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5 **METHYLMERCURY COMPLEXES: SELECTION OF THERMODYNAMIC PROPERTIES**
6 **AND APPLICATION TO THE MODELLING OF A COLUMN EXPERIMENT**
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18 **Abstract**
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20 Complexation with methyl groups produces the most toxic form of mercury, especially
21 because of its capacity to bioconcentrate in living tissues. Understanding and integrating
22 methylation and demethylation processes is of the utmost interest in providing geochemical
23 models relevant for environmental assessment. In a first step, we investigated methylation at
24 equilibrium, by selecting the thermodynamic properties of different complexes that form in the
25 chemical system Hg-SO₃-S-Cl-C-H₂O. The selection included temperature dependencies of
26 the equilibrium constants when available. We also considered adsorption and desorption
27 reactions of both methylated and non-methylated mercury onto mineral surfaces. Then we
28 assessed the kinetics of methylation by comparing a dedicated column experiment with the
29 results of a geochemical model, including testing different methylation and demethylation
30 kinetic rate laws. The column system was a simple medium: silicic sand and iron hydroxides
31 spiked with a mercury nitrate solution. The modelling of methylmercury production with two
32 different rate laws from the literature is bracketing the experimental results. Dissolved
33 mercury, iron and sulfate concentrations were also correctly reproduced. The internal
34 evolution of the column was also correctly modeled, including the precipitation of
35 mackinawite (FeS) and the evolution of dissolved iron. The results validate the conceptual
36 model and underline the capacity of geochemical models to reproduce some processes
37 driven by bacterial activity.
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40 *Keywords:* Methylmercury, reactive transport, percolation, sulfate reduction
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45 **Introduction**

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47 Mercury (Hg) is among the most toxic elements, and has many natural sources. Human
48 activity, especially mining and the burning of coal, has increased the mobilization of mercury
49 into the environment. For about 200 years, anthropogenic emissions have been greater than
50 natural emissions (UNEP, 2013). Mercury occurs in various chemical forms. Most
51 atmospheric Hg is gaseous elemental mercury (Hg^0). In surface water and soils it occurs as
52 elemental mercury (droplets of liquid mercury) and as Hg(II) complexes (Kim et al., 2003).
53 Hg-containing minerals, such as cinnabar and metacinnabar (two polymorphs of HgS) and
54 montroydite (HgO), can control its solubility (Kim et al., 2003). Much human exposure to
55 mercury is through the consumption of fish and other marine foods, since mercury is mainly
56 introduced into the food chain as methylmercury (MeHg). In soils, the presence of MeHg
57 results from a balance between different competing processes (Skylberg, 2012): methylation
58 and demethylation (Cossa et al., 2014) reactions, formation of aqueous complexes and
59 gaseous species and adsorption/desorption reactions onto inorganic and organic substrates.
60 The balance between those different mechanisms determines bioaccumulation and MeHg
61 transportation.

62

63 Researchers have begun to use geochemical modelling to assess the fate of mercury in the
64 environment. Bessinger et al. (2012) have proposed a comprehensive model to reproduce
65 mercury and arsenic speciation in sediment caps and how it changes over time, including
66 MeHg. Leterme et al. (2014) also developed geochemical modelling of a conceptual soil, to
67 assess the relative proportion of mercury release in the atmosphere or transported through
68 the soil column or trapped, either onto mineral surfaces or as minerals precipitated along the
69 profile.

70

71 Leterme et al. (2014) explained that in spite of being an important tool, geochemical
72 modelling suffers from the lack of well characterized sites. Actually, the counterpart of being

73 able to reproduce detailed reactive mechanisms is that those models may require an
74 important input dataset, including site-specific parameters. Even if determined, the values
75 may suffer from variability and heterogeneities. As an alternative, we propose building a
76 model to reproduce the results of a less complex column experiment. The model itself would
77 include all the complexity governing MeHg fate, including methylation/demethylation
78 reactions, the formation of aqueous complexes and gaseous species and surface
79 complexation reactions. Johannesson and Neumann (2013) conducted a comprehensive set
80 of measurements in groundwater along a 13 km flowpath located within a confined aquifer in
81 southeastern Texas, USA. Their biogeochemical model was able to highlight the main
82 mechanisms (mineral dissolution and sorption onto oxide surfaces) responsible for the
83 speciation of total Hg.

