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Organic carbon induced mobilization of iron and manganese in a West Bengal aquifer and the muted response of groundwater arsenic concentrations

Harald Neidhardt [a,*], Zsolt Attila Berner [a], Dominik Freikowski [b], Ashis Biswas [c], Santanu Majumder [d], Josef Winter [b], Claudia Gallert [f], Debashis Chatterjee [e], Stefan Norra [a]

[a] *Institute of Mineralogy and Geochemistry, Karlsruhe Institute of Technology, Adenauerring 20b, D-76131 Karlsruhe, Germany*
[b] *Institute of Biology for Engineers and Biotechnology of Waste Water Treatment, Karlsruhe Institute of Technology, Am Fasanengarten, D-76131 Karlsruhe, Germany*
[c] *Department of Land and Water Resource Engineering, Royal Institute of Technology, Teknikringen 76, SE-100 44 Stockholm, Sweden*
[d] *Department of Chemistry, University of Girona, Campus Montilivi, 17071 Girona, Spain*
[e] *University of Kalyani, Department of Chemistry, Kalyani, 741235 Nadia, West Bengal, India*
[f] *Department of Microbiology - Biotechnology, Faculty of Technology, University of Applied Science, Hochschule Emden/Leer, Constantiaplatz 4, 26723 Emden, Germany*

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ABSTRACT

The exact circumstances that cause the widespread enrichment of Mn and As in groundwater of the Bengal Delta Plain (BDP) and many other Asian delta areas still remain a matter of debate in the scientific community. We conducted an *in situ* field experiment in the central BDP region to investigate the influence of organic matter on the mobility of Fe, Mn and As in shallow aquifers. The groundwater at our study site was initially characterized by a circum-neutral pH, low concentrations of O_2, NO_3^- and SO_4^{2-}, and increased Fe, Mn and As concentrations, reflecting reducing conditions in the aquifer. Since organic matter controls microbially mediated redox processes which are believed to result in the mobilization of Fe, Mn and As from Holocene aquifer sediments, an easily degradable carbon source (sucrose) was introduced into a shallow aquifer via four nested monitoring wells and distributed by circular pumping. Initial sucrose concentrations reached up to 2.55 mM in the local groundwater and induced a strong increase in the activity of indigenous microbes that decomposed the sucrose within the following 14 days stepwise into intermediate catabolic products (e.g., acetic acid), and finally to CO_2/HCO_3^-. The formation of organic acids was accompanied by a temporary decline in the pH and the redox potential, as well as an increase in the concentration of most major and trace elements in the groundwater by several times. While Mn concentrations rose up to 81.3 μM (representing a 7.5 fold increase), Fe (on average 96.7% Fe(II)) concentrations reached a considerable transient maximum of 1390 μM, which was 36 times higher than the initial baseline value. The most significant observation of this experiment is that the relative increments of dissolved As (on average 95.8% As(III)) reached between 19 and 49% only, which is in clear contrast to the pronounced mobilization of Fe, Mn and other trace elements. Changes in the groundwater composition during the experiment imply that the mobilization of Fe and Mn was primarily caused by a reductive dissolution of Mn-oxides and Fe-(oxyhydr)oxides, resulting from the stimulation of indigenous bacteria by the addition sucrose. In this context, the release of As can be attributed to the dissolution of Fe-(oxyhydr)oxides, which constitute the principal source of As in the aquifer sediments according to mineralogical and geochemical analyses. In contrast to the pronounced mobilization of Fe, the response of groundwater arsenic concentrations appeared to be muted, as indicated by subsequently declining As to Fe mol ratios that dropped one order in magnitude. The remarkable decoupling of As from Fe mobilization indicates that the aquifer sediments were apparently capable of compensating for the additional release of As. We attribute this As buffer potential to remaining Fe-minerals and potentially newly formed Fe(II)- and mixed Fe(II/III)-mineral phases, which were able to readily immobilize dissolved As. Sequential extraction results of the initial aquifer sediments further support this interpretation, revealing that up to 85% of the total As in the sediments was already present in adsorbed form, with Fe-minerals as principal hosts. Hence, the experimental data implies that a biogeochemically controlled environment of competing As release and retention arose after the addition of sucrose, where Fe-mineral phases played a key role in buffering the release of As. We further conclude that organic carbon limited aquifer systems in the BDP with increased As concentrations in groundwater may exhibit an unexpected buffer potential towards an additional As release, even when vast amounts of easily degradable organic carbon are introduced into the system.

