Occurrence of Arsenic in Groundwater: Speciation, Mobilisation and Spatio-temporal Trends

By

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1. Introduction

1.1 Background

Groundwater is a crucial resource of our life support system. The groundwater resources are being utilised for drinking, irrigation and industrial purposes. However, due to rapid urbanization and industrialisation, groundwater resources are exploited thereby not only deplenishing the quantity but alsodeteriorating the quality. Since Independence, the Government of India has attempted to provided most of the population with bacteriogically safe drinking water by providing tube wells that draw ground water from subsurface aquifer. In India, around 80% of the rural population and 50% of urban population depend on groundwater for domestic purposes. More than 33% of the country's groundwater resources are not fit for consumption(Dipankar Chakraborti, Bhaskar Das, 2011).Various anthropogenic and geogenic contaminants have emerged over the last several decades as serious threats to human health due toanthropogenic activities on the surface (e.g. open defication, disposal of domestic and industrial wastes, agriculture, etc.) andintense groundwater exploration. Among these contaminants, arsenic has been causing various health problems among millions of people since the last several decades. Humans are essentially exposed to arsenic through groundwater utilization. The metalloid arsenic is ubiquitous element found in rocks, soils and water in contact with it. Being a toxic element, arsenic is considered a human health hazard (Chakraborti *et al*., 2009).Groundwater containing arsenic is used for various purposes such as drinking, cooking and irrigation in many parts of the world. The widespread distribution and high toxicity of arsenic in groundwater is as serious environmental issue which threatens human health in many countries such as Bangladesh, India, China, Cambodia, Japan, Argentina, Chile and USA (Nordblrom, 2002).Groundwater arsenic contamination is mainly found in the floodplains of the river originating from the Himalayas, especially the Ganga-Meghna-Brahmaputra (GMB) plain of India and Bangladesh. In GMB plain alone, more than 100 million people are at potential risk from arsenic contamination (Chakraborti, Mahmudur, Bhaskar, Bishwajit, & Arup, 2013). Long term exposure to arsenic may cause gastro-intestinal damages, diarrhoea and cardiac abnormalities. In West Bengal and Bangladesh, it is reported that people are suffering from leuco-melanosis, keratosis, spotted and diffused melanosis (Chakraborti *et al*., 2002). In order to reduce the impactof the toxicity of As mainly carcinogenicity, the WHO guideline for arsenic in drinking water was reduced from 50 µg/L to 10 µg/L in 1993 (Edition & First, 2008). In India permissible limit for drinking water is 50 µg/L and acceptable limit is 10 µg/L (Kisan, Sangathan, Nehru, & Pitroda, 2012). The toxicity depends on the form of the arsenic compounds; the inorganic forms being more toxic than organic forms. Among the inorganic forms, As (III) is more hazardous than As (V) (Edition & First, 2008).

1.2 Problem Overview

In recent years, both WHO and national standards are quite frequently exceeded in drinking water sources. Most arsenic problems in the environment are the result of mobilisation under natural conditions. Arsenic is mobilised under a combination of natural processes such as weathering reactions, volcanic emissions and biological activities. However, these natural processes of arsenic mobilisation are enhanced with anthropogenic activities such as mining activity, burning of fossil fuels, use of fertilisers and pesticides. Further the mobilisation and spread depend upon various physicochemical parameters such as pH, redox potential, presence of other major ions, organic matter that influence adsorption/desorption, precipitation/dissolution, biological transformation, etc. These factors may vary from aquifer to aquifer depending on the geological settingand bio-geochemical environment of the aquifer. The ambivalence nature of the influencing factors poses big challenge to scientists to understand causes of increasing arsenic contamination in groundwater. This research was initiated to collate relevant information on arsenic contamination in groundwater, particularly in the context of Ganga River Basin, to advance the state-of-the-art.

2. Literature Review

- ## Past Study

2.1 Arsenic speciation in water

Arsenic mobilisation is sensitive at pH values typically found in groundwater (6.5-8.5) under both oxidising and reducing conditions. Arsenic can be found in several oxidation states (0, +3 and +5) but in natural waters, inorganic forms of arsenic mainly exist as oxyanions of trivalent arsenite [As(III)] and pentavalent arsenate [As(V)]. Organic forms of arsenic are formed due to biological activity but are rarely important in the environment. Organic forms may also be formed due to industrial activities (Smedley & Kinniburgh, 2002). Because of its mobility in wide range of redox conditions, Arsenic is one of the most problematic compounds in the environment. Relative concentrations of As (III) and As (V) is a function of Eh and pH, main factors for determining the arsenic speciation in the aquatic systems. Arsenic speciation in water is affected by the presence of other ions such as iron and sulphur(Cullen & Reimer, 1989).

2.2 Mobilisation of arsenic in groundwater

Nowadays, arsenic occurrence has been a subject of raging debate. Natural contamination of arsenic in groundwater and threat to human health worldwide has led to extensive studies on various factors controlling conditions leading to mobilization of arsenic in different arsenic contaminated areas. Geogenic, non-point source and carcinogenic arsenic is now considered as one of the most important contaminants in groundwater worldwide (Plain, 2001; Smedley and Kinniburgh, 2002). Although various hypothesis for arsenic release have been proposed, no consensus has been achieved as to the exact reasons controlling arsenic mobilization in the groundwater. Similarly, the primary source of arsenic in the aquifers are not known with certainty (Mukherjee *et al.*, 2008).

There have been many investigations and reconnaissance studies to understand the mechanisms of mobilization of arsenic into the groundwater such as oxidation of pyrite (Mandal *et al.*, 1998; Chowdhury *et al.*, 1999; BGS and DPHE, 2001), competitive anion exchange with phosphates from fertilizers (Acharyya, Lahiri, Raymahashay, & Bhowmik, 2000) and dissolution of ironoxyhydroxides (Nickson *et al.*, 1998; Nickson *et al.*, 2000; P. Ravenscroft, 2001). The pyrite oxidation process has been discarded by various authors (Nickson *et al.*, 2000; Ravenscroft, 2001). Phosphate, an important component in fertilizers is extensively used in irrigation and may replace sorbed arsenic in the surface of sediments and release arsenic in the groundwater. Some studies have focused that iron oxyhydroxides strongly adsorb arsenic in the river water (Loeppert, 1999). Many authors found correlation between arsenic and iron and suggested that dissolution of iron hydroxide releases arsenic into groundwater (Nickson *et al.*, 1998; Nickson *et al.*, 2000; Cummings and Caccavo, 1999). It was further proposed that arsenic is released from the sediments during the microbial degradation of organic matter and decrease in reduction potential of groundwater caused dissolution of iron oxyhydroxides and release the adsorbed arsenic into dissolved form (Nickson *et al.*, 1998; Nickson *et al.*, 2000; Poreda, 2002; Badruzzaman *et al.*, 2002).

$$8FeOOH\text{-}As_{(s)} + CH_3COOH + 14H_2CO_3 \rightarrow 8Fe^{2+} + As_{(d)} + 16HCO_3^{-} + 12H_2O$$

where As $_{(s)}$ is sorbed As and As $_{(d)}$ is dissolved As.

Arsenic and organic matter are closely associated in sediments of the Bengal delta and other parts of the world (Ravenscroft, 2001; Anawar *et al.*, 2003). Strong correlations among arsenic, iron and organic matter further provide evidence that arsenic mobilization mainly occur via microbial degradation of organic matter and reductive dissolution of iron oxides (Anawar *et al.*, 2003; Islam *et al.*, 2004; McArthur *et al.*, 2004).

Natural organic matter serves as a source of energy for micro-organisms in the aquatic environment. Heterotrophic micro-organisms present in the subsurface water oxidize dissolved organic carbon to CO_2 and thus deplete dissolved oxygen.

$$CH_2O + O_2 \rightarrow CO_2 + H_2O$$

Here, oxygen acts a terminal electron acceptor for the carbon oxidation process and as an energy source for respiration for the microbes (Akai *et al.*, 2004; Rowland *et al.*, 2006).

Addition of fertilizers and sewage also increase the concentration of ammoniacal nitrogen in groundwater. A group of autotropic micro-organisms called nitrifying bacteria convert ammoniacal nitrogen into nitrates in the presence of bicarbonate and dissolved oxygen (Wezernak, 1967).

$$NH_3 + 1.5O_2 \rightarrow NO_2^{-} + H_2O + H^{+}$$

$$NO_2^{-} + 0.5O_2 \rightarrow NO_3^{-}$$

This process of nitrification depletes dissolved oxygen in groundwater and causes anaerobic conditions. Arsenic is directly or indirectly associated with organic matter. A study by Anawar *et al.* (2013) showed that strong correlation by ammoniacal nitrogen and dissolved organic matter indicate reducing environment in the aquifers. Further the reduced concentrations of dissolved O_2, nitrate and sulphate, and high concentrations of dissolved organic carbon, bicarbonate and ammoniacal nitrogen indicate reducing geochemical conditions (Anawar, *et al.*, 2013).

Anawar *et al.* (2004) claimed that high concentrations of bicarbonate in water caused mobilisation of arsenic. Another proposed mechanism is the competitive anion exchange between sorbed arsenic and phosphate. Phosphate has a higher affinity to get adsorbed on the surface of iron oxyhydroxide than arsenic (Chowdhury *et al.*, 1999). Acharyya *et al.*(1999) stated that during the past thirty years, groundwater has been extensively used for irrigation and the use of fertilizers have increased three-fold (Acharyya *et al.*, 2000). This widespread use of groundwater might have released phosphates from fertilizers and could promote growth of sediment biota thereby releasing arsenic from iron oxyhydroxide sediments. These combined biological and chemical processes have increased the mobility of arsenic in groundwater.

Contrary to the current hypotheses, some authors presented a sequence of evidence that arsenic may be released in the near surface but then transported to depth. Erban *et al.* (2013) suggested that downward leakage in the bore wells may cause deep arsenic contamination. This is further supported by Polizzotto *et al.* (2005) that arsenic is released from near surface sediments which corresponds to reducing zones and then further transported deeper by seasonally shifting hydrologic gradient due to the cracks in underlying confining layers. This affects both geochemical release of arsenic in near surface and transport of arsenic into deeper aquifers. A recent study by BGS confirmed that shallow tube wells in Bangladesh have distinctly higher arsenic concentrations than deep tub wells (BGS and DPHE, 2001). Thus arsenic mobilisation is controlled by a set of complex processes and conditions.

2.3 Spatial and temporal variation of arsenic in India

During the last two decades, high concentrations of arsenic have been detected in groundwater in many countries around the world originating from natural geochemical processes. To date, arsenic has been identified in 105 countries affecting 200 million people worldwide at concentrations greater than the WHO specified guideline value of 10 µg/L (Naujokas *et al.*, 2013). In India, the first arsenic contamination was reported in 1979 in Chandigarh where some people suffered from arsenic toxicity (Datta, Mitra, Chhuttani, &Chakravarti, 1979). The following table shows the chorological years of discovery and places of groundwater arsenic contamination (Chakraborti *et al.*, 2017).

Table 1: Chronological Years of Discovery and Places of Groundwater Arsenic Contamination

Year	Place
1979	Chandigarh
1984	West Bengal
1999	Madhya Pradesh
2003	Bihar
2004	Uttar Pradesh
2004	Jharkhand

2004	Assam
2009	Manipur
2009	Allahabad-Kanpur, Upper Ganga Plain
2013	Karnataka
2014	Majuli, Assam

- ## Summary Remarks

Of several proximate mechanisms suggested for elevated arsenic in groundwater, two that appear most possible are 1) reductive dissolution of iron oxyhydroxide and 2) competitive anion exchange between phosphate. But the heterogenous distribution of arsenic in the complex aquifer stratigraphy suggest that multiple processes may be evoked to explain the elevated levels of arsenic in groundwater. Based on the studies done by many authors, we can say that no consistent mobilisation processes have been provided. The sedimentary origin of arsenic and precise mobilisation into the groundwater in different locations are yet to be equivocally determined.

3. Objective

Understanding the source and mobilization of the severe arsenic contamination has a number of benefits. It will help to identify the contaminated aquifers and help in predicting future trends of arsenic in groundwater. Given the present gaps in understanding the mobilisation process of arsenic in groundwater, it is necessary to investigate the geochemical properties of the aquifers of many arsenic affected regions. Changes in arsenic speciation also play an important role in mobilisation into groundwater. There is common agreement among scientists that arsenic contamination is a result of natural geogenic process, and are enhanced by anthropogenic intervention.

In this regard, various parameters such as presence of major ions, role of organic matter as well as lithological aspects seem to play an important role which will be discussed in detail.

In this thesis, an attempt is made to study the speciation of arsenic in water in presence of different ions. The objective of the research is to scrutinize geochemical evidence in support of the mobilisation mechanisms and indicate the potential causes responsible for mobilising arsenic in the subsurface system.In the end, conceptual maps are developed to show the spatial and temporal trends of arsenic contamination in groundwater in India based on data collected.

4. Methodology

- ## Arsenic speciation in water

4.1 Thermodynamic data

Eh-pH diagrams serve as a useful guide for determining predominance of dissolved species and stability of solids. Recently various versions of Eh-pH diagrams of arsenic have been constructed. These diagrams mainly differ because of 1) different thermodynamic properties of aqueous species and solids used, 2) inclusion and exclusion of certain species, and 3) different geochemical system of interest. Marini and Accornero (2017) focused on the thermodynamic properties of metal arsenates and metal arsenite complexes (Accornero, Appolonia, Marini, & Accornero, 2017). Nordstrom and Archer (2003) presented the thermodynamic properties of elemental arsenic, arsenic oxides, arsenic sulphides, aqueous arsenic species and other related species (Kirk, United, Geological, & Nordstrom, 2014). Langmuir *et al.*(2006) critically reviewed the solubility data of iron bearing aqueous arsenic species and scorodite solid.

Using the above contribution by various scientists, a thermodynamic database of equilibrium constants for different arsenic species was compiled for arsenic aqueous species and complexes and arsenic oxides, sulphides and ferric arsenic species as the basis for Eh-pH diagrams and the plots are done at 25° C and 1 bar for various systems relevant to the environment.

The following set of aqueous species are included in the database:

1. H_3AsO_3, $H_2AsO_3^-$, $HAsO_3^{--}$, AsO_3^{---}, H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{--}$, AsO_4^{---}.
2. $As_3H_4\ (HS)^-$, $AsS(OH)HS^-$.
3. $FeAsO_4$, $FeAsO_4^-$, $FeH_2AsO_3^{++}$, $FeH_2AsO_4^+$, $FeH_2AsO_4^{++}$, $FeHAsO_4$, $FeHAsO_4^+$.