84

85 The aim of this study is to test geochemical modelling in a more controlled context like the
86 column experiment performed by Hellal et al. (2015). The geochemical calculations on Hg
87 fate can then be somehow constrained or compared with respect to those experimental
88 results. In addition, taking advantage of the analyses performed by Hellal et al. (2015), the
89 calculations are especially focused on methylmercury fate (methylation/demethylation and
90 transportation), allowing testing of the methylation/demethylation rates available to date in
91 the literature. Before comparing the calculations with the experimental results, we include a
92 critical selection for MeHg complexes, consistent with the database built up by Leterme et al.
93 (2014) for Hg-bearing species. The selection extended to surface complexation reactions
94 and methylation/demethylation rates, following the review and case study proposed by
95 Bessinger et al. (2012) and Cossa et al. (2014).

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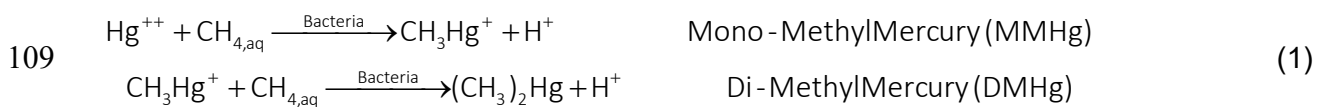
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102 1. Selection of thermodynamic properties for methylmercury aqueous complexes

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

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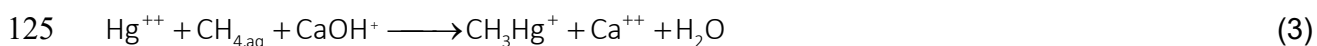


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111 Dimethyl products are found as both aqueous complexes (in basic solutions) and in gaseous
112 form. Methylation of mercury is reversible. We selected MeHg species using thermodynamic
113 data processed according to guidelines describes by Blanc et al. (2012) and consistent with
114 the previous selection by Leterme et al. (2014). The thermodynamic parameters associated
115 with complexation reactions have been collected and discussed from Erni (1977), Alderighi et
116 al. (2003), Loux (2007) and Skyllberg (2012), for various chemical systems, at 25°C. Loux
117 (2007) are especially important, resulting from an extrapolation to infinite dilution of large
118 experiment datasets. Alderighi et al. (2003) have measured, by calorimetry, the heat
119 exchanged during various complexation reactions involving methylmercury. From these
120 measurements, we were able to calculate the entropy of complexes, which are reported in
121 Table 1. Actually, they provided ΔS_r for reactions involving CH_3Hg^+ as primary specie. In
122 order to use these measurements, we have considered the reaction:



124 It was converted into an isocoulombic equilibrium using Ca^{++} and $\text{Ca}(\text{OH})^+$ species:



126 The third law entropy was calculated considering the one term approximation method from
 127 Gu et al. (1994) and entropies from the Thermoddem database (Blanc et al., 2012). The
 128 result allows obtaining the third law entropies from Alderighi et al. (2003) measurements. The
 129 whole results are reported in Table 1. In addition to the aqueous complexes we have
 130 included a gas phase, $\text{Hg}(\text{CH}_3)_{2,\text{g}}$ which represents an extreme stage of the methylation
 131 process (Thomassin and Touze, 2003).

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Table 1 – Selection for thermodynamic properties of MeHg-bearing species

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

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

139 a. Not selected (see text)

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143 For the selection, we followed the approach promoted by Stumm and Morgan (1996) where

144 the methyl group is represented by the CH₃⁻ anion. This formally identifies the methylated

145 complexes and easily separates the inorganic and organic chemical system when required.

146 The selection was integrated in the Thermoddem database (Blanc et al., 2012) in order to

147 use it with geochemical codes GWB (Bethke, 2004) and PhreeqC (Parkhurst and Appelo,
148 1999).

149

150 A first test of the database consisted in calculating the production of methyl complexes which
151 would arise from the speciation model detailed in Table 1. After Leterme and Jacques
152 (2012), the amount of MeHg in waters in contact with soil systems is usually close to 2%. A
153 speciation calculation is conducted, using PhreeqC-2 with the above database and
154 considering a solution with $[\text{NaCl}] = 10^{-3} \text{ M}$ and $[\text{Hg}] = 10^{-9} \text{ M}$. This amount was reached
155 applying two different corrections:

- 156 - by modifying reaction (2) equilibrium constant from $\log_{10}K = 3$ to 2.5 when reactions
157 from Table 1 are written with $\text{CH}_{4,\text{aq}}$ as primary specie
- 158 - or by modifying $\text{CH}_{4,\text{aq}} = \text{CH}_3^- + \text{H}^+$ equilibrium constant from $\log_{10}K = -46$ to -52.5 when
159 reactions from Table 1 are written with CH_3^- as primary specie.

