Multivariate Statistics Applied on Groundwater Geochemical Data to Identify Arsenic Release Mechanism and Related Microenvironments - A Case Study from Nakashipara, Tahatta-I and II Blocks of Nadia District, West Bengal, India.

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Abstract

The distribution of arsenic content and other variables in groundwater data of 302 tube-wells in Nakashipara and Tehatta I and II blocks of Nadia district, West Bengal, India are analysed. The arsenic content of 255 tube-wells out of 302 are above permissible limit of 10 ppb and thus contaminated. As per the spatial buffer analysis, the contaminated tube-wells are found to be within 500m distance from waterbody/abandoned/meander/palaeo channels; interior of which, in presence of fresh organic carbon and arsenic bearing fines, the reductive dissolution and desorption processes operate. From the identified three types of aquifers (1, 2, 2A), the semi to leaky-confined aquifer of Type-2 is presumably more susceptible to create arsenic release environment from sediment to groundwater due to elevated organic carbon content in clay layer that boosts bacteriogenic reductive dissolution process. The Principal Component Analysis performed on 23 variables of 302 water samples has identified five physico-chemical factors responsible for arsenic release in aqueous system from sediment. The Hierarchical Agglomerative Cluster Analysis on these five factors using ‘Euclidean distances’ as a measure of similarity has classified the tube-wells into three distinct clusters (I, II, III). With careful analysis, it is concluded that they actually represent the different stages of reductive dissolution process of arsenic release in an order of cluster II ◊ cluster I ◊ cluster III (initial to advance state). We propose that these stages mimic probable microenvironments within a broad realm of reducing environment of arsenic release, microenvironments alter rapidly within small areal distance.

1. Introduction

More than 4 million people in West Bengal, India and 20 million people in Bangladesh are exposed to a severe health hazard as a result of drinking arsenic contaminated (> 10 ppb, the WHO standard) groundwater from tube-wells (Chakraborti et al. 2009; Fendorf et al. 2010; Flanagan et al. 2012). In West Bengal, 19 districts have 48.1% tube-wells with arsenic concentrations above 10 ppb level (Chakraborti et al. 2009; Rahman et al. 2014); nine districts (Malda, Murshidabad, Nadia, North 24 Parganas, South 24 Parganas, Bardhaman, Howrah, Hoogly and Kolkata) show arsenic concentrations more than 300 ppb in tube-wells and thus categorized as highly affected. Out of these highly affected nine districts of West Bengal, five districts (South 24 Parganas, North 24 Parganas, Nadia, Murshidabad, and Malda) are severely affected and having patients with arsenical skin lesions (Rahman et al. 2014). The magnitude of the arsenic catastrophe in Nadia district is extremely alarming and comparable to other two severely arsenic contaminated districts (North 24 Parganas and Murshidabad) of West Bengal (Rahman et al. 2014). In Nadia district, groundwater of all 17 blocks contained arsenic above 50 ppb with maximum observed level of 3200 ppb. Thus an estimated 0.048 million of people in Nadia district are at risk of drinking arsenic contaminated water above 300 ppb and in danger of developing skin manifestations (Rahman et al. 2014). For these detailed hazard scenario, Nakashipara and Tehatta I and II blocks of Nadia district, West Bengal, India has been selected in the present study where presence of high arsenic in groundwater and manifestation of Arsenicosis in human body have been already reported (Mukherjee et al. 2010; Rahman et al. 2014).

The scientific community agrees that the source of arsenic in groundwater is the river borne sediments of the Ganges brought from the Himalayan uplands in the north and Precambrian basement gneissic complexes in the west by the drainages (Nickson et al. 1998). The tube-wells in the deltaic West Bengal and Bangladesh draw water from aquifers of the Holocene sequence constituted of basal Older Alluvium Plain (OAP) overlain by the Young Delta Plain (YDP) (Acharyya et al. 2000). The contamination is mostly restricted to the sedimentary layers of Pleistocene to Meghalayan age, and also in the groundwater drawn from grey sand aquifer capped with soft carbon rich clay of the Early Holocene to Meghalayan age (Mukherjee et al. 2001; Pal and Mukherjee 2009). Contrarily, the groundwater tapped from oxidised Pleistocene "Orange Sand" with capping of hard montmorillonite rich sticky clay horizon is arsenic free (Pal and Mukherjee 2009); but the orange sand horizon is of limited areal extent. Further, out of the six types of aquifers (Type-1 to Type-6) identified by Pal and Mukherjee (2009) based on nature of sediments and its arsenic content in West Bengal, Type-2 and Type-5 aquifer sequences which are capped by a grey to dark grey soft organic carbon rich clay unit of different age yields arsenic contaminated groundwater, while other aquifers (Type 1, 3, 4 and 6) are generally arsenic free. Age of the sediments also significantly influence arsenic contamination as revealed clearly by the higher dissolved arsenic in the groundwater drawn.
from grey sand aquifers of ≤ 7000 years of age at 40m depth while low dissolved arsenic content is observed in deep Plio-
Pleistocene aquifers of age ranging between 12300 and 48600 years (Acharyya et al. 1999; Acharyya et al. 2000; Moran et al. 2000; Eiche et al. 2008; Burgess et al. 2010; Fendorf et al. 2010; Datta et al. 2011; Hoque et al. 2011; Neidhardt et al. 2013; Knappett et al. 2016). Geomorphology also plays a critical role in arsenic contamination as evident from the spatial association between arsenic contamination and water bodies /palaeo/ cut-off/ abandoned channels (Pal and Mukherjee 2002; Sengupta et al. 2004; Mukhopadhyay et. al. 2006).

As per the available data in West Bengal and Bangladesh, arsenic content of the aquifer sediments is nowhere exceptionally high (Datta and Subramanian 1977; BGS 1999) and it is not significantly different in aquifer sediments from areas yielding contaminated or safe groundwater (Pal et al. 2002; Sengupta et al. 2004; Pal and Mukherjee 2009). Researchers unanimously agree that dissolved arsenic in groundwater is sourced from aquifer sediments (McArthur et al. 2001; Harvey et al. 2005; Pal et al. 2002; Sengupta et al. 2004; Pal and Mukherjee, 2009). Arsenic concentrations in aquifer sediments is typically less than 10 ppm in sandy layers and less than 100 ppm in clay and peat (McArthur et al. 2001). From the West Bengal part of the Bengal Delta, the pattern of arsenic distribution in sediments is more or less uniform in the arsenic affected and arsenic free areas (Pal et al. 2002; Sengupta et al. 2004; Pal and Mukherjee, 2009). As presence of arsenic in aquifer sediments is almost ubiquitous, its release in groundwater is governed by a complex bio-geo-chemical processes known as reductive dissolution aided by bacteria. The distinct procedure of release of arsenic into the groundwater takes place through this bio-geo-chemical release of arsenic adsorbed on the outer surface of the ferric oxy-hydroxide (FeOOH) grains into the groundwater (Nickson et. al. 1998; Nickson et. al. 2000; McArther et. al. 2001). However, other researchers stated that beside ferric oxy-hydroxide, phyllosilicate in sediment also play a significant role as arsenic sink (Mukherjee et al. 2001; Pal et al. 2002; Sengupta et al. 2004). Hence, in such a complex bio-geochemical environment, release of arsenic is closely associated with geology, geomorphology, land use, irrigation pattern and drainage pattern of the area; a detailed geochemical study of the underground aquifer system to understand the complete arsenic pollution scenario of a particular area is very critical.

