



## Ground water geochemistry of Ballia district, Uttar Pradesh, India and mechanism of arsenic release

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### ABSTRACT

Threat to human health worldwide due to the natural contamination of arsenic in ground waters has led to extensive studies on factors controlling the distribution of arsenic and conditions leading to arsenic mobilization in different arsenic contaminated areas. Another aspect of the arsenic crisis, especially in South Asia, is the degree of spatial variability of ground water arsenic concentrations. Thus it becomes necessary to study the source and the processes involved in arsenic mobilization into ground water under such conditions. An arsenic contaminated area namely, Ballia district of UP was chosen for this study. A set of 56 samples were collected from India Mark II hand pumps (30–33 m depth) thrice in a year namely pre-monsoon (April '07), monsoon (July '06) and winter seasons (December '06). Nine samples were also collected from deep bore well hand pumps (66–75 m) to study the difference in geochemistry with the shallow pumps. Various water quality parameters like As(III), As(V), sulfate, nitrate, phosphate, bicarbonate, ammonia, were determined. Arsenic concentrations ranged from 0 to 468  $\mu\text{g L}^{-1}$  in ground water collected from depths of 30–33 m. In the deeper wells (66–75 m), arsenic concentrations ranged from 12 to 20  $\mu\text{g L}^{-1}$ . Most samples contained both As(III) and As(V) and the concentration of As(III) was generally equal/higher than As(V). Not much variation of arsenic concentration was observed when sampled in summer, monsoon and winter seasons. Correlation studies among various water quality parameters revealed that reductive dissolution of FeOOH was the most probable mechanism for release of arsenic.

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### 1. Introduction

The presence of arsenic in ground water has been reported from many parts of the world particularly in the Bengal delta and Bangladesh (Berg et al., 2001), China (Kinniburgh and Smedley, 2001), Vietnam (UNESCAP-UNICEF-WHO, 2001) and Nepal (Tandukar et al., 2001). Arsenic contamination in India is well documented (Datta and Kaul, 1976; Garai et al., 1984; Dhar et al., 1997; Chakraborti et al., 2002, 2003). It is reported that parts of all the states and countries surveyed in the Ganga–Meghna–Brahmaputra (GMB) plain, which has an area of approximately 500,000  $\text{km}^2$  and a population over 500 million, are at risk from ground water arsenic contamination (Chakraborti et al., 2004). However, recent studies by Acharyya and Shah (2004, 2005, 2007) and Shah (2008) have shown that arsenic contamination in Middle Ganga plains are restricted to narrow entrenched channels, and major part of the Ganga plains' interfluvial upland is found to be unaffected, thus questioning the extent of population at risk in this re-

gion. Current knowledge on the contamination status of arsenic in ground water in five states of India namely, Uttar Pradesh, Bihar, Jharkhand, Assam and West Bengal has been discussed in detail (Nickson et al., 2007). Recently, Ahamed et al. (2006) conducted a survey in Ballia, Gazipur and Varanasi districts of Uttar Pradesh. Analyses of 4780 tube well water samples revealed that arsenic concentrations exceeded 10  $\mu\text{g L}^{-1}$  in 46.5%, 50  $\mu\text{g L}^{-1}$  in 26.7% and 300  $\mu\text{g L}^{-1}$  in 10% of the samples. It is reported that in Ballia district, around 4.4% of the sources contained arsenic concentration >50  $\mu\text{g L}^{-1}$  (Nickson et al., 2007). It is well known that consumption of arsenic contaminated ground water leads to chronic health effects. Signs of chronic arsenicalism include dermal lesions, peripheral neuropathy and skin cancer. These clinical symptoms, especially dermal lesions (the most commonly observed symptom) generally occur after some years of consumption of arsenic contaminated drinking water. The upper permissible limit of arsenic in potable water is 50  $\mu\text{g L}^{-1}$  in India, Bangladesh and some other countries. WHO (2004) recommended reduction of this limit to 10  $\mu\text{g L}^{-1}$ , which has been endorsed by BIS (2003). The permissible limit of arsenic concentration in potable water is recommended at 10  $\mu\text{g L}^{-1}$  in India.

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In India and Bangladesh, the problem of arsenic in ground water arises because of an unfortunate combination of three factors: a source of arsenic present in the aquifer sediments, its mobilization into the ground water & the use of arsenic-rich water for drinking. A detailed analysis by the British Geological Survey (BGS) has shown that water from shallow aquifers with recent alluvial sediments carry distinctly higher (arsenic) than the water from deeper aquifers with presumed pre-Holocene sediments: only 1% of wells in the depth range of 150–200 m have aqueous arsenic above  $50 \mu\text{g L}^{-1}$  (BGS/DPHE, 2001). The BGS study reveals relationships between the occurrence of aqueous arsenic, the geology, geomorphology and hydrogeology of the area, as well as land and water use. The role of quaternary stratigraphy on arsenic contaminated ground water from parts of Middle Ganga Plain (UP–Bihar), India has been discussed in great detail (Acharyya, 2005; Acharyya and Shah, 2005, 2007; Shah, 2008). Together, these observations demonstrate that arsenic concentrations in ground water are controlled by many complex sets of conditions and processes (Smedley and Kinniburgh, 2002, 2005).

Thus, arsenic mobilization mechanism may vary with the location depending on hydro-geological conditions. Hence it is important to study the correlation of arsenic with various species like nitrate, sulfate, iron, bicarbonate, dissolved oxygen, phosphate etc. for assessing the likely mechanism of arsenic mobilization. Understanding the mechanism for mobilization may elucidate the predominant arsenic species to plan for proper mitigation steps in arsenic-affected areas of Ballia district.

