Universitat de Girona

POLLUTION ASSESSMENT OF ARSENIC IN GROUNDWATER: GEOCHEMISTRY AND ANALYTICAL ASPECTS

Santanu Majumder

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Doctoral Thesis

Pollution Assessment of Arsenic in Groundwater: Geochemistry and Analytical Aspects

Santanu Majumder

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Doctoral programme in Experimental Sciences and Sustainability

Supervised by:

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Presented in partial fulfillment of the requirements for a doctoral degree from the University of Girona

Dra. Manuela Hidalgo Muñoz of University of Girona, **Prof. Debashis Chatterjee** of Univeristy of Kalyani and **Dra. Gabriela Roman-Ross** of AMPHOS 21,

WE CERTIFY:

That the thesis entitled as "**Pollution Assessment of Arsenic in Groundwater: Geochemistry and Analytical Aspects**" has been completed under our supervision to obatain a Doctoral degree and meets the requirements to qualify for an International Doctorate.

For all intents and purposes, we hereby sign this document.

Chatterji

Prof. Manuela Hidalgo **Prof. Debashis Chatterjee** **Dr. Gabriela Roman-Ross**

Girona 1st October, 2013

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Dedicated to my family and friends

"I have not failed. I've just found 10,000 ways that won't work"

– Thomas A. Edison

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Summary

The presence of natural arsenic (As) in groundwater is a wide-spread problem in south-east Asia. Surface water is generally not suitable for drinking purposes due to pathogenic contamination. Due to this reason and easier accessibility, groundwater is now almost the exclusive source of drinking water in Bengal Delta Plain (BDP). The source of As in the groundwater of BDP and south-east Asia is geogenic. However, anthropogenic systems may also influence its release in small patches. Increasing groundwater abstraction for agricultural irrigation makes the situation even worse. The health of millions of people through consumption of As-rich groundwater in BDP and in south-east Asia calls for immediate action on various levels. The probable reasons causing spatio-temporal heterogeneity of groundwater As distribution is very crucial to assess. The role of monsoon and the change in redox signature therein the aquifers needed to be investigated in detail to explain the As release and mobility at ground level.

In this context, a study area has been selected in the state of West Bengal, India located within the BDP that is well reported to be highly affected by groundwater As. The water quality and chemistry of the groundwater surveyed from the area have been investigated by a systematic screening operation. The groundwater is predominantly of Ca-HCO_3^- type. Factor analysis is employed to delineate the inter-relationship among the analyzed hydrochemical parameters and their association to understand the nature of the local hydrogeochemical features of groundwater. Initial part of this thesis focuses on the multiple As mobilization processes playing simultaneously that may cause the release of As rather than supporting any individual process (mechanism). The study suggests that Fe-(oxyhydr)oxide reduction may not be the only possible mechanism for As mobilization. In the sediment, Fe bearing aluminosilicates (altered mica/biotite) could also be important to host As. The groundwater As distribution and their relationship with land-use pattern suggest that As release is possibly linked with the local conditions (e.g. sanitation, presence of surface water bodies, agricultural practice). The interconnectivity of these local conditions with aquifer sediment and the proximate land-use (morphology) in and around the water wells may often facilitate the heterogeneity in As distribution. The local hydrogeological regime (sediment-water

interaction) may also play a key role to regulate aqueous distribution of As. Finally, the As release mechanism is complex as well as patchy (spatio-vertical heterogeneity). Unique/individual mechanism may not be universally applied to address the heterogeneous distribution of As. Thus, in addition to the regional geology and hydrogeology, local conditions may also add to the heterogeneous As distribution and mobilization patterns.

Large-scale groundwater abstraction was hypothesized to be one of the important factors controlling release and distribution of arsenic (As) in the aquifer. In the next study, we examined stable isotopic signatures of O and H in groundwater of two different geomorphic domains in Chakdaha Block, West Bengal, in an attempt to decipher potential influences of groundwater abstraction on the hydrochemical evolution and concomitant As release. Although isotopic signatures are largely controlled by local precipitation, the isotopic composition falls sub-parallel to the Global Meteoric Water Line (GMWL) – indicating widespread usage of groundwater for agriculture may have contributed to the drawdown of evaporation influenced surface waters. The stable isotope composition in several wells of the flood plain has similar values with the stable isotope signature of the adjacent ponds, mostly during post-monsoon season, which might evoke closer look at a possible link between aquifer and pond waters. The Cl/Br molar ratio in the groundwater suggests vertical recharge process in the wells within the flood plain area, especially during the post-monsoon season, whereas, strong evaporation is controlling the recharge process in case of the natural levee wells. In the flood plain area, the mean As(III) concentration increased dramatically (223%) in comparison to As_T concentration (6.6%) after the monsoon period. Similarly, in the natural levee wells, As(III) increased drastically (217%) after the monsoon season. However, As_T concentration decreased noticeably (17.7%) in natural levee wells. Dissolved organic carbon (DOC) concentrations in the flood plain wells increased significantly after the monsoon period (from 1.33 to 6.29 mg/L), indicating a possible inflow of organic carbon to the aquifer. The decrease in Eh along with the increase in Fe^{2+} and positive correlation of DOC with As(III) in the flood plain samples during post-monsoon season indicate possible microbe enhanced As release in groundwater.

Earlier studies have suggested that the mobility of As can be influenced by the presence of DOC and Fe mineral phases. Arsenic can be associated with colloidal particles containing organic matter and Fe. Currently, no data is available on the dissolved phase/colloidal association of As in groundwater of alluvial aquifers in West Bengal, India. We investigated the fractional distribution of As (and other metals/metalloids) among the particulate, colloidal and dissolved phases in groundwater to understand the control of both organic and inorganic colloids on As mobility. The result shows that 83-94% of As remained in the 'truly dissolved phases' of groundwater. Strong positive correlation between Fe and As (r^2 between 0.65 and 0.94) is observed in different size fractions, especially in the larger (i.e., >0.05 μm size) colloidal particles, which indicate the close association of As with larger Fe-rich inorganic colloids. In contrast strong positive correlation is observed between As and DOC ($r^2 = 0.85$) in the smaller (i.e., <0.05 μm size) pore-sized fraction which highlights the strong association of smaller organic colloids with As. As(III) is mainly associated with the larger inorganic colloids, whereas, As(V) is associated with smaller organic/organometallic colloids. SEM and EDX result confirms an association of As with DOC and Fe mineral phases, suggesting the formation of dissolved organo-Fe complexes and colloidal organo-Fe oxide phases. ATR-FTIR spectra further confirms the formation of As-Fe-NOM organometallic colloids, however, detailed study of these colloids in natural waters are necessary to underpin its controlling behaviour.

In addition to the investigation on the distribution and mobility of groundwater As, studies related to probable mitigation options has also been carried out simultaneously. Field experience reveals that although there is number of As removal and treatment plants available, however, most of them are either very expensive or not so efficient. Additionally, they may also cause environmental hazards due to the use of various chemicals. Keeping in mind that majority of the population of these rural areas are very poor and not so skilled with sophisticated machines, any groundwater As removal method should be very much user-friendly and cost-effective.

In this regard, we re-examine the Solar Oxidation and Removal of Arsenic (SORAS) method to modify its efficiency using locally available household materials. SORAS

is a low-cost non-hazardous technique for the removal of As from groundwater. In this study, we tested the efficiency of natural citric acid sources extracted from tomato, lemon and lime to promote SORAS for As removal at the household level. The experiment was conducted in the laboratory using both synthetic solutions and natural groundwater samples collected from As-polluted areas in West Bengal. The role of As/Fe molar ratios and citrate doses on As removal efficiency were checked in synthetic samples. The results demonstrate that tomato juices (as citric acid) was more efficient to remove As from both synthetic (removal percentage: 78-98%) and natural groundwater (90-97%) samples compared to lemon (61-83% and 79-85%, respectively) and lime (39-69% and 63-70%, respectively) juices. The As/Fe molar ratio and the citrate dose showed an 'optimized central tendency' on As removal. Anti-oxidants, e.g. 'hydroxycinnamates', found in tomato, was shown to have a higher capacity to catalyze SORAS photochemical reactions compared to 'flavanones' found in lemon or lime. The application of this method has several advantages, such as eco- and user friendliness and affordability at the household level compared to other low-cost techniques.

Arsenic is the most carcinogenic element listed in the drinking water guidelines and may cause health catastrophes even at μg/L levels. Thus, it is absolutely important to measure the concentration of As even at ultra-trace levels in wide range of environmental samples, especially in waters. There are several methods available for the measurement of As in water. However, either these techniques are very costly (operation and maintenance wise) or they suffer from various interferences and matrix effects. Some of them are also not that sensitive for direct measurement. Hence, there is a room for improvement and developing new methods for the measurement of As that are cost-effective and at the same time very sensitive.

In the last part of this thesis, we investigated the hollow fiber liquid phase microextraction system (HF-LPME) combined with total reflection X-ray fluorescence (TXRF) for the determination of low amounts of inorganic As species in water samples. The obtained results showed the 3-phase system was more suitable to be used in combination with TXRF than the 2-phase configuration, since higher sensitivity and better precision for As determination can be attained. The influence of the relevant experimental parameters affecting As extraction (i.e. extractant, organic solvent, agitation speed, pH and extraction time) was systematically evaluated. It was found that As(III) was more efficiently extracted at pH 13, whereas, As(V) was extracted almost completely at pH 8.5. Controlling factors such as deposition volume for the favourable operating conditions for the use of TXRF spectrometry was evaluated. Moreover, the limits of detection achieved using the best analytical conditions meet the requirements of current legislation and allow the determination of inorganic As(V) and As(III) in water. The proposed method was also successfully applied to different environmental water samples for the preconcentration and subsequent determination of trace inorganic As species.

Resum

La presència d'arsènic (As) d'origen natural en l'aigua subterrània és un problema molt estès a l'Àsia sud-oriental. L'aigua superficial generalment no és adequada per consum humà a causa de la contaminació patògena. Per aquesta raó i, degut a la més fàcil accessibilitat, l'aigua subterrània és actualment font quasi exclusiva d'aigua potable en zones com la planícia del delta a Bengala (Bengala Delta Plain, BDP). L'origen de l'arsènic a l'aigua subterrània en el BDP i el sud-est d'Àsia en general és fonamentalment geogènic, encara que l'activitat antropogènica també pot influir en la seva presència en determinades àrees. L'increment de l'extracció d'aigüa subterrànies per a reg agrícola fa que el problema s'agreugi. La salut de milions de persones esta en risc degut al consum de les aigües subterrànies riques en As en BDP i al sud-est d'Àsia exigeix una acció immediata a diversos nivells. És molt important avaluar les causes probables de l'heterogeneïtat espacio-temporal de les aigües subterrànies així com la distribució de l'arsènic en la zona. El paper dels monsons i el canvi de la signatura redox en els aqüífers han de ser investigats en detall a fi d'explicar l'alliberament i mobilitat de l'As.

En aquest context, s'ha seleccionat una àrea d'estudi en l'estat de Bengala Occidental, Índia, dins del BDP, greument afectada per la presència de As en les aigües subterrànies. S'ha realitzat una investigació sistemàtica de la qualitat i la química de l'aigua subterrània de la zona. Es tracta d'aigües predominantment de tipus Ca-HCO_3^-. S'ha emprat l'Anàlisi de Factors per definir la interrelació entre els paràmetres hidroquímics analitzats i la seva associació per tal de comprendre la naturalesa de les característiques hidrogeoquímiques de les aigües subterrànies locals. La investigació ha considerat el múltiples processos causants de l'alliberament d'As que tenen lloc simultàniament. Els resultats de l'estudi suggereixen que la reducció de Fe-oxihidròxid pot no ser l'únic mecanisme possible de mobilització del l'As. En el sediment, els aluminosilicats que contenen Fe (mica/biotita alterats) també podrien ser importants com a font d'As. La distribució d'As a l'aigua subterrània i la seva relació amb el patró d'ús de la terra suggereixen que l'alliberament està possiblement relacionat amb les condicions locals (per exemple, el sanejament de les aigües residuals, la presència d'aigües superficials, les pràctiques agrícoles). La interconnexió d'aquestes condicions locals amb els

sediments de l'aqüífer i l'ús de la terra (morfologia) al voltant dels pous d'aigua sovint pot facilitar l'heterogeneïtat en la distribució de l'As. El règims hidrogeològics locals (interacció aigua-sediment) també poden tenir un paper clau per regular la distribució d'As a l'aigua. Finalment, el mecanisme d'alliberament d'As és complex, així com localment desigual (heterogeneïtat espacial i vertical). Així, no es pot aplicar universalment un únic mecanisme individual per abordar la distribució heterogènia d'As. Per tant, a més de la hidrogeologia regional, les condicions locals poden també influir en la distribució heterogènia d'arsènic i els seus patrons de mobilització.

L'extracció d'aigua subterrània a gran escala es va plantejar com un dels factors importants que controlen l'alliberament i distribució d'arsènic (As) a l'aqüífer. En el següent estudi es van analitzar les signatures isotòpiques d'O i H en l'aigua subterrània de dos dominis geomorfològics diferents en Chakdaha Block, Bengala Occidental, en un intent de desxifrar les possibles influències de l'extracció d'aigua subterrània en l'evolució hidroquímica i concomitant alliberament d'As. Tot i que les signatures isotòpiques estan controlades en gran mesura per les precipitacions locals, la composició isotòpica cau sub-paral·lela a la Línia d'Aigua Meteòrica Global (GMWL), indicant que l'ús generalitzat de les aigües subterrànies per a l'agricultura pot haver contribuït a la disminució de les aigües superficials influenciades per l'evaporació. La composició d'isòtops estables de l'aigua en diversos pous de la plana d'inundació té valors similars a la signatura isotòpica dels estanys adjacents, sobretot durant la temporada post-monsó, que podrien indicar un possible vincle entre l'aqüífer i les aigües de l'estany. La relació molar Cl/Br en las aguas subterráneas suggereix un procés de recàrrega vertical en els pous a la plana d'inundació, especialment durant l'època post-monsó, mentre que la forta evaporació controla el procés de recàrrega en el cas dels pous en la zona de dics naturals. A la plana d'inundació, la concentració mitjana d'As(III) va augmentar dramàticament (223%) en comparació amb la concentració d'As total (6.6%) després del període dels monsons; de manera similar, als pous de la zona de dics naturals, l'As(III) va augmentar dràsticament (217%) després de la de temporada del monsó. No obstant això, la concentració total d'As va disminuir notablement (17.7%) en els pous de la zona de dics naturals. Les concentracions de carboni orgànic dissolt

(DOC) en els pous de la plana d'inundació van augmentar significativament després del període del monsó (1.33-6.29 mg/L), el que indica un possible flux d'entrada de carboni orgànic a l'aqüífer. La disminució de Eh, juntament amb l'augment de Fe^{2+} i la correlació positiva de DOC amb As(III) en les mostres de la plana d'inundació durant la temporada post-monsó indiquen un possible paper dels microorganismes en alliberament d'As en l'aigua subterrània.

Estudis anteriors han suggerit que la mobilitat d'As es pot veure influïda per la presència de carboni orgànic dissolt (DOC) i les fases minerals de Fe. L'arsènic pot estar associat amb partícules col·loïdals que contenen matèria orgànica i Fe En l'actualitat, no es disposa de dades sobre la fase dissolta/associació col·loïdal d'As en les aigües subterrànies dels aqüífers al·luvials de Bengala Occidental, Índia. En aquesta tesis s'ha investigat la distribució fraccionada d'As (i altres metalls/metal·loides) entre el material particulat, les fases col·loïdals i dissolta en l'aigua subterrània per comprendre el control d'ambdós, els col·loides orgànics i inorgànics, en la mobilitat d'As. El resultats mostren que el 83-94% d'As es va mantenir en les fases 'veritablement' dissoltes de les aigües subterrànies. Es va observar una elevada correlació positiva entre ferro i arsènic ($0.65< r^2<0.94$) en diferents fraccions especialment en les partícules col·loïdals més grans (>0.05 μm), que indiquen l'estreta associació d'As amb col·loides inorgànics més grans rics en Fe. Contràriament, s'observa una forta correlació positiva entre As i DOC ($r^2 = 0.85$) en la fracció més petita (<0.05 μm) que posa de relleu la forta associació dels col·loides orgànics de mida més petita amb As. L'As(III) s'associa principalment amb els col·loides inorgànics més grans, mentre que, l'As(V) s'associa amb col·loides orgànics/organometàl·lics de mida més petita. Els resultats de SEM i EDX confirmen una associació d'As amb DOC i les fases minerals de Fe, el que suggereix la formació de complexos orgànics de Fe dissolts i fases col·loïdals d'òxids de Fe. Els resultats de ATR-FTIR confirmen la formació de col·loides organometàl·lics As-Fe-NOM, encara que són necessaris estudis més detallats d'aquests col·loides en aigües naturals per corroborar els seu paper en el control de la mobilitat de l'As.

A més de la investigació sobre la distribució i la mobilitat d'As en les aigües subterrànies, s'han dut a terme de forma simultània estudis relacionats amb les probables opcions de mitigació. L'experiència de camp revela que, encara que existeixen diferents sistemes d'eliminació i tractament disponibles, la majoria d'ells són molt cars o no són molt eficients. A més, també poden causar problemes ambientals a causa de la utilització de diversos productes químics. Tenint en compte que la major part de la població d'aquestes zones rurals és molt pobre i no es disposa de personal qualificat, les tecnologies per a l'eliminació d'As de les aigües subterrànies han de ser molt fàcils d'implementar i de baix cost.

En aquest sentit, s'ha tornar a examinar el mètode d'oxidació solar i eliminació d'arsènic (Solar Oxidation and Removal of Arsenic, SORAS) per tal de modificar la seva eficiència utilitzant materials casolans fàcilment disponibles en les zones afectades. SORAS és una tècnica de baix cost i que no utilitza materials perillosos per a l'eliminació d'arsènic de les aigües subterrànies. En aquest estudi, es va avaluar l'eficiència de les fonts d'àcid cítric natural extret de tomàquet, llimona i llima per promoure SORAS per a la remoció d'As a les llars. Els experiments es van dur a terme al laboratori utilitzant tant solucions sintètiques com mostres d'aigües subterrànies naturals de les zones contaminades amb As a Bengala Occidental. El paper de les relacions molars As/Fe i de les dosis de citrat en l'eficiència d'eliminació d'As es van comprovar en mostres sintètiques. Els resultats demostren que els sucs de tomàquet (com a font d'àcid cítric) eren més eficaços per eliminar As tant en les solucions sintètiques (percentatge de remoció: 78-98%) com en les aigües subterrànies naturals (90-97%) en comparació amb els sucs de llimona (61-8 % i 79-85%, respectivament) i llima (39-69% i 63-70%, respectivament). La relació molar As/Fe i la dosi de citrat van mostrar una "tendència central optimitzada" en l'eliminació d'As. S'ha demostrat que els antioxidants, per exemple, hidroxicinamats, que es troben en el tomàquet, tenen una major capacitat per catalitzar reaccions fotoquímiques SORAS en comparació amb les flavanones que es troben en llimona o llima. L'aplicació d'aquest mètode té diversos avantatges, com la facilitat d'ús i l'accessibilitat dels materials y baix impacte ambiental en comparació amb altres tècniques de baix cost.

L'elevada toxicitat de l'arsènic, que pot causar problemes gravíssims en la salut fins i tot a nivells de µg/L, fa que es trobi regulat de forma estricta en diferents directives, tant en les cas de les aigües naturals com en les aigües potables. Per tant, és absolutament important mesurar la concentració d'As fins i tot a nivells ultra traça en una àmplia gamma de mostres ambientals, especialment en les aigües. Hi ha diversos mètodes disponibles per a la determinació i especiació d'As en l'aigua. No obstant això, aquestes tècniques són costoses (operació i manteniment) o pateixen de diverses interferències i efectes de matriu. La sensibilitat d'algunes d'elles no permeten la mesura directa. Per tant, hi ha un marge per a la millora i desenvolupament de nous mètodes per a la determinació i especiació d'As.

En l'última part d'aquesta tesi, s'ha investigat la tècnica de microextracció en fase líquida amb fibra buida (HF-LPME) combinada amb la fluorescència de raigs X amb reflexió total (TXRF) per a la determinació de les espècies inorgàniques d'arsènic a nivells traça en aigües. Els resultats obtinguts mostren que el sistema de LPME de tres fases en combinació amb TXTF és més eficient que la configuració en dues fases, ja que permet assolir millor precisió i exactitud. Es va avaluar de forma sistemàtica la influència dels paràmetres experimentals més rellevants que afecten l'extracció de les espècies d'As (extractant, solvent orgànic, velocitat d'agitació, pH i temps d'extracció). L'ió arsenit va ser extret de forma mes eficient a pH 13, emprant Aliquat 336 com a transportador, mentre que el pH òptim per l'extracció de l'ió arsenat va ser de 8.5. Així mateix, es van estudiar els factors que controlen les condicions més favorables d'operació de la tècnica TXRF emprada en la detecció d'As, com el volum de deposició en els reflectors. Els límits de detecció obtinguts en les millors condicions experimentals compleixen els requeriments establerts per la legislació en vigor i permeten la determinació de les espècies inorgàniques d'As(III) i As(V) en aigua. El mètode proposat es va aplicar satisfactòriament a la determinació de les espècies inorgàniques d'arsènic a nivells de traces en diferents tipus d'aigües: superficials i subterrànies.

Resumen

La presencia de arsénico (As) de origen natural en el agua subterránea es un problema muy extendido en Asia suroriental. El agua superficial generalmente no es adecuada para consumo humano debido a la contaminación patógena. Por esta razón, y debido a la más fácil accesibilidad, el agua subterránea es actualmente fuente casi exclusiva de agua potable en zonas como la planicie del delta en Bengala (Bengal Delta Plain, BDP). El origen del arsénico en las aguas subterráneas en el BDP y el sudeste de Asia en general es fundamentalmente geogénico, aunque la actividad antropogénica también puede influir en su presencia en determinadas áreas. El incremento de la extracción de aguas subterráneas para riego agrícola hace que el problema se agrave. El riesgo para la salud de millones de personas a través del consumo de las aguas subterráneas ricas en As en BDP y el sureste de Asia exige una acción inmediata a varios niveles. Es muy importante evaluar las causas probables de la heterogeneidad espacio-temporal de las aguas subterráneas así como la distribución del arsénico en la zona. El papel de los monzones y el cambio de la signatura redox en los acuíferos deben ser investigados en detalle a fin de explicar la liberación y movilidad del As.

En este contexto, se ha seleccionado un área de estudio en el estado de Bengala Occidental, India, dentro del BDP, gravemente afectada por la presencia de As en las aguas subterráneas. Se ha realizado una investigación sistemática de la calidad y la química del agua subterránea de la zona. Se trata de aguas predominantemente de tipo Ca-HCO_3^- . Se ha empleado el Análisis de Factores para definir la interrelación entre los parámetros hidroquímicos analizados y su asociación con el fin de comprender la naturaleza de los características hidrogeoquímicas de las aguas subterráneas locales. La investigación ha considerado los múltiples procesos causantes de la liberación de As que tienen lugar simultáneamente. Los resultados del estudio sugieren que la reducción de Fe-oxihidróxido puede no ser el único mecanismo posible de movilización del el As. En el sedimento, los aluminosilicatos que contienen Fe (mica/biotita alterados) también podrían ser importantes como fuente de As. La distribución de As en el agua subterránea y su relación con el patrón de uso de la tierra sugieren que la liberación está posiblemente relacionada con las condiciones locales (por ejemplo, el saneamiento de las aguas residuales, la

presencia de aguas superficiales, las prácticas agrícolas). La interconexión de estas condiciones locales con los sedimentos del acuífero y el uso de la tierra (morfología) alrededor de los pozos de agua a menudo pueden facilitar la heterogeneidad en la distribución del As. Los regímenes hidrogeológicos locales (interacción agua-sedimento) también pueden tener un papel clave para regular la distribución de As en el agua. Finalmente, el mecanismo de liberación de As es complejo, así como localmente desigual (heterogeneidad espacial y vertical). Así, no se puede aplicar universalmente un único mecanismo individual para abordar la distribución heterogénea de As. Por tanto, además de la hidrogeología regional, las condiciones locales pueden también influir en la distribución heterogénea de arsénico y sus patrones de movilización.

La extracción de agua subterránea a gran escala se planteó como uno de los factores importantes que controlan la liberación y distribución de arsénico (As) en el acuífero. En el siguiente estudio se analizaron las firmas isotópicas de O y H en el agua subterránea de dos dominios geomorfológicos diferentes en Chakdaha Block, Bengala Occidental, en un intento de descifrar la posible influencia de la extracción de agua subterránea en la evolución hidroquímica y concomitante liberación de As. Aunque las signaturas isotópicas están controladas en gran medida por las precipitaciones locales, la composición isotópica cae sub-paralela a la línea de agua meteórica Global (GMWL), indicando que el uso generalizado de las aguas subterráneas para la agricultura puede haber contribuido a la reducción de las aguas superficiales influenciadas por la evaporación. La composición de isótopos estables en varios pozos de la llanura de inundación tiene valores similares a la firma isotópica de los estanques adyacentes, sobre todo durante la temporada post-monzón, que podrían indicar un posible vínculo entre el acuífero y las aguas superficiales. La relación molar Cl/Br en las aguas subterráneas sugiere un proceso de recarga vertical en los pozos en la llanura de inundación, especialmente durante la época post-monzón, mientras que la fuerte evaporación controla el proceso de recarga en el caso de los pozos en la zona de diques naturales. En la llanura de inundación, la concentración media de As(III) aumentó dramáticamente (223%) en comparación con la concentración de As total (6.6%) tras el periodo de los monzones; de manera similar, en los pozos en la zona de diques naturales, el As(III) aumentó drásticamente (217%) después de la de temporada del monzón. Sin embargo, la concentración total de As disminuyó notablemente (17.7%) en los pozos de la zona de diques naturales. Las concentraciones de carbono orgánico disuelto (DOC) en los pozos de la llanura de inundación aumentaron significativamente después de que el periodo del monzón (1.33-6.29 mg/L), lo que indica un posible flujo de entrada de carbono orgánico en el acuífero. La disminución de Eh, junto con el aumento de Fe^{2+} y la correlación positiva de DOC con As(III) en las muestras de la llanura de inundación durante la temporada post-monzón indican un posible papel de los microorganismos en liberación de As en el agua subterránea.

Estudios anteriores han sugerido que la movilidad de As se puede ver influida por la presencia de carbono orgánico disuelto (DOC) y las fases minerales de Fe. El arsénico puede estar asociado con partículas coloidales que contienen materia orgánica y Fe En la actualidad, no se dispone de datos sobre la fase disuelta/asociación coloidal de As en las aguas subterráneas de los acuíferos aluviales de Bengala Occidental, India. En esta tesis se ha investigado la distribución fraccionada de As (y otros metales/metaloides) entre el material particulado, las fases coloidales y disuelta en el agua subterránea para comprender el control de los coloides orgánicos e inorgánicos en la movilidad de As. Los resultados muestran que el 83-94 % de As se mantuvo en las fases 'verdaderamente' disueltas de las aguas subterráneas. Se observó una elevada correlación positiva entre hierro y arsénico ($0.65< r^2<0.94$) en diferentes fracciones especialmente en las partículas coloidales de mayor tamaño (>0.05 micras), que indican la estrecha asociación de As con coloides inorgánicos mayores ricos en Fe. Por el contrario, se observa una fuerte correlación positiva entre As y DOC ($r^2 = 0.85$) en la fracción de menor tamaño (<0.05 micras) que pone de relieve la fuerte asociación de los coloides orgánicos más pequeños con As. El As(III) se asocia principalmente con los coloides inorgánicos más grandes, mientras que, el As(V) se asocia con coloides orgánicos/organometálicos más pequeños. Los resultados de SEM y EDX confirman una asociación de As con DOC y las fases minerales de Fe, lo que sugiere la formación de complejos orgánicos de Fe disueltos y fases coloidales de óxidos de Fe. Los resultados de ATR-FTIR confirman la formación de coloides organometálicos As-Fe-NOM, aunque son necesarios estudios más detallados de estos coloides en aguas naturales para corroborar su papel en el control de la movilidad del As.

Además de la investigación sobre la distribución y la movilidad de As en las aguas subterráneas, se han llevado a cabo de forma simultánea estudios relacionados con las probables opciones de mitigación. La experiencia de campo revela que, aunque existen diferentes sistemas de eliminación y tratamiento disponibles, la mayoría de ellos son muy caros o no son muy eficientes. Además, también pueden causar problemas ambientales debido a la utilización de diversos productos químicos. Teniendo en cuenta que la mayor parte de la población de estas zonas rurales es muy pobre y no se dispone de personal cualificado, las tecnologías para la eliminación de As de las aguas subterráneas deben ser muy fáciles de implementar y de bajo coste.