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161 Actually, we did not expect the relation between organic and inorganic carbon to be driven by
162 thermodynamic equilibrium. The correction considered in the first test is still of small extent,
163 especially because the value originally given by Erni (1977) was calculated and not
164 measured and the uncertainty can be larger in that case. In addition, the fact that the results
165 obtained for MeHg speciation may depend on the way the database is written is to be
166 underline. For the rest of the calculations, we no longer consider the equilibrium between
167 organic and inorganic reduced carbon. However it is important to note that when the
168 database uses $\text{CH}_{4,\text{aq}}$ or CH_3^- complexes as primary specie for the methylation reactions, this
169 allows considering also the methylation for other metals like Sn or Pb (Stumm and Morgan,
170 1996), jointly with Hg methylation. The database in Table 1 was also tested using activity
171 diagrams of which examples are displayed in Figure 1

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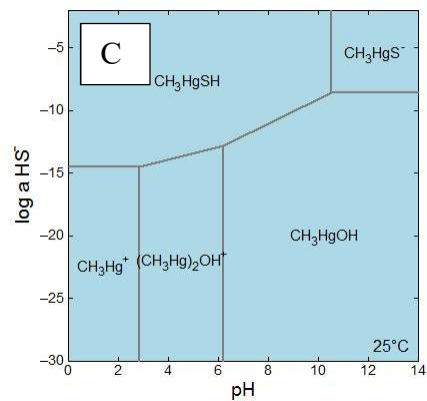
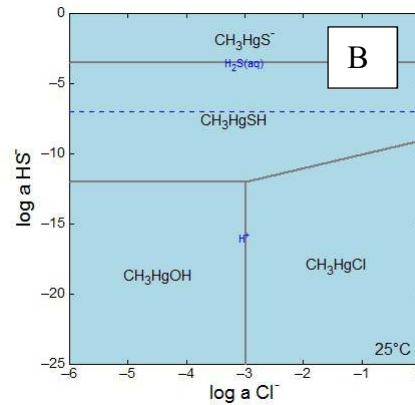
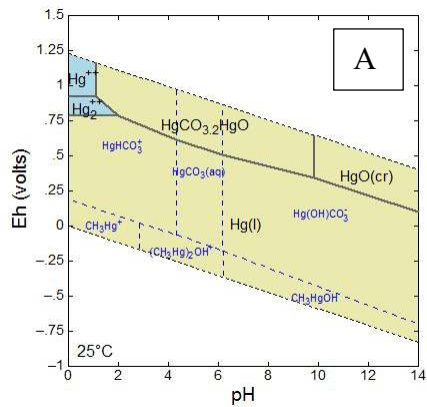


Figure 1 – Stability relation between MeHg aqueous complexes at 25°C: A – for the carbonate sub-system; B - depending on sulfide and chloride activity; C – depending on sulfide activity and pH

In yellow: solid phase stability domains; in blue: aqueous complexes stability domains

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The carbonate stability domains (Figure 1.A) are in agreement with Powell et al. (2005) calculations. As for methylmercury species, they are dominated by CH_3Hg^+ , $(\text{CH}_3\text{Hg})_2\text{OH}^+$ and CH_3HgOH complexes and located in the reduced part of the predominance diagram. The equilibrium with dissolved carbonate species strongly reduces the methylmercury stability domain. Since most of the contaminated water contains 1% of total mercury as MeHg, this would imply kinetic control of MeHg speciation. Figures 1.B and 1.C display a transition between sulfide and hydroxylated species for a total sulfide concentration close to 10^{-12} mol/L, whereas Boszke et al. (2002) proposed 10^{-11} mol/L. On the other hand the transition between chlorinated and hydroxylated methyl complexes occurs according to Boszke et al.'s calculation at $\text{pH} = 7$ (for a chloride concentration of about 10^{-3} mol/L). Previous results could only be obtained only by removing the $(\text{CH}_3\text{Hg})_2\text{S}$ complex which displayed an exaggerated stability, covering most of the area in figures 1.B and 1.C.