The following mineral species are included in the database:

5. Arsenolite, Arsenopyrite, As mineral, As_2O_5, Claudetite, Orpiment, Realgar, Scorodite.

The range of arsenic concentration in natural waters is large (Smedley & Kinniburgh, 2002). Hence a wide range of arsenic concentration (10^{-3} to 10^{-8} M) was chosen in this study. In this study, Eh-pH diagrams for sulphur and iron species are considered. Instead of molarity, activities are taken into consideration for the influence of ionic strength. These calculations are done with the help of geochemical modelling aid.

4.2 Software for plotting the Eh-pH diagrams

Construction of Eh-pH plots was done using the computer code Geochemist Workbench (GWB) student version 11.0. Act2 program in the GWB code is used to calculate and plot Eh-pH diagrams. Geochemist workbench was introduced in 1991 and since its introduction, Geochemist Workbench has set the standard in geochemical modelling. This software solves chemical equilibrium problem with user provided thermodynamic data and produces Eh-pH diagrams and activity diagrams with highly optimized algorithm and advanced software architecture.

• Correlations Among Major Ions

In order to understand the association of arsenic and other major species in groundwater, correlation analysis is done using a statistical modelling tool ‘R-studio’. It is an open source language for statistical computing and visualization. The correlation coefficient (R-value) between -1 and 1 is determined to know whether two paired sets of data are related. The closer to 1, the more related we are with a positive linear correlation and the closer to -1, the more unrelated we are with a negative linear correlation. Further, the confidence in a relationship is supported by the numbers of pairs in a dataset. This is done by adding significance value (p-value) to the pairs varying between 0 to 1. A low p-value such as 0.01 says that null hypothesis can be rejected and the data is significant at 99% level. Typically, values of 0.01 or 0.05 are used. In this study, p-value of 0.01 is considered.

This study analyses a suite of components in samples covering broad range of groundwater conditions at 11 locations. The following table shows the details of the data collected from different sources.

Table 2: Details of Collected Data for Correlation Analysis

Case No.	Year of Sampling	Location	Researchers Involved
1.	August 2010	North China	Pi *et al.*, 2015
2.	1998-2001	Bangladesh	BGS and DPHE, 2001
3.	2004-2005	Western Bengal Basin	Mukherjee and Fryar, 2008
4.	July 2006- April 2007	Balia,Uttar Pradesh	Chauhan *et al.*, 2009
5.	May 2007 and October 2007	Ghazipur, Uttar Pradesh	Kumar *et al.*, 2010
6.	2001	Sonargaon, Bangladesh	Anawar *et al.*, 2003

A map showing the locations from where sampled data have been analysed is shown in Appendix. 1.

• Variation of Arsenic in Shallow and Deep Tube Wells in India

As a part of survey covered through the National Rural Drinking Water Programme of the Ministry of Drinking water and Sanitation, Government of India, arsenic contamination in drinking water in the habitations of India was measured from 2010-2011 to 2016-2017. Using the data, maps are constructed using the geographic information system ‘QGIS’ application. The shape file of India administrative areas has been collected from ArcGIS website.

5. Results and Discussions

• Arsenic Speciation in Water

5.1 Arsenic speciation in absence of other species

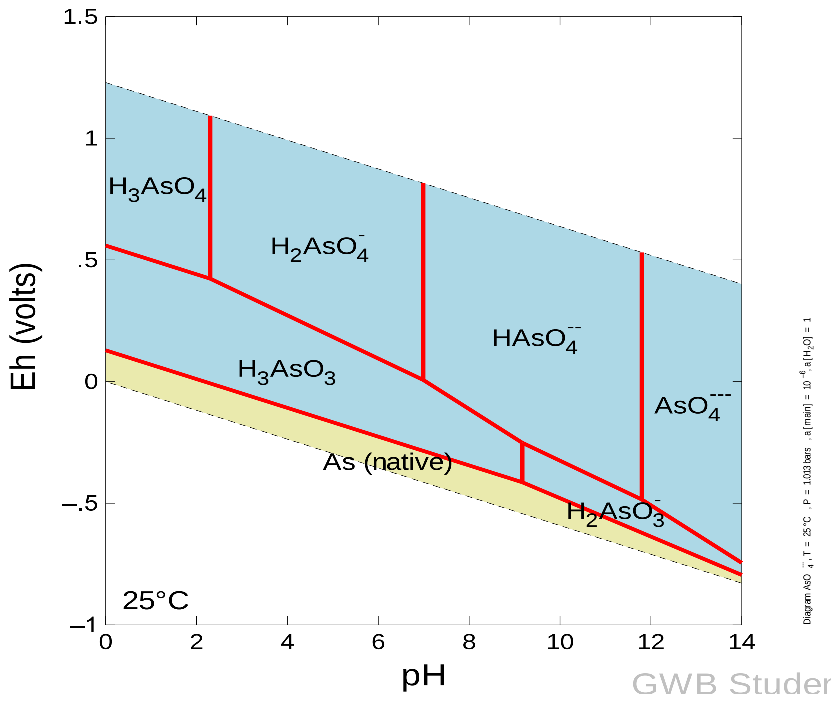


Figure 1: Eh-pH diagram for As-O-H system at 25°C and 1 bar. {As} = 10^{-6}

Arsenic forms anionic species in aqueous medium. From Figure 1, we find that As (III) gets converted to As (V) under oxidising conditions and likewise, As (V) gets converted to As (III) under reducing conditions. Among the major arsenic species, the main ones are As(III), As(V), arsenious acids (H_3AsO_3, $H_2AsO_3^-$, $HAsO_3^{--}$, AsO_3^{---}) and arsenic acids (H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{--}$,AsO_4^{---}). Arsenate is dominant under oxidizing conditions, as the $H_2AsO_4^-$is formed at low pH (less than 6.9) as well as $HAsO_4^{---}$ is formed at higher pH. The arsenite species H_3AsO_3 predominates under reducing conditions at pH less than 9.2.

5.2 Arsenic speciation in presence of reduced sulphur

In presence of high concentrations of reduced S, dissolved species of As-sulphides are predominant. Reducing acidic conditions favour the formation of orpiment (As_2S_3), realgar (AsS) and other As minerals (Cullen & Reimer, 1989).

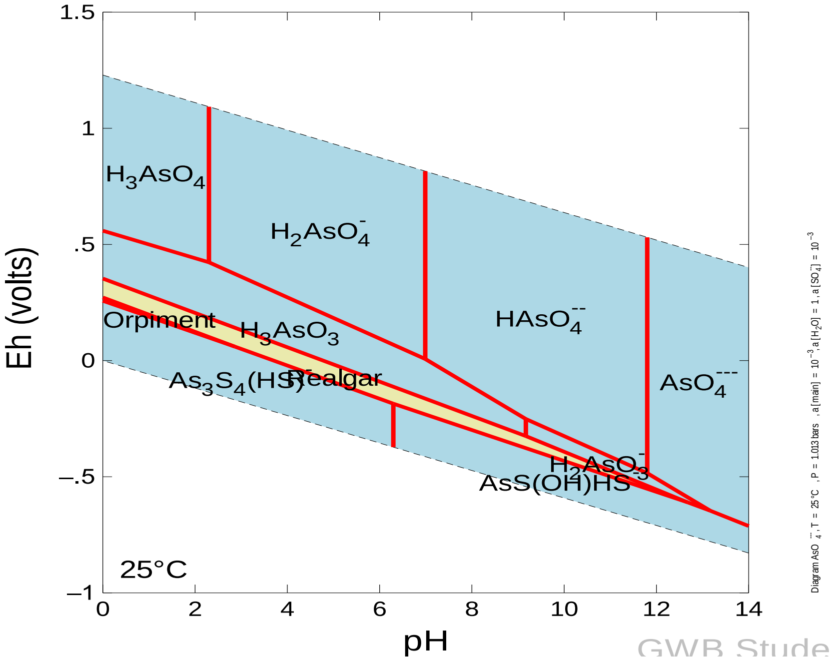


Figure 2: Eh-pH diagram for As-O-H-S system at 25°C and 1 bar.{As} = 0.001, {S} =0.001

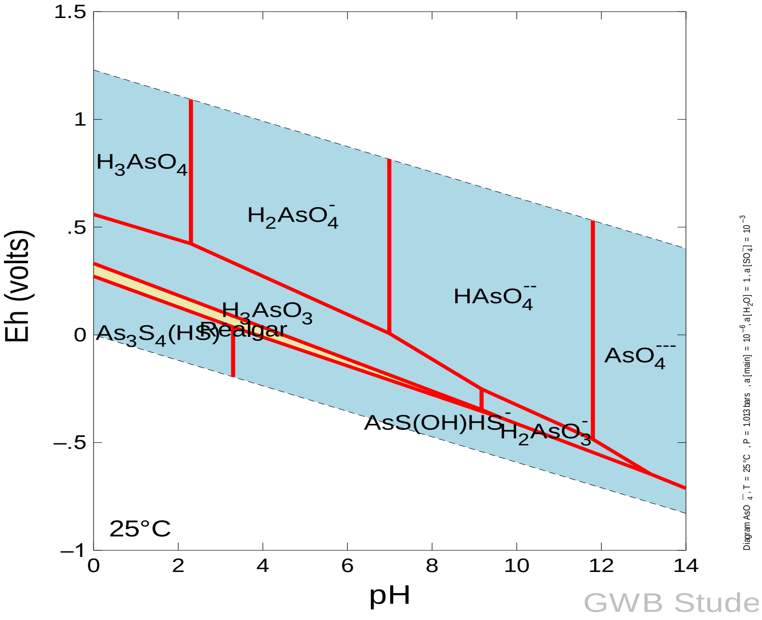


Figure 3: Eh-pH diagram for As-O-H-S system at 25°C and 1 bar.{As} = 10^{-6}, {S} =0.001

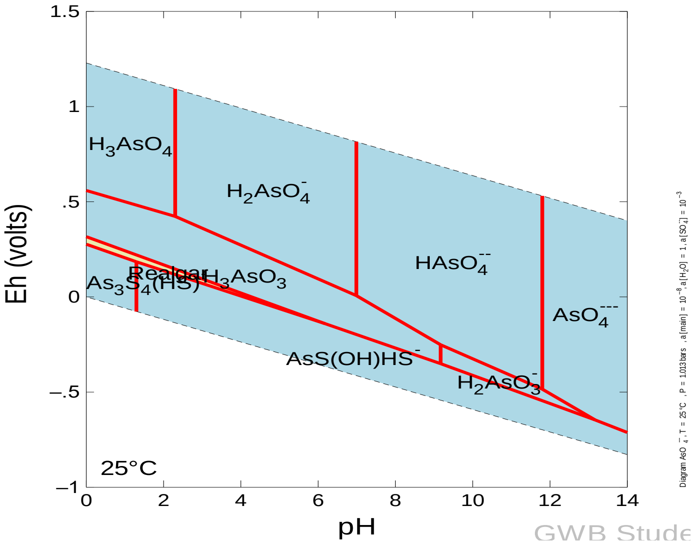


Figure 4: **Eh-pH diagram for As-O-H-S system at 25°C and 1 bar. {As} = 10^{-8}, {S} =0.001**

From Figures 2, 3 and 4, we can say that higher the activity of As, higher is the stability of orpiment and realgar. The predominance field of thioarsenite species $As_3S_4(HS)^-$ and $As(OH)SH^-$ increases with the decrease in activity of As. Arsenic partitions significantly into aqueous species $As_3S_4(HS)^-$ and $As(OH)SH^-$ under mildly reducing and acidic conditions.

4..1. Arsenic speciation in presence of reduced sulphur and iron

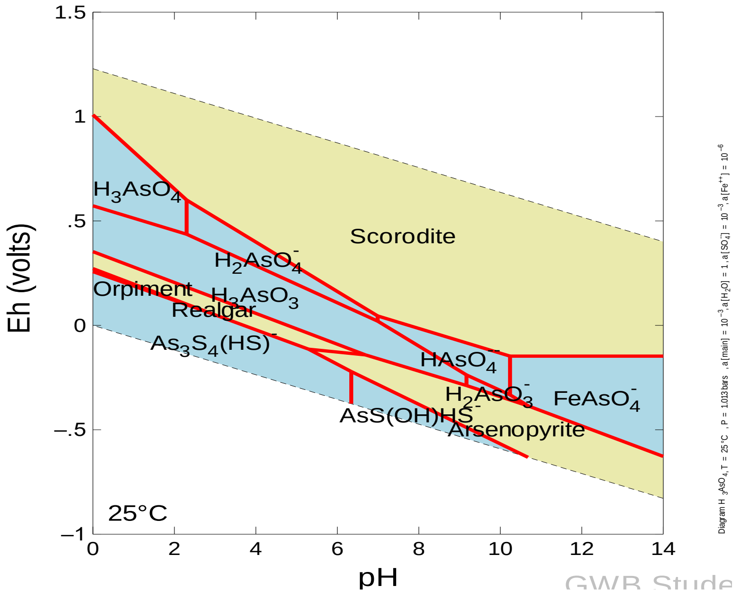


Figure 5: **Eh-pH diagram for As-O-H-S-Fe system at 25°C and 1 bar. {As} = 0.001,{S} =0.001 and {Fe} = 10^{-6}**

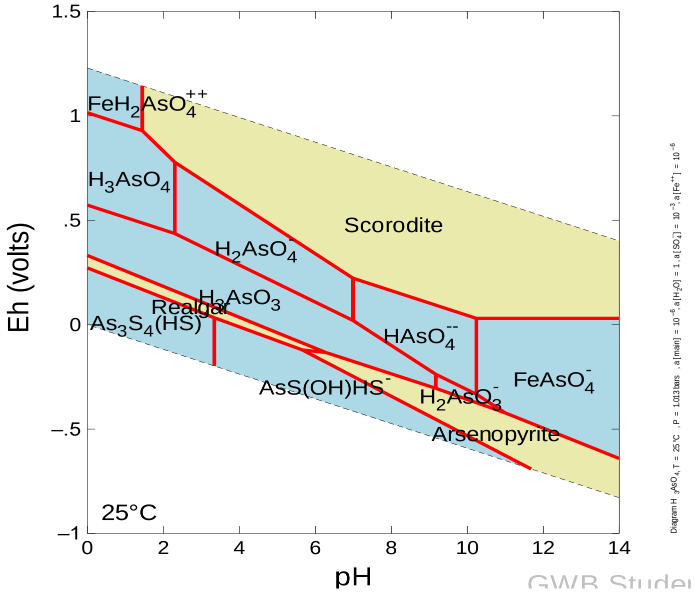


Figure 6: **Eh-pH diagram for As-O-H-S-Fe system at 25°C and 1 bar.{As} = 10^{-6}, {S} =0.001 and {Fe} = 10^{-6}**