In the present study, correlation of the different influencing factors responsible for the arsenic release have been extracted from the trace element distribution in the groundwater from 302 tube-wells data. These factors are further used to classify possible microenvironments within a broad regional environmental framework responsible for the release of arsenic from sediment to groundwater and the role of type of aquifer systems in the release process. Further the pattern of distribution of arsenic and related trace-elements in groundwater geochemistry and their correlation with other factors have been extracted and analysed with the help of two well constrained statistical techniques; the Principal Component Analysis (PCA) and the Hierarchical Agglomerative Cluster Analysis (HACA). These multivariate statistical techniques have been applied widely on groundwater chemical data elsewhere to classify the groundwater areas on the basis of explanatory models for mobilisation of arsenic (Baig et al. 2010; Mukherjee et al. 2012; Lu et al., 2012; Andrade and Stigter 2013; Jiang et al. 2015). The PCA on the chemical variables in groundwater data is used for evaluating factors responsible for high arsenic concentrations in groundwater whereas HACA technique is used for classifying the tube-wells to decipher the micro-environments and geo-chemical processes that influence the aqueous arsenic distribution.

2. Physiography And Geomorphology Of The Study Area

The study area containing Nakashipara, Tahat-ta-I and Tehatta-II of Nadia District, West Bengal, India falls within the “old” Ganges river delta region (Fig. 1) and form a terraced landscape marked by multicycle erosional and depositional surfaces. Bhagirathi, the present day river channel, incises the sediments of the delta plain and marks the south-western boundary of the study area (Fig. 1). The Bhagirathi river drives major erosion of the older landscape, followed by sediment deposition in the low lying areas. Among the other rivers, Jalangi is the most important one that flows southward along the political boundary between Tehatta-I and Tehatta-II blocks. The rivers in this part of old gangetic plain are often heavily silted, slow, meandering ones and frequently shifts their courses creating swamps, small water bodies, ponds, ox-bow lakes, abandoned channels and meander cuts with presence of natural levees along the river banks in the study area. The area
contains grey sand-silt-clay package in the channel domain and over-bank, represent a youngest fluvial cycle (Young Delta Plain (YDP)) of Holocene age.

3. Materials And Method

3.1. Satellite Imagery Study

The 800 sq. km area of Nakashipara, Tahatta-I and Tehatta-II of Nadia District, West Bengal is examined from both LISS3 satellite imagery and post monsoon Sentinel Data of October, 2017. The detailed geomorphological elements (river channel, water bodies, abandoned channels, meander scars, meander cuts, paleo-channels, back-swamps, ox-bow lakes etc.) are extracted from LISS3 satellite imagery. Other than these, numerous hidden palaeo / abundant channels and associated geomorphic features are also identified from the post monsoon Sentinel data of October, 2017 because of its increasing moisture content. Most prominent geomorphological elements mapped for the blocks are illustrated in Fig. 1.

3.2. Sample collection and preparation

Water samples were collected from 302 sample points (locations given in Fig. 1) of mostly domestic tube-wells in Nakashipara, Tehatta-I and Tehatta-II Blocks, Nadia district for elemental analysis. Tube-well locations were mapped using a portable GPS unit. One liter of non-acidified water was collected from each of the sample location for cation, anion and major elements analysis. 100 ml of water, after addition of 2 ml suprapure nitric acid, was collected from the same tube-wells in HDPE bottles for trace element analysis. Before sample collection, the domestic tube-well was first purged by removing approximately 15 liters of water using the pre-existing hand pumps found on all the tube-wells. Irrigation tube-wells were sampled directly from the outflow.

In addition, 40 numbers of sediment samples (sand and clay) of different depths are collected from the 7 disturbed boreholes for major, minor and trace element analysis. Sediment samples are dried at sunlight for 72 hours and homogenised by hand auger. Dry samples from sandy horizon are sieved successively through 60 (0.25 mm), 230 (0.0625 mm) ASTM mesh. After cone and quartering of (–60 + 230 ASTM) sand, the samples are fused with pyro-sulfate followed by leaching with dilute hydrochloric acid.

3.3. Instruments used for chemical analysis

The minor and trace elements in the samples (water and sediment) are analysed through ICP-MS. The pH and TDS of water samples are measured by Water Analysis Kit; Na⁺ & K⁺ are analysed by Flame Photometer; the analysis of NO₃⁻, SO₄²⁻ and PO₄³⁻ is done by UV visible spectrometer; and the content of Ca²⁺, Mg²⁺, HCO₃⁻, CO₃²⁻, Cl⁻ are measured by ICPMS in GSI lab, Kolkata, India. The major oxides and trace elements are in ppm and ppb respectively. Total Organic Carbon (TOC) in sediment samples of clay layers from different aquifers is analysed by TOC analyser in Marine & Coastal Survey Division, GSI, Visakhapatnam, India. Results of TOC are in percentage. For sediment samples, the major and minor elements are analysed in WD-XRF and trace elements by ICPMS in GSI Chemical Laboratory, Kolkata, India.

3.4. Statistical methods

To quantitatively investigate relationships among the trace-elements in groundwater data, PCA and HACA are performed for 23 geochemical variables in 302 analysed samples using the software XLSTAT 2021.2. The methodology of PCA analysis is following Hotelling (1933). Using PCA, dimension of the data set with 6946 values is reduced and summarized by determining the linear combinations of the original variables. From these variables, linearly combined unrelated new set of factors are extracted to represent the data (Brown and Brown, 1998). Further, varimax rotation factors are extracted based on the importance of the factor (eigenvalues > 1) and on the basis of cumulative percentage of data variance explained (Mahmud et.al. 2007; Eqani et al. 2011; Phung et al. 2015; Jiang et.al., 2015). These factors are interpreted according to the hydro-geochemistry of groundwater present in each tube-well and the influence over the arsenic release and distribution.
On top of this, to understand the influence of the factors extracted from PCA on groundwater samples and for clustering of similar data, Hierarchical Agglomerative Cluster Analysis (HACA) is performed on the dataset using squared ‘Euclidean distances’ as a measure of similarity (Jalbani et al. 2007; Jiang et al. 2015). In this method, the similarity between the data objects to be clustered are tested, clusters are formed sequentially on the most similar pair of objects and forming higher clusters subsequently. In the present study, dendrogram is also constructed after HACA which in turn depict the progression of levels of similarity at which the data merges and finally displayed the distinct clusters.