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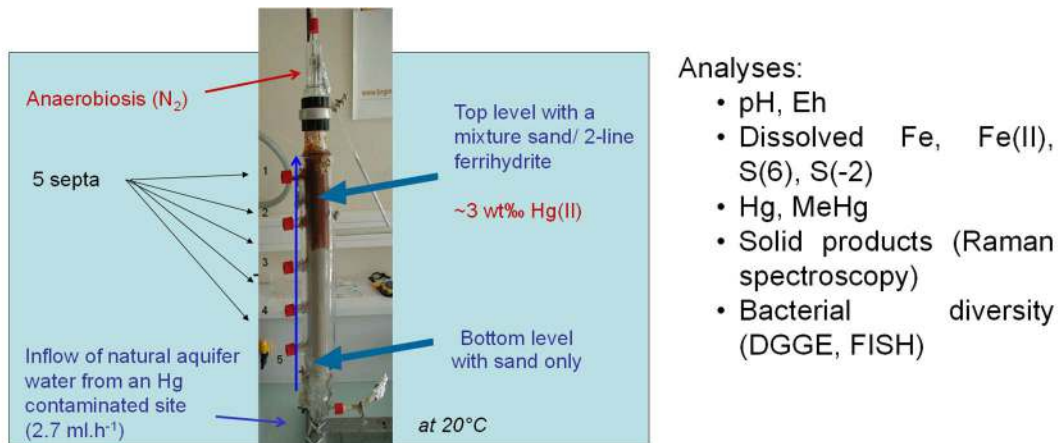
2. Column experiment (Hellal et al., 2015)

193 The database set up previously is now tested by modeling the MeHg rate obtained
194 experimentally by Hellal et al. (2015) in a companion. To our knowledge, such comparison is
195 rather unique for Hg methylation, up to now.

196

197 Only a brief description is given here and the reader referred to Hellal et al. (2015) for
198 additional details. The experiment design is reported in Figure 2. The lower half the column is
199 filled with sterile sand and the upper half with a sterile mixture of sand and iron oxides,
200 initially enriched with Hg(+2). The column is inoculated with a bacterial consortium and the
201 inflowing solution is supplemented with magnesium sulfate and sodium lactate to enhance
202 the growth and activity of sulfate-reducing bacteria (SRB). The water flow is ascendant. Five
203 septa set regularly along the columns enable water sampling from the different layers of the
204 column without perturbing water flow or in situ experimental conditions. After an abiotic
205 rinsing period, the system is inoculated with a bacterial consortium, and physical, chemical
206 and microbial parameters are monitored in time and space, up to 143 days.

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- **Percolating water (mmol.L⁻¹):** pH 7.22, pe 2.28, [Ca] 1.41, [Cl] 0.42, [Na] 0.30, [S] 0.75, [Lactate] 0.01, [Fe] 1.80.10⁻⁷, [Hg] 1.6.10⁻⁹
- **Solid matrix:** 0-15 cm sand ; 15-30 cm sand + Ferrihydrite 2L (5.7 %)
- Percolating water inoculated with SRB and FRB
- Percolating for 143 days

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Figure 2 – Experimental design developed by Hellal et al. (2015)

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217 3. Model development

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219 A specific reactive transport model was developed to reproduce the experimental conditions.

220 Methylation is described in the model following a suite of chemical reactions described in

221 Figure 3, where MeHg formation arises from a rather complex process including different

222 steps:

- 223 - a first step corresponds to the reduction of Fe(+3) from the dissolution of ferrihydrite.

224 It is reproduced using the model developed by Poulton (2003)

- 225 - meanwhile, sulfate undergoes a reduction induced by the activity and growth of SRB

226 bacteria. The reduction is modeled using a first order rate law which rate constant is