En este sentido, se ha reexaminado el método de oxidación solar y eliminación de arsénico (Solar Oxidation and Removal of Arsenic, SORAS) para modificar su eficiencia utilizando materiales caseros fácilmente disponibles en las zonas afectadas. SORAS es una técnica de bajo coste y que no utiliza materiales peligrosos para la eliminación de arsénico (As) de las aguas subterráneas. En este estudio, se evaluó la eficiencia de las fuentes de ácido cítrico natural extraído de tomate, limón y lima para promover el proceso SORAS para la remoción de As en los hogares. Los experimentos se llevaron a cabo en el laboratorio utilizando tanto soluciones sintéticas como muestras de aguas subterráneas naturales de las zonas contaminadas con As en Bengala Occidental. El papel de las relaciones molares As/Fe y de las dosis de citrato en la eficiencia de eliminación de As se comprobaron en muestras sintéticas. Los resultados demuestran que los zumos de tomate (como fuente de ácido cítrico) son más eficaces para eliminar As tanto en las soluciones sintéticas (porcentaje de remoción: 78-98%) como en las aguas subterráneas naturales (90-97%) en comparación con los zumos de limón (61-83% y 79-85%, respectivamente) y lima (39-69% y 63-70%, respectivamente). La relación molar As/Fe y la dosis de citrato mostraron una "tendencia central óptima" en la eliminación de As. Se ha demostrado que los antioxidantes, por ejemplo, hidroxicinamatos, que se encuentran en el tomate, tienen una mayor capacidad para catalizar reacciones fotoquímicas SORAS en comparación con las flavanonas que se encuentran en limón o lima. La aplicación de este método tiene varias ventajas, como la facilidad de uso y la accesibilidad de los materiales y bajo impacto ambiental en comparación con otras técnicas de bajo coste.

La elevada toxicidad del arsénico, que puede causar problemas gravísimos en la salud incluso a niveles de mg/L, hace que se encuentre regulado de forma estricta en diferentes directivas, tanto en las caso de las aguas naturales como en las aguas potables. Por tanto, es indudable la importancia de la determinación de la concentración de As incluso a niveles ultra traza en amplia gama de muestras ambientales, especialmente en las aguas. Hay varios métodos disponibles para la determinación y especiación de As en el agua. Sin embargo, estas técnicas son costosas (operación y mantenimiento) o sufren de varias interferencias y efectos de matriz. La escasa sensibilidad de algunas de ellas no permite la medida directa. Por lo tanto, hay un margen para la mejora y desarrollo de nuevos métodos para la determinación y especiación de As.

En la última parte de esta tesis, se ha investigado la técnica de microextracción en fase líquida con fibra hueca (HF-LPME) combinada con la fluorescencia de rayos X con reflexión total (TXRF) para la determinación de las especies inorgánicas de arsénico a niveles traza en aguas. Los resultados obtenidos muestran que el sistema de LPME de tres fases en combinación con TXRF es más eficiente que la configuración en dos fases, ya que permite alcanzar mejor precisión y exactitud. Se evaluó de forma sistemática la influencia de los parámetros experimentales más relevantes que afectan la extracción de las especies de As (extractante, solvente orgánico, velocidad de agitación, pH y tiempo de extracción). El ión arsenito fue extraído de forma más eficiente a pH 13, empleando Aliquat 336 como transportador, mientras que el pH óptimo para la extracción del ión arsenato fue de 8.5. Asimismo, se estudiaron los factores que controlan las condiciones más favorables de operación de la técnica TXRF empleada en la detección de As, como el volumen de deposición en los reflectores. Los límites de detección obtenidos en las mejores condiciones experimentales cumplen los requerimientos establecidos por la legislación en vigor y permiten la determinación de las especies inorgánicas de As(III) y As(V) en agua. El método propuesto se aplicó satisfactoriamente en la determinación de las especies inorgánicas de arsénico a niveles de trazas en diferentes tipos de aguas: superficiales y subterráneas.

CHAPTER 1: GENERAL INTRODUCTION

1.1. Arsenic in environment

Arsenic (As) is a metalloid placed in the nitrogen group row in the periodic table having atomic number of 33, five valence electrons and molecular weight of 74.9 g/mol. The only naturally occurring isotope is ^{75}As (De Laeter et al., 2003). It is the 20th most abundant naturally occurring element in the Earth's crust. It has four possible oxidation states: As(-III) (arsenide), As(0) (elemental arsenic), As(III) (arsenite) and As(V) (arsenate). Inorganic As occurs in natural groundwater in two different oxidation states, arsenate and arsenite. Arsenic(V) tends to predominate in oxidizing water (arsenate oxy-anions, $H_2AsO_4^-$, $HAsO_4^{2-}$) while As(III) is associated with reducing conditions (arsenite oxy-anions, H_3AsO_3, $H_2AsO_3^-$, $HAsO_3^{2-}$). Monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) and Arsenobetain (AsB) are the dominant organic species that are mostly found in groundwaters at ultra-trace levels (Bhattacharya et al., 2002a; Sharim et al., 2002; Gault et al., 2003). Inorganic trivalent arsenite is more toxic to organisms/human beings, and also more mobile in the environment than the pentavalent arsenate. Arsenic is found in a large variety of chemical forms/compounds in the environment. Changes in geochemical redox conditions (such as redox potential, pH), microbial activity can affect the natural transformations of these forms. Arsenic is involved in forming the crystal lattice of several minerals, such as arsenides, sulphides, oxides, arsenates and arsenites (Smedley and Kinniburgh, 2002). Arsenic was the first natural chemical element to be attributed as carcinogenic and the most carcinogenic element in the current drinking water regulations. However, it is an essential element for the development and growth of some organisms (Cullen and Reimer, 1989; Reimann et al., 2009).

Exposure of prolonged and high concentrations of As in the environments such as in water, sediment, and soil, has proved to be harmful to the living beings (Nriagu et al., 2007). Consumption of As contaminated drinking water, food and sometimes inhalation of air are the major routes of human exposure. In most parts of the world, groundwater has been used as the dominant drinking water resource. Several researchers have reported the groundwater to be contaminated with naturally occurring As from around the globe and thereby causing human health hazards (Bhattacharya et al., 1997, 2002b; Garcia-Sanchez et al., 2002; Smedley and Kinniburgh, 2002; Bundschuh et al., 2004, 2007, 2012).

In addition to the natural occurrence, it may also be found as a result of human activities – from widely used herbicides, insecticides, feed additives and especially wood preservatives. Industrial activities such as leather and metal (alloys and bronze) treatments can also produce large volume of As in addition to some of the pharmaceutical industries (Yusfin et al., 2001). Furthermore, a large percentage of the anthropogenic As enters directly into the environment due to mining activities and emissions due to burning of oil and coal (Melamed, 2005; Reimann et al., 2009).

1.2. Arsenic in groundwater

Water is vital for human existence. Today, more than half of the world's population depends on groundwater as drinking water source. Approximately a population of more than 100 million people depends on groundwater as their only available drinking water source (Nriagu et al., 2007). A survey of the groundwater quality indicates that As concentrations are often exceeding World Health Organization (WHO) guideline value (>10 µg/L) (WHO, 2011) in several parts of the globe. While it is well known that As represents a major risk for human health (Pontius et al., 1994), lately it has turned out that groundwater is highly enriched in As in large areas worldwide. The use of such groundwaters in households and for irrigation of agricultural crops became a problem of global concern.

1.2.1. Global phenomenon

High concentrations of As in groundwater have been reported from countries like USA, Canada, China, Argentina, Chile and many parts of south and south-east Asia (Figure 1.1) (Chen et al., 1985; Welch and Lico, 1988; BGS and DPHE, 2001; Smedley and Kinniburgh, 2002; Bhattacharyya et al., 2003a; Chatterjee et al., 2005; Nath et al., 2005, 2008a; Charlet and Polya, 2006). Very natural aquifers exceed 10 µg/L from all over the world, e.g., Argentina, Australia, Bolivia, Cambodia, Chile, Ecuador, El Salvador, Honduras, Hungary, Mexico, Nepal, New Zealand, Nicaragua, Myanmar, Philippines, Taiwan, Thailand, Uruguay and the United States (Figure 1.1). Mostly, the aquifers of river deltas in Asia are often found to be contaminated with As including the Bengal Delta Plain (BDP) in India and Bangladesh and the Red River

Delta in Vietnam (Bhattacharya et al., 1997; Acharyya et al., 1999; Berg et al., 2001; van Geen et al., 2006).

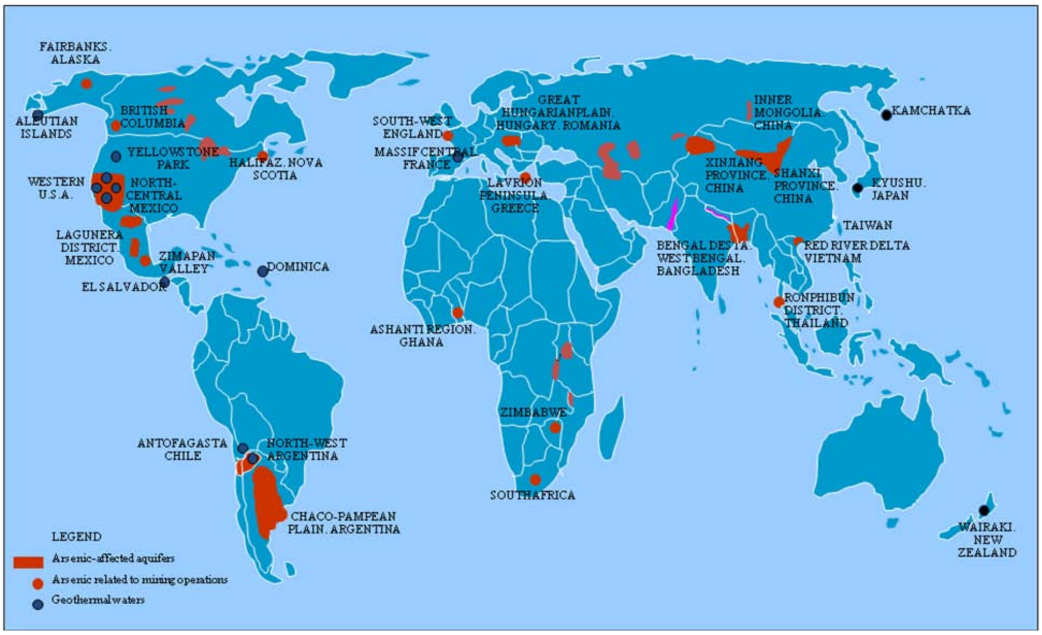


Figure 1.1. Global scenario of As in groundwater (source: http://www.bgs.ac.uk/arsenic/).

The reports from Latin America are relatively newer and each day fresh studies are being registered from different parts of the continent (Budschuh et al., 2012). Very little information is available though regarding the African continent. Amongst all countries worldwide, India (especially West-Bengal) and Bangladesh is facing the most severe threat (PHED, 1993; BGS and DPHE, 2001), with several millions of people being endangered to be affected by As induced diseases (Acharyya et al., 1999; Chakraborty et al., 2002; Bhattacharyya et al., 2003b; Chatterjee et al., 2003).

1.2.2. Local scenario

Millions of tube wells were installed in the BDP (Figure 1.2) to provide groundwater (as drinking water source and irrigation to support agriculture) (Charlet and Polya, 2006; Polya and Charlet, 2009) and later on this triggered the wide spread threat of Arsenicosis. The easily accessible surface water was not suitable for drinking purposes as being affected with pathogenic contamination. This encouraged the local population to look for an easily accessible and safer alternative drinking water source – groundwater. However, nobody was aware of an underlying, potential threat of groundwater As [especially As(III)] contamination, which was later considered as the largest mass poisoning of a population in human history by WHO (Smith et al., 2000). In the recent past, skin, lung and liver cancers are the most common consequences of high As exposure among the population in rural West-Bengal and Bangladesh (Das et al., 1994; Rahman, 1999; Bhattacharyya et al., 2003b; Yu et al., 2003). In addition, the widespread use of groundwater for irrigation causes the risk of As entering the food chain. Although, the major crop and the dominant stable food Rice, can be considered to be safe as the rice roots are covered with Fe-(oxyhydr)oxides and prevents As entering the rice grains (Norra et al., 2005). However, there are reports on As-enriched rice, specially the brown rice from some parts of this region (Chatterjee et al., 2010; Halder et al., 2012). In case of some other crops, As may accumulate into the roots or leaves, though not very often in the grains (Neidhardt et al., 2012).

1.2.2.1. Arsenic in the Bengal Delta Plain

The BDP is known as one of the most affected areas worldwide (Figure 1.2) with naturally occurring inorganic As in groundwater (Charlet and Polya, 2006; Polya and Charlet, 2009). To provide suitable mitigation options one need to know the dimension and dynamics of the As distribution in groundwater. Number of studies have been reported in the past two and half decades in this regard (e.g., Berg et al., 2001; McArthur et al., 2001,2004; van Geen et al., 2004; Harvey et al., 2002,2005; Neumann et al., 2009; Fendorf et al., 2010; Postma et al., 2010). Arsenic in groundwater has been found to reach up to 3200 µg/L in the contaminated tube wells in depths down to 150 m, with As(III) as dominating species (Kinniburgh and Smedley, 2001). The chemical composition of the groundwater varies both regionally and also from aquifer to aquifer. The physico-chemical composition of groundwater shows large variation and it has been found that groundwaters contain high concentration of redox sensitive species (As, Fe, Mn) and relatively low concentration of dissolved oxygen (D.O.) (<1 mg/L), NO_3^- and SO_4^{2-}. The most dominant anion is HCO_3^- and the cation is Fe(II) (2–14 mg/L). The water is generally fresh (electrical conductivity 580-1100 µs/cm) and Ca–HCO_3 type (electrical conductivity 580–1100 µs/cm) (Chatterjee et al., 2003; Mukherjee–Goswami et al., 2008; Nath et al., 2008). This distribution of terminal electron acceptor (TEA) clearly highlights influences of microbial processes involving Mn(IV), Fe(III) and SO_4^{2-} reduction in the shallow aquifer parts.

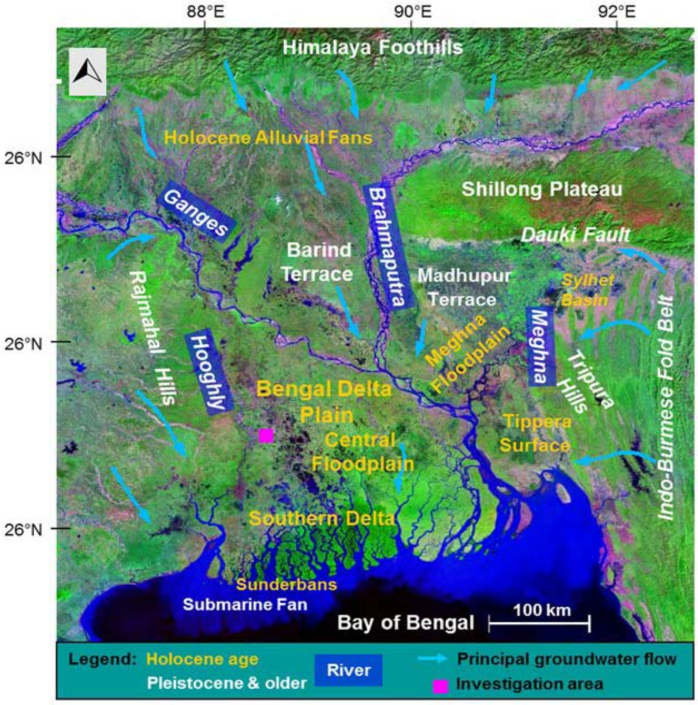


Figure 1.2. Pseudo colour mosaic picture of the Bengal Delta Plain (BDP) created with NASA World Wind (Landsat 7 image). Coloration emphasizes the presence of water (blue), vegetation (green) and bare soil (purple) (picture taken from Neidhardt et al., 2013).

The As-bearing groundwater is largely hosted by the sediments deposited by the meandering river channels during the Early-Mid Pleistocene and Holocene deposits (Chatterjee et al., 2005). However, reportedly organic-enriched, reduced Holocene sand aquifers of the Ganges-Brahmaputra-Meghna delta (especially flood plain areas) of eastern India, as well as in the Sylhet Basin in Bangladesh are more frequently contaminated with inorganic As (Acharyya et al., 2000). The older Pleistocene units are usually As-free (McArthur et al., 2004; Mukherjee et al., 2011). The spatial variation and concentration of As may change from one place to another significantly within a couple of meters (Ravenscroft et al., 2001; Charlet et al., 2007; Mukherjee et al., 2008; Nath et al., 2008). In addition to the spatial variation, As concentration may also very to some degree vertically down the aquifer (van Geen et al., 2006; Charlet et al., 2007). Recent studies found that the regression and transgression can influence the spatial heterogeneity of As distribution in groundwater (Sarka et al., 2009) and some studies reported that As release mechanism could also depend on the depth profile (Biswas et al., 2011). Therefore, the local geology and geomorphology can be very much linked with the spatial and veridical heterogeneity of As. A major challenge is the substantiation/concretization of the role of the host sedimentary environment in the release of arsenic into the groundwater and the elucidation of the causes for the often observed very heterogeneous arsenic distribution in the groundwater of contaminated areas (Wagner, 2005).

In spite of volumes of studies have been carried out on As contamination in groundwater in BDP, very is less is known about the sources and transport of As into these basinal aquifers. The Bengal basin is an asymmetric pericratonic basin, whose formation was initiated in the cretaceous. BDP is bound by the Himalayas and the Shillong massif in the north, the Indo-Burman ranges (Assam-Arakan-Geosynclinical) in the east, and the Indian shield in the west. (Barman, 1992). It is quite clear that the source is geogenic as the host Holocene units formed from the Himalayan Mountain Range carrying the arsenic-bearing phases like apatite, pyrite and magnetite (Hattori et al., 2005; Mailloux et al., 2009). Arsenic trapped in these mineral phases can be mobilized directly down to the basinal plains through weathering of the As-bearing host parent rocks and subsequently co-precipitated with Fe-(oxyhydr)oxides. These secondary Fe-mineral phases act as primary carrier phases for As (Raiswell, 2011). Finally, As is transported via surface runoff to the basinal flood plains and deposited (Kinniburgh and Smedley, 2001).

1.2.2.2. The study area – Chakdaha city

The study area selected for this thesis work, have been previously investigated by various international research groups. Chakdaha block (Figure 1.3) located in the district of Nadia, West Bengal, India is one of the most recent investigation site in BDP dealing with the growing threats of As contamination in groundwater as well as in food chain and to its surrounding living bodies. The city is situated on the western river bank of the Hooghly river and about 65 km north of Kolkata (Charlet et al., 2003). Chakdaha city is mainly a sub-urban area with mostly surrounding with villages with the main city at the center. The estimated population is around 75,000 which are denser in the main city. Series of oxbow lakes, meander scars, swamps, natural levees and ponds are frequently found in the study area due to very dynamic geomorphological shifts of Hooghly river channel in the past. The area is hugely cultivated all year around and the main crop being rice, jute and vegetables. The principle source of irrigation and drinking water is groundwater of course. Although, very recently, the local government has started to built the large-scale treated surface water supply, which is at its very early stage development.

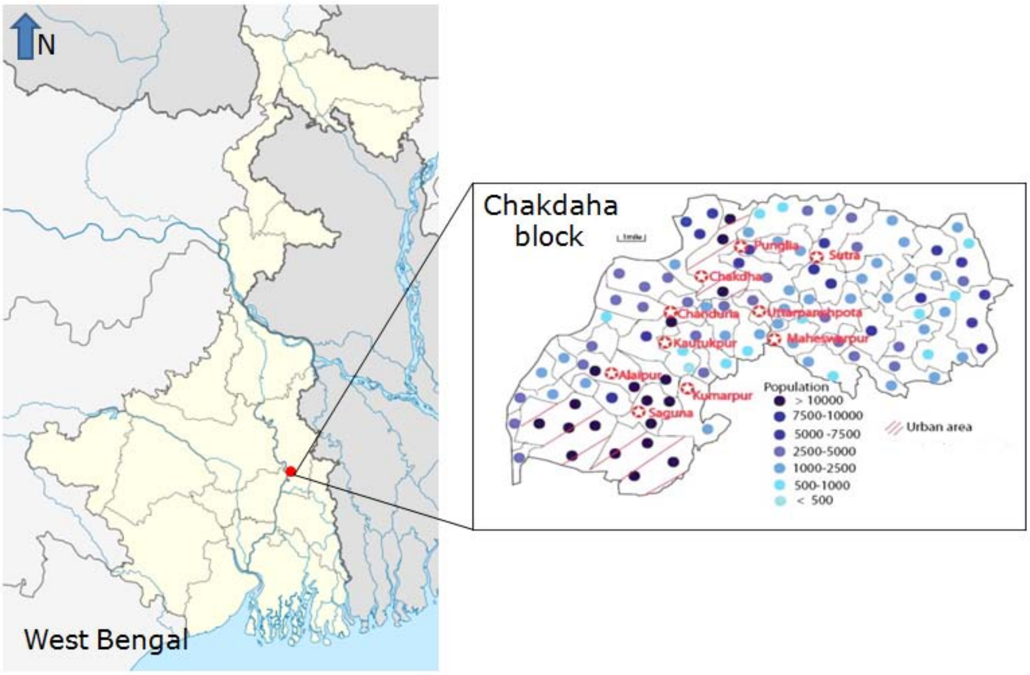


Figure 1.3. Chakdaha block (study area) (modified after Mondal and Polya, 2008).

As found by Nath et al. (2008), during 1998-1999, about 60% of 8,450 ha agricultural fields were irrigated with a total of more than thousands of deep, medium deep and shallow tube wells together with 319 river lift pumps. The installation of more shallow irrigation pumps are growing each day in these areas.

Groundwater As concentrations in the area may reach up to 500 µg/L showing a overall reducing nature with mostly negative redox potential (Eh), including prominent spatial variations in As concentrations (Charlet et al., 2003,2007). Groundwater HCO_3^- concentration is often very high and can be attributed to the microbial degradation of organic matter (OM) (Metral et al., 2008). Hooghly River acts as recharge source during the dry season and as drainage during the monsoon (Nath et al., 2008). Piezometric measurements showed that aquifer hydraulic head may fluctuate seasonally and vertically.

Regular and excessive groundwater withdrawal in depths around and so on, formed a local depression cone near the shallow aquifer. This subsequently attracts nearby fluxes of As-rich groundwater causing drawdown and further mixing with the deeper wells (Charlet et al., 2007; Lawson et al., 2008). Previous investigations confirmed the possible role of Fe-(oxyhydr)oxides as key mineral phase hosting low As contents (~ 2.5 mg/kg) and the dominance of As(III) (>70%) in the reduced sediments (Rowland et al., 2005). The high As groundwaters are associated with relatively low As (nearly 7-26 mg/kg) content in sediments and the average is not very high when compared with world average values (earth crust -1.8 mg/kg; rocks - 0.5-2.5 mg/kg; coal - average 10 mg/kg) (NAS, 1997). The As content of regional river bed samples of the BDP (Ganges - 2.03 mg/kg, Brahmaputra - 2.79 mg/kg and Meghna - 3.49 mg/kg) are also reported lower than the Arsenic contents in BDP sediments (Chatterjee et al., 2005). A survey of the groundwater quality indicates that As concentrations are often exceeding WHO guideline values (>10 µg/L) and also exceed the national safe limit (>50 µg/L). The As concentrations in groundwater vary over wide range of magnitude (sub milligram to milligram level). Arsenic concentrations show limited distinct regional trend along with many other dissolved elements and also display a significant short range spatial variability.

1.3. Hydrogeochemistry of inorganic arsenic

The water-rock interactions are very crucial for the mobility and transport of As in groundwater. Depending on the ambient environment, sediments can act both as source and sink for As. Geochemical processes such as complexation, redox reactions and competitive anion exchange have the most important influence on the mobility of As depending on the Eh-pH status of the aquifer. Both, As(III) and As(V) can form strong bidentate complexes via ligand exchange (Dixit and Hering 2003; Ona-Nguema et al., 2005; Borch et al., 2010; Muller et al., 2010) owing to their strong binding affinity towards the Fe-(oxyhydr)oxide surfaces. Usually, sedimentary inorganic As is attached with Mn- and Al-(oxyhydr)oxides, clay minerals, sulphates, calcium carbonates and organic acids (O'Day, 2006). The proportion ratio of As(III) and total arsenic (As_T) normally seems to be in the range of 55–70% in shallow aquifers. This highlights that the weakness exists in the redox equilibrium in the aquifer and such weakness is varying in the multilevel sedimentary aquifer of the

BDP (Gault et al., 2005). The disequilibria with respect to reduction of As(III)/As(V) suggest that As(V) may fall short of As(III) concentration in groundwater due to the higher charge of the arsenate species.

Arsenate has relatively higher sorption affinity for the binding sites of potential host mineral phases or organic compounds in aquifer sediment. The sorption efficiency is primarily controlled by the redox state of the solution and the presence of available binding sites on potential sorbing mineral phases (Dixit and Hering, 2003; Goh and Lim, 2004). Although the natural aquifers are quite complex, however, As sorption experiments has been studied using simple reaction steps (Mohan and Pittman, 2007). Competition from PO_4^{3-} and other anions plays an imperative role regarding competitive ion exchange and adsorption (Postma et al., 2007). Appelo et al. (2002) proposed competitive exchange of anions (bicarbonate, phosphate, silicate) in solution with As species (arsenate or arsenite) that also lead to an additional desorption of As from mineral surfaces. In case of Fe-(oxyhydr)oxides rich soils, As exchange potentials declined in order of $PO_4^{3-} >> CO_3^{2-} > SO_4^{2-} \approx Cl^-$ (Goh and Lim, 2005).

1.4. Arsenic hydrochemistry and redox changes

The mobilization, geochemical transformation and speciation of As in groundwater is primarily controlled by the redox state (Eh and pH) of the aquifer. In oxidizing environment, the dominant and thermodynamically favoured species is inorganic arsenate [As(V)], in the form of oxyanions such as AsO_4^{3-}. In acidic environments, $H_2AsO_4^-$ dominates, whilst $HAsO_4^{2-}$ appears with a shift to neutral or alkaline pH conditions (Figure 1.4). Two other species H_3AsO_4 and AsO_4^{3-} can only form either at extremely acidic, or alkaline pH's respectively. The dominant species in reducing environments is arsenite [As(III)]. Until a pH value up to ~ 9, neutral H_3AsO_3 dominates (Smedley and Kinniburgh, 2002). Above that pH range, anionic $H_2AsO_3^-$ appears. As(V) and As(III) can also exist together at a given Eh-pH range depending upon certain hydrogeochemical conditions (Inskeep et al., 2002; Nriagu et al., 2007).

The summarized picture of different As species controlled by Eh and is presented in the Eh-pH diagram based on thermodynamic calculations (Stumm and Morgan, 1996; Figure 1.4).

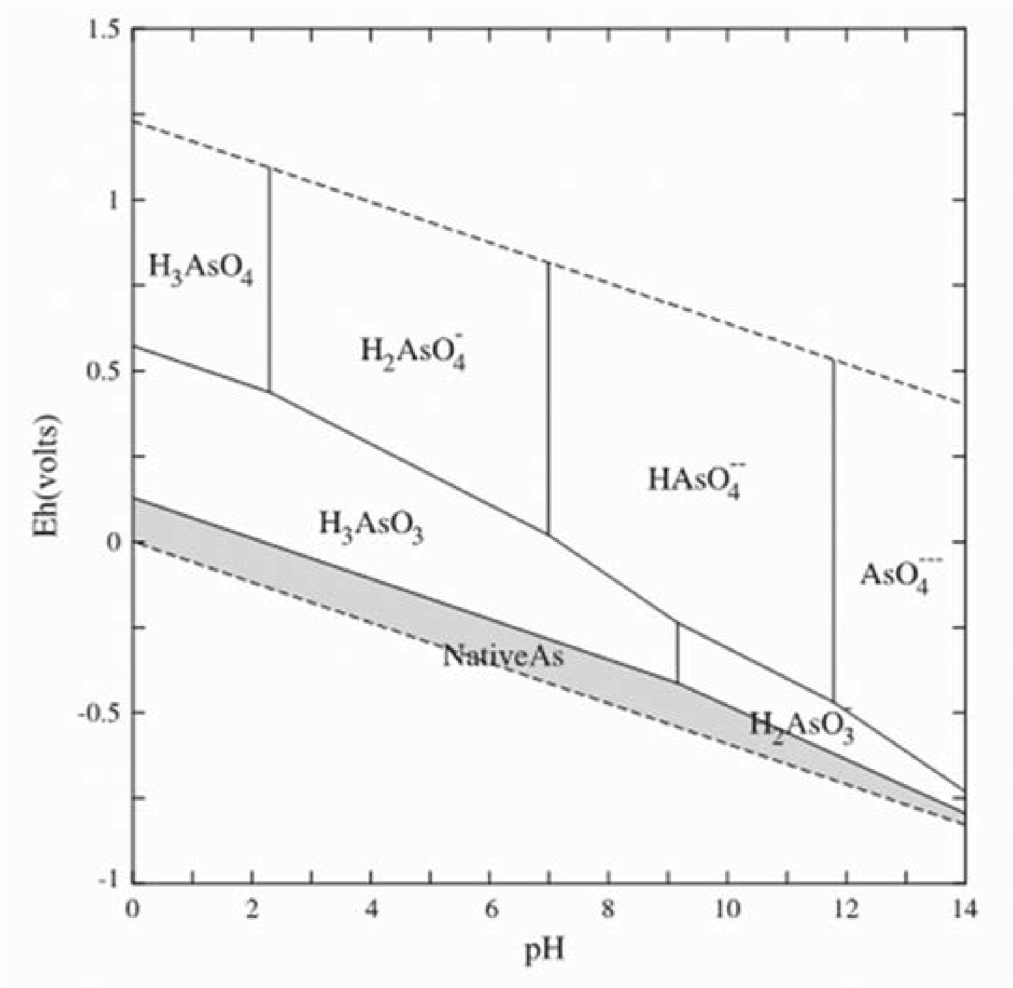


Figure 1.4. Characteristic Eh-pH diagram for the system As-O_2-H_2O at 25°C and 0.1 MPa based on latest thermodynamic data (after Lu and Zhu, 2011).

