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Monsoonal influence on variation of hydrochemistry and isotopic signatures: Implications for associated arsenic release in groundwater

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S U M M A R Y

The present study examines the groundwater and surface water geochemistry of two different geomorphic domains within the Chakdaha block, West Bengal, in an attempt to decipher potential influences of groundwater abstraction on the hydrochemical evolution of the aquifer, the effect of different water inputs (monsoon rain, irrigation and downward percolation from surface water impoundments) to the groundwater system and concomitant As release. A low-land flood plain and a natural levee have been selected for this purpose. Although the stable isotopic signatures of oxygen ($\delta^{18}O$) and hydrogen ($\delta^{2}H$) are largely controlled by local precipitation, the isotopic composition falls sub-parallel to the Global Meteoric Water Line (GMWL). The Cl/Br molar ratio indicates vertical recharge into the wells within the flood plain area, especially during the post-monsoon season, while influences of both evaporation and vertical mixing are visible within the natural levee wells. Increase in mean DOC concentrations (from 1.33 to 6.29 mg/L), from pre- to post-monsoon season, indicates possible inflow of organic carbon to the aquifer during the monsoonal recharge. Concomitant increase in As_T, Fe(II) and HCO_3^- highlights a possible initial episode of reductive dissolution of As-rich Fe-oxyhydroxides. The subsequent sharp increase in the mean As(III) proportions (by 223%), particularly in the flood plain samples during the post-monsoon season, which is accompanied by a slight increase in mean As_T (7%) may refer to anaerobic microbial degradation of DOC coupled with the reduction of As(V) to As(III) without triggering additional As release from the aquifer sediments.

1. Introduction

In the Bengal Delta Plain (BDP), groundwater arsenic (As) concentrations have been found to frequently exceed the WHO drinking water guideline of 10 μg/L (WHO, 2011). Amongst other countries worldwide, parts of SE Asia including India and Bangladesh are facing severe threats of limited As safe drinking water sources (Nath et al., 2008a; van Geen et al., 2008; Fendorf et al., 2010; Datta et al., 2011). Toxic inorganic forms, arsenite [As(III)] and arsenate [As(V)], are the most dominant species of As in groundwater (Majumder et al., 2014). The concentration of organic As species are negligible throughout the BDP aquifers (Sharim et al., 2002; Gault et al., 2005). This situation is currently affecting the health of millions of people and has become one of the world's worst health catastrophes (Smith et al., 2000; Nriagu et al., 2007).

It has been proposed that the local groundwater pumping for irrigation and/or community drinking water supply may draw young, organic-rich water into the shallow aquifers (Neumann et al., 2010), accelerating the release of As to groundwater

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(Harvey et al., 2002). The organic carbon transported in this process can be used as an electron donor in microbially mediated redox reactions where metal reducing bacteria are believed to play a key role in As mobilization (Islam et al., 2004). In addition, ponds can act as potential contributors to groundwater recharge when they are hydraulically connected with the underlying shallow aquifers (Lawson et al., 2013). Wetlands and ponds are known to serve as potential sources of infiltrating dissolved organic carbon (DOC), especially during monsoon rains, when the surface recharge increases (Kocar et al., 2008; Polizzotto et al., 2008; Lawson et al., 2013). However, the potential influence of ponds as a source of organics to underlying aquifers is still a matter of controversy and speculation (e.g., Harvey et al., 2006; Sengupta et al., 2008; Neumann et al., 2010; Datta et al., 2011; McArthur et al., 2011) and certainly needs further investigations.

In the BDP, several studies have been conducted showing the relevance of isotopic proxies in groundwater to delineate its hydrogeological environment and recharge processes in As-enriched aquifers (Shivanna et al., 1999; Aggarwal et al., 2000; Basu et al., 2002; Harvey et al., 2002; Klump et al., 2006; Sengupta et al., 2008; Sikdar and Sahu, 2009; Saha et al., 2011). Oxygen ($\delta^{18}O$) and hydrogen ($\delta^{2}H$) stable isotopic analysis have been successfully established as methods of choice for the investigation of groundwater flow systems (Chen et al., 2006; Zhu et al., 2007; Datta et al., 2011; Xie et al., 2012). Due to the conservative behavior of $\delta^{18}O$ and $\delta^{2}H$, mixing models can be applied as an additional key feature in hydrogeochemical studies (Clark and Fritz, 1997). Thus, stable isotopic ratios of groundwater can yield valuable information complementary to the elemental hydrogeochemistry, allowing to understand the geological alterations and aquifer dynamics (Soulsby et al., 2000; Mukherjee et al., 2007; Sengupta et al., 2008; Saha et al., 2011). In addition, other naturally occurring environmental tracers such as chloride (Cl^-) or bromide (Br^-) and the Cl/Br molar ratio has been used to determine modes and rates of groundwater recharge (Allison and Hughes, 1978; Whittemore and Pollock, 1979; Phillips, 1994; Davis et al., 1998; Zagana et al., 2007; Katz et al., 2011). Hydrochemical processes can influence the Cl/Br ratio in groundwater during the course of variable solute transport and recharge processes (Cartwright and Weaver, 2005; Cartwright et al., 2006; Zhu et al., 2007). The Cl/Br ratio is useful to distinguish different water sources. Since Cl^- and Br^- represent stable and conservative elements in groundwater, changes in the Cl/Br ratio can be applied to delineate the nature of groundwater recharge as well as the extent of mixing (Whittemore and Pollock, 1979; Katz et al., 2011; Xie et al., 2012).

