



Mercury mobilization and speciation linked to bacterial iron oxide and sulfate reduction: A column study to mimic reactive transfer in an anoxic aquifer



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ABSTRACT

Mercury (Hg) mobility and speciation in subsurface aquifers is directly linked to its surrounding geochemical and microbial environment. The role of bacteria on Hg speciation (i.e., methylation, demethylation and reduction) is well documented, however little data is available on their impact on Hg mobility.

The aim of this study was to test if (i) Hg mobility is due to either direct iron oxide reduction by iron reducing bacteria (IRB) or indirect iron reduction by sulfide produced by sulfate reducing bacteria (SRB), and (ii) to investigate its subsequent fate and speciation.

Experiments were carried out in an original column setup combining geochemical and microbiological approaches that mimic an aquifer including an interface of iron-rich and iron depleted zones. Two identical glass columns containing iron oxides spiked with Hg(II) were submitted to (i) direct iron reduction by IRB and (ii) to indirect iron reduction by sulfides produced by SRB. Results show that in both columns Hg was leached and methylated during the height of bacterial activity. In the column where IRB are dominant, Hg methylation and leaching from the column was directly correlated to bacterial iron reduction (i.e., Fe^{II} release). In opposition, when SRB are dominant, produced sulfide induced indirect iron oxide reduction and rapid adsorption of leached Hg (or produced methylmercury) on neoformed iron sulfides (e.g., Mackinawite) or its precipitation as HgS. At the end of the SRB column experiment, when iron-oxide reduction was complete, filtered Hg and Fe concentrations increased at the outlet suggesting a leaching of Hg bound to FeS colloids that may be a dominant mechanism of Hg transport in aquifer environments.

These experimental results highlight different biogeochemical mechanisms that can occur in stratified sub-surface aquifers where bacterial activities play a major role on Hg mobility and changes in speciation.

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1. Introduction

In temperate continental watersheds, mercury (Hg) loading to freshwater ecosystems originates from atmospheric

deposition, mobilization from watersheds and groundwater discharges (Johannesson and Neumann, 2013). Several authors suggested that mobilized Hg leaves the watershed as Hg(II) complexed to dissolved organic carbon (DOC) compounds through overland flow and, to a lesser extent, groundwater flow (Krabbenhof et al., 1995; Babiarez et al., 2003; Brigham et al., 2009; Bradley et al., 2012; Lamborg et al., 2013).

Although several investigations have studied Hg cycling in continental aquifers (Dooley, 1992; Krabbenhof et al., 1992; Krabbenhof et al., 1995; Bollen et al., 2008; Bagnato et al., 2009; Bradley et al., 2012; Johannesson and Neumann, 2013; Lamborg et al., 2013; Guédron et al., 2014) our knowledge related to Hg reactivity, mobility and speciation in groundwater remains limited. Recently, Lamborg et al. (2013) studied the concentration and speciation of Hg in groundwater down-gradient from wastewater infiltration beds in Massachusetts. They observed substantial reduction of Hg(II) to Hg⁰ within an anoxic sediment zone when iron reduction was evident and suggested that anoxia and eutrophication in groundwater facilitate the mobilization and transport of natural and anthropogenic Hg from aquifers to freshwaters. Besides, Johannesson and Neumann (2013) highlighted through an in situ and reactive transport modeling study of Hg geochemical cycling in the Carrizo aquifer that Hg was chiefly complexed with dissolved sulfide rather than organic complexes. They also suggested that Hg was released to the aquifer groundwater by dissimilatory reduction of Fe(III) oxides/oxyhydroxides (goethite and hematite) and was removed along the flow path by adsorption onto goethite and hematite.

Although some information exists regarding Hg reactivity and mobility in aquifers, only few data exist regarding the role of bacteria in (i) these mobilization/sequestration processes and in particular in (ii) the production of monomethylmercury (MMHg), the neurotoxic organic form of Hg that bioaccumulates in the food webs (Ullrich et al., 2001; Žižek et al., 2007). Especially, little is known about the dual effect of iron- and sulfate-reducing bacterial activities in the Hg mobilization/retention and alkylation processes in aquifer environments.