4. Analysis, Results And Inferences

4.1. Arsenic distribution map

The distribution of 302 tube-wells with arsenic content in three blocks (Nakashipara, Tahatta-I and Tehatta-II) of Nadia District, West Bengal is illustrated in Fig. 1. Out of 302 tube-wells, 47 tube-wells contains ≤ 10 ppb arsenic, 149 tube-wells with > 10–100 ppb arsenic, 41 tube-wells with > 100–200 ppb arsenic, and 65 tube-wells with > 200 ppb arsenic. Hence, by WHO standard 255 tube-wells i.e. 84.44% of total tube-wells sampled are above permissible limit of human consumption and designated as contaminated tube-wells.

Tube-wells with less arsenic values are mostly concentrated for a limited area around the river banks of the Bhagirathi and Jalangi rivers, that covers the south-western part of the Nakashipara block and parts of Tehatta-I and Tehatta-II blocks. The tube-wells are drilled within the fluvial sedimentary deposits of the Bhagirathi and Jalangi rivers, that is mostly composed of fine to coarse sand. As the paleo-lacustrine environment (Dasgupta et al. 2017) prevails towards the north-eastern part of the Nakashipara and Tehatta-I blocks, the tube-wells are drilled within the thick organic carbon rich clay bed showing elevated arsenic concentrations in the groundwater samples (Fig. 1).

4.2. Buffer analysis

The contaminated tube-wells are spatially mapped by applying variable buffer distances of 200 to 800m from the waterbody/abandoned/meander/palaeo channels and number of contaminated tube-wells coming within that zone is counted. The analysis is done following the methodology described in Mukhopadhyay et al. (2006) using the spatial tools in GIS software. The number of contaminated tube-wells lies within the buffer distance from waterbody/abandoned/meander/palaeo channels is summarized as follows: 200m (105 number of contaminated tube-wells), 300m (125), 400m (164), 500m (204), 600m (215), 700m (220) and 800m (255). The result shows that 80% of contaminated tube-wells (i.e. 204 out of 255) in the study area are occurring within 500-meter distance on either side of waterbody/abandoned/meander/palaeo channels.

4.3. Arsenic - source and release mechanism

4.3.1. Types of aquifers and arsenic content in sediments

The shallow unconfined aquifers of Type - 1 (Pal and Mukherjee 2009) variety with low arsenic content in groundwater, mostly observed towards the southwest of Nakashipara block and northern parts of the Tehatta I and II blocks (Fig. 1). These aquifers contain sand rich sediments of upper fluvial deposits with arsenic content in the sediment illustrated in Fig. 2. Water from these aquifers being generally rich in iron, manganese and other harmful bacteria (Wasserman et al. 2006), is mostly avoided for drinking purposes though arsenic concentrations is less.

Shallow to intermediate depth semi-confined to leaky-confined aquifer of grey sand with its overlying grey to dark grey soft clay is designated as Type - 2 (Pal and Mukherjee 2009) aquifer with arsenic content in groundwater ranges from 100 to 500 ppb (Fig. 3). This aquifer is mostly concentrated in the Nakashipara block and the north-eastern part of the Tehatta - I block (Fig. 1). This aquifer with high arsenic concentration is mostly placed in the sediments of younger fluvial deposits, varies in depth from 50 feet to 150 feet approximately. Dark grey and soft clay overlying this aquifer contain more water
(30–35 wt%) and higher biodegradable organic matter (1–6 wt%) favorable for bacterial population (Macur et al. 2004). Concentration of the organic carbon reaches up to 6% in aquifer sediments (Nickson et al. 2000) but in the present case it is below 1.12%. Mukherjee and Fryar (2008) opined that elevated arsenic level in groundwater is strongly influenced by coupled Fe–S–C redox cycles.

During the present study, apart from the aquifer types mentioned above, a new type of aquifer named as Type − 2A, slightly distinct from Type − 2 aquifer in physical characteristics is identified for the first time in Bengal delta. This semi- to leaky confined aquifer bears most of the morphological characters of Type-2 aquifer but the sticky clay layer overlying the sand aquifer is less dark in colour and contains less carbonaceous/organic carbon in comparison to typical Type-2 aquifer (Fig. 4). The Type − 2A releases less arsenic in groundwater in comparison to Type 2 aquifer.

It is evident from the plots (Figs. 2 to 4) that irrespective of the aquifer type, top most layers are rich in adsorbed arsenic. Incidentally, among these top most sediment layers, coarse oxidized sand layer in Type-1 aquifer and calcrite concretion layer in Type-2 aquifer display the high arsenic concentration (Figs. 2 and 3). Among the deeper layers, sand layers are mostly devoid of high arsenic concentration in Type-1 aquifer. Sand layers just below the foul smelling black coloured soft clay layer with high carbon content in Type − 2 are also of comparatively low arsenic concentration (4.3–5.8 ppm). The arsenic concentration in the clay layers are 3.87–9.33 ppm and 5.03–9.13 ppm for Type-2A and Type-2 aquifers respectively. The TOC (Total Organic Carbon) in the clay layer varies from 0.21–0.34% for Type-2A aquifer, where for Type-2 aquifer it varies from 0.58–1.12% (Figs. 3 and 4). A comparison between the arsenic concentration of the clay layers of Type-2 and Type-2A aquifers is made. It is evident that less organic carbon rich clay layer of Type-2A aquifer (20–25 feet depth) contains less arsenic (5.87 ppm) than the dark coloured black soft carbon rich clay layer (9.13 ppm) of Type-2 aquifer (29–48 feet depth) (Figs. 3 and 4).

**4.3.2. Condition of aquifer and arsenic release**

In Bengal Delta, arsenic mobilization occurs under reducing conditions (Kinniburgh and Smedley 2001). Several workers opined that reducing conditions generated by rapid consumption of oxygen by oxidation of fresh organic matter in recently buried sediments during diagenetic processes are responsible for arsenic mobilization from sediment to groundwater (McArthur et al. 2001; Dowling et al. 2002; Acharyya 2002; Harvey et al. 2005). The mineral phases that host arsenic chiefly includes iron oxy-hydroxides with their adsorbed arsenic and iron bearing alumino-silicates or their alteration products (Dowling et al. 2002; Sengupta et al. 2003; Nath et al. 2008a). For arsenic to be released from these phases, dissolution and desorption process have to operate. Desorption can take place by reduction in surface area of iron oxy-hydroxides following their partial re-crystallisation (ageing) or due to changes in their surface chemistry as a result of formation of a mixed-oxidation state. Along with these, reduction of strongly adsorbed As (V) to less strongly adsorbed As (III) can also result in increased release of arsenic.