In spite of considerable progress towards understanding As mobilization processes in the aquifers, not much has been reported on the monsoonal rainfall and related recharge processes as a potential controlling factor of As release (and its speciation changes). The current study combines hydrochemical and isotopic data collected from wells within a low As bearing natural levee and a high As flood plain area to investigate the impact of monsoonal recharge processes on As release and its speciation changes. Furthermore, an attempt is made to relate the diverse geomorphology of the study area to the subsurface geochemistry of the groundwater. This study further depicts possible redox interactions between As and DOC in the aquifer.

2. Study area

The study area (part of Chakdaha block, ~65 km north of Kolkata; area ~150 km^2) is located in the alluvial plain of the Ganges river delta in Nadia district, West Bengal, India, which is known for the widespread occurrence of high As concentrations in groundwater (Bhattacharyya et al., 2003; Charlet et al., 2007; Majumder et al., 2010, 2013, 2014) (Fig.1). A field survey conducted in 2010 as part of this study recorded areas of low flat relief (average ~9 m above mean sea level) flood plains as well as high relief (average ~12 m above mean sea level) natural levees.

The flood plain area is adorned with impounded surface water bodies such as ponds with varying shapes, sizes and depths which are surrounded by rice fields and partly non-arable lands (Nath et al., 2010). Surface water bodies are considered as local recharge sites for shallow aquifers (Ahmed et al., 2004). These water bodies also have a social importance and are often used for jute retting, cattle bathing and aquaculture (Farooq et al., 2010).

A natural levee is an upland terrace which is predominantly used for the construction of roads and highways. The area is more densely inhabited along with relatively lesser number of ponds.

The regional annual rainfall ranges between 1295 and 3945 mm (Nath et al., 2008b), where 90% of the precipitation occurs during the monsoonal months (considering the actual monsoon to prevail between June through September). Recharge in the study area is governed by monsoonal rain and groundwater abstraction in the Nadia district was estimated to be 1×10^{-8} m^3/s/m^2 (Michael and Voss, 2009). Groundwater constitutes an important source of irrigation water, especially during the dry season (summer) paddy cultivation (Chatterjee et al., 2010). Considerable water table fluctuations occur between the pre- and post-monsoon seasons. Pre-monsoon water tables are generally lower (2.2–5.5 m, bsl) in comparison to the post-monsoon (0.1–6.4 m, bsl) season, while fluctuations of groundwater levels are more pronounced in the flood plain area than in case of the natural levee (Nath et al., 2008b).

Apart from a clay layer at the surface (down to ~5 m), the lithology of the flood plain is dominated by medium to coarse sands down to the depth of ~80 m and gravels at a depth of 125 m (Sarkar, 2012). In case of the natural levee, interchanging sequence of clay (hard and soft) and sand (mostly fine) layers are present throughout the lithological strata down to ~125 m (Sarkar, 2012). Color of the sediments within the flood plain is blackish gray (reducing sediments) where maximum groundwater As concentration is up to 300 μg/L. The color of the sediments in natural levee boreholes between 5 and 35 m depth is off-white where maximum groundwater As concentration reaches up to 60 μg/L. The general mineralogy of the study area is dominated by detrital quartz followed by feldspar, carbonates (calcite), mica and chlorite (clinochlore). Traces of Fe-oxides (magnetite, hematite), garnet (almandine), biotite (phlogopite), chloritoid and actinolite could be identified. High contents of smectite and carbonates are also found that indicate deposits from River Ganges (Datta and Subramanian, 1997; Allison et al., 2003; Heroy et al., 2003; Neidhardt et al., 2013).

Organic carbon is either available in the form of DOC in groundwater, or as sedimentary organic matter (SOM) in the aquifer systems. Additional sources of organic matter are surface recharge during irrigation and monsoon flooding and the drawdown of organic-rich water in the areas of extensive pumping (Harvey et al., 2002; Sutton et al., 2009; Farooq et al., 2010; Neumann et al., 2010).

3. Methods

Groundwater samples have been collected from wells in the flood plain ($n = 21$ and 22 in the pre- and post-monsoon season, respectively) as well as from wells located in the natural levees ($n = 10$ and 13 wells during pre- and post-monsoon season, respectively) for hydrochemical and stable isotopic ($\delta^{18}O$ and $\delta^{2}H$) analyses. In this study, pre-monsoon (PRM) indicates samples collected in April–May and post-monsoon (PSTM) in December. In addition, samples have been collected from four ponds – two