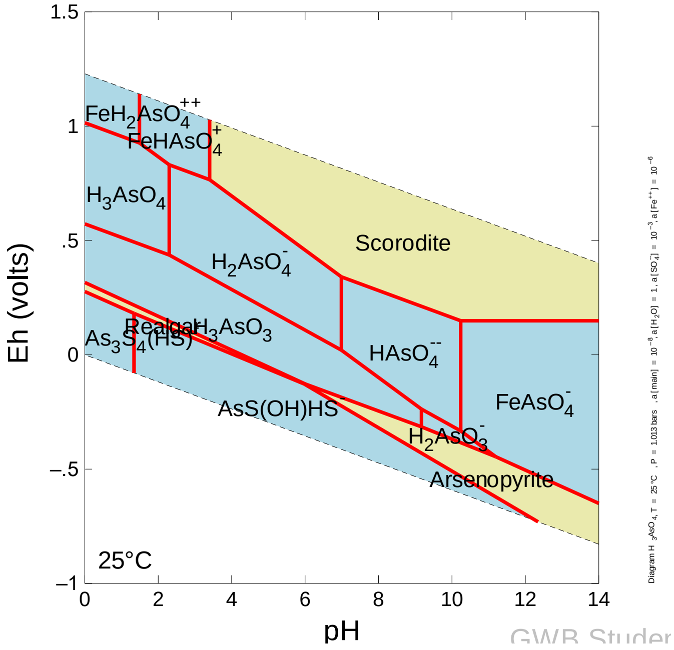


Figure 7: **Eh-pH diagram for As-O-H-S-Fe system at 25°C and 1 bar. {As} = 10^{-6}, {S} =0.001 and {Fe} = 10^{-6}**

The Eh-pH plot for As-O-H-S-Fe system is characterised by a large stability field for scorodite ($FeAsO_4.2H_2O$) under a wide range of pH which reduces the stability fields of As (V) aqueous species under oxidising conditions. Addition of Fe into As-O-H-S system shrinks the stability fields of orpiment and realgar due to the formation of arsenopyrite. Arsenopyrite is stable under basic, reducing conditions. Arsenopyrite field replaces part of the thioarsenite species and arsenous acid fields in the As–O–H–S system. Predominance of aqueous species fields in

Figure 6 results from the inclusion of ferric and ferrous arsenate species(Accornero *et al.*, 2017). As a result, $FeH_2AsO_4^{++}$ reduce the predominance fields of H_3AsO_4 and $H_2AsO_4^-$ under extremely acidic pH with {As} = 10^{-6}, {S} =0.001 and {Fe} = 10^{-6}. Figure 7 shows that further decreasing the activity of arsenic increase the predominance fields of $FeH_2AsO_4^{++}$and $FeHAsO_4^+$ and reduces the stability of arsenic species.

• Potential Causes of Mobilisation of Arsenic in the Groundwater

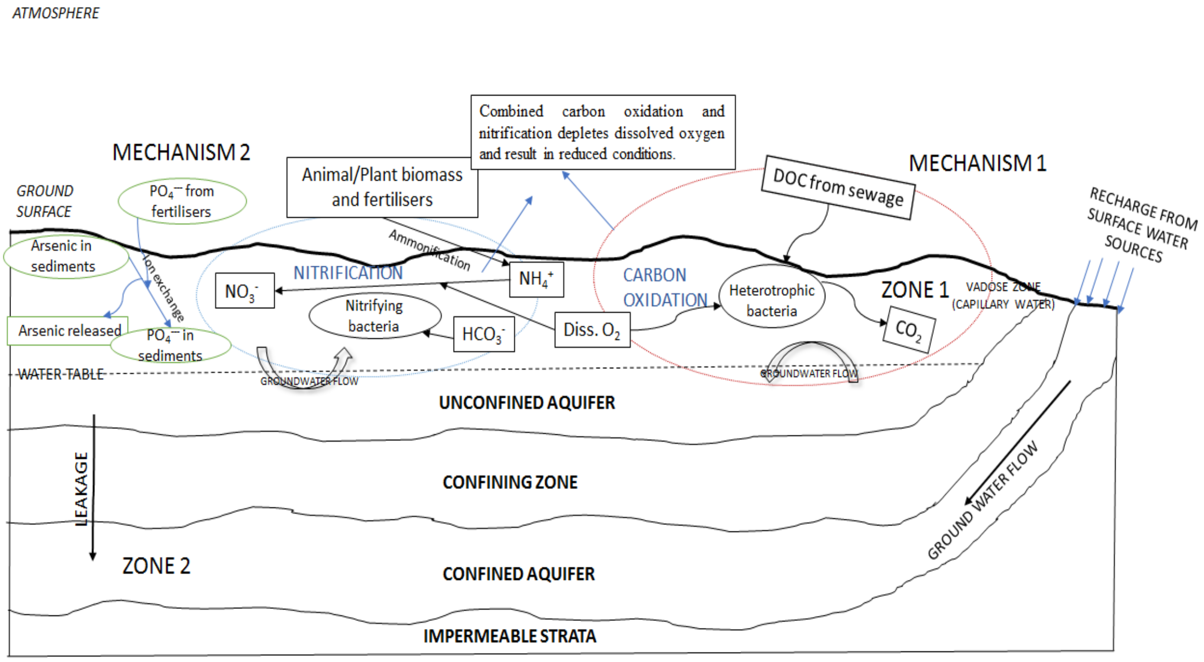


Figure 8: **Flow diagram showing various mechanisms of arsenic release**

Case 1:Dantong Basin, North China

The correlation scatter plot matrix is prepared using R-studio and following observations are made using the data:

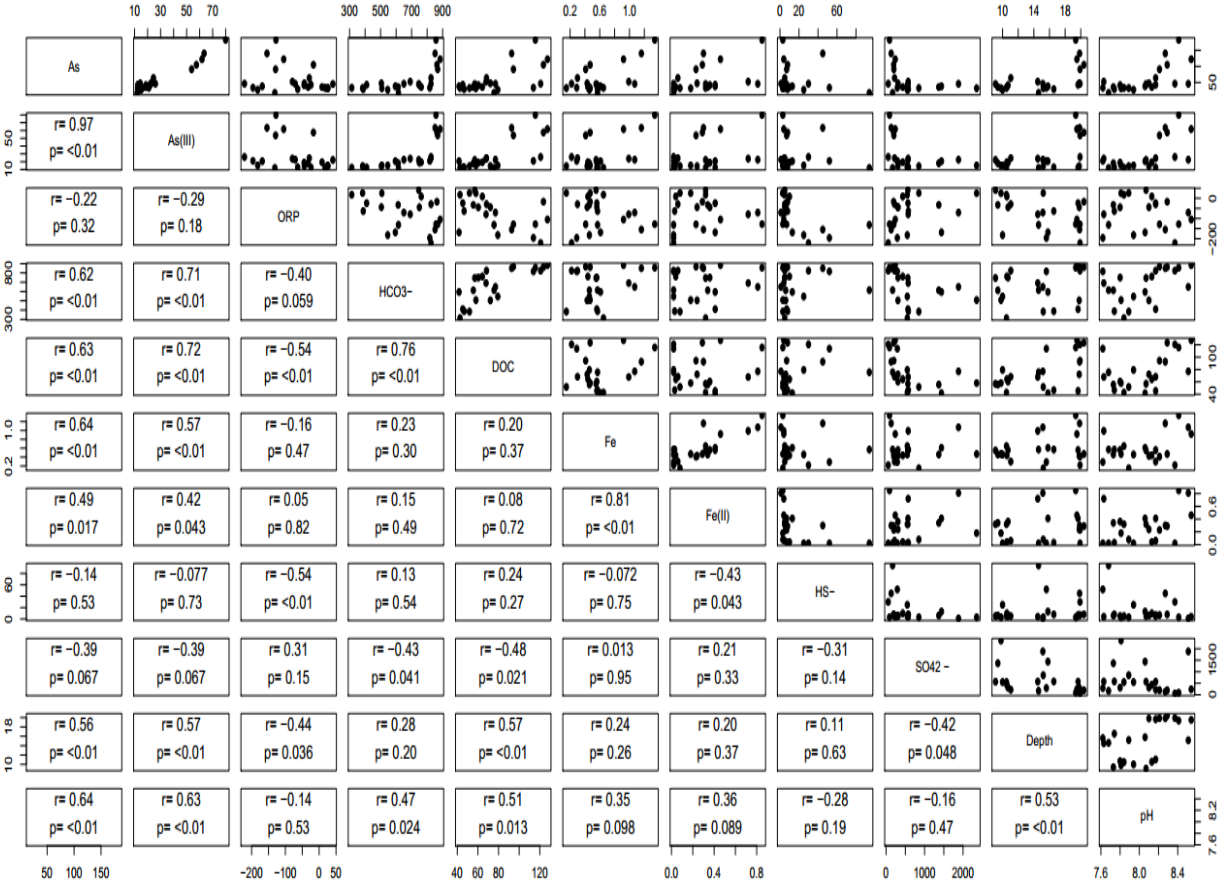


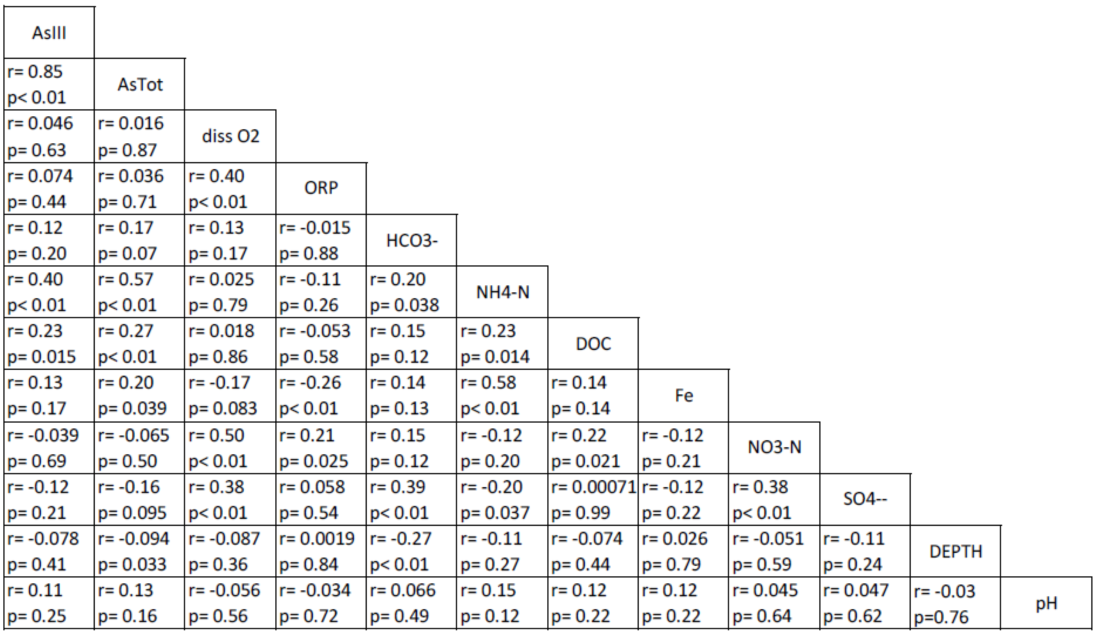
Figure 9: **Correlation matrix for various physicochemical parameters measured in Dantong Basin, North China**

- The total arsenic concentration varied from 182 µg/L to 18.0 µg/L with an average of 58.4µg/L and As (III) ranged from 12.0 to 79.9 µg/L with an average of 27.9 µg/L. As (III) is predominately present in comparison to As (V) as evident from the strong positive correlation between As (III) and As (tot).
- DOC concentration was found to be 40.8-127.4 mg/L in the groundwater and DOC is negatively correlated with ORP at 99% significance level. Also, DOC has a strong positive correlation with arsenic. This implies that DOC has reduced the ORP in the subsurface water and enhanced arsenic levels. The negative values of ORP (-221.2 to 8.7 mV) also indicate reducing nature of the subsurface water.
- Bicarbonate concentration is found to be in the range of 214 mg/L to 884 mg/L in the groundwater samples. Bicarbonate has a weak negative correlation with ORP but very strong positive correlation with arsenic and iron.
- As and ORP are negatively correlated at 64% significance level. This can be related to the fact that out of 100 samples, 64 samples contain arsenic in the reduced region of the unconfined aquifer (Zone 1 in 8) and 32 samples contain transported arsenic in the confined aquifer (Zone 2 in 8) which can have positive ORP.

- The dissolved Fe concentrations varied from 0.15 to 1.34mg/L and Fe(II) varied from 0.02 to 0.85 mg/L. Fe (II) has a strong positive correlation with total Fe concentration which implies that Fe(II) is the dominant dissolved Fe species in groundwater.
- Iron and arsenic are positively correlated at 99% significance level which can be attributed to the simultaneous release of Fe and As controlled by reductive dissolution of iron oxyhydroxides.
- Interestingly, dissolved sulphide is also prevalent in the groundwater. The sulphide is measured in the form of HS^- and ranged from 1 to 94 µg/L with an average of 15µg/L. The negative strong correlation between ORP and HS^- is evident. A negative correlation between SO_4^{--} and arsenic indicates that reduction of sulphur occurs in the reducing aquifers (Guo *et al.*, 2011). Formation of dissolved sulphide from reduction of $SO_4^{--}$and oxidation for organic matter also contributed to the reduced environment in groundwater.

Case 2: Nawabganj, Faridpur, Lakhimpur and Naokhali (Bangladesh)

Using the data, correlation matrix has been prepared to study the potential causes of arsenic pollution. pollution.