1.5. Proposed release mechanism in groundwater

Many studies exist trying to explain the mechanism that generates these high As concentrations in groundwater. The most popular models include:

- Arsenic is released into the groundwater by the oxidation of As-bearing pyrite present in aquifer sediments (Das et al., 1996; Chowdhury et al., 1999). However, since the Fe-(oxyhydr)oxides which result from pyrite oxidation strongly adsorb As, this may not be the basic mechanism for As mobilization (Stüben et al., 2003). In addition, SO_4^{2-} and As concentrations in the groundwater often do not show any correlation with each other, as expected if As would have been chiefly released during pyrite oxidation (Ahmed et al., 2004).

- Arsenic in groundwater results from the reduction and concomitant dissolution of As-rich Fe-/Mn-oxides/hydroxides promoted by organic matter, such as buried peat (McArthur et al., 2001), or by dissolved organics in recharging water (Harvey et al., 2002). Many of these redox processes are coupled with the mineralization of natural organic matter (NOM) and their distribution may control to a large extent the mobilization of As in a sedimentary environment (Lovley, 1987,1993,1996; McArthur et al., 2004; Charlet and Polya, 2006).
- Recently, Oremland and Stolz (2003) and Akai et al. (2004) emphasized the role of microorganisms in the enrichment of As in the groundwater.

Nevertheless, despite of intensive scientific research there is no adequate answer to the question on the ultimate cause for the occurrence of the high As concentrations in the groundwater of these areas and none of the above models can explain in a satisfactory way all the observed features in the distribution of As in groundwater, such as the spatio-temporal heterogeneity of the As concentrations, their incidental variation with local geomorphological elements, aquifer lithology, geochemistry, and microbial activity. Only a detailed understanding of the complex inter-relationships among the different parameters can shed light on the ultimate cause responsible for the occurrence of As contaminated groundwater reservoirs with regional extent. The geochemical environment and aquifer condition (oxic or anoxic), aquifer age, the occurrence of key mineral phases in the sediment, anthropogenic recharge - to mention only a few of major potential factors - may all influence the mechanism of As release to a considerable amount and should be therefore carefully considered in any attempt to solve this long lasting scientific debate with dramatic practical consequences.

But a thorough chemical characterization of the waters and the detailed knowledge of the hydrogeochemical environment in which high As groundwaters occur are essential also for the elaboration of efficient treatment technologies for the reduction of the As concentrations. The optimal treatment method for any particular water depends not only on the chemical speciation of As, but also on further specific qualitative attributes at that location (Chen et al., 1999). In order to elaborate an adequate strategy for the protection of the population it is essential to investigate any specific drinking water source in context of its local hydrogeological and hydrogeochemical environment.

1.6. Health implications

For centuries, As has been one of the biggest threats to living organisms due to its extremely high toxicity and can therefore be regarded as the "king of poisons"(Nriagu et al., 2007). On the other hand, a specified dose of As has also been used in medicines. For millions of people, As enters into the lives of millions of people worldwide everyday through foods, water, air and remains as one of the dreadful integral part of the human civilization. Consumption of As even at low doses can cause acute as well as chronic intoxications.

Inorganic As [especially As(III)] is more active to harm body tissues than organic As as the later is excreted through urine (Knowles and Benson, 1983; WHO, 2003; Hopenhyn, 2006). As(III) hinders the human methylation mechanisms (Hughes and Kenyon, 1998; Jing et al., 2006) and it also can damage the neurological systems at very low concentrations. Initial manifestations on human body are skin pigmentation and keratosis (Nriagu et al., 2007). Male are found to be more susceptible to keratosis and skin pigmentation than female (Guha Mazumder et al., 1988,1999). Chronic As poisoning can cause skin cancer and liver diseases due to prolonged consumption of high-As drinking water. Arsenic health effect is to some extent linked with the poor diet (less protein and vitamins) of the rural population of BDP (Huq et al., 2001). The half-life of inorganic As compounds in the human body is 2-40 days after resorption, however, long-term ingestion causes enrichment in liver, kidneys, heart, lungs and ectodermic tissues (Pomroy et al., 1980). Another typical manifestation is arsenicosis, a collective term used for extreme skin lesions like keratosis, hyperkeratosis and hyperpigmentation (Ahmad et al., 1997). Several reports from affected villages of Vietnam, China and Bangladesh depict that chronic exposure of As (mostly from drinking water) may trigger fatal loss and infant death, development of diabetes mellitus (Smith et al., 2000), cardio-vascular disease and eventually neurotoxic effects and inhibition of children's mental development (Rahman et al., 1998,2007; Alam et al., 2002; Lin et al., 2004; Fujino et al., 2006; Argos et al., 2010). There is no proper treatment available for arsenicosis till today, which is why mitigation strategies and sustainable water development are the only hope to avoid diseases related to fight As menace. Additionally, there is no dose-response relationship to assess the carcinogenicity of As making it difficult to fix a maximum value in water and food. The WHO provisional guideline value for total As (As_T) in drinking water is 10 µg/L (WHO, 2011). In India, the national legal limit is currently 50 µg/L for the total As concentration in drinking water, where there is no other suitable alternative available (Indian Standard Specifications for drinking water IS 10500, reaffirmed 1993).

1.7. Available removal techniques and mitigation options

There are manly two options available to avoid exposure from high As drinking water – 1) develop affordable As removal techniques for groundwater, 2) seek for alternative safer drinking water source. There are number of proposed techniques available for the removal of As from groundwater. For example, iron and alum coagulation (Shen, 1973), lime softening (McNeill and Edwards, 1995), reverse osmosis (Schneiter and Middlebrooks, 1983), zero-valent iron and nano-particulate zero-valent iron (Lien and Wilkin, 2005; Morgada et al., 2009), natural/synthetic metal oxides (Guo et al., 2007; Chang et al., 2009), iron doped activated carbons (Fierro et al., 2009), granular TiO_2 adsorbent (Bang et al., 2005), hybrid materials (Mandal et al., 2011) are some of the many proposed removal techniques. Among these, some are efficient but expensive whereas others are cheaper but not efficient. Pond sand filters and rain water harvesting are other alternative options that have been proposed, however, there is always the risk of contamination with pathogenic microorganisms (Ahuja, 2008).

The developing countries (especially around BDP) do not have large-scale centralized water supply due to financial constraints. Therefore, thorough screening and identification of safe wells by using cheap and simple As measuring field test kits is important (Kinniburgh and Smedley, 2001; Yu et al., 2003; World Bank, 2005). Recently advanced use of topographical survey to delineate the As affected area and related modeling to identification of potential aquifers prone to contamination in near future is gradually earning popularity for the policy makers (Winkel et al., 2008). Installation of deep tube wells (>150 m depth) to access As-free water is also a useful alternative that is being adopted by the rural governments in recent times.

However, large-scale supply of treated surface water is essential in these affected areas in near future. Economic hurdles are the main problem to do so.

1.8. Analytical aspects and potential improvements for ultra-trace measurements

1.8.1. Measurement and speciation of arsenic

Inorganic As is regarded as one of the most toxic contaminants in nature, especially in water, and therefore its measurement and speciation is very crucial for safe drinking water supply and public health. Several methodologies have been developed and published for the determination of both total elemental As and it's species in various environmental samples, including water.

It is a well established fact that determination of total elemental composition is not sufficient to assess the potential biochemical, biophysical, biomedical, toxicological and environmental threats to the living orgasms (Radke et al., 2012). The scale of hazardous effect is different from one species to another for each element. Any changes in the redox environment (e.g., pH, redox potential, salinity, temperature) of the matrix can strongly influence the stability of different species (Radke et al., 2012). The term "speciation" was attributed to certain methods of analysis that determined the available species and their concentration in a sample under investigation for a given metal. According to the current IUPAC guidelines, speciation is defined as "identification and determination of all the chemical and physical species of a given element in which it occurs in a specific part of the environment" (Radke et al., 2003).

Arsenic speciation in different environmental samples, especially in liquid samples (e.g., water and urine) has emerged as one of the most important aspects in recent times. However, speciation in more complex matrices like soil, sediment, food and other biological samples still poses bigger challenge due to the difficulty of separation and detection of various species and of course to overcome different interferences. Moreover, speciation involves expensive, analytical instrumentation and good laboratory practice (GLP) (Radke et al., 2012). The advanced technologies are multistep processes consisting of extraction, preconcentration, chromatographic separation (in some cases) and detection. Thus, these methods are susceptible to analyte loss and experimental errors. Some of them are also time consuming. Hence, speciation of As is complicated and presents wide range of difficulties to deal with.

Amongst the available existing techniques, colorimetric methods are perhaps the cheapest for in-situ measurement of As. Usually, this involves the "Gutzei" method that involves using a reducing agent to form the As-trihydride (arsine, AsH_3) gas. Then this gas is imposed on a paper impregnated with mercuric bromide to form a strong colored compound. Then the color intensity of this compound is measured using various techniques (e.g., using a calibrated standard colour scale, a colorimeter). However this method suffers from interference from sulfur, selenium and tellurium (Cullen and Reimer, 1989).

Regarding electrochemical methods, anodic stripping voltammetric (ASV) technique is one of the widely used techniques for the determination of inorganic As at trace levels. The basic principle is the anodic stripping of the metallic As deposited on various electrodes like graphite, platinum, gold, diamond (Kaponica and Novotny, 1998; Song and Swain, 2007; Long and Nagaosa, 2008).

Another well known technique is the cathodic stripping voltammetry (CSV). This involves a mercury working electrode. A modified use of hanging drop mercury electrode is based on pre-concentration of As in highly acidic media and subsequent scanning of a peak that corresponds to the formation of arsine. The use of this technique is cumbersome and suffers from interference from organic matter. However, it does not require electrode regeneration and cleaning (Mays and Hussam, 2008).

For the last few decades, atomic absorption spectrometry (AAS) and atomic fluorescence spectrometry (AFS) have been exceedingly used as a technique for trace determination of As. Both total As and differential concentration of As(III) and As(V) can be measured using the hydride generation method. Although, this method is free of potential matrix effects, however, it can face atomization interference caused by the formation of additional volatile hydrides due to presence of transition elements in form of aerosols that can trespass into the atomizer (Erdem and Henden, 2004; Hung et al., 2004).

Electrothermal atomic absorption spectrometry (ETAAS) is another widely used method. It is free of volatile impurities and consumes less time and energy due to simpler and faster heating methods. However, for the direct determination of As, the sensitivity is low and therefore needs pre-concentration of the analyte (Lima et al., 2003; Hung et al., 2004).

Inductively coupled plasma atomic emission spectrometry (ICP-AES) with ultrasonic nebulizer is highly used as it guarantees lower detection limits in comparison to pneumatic nebulizers (Vassileva and Hoenig, 2001). However, in presence of high concentrations Mn, Cr, Fe and some other elements in the same matrix, it suffers through spectral interferences.

Now-a-days, inductively coupled plasma mass spectrometer (ICP-MS) is preferred over the ICP-AES for the determination of trace/ultra-trace As due to its high precision and sensitivity, lower detection limits and ability to measure the isotopic composition. Highly resolution detectors are used to eliminate the $^{40}Ar^{35}Cl$ signal interference (Fiket et al., 2007) and collision cells are reported to combat the polyatomic intereferences produced inside the plasma (Dufailly et al., 2008). High performance liquid chromatography (HPLC) has also been used successfully in tandem with ICP-MS for the determination and simultaneous speciation of As.

Chromatographic techniques play a crucial role for the selective determination and speciation of As. This can be applied for very low concentrations and for the selective determination of wide range of organic and inorganic As species. The major disadvantage is the high instrumental and operational cost. Relatively cheaper gas chromatography (GC) is mostly used in case of volatile and thermally stable compounds. However, GC involves extraction, derivatization and clean up steps prior to introduction of the samples. Liquid chromatography (LC) is used in case of non-volatile and thermally unstable compounds as well as for polar and ionic substances (Radke et al., 2012). LC is commonly used in combination with spectrometric techniques for As speciation.

1.8.2. Improving the sensitivity for aqueous samples by extraction/pre-concentration techniques

Development of new, eco-friendly, cheaper analytical methods, including sample pretreatment steps, are one of the most important objectives. Sample preparation constitutes a basic and crucial step in the success of any analytical method. It is generally analyte and matrix dependent, requiring a suitable optimization of its different influencing parameters. Although in the past enough attention has not been paid, especially due to the advances in the analytical instrumentation, now-a-days efforts are being focused on its improvement. In this sense, current trends are moving towards its simplification, miniaturization and automation involving also the use of solvent free or environmentally friendly procedures, and maintaining at the same time good/acceptable extraction efficiencies. Such enhancement constitutes a challenging task, especially for samples having a high complexity.

Several extraction and preconcentration techniques have been designed for the extraction of metals and metalloids from aqueous samples. Liquid-liquid extraction (LLE) and solid-phase extraction are the most used of them, however, they are time consuming procedures and use large volume of organic solvents. Therefore, in recent times, miniaturized extraction techniques such as solid-phase microextraction (SPME) and liquid-phase microextraction (LPME) have been proposed as they are user-friendly, eco-friendly and do not require multi-stage operations.

LLE is a conventional preconcentration and clean-up technique based upon transfer of analyte from the aqueous sample to a water immiscible organic solvent. LLE has been applied extensively, although it involves use of high organic solvent volume, emulsion formation or precipitation, loss of analyte during the course of the process (Psillakis and Kalogerakis, 2003).

The basic principle of SPE is sorption on a solid sorbent surface and then re-extraction with the help of a solvent into a liquid phase. It needs lesser solvent volume than the LLE method and the enrichment factor is also higher (Poole, 2003). Availability of wide range of solid sorbent makes this method easy and simple. However, the method is time-consuming, costly and not very suitable for complex matrices. SPE is mostly used for the extraction and preconcentration of organic compounds in aqueous samples (Fritz, 1999; Richardson and Ternes, 2011).

SPME is a simple method in which the analyte, most commonly an organic compound, is being extracted from an aqueous or gaseous phase on to a solid sorbent coated with a fiber that carries a thin layer of solid polymeric material. However, the limitations are high cost of the coated fibers, short lifetime, contamination risk between analyses and low capacity (Psillakis and Kalogerakis, 2003; Sarfaraz-Yazdi and Amiri, 2010). Recently, dispersive-based procedures have gained importance as rapid and efficient sample treatment methodologies also for inorganic analytes. In dispersive solid phase microextraction the solid sorbent in the µg or mg range is dispersed in the sample solution. After sorption the analytes are eluted or directly determined by a suitable spectroscopic technique (Alcudia-León et al., 2009; Zawisza et al., 2012; Sitko et al., 2012).

1.8.2.1. Liquid phase microextraction (LPME)

LPME is the miniaturized LLE technique. Its advantages over conventional extraction procedures (simplicity, effectiveness, rapidity and low consumption of organic solvents) has also attracted its application in the complex food analysis field, in which it has clearly provided good and challenging results (Asensio-Ramos et al., 2011). Over the last few years, liquid-phase microextraction (LPME) in its different application modes, namely single drop microextraction (SDME), dispersive liquid–liquid microextraction (DLLME) and hollow fiber-liquid phase microextraction (HF-LPME) (Figure 1.5) has been increasingly applied for the extraction of both inorganic and organic analytes from different matrices.

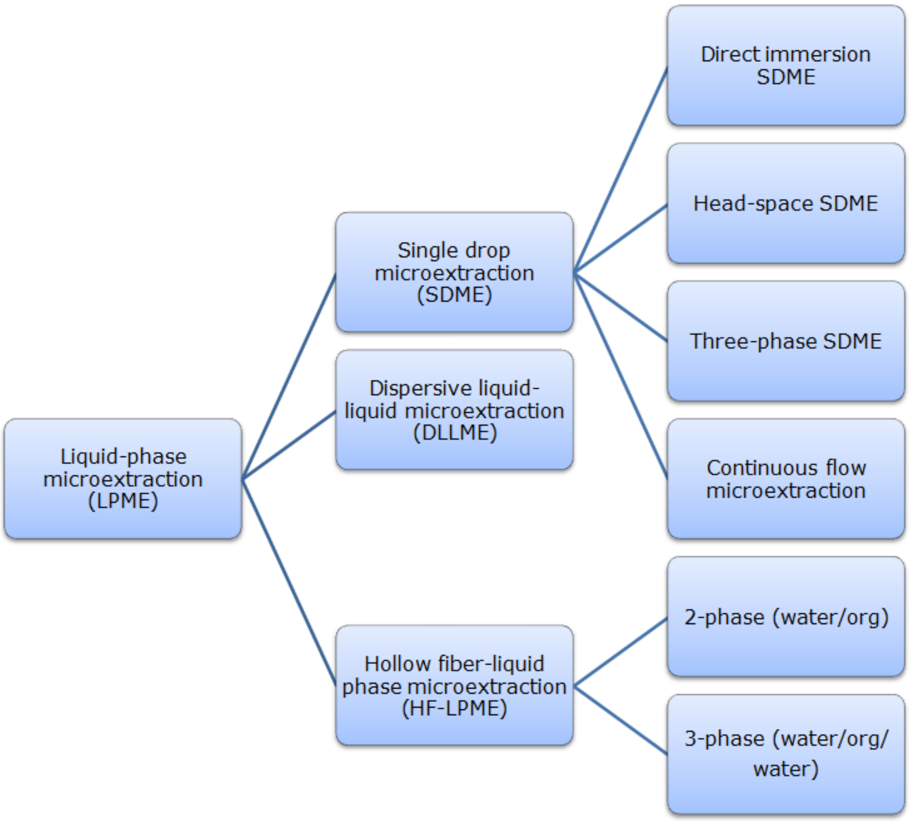


Figure 1.5. Summary tree for the different of liquid phase microextraction techniques.

1.8.2.1.1. Single-drop microextraction (SDME)

SDME is the LPME technique in which the extraction medium is in the form of a microdrop of an organic solvent suspended from the tip of a microsyringe into the liquid sample medium (Dadfarnia and Haji Shabani, 2010). The analytes are extracted from the sample solution into the droplet using passive diffusion (Pedersen-Bjergaard and Rasmussen, 2008). This is not a very robust method due to the instability and irregular formation of the droplet (Psillakis and Kalogerakis, 2003; Mahugo-Santana et al., 2011). Different modes of SDME such as direct immersion SDME, headspace SDME, 3-phase SDME and continuous flow microextraction have been developed for various analytical requirements (Jeannot and Cantwell, 1996). Headspace SDME was first used in combination with ETAAS for the determination of aqueous As (Chamsaz et al., 2003).

1.8.2.1.2. Dispersive liquid-liquid microextraction (DLLME)

DLLME is a ternary solvent system very similar to homogeneous LLE or cloud point extraction (CPE), involving a water immiscible, extracting organic solvent and a dispersing soluble with both the extracting andd the aqueous phase (e.g., acetone, methanol, ethanol or acetonitrile) (Pena-Pereira et al., 2009; Dadfarnia and Haji Shabani, 2010). This method was originally designed for extraction of organic compounds (Rahnama Kozani et al., 2007), however, very soon the application switched to inorganic analytes. This technique involves rapid injection of both the extracting and disperser solvents into the aqueous sample containing the analyte, thereby creating a large interface (between the extracting solvent and the aqueous sample) helping the equilibrium in few seconds. Then these phases are separated by centrifugation with the settling of fine droplets at the bottom (Rezaee et al., 2006; Sarfaraz-Yazdi and Amiri, 2010). DLLME has been applied to determine cadmium in water samples (Jahromi et al., 2007) and Rivas et al. (2009) studied the speciation of As and Sb in water samples using DLLME combined with ETAAS.

1.8.2.1.3. Hollow fiber-liquid phase microextraction (HF-LPME)

Pedersen-Bjergaard and Rasmussen used the core principle of supported liquid membranes (SLM) and transformed into a simple, low-cost units for liquid-liquid microextraction using commercial polypropylene fibers as membrane. In case of the hollow-fiber liquid-phase microextraction (HF-LPME), analytes are firstly extracted into a solvent sustained in the pores of a hydrophobic porous hollow fibers in rod configuration or U-shape (Jonsson and Mathiasson, 2001; Psillakis and Kalogerakis, 2003; Chimuka et al., 2011; Mahugo-Santana et al., 2011), and later into an acceptor solution placed inside the lumen of the fiber. HF-LPME modes can be classified according to the number of phases involved in the system into 2-phase or 3-phase HF-LPME. In these systems, sample donor and the acceptor phases are separated by the porous membrane of the hollow fiber, so they are not in direct contact. However, some modifications have been introduced in the last years, which will be later commented together with some of its applications. The pores of the fiber are impregnated with an organic solvent and the lumen of the hollow fiber is filled with µL volume of acceptor phase that can be the same organic solvent (2-phase system) or an aqueous stripping solution (3-phase system) as shown in Figure 1.6 (Psillakis and Kalogerakis, 2003; Rasmussen and Pedersen-Bjergaard, 2004; Mahugo-Santana et al., 2011). Then the hollow fiber is placed into a aqueous solution of target analyte called donor/feeding phase for extraction into the extraction/stripping phase prior to subsequent analysis of the extracted specific analyte. In this system, feeding/donor phase to acceptor/stripping phase volume solution can be kept very high resulting in high enrichment factor. Having all the benefits of the LPME, HF-LPME additionally prevents the transport of macromolecules, particles and molecules insoluble in the organic solvent used to the acceptor phase (Jonsson and Mathiasson, 2001; Psillakis and Kalogerakis, 2003; Lee et al., 2008; Sarfaraz-Yazdi and Amiri, 2010).

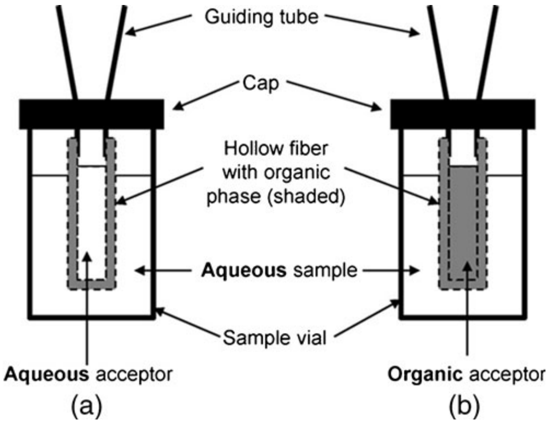


Figure 1.6. Outline of the a) 3-phase and b) 2-phase HF-LPME set-ups (after Han and Row, 2012).

The efficiency of HF-LPME is controlled by the enrichment factor of the method and extraction efficiency (E). Extraction efficiency is the measure of amount of analyte recovered in the acceptor phase from the donor phase and calculated as:

$E = (C_A/C_D) \times 100\%$

where C_A is the amount of analyte in the acceptor phase and C_D is amount of analyte present in the donor phase at equilibrium.

Enrichment factor (Ee) is defined as how many fold the analyte amount has increased in the acceptor phase after preconcentration as compared actual initial concentration of the analyte in the donor phase, and measured as:

$Ee = (m_A{}^t/m_D{}^i)$

where m_A^t is the concentration of the analyte in acceptor phase at equilibrium and m_D^i is the initial concentration of analyte in the donor phase.

1.8.2.1.3.1. Principles of 2-phase HF-LPME

Analytes are extracted from an aqueous phase into an organic acceptor solvent impregnated within the pores and in the lumen of the hollow fiber. The membrane wall acts as the barrier between the organic and the aqueous phase, and the extracted analyte in the acceptor phase can be measured using chromatographic techniques. The basic principle can be described by the following equation:

$A_{donor} \leftrightarrow A_{acceptor}$

where A_{donor} is the target analyte in donor aqueous solution and $A_{acceptor}$ is the analyte in acceptor organic solution.

In this system, the final acceptor phase containing the analyte is an organic phase.

1.8.2.1.3.2. Principles of 3-phase HF-LPME

In this method, analytes are extracted from an aqueous donor phase (feeding phase) into an aqueous acceptor phase (stripping phase) present inside the lumen of the hollow fiber membrane. They are separated by a water immiscible organic solvent (membrane phase) impregnated within the pores of the hollow fiber. The following equation can explain the basic principle:

$A_{aqueous/feeding} \leftrightarrow A_{organic/membrane} \leftrightarrow A_{aqueous/stripping}$

where $A_{aqueous/feeding}$ is the target analyte in the aqueous feeding solution, $A_{organic/membrane}$ is the target analyte in the organic membrane phase and $A_{aqueous/stripping}$ is the target analyte in the aqueous stripping phase.

In this system, the final acceptor phase containing the analyte is an aqueous phase.

The basic mechanism for both two and 3-phase HF-LPME is diffusion, in which hydrophobic analytes are extracted due to partition co-efficients. However, metal ions are hydrophilic in nature and thus produce low partition co-efficient resulting in poor extraction. This can be achieved in a active transport mode (Ho et al., 2003;

Jiang et al., 2008), in which a complexing agent or a extractant can be added to form a hydrophobic complex or ion-pair with the analyte that can be extracted into the organic phase either present in the hollow fiber lumen (2-phase) or inside the pores (3-phase).

This thesis has focused on the applicability of HF-LPME as an extracting and preconcentration technique for the determination and speciation of As in aqueous samples in combination with total X-ray fluorescence (TXRF).

1.8.3. Liquid-phase microextraction (LPME) combined with total reflection X-ray fluorescence (TXRF) spectrometry

LPME has been used to determine As species in water samples in combination with HPLC-ICP-MS or GC-MS techniques (Radke et al., 2012). HF-LPME has been reported for the measurement of antimony species in tandem with thermospray flame furnace AAS (Zeng et al., 2011). Very recently, speciation of As has been reported using DLLME as the preconcentration technique and ETAAS as the measuring instruments (Rabieh et al., 2013). Most of the techniques mentioned above suffers from matrix effect and quite expensive. A relatively inexpensive alternative microanalytical technique could be total reflection X-ray fluorescence (TXRF) spectrometry. TXRF is a well established multielemental technique especially suitable for liquid and powdered samples (Margui et al., 2010) (Figure 1.7).

Figure 1.7. A benchtop total reflection X-ray fluorescence (TXRF) spectrometer "S2 PICOFOX".

In 1971, Yoneda and Horiuchi (1971) reported the advantages of total reflection of X-rays falling at an optically flat, smooth surface of a reflector at an angle smaller than the critical angle ($\theta_c \sim 0.1^{\circ}$), and causing in total reflection. Therefore, most of the primary beam gets reflected and subsequently spectral background is significantly reduced (Margui and van Grieken, 2013). Critical angle (θ_c) can be calculated following the equation below:

$$\theta_c = 1.65/E \times \surd(Z/A)\rho$$

where E represents the photon energy (kV), Z is the atomic number of the reflector, A is the atomic mass (g/mol), and ρ is the density (g/cm^3).

In addition to the background reduction, reflected beams also induce excitation, resulting in doubling of the fluorescence signal intensity. Moreover, the detector can be positioned very close to the sample leading to availability of large solid angle for detection of fluorescence signal (Figure 1.8).