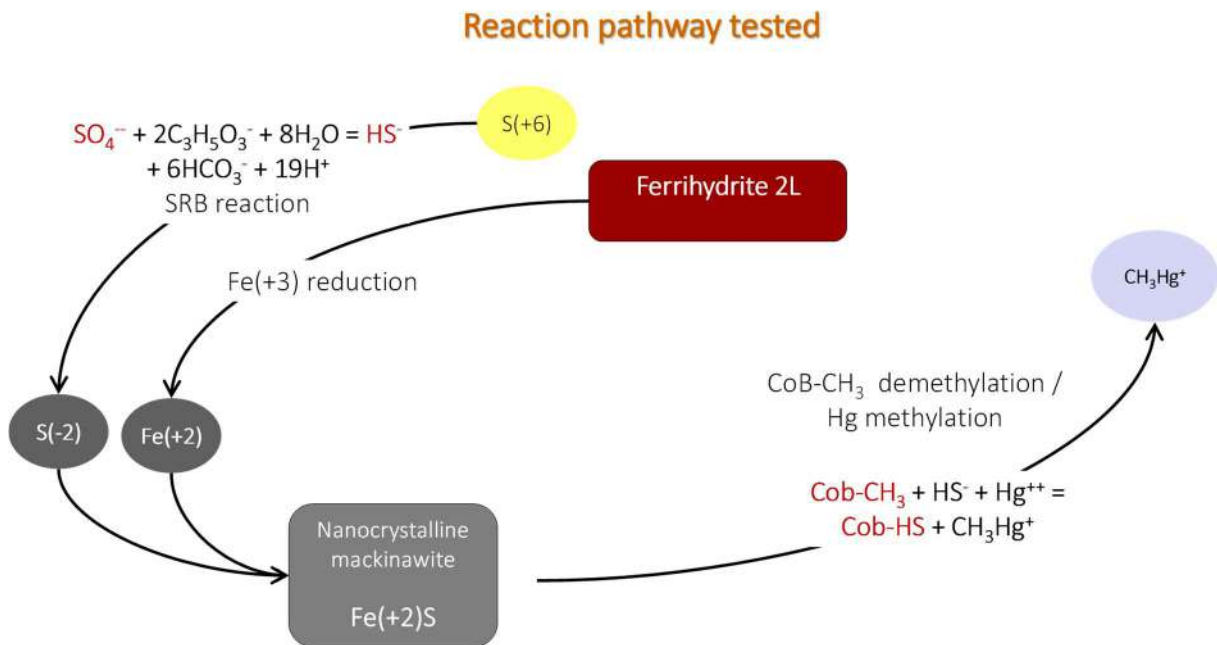
227 extracted from Bharati and Kumar (2012) experiment (Table 2)

- 228 - both Fe(+2) and S(-2) are consumed to precipitate mackinawite (FeS_{cr})

229 - cobaltihexamine (CoB-CH₃) complexes with mackinawite surfaces, the methyl group
 230 CH₃⁻ is released and combines in solution with dissolved mercury Hg⁺⁺ to form
 231 eventually the methylmercury complex CH₃Hg⁺. Two rate laws were tested, a first
 232 order proposed by Bessinger et al. (2012) and a second law based on the work by
 233 Heyes et al. (2006) (Table 2) and which rate corresponds to a balance between both
 234 methylation and demethylation rates.

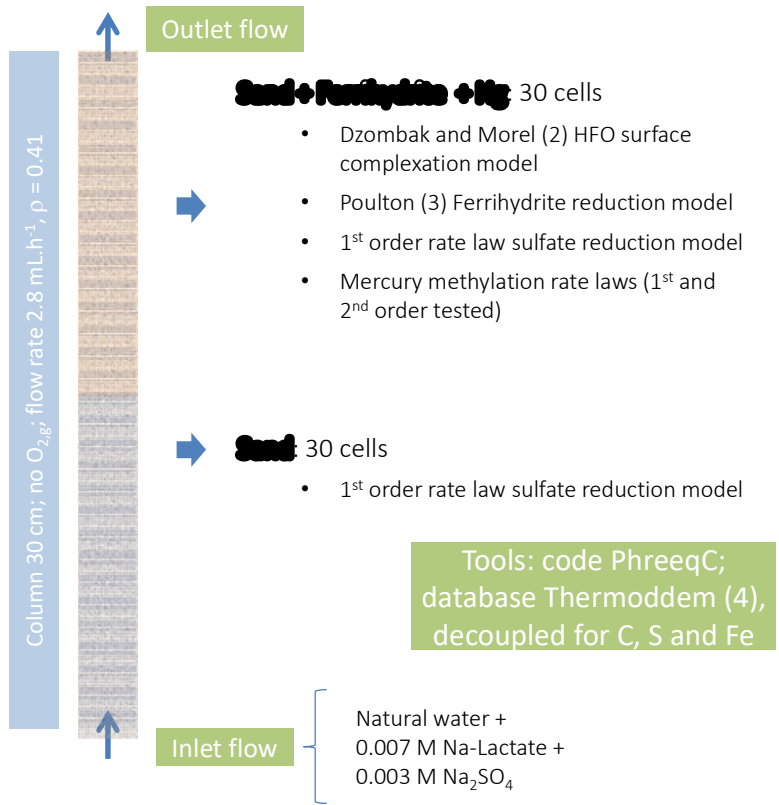
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 236 The possible formation of complexes at the ferrihydrite surface is implemented, using
 237 capacity of ferrihydrite, using the Dzombak and Morel (1990) model and database. Numerical
 238 modelling uses PhreeqC-2 code (Parkhurst and Appelo, 1999) and the Thermodem
 239 database (Blanc et al., 2012). The conceptual model is based on 1D-cartesian geometry, as
 240 displayed in Figure 4. A tracer test has been successfully simulated to verify the
 241 hydrodynamic set of parameters used.

