Universitat de Girona

ARSENIC AND ITS SPECIATION ANALYSIS IN BIOLOGICAL AND ENVIRONMENTAL SAMPLES USING ICP TECHNIQUES

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Arsenic and its speciation analysis in biological and environmental samples using ICP techniques

SUBHAMOY BHOWMICK

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WE DECLARE:

That the thesis titles “***Arsenic and its speciation analysis in biological and environmental samples using ICP techniques***” to obtain a doctoral degree, has been completed under our supervision and meets the requirements to opt for an International Doctorate.

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Dedicated to my family

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CONTENTS

SUMMARY

Arsenic is one of the carcinogenic metalloid that is omnipresent in natural water, soils and atmosphere. Because of this wide distribution, millions of people across the globe are being continuously exposed to high levels of arsenic. As a result of these high exposure to arsenic, the health effect are enormous and includes carcinogenic effect of skin, liver, kidney and other organs which ultimately leads to death. The state of West Bengal, India is one such arsenic endemic area of the World where arsenic possesses the biggest threat to large number of populations of this area. Thus, in this thesis, the state of West Bengal, India was considered as a representative area to study the various aspects of arsenic.

Firstly, the groundwater arsenic mobilization process was studied by comparing the groundwater chemistry of three geographically district areas of West Bengal. The effects of local anthropogenic factors as well as regional scale lithological and hydrological variations were considered for arsenic release processes. The low redox potential (Eh = −185 to −86 mV) and dominant As(III) and Fe(II) concentrations are indicative of the anoxic nature of the aquifers. The equilibrium of groundwater with respect to carbonate minerals and their precipitation/dissolution showed to be controlling the overall groundwater chemistry of these areas. Speciation of arsenic in the groundwater [As(III) and As(V)] and the relative distribution of this species were examined and were categorized not only according to their respective areas but also in deep and shallow aquifers. The data showed that the shallow aquifers were mainly contaminated with high concentrations of arsenic while the deeper aquifers were relatively safe ($< 50\ \mu g\ L^{-1}$). The As(III)/As(V) ratio was highly variable in the shallow aquifers compared to the deeper aquifers and suggested that the shallow groundwater were highly influenced by anthropogenic activities. We found low concentrations of SO_4^{2-} and high concentration of DOC, PO_4^{3-} and HCO_3^- in groundwater which signified ongoing microbial mediated redox processes favoring arsenic mobilization in the aquifer. The arsenic release is influenced by both geogenic (i.e. geomorphology) and anthropogenic (i.e. unsewered sanitation) processes. No single arsenic release mechanism but multiple geochemical processes, e.g., Fe-oxyhydroxides reduction and carbonate dissolution, are responsible for high arsenic occurrence in groundwaters.

Thereafter we identified some people of this area with varying degree of arsenic-induced skin lesions. Controls without skin lesion were also chosen from the same area. Urine and saliva was taken from the recruited participants and arsenic in these biological fluids was measured. We developed an analytical methodology for measurement of trace levels of arsenic in saliva using ICP-MS by diluting saliva with methanol, nitric acid and internal standard (Rhodium solution). The developed method was sensitive and reproducible and was used for arsenic determination in the collected saliva samples. Arsenic content in water and rice was used as an estimate to measure the total daily intake of arsenic. Arsenic in saliva showed good reflection of the daily ingested arsenic of the participants. Since arsenic content in urine is already an established biomarker of arsenic exposure, positive correlation of salivary and urinary arsenic demonstrated saliva as a surrogate of urine in arsenic exposure studies.

Later we tried to speciate the various forms of arsenic in saliva. We were successful to develop a speciation technique with an anion exchange PRP-X100 column using a gradiant elution of $(NH_4)_2CO_3$ at pH 9. The speciation protocol was able to speciate arsenobetaine, monomethyl arsenic acid, dimethyl arsenic acid, As(III) and As(V) in the saliva samples. Our analyses suggested As(V) was the predominant species while the concentration of arsenobetaine was low or even not detectable in most of the collected saliva samples. Female and control without skin lesion showed greater methylation capacity of the ingested inorganic arsenic compared to male and cases of skin lesion, respectively. Thus the study exhibited the variation of individual methylation capability and subsequently susceptibility to arsenic-induced skin lesions.

Finally, we tried to find an ecofriendly arsenic removal technique suitable for Bengal groundwater. nano Zerovalent Iron (nZVI) are now being used for arsenic removal from contaminated water but poses some field limitations. Hence we synthesized nZVI on montmorillonite clay which was used as an inert material. Such procedure decreased the agglomeration of the nZVI and was confirmed through SEM, EDX, XRD and XPS analysis. Montmorillonite-supported nZVI had a core shell Fe(0) structure with an outer oxide/hydroxide shell and had high affinity for As(III) and As(V) over a wide range of pH (4-8) but decreased for pH> 9. In solution, As(V) was adsorbed and/or co-precipitated onto the corrosion product formed from the reaction of nZVI with water. However, As(III) in solution was adsorbed and subsequently oxidized to As(V). Thus the study demonstrated montmorillonite-supported nZVI as a potential adsorbent to reduce elevated levels of arsenic in groundwater.

RESUM

L'arsènic és un metal·loide carcinogen omnipresent en aigües naturals, sòls així com a l'atmosfera. A causa d'aquesta àmplia distribució, milions de persones a tot el món estan contínuament exposades a alts nivells d'arsènic. Com a resultat d'aquesta alta exposició, els efectes sobre la salut són enormes i inclouen efectes cancerígens a la pell, el fetge, el ronyó i altres òrgans que poden conduir finalment a la mort. L'estat de Bengala Occidental (Índia) és una de les zones més afectades per la presència d'arsènic del món, el qual representa la amenaça més important per a gran part de la població d'aquesta zona. Per tant, en aquesta tesi, l'estat de Bengala Occidental va ser considerada com una àrea representativa per estudiar els diversos aspectes relacionats amb l'arsènic.

En primer lloc, el procés de mobilització de l'arsènic en les aigües subterrànies es va estudiar mitjançant la comparació de la composició química de les aigües subterrànies de les tres àrees geogràfiques del districte de Bengala Occidental. L'efecte de factors antropogènics locals, així com les variacions litològiques i hidrològiques a escala regional varen ser considerats per a l'estudi dels processos d'alliberament d'arsènic. El baix potencial redox (Eh = -185 a -86 mV) i el predomini d'As (III) i de Fe (II) són indicatius de la naturalesa anòxica dels aqüífers. L'equilibri de les aigües subterrànies d'aquestes àrees es va veure que estava controlat pels carbonats i els seus processos de precipitació/dissolució. Es va examinar l'especiació d'arsènic en les aigües subterrànies [As (III) i As (V)] i la seva distribució relativa. A continuació, les aigües es varen classificar no només en funció de les seves respectives àrees de procedència, sinó també en relació a si es tractava d'aqüífers profunds o poc profunds. Les dades van mostrar que els aqüífers poc profunds estan contaminats presentant altes concentracions d'arsènic, mentre que els aqüífers més profunds eren relativament segurs (amb concentracions d'As per sota dels 50 g L^{-1}). La relació As(III)/As(V) es va trobar que és molt variable en els aqüífers poc profunds en comparació amb els aqüífers més profunds, la qual cosa va suggerir que la composició de l'aigua subterrània poc profunda, està fortament influenciada per les activitats antropogèniques.

S’han trobat concentracions baixes de SO_4^{2-} i altes de DOC, PO_4^{3-} i HCO_3^- en l'aigua subterrània que indica processos microbiològics redox continus que afavoreixen la mobilització de l’arsènic a l'aqüífer. L'alliberament de l’arsènic està influenciat tant per processos geogènics (com la geomorfologia) com antropogènics (com el sanejament sense clavegueram). Cap mecanisme d'alliberament d'arsènic, però diversos processos geoquímics, per exemple, la reducció dels oxihidròxids de ferro i la dissolució dels carbonats, són els responsables dels alts nivells d'arsènic a les aigües subterrànies.

A continuació es varen identificar algunes persones d'aquesta zona amb diversos graus de lesions cutànies induïdes per l'arsènic, també es van triar persones sense lesions a la pell, com a controls, procedents de la mateixa zona. Es va obtenir l'orina i la saliva dels participants reclutats per a l’estudi i es va mesurar el contingut d’arsènic en aquests fluids biològics. En aquest sentit, s’ha desenvolupat una metodologia analítica per a la mesura de traces d'arsènic a la saliva utilitzant ICP-MS mitjançant la dilució de la saliva amb metanol, àcid nítric i un patró intern (patró de rodi). El mètode desenvolupat és sensible i reproduïble i es va utilitzar per a la determinació d'arsènic en les mostres de saliva recollides. D’altra banda, el contingut d'arsènic en aigua i arròs es va utilitzar com a estimació per mesurar la ingesta diària total d'arsènic. L'arsènic a la saliva va mostrar ser un bon reflex de l'arsènic ingerit diàriament pels participants. Atès que el contingut d'arsènic en l'orina ja és un biomarcador establert d'exposició a l'arsènic, la correlació positiva de l’arsènic en saliva i en orina va demostrar que la saliva pot ser un substitut adequat a l'orina en els estudis d'exposició a l'arsènic.

A continuació varem intentar determinar l’especiació de l'arsènic en saliva. En aquest sentit, hem desenvolupat un mètode d'especiació amb una columna PRP-X100 d'intercanvi aniònic usant una elució en gradient de $(NH_4)_2CO_3$ a pH 9. Amb el mètode desenvolupat varem poder determinar: arsenobetaina, àcid monometilarsènic, àcid dimetilarsènic, As (III) i As (V) en les mostres de saliva. Les nostres anàlisis indiquen que l’As (V) es l'espècie predominant, mentre que la concentració de arsenobetaina es baixa o no detectable en la majoria de les mostres de saliva recollides. L'anàlisi dels resultats indica que les dones i les persones sense lesió cutània (utilitzades com a control) mostren una major capacitat de metilació de l'arsènic inorgànic ingerit en comparació amb homes i els casos de lesió a la pell, respectivament. Així doncs, l'estudi mostra la variació de la capacitat de metilació de l'individu i, per tant, la susceptibilitat a les lesions cutànies induïdes per l'arsènic.

Finalment, varem tractar de trobar una tècnica d'eliminació d'arsènic respectuós amb el medi ambient i adequat per a les aigües subterrànies de Bengala. Les Nanopartícules de ferro amb valència zero (nZVI) han estat utilitzades per a l'eliminació d'arsènic d'aigua contaminada, però la seva utilització planteja algunes limitacions sobre tot en la implanació sobre el terreny. S'han sintetitzat nZVI sobre argila de montmorillonita que va ser utilitzada com a material inert. Aquest procediment va reduir l'aglomeració de les nZVI, la qual cosa va ser confirmada a través de diverses tècniques com SEM, EDX, XRD i XPS. nZVI sobre montmorillonita tenien una estructura amb un nucli de Fe(0) i una capa externa d'òxid/hidròxid; les nanopartícules tenen una alta afinitat per l'As (III) i As (V) en un ampli interval de pH (4-8) que disminueix, però, a pH> 9. En solució, l'As (V) va ser adsorbit i/o coprecipitat en el producte de la corrosió format a partir de la reacció de les nZVI amb aigua. Per contra, l'As (III) en solució va ser adsorbit i posteriorment oxidat a As (V). L'estudi demostra que les nZVI recolzades sobre montmorillonita representen un adsorbent potencial per reduir els nivells elevats d'arsènic en les aigües subterrànies.

RESUMEN

El arsénico es un metaloide carcinógeno omnipresente en aguas naturales, suelos así como en la atmósfera. Debido a esta amplia distribución, millones de personas en todo el mundo están continuamente expuestos a altos niveles de arsénico. Como resultado de esta alta exposición, los efectos sobre la salud son enormes e incluyen efectos cancerígenos en la piel, el hígado, el riñón y otros órganos que pueden conducir finalmente a la muerte. El estado de Bengala Occidental (India) es una de las zonas más afectadas por la presencia de arsénico del mundo, el cual representa la amenaza más importante para gran parte de la población de esta zona. Por tanto, en esta tesis, el estado de Bengala Occidental fue considerada como un área representativa para estudiar los diversos aspectos relacionados con el arsénico.

En primer lugar, el proceso de movilización del arsénico en las aguas subterráneas se estudió mediante la comparación de la composición química de las aguas subterráneas de las tres áreas geográficas del distrito de Bengala Occidental. El efecto de factores antropogénicos locales, así como las variaciones litológicas e hidrológicas a escala regional fueron considerados para estudiar los procesos de liberación de arsénico. El bajo potencial redox (Eh = -185 a -86 mV) y el predominio de As (III) y de Fe (II) son indicativos de la naturaleza anóxica de los acuíferos. El equilibrio de las aguas subterráneas de estas áreas se vio que estaba controlado por los carbonatos y sus procesos de precipitación / disolución. Se examinó la especiación de arsénico en las aguas subterráneas [As (III) y As (V)] y su distribución relativa. A continuación las aguas se clasificaron no sólo en función de sus respectivas áreas de procedencia, sino también en relación a si se trataba de acuíferos profundos o poco profundos. Los datos mostraron que los acuíferos poco profundos están contaminados, presentando altas concentraciones de arsénico, mientras que los acuíferos más profundos eran relativamente seguros (con concentraciones de As por debajo de los 50 g L^{-1}). La relación As (III) / As (V) se encontró que es muy variable en los acuíferos poco profundos en comparación con los acuíferos más profundos, lo que sugirió que la

composición del agua subterránea poco profunda está fuertemente influenciada por las actividades antropogénicas. Se han encontrado concentraciones bajas de SO_4^{2-} y altas de DOC, PO_4^{3-} y HCO_3^-en el agua subterránea que indica procesos microbiológicos redox continuos que favorecen la movilización del arsénico en el acuífero. La liberación del arsénico está influenciado tanto por procesos geogénicos (como la geomorfología) como antropogénicos (como el saneamiento sin alcantarillado). Ningún mecanismo de liberación de arsénico, pero varios procesos geoquímicos, por ejemplo, la reducción de los oxihidróxidos de hierro y la disolución de los carbonatos, son los responsables de los altos niveles de arsénico en las aguas subterráneas.

A continuación se identificaron algunas personas de esta zona, con diversos grados de lesiones cutáneas inducidas por el arsénico. también se eligieron personas sin lesiones en la piel, como controles, procedentes de la misma zona. Se obtuvo la orina y la saliva de los participantes reclutados para el estudio y se midió el contenido de arsénico en estos fluidos biológicos. En este sentido, se ha desarrollado una metodología analítica para la medición de trazas de arsénico en la saliva utilizando ICP-MS mediante la dilución de la saliva con metanol, ácido nítrico y un patrón interno (patrón de rodio). El método desarrollado es sensible y reproducible y se utilizó para la determinación de arsénico en las muestras de saliva recogidas. Por otra parte, el contenido de arsénico en agua y arroz se utilizó como una estimación para medir la ingesta diaria total de arsénico. El arsénico en la saliva mostró ser una buen reflejo del arsénico ingerido diariamente por los participantes. Dado que el contenido de arsénico en la orina ya es un biomarcador establecido de exposición al arsénico, la correlación positiva del arsénico en saliva y orina demostró que la saliva puede ser un sustituto adecuado a la orina en los estudios de exposición al arsénico.

A continuación intentamos determinar la especiación del arsénico en saliva. En este sentido, hemos desarrollado un método de especiación con una columna PRP-X100 de intercambio aniónico usando una elución en gradiente de $(NH_4)_2CO_3$ a pH 9. Con el método desarrollado pudimos determinar:

arsenobetaina, ácido monometilarsénico, ácido dimetilarsénico, As (III) y As (V) en las muestras de saliva. Nuestros análisis indican que el As (V) es la especie predominante, mientras que la concentración de arsenobetaina es baja o no detectable en la mayoría de las muestras de saliva recogidas. El análisis de los resultados muestra que las mujeres y las personas sin lesión cutánea (utilizadas como control) muestran una mayor capacidad de metilación del arsénico inorgánico ingerido en comparación con hombres y los casos de lesión en la piel, respectivamente. Así pues, el estudio muestra la variación de la capacidad de metilación del individuo y, por tanto, la susceptibilidad a las lesiones cutáneas inducidas por el arsénico.

Finalmente, tratamos de encontrar una técnica de eliminación de arsénico respetuoso con el medio ambiente y adecuado para las aguas subterráneas de Bengala. Las Nanopartículas de hierro con valencia cero (nZVI) han sido utilizadas para la eliminación de arsénico de agua contaminada, pero su utilización plantea algunas limitaciones sobre todo en la implanació sobre el terreno. Hemos sintetizado nZVI sobre arcilla de montmorillonita que fue utilizada como material inerte. Este procedimiento redujo la aglomeración de las nZVI, lo cual fue confirmado a través de diversas técnicas como SEM, EDX, XRD y XPS. nZVI sobre montmorillonita tenían una estructura con un núcleo de Fe (0) y una capa externa de óxido/hidróxido. Las nanopartículas tenían una alta afinidad por el As (III) y As (V) en un amplio intervalo de pH (4 -8) que disminuye a pH> 9. En solución, el As (V) es adsorbido y/o coprecipita en el producto de la corrosión formado a partir de la reacción de las nZVI con agua. Por el contrario, el As (III) en solución fue adsorbido y posteriormente oxidado a As (V). El estudio demuestra que las nZVI apoyadas sobre montmorillonita representan un adsorbente potencial para reducir los niveles elevados de arsénico en las aguas subterráneas.

CHAPTER 1: GENERAL INTRODUCTION

Arsenic is one of the handy but deadly elements that have been associated from the very onset of human civilization. For thousands of years, human have lived in contact with this mysterious element because of its wide distribution in nature ranging from the atmosphere, soils, rocks, natural waters to the organisms. Tens of thousands of people have been sickened and died in the past because of arsenic, and still today, millions of people across the globe are suffering from the consequences of exposure to high arsenic concentration.

In the environment, arsenic can exist in several oxidation state (+5, +3, 0 and -3) of inorganic and organic species. In natural water, arsenic is usually present as inorganic oxyanions of As(III) and As(V). The distribution of these inorganic species is dependent upon the redox condition. In waters which are oxidizing, As(V) is predominant whereas in reducing environment, the major species are those of As(III) [1]. Therefore, waters from reducing environment are more toxic than those from oxidizing environment as As(III) is more toxic and mobile than As(V) species. The organic forms are mostly common where the water is industrially polluted or influenced by microbial activity [2]. In living system, arsenic is widespread in various organic forms but the major portion is monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA). Arsenobetaine (AsB) is common in marine biological system and is the main source of arsenic in fish and seafood [3].

Exposure to inorganic arsenic of sufficient concentration has proved to be detrimental for the living communities. The principal sources of arsenic poisoning for human health includes arsenic contaminated drinking water and foods while a very little contributes from the inhalation of air [4]. There are several regions in the World where arsenic contaminated groundwater is still the only source of drinking water for large number of population [2,5]. Therefore due to growing concern of the arsenic induced health effects, various environmental regulatory boards and National Standards have set a low values for the permissible level of arsenic in drinking water.

1.1. OCCURRENCE AND DISTRIBUTION OF ARSENIC

1.1.1. Distribution of arsenic in minerals

Arsenic is a common constituent of the earth crust with an average concentration of 2 – 3 mg kg^{-1} of arsenic in continental crust [6]. Arsenic is the integral component of several minerals (> 200) e.g. elemental arsenic, arsenides, arsenites, sulfides, oxides and is therefore, considered as an important sources of environmental poisoning. Arsenopyrite (FeAsS) is the most abundant among all the arsenic minerals and it contains around 46% of arsenic by mass [7]. Various rock forming minerals (sulfate, oxide, phosphate etc) are also an important source of arsenic into the environment although in these minerals arsenic is not a major constituent [4].

The arsenic and sulphur chemistry has some similarities and therefore, arsenic is present in many sulfide minerals crystals as a substitute of sulfur. Pyrite, marcasite, galena, chalcopyrite are the example of some arsenic rich sulfide minerals which contains more than 10% arsenic by mass [8]. Low temperature sedimentary environment under reducing condition is considered as one of the principal state for pyrite mineral formation. Pyrite is very unstable in aerobic condition and therefore, arsenic is released from this mineral along with sulfate ions when it comes in contact with aerobic environment [9].

Several metal oxides and hydrous minerals are enriched with arsenic either as a mineral structure or as a sorbed species. Hematite, magnetite, illmenite, iron(II) oxides, iron(III) oxyhydroxides are the examples of such oxide minerals. Arsenic is also adsorbed on the surface of hydrous aluminum, manganese oxides, calcite and hydrous iron oxides [10–13]. Iron oxides are most significant among all these oxides due to high arsenic loading compared to other metallic oxides [13].

Phosphate minerals contribute less severely compared to oxide minerals as they are less abundant than the former ones [2]. Apatite is an example of phosphate rich mineral that sometime contains very high concentration of arsenic (1000 mg kg^{-1}). Arsenic is also presents in several other rock forming minerals and can substitutes Si^{4+}, Al^{3+}, Fe^{3+}, Ti^{4+} in many mineral structures. However, the concentration of arsenic on those substituted minerals is very low [14].

1.1.2. Distribution of arsenic in rocks

The average concentration of arsenic in sedimentary rock is typically in the range of 5 – 10 mg kg^{-1} [15]. The concentration of arsenic in sand and sandstone (quartz and feldspars) is much lower (4 mg kg^{-1}) compared to argillaceous (13 mg kg^{-1}) [16]. High concentration of arsenic in argillaceous rocks is observed due to the presence of larger proportion of sulfide minerals, oxides, organic matters and clays. Coals and bituminous contains a large amount of arsenic and sometimes reaches upto 35000 mg kg^{-1} [17] and therefore, burning of these fossil fuels may introduce arsenic in the environment. Additionally, ironstones and iron rich rocks also contain a large amount of arsenic (2900 mg kg^{-1}) [9].

Arsenic concentrations in igneous rocks are much lower compared to sedimentary ones. Among all the igneous rocks, volcanic ashes contribute the highest arsenic concentration in aqueous environment [18]. Additionally, pelitic rocks (slates, phyllites) also implicate around 18 mg kg^{-1} of arsenic into the environment [19].

1.2. SOURCES OF ARSENIC CONTAMINATION

Arsenic is omnipresent in rocks, minerals and also in chemicals, concentrate, coal and industrial products and the various interactions of these components with the ecosystem results in the multi-faced contamination of arsenic [2,4]. Broadly the sources can be grouped as (i) natural and (ii) man-made.

1.2.1. Natural sources

Release of arsenic in the environment by natural process includes weathering of rocks and sediments, geothermal and volcanic activities, hydrothermal ore deposit and forest fires and sea salt spays [7,20]. Nriagu [21] in an earlier report had estimated a global emission of 12 million metric tons of arsenic per year from natural sources.

Interaction of natural water with the bedrocks, sediments and soils is one of the important processes for turning the arsenic cycle [2]. Arsenic has been reported to be present in groundwaters from several parts of the world and the concentration as well as the species of arsenic varies depending upon the redox condition of the groundwater and the lithological characteristics of the aquifer sediments and bedrock formation [22]. In sedimentary environment, arsenic is sorbed onto the oxidized sediments and the concentration may vary from 0.6 mg kg^{-1} in sand to 490 mg kg^{-1} in shale and clays [23]. Pyrites are formed diagenetically in reduced condition rich in organic matter and arsenic gets incorporated into it [7].

Arsenic contamination of the aquatic system results from the natural weathering of the soil, rock and volcanism. The marine water arsenic concentration is usually between 1-2 μg L^{-1} where As(V) is the predominant species [24]. However, the marine organism detoxifies the As(V) to MMA and DMA which is also later transformed to AsB and arsenoribosides [24]. Although the concentration of arsenic in river water is low (< 10 μgL^{-1}), the suspended particulate and the aqueous phase arsenic concentration differ significantly [25]. In several regions of the South America, volcanic rocks and its weathering products along with geothermal and mining activities are responsible for the high arsenic concentration in river water [18]. The arsenic contamination in the river of Chile (Atacama Desert) and the Aricota Lake of Peru are such examples.

1.2.2. Anthropogenic sources

1.2.2.1. Mining

Several parts of the world are affected by arsenic due to poisoning in soils, sediments and water through mining activities. Arsenic contaminations in parts of US, South West England, Thailand, Ghana, Chile etc are such examples [2].

Gold mining is considered as one of the major source of arsenic pollution in many countries [26–28]. Arsenic has been detected in the environment due to weathering of the arsenic-bearing metal sulfides (e.g. pyrite). The concentration of arsenic in specific mining sites depends on the type of the ore that are being mined, type of ore processing and waste disposal [29]. Borba et al. [30] found around 300 µg L^{-1} of arsenic in surface water and 20-4000 mg kg^{-1} of arsenic in the sediments due to gold mining. Similarly, Ellice et al. [29] also reported 280-15000 mg kg^{-1} of arsenic in mullock heaps and waste disposal areas in Victoria.

1.2.2.2. Fossil fuel burning

Coal is considered as one of the important fossil fuel that contaminates air, soil and water with arsenic through burning, deposition and leaching. Yudovic and Ketris [31] reported that the average arsenic content for bituminous and lignite coal in the world is 9.0 ± 0.8 and 7.4 ± 1.4 mg kg^{-1}, respectively and estimated that 2 – 47% of arsenic from coal is released into the environment from power plant. They also opined that the coal with high arsenic content are enriched with sulfide (pyrite and other sulfides) while coals with low arsenic content are associated with organic matter. The leaching of arsenic from acid bituminous coal ashes (SiO_2 rich) is very rapid compared to the alkali lignite ashes (CaO rich) in natural environment [31]. The extensive exposure of arsenic due to burning of arsenical coal has been reported in Slovakia [32] and Guizhou Province of China [33,34].

1.2.2.3. Agricultural use

Arsenical pesticides and insecticides have been extensively used in many countries for several decades until the introduction of DDT [14]. Therefore, soils and aquatic environment are vastly contaminated with arsenic either directly or by leaching due to the use of various arsenical pesticides and insecticides such as lead arsenate, zinc arsenate, calcium arsenate, zinc arsenite, Paris green, magnesium arsenate [35,36]. Additionally, some arsenical products (arsenous acid, 4-nitrophenyl arsenic acid etc) were also used as animal feed additives [37]. Sodium arsenite was also used for past few decades as soil sterilants for agricultural purpose [38]. These arsenical products contribute to a considerable amount for arsenic loading in soils and aquatic environment in different countries. McLaren et al. [39] reported that in New Zealand, the soil of 0-10 cm depth and the soil of 20-40 cm depth are affected with 37-3542 and 2282 mg kg^{-1} of As, respectively due to the use of arsenical insecticides in sheep and cattle dips. Similarly, Smith et al. [40] reported that due to the use of arsenical pesticides several sites of Australian land are contaminated with leached arsenic ranging from <0.5 to 115 mg kg^{-1}. Therefore, many arsenical products are restricted by USEPA [23]. However, several organic arsenical compounds (monomethylarsenic acid, dimethylarsenic acid, etc) are permitted to be used as they are considered to be non-carcinogenic. Although the stability of these compounds is questionable and further confirmation are needed about their toxicity, degradation or transformations in soil [41].

1.2.2.4. Wood preservation

Arsenic compounds have been used in wood industry to preserve the woods from water and microorganism [42]. Chromated-copper-arsenate (CCA) is one such wood preservative that have been used widely for several years in Europe and North America [43]. Waste from timber industry [44,45] and timber treatment effluent [43,45] are considered as very important source of aqueous arsenic contamination. Therefore, CCA-treated woods are legally banned for residential use and marine water installation [42], and the industrial or professional use is permitted under strict conditions [44].

1.3. CONTAMINATION OF ARSENIC IN GROUNDWATER

A good number of aquifers in different parts of the world have been identified with high arsenic concentration (several South-East Asian countries, Mexico, Hungary etc) [2]. Additionally arsenic contaminated geothermal water has also been reported from various regions of the globe (France, New Zealand, Chile, and USA etc) [4,46]. The concentration of arsenic and the distribution of the species in groundwater depend on the redox condition of groundwater and climate [2,4,46]. Depending upon the groundwater environment and the mobilization process, arsenic affected groundwater is divided into three types; reducing environment, arid oxidizing environment and mixed reducing and oxidizing environment [2,4].

1.3.1. Arid oxidizing environment

The groundwater from Mexico, Chile and Argentina are considered in arid oxidizing environment. Del Razo et al. [47] found that the pH values for the groundwater in Lagunera region of north central Mexico were in the range of 6.3 to 8.9 with an average arsenic concentration of 8 – 624 μgL^{-1} where As(V) (>90%) was the predominant species. Similarly, Wyatt et al. [48] also found the arsenic concentration in the range of 2 – 305 μg L^{-1} in Sonora state of NW Mexico. All of these places are also contaminated with high fluoride content, although there is no fixed correlation between arsenic and fluoride. The groundwaters from arsenic affected areas in Chile are predominantly oxidizing [49] and the aquifers are composed of volcanic rocks and sediments. The arsenic concentrations in surface and groundwater have been found up to 21000 μg L^{-1} in northern Chile [50]. Although major cities of Chile are supplied with treated water, several rural areas are still using the arsenic contaminated untreated water [2]. The groundwater of Chaco-Pampean Plain is the largest arsenic affected area in Argentina. The groundwater of Argentina has high salinity and high pH value due to weathering of silicate and carbonates [5]. The main mechanism for arsenic mobilization reported in this region are: (i) desorption of arsenic from oxyhydroxides of Al, Mn, and to a limited extent from Fe in response to changes in pH and Eh of the adsorbent, and (ii) competition for adsorption sites with other oxyanions such as V, Mo, PO_4^{3-}, and HCO_3^- [5,51].