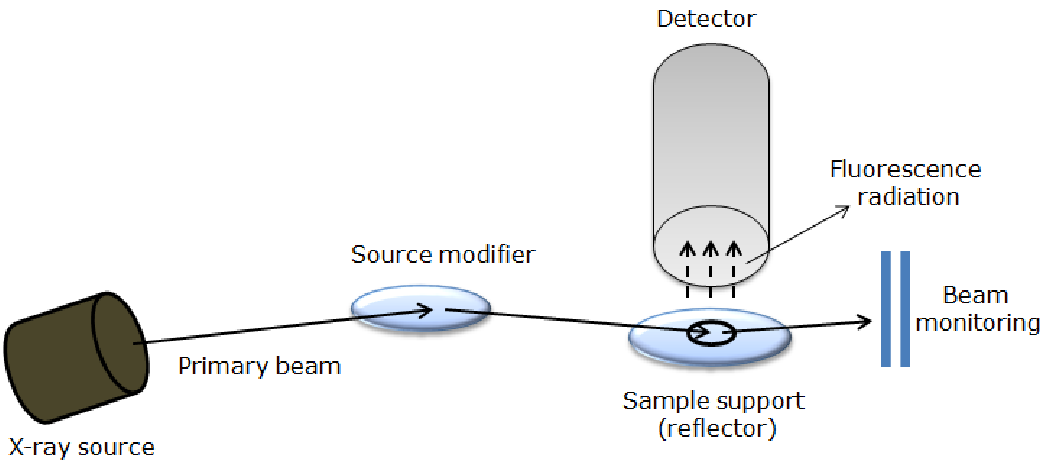


Figure 1.8. Arrangement of a TXRF system, modified after Margui and Van Grieken (2013).

Extremely small amounts of samples (in microliters or micrograms) should be introduced on the sample carriers as thin layers. This helps to avoid possibility of matrix influence. The deposited samples are generally dried before exposing them to the final X-ray measurement. This technique is also very simple, versatile and cost effective.

LPME followed by TXRF analysis for the determination of metals in various environmental matrices have been proposed in recent times for selenium, antimony (Margui et al., 2010, 2013). However, there is no report on determination and speciation of As using combined LPME-TXRF technique. This thesis is focused on using the HF-LPME-TXRF technique for the determination and speciation of As in water samples.

References

Acharyya S. K., Chakraborty P., Lahiri S., Raymahashay B. C., Guha S., Bhowmik A. (1999) Comment on Nickson et al. Arsenic poisoning of Bangladesh groundwater. *Nature* **401**, 545.

Ahmad S. A., Bandaranayake D., Khan A. W., Hadi S. A., Uddin G., Abdul M. (1997) Arsenic contamination in groundwater and arsenicosis in Bangladesh. *Int. J. Environ. Health Res.* **7**, 271–276.

Ahmed K. M, Bhattacharya P., Hasan M. A., Akhter S. H., Alam S. M. M, Bhuiyan M. A. H., Imam M. B., Khan A. A., Sracek O. (2004) Arsenic enrichment in groundwater in the alluvial aquifers in Bangladesh: an overview. *Appl. Geochem.* **19**, 215–130.

Ahmed K. M., Rahman M. W., Cheng Z., van Geen A. (2008) Comparison of dissolved and particulate arsenic distributions in shallow aquifers of Chakdaha, India, and Araihazar, Bangladesh. Geochem. Trans. 9, DOI:10.1186/1467-4866-9-1.

Ahuja S. (2008) Solutions for Arsenic Contamination of Groundwater. In: Ahuja, S., Ed. Arsenic contamination of groundwater: Mechanism, Analysis, and Remediation. 367-376, John Wiley & Sons, Hoboken, New Jersey.

Akai J., Izumi K., Fukuhara H., Masuda H., Nakano S., Yoshimura T., Ohfuji H., Anawar H. M., Akai K. (2004) Mineralogical and Geomicrobiological investigations on groundwater arsenic enrichment in Bangladesh. *Appl. Geochem.* **19**, 215–230.

Alam M. G. M., Allinson G., Stagnitt F., Tanaka A., Westbrooke M. (2002) Arsenic contamination in Bangladesh groundwater: a major environmental and social disaster. *Int. J. Environ. Health Res.* **12**, 236–253.

Alcudia-León M. C., Lucena R., Cárdenas S., Valcárcel M. (2009) Dispersive solid phase extraction for in sorbent surface attenuated total reflection infrared detection. *Anal. Chem.* **81**, 1184-1190.

Appelo C. A. J., van der Weiden M. J. J., Tournassat C., Charlet L. (2002). Surface complexation of ferrous iron and carbonate on ferrihydrite and the mobilization of arsenic. *Environ. Sci. Technol.* **36**, 3096–3103.

Argos M., Kalra T., Rathouz P. J., Chen Y., Pierce B., Parvez F., Islam T., Ahmed A., Rakibuz-zaman M., Hasan R., Sarwar G., Slavkovich V., van Geen A., Graziano J., Ahsan H. (2010) A prospective cohort study of arsenic exposure from drinking water and all-cause and chronic disease mortality in Bangladesh. *The Lancet* **376**, 252–258.

Asensio-Ramos M., Ravelo-Perez L. M., Gonzalez-Curbelo M. A., Hernandez-Borges J. (2011) Liquid phase microextraction applications in food analysis. *J. Chromatogr. A* **1218**, 7415–7437.

Bang S., Patel M., Lippincott L., Meng X. (2005) Removal of arsenic from groundwater by granular titanium dioxide adsorbent. *Chemosphere* **60**, 389–397.

Barman A. R. (1992) Geological history and hydrocarbon exploration in Bengal Basin. *Indian Journal of Geology* **64**, 235–258.

Berg M., Tran H. C., Ngyen T. C., Pham H. V., Schertenleib R., Giger W. (2001) Arsenic Contamination of Groundwater and Drinking Water in Vietnam: A Human Health Threat. *Environ. Sci. Technol.* **35**, 2621–2626.

BGS and DPHE (2001) In: Kinniburgh, D.G., Smedley, P.L. (Eds.), Arsenic contamination of groundwater in Bangladesh. British Geological Survey WC/00/19, Keyworth.

Bhattacharya P., Chatterjee D., Jacks G. (1997) Occurrence of arsenic-contaminated groundwater in alluvial aquifers from delta plains, Eastern India: Options for safe drinking water supply. *Int. J. Water Resour. Dev.* **13**, 79–92.

Bhattacharya P., Frisbie S. H., Smith E., Naidu R., Sarkar B. (2002a) Arsenic in the environment: a global perspective. In: Sarkar, B. (ed.) Hand Book of Heavy Metals in the Environment. Marcel Dekker, New York, pp. 145–215.

Bhattacharya P., Jacks G., Ahmed K. M., Routh J., Khan A. A. (2002b) Arsenic in groundwater of the Bengal Delta Plain aquifers in Bangladesh. *Bull. Environ. Contam. Toxicol.* **69**, 538–545.

Bhattacharyya R., Chatterjee D., Nath B., Jana J., Jacks G., Vahter M. (2003b): High arsenic groundwater: Mobilization , metabolism and mitigation – An overview in the Bengal Delta Plain. *Mol. Cell. Biochem.* **253**, 347–355.

Bhattacharyya R., Jana J., Nath B., Sahu S. J., Chatterjee D., Jacks G. (2003a). Groundwater As mobilization in the Bengal Delta Plain, the use of ferralite as a possible remedial measure – A case study. *Appl. Geochem.* **18**, 1435–1451.

Biswas A., Majumder S., Neidhardt H., Halder D., Bhowmick S., Mukherjee-Goswami A.,Kundu A., Saha D., Berner Z., Chatterjee D. (2011) Groundwater chemistry and redoxprocesses: Depth dependent arsenic release mechanism. *Appl. Geochem.* **26**, 516–525.

Borch T., Kretzschmar R., Kappler A., Cappelen P. V., Gindervogel M., Voegelin A., Campbell K. (2010) Biogeochemical redox processes and their impact on contaminant dynamics. *Environ. Sci. Technol.* **44**, 15–23.

Bundschuh J., Farias B., Martin R., Storniolo A., Bhattacharya P., Cortes J., Bonorino G., Albouy R. (2004) Grounwater arsenic in the Chaco- Pampean Plain, Argentina: case study from Robles county, Santiago del Estero Province. *Appl. Geochem.* **19**, 231–243.

Bundschuh J., Litter M. I., Parvez F., Román-ross G., Nicoli H. B., Jean J-S., Liu C-W., Lopez D., Armienta M. A., Guilherme L. R. G., Cuevas A. G., Cornejo L., Cumbal L., Toujaguez R. (2012) One century of arsenic exposure in Latin America: A review of history and occurrence from 14 countries. *Sci. Total Environ.* **429**, 2–35.

Bundschuh, J., Garcia, M. E., Birkle, P., et al. (2007) Groundwater arsenic in rural Latin America – occurrence, health effects and remediation experiences. In: Bundschuh, J., Armienta, M. A., Bhattacharya, P., Matschullat, J., Mukherjee, A. B. (eds.) Geogenic Arsenic in Groundwater of Latin America. A. A. Balkema Publisher, The Netherlands.

Chakraborti, D., Rahman,. M.M., Paul, K., Chowdhury, U.K., Sengupta, M.K., Lodh, D., Chanda C. R., Saha K. C., Mukherjee S. C. (2002) Arsenic calamity in the Indian subcontinent. What lessons have been learned? *Talanta*. **58**, 3–22.

Chamsaz M., Arbab-Zavar M. H., Nazari S. (2003) Determination of arsenic by electrothermal atomic absorption spectrometry using headspace liquid phase microextraction after in situ hydride generation. *J. Anal. At. Spectrom.* **18**, 1279–1282.

Chang Y. Y., Lee S. M., Yang J. K. (2009) Removal of As(III) and As(V) by natural and synthetic metal oxides. *Colloid Surf. A-Physicochem. Eng. Asp.* **346**, 202–207.

Charlet L., Chakraborty S., Appelo C. A. J., Roman-Ross G., Nath B., Ansari A. A., Lanson M., Chatterjee D., Basu Mallik S. (2007) Chemodynamics of an arsenic ''hotspot'' in a West Bengal aquifer: A field and reactive transport modelling study. *Appl. Geochem.* **22**, 1273–1292.

Charlet L., Polya D. A. (2006) Arsenic in shallow, reducing groundwaters in southern Asia: An environmental health disaster. *Elements.* 2, 91–96.

Charlet L., Roman-Ross G., Spadini L., Rumbach G. (2003) Propagation of a natural arsenic plume in West Bengal, India. *J. de Physique IV* **107**, 285–288.

Chatterjee D., Chakraborty S., Nath B., Jana J., Bhattacharya R., Basu Mallik S., Charlet L. (2003) Mobilization of arsenic in sedimentary aquifer vis-à-vis subsurface iron reduction processes. *Journal de Physique IV* **107**, 293–296.

Chatterjee D., Halder D., Majumder S., Biswas A., Bhattacharya P., Bhowmick S., Mukherjee-Goswami A., Saha D., Maity P. B., Chatterjee D., Nath B., Mukherjee A., Bundschuh J. (2010) Assessment of arsenic exposure from groundwater and rice in Bengal Delta Region, West Bengal, India. *Water Res.* **44**, 5803–5812.

Chatterjee D., Roy K. K., Basu B. B. (2005) Riddle of arsenic in groundwater of Bengal Delta Plain – Role of non-inland source and redox traps. *Environ. Geol.* **49**, 188-206.

Chen C. J., Chuang Y. C., Lin T. M., Wu H. Y. (1985) Malignant neoplasms among residents of a blackfoot disease endemic area in Taiwan: High-arsenic artesian well water and cancers. *Cancer Res.* **45**, 5895–5899.

Chen S.-L., Dzeng S. R., Yang M.-H., Chiu K.-W., Shieh G.-M., Wai M. W. (1994) Arsenic Species in Groundwaters of the Blackfoot Disease Area, Taiwan. *Environ. Sci. Technol.* **28**, 877–881.

Chimuka L., Michel M., Cukrowska E., Buszewski B. (2011) Advances in sample preparation using membrane based liquid-phase microextraction techniques. *Trends Anal. Chem.* **30**, 1781–1792.

Chowdhury T. R., Basu G. K., Mandal B. K., Biswas B. K., Samanta G., Chowdhury U. K., Chanda C. R., Lodh D., Lal Roy S., Saha K. C., Roy S., Kabir S., Quamruzzaman Q., Chakraborti D. (1999) Arsenic poisening in the Ganges Delta. *Nature* **401**, 545–546.

Cullen W., Reimer K. (1989) Arsenic speciation in the environment. *Chem. Rev.* **89**, 713–764.

Dadfarnia S., Haji Shabani A. M. (2010) Recent development in liquid phase microextraction for determination of trace level concentration of metals – A review. *Anal. Chim. Acta* **658**, 107–119.

Das D., Chatterjee A., Samanta G., Mandal B., Chowdhury T. R., Samanta G., Chowdhury P. P., Chanda C., Basu G., Lodh D., Nandi S., Chakraborty T., Mandal S., Bhattacharya S. M., Chakraborti. (1994) Arsenic contamination in groundwater in six districts of West Bengal, India: The biggest arsenic calamity in the world. *Analyst* **119**, 168N–170N.

De Laeter J. R., Bohlke J. K., De Bievre P., Hidaka H., Taylor P. D. P. (2003) Atomic weights of the elements: Review 2000 (IUPAC Technical Report). *Pure Appl. Chem.* **75**, 683–800.

Dixit S., Hering J. G. (2006) Sorption of Fe(II) and As(III) on goethite in single and dual-sorbate systems. *Chem. Geol.* **228**, 6–15.

Dufailly V., Noel L., Guerin T. (2008) Optimization and critical evaluation of a collision cell technology ICPMS system for the determination of arsenic in the food stuffs of animal original. *Anal. Chim. Acta* **611**, 134–142.

Erdem N., Henden E. (2004) Inter-element interferences in the determination of arsenic and antimony by hydride generation atomic absorption spectrometry with a quartz tube atomizer. *Anal. Chim. Acta* **505**, 59–65.

Fendorf S., Michael H. A., van Geen A. (2010) Spatial and temporal variations of groundwater arsenic in south and Southeast Asia. *Science* **328**, 1123–1127.

Fierro V., Muniz G., Gonzalez-Sánchez G., Ballinas M. L., Celzard A. (2009) Arsenic removal by iron-doped activated carbons prepared by ferric chloride forced hydrolysis. *J. Hazard. Mater.* **168**, 430–437.

Fiket Z., Roje V., Mikac N., Kniewald G. (2007) Determination of arsenic and other trace elements in bottled waters by high resolution inductively coupled plasma mass spectrometry. *Croat. Chem. Acta* **80**, 91–100.

Fritz J. S. (1999) Analytical solid-phase extraction. Wiley-VCH, ISBN: 0-471-24667-0.

Fujino Y., Guo X., Shiranr K., Liu J., Wu K., Miyatake M., Tanabe K., Kusuda T., Yoshimura T. (2006) Arsenic in Drinking Water and Peripheral Nerve Conduction Velocity among Residents of a Chronically Arsenic-affected Area in Inner Mongolia. *J. Epidemiol.* **16**, 207–213.

Gault A. G., Davidson L. E., Lythgoe P. R., Polya D. A., Abou-Shakra F. R., Walker H. J., Chatterjee D. (2003) Iron and arsenic speciation in groundwater from West Bengal, India by coupled HPLC-ICPMS utilizing a hexapole collision cell in plasma source mass spectrophotometer: application and emerging technologies. *Roy. Soc. Chem. Spec. Publ.* **288**, 112–126.

Gault A. G., Jana J., Chakraborty S., Mukherjee P., Sarkar M., Nath B., Polya D. A., Chatterjee D. (2005) Preservation strategies for inorganic As species in high iron, low-Eh groundwater from West Bengal, India. *Anal. Bioanal. Chem.* **381**, 347–353.

Goh K. H., Lim T. T. (2004) Geochemistry of inorganic arsenic and selenium in a tropical soil: effect of reaction time, pH, and competitive anions on arsenic and selenium adsorption. *Chemosphere* **55**, 849–859.

Goh K. H., Lim T. T. (2005) Arsenic fractionation in a fine soil fraction and influence of various anions on its mobility in the subsurface environment. *Appl. Geochem.* **20**, 229–239.

Gracia Sanchez A., Alvarez-Ayuso E., Rodriguez F. (2002) Sorption of As(V) by some oxyhydroxides and clay minerals. Application to its immobilization in two polluted mining soils. *Clay Miner.* **37**, 187–194.

Guha Mazumder D. N., Chakraborty A. K., Ghose A., Gupta J. D., Chakraborty D. P., Dey S. B., Chattopadhyay N. (1988) Chronic arsenic toxicity from drinking tubewell water in rural West Bengal. *Bull. World Health Org.* **66**, 499–506.

Guha Mazumder D. N., De B. K., Santra A., Dasgupta J., Ghosh N., Roy B. K., Ghoshal U. C., Saha J., Chatterjee A., Dutta S., Haqu R., Smith A. H., Chakraborty D., Angle C. R., Centeno J. A. (1999) Chronic arsenic toxicity: Epidemiology, natural history and treatment. In: Chappell, W.R., Abernathy, C.O. & Calderon, R.L., eds, *Arsenic Exposure and Health Effects*, Amsterdam, Elsevier Science, pp. 335‑347.

Guo H., Stüben D., Berner Z. (2007) Removal of arsenic from aqueous solution by natural siderite and hematite. *Appl. Geochem.* **22**, 1039–1051.

Guo H., Yang S., Tang X., Li Y., Shen Z. (2008) Groundwater geochemistry and its implications for arsenic mobilization in shallow aquifers of the Hetao Basin, Inner Mongolia. *Sci. Total. Environ.* **393**, 131–144.

Halder D., Bhowmick S., Biswas A., Mandal U., Nriagu J., Guha Mazumdar D. N., Chatterjee D., Bhattacharya P. (2012) Consumption of brown rice: a potential pathway for arsenic exposure in rural Bengal. *Environ. Sci. Technol.* **46**, 4142–4148.

Han D., Row K. H. (2012) Trends in liquid-phase microextraction, and its application to environmental and biological samples. *Microchim. Acta* **176**, 1–22.

Harvey C. F., Swartz C. H., Badruzzaman A. B. M., Keon-Blute N., Yu W., Ali M. A., Jay J., Beckie R., Niedan V., Brabander D., Oates P. M., Ashfaque K. N., Islam S., Hemond H. F., Ahmed M. F. (2005) Groundwater arsenic contamination on the Ganges Delta: biogeochemistry, hydrology, human perturbations, and human suffering on a large scale. *C.R. Geosci.* **337**, 285–296.

Harvey C. F., Swartz C. H., Badruzzaman A. B. M., Keon-Blute N., Yu W., Ali M. A., Jay J., Beckie R., Niedan V., Brabander D., Oates P. M., Ashfaque K. N., Islam S., Hemond H. F., Ahmed M. F. (2002) Arsenic Mobility and Groundwater Extraction in Bangladesh. *Science* **298**, 1602–1606.

Hattori K., Takahasi Y., Guillot S., Johanson B. (2005) Occurrence of arsenic(V) in forearc mantle serpentinites based on X-ray absorption spectroscopy study. *Geochim. Cosmochim. Acta* **69**, 5585–5596.

Ho T. S., Halvorsen T. G., Pedersen-Bjergaard S., Rasmussen E. (2003) Liquid-phase microextraction of hydrophilic drugs by carrier-mediated transport. *J. Chromatogr. A* **998**, 61–72.

Hopenhayn C. (2006) Arsenic in Drinking Water: Impact on Human Health. *Elements* **2**, 103–107.

http://www.bgs.ac.uk/arsenic/ (last accessed on 24th June, 2013)

Hughes, M. F., Kenyon, E. M. (1998) Dose-dependent effects on the disposition of monomethylarsonic acid and dimethylarsenic acid in the mouse after intravenous administration. *J. Toxicol. Environ. Health* A **53**, 95–112.

Hung D. Q., Nekrassova O., Compton R. G. (2004) Analytical methods for inorganic arsenic in water: a review. *Talanta* **64**, 269–277.

Huq S. M. I., Jahan A., Quazi A., Islam K., Zaher A., Naidu R. (2001) The possible contamination from arsenic through food chain. In: Jacks, G., Bhattacharya, P., Khan, A. A. (eds.) Groundwater Arsenic Contamination in the Bengal Delta Plain of Bangladesh: Proceedings of the KTH-Dhaka University Seminar. University of Dhaka, Bangladesh, KTH Special Publication, TRITA-AMI Report 3084, pp. 91–96.

Indian Standard Specifications for Drinking Water (1992) IS 10500. Available from: http://hppcb.gov.in/eiasorang/spec.pdf (last accessed on 26th June, 2013).

Inskeep W. P., McDermott T. R., Fendorf S. (2002) Arsenic (V)/(III) Cycling in Soils and Natural Waters: Chemical and Microbiological Processes. In: Frankenberger Jr., W.T., Ed. (2002): Environmental Chemistry of Arsenic. 183-215, Marcel Dekker Inc., New York.

Jahromi E. Z., Bidari A., Assadi Y., Milani Hosseini M. R., Jamali M. R. (2007) Dispersive liquid-liquid microextraction combined with graphite furnace atomic absorption spectrometry: Ultra trace determination of cadmium in water samples. *Anal. Chim. Acta* **585**, 305–311.

Jeannot M. A., Cantwell F. F. (1996) Solvent microextraction into a single drop. *Anal. Chem.* **68**, 2236–2240.

Jiang H., Hu B., Chen B., Zu W. (2008) Hollow fiber liquid phase microextraction combined with graphite furnace atomic absorption spectrometry for the determination of methylmercury in human hair and sludge samples. *Spectroc. Acta Pt. B-Atom. Spectr.* **63**, 770–776.

Jing C., Meng X., Liu S., Baidas S., Patraju R., Christodoulatos C., Korfiatis G. P. (2006) Surface complexing of organic arsenic on nanocrystalline titanium oxide. *J. Colloid Interface Sci.* **290**, 14–21.

Jonsson J. A., Mathiasson L. (2001) Membraane extraction in analytical chemistry. *J. Sep. Sci.* **24**, 495–507.

Kaponica M., Novotny L. (1998) Determination of traces arsenic(III) by anodic stripping voltammetry in solutions, natural waters and biological material. *Anal. Chim. Acta* **368**, 211–218.

Kinniburgh D. G., Smedley P.L. (2001): Arsenic contamination of groundwater in Bangladesh, Vol. 1: Summary. Bangladesh Department for Public Health Engineering and British Geological Survey, Keyworth. Available from: http://www.bgs.ac.uk/arsenic (last accessed on 26th June, 2013)

Knowels F. C., Benson A. A. (1983) The biochemistry of arsenic. *Trends Biochem. Sci.* **8**, 178–180.

Lawson M., Ballentine C. J., Polya D. A., Boyce A. J., Mondal D., Chatterjee D., Majumder S., Biswas A. (2008) The geochemical and isotopic composition of groundwaters in West Bengal: tracing ground-surface water interaction and its role in arsenic release. *Min. Mag.* **72**, 107–110.

Lee J., Lee H. K., Rasmussen K. E., Pedersen-Bjergaard S. (2008) Environmental and bioanalytical application of hollow fiber membrane liquid-phase microextraction: A review. *Anal. Chim. Acta* **624**, 253–268.

Lien H. L., Wilkin R. T. (2005) High-level arsenite removal from groundwater by zero-valent iron. *Chemosphere* **59**, 377–386.

Lima E. C., Brasil J. L., Vaghetti J. C. P. (2003) Evaluation of different permanent modifiers for the determination of arsenic in environmental samples by electrothermal atomic absorption spectrometry. *Talanta* **60**, 103–113.

Lin N.-F., Tang J., Bian J.-M. (2004) Geochemical environment and health problems in China. *Environ. Geochem. Health* **26**, 81–88.

Long J., Nagaosa Y. (2008) Determination of trace arsenic(III) by differential-pulse anodic stripping voltammetry with in-situ plated bismuth-film electrode. *Intern. J. Environ. Anal. Chem.* **88**, 51–60.

Lovey D.R., Phillips E. J. P. (1987) Rapid Assay for Microbially Reducible Ferric Iron in Aquatic Sediments. *Appl. Environ. Microbiol.* **53**, 1536–1540.

Lovley D. R. (1993) Dissimilatory metal reduction. *Annu. Rev. Microbiol.* **47**, 263–290.

Lovley D. R., Coates J. D., Bluny-Harris E. L., Phillips E. J. P., Woodward J. C. (1996) Humic substances as electron acceptors for microbial respiration. *Nature* **382**, 445–448.

Lu P., Zhu C. (2011) Arsenic Eh–pH diagrams at 25°C and 1bar. *Environ. Earth Sci.* **62**, 1673–1683.

Mahugo-Santana C., Sosa-Ferrera Z., Torres-Padron M. E., Santana-Rodriguez J. J. (2011) Application of approaches to liquid-phase microextraction for the determination of emerging pollutants. *Anal. Chem.* **30**, 731–748.

Mailloux B. J., Alexandrova E., Keimowitz A. R., Wovkulich K., Freyer G. A., Herron M., Stolz J.F., Kenna T. C., Pichler T., Polizzotto M. L., Dong H., Bishop M., Knappet P. S. K. (2009) Microbial Mineral Weathering for Nutrient Acquisition Releases Arsenic. *Appl. Env. Microbiol.* **75**, 2558–2565.

Mandal S., Padhi T., Patel R. K. (2011) Studies on the removal of arsenic (III) from water by a novel hybrid material. *J. Hazard. Mater.* **192**, 899–908.

Margui E., Floor G., Hidalgo M., Kregsamer P., Roman-Ross G., Streli C., Queralt I. (2010) Analytical possibilities of total reflection X-ray spectrometry (TXRF) for trace selenium determination in soils. *Anal. Chem.* **82**, 7744–7781.

Margui E., Sague M., Queralt I., Hidalgo M. (2013) Liquid phase microextraction strategies combined with total reflection X-ray spectrometry for the determination of low amounts of inorganic antimony species in waters. *Anal. Chim. Acta* **786**, 8–15.

Margui E., van Grieken R. (2013) X-ray fluorescence spectrometry and related techniques: An introduction. Momentum Press, NY.

Mays D. E., Hussam A. (2008) Voltammetric methods for determination and speciation of inorganic arsenic in the environment – a review. *Anal. Chim. Acta* **646**, 6–16; B. Daus, Topical issue: “The fate of arsenic in environment”, *Engi. Life Sci.* **6** (2008) 8, 571–572.

McArthur J. M., Banerjee D. M., Hudson-Edwards K. A., Mishra R., Purohit R., Ravenscroft P., Cronin A., Howarth R. J., Chatterjee A., Talukder T., Lowry D., Houghton S., Chadha D. K. (2004) Natural organic matter in sedimentary basins and its relation to arsenic in anoxic groundwater: the example of West Bengal and its worldwide implications. *Appl. Geochem.* **19**, 1255–1293.

McArthur J. M., Ravenscroft P., Safiulla S., Thirlwall M. F. (2001) Arsenic in groundwater: Testing pollution mechanisms for sedimentary aquifers in Bangladesh. *Water Resour. Res.* **37**, 109–117.

McNeill L. S., Edwards M. A. (1995) Soluble Arsenic Removal at Water Treatment Plants. *J. Am. Water Works Assoc.* **87**, 105–113.

Melamed D. (2005) Monitoring arsenic in the environment: a review of science and technologies with the potential for field measurements. *Anal. Chim. Acta* **532**, 1–13.

Metral J., Charlet L., Bureau S., Mallik S. B., Chakraborty S., Ahmed K. M., Rahman M. W., Cheng Z., van Geen A. (2008) Comparison of dissolved and particulate arsenic distributions in shallow aquifers of Chakdaha, India, and Araihazar, Bangladesh. *Geochem. Trans.* **9**, DOI:10.1186/1467-4866-9-1.

Mohan D., Pitman C. U. Jr. (2007) Arsenic removal from water/wastewater using adsorbents – A critical review. *J. Hazard. Mater.* **142**, 1–53.

Mondal D., Polya D. A. (2008) Rice is a major route for arsenic in Chakdaha block, Nadia district, West Bengal, India: A probabilistic risk assessment. *Appl. Geochem.* **23**, 2987–2998.

Morgada M. E., Levy I. K., Salomone V., Farias S. S., Lopez G., Litter M. I. (2009) Arsenic(V) removal with nanoparticulate zerovalent iron: Effect of UV light and humic acids. *Catal. Today* **143**, 261–268.

Mukherjee A., Fryar A. E., Scanlon B. R., Bhattacharya P., Bhattacharya A. (2011) Elevated arsenic in deeper groundwater of western Bengal basin, India: Extents and controls from regional to local-scale. *Appl. Geochem.* **26**, 600–613.

Mukherjee A., von Bromssen M., Scanlon B. R., Bhattacharya P., Fryar A. E., Hasan M. A., Ahmed K. M., Chatterjee D., Jacks G., Sracek O. (2008) Hydrogeochemical comparison and effects of overlapping redox zones on groundwater arsenic near the western (Bhagirathi sub-basin, India) and Eastern (Meghna sub-basin, Bangladesh) margins of the Bengal Basin. *J. Contam. Hydrol.* **99**, 31–48.