The identified correlation between Fe and arsenic in groundwater has led several workers (Nickson et al. 1998; Cummings et al. 1999; Nickson et al. 2000; McArthur et al. 2001; Dowling et al. 2002; Hasan et al. 2007; Donselaar et al. 2017) to hypothesize that the dissolution of iron hydroxides from sediment is responsible to release arsenic into groundwater. Based on high correlation of arsenic along with iron, methane and ammonia in groundwater, Dowling et al. (2002) suggested microbial mediated reductive dissolution of iron hydroxides as the main mechanism of arsenic mobilisation into groundwater. The organic carbon content in the aquifer sediments is the prime energy source for microbial reductive dissolution process (McArthur et al. 2004; Harvey et al. 2006; Donselaar et al. 2017; Sengupta et al. 2008; Datta et al. 2011; Neumann et al. 2014; Lawson et al. 2016; Kulkarni et al. 2018a). The higher biodegradable material with organic carbon in clay favours the formation of bacterial colony eventually form a reducing closed environment to generate CH₄ and NH₄ which controls consequent arsenic release into the groundwater of the underlying aquifer from sediment (Dowling et al. 2002; Harvey et al. 2002, 2006; Stuben et al. 2003; Horneman et al. 2004; McArthur et al. 2004; Bauer and Blodau 2006; Herbel and Fendorf 2006; Lim et al. 2007; Radloff et al. 2007).
Moreover, the dissolved organic matter (DOM) promotes the intermediate electron shuttle for the microbes to grow (Kulkarni et al. 2018b) and subsequently generating the aqueous complexes with Fe and arsenic (Sharma et al. 2010; Liu et al. 2011), and competing with the arsenic in the sorption sites (Bauer and Blodau 2006). In the same line, Swartz et al. (2004) opined that introduction of labile organic matter presumably stimulates microbial respirations and induce further reductive dissolution of Fe (III) solids to which the released arsenic is associated.

Hence, the widely accepted school of thought of present day suggests that the arsenic in groundwater is derived from reductive dissolution of arsenic containing FeOOH driven by the oxidation of organic carbon driven by microbial degradation (Nickson et al. 1998, 2000). These microbes need to form bicarbonate (HCO$_3^-$) by breaking organic carbon through oxidation for survival which requires ample amount of dissolved O$_2$. If oxygen saturation is low on water, the process of bicarbonate (HCO$_3^-$) formation through oxidation is low. This takes place in two steps; i) microbial oxidation of organic carbon and ii) NO$_3^-$ reduction. The redox process occurred after microbial oxidation consumes most of the dissolved O$_2$ and NO$_3^-$, After the exhaustion of free molecular O$_2$ and NO$_3^-$, more thermodynamically favourable oxygen sources, microbiological reduction of Fe oxyhydroxide starts (Nickson et al. 1998). During this process, the arsenic adsorbed as coating in FeOOH is released to groundwater through reduction of arseniferous Fe-oxyhydroxides when anoxic conditions develop during the burial of sediment (Nickson et al. 1998).

### 4.3.3. Probable physiographic and geological control on arsenic release

While attempting to correlate arsenic in groundwater with geological formations as well as physiographic units, certain systematic variations in arsenic content in groundwater vis-à-vis geological formations have been observed on regional scale (BGS 1999; Ravenscroft et al. 2005). But the arsenic maps produced by us from the present study area (Fig. 1) of West Bengal clearly demonstrate that although a pattern exists in regional scale, the same is lost when we scale down to village/block level, where both contaminated and arsenic free tube-wells exist side by side (also observed by Van Geen et al. 2003 in Araihazar upazilla area of Bangladesh). This non-homogenous distribution of contaminated tube-wells is mostly responsible for the variation in depth of adjacent tube-wells where underground bio-geo-chemical environment changes with depth in presence of organic carbon bearing clay.

The alluvial landscape of the upper part of the Bengal Delta in general and the present study area in particular may be divided into three domains; channel deposits of predominantly sand, floodplain deposits of predominantly clay and silty clay, and a mixed domain where constituents of these two inter-finger. Considering the fact that aquifers studied are shallow in nature (Figs. 2 to 4) and there is a general depth continuity of up to 100m of geological units exposed at surface (Ravenscroft et al. 2005), we nullify the transgress of one landform into another at depth. Geologically, the first domain where a sand sequence underlies the thin topsoil represents the zone of coalescing channel bars and palaeo/abandoned/cut-off channels. Width of this domain corresponds to the valley span in which channel shifting has been confined and channel bars have formed. Similarly, it has been ascertained in the present study that almost 80% of the contaminated tube-wells lie within a 500m wide corridor, which includes the palaeo/abandoned/cut-off channels/river/water-body and coincide with the first domain (Fig. 1). Hence, spatial association of contaminated tube-wells with present day geomorphic units or palaeo channels becomes a reflection of the fact that the contamination has very close connection with the present day landform along with the palaeo-environments which in the past had created the aquifers at depth.

The valley span of 500m on both side of palaeo/abandoned/cut-off channels/river/water-body is submerged at least for part of every year due to flooding which adds arsenic to the aquifer both in dissolved and particulate form. The characteristic sedimentary packet in this corridor is a continuous grey coloured sand sequence with high permeability that facilitates downward and lateral migration of the arsenic. Harvey et al. (2005) from their study at Munshiganj, Bangladesh
described about the nature of this convergent vertical flow and the resultant mixing of floodwater with groundwater, which is again supported by $^{18}$O isotope profile and arsenic profile in response to depth (Yu et al. 2003).

4.4. Descriptive statistics and scatter plots of groundwater geochemical data

The descriptive statistics of arsenic and other physicochemical parameters measured in the chemical laboratory for groundwater samples are listed in Table 1. High variation in values with remarkably high standard deviation are illustrated by As (total), Mn, Fe, Ba, TDS and HCO$_3^-$ . Arsenic values range from 1.01 to 1070.83 ppb with a mean of 120.6 ppb. Scatter plots show that As (total) is having a visual positive relation with Mn, Fe and Mg (Fig. 5a, b, i) but having a negative relation with redox sensitive parameters like U, SO$_4^-$ and NO$_3^-$ (Fig. 5c, d, j) indicating the association of arsenic in reducing environment.
Table 1
Descriptive statistics of Arsenic (As) with other parameters in groundwater samples.