1.3.2. Mixed oxidizing and reducing environment

The groundwater of the South Western USA such as Nevada, Arizona, California, Dakota etc along with parts of Argentina, Chile, Bolivia, Peru, Ecuador, Mexico are mainly affected by arsenic with mixed oxidizing and reducing environment. In arid regions, evaporation near the surface is thought to be an important mechanism in regulating the groundwater chemistry [52]. The arsenic concentration up to 2600 µg L^{-1} was reported by Welch and Lico [53] in the groundwater of southern Carson Desert. The redox condition of San Joaquin Valley is variable and high arsenic concentration is noticed in both oxidizing and reducing condition in the range of <1-2600 µg L^{-1} [54].

1.3.3. Reducing environment

The groundwater environment of India, Bangladesh, Taiwan, Vietnam, Northern China, Hungary and Romania are considered in the category of reducing environment. The characteristic chemical features of the this type of groundwater are pH values close to or greater than 7, redox potential less than 100 mV and high concentration of the reduced aqueous species such as Fe(II), Mn(II), NH_4^+ and As(III) [2,46]. It is estimated that 36 million people in Bengal delta (West Bengal and Bangladesh jointly) and over 200 million people in Asia are exposed to unsafe levels of arsenic in their drinking water [7,23].

In North-West of China, the groundwaters of Inner Mongolia as well as Xinjiang and Shanxi Provinces are arsenic contaminated [55]. In Inner Mongolia, concentrations of arsenic in excess of 50 µg L^{-1} have been found in groundwaters from aquifers in Keshenketeng County, the Hetao Basin, and the Tumote Basin [56,57]. In the Datong basin of Shanxi Province, the affected groundwaters are found in alluvial–lacustrine aquifers containing relatively high organic matter [58]. The arsenic-affected areas of Xinjiang province are mainly distributed between the Aibi Lake (in the southwest of the Zhunge'er Basin) and Manasi River, paralleling the Tianshan Mountain [59].

South-West and North-East part of Taiwan are similar arsenic-affected areas where the previous studies carried out by the Taiwan Provincial Institute of Environmental Sanitation have shown that 119 townships has arsenic concentrations in groundwater greater than 50 mg L^{-1} while 58 townships present value above 350 mg L^{-1} [60]. The Mekong and the Red river delta are similar representative arsenic-contaminated regions of Vietnam and Cambodia [61–63]. These areas are typically young Quaternary deltaic and alluvial sediments comprising of highly reducing aquifers [63,64].

In the affected areas of West Bengal, India and Bangladesh, the aquifer sediments are covered by a layer of clay or silt of variable thickness, which restricts the entry of air in to the aquifers. Thus, the recent solid organic matters that are deposited with the sediments along with the capped clay structure results in the development of highly reducing conditions in the aquifers which favor the mobilization of arsenic [65]. The distribution of arsenic is patchy with the shallow aquifers (< 100 m) being more contaminated compared to the deeper aquifers of this region [22], although, the reason for this distinction is not fully understood. The differences in sediment properties, redox state of the groundwater and the availability of fresh organic matter might be some of the possible reasons for this discrepancy [23,46].

1.4. ARSENIC EXPOSURE AND THE ASSESSMENT OF BIOMARKERS

1.4.1 Exposure pathways of arsenic

Although drinking water remains the primary route of arsenic exposure in most cases, recent studies are increasingly showing that the use of arsenic rich groundwater for irrigation purposes constitutes an additional health risk to the people consuming such irrigated crops [66]. Local farmers are now cultivating their land three-four times a year to meet with the increasing food demand of the growing populations, and hence are largely dependent upon the shallow groundwater for irrigation purpose [4,67]. Huq and Naidu [68] in their study have indicated that considerable amount of arsenic accumulates in the tissue of the vegetables when are irrigated with arsenic rich water. The average value of arsenic in a crop is 1 mg kg^{-1}, but the crops grown in arsenic contaminated area exceed this average value. The concentrations of arsenic are found to be higher for leafy vegetables than the non-leafy or root vegetables [69]. The situation becomes complex when the irrigated crops are feed by the animals and thereafter cumulate arsenic in the animal kingdom. Additionally, human are also dependent upon the animals for food, and thus, arsenic distributes in a multiple way throughout the food chain.

Among all the cultivated crops, rice remains the second largest produced cereal in the world. At the beginning of the 1990s, worldwide annual production was about 350 million tons and by the end of the century had reached 410 million tons (milled). World production totaled 450 million tons of milled rice in 2010. The largest producers of rice are concentrated in Western and Easter Asia and accounts for more than 90 percent of world output [70]. Rice is considered a principal dietary component, particularly in the Asian countries, where per person daily rice consumption may be up to 0.5 kg (dry weight) [71]. In West Bengal and Bangladesh, rice consumption provides an average of 72.8% of the daily caloric intake per capita [72,73]. In rice, arsenic is mostly present in inorganic and methylated forms [66] but their distribution varies genetically [74]. The general practice for cultivation of rice needs continuous flooding of irrigation land [75] and as a result, tons of arsenic is being released each year to the top soil of the irrigated lands [76,77]. Brammer and Ravenscroft [67] in their report had estimated that a soil irrigated with 1000 mm of water containing 100 ppb arsenic would receive 1 kg/ha of arsenic per year. They opined that the soil would exceed the safe limit by irrigating with water containing 250 $\mu g\ L^{-1}$ arsenic over a 20-year period, which however would be safe in the range of 25–50 $\mu g\ g^{-1}$ [78,79]. Field study carried out by Hossain [80] also support such hypothesis as it found that the arsenic concentrations in the top soils at the Faridpur site (Bangladesh), which had been irrigated for about 20 years, ranged from 61 $\mu g\ g^{-1}$ in the field nearest to the well-head, and 11 $\mu g\ g^{-1}$ in a field at the far side of the area. Even though the background levels of arsenic in soils of Bangladesh typically are < 10 $\mu g\ g^{-1}$, concentrations significantly higher than 40 $\mu g\ g^{-1}$ have been reported in soils that have been intensively irrigated with the arsenic contaminated groundwater [81].

The important concern is the higher efficiency in the bioaccumulation of arsenic in rice compared to other crops and cereals. William et al. [82] analyzed 173 paired soil, shoot and grain samples of the three cereal crops collected from different regions of the world. The study showed higher transfer factor for arsenic from soil to the shoots of rice (0.05–3.8, mean=0.76) compared to the values for wheat (0.002–0.14, mean=0.018) and barley (0.002–0.095, mean=0.013). The enrichment factor (the ratio of plant arsenic concentration to soil arsenic concentration) of arsenic from soil to rice grain (0.01–0.12, mean=0.04) was also much higher than that of wheat (0.000–0.024, mean=0.004) or barley (0.000–0.019, mean=0.003). This implies that rice grown in soils that are contaminated with arsenic is able to accumulate high levels of arsenic in the grain. It is the accumulation of arsenic in soil from the application of arsenic-contaminated water that has been associated with substantial elevated levels of arsenic in rice-grain and represents an important threat to the food security, particularly in South Asia.

1.4.2. Evaluation of the biomarkers of arsenic exposure

As discussed in the previous section, populations living in arsenic affected areas are exposed to multiple pathways of arsenic and that includes not only drinking water but also the foods that are consumed daily. Once the arsenic is ingested, it is adsorbed from the gastro-intestinal tract and is distributed in the tissues. Liver is the principal organ for the metabolism of arsenic and it is transformed to monomethyl and dimethyl arsenical which is later excreted *via* urine and a part accumulates in the biological structure [83]. Although the primary metabolic pathway for inorganic arsenic is methylation [84,85], the exact reaction is not yet fully understood. At present there are two conceptual models for the enzymatically catalyzed methylation of arsenic. Whereas the first model hypothesizes alternating reduction of As(V) to As(III) and oxidative addition of methyl group [86,87], the second model describes thiol-containing complexes of arsenicals (mainly the pentavalent methylmonothioarsonic acid, the dimethylmonothioarsinic acid and the dimethyldithioarsinic acid) as substrates for the transfer of methyl groups to the arsenic species [88–90]. In this pathway, the reduced trivalent methylated arsenic is formed before the pentavalent species [91]. Nevertheless at present, the second model is not universally accepted in the scientific community and more detailed studies are needed.

A biomarker is a useful tool to measure the environmental impact on an individual over space and time. Various biomarkers of exposure, effect and sustainability has been identified and are used for arsenic epidemiological study. Speciation of the various forms of arsenic in these fluids and tissues used as biomarkers is needed for the understanding of the mechanism of arsenic toxicity and to properly access the risk associated with arsenic in a population [92].

Determination of arsenic and its metabolites in blood provides information about the recent exposure to arsenic [93–95]. Blood analysis is particularly useful for dose-response studies where the population is exposed to a wide range of arsenic concentration. Studies have shown moderate relationship between arsenic in blood and that of drinking water [93,94]. However, the use of blood as a biomarker is difficult as the sampling procedure is invasive and people usually tends to avoid giving blood samples because of the risk of blood related diseases. Moreover, speciation of the various species of arsenic in blood is difficult as it involves plasma, serum or blood cells [94,96]. Hair and nail are other biological structure rich in keratin which has been used as a biomarker of arsenic exposure [94,97–100]. Arsenic has high affinity for keratin and is deposited by forming bonds with the sulphydyl group of keratin [101,102]. Since the growth rate of hair is ~1-2 mm per day [103] while that of fingernail and toenail is 0.1 mm per day and 0.03–0.05 mm/day, respectively, analysis of the total as well as the various species of arsenic provides reflection of past exposure [104]. Although, hair and nail can be collected by non-invasive method, the problem that mainly persists is related to external contamination [103,104]. Erroneous results might be encountered because of the difficulty to distinguish between endogenous and exogenous sources of arsenic adsorbed in hair and nail [103,105]. Speciation of arsenic from hair and nail involves digestion of the sample at high temperature and measuring the extract [101]. Reports suggest that species transformation might take place during such extraction [102]. Moreover, arsenic in hair and nail has limited applicability for a population exposed to high amount of arsenic. Schmitt et al. [106] showed that for a 50-fold increase of arsenic concentration in water for arsenic exposed and non-exposed population in Inner Mongolia, an increase of only 20-fold took place for nail arsenic, suggesting that hair and nail may be saturated with arsenic.

Arsenic in urine is probably the most used biomarker in arsenic epidemiological study [94,107–110]. Since most of the ingested arsenic is excreted through urine, examination of urinary arsenic serves as one of the potent indicator of arsenic exposure [94]. Earlier studies measured total arsenic in urine for the population that has been exposed to arsenic. In recent times, with the advancement of analytical techniques, speciation of urinary arsenic has gained considerable interest [111–113]. Determination of the different species such as As(III), As(V), dimethylarsinic acid (DMA) and monomethylarsonic acid (MMA) is described to be better indicator of arsenic exposure [85,94] and can be related to individual capacity to methylate inorganic arsenic and subsequently accessing risk toxicity [114]. There have also been some studies that have identified MMA and DMA in lower oxidation state [MMA(III) and DMA(III)] in human urine [115–118]. Results suggest that a higher concentration of urinary MMA(III) has been related to higher risk of arsenic-induced cancers [91,119]. For example, studies carried out in an endemic areas of central Mexico by Valenzuela et al. [118] have shown higher concentration of urinary arsenic and MMA(III) for subjects with skin lesions of arsenism than subjects without skin lesions. Thus these findings shows that the concentration of MMA(III) in urine can reflect some light on the individual susceptibility to arsenic.

Interpretation of the arsenic results in urine is difficult and there are several limitations for the use of urine in arsenic epidemiological study. Urinary arsenic gives information about the excretion and the metabolism of arsenic but falls silent about the actual tissue burden [120]. Thus any factors that affect the metabolism of arsenic can have a severe impact on the concentration of urinary arsenic. Studies have shown that consumption of seafood and marine fish containing organic arsenic can interfere with the total urinary arsenic and the distribution of arsenic derivatives such as arsenobetaine and arsenocholine [92]. Organo arsenic species are non-toxic, chemically stable and are excreted rapidly intact but its consumption can significantly increase the concentration of urinary arsenic. Therefore before performing the study, restriction in food consumption needs to be taken and participants are refrained from consuming seafood for 2-3 days before collection of the urine samples [92]. Sometimes rapid analysis of the urine samples are required as the reduced arsenic species present in urine [MMA(III) and DMA(III)] are rapidly oxidized even when kept frozen, and thus, underestimation of these arsenic species may take place [118]. Although spot urine are the preferred collection procedure for urine samples, the major disadvantage that usually persists is inter-individual matrix variation due to difference in fluid intake, physical activity and temperature between the individuals [121]. As a result, hydration correction is necessary to account for the differences while omitting such corrections may lead to highly significant correlations as dilution of urine samples are not accounted [107]. For hydration correction, there are studies where urine arsenic has been normalized with urine creatinine [122,123]. However such method of adjusting the arsenic-level with the concentration of creatinine in urine has limitations as the excretion of creatinine is dependent on factors such as age, sex, body mass index (BMI) and race [107,124]. Moreover, concentration of creatinine is significantly related to the concentration of the arsenic metabolites present in the urine and changes for creatinine adjustment may give erroneous results [122]. Gamble and Liu [123] in their report concluded that urinary creatinine should be included as an independent variable in multiple regression analysis and the role of one-carbon metabolism as a predictor of creatinine must also be considered for the interpretation of the result.

From the above discussion, it is clear that none of the conventional biomarkers of arsenic exposure is universally suitable for every arsenic epidemiological study and the selection of the appropriate biomarker should be considered after gaining sufficient knowledge about the characteristic of the selected area and the populations.

1.5. REMOVAL OF ARSENIC FROM CONTAMINATED WATER

With the aim of providing a solution to populations exposed to high levels of arsenic through drinking water, several methods have been developed for the treatment of arsenic contaminated water. They include a large range of processes such as co-precipitation, flotation, ion-exchange, ultrafiltration, and reverse osmosis [125]. However among all the various techniques adopted for arsenic removal, adsorption has received much attention because of its low cost and high removal efficiency [126]. Since arsenic has a high affinity towards iron, iron based adsorption has been widely used for treatment of arsenic contaminated groundwater [126]. Depending on the chemistry of the remediation process, iron based technologies can be divided into two overlapping groups; one is when iron acts as sorbent, co-precipitant or contaminant immobilizing agent and the other is when iron behaves as a reductant (convert contaminants into lower oxidizing state or used as an electron donor) [125]. Goethite and Hydrous Ferric Oxide (HFO) are two important iron based materials that are used as sorbent but goethite is less reactive than HFO due to the lack of sufficient surface area [2]. Previous studies have demonstrated that As(V) and As(III) forms a strong inner sphere complex on the ferrihydrite surface of HFO and thus can acts as a potent adsorbent for arsenic [127,128]. Among the natural minerals, much attention has been given to iron containing natural magnetite, siderite, and hematite [129–131]. In one such study, Guo et al. [132] found that natural siderite and hematite removed arsenic through electrostatic attraction and surface complexation with the Fe hydroxides in the minerals. However, the rate of reaction was slow and common anions such as bicarbonate and phosphate decreased the adsorption capacity of arsenic.

Metallic iron as zero valent iron (ZVI) has been used in the past for the treatment of groundwater and also as a reactive media in a number of field scale permeable reactive barrier systems [133–135]. Iron has an advantage over other metals as they are non-toxic (environmentally friendly), inexpensive and readily available in bulk quantities (cost-effective). Since the development of ZVI in 1990, by Canadian hydrogeologist, approximately 120 iron walls have been constructed worldwide as permeable reactive barrier so as to remove contaminants from groundwater [136,137]. Laboratory scale studies have shown that ZVI oxidizes spontaneously in water to form a number of Fe(II) and Fe(III) oxides/hydroxides and As(III) and As(V) forms inner-sphere complexes with the corrosion products [138,139]. Sun et al. [140] observed that oxidation of As(III) to As(V) in aerobic conditions plays an important role for the removal of As(III), and As(III) and As(V) are removed from solution via adsorption onto the corrosion product. In another study, Bang et al. [133] observed a rapid rate of arsenic removal from aqueous solution via precipitation/co-precipitation on iron hydroxide precipitation product in aerobic condition and the uptake of As(V) was faster than As(III) at pH 7. However, for anaerobic conditions, the rate of reaction was considerably slower compared to aerobic environment and the removal rate of As(III) was faster than As(V) at pH 4 and 7. Moreover, their study also demonstrated that reduction of As(V) to As(III) and As(III) to metallic As takes place upon reaction with ZVI in the absence of O_2. Thus, different reaction mechanisms of arsenic with ZVI predominate in aerobic and anaerobic environments. Due to the absence of O_2, ZVI is able to act as a reductant and to reduce As(V) and As(III). The presence of As(0) was also reported by Sun et al. [141], who demonstrated that disruption of the outer oxide layer by acid treatment enabled As(V) to reacts with the core Fe^0 of the ZVI and as a result, sufficient redox potential is achieved for reduction of As(V) to As(0).

Recent advances in nanoscience and nanotechnology have led to the development of a number of nanoparticles for the environmental remediation of various contaminants from groundwater [142]. Due to their high specific surface area and reactivity, nanoparticles are considered as a suitable option for fast removal of contaminants from aqueous solution [143]. Nano-ZVI (nZVI) is one such nanoparticle that is now being used extensively for removal of arsenic from aqueous solution [144]. The mechanism of arsenic removal by nZVI is similar to that of ZVI where As(III) and As(V) forms an inner sphere complex with the iron oxide/hydroxide corrosion product formed in solution under open atmosphere along with simultaneous oxidation of As(III) to As(V) [145,146]. The major limitation that usually persists is the free release of the nanoparticles to the environment which has a potential impact on human health [147]. Recent trends in research have shown that doping such nZVI on an inert material can be an option to increase the stability of nZVI and thereby arrest the limitations of the use of nZVI [148]. However little reports are currently available about the use of such adsorbent for the removal of arsenic and particularly its suitability in groundwater remediation.

1.6. ANALYTICAL METHODS FOR ARSENIC DETERMINATION

There are several methodologies that have been developed for the determination of total as well as arsenic species in wide range of environmental matrices. The Molybdenum blue and the silver diethyldithiocarbamate (SDDC) method are probably the cheapest and the most common for arsenic determination. However, in recent times, the methods has become obsolete, in particular for analyses of environmental samples, as the method is time consuming and do not ensure sufficient detection limit. In molybdenum blue method, the arsenic is extracted by mineral acid and is oxidized to As(V) which reacts with ammonium molybdate (VI) to forms a characteristic blue color and is detected at the wavelength 825 nm [149]. On the other hand, in SDDC method, arsenic is reduced to arsenic hydride which absorbs in the solution of SDDC with chloroform or pyridine. The red-violet complex formed as a result, is measured at a wavelength of 510 or 525 nm. However for both this method, there are potential interferences from sulphur, germanium, selenium and tellurium compounds [149].

Among the electrochemical techniques used for arsenic determination, stripping analysis is best suited as no current passes through the working electrode during stripping and thus there is less interference from electro-active species [150]. In anodic stripping voltammetry (ASV), arsenic is deposited at the working electrode with subsequent stripping from the anodic surface. Several electrodes have been used for this purpose and include graphite, platinum, gold, boron, diamond etc [151,152]. For cathodic stripping voltammetry (CSV), mercury as working electrodes has been mostly recommended [153]. There has been studies where hanging mercury drop electrode (HMDE) has been used to determine arsenic in acidic medium where arsenic is pre-concentrated as intermetallic compounds in the HMDE and then stripped cathodically [154,155]. However, arsenic has a poor sensitivity on mercury surface and also there are possible interferences of ions which are co-deposited [156].

Atomic absorption spectrometry (AAS) and atomic fluorescence spectrometry (AFS) are the most used among the atomic spectrometric method for arsenic determination in wide range of water, geological and biological samples. For both techniques, quite lower detection limit can be obtained by integration with a hydride generator. In hydride generation, arsenic reacts with a reducing agent (mostly borohydride ion) and form a volatile arsenic hydride which is then transported to the spectrometer and measured for arsenic. Thus the process ensures more efficient sample introduction system and also to avoid matrix interferences. However the method has some interference as there are matrix elements that suppress the formation of the volatile hydrides as well as interfere in the atomizer process [157].

Inductively coupled plasma (ICP) has also been used for arsenic determination conjugated with detection techniques such as atomic emission spectrometry (AES) and Mass Spectrometry (MS) [158]. The plasma atomizes and partially ionizes all the forms of arsenic and therefore such analyses are not dependent upon the arsenic species. However among these techniques, ICP-AES are less used and normally applied for comparison and accurate analysis in multi-element samples [158]. Moreover arsenic determination also suffers from spectral interferences at high concentration of titanium, manganese, chromium and iron, due to vacuum ultraviolet lines and also high concentration of vanadium and chromium due to ultraviolet lines. On the other hand, ICP-MS is one of the widely and robust techniques that has been used for arsenic. The main advantage of ICP-MS over ICP-AES is its isotope analysis capability with higher precision and lower detection limit. However, there are also several spectral and non-spectral interferences. Among them, high level of chlorides (Cl^-) is the main challenge for the determination of arsenic. Chloride and argon combines in the plasma to form argon chloride ($^{40}Ar^{35}Cl$) which has similar mass to arsenic (^{75}As) [159]. Nevertheless, electrothermal vaporization, high resolution detectors and collision/reaction cell devices has successfully been used to overcome this interference [160,161]. Arsenic also suffers from poor ionization efficiency in the ICP source that can be a problem for the determination of low concentration of arsenic in real samples. It has been seen that addition of C-containing compounds such as methanol and ethanol in plasma enhances the ionization efficiency in the plasma and as a result, increases the sensitivity of arsenic [162]. Thus several applications have been adopted to overcome such challenge and hydride generation is one of them [158].

For speciation of arsenic in samples, high performance liquid chromatography (HPLC) coupled with ICP-MS are the most frequently used hyphenated techniques. The different arsenic species directly interacts with the stationary phase and depending upon the nature of interactions, are sequentially eluted and finally measured. Compared to ion-pair reverse phased column, an ion exchange column is found to be superior for the arsenic speciation process [163]. The combination of anion and cation exchange column in-series has also been shown to separate arsenite, arsenate as well as other organo arsenic species [164].

1.7. GEOGRAPHIC AREAS INVOLVED IN THIS PRESENT STUDY

To study the endemic problems of arsenic, the state of West Bengal in India was chosen as a representative arsenic affected area. The study areas, Debagram and Chakdaha are situated in the northern and southern part of the Nadia district, respectively, and Baruipur is situated in the South 24 Parganas district of West Bengal, India (Fig. 1.7).

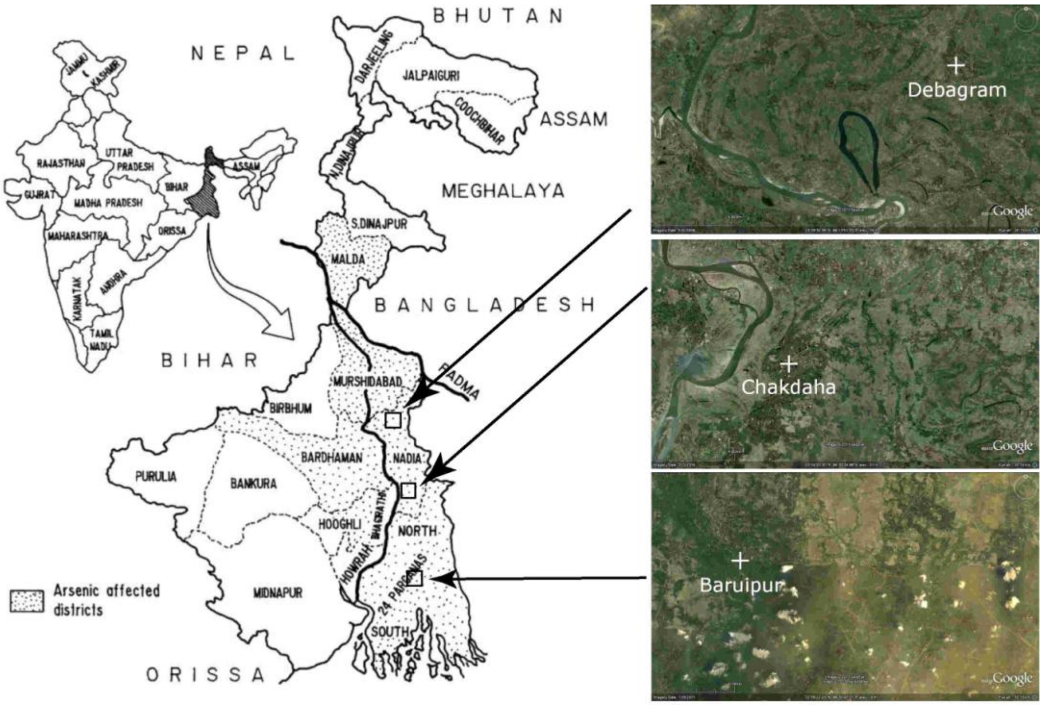

Figure 1.7. Map of the study areas (1: Debagram; 2: Chakdaha; 3: Baruipur) in West Bengal, India showing arsenic affected districts. Map also shows Google Earth imagery of the areas surrounding three study areas. The central study area locations were marked with a cross in each of the Google Earth imagery.

1.7.1 Location and climate

The study areas have tropical climate with annual rainfall ranges between 1295 and 3945 mm. The temperature ranges between 16 to 42^{o}C and average relative humidity is >65%. The study areas have three distinct seasons: summer (February to May), monsoon (June to September) and winter (October to January). The bulk of the rainfall (82%) takes place during monsoon periods due to moisture-laden winds from the Bay of Bengal. The local conventional rainfall contributes during pre-monsoonal (16%) and winter (2%) periods.

1.7.2 Physiography and geomorphology

The state of West Bengal can be divided into six macro-physiographic regions: i) laterite upland and barind tract; ii) upper delta plain (UDP); iii) valley margin fan; iv) marginal plain; v) lower delta plain (LDP), and vi) delta front [165]. The upper- and lower- delta plain is basically surrounded by the river Ganges-Padma, river Bhagirathi-Hooghly, and the Bay of Bengal in the east, west and south, respectively.

The major geomorphic units of the delta plain can be divided into two distinct divisions: i) the UDP of meander belts of river Bhagirathi-Hooghly in the north, and (ii) the LDP and delta fronts with several tidal creeks in the south. A series of meander scars, abandoned channels and oxbow lakes are the common geomorphic features of this region [166]. Abandoned meander scrolls may be representative of the flood plains in the UDP with a very gentle slope towards south. Levees and back swamps in between inter-distributary levees are the other landform features. Fining upward sedimentary sequence (sand-silt-clay) or such cyclothems are the characteristic lithology of the aquifer sediments [167]. The geomorphology of the LDP and delta front is characterized by several tidal creeks, tidal mudflats, distributary levees and inter-distributary marsh complexes, formed under fluvial, estuarine and marine environment as a consequence of fluctuating sea level during geologically Recent time [168,169].

1.7.3 Depositional environment

The depositional behaviour of the sediment in Nadia (Debagram and Chakdaha) and South 24 Parganas (Baruipur) districts are distinctly different in terms of geomorphologic and physiographic settings. Debagram and Chakdaha are situated within the UDP (i.e. Bhagirathi-Hooghly alluvial plain), of which, Debagram is located ~10 km east of the major meander belt of Bhagirathi-Hooghly river, while Chakdaha is located beside the recent meander and the present river channel of Bhagirathi-Hooghly river. Baruipur is located at the delta front and near to the Bay of Bengal in the south.

The Bhagirathi-Hooghly alluvial plain are mainly represented by the overlapping sub-delta, where fluvial processes might have resulted in extensive Holocene flood plains with the dominance of coarse grained sediments [165]. The breakthrough of numerous tributaries and distributaries of river Ganges within the time scale of 100 years have been resulted in the deposition of thick layers of overbank silts and clays engraved by the channel sands [168,170,171]. On the contrary, the delta front lithology has been represented by the extensive clay capping of variable thickness (15 and 75 m), underlain by the mixture of fine grained sand and mud deposits[172].

1.7.4. Overview of the various geochemical processes responsible for arsenic mobilization in the study area

Various hypotheses related to release mechanisms of arsenic in shallow aquifers, have been put forwarded over the past decades. Among these hypotheses (also popular as models), the oxidation and reduction models have been widely employed to explain high arsenic groundwater in the Bengal Delta Plain [167,173–177]. However, the ‘‘oxidation model’’, that is oxidation of sulfide minerals by air reaching the underground aquifer and subsequent release of arsenic, as a mechanism, has now been discarded by research workers [166,178–180]. In contrast, the ‘‘reduction model’’, that is reductive dissolution of arsenic rich Fe/Mn oxyhydroxide has been largely supported by several researchers [166,167,177](. The West Bengal groundwater hydrochemistry studies have revealed that mobility of arsenic is primarily controlled by the availability of organic matter in the young Gangetic sediment [181–183]. Fermentation of organic matter produces intermediate products like acetate and formate as nutrient for bacteria along with HCO_3^- and thereby accelerates various geochemical processes (denitrification → Fe reduction) [178,181,184]. Thus, in thermodynamically favored conditions, these processes generally provide mutual positive relationships between reduced species like As(III), Fe(II), Mn(II), NH_4^+, etc. and HCO_3^- [185]. However, the Fe/Mn hydroxide reduction hypothesis has not been rigorously proven. It is still not clear how sandy aquifer materials containing arsenic mostly below 10 mg kg^{-1} on average along with a very low amount of C (~ up to 0.5%) produce such high levels of dissolved arsenic in Bengal groundwater [183,186,187]. Moreover, sometimes no correlation is observed between Fe and/or Mn and arsenic concentration either in the sediment or in the groundwater, a matter which sometimes is invoked to play down the role of these processes in the occurrence of natural high arsenic in groundwater.

1.8. REFERENCES

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CHAPTER 2: OBJECTIVE

The main objective of this thesis is focused on the understanding of arsenic interactions in environmental and biological system through chemical speciation of its major species. Thus, taking into consideration the above objective, the more specific and detailed description is as follow:

1. Although there has been extensive research on the groundwater mobilization of arsenic, there is actually lack of our understanding about the various local anthropogenic as well as the geogenic effects that may exert control on the elevated levels of arsenic in groundwater. Therefore, to understand these factors, we studied the groundwater chemistry and the arsenic mobilization process by comparing three physicologically different areas.

