



# Coupling fractionation and batch desorption to understand arsenic and fluoride co-contamination in the aquifer system



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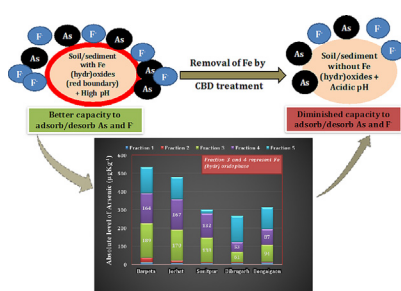
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## HIGHLIGHTS

- Organic matter, clay and Fe (hydr) oxide content governs partition coefficient of As.
- Outer and inner surface complexed As were easily leachable but small As reserves.
- Fe (hydr)oxide bound arsenic was the most prominent single redox dependent fraction.
- Fe (hydr)oxide fraction play the major role in co-evolution of As and F<sup>-</sup>.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The present work is an attempt to study As and F<sup>-</sup> coevality using laboratory based assays which couples fractionation and batch dissolution experiments. Sequential extraction procedure (SEP) resulting into five “operationally defined phases”, was performed on sediment and soil samples collected from the Brahmaputra flood plains, Assam, India. High correlation between the Fe (hydr)oxide fraction and total As content of the soil/sediment sample indicates the involvement of Fe (hydr)oxides as the principal source of As. F<sup>-</sup> being an anion has high potential to be sorbed onto positively charged surfaces. Findings of the SEP were used to design the batch desorption experiments by controlling the Fe (hydr)oxide content of the soil/sediment. Desorption of As and F<sup>-</sup> was observed under acidic, neutral and alkaline pH from untreated and Fe (hydr)oxide removed samples. Highest amount of As and F<sup>-</sup> were found to be released from untreated samples under alkaline pH, while the amount leached from samples with no Fe (hydr)oxide was low. The study showed that the Fe (hydr)oxide fraction commonly found in the soils and sediments, had high affinity for negatively charged species like F<sup>-</sup> oxyanions of As, AsO<sub>4</sub><sup>3-</sup> (arsenate) and AsO<sub>3</sub><sup>3-</sup> (arsenite). Fe (hydr)oxide fraction was found to play the major role in co-evolution of As and F<sup>-</sup>. Two sorption coefficients were proposed based on easily leachable fraction and As present in the groundwater of sampling location for understanding of contamination vulnerability from the leaching.

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## 1. Introduction

Arsenic and fluoride are reported to be two of the most common

geogenic inorganic pollutants in groundwater, in many regions of the world (Farooqi et al., 2007; Armienta and Segovia, 2008; Kim et al., 2012; Kumar et al., 2016a). Arsenic is a known carcinogen in human beings (Kumar et al., 2010a), while  $F^-$  cripples the body by causing fluorosis (Fantong et al., 2010). Of late some of the studies have pertained to the phenomenon of “co-occurrence” of the two contaminants as it represents a greater danger to human health and society (Armienta and Segovia, 2008; Gomez et al., 2009; Kim et al., 2012; Kumar et al., 2016a). The amount of As adsorbed or desorbed has been found to be controlled by the Fe content of the aquifer materials and the sediments (Smedley and Kinniburgh, 2002; Bhattacharya et al., 2006; Sharif et al., 2008). Co-occurrence of the two pollutants has been found to be more common in the arid parts of the world where rock-water interaction is adequate and the groundwater condition is oxidizing. Regions like Arizona and California in the USA (Levy et al., 1999; Kim et al., 2012), Mexico (Armienta and Segovia, 2008; Kim et al., 2012), Argentina (Smedley and Kinniburgh, 2002; Bhattacharya et al., 2006; Gomez et al., 2009; Kim et al., 2012), China (Currell et al., 2011), Pakistan (Farooqi et al., 2007; Kim et al., 2012) thus have acknowledged areas of As- $F^-$  co-occurrence. Although co-occurrence is more common in arid oxidizing conditions, yet some notable cases of As and  $F^-$  co-occurrence involving reducing aquifers include three basins in China, the Hetao (Guo et al., 2008; He et al., 2009; Deng et al., 2009; Kim et al., 2012), the Huhhot and (Smedley et al., 2002; Kim et al., 2012), the Datong (Guo et al., 2003; Kim et al., 2012) basins along with Montana, USA (Nimick, 1998; Kim et al., 2012). In India although both As (Singh, 2004; Acharyya, 2005; Kumar et al., 2010, 2016b; Sailo and Mahanta, 2014; Das and Kumar, 2015; Das et al., 2016) and  $F^-$  have been detected (Saxena and Ahmed, 2001, 2002; Das et al., 2003), yet co-occurrence studies are missing and the lacunae requires urgent attention.

