Science of the Total Environment 539 (2016) 36–44

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Mercury (II) reduction and co-precipitation of metallic mercury on hydrous ferric oxide in contaminated groundwater

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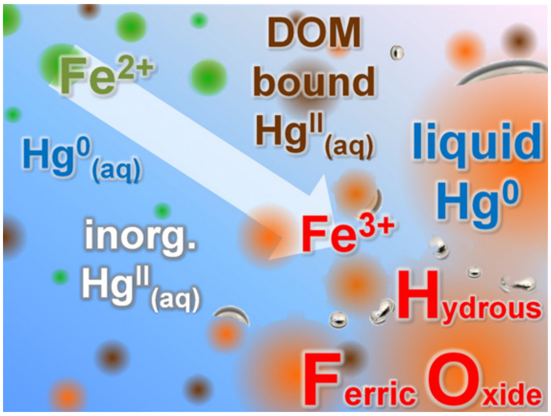
HIGHLIGHTS

- We analyzed Hg on hydrous ferric oxides (HFOs) from contaminated groundwater.
- Hg species were determined using thermo-desorption, CV-AAS, geochemical modeling.
- On HFO Hg was in elemental form (Hg^0) and showed concentrations of up to 4 wt.%.
- In solution mercury was present as inorganic Hg, humic matter bound Hg, and Hg^0.
- Aqueous Hg species were predicted well by geochemical model, Hg sorption was not.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 14 June 2015
Received in revised form 19 August 2015
Accepted 20 August 2015
Available online 6 September 2015

Editor: D. Barcelo

Keywords:
Elemental mercury
Hg thermo-desorption
Geochemical modeling
HgCl2
DOM bound mercury
Dissolved gaseous mercury

ABSTRACT

Mercury (Hg) speciation and sorption analyses in contaminated aquifers are useful for understanding transformation, retention, and mobility of Hg in groundwater. In most aquifers hydrous ferric oxides (HFOs) are among the most important sorbents for trace metals; however, their role in sorption or mobilization of Hg in aquifers has been rarely analyzed. In this study, we investigated Hg chemistry and Hg sorption to HFO under changing redox conditions in a highly $HgCl_2$-contaminated aquifer (up to 870 $\mu g\ L^{-1}$ Hg). Results from aqueous and solid phase Hg measurements were compared to modeled (PHREEQC) data. Speciation analyses of dissolved mercury indicated that Hg^{II} forms were reduced to Hg^0 under anoxic conditions, and adsorbed to or co-precipitated with HFO. Solid phase Hg thermo-desorption measurements revealed that between 55 and 93% of Hg bound to HFO was elemental Hg (Hg^0). Hg concentrations in precipitates reached more than 4 weight %, up to 7000 times higher than predicted by geochemical models that do not consider unspecific sorption to and co-precipitation of elemental Hg with HFO. The observed process of Hg^{II} reduction and Hg^0 formation, and its retention and co-precipitation by HFO is thought to be crucial in $HgCl_2$-contaminated aquifers with variable redox-conditions regarding the related decrease in Hg solubility (factor of ~10^6), and retention of Hg in the aquifer.

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http://dx.doi.org/10.1016/j.scitotenv.2015.08.116

1. Introduction

Mercury (Hg) is among the most toxic contaminants, but the actual toxicity and harmful potential are strongly dependent on its chemistry (UNEP 2002). Inorganic ionic, mainly divalent mercury, Hg^{II}, and metallic mercury, $Hg^0_{(l)}$, have been used in numerous industrial processes resulting in soil and groundwater contamination. In the environment, mercury is subject of several species transformation processes resulting in changes of mobility and toxicity of which the formation of methyl-Hg is most relevant for Hg uptake in aquatic food chains. As a type B metal, Hg shows strong affinity for sulfur and its transport in aquatic systems is mainly determined by sulfur bearing dissolved organic matter (DOM) (Ravichandran, 2004; Nagy et al., 2011). However, DOM concentrations in groundwater are usually low (<1 mg L^{-1}) (Malcolm, 1991). As a noble metal, Hg is easily reduced to its elemental form, either by humic matter enhanced photoreduction (Si and Ariya, 2011) or in oxygen depleted (subsurface) environments (Lamborg et al., 2013).