AsIII											
r= 0.85 p< 0.01	AsTot										
r= 0.046 p= 0.63	r= 0.016 p= 0.87	diss O2									
r= 0.074 p= 0.44	r= 0.036 p= 0.71	r= 0.40 p< 0.01	ORP								
r= 0.12 p= 0.20	r= 0.17 p= 0.07	r= 0.13 p= 0.17	r= -0.015 p= 0.88	HCO3-							
r= 0.40 p< 0.01	r= 0.57 p< 0.01	r= 0.025 p= 0.79	r= -0.11 p= 0.26	r= 0.20 p= 0.038	NH4-N						
r= 0.23 p= 0.015	r= 0.27 p< 0.01	r= 0.018 p= 0.86	r= -0.053 p= 0.58	r= 0.15 p= 0.12	r= 0.23 p= 0.014	DOC					
r= 0.13 p= 0.17	r= 0.20 p= 0.039	r= -0.17 p= 0.083	r= -0.26 p< 0.01	r= 0.14 p= 0.13	r= 0.58 p< 0.01	r= 0.14 p= 0.14	Fe				
r= -0.039 p= 0.69	r= -0.065 p= 0.50	r= 0.50 p< 0.01	r= 0.21 p= 0.025	r= 0.15 p= 0.12	r= -0.12 p= 0.20	r= 0.22 p= 0.021	r= -0.12 p= 0.21	NO3-N			
r= -0.12 p= 0.21	r= -0.16 p= 0.095	r= 0.38 p< 0.01	r= 0.058 p= 0.54	r= 0.39 p< 0.01	r= -0.20 p= 0.037	r= 0.00071 p= 0.99	r= -0.12 p= 0.22	r= 0.38 p< 0.01	SO4--		
r= -0.078 p= 0.41	r= -0.094 p= 0.033	r= -0.087 p= 0.36	r= 0.0019 p= 0.84	r= -0.27 p< 0.01	r= -0.11 p= 0.27	r= -0.074 p= 0.44	r= 0.026 p= 0.79	r= -0.051 p= 0.59	r= -0.11 p= 0.24	DEPTH	
r= 0.11 p= 0.25	r= 0.13 p= 0.16	r= -0.056 p= 0.56	r= -0.034 p= 0.72	r= 0.066 p= 0.49	r= 0.15 p= 0.12	r= 0.12 p= 0.22	r= 0.12 p= 0.22	r= 0.045 p= 0.64	r= 0.047 p= 0.62	r= -0.03 p=0.76	pH

Figure 10: Summary of correlation matrix in Nawabganj, Bangladesh

- As(III) has a strong positive correlation with Tot As in all the four districts. Hence, we can say that the predominate As species is As (III) in the groundwater of the four districts.
- The maximum Total As concentration of 2340 µg/L is found in Nawabganj district at depth of 21m. As(III) at this depth is found to be 2210 µg/L.
- Very low concentration of dissolved O_2 (0-4.1mg/L) is found in the groundwater of Nawabganj and has a strong positive correlation with ORP. This indicates a reducing

condition in the subsurface water. This is further supported by the negative correlation between dissolved organic carbon and ORP.

- Dissolved organic carbon concentration varied from 0-9.4 mg/L in Nawabganj and it has a very weak positive correlation with dissolved O_2 which implies a mildly reducing condition in the groundwater. Further, dissolved organic carbon has a very strong positive correlation with arsenic and this is the main condition which indicates reducing environment in the groundwater.
- Bicarbonate and ammoniacal nitrogen have weak negative correlation with ORP which is an indication of mildly reducing environment. Ammoniacal nitrogen also has a weak negative correlation with dissolved O_2.
- Both bicarbonate and ammoniacal nitrogen has good positive correlation with arsenic. This shows that reducing conditions due to nitrification favour release of arsenic into dissolved form.
- Arsenic and ORP has a very weak positive correlation of 0.036 at 29% significance level. This shows that some samples have high arsenic concentration in areas where oxidizing conditions prevail. This is possible only when arsenic has been transported to confined aquifers through cracks in the confining zones.
- Iron and arsenic have a weak positive correlation implying that both exist together in the groundwater.

As(III)											
r=0.96 p<0.01	As(Tot)										
r=-0.022 p=0.88	r=-0.088 p=0.54	Diss O2									
r=-0.27 p=0.051	r=-0.30 p=0.031	r=0.082 p=56	ORP								
r=0.017 p=0.91	r=-0.031 p=0.83	r=0.12 p=0.38	r=0.054 p=0.70	HCO3-							
r=-0.027 p=0.85	r=-0.021 p=0.88	r=-0.082 p=0.56	r=-0.05 p=0.73	r=0.21 p=0.14	NH4-N						
r=0.014 p=0.92	r=0.018 p=0.90	r=-0.16 p=0.26	r=-0.12 p=0.41	r=0.24 p=0.081	r=0.68 p<0.01	DOC					
r=0.011 p=0.94	r=0.025 p=86	r=-0.045 p=0.75	r=-0.16 p=0.27	r=0.17 p=0.22	r=0.59 p<0.01	r=0.50 p<0.01	Fe				
r=0.011 p=0.94	r=0.013 p=0.93	r=-0.058 p=0.68	r=-0.057 p=0.69	r=0.19 p=0.18	r=-0.22 p=0.12	r=0.058 p=0.6	r=0.13 p=0.36	NO3-N			
r=-0.11 p=0.46	r=-0.13 p=0.34	r=-0.038 p=0.79	r=0.15 p=0.30	r=-0.019 p=0.89	r=-0.20 p=0.16	r=-0.23 p=0.098	r=-0.35 p=0.01	r=-0.11 p=0.44	SO4--		
r=-0.10 p=0.47	r=-0.10 p=0.46	r=-0.089 p=0.53	r=-0.09 p=0.52	r=0.18 p=0.21	r=0.10 p=0.47	r=0.14 p=0.32	r=0.073 p=0.61	r=-0.062 p=0.66	r=-0.17 p=0.23	DEPTH	
r=0.21 p=0.13	r=0.26 p=0.067	r=-0.047 p=0.74	r=-0.094 p=0.51	r=-0.39 p<0.01	r=-0.49 p<0.01	r=-0.47 p<0.01	r=-0.54 p<0.01	r=-0.034 p=0.81	r=0.047 p=0.74	r=0.054 p=0.70	pH

Figure 11: Summary of Correlation Matrix in Faridpur, Bangladesh

- Faridpur district has a maximum As (tot) concentration of 1460 µg/L at 27.6 m and maximum As(III) of 990 µg/L at the same depth.
- In Faridpur, dissolved organic carbon varied from 0.1-13 mg/L and negligible concentration of O_2 (0-1.4 mg/L) is found in the groundwaters of Faridpur indicating reducing conditions.
- Weak negative correlation between dissolved organic carbon and dissolved O_2 of -0.16 at 74% significance level and -0.12 at 59% significance level between dissolved organic carbon and ORP indicate mild reducing conditions in the upper unconfined aquifer only where very low values of dissolved O_2 and ORP are obtained. But organic matter may be transported into deeper aquifers where oxidizing conditions exist due to leakage.
- Further Arsenic (Tot) and ORP are negatively associated with correlation value of -0.031 at significance level of 97%. Similar variation is found between arsenic (tot) and dissolved O_2. This shows that some samples contain arsenic in the reduced aquifer where reducing condition is prevalent and some samples also contain arsenic in the deeper aquifer where oxidizing conditions still prevail.
- Bicarbonate and ammoniacal nitrogen has a similar trend with ORP. Both are negatively associated with ORP with a weak correlation value of -0.05 at 30% significance level.
- Arsenic is also weakly associated with bicarbonate and ammoniacal nitrogen with a negative correlation at 10% significance level. This indicates that nitrification doesn't contribute to the reducing condition in a significant way in the Faridpur groundwater.

AsIII												
r= 0.93 p< 0.01	AsTot											
r= -0.14 p= 0.26	r= -0.14 p= 0.25	diss O2										
r= -0.45 p < 0.01	r= -0.51 p < 0.01	r= 0.30 p= 0.012	ORP									
r= 0.17 p= 0.15	r= 0.24 p= 0.049	r= -0.071 p= 0.56	r= -0.19 p= 0.12	HCO3-								
r= 0.48 p< 0.01	r= 0.54 p< 0.01	r= -0.11 p= 0.37	r= -0.37 p< 0.01	r= 0.48 p< 0.01	NH4-N							
r= 0.42 p< 0.01	r= 0.47 p< 0.01	r= -0.14 p= 0.26	r= -0.33 p< 0.01	r= 0.41 p< 0.01	r= 0.49 p< 0.01	DOC						
r= 0.13 p= 0.28	r= 0.24 p= 0.044	r= -0.13 p= 0.28	r= -0.18 p= 0.13	r= 0.048 p= 0.69	r= 0.44 p< 0.01	r= 0.44 p< 0.01	Fe					
r= 0.0081 p= 0.95	r= -0.021 p= 0.86	r= -0.036 p= 0.77	r= 0.055 p= 0.65	r= 0.044 p= 0.72	r= -0.021 p= 0.87	r= 0.0054 p= 0.96	r= -0.11 p= 0.38	NO3-N				
r= -0.17 p= 0.16	r= -0.17 p= 0.17	r= -0.036 p= 0.76	r= 0.34 p< 0.01	r= 0.36 p< 0.01	r= -0.57 p= 0.64	r= -0.16 p= 0.19	r= -0.15 p= 0.22	r= 0.029 p= 0.81	SO4--			
r= -0.37 p< 0.01	r= -0.39 p< 0.01	r= 0.23 p= 0.06	r= 0.28 p= 0.021	r= -0.58 p< 0.01	r= -0.32 p< 0.01	re= -0.28 p= 0.021	r= 0.093 p= 0.44	r= -0.10 p= 0.41	r= -0.15 p= 0.21	DEPTH		
r= 0.34 p< 0.01	r= 0.34 p< 0.01	r= -0.0097 p= 0.94	r= -0.33 p< 0.01	r= 0.46 p< 0.01	r= 0.22 p= 0.074	r= 0.21 p= 0.078	r= -0.48 p< 0.01	r= 055 p= 0.65	r= 0.11 p= 0.36	r= -0.56 p< 0.01	pH	

Figure 12: Summary of correlation matrix in Lakhimpur, Bangladesh

- The maximum concentration of As (Tot.) in Lakhimpur is 986 µg/L at 11m.
- The dissolved O_2 in the Lakhimpur waters varied from 0 to 2.1 mg/L. These low values indicate reduced groundwater. Further, correlation coefficient between dissolved organic carbon and dissolved O_2 is found to be -0.14 at 74% significance level which indicates that dissolved organic carbon is the potential cause for lowering the dissolved O_2 levels in groundwater.Further ORP(Oxidation-Reduction potential) has a negative association with a correlation value of -0.33 with dissolved organic carbon indicating the reduced conditions in the groundwater.
- Arsenic (tot) and dissolved organic carbon are very strongly correlated at 99% significance level. This shows that the potential cause of arsenic release into the groundwater in Lakhimpur is dissolved organic carbon.
- Ammoniacal nitrogen has a very strong correlation of -0.37 with ORP and 0.54 with arsenic at 99% significance level which indicates that nitrification may also be responsible for creating reducing conditions in Lakhimpur waters.
- Arsenic and ORP are strongly associated with a negative correlation of -0.51 at 99% significance level indicating that reducing conditions is responsible for arsenic release into dissolved form. The positive correlation between arsenic and iron shows that both are found together in Lakhimpur groundwater.

AsIII											
r= 0.99 p< 0.01	AsTot										
r= -0.33 p= 0.42	r= -0.32 p= 0.44	diss O2									
r= -0.30 p= 0.47	r= -0.30 p= 0.47	r= -0.54 p= 0.17	ORP								
r= 0.72 p= 0.044	r= 0.61 p= 0.11	r= -0.21 p= 0.62	r= -0.26 p= 0.53	HCO3-							
r= -0.10 p= 0.81	r= -0.093 p= 0.83	r= 0.17 p= 0.69	r= -0.15 p= 0.73	r= -0.083 p= 0.85	NH4-N						
r= 0.62 p= 0.10	r= 0.51 p= 0.19	r= -0.37 p= 0.37	r= -0.22 p= 0.60	r= 0.79 p= 0.021	r= -0.20 p= 0.63	DOC					
r= 0.45 p= 0.26	r= 0.49 p= 0.22	r= -0.35 p= 0.40	r= 0.072 p= 0.86	r= 0.051 p= 0.90	r= 0.65 p= 0.081	r= 0.069 p= 0.87	Fe				
r= 0.76 p= 0.028	r= 0.67 p= 0.067	r= -0.45 p= 0.27	r= -0.029 p= 0.95	r= 0.88 p< 0.01	r= -0.44 p= 0.28	r= 0.84 p< 0.01	r= -0.021 p= 0.96	NO3-N			
r= -0.15 p= 0.73	r= -0.17 p= 0.69	r= -0.24 p= 0.57	r= 0.23 p= 0.58	r= 0.20 p= 0.63	r= -0.19 p= 0.65	r= -0.16 p= 0.71	r= -0.45 p= 0.27	r= 0.15 p= 0.72	SO4--		
r= -0.61 p= 0.11	r= -0.58 p= 0.13	r= 0.074 p= 0.786	r= 0.44 p= 0.28	r= -0.72 p= 0.043	r= -0.30 p= 0.47	r= -0.40 p= 0.32	r= -0.21 p= 0.62	r= -0.49 p= 0.22	r= -0.39 p= 0.34	DEPTH	
r= 0.86 p< 0.01	r= 0.83 p= 0.01	r= -0.50 p= 0.21	r= -0.069 p= 0.87	r= 0.77 p= 0.026	r= -0.38 p= 0.35	r= 0.57 p= 0.14	r= 0.88 p< 0.01	r= 0.88 p< 0.01	r= 0.32 p= 0.44	r= -0.63 p= 0.096	pH

Figure 13: Summary of correlation matrix in Naokhali, Bangladesh

- In Naokhali, maximum arsenic (tot) concentration is found to be 670µg/L at 15.2m with ORP at -14mV.
- The dissolved O_2 concentration varied from 0 to 1.2 mg/L in Naokhali groundwater indicating reduced conditions.

- Dissolved organic carbon has negative correlation with dissolved O_2 and ORP at low level of significance. This shows that at some depths, organic matter may be a cause for reduced condition. Dissolved organic carbon has a positive correlation of 0.51 with arsenic at 80% significance level.
- Arsenic and ORP are negatively correlated at 53% significance level. This shows that arsenic has been transported to some places where oxidizing conditions prevail.
- Bicarbonate and ammoniacal nitrogen are negatively related with ORP and dissolved O_2 indicating that nitrification can also be a potential cause for reducing environment in Naokhali groundwater. This is further supported by the strong positive correlation of 0.88 between bicarbonate and nitrate.
- The positive correlation value of 0.49 between arsenic and iron shows that both exist together in Naokhali waters.

Case 3: Western Bengal Basin

Correlation analysis is being done with the available data to find the potential causes of arsenic mobilization.