Muller K., Ciminelli V. S. T., Dantas M. S. D., Willscher S. (2010) A comparative study of As(III) and As(V) in aqueous solutions and adsorbed on ironoxyhydroxides by Raman spectroscopy. *Water Res.* **44**, 5660–5672.

Nath B., Berner Z., Basu Mallik S., Chatterjee D., Charlet L., Stüben D. (2005) Charachterization of aquifers conducting groundwaters with low and high arsenic concentrations: A comparative case study from West Bengal, India. *Min. Mag*. **69**, 841–853.

Nath B., Berner Z., Chatterjee D., Basu Mallik S., Stüben D. (2008) Mobility of arsenic in West Bengal aquifers conducting low and high groundwater arsenic. Part I: Comparative hydrochemical and hydrogeological characteristics. *Appl. Geochem.* **23**, 977–995.

National Academy of Sciences (NAS) (1977) Medical and biological effects of environmental pollutants: arsenic. National Academy of Sciences, Washington DC.

Neidhardt H., Biswas A., Freikowski D., Majumder S., Chatterjee D., Berner Z. A. (2013) Reconstructing the sedimentation history of the Bengal Delta Plain by means of geochemical and stable isotopic data. *Appl. Geochem.* **36**, 70–82.

Neidhardt H., Norra S., Tang X., Guo H., Stüben D. (2012) Impact of irrigation with high arsenic burdened groundwater on the soil-plant system: Results from a case study in the Inner Mongolia, China. *Environ. Pol.* **163**, 8–13.

Neumann R. B., Ashfaque K. N., Badruzzaman A. B. M., Ali M. A., Shoemaker J. K., Harvey C. H. (2010) Anthropogenic influences on groundwater arsenic concentrations in Bangladesh. *Nat. Geosci.* **3**, 46–52.

Norra S., Berner Z. A., Agarwala P., Wagner F., Chandrasekharam D., Stüben D. (2005) Impact of irrigation with As rich groundwater on soil and crops: a geochemical case study in West Bengal Delta Plain, India. *Appl. Geochem.* **20**, 1890–1906.

Nriagu J. O., Bhattacharya P., Mukherjee A. B., Bundschuh J., Zevenhoven R., Loeppert R. H. (2007) Arsenic in soil and groundwater: an overview. In:

Bhattacharya P., Mukherjee A. B., Bundschuh J., Zevenhoven R., Loeppert R. H., Eds. (2007): Arsenic in soil and groundwater environment: Biogeochemical Interactions, Health Effects and Remediation (Trace Metals and Other Contaminants in the Environment). 3-63, Elsevier, Amsterdam.

O'day P.A. (2006) Chemistry and Mineralogy of Arsenic. *Elements* **2**, 77–83.

Ona-Nguema G., Morin G., Juillot F., Calas G., Brown Jr. G. E. (2005) EXAFS Analysis of Arsenite Adsorption onto Two-Line Ferrihydrite, Hematite, Goethite, and Lepidocrocite. *Environ. Sci. Technol.* **39**, 9147–9155.

Oremland R. S., Stolz J. F. (2003) The Ecology of Arsenic. *Science* **300**, 939–944.

Pedersen-Bjergaard S., Rasmussen K. E. (2008) Liquid-phase microextraction with porous hollow fibers, a miniaturized and highly flexible format for liquid-liquid extraction. *J. Chromatogr. A* **1184**, 132–142.

Pena-Perreira F., Lavilla I., Bendicho C. (2009) Miniaturized preconcentration methods based on liquid-liquid extraction and their application in inorganic ultra-trace analysis and speciation: A review. Spectroc. Acta Pt. B-Atom. Spectr. **64**, 1–15.

Polya D., Charlet L. (2009) Rising arsenic risk? *Nat. Geosci.* **2**, 383–384.

Pomroy C., Charbonneau S. M., McCullough R. S., Tam G. K. H. (1980) Human retention studies with ^{74}As. *Toxicol. Appl. Pharmacol.* **53**, 550–556.

Pontius F. W., Brown K. G., Chen C. J. (1994) Health implications of Arsenic in drinking water. *J. Am. Water Work Ass.* **86,** 52–63**.**

Poole C. F. (2003) New trends in solid-phase extraction. *Trends Anal. Chem.* **22**, 362–373.

Postma D., Jessen S., Hue N. T. H., Duc M. T., Koch C. B., Viet P. H., Nhan P. Q., Larsen F. (2010) Mobilization of arsenic and iron from Red River floodplain sediments, Vietnam. *Geochim. Cosmochim. Acta* **74**, 3367–3381.

Postma D., Larsen F., Hue N. T. M., Duc M. T., Viet P. H., Nhan P. Q., Jessen S. (2007) Arsenic in groundwater of the Red River floodplain, Vietnam:

Controlling geochemical processes and reactive transport modeling. *Geochim. Cosmochim. Acta* **71**, 5054–5071.

Psillakis E., Kalogerakis N. (2003) Developments in liquid-phase microextraction. *Trends Anal. Chem.* **22**, 565–574.

Public Health Engineering Directorate (PHED) (1993) National Drinking Water Mission project on Arsenic pollution of groundwater in West Bengal. Final report, Steering Committee on Arsenic investigation. Government of West Bengal, India.

Rabieh S., Bagheri M., Planer-Friedrich B. (2013) Speciation of arsenite and arsenate by electrothermal AAS following ionic liquid dispersive liquid-liquid microextraction. *Microchim. Acta* **180**, 415–421.

Radke B., Jewell L., Namiesnik J. (2012) Analysis of arsenic species in environmental samples. *Clin. Rev. Anal. Chem.* **42**, 162–183.

Radke B., Namiesnik J., Bolalek J. (2003) Pathways and determinations of organometallic compounds in the marine environment with a particular emphasis on organotin. *Oceanol. Hydrobiol. Stud.* **32**, 43–71.

Rahman A., Vahter M., Ekstrom E. C. (2007) Association of arsenic exposure during pregnancy with fetal loss and infant death: a cohort study in Bangladesh. *Am. J. Epidemiol.* **165**, 1389–1396.

Rahman M. M., Sengupta M. K., Ahamed S., Chowdhury U. K., Lodh D., Hossain A., Das B., Roy N., Saha K. C., Palit S. K., Chakraborti D. (2005) Arsenic Contamination of Groundwater and it's Health Impact on Residents in a Village in West Bengal, India. *Bulletin of the World Health Organisation.* **83**, 49–57.

Rahman M., Tondel M., Ahmad S. A., Axelson O. (1998) Diabetes mellitus associated with arsenic exposure in Bangladesh. *Am. J. Epidemiol.* **148**, 198–203.

Rahnama-Kozani R., Assadi Y., Shemirani F., Milani Hosseini M-R., Jamali M. R. (2007) Part-per-trillion determination of chlorobenzenes in water using dispersive liquid-liquid microextraction combined gas chromatography-electron capture detection. *Talanta* **72**, 387–393.

Raiswell R. (2011) Iron Transport from the Continents to the Open Ocean: The Aging-Rejuvenation Cycle. *Elements* **7**, 101–106.

Rasmussen K. E., Pedersen-Bjergaard S. (2004) Developments in hollow fiber-based, liquid-phase microextraction. *Trends Anal. Chem.* **23**, 1–10.

Reimann C., Matschullat J., Birke M., Salminen R. (2009) Arsenic distribution in the environment: the effects of scale. *Appl. Geochem.* **24**, 1147–1167.

Rezaee M., Assadi Y., Hosseini M. M., Aghaee E., Ahmadi F., Berijani S. (2006) Determination of organic compounds in water using dispersive liquid-liquid microextraction. *J. Chromatogr. A* **1116**, 1-9.

Richardson S. D., Ternes T. A. (2011) Water analysis: emerging contaminants and current issues. *Anal. Chem.* **83**, 4614–4648.

Rivas R. E., Lopez-Garcia I., Hernandez-Cordoba M. (2009) Speciation of very low amounts of arsenic and antimony in waters using dispersive liquid-liquid microextraction and electrothermal atomic absorption spectrometry. Spectrochimica Acta Part B: Atomic Spectroscopy 64, 329-333.

Rowland H. A. L., Gault A. G., Charnock J. M., Polya D. A. (2005) Preservation and XANES determination of the oxidation state of solid-phase arsenic in shallow sedimentary aquifers in Bengal and Cambodia. *Mineral. Mag.* **69**, 825–839.

Sarafraz-Yazdi A., Amiri A. (2010) Liquid-phase microextraction. *Trends Anal. Chem.* **29**, 1–14.

Sarka A., Sengupta S., McArthur J. M., Ravenscroft P., Bera M. K., Bhushan R., Samanta A., Agrawal S. (2009) Evolution of Ganges–Brahmaputra western delta plain: clues from sedimentology and carbon isotopes. *Quat. Sci. Rev.* **28**, 2564–2581.

Schneiter R. W., Middlebrooks E. J. (1983) Arsenic and Fluoride Removal from Groundwater by Reverse Osmosis. *Environ. Int.* **9**, 289–291.

Sharim A., Shekharan N. C., Anuradha C. D., Hirano S. (2002) Speciation of arsenic in tube-well water samples collected from West Bengal, India, by high-performance liquid chromatography-inductively coupled plasma mass spectrometry. *Appl. Organomet. Chem.* **16**, 202–206.

Shen Y. S. (1973) Study of arsenic removal from drinking water. *J. Am. Water Works Assoc.* **65**, 543–547.

Sitko R., Zawisza B., Malicka E. (2012) Modification of carbon nanotubes for preconcentration, separation and determination of trace-metal ions. Trends Anal. Chem. **37**, 22-31.

Smedley P. L., Kinniburgh D. G. (2002) A review of the source, behaviour and distribution of arsenic in natural waters. *Appl. Geochem.* **17**, 517–568.

Smith A. H., Lingas E. O., Rahaman M. (2000) Contamination of drinking water by arsenic in Bangladesh: a public health emergency. *Bull. WHO* 78, 1093–1103.

Song Y., Swain G. M. (2007) Total inorganic arsenic detection in real water samples using anodic stripping voltammetry and a gold-coated diamond thin-film electrode. *Anal. Chim. Acta* **593**, 7–12.

Stüben D., Berner Z., Chandrasekharan D., Karmakar J. (2003) Arsenic Enrichment in Groundwater of West Bengal, India: Geochemical Evidence for Mobilization of As Under Reducing Conditions. *Appl. Geochem.* **18**, 1417–1434.

Stumm W., Morgan J. J. (1996) Aquatic chemistry: Chemical equilibria and rates in natural waters, 3rd edition. John Wiley & Sons, N.Y.

van Geen A. (2008) Arsenic meets dense populations. *Nat. Geosci.* **1**, 494–496.

van Geen A., Rose J., Thoral S., Garnier J. M., Zheng Y., Bottero J. Y. (2004) Decoupling of As and Fe release to Bangladesh groundwater under reducing conditions. Part II: Evidence from sediment incubations. *Geochim. Cosmochim. Acta* **68**, 3475–3486.

van Geen A., Zhang Y., Cheng Z., Aziz Z., Horneman A., Dhar R. K., Mailloux B., Stute M., Weinmand B., Goodbred S., Seddique A. A. (2006) A transect of groundwater and sediment properties in Araihazar, Bangladesh: Further evidence of decoupling between As and Fe mobilization. *Chem. Geol.* **228**, 85–96.

Vassileva E., Hoenig M. (2001) Determination of arsenic in plant samples by inductively coupled plasma atomic emission spectrometry with ultrasonic nebulization: a complex. *Spectroc. Acta Pt. B-Atom. Spectr.* **56**, 223–232.

Wagner F. (2005) Prozessverständnis einer Naturkatastrophe: eine geo- und hydrochemische Untersuchung der regionalen Arsen-Anreicherung im Grundwasser West Bengalens, (Indien). Dissertation an der Fakultät für Bauingenieur-, Geo- und Umweltwissenschaften, Universität Karlsruhe. *Karlsruher Mineralogische und Geochemische Hefte.* **29**, *165S.*

Welch A. H., Lico M. S. (1988) Factors controlling Arsenic and U in shallow groundwater, southern Carson Desert, Nevada. *Appl. Geochem.* **13**, 521–539.

Winkel L. H. E., Berg M., Amini M., Hug S. J., Johnson A. (2008) Predicting groundwater arsenic contamination in Southeast Asia from surface parameters. *Nat. Geosci.* **1**, 536–542.

World Health Organization (WHO) (2003) Arsenic in Drinking-water - Background document for development of WHO Guidelines for Drinking-water Quality. WHO/SDE/WSH/03.04/75. Available from: http://www.who.int/water_sanitation_health/dwq/chemicals/arsenic.pdf (last accessed on 15th July, 2013)

World Health Organization WHO (2011) Guidelines for Drinking-water Quality. 4th edition. World Health Organization, Geneva. Available from: http://whqlibdoc.who.int/publications/2011/9789241548151_eng.pdf (last accessed on 15th July, 2013)

Yoneda Y., Horiuchi T. (1971) Optical flats for use in X-ray spectrochemical microanalysis. *Rev. Sci. Instrum.* **42**, 1069.

Yu W. H., Harvey C. M., Harvey C. F. (2003) Arsenic in Groundwater in Bangladesh: A geostatistical and epidemiological framework for evaluating health effects and potential remedies. *Water Resour. Res.* **39,** 1146.

Zawisza B., Skorek R., Stankiewicz G., Sitko R. (2012) Carbon nanotubes as a solid sorbent for the preconcentration of Cr, Mn, Fe, Co, Ni, Cu, Zn and Pb prior to wavelength-dispersive X-ray fluorescence spectrometry. *Talanta* **99**, 918–923.

OBJECTIVES

Objectives

Arsenic (As) contamination of groundwater and related environmental hazard is a worldwide phenomenon, especially in south-east Asia. Number of studies have been propsed various As release mechanisms in groundwater and its distribution. However, there is still a gap to assess the role of hydrogeochemical and anthropogenic factors operating at regional to local scale. Innovation and improvement of household, cost-effective, user-friendly and eco-friendly As removal techniques is also necessary for the rural population of the As-affected areas. Developing new inexpensive, non-hazardous analytical methodologies for the determination of ultra-trace As and its speciation is another very interesting aspect. Thus, considering the aforementioned objectives, the more precise aims of the study were the followings:

1. An As affected study area was selected in Bengal Delta Plain (BDP), India to study the spatio-temporal effect of hydrochemistry, land-use pattern, redox changes due to monsoon and related recharge processes in connection with As distribution and transport in groundwater.

2. To study the colloidal distribution and fractionation of inorganic As for the first time in the area and to assess the possible role of organic vs. inorganic control over its transport in groundwater.

3. To develop cost-effective, environment friendly, household As removal techniques using only naturally available materials and resources that can be easy-to-use for the affected rural populations.

4. To develop novel, cheaper, eco-friendly analytical methodologies for the determination and speciation of ultra-trace As in water based on the HF-LPME combined with TXRF analysis.

RESULTS

CHAPTER 2: HETEROGENEOUS ARSENIC DISTRIBUTION IN A HOMOGENEOUS AQUIFER

A hydrogeochemical screening and field survey was carried out in the study area Chakdaha block, West Bengal to investigate the local scale spatial heterogeneity of arsenic (As) and to have an idea regarding the overall groundwater chemistry. It seems that one single proposed mechanism is perhaps not sufficient to describe the heterogeneous distribution of groundwater As, and it is possibly due to a combination of all the release mechanisms working together in patches.

2.1. Introduction

Naturally occurring, carcinogenic, arsenic (As) is omnipresent in hydrological systems, and is considered as the most serious abiotic contaminant of groundwater in several parts of the world (Chatterjee et al., 2005; Mukherjee et al., 2008a). The Quaternary aquifers of south-east Asia (mostly shallow, <50 m) are now often yielding high As groundwater. It is extensively used for irrigation and domestic purposes (cooking/drinking/bathing etc.) (Gault et al., 2005). In south-east Asia, As-rich groundwaters are often found in alluvium plains of regional rivers (Bhattacharya et al., 1997; Mukherjee-Goswami et al., 2008). Prolonged consumption of groundwater with elevated level of As may cause a formidable threat on human health (national guideline value >50 µg/L; WHO guideline value >10 µg/L) and millions of people are now at risk (Bhattacharyya et al., 2003a; Nath et al., 2008a; Chatterjee et al., 2010). In south-east Asia, the geographical extent (173 x 10^3 km^2) and human exposure (19 million affected and 55 million at risk) of As menace in BDP [Bengal Delta Plain, Bangladesh and West Bengal (India)] of As contamination in groundwater is reported as the greatest mass poisoning in human history (Smith et al., 2000; Bhattacharyya et al., 2003a; Chatterjee et al., 2004).

In Bengal Delta Plain (BDP), the spatial distribution of groundwater As is complex and patchy (contaminated areas interspersed with non-contaminated areas) (Chatterjee et al., 2005). The total arsenic (As_T) content of the BDP Holocene sediments is generally low (Table 2.1). These values [As (sediment)] are often within the typical range (0.5–2.5 mg/kg) of most rocks (primarily igneous and sedimentary rocks) (NAS, 1977). The sediment As depends on texture and mineralogy (Pal et al., 2002a). In surface soil, the As concentration is also low (0.4-2 mg/kg) (Kabata-Pendias and Pendias, 2001; Chatterjee et al., 2005) although the high As groundwater is frequently encountered in shallow (<50 m) BDP aquifers. The As contents of the deltaic (regional) river bed sediments (1.3-5.6 mg/kg) and their waters (0.33-3.83 µg/L) are also generally low (Datta and Subramanian, 1998; Stüben et al., 2003; Chatterjee et al., 2005), whereas the extensively exploited adjacent alluvial and deltaic shallow aquifers (<50 m) are contaminated with high As.

Table 2.1. As concentration in BDP sediments (at different depth levels).

Meherpur, Bangladesh[a]			**Baruipur (BH-1), West Bengal, India**[b]			**Baruipur (BH-2), West Bengal, India**[b]		
Depth (m)	As (mg/kg)	Mean As (mg/kg)	Depth (m)	As (mg/kg)	Mean As (mg/kg)	Depth (m)	As (mg/kg)	Mean As (mg/kg)
3	9.6	-	0.42-0.74 2.42-2.74	30 23	26.5	0.96-1.00 2.96-3.00	8 9	8.5
6 9	2 6.4	4.2	7.74-8.06	12	-	7.96-8.00 8.60-9.00 9.96-10.00	3 42 5	16.67
15	5.2	5.2	12.06-13.38	21	-	11.96-12.00	3	-
21	35	-	17.74-18.06 20.90-21.35 21.90-22.35	6 5, <1, 8 4, <1, 10	5	17.37-17.40 19.36-19.40 21.36-21.40	6 3 4	4.33
27 33	3 1.8	2.4	26.90-27.35	3, <1, 10	4.67	24.36-24.40 26.36-26.40 28.96-29.40 31.36-31.40	12 6 5 5	7
39	1.4	-	34.60-35.05 37.60-38.05 38.60-39.05 39.60-40.05	25, <1, 14 24, <1, <1, 12 17, <1, 12 26, <1, 14	11.46	33.06-33.10 33.10-33.55 36.10-36.55 39.10-39.55	6 8, <1 16, <1 20, <1	5.89
42 46	2.8 27	14.9	42.60-43.05	24, <1, 14	13	45.10-45.55	24, <1, 9	11.33
51 57	2.4 2	2.2	52.60-53.05 58.60-59.06	21, <1, 14 27, <1	12.8	52.10-52.50 60.10-60.50	18,<1, 10 8, <1	7.6

[a]Chowdhury et al., 2000; [b]Pal et al., 2002b.

The occurrence of As-rich groundwater is, therefore, difficult to explain by the low As contents of the BDP sedimentary environment. In contrast, over the years, it has became gradually evident that instead of a local high As distributive source in the Holocene sediment, several hot-spots (As-rich groundwater >150 µg/L) have been identified in various parts of BDP (Bhattacharyya et al., 2003b).

One of the major concerns of the BDP groundwater is the unpredictable nature of spatial variation in As concentration (van Geen et al., 2003; Fendorf et al., 2010). In BDP, the As spatial variability and depth distribution of redox elements are atypical. This heterogeneity is a matter of ongoing debate. A major challenge is the substantiation/concretization of the role of host sedimentary environment in the release of As to the groundwater and the elucidation of the causes for the often observed heterogeneous As distribution pattern.

In this chapter, we would like to document the spatial scale of As heterogeneity in a deltaic region of the BDP (Chakdaha block, Nadia district) of Bengal where a large number of high As wells have already been identified (RGNDWM, 2001; IFCPAR, 2004; Jana, 2004). The paper initiates with groundwater quality (mostly collected from hand-operated drinking wells of the rural areas) and chemistry to demonstrate the degree of the As heterogeneity in the young deltaic plain of Bengal. A statistical evaluation of the hydrochemical features, for the explanation of the geochemical processes that may regulate spatial As distribution pattern and its mobilization, is presented. Finally, the inter-relationship between the prevailing local conditions and surveyed wells is studied carefully that often regulates the hydrochemical environment. Ultimately, this helps to demonstrate typical spatial heterogeneity of As distribution in BDP.

2.2. Study area

2.2.1. Physiography and setting

The study area [latitude 23^{o} 00/ 20//–23^{o} 05/ 20// N; longitude 88^{o} 31/ 40//–88^{o} 49/ 00// E, Nadia district, 65 km north of Calcutta (Kolkata), West Bengal, India; Figure 2.1], encompasses an integral part of the BDP. BDP is the main geomorphic component of the world's largest fluvio-deltaic system (combined delta system of the River Ganges and River Brahmaputra delta).

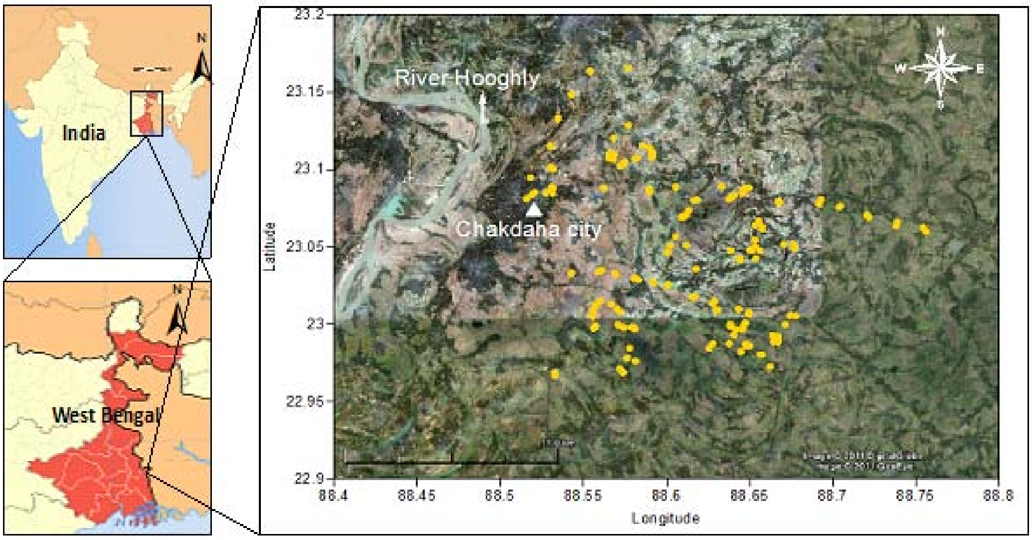


Figure 2.1. Study area (Chakdaha block, Nadia District, West Bengal); sampling locations highlighted in yellow dots.

The area under investigation spans over approximately 200 km^2. Geologically, the area is a part of the stable shelf part of the western Bengal Basin (Mukherjee et al., 2009). The quaternary sedimentary succession of the fluviatile deposit comprises of Fe-coated micaceous sand, silt and clay. The sediment sequences mostly demonstrate fining upward cycles of variable thickness (often truncated) that has been deposited by regional meandering rivers (PHED, 1993; Bhattacharya et al., 1997; CGWB, 1999; Pal et al., 2002b; Mukherjee et al., 2009). The young, Gangetic low-land flood plains deposits are characterized by a series of meander scars of varied wavelengths and amplitudes, abandoned channels and ox-bow lakes with a gradual southward slope. Other landform features are levees, back swamps in between inter-distributary levees with a relief difference of a few metres (Bhattacharya et al., 1997; Pal et al., 2002a). The climate is tropical, hot and humid (temperature range 16–42 ^{o}C; average relative humidity >65%) with annual rainfall ranging between 1295 mm and 3945 mm (Bhattacharyya and Chatterjee, 2001).

A large part of the study area (>70%) is characterized by shallow (10–50 m) groundwater wells (hand operated: privately owned ~80%; government-owned ~20%). Apart from these, a few motorized large-diameter deep wells (depth >100 m) for community water supply are also available. A large number of shallow motorized irrigation wells (10–20 m) aid the practice of sustainable agriculture all year round. These significantly support the high delta Boro (summer paddy;

February–June) cultivation. The gross crop area reported is ~1.0 million ha. with a cropping intensity of 140% (PHED, 1993; Bhattacharyya and Chatterjee, 2001).

2.2.2. Hydrogeology

The regional hydrostratigraphic characterization of the study area and surrounding [up to a depth of 300 m below mean sea level (MSL)] has resulted in delineation of a major aquifer, named as Bengal Alluvial Aquifer (BAA) (Mukherjee et al., 2007). This aquifer is a continuous, semi-confined sand aquifer, underlained by a thick clay aquitard. This BAA, deepens from a maximum of ~ 50-80 m below ground level (bgl) in the north to ~180 to > 200 m bgl in the south. The BAA constitutes most of the BDP that is present in the western Bengal Basin (geologically) or West Bengal, India (geographically). The groundwater in the aquifers is often associated with elevated level of As (>50 µg/L). These have been extensively developed due to their high potential yield and shallow accessibility. The upper most part of the BDP aquifer (4–12 m) generally has a capping of silt and/or silty clay, thus creating semi-confining conditions. The piezometric surface is usually within 3–6 m of the ground level (RGNDWM, 2001; IFCPAR, 2004). The water table (piezometric surface) gradually declines during the summer by a few meters. The regional groundwater flow is very slow (generally a few centimeters per year). The flow direction is from west to east and much influenced by local scale flow systems and pumping (Mukherjee et al., 2008b).

2.3. Materials and Methods

2.3.1. Sampling and analytical techniques

The groundwater samples (n = 181) are collected from the tube wells (mostly private) in acid washed pre-cleaned polyethylene (PE) bottles (capacity, 100–200 mL). Prior to sampling, tube well waters are flushed for several minutes to discharge the standing volume of water [~ 40-60 L, 2/3 buckets (each of 20 L capacity)]. This is done to get the fresh water from the aquifer. Water samples are filtered (0.45 µm cellulose nitrate membrane filter) on-site and divided into two groups. First group is acidified with HNO_3 (0.2% v/v, suprapur, MERCK, Germany) for the analysis of cation and As using double focusing High Resolution Inductively Coupled Plasma Mass Spectrometer (HR-ICP-MS VG AXIOM, VG

Elemental) in a clean room (sample dilution 1:1 with 1% HNO_3 of sub-boiled quality). The second group is left un-acidified for anion analysis with the help of Ion Chromatograph (IC, DIONEX ICS 1000) with a separating column (DIONEX AS 4 SC). Analytical quality controls with GLP were regularly practiced using commercial CRM materials (SRM 1643e). Samples were measured in triplicates, showing average precisions of within ± 5%. A few field parameters pH, Eh, conductivity, temperature (WTW multimeters) and HCO_3^- (titrating with 0.2 M H_2SO_4) are measured at the well head.

2.3.2. Statistical and thermodynamic calculations

The software package STATISTICA 6.0 (StatSoft Inc., USA) is used to evaluate the geochemical variation of groundwater. Factor analysis has been adopted to demonstrate the variation of groundwater composition including As (heterogeneity in relation with the groundwater quality) (Liu et al., 2003; Nath et al., 2008b). This has been used to evaluate elemental association in the hydrochemical environment. Factor analysis attempts to simplify the complex relationships within a multivariate data matrix. The reduced and comprehensive data volume will ultimately produce a meaningful number of new variables (factors). These factors cumulate those of the initial variables which are inter-correlated amongst them (Usunoff and Guzman-Guzman, 1989; Evans et al., 1996; Helena et al., 2000; Lee et al., 2001; Nath et al., 2008b). Principal Component Analysis (PCA) has been used to derive the factor loadings limiting the maximum eigenvalue to 1.0. To facilitate the interpretation of the factor analysis (loadings), the factor axis is rotated by the normalized varimax method, i.e., the extracted factors are rotated in such a way that the variance of the factor loadings tends to be maximum. A loading (high) close to ±1.0 indicates a strong relationship between factor and variable, while a loading (low) close to zero or negative means that there is no correlation (Davis, 1986).