There are only few studies of mercury in groundwater that mainly focus on total or methyl-Hg. A summary of the existing work is given elsewhere (Barringer et al., 2013). Even fewer studies address the fate of $HgCl_2$ and Hg^0 in groundwater. Bollen et al. (2008) observed the formation of Hg^0 in aquifer sediments at a mercury(II)chloride ($HgCl_2$) contaminated site and dissolved gaseous mercury (DGM) has been shown to occur in an anoxic groundwater contaminated by a wastewater plume (Lamborg et al., 2013). Under anoxic conditions, iron (Fe) containing minerals are important electron acceptors (Ehrlich and Newman, 2008) for the microbial degradation of organic matter, and are dissolved as Fe^{II} ions (Liang et al., 1993). Upon contact with oxygen, Fe^{II} gets oxidized and starts to precipitate as ferrihydrite ($Fe(OH)_3$) and other amorphous or poorly crystalline hydrous ferric oxides (HFOs). HFO formation and dissolution is an important process in many aquifers (Herbert, 1996) and groundwater/freshwater interfaces (Dekov et al., 2014). Moreover, HFOs are known to be important temporary sinks, but also carriers of pollutants due to their large reactive surface areas including inner and outer sorption sites (Dzombak and Morel, 1990; Sparks, 2005). Hg sorbed to Fe-minerals can get exchanged (Jiskra et al., 2014), and dissolution of HFO can lead to the release of trapped Hg (Johannesson and Neumann, 2013). Large efforts were made in the past to determine sorption constants for many pollutants, including Hg (Dzombak and Morel, 1990), in order to predict their sorption behavior on HFO precipitates by geochemical modeling. Such constants are based on lab experiments with HFO derived from Fe(III) salts and equilibrated with Hg^{II} solutions (Dzombak and Morel, 1990). Other important Hg species such as DOM-bound Hg or Hg^0 were disregarded and possible effects on the oxidation state of Hg resulting from redox changes have been widely neglected. Less is known about the role of HFOs for Hg^{II} reduction, but recent laboratory studies (Charlet et al., 2002; Peretyazhko et al., 2006; Wiatrowski et al., 2009; Amirbahman et al., 2013; Pasakarnis et al., 2013) have shown the importance of Fe^{II} as a reducing agent for Hg^0 formation. Recently, Lamborg et al. (2013) found indications for the relevance of this process in the iron reducing zone of an anoxic aquifer. It is not known, however, how important HFOs are for precipitation and retention of Hg^0 in contaminated aquifers. In this study, we investigated the role of HFO as Hg sorbent in a $HgCl_2$-contaminated aquifer showing variable redox conditions. We analyzed Hg speciation in aqueous phase and on HFO, quantified Hg retained, and compared the results to those obtained by geochemical modeling to evaluate to what extent geochemical models are able to reproduce measured Hg compounds and their quantities.

2. Materials and methods

2.1. Sampling site

The sampling site (Fig. 1) is a former wood impregnation facility located in the Black Forest (Southern Germany). $HgCl_2$ had been used as a wood preservative for decades, resulting in extensive contamination of soil and groundwater. Hydrogeology of the site is characterized by late Quarternary fluvial sediments overlaying Paleozoic granite basement (LUBW, 2014). Part of the affected aquifer is rich in organic material (peat), which causes depletion of oxygen and temporary anoxic conditions. Multiple groundwater wells have been installed on the site for monitoring purposes, and a pump & treat remediation facility is operated. Water is pumped through high-density polyethylene (HDPE) pipes from several oxic wells (W2, W35–W38) and one mostly anoxic well W7a that becomes oxic when groundwater levels are low. W7a water can also mix with oxygen rich groundwater or river water, depending on groundwater levels and flow. This leads to periodic oxidation events and formation of HFO colloids and particles.

2.2. Sampling and sample treatment

Precipitate samples were collected from filters inside the pump & treat facility and from the temporarily anoxic well W7a. Filters inside the pump & treat facility consisted of six synthetic fiber filter pads with undefined pore size, that had been installed for 200 days in parallel between a mixing chamber for oxic- and anoxic groundwater and the treatment units (see also Figure S4). How many redox cycles well W7a went through during this time period was not monitored, but redox conditions inside the mixing chamber were always oxic. Filter pads were installed behind cartridge filters (5 μm) monitored for oversaturation by the plant operator, thus solely freshly precipitated, not yet coagulated material was obtained. Precipitates were washed off the filter pads using Milli-Q water (18.2 MΩ cm) and suspensions were centrifuged at 5000 rpm. The supernatant was discarded and the retained precipitate was stored in sealed polypropylene (PP) containers below 8 °C until further analysis. To obtain precipitate samples from the temporarily anoxic groundwater well 50 L of unfiltered water were collected in a PP container during a suboxic event (0.9 mg L^{-1} O_2, 9.7 °C). Sampling was done after stationary conditions of field parameters (pH, electric conductivity) were reached, using a 1.4 in. polybutylene terephthalate (PBT) groundwater testing pump (WP 4012, Whale Pumps, U.K.). Sample for extraction of precipitates was transported to the lab under oxic conditions at ambient temperature (~15 °C) to allow complete oxidation and HFO precipitation and filtered through 0.45 μm polyamide (PA) membrane filters within 48 h. Precipitates were rinsed from the filters with Milli-Q water, centrifuged, collected after the supernatant was discarded, split into 6 replicates, and stored in sealed PP containers below 8 °C until further analysis.

All water samples were taken in a 500 mL fluorinated polyethylene (FLPE) bottle, thoroughly washed with demineralized water and double distilled nitric acid (HNO_3), and preconditioned with sample water. Samples for determination of dissolved concentrations were filtered through 0.45 μm polyamide (PA) membrane syringe filters in the field directly after sampling. Total concentrations were determined from unfiltered samples and particulate concentrations were calculated by subtracting dissolved from total concentrations. To avoid precipitation subsamples for cation analysis were acidified immediately after extraction by adding one percent (*v*/*v*) of double distilled HNO_3 and stored in sealed PP containers below 8 °C until analysis. Subsamples for anion analysis were kept in air free, sealed PP containers below 8 °C until analysis. Because sampling was done in an oxic environment oxidation of reduced nitrogen forms to nitrate cannot be ruled out except for well 7a, where a field photometer was used to determine ammonium and nitrite in the field. However, Eh, pH, electric conductivity, temperature, and oxygen content were determined using an air free flow chamber to avoid contact with the atmosphere. Subsamples for total Hg and total filtered Hg determination were stabilized with 1/60 M $K_2Cr_2O_7$–HNO_3 in the field and oxidized in the lab with BrCl solution according to EN standard method 1483 (EN, European Committee for Standardization, 2007) and USEPA method 1631 (USEPA, Office of Science and