Astot											
r= 0.96 p< 0.01	As(III)										
r= 0.023 p= 0.87	r= 0.017 p= 0.90	ORP									
r= -0.029 p= 0.84	r= -0.11 p= 0.45	r= 0.21 p= 0.13	diss O2								
r= -0.18 p= 0.20	r= -0.22 p= 0.11	r= -0.15 p= 0.28	r= 0.16 p= 0.26	HCO3-							
r= 0.20 p= 0.15	r= 0.15 p= 0.27	r= -0.11 p= 0.43	r= -0.19 p= 0.17	r= -0.17 p=0.23	NH4+						
r= -0.051 p= 0.72	r= -0.14 p= 0.32	r= -0.21 p= 0.13	r= 0.11 p= 0.44	r= 0.28 p= 0.043	r= 0.028 p= 0.84	DOC					
r= 0.52 p< 0.01	r= 0.56 p< 0.01	r= -0.061 p= 0.66	r= -0.082 p= 0.56	r= -0.15 p= 0.27	r= 0.21 p= 0.12	r= -0.16 p= 0.26	Fetot				
r= 0.52 p< 0.01	r= 0.57 p< 0.01	r= -0.05 p= 0.72	r= -0.085 p= 0.54	r= -0.16 p= 0.26	r= 0.22 p= 0.11	r= -0.16 p= 0.25	r= 1.00 p< 0.01	Fe(II)			
r= -0.074 p= 0.60	r= -0.075 p= 0.59	r= 0.60 p< 0.01	r= 0.19 p= 0.17	r= 0.099 p= 0.48	r= -0.10 p= 0.46	r= 0.016 p= 0.91	r= -0.15 p= 0.28	r= -0.15 p= 0.29	NO3-N		
r= -0.036 p= 0.80	r= -0.017 p= 0.90	r= 0.41 p< 0.01	r= 0.29 p= 0.032	r= -0.093 p= 0.051	r= -0.24 p= 0.077	r= -0.12 p= 0.39	r= 0.037 p= 0.79	r= 0.02 p= 0.89	r= 0.41 p< 0.01	SO4--	
r= -0.39 p< 0.01	r= -0.41 p< 0.01	r= -0.62 p< 0.01	r= -0.047 p= 0.74	r= 0.050 p< 0.01	r= -0.053 p= 0.71	r= 0.39 p< 0.01	r= -0.47 p< 0.01	r= -0.48 p< 0.01	r= -0.11 p= 0.45	r= -0.26 p= 0.056	pH

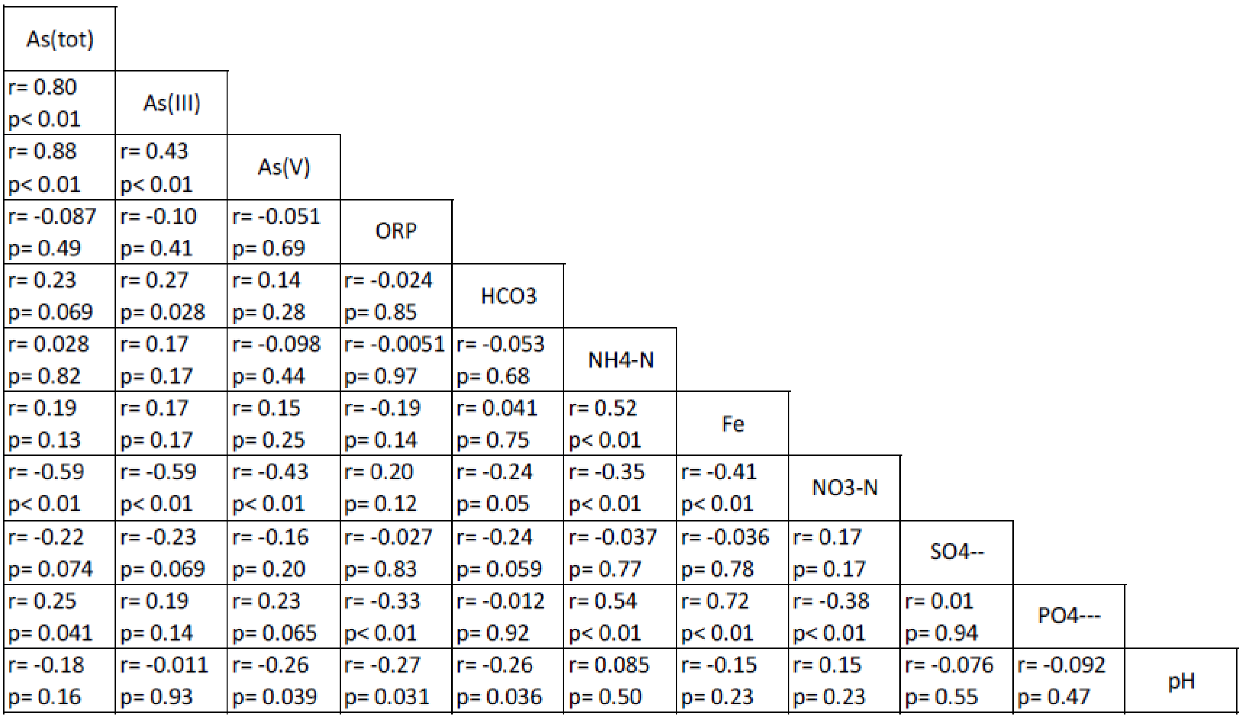
Figure 14: Summary of correlation matrix in Western Bengal Basin

- The depth of the wells varied from 50-200 m below ground level.
- The total arsenic concentration varied from 0 to 137 µg/L and As (III) from 0 to 82 µg/L. As (III) and As (tot) have a correlation of 0.96 at 99% significance level which implies that the dominant species in the groundwater is As (III).

- Low levels of dissolved O_2 is detected (mean 1.04 mg/L) and the ORP is found to be in low range (15-120 mV). These conditions indicate reduced environment in the groundwater.
- Further the weak negative correlation value of -0.21 between dissolved organic matter and ORP also support mildly reduced nature. Also dissolved organic matter and dissolved O_2 have very weak positive correlation of 0.11 which may indicate that organic matter may be responsible for mildly reducing conditions at some locations.
- ORP and dissolved O_2 are weakly related to arsenic in these samples. This shows that few samples have arsenic concentrations in the reduced zone of the aquifer. Other samples may have arsenic contamination that have been transported due to groundwater flow.
- Ammoniacal nitrogen has weak negative correlation of -0.11 and -0.19 with ORP and dissolved O_2respectively at very low level of significance. This shows that nitrification has an insignificant role in creating reduced conditions in the Bengal groundwater.
- Fe(tot) concentration in this region is found to be in the range 0-5.23 mg/L and Fe(II) in the range 0-5.2 mg/L. The correlation value between Fe(tot) and Fe(II) is 1 at 99% significance level. This indicates that the dominant iron species is Fe(II) due to reductive dissolution of iron oxyhydroxides. Fe(II) and As (III) are also strongly correlated (0.57) with each other suggesting that both exist simultaneously in groundwater.

Case 4: Ballia, Uttar Pradesh

Sixty-five ground water samples were collected in Ballia district during July 2006 to April 2007 by Chauhan and co-workers (Chauhan *et al.*, 2009). They measured various physicochemical parameters of the samples. Using the data, correlation matrix has been prepared to analyse the potential cause of arsenic mobilization in this region.



As(tot)										
$r = 0.80$ $p < 0.01$	As(III)									
$r = 0.88$ $p < 0.01$	$r = 0.43$ $p < 0.01$	As(V)								
$r = -0.087$ $p = 0.49$	$r = -0.10$ $p = 0.41$	$r = -0.051$ $p = 0.69$	ORP							
$r = 0.23$ $p = 0.069$	$r = 0.27$ $p = 0.028$	$r = 0.14$ $p = 0.28$	$r = -0.024$ $p = 0.85$	HCO3						
$r = 0.028$ $p = 0.82$	$r = 0.17$ $p = 0.17$	$r = -0.098$ $p = 0.44$	$r = -0.0051$ $p = 0.97$	$r = -0.053$ $p = 0.68$	NH4-N					
$r = 0.19$ $p = 0.13$	$r = 0.17$ $p = 0.17$	$r = 0.15$ $p = 0.25$	$r = -0.19$ $p = 0.14$	$r = 0.041$ $p = 0.75$	$r = 0.52$ $p < 0.01$	Fe				
$r = -0.59$ $p < 0.01$	$r = -0.59$ $p < 0.01$	$r = -0.43$ $p < 0.01$	$r = 0.20$ $p = 0.12$	$r = -0.24$ $p = 0.05$	$r = -0.35$ $p < 0.01$	$r = -0.41$ $p < 0.01$	NO3-N			
$r = -0.22$ $p = 0.074$	$r = -0.23$ $p = 0.069$	$r = -0.16$ $p = 0.20$	$r = -0.027$ $p = 0.83$	$r = -0.24$ $p = 0.059$	$r = -0.037$ $p = 0.77$	$r = -0.036$ $p = 0.78$	$r = 0.17$ $p = 0.17$	SO4--		
$r = 0.25$ $p = 0.041$	$r = 0.19$ $p = 0.14$	$r = 0.23$ $p = 0.065$	$r = -0.33$ $p < 0.01$	$r = -0.012$ $p = 0.92$	$r = 0.54$ $p < 0.01$	$r = 0.72$ $p < 0.01$	$r = -0.38$ $p < 0.01$	$r = 0.01$ $p = 0.94$	PO4---	
$r = -0.18$ $p = 0.16$	$r = -0.011$ $p = 0.93$	$r = -0.26$ $p = 0.039$	$r = -0.27$ $p = 0.031$	$r = -0.26$ $p = 0.036$	$r = 0.085$ $p = 0.50$	$r = -0.15$ $p = 0.23$	$r = 0.15$ $p = 0.23$	$r = -0.076$ $p = 0.55$	$r = -0.092$ $p = 0.47$	pH

Figure 15: Summary of correlation matrix in Ballia, UP

- The groundwater samples are reducing in nature as evident from negative ORPs. ORP ranged from 33mV to -130mV.
- Arsenic (tot) concentration varied from 0 to 468 µg/L, As (III) from 0 to 218 µg/L and As (V) from 0 to 315 µg/L. The strong positive correlation between arsenic species indicate that both the species exist in the groundwater in nearly equal proportion.
- The mildly reducing nature of the groundwater is also evident from weak negative correlation between bicarbonate and ammoniacal nitrogen. This shows that nitrification may be a reason for the reducing environment.
- Iron concentration varied from <1 to 13.2 mg/L and the positive correlation between ORP and iron suggest that bulk of iron is present in reduced form. Iron has a positive correlation with arsenic too which suggests that both exist together.
- We also found out that arsenic and ORP are very weakly correlated. This may be due to mixing of groundwater from different redox zones.
- Further, we could see phosphate concentration of 0.11 to 0.97 mg/L. This is mainly due to widespread use of fertilizers in irrigation. Phosphate has a weak correlation with arsenic indicating that phosphate has replaced arsenic in the groundwater.

Case 5:Ghazipur, Uttar Pradesh

The depth of tube wells varied from 11 to 62m with an average of 26.5m. To evaluate the potential cause of arsenic release, correlation matrix is prepared using the data.

As										
r= 0.98 p< 0.01	As(III)									
r= 0.97 p< 0.01	r= 0.90 p< 0.01	As(V)								
r= -0.16 p= 0.40	r= -0.14 p= 0.47	r= -0.18 p= 0.35	ORP							
r= -0.30 p= 0.10	r= -0.31 p= 0.096	r= -0.28 p= 0.14	r= 0.27 p= 0.15	HCO3-						
r= -0.27 p= 0.16	r= -0.24 p= 0.21	r= -0.28 p= 0.13	r= 0.53 p< 0.01	r= 0.19 p= 0.32	Fe					
r= -0.20 p= 0.29	r= -0.22 p= 0.25	r= -0.17 p= 0.38	r= 0.17 p= 0.38	r= -0.014 p= 0.94	r= 0.068 p= 0.72	NO3-				
r= 0.038 p= 0.84	r= 0.053 p= 0.78	r= 0.018 p= 0.93	r= 0.12 p= 0.54	r= 0.13 p= 0.48	r= 0.21 p= 0.27	r= 0.55 p< 0.01	SO4--			
r= 0.00098 p= 1.00	r= 0.039 p= 0.84	r= -0.046 p= 0.81	r= 0.15 p= 0.44	r= 0.22 p= 0.24	r= 0.0058 p= 0.98	r= 0.15 p= 0.42	r= 0.16 p= 0.41	PO4---		
r= -0.34 p= 0.065	r= -0.36 p= 0.048	r= -0.29 p= 0.12	r= 0.16 p= 0.41	r= 0.22 p= 0.24	r= 0.20 p= 0.29	r= -0.14 p= 0.46	r= -0.11 p= 0.56	r= -0.25 p= 0.18	Depth	
r= 0.54 p< 0.01	r= 0.53 p=< 0.01	r= 0.53 p< 0.01	r= -0.36 p= 0.049	r= -0.34 p= 0.062	r= -0.26 p= 0.17	r= -0.027 p= 0.89	r= 0.12 p= 0.51	r= 0.17 p= 0.37	r= -0.44 p= 0.014	pH

Figure 16: **Summary of correlation matrix in Ghazipur, UP (May 2007)**

As										
r= 1.00 p< 0.01	As(III)									
r= 0.97 p< 0.01	r= 0.94 p< 0.01	As(V)								
r= -0.16 p= 0.40	r= -0.15 p= 0.43	r= -0.17 p= 0.36	ORP							
r= -0.28 p= 0.13	r= -0.23 p= 0.21	r= -0.40 p= 0.028	r= -0.057 p= 0.76	HCO3-						
r= 0.032 p= 0.87	r= 0.03 p= 0.87	r= 0.035 p= 0.85	r= 0.12 p= 0.51	r= 0.18 p= 0.33	Fe					
r= -0.20 p= 0.29	r= -0.20 p= 0.29	r= -0.19 p= 0.32	r= 0.26 p= 0.17	r= 0.0069 p= 0.97	r= 0.16 p= 0.40	NO3-				
r= -0.21 p= 0.27	r= -0.21 p= 0.26	r= -0.19 p= 0.31	r= 0.25 p= 0.19	r= 0.00052 p= 1.00	r= 0.15 p= 0.41	r= 1.00 p< 0.01	SO4--			
r= -0.0063 p= 0.97	r= 0.00051 p= 1.00	r= -0.025 p= 0.90	r= 0.29 p= 0.12	r= 0.046 p= 0.81	r= -0.063 p= 0.74	r= 0.061 p= 0.75	r= 0.037 p= 0.85	PO4---		
r= -0.34 p= 0.065	r= -0.33 p= 0.075	r= -0.36 p= 0.053	r= -0.098 p= 0.61	r= 0.20 p= 0.30	r= -0.31 p= 0.092	r= -0.14 p= 0.46	r= -0.13 p= 0.50	r= -0.19 p= 0.32	Depth	
r= 0.0098 p= 0.96	r= 0.024 p= 0.90	r= -0.029 p= 0.88	r= 0.057 p= 0.77	r= 0.17 p= 0.36	r= 0.26 p= 0.17	r= -0.071 p= 0.71	r= -0.089 p= 0.64	r= 0.021 p= 0.91	r= -0.21 p= 0.26	pH

Figure 17: **Summary of Correlation Matrix in Ghazipur, UP (Oct 2007)**

- Arsenic concentration varied from 6.4 to 259.5 µg/L and from 5.1 to 205.5 µg/L during May 2007 and October 2007 respectively.
- Both the species of arsenic have strong positive correlation with total arsenic concentration at high level of significance during both the seasons. Hence, nearly equal proportions of the species are present in the groundwater.
- Range of ORP observed during May 2007 is 346-640 mV and during October 2007 is 401-747 mV.