2. The arsenic effect on human has been measured by measuring arsenic on various biological fluids and structures but each of these has some drawbacks. Saliva is a biological fluid that has not been used in arsenic study. Thus we aimed to develop a method for easy determination of total arsenic in saliva.

3. Additionally we also intended to speciate the various forms of arsenic in saliva. Such information would not only give us knowledge about the body burden of the ingested arsenic, but also individual susceptibility to arsenic-induced skin lesion.

4. Lastly, we try to find a simple and robust method for providing arsenic free water to the population exposed to arsenic. Although the proper understanding of the arsenic mobilization mechanism and the health effect of arsenic is of utmost importance, treatment technologies targeted on removal of arsenic is equally important that needs to be addressed, as delivering safe water to the arsenic affected patients is the only effective alternative for curing

arsenicosis. With this objective, we tried to develop an adsorbent that can reduce the elevated levels of arsenic in aqueous solution. Even though nZVI has been used effectively for laboratory scale arsenic removal, there are some intrinsic properties of nZVI that inhibit for the direct application in field. We doped nZVI on the surface of an inert material (Montmorillonite) and tried to investigate the removal efficiency. We also studied the speciation of arsenic after adsorption onto the absorbent material so as to understand the mechanism of arsenic removal from aqueous solution.

CHAPTER 3: EXPERIMENTS AND RESULTS

3.1: Arsenic mobilization in the aquifers of West Bengal, India

A hydrogeochemical study was carried out in West Bengal, India to demonstrate the control of geogenic and anthropogenic influences on groundwater arsenic mobilization. Our result shows that the arsenic release is influenced by both geogenic (i.e. geomorphology) and anthropogenic (i.e. unsewered sanitation) factors. Thus multiple geochemical processes, such as Fe-oxyhydroxides reduction and carbonate dissolution, are responsible for high arsenic occurrence in groundwaters of the studied area.

3.1.1. INTRODUCTION

The state of West Bengal in India is representative of one of the diverse arsenic (As) effected groundwater zones of the Bengal Delta Plain [1,2]. The occurrences of As in West Bengal have been widely reported from the districts of Maldah, Murshidabad, Nadia, North & South 24 Parganas, Burdwan, Howrah and Hooghly, and more recent observations from Kolkata, Koch Bihar, North & South Dinajpur districts [3]. The affected districts include one hundred and eleven blocks and more than three thousand villages [4]. The high As groundwater in West Bengal stretches ~400 km (Maldah district in the north to South 24 Parganas district in the south) and was typically characterized by heterogeneous and patchy distribution of hot spots, interspersed with low/safe As-areas [5,6].

In West Bengal, previous studies has demonstrated the role of depositional behavior of aquifer sediments on the geochemical processes leading to the release of high As concentrations in the groundwater [7,8]. The processes of As mobilization is mainly governed by the complex biogeochemical interactions regulated by a number of physical, chemical and biological factors, such as sedimentological settings, sedimentation history, groundwater abstraction, adsorption and desorption behavior of sediments, dissolved organic carbon and microbes [9–14]. Such biogeochemical interactions can further be complicated by the local anthropogenic activities, such as unsewered sanitations, domestic wastes and ponds [15–17]. However, only a few studies [18–20] have attempted to demonstrate the controlling behavior of regional scale lithological and hydrological variations on As release processes by comparing As-contamination scenarios in different physiographic settings of the delta plain. The effect of different local factors including land use pattern towards As release have not been demonstrated in details. Thus there are considerable knowledge-gaps to our scientific understanding of the cumulative controlling mechanism of geogenic and anthropogenic factors in release of As into groundwater of the deltaic basin.

CHAPTER 3.1

The objective of this chapter is to elucidate the mechanism of As release into groundwater of deltaic West Bengal, India. The study areas are Debagram and Chakdaha located within the Bhagirathi-Hooghly alluvial plain and Baruipur located within the Delta front (head of Bay of Bengal). We examined the salient hydrogeochemical features of groundwater in drinking water wells. The role of geomorphology and land use including the influence of anthropogenic activities (e.g. sanitation, pond, domestic wastes, etc.) on As release processes was also examined.

3.1.2. MATERIALS AND METHODS

3.1.2.1. Sampling and analysis

Thirty groundwater samples from tube wells of each study area were collected in acid washed, pre-cleaned polyethylene (PE) bottles. The selection of tube wells have been made on a random basis to have wider coverage and to provide representative dataset of the studied localities. Prior to sampling, tube wells were flushed for several times to collect fresh water from the aquifer. The Eh, pH and electrical conductivity (EC) were measured on-site using a WTW multimeter (WTW, Germany). Samples for As(III) and As(V) analyses were separated on-site by passing (~5ml/min) water samples (~50 ml) through a disposable cartridge packed with ion exchange resins (Metal Soft Centre, Highland Park, USA). The cartridge selectively adsorbs As(V) and the eluents were stored after acidified with few drops of HNO3 for As(III) measurement. Anion analyses were performed by an Ion Chromatograph (DIONEX ICS 1000) with a separating column (DIONEX AS 4 SC), while the cation and trace elements were analyzed using ICP-AES (Perkin Elmer 3300 DV optima). Total Fe and Fe(II) concentrations were measured spectrophotometrically (Perkin Elmer, Lamda 20 UV-VIS) using 1, 10 phenanthroline [21].

3.1.2.2. Geochemical modeling

Saturation indices (SI) of major mineral phases in groundwater were calculated as the quotient of ion activity product (IAP) and saturation product (Ksp), using PHREEQC version 2.8 [22]. The program evaluates the SI values of minerals in groundwater by solving mass balance and mass action (chemical reaction) equations. The SI values (positive and negative) represent the thermodynamic potential for precipitation and dissolution, respectively. The major mineral phases include aragonite, calcite, dolomite, ferrihydrite, goethite, hematite, magnetite, pyrolusite, rhodochrosite, siderite, and vivianite. The SI calculations were done on individual sample and reported as mean values by grouping the result from each study area. These calculations were useful to identify the geochemical reactions in liquid phases linked to the release of As in groundwater (e.g. Fe-oxide precipitation or dissolution).

3.1.3. RESULTS AND DISCUSSION

3.1.3.1. Groundwater chemical composition

The results of the detailed chemical analyses of groundwater from Debagram, Chakdaha and Baruipur are presented in Table 3.1.1. In general, the groundwater contains high values of EC, HCO_3^-, Na^+, Ca^{2+}, Mg^{2+}, Cl^- and low values of SO_4^{2-} and K^+. The pH is circum-neutral (7.5 ± 0.28, 7.6 ± 0.28, and 7.6 ± 0.23, respectively), while Eh is negative (-142 ± 25, -118 ± 20, and -131 ± 15 mV, respectively) suggesting reduced condition. Throughout this chapter, reported values in the parentheses are the respective mean and standard deviation of the chemical parameters of groundwater following order of Bhagirathi-Hooghly alluvial plain (Debagram and Chakdaha) and delta front (Baruipur) unless otherwise specified.

In Bhagirathi-Hooghly alluvial plain, the shallow aquifer (<100 m) are relatively enriched with Cl^- (36 ± 24 and 31 ± 16 mgL^{-1} respectively in Debagram and Chakdaha) compared with the deeper aquifer (>100 m) (8.3 ± 5.9 and 6.1 ± 0.30 mgL^{-1} respectively). However, in the delta front, the deeper aquifer are enriched with Cl^- (426 ± 304 mgL-1) compared with the shallow aquifer (65 ± 102 mgL^{-1}). The SO_4^{2-} concentrations are higher in shallow aquifers of Bhagirathi-Hooghly alluvial plain (11 ± 16 and 4.1 ± 4.2 mgL^{-1} respectively) than deeper aquifers (1.7 ± 2.0 and 0.25 ± 0.24 mgL^{-1} respectively). In the delta front, the deeper aquifers have a higher concentration of SO_4^{2-} (52 ± 40 mgL^{-1}) compared to shallow aquifers (2.9 ± 6.1 mgL^{-1}). The Na^+ concentrations are also higher in shallow aquifers of Bhagirathi-Hooghly alluvial plain (21 ± 7.6 and 26 ± 13 mgL^{-1} respectively) than deeper aquifers (8.0 ± 0.82 and 15 ± 3.7 mgL^{-1} respectively). On the contrary, the deeper aquifer of delta front are enriched with Na^+ (209 ± 148 mgL^{-1}) compared with shallow aquifers (65 ± 73 mgL^{-1}). Such chemical features signify potential seawater intrusion in the deeper aquifer of the delta front and/or dissolution of connate water that were entrapped during Pleistocene-Holocene glacial maxima [23].

Table 3.1.1. The results of the detailed chemical analysis of groundwater collected form Debagram (a), Chakdaha (b) and Baruipur (c).

(a) Debagram groundwater

Well No.	Latitude	Longitude	Land use	Geomorphology	Depth (m)	pH	EC (μScm^{-1})	DOC (mgL^{-1})	Eh (mV)
1	23.6892	88.2922	Habitation	Palaeo-channel	20	7.2	1020	5.5	-127
2	23.6883	88.3128	Habitation	Palaeo-interfluve	20	7.4	901	2.4	-175
3	na	na	Sanitation	na	20	7.3	620	6.1	-175
4	23.6892	88.3158	Pond	Palaeo-interfluve	20	7.3	945	8.4	-185
5	23.6883	88.3169	Habitation	Palaeo-interfluve	20	7.1	720	5.5	-150
6	23.6886	88.3108	Agriculture	Palaeo-interfluve	23	7.0	620	6.2	-121
7	na	na	Sanitation	na	24	7.1	707	9.5	-155
8	na	na	Sanitation	na	27	7.9	450	2.1	-152
9	23.6861	88.2964	Habitation	Palaeo-channel	27	8.0	650	5.4	-173
10	na	na	Sanitation	na	27	7.6	478	3.3	-160
11	23.6881	88.3089	Agriculture	Palaeo-interfluve	27	7.1	720	7.3	-162
12	na	na	Sanitation	na	30	7.3	530	4.5	-152
13	na	na	Sanitation	na	30	7.2	800	5.9	-165
14	23.6881	88.3108	Agriculture	Palaeo-interfluve	30	7.9	460	5.1	-182
15	23.6886	88.3169	Pond	Palaeo-interfluve	33	7.9	530	3.7	-153
16	23.6892	88.3006	Habitation	Palaeo-channel	33	7.8	841	2.9	-151
17	23.6881	88.3067	Habitation	Palaeo-interfluve	35	7.4	420	6.6	-121
18	na	na	Sanitation	na	37	7.8	550	7.8	-132
19	na	na	Sanitation	na	40	7.9	721	5.9	-118
20	23.6872	88.3028	Habitation	Palaeo-channel	40	7.6	498	7.0	-134
21	23.6889	88.3025	Habitation	Palaeo-channel	40	7.5	550	7.5	-125
22	na	na	Sanitation	na	40	7.6	478	10	-128
23	23.6869	88.2922	Agriculture	Palaeo-channel	43	7.7	874	9.0	-155
24	na	na	Sanitation	na	47	7.4	754	5.4	-112
25	na	na	Sanitation	na	67	7.4	671	2.5	-142
26	23.6886	88.2914	Agriculture	na	67	7.2	391	1.6	-117
27	na	na	na	Deeper aquifer	120	7.3	352	1.2	-105
28	23.6875	88.3042	na	Deeper aquifer	120	7.2	420	2.2	-110
29	23.6878	88.2983	na	Deeper aquifer	134	7.5	312	1.9	-111
30	na	na	na	Deeper aquifer	134	7.3	350	1.5	-103

Note: na- not available, bdl- below detection limit.

(a) continued..

Well No.	HCO_3^- (mgL^{-1})	PO_4^{3-} (mgL^{-1})	NH_4^+ (mgL^{-1})	NO_3^- (mgL^{-1})	SO_4^{2-} (mgL^{-1})	Cl^- (mgL^{-1})	As (μgL^{-1})	As(III) (μgL^{-1})	As(V) (μgL^{-1})
1	307	0.30	0.10	0.43	4.7	16	110	80	30
2	408	1.5	1.3	5.6	0.01	18	178	135	43
3	413	3.0	bdl	bdl	5.5	26	12	na	na
4	548	3.0	1.9	8.4	0.09	61	242	199	43
5	444	0.41	bdl	bdl	14	32	42	32	10
6	597	5.6	7.4	33	0.12	60	969	832	137
7	814	26	4.8	21	0.13	87	176	122	54
8	619	6.2	7.5	33	0.11	37	961	854	107
9	641	7.7	10	45	0.06	17	683	537	146
10	410	0.75	0.49	2.2	8.7	41	96	77	19
11	401	2.2	2.2	9.5	0.49	15	226	161	65
12	665	10	3.2	14	2.0	111	30	21	9
13	617	2.9	3.7	16	bdl	23	434	347	87
14	399	0.10	0.05	0.24	0.61	10	1.0	na	na
15	496	1.1	3.8	17	0.96	30	693	627	66
16	503	0.54	3.1	14	1.5	29	133	91	42
17	429	0.19	0.25	1.1	3.2	56	17	na	na
18	578	2.6	3.9	17	0.31	17	878	689	189
19	518	6.8	8.6	38	0.08	58	470	306	164
20	655	1.8	5.9	26	0.41	122	1059	858	201
21	653	1.2	1.0	4.5	0.69	104	78	62	16
22	740	3.0	4.2	18	0.14	67	416	268	148
23	547	4.4	2.8	12	bdl	52	498	357	141
24	291	4.3	2.3	9.9	0.72	12	366	253	113
25	179	0.14	bdl	bdl	27	529	2.1	na	na
26	270	0.15	bdl	bdl	26	538	1.2	na	na
27	503	bdl	0.20	0.87	0.03	120	3.0	na	na
28	431	0.13	0.66	2.9	59	183	1.2	na	na
29	458	0.14	1.3	5.7	106	878	1.3	na	na
30	421	0.13	1.1	5.0	68	410	1.1	na	na

Note: na- not available, bdl- below detection limit.

(a) continued..

Well No.	**Fe (mgL^{-1})**	**Fe(II) (mgL^{-1})**	**Fe(III) (mgL^{-1})**	**Na^{+} (mgL^{-1})**	**K^{+} (mgL^{-1})**	**Mg^{2+} (mgL^{-1})**	**Ca^{2+} (mgL^{-1})**	**Ba (μgL^{-1})**	**Mn (μgL^{-1})**	**Sr (μgL^{-1})**	**Al (μgL^{-1})**
1	0.39	0.28	0.11	15	2.8	14	80	81	544	132	54
2	3.5	2.7	0.76	13	3.8	17	94	140	828	244	46
3	4.0	2.9	1.1	10	3.2	21	100	126	208	167	53
4	8.3	7.1	1.2	39	5.3	27	120	387	1394	416	49
5	1.0	na	na	14	11	29	145	198	911	269	125
6	6.2	5.2	1.1	47	5.9	28	120	248	680	495	100
7	1.6	1.0	0.53	316	5.6	9.0	23	42	50	78	51
8	5.9	4.9	1.0	44	5.9	30	128	254	408	502	57
9	7.8	6.3	1.6	55	6.3	28	111	268	393	479	66
10	3.2	2.5	0.74	26	2.9	19	100	264	888	165	36
11	10	7.4	2.9	16	4.7	18	84	210	522	294	95
12	3.9	2.8	1.1	195	9.2	40	54	267	182	330	50
13	3.3	2.5	0.78	41	8.2	38	101	106	95	442	43
14	2.0	na	na	12	1.3	29	79	31	384	358	47
15	5.7	5.0	0.76	34	7.4	26	92	400	112	405	63
16	3.8	2.9	0.91	26	5.4	29	111	80	368	415	128
17	0.87	na	na	29	3.2	26	100	85	402	420	57
18	4.7	4.0	0.71	38	5.9	32	126	198	1082	484	73
19	11	8.2	2.4	39	7.4	37	108	235	256	441	35
20	7.4	6.2	1.3	118	7.8	37	99	529	224	526	38
21	1.7	1.4	0.30	189	5.8	22	68	123	211	327	71
22	2.7	2.1	0.54	63	8.9	47	111	164	242	508	143
23	4.6	3.9	0.67	98	7.4	38	96	48	606	457	52
24	5.9	4.6	1.2	18	4.2	21	101	245	882	343	53
25	0.36	na	na	119	5.3	44	207	239	1259	901	40
26	0.50	na	na	128	5.6	47	214	301	1344	933	36
27	1.1	na	na	115	5.6	32	99	226	147	509	106
28	0.31	na	na	133	6.1	41	91	97	46	643	35
29	2.91	na	na	467	7.6	69	140	253	84	1015	60
30	0.52	na	na	200	7.4	54	111	157	62	919	54

Note: na- not available, bdl- below detection limit.

(a) continued..

Well No.	Zn (μgL^{-1})	Cu (μgL^{-1})	Pb (μgL^{-1})	Ni (μgL^{-1})	Cr (μgL^{-1})	Co (μgL^{-1})	U (μgL^{-1})	Co (μgL^{-1})	Mo (μgL^{-1})	U (μgL^{-1})	V (μgL^{-1})
1	21	2.6	9.9	9.0	6.5	0.40	0.30	1.9	2.8	0.03	0.53
2	148	3.0	10	11	12	0.43	0.10	0.80	3.7	0.80	0.84
3	3123	5.3	8.6	7.5	1.4	0.20	0.02	0.90	1.3	0.05	0.53
4	245	7.6	21	12	1.8	0.39	0.02	1.9	2.9	0.10	bdl
5	70	6.3	18	14	8.6	0.52	1.4	2.1	3.5	0.04	0.61
6	245	8.2	17	15	8.4	1.2	0.02	1.2	7.0	0.05	0.83
7	15	3.8	7.7	9.3	9.3	0.42	0.02	1.8	3.5	3.2	1.5
8	94	6.5	8.5	15	9.1	0.69	0.02	2.9	7.1	0.40	0.47
9	107	3.8	9.2	16	11	0.95	0.02	1.1	5.9	0.20	0.61
10	28	3.1	6.9	5.6	1.5	0.23	0.07	1.0	1.1	0.09	0.47
11	21	6.1	7.7	11	3.0	0.75	0.02	6.1	3.0	0.50	1.6
12	12	3.7	4.8	4.8	1.8	0.43	0.01	2.3	1.5	1.2	0.43
13	24	3.5	8.4	6.7	1.3	0.33	0.01	0.90	3.4	0.50	0.59
14	172	1.7	6.6	4.9	4.0	0.33	0.87	1.9	1.1	1.9	0.64
15	115	5.5	8.3	16	13	0.50	0.19	1.2	8.2	0.40	0.56
16	1842	6.8	18	13	12	0.76	0.26	1.0	3.3	0.07	0.67
17	94	5.0	11	6.5	4.8	0.34	6.0	1.1	0.91	0.06	0.52
18	121	7.2	5.8	12	4.9	0.60	0.07	1.7	7.7	3.4	0.65
19	164	3.8	11	6.8	bdl	0.75	0.02	1.5	2.5	0.80	bdl
20	99	4.4	3.1	10	2.8	1.1	0.07	1.4	4.3	0.07	0.93
21	54	29	13	8.0	4.9	0.34	0.34	1.8	4.3	0.06	0.48
22	8168	15	22	22	11	0.66	0.04	1.7	6.1	2.4	0.57
23	94	4.8	8.0	10	3.2	0.51	0.02	1.6	5.7	0.02	0.59
24	281	7.2	8.6	7.4	1.2	0.23	0.02	2.1	3.6	0.30	0.53
25	36	2.4	9.7	4.4	3.2	0.39	4.1	0.70	1.9	0.60	bdl
26	44	57	11	4.0	2.6	0.33	3.2	0.80	2.0	0.40	bdl
27	1330	9.6	13	43	149	0.78	0.12	1.6	5.7	0.08	0.40
28	1153	2.8	7.5	5.1	4.3	0.18	0.07	0.90	1.4	0.05	0.29
29	2072	4.3	9.3	5.9	4.6	0.28	0.03	2.6	2.7	0.01	0.51
30	1132	2.9	5.4	2.5	0.72	0.16	0.06	1.9	1.2	bdl	0.46

Note: na- not available, bdl- below detection limit.

(b) Chakdaha groundwater

Well No.	**Latitude**	**Longitude**	**Land use**	**Geomorphology**	**Depth (m)**	**pH**	**EC (µScm^{-1})**	**DOC (mgL^{-1})**	**Eh (mV)**
1	23.0864	88.5353	Pond	Palaeo-channel	7.0	7.7	770	5.3	-110
2	23.0764	88.5314	Habitation	Palaeo-channel	19	7.6	530	4.2	-135
3	23.0811	88.5253	Pond	Palaeo-channel	19	7.9	615	3.3	-105
4	23.0831	88.5394	Sanitation	Palaeo-channel	20	8.0	763	3.8	-154
5	23.0772	88.5356	Habitation	Palaeo-channel	20	7.5	772	3.8	-134
6	23.0783	88.5322	Pond	Palaeo-channel	20	7.9	749	3.3	-121
7	23.0817	88.5450	Habitation	Palaeo-channel	21	8.0	529	5.5	-132
8	23.0775	88.5222	Pond	Palaeo-channel	21	7.3	1062	5.8	-95
9	23.0878	88.5308	Habitation	Palaeo-channel	21	7.9	671	2.0	-130
10	23.0803	88.5469	Pond	Palaeo-channel	21	7.9	585	3.2	-139
11	23.0850	88.5208	Pond	Palaeo-channel	22	8.1	892	3.3	-143
12	23.0814	88.5325	Pond	Palaeo-channel	23	7.4	674	3.5	-110
13	23.0883	88.5317	Sanitation	Palaeo-channel	23	7.9	536	2.3	-107
14	23.0842	88.5439	Habitation	Palaeo-channel	23	7.7	754	2.3	-145
15	23.0875	88.5408	Habitation	Palaeo-channel	26	7.8	788	5.2	-102
16	23.0781	88.5486	Sanitation	Palaeo-channel	26	7.7	841	3.5	-109
17	23.0789	88.5369	Habitation	Palaeo-channel	26	7.6	880	7.0	-125
18	23.0750	88.5381	Habitation	Palaeo-channel	26	7.0	1074	4.7	-121
19	23.0786	88.5364	Pond	Palaeo-channel	27	7.2	957	5.8	-129
20	23.0786	88.5403	Pond	Palaeo-channel	30	7.2	991	5.2	-137
21	23.0828	88.5408	Sanitation	Palaeo-channel	30	7.3	872	5.6	-131
22	23.0808	88.5539	Sanitation	Palaeo-channel	32	7.8	704	5.6	-154
23	23.0839	88.5467	Sanitation	Palaeo-channel	34	7.8	561	3.2	-132
24	23.0806	88.5514	Sanitation	Palaeo-channel	36	7.9	689	3.4	-109
25	23.0822	88.5508	Habitation	Palaeo-interfluve	75	7.4	642	1.9	-96
26	23.0764	88.5342	Habitation	Palaeo-interfluve	78	7.5	601	1.1	-92
27	23.0842	88.5508	Pond	Palaeo-interfluve	86	7.2	676	1.8	-91
28	23.0808	88.5431	Habitation	Palaeo-interfluve	94	7.7	616	1.6	-86
29	23.0850	88.5283	na	Deeper aquifer	133	7.4	564	1.2	-89
30	23.0778	88.5272	na	Deeper aquifer	133	7.3	550	1.0	-90

Note: na- not available, bdl- below detection limit.

(b) continued..

Well No.	HCO_3^- (mgL^{-1})	PO_4^{3-} (mgL^{-1})	NH_4^+ (mgL^{-1})	NO_3^- (mgL^{-1})	SO_4^{2-} (mgL^{-1})	Cl^- (mgL^{-1})	As (μgL^{-1})	As(III) (μgL^{-1})	As(V) (μgL^{-1})
1	471	5.0	0.59	2.5	5.8	25	402	326	76
2	468	3.6	1.2	0.30	4.2	28	185	132	53
3	418	2.9	0.80	0.10	1.6	37	93	52	41
4	476	5.1	1.6	2.9	5.6	51	421	350	71
5	558	4.8	1.8	bdl	0.30	26	254	191	63
6	573	5.0	2.4	3.2	1.8	35	375	300	75
7	423	2.9	0.29	bdl	1.5	32	182	132	50
8	368	2.2	0.86	9.6	8.9	69	113	86	27
9	348	1.9	bdl	8.9	8.9	33	57	32	25
10	496	3.9	0.29	2.7	1.7	15	298	219	79
11	363	2.1	1.6	bdl	16	39	93	66	27
12	418	2.9	3.9	1.6	8.7	15	122	106	16
13	392	2.5	3.7	1.5	2.9	56	56	34	22
14	531	4.4	2.4	2.4	1.6	61	149	124	25
15	707	6.9	0.57	2.7	1.7	25	425	348	77
16	600	5.4	0.21	bdl	0.20	15	359	282	77
17	684	6.6	0.39	2.9	13	19	469	418	51
18	800	6.5	0.41	bdl	0.20	13	456	397	59
19	842	6.7	0.48	bdl	0.50	15	596	501	95
20	745	6.0	0.78	0.30	1.2	12	541	466	75
21	810	6.2	0.56	0.70	2.4	14	602	512	90
22	796	7.6	1.1	2.7	5.9	51	550	477	73
23	424	2.9	2.4	3.0	2.2	27	138	99	39
24	439	3.2	0.21	1.8	1.1	23	191	155	36
25	282	0.67	0.97	bdl	0.70	6.0	51	27	14
26	257	0.21	3.6	0.40	0.20	6.0	15	13	2.0
27	268	0.47	1.1	bdl	0.10	6.5	40	29	11
28	250	0.22	2.3	bdl	0.30	6.3	34	20	14
29	248	0.26	5.3	0.30	0.20	5.7	19	16	3.0
30	252	0.20	1.5	bdl	bdl	5.8	12	8.0	4.0

Note: na- not available, bdl- below detection limit.

(b) continued..

Well No.	Fe (mgL^{-1})	Fe(II) (mgL^{-1})	Fe(III) (mgL^{-1})	Na^+ (mgL^{-1})	K^+ (mgL^{-1})	Mg^{2+} (mgL^{-1})	Ca^{2+} (mgL^{-1})	Al (μgL^{-1})	Ba (μgL^{-1})	Mn (μgL^{-1})
1	5.9	4.9	1.0	23	4.4	24	90	116	330	105
2	5.0	3.2	1.8	21	4.8	25	88	120	282	178
3	2.4	1.9	0.53	19	1.8	21	98	65	187	111
4	7.3	6.0	1.3	22	4.6	27	103	128	250	169
5	5.2	4.5	0.71	21	5.3	32	95	110	242	147
6	5.0	4.4	0.64	14	6.3	42	101	90	274	156
7	4.3	3.4	0.88	21	3.5	21	98	81	239	162
8	3.0	2.4	0.68	37	2.5	38	88	128	288	296
9	1.2	0.8	0.37	19	2.7	23	94	56	207	202
10	2.4	2.1	0.29	27	3.3	28	89	98	221	349
11	3.2	2.7	0.44	18	2.7	16	88	56	253	374
12	4.3	3.6	0.75	22	4.7	20	94	228	237	283
13	0.57	0.51	0.06	6.9	2.1	37	108	90	164	98
14	3.8	2.5	1.3	19	7.0	42	99	108	209	77
15	4.4	3.5	0.88	32	3.5	39	127	154	383	228
16	3.2	2.5	0.68	29	3.9	34	100	119	125	155
17	3.8	2.8	0.99	22	4.2	39	120	195	439	130
18	3.6	2.6	1.0	56	4.1	37	125	178	514	71
19	4.0	2.9	1.1	52	4.8	45	147	152	415	129
20	7.0	5.7	1.2	47	5.4	41	138	145	357	157
21	6.4	4.9	1.5	39	4.3	49	147	124	394	155
22	7.4	5.2	2.3	35	4.1	56	140	198	464	164
23	2.9	2.1	0.78	12	3.5	29	94	84	169	303
24	1.7	1.1	0.53	13	2.5	21	97	75	71	331
25	0.45	0.38	0.07	21	3.6	8.0	73	36	191	123
26	0.10	0.07	0.03	12	3.1	25	58	24	99	110
27	0.35	0.26	0.10	12	2.9	12	55	32	92	119
28	0.27	0.15	0.12	18	2.3	13	50	30	104	108
29	0.10	0.08	0.02	15	2.5	22	63	32	101	103
30	0.09	0.07	0.02	13	2.4	23	55	25	95	100

Note: na- not available, bdl- below detection limit.

(b) continued..