<table>
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<tr>
<th>Variable</th>
<th>Units</th>
<th>No. of sample (N)</th>
<th>Minimum</th>
<th>Maximum</th>
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<td>K⁺</td>
<td>ppm</td>
<td>302</td>
<td>0.60</td>
<td>220.00</td>
<td>7.02</td>
<td>22.71</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>ppm</td>
<td>302</td>
<td>24.04</td>
<td>192.34</td>
<td>89.79</td>
<td>31.46</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>ppm</td>
<td>302</td>
<td>1.94</td>
<td>77.76</td>
<td>23.47</td>
<td>13.09</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>ppm</td>
<td>302</td>
<td>158.60</td>
<td>719.80</td>
<td>407.14</td>
<td>102.20</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>ppm</td>
<td>302</td>
<td>0.00</td>
<td>255.24</td>
<td>35.33</td>
<td>34.85</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>ppm</td>
<td>302</td>
<td>0.10</td>
<td>240.00</td>
<td>9.36</td>
<td>27.09</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>ppm</td>
<td>302</td>
<td>0.10</td>
<td>155.98</td>
<td>13.90</td>
<td>22.48</td>
</tr>
<tr>
<td>PO₄³⁻</td>
<td>ppm</td>
<td>302</td>
<td>0.10</td>
<td>64.00</td>
<td>1.47</td>
<td>5.57</td>
</tr>
</tbody>
</table>

4.5. Principal Component Analysis (PCA)

PCA has been carried out with 23 variables on 302 water analysis data and the results of the analysis are illustrated in Table 2 and Fig. 6. PCA on 23 variables has retrieved five major principal components i.e., F1, F2, F3, F4 and F5 explaining a total of 62.687% variance of the original 302 datasets. In Table 2, the variables with significant loading (both positive and negative) on the corresponding components are highlighted in bold letters for understanding.
Table 2
Rotated factor loadings of principal components of variables in groundwater samples.

<table>
<thead>
<tr>
<th>Variables</th>
<th>F1</th>
<th>F2</th>
<th>F3</th>
<th>F4</th>
<th>F5</th>
</tr>
</thead>
<tbody>
<tr>
<td>As (total)</td>
<td>-0.053</td>
<td>-0.121</td>
<td>0.035</td>
<td>0.169</td>
<td>0.675</td>
</tr>
<tr>
<td>Al</td>
<td>-0.018</td>
<td>0.757</td>
<td>0.395</td>
<td>-0.091</td>
<td>0.058</td>
</tr>
<tr>
<td>Sc</td>
<td>-0.014</td>
<td>0.952</td>
<td>-0.099</td>
<td>-0.061</td>
<td>-0.007</td>
</tr>
<tr>
<td>V</td>
<td>0.258</td>
<td>0.720</td>
<td>0.366</td>
<td>-0.146</td>
<td>-0.208</td>
</tr>
<tr>
<td>Mn</td>
<td>0.138</td>
<td>-0.314</td>
<td>0.345</td>
<td>0.391</td>
<td>-0.127</td>
</tr>
<tr>
<td>Fe</td>
<td>-0.024</td>
<td>0.043</td>
<td>0.007</td>
<td>0.433</td>
<td>0.742</td>
</tr>
<tr>
<td>Cu</td>
<td>0.015</td>
<td>0.051</td>
<td>0.911</td>
<td>-0.016</td>
<td>0.011</td>
</tr>
<tr>
<td>Ga</td>
<td>-0.015</td>
<td>0.179</td>
<td>0.926</td>
<td>-0.047</td>
<td>0.022</td>
</tr>
<tr>
<td>Y</td>
<td>0.234</td>
<td>-0.017</td>
<td>0.674</td>
<td>0.300</td>
<td>-0.001</td>
</tr>
<tr>
<td>Ru</td>
<td>0.074</td>
<td>0.911</td>
<td>-0.078</td>
<td>0.108</td>
<td>-0.068</td>
</tr>
<tr>
<td>Ba</td>
<td>0.439</td>
<td>-0.199</td>
<td>0.026</td>
<td>0.125</td>
<td>0.609</td>
</tr>
<tr>
<td>U</td>
<td>0.434</td>
<td>-0.192</td>
<td>0.227</td>
<td>0.123</td>
<td>-0.510</td>
</tr>
<tr>
<td>pH</td>
<td>-0.093</td>
<td>0.288</td>
<td>-0.184</td>
<td>-0.715</td>
<td>-0.016</td>
</tr>
<tr>
<td>TDS</td>
<td>0.814</td>
<td>0.017</td>
<td>0.118</td>
<td>0.459</td>
<td>0.114</td>
</tr>
<tr>
<td>Na</td>
<td>0.754</td>
<td>0.156</td>
<td>0.172</td>
<td>0.159</td>
<td>0.170</td>
</tr>
<tr>
<td>K</td>
<td>0.709</td>
<td>-0.034</td>
<td>-0.103</td>
<td>-0.097</td>
<td>-0.051</td>
</tr>
<tr>
<td>Ca</td>
<td>0.059</td>
<td>0.204</td>
<td>-0.035</td>
<td>0.776</td>
<td>0.197</td>
</tr>
<tr>
<td>Mg</td>
<td>0.682</td>
<td>0.054</td>
<td>0.137</td>
<td>-0.062</td>
<td>0.017</td>
</tr>
<tr>
<td>HCO3^-</td>
<td>0.408</td>
<td>-0.146</td>
<td>0.022</td>
<td>0.728</td>
<td>0.097</td>
</tr>
<tr>
<td>Cl^-</td>
<td>0.715</td>
<td>0.287</td>
<td>0.092</td>
<td>0.375</td>
<td>0.007</td>
</tr>
<tr>
<td>NO3^-</td>
<td>0.806</td>
<td>-0.088</td>
<td>-0.042</td>
<td>-0.048</td>
<td>-0.169</td>
</tr>
<tr>
<td>SO4^-</td>
<td>0.507</td>
<td>0.162</td>
<td>0.125</td>
<td>-0.451</td>
<td>0.428</td>
</tr>
<tr>
<td>PO4---</td>
<td>0.188</td>
<td>-0.047</td>
<td>-0.001</td>
<td>-0.473</td>
<td>0.215</td>
</tr>
<tr>
<td>Cumulative (%)</td>
<td>17.285</td>
<td>30.779</td>
<td>42.095</td>
<td>54.272</td>
<td>62.687</td>
</tr>
</tbody>
</table>

The F1 factor, explaining 17.28% of total variance of dataset, shows high loading for elements like Ba, U, TDS, Na, K, Mg, Cl, NO3^−, and SO4^−− with a negative loading of As. The higher positive loading of hydro-chemical variables such as Cl, Mg, K, Na and Ba derived from mineral weathering and water-sediment interaction in the aquifer system on F1 indicate that this factor is controlled by geological and climatic processes. The positive loading of TDS indicates higher amount of dissolved ions in the groundwater. The moderate loading of the water quality variable HCO3^- is attributed to be derived from sediment with elevated content of organic carbon. The moderate loading of U and high loading of NO3^- with negative loading of Fe
and As indicate relatively oxic micro environment leading to consumption of free molecular oxygen by the microbes. This environment promotes restricted release of arsenic from sediment to water as shown by negative loading of As.