- In both the seasons, ORP and arsenic have negative correlation but at low significance levels. This indicates that the upper aquifer may be reducing in nature and has low levels of ORP and high levels of arsenic. In addition to that arsenic is also present in areas of oxidizing conditions because of leakage in the redox zones.
- Although the groundwater is reducing, there exists poor correlation between arsenic and iron. This may be due to the precipitation of Fe^{2+} as $FeCO_3$(Welch & Lico, 1998).
- The reducing nature of groundwater is further supported by poor correlation between arsenic and nitrate in both seasons which reveals that apart from dissolved O_2, nitrate is considered as thermodynamically favored electron acceptor for reducing condition.
- Considerable amount of phosphates is also present in the groundwater. This is mainly due to the application of fertilizers for irrigation.

Case 6: Sonargaon Thana, Bangladesh

Using the data, correlation matrix is being prepared to find out the potential cause of arsenic release.

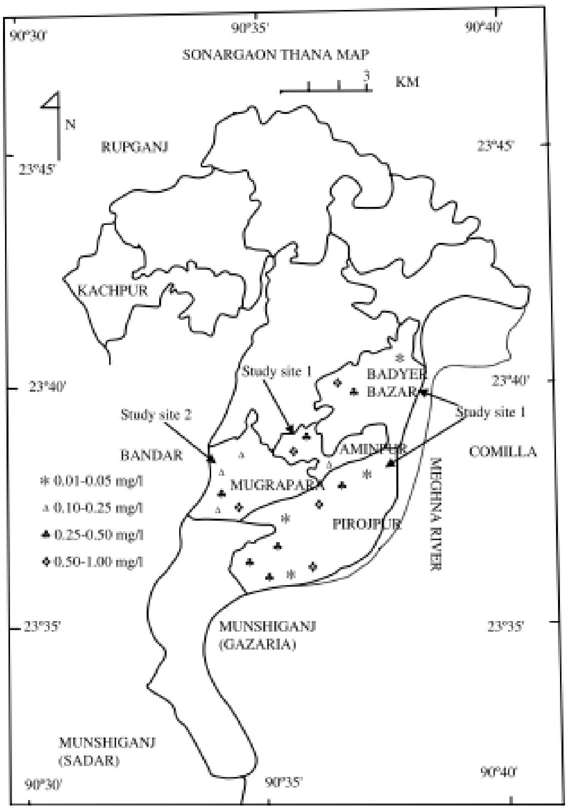


Figure 18: Map showing two different sites for analysis in Sonargaonthana, Bangladesh(H. M. Anawar *et al.*, 2003)

As									
r= 0.24 p= 0.27	Diss O2								
r= 0.63 p< 0.01	r= 0.051 p= 0.81	HCO3-							
r= 0.43 p= 0.038	r= 0.10 p= 0.64	r= 0.52 p< 0.01	NH4+						
r= 0.65 p< 0.01	r= 0.047 p= 0.83	r= 0.50 p= 0.012	r= 0.67 p< 0.01	DOC					
r= 0.34 p= 0.10	r= 0.026 p= 0.90	r= 0.70 p< 0.01	r= 0.63 p< 0.01	r= 0.52 p< 0.01	Fe				
r= -0.20 p= 0.35	r= -0.097 p= 0.65	r= -0.22 p= 0.30	r= -0.32 p= 0.12	r= -0.40 p= 0.055	r= -0.47 p= 0.021	SO4--			
r= -0.45 p= 0.027	r= -0.12 p= 0.59	r= -0.12 p= 0.59	r= 0.12 p= 0.59	r= -0.26 p= 0.22	r= 0.096 p= 0.65	r= -0.058 p= 0.79	NO3-		
r= -0.78 p< 0.01	r= -0.12 p= 0.59	r= -0.66 p< 0.01	r= -0.42 p= 0.042	r= -0.54 p< 0.01	r= -0.50 p= 0.012	r= 0.16 p= 0.45	r= 0.19 p= 0.37	Depth	
r= 0.53 p< 0.01	r= 0.22 p= 0.31	r= 0.24 p= 0.25	r= 0.11 p= 0.62	r= 0.017 p= 0.94	r= 0.095 p= 0.66	r= -0.071 p= 0.74	r= -0.16 p= 0.46	r= -0.46 p= 0.022	pH

Figure 19: Summary of correlation matrix in Site-1, Sonargaonthana, Bangladesh

The following findings are for Site 1.

- Low concentrations of dissolved O_2 from 0 to 2.1 mg/L is detected and the concentrations of organic carbon varied from 0.2 to 5.09 mg/L. Very weak positive correlation between dissolved O_2 and dissolved organic carbon shows that the groundwater is mildly reducing nature. Arsenic and dissolved organic carbon are positively correlated (0.65) at 99% significance level indicating that sedimentary organic matter and dissolved arsenic are associated. Dissolved organic matter is also positively correlated with iron suggesting that both As and iron exist together in the groundwater and reductive dissolution of iron oxyhydroxides release sorbed arsenic into the groundwater.
- Further, bicarbonate and ammoniacal nitrogen also show weak positive correlation with dissolved O_2 indicating that nitrification is also responsible for reducing conditions. Very high concentration of ammoniacal nitrogen is detected in these waters (2.27-19.93 mg/L). Positive correlations of 0.63 and 0.43 are also obtained between arsenic with bicarbonate and ammoniacal nitrogen respectively. These relations indicate that anoxic conditions are created by microbial oxidation of dissolved organic carbon and subsequent depletion of dissolved O_2 resulting in the formation of ammoniacal nitrogen and bicarbonate.
- Nitrate concertation varied from 0 to 5.93 mg/L and sulfate from 0 to 10.5 mg/L. The reduced concentrations of terminal electron acceptors (dissolved O_2, nitrate and sulfates) and high concentrations of dissolved organic carbon and ammoniacal nitrogen indicate the reducing environment of the subsurface aquifer.

As								
r= 0.027 p= 0.94	Diss O2							
r= 0.81 p< 0.01	r= -0.0012 p= 1.00	HCO3-						
r= 0.84 p< 0.01	r= 0.21 p= 0.54	r= 0.59 p= 0.0057	DOC					
r= 0.74 p< 0.01	r= -0.45 p= 0.17	r= 0.40 p= 0.22	r= 0.61 p= 0.046	NH4+				
r= 0.23 p= 0.49	r= -0.44 p= 0.18	r= 0.13 p= 0.71	r= 0.37 p= 0.26	r= 0.37 p= 0.26	Fe			
r= -0.57 p= 0.07	r= -0.092 p= 0.79	r= -0.42 p= 0.20	r= -0.82 p< 0.01	r= -0.34 p= 0.30	r= -0.64 p= 0.036	SO4--		
r= -0.86 p< 0.01	r= -0.34 p= 0.30	r= -0.84 p< 0.01	r= -0.74 p< 0.01	r= -0.39 p= 0.24	r= -0.072 p= 0.83	r= 0.57 p= 0.067	Depth	
r= 0.062 p= 0.86	r= -0.14 p= 0.68	r= 0.28 p= 0.41	r= -0.15 p= 0.66	r= -0.29 p= 0.38	r= 0.031 p= 0.93	r= -0.13 p= 0.71	r= -0.16 p= 0.65	pH

Figure 20: Summary of correlation matrix in Site-2, Sonargaon Thana, Bangladesh

- Very low concentrations of dissolved O_2 (0-0.1mg/L) is detected in site 2 of Sonargaon Thana which indicates reduced nature of the subsurface water. Similarly, dissolved organic carbon varied from 0 to 3.96 mg/L and ammoniacal nitrogen from 2.42 to 17.42 mg/L.
- Strong positive correlation between arsenic and dissolved organic carbon reveals that organic matter is one the most important parameters in increasing arsenic concentration in water.
- Although there exists a weak positive correlation between dissolved O_2 and organic carbon, we can say that organic matter depleted dissolved O_2 only in the near surface zone of groundwater. In deeper zones, the condition is oxic.
- Ammoniacal nitrogen also shows good negative correlation with dissolved oxygen indicating that nitrification also depletes dissolved O_2 and causes anoxic conditions.
- Further, the strong positive correlation of arsenic with dissolved organic carbon (0.84) and ammoniacal nitrogen (0.74) at 99% significance level shows that these are the potential cause for depleting dissolved O_2 and mobilizing arsenic into the water
  .

• Spatial and Temporal Trend of Arsenic in India

Based on the reported data by National Rural Drinking Water Programme of the Ministry of Drinking Water and Sanitation, Government of India, tube wells in around 6800 villages in 96 districts have shown arsenic levels more than the WHO specified guideline value of 10 μg/L in 2016-2017. Population in more than 43000 habitations in India have been affected with arsenic in 2016-2017. Figures 21 and 22 show the increase in the number of villages and districts with arsenic contamination from 2010-2011 to 2016-2017.

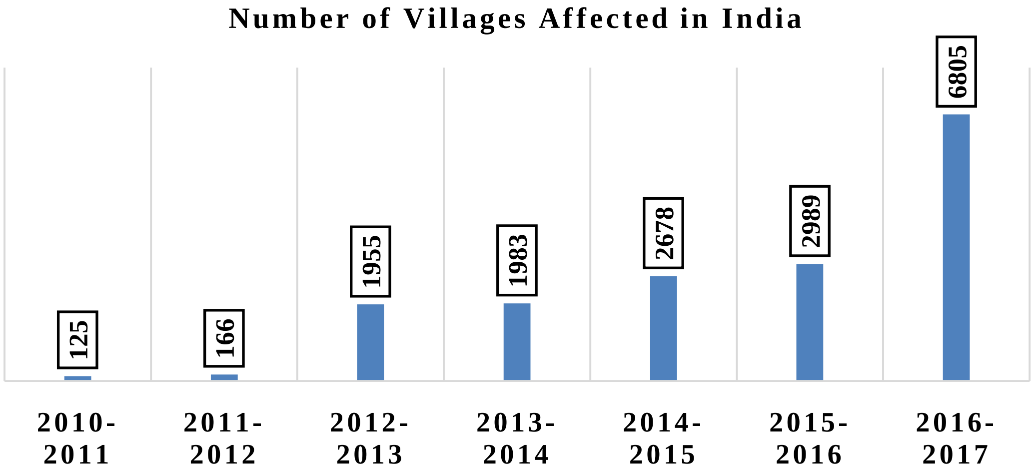


Figure 21: Number of villages with arsenic contamination

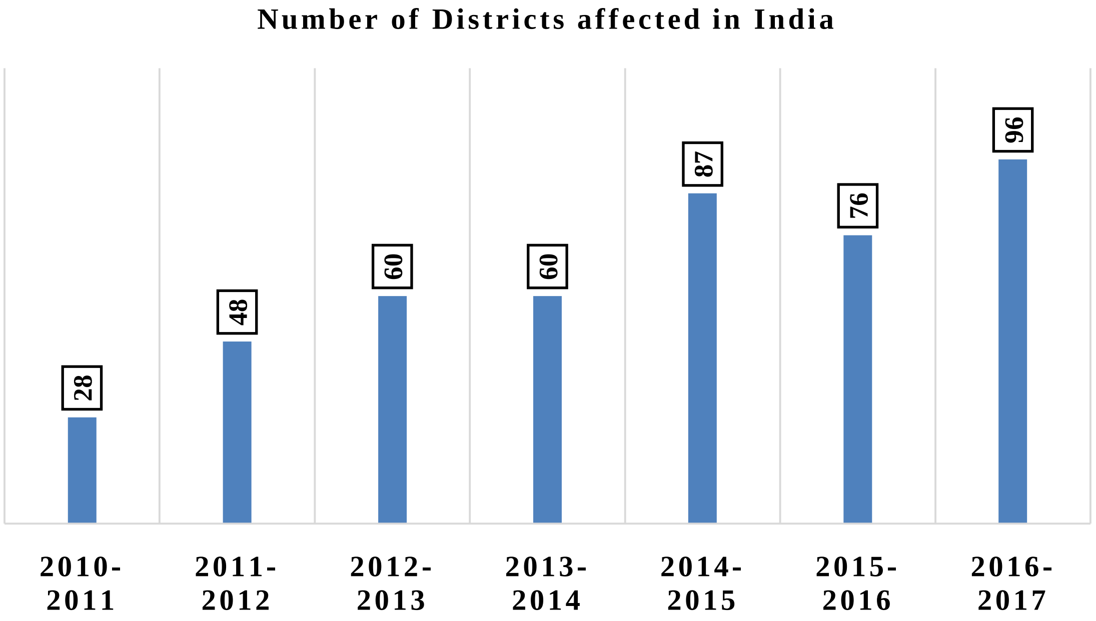


Figure 22: Number of districts with arsenic contamination

Figures 23 and 24 show the spatial and temporal variation of arsenic in deep and shallow tubewells respectively in India. We see that values are increasing with year. Some of the data reflect very high concentration of arsenic which appear to be unrealistic and need to be verified.