Well No.	Sr (μgL^{-1})	Zn (μgL^{-1})	Cu (μgL^{-1})	Pb (μgL^{-1})	Ni (μgL^{-1})	Cr (μgL^{-1})	Mo (μgL^{-1})	Co (μgL^{-1})	U (μgL^{-1})	V (μgL^{-1})
1	400	38	4.0	2.1	2.5	1.2	0.70	0.40	0.01	0.26
2	344	248	11	14	5.3	5.9	1.7	0.50	0.02	0.51
3	290	137	5.2	5.7	25	3.9	1.5	0.40	0.02	0.53
4	383	61	4.8	3.2	9.0	49	3.7	0.30	0.02	0.29
5	291	24	6.5	1.1	2.6	1.8	1.0	0.20	0.01	0.28
6	330	32	3.7	2.1	2.9	140	1.1	0.30	0.01	0.35
7	375	295	7.9	18	7.4	5.6	2.4	0.50	0.02	0.47
8	610	305	9.1	14	9.0	5.4	1.1	1.0	0.09	1.3
9	258	42	4.5	3.1	5.1	2.6	0.80	0.20	0.01	0.18
10	238	52	4.9	1.9	2.9	1.8	1.2	0.20	0.01	0.11
11	256	213	5.6	12	7.2	4.0	3.1	0.40	0.01	0.35
12	269	220	7.9	64	9.8	26	2.3	0.50	0.03	0.76
13	243	166	9.3	14	63	4.9	2.8	0.30	0.02	0.59
14	376	130	3.5	2.9	2.9	1.3	0.50	0.30	0.01	0.19
15	472	88	8.3	12	7.3	24	1.0	0.60	0.07	0.66
16	338	22	1.6	bdl	7.4	2.2	0.30	0.20	bdl	0.05
17	463	82	4.3	5.6	3.1	5.2	0.90	0.50	0.02	0.41
18	487	68	1.9	7.7	2.3	1.8	0.80	0.30	0.01	0.31
19	397	72	2.5	6.8	6.1	4.2	1.5	0.50	0.05	0.27
20	351	84	2.1	4.6	6.7	4.8	0.70	0.80	0.08	0.27
21	428	77	2.7	5.7	7.9	5.5	1.2	0.40	0.06	0.31
22	552	53	3.9	2.2	7.9	5.0	0.80	0.50	0.01	0.34
23	237	211	6.4	9.0	5.0	3.0	1.4	0.40	0.01	0.21
24	361	87	3.5	3.2	2.7	1.2	0.90	1.4	1.5	1.1
25	592	1396	7.2	14	7.4	5.2	2.5	0.40	0.03	0.49
26	344	745	5.1	3.8	3.1	1.6	1.2	0.20	0.01	0.20
27	397	549	4.5	4.4	3.2	1.5	1.0	0.10	0.02	0.60
28	304	1565	4.6	4.0	3.0	2.3	1.0	0.20	0.01	0.15
29	319	829	4.6	3.9	3.0	1.7	1.3	0.10	0.02	0.13
30	320	815	5.0	3.0	2.8	1.6	1.2	bdl	0.01	0.14

Note: na- not available, bdl- below detection limit.

(c) Baruipur groundwater

Well No.	Latitude	Longitude	Land use	Geomorphology	Depth (m)	pH	EC (μScm^{-1})	DOC (mgL^{-1})	Eh (mV)
1	22.3490	88.4600	Habitation	Palaeo-channel	14	8.0	534	2.0	-129
2	22.3257	88.4605	Habitation	Palaeo-channel	14	7.4	685	2.9	-120
3	22.3357	88.4502	Habitation	Palaeo-channel	15	7.3	681	4.6	-128
4	22.3188	88.4495	Habitation	Palaeo-channel	15	7.3	1009	2.2	-132
5	22.3275	88.4575	Pond	Palaeo-channel	15	7.6	810	2.3	-137
6	22.3092	88.4623	Pond	Palaeo-channel	18	7.4	1085	6.6	-152
7	22.3613	88.4770	Agriculture	Palaeo-channel	18	7.8	1511	11	-135
8	22.3075	88.4607	Sanitation	Palaeo-channel	24	7.3	1111	5.2	-145
9	22.3503	88.4642	Pond	Palaeo-channel	24	7.6	1032	7.0	-138
10	22.3347	88.4487	Pond	Palaeo-channel	27	7.6	780	1.1	-147
11	22.3195	88.4685	Pond	Palaeo-channel	30	7.3	655	3.9	-129
12	22.3615	88.4783	Agriculture	Palaeo-channel	30	7.8	1370	4.1	-128
13	22.3292	88.4820	Agriculture	Palaeo-channel	30	7.5	980	3.2	-132
14	22.3615	88.4670	Pond	Palaeo-interfluve	31	7.9	619	0.76	-135
15	22.3048	88.4642	Habitation	Palaeo-channel	32	7.4	859	4.6	-125
16	22.3572	88.4672	Pond	Palaeo-channel	34	7.4	842	4.3	-125
17	22.3035	88.5315	Agriculture	Palaeo-interfluve	37	7.8	801	1.5	-132
18	22.3102	88.4607	Pond	Palaeo-channel	37	7.3	1014	3.4	-154
19	22.3337	88.4733	Pond	Palaeo-channel	37	7.3	1002	4.7	-134
20	22.3308	88.4768	Sanitation	Palaeo-channel	37	7.5	1810	3.9	-156
21	22.3107	88.4607	Habitation	Palaeo-channel	40	7.4	1273	1.1	-124
22	22.3290	88.4797	Habitation	Palaeo-channel	43	7.5	1168	13	-139
23	22.3288	88.4788	Pond	Palaeo-channel	43	7.5	1192	5.9	-143
24	22.3188	88.4657	Pond	Palaeo-channel	55	7.4	704	2.3	-146
25	22.3400	88.4672	Agriculture	Palaeo-interfluve	74	7.6	2180	0.50	-134
26	22.3402	88.5465	na	Deeper aquifer	107	7.7	2400	0.38	-99
27	22.3090	88.4598	na	Deeper aquifer	244	7.5	1256	1.7	-104
28	22.3330	88.5167	na	Deeper aquifer	244	8.1	1363	0.61	-110
29	22.3345	88.5315	na	Deeper aquifer	259	7.8	3440	0.92	-109
30	22.3388	88.5053	na	Deeper aquifer	305	8.0	1960	0.40	-102

Note: na- not available, bdl- below detection limit.

(c) continued..

Well No.	HCO_3^- (mgL^{-1})	PO_4^{3-} (mgL^{-1})	NH_4^+ (mgL^{-1})	NO_3^- (mgL^{-1})	SO_4^{2-} (mgL^{-1})	Cl^- (mgL^{-1})	As (μgL^{-1})	As(III) (μgL^{-1})	As(V) (μgL^{-1})
1	307	0.30	0.10	0.43	4.7	16	110	80	30
2	408	1.5	1.3	5.6	0.01	18	178	135	43
3	413	3.0	bdl	bdl	5.5	26	12	na	na
4	548	3.0	1.9	8.4	0.09	61	242	199	43
5	444	0.41	bdl	bdl	14	32	42	32	10
6	597	5.6	7.4	33	0.12	60	969	832	137
7	814	26	4.8	21	0.13	87	176	122	54
8	619	6.2	7.5	33	0.11	37	961	854	107
9	641	7.7	10	45	0.06	17	683	537	146
10	410	0.75	0.49	2.2	8.7	41	96	77	19
11	401	2.2	2.2	9.5	0.49	15	226	161	65
12	665	10	3.2	14	2.0	111	30	21	9
13	617	2.9	3.7	16	bdl	23	434	347	87
14	399	0.10	0.05	0.24	0.61	10	1.0	na	na
15	496	1.1	3.8	17	0.96	30	693	627	66
16	503	0.54	3.1	14	1.5	29	133	91	42
17	429	0.19	0.25	1.1	3.2	56	17	na	na
18	578	2.6	3.9	17	0.31	17	878	689	189
19	518	6.8	8.6	38	0.08	58	470	306	164
20	655	1.8	5.9	26	0.41	122	1059	858	201
21	653	1.2	1.0	4.5	0.69	104	78	62	16
22	740	3.0	4.2	18	0.14	67	416	268	148
23	547	4.4	2.8	12	bdl	52	498	357	141
24	291	4.3	2.3	9.9	0.72	12	366	253	113
25	179	0.14	bdl	bdl	27	529	2.1	na	na
26	270	0.15	bdl	bdl	26	538	1.2	na	na
27	503	bdl	0.20	0.87	0.03	120	3.0	na	na
28	431	0.13	0.66	2.9	59	183	1.2	na	na
29	458	0.14	1.3	5.7	106	878	1.3	na	na
30	421	0.13	1.1	5.0	68	410	1.1	na	na

Note: na- not available, bdl- below detection limit.

(c) continued..

Well No.	Fe (mgL^{-1})	Fe(II) (mgL^{-1})	Fe(III) (mgL^{-1})	Na^{+} (mgL^{-1})	K^{+} (mgL^{-1})	Mg^{2+} (mgL^{-1})	Ca^{2+} (mgL^{-1})	Al (µgL^{-1})	Ba (µgL^{-1})	Mn (µgL^{-1})
1	0.39	0.28	0.11	15	2.8	14	80	54	81	544
2	3.5	2.7	0.76	13	3.8	17	94	46	140	828
3	4.0	2.9	1.1	10	3.2	21	100	53	126	208
4	8.3	7.1	1.2	39	5.3	27	120	49	387	1394
5	1.0	na	na	14	11	29	145	125	198	911
6	6.2	5.2	1.1	47	5.9	28	120	100	248	680
7	1.6	1.0	0.53	316	5.6	9.0	23	51	42	50
8	5.9	4.9	1.0	44	5.9	30	128	57	254	408
9	7.8	6.3	1.6	55	6.3	28	111	66	268	393
10	3.2	2.5	0.74	26	2.9	19	100	36	264	888
11	10	7.4	2.9	16	4.7	18	84	95	210	522
12	3.9	2.8	1.1	195	9.2	40	54	50	267	182
13	3.3	2.5	0.78	41	8.2	38	101	43	106	95
14	2.0	na	na	12	1.3	29	79	47	31	384
15	5.7	5.0	0.76	34	7.4	26	92	63	400	112
16	3.8	2.9	0.91	26	5.4	29	111	128	80	368
17	0.87	na	na	29	3.2	26	100	57	85	402
18	4.7	4.0	0.71	38	5.9	32	126	73	198	1082
19	11	8.2	2.4	39	7.4	37	108	35	235	256
20	7.4	6.2	1.3	118	7.8	37	99	38	529	224
21	1.7	1.4	0.30	189	5.8	22	68	71	123	211
22	2.7	2.1	0.54	63	8.9	47	111	143	164	242
23	4.6	3.9	0.67	98	7.4	38	96	52	48	606
24	5.9	4.6	1.2	18	4.2	21	101	53	245	882
25	0.36	na	na	119	5.3	44	207	40	239	1259
26	0.50	na	na	128	5.6	47	214	36	301	1344
27	1.1	na	na	115	5.6	32	99	106	226	147
28	0.31	na	na	133	6.1	41	91	35	97	46
29	2.91	na	na	467	7.6	69	140	60	253	84
30	0.52	na	na	200	7.4	54	111	54	157	62

Note: na- not available, bdl- below detection limit.

(c) continued..

Well No.	Sr (μgL^{-1})	Zn (μgL^{-1})	Cu (μgL^{-1})	Pb (μgL^{-1})	Ni (μgL^{-1})	Cr (μgL^{-1})	Mo (μgL^{-1})	Co (μgL^{-1})	U (μgL^{-1})	V (μgL^{-1})
1	132	21	2.6	9.9	9.0	6.5	2.8	0.40	0.30	0.33
2	244	148	3.0	10	11	12	3.7	0.43	0.10	0.12
3	167	3123	5.3	8.6	7.5	1.4	1.3	0.20	0.02	1.1
4	416	245	7.6	21	12	1.8	2.9	0.39	0.02	0.41
5	269	70	6.3	18	14	8.6	3.5	0.52	1.4	0.33
6	495	245	8.2	17	15	8.4	7.0	1.2	0.02	0.43
7	78	15	3.8	7.7	9.3	9.3	3.5	0.42	0.02	2.5
8	502	94	6.5	8.5	15	9.1	7.1	0.69	0.02	0.27
9	479	107	3.8	9.2	16	11	5.9	0.95	0.02	0.41
10	165	28	3.1	6.9	5.6	1.5	1.1	0.23	0.07	0.27
11	294	21	6.1	7.7	11	3.0	3.0	0.75	0.02	0.23
12	330	12	3.7	4.8	4.8	1.8	1.5	0.43	0.01	0.44
13	442	24	3.5	8.4	6.7	1.3	3.4	0.33	0.01	0.39
14	358	172	1.7	6.6	4.9	4.0	1.1	0.33	0.87	1.4
15	405	115	5.5	8.3	16	13	8.2	0.50	0.19	0.36
16	415	1842	6.8	18	13	12	3.3	0.76	0.26	0.47
17	420	94	5.0	11	6.5	4.8	0.91	0.34	6.0	0.97
18	484	121	7.2	5.8	12	4.9	7.7	0.60	0.07	0.32
19	441	164	3.8	11	6.8	bdl	2.5	0.75	0.02	0.45
20	526	99	4.4	3.1	10	2.8	4.3	1.1	0.07	0.73
21	327	54	29	13	8.0	4.9	4.3	0.34	0.34	0.28
22	508	8168	15	22	22	11	6.1	0.66	0.04	2.9
23	457	94	4.8	8.0	10	3.2	5.7	0.51	0.02	0.39
24	343	281	7.2	8.6	7.4	1.2	3.6	0.23	0.02	0.33
25	901	36	2.4	9.7	4.4	3.2	1.9	0.39	4.1	bdl
26	933	44	57	11	4.0	2.6	2.0	0.33	3.2	0.16
27	509	1330	9.6	13	43	149	5.7	0.78	0.12	2.1
28	643	1153	2.8	7.5	5.1	4.3	1.4	0.18	0.07	0.09
29	1015	2072	4.3	9.3	5.9	4.6	2.7	0.28	0.03	bdl
30	919	1132	2.9	5.4	2.5	0.72	1.2	0.16	0.06	bdl

Note: na- not available, bdl- below detection limit.

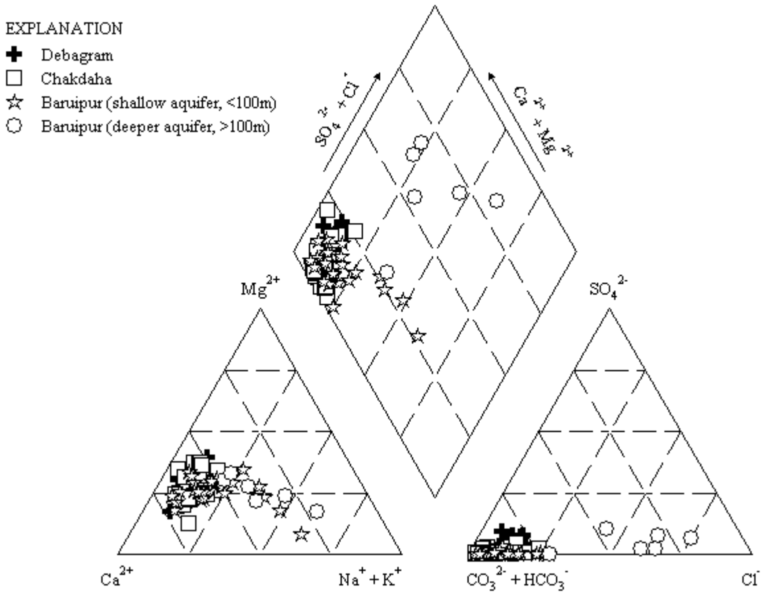

Figure 3.1.1. Piper diagram illustrating the main hydrochemical facies of Debagram, Chakdaha and Baruipur groundwaters.

The Piper plot (Fig. 3.1.1) demonstrates Ca^{2+}-HCO_3^- type water in the Bhagirathi-Hooghly alluvial plain (i.e. in Debagram and Chakdaha) which is indicative of fresh water recharge consistent with the dissolution of carbonate rocks or minerals. In contrast, the groundwaters of the delta front are characterized by the diffused hydrochemical facies: i) shallow aquifers contain admixture of Ca^{2+}-HCO_3^- type (fresh groundwater) and Ca^{2+}-Na^+-HCO_3^- type (cation exchange) water, whereas, ii) deeper aquifers show nature of mild saline water intrusion with cation exchange as evidenced by Ca^{2+}-HCO_3^--Cl^- type water. In addition, few shallow wells in Baruipur are enriched with Cl^- and Na^+, possibly sourced from local anthropogenic inputs. The composition of major solutes in groundwater are mainly governed by the mineralogy of the aquifer sediment and the kinetics of chemical weathering and mineral dissolution reactions [24,25]. In BDP, the chemical evolution of groundwater results from interaction of various processes, and because of highly heterogeneous aquifer system, it is difficult to identify the source and contribution of any single chemical processes. Galy and France-Lanord [26] observed that weathering of silicate minerals play a dominant role in the evolution of BDP groundwater, while Dowling et al. [27] argued for carbonate weathering. The bivariate plot of Na-normalized Ca^{2+} vs HCO_3^- and Na-normalized Ca^{2+} vs Mg^{2+} showed that the groundwater is mainly influenced by silicate weathering and carbonate dissolution (Fig. 3.1.2).

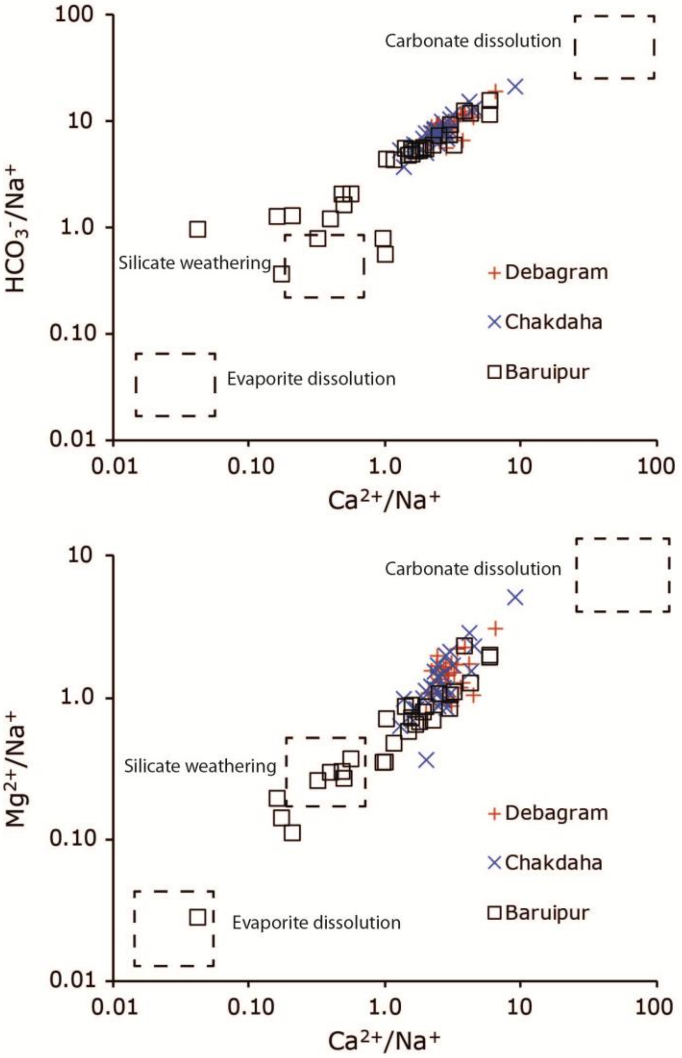

Figure 3.1.2. Bivariate plot of Na^+ normalized HCO_3^- and Mg^{2+} versus Na^+ normalized Ca^{2+} to understand the processes related to geochemical evolution of groundwater in the study areas.

However within the majority of the samples, a few shallow groundwater from Baruipur shows evidence of evaporite dissolution. On the other hand, the plot of Ca^{2+} + Mg^{2+} vs HCO_3^- shows that the groundwater falls close to y = 2x line suggesting dominance of carbonate dissolution (Fig. 3.1.3). However, an exception occurs for some shallow and deeper groundwater samples of Baruipur. This artefact has also been reflected in the Piper plot (Fig. 3.1.1).

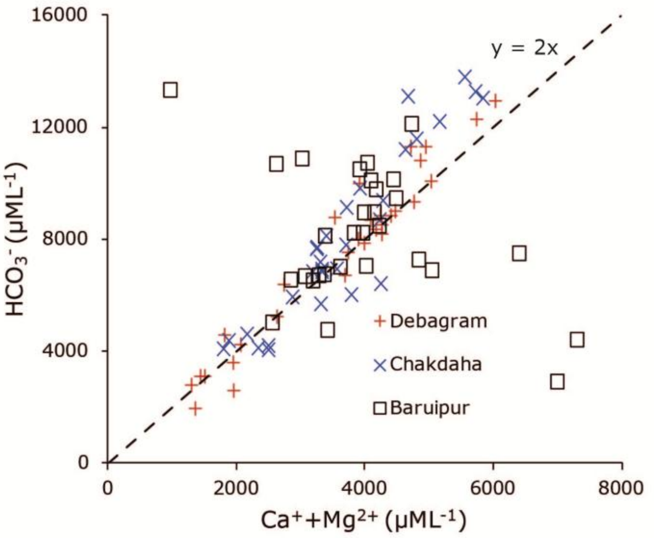

Figure 3.1.3. Bivariate plot of HCO_3^- versus Ca^{2+} + Mg^{2+} to compare the extents of carbonate dissolution in groundwater of the study areas.

3.1.3.2. Distribution of redox sensitive elements in groundwater

The As concentrations in the shallow aquifer of Bhagirathi-Hooghly alluvial plain and delta front are high (481 ± 317, 297 ± 182, and 351 ± 342 μgL^{-1} respectively) compared with deeper aquifers (25 ± 3.3, 29 ± 16, and 1.4 ± 0.76 μgL^{-1} respectively), those distributions also exhibit a strong depth dependency (Fig. 3.1.4a). The highly contaminated aquifer zone lies between 20 and 55 m. Similar depth distribution was also reported from other parts of the Bengal Delta Plain (BDP) [7,28,29]. The Fe concentrations in shallow aquifers of the Bhagirathi-Hooghly alluvial plain and delta front are also high (5.2 ± 2.4, 4.1 ± 1.8, and 4.4 ± 2.9 mgL^{-1}, respectively) compared with deeper aquifers (0.20 ± 0.05, 0.22 ± 0.15, and 1.1 ± 1.1 mgL^{-1}, respectively) with a trend similar to As (Fig. 3.1.4b). However, some of the low Fe containing groundwaters also show high As concentrations (Table 3.1.1), and overall predominance of As(III) over As(V) was observed irrespective of Fe content and aquifer depth. The co-existence of As(III) and As(V) in groundwater is generally due to slow kinetics of As(V) during reductive dissolution of Fe-oxyhydroxides [1,30] and seasonal fluctuation of subsurface redox conditions from oxic to anoxic and vice-versa consistent with the large-scale anthropogenic activities (e.g. groundwater extraction for domestic use and irrigation) [31,32]. Such behavior has been reflected in the As(III)/As(V) ratios which are highly variable within the shallow aquifers (< 100 m) while the ratio reaches a low stable value at depths (Table 3.1.1). Large amount of fresh organic material may be introduced to the shallow aquifer through recharging groundwater and making the aquifer highly reducing. The availability of fresh surface-derived organic material is mainly dependent on the extent of anthropogenic activities. Some samples in deeper aquifers of Chakdaha show high As(III)/As(V) ratios, possibly suggests contamination of deeper aquifers through recharging As-enriched groundwater from shallow aquifers. Such anthropogenic effects and their impact on the distribution of groundwater As has also reported earlier by other researchers [25,31–33].

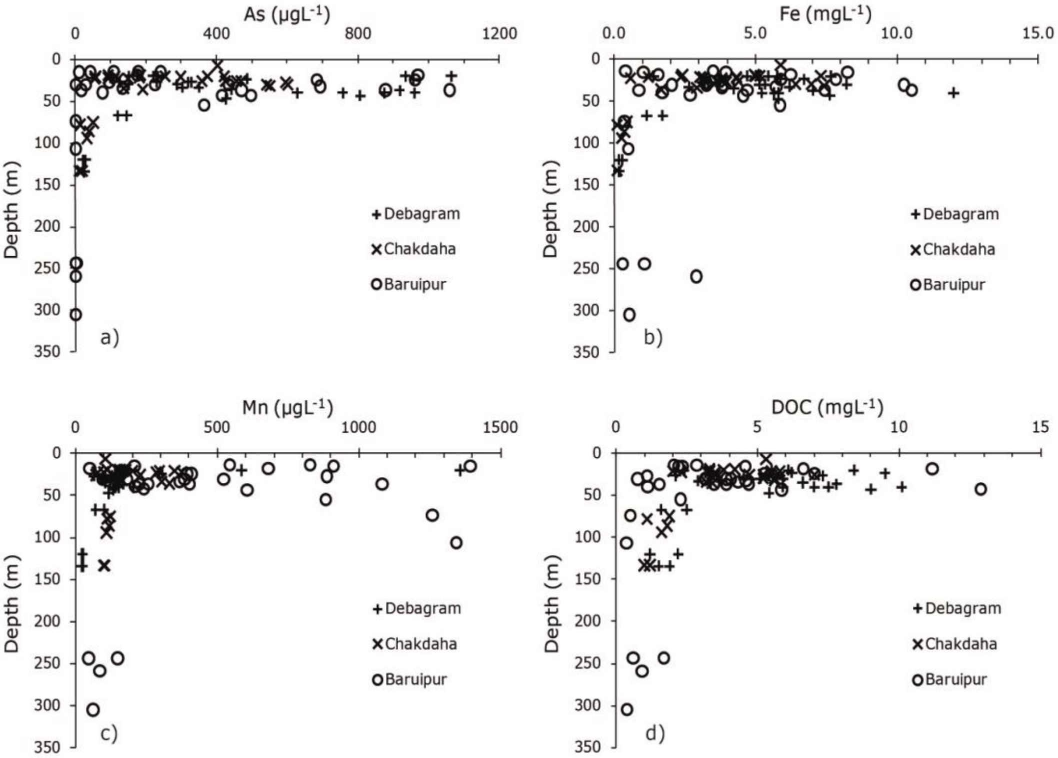

Figure 3.1.4. Depth profile of the concentrations of (a) As, (b) Fe, (c) Mn, and (d) DOC in three study areas (Debagram, Chakdaha and Baruipur)

The Eh values in shallow aquifers of Bhagirathi-Hooghly alluvial plain and delta front show stronger reducing nature (-147 ± 22, -125 ± 17, and -136 ± 9.7 mV, respectively) than deeper aquifers (-107 ± 3.9, -91 ± 3.3, and -105 ± 4.7 mV, respectively). The Mn concentrations in shallow aquifers of the Bhagirathi-Hooghly alluvial plain are low (205 ± 255 and 189 ± 88 μgL^{-1} in Debagram and Chakdaha respectively) compared with the delta front (384 ± 167 μgL^{-1}). While, deeper aquifers of the Bhagirathi-Hooghly alluvial plain are relatively Mn-free (24 ± 1.3 and 111 ± 9.0 μgL^{-1}, respectively) compared with the delta front groundwater (804 ± 216 µgL-1) (Table 3.1.1, Fig. 3.1.4c). The HCO_3^- concentration is always high in shallow aquifers, both in the Bhagirathi-Hooghly alluvial plain (503 ± 160 and 548 ± 161 mgL^{-1}, respectively) and the delta front (515 ± 149 mgL^{-1}) compared with deeper aquifers (168 ± 33, 260 ± 13, and 417 ± 88 mgL^{-1}, respectively) (Table 3.1.1). The DOC concentration is also relatively high in shallow aquifers of the Bhagirathi-Hooghly alluvial plain and the delta front (5.7

± 2.3, 4.2 ± 1.3, and 4.1 ± 3.0 mgL^{-1}, respectively) compared with deeper aquifers (1.7 ± 0.44, 1.3 ± 0.38, and 0.80 ± 0.55 mgL^{-1}, respectively) (Fig. 3.1.4d). The values of redox sensitive elements and Eh suggest less reducing nature of the deeper aquifers compared to the shallow aquifers. Under such conditions, Fe-oxyhydroxide reduction seems unlikely to follow and release As and HCO_3^- concentrations in the deeper aquifers. However, reduction of Mn-oxyhydroxides may be possible under such redox state in the deeper aquifers and release high Mn concentrations, especially in the delta front.

3.1.3.3. Thermodynamic calculations

The saturation indices (mean values) of mineral phases in groundwater of the Bhagirathi-Hooghly alluvial plain and the delta front are shown in Fig. 3.1.5. Groundwaters are mostly in equilibrium with carbonate minerals, such as aragonite [$CaCO_3$], calcite [$CaCO_3$], dolomite [$CaMg(CO_3)_2$], siderite [$FeCO_3$] and rhodochrosite [$MnCO_3$]. This suggests that the groundwater chemistry is merely controlled by the precipitation/dissolution of carbonate minerals. The SI values of dolomite in groundwater are highly variable in the Bhagirathi-Hooghly alluvial plain and the delta front (data not shown). The variability in the chemical equilibrium (i.e. over- and under- saturation) of carbonate minerals is important, because dolomitization of calcite and aragonite may occur by reaction with Mg-bearing connate water, especially in the delta front.

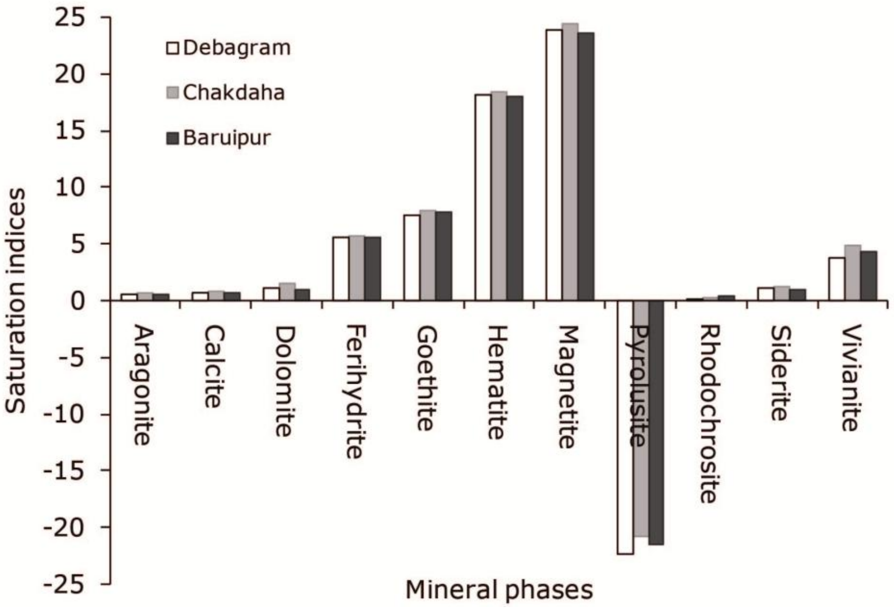

Figure 3.1.5. Plot of mean saturation indices of important mineral species in groundwater of Debagram, Chakdaha and Baruipur

Calcium in $CaCO_3$ may partially be substituted by Mn in the aquifer as evidenced from the precipitation of rhodochrosite, calcite and aragonite [34]. Furthermore, calcite, aragonite and rhodochrosite can act as a sink for Fe(II) and Mn(II) by adsorption onto and/or co-precipitation with $CaCO_3$ in anoxic groundwater [35]. The presence of calcite, aragonite and rhodochrosite mineral phases in the sediment of the Bhagirathi-Hooghly alluvial plain and the delta front was earlier reported by other workers [36,37].