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Figure 3 – Main reactions involved



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Figure 4 – Conceptual model

Table 2 – Main parameters for reactive transport modeling

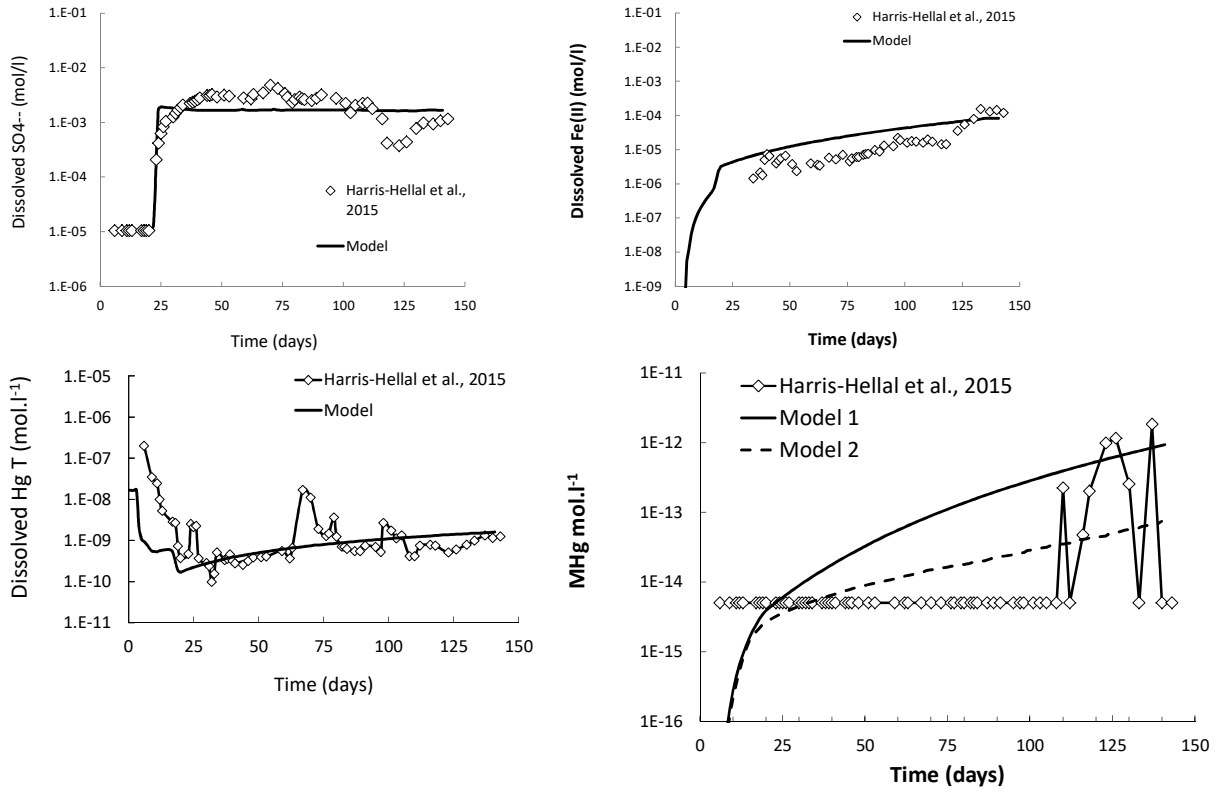
Chemical system			
Minerals			
Ferrihydrite	$\text{Fe}(\text{OH})_3 + 3\text{H}^+ = \text{Fe}^{+++} + 3\text{H}_2\text{O}$	$\text{Log}_{10}\text{K}^\circ = 3.40$	Blanc et al. (2012)
Mackinawite	$\text{FeS} + \text{H}^+ = \text{Fe}^{++} + \text{HS}^-$	$\text{Log}_{10}\text{K}^\circ = -3.54$	Blanc et al. (2012)
Schwertmannite	$\text{Fe}_8\text{O}_8(\text{OH})_6\text{SO}_4 \cdot 8\text{H}_2\text{O} + 22\text{H}^+ = 8\text{Fe}^{+++} + \text{SO}_4^- + 22\text{H}_2\text{O}$	$\text{Log}_{10}\text{K}^\circ = 8.95$	Blanc et al. (2012)
Calcite	$\text{CaCO}_3 + \text{H}^+ = \text{HCO}_3^- + \text{Ca}^{++}$	$\text{Log}_{10}\text{K}^\circ = 1.85$	Blanc et al. (2012)
Aqueous species			
Thermodynam database, decoupled	C decoupled into C(+4) and C(-4) S decoupled into S(+6) and S(-2) Fe decoupled into Fe(+2) and Fe(+3)	Percolating solution given Figure 2	
Surface complexation			