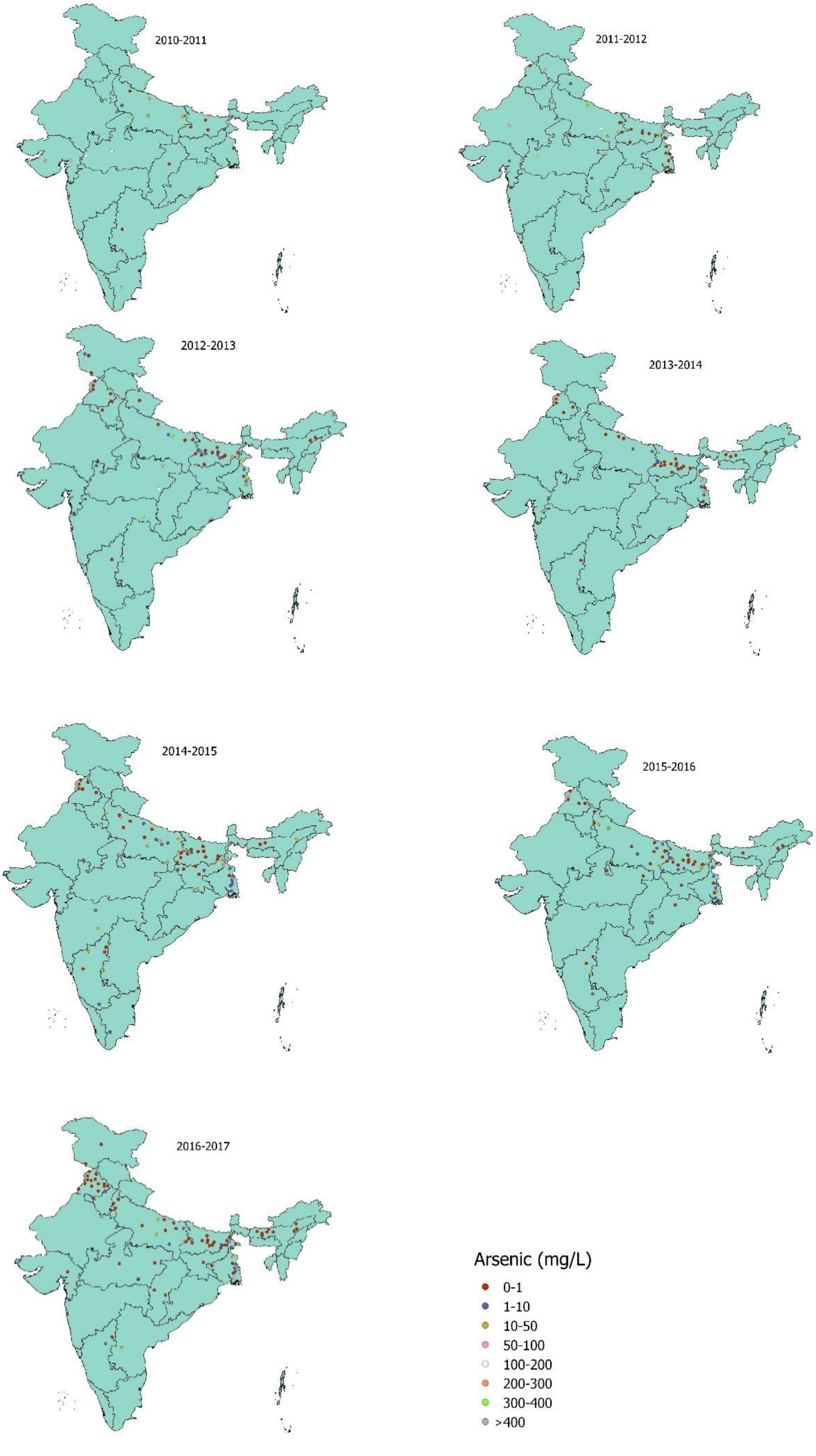
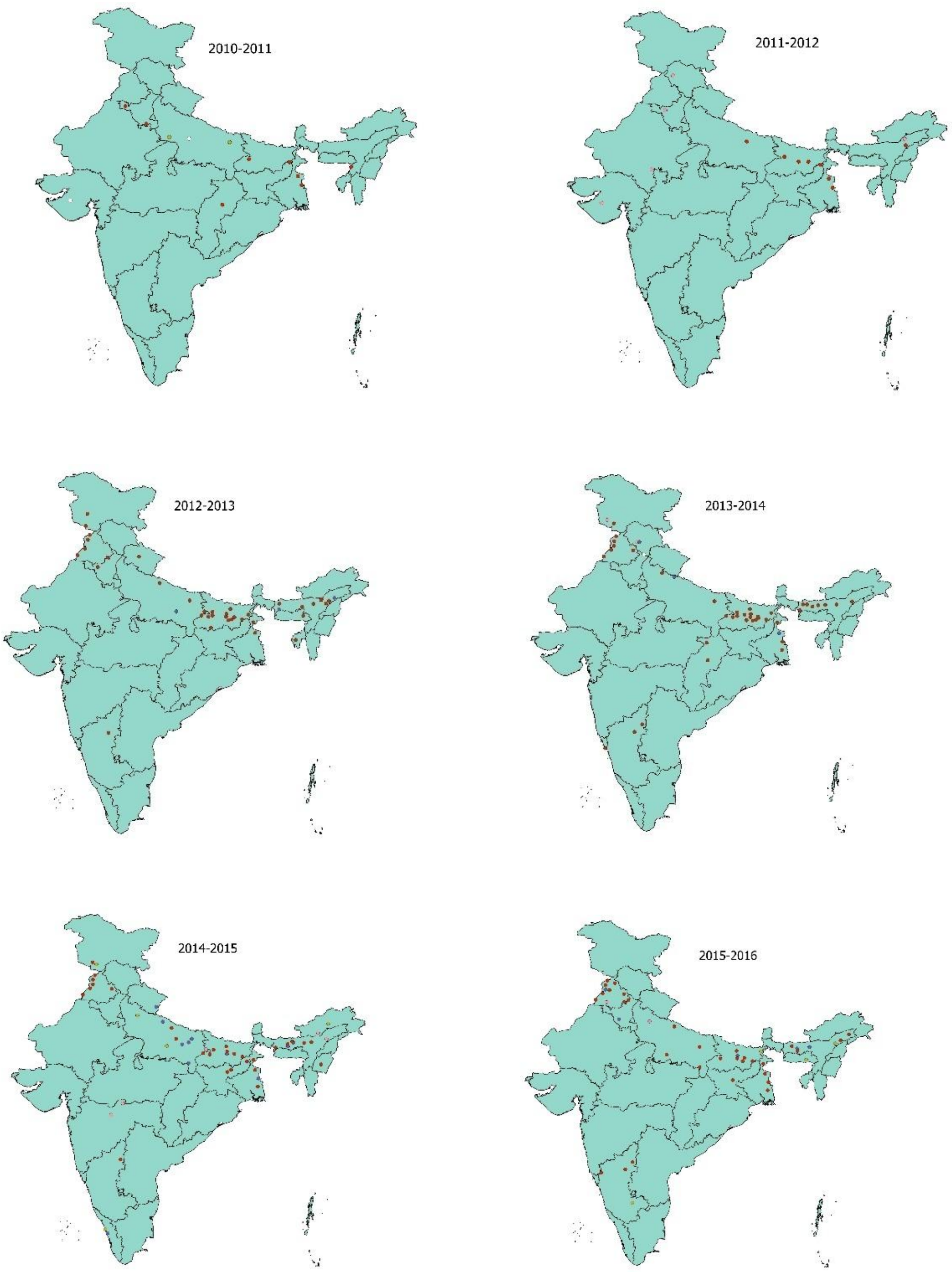

2010-2011
2011-2012
2012-2013
2013-2014
2014-2015
2015-2016
2016-2017
Arsenic (mg/L)
0-1
1-10
10-50
50-100
100-200
200-300
300-400
>400

Figure 23: Spatial and tremporal variation of arsenic in deep tube wells



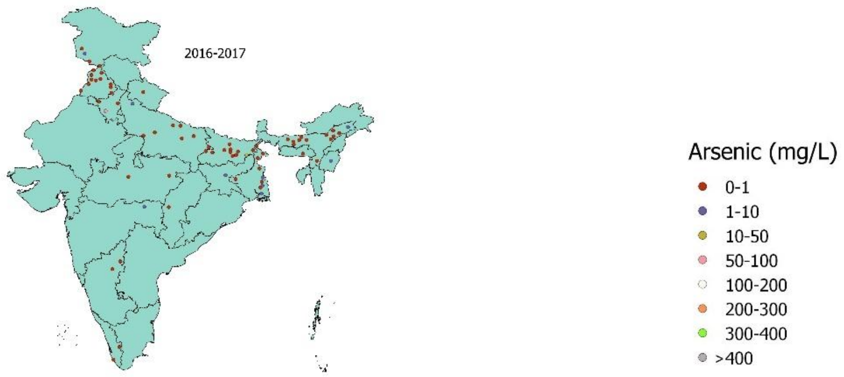


Figure 24: **Spatial and tremporal variation of arsenic in shallow tube wells**

6. Conclusion

It appears from the overall study that arsenic in groundwater is mainly mobilised by two major mechanisms: 1) microbial degradation of organic matter and further reductive dissolution of iron oxyhydroxide, and 2) competitive anion exchange with phosphate. Redox potential and pH play an important role in the speciation of arsenic in groundwater. Geochemical data in all the locations showed that reduced concentrations of electron acceptors and high concentrations of dissolved organic matter, bicarbonate and ammoniacal nitrogen indicate the reducing environment of the subsurface aquifer. This is further supported by the negative correlation between dissolved organic matter and dissolved oxygen i.e. microbial degradation of organic matter depleted dissolved oxygen creating reduced conditions. The reduced environment is also demonstrated by low levels of redox potential and strong negative correlation between redox potential and dissolved organic matter exists. The positive strong correlation between arsenic and dissolved organic matter demonstrate that DOM has the potential to mobilize arsenic into dissolved form. The positive correlation between iron and arsenic suggest that both exist together i.e. arsenic may be strongly adsorb on the surface of iron oxyhydroxides. The process of nitrification also depletes dissolved oxygen by converting ammoniacal nitrogen into nitrates. This is supported by the negative correlation among bicarbonate and ammoniacal nitrogen with dissolved oxygen and redox potential. This combined process of carbon oxidation and nitrification is the main redox driver to release arsenic from the surface of iron oxyhydroxide into groundwater. In some locations, arsenic has a strong positive correlation with phosphates. Addition of phosphate based fertilisers have increased and this might serve another mechanism for releasing arsenic into groundwater by competitive exchange on the surface of iron oxyhydroxides.

The mechanisms may be operative on the surface of sediments in the biofilm in the saturated and capillaries just above and/or beneth the water table and then transported to depths. This is evident from the significance values in the correlation models which may indicate that arsenic is found in certain locations where reduced condition does not exist ($p>0.01$). Arsenic may get transported to deeper aquifer through the cracks developed in the confining zones. Groundwater flow pattern plays an important role in arsenic spread in the subsurface system.

The spatial and temporal study of arsenic distribution showed variation over space and time in India. Geospatial conditions such as latitude, longitude as well as depth of the tube wells may attribute to the difference in arsenic concentrations over space and time.

7. Future Work

Based on the correlation among major species responsible for releases arsenic into the groundwater, experiments can be conducted to show that organic matter and reduced conditions cause release of arsenic into dissolved form and also cracks in the lower strata cause transport of arsenic into deeper zones.

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Appendix

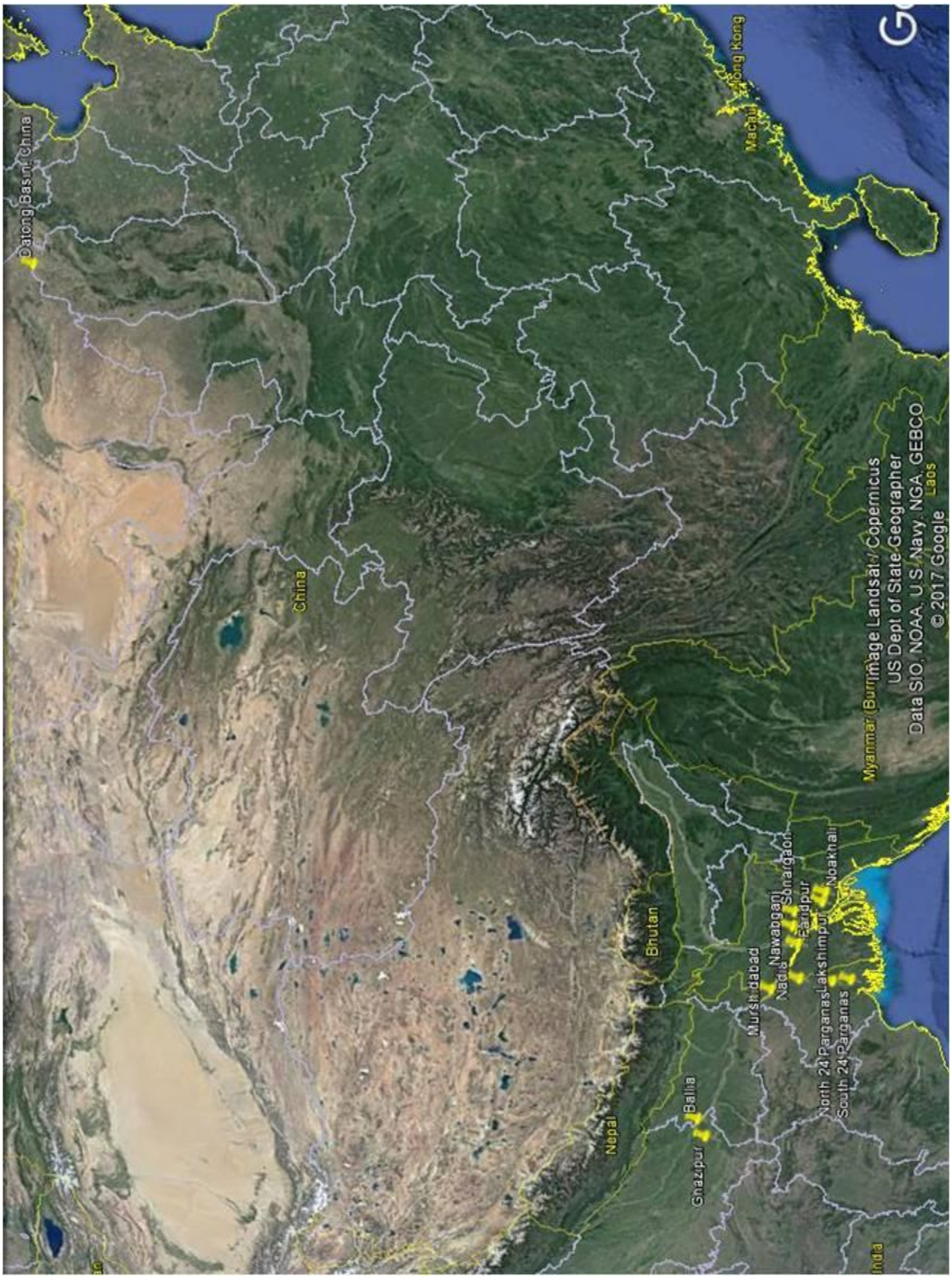

Figure A 1: Map showing locations from where various Authors have collected arsenic and other physicochemical Parameters

Figure A 2: **Correlation matrix for various physicochemical parameters measured in Nawabganj, Bangladesh**

Figure A 3: **Correlation matrix for various physicochemical parameters measured in Faridpur, Bangladesh**

Figure A 4: Correlation matrix for various physicochemical parameters measured in Lakhimpur, Bangladesh

Figure A 5: Correlation matrix for various physicochemical parameters measured in Naokhali, Bangladesh