The high contribution of Al, Sc, V and Ru with absence of Fe, Mn and Mg on the F2 factor (accounts 13.49% of the total variance) show the dominance of sedimentological (lithological) processes controlling this factor. The negative contribution of U and NO$_3$ signifies that the water is reducing but the arsenic is not getting released from sediment to water due to probable non-activity of the bacteria responsible for its release.

The factor F3 (explains 11.31% variance) indicates a mild reducing environment in the groundwater as evident from the negative loading of NO$_3$ with positive loading of Cu and Ga which are associated with As as per affinity in the Periodic Table (Period IV elements). The negative loading of NO$_3$ probably indicates complete consumption of dissolved O$_2$ and subsequent breaking of NO$_3$ by the microbes. It is to be noted that here arsenic released in a small quantity as shown by low positive loading of As and Fe which probably indicate the breaking Fe-oxyhydroxide has just initiated.

Factor F4 (accounts 12.178% variance) is characterized by high loading of Ca and HCO$_3$, moderate loading for TDS, Fe and Mn along with increasingly positive loading of As indicate the breaking of Mn-oxyhydroxide and Fe-oxyhydroxide. As loading of NO$_3$ remains more or less unchanged from F3 to F4, though As loading has increased, indicates rate of breaking of NO$_3$ by the microbes has been saturated and excess As is being released by reductive dissolution of FeOOH and MnOOH. Incidentally, reductive dissolution of Mn-oxyhydroxide occurs prior to the reduction of Fe-oxyhydroxide and releases arsenic in the groundwater (Biswas et. al. 2014). Also, salt formation due to the reaction between HCO$_3$ and Ca is evident under increasingly reducing condition. This micro environment further indicates the release of As into groundwater during reductive dissolution of Fe-oxyhydroxide.

Factor F5 which accounts for 8.415% of variance is characterized by the high positive loading for As & Fe and negative loading for U & NO$_3$, indicate a highly anoxic/reducing condition where arsenic is released by breaking of Fe-oxyhydroxide by reductive dissolution process and thereby release of high quantity of Fe in water. Negative loading of Mn indicates that reductive dissolution of Mn-oxyhydroxide has probably stopped. Slight decrease of NO$_3$ loading from the previous factor indicates breaking of NO$_3$ by the microbes is still going on, but due to gradual exhaustion of thermodynamically favorable oxygen sources (Nickson & McArthur 2000), large amount of FeOOH being broken which is indicated by the increase of Fe loading. The positive factor of Fe and Ba indicate the bearing of Fe and Ba minerals in arsenic release, and role of bacteria in reductive dissolution process. The increased loading of SO$_4$ is possibly due to presence of sulphate fertilizer (used for cultivation of paddy) in the groundwater.

It is apparent from the above discussion that factors F1 and F2 are represented by a common geological factors whereas F5 along with factors F3 and F4 are representing biogeochemical process of arsenic release microenvironments. Taking this into consideration and for representation, the F1 and F5 factors of 23 variables are plotted in a scatter diagram to understand the presence of sub-environments pertaining to arsenic release and role of the variables in it (Fig. 6). The negative direction of F1 represents the reducing condition and predominance of arsenic and Fe whereas the positive direction of F1 indicates predominantly oxidized condition with prevalence of NO$_3$ and other sedimentological condition in the aquifer system for arsenic release. The coexistence of arsenic and Fe in the plot is indicative of content of Fe-oxyhydroxide in sediment and also role of reducing environmental condition in the aquifer for release of arsenic and iron by breaking down of Fe-oxyhydroxide.

4.6. Hierarchical agglomerative cluster analysis (HACA)

The PCA factor (F1 to F5) scores obtained for the 302 samples are then subjected to Hierarchical Agglomerative Cluster Analysis (HACA) for statistical grouping in terms of similarity. The analysis produces three prominent clusters (I to III) in terms of dissimilarity and represented in the dendrogram (Fig. 7) where the Phenon line is placed at a distance of 750. Here
the cluster II has the least dissimilarity followed by cluster III and cluster I. With this classification, the cluster I is represented by 194 tube-wells, cluster II with 35 tube-wells and cluster III with 73 tube-wells. On the basis of these grouping, the tube-wells are spatially mapped and represented in Fig. 8. It is to be noted that tube-wells of cluster II is spatially clustered in and around Bethuadahori along NE-SW direction, whereas the cluster I is predominant in Nakashipara block. There is an equal abundance of cluster I and III tube-wells in Tehatta I and II blocks, and most importantly they occur side by side forming small individual clusters of limited areal extent.