In surface ecosystems (i.e., wetlands, river and lake sediments), Hg mobility is controlled by carrier phases such as dissolved organic matter (OM; mainly thiol groups) or colloidal manganese and iron oxides (Andersson, 1979; Khwaja et al., 2006; Neculita et al., 2005; Schuster, 1991; Wallschläger et al., 1998). Amorphous iron oxides are also known as major sorbents for Hg in soils and sediments as they have large surface areas (Stumm, 1992; Cornell and Schwertmann, 2003) and have been shown to be efficient Hg sorbents in iron-rich and OM-depleted mineral environments (Roulet and Lucotte, 1995; Roulet et al., 1998; Guedron et al., 2009). In subsurface aquifers, iron oxides can undergo non-reductive and reductive dissolution forming Fe^{II} and releasing associated contaminants (Luther et al., 1992). Direct microbial reduction is the dominant pathway for Fe^{III} reduction in non sulfidogenic anaerobic soils and sediments (Lovley, 1991; Lovley et al., 2000), whereas sulfide (S²⁻) drives much of Fe^{III} reduction in sulfur-rich sediments (Thamdrup et al., 1994). In iron-rich tropical ferrallitic soils, recent work has shown that Hg was also mobilized by bacterial iron reduction (Harris-Hellal et al., 2011). However, few studies have focused on Hg mobility and reactivity when iron and sulfate reduction occurs

simultaneously (Slowey and Brown, 2007). Recently, Yu et al. (2011) suggested that coexisting sulfate reducing bacteria (SRB) and iron reducing bacteria (IRB) populations in river sediments contribute to Hg methylation, possibly by temporally and spatially separated processes. Since methylation is governed by several factors including bacterial activity (mainly SRB and IRB – Benoit et al., 1999; Compeau and Bartha, 1985; Gilmour et al., 1992; Fleming et al., 2006; Kerin et al., 2006; King et al., 2000; Si et al., 2014) and Hg availability for methylation, Hg sorption processes in aquifers are determinant parameters for estimating its potential toxicity. In theory, sulfate reduction should occur where electron acceptors with a higher energy yield, are depleted, thus where Fe^{III} is not available; however aquifers can present heterogeneous materials with iron-rich zones, where IRB may be active, and iron-depleted zones, where SRB metabolism could be expressed. In such systems, dissolved sulfide and Fe^{II} can diffuse or be transported from a zone to another.

The aim of this study was to i) improve knowledge on Hg mobility in anoxic aquifers due to either direct iron oxide reduction by IRB or indirect reduction by sulfide produced by SRB and ii) to bring new information on the potential subsequent Hg methylation. An experimental column setup was designed to integrate both temporal and spatial dimensions, including heterogeneity in terms of Fe^{III} availability, in order to understand the kinetics and dynamics of Hg sorption, mobility and alkylation with regard to the surrounding geochemical environment. This work combines geochemical and microbiological approaches to understand the mutual catalysis processes implied in the speciation equilibria of Hg between solid and filtered phases (i.e., biosorption, solubilization versus sequestration: dual effect of S, Fe).

2. Materials and methods

Two identical glass columns with an ascendant water-flow, were filled in the lower half with sterile sand and in the upper half with a sterile mixture of sand and iron oxides, initially spiked with Hg(II). In one column, sulfate reduction was favored (SRB column) whereas iron-reducing activity was stimulated in the other column (IRB column). This experimental device enabled a comparison of the influence of the two different bacterial activities on Hg mobility in a heterogeneous system presenting an interface between iron-depleted and iron-rich solid phases. The IRB column was meant as a control column representing bacterial iron reduction only, whereas the SRB column combines both sulfate and iron reduction. Accordingly, the more thorough observations on bacterial diversity, Hg carrier phases, including SEM observations and Raman spectrometry were only carried out on the SRB column.

2.1. Column setup

Two thermostated (20 °C, water jacket) glass columns (internal volume = 400 mL, height = 30 cm, diameter 3.5 cm) were designed to follow iron oxide reduction in a continuous system containing different compartments that mimic heterogeneity of iron distribution in an aquifer and favoring either sulfate reduction (SRB column) or iron reduction (IRB column). Five septa set regularly (every 5 cm) along

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