Saturation indices ($SI = \log [IAP\ K_T^{-1}]$, where IAP is the ion activity product and K_T is the equilibrium solubility constant of a mineral phase at ambient temperature) for groundwater of surveyed wells are calculated using PHREEQC version 2.15 (Parkhurst and Appelo, 1999).

2.4. Results

2.4.1. Groundwater Chemistry

A survey (between 2007 and 2008) of groundwater quality of mostly privately owned wells (individual ownership) has been carried out in rural West Bengal (Chakdaha block, Nadia). The representative chemical analysis of the samples (selected over a ~300 km^2 area) is shown in Table 2.2.

Groundwater temperatures (17-29 ^{o}C) are often variable as a result of variation in water table (Table 2.2). The analytical results indicate large variation in chemical composition and also show high (>100 µg/L) As values (range 101-333 µg/L) in many of the samples (n = 27, 15% of total 181 samples). The As contamination in water wells are much above the WHO guideline value (10 µg/L). This also exceeds the national safe limits of India and Bangladesh (50 µg/L). The As concentration varies (both spatially and vertically) widely within the study area (sub-mg to mg level). The summarized chemical features of the groundwater indicate a widespread contamination of As. This contaminated water is often a source of water supply for local villagers to meet up their various domestic demands (drinking, cooking, bathing etc.).

The moderate conductivity (mean 707.38 µS/cm, range 200-1514 µS/cm) and circumneutral pH (mean 7.12, range 5.95-7.99) of groundwater suggest that the groundwater is fresh and well buffered. The low Eh [range -238-(+)56 mV, mean -109 mV] and low to very low Dissolved Oxygen (D.O.) [<0.1 mg/L, often absent (Below Detection Limit, BDL)] indicate that affected aquifers are generally anoxic in nature. The anoxic condition is further demonstrated by the presence of high redox sensitive elements (Fe, Cu, Mn, As, Co, Ni etc. with the mean value of 3415.3 µg/L, 2.64 µg/L, 321.35 µg/L, 52 µg/L, 0.27 µg/L, 1.14 µg/L respectively) and low to very low NO_3^- (43% below the detection limit). SO_4^{2-} concentrations (mean 7.32 mg/L, range 0.14-50.34 mg/L) reach upto 50.34 mg/L, whereas the Cl^- concentrations (mean 22.77 mg/L, range 0.67-146.85 mg/L) goes upto 146.85 mg/L. High Cl^- is often experienced in shallow aquifers.

During investigation, relatively low SO_4^{2-} and high Cl^- are noticed in shallow aquifers (<50 m). Both the distribution of Cl^- and SO_4^{2-} (Figures 2.2a and b) are depth dependent and drastically go down with depth (> ~50 m). The concentrations of Cl^- and SO_4^{2-} are only restricted within the shallow aquifer (~15-50 m) and practically absent (BDL) in the deeper aquifer.

Table 2.2. Statistical summary data of the screened wells (n = 181).

Measured parameters	Min	Max	Mean	Median	SD (±)
Depth (m)	7	271	39	24	42.6
pH	5.95	7.99	7.12	7.12	0.37
Eh (mV)	-238	56	-109	-112	37.30
Conductivity (µS/cm)	200	1514	707.38	672	186.67
Temp (°C)	25	31	27	26	0.74
As (µg/L)	0.31	333	52	34	61.78
Fe (µg/L)	8	19408	3415.3	2467	3.647.4
DOC (mg/L)	BDL	20.53	2.11	1.73	1.79
Na (mg/L)[a]	4.41	111.79	21.87	17.61	14.55
Mg (mg/L)[b]	5.41	43.65	22.84	21.88	6.41
K (mg/L)[a]	0.77	44.48	3.76	3.03	3.83
Ca (mg/L)[b]	20.33	178.16	100.15	98.51	25.52
Li (µg/L)	0.42	14.59	4.08	2.96	2.87
B (µg/L)	9.64	85.73	28.65	25.81	11.49
Al (µg/L)	2.42	912.67	22.22	11.09	75.02
P (µg/L)	2.16	3196.23	627.92	405.69	651.42
V (µg/L)	0.03	15.03	0.74	0.11	1.92
Cr (µg/L)	0.04	39.17	0.76	0.13	3.49
Mn (µg/L)	5.26	2524.45	321.35	263.13	283.83

Measured parameters	Min	Max	Mean	Median	SD (±)
Co (µg/L)	0.02	9.43	0.27	0.10	0.87
Ni (µg/L)	0.26	26.21	1.14	0.71	2.22
Cu (µg/L)	0.39	99	2.64	1.05	8.44
Zn (µg/L)	5.16	6964.34	272.09	33.14	805.39
Rb (µg/L)	0.06	8.24	2.22	1.90	1.52
Sr (µg/L)	103.13	656.08	294.75	266.71	109
Mo (µg/L)	0.21	8.43	1.06	0.88	0.84
Cd (µg/L)	0.01	0.52	0.07	0.05	0.05
Sb (µg/L)	0.3	0.5	0.4	0.4	0.06
Ba (µg/L)	28.29	591.77	175.87	162.67	85.7
Tl (µg/L)	0.02	0.71	0.09	0.06	0.09
Pb (µg/L)	0.08	77.52	1.9	0.82	6.18
Th (µg/L)	0.1	0.3	0.2	0.1	0.1
U (µg/L)	0.01	11.52	0.6	0.03	1.66
HCO_3^- (mg/L)	200	587.8	424.53	422	50.36
Fl^- (mg/L)	0.009	1.55	0.12	-	0.24
Cl^- (mg/L)	0.67	146.85	22.77	14.39	24.75
NO_3^- (mg/L)	BDL	12.68	1.57	1.23	2.12
PO_4^{3-} (mg/L)	0.11	3.99	0.71	0.48	0.68
SO_4^{2-} (mg/L)	0.14	50.34	7.32	4.6	8.33

[a] K/Na molar ratio: range 0.02-0.96; mean 0.12

[b] Mg/Ca molar ratio: range 0.16-0.58; mean 0.39

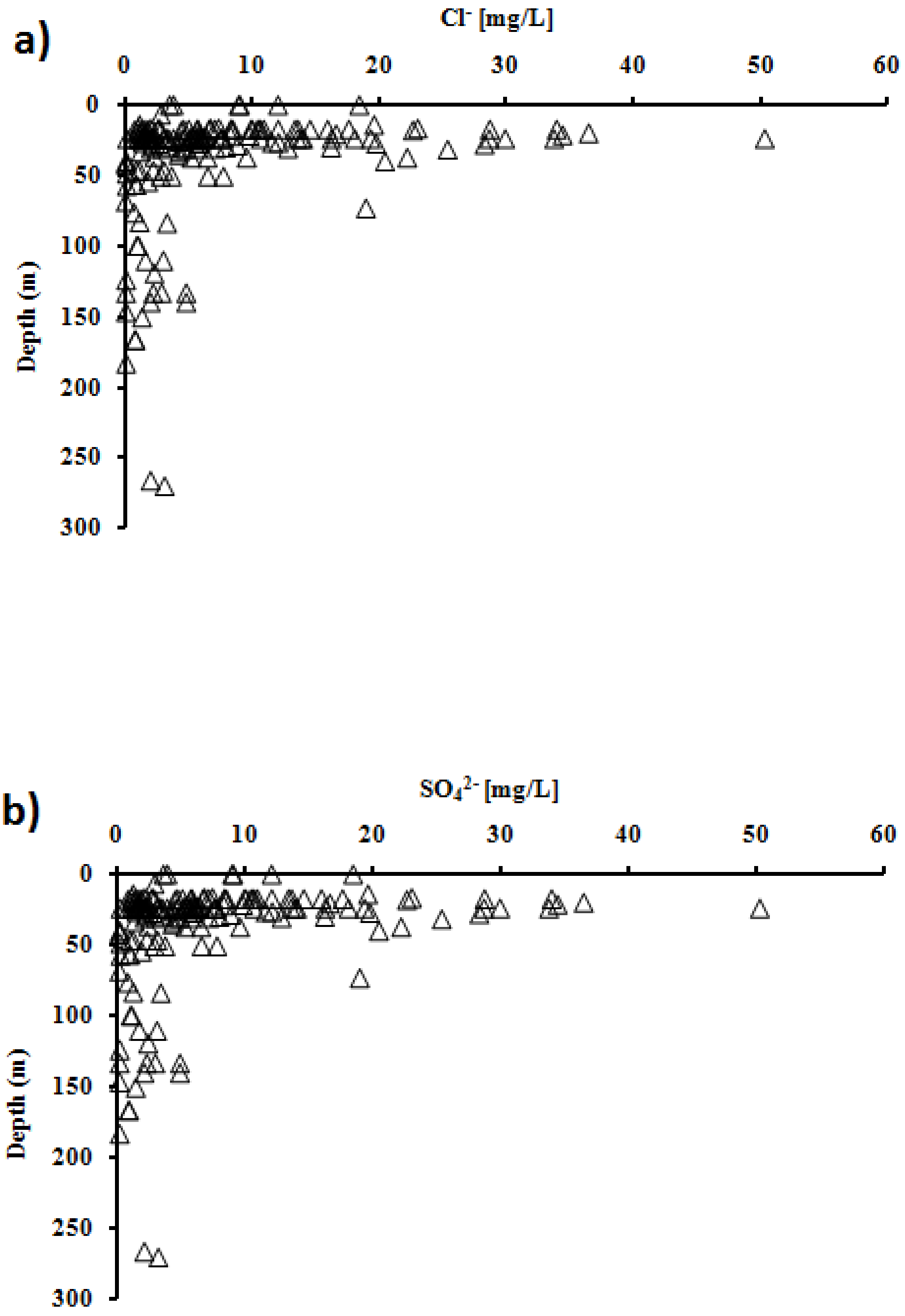
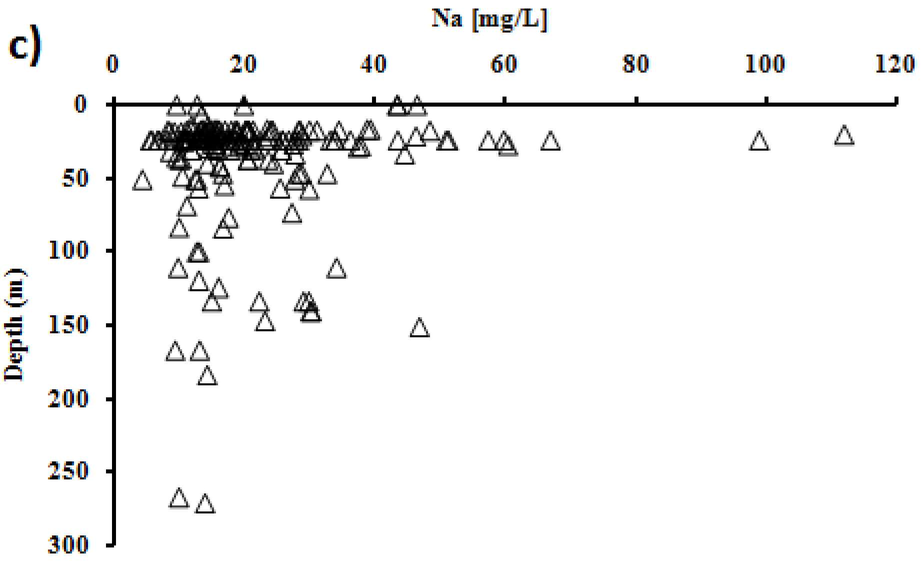


Figure 2.2. Scatter diagram of (a) Cl$^-$, (b) SO$_4^{2-}$.



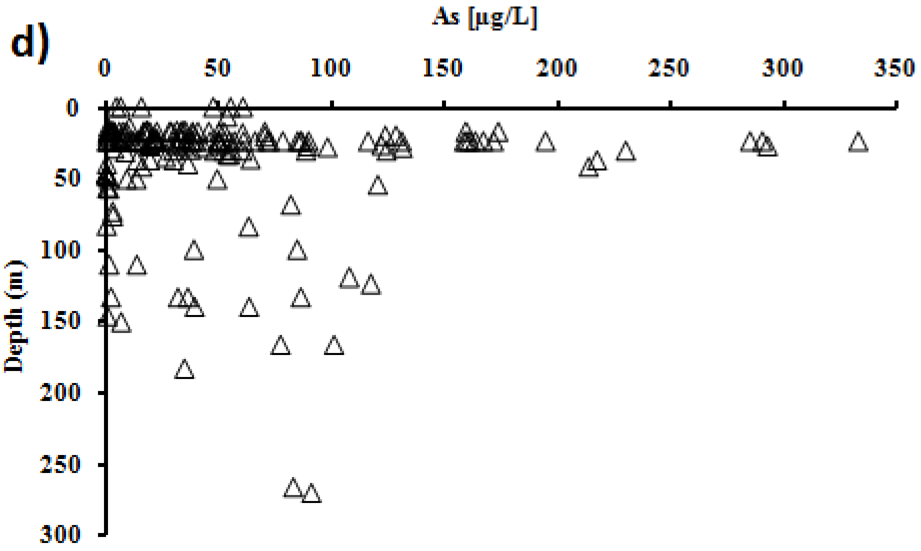


Figure 2.2. Scatter diagram of (c) Na, (d) As.

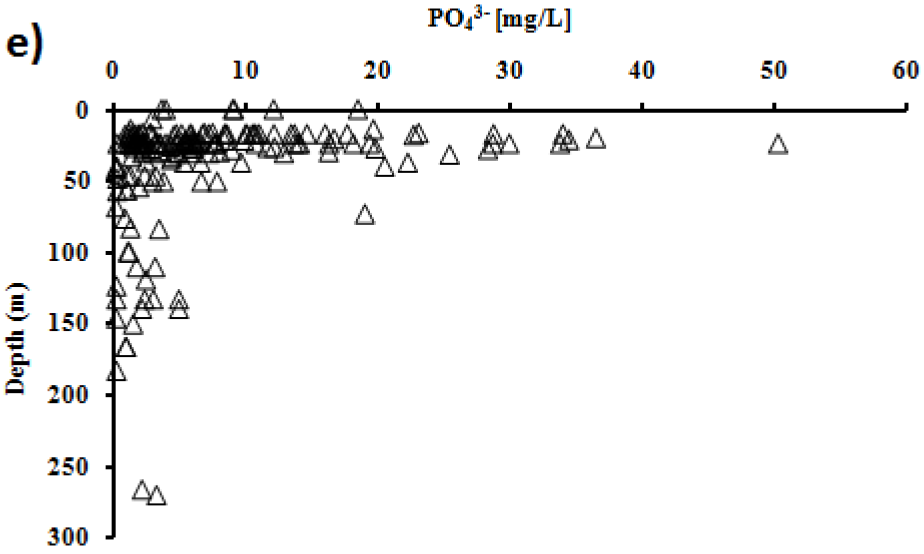


Figure 2.2. Scatter diagram of (e) PO$_4^{3-}$ with respect to depth.

Among the trace elements Fe, P, Mn, Zn, Sr and Ba show relatively higher values. The rest of the trace elements are comparatively in the lower range. The special feature of the chemical characteristics is the measurement of the ultra-trace elements including lanthanides and actinides (Table 2.2). Their concentration shows relatively higher values in comparison with earlier results of BDP groundwater (BGS and DPHE, 2001).

The most dominant anion is HCO$_3^-$ (mean 424.53 mg/L, range 200-587.8 mg/L) while the cation is Fe (mean 3415.3 µg/L, range 8-19408 µg/L) followed by Mn, Sr, Zn and As (Table 2.2). Like Ca (mean 100.15 mg/L, range 20.33-178.16 mg/L), concentration of Mg is also high (mean 22.84 mg/L, range 5.41-43.65 mg/L). Molar ratios (Mg/Ca) are variable and ranging from 0.16 to 0.58, whereas, the average is around 0.39 (Table 2.2). Among the alkali metal concentrations, Na (mean 21.87 mg/L, 4.41-111.79 mg/L) is throughout much higher than K (mean 3.76 mg/L, range 0.77-44.48 mg/L). The mole ratios are also variable (mean 0.12, range 0.02-0.96). Among the other alkaline earth metals, concentration of Sr and Ba are relatively higher and does not show much fluctuation.

It is pertinent to mention that the easily soluble alkali metal (Na) is consistent with the average values of Cl$^-$ (Table 2.2). Nevertheless, their ranges are quite variable. Na content in groundwater is found to be generally high along with high Cl$^-$.

However, high Na and low Cl^- are also observed in few cases (Figures 2.2a and c). The distribution pattern of Na and Cl^- (high Na and high Cl^-, high Na and low Cl^-) can only be possible when local anthropogenic sources (pollution) prevail.

The shallow groundwaters generally contain high P. The concentrations of P (mean 627.92 µg/L, range 2.16-3196.23 µg/L) in the surveyed wells are considerably higher than the general BDP trends (BGS and DPHE, 2001). The variation of P concentration in groundwater follows a similar trend that of the concentration of As in groundwater. Highest concentrations of P and As are generally found in the groundwater from shallow depth. The deeper wells are much lower in P concentrations and hence may not be linked with As contamination. Overall concentration of P is variable, often high (>1 mg/L) and shows little consistent trend.

The hydrochemistry indicates that the groundwaters are enriched with As (often exceeding safe limits). The As contamination in many wells are relatively high (upto 333 mg/L). The distribution of high As wells are patchy with some areas more enriched than others. These results also confirm the BDP regional As distribution trends (van Geen et al., 2003; Zheng et al., 2004; Polizotto et al., 2006; Fendorf et al., 2010; Bhattacharya et al., 2007).

2.4.2. Hydrochemical facies

The Piper plot (Figure 2.3) shows that the groundwater is predominantly Ca-HCO_3^- type. A few groundwater samples [generally shallow aquifer (generally <50 m)], are found to have distinct higher concentrations of Na and Cl^- than the predominantly Ca-HCO_3^- water. In contrast, a few wells are suspected to have semi-isolated condition (high Na–low Cl^-) (Figure 2.3). The present study indicates additional NaCl-enrichment along with earlier reported Ca-HCO_3^- type (RGDWM, 2001; Bhattacharyya et al., 2003b; Jana, 2004; Zheng et al., 2004). This has been clearly reflected in the non-clustered tail-end part of the plot (Figure 2.3). Surveyed wells have large variation of Cl^- concentrations (mean 22.77 mg/L, range 0.67-146.85 mg/L). The distribution of Cl^- concentrations generally follows that of Na with respect to depth (Figure 2.2a and c). The high degree of similarity in distribution pattern has been observed for both Na and Cl^- in the shallow aquifers (upto ~50 m).

These wells are relatively young (≤15 years) and located very near (~1-3 m) to sanitation (pit latrines). The enriched Na and Cl^- groundwaters are result of pollution from local sanitation rather than the result of sediment-water interaction.

Most significant observation is the high As concentrations that are often found in shallow aquifers where Na and Cl^- levels are high. Cl^- in groundwater is most probably derived from the sanitary systems. Such local pollutions were earlier reported from BDP (Chatterjee et al., 2010). In the deeper aquifers, generally the Na concentrations are varying and the Cl^- concentrations remain unchanged (Figure 2.2a and c). High Na (low Cl^-) groundwater may be caused due to the reverse ion exchange process and thereby groundwater contains relatively low alkalinity, low Cl^- with high alkali and redox elements.

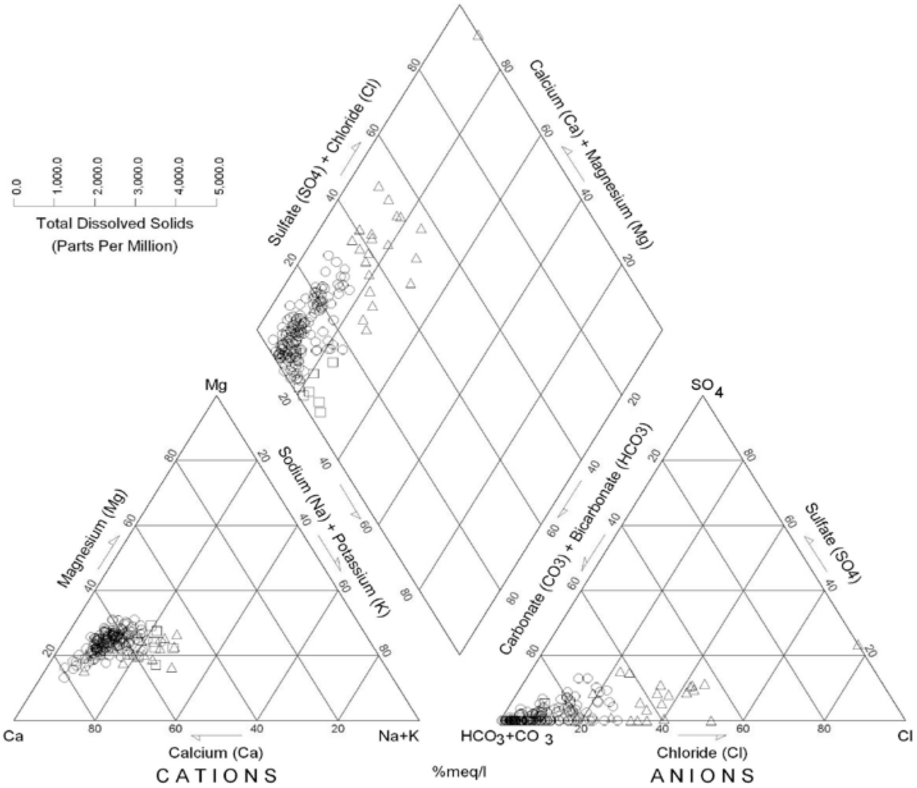


Figure 2.3. Piper diagram.

2.4.3. *Vertical distribution of arsenic*

The study indicates that the As concentration varies with depth as reported earlier in BDP (Bhattacharyya et al., 2003b; Nath et al., 2008a). Evidence of depth control on the As occurrence in the study area [shallow (21-50 m) - high release zone of As;

deep (81-150 m) - low release zone of As] has also been observed. As concentration tend to be highest (up to 333 μg/L) in the intensively exploited shallow aquifer (<50 m), where millions of water wells has been installed by the rural villagers (Smedley and Kinniburgh, 2002; Bhattacharyya et al., 2003a). On the other hand, waters from deeper aquifers (>100 m) generally have low concentration of As (~7-8 fold lower).

The most important feature is the inability to observe any clear trend between As concentration and depth. On the contrary, depth distribution (Table 2.3) shows much variability in As concentration. The depth complexity (vertical heterogeneity) is possibly the most critical component of BDP As occurrence. Depth profiling (stratification) (Table 3.3) along with As concentration has been constructed to focus on the nature as well as pattern of such vertical distribution. It reveals that the near-surface aquifer [depth <20 m, n = 29; 21 wells from Set II (above the WHO guideline value), 6 wells from Set III and 2 wells from Set IV (both above the WHO as well as national safe limit)] is contaminated with As. However, in a few shallow wells (depth ≤50 m) As concentrations are lower than below WHO guideline value (n = 37; 19 wells from near–surface aquifer (<20 m) and 18 from shallow aquifer (21-50 m).

The most contaminated aquifer is the 'shallow' aquifer where 40.82% of the wells (n = 40; 26 wells from Set III and 14 wells from Set IV, out of total n = 98 wells falling in this depth level) are above the national standard. Again, 40.82% of the wells (n = 40 out of total 98 wells) are above the WHO guideline value. A limited number of wells (n = 18) have As concentration below WHO guideline value. This suggests that even in the high contaminated zone the As concentration is varying. This advocates the heterogeneity in the As distribution pattern. The deep (81-150 m)/very deep (>150 m) aquifer (even that of intermediate) is generally found to be low/very low in As concentration (Table 2.3). However, it is astounding to observe that dissolved As concentration in some of the deeper wells [n = 10; 6 wells falling in the deeper aquifer and 4 wells falling in the very deep aquifer (both grouping in Set III)] is high (>50 μg/L) even exceeding both WHO and national standard value. These deeper aquifers are often considered safe for drinking purpose. This again reinforces the vertical heterogeneity of As distribution pattern in BDP groundwater.

2.4.4. Spatial distribution of arsenic

High As groundwater is often concentrated in patches/pockets surrounded by low/free As zones (Figure 2.4a). This favours the regional As distribution pattern of the BDP (BGS and DPHE, 2001; Chatterjee et al., 2004; Nath et al., 2008b). The present investigation emphatically highlights the bewildering nature of spatial variation of As concentration in the study area. The major important issue is the spatio-vertical variability of As (Table 2.3).

The spatial distribution pattern indicates that the contaminated wells are generally surrounded by the safe wells (Figure 2.4a). This is more pronounced in the south and south-eastern part of the study area. The distribution of hot-spots is also interesting and its orientation is from south-east to north-west. On the contrast, another hot-spot has been identified further east where safe water wells are limited as per WHO guideline. Safe water wells are much less in the flood basin area where sediments are generally channel-filled depositions (Bhattacharya et al., 1997; Bhattacharyya et al., 2003b).

Table 2.3. Depth profiling (stratification) with respect to well As concentration.

	Near-surface Aquifer (<20 m)	**Shallow Aquifer (21-50 m)**	**Intermediate Aquifer (51-80 m)**	**Deeper Aquifer (81-150 m)**	**Very Deep Aquifer (>150 m)**
Set I[a] (n=49)	19(38.8%)	18(36.7%)	6(12.2%)	4(8.2%)	1(2%)
Set II[b] (n=69)	21(30.4%)	40(57.9%)	2(2.9%)	5(7.2%)	1(1.4%)
Set III[c] (n=47)	6(12.8%)	*26(55.3%)	2(4.2%)	6(12.8%)	4(8.5%)
Set IV[d] (n=16)	2(12.5%)	*14(87.5%)	0(0.0%)	0(0.0%)	0(0.0%)

[a]Set I (As <10 µg/L), [b]Set II (As 10-50 µg/L), [c]Set III (As 50-150 µg/L), [d]Set IV (As >150 µg/L); the values in the brackets denote the % of wells falling in each depth level out of total wells grouping in each "Set" with respect to As concentration.

*(26+14) = 40 wells out of total 98 wells falling in the shallow aquifer (21-50 m); hence, 40.82% of the wells are contaminated.

2.4.5. Spatial distribution of redox-sensitive solutes

Redox-sensitive solute distribution maps (Fe, Mn) are shown in Figures 2.4b and c. Concentration (mean) of Fe is generally high in groundwater. Such high average values of redox elements (Table 2.2) also indicate the possibility of predominant local reducing environment in the aquifer. The distribution of Fe with respect to As shows strong relationship within the south-eastern part of the study area (Figures 2.4a and b), whereas, The distribution of Mn also follows the spatial contour of As (Figures 2.4a and c) in the north-western parts.

It is worthwhile to mention that the spatial distribution pattern of the redox elements (Fe, Mn) shows different behaviour (distribution pattern) (Figures 2.4b and c) amongst themselves. This is not unanimously consistent with respect to the spatial distribution of As. Hence, the reductive dissolution of Fe/Mn – (oxyhydr)oxides is unlikely to be the major process for As release. The spatial distribution of redox elements (Fe/Mn/As) reveals that the observed distribution pattern is locally occurring (As vs. Fe – south-eastern; As vs. Mn – north-western). The reductive dissolution of Fe/Mn – (oxyhydr)oxides is possibly causative mechanism for As release in few spatial pockets where As and Fe/Mn distribution contours follow each other. However, the overall distribution pattern is weak and do not fit with earlier suggested “Fe/Mn reduction model” (Smith and Kinniburgh, 2002; McArthur et al., 2004; Zheng et al., 2004; Charlet et al., 2007; Sracek et al., 2005). Recent studies (Nath et al., 2008a; Chatterjee et al., 2010, 2012; Majumder et al., 2010) reported that local geology (altered mica/carbonate/clay) coupled with land-use pattern may also play crucial role to release As into the groundwater. Researchers further highlighted that heterogeneous As distribution is linked with land-use pattern (Nath et al., 2008a; Chatterjee et al., 2010).