* Corresponding author at: Department of Water Resources and Drinking Water, Eawag, Swiss Federal Institute of Aquatic Science and Technology, Überlandstrasse 133, 8600 Dübendorf, Switzerland. Tel.: +41 58 765 5578; fax: +41 58 765 5028.
E-mail address: harald.neidhardt@eawag.ch (H. Neidhardt).

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1. Introduction

1.1. Arsenic and manganese in the groundwater of the Bengal Delta Plain

Naturally occurring arsenic-rich groundwater threatens the health of millions of residents in the Bengal Delta Plain (BDP), which is situated in Bangladesh and the Indian state of West Bengal (Mukherjee and Bhattacharya, 2001; Ravenscroft et al., 2001). The chronic exposure to As in these countries gained notoriety because villagers preferentially use shallow groundwater as drinking water supply, resulting in an increased risk of cancer and the widespread occurrence of skin lesions (Bhattacharya et al., 2002; Charlet and Polya, 2006). According to the Indian standard specifications for drinking water (IS 10500 from 2012), the maximum concentration for total As in drinking water was recently set to 10 μg/L, but may be extended to a permissible limit of 50 μg/L in the absence of alternative drinking water sources. The WHO recommends a provisional guideline value of 10 μg/L (WHO, 2011). In addition to As, concentrations of dissolved Mn are in many cases elevated as well, which aggravates the situation. Although shallow groundwater in the BDP often exceeds the national guideline value with respect to As and Mn, the spatial distribution pattern of these two trace elements often differs (BGS and DPHE, 2001; van Geen et al., 2007; McArthur et al., 2012). While increased and anti-correlated Mn and As concentrations have also been reported from other delta and floodplain areas in SE Asia (Berg et al., 2001; Winkel et al., 2011), the underlying mechanisms of Mn mobilization and enrichment in groundwater as well as potentially toxic health effects have barely been investigated thus far. On the one hand, Mn serves as an essential nutrient, but on the other hand, chronic exposure to high concentrations was found to be associated with neurotoxic health effects (ATSDR, 2008). Recent studies strengthen the assumption that chronic exposure to elevated Mn concentrations causes neurological effects in children, which may be additionally superimposed by elevated As concentrations (Khan et al., 2011; Wasserman et al., 2011). The Indian drinking water standard (IS 10500 from 2012) set the maximum admissible Mn concentration in drinking water to 0.1 mg/L, which may be extended to 0.3 mg/L in cases where no alternative drinking water sources are available. In the latest WHO guidelines for drinking water quality, the formerly specified provisional guideline value for Mn of 0.4 mg/L was discarded on the grounds that such concentrations would usually not occur in drinking water (WHO, 2011). However, Mn concentrations in the groundwater of most reducing shallow aquifers in the BDP clearly exceed this value (McArthur et al., 2012).