Ferrihydrite surface	$>\text{Fe}^z\text{OH} + \text{X}^z = >\text{FeOX}^{(z-1)} + (z-1)\text{H}^+$ $>\text{Fe}^w\text{OH} + \text{X}^z = >\text{FeOX}^{(z-1)} + (z-1)\text{H}^+$	$\text{X}^z = \text{Fe}^{++}, \text{Hg}^{++}, \text{Ca}^{++}, \text{SO}_4^-, \text{H}^+$	Dzombak and Morel (1990)
Mackinawite surface	$>\text{FeS} + \text{CH}_3\text{Hg}^+ = >\text{FeS} - \text{CH}_3\text{Hg}^+$	$\text{Log}_{10}\text{K}^\circ = 4.5$	This study
Kinetic transformations			
Sulfate reduction	$\text{SO}_4^- + 2\text{C}_3\text{H}_5\text{O}_3^- + 8\text{H}_2\text{O} = \text{HS}^- + 6\text{HCO}_3^- + 19\text{H}^+$	$k_{\text{sr}} = 6 \cdot 10^{-7} \text{ s}^{-1}$	Extracted from Bharati and Kumar (2012)
MeHg formation	Model1: $k_1 (\text{s}^{-1}) = [\text{Hg}(\text{HS})_2] \cdot k_{\text{sr}} \cdot 4.2 \cdot 10^5$		Bessinger et al. (2012)
Fe reduction	Model2: $\text{Cob-CH}_3 + \text{HS}^- + \text{Hg}^{++} = \text{Cob-HS} + \text{CH}_3\text{Hg}^+$ $k_{\text{fe}} (\text{s}^{-1}) = 0.92 \cdot 10^{-6} \cdot [\text{Ferrihydrite}] \cdot [\text{S}(-2)]^{0.5}$	$k_2 = 1.3 \cdot 10^{-7} \text{ s}^{-1}$	Heyes et al. (2006) Poulton (2003)
Physical parameters			
Porosity = 0.41	Extracted from a preliminary tracing test	0.41	This study
Inlet solution flow		2.8 mL/h	Hellal et al. (2015)