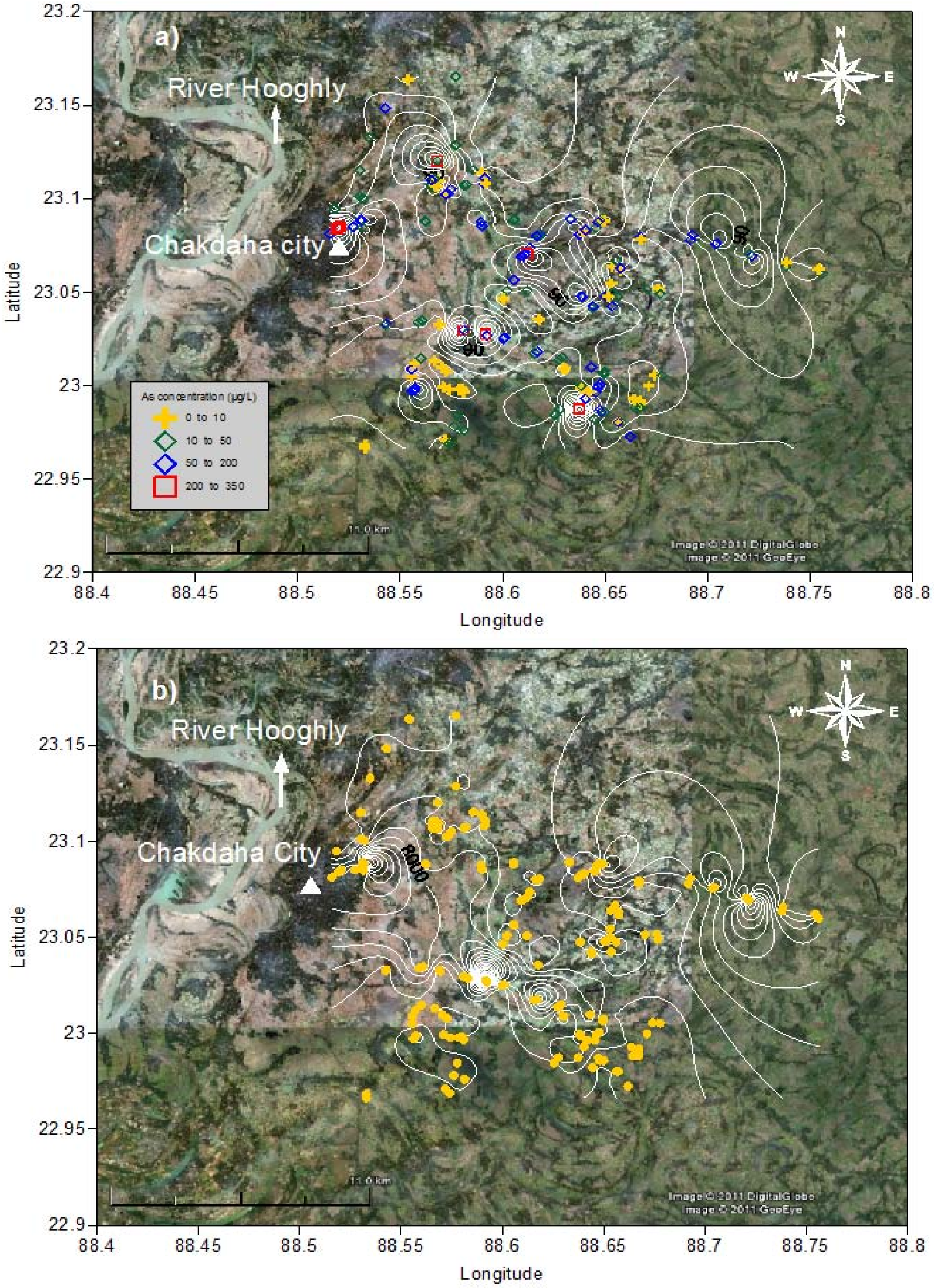


Figure 3.4. Contour maps of (a) As, (b) Fe.

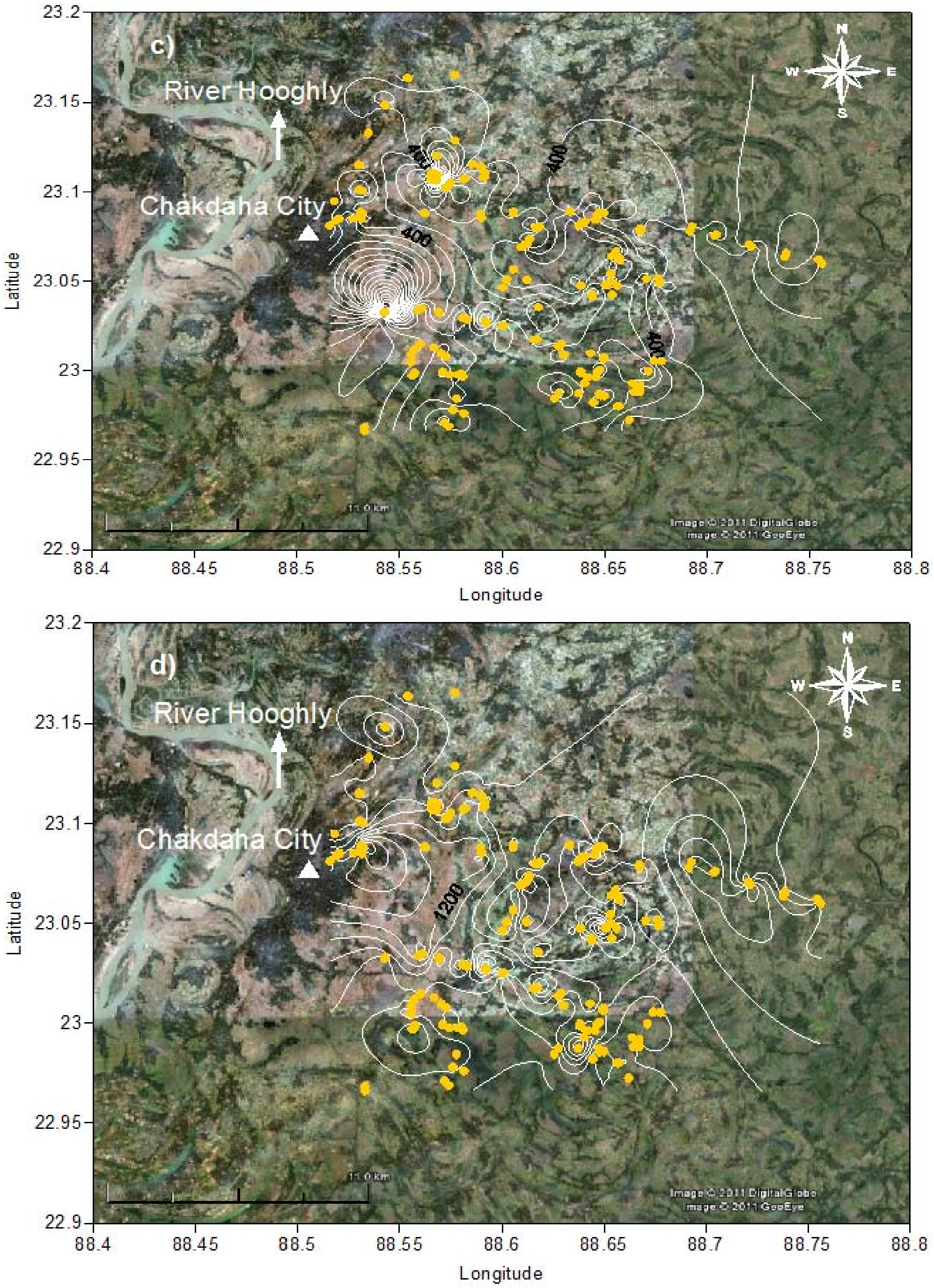


Figure 3.4. Contour maps of (c) Mn, (d) P.

The spatial distribution of As often follows the contour of P (Figures 2.4a and d). The similar depth distribution of groundwater PO_4^{3-} and As at shallow/intermediate aquifers has also been observed (Figures 2.2d and e). High PO_4^{3-} areas are often arsenical ($r^2 \sim 0.54$).

2.4.6. Heterogeneity in distribution of arsenic – key features of well site

A surrounding site characteristics survey has been conducted in the study area during monitoring of the groundwater quality. The study demonstrates that the concentration and distribution of As is a function of site characteristics and surroundings of monitored wells such as well location, well depth and age (Nath et al., 2008a; Chatterjee et al., 2010).

The distribution of monitored wells along with four major site characteristics is shown in Table 2.4. The highest numbers of wells (40.88%) are adjacent to sanitary installations followed by sanitation coupled with surface water body, agricultural field, and surface water body.

Table 2.4. As distribution profile in relation with prevailing site characteristics.

Adjacent site characteristics	No. of adjacent wells (n)	% of total no. of wells	As range (μg/L)	Mean As (μg/L)	Wells (n) having As ≥50 μg/L	% of affected wells
Sanitational installations	74	40.88	0-217	44	26	35.13
Sanitation coupled with surface water body	50	27.62	0-290	49	17	34
Surface water body	22	12.15	0-285	60	9	40.9
Agricultural field	35	19.34	0-333	67	12	34.28

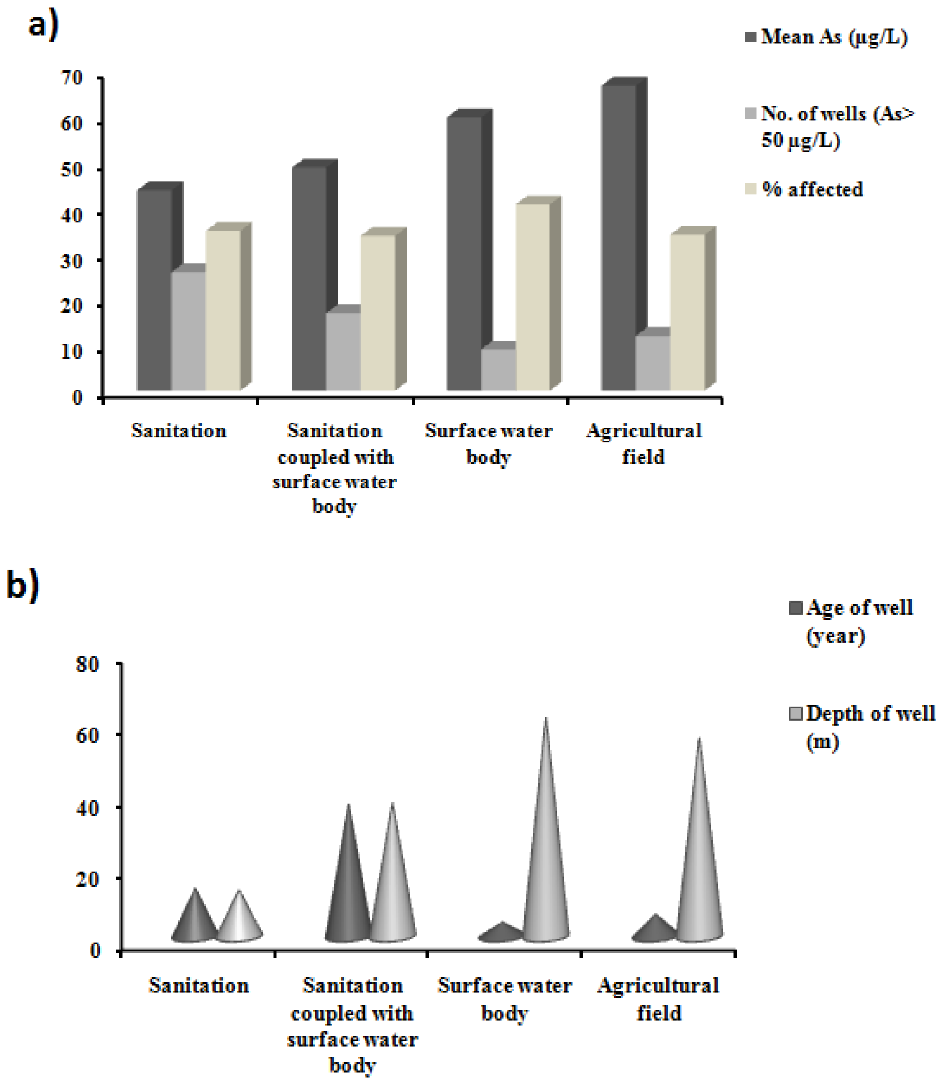


Figure 2.5. Relation of various site characteristics with a) distribution of As content; b) age and depth distribution of wells.

The mean As concentration varies among the selected site characteristics (Table 2.4 and Figures 2.5a) where wells adjacent to agricultural fields have the highest mean value (67 µg/L) followed by surface water body, sanitation coupled with surface water body, sanitary installations.

It is interesting to note that number of contaminated wells (> 50 µg/L) are mostly associated with sanitary installations (35.13%) followed by sanitation coupled with surface water body, agricultural field, and surface water body. However, the well distribution scenario has been changed when percentage of affected wells (> 50 μg/L) is considered. Wells located near to surface water bodies are found to be affected mostly (Table 2.4 and Figures 2.5a).

As distribution pattern distinctly changes with relation to As concentration, number of contaminated wells and percentage of affected wells amongst the various site characteristics and further encourages to examine the role of well depth and age of the monitored wells in such situation.

The average depth and age distribution of the wells with respect to site characteristics have also been plotted (Figures 2.5b). The figure illustrates the contaminated wells are generally young (4-7 years) and often found to be located near surface water bodies and agricultural field (~within 5-10 m). These wells are also happened to be the most affected wells with higher mean As value. Relatively older wells are placed (~within 10m) near to sanitation installations and sanitation coupled with surface water bodies. The figure (Figures 2.5b) also indicates that the deeper wells are located near surface water bodies and agricultural field, whereas, relatively shallower wells have been found to be located near sanitary installations and sanitation coupled with surface water bodies.

2.4.7. Statistical evaluation (Factor analysis)

The analysis reduces the initial 21 variables to four factors (Table 2.5). Factor-1 has loadings >0.5 for Fe, V, Cr, Co, Ni. All these transition metals are typically associated with mafic minerals (silicates) to which biotite also belongs. Factor-2 exhibits higher loadings for Na, Mg, Ca, Cl^- and SO_4^{2-}. The combination of these variables into a common factor corresponds to the major dissolved ionic load of the groundwater. This has resulted from the interaction of the groundwater with the aquifer materials and rocks of the catchment area. Factor-3 shows higher loading for As and PO_4^{3-}. Their similar algebraic sign suggests that the mobilization of both elements is coupled by the alike processes. Factor-4 contains Al, Co, Zn, Cd and Pb.

Table 2.5. Factor Loadings (varimax normalized).

Variables	Factor 1	Factor 2	Factor 3	Factor 4
pH	0.014	-0.158	-0.424	0.014
Eh	-0.118	-0.201	-0.291	-0.046
Conductivity	-0.091	**0.884**	0.242	0.056
HCO_3^-	-0.234	0.477	0.491	0.232
As	0.261	-0.113	**0.708**	0.041
Fe	**0.753**	0.014	0.487	0.223
Na	0.029	**0.763**	0.078	0.175
Mg	-0.039	**0.810**	0.289	0.067
K	0.125	0.471	-0.279	-0.057
Ca	-0.010	**0.749**	0.218	0.054
Al	0.409	0.024	0.116	**0.789**
V	**0.836**	0.176	-0.091	0.183
Cr	**0.855**	0.004	0.163	0.198
Co	**0.709**	0.018	0.132	**0.639**
Ni	**0.831**	-0.024	0.083	0.139
Zn	-0.062	-0.014	0.052	**0.838**
Cd	0.462	0.105	-0.037	**0.679**
Pb	0.296	0.079	0.041	**0.852**
Cl^-	0.109	**0.789**	-0.092	-0.141
SO_4^{2-}	0.141	**0.691**	-0.483	-0.008
PO_4^{3-}	0.468	-0.065	**0.601**	0.060

Extraction: Principal Component Method

[Marked (Bold-Underlined) loadings are >0.5)].

2.4.8. Thermodynamic saturation index (SI)

The groundwaters of the surveyed wells are saturated with carbonates (aragonite, calcite, dolomite, siderite, rhodochrosite), along with oxide (hematite), hydroxide (gibbsite), oxi-hydroxide (goethite) and phosphates (hydroxyapatite, vivianite) minerals (Table 2.6). The groundwater is always supersaturated with hematite in all the cases.

Table 2.6. Saturation indices of mineral phases controlling the water chemistry.

Minerals	**Saturation Indices (SI) value of wells adjacent to -**			
	Agricultural field	**Sanitational installations**	**Sanitation coupled with surface water body**	**Surface water body**
Aragonite ($CaCO_3$)	0.15	0.09 (near equilibrium)	0.09 (near equilibrium)	0.27
Calcite ($CaCO_3$)	0.29	0.24	0.24	0.42
Dolomite [$CaMg(CO_3)_2$]	0.30	0.12	0.12	0.53
Hydroxyapatite [$Ca_5(PO_4)_3OH$]	1.49	1.29	1.65	1.88
Goethite ($FeOOH$)	2.83	2.62	2.68	3.05
Hematite (Fe_2O_3)	7.66	7.23	7.34	8.09
Vivianite [$Fe_3(PO_4)_2$, $8H_2O$]	0.98	0.90	1.23	0.75
Siderite ($FeCO_3$)	0.93	0.86	0.89	0.89
Rhodochrosite ($MnCO_3$)	0.16	0.03 (near equilibrium)	0.13	0.10
Gibbsite [$Al(OH)_3$]	1.43	1.33	1.37	1.18

Calculated SI value (0.03) also indicates that rhodochrosite (for wells nearby the sanitational installations) and aragonite (for wells nearby the sanitational installations and sanitation coupled with surface water bodies). Samples near the agricultutral fields and surface water bodies are generally saturated with respect to carbonate, oxide-hydroxide and phosphate minerals. Hence, hydrogeology, local recharge from agricultural fields and surface water bodies play a vital role in controlling release of As in groundwater.

2.5. Discussion

The hydrochemistry indicates that the groundwater is enriched with As. The As contamination in many wells are relatively high (>300 µg/L). The distribution of high As wells are heterogeneous with some areas more enriched than others. These results also confirm the BDP regional As distribution trends (van Geen et al., 2003; Zheng et al., 2004; Polizotto et al., 2006; Bhattacharya et al., 2007, Mukherjee and Fryar, 2008; Fendorf et al., 2010; Mukherjee et al., 2011).

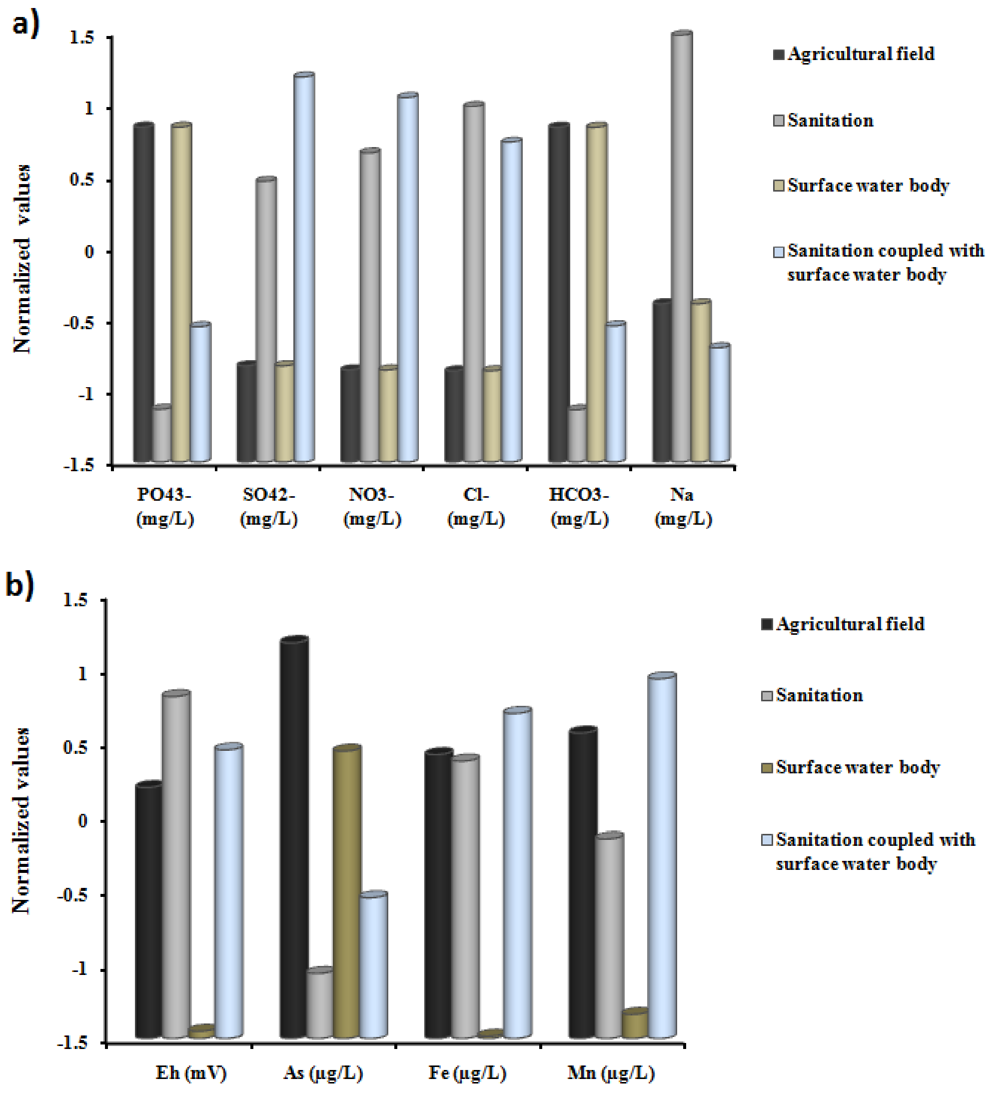
Most significant observation is the high As concentrations that are often found in shallow aquifers where Na and Cl^- levels are high. Cl^- in groundwater is most probably derived from the sanitary systems (Jacks et al., 1999). In these wells, SO_4^{2-} and NO_3^- are also high (Figure 2.6a). Such local pollutions were earlier reported from BDP (Chatterjee et al., 2010). In the deeper part of the aquifers, generally the Na concentrations are varying and the Cl^- concentrations remain unchanged (Figures 2.2a and c). High Na (low Cl^-) groundwater may be caused due to the reverse ion exchange process (Mukherjee and Fryar, 2008), and thereby groundwater contains relatively low alkalinity, low Cl^- with high alkali and redox elements.

SO_4^{2-} concentrations are generally low. The low concentration of SO_4^{2-}, (mean: 7.32 mg/L), tends to be associated with strongly reducing groundwater. The lack of positive correlation between dissolved As and SO_4^{2-} may suggest that the removal of SO_4^{2-} from groundwater has occurred. One of the possible mechanisms is likely to be bacterial reduction of SO_4^{2-} that is possibly operating in the aquifer (Radu et al., 2005; Lowers et al., 2007; Mukherjee et al., 2008b). SO_4^{2-} reduction further indicates that the reduction process has been accompanied by As mobilization (denitrification → Fe-reduction → SO_4^{2-} reduction).

In BDP, Ca-HCO_3^- type groundwater is most common and reported by several workers (Bhattacharya et al., 1997; Bhattacharyya et al., 2003b; Nath et al., 2005, 2008a; Mukherjee et al., 2008b; Fendorf et al., 2010; Neumann et al., 2010). Unlike Ca, concentration of Mg is relatively low and the molar Mg/Ca ratio is also variable. This indicates dissolution of Ca and Mg from different mineral sources. Similarly, the molar K/Na ratio is also varying and suggests that Na might have occurred in groundwater from the local source (pollution) rather than conservatively mineral dissolution. However, the enrichment of NaCl and the semi-isolated characters are interesting and may be a signature of the site specificity of the wells and characteristics of the surrounding (Figures 2.2a and c).

The importance of local anthropogenic influence and its possible sources (surface water body, sanitary systems, and agricultural field) may contribute on As mobilization. The hydrochemical features (normalized values) and site specific well associated features are plotted (Figures 2.6a and 6b) to explain the importance of local anthropogenic influence on groundwater quality as well as heterogeneous As distribution. The higher concentrations of NO_3^-, SO_4^{2-} and Cl^- in groundwater are found to be associated with sanitation systems as well as sanitation coupled with surface water body. The site specificity of the wells in relation with sanitation is further conformed when high Na groundwater is also found in wells located near the sanitary systems. The groundwater PO_4^{3-} concentration is also relatively high in agricultural wells (Figure 2.6a). The higher concentrations of PO_4^{3-} and HCO_3^- are primarily linked with agricultural fields and surface water body. The relatively higher mean HCO_3^- value (424.53 mg/L) further advocates the surface input of dissolved organic material from agricultural field and surface water bodies. The oxidation of these organic matters leads to the successive appearance of redox elements [As (mean 52 μg/L), Fe (mean 3415.3 μg/L), Mn (mean 321.35 μg/L)] (Stüben et al., 2003; Zheng et al., 2004; Bhattacharya et al., 2007). PO_4^{3-} input is common from agricultural (irrigated) field as wells as local infiltration from ponds into the groundwater. During field investigation, the location of the pond is often in between agricultural field and habitation where surface run-off from agricultural fields takes place (Biswas et al., 2011; Sahu et al., 2011).

The further examination of hydrochemical features has also been carried out on spatial scale (Figures 2.4a-d) to examine the pattern of spatial heterogeneity. The As distribution pattern is not equivocally following the Fe/Mn distribution pattern. This suggests that possibly single mechanism (reductive dissolution of Fe/Mn-(oxyhydr)oxides) is not sufficient to explain heterogeneous As distribution pattern. It is likely that multiple mechanisms are operating to maintain As release and



Figures 2.6(a) and (b). Distribution of hydrochemical paramteres among various site charachteristics.

distribution pattern (Neumann et al., 2010; Biswas et al., 2011). Heterogeneity of As occurrences can be further resolved by the competitive ion-exchange process where local anthropogenic input is regulating the system (Figure 2.4a). The concentrations of NO_3^- and SO_4^{2-} are important because they act as a terminal electron acceptor in water systems (Appelo and Postma, 2004). It has been observed that As concentration (mean: 17 µg/L) in groundwater is relatively low where NO_3^- is high (mean: 9 mg/L). This suggests that the groundwater chemistry of the aquifer is influenced by local anthropogenic influence and thereby gradually becoming less anoxic. The appearance and disappearance of SO_4^{2-} are also regulated by the local anthropogenic influence where microbial reduction of SO_4^{2-} may have often occurred (Postma and Jakobsen, 1996), though, H_2S is mostly below detection limit. BDP groundwater does not support the predominant presence of sulphidic minerals rather supporting the presence of aluminosilicates/clay minerals (Swartz et al., 2004; Chatterjee et al., 2010).

In summary, the spatio-vertical heterogeneity of the As concentrations in groundwater is an important issue in BDP. The present study suggests that this heterogeneity may be a matter of aquifer perturbation. Local land-use pattern influences the natural cycling of As between sediment and water, ultimately releasing As in the aqueous environment. In the absence of primary sources (arsenopyrite/pyrites), secondary metal oxides/hydroxides, especially of Fe and Mn along with micas (altered aluminosilicates) are considered to be important. These are dominant sources as they are abundant in the sediments of BDP (Swartz et al., 2004; Polizzotto et al., 2006; Chakraborty et al., 2007). In addition, fluvial geomorphology and their physical location within land-use pattern are also influencing heterogeneity of As distribution and thereby regulating the patchiness. Local land-use pattern, fluvial geomorphology and hydrogeological conditions (sediment-water interaction) are controlling such heterogeneity in terms of nature, shape and size.

The presence of saturated carbonate minerals (aragonite, calcite, dolomite, siderite, rhodochrosite) (Table 2.6) and high values of Ca, Mg, Fe, HCO_3^- in groundwater with circumneutral to slightly alkaline pH (Table 2.2), is an indication of carbonate mineral dissolution process, in addition to the Fe-oxides/hydroxides. This often indicates that carbonate reactions are important for influencing groundwater hydrochemistry in the surveyed wells. It is pertinent to mention that SI values for dolomite fluctuate to certain extent (0.12-0.53), which might be indication of dolomitization of calcite and aragonite that may have been taken place by reaction with Mg-bearing sea water during sea-level changes in the BDP (Chatterjee et al., 2005). However, the SI values for siderite are virtually remaining unaffected amongst the various site characteristics around the wells, reflecting that the influence of these local features on the thermodynamic equilibrium of siderite in groundwater is not sufficient. The minerals (siderite and rhodochrosite) have also been identified earlier in the study area (Pal et al., 2002b; Mukherjee et al., 2008b).

Groundwater is commonly super-saturated with hematite and saturated with siderite. This suggests that the precipitation of Fe(III) phases from groundwater is thermodynamically favourable and thereby regulating As concentration in groundwater. The mean As concentration is relatively higher in wells nearby agricultural fields and surface water bodies where PO_4^{3-} (run-off from agricultural fields) and HCO_3^- (bio-indicator and end product of degraded natural organics) are high and Dissolved Organic Carbon (DOC), NO_3^- and SO_4^{2-} are relatively low (Table 2.4, Figures 2.6a and b). This supports the combined release mechanism (Fe reduction and PO_4^{3-} competitive exchange process) for the occurrence of high As in groundwater (Biswas et al., 2011). In contrast, mean As concentration is relatively low (Table 2.4) in case of wells adjacent to sanitary installations and sanitation coupled with surface water bodies, where SO_4^{2-}, NO_3^-, Cl^- and Fe are relatively high and PO_4^{3-}, HCO_3^- are relatively low. This suggests that Fe reduction is the principal process for release of As in groundwater in case of these type of wells. Several workers have already identified these minerals principally hematite in the sediment (Pal et al., 2002b; Bhattacharyya et al., 2003b; Nath et al., 2005,2008c).