The statistics of these three classes for 23 variables with minimum, maximum and mean values are placed in Table 3 for comparison. The pH of water in the study area ranges between 7 and 8.5 with mean 7.58 and standard deviation 0.34 (Table 1). The variation of pH of water in the clusters vary with mean value, which is least in cluster III followed by cluster I and cluster II in increasing order (Table 3). The narrow pH range indicates reducing condition where near neutral environment promotes arsenic mobilisation from sediment to groundwater (Smedley and Kinniburgh 2002). The mean value and range in arsenic content is maximum in cluster I followed closely by cluster III and least in cluster II. The variables Fe, Mn, Ba, U, TDS, HCO$_3^-$, NO$_3^-$ are highest in cluster III followed by cluster I and least in cluster II (Table 3). The results indicate that within a broad realm of reducing environment in the aquifer system there are sub-environments which probably controls the degree and extent of arsenic release from sediment to water.
Table 3
Description and statistics of variables in the three clusters (I, II, and III) obtained from PCA and HACA analyses. N: Number of tube-wells.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Cluster I (N = 194)</th>
<th>Cluster II (N = 35)</th>
<th>Cluster III (N = 73)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Minimum</td>
<td>Maximum</td>
<td>Mean</td>
</tr>
<tr>
<td>As (total)</td>
<td>1.01</td>
<td>1070.83</td>
<td>142.47</td>
</tr>
<tr>
<td>Al</td>
<td>1.80</td>
<td>57.19</td>
<td>8.28</td>
</tr>
<tr>
<td>Sc</td>
<td>3.71</td>
<td>15.30</td>
<td>7.60</td>
</tr>
<tr>
<td>V</td>
<td>0.17</td>
<td>11.60</td>
<td>0.72</td>
</tr>
<tr>
<td>Mn</td>
<td>3.15</td>
<td>1217.78</td>
<td>311.48</td>
</tr>
<tr>
<td>Fe</td>
<td>52.44</td>
<td>1171.32</td>
<td>403.88</td>
</tr>
<tr>
<td>Cu</td>
<td>0.31</td>
<td>7.30</td>
<td>1.11</td>
</tr>
<tr>
<td>Ga</td>
<td>0.02</td>
<td>0.35</td>
<td>0.06</td>
</tr>
<tr>
<td>Y</td>
<td>0.01</td>
<td>0.58</td>
<td>0.09</td>
</tr>
<tr>
<td>Ru</td>
<td>0.00</td>
<td>0.01</td>
<td>0.00</td>
</tr>
<tr>
<td>Ba</td>
<td>40.16</td>
<td>413.75</td>
<td>139.89</td>
</tr>
<tr>
<td>U</td>
<td>0.00</td>
<td>10.70</td>
<td>0.84</td>
</tr>
<tr>
<td>PH</td>
<td>7.10</td>
<td>8.50</td>
<td>7.64</td>
</tr>
<tr>
<td>TDS</td>
<td>208.00</td>
<td>665.00</td>
<td>351.50</td>
</tr>
<tr>
<td>Na⁺</td>
<td>5.70</td>
<td>103.00</td>
<td>25.34</td>
</tr>
<tr>
<td>K⁺</td>
<td>0.60</td>
<td>81.10</td>
<td>3.67</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>24.04</td>
<td>148.26</td>
<td>79.37</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>1.94</td>
<td>48.60</td>
<td>20.65</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>158.60</td>
<td>566.08</td>
<td>375.39</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>0.00</td>
<td>127.63</td>
<td>20.46</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>0.10</td>
<td>64.00</td>
<td>4.22</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>0.10</td>
<td>155.98</td>
<td>13.22</td>
</tr>
<tr>
<td>PO₄³⁻</td>
<td>0.10</td>
<td>64.00</td>
<td>2.10</td>
</tr>
</tbody>
</table>

5. Discussion

5.1. Factors affecting the groundwater geochemistry

The association of arsenic with other redox sensitive parameters are established in the scattered plots (Fig. 5). It has been indicated from earlier discussion that reducing condition in the aquifer system is responsible for release of arsenic from
sediment. It is to be noted that degree of reducing condition varies within the same aquifer system and changes rapidly within short spatial distance (Fig. 8). On the same line, the change in cluster type is also characterize the area. To understand the relative importance of factors to form three clusters and redox condition, the representative factor scores of F1 and F5 belonging to all 302 tube-wells with designated cluster numbers (I, II and III) are plotted in a scatter plot (Fig. 9). The dendrogram (Fig. 7) and distribution of factors (Fig. 9) denote that that cluster I and II tube-wells are concentration mainly where F1 is negative i.e. less than 0; whereas majority of cluster II tube-wells are placed where F1 > 0. Though the overall condition of aquifer for all the tube-wells is reducing as also shown by cluster I and II tube-wells due to very less amount of NO$_3$ and U present in the system, the cluster III tube-wells though by and large in the reducing domain get some fresh oxygenated water from outside (due to probable flooding) which also increases the NO$_3$ content a little bit in the system (Table 3).

5.2. Arsenic release process vis-à-vis elemental distribution and clustering of tube-wells

The mentioned process of reductive dissolution responsible for Arsenic release in groundwater is operative throughout the study area in two phases. In phase I, the oxidation of organic carbon takes place either in presence of free oxygen or by breaking down of NO$_3^-$ through reduction. Therefore, as reduction of NO$_3^-$ takes place in primary phase of arsenic release, the content of NO$_3^-$ has to be low as well as the arsenic concentration (Fig. 5J). This phase is mostly operating in the cluster II tube-wells with low arsenic and NO$_3^-$ content (Table 3). In phase II, gradually due to lack of free oxygen in the aquifer, environment starts to become more reducing and microbes start to break down Fe-oxyhydroxide where much of Arsenic is released in the system by the reductive dissolution of Fe-oxyhydroxide (Nickson et al. 2000) and not by oxidation of organic carbon by NO$_3^-$

Therefore, in the later phase, as the reduction of NO$_3^-$ stops, the amount of NO$_3^-$ increases along with the arsenic concentration (see cluster III tube-wells in Table 3). Moreover, during the reductive dissolution of Fe-oxyhydroxide, due to the breaking of Fe-oxyhydroxide, increase of Fe$^{2+}$ in the system is obvious, as described in many of the previous studies (Desbarats et al. 2017). Also bicarbonate (HCO$_3^-$) is released in the system during the reductive dissolution of Fe-oxyhydroxide (Nickson et al. 2000; Saha et al. 2010; Andrade and Stigter 2013). This is the reason behind the gradual increase of Fe$^{2+}$ and HCO$_3^-$ with the increase of arsenic concentration (Figs. 5b and 5e). Apart from the mentioned cations and anions, increase of K$^+$ and Ca$^{2+}$ is also observed, which possibly responsible for the increase of TDS and decrease in NO$_3^-$ in later phase of arsenic release. Bicarbonate (HCO$_3^-$) released during the reductive dissolution of Fe-oxyhydroxide cannot stay in the system for long and often reacts with calcium ions (Ca$^{2+}$) and precipitates as salt and thereby increasing the Total Dissolved Solids (TDS) during the later phase of arsenic release (Table 3). This process is evident from the results of the chemical analysis that shows positive trend between Ca$^{2+}$ and HCO$_3^-$ and increasingly positive trend of TDS with the change in Arsenic values. Also, decrease of K$^+$ and NO$_3^-$ in this later phase of reductive dissolution probably indicates formation of KNO$_3$ eventually increasing the TDS.

The phase II is characteristic of cluster III which is followed very strongly by cluster I as reducing condition becoming more intense.