It has been reported that in natural media like groundwater, metal contaminants could undergo reactions with ligands in water and with surface sites on solid materials present in the water (EPA, 2005). The metal that is bound to the solid matrix is termed “sorbed”, and such reactions are termed as sorption reactions (EPA, 2005). The partition coefficient ( $K_d$ ) or the ability of a contaminant to separate out into the groundwater system depends on a number of factors. The total concentration of the pollutant in the soil/sediment is not an accurate indicator of their leaching potential to contaminate groundwater. For every particular metal,  $K_d$  values in soil actually depend on various geochemical characteristics of the soil as well as the pore water. In the case of As, total As content, pH, organic matter content, CEC, presence of Fe and Al oxides, clay content, grain size, parent material are some of the factors which can influence the leaching potential (Janssen et al., 1997; Smedley and Kinniburgh, 2002; Carlon et al., 2004; Lee, 2006; Chen et al., 2009; Yang et al., 2012).

One of the primary factors which governs the mobilization of contaminants like As and  $F^-$  is their distribution in different soil/sediment phases (Tessier et al., 1979). Actual toxicity of many contaminants like As which occur in soils and sediments have been found to be dependent on the relative ease with which the fractions leach out of solid phase rather than their total concentrations (in soil, sediments and minerals) (Wenzel et al., 2001; Kumar et al., 2009). Therefore in light of the above factors, it is essential to understand phase distribution of different fractions of “interest” in soil and aquifer materials. Sequential extraction procedure (SEP), is one of the most well established methods for extracting and understanding these “operationally defined phases” or fractions of soils/sediments with the help of “reagents of increasing dissolution strength” under laboratory conditions (Wenzel et al., 2001). However, field conditions present a completely different perspective in

comparison to the laboratory environment as the former is much more complex, and cannot be predicted or controlled. Although examination of aquifer materials provides a better understanding of the actual groundwater environment, yet roles of soil and sediment cannot be neglected. This may be attributed to two main reasons, viz., first that both soils and sediments undergo deposition and compaction to form aquifers in the future and secondly, they provide a better insight into the role of anthropogenic activities in the particular region.

Physico-chemical parameters like pH and alkalinity have been found to positively affect the mobility of As and  $F^-$  in groundwater (Smedley and Kinniburgh, 2002; Kim et al., 2012). Batch sorption/desorption and column experiment based studies to understand As and  $F^-$  co-occurrence are few in number but present a much deeper understanding of release and co-occurrence mechanisms that may be further verified in the natural settings. It is imperative to realise that both As and  $F^-$  released into the aqueous solution from adsorption surfaces and further resulting ionic species will be re-adsorbed depending on saturation conditions of the groundwater and availability of adsorptive sites. Thus an effort is required to understand the dynamics of origin from one phase to adsorption to another. However, very few laboratory based studies have attempted to understand the mobility dynamics and co-occurrence of As and  $F^-$  around the world and are ironically lacking in India which is a hotspot of As contamination. A batch desorption study in the alluvial plains of Mankyeong river by Kim et al. (2012) reported that hydrolysis of Fe (hydr) oxides released As and  $F^-$  under reducing conditions, however the same study also found that under oxidizing conditions, increase in pH was the main mode of As and  $F^-$  mobilization. The later phenomenon was attributed to the achievement of the “Point of Zero Charge (PZC)” with an increase in pH. Metal (hydr)oxides like those of Fe have an innate positive charge in a pH range from <7 to about 8.5, increase in pH results in development of a net negative charge resulting in the desorption of negative ions like As oxyanions and  $F^-$ . The Brahmaputra Flood Plains (BFP) of Assam, India is a very large region with a dominantly alluvial condition and such a detailed study as the one cited above is lacking. The population is also at risk from drinking As and  $F^-$  contaminated groundwater as both these pollutants have been reported from this region (Singh, 2004).

Works on naturally porous mediums like soil and sediments based on the sorption coefficients and phase distribution of As and  $F^-$  have received much less attention. Soil types and conditions are therefore important considerations. Since increasing trends of pesticide and fertilizer usage affect the groundwater As levels (Davenport and Peryea, 1991); there is a need to understand contributing factors and the mass balance involved in mobilization of As and  $F^-$  in groundwater. Thus we made an attempt to understand the distribution of different phases in the soil and sediments of the region, correlation of Fe on total As, leaching of As and  $F^-$  in the system and pH change related mobilization of As and  $F^-$  in the groundwater from porous medium.

## 2. Materials and methods

### 2.1. Groundwater, sediment sampling, and analyses

Two grab river sediments [Dibrugarh (SD1) and Bongaigaon (SD2)] and three soil grab samples [Jorhat (S1), Sonitpur (S2) and BARPETA (S3)] were collected from the BFP during 2014 (Supplementary Fig. 1, Table 1). The soil and sediment samples were brought to the laboratory and dried at 50 °C for 24 h and stored at 4 °C until further analysis (Kim et al., 2012). Detection of elements was done by scanning electron microscope coupled with an energy dispersive X-ray analyzer (SEM EDX, JEOL, JSM-6390LV, Japan).

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