The groundwater is undersaturated with respect to Mn-oxide minerals (e.g. pyrolusite) in three study areas. This suggests strong reducing conditions in groundwater and high concentrations of dissolved Mn from reduction of Mn-oxide minerals. However, some of the Mn may be removed from groundwater due to precipitation of rhodochrosite and/or incorporation by solid solution onto other carbonate minerals, such as siderite. The groundwater is supersaturated with respect to Fe-oxide/hydroxide minerals, such as hematite [Fe_2O_3], goethite

[FeOOH], ferrihydrite [$Fe(OH)_3$] and magnetite [Fe_3O_4], suggesting precipitation of Fe(III) phases in groundwater.

3.1.3.4. Factors controlling arsenic mobilization in groundwater

Arsenic is positively correlated with Fe ($R^2 = 0.63$, $p < 0.05$) in Chakdaha, whereas weak correlation is found in Debagram and Baruipur groundwater (Debagram: $R^2 = 0.36$, $p < 0.05$ and Baruipur: $R^2 = 0.38$, $p < 0.05$) (Fig. 3.1.6a, Table 3.1.2). The lack of correlation between As and Fe, especially in Debagram and Baruipur groundwater suggests that the desorption of As from Fe- oxyhydroxides may not be the sole process accounting for the mobilization of As in groundwater. However, regionally, several wells were reported to contain high As and Fe concentrations [11,20,38].

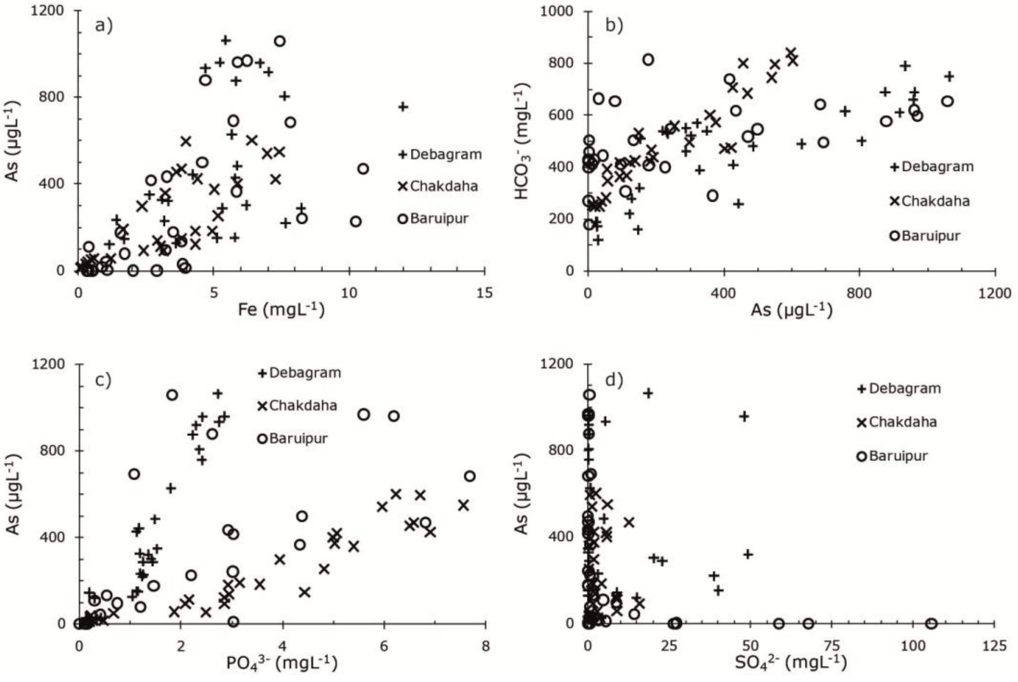

Figure 3.1.6. Correlation between (a) As and Fe, (b) HCO_3^- and As, (c) As and PO_4^{3-}, and (d) As and SO_4^{2-} in the study areas (Debagram, Chakdaha and Baruipur).

Strong positive correlation is observed between HCO_3^- and As in the Bhagirathi-Hooghly alluvial plain and the delta front (Fig. 3.1.6b, Table 3.1.2). The positive correlation is also entangled with high intercept values of 268, 274 and 440 mgL^{-1} for Debagram, Chakdaha and Baruipur, respectively. High HCO_3^- concentrations may generate due to: i) oxidation of organic matter associated with reductive dissolution of Fe-oxyhydroxides and As release to groundwater [1,10], and/or ii) partial dissolution of metal carbonates [39–41]. Therefore, the samples with HCO_3^- concentrations below the intercept are possibly resulted from the dissolution of carbonate minerals, whereas the sample with HCO_3^- concentrations above the intercept are cumulatively contributed by the degradation of organic matter and carbonate mineral dissolution. Moreover, Saalfield and Bostick [41] opined that HCO_3^- produced during microbial processes is not sufficient to release additional As rather CO_2 produced during microbial decomposition which when buffered by carbonate dissolution yields high As in the aquifer. In Chakdaha, HCO_3^- concentrations below the intercept yielded low As (<50 μgL^{-1}) in groundwater (Table 3.1.1). However, in Baruipur and Debagram, a few tube wells have shown As concentrations above 50 μgL^{-1}, suggesting increase in As solubility with carbonate mineral dissolution [39–41].

Table 3.1.2. Comparison of major chemical characteristics and arsenic mobilization processes in groundwaters of Bhagirathi-Hooghly alluvial plain (Debagram and Chakdaha), and Delta front (Baruipur).

Chemical compositions	***Bhagirathi-Hooghly alluvial plain***		***Delta front***
	Debagram	***Chakdaha***	***Baruipur***
Electrical Conductivity	650 ± 174 µscm^{-1}	743 ± 157 µscm^{-1}	1028 ± 383 µscm^{-1}
Na^+, Cl^-, and SO_4^{2-}	21 ± 7.6, 36 ± 24, and 11 ± 16 mgL^{-1}	25 ± 12, 27 ± 18, and 3.5 ± 4.1 mgL^{-1}	65 ± 73, 65 ± 102, and 2.9 ± 6.1 mgL^{-1}
Groundwater type	Ca^{2+}-HCO_3^- type	Ca^{2+}-HCO_3^- type	Shallow aquifers- mostly Ca^{2+}-HCO_3^- type, deeper aquifers- seawater salinization (enrichment of Na^+ and Cl^-)
As, Fe, and Mn	481 ± 317 µgL^{-1}, 5.2 ± 2.4 mgL^{-1}, and 205 ± 255 µgL^{-1}	260 ± 192 µgL^{-1}, 3.5 ± 2.2 mgL^{-1}, and 178 ± 85 µgL^{-1}	351 ± 342 µgL^{-1}, 4.4 ± 2.9 mgL^{-1}, and 525 ± 375 µgL^{-1}
DOC, NH_4^+, and PO_4^{3-}	5.7 ± 2.3, 3.6 ± 3.8, 1.6 ± 0.71 mgL^{-1}	3.8 ± 1.5, 1.3 ± 1.1, 3.9 ± 2.2 mgL^{-1}	4.1 ± 3.0, 3.1 ± 2.9, 3.8 ± 5.4 mgL^{-1}
As vs Fe	Weak correlation ($y = 72x+97$; $R^2 = 0.36$)	Positive correlation ($y = 69x+16$; $R^2 = 0.63$)	Weak correlation ($y = 71x+23$; $R^2 = 0.38$)
As vs HCO_3^-	Positive correlation with moderate intercept values ($y = 0.45x+268$; $R^2 = 0.64$)	Strong positive correlation with moderate intercept values ($y = 0.89x+274$; $R^2 = 0.88$)	Weak correlation with high intercept values ($y = 0.20x+440$; $R^2 = 0.22$)
As vs PO_4^{3-}	Strong positive correlation ($y = 389x-129$; $R^2 = 0.88$)	Strong positive correlation ($y = 80x-47$; $R^2 = 0.88$)	No correlation ($y = 13x+251$; $R^2 = 0.04$)
Arsenic mobilization processes	Fe-oxyhydroxide reduction and carbonate dissolution	Fe-oxyhydroxide reduction	Fe-oxyhydroxide reduction and carbonate dissolution

The plot of As vs PO_4^{3-} depicted a strong positive correlation in three study areas (Fig. 3.1.6c, Table 3.1.2). The concentration of PO_4^{3-} is generally 1-fold higher in the shallow aquifer of Bhagirathi-Hooghly alluvial plain and the delta front (1.6 ± 0.71, 4.5 ± 1.8 and 3.8 ± 5.4 mgL^{-1} respectively) than the deeper aquifer (0.27 ± 0.14, 0.34 ± 0.19 and 0.11 ± 0.06 mgL^{-1} respectively). The observed high PO_4^{3-} concentrations in shallow aquifers of Chakdaha and Baruipur might have reductively dissolved from the accumulated P in soils and sediments. High levels of P in soils/sediments may accumulate due to prolonged application of fertilizers for agricultural productivity, untreated sewage or domestic wastes associated with large-scale human settlements and occupations [42,43]. In our study areas, agricultural practices and application of fertilizers are pronounced both in terms of rate and frequency and can substantially accumulate P in the soil [17,44]. The released PO_4^{3-} may compete with AsO_4^{3-} for the sorption site and increase the solubility of As in the aquifer. The correlation between As vs SO_4^{2-} (Fig. 3.1.6d) is absent in the Bhagirathi-Hooghly alluvial plain and the delta front. Low SO_4^{2-} concentrations in groundwater suggest anoxic condition of the aquifer and could be associated with the biotic and/or abiotic oxidation of organic matters [45]. We observed As concentrations in groundwater increases with decrease in SO_4^{2-} concentrations. The low SO_4^{2-} concentration in groundwater is indicative of bacterial SO_4^{2-} reduction which may potentially limit As in groundwater through the formation of biogenic sulfides (e.g. pyrite), a potential sink for As in groundwater [46].

3.1.3.5. Geomorphology and land use control of arsenic mobilization

The Bhagirathi-Hooghly alluvial plain was characterized by several geomorphic features, such as abandoned meanders, abandoned channels and oxbow lakes [7]. Such geomorphic features were formed mainly due to varied hydrodynamic condition of the river, e.g. sediment load, stream movement and stream current. The formation of a new river channel leaves the cut-off channel abandoned, where fine grained colloidal sized particles and organic matter may deposits due to swampy condition together with the development of large vegetative cover [47]. The above facet makes these zones highly anaerobic and facilitates Fe-reduction to release As. The prevailing geochemical conditions of the Bhagirathi-

Hooghly alluvial plain were linked to the reductive dissolution of Fe-oxyhydroxides concurrent with the oxidative breakdown of organic matter [1,9,28,37]. Nevertheless, anaerobic metal-reducing bacteria were proved to be playing an important role in releasing As to groundwater [48]. However, the operating scale of geochemical processes was dependent on the nature, composition, concentration and distribution (i.e. spatio-temporal variability) of organic matter in the alluvium. The resulting geochemical processes may further be complicated by the presence of land-surface (i.e. anthropogenic) source of dissolved organic carbon in the aquifer to enhance As release process [17,23,31–33]. Therefore, combination and contribution of organic carbon sources are important and should play a pertinent role in the enrichment of As in the BDP.

The groundwater sampling point in Chakdaha was mostly located within and/or proximately to meander belts of Bhagirathi-Hooghly river. Numerous palaeo-rivers have cut deep and wide channels and later filled with sediments during Holocene period concurrent with the changes in eustatic sea level [49–51]. It is well known that the aquifer containing Holocene sediments are vulnerable to As contamination [52,53]. Therefore, high As concentrations in groundwater of our study areas might be controlled by the recent geomorphology [7]. Our statistical results supports such assumptions which show that groundwaters in palaeo-channel aquifer (i.e. recent geomorphology) contain considerably high As concentrations compared with the groundwaters in the palaeo-interfluvial aquifers (Fig. 3.1.7a). McArthur et al. [53] also demonstrated a link between subsurface sedimentology (i.e. the distribution of palaeosol, an ancient land surface) and depth heterogeneity of As in groundwaters of southern West Bengal. The depth heterogeneity in As concentrations can be explained by the differences in mean Eh values, which is slightly high for the deeper aquifer (Table 3.1.1). The reason for such depth heterogeneity and less anoxic nature of the deeper aquifers could also be explained by sediment color, where, deeper aquifer sediments are oxidized and brown in color whereas shallow aquifers are mostly reduced and gray in color [52,53].

In Chakdaha, some areas remain water logged for most part of the year and thus favor the accumulation of fine grained sediments and fresh organic matter. The observation of large surface water bodies, i.e. abandoned ponds of cut-off channels, suggests the source of young and labile organic carbon in the area. This implies that local land use is also important which may further influence the aquifer biogeochemistry. Our data clearly shows the link between local land use and As distribution in shallow aquifers, for those wells located close to the source of sewage and/or domestic wastes (i.e. sanitation) has the highest mean As concentrations (331 ± 209 μgL^{-1}) compared with the wells located close to pond and habitation (267 ± 203 and 207 ± 173 μgL^{-1}, respectively) (Fig. 3.1.7b). In Debagram, we observed no significant control of subsurface sedimentology on As distribution and heterogeneity. This is perhaps due to the location of the study area which is outside the proximity to recent meander belts of Bhagirathi-Hooghly river. However, the concentration of As and DOC in shallow aquifers of Debagram is higher than that observed in Chakdaha (Table 3.1.1). This behavior is consistent with the observed low Eh values in shallow aquifers of Debagram compared to Chakdaha (-147 ± 22 and -125 ± 17 mV, respectively). In Debagram, most of the wells are located within the habitation where land-surface source of DOC from untreated sewage and/or domestic wastes can make way to the shallow aquifer and providing conditions necessary for Fe-oxyhydroxides reduction to occur and release of As into groundwater.

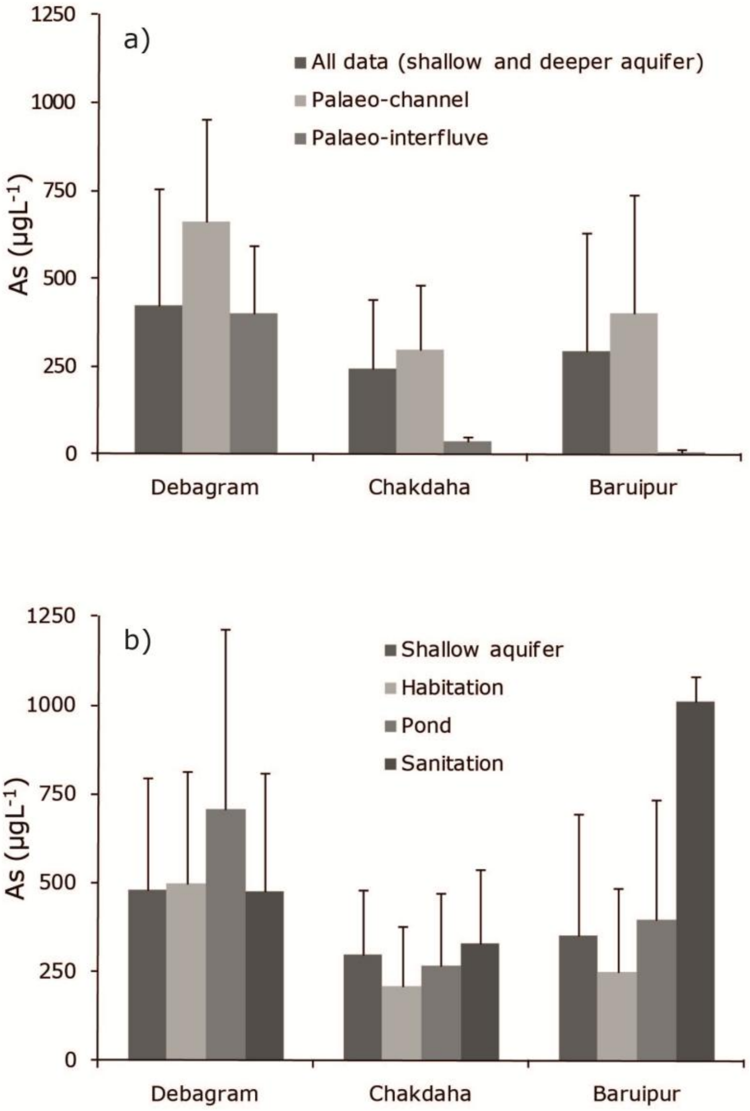

Figure 3.1.7. Histogram showing the distribution of As under (a) geomorphological settings, and (b) land use characteristics. The values are expressed as mean ± 1σ (standard deviation).

In Baruipur, Pal et al. [36] observed palaeo-channel settings in the western edge of the study area, where groundwater contains high As concentrations (Fig. 3.1.7a). This is consistent with the findings in Chakdaha study area where subsurface sedimentology has a strong control on groundwater As distribution. Nath et al. [17] pointed out that the shallow wells located close to sanitation and/or surface water body (i.e. pond) has the highest As concentrations. This has also been reflected through our study where land-surface sources of DOC might be leached to the shallow aquifer and controlling the redox reactions (Table 3.1.1, Fig. 3.1.7b). The observation of high PO_4^{3-} concentrations in the shallow aquifer of the delta front clearly suggests extensive anthropogenic activities which may further controls the solubility of As in the aquifer.

3.1.4. CONCLUSIONS

Groundwater redox chemistry of three physiographic settings of deltaic West Bengal was evaluated to identify the geogenic and anthropogenic controls on As release mechanism. High As concentrations in groundwater of the study areas were mainly controlled by the reductive dissolution of Fe-oxyhydroxides catalyzed by the oxidation of organic matter. The source, distribution and type of the organic matter were important, which were observed to be linked with geomorphological features (e.g. abandoned channels) and local anthropogenic activities (e.g. sanitation, domestic wastes, etc). Additionally, the release of As in groundwaters of Debagram and Baruipur were due to a complex combination of processes such as carbonate mineral dissolution and reduction of Fe-oxyhydroxides.

3.1.5. REFERENCES

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3.2: Saliva as a biomarker of arsenic exposure

Saliva is a biological fluid that has not been used extensively as a biomonitoring tool in epidemiological studies. This chapter presents the As concentrations in saliva and urine samples collected from populations of West Bengal, India who had been previously exposed to high As levels in their drinking water. Our findings show that saliva is a useful biomarker of As exposure in our study population.

3.2.1. INTRODUCTION

Exposure to elevated levels of arsenic results in several manifestations of arsenicosis (As toxicity due to chronic exposure) which include a range of cardiovascular, hepatic, hematological, endocrine, renal and dermal diseases as well as cancers of the various organs [1-3]. As mentioned in our introduction, all the conventional biomarkers that has been used for arsenic exposure has some limitations where either the analytical methodologies applied for arsenic determination are complicated or the interpretation of the results are misinformative.

Saliva is an easily accessible bio-fluid which is secreted in salivary glands including parotid, submandibular, and sublingual glands by active transport of water and ion from plasma. Water is the main constituent of saliva (98%) along with electrolytes, enzymes, mucus and antibacterial constituents [10]. The daily secretion of saliva ranges from 800 ml to 1500 ml and represent a relatively simple matrix compared to blood and urine [11]. Because of the non-invasive nature, ease of collection and storage, saliva can be helpful for studying large population and particularly advantageous when children are involved [12]. Methods have already been established to quantify several heavy metals in saliva [13,14] and have been used for biomonitering of lead exposure [15,16], mercury release from amalgam fillings [17,18], cadmium exposure via smoking addiction [19] and atrazine exposure from herbicides [20]. For lead exposed populations, the concentration of Pb in saliva is closely related to blood, plasma and hair metal concentration, thus rendering saliva as a potential biomarker of lead exposure [15,16]. However, there have been limited numbers of studies that have detected As in saliva [21,22]. Fängström et al. [23] stated that because of low concentration and lesser variation in As concentration, saliva is unsuitable for use as a biomarker in epidemiological studies. In a different study, Lew et al. [24] did not find any significant relationship in As concentration and speciation pattern in saliva samples from children that were exposed to As via hand to mouth transfer by playing in Chromated Copper Arsenate (CCA) treated wood playground compared to those that did not play in CCA-treated wood. Thus there exists serious knowledge gap in the use of salivary As as a biomarker in epidemiological study.

The aims of this chapter is to (i) develop a simple analytical protocol to determine As in saliva and test the method on saliva samples collected from the people residing in three villages in Nadia district, West Bengal, and (ii) we examine the correlation between As in urine and saliva samples from the study population. The overarching objective of the study is to assess whether saliva is a suitable biomarker for biomonitoring As exposure.

3.2.2. MATERIALS AND METHODS

3.2.2.1. Study population and sample collection

Saliva (n= 101) and urine (n= 101) samples were collected from participants of three villages (Chhoto-Itna, Debagram and Tehatta) of Nadia district, West Bengal, India. Participants were recruited from the cross-sectional study (2006-2007) carried out by Guha Mazumder et al. [25] in Nadia district, West Bengal, India. Local volunteers were employed to identify the selected participants from the study areas who have been residing in the same locality for a minimum of 10 years prior to the interview and were between 18-65 years of age. Since the control was also taken from the same areas, such criteria enabled us to compare the case-control who was exposed to compatible As for a long period of time. The region has been documented to have high As concentrations in groundwater [26]. Most of the people of these villages used to consume groundwater with high As levels in the past but for the last few years (3-4 years) are now relying on safe municipal water supply. However there are few families that are still using As-contaminated groundwater for drinking purpose. The villages are surrounded by agricultural lands and cultivation of jute and rice are the most common practice.

Trained interviewers conducted face-to-face interview with the participants in their residence. Before the interview, experienced physician conducted a clinical examination of the participants and those suffering from contagious disease and/or renal dysfunction were excluded from the study. Detailed information (age, body height and weight, body mass index (BMI), occupation, residential years, drinking and smoking habits) about the selected participants were obtained using a questionnaire. Participants were characterized as cases of skin lesions and control (with no skin lesions). The severity of the skin lesions was scored following standard protocol [25,27–29].

After the interview, participants were asked to provide saliva and urine samples. Spot urine samples were taken in prewashed (with 5% HNO_3 acid and then several times with Milli-Q water) polyethylene bottles in the day time (10.00 to 16.00 IST). For saliva, the participants were asked not to eat or drink for 1 hr prior to the sample collection. The participants rinsed their mouths with Milli-Q water and discarded the saliva which was formed immediately. After 2-3 min, the participants were given 15 mL LDPE bottles and the saliva was collected. Both urine and saliva was collected simultaneously in the day time. The minimum saliva sample required was 3 mL. Immediately after the sample collection, the bottle was placed in separate zip lock bag with printed sticker code of the participant and then stored in a salt–ice mixture and kept frozen until returned to the home laboratory. Later the samples were stored in -20°C freezer until analysis. Drinking water samples (n = 16) were also collected in acid washed, pre-cleaned polyethylene (PE) bottles from the sources mentioned by the participants as the primary supplier of their drinking water. The water samples were acidified with HNO_3 (pH <2) on the spot and were preserved at 4°C until further analysis.

3.2.2.2. Sample preparation and analysis

Urine samples were brought to room temperature and filtered with 0.45 µm syringe filter. The specific gravity of each sample was measured. The concentrations of As in the urine samples were corrected to the mean specific gravity of the samples (1.01 gmL^{-1}). The filtered urine samples were digested with HNO_3 and H_2O_2 (Merck). 1 mL of filtered urine sample was mixed with 3 mL of concentrated HNO_3 (suprapur, Merck) and the solution was heated for ~4 hrs at 120^{o}C until the solution turned colourless. To remove the excess organics, 1 mL of 30% H_2O_2 (Merck) was added and the heating was continued. The digestion was marked complete when the evolution of gas from the solution stopped. The digested sample was cooled and measured for As using HG-AAS (Varian, AA220) following manufacturer instruction. The water samples collected during the survey were also measured for total As using HG-AAS.

As contents of the saliva samples were measured with inductively coupled plasma/mass spectrometer (ICP-MS) (Agilent 7500c) equipped with collision cell. The samples were thawed to room temperature, centrifuged and 1 mL of the sample was transferred to a plastic vial. To the sample, appropriate amount of HNO_3 (2% v/v), ethanol (2% v/v) and internal standard (I.S) (10 $\mu g\ L^{-1}$ Rhodium standard) was added. The volume was made up to 3 mL using Milli-Q water and was analyzed for As following the operational parameter as described in Colon et al. [30].

The reproducibility of the data (± 0.2 – 0.4 %) was checked through frequently run laboratory standards. Detection limits were calculated as three times the standard deviation for the reagent blanks.

3.2.2.3. Estimation of total inorganic As exposure

Studies on dose-response relationship have shown that consumption of inorganic As (iAs) in drinking water is one of the route of As intake in human [27,31,32]. Since, the As in water of our study area is primarily composed of inorganic As [As (III) and As (V)] [26], the As exposure via drinking water of each participant was estimated following the equation:

$$I_{As,i}\ (\mu g\ day^{-1}) = (C_{W,i} \times V_i) \qquad \text{(I)}$$

where, $I_{As,i}$ represents amount of ingested iAs from water, $C_{W,i}$ represents the concentration of As in drinking water ($\mu g\ L^{-1}$) and V_i represents the volume of daily water intake of each participant, collected during questionnaire survey (L day^{-1}).

In a recent study in the same cohort, Halder et al. [33] had estimated the extent of As ingestion through rice by measuring the As concentration of the household rice samples and from the amount of daily rice consumption for each participants. Out of the 157 participants investigated by Halder et al. [33], the number of participants recruited in this present study was included and thus the amount of As intake through rice was quantified. Additionally, speciation of the rice samples consumed by the participants in our study area was also done in that study and it was reported that the rice accounts to 0.92 fractions of the inorganic As.Therefore, the total amount of iAs ingested was calculated as:

$$TDI_i\ (\mu g\ day^{-1}) = I_{As,i} + (C_{R,i} \times W_i \times 0.92) \qquad \text{(II)}$$

where, TDI$_i$ represent the total daily ingestion of iAs, $C_{R,i}$ represent the concentration of As in rice (µg Kg^{-1}) and W_i represent the amount of rice consumed daily (Kg day^{-1}) for each participants.

3.2.2.4. Data analysis

The detailed statistical analyses were performed using SPSS statistical software, version 17.0 by IBM. Although statistical analyses are highly dependent on the sample size and its biasness, but such evaluation are important for the better understanding of the association between different parameters. Moreover in comparison to past As epidemiological studies [7, 24], our sample size (n) was good enough to provide statistical significant results. Histogram and normal probability plot of the tabulated TDI, As concentration in urine and saliva revealed that the distributions were right skewed and deviated from normality. Thus all the data was Log transformed prior to use for statistical analysis.

Linear regression analysis was performed to evaluate the strength of the association between TDI with total urinary As and salivary As. Additionally, regression analysis was also estimated between salivary and urinary As so as to assess the relationship between these parameters. Influence of the different demographic variables on the As concentration in urine and saliva was tested by the analysis of variance (ANOVA). The independent variables include age, gender, smoking status, Body Mass Index (BMI) and score of skin lesion. The variables were later tested for multiple linear regression analysis with As concentration in urine and saliva. Statistical significance was indicated by values of $p < 0.05$.

3.2.3. RESULTS AND DISCUSSION

3.2.3.1. Analytical protocol and quality control

Standard reference material (SRM) for water (SRM 1643e) and urine (SRM 2670a) from the US National Institute of Standards and Technology (NIST) was used for quality assurance. The As concentration in the standard water reference material was found to be in agreement with the certified value. The measurement of total As in urine was confirmed by means of total As recovered from digesting the SRM of urine using the protocol as that described for urine samples. Our result showed mean percentage recovery of 99 ± 15 % (n = 8).

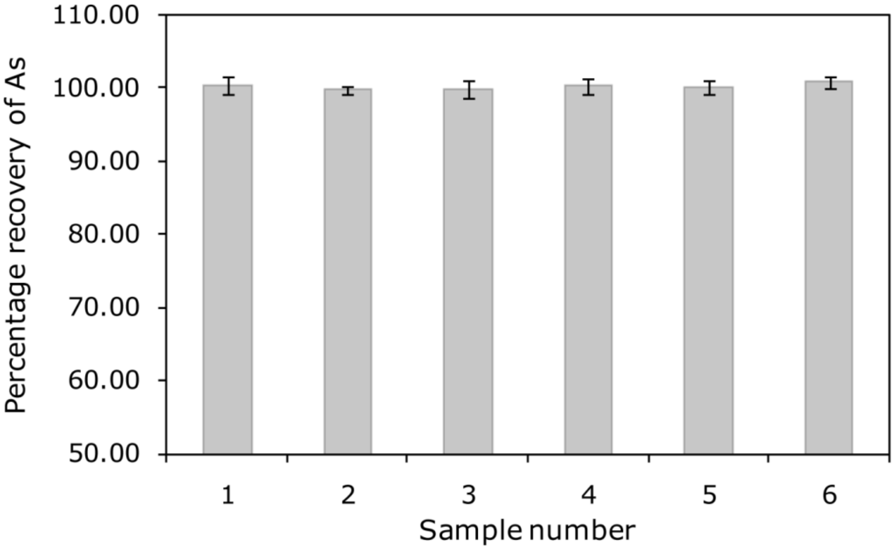

Figure 3.2.1. Percentage recovery of As from spiked saliva samples. Error bar represents standard deviation (SD).