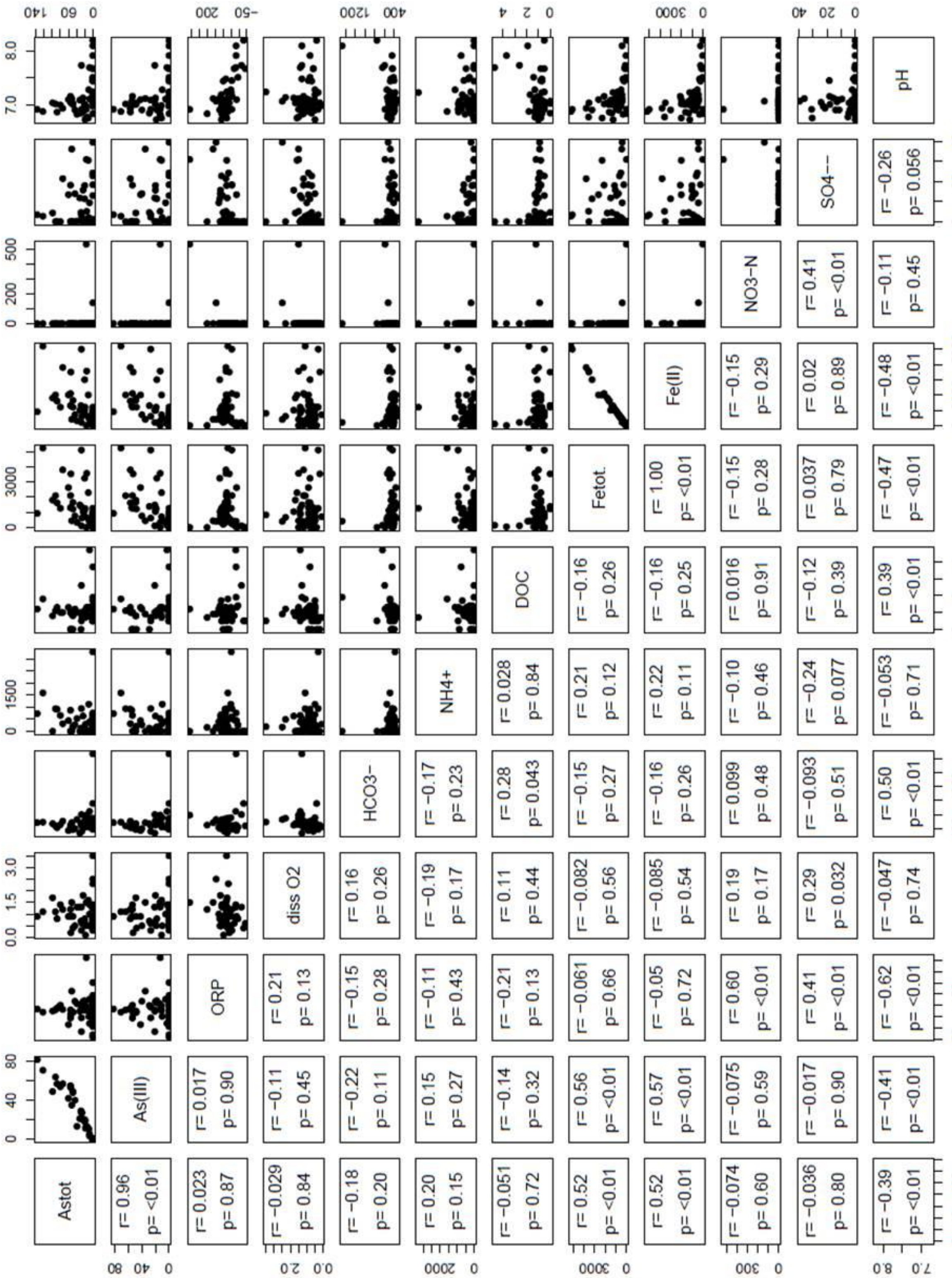

Figure A 6: Correlation matrix for various physicochemical parameters measured in Western Bengal Basin

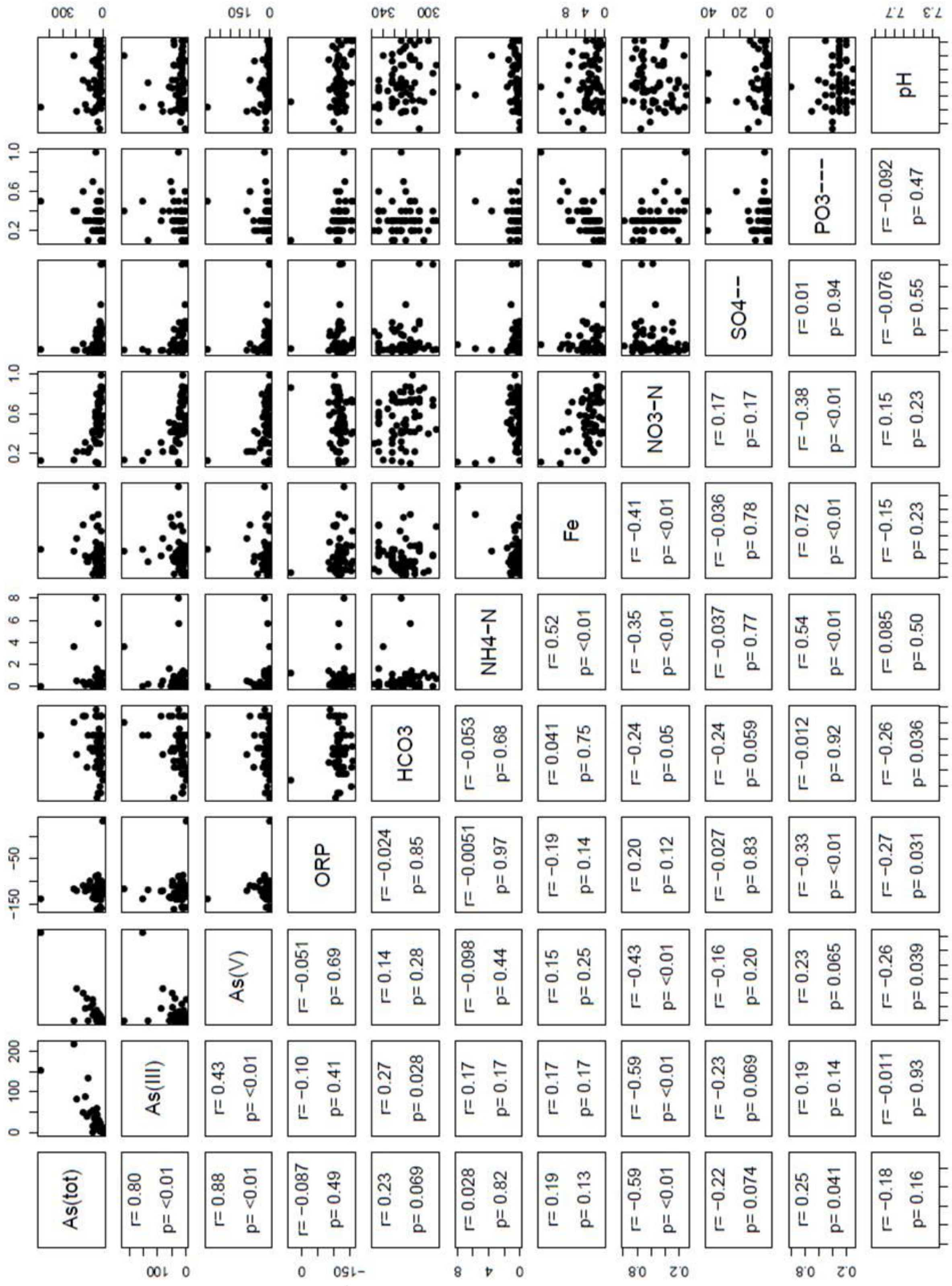

Figure A 7: Correlation matrix for various physicochemical parameters measured in Ballia, UP

Figure A 8: Correlation matrix for various physicochemical parameters measured in Ghazipur, UP During May 2007

Figure A 9: Correlation matrix for various physicochemical parameters measured in Ghazipur, UP During October 2007

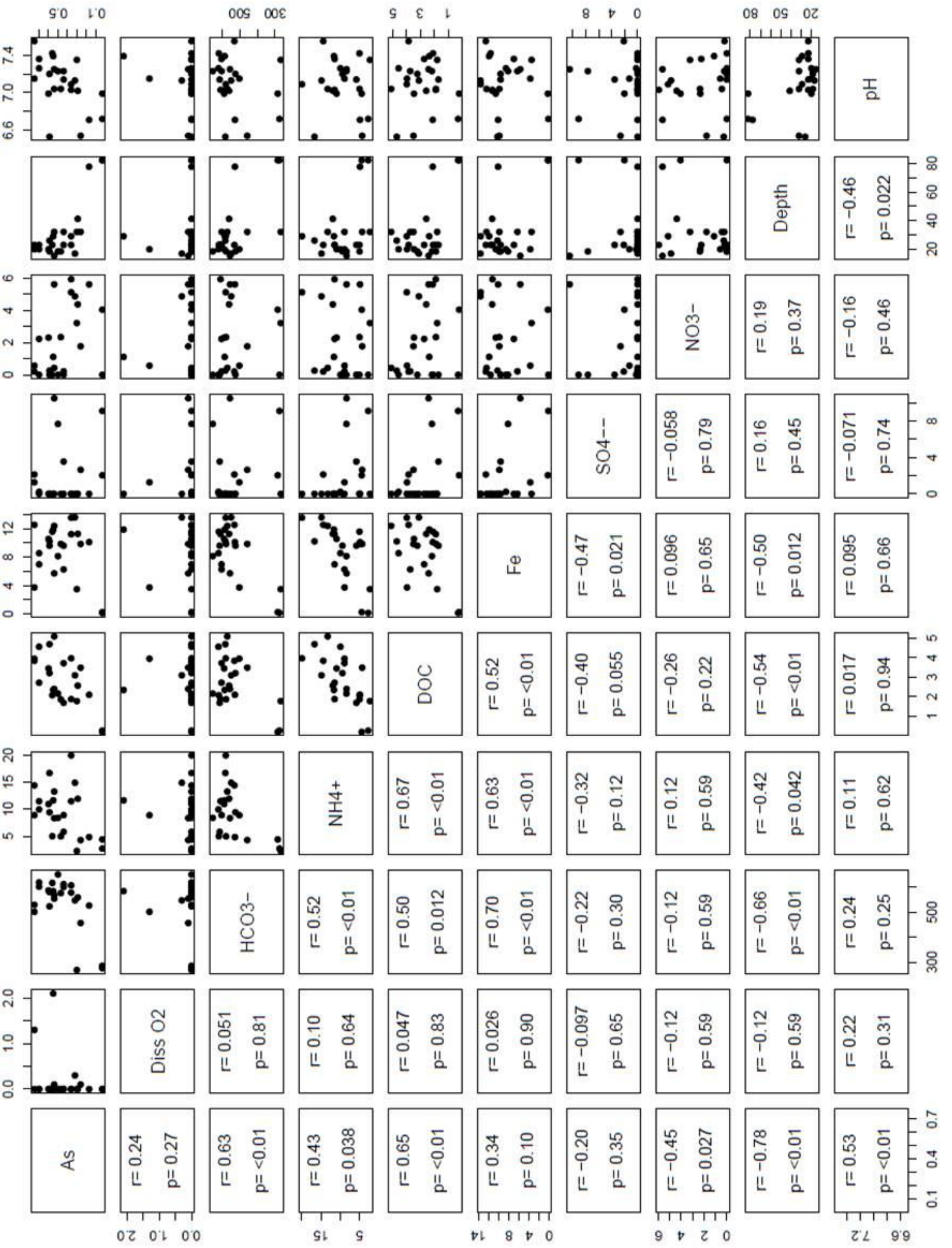

Figure A 10: Correlation matrix for various physicochemical parameters measured in Site-1, Sonargaon Thana, West Bengal

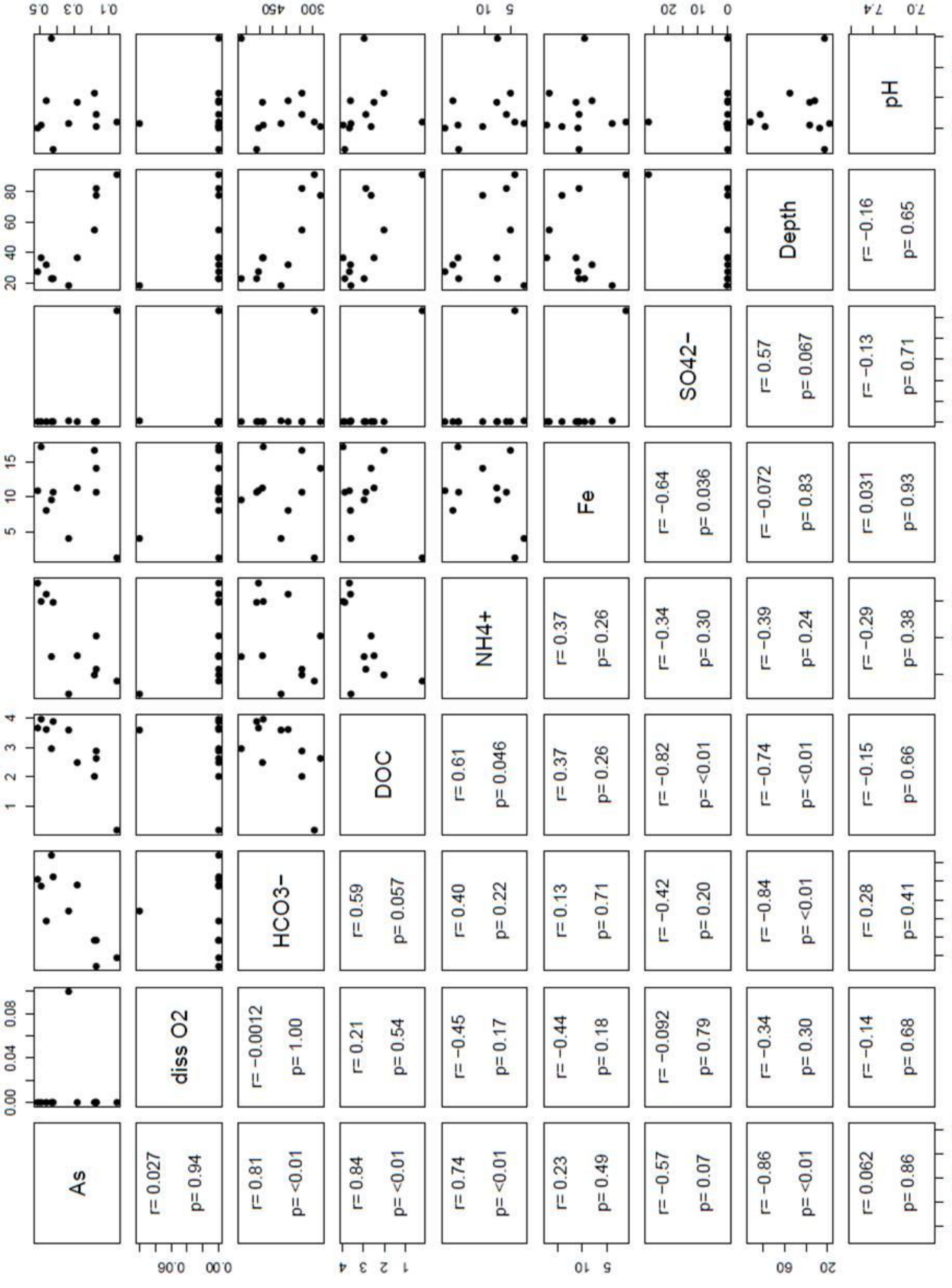

Figure A 11: **Correlation matrix for various physicochemical parameters measured in Site-2, Sonargaon Thana, West Bengal**