(2), (3)
$\text{CH}_3\text{HgOH}$	$\text{CH}_3\text{Hg}^+ + \text{H}_2\text{O} = \text{CH}_3\text{HgOH} + \text{H}^+$	-4.53	110.71	(2), (3)
$\text{CH}_3\text{HgS}^-$	$\text{CH}_3\text{Hg}^+ + \text{HS}^- = \text{CH}_3\text{HgS}^- + \text{H}^+$	4.00		(2)
$\text{CH}_3\text{HgSH}$	$\text{CH}_3\text{Hg}^+ + \text{HS}^- = \text{CH}_3\text{HgSH}$	14.50		(2)
$(\text{CH}_3)_2\text{Hg}$	$2\text{CH}_3\text{Hg}^+ = (\text{CH}_3)_2\text{Hg} + \text{Hg}^{++}$	13.00		(1)
$\text{CH}_3\text{HgCO}_3^-$	$\text{CH}_3\text{Hg}^+ + \text{HCO}_3^- = \text{CH}_3\text{HgCO}_3^- + \text{H}^+$	-4.23		(2)
$\text{CH}_3\text{HgHCO}_3$	$\text{CH}_3\text{Hg}^+ + \text{HCO}_3^- = \text{CH}_3\text{HgHCO}_3$	2.60		(2)
$\text{CH}_3\text{HgSO}_4^-$	$\text{CH}_3\text{Hg}^+ + \text{SO}_4^{--} = \text{CH}_3\text{HgSO}_4^-$	2.64		(2)
$(\text{CH}_3\text{Hg})_2\text{OH}^+$	$2\text{CH}_3\text{Hg}^+ + \text{H}_2\text{O} = (\text{CH}_3\text{Hg})_2\text{OH}^+ + \text{H}^+$	-2.15	167.62	(2), (3)
$(\text{CH}_3\text{Hg})_2\text{S}^a$	$\text{CH}_3\text{Hg}^+ + \text{CH}_3\text{HgS}^- = (\text{CH}_3\text{Hg})_2\text{S}$	20.32		(2)
$\text{Hg}(\text{CH}_3)_{2,g}$	$\text{Hg}^{++} + 2\text{CH}_{4,\text{aq}} = \text{Hg}(\text{CH}_3)_{2,g} + 2\text{H}^+$	8.82	306.00	(4)

(1) Erni (1977); (2) Loux (2007); (3) recalculated using reaction entropy from Alderighi et al. (2003); (4) Wagman et al. (1982).

<sup>a</sup> Not selected (see text).

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