Measuring As in saliva is relatively new and currently there is no SRM for salivary As. Thus in absence of SRM, our protocol involved in-house secondary standards created by spiking different concentration of As in non-contaminated saliva samples collected from volunteers of different ages and sex. The percentage As recovery ranged from 99 % to 101 % (Fig. 3.2.1). The results showed good agreement when the spiked saliva samples were diluted three folds (data not shown), thus suggesting minimum matrix effect. The sensitivity of As measurement increased on addition of 2 % ethanol (EtOH) as evidenced from the increase in slope of the curve (Fig. 3.2.2a). The increase in As signal owing to addition of small amount of alcohol (2 % EtOH) is due to charge transfer reaction between positively charged carbon and ^{75}As in the plasma [30,34,35]. However, addition of excess alcohol may cause local cooling in the centre of the plasma and a reduction of analyte signal can take place [34]. Additionally, effect of various internal standards (IS) was also evaluated to minimize, if necessary, possible matrix effects and/or instrumental drift. Rhodium (Rh) and Yttrium (Y) are some of the most commonly used IS for ICP-MS and their masses are not so different from that of the As. Although their ionization potential is quite lower in comparison with that of the As, they had showed good behaviour in previous studies [30]. Figure 3.2.2b shows the curve of CPS (counts per second) of As (normalized with IS) against the concentration of spiked As. It was found that although Y had a higher CPS ratio than Rh but the linearity was poor even at higher concentration of As in the spiked samples. In comparison, Rh had a better sensitivity for As measurement in our spiked saliva sample than Y and therefore Rh was used as an IS for measurement of all saliva samples.

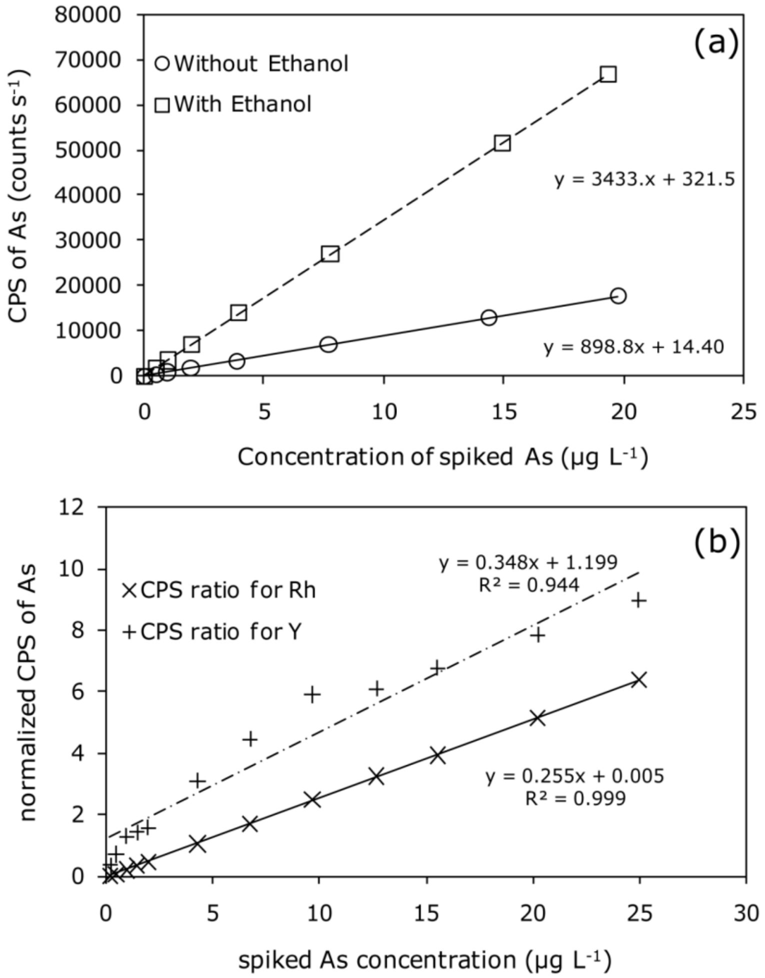

Figure 3.2.2. (a) Effect of ethanol on the sensitivity of As measurement in ICP-MS and (b) effect of internal standard (Rh and Y) for measurement of As in ICP-MS.

3.2.3.2. Arsenic exposure and total arsenic concentration in urine and saliva

The statistical results of the As level in drinking water, tabulated TDI, As concentration in urine (U_{As}) and saliva (S_{As}) are represented in Table 3.2.1 and the Log transformed data is shown in Fig. 3.2.3. Our results are in accordance with the study of Yuan et al. [21] which found the mean concentration of saliva As up to 11.9 μg L^{-1} for residents of Inner Mongolia, China who were exposed to As concentrations up to 826 μg L^{-1} in drinking water. By comparison, the salivary As value of 0.79 μg L^{-1} has been reported for populations of Edmonton, Alberta, Canada who were consuming As concentration < 5 µg L^{-1} in drinking water. Although the groundwater in our study area have high concentration of As, due to increased social awareness, the participants are now sharing the low As common water sources for drinking purpose [25]. However, the local farmer still uses high As concentration groundwater for irrigation and crop cultivation. Studies have revealed that because of the use of such groundwater for agricultural purpose, there are additional exposures of bioavailable As from foods consumed by the participants [36,37]. In a recent publication on the same participants, Halder et al. [35] has explicitly measured the As exposure from dietary sources and it was shown that for people consuming safe water (< 10 µg L^{-1}), the major contribution of inorganic As is from rice consumption and for

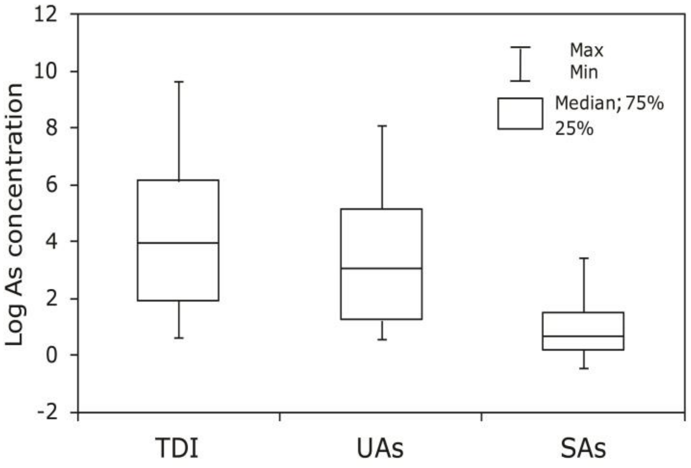

Figure 3.2.3. Box plot of Log transformed Total Daily Ingestion of As (TDI), As concentration in urine (U_{As}) and saliva As concentration (S_{As}) of 101 participants. Concentration of TDI is in µg day^{-1} and concentration of U_{As} and S_{As} is in µg L^{-1}.

35% cases, the total As intake from water and rice exceeds the previous provisional tolerable daily intake of 2.1 µg day^{-1} kg^{-1} BW as recommended by WHO. Additionally, for the participants consuming water with As concentration >10-50 µg L^{-1}, the intake of inorganic As from water and rice are almost equal and therefore, the cumulative contribution of the As ingested through rice and water may be sufficient to cause a potential threat to the inhabitants of these areas.

Table 3.2.1. Statistical table of the measured As concentration in drinking water, TDI, U_{As} and S_{As} of all the participants.

Medium	N	x ±S.D	Median	Range
C_W ($\mu g\ L^{-1}$)	16	120 ± 239	18.0	806 – 2.50
TDI ($\mu g\ day^{-1}$)	101	235 ± 531	113	3172 – 19.9
U_{As}($\mu g\ L^{-1}$)	101	110 ± 154	67.7	883 – 0.22
S_{As} ($\mu g\ L^{-1}$)	101	7.84 ± 12.6	2.99	84.3 – 0.22

C_W – Concentration of As in drinking water
TDI – Total Daily Ingestion of inorganic As
U_{As} – Urinary As concentration
S_{As} – Salivary As Concentration

Simple regression analysis between TDI and U_{As} as well as S_{As} was done to evaluate the viability of the excreted As as a measure of As exposure (Fig. 3.2.4; Table 3.2.2). Our study shows that TDI has a positive correlation with both U_{As} ($r = 0.50$, $p < 0.05$) as well as S_{As} ($r = 0.68$, $p < 0.05$). This suggests that similar to urinary As, salivary As can also act as a predictor of As exposure. However the results of our study shows that S_{As} has a better correlation with TDI than U_{As}, signifying As in saliva as a superior reflection of the ingested As compared to urine. A number of previous epidemiological studies on As have used urinary As as a biomarker of As exposure [38-42]. The ingested As is quickly eliminated within 2-3 hrs from blood through kidney and from urine in 2-3 days [40]. Therefore, urinary As indicates recent exposure. Nevertheless, As concentration in urine reaches a steady state and may thus reflect past exposure for populations exposed to continuous chronic levels [43]. Simple regression analysis was done between U_{As} and S_{As} and there exist a positive, significant correlation between the two parameters ($r = 0.60$, $p < 0.05$; Fig. 3.2.5). This suggests that ingestion of inorganic As is important in determining the As concentration in saliva. Thus S_{As} can be regarded as biomarker of As exposure and can be used as a surrogate of urine in As epidemiological study.

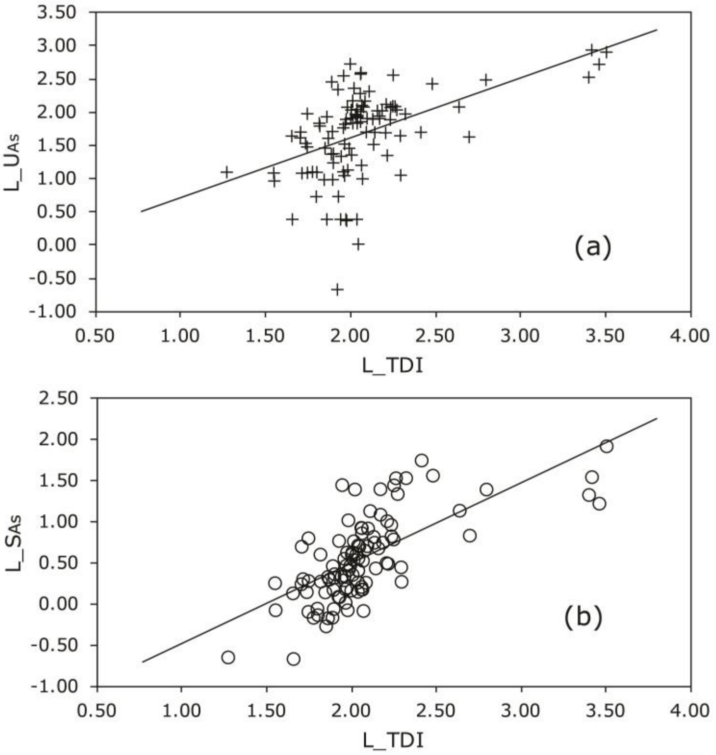

Figure 3.2.4. Plot of (a) Log-transformed urine As concentration (U_{As}) versus Total Daily Ingestion of As (TDI) and (b) saliva As concentration (S_{As}) vs Total Daily Ingestion of As (TDI). Concentration of TDI is in µg day^{-1} and concentration of U_{As} and S_{As} is in µg L^{-1}.

Additionally there are several field problems for the collection of urine samples. Our field experience shows that participants, particularly village women were much reluctant to provide samples for research. We also observed that ethnic barrier is another important factor for the collection of urine sample and participants of certain race are conservative and are unwilling to give urine sample even after long persuasion. Moreover participants needed to feel the urge of urination to provide urine samples and this was often a time taking process. Difficulties in the collection of urine samples may be compounded when the studies involve children and especially young children who are still in diapers [12]. Such drawbacks can be eliminated by using saliva as a biomarker since no prior adjustment of the samples is necessary for interpretation of the results and the samples can be collected easily on-spot in few minutes.

Table 3.2.2. Correlation matrix of the bivariate relation between Log Total Daily Ingestion of As, Log As in urine and saliva

	L_ TDI	*L_U$_{As}$*	*L_S$_{As}$*
L_ TDI	–	$r = 0.50; p < 0.05$ Rsq = 0.25 Adj Rsq = 0.24 SEE = 0.57 $L\_U_{As} = -0.25 + 0.92\ L\_TDI$	$r = 0.68 ; p < 0.05$ Rsq = 0.46 Adj Rsq = 0.45 SEE = 0.38 $L\_S_{As} = - 1.52 + 0.99\ L\_TDI$
L_U$_{As}$	$r = 0.50; p < 0.05$ Rsq = 0.25 Adj Rsq = 0.24 SEE = 0.57 $L\_U_{As} = -0.25 + 0.92\ L\_TDI$	–	$r = 0.60 ; p < 0.05$ Rsq = 0.36 Adj Rsq = 0.36 SEE = 0.42 $L\_S_{As} = - 0.24 + 0.48\ L\_U_{As}$
L_S$_{As}$	$r = 0.68 ; p < 0.05$ Rsq = 0.46 Adj Rsq = 0.45 SEE = 0.38 $L\_S_{As} = - 1.52 + 0.99\ L\_TDI$	$r = 0.60 ; p < 0.05$ Rsq = 0.36 Adj Rsq = 0.36 SEE = 0.42 $L\_S_{As} = - 0.24 + 0.48\ L\_U_{As}$	–

L_TDI - Log Total Daily Ingestion of As
L_U$_{As}$- Log of As concentration in urine
L_S$_{As}$– Log of As concentration in saliva
r – Pearson correlation coefficient
SEE – Standard Error of the Estimate

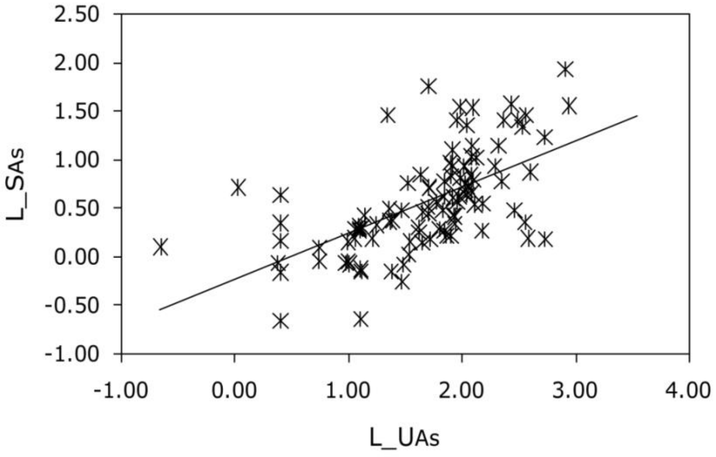

Figure 3.2.5. Log-transformed saliva As concentration (S_{As}) versus urine As concentration (U_{As}). Concentration of U_{As} and S_{As} is in µg L^{-1}.

3.2.3.3. Factors regulating As concentration in urine and saliva

Influence of age, sex, smoker, BMI and score of skin lesion on urinary and saliva As concentration is shown in Table 3.2.3. Our results indicates significant association of U_{As} with sex ($p < 0.0001$), age ($p = 0.003$), smoker ($p = 0.002$) and prevalence of skin lesion ($p = 0.000$). However, there were no significant differences of urinary As concentration with BMI ($p = 0.44$). Previous studies on Asian countries have observed that male, smokers and older participants are likely to be more affected from their respective counterparts [31,42,50,51]. The possible explanation for such observation has been suggested to decreased methylation capacity of the participants [42,50] and this has also been reflected in our study (Table 3.2.3). Manifestation of skin lesion has been positively associated with As exposure [51–53]. Our study shows that the controls have lower concentration of U_{As} than cases with skin lesions (Table 3.2.3). However, among the various cases of skin lesion, participants categorized as moderate (score ≤ 4) have a higher concentration of U_{As} than severe (score ≤6) and mild (score ≤ 2) cases (Table 3.2.3).

Table 3.2.3. Association of urinary and salivary As concentration with study variables

Variables	Sample number	*urinary As concentration*			*saliva As concentration*		
		mean ± S.D	95 % CI for mean*	*p*-value*	mean ± S.D	95 % CI for mean*	*p*-value*
Sex							
Male	48	143 ± 160	1.81 - 2.08	0.00	10.4 ± 12.8	0.58-0.88	0.00
Female	53	79.9 ± 144	1.24 - 1.63		5.56 ± 12.1	0.28-0.54	
Age							
<35	11	22.8 ± 27.6	0.79 - 1.46	0.00	4.83 ± 9.97	-0.11-0.64	0.15
36-45	42	95.9 ± 150	1.39 - 1.81		7.89 ± 15.7	0.37-0.69	
46-55	35	156 ± 183	1.70 - 2.11		8.27 ± 9.85	0.47-0.82	
>55	13	102 ± 106	1.44 - 2.08		9.10 ± 10.4	0.38-0.99	
Smoker							
No	63	90.4 ± 143	1.34 - 1.70	0.00	5.12 ± 11.2	0.29-0.52	0.00
Yes	38	142 ± 167	1.78 - 2.09		12.4 ± 13.7	0.65-0.99	
BMI							
<18	22	118 ± 132	1.49 - 2.04	0.73	8.99 ± 11.4	0.34-0.88	0.87
18-25	70	107 ± 164	1.48 - 1.80		7.77 ± 13.6	0.44-0.67	
>25	9	114 ± 139	1.17 - 2.22		5.60 ± 6.70	0.14-0.89	
Score							
control	37	31.6 ± 48.3	0.94 - 1.35	0.00	2.92 ± 5.95	0.09-0.36	0.00
mild	19	137 ± 185	1.71 - 2.12		10.1 ± 19.5	0.38-0.87	
moderate	38	168 ± 180	1.93 - 2.18		9.03 ± 9.47	0.61-0.90	
severe	7	131 ± 132	1.08 - 2.47		21.2 ± 18.8	0.62-1.61	

* ANOVA of Log transformed dependent variables

Similar to urinary As, male participants and smokers had a higher concentration of S_{As} compared to female and non-smokers respectively, while association of S_{As}

with BMI (p = 0.871) and age (p = 0.440) was not statistically significant (Table 3.2.3). Control had lower concentration of S_{As} and the concentration for severe cases was 2-fold higher than the mild and moderate cases of skin lesion (Table 3.2.3). Results of multiple regression analysis for U_{As} and S_{As} are shown in Table 3.2.4. It is interesting to note that while considering the concurrent effect, TDI and scores of skin lesion had significant effect on U_{As} while for saliva, sex, smokers, score and TDI was positively related with S_{As}. This suggest that compared to U_{As}, S_{As} provides better information about the confounding factors which in turn are directly related to the individual As exposure.

Table 3.2.4. Results of multiple regression analysis of Log transformed urinary As and saliva As concentration with selected study variables.

	Log urinary As			***Log saliva As***		
	Beta coefficient ± S.E	95% CI	*p*-value	Beta coefficient ± S.E	95% CI	*p*-value
Log TDI	0.64 ± 0.15	0.38–0.95	0.00	0.77 ± 0.10	0.57–0.97	0.00
Sex	0.19 ± 0.19	-0.19–0.58	0.32	-0.30 ± 0.13	-0.55– -0.04	0.02
Age	0.01 ± 0.01	0.00–0.02	0.08	0.01 ± 0.00	0.00–0.01	0.16
Smoker	-0.02 ± 0.19	-0.39–0.35	0.90	0.40 ± 0.12	0.16–0.65	0.00
BMI	-0.01 ± 0.02	-0.04–0.02	0.50	-0.01 ± 0.01	-0.03–0.01	0.48
Score	0.11 ± 0.03	0.04–0.17	0.00	0.09 ± 0.02	0.05–0.13	0.00

3.2.4. CONCLUSIONS

The use of saliva for exposure assessment has several advantages compared to other already established biomarkers. Saliva, secreted in the salivary gland, consist of ingredients of extra-cellular fluids. Thus the chemical composition and the chemistry are widely different from that of plasma and serum. The metal ions are actively transported from the plasma and thus represent a measure of internal dose. So monitoring saliva data may provide insight to the As metabolic process. This study demonstrated S_{As} as a potent biomarker of As exposure in our study population that has been exposed to high As concentration groundwater in the past. The strong positive correlation between the TDI and S_{As} suggests that As concentration in saliva provides a good reflection of As exposure. Since urine is considered as a surrogate of As intake, the positive correlation between U_{As} and S_{As} strengthens the case for the use of saliva as biomarker of As exposure.

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3.3: Speciation of salivary arsenic

Saliva was used as a biomarker of arsenic exposure for the population of West Bengal, India and arsenic speciation of the saliva samples was carried out. As(V) was the predominant species, with the amount of inorganic As [As(V) and As(III)] being more than half of the total As in saliva. The chapter shows higher As exposure and a lower methylation capacity were responsible for developing As-induced health effects.

S. Bhowmick, D. Halder, J. Nriagu, D.N. Guha Mazumder, G. Roman-Ross, D. Chatterjee, M. Iglesias. "Speciation of Arsenic in Saliva Samples from a Population of West Bengal, India". *Environmental Science and Technology*, 48 (2014) : 6973-6980

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Abstract

Saliva, an easily accessible biofluid, is validated as biomarker of arsenic (As) exposure in several villages of West Bengal, India. Pentavalent arsenic [As(V)] was found to be the predominant species in saliva, with the amount of inorganic As [As(V) and trivalent form, As(III)] being more than half of the total As in the samples. Significant association was found between total daily ingestion of As and As(V) ($r = 0.59$; $p = 0.000$), As(III) ($r = 0.60$; $p = 0.000$), dimethylarsinous acid (DMAV) ($r = 0.40$; $p = 0.000$), and monomethylarsonous acid (MMAV) ($r = 0.44$; $p = 0.000$), implying that these species have mainly been derived from the methylation of the inorganic As in the water that study participants drank and the food they ate. Analysis of confounding effects of age, sex, smoking, body mass index and the prevalence of skin lesion suggests that women and controls with no skin lesion had a higher capacity to methylate the ingested As compared to the rest of the population. Thus, our study demonstrates that As species in saliva can be an useful tool to predict the individual susceptibility where higher As exposure and a lower methylation capacity are implicated in the development of As-induced health effects.

3.4: Montmorillonite-supported nanoscale zerovalent iron for removal of arsenic from aqueous solution

Montmorillonite-supported nanoscale zero-valent iron (Mt-nZVI) has been synthesized to remove inorganic arsenic from aqueous solutions. The dispersion of nZVI onto montmorillonite was found to be increased with decreasing tendency to agglomerate into larger particles. Batch experiments revealed that adsorption kinetics followed pseudo-second order rate equation with high affinity towards both As(III) and As(V) over a wide pH range (4-8) which was decreased at pH>9. Thus this chapter shows Mt-nZVI as a potential adsorbent to reduce elevated levels of arsenic in groundwater.

3.4.1. INTRODUCTION

As mentioned in Chapter 2 and 3, chronic exposure to arsenic (As) via drinking water is one of the major cause of As poisoning and currently, millions of people are at risk from consuming As contaminated water [1]. The grave of the problem lies in the fact that exposure to low concentration (<50 μgL^{-1}) can cause chronic toxicity of As. Thus various environmental protection agencies and National Standards are lowering the permissible level of As below $10\mu gL^{-1}$ in drinking water. It is therefore necessary to develop simple, fast and low cost method for removal of As from aqueous environment so as to provide safe water to the community.

Nanoscale zero-valent iron (nZVI) has been used for treatment of As contaminated groundwater [2–5]. Because of its large active surface area and high As adsorption capacity, nZVI acts as promising material for removal of As from aqueous solution [6]. However, tiny particle size and powder state along with lack of durability and mechanical strength restricts the direct use of nZVI [7]. The intrinsic characteristics of nZVI to agglomerate during preparation decreases the reactivity of the particle and also results in poor mobility and successful transport of nZVI to the contaminated area for *in-situ* remediation [8]. Moreover, agglomeration of iron particles in fixed bed column or any other dynamic flow system results in high-pressure drop, thus restricting the direct use of nZVI for field scale application. Hence, loading nZVI onto supporting material may be a potential method to decipher the problem [7]. Clay is an abundant natural resource and can be a suitable supporting material due to its potential applicability in catalysis and various composites [9,10]. Clay-nZVI is known to remove heavy metals (Cr, Pb, Co) from aqueous solution [11–13]. However little is known about the use of such material for removal of As from aqueous solution.

The primary objectives of the present chapter were to: (1) synthesis and characterize the montmorillonite-supported nanoscale zero-valent (Mt-nZVI); (2) investigate the adsorption kinetics of As onto Mt-nZVI and (3) study the effect of solution pH and chemical competition on the adsorption. A mechanism of As removal and method of regeneration of Mt-nZVI after repetitive use have been proposed.

3.4.2. MATERIALS AND METHODS

3.4.2.1 Materials and chemicals

The natural Na-Montmorillonite (SWy-2, abbreviated as Mt) obtained from Source Clay Mineral Repository, University of Missouri, Columbia, USA was used without any pre-chemical treatment. The X-ray diffraction pattern showed that the clay consists primarily of Mt with minor impurities of quartz and muscovite.

All the chemicals were analytical grade and used without further purification. Sodium borohydride ($NaBH_4$), iron(III) chloride hexahydrate ($FeCl_3.6H_2O$), hydrochloric acid (HCl), sodium hydroxide (NaOH) and absolute ethanol (99%) were obtained from Panreac (Spain). Stock solutions of As(V) and As(III) were prepared by dissolving appropriate amount of di-sodium hydrogen arsenate-heptahydrate (Na_2HAsO_4, $7H_2O$) (Merck) and sodium (meta) arsenite ($NaAsO_2$) (Fluka) respectively in deionized water (Millipore Milli-Q 18 MΩ).

3.4.2.2 Preparation of Mt-nZVI

Montmorillonite-supported nanoscale zero-valent iron (Mt-nZVI) was synthesized under N_2 atmosphere by conventional method of reducing Fe(III) with $NaBH_4$ in presence of Mt as a supporting material [12,13]. $FeCl_3.6H_2O$ (corresponding to 0.30g of Fe) was dissolved in 100 ml of ethanol water mixture (4:1, v/v) and was purged with N_2 for 1 hr. Three g montmorillonite was added to the above mixture and stirred for another 1 hr. Freshly prepared 100 ml 1 (M) $NaBH_4$ solution was added dropwise (at a rate of 1-2 drops per second) into the montmorillonite/Fe^{3+} dispersion and was stirred vigorously. The solution was agitated additionally for another 2 hrs for complete reduction of Fe^{3+} and depletion of the $NaBH_4$. The reaction can be represented as:

$4Fe^{3+} (aq) + 3BH_4^- + 9H_2O \rightarrow 4Fe^0 + 3H_2BO_3^- + 12H^+ + H_2 \uparrow$

All the above experiment was carried under N_2 atmosphere. The black nanoparticles formed onto supporting montmorillonite were separated from the solution by centrifugation at 4000 rpm. It was washed three times with absolute ethanol and dried overnight in vacuum at 60°C. An excess of $NaBH_4$ was used to ensure complete reduction of Fe(III). nZVI without supporting clay were also prepared in similar way. After the synthesis, Mt-nZVI and nZVI were dried in vacuum and stored under N_2 atmosphere to prevent aerial oxidation prior to experiment.

3.4.2.3 Characterization and measurement

Zero point charge pH (pH_{ZPC}) of the Mt-nZVI was determined by acid-base titration method as described by Stumm and Morgan [14]. The surface morphology images of Mt-nZVI were taken by scanning electron microscope (SEM) (CARL-ZEISS model DSM 960 A, Germany) operating at 30 kV and equipped with energy dispersive X-ray (EDX) analysis. The dried samples were coated on gold and carbon for SEM and EDX analyses respectively. X-ray diffraction (XRD) pattern of Mt and Mt-nZVI were performed in a Bruker X-ray powder diffractometer (model D8) using Cu-Kα radiation source operating at 40 kV and 40 mA. The specific surface area was measured by Brunauer–Emmett–Teller (BET) N_2 adsorption method using a Micromeritics Gemini V2.00 (Model 2380) instrument where the samples were dried with a constant flow of N_2 at 60°C for 24 hours.

X-ray photoelectron spectroscopy (XPS) was used to analyze the surface composition of Mt-nZVI within a depth of <10 nm. The analysis was performed with an upgraded ESCALAB 220i-XL spectrometer using monochromatic Al - Kα radiation operated at 15 kV and 150 W. Charge corrections were applied on the spectra using the C1s line (284.6 eV) of adventitious aliphatic carbon as an internal reference. Data acquisition and processing was done using Advantage Data Spectrum Processing Package (Thermo VG Scientific, U.K).

3.4.2.4 Adsorption experiment

The adsorption experiments were performed in batch method at room temperature (25 ± 1°C). The vials containing suspensions of Mt-nZVI were equilibrated with appropriate concentrations of either As(III) or As(V) solutions. The pH of the suspensions was adjusted using an aqueous solution of HCl and NaOH. After certain intervals, ~5 ml of clay suspensions were sampled, filtered through 0.45 μm filter (Minisart- GF, Sartorius Stedim Biotech) and the filtrates were stored at 4°C after acidification until analyses of total As concentration by inductively coupled plasma mass spectroscopy (ICP-MS, Agilent 7500C). The detailed experimental conditions are listed in Table 3.4.1.

Table 3.4.1. Experimental conditions of adsorption kinetics, edge and isotherm experiments

	Adsorption kinetics		Adsorption edge		Adsorption isotherm	
	As(III)	As(V)	As(III)	As(V)	As(III)	As(V)
pH	7.02	7.03	4 –10	4 –10	7.00	7.00
[Mt-nZVI] (gL^{-1})	1.00	1.13	1.07 ± 0.02	1.10 ± 0.03	1.29 ± 0.05	1.26 ± 0.08
$[As]_0$ (mgL^{-1})	5.54	5.52	5.65 ± 0.17	5.15 ± 0.19	2 –345	2 –200
time (hr)	0.02 – 48	0.02 – 48	4	4	4	4

[Mt-nZVI] = concentration of Mt-nZVI, $[As]_0$ = initial As concentration.

All the experiments were performed in triplicates and blanks containing no solid were prepared under identical experimental conditions. The amount of As adsorbed onto Mt-nZVI was calculated using the following equation:

$$q = V(Ci - Ct)/M \qquad (1)$$

where, q = mass of As adsorbed; V = volume of solution; C_i and C_t = initial As concentration and As concentration at time t respectively; M = mass of the adsorbent.