1.2. The role of organic matter in the mobilization of iron, manganese and arsenic

In the BDP, the release of both Mn and As is believed to be closely linked to the decomposition of organic matter by anaerobic microbes that use Mn(IV) and Fe(III) as terminal electron acceptors (TEA) (Nickson et al., 1998; Rowland et al., 2009; Borch et al., 2010). Manganese-oxides, and in particular Fe-(oxyhydr)oxides, were identified as primary As-hosting mineral phases in the sediments of the BDP (Harvey et al., 2005; McArthur et al., 2008). Hence, the microbially mediated reductive dissolution of Mn- and Fe-(oxyhydr)oxides supposedly causes a concurrent release of Mn(II) and Fe(II) into the groundwater, which is accompanied by the passive mobilization of adsorbed and/or co-precipitated As (Lovley et al., 2004; Konhauser et al., 2011). In addition, some microbes are able to reduce As(V) via detoxification or respiration pathways, which might influence its toxicity (Smith et al., 1992) and its mobility within aquifer systems, depending on the prevailing hydrogeochemical conditions (Dixit and Hering, 2003; Oremland and Stolz, 2005). Available organic matter triggers geomicrobiological processes, while the interplay of local hydrological and geochemical conditions fosters the development of specific redox zones in different parts of the aquifer (McArthur et al., 2004). As soon as microbes start using Mn(IV), Fe(III) and/or As(V) as TEA, these elements are likely to become mobilized (Stüben et al., 2003). The availability of organic carbon either in the form of dissolved organic carbon (DOC) in groundwater, or as sedimentary organic matter, is considered to be a limiting factor for microbially mediated redox reactions in aquifer systems (Radloff et al., 2008). Thus, it can be expected that most biogeochemical processes involved in the mobilization of Fe, Mn and As take place within the near surface sediments, where the pool of organic carbon is not yet exhausted (Polizzotto et al., 2005). An additional supply of organic matter (caused for example by surface recharge during irrigation and monsoon flooding, or by the drawdown of organic-rich water in areas of extensive pumping) may promote a release of supplemental amounts of Fe, Mn and As and into the groundwater as suggested by several studies conducted in West Bengal and Bangladesh (Harvey et al., 2002; Neumann et al., 2009; Sutton et al., 2009; Farooq et al., 2010). However, the Fe, Mn and As mobilization potential of allochthonous organic carbon strongly depends on various factors, such as reactivity and concentration, as well as the prevailing geomicrobial and geochemical environment (Rowland et al., 2009; Wolf et al., 2009; Selim Reza et al., 2010). Besides, other potential mobilization mechanisms and sources must be taken into account as well when investigating a specific study site or area, especially in the case of As. For example, thermal springs or anthropogenic sources like heavy industry, mining activities or agricultural fertilizer application may locally contribute to the problem of increased As groundwater concentrations (Matschullat, 2000; Farooqi et al., 2009). After mobilization, slow groundwater flow is believed to favor the accumulation of mobilized trace elements in the characteristically flat delta plain (Michael and Voss, 2009; Mukherjee et al., 2009).

1.3. Study aim

In contrast to the extensively investigated distribution and enrichment of As in groundwater of the BDP, there is a substantial lack of studies that consider the occurrence and health effects related to increased Mn concentrations. Laboratory column and batch experiments indicate, without a doubt, the potential role of geomicrobiological processes in the mobilization of As (Islam et al., 2004; Radloff et al., 2008), but only a few field experiments have been carried out so far in the BDP to directly prove and document the actual role of such mechanisms in the occurrence of arsenic-rich groundwater (Harvey et al., 2002; Saunders et al., 2008). Supplemental microbial column experiments indicated a significant biogenic mobilization potential for Fe, Mn and As in the aquifer sediments from our study site (Freikowski et al., 2013). We have therefore performed an *in situ* field experiment in the central BDP to stimulate the activity of indigenous microbes by providing sucrose as an easily degradable carbon source. The subject of this experiment was to verify the outcomes of the complementary column experiments and to characterize the biogenic mobilization potential of geogenic As and Mn in a typical shallow aquifer under field conditions.

2. Methods

2.1. Coring and multi-level well installation

Our study site is located at the periphery of Chakudanga (N23°04′58″, E88°38′13″), a small farming village in the Nadia district of West Bengal, India (Fig. 1). It is situated about 12.5 km to the east of the city of Chakdah, a well-known As hot spot area (Charlet et al., 2007). Five nested monitoring wells with well screens located at different depth intervals (Fig. 2) were installed according to common practice (well design after Lapham et al., 1997). All wells are equipped with a bottom sump 100 cm in length with a well screen above (slit width: 2 mm, length: 3 m, diameter: 7.5 cm; except central well A, where the well screen is 9 m in length with a diameter of 20 cm). The well screens are surrounded by filter gravel, which is separated from the PVC casing above by a 30 cm bentonite seal. At the surface, the well