## 2. Geography, geomorphology and climate of the study area

The geography, geomorphology and quaternary stratigraphy of the study area has been detailed by Ahamed et al. (2006) and Acharyya and Shah (2007) from whose work the account of the Ballia district is summarized in the following three paragraphs.

The area of Uttar Pradesh (UP) located in upper and middle Ganga plain is  $238,000 \text{ km}^2$  and its population is reported to be 166 million. The climate of the state is tropical monsoon but variations exist due to differences in altitude. The majority of the population depends on farming as its main occupation. Uttar Pradesh consists of 70 districts. Each district is divided into several blocks and each of these blocks have several Gram Panchayats, which are the clusters of villages. We focused mainly on the Ballia district (area  $3168 \text{ km}^2$ , population 2.75 million) which stretches from  $83^\circ 38'$  to  $84^\circ 39'$  East longitudes and  $25^\circ 33'$  to  $26^\circ 11'$  North latitudes. The location of Ballia district located between Ghaghra and Ganga rivers is shown in Fig. 1a. The blocks sampled in Ballia are Belhari, Dubhav, Bairia, Hanumanganj and Murli Chhapra. Detailed sampling locations are shown in Fig. 1b.

The large-scale features of the Ganga plain correspond to major climate changes in the late Quaternary (Singh, 2004). The geomorphic surfaces identified in the regional mapping of the Quaternary deposits of the Ganga plain are upland interfluvial surface ( $T_2$ ), marginal fan upland surface (MP), megafan surface (MF), piedmont fan surface (PF), river valley terrace surface ( $T_1$ ) and active flood plain surface ( $T_0$ ). A significant aspect of these surfaces is that all of them are depositional surfaces, having a succession of overlying sediments. The Uttar Pradesh Ganga plain (50–200 m above the ASL, and 550–1000 km from the sea coast) shows prominent distinction between  $T_0$ ,  $T_1$  and  $T_2$  surfaces. The Holocene aggradations, mostly due to rising base level and climate-driven sediment supply, are less pronounced here compared with Bihar and delta plain, although Holocene cover of 5–10 m thickness is present.

The Ganga plain foreland basin is a repository of sediments derived from the Himalayas and from Peninsular Craton. The weathered material brought from the Himalaya is deposited in the

alluvial plain where they undergo further chemical weathering, mobilizing several anions and cations.

The year is divided into three seasons: the cold season (November–February), the hot season (March–June) and the monsoon season (July–October). The mean maximum monthly temperature ( $41.7^\circ\text{C}$ ) has been recorded during May and minimum ( $22.8^\circ\text{C}$ ) in January. During peak summer, the temperature sometimes shoots up to  $46^\circ\text{C}$  while in peak winter it becomes as low as  $4^\circ\text{C}$ .

## 3. Methodology

### 3.1. Sample collection

Ground water sampling in the Ballia district was carried out during pre-monsoon (April '07), monsoon (July '06) and winter seasons (December '06). Samples were collected from 65 water sources in total, 56 being from tube wells of 30–35 m deep and 9 from 66 to 75 m deep. All tube wells had concrete apron. On-site measurements included pH and ORP. Site locations were determined by GPS (12-channel Garmin 12, UTM system), which is accurate to around 5 m.

Ground water samples were collected in polyethylene bottles for subsequent laboratory chemical analysis. Prior to sampling, the hand pumps were flushed with 30–40 L of water. Two sets of samples were collected from each location. One set of samples were collected without any preservative for the analysis all other parameters and in the other set of samples, 1 mL of Conc. HCL was added to 500 mL sample bottles to preserve As(III), As(V) and iron (Gault et al., 2005). Samples were stored where possible in refrigerators before analysis. All analyses were completed within one week of sample collection. Water was filled to the brim of the bottle without any air bubbles.

### 3.2. Field and laboratory measurements

Samples were immediately analyzed in the field for ORP and pH measurements by Wagtech ORP/pH electrode. In the case of ORP electrode, standardization was performed using 0.36 M KF solution. For the pH electrode, standardization was performed with pH 4 and 7 buffers. Procedures used for the analysis of other parameters were as per standard methods for water and waste water analysis (APHA, 1998). Analysis of total inorganic arsenic was carried out for all the three seasons. However, speciation of arsenic and other water quality parameters were analyzed only for the samples collected during December '06.

Total inorganic arsenic and As(III) analyses were carried out using spectrophotometric silver diethyl dithiocarbamate method (APHA, 1998). For As(III) determination, a small modification of the standard method (0.6 M acetate buffer was used instead of 0.2 M acetate buffer) was found necessary to take care of the acidity of the preserved samples. The lower limit of detection was found to be  $4 \mu\text{g L}^{-1}$ . Each sample was analyzed twice. The co-efficient of variation in the duplicate samples was 2.5%. The average total arsenic level in 20 aqueous calibration check samples spiked with  $50 \mu\text{g L}^{-1}$  As was  $52 \pm 4.0 \mu\text{g L}^{-1}$ . Calibration was carried out daily with freshly prepared As standards, before the sample analysis. Iron(II), ammonia, and phosphate analyses were carried out by 1.10 phenanthroline, Nessler's reagent and molybdenum blue spectrophotometric methods, respectively. Turbidimetry method was followed for sulfate analysis and bicarbonate was analyzed by titrimetry. Nitrate ion selective electrode ORION 97-07 equipped with an ion meter (Model, 290A Thermo Orion, USA) was used for the analysis of nitrate ions. Nitrate interference suppresser solution (Orion 930710) was used for its determination.

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