The effects of oxy-anion like PO_4^{3-}, SO_4^{2-}, HCO_3^- and NO_3^- on the adsorption of As was investigated at pH 7.0 in a solution with an initial As concentration of 5 mg L^{-1}. The efficiency of Mt-nZVI to remove As from As-spiked tap water as well as natural As contaminated groundwater was also investigated. To know the distribution of inorganic As species in groundwater, separation of As(III) and As(V) was done on-site. The groundwater is passed through an ion-exchange resin cartridge (Metal Soft Centre, Highland Park, USA), where As(V) is selectively adsorbed and only As(III) is eluted out. The difference between the total As and As(III) gives the concentration of As(V).

The possible re-use of Mt-nZVI was further tested by shaking samples (2 mg L^{-1} of either As(III) or As(V) solution spiked to and agitated with 5 g L^{-1} of Mt-nZVI suspension for 24 hours and then centrifuged) with 0.1 M NaOH for 4 hrs. The solution was centrifuged for 10 min at 3000 rpm and the supernatant was decanted. The composite was washed 3 times with distilled water and the above cycle was repeated for 5 times.

3.4.3. RESULTS AND DISCUSSION

3.4.3.1 Characterization

The BET calculated specific surface areas for Mt-nZVI and Mt were 36.97 and 14.85 m^2 g^{-1}, respectively. Thus the surface area was enhanced and was attributed to the increase in reactivity by incorporating nZVI on the montmorillonite. The surface morphology of dispersed nZVI with and without supporting montmorillonite is shown in Figure. 3.4.1. In absence of supporting clay, nZVI showed chain-like morphology with occasional agglomerations due to the combined effect of their intrinsic magnetic property and its preference to remain in thermodynamically favorable state (Fig. 3.4.1b) [8]. The agglomeration expectedly decreased with increase of dispersion and mechanical strength of nZVI when Mt was used as the supporting material (Fig. 3.4.1c). Üzüm et al. [11] and Zhang et al. [12] also observed similar phenomenon on using bentonite and kaolinite as supporting clay. However after reaction with As (Fig. 3.4.1d), the agglomeration as well as size of the nanoparticles increased probably due to the formation of iron corrosion products and the adsorption /co-precipitation of As on such corrosion surface [2,15]. Quantitative EDX analyses showed the abundance of Fe in Mt-nZVI compared to Mt alone (Fig. 3.4.2) and clearly demonstrate that the nZVI were successfully loaded onto Mt. The peak of As in Mt-nZVI after reaction (Fig. 3.4.2) further confirmed that As was adsorbed on the solid surface.

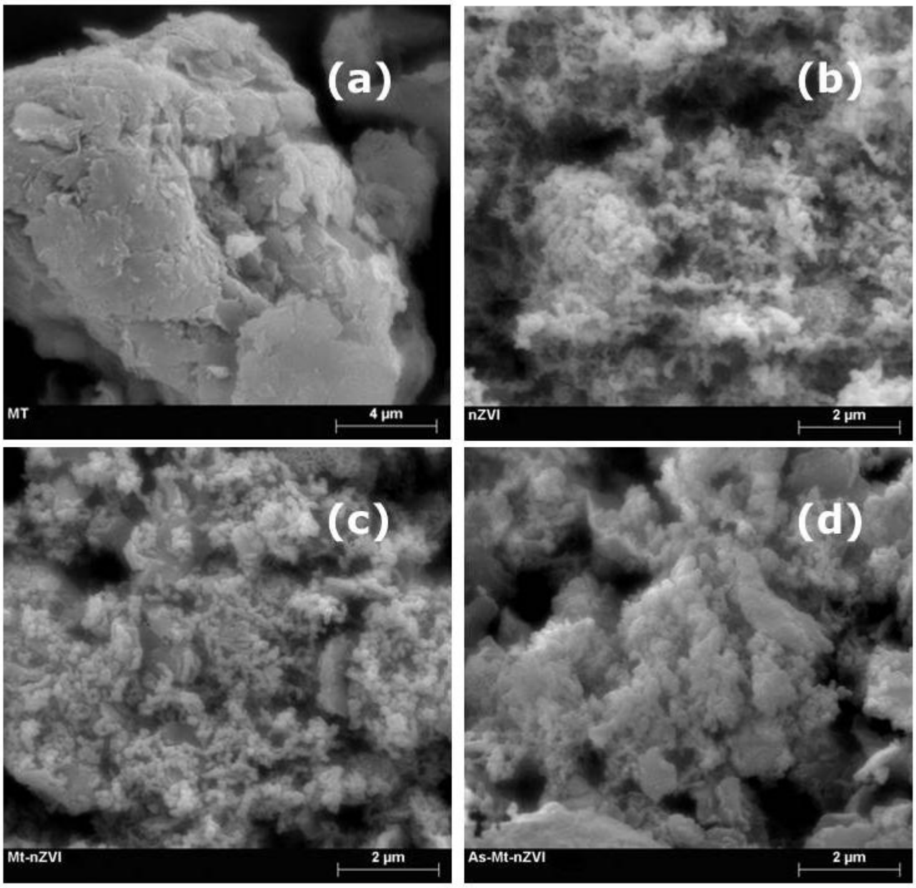

Figure 3.4.1. SEM image of (a) Mt, (b) nZVI, (c) Mt-nZVI before reaction, (d) Mt-nZVI after reaction with 100 mgL^{-1} of As(V) at pH 7.0.

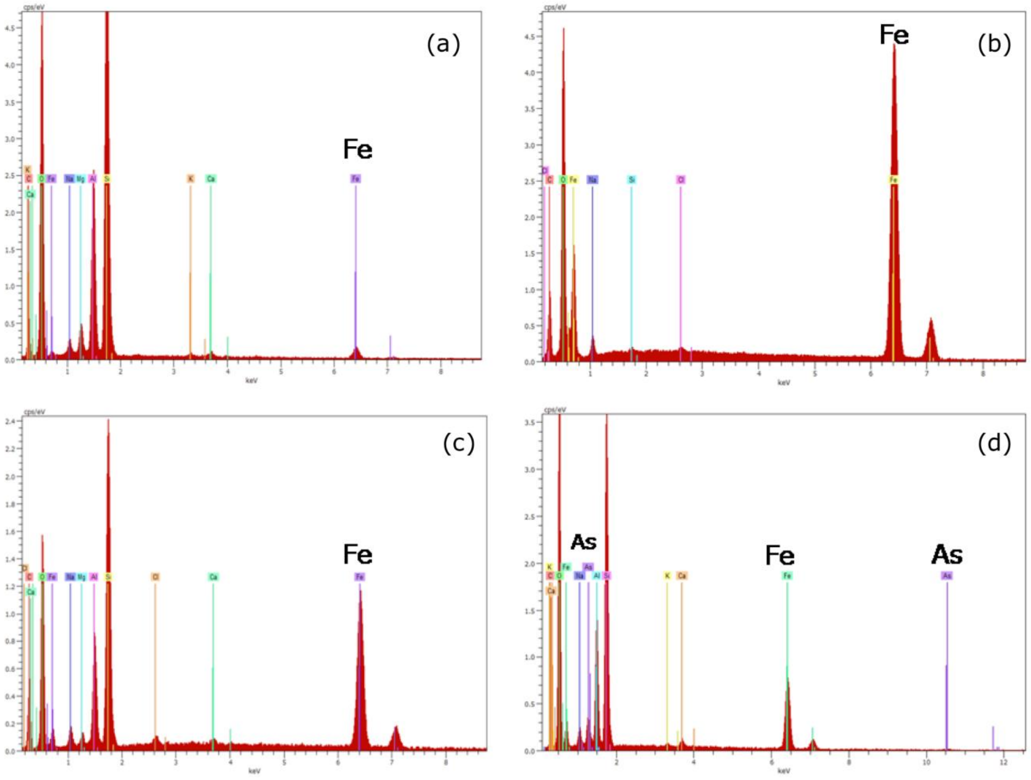

Figure 3.4.2. EDX spectra of (a) Mt, (b) Fe nanoparticle, (c) Mt-nZVI before reaction, (d) Mt-nZVI after reaction with 100 mgL^{-1} of As at pH 7.

The XRD patterns of Mt and Mt-nZVI are shown in Fig. 3.4.3. The supporting clay (Na$^+$ - montmorillonite) used in our study represents a characteristic d(0 0 1) value of 1.19 nm and consists mainly of Mt with minor presence of quartz and muscovite (Fig. 3.4.3a). However increase in d-spacing to 1.50 nm in Mt-nZVI (Fig. 3.4.3b) implies the possible replacement of interlayer cation, Na$^+$ with Fe^{3+} which can be subsequently reduced to Fe(0) by BH_4^- [16]. Thus the layer structure of Mt can serve as a perfect host for nZVI which thereby also increases the stability of the nZVI particle [16]. In addition, reflections at 2θ = 44.50°, 30° and 35° indicate the presence of elemental iron (α-Fe) along with iron oxides crystalline phases [maghemite (γ-Fe_2O_3) and/or magnetite (Fe_3O_4)] [2,17]. Further characterization of Mt-nZVI was done by using XPS. The broad survey scan containing surface composition (Fig. 3.4.4a) indicates the Mt-nZVI consists primarily of Fe and O, while a small amount of C, Cl, Si and Al were also detected, which might be contributed from Mt or the chemicals used. Additionally, to investigate the detected Fe and O, examination of the Fe2p (Fig. 3.4.4b) and O1s core level (Fig. 3.4.4c) was also evaluated. The spectra of O1s consist of peaks at 527.7, 530.5 and 532.6 eV and represent the binding energies

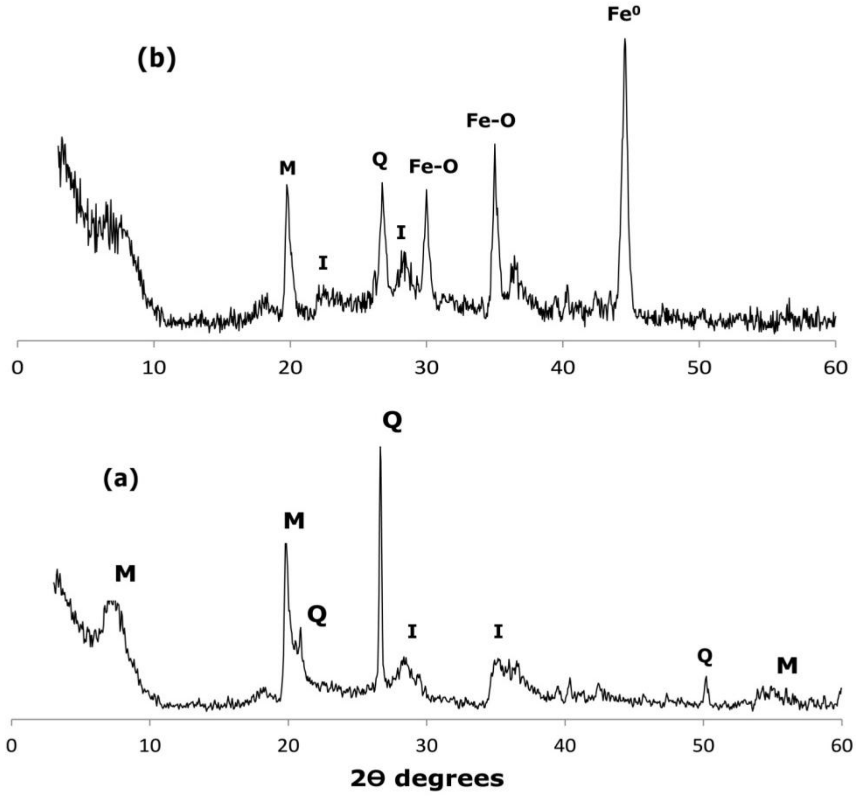

Figure 3.4.3. X-ray diffraction patterns of (a) Mt and (b) Mt-nZVI [M-montmorillonite, I-illite/muscovite, Q-quartz, Fe-O-iron oxide nanoparticles, Fe^0-nano zerovalent iron].

of O^{2-}, OH^- and physically or chemically adsorbed water, respectively [18]. The Fe2p photoelectrons shows distinct peaks corresponding to the binding energy of Fe $2p_{3/2}$ (ca. 711 eV) and $2p_{1/2}$ (ca. 725 eV) of oxidized iron [Fe(III)] while, a small shoulder at 707.2 eV indicate the peak of zero-valent iron ($2p_{3/2}$) [18–20]. Moreover, a shoulder at 719.9 eV was also observed and results from the overlap of the shakeup satellite of oxidized iron ($2p_{3/2}$) and zerovalent iron ($2p_{1/2}$) [17,19]. Thus the above X-ray analyses conclusively demonstrate that the nZVI, which is loaded on Mt has an envelope of Fe oxide likely in the form of Fe_2O_3, Fe_3O_4 and

FeOOH [17,18]. Earlier studies also reported that nZVI synthesized following similar reduction of iron salts by BH_4^- have such characteristic core shelled Fe(0) structure with Fe oxide/hydroxide envelope protecting the highly reactive Fe(0) from fast oxidation [17,19,20].

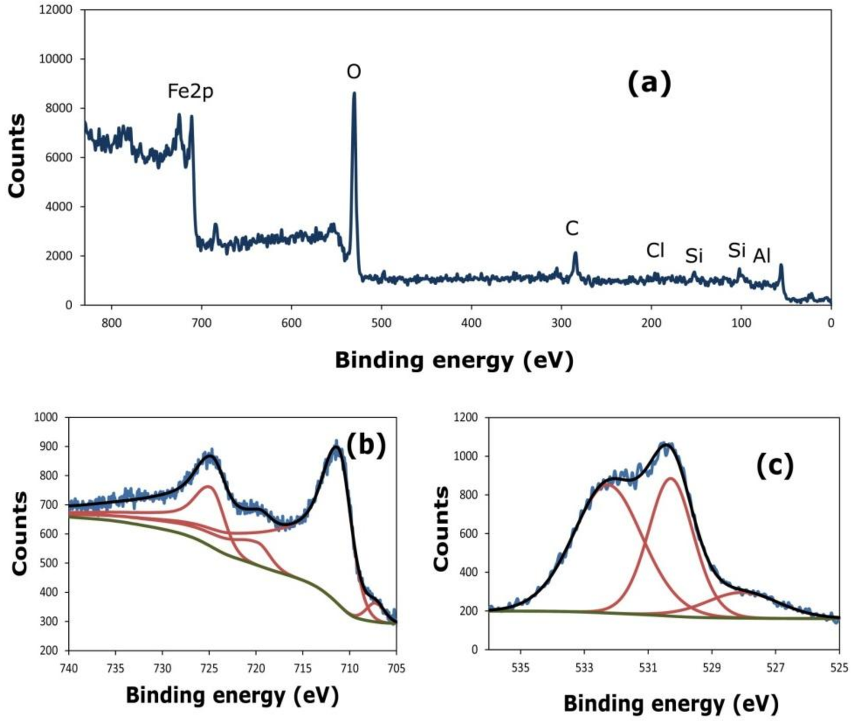

Figure 3.4.4. XPS spectra of (a) survey scan; (b) Fe2p region and (c) O1s region of unreacted Mt-nZVI

3.4.3.2 Adsorption kinetics of As onto Mt-nZVI

Adsorption of As(III) and As(V) was investigated by adding 1 g L^{-1} Mt-nZVI to a solution of 5 mg L^{-1} As at pH 7.0. For both As(III) and As(V), the initial fast uptake of As was followed by a much slower step (Fig. 3.4.5). The removal of As(III) and As(V) also decreased with decreasing concentration of Mt-nZVI from 1 to 0.1 mg L^{-1} (data not shown). Such slower uptake of As from solution with increasing time and reducing Mt-nZVI concentration may be attributed to the decrease in adsorption sites of Mt-nZVI [21,22].

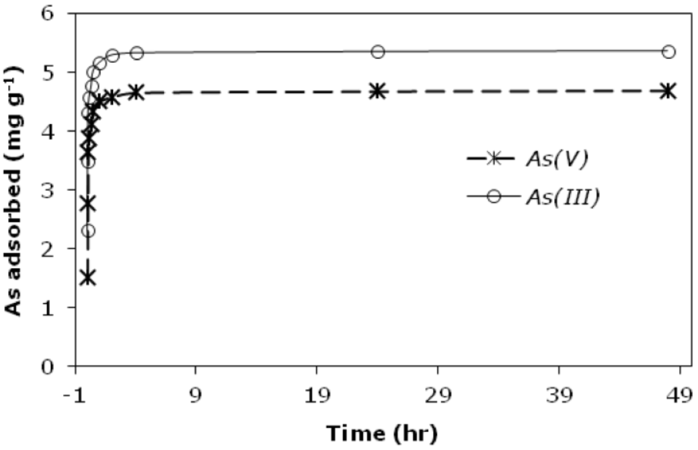

Figure 3.4.5. Kinetics of As(III) and As(V) adsorbed onto Mt-nZVI [Reaction condition: 2.0 mgL^{-1} of As(III)/As(V), 1.0 gL^{-1} of Mt-nZVI, pH 7.0, 25^{o}C]

The data obtained from adsorption kinetics were fitted with pseudo-first order, pseudo-second order and intra particle diffusion models. Due to poor regression coefficient (R^2) values for pseudo-first order and intra particle diffusion models were not included in the text. The pseudo-second order rate equation can be written as follow:

$$dq_t/dt = k_2(q_e - q_t)^2 \qquad (2)$$

where, q_e and q_t are the amount of As adsorbed (mg g^{-1}) at equilibrium and at time t (hr) respectively and k_2 (g mg^{-1} hr^{-1}) represents the pseudo-second-order rate constant. Integrating Eq. (2) with the boundary condition of $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ and on subsequent rearranging, the following linear form is obtained.

$$t/q_t = 1/k_2q_e^2 + t/q_e \qquad (3)$$

The plot of t/q_t vs t for both As(III) and As(V) is shown in Fig. 3.4.6a. The values of q_e and k_2 were calculated from the slope and intercept of the curve respectively, and are listed in Table 3.4.2. The positive correlation between k_2 vs concentration of Mt-nZVI (Fig. 3.4.6b) suggests that the overall rate of As adsorption onto Mt-nZVI was controlled by pseudo-second order reaction mechanism.

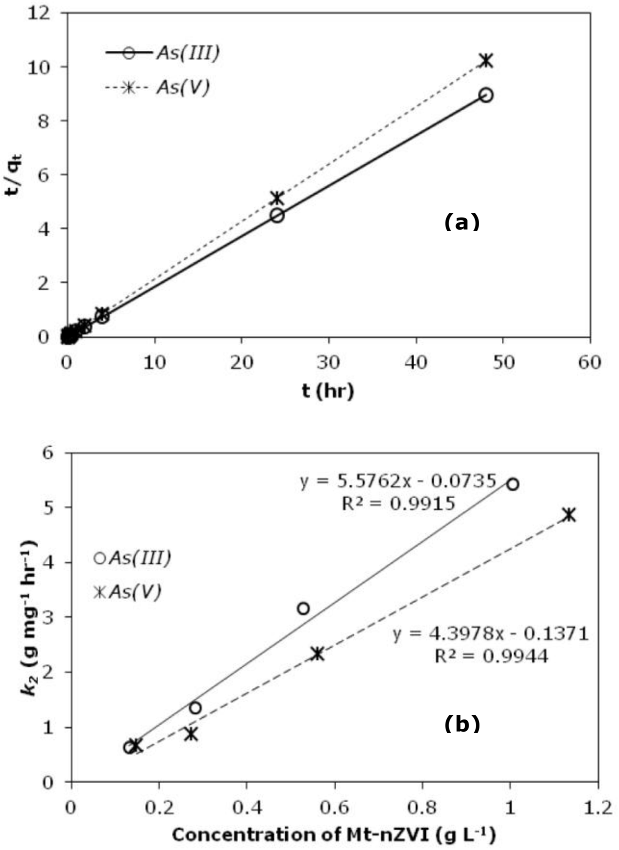

Figure 3.4.6. Plot of (a) pseudo-second-order kinetics of As(III) and As(V) adsorption onto Mt-nZVI; (b) pseudo-second-order rate constant as a function of concentration of Mt-nZVI.

Table 3.4.2. Pseudo-first order rate constant (K_{ads}) for As(III) and As(V) adsorbed on Mt-nZVI

As (III)				As (V)			
Mt Fe (gL^{-1})	k_2 (g mg^{-1} hr^{-1})	q_e (mg/g)	R^2	Mt Fe (gL^{-1})	k_2 (g mg^{-1} hr^{-1})	q_e (mg/g)	R^2
0.13	0.62	27.70	1.00	0.15	0.67	20.1	1.00
0.28	1.36	15.67	1.00	0.27	0.87	13.4	1.00
0.53	3.16	8.79	1.00	0.56	2.34	7.87	1.00
1.00	5.42	5.37	1.00	1.13	4.87	4.70	1.00

3.4.3.3 As adsorption edge

Adsorption edge experiments were performed in the pH range from 4 to 10 for both As(III) and As(V). Mt-nZVI showed higher affinity towards As(III) than As(V) and the adsorbed amount remained nearly constant from pH 4 – 8.5 for both As(III) and As(V) while decreasing sharply at higher pH (Fig. 3.4.7). Similar pH dependent As adsorption on nZVI has been documented previously [2,3].

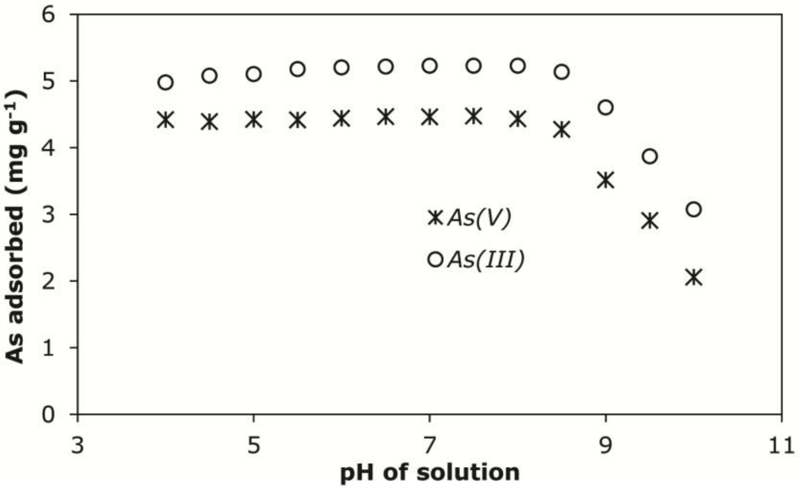

Figure 3.4.7. Adsorption edges of As(III) and As(V) on Mt-nZVI.

The As(V) adsorption edge curve can be explained by considering ionization of oxy-anionic species of As in solution as well as Mt-nZVI surface charge. As(V) exhibits varying forms in aqueous solution and $H_2AsO_4^-$ (pK_{a1} = 2.3), $HAsO_4^{2-}$ (pK_{a2} = 6.8) and AsO_4^{3-} (pK_{a3} = 11.6) are the predominant species when the pH is increased from acidic to alkaline range [23]. On the other hand, pH of zero point charge (pH_{ZPC}) of the synthesized Mt-nZVI was determined to be 8.2. Solid surfaces are positively and negatively charged at pH below and above pH_{ZPC} respectively. Thus on increasing pH> 8.5, negatively charged Mt-nZVI surface shows less attraction towards oxy-anionic As(V) species and as a result, adsorption of As(V) decreases. According to pe-pH diagram, H_3AsO_3 and $H_2AsO_3^-$ are the dominant As(III) species adsorbed at pH< 9 and at pH 9-12 respectively [24]. So at pH> 9, electrostatic repulsion takes place between $H_2AsO_3^-$ species and the negatively charged Mt-nZVI surface, and consequently adsorption decreases. However for pH below 9, electrostatic attraction and repulsion is not important for neutral H_3AsO_3 species as the adsorption is dominated by deprotonation/dissociation of H_3AsO_3 before surface complexation with Mt-nZVI [25]. For highly acidic medium, deprotonation of H_3AsO_3 is suppressed and therefore there is a slight decrease of adsorption of As(III) as the acidity of the solution is increased. Thus the maximum adsorption of As(III) occurs close to the near neutral pH range (6.5–8.0).

3.4.3.4 Arsenic adsorption isotherm

Langmuir and Freundlich isotherm equations were used to quantitatively describe the effect of increased aqueous As concentrations on the surface loadings of As(III) and As(V) on Mt-nZVI. While Langmuir model assumes monolayer adsorption onto homogeneous adsorbent surface with finite number of identical sites, Freundlich model is empirical in nature and allows multilayer adsorption. The linear form of Freundlich model is given as:

$$\log q_e = \log K_f + (1/n) \log C_e \qquad (4)$$

where, q_e is the amount of As uptake at equilibrium (mg g^{-1}), K_f and n are the Freundlich constant related to adsorption capacity and adsorption intensity respectively, and C_e is the equilibrium concentration of As in liquid phase (mg L^{-1}). The linear form of the Langmuir equation is expressed as:

$$Ce/q_e = (Ce/q_m) + (1/K_L q_m) \qquad (5)$$

where, K_L is the Langmuir constant related to the energy of adsorption and q_m is the monolayer maximum adsorption capacity (mg g^{-1}).

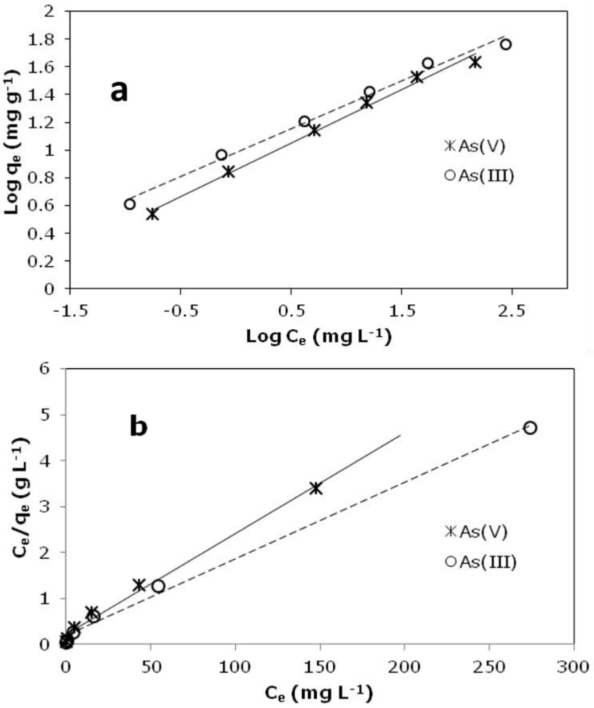

Figure 3.4.8. (a) Freundlich and (b) Langmuir adsorption isotherm of As(III) and As(V) on Mt-nZVI at pH 7.0, equilibration time 4 hr.

The adsorption data fitted well with both the models (Fig. 3.4.8). The values of the constants calculated from the isotherms are listed in Table 3.4.3. The maximum adsorption capacity was found to be 59.9 mg g^{-1} and 45.5 mg g^{-1} for As(III) and As(V) respectively. The process of adsorption is considered favorable and are indicative of chemisorption if the value of *n* is in the range of 0 – 10 [26]. Our results show that the values of *n* are within this range (Table 3.4.3), thus signifying favorable adsorption of As(III) and As(V) onto Mt-nZVI. The applicability of the Langmuir adsorption isotherm is studied by the dimensionless equilibrium constant called separation factor (R_L) and is expressed as:

$$R_L = 1 / (1 + K_L C_0) \qquad (6)$$

The value of R_L for adsorption of As(III) and As(V) on Mt-nZVI was in between 0 and 1 (Table 3.4.3), which further indicates favorable adsorption of As [26].

Table 3.4.3. Parameters of Langmuir and Freundlich adsorption isotherm equations

	Langmuir constants				Freundlich constants		
	Q_m (mgg^{-1})	K_L (Lmg^{-1})	R_L	R^2	n	K_f (Lg^{-1})	R^2
As (III)	59.9	0.003	0.98 - 0.48	0.99	2.90	9.64	0.99
As (V)	45.5	0.005	0.98 - 0.52	0.99	2.60	7.24	0.99

3.4.3.5 Characterization of the reaction product

To characterize the As species after reaction and to delineate the mechanism of As removal from aqueous solution, XPS analysis of the reacted Mt-nZVI was performed. The survey spectrum of unreacted Mt-nZVI (Fig. 3.4.4a) shows no peak in the range of 39 - 48 eV indicating that Mt-nZVI has not been contaminated with As. A number of previous studies have shown the reduction of As(V) by ZVI under anoxic conditions [4,27,28], however for an open batch reactor, no reduction of As(V) has been documented [21,29]. Our results showed no reduction of As(V) even after 72 hrs of reaction and only one doublet peak, consisting of the overlapping As(V) 3d5/2 and As(V) 3d3/2 peaks was observed (Fig. 3.4.9a). On the other hand, for As(III) reacted Mt-nZVI, the XPS analysis also showed the presence of As(V) alone, suggesting complete oxidation of As(III) by Mt-nZVI surface (Fig. 3.4.9b). Similar results in open atmospheric condition were also found by other researchers [2,30,31].

In aqueous phase, Fe(0) spontaneously reacts with water and oxygen to produce Fe^{2+} and Fe^{3+} which on further reaction, forms a series of iron oxide, hydroxides and oxyhydroxides such as ferrous hydroxide, ferric hydroxide, iron rusts, magnetite, lepidocrocite, maghemite; depending upon the redox and pH of the solution [2,22,27,29].