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4. Results and discussion

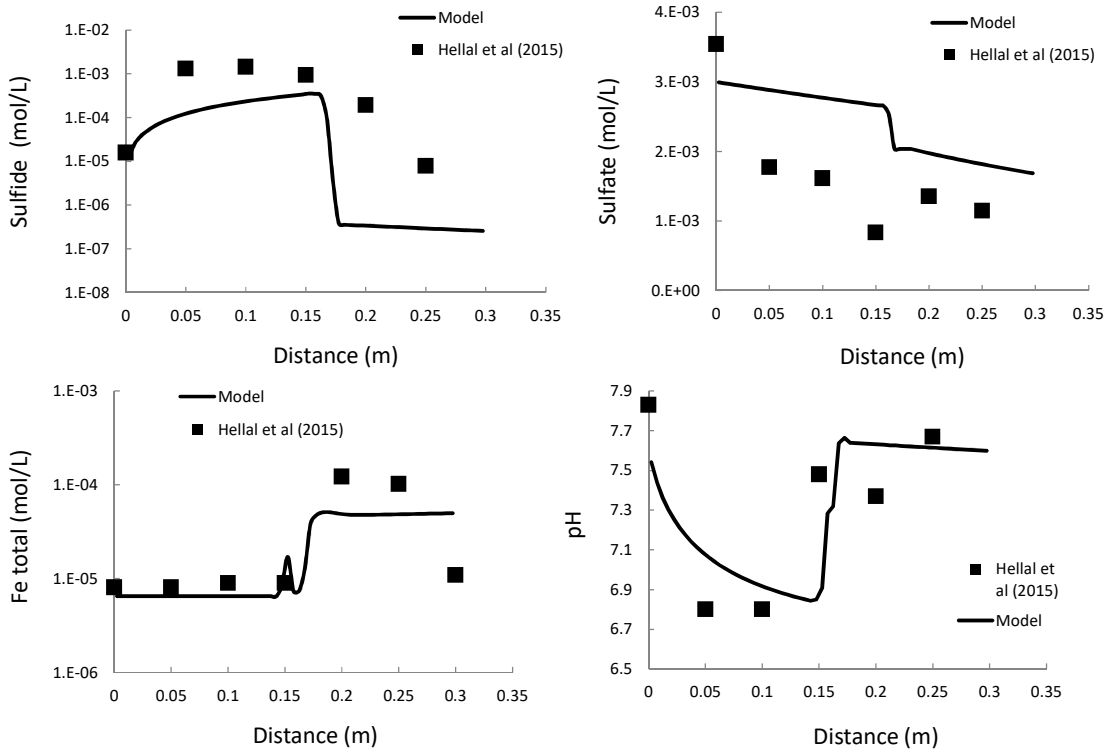
The results were first verified at the column breakthrough point (Figure 5) and along the column (Figure 6) for the longest reaction time (143 days). The reduction of sulfates was correctly reproduced, globally. In that regard, Bharati and Kumar (2012) experiment was selected because they were performing sulfate reduction by using lactate as substrate and carbon source, as in our case. However, sulfate reduction appears somewhat underestimated by the model, especially concerning sulfide production. The redox conditions in the column (and departure to equilibrium conditions) could be questioned in that regard. Dissolved Fe(+2) at the outlet was quite correctly predicted and calculations corresponding to the concentrations measured in the different septa even matched the abrupt increase observed in the ferrihydrite-loaded part of the column. Such increase happens during a period when calcite precipitates. It also corresponds to the precipitation of Mackinawite, observed in the experiments by Hellal et al. (2015), using Raman spectroscopy. From the reaction displayed in Table 2, mackinawite precipitation happens to consumes protons which increases pH and can lead induce the precipitation of carbonates.

For dissolved mercury (Figure 5), the total concentrations were correctly predicted. Methylmercury concentrations analyzed were somewhat bracketed by the calculation performed with the model proposed by Bessinger et al. (2012) and Heyes et al. (2006) (Model 1 and Model 2 in Figure 5, and Table 2 respectively). The lowest concentrations found using Heyes et al (2006) methylation rate law may possibly be explained because the first order rate constant reported in Table 2 represent a balance between both methylation and demethylation rates. Actually the global methylation budget usually arises from the competition between both mechanisms.



312 *Figure 5 – Concentration in dissolved elements analysed at the outlet of the column*

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Figure 6 – Concentration in dissolved elements in the length of the column, after 143 days. 0 (m) corresponds to the inlet solution

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321 **Conclusion**

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323 The results obtained here are in line with previous works from Bessinger et al. (2012) and
324 Leterme et al. (2014). However, it displays a rare comparison between experiment and
325 reactive transport modelling results. It confirms the rate obtained by previous authors
326 concerning the mercury methylation process and it brings a confirmation to the reaction
327 pathways first proposed by Hellal et al. (2015) to explain their evolutions. The selection of
328 thermodynamic properties for MeHg complexes gave the opportunity to test different writing
329 for the MeHg database. The testing favored the discarding of the dimethyl complex $(\text{CH}_3)_2\text{Hg}$
330 from the thermodynamic dataset. In addition, it enhances possible connections between
331 inorganic and organic dissolved carbon forms, from the point of view of methylation
332 processes. Such relations do probably not involve equilibrium reaction. There is a strong
333 need for additional experiment data to test such hypotheses, including measurements that
334 does not seems to be related, at first sight, like dissolved CH_4 concentrations, for instance.

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