The presence of organic carbon in sediment is extremely important for arsenic release and formulation of clusters in the tube-wells. There are two views regarding the source of organic carbon within the aquifer. According to the “recharge” hypothesis, the source of organic carbon is infiltration from surface waters, such as ponds / stagnant water bodies or rice paddies (Harvey et al. 2002; Neumann et al. 2010; Lawson et al. 2013; Mailloux et al. 2013). According to the “in situ” hypothesis, the organic carbon is of sedimentary origin and co-deposited along with arsenic bearing sediments (Desbarats et al. 2014; Postma et al. 2007; Polizzotto et al. 2008). Compelling evidences supporting “in situ” carbon hypotheses have been presented by Polizzotto et al. (2008). We strongly believe that oxidation of organic carbon from whatever source may be have been started in all tube-wells in the phase I. Cluster II tube-wells have experienced only a part of phase II whereas, cluster I followed by cluster III tube-wells experienced the entire phase II process of arsenic release in an order of cluster II ◦ cluster I ◦ cluster III. Reflection of these are represented by the summary statistics of Table 3 and its representations in the
box-whisker plots of the redox sensitive elements (Figs. 10 and 11). Arsenic and HCO\textsubscript{3}\textsuperscript{−} in groundwater is least in cluster II followed by cluster III and maximum in cluster I (Fig. 10a, 10c). The recovery of NO\textsubscript{3}\textsuperscript{−} in the middle process otherwise having lower values all along are shown in Fig. 10b. The content of Fe, Mn, Ba and K (Fig. 10e, 11e, 11d, 10d) is lowest in cluster II, increased in cluster I and highest in cluster III. Here they are lower in Cluster I because as per maturity of the process some of the salts are formed in combination with HCO\textsubscript{3}\textsuperscript{−} and lowers down the TDS (Fig. 11a). The Cl content increases from cluster II to III but reduces in cluster I due to probable formation of salt with Na (Fig. 11c and Table 3).

The role of inorganic fertilizer used in cultivation and percolated in the shallow aquifer system is probably also responsible in release of arsenic in the sediment – water interaction. The SO\textsubscript{4} is generally significant in all clusters (Table 3; Fig. 11b) and in some samples increases with the arsenic content (Fig. 5d); it indicates that SO\textsubscript{4} is probably not coming from arsenic sulphide minerals but possibly from the inorganic sulphate fertilizer being used in the paddy cultivation. This is even supported by the fact that most of the contaminated tube-wells are located in the agricultural land supporting the dominantly agrarian population in the study area. Similarly, the PO\textsubscript{4} content in the water samples in the clusters can be explained as (i) the phosphate fertilizer used in cultivation may increase the solubility of arsenic due to competitive PO\textsubscript{4} – AsO\textsubscript{4}\textsuperscript{−} exchange in the soil (Smedley and Kinniburgh 2002; Andrade and Stigter 2013) and (ii) then the low mobility of PO\textsubscript{4} also helps its precipitation with Ca by forming salt.

6. Conclusion

The spatial mapping and multivariate statistical analysis performed on the chemical analysis data of 302 tube-well water samples make some interesting revelations:

1. The distribution of 302 tube-wells with arsenic content shows that 84.44% of total tube-wells sampled are above permissible limit of 10 ppb and designated as contaminated tube-wells. The contaminated tube-wells are spatially associated with distinct geomorphic elements where they show very close association (within 500-meter distance) with waterbody/abandoned/ meander channels and palaeochannels. These 500m corridors on either side of channels present conditions whereby not only reductive dissolution and desorption processes operate but also a steady inflow of fines loaded with arsenic maintains the level of arsenic accumulation. Beyond this distance limit, the tube-wells are generally uncontaminated due to lack of supply of organic carbon and arsenic fines from source. The result indicates a strong geomorphological control on distribution of contaminated tube-wells.

2. Out of three types of aquifers (Type 1, 2 and 2A) identified in the study area, the semi-confined to leaky-confined aquifer of Type – 2 is presumably more prone to release arsenic from sediment to groundwater due to more organic carbon content in clay layer which help biogenic reductive dissolution process.

3. The PCA carried out on the redox sensitive variables of 302 water samples has identified five distinct factors representing the contributions of various physical, sedimentological, environmental and chemical factors in arsenic release process within aquifer. When these factors are combined in HACA using ‘Euclidean distances’ as a measure of similarity, the process generate three distinct tube-well clusters (I, II and III) having distinct spatial connotation. These clusters indicate that within a broad realm of reducing environment in the aquifer system for arsenic release from sediment to water, there are microenvironments which probably controls the quantum of arsenic release. More explicitly, the microenvironments actually represent the stages of reductive dissolution process of arsenic release; which is in the present case in an order of cluster II ◊ cluster I ◊ cluster III i.e. from initial to more advance state of arsenic release process within an overall reducing environment in aquifer for arsenic release from sediment to groundwater. However, these microenvironments change rapidly within small spatial distance.

Declarations

Funding:

Declaration of competing interest:

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Author statement

D. S., P. K. M., and B. M. conceived the idea; D. S. and B. M. wrote the manuscript and subsequently improved with inputs from all authors. All the authors contributed during analyzing & interpreting field data, and final editing of the paper.

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**Figures**

**Figure 1**

Map showing the distribution of arsenic content in 302 tube-wells, area of distribution of types of aquifer, and geomorphological elements mapped in Nakashipara, Tehatta I and II blocks of Nadia district, West Bengal, India

**Type - I**

[Soil, Sandy Silt, Mica Rich Oxidised Fine to Medium Sand]

0 - 2 ft Top Soil

**Figure 2**
Depth-wise log of the sediments and its arsenic content in aquifer Type - 1.

Figure 3

Depth-wise log of the sediments and its arsenic content in aquifer Type - 2. Note the type of clay in the inset figure and its arsenic & TOC content.
Figure 4

Depth-wise log of the sediments and its arsenic content in aquifer Type - 2A. Note the type of clay in the inset figure and its difference from Type - 2 clay. Further account for the arsenic & TOC content in clay sediment which is lower than Type - 2.

Figure 5

Scatter plot of As (total) against other variables in groundwater; (a) Mn, (b) Fe, (c) U, (d) SO₄, (e) HCO₃, (f) Cl, (g) PO₄, (h) Ca, (i) Mg, (j) NO₃.
Figure 6

Plot of PCA factors F1 against F5 for As (total) and other related variables in groundwater.

Figure 7

Cluster I
Cluster II
Cluster III
Phenon Line

Dissimilarity

0 100 200 300 400 500 600 700 800 900 1000

Fe As Ba SO4 Na Ca PO4
Dendogram of the 302 groundwater samples. The plot identifies three distinct clusters (I, II and III) on the basis of dissimilarity where Phenon line is placed at 750.

**Figure 8**

Map illustrates the distribution of three clusters of tube-wells obtained from PCA and HACA analyses along with types of aquifer and geomorphological elements mapped in Nakashipara, Tehatta I and II blocks of Nadia district, West Bengal, India.
Figure 9

Distribution of factors on 302 groundwater samples of three tube-well clusters (I, II, and III).
Figure 10

Box-whisker plots of the segregated groundwater samples in three clusters (I, II, and III) given in table 3; (a) As, (b) NO$_3$, (c) HCO$_3$, (d) K, (e) Fe and (f) Ca.
Figure 11

Box-whisker plots of the segregated groundwater samples in three clusters (I, II, and III) given in table 3; (a) TDS, (b) SO₄, (c) Cl, (d) Ba, and (e) Mn.