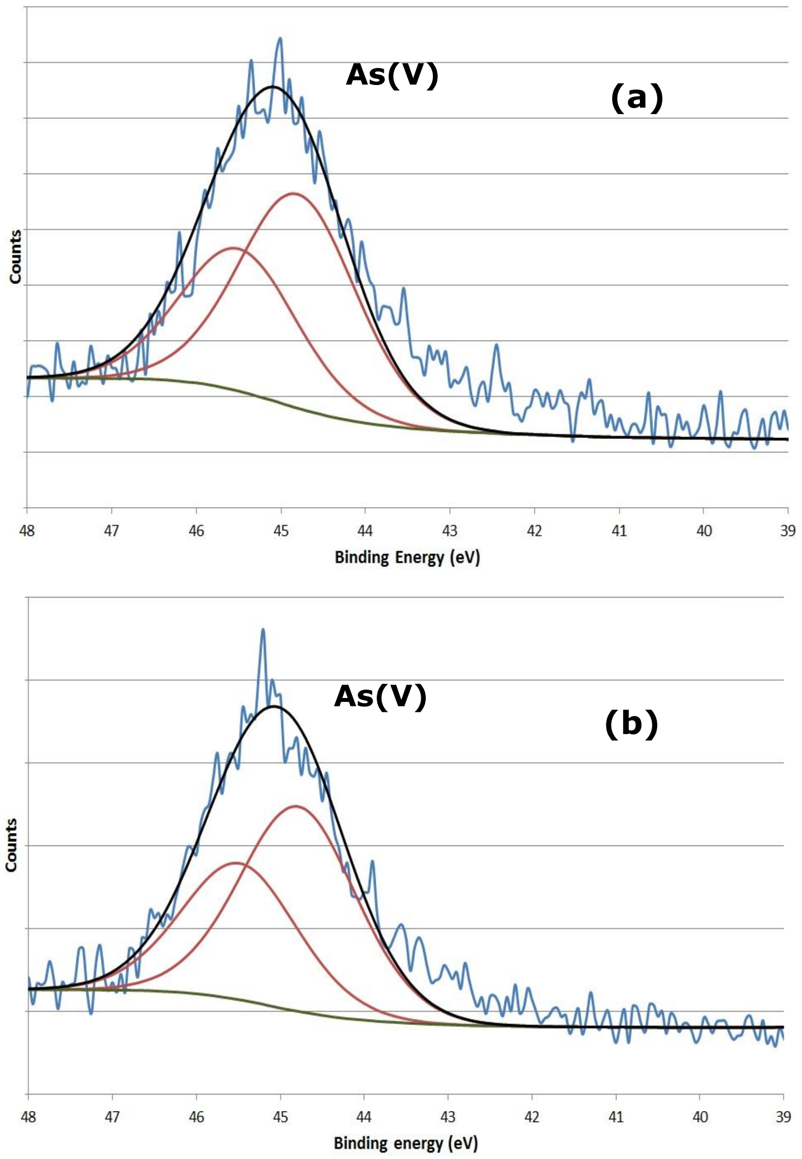

Figure 3.4.9. As3d XPS spectra of Mt-nZVI after reaction with 100 mgL^{-1} (a) As(V) and (b) As(III) at pH 7.0.

$2\ Fe(0) + O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4OH^-$ (7)

$4\ Fe^{2+} + 2\ H_2O + O_2 \rightarrow 4\ Fe^{3+} + 4\ HO^-$ (8)

Earlier studies have shown that As(V) and As(III) are capable of forming inner sphere bidentate surface complexes with the surface bonded OH$^-$(> Fe-OH) [21,29]. Thus the hydroxyl group at the Mt-nZVI/H$_2$O interface forms surface complexes with the aqueous As and thus subsequently remove As from the aqueous solution. Moreover As may also be trapped on the matrix of the growing corrosion product and are thus removed from the solution via precipitation/co-precipitation [3,32]. On the other hand, the Fe^{2+} formed from oxidation of Fe(0) also reacts with water and O_2 to produce oxidizing intermediate in solution such as H_2O_2, HO^{o}, O_2^{o-} [30,31]

$Fe^{2+} + O_2 \rightarrow Fe^{3+} + O_2^{o-}$ (9)

$Fe^{2+} + O_2^{o-} + 2\,H^{+} \rightarrow Fe^{3+} + HO^{o} + HO^{-}$ (10)

$Fe^{2+} + O_2^{o-} + 2H^{+} \rightarrow 2Fe^{3+} + H_2O_2$ (11)

These oxidizing intermediate are responsible for the oxidation of As(III) to As(V) following Fenton like reaction mechanism [31,33]. Thus our experimental finding shows that As(V) and As(III) in aqueous solution forms surface complexes with Mt-nZVI and the As(III) are consecutively oxidized to As(V) by oxidizing intermediate that are produced *in-situ* from the oxidation of Fe(0).

3.4.3.6 Effect of coexisting oxy-anions

Phosphate (PO_4^{3-}), sulphate (SO_4^{2-}), nitrate (NO_3^{-}) and bicarbonate (HCO_3^{-}) represent the common oxy-anions found in As rich natural groundwater [34–36] and the chemical competition of these anions on the adsorption of As are shown in Table 3.4.4. Our results suggest that NO_3^{-}, SO_4^{2-}, HCO_3^{-} have insignificant effect on adsorption for both the species of As on Mt-nZVI (Table 3.4.4). However, the adsorption of As decreased with the increase of PO_4^{3-} concentration. On increasing PO_4^{3-} concentration from 2 - 5 mg L^{-1}, the percentage reduction of As adsorption increased from 11.0% to 28.4% for As(V) and 13.0% to 35.5% for As(III). Similar decrease of As adsorption on Fe containing adsorbent in presence of PO_4^{3-} in aqueous solution has been reported previously [3,37]. PO_4^{3-} like H_3AsO_3 and $H_2AsO_4^{-}/HAsO_4^{2-}$ forms inner sphere complex and thus compete for the adsorption site on the adsorbent surface [37,38].

Table 3.4.4: Effect of oxy-anion on adsorption of As(III) and As(V) on Mt-nZVI

Anions	Concentration (mgL^{-1})	$[As (V)] = 5 mgL^{-1}$		$[As (III)] = 5 mgL^{-1}$	
		Amount adsorbed (mgg^{-1})	% reduction of As (V) adsorbed	Amount adsorbed (mgg^{-1})	% reduction of As (III) adsorbed
None	0	0.96	0.00	0.97	0.00
PO_4^{3-}	2	0.86	11.0	0.85	13.0
	5	0.69	28.4	0.63	35.5
HCO_3^-	250	0.91	5.76	0.91	6.00
	500	0.89	7.53	0.90	7.63
SO_4^{2-}	10	0.92	4.35	0.93	4.56
	20	0.90	6.79	0.90	7.84
NO_3^-	5	0.94	2.60	0.94	3.74
	10	0.92	4.51	0.92	5.53

Reaction condition: pH- 7.0, reaction time- 4 hr.

3.4.3.7 Applicability of Mt-nZVI to natural system

Batch studies on As removal were carried out using As-spiked tap water and contaminated groundwater obtained from West Bengal, India. The result shown in Table 3.4.5 suggest that Mt-nZVI can act as promising adsorbent for removal of As from contaminated waters to provide safe levels of As concentration below 10 μg L^{-1}.

Table 3.4.5: Application of Mt-nZVI to As-spiked and natural water samples

Sample	Initial concentration (μgL^{-1})		Initial total As concentration (μgL^{-1})	Final total As concentration (μgL^{-1})	% As removed
	As (III)	As (V)			
As spiked tap water	369	398	767	8.58	98.9
ACG I	143	85.1	228	1.28	99.4
ACG II	327	102	429	2.78	99.3
ACG III	199	96.4	295	1.29	99.6
ACG IV	86.2	36.8	123	0.64	99.5

ACG: As contaminated groundwater
Reaction condition:
pH- 7.0, [Mt-nZVI]- 1gL^{-1}, reaction time- 4 hr.

3.4.3.8 Reusability of the composite

The spent Mt-nZVI was regenerated by shaking the As loaded adsorbent with 0.1 M NaOH solution for 4 hrs. Around 50 % of the total adsorbed As was desorbed within 4 hr (Fig. 3.4.10). To test the integrity of the material, repeated adsorption-desorption experiments had been carried out. It was seen that even after 5 cycles, the performance of Mt-nZVI was not appreciably deteriorated and there was no decrease in the uptake of both As(III) and As(V) (Fig. 3.4.10). This indicates that the synthesized Mt-nZVI was chemically and mechanically robust enough for treatment of As in drinking water. Thus additional advantage results from the repeated utilization of the used material for such water treatment.

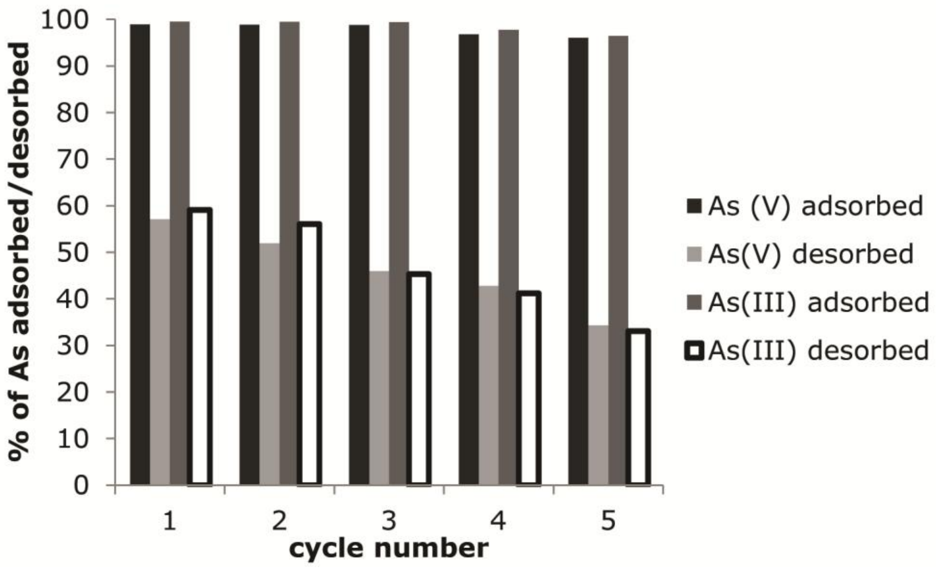

Figure 3.4.10. Regeneration of Mt-nZVI adsorbent.

3.4.4. CONCLUSIONS

Mt-nZVI adsorbent was prepared by loading nZVI onto Mt via chemical reduction of Fe^{3+} by BH_4^-. SEM image revealed dispersed nZVI on the Mt surface with decreased agglomeration and dispersion compared to nZVI alone. XRD and XPS analyses confirmed the presence of a Fe(0) core-iron oxide/hydroxide montmorillonite compound in the adsorbent material. Batch adsorption studies showed that Mt-nZVI nanoparticles are effective in removal of both As(III) and As(V) with fast kinetics and the rate of adsorption that followed pseudo-first order with slightly higher rate constant (K_{ads}) for As(III) than As(V). The adsorbent has high affinity for both As(III) and As(V) over a wide range of pH which is decreased at pH> 9. The adsorption isotherm results fitted well with Langmuir and Freundlich models and the maximum adsorption capacity for As(III) and As(V) was 59.9 mg g^{-1} and 45.5 mg g^{-1} respectively. The Mt-nZVI upon reacting with water and oxygen forms a number of iron corrosion product and provides new adsorption sites for As(III) and As(V). While reduction of As(V) was not observed in our experimental condition, complete oxidation of As(III) to As(V) took place in presence of Mt-nZVI, as evidenced from XPS analyses. Phosphate in solution had an inhibitory effect on the adsorption of As, suggesting competition for adsorption site. The Mt-nZVI was effective to reduce As below 10 μgL^{-1} from synthetic as well as As contaminated groundwater at neutral pH and the spent (As loaded) adsorbent could be effectively regenerated using 0.1 M NaOH solution. Thus we hypothesize that the Mt-nZVI reported in this chapter are relevant for preparing low cost adsorbent to remediate inorganic As from contaminated water.

3.4.5. REFERENCES

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CHAPTER 4: GENERAL DISCUSSION

Arsenic has gained significant importance in the last past decades because of its potential toxicity. It is now well known that the potential health impact of chronic arsenic exposure includes disorders of the circulatory and nervous system as well as cancer of the skin, urinary bladder, kidney, lung, and liver. There are large numbers of aquifers across the world with elevated levels of arsenic having different groundwater characteristics. Therefore the scientific communities are now engaged to understand the different release mechanism that result in high concentration of arsenic in groundwater of various parts of the world. The situation has now become more complicated when different mechanism has been shown to be responsible for the release of high arsenic in same area.

Currently in the state of West Bengal, India, it has been estimated that more than 25 million people are exposed to arsenic concentration greater than the WHO guideline of 10 μgL^{-1}. In West Bengal, there are reports that have documented high arsenic concentration in groundwater from the district of Maldah, Murshidabad, Nadia, North & South 24 Parganas, Burdwan, Howrah and Hooghly, and more recent observations from Kolkata, Koch Bihar, North & South Dinajpur districts. The distribution of groundwater arsenic in the area is heterogeneous and patchy with arsenic hot-spots being interspaced between low/safe arsenic areas. In recent years, several hypotheses have been put forwarded to explain the occurrence of high arsenic in West Bengal groundwater. Among them, the iron reduction model catalyzed by the oxidation of organic matter is now widely accepted in the scientific community. Nevertheless, anaerobic metal-reducing bacteria were proved to be playing an important role in releasing arsenic to groundwater. However there are several complexities and observations that cannot still be explained by considering the reduction model. For example, if the Fe-reduction model were solely responsible for the high occurrence of arsenic in groundwater, the concentrations of iron and arsenic should be related. Although the groundwaters were reported to contain high arsenic and iron concentrations, in some cases, there actually exists lack of correlation between these two elements which cannot be explained by the above model. Moreover, the availability of the organic matter is another important factor and ambiguities exist upon its source and the distribution. Therefore to understand the occurrence of high arsenic in the groundwater, a comparative study of the groundwater of geologically different areas were carried out.

With this objective in mind, we studied the groundwater samples of Debagram, Chakdaha and Baruipur areas in West Bengal. The surrounding environment of the selected areas were quite different with Debagram located ~10km east of the major meander belt of the Bhagirathi-Hooghly river, while Chakdaha is located beside the recent meander and the present river channel of the Bhagirathi Hooghly river. On the other hand, Baruipur is located at the delta front and proximity to the Bay of Bengal in the south. The chemical analyses of groundwater from the studied areas showed the reducing nature of groundwaters with negative Eh potentials. It is known that the chemical evolution of the groundwater result from the interaction of several chemical processes and in this study, it was seen that the groundwater was influenced from silicate weathering to carbonate dissolution for all the areas. However there were few shallow groundwater from Baruipur that showed evidence of evaporate dissolution.

The separation of the inorganic arsenic showed As(III) was always predominant over As(V) in the groundwater of our study areas. The co-existence of both forms of arsenic in reduced groundwater is known to be due to slow reduction kinetics of As(V) released during ongoing reductive dissolution of Fe-oxyhydroxides and for the seasonal fluctuation of subsurface redox conditions with the large-scale groundwater abstraction for domestic use and irrigation which may partially diminish the reductive nature of the aquifer. This has been reflected from the As(III)/As(V) ratio which was highly variable in the shallow aquifers and reaches a steady value with depth. Under such seasonal groundwater fluctuation, large amount of organic matter are introduced into the shallow aquifer as a result of groundwater recharge. However, the deeper aquifers showed less reducing nature compared to the shallow aquifers and therefore, Fe-oxyhydroxide reduction seems less probable for the release of arsenic.

Thermodynamic calculations showed the groundwater to be in equilibrium with carbonate minerals, thereby suggesting that the groundwater chemistry is controlled by the precipitation/dissolution of carbonate minerals. The groundwater is also supersaturated with respect to Fe-oxide/hydroxide minerals, suggesting precipitation of Fe(III) phases in groundwater. Except for Chakdaha, in Debagram and Baruipur, there was lack of correlation between arsenic and iron which suggested that desorption of arsenic from Fe-oxyhydroxides may not be the sole process accounting for the mobilization of arsenic in groundwater. For all the studied areas, strong positive correlation was observed between bicarbonate and arsenic linked with high intercept values. Bicarbonate in groundwater result from the oxidation of organic matter associated with the reductive dissolution of Fe-oxyhydroxides and from the dissolution of metal carbonates. Thus the samples with bicarbonate concentrations below the intercept are resulted from the dissolution of carbonate minerals, whereas the sample with bicarbonate concentrations above the intercept are cumulatively contributed by the degradation of organic matter and the carbonate dissolution. In Chakdaha, bicarbonate concentrations below the intercept yielded low arsenic concentration in groundwater. However, in case of Baruipur and Debagram, there were few tube wells which showed high arsenic concentrations thereby, suggesting increase in arsenic solubility with carbonate mineral dissolution. Therefore while the release of arsenic in the groundwater of Chakdaha were mainly governed by the reductive dissolution of Fe-oxyhydroxide, in case of Debagram and Baruipur were due to the complex combination of processes such as carbonate mineral dissolution and reduction of Fe-oxyhydroxides.

The study area Chakdaha and Debagram is situated in the close proximity to the river Bhagirathi-Hooghly. The places are characterized by several geomorphic features which are mainly formed due to varied hydrodynamic condition of the river, e.g. sediment load, stream movement and stream current. As a result, fine grained colloidal sized particles and organic matter may deposit due to swampy condition together with the development of a large vegetative cover which makes these zones highly anaerobic. Such anaerobic condition with the availability of organic matter facilitates the reductive dissolution of Fe-oxyhydroxides. The statistical analysis of the groundwater in Chakdaha shows that the groundwaters in palaeochannel aquifer contain considerably high arsenic concentrations compared with the groundwaters in the palaeo-interfluvial aquifers. However in Debagram, we observed no significant control of subsurface sedimentology on arsenic distribution and heterogeneity and were perhaps due to the location of the study area which was outside the proximity to recent meander belts of the Bhagirathi-Hooghly River.

The resulting geochemical processes may further be complicated by the presence of surface-derived (i.e. anthropogenic) source of dissolved organic carbon in the aquifer which enhances the arsenic release process. In Chakdaha, our data showed the link between local land use and arsenic distribution in shallow aquifers, and for wells located close to the source of sewage and/or domestic wastes (i.e. sanitation) has the highest mean arsenic concentration compared with the wells located close to pond and habitation. On the other hand, in Debagram, most of the sampling points were located within the habitation where surface-derived source of DOC from untreated sewage and/or domestic wastes may make way to the shallow aquifer and provide conditions necessary for Fe-oxyhydroxides reduction to occur and release arsenic in to groundwater. In Baruipur, we observed palaeo-channel settings with strong control of subsurface sedimentology where groundwater contains high arsenic concentrations as well as the effect of surface-derived organic, which might be leached to the shallow aquifer and thereby controlling the redox reactions.

Thus the groundwater chemistry in West Bengal and the arsenic release mechanism is complicated and there are multiple processes that act simultaneously for the elevated levels of arsenic. Unfortunately in the state of

West Bengal, large amount of populations are dependent on groundwater for drinking purpose. Moreover arsenic contaminated groundwater is used for irrigation where a substantial amount of arsenic is accumulated in the irrigated crops. In West Bengal, rice is not only the widely cultivated crops but also the most consumed staple food of the population. Rice consumption accounts to an average of 72.8% of the daily caloric intake per capita. Rice irrigation requires high amount of water with continuous flooding during the growing season. The use of large amount of arsenic rich water not only increases the arsenic loading of the soil but also elevates the arsenic content in rice grain. Therefore the exposure level of arsenic is quite high and poses a threat to the residents of the area.

To measure the arsenic exposure, wide range of biological fluids and tissues has been used as biomarkers in the past so as to monitor the behavior of arsenic inside the body. However each of the previously used biomarkers represents some drawbacks either in the form of complicated analysis of arsenic or misinterpretation of data. Saliva is one biological fluid that has not been used extensively for arsenic exposure. Saliva has advantage over other conventional arsenic biomarkers because of easy sample collection procedure, storage and analysis. It is also known that saliva reflects the body burden of the metals which other conventional biomarkers fails to light upon. Thus we measured the arsenic in the saliva samples collected from the residents of arsenic affected areas of West Bengal. The participants were chosen with varying degree of arsenic induced skin lesions and also without skin lesions. Such criteria helped us to compare the cases and controls that were exposed to compatible levels of arsenic exposure. Our developed method of measuring arsenic in saliva was robust with high sensitivity and low detection limit. The addition of alcohol in the samples prior to analysis in ICP-MS increased the arsenic sensitivity which was attributed to the charge transfer reaction between the carbon and the ^{75}As in the plasma. For internal standard, rhodium was found to be better suited. The method show good linear characteristics over a wide range of arsenic concentration. For the estimate of arsenic exposure, water and rice was considered as the principal sources. Our analysis showed that salivary arsenic was a good predictor of the arsenic exposure. Cases of skin lesion and male participants were found to have higher concentration of salivary arsenic compared to controls and female counterparts. Additionally, urine which is a well-known biomarker of current arsenic exposure, the good correlation of the salivary arsenic with urinary arsenic further strengthen the case of arsenic in saliva as a biomarker of arsenic exposure.

Later we tried to speciate the various forms of arsenic is saliva so as to estimate the fate of arsenic inside the body and also to predict the individual susceptibility. We used a PRP-X100 anion exchange column to separate the arsenic species where the outlet of the column was directly connected to the nebulizer of the ICP-MS. A gradient flow of 10mM to 50 mM $(NH_4)_2CO_3$ at pH 9.0 was used as a mobile phase. According to the charge and acidity of the arsenic species at this particular pH, As(III), DMA, MMA and As(V) were eluted in sequence. At the working pH, AsB exhibit neutral form and is eluted in the void volume. Although there has been studies that have detected MMA(III) and DMA(III) in various biological structures and tissues, these were not included in our study since such species are normally found when the populations are chronically exposed to very high levels of arsenic. The analysis of the saliva samples depicted that As(V) was the major species and the fraction of inorganic species [As(V) and As(III)] accounts to half of the total salivary arsenic. The availability of sea foods are very rare in our study area and as seafood are the main source of AsB, this species was often undetected in the saliva samples.

Statistical analysis of the results showed significant positive correlation of the ingested arsenic with all the salivary arsenic species including MMA and DMA. The results suggested that the methylated arsenic results from the methylation of the ingested arsenic. Male and cases of skin lesion showed higher concentration of As(III) and As(V) while female and control without skin lesion showed higher concentration of MMA and DMA. These results indicate that female and control have higher methylation capacity compared to their male and cases counterparts. Thus we find that measuring the different forms of arsenic in the saliva may help us to understand the individual susceptibility where higher arsenic exposure and a lower methylation capacity are implicated in the development of arsenic-induced health effects.

Lastly in this thesis, we develop an adsorbent to reduce the concentration of arsenic in aqueous solution. Adsorption is the preferred method among all the removal techniques because of the simplicity, treatment stability and cost effectiveness. Nano zerovalent iron (nZVI) has been widely used for arsenic removal from aqueous solution. The large active surface area and high arsenic adsorption capacity makes nZVI a promising material for removal of arsenic from aqueous solution. However, there are several limitations for the direct use of nZVI. Among them are the tiny particle size and powder state along with lack of durability and mechanical strength. Moreover nZVI tends to agglomerate during preparation and thus there is a decrease in reactivity of the particle and also poor mobility and transport to the contaminated area for in-situ remediation. However, loading nZVI onto supporting material has been shown to be a potential method to overcome such problem.

Therefore we prepared nZVI on montmorillonite by chemical reduction of Fe^{3+} with BH_4^-. The characterization of the adsorbent showed the existence of core shell Fe(0) structure with an outer oxide/hydroxide shell. Further analysis suggested that the layer structure of the clay can serve as a perfect host for nZVI where some of the interlayer cations were replaced with the Fe^{3+} and then successively reduced to nZVI. Batch experiments revealed adsorption kinetics followed pseudo-second order rate equation with high affinity towards both As(III) and As(V) over a wide pH range (4-8) which was decreased at pH>9. Such decrease in adsorption capacity was because of the increased repulsion between the negatively charged arsenic species at pH>9 in solution and the negatively charged adsorbent above the isoelectric point (8.2). As(III) showed higher adsorption than As(V) where the adsorption capacity calculated from the Langmuir adsorption isotherm was found to be 59.9 and 45.5 mg g^{-1} for As(III) and As(V) respectively at pH 7.0.

nZVI reacts with water to form a number of iron oxide and hydroxides and these acts as suitable sites for arsenic adsorption. It is well known that As(V) and As(III) are capable of forming inner sphere bidentate complex with the hydroxyl group at the nZVI/H_2O interface and is therefore removed from aqueous solution. From our study we find that in open atmospheric condition, As(V) reduction did not take place but As(III) was rapidly oxidized to As(V). This was due to the reaction of the nZVI with oxygen and water which produces oxidizing intermediate and these intermediates are responsible for the oxidation of As(III) following Fenton like reaction mechanism. Phosphate in solution decreased the adsorption of arsenic and was attributed because of the competition for the same adsorption site on the adsorbent surface. However the presence of other anions didn't show pronounced decrease on arsenic absorption. The montmorillonite-nZVI was also shown to be applicable to reduce arsenic from contaminated groundwater from West Bengal below WHO safe limit. Thus the synthesized montmorillonite-nZVI acts as potential adsorbent to reduce elevated levels of arsenic in groundwater and provide safe water to the community.

CHAPTER 5: GENERAL CONCLUSIONS

The main conclusions of the present thesis are as follows:

1. Reductive dissolution of iron oxyhydroxides catalyzed with the oxidation of organic matter was the main mechanism for the elevated arsenic concentration in all the studied groundwater. However the source, distribution and the type of the available organic matter was linked with geomorphological features (e.g. abandoned channels) and local anthropogenic activities (e.g. sanitation, domestic wastes, etc.).

2. The release of arsenic in groundwaters of Debagram and Baruipur were complex and due to the combination of processes such as carbonate mineral dissolution and reduction of Fe-oxyhydroxides. Thus one single arsenic mobilization mechanism was not able to explain the release of arsenic of these areas but was controlled by simultaneous occurrence of multiple processes.

3. Our developed method for determination of total arsenic in saliva was able to quantify low levels of arsenic in the collected saliva samples. While Rhodium was best suited as an internal standard, the addition of ethanol to the sample prior to analysis increased the sensitivity of arsenic in ICP-MS. Arsenic in saliva displayed good correlation with the ingested inorganic arsenic and also with urinary arsenic, which is already an established biomarker of arsenic exposure. Thus salivary arsenic was proved to be an effective indicator for arsenic exposure in a population based study.

4. The arsenic speciation protocol involving gradient elution with stepwise increase in mobile phase concentration was applied for saliva to speciate arsenobetaine, As(III), DMA, MMA and As(V). $(NH_4)_2CO_3$ as mobile phase has an advantage as it leaves little residue on the sampler and cones of the ICP-MS and thus there is little signal drift even after prolonged use. The speciation method was robust with low detection limit and was tested with spiked non-contaminated saliva samples which gave satisfactory results. Our results showed As(V) was the major arsenic species in saliva for our studied population and the

amount of inorganic arsenic was approximately half of the total salivary arsenic while the other organo arsenic species comprise the rest.

5. Male and cases of skin lesion showed higher concentration of salivary arsenic and decreased tendency to methylate ingested arsenic compared to female and controls without skin lesion. Therefore arsenic species in saliva was able to provide insight on the internal dose and any individual differences in susceptibility to arsenic exposure.

6. nZVI was successfully loaded onto montmorillonite (Mt-nZVI) with decreased agglomeration and dispersion compared to nZVI alone. The adsorbent material showed Fe(0) core-iron oxide/hydroxide montmorillonite structure with high affinity for As(III) and As(V).

7. The Mt-nZVI upon reacting with water and oxygen forms a number of iron corrosion product and these acts as the potential adsorption site for As(III) and As(V). While reduction of As(V) was not observed in our experimental condition, surface oxidation of As(III) to As(V) took place in presence of Mt-nZVI. The Mt-nZVI was also effective to reduce arsenic below 10 μgL^{-1} from arsenic contaminated groundwater of Bengal at neutral pH.

CHAPTER 6: FUTURE TRENDS

The future scope of the potential research work is as follow:

1. Study of stable isotope ratios and radioactive isotope compositions in arsenic enriched groundwater. Such study can delineate the groundwater recharge and as a result, better identify the possible sources of organic carbon input that catalyzes arsenic mobilization process. Moreover, from the isotope signature of deeper and shallow aquifer, the influence of anthropogenic activities (such as groundwater abstraction, infiltration from nearby sources) can accurately be predicted.

2. It would be interesting to study the arsenic composition of saliva collected from people of different ethnic groups. Since we have already demonstrated saliva as a suitable biomarker of arsenic exposure, such study on different arsenic exposed group would enable us to have a better insight on the arsenic metabolism process.

3. Our laboratory scale experiment has showed Montmorillonite-nano Zero Valent Iron (Mt-nZVI) to be a potent absorbent to decrease the concentration of arsenic in aqueous solution. However, field based experiment where the adsorbent acting as permeable reactive barrier can be one of the interesting aspects of research and also a groundwater arsenic remediation technique.

Finally it is the time to show my gratitude to all the people that have been with me in this incredible journey of my life. This present thesis would not have been possible without the help and co-operation from a lot of people. During the years of my doctoral study, I came to meet with some lovely people and my interactions with all of them have only increased my passion and energy towards my work.

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ICP or other things, I would confidently discuss with her and every time, she would help me to the best off her abilities. I came to know many things from her particularly technical details related to speciation. There would also be a smiling girl and whatever happened, you would always see a smile in Aida´s face. She has the natural tendency to go deep in the details of the matter and hence is the ``CSI women´´. Our morning cup of *caffe amb llet* at the parc cafeteria was refreshing and was the perfect place to speak our mind. Every day I would come up with some strange questions about Catalan and its pronunciation and both Carme and Aida would be kind enough to give me some information so as to increase my knowledge about the language. As a result I developed immense skill in saying *que si que si, ja està* and *tigismiguis*. Anna was always been very polite. Never have I seen her angry and hence I could always seek for her help. Dolors was very sporting but little *cansada*. My conversation with Dolors would last long and we would use much of hand movement and signs. Both Anna and Dolors amazed me with the amount of research work they did every day. I will also like to acknowledge the past members of analytical chemistry (Geerke, Raquel, Ester and Mònica A) with whom I had spent few days.

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