Calculated SI values indicate that vivianite is saturated in many of the groundwaters where As concentration varies largely (mean 49-67 µg/L). However, this has not been identified mineralogically.

Saturation indices of rhodochrosite and gibbsite are also important because the formation of rhodochrosite and gibbsite can regulate As concentration in groundwater. These minerals can act as a sink for As by co-precipitation with

Mn(II), Al(III) ions from the anoxic groundwater. This processes can accelerate the rate of reduction of metal(s) oxide/hydroxides by shifting the equilibrium, thereby, increasing concentration of dissolved As in groundwater. However, when the minerals are in equilibrium (rhodochrosite in case of sanitary installations), the process gets slowed and As release is hindered (mean As concentration 44 μg/L). This further reinforces that the combined release mechanisms are important and operated by the various local features around the well site.

Finally, the heterogeneous As distribution (spatial and vertical variability) can be linked with multiple natural geochemical processes playing simultaneously and thereby enriching the groundwater with As. Nevertheless, ion exchange and ion concurrence with PO_4^{3-} from anthropogenic sources (fertilizers) together with the complex deltaic environment may also have some impact on the spatio-vertical heterogeneity of As.

2.6. Conclusion

Currently the BDP groundwater indicates large spatial variability of As concentration along with variable redox element depth distribution. This heterogeneity is a matter of intense debate. The present study demonstrates the groundwater chemistry of As affected aquifers in BDP (Chakdaha block, Nadia district, West Bengal) predominantly under anoxic condition (low to very low NO_3^-, absent D.O., high HCO_3^- and redox elements). The groundwater is generally HCO_3^- type, occasionally enriched with Na and Cl^- in shallow aquifers and possibly a signature of local pollution. The critical examination (statistical evaluation) of the groundwater composition reveals that Fe – (oxyhydr)oxide reduction and As mobilization may not be the only process to explain high As groundwater in BDP. Altered mica (like biotite) which accommodates both Fe(II) and Fe(III) may be another potential host in BDP sediment to release As in groundwater. The major breakthrough is the morphology of land-use pattern (surface water body/sanitation/agriculture-aquifer-sediment interactions). This can suitably explain the heterogeneity of As distribution in BDP. Apart from land-use pattern, the local hydrogeological regime (sediment-water interaction) is important to explain patchy distribution of As. The competitive exchange of ions can also influence As distribution when the wells are located nearby the agricultural field.

The extent and their inter-connectivity of all these processes vary considerably from place to place. The calculated SI values also suggest that there may be a relation between the well site characteristics and the mineralogical distribution, influencing the thermodynamic equilibrium of the sediment-water interaction and the release of As. Finally, the As release mechanism is complex and no unique/individual mechanism can be universally applied to explain such heterogeneous distribution of As.

References

Appelo C. A. J., Postma D. (2004) Geochemistry, groundwater and pollution. Balkema.

BGS and DPHE (2001) In: Kinniburgh, D.G., Smedley, P.L. (Eds.), Arsenic contamination of groundwater in Bangladesh. British Geological Survey WC/00/19, Keyworth.

Bhattacharya P., Chatterjee D., Jacks G. (1997) Occurrence of arsenic-contaminated groundwater in alluvial aquifers from delta plains, Eastern India: Options for safe drinking water supply. *Int. J. Water Resour. Dev.* **13**, 79–92.

Bhattacharya P., Welch A. H., Stollenwerk K. G., McLaughlin M. J., Bundschuh J., Panaullah G. (2007) Arsenic in the environment: biology and chemistry. *Sci.Total Environ.* **379**, 109–120.

Bhattacharyya R., Chatterjee D. (2001) Technique for arsenic removal from groundwater utilizing geological options – An innovative low cost remediation. *International Association of Hydrological Society* **275**, 391–396.

Bhattacharyya R., Chatterjee D., Nath B., Jana J., Jacks G., Vahter M. (2003a) High arsenic groundwater: Mobilization, metabolism and mitigation – An overview in the Bengal Delta Plain. *Mol. Cell. Biochem.* **253**, 347–355.

Bhattacharyya R., Jana J., Nath B., Sahu S. J., Chatterjee D., Jacks G. (2003b) Groundwater As mobilization in the Bengal Delta Plain, the use of ferralite as a possible remedial measure – A case study. *Appl. Geochem.* **18**, 1435–1451.

Biswas A., Majumder S., Neidhardt H., Halder D., Bhowmick S., Mukherjee-Goswami A.,Kundu A., Saha D., Berner Z., Chatterjee D. (2011) Groundwater chemistry and redoxprocesses: Depth dependent arsenic release mechanism. *Appl. Geochem.* **26**, 516–525.

CGWB (1999) High Incidence of As in groundwater in West Bengal. Central Groundwater Board (CGWB), India. Ministry of Water Resources, Government of India.

Chakraborty S., Wolthers M., Chatterjee D., Charlet L. (2007) Adsorption of arsenite and arsenate onto muscovite and biotite mica. *J. Colloid Interface Sci.* **309**, 392–401.

Charlet L., Chakraborty S., Appelo C. A. J., Roman-Ross G., Nath B., Ansari A. A., Lanson M., Chatterjee D., Basu Mallik S. (2007) Chemodynamics of an As "hotspot" in a West Bengal aquifer: A field and reactive transport modeling study. *Appl. Geochem.* **22**, 1273–1292.

Chatterjee D., Chakraborty S., Nath B., Jana J., Mukherjee P., Sarkar M. (2004) Geochemistry of arsenic in deltaic sediment. *Geochim. Cosmochimi. Acta* **68**, 514.

Chatterjee D., Halder D., Majumder S., Biswas A., Bhattacharya P., Bhowmick S., Mukherjee-Goswami A., Saha D., Maity P. B., Chatterjee D., Nath B., Mukherjee A., Bundschuh J. (2010) Assessment of arsenic exposure from groundwater and rice in Bengal Delta Region, West Bengal, India. *Water Res.* **44**, 5803–5812.

Chatterjee D., Majumder S., Mukherjee-Goswami A., Jana J., Biswas A., Halder D., Bhowmick S., Chatterjee D. (2012) Young Bengal Delta Plain and Arsenic in groundwater: distribution and geochemistry. *Indian Journal of Applied Geochemistry* 170–185.

Chatterjee D., Roy R. K., Basu B. B. (2005) Riddle of arsenic in groundwater of Bengal Delta Plain – role of non-inland source and redox traps. *Environ. Geol.* **49**, 188–206.

Chowdhury M. K. I., Ahmed F. M., Ali M. A. (2000) Influence of upstream sediment on As contamination of groundwater in Bangladesh. Proceeding of International Conference on Geoenvironment, Sultan Qabus University, Muacat, Oman (March 4-7, 2000) 1, 21– 35.

Datta, D. K., Subramanian V. (1998) Distribution and fractionation of heavy metals in the surface sediments of the Ganges–Brahmaputra-Meghna river system in the Bengal Basin. *Environ. Geol.* **36**, 93–101.

Davis J. C. (1986) Statistics and data analysis in geology. John Wiley and Sons, New York.

Evans, C. D., Davies T. D., Wigington P. J., Tranter J. M., Kretser. W.A. (1996) Use of factor analysis to investigate processes controlling the chemical composition of four streams in the Adirondack Mountains, New York. *J. Hydrol.* **185**, 297–316.

Fendorf S., Michael H. A., van Geen A. (2010) Spatial and temporal variations of groundwater arsenic in south and south East Asia. *Science* **328**, 1123.

Gault A. G., Islam F. S., Polya D. A., Charnock J. M., Boothman C., Chatterjee D., Lloyd J. R. (2005) Microcosm depth profiles of arsenic release in a shallow aquifer, West Bengal. *Miner. Mag.* **69**, 855–863.

Helena B., Pardo R., Vega M., Barrado E., Fernandez J. M., Fernandez L. (2000) Temporal evolution of groundwater composition in an alluvial aquifer (Pisguera river, Spain) by Principal Component Analysis. *Water Res.* **34**, 807–816.

IFCPAR (Indo-French Centre for the Promotion of Advance Research) (2004) Report on “Geochemistry of Ganga Sediment and Groundwater: Arsenic Mobilization”. University of Kalyani, Nadia, West Bengal, India and University of Grenoble, France.

Jacks G., Sefe F., Carling M., Hammar M., Letsamao P. (1999) Tentative nitrogen budget for pit latrines – Eastern Botswana. *Environ. Geol.* **8**, 199–203.

Jana J. (2004) Jenesis of arseniferrous groundwater in the Bengal Delta Plain in West Bengal, Eastern India. Unpublished Ph.D. thesis, University of Kalyani, India.

Kabata-Pendius A., Pendius H. (2001) Trace elements in soils and plants, 3rd edn., CRC press, Boca Raton, FL.

Lee J. Y., Cheon J. Y., Lee K. K., Lee S. Y., Lee M. H. (2001) Statistical evaluation of geochemical parameter distribution in a groundwater system contaminated with petroleum hydrocarbons. *J. Environ. Qual.* **30**, 1548–1563.

Liu C. W., Lin K. H., Kuo Y. M. (2003) Application of factor analysis in the assessment of groundwater quality in a blackfoot disease area in Taiwan. *Sci. Total Environ.* **313**, 77–89.

Lowers H. A., Breit G. N., Foster A. L., Whitney J., Yount J., Uddin M. N., Muneem A. A. (2007) Arsenic incorporation into authegenic pyrite, Bengal Basin sediment, Bangladesh. *Geochim. Cosmichim. Acta* **71**, 2699–2717.

Majumder S., Chatterjee D., Biswas A., Berner Z., Neidhardt H. (2010) Factor analysis to explain arsenic mobilization: a case study for an area in West Bengal, India. Water-Rock Interaction 13, Guanajuato, Mexico, 264-267.

McArthur J. M., Banerjee D. M., Hudson-Edwards K. A., Mishra R., Purohit R., Ravenscroft P., Cronin A., Howarth R.J., Chatterjee A., Talukder T., Lowry D., Houghton S., Chadha D. K. (2004) Natural organic matter in sedimentary basins and its relation to As in anoxic groundwater: The example of West Bengal and its worldwide implications. *Appl. Geochem.* **19**, 1255–1293.

Mukherjee A., Bhattacharya P., Savage K., Foster A., Bundschuh J. (2008a) Distribution of geogenic arsenic in hydrologic systems: controls and challenges. *J. Contam. Hydrol.* **99**, 1–7.

Mukherjee A., Fryar A. E. (2008) Deeper groundwater chemistry and geochemical modeling of the arsenic affected western Bengal basin, West Bengal, India. *Appl. Geochem.* **23**, 863–892.

Mukherjee A., Fryar A. E., Howell P. (2007) Regional hydrostratigraphy and groundwater flow modeling of the arsenic contaminated aquifers of the western Bengal basin, West Bengal, India. *Hydrogeol. J.* **15**, 1397–1418.

Mukherjee A., Fryar A. E., Scanlon B. R., Bhattacharya P., Bhattacharya A. (2011) Elevated arsenic in deeper groundwater of western Bengal basin, India: Extents and controls from regional to local-scale. *Appl. Geochem.* **26**, 600–613.

Mukherjee A., Fryar A. E., Thomas W. A. (2009) Geologic, geomorphic and hydrologic framework and evolution of the Bengal basin, India. *J. Asian Earth Sci.* **34**, 227–244.

Mukherjee A., von Bromssen M., Scanlon B. R., Bhattacharya P., Fryar A. E., Hasan M. A., Ahmed K. M., Chatterjee D., Jacks G., Sracek O. (2008b) Hydrogeochemical comparison and effects of overlapping redox zones on groundwater arsenic near the western (Bhagirathi sub-basin, India) and Eastern (Meghna sub-basin, Bangladesh) margins of the Bengal Basin. *J. Contam. Hydrol.* **99**, 31–48.

Mukherjee-Goswami A., Nath B., Jana J., Sahu S. J., Sarkar M. J., Jacks G., Bhattacharya P., Mukherjee A., Polya D. A., Jean J.-S., Chatterjee D. (2008) Hydrogeochemical behavior of arsenic-enriched groundwater in the deltaic environment: Comparison between two study sites in West Bengal, India. *J. Contam. Hydrol.* **99**, 22–31.

NAS (1977) Medical and biological effects of environmental pollutants: arsenic. National Academy of Sciences, Washington, DC.

Nath B., Berner Z., Basu Mallik S., Chatterjee D., Charlet L., Stüeben D. (2005) Characterization of aquifers conducting groundwaters with low and high arsenic concentrations: A comparative case study from West Bengal, India. *Miner. Mag.* **69**, 841–853.

Nath B., Berner Z., Chatterjee D., Basu Mallik S., Stüben D. (2008c) Mobility of arsenic in West Bengal aquifers conducting low and high groundwater arsenic. Part II: Comparative geochemical profile and leaching study. *Appl. Geochem.* **23**, 996–1011.

Nath B., Sahu S. J., Jana J., Mukherjee-Goswami A., Roy S., Sarkar M. J., Chatterjee D. (2008a) Hydrochemistry of arsenic-enriched aquifer from rural West Bengal, India: a study of the arsenic exposure and mitigation option. *Water Air Soil Pollut.* **190**, 95–113.

Nath B., Stuben D., Basu Mallik S., Chatterjee D., Charlet L. (2008b) Mobility of arsenic in West Bengal aquifers conducting low and high groundwater arsenic. Part I: Comparative hydrochemical and hydrogeological characteristics. *Appl. Geochem.* **23**, 977–995.

Neumann R. B., Ashfaque K. N., Badruzzaman A. B. M., Ali M. A., Shoemaker J. K., Harvey C. H. (2010) Anthropogenic influences on groundwater arsenic concentrations in Bangladesh. *Nat. Geosci.* **3**, 46–52.

Pal T., Mukherjee P. K., Sengupta S. (2002a) Nature of arsenic pollutants in groundwater of Bengal Basin – A case study from Baruipur area, West Bengal, India. *Curr. Sci.* **82**, 554–561.

Pal T., Mukherjee P. K., Sengupta S., Bhattacharya A. K., Shome S. (2002b) Arsenic pollution in groundwater of West Bengal, India – an insight into the problem by sub-surface sediment analysis. *Gondwana Res.* **5**, 501–502.

Parkhurst D. L., Appelo C. A. J. (1999) Users guide to PHREEQC (version 2): A computer program for speciation, batch–reaction, one–dimensional transport, and inverse geochemical calculation. U. S. Geol. Surv. Water Resour. Invest. Rep. 99–425.

PHED (Public Health and Engineering Directorate) (1993) National Drinking Water Mission project on Arsenic pollution on groundwater in West Bengal. Final report, Steering Committee on As investigation. Government of West Bengal, India.

Polizzotto M. L., Harvey C. F., Li G., Badruzzman B., Ali A., Newville M., Sutton S., Fendorf S. (2006) Solid-phases and desorption processes of arsenic within Bangladesh sediments. *Chem. Geol.* **228**, 97–111.

Postma D., Jakobsen R. (1996) Redox zonation: equilibrium constraints on the Fe(III)/SO_4^{2-}-reduction interface. *Geochim Cosmochim Acta* **60**, 3169–3175.

Radu T., Subacz J. L., Philippi J. M., Barnett M. O. (2005) Effects of dissolved carbonate on arsenic adsorption and mobility. *Environ. Sci. Technol.* **39**, 7875–7882.

RGNDWM (Ministry of Rural Water and Development, Government of India) (2001) Phase-II Report, University of Kalyani, Nadia, West Bengal, India.

Sahu S. J., Nath B., Roy S., Mandal B., Chatterjee D. (2011) A laboratory batch study on arsenic sorption and desorption on guava orchard soils of Baruipur, West Bengal, India. *J. Geochem. Explor.* **108**, 157–162.

Smedley P. L., Kinniburgh D. G. (2002) A review of the source, behaviour and distribution of arsenic in natural waters. *Appl. Geochem.* **17**, 517–568.

Smith A. H., Lingas E. O., Rahaman M. (2000) Contamination of drinking water by arsenic in Bangladesh: A public health emergency. *Bulletin World Health Organization* **78**, 1093–1103.

Sracek O., Bhattacharya P., von Brömssen M., Jacks G., Ahmed K. M. (2005) In: Bundschuh, J., Bhattacharya, P., Chandrashekharam, D. (Eds.), Natural enrichment of arsenic in groundwaters of Brahmanbaria district, Bangladesh: geochemistry, speciation modeling and multivariate statistics. Natural Arsenic in Groundwater: Occurrence, Remediation and Management. A.A. Balkema, Taylor and Francis Group, London, 133–144.

Stüben D., Berner Z., Chandrasekharam D., Karmakar J. (2003) Arsenic enrichment in groundwater of West Bengal, India: geochemical evidence for mobilization of As under reducing conditions. *Appl. Geochem.* **18**, 1417–1434.

Swartz C. H., Blute N. K., Badruzzman B., Ali A., Brabander D., Jay J., Besancon J., Islam S., Hemond H. F., Harvey C. F. (2004) Mobility of arsenic in a Bangladesh aquifer: Inferences from geochemical profiles, leaching data, and mineralogical characterization. Geochem. Cosmichim. Acta **68**, 4539–4557.

Usunoff E. J., Guzman-Guzman A. (1989) Multivariate analysis in hydrochemistry: An example of the use of factor and correspondence analyses. *Groundwater* **27**, 27–34.

van Geen A., Zheng Y., Versteeg R., Stute M., Horneman A., Dhar R., Steckler M., Gelman A., Small C., Ahsan H., Graziano J. H., Hussain I., Ahmed K. M. (2003) Spatial variability of arsenic in 6000 tube wells in a 25 km^2 area of Bangladesh. *Water Resour. Res.* **39**, 1140.

Zheng Y., Stute M., van Geen A., Gavrieli I., Dhar R., Simpson H. J., Schlosser P., Ahmed K. M. (2004) Redox control of arsenic mobilization in Bangladesh groundwater. *Appl. Geochem.* **19**, 201-214.

CHAPTER 3: MONSOONAL INFLUENCE ON STABLE ISOTOPE SIGNATURES AND ASSOCIATED ARSENIC DISTRIBUTION IN GROUNDWATER

The influence of monsoon on variation of aquifer redox changes and related arsenic (As) release processes in groundwater was studied. The control of geochemical processe on passing from pre-monsoon to post-monsoon season was investigated. The associated recharge processes were also studied. It was found that after the monsoon rainfall, As(III) increases drastically in caomparison to the increase in total As. The increase is higher in flood plain areas than in natural levee areas. Stable isotope signature and Cl/Br molar ratio has shown that vertical mixing could be the major recharge process, especially during the post-monsoon season.

3.1. Introduction

In the Bengal Delta Plain (BDP), groundwater arsenic (As) concentrations has been found to frequently exceed the WHO drinking water provisional guide value of 10 μg/L (WHO, 2011). Amongst other countries worldwide, parts of south-east Asia including India and Bangladesh are facing the most severe threats of safe drinking water sources (Nath et al., 2008a; van Geen et al., 2008; Fendorf et al., 2010; Datta et al., 2011). Skin, lung, and liver cancers are the most common consequences of high As exposure among the population in rural West Bengal and Bangladesh (Das et al., 1996; Rahman et al., 2001; Bhattacharyya et al., 2003; Yu et al., 2003). This situation is currently affecting the health of millions of people (Bhattacharyya et al., 2003; Chatterjee et al., 2003) and has become one of the world's worst health catastrophes (Smith et al., 2000; Nriagu et al., 2007).

It has recently been suggested that extensive groundwater withdrawal for agriculture and domestic purposes in these areas may accelerate the release of As to groundwater (Harvey et al., 2002; McArthur et al., 2012; Xie et al., 2012). Oxygen-18 ($\delta^{18}O$) and deuterium ($\delta^{2}H$) stable isotopes have been successfully applied to investigate groundwater flow systems (Chen et al., 2006; Zhu et al., 2007; Datta et al., 2011). The Cl/Br ratio has been frequently used in recent times to assess various hydrogeochemical processes of groundwater evolution (McArthur et al., 2012; Xie et al., 2012). Hydrochemical processes can readily influence the Cl/Br ratio in groundwater during the course of variable solute transport and recharge processes (Cartwright and Weaver, 2005; Cartwright et al., 2006; Zhu et al., 2007). Thus, Cl^- and Br^-, being stable and conservative elements in groundwater, the change in the Cl/Br ratio can be applied to delineate the nature of groundwater recharge and mixing (Xie et al., 2012).

It has been postulated that the local groundwater pumping for irrigation and/or community drinking water supply may draw young, organic-rich water into the aquifer (Neumann et al., 2009). As a result, pumping-driven groundwater movements may flush As from the aquifers (Harvey et al., 2002). The organic carbon transported in this process can be used as an electron donor in microbially mediated redox reactions where metal reducing bacteria are believed to play a key role in As mobilization (Islam et al., 2004). Therefore, it is important to understand the link of hydrogeological environments and the As mobilization processes.

A number of studies have been carried out on the effect of natural organic matter (NOM) influencing the fate of As in the environment (McArthur et al., 2001; Bauer and Blodau, 2006, 2009). For example, microbial degradation of NOM and consequent reductive dissolution of As bearing iron oxy-hydroxides (Bhattacharya et al., 1997; Nickson et al., 2000; McArthur et al., 2001; Swartz et al., 2004), competition between As and dissolved organic carbon (DOC) for the binding sites of goethite, alumina or hematite (Redman et al., 2002; Bauer and Blodau, 2006), metal enhanced complexation of As with DOC are the few reported till date. However, the binding nature of As(III)/As(V) with DOC, the kinetic and thermodynamic detail for the necessary reactions are still to be explored (Thanabalasingam and Pickering, 1986; Warwick et al., 2005; Buschmann et al., 2006). Kanematsu et al. (2013) stated that the major oxyanions of As(III) and As(V) may react differently to goethite-based adsorbent in presence of competitive ions.

This study uses hydrochemical and isotopic data collected from a hotspot (high As area – flood plain wells) and a low As area – natural levee wells to understand the impact of monsoonal influence on As release and it's species distribution in groundwater. Systematic analysis of hydrogeological features of groundwater combined with isotope geochemistry was carried out to test the applicability of environmental isotopes and Cl/Br molar ratios in delineating groundwater recharge patterns. This study depicts the possible redox interactions between As and DOC in the aquifer. Throughout this manuscript, we have used the acronyms 'PRM' to denote the 'pre-monsoon' and 'PSTM' to denote 'post-monsoon' water samples.

3.2. Study area

The study area is located in Chakdaha block of Nadia district, 65 km north of Kolkata, West Bengal, India (Figure 3.1). A high As and a low As site were selected depending on a previously executed hydrochemical survey (Chatterjee et al., 2010; Majumder et al., 2010, 2013).

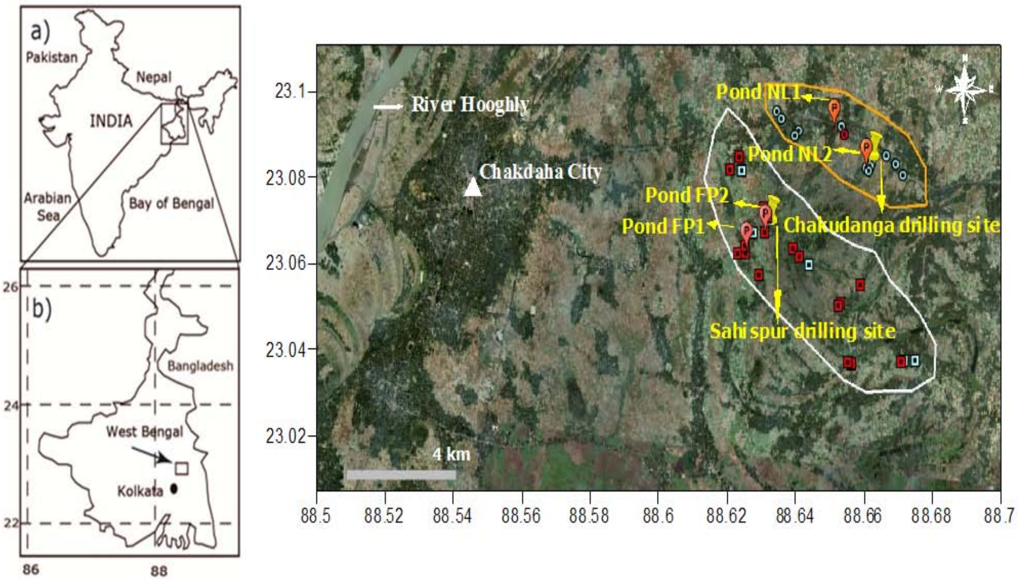


Figure 3.1. Study area (the polygon with white color boundary line represents the flood plain area and the polygon with orange color boundary line represents the natural levee area). All the red colored points (squares in case of flood plain and circles in case of natural levee) denote samples exceeding 50 µg/L of As_T and the light blue colored points denote samples below 50 µg/L of As_T concentration. The 'p' balloons represent the pond samples from the respective areas.

The water samples were collected during the pre-monsoon season (April-May, 2009) and the post-monsoon season (October-November, 2009). As per previous studies of geomorphological characteristics of the region and interpretation of the satellite imagery, the high As (hotspot) localities are situated within the flood plain of the Hooghly-Bhagirathi river, while the low As localities are situated within natural levees (Figure 3.1). The flood plain includes numerous large and small natural and/or man-made ponds with areas mostly used for agricultural purposes being cultivated all around the year. Irrigation with shallow groundwater is common practice in the study area, especially during the dry season. During 1998–1999, about 60% of 8,450 ha agricultural fields were irrigated with shallow groundwater (Nath et al., 2008b). The natural levees are used for habitation and highways. The temperature of the study area is ~ 16-42^{o}C and average relative humidity>65%. The annual rainfall ranges between 1295 and 3945 mm (Bhattacharyya, 2001).

3.3. Methods

Groundwater samples (n = 49, 22 wells from flood plains and 13 from natural levees) have been collected from the study area for hydrochemical and stable isotope ($\delta^{18}O$ and $\delta^{2}H$) analysis during pre-monsoon (PRM, April–May, 2009) and post-monsoon (PSTM, October–November, 2009) season. Four pond samples were also collected (2 from flood plain area and 2 from natural levee) during both PRM and PSTM sampling (Figure 3.1). All the sampled wells were within the shallow depth levels (<40 m). Rainwater samples could not be analysed during our study period, therefore, we used rainwater data (both pre-monsoon and monsoon) from Mukherjee et al. (2007) as their study site was within the 50 km of the present study site. Both the groundwater and pond water samples were filtered (0.45 µm cellulose nitrate membrane filter) on-site and divided into two groups. First group was acidified with HNO_3 (0.2% v/v, suprapur, MERCK, Germany) for the analysis of cation and As, using a high resolution inductively coupled plasma mass spectrometer (HR-ICP-MS VG AXIOM, VG Elemental). The second group was left unacidified to determine anions by Ion Chromatography (IC, DIONEX ICS 1000 equipped with a DIONEX AS 4 SC column). Samples for As(III) speciation were additionally injected onsite through a disposable cartridge® packed with an ion exchanger resin at a flow rate of 5 mL/min (MetalSoft Centre, NJ, USA). The samples for Fe(II) were filtered into a separate 50 mL amber glass bottle containing 2 mL concentrated HCl (Suprapure, MERCK) whereas samples for major cations and trace elements were acidified with HNO3 (1% v/v, Suprapure, MERCK). The limit of detection of the HR-ICP-Ms for the determination of As and Fe was 0.25 ± 0.08 and 1.55 ± 0.72 (in µg/L) respectively. Analytical quality controls with GLP were regularly practiced using commercial CRM materials (SRM 1643e). Samples were measured in triplicates, showing average precisions of within ± 5%. Dissolved organic carbon (DOC) was determined with a high TOC analyzer (Elementar, Hanau). Water quality parameters pH, Eh, conductivity, temperature (using WTW multimeters) and HCO_3^- (titrating with 0.2 M H_2SO_4) were measured on site.

Sediment core drilling samples were collected from two sites – one within the flood plain area in the village of Sahispur, Chakdaha Block (N23°04'15.5'', E88°36'33.5''), located about 25 km west of the River Ganges, another one far west within the natural levee area in the Chakudanga village, Chakadaha block (N23°04'58'', E88°38'13'') (Figure 3.1). Sediment core samples of 0.65 m in length were collected by means of split spoon core sampling device. The deepest samples in the flood plain sediment sample site and for the natural levee sampling site were 39.2 m and 45.5 m below surface respectively. Major and trace element concentrations in sediments were measured by means of energy dispersive X-ray fluorescence spectroscopy (EDX; Epsilon5, PANanalytical), grain size was determined by sieving, and primary mineral phases were analyzed by X-ray diffraction (XRD; D500 Kristalloflex, Siemens) at the Institute of Mineralogy and Geochemistry, Karlsruhe Institute of Technology, Karlsruhe, Germany. Certified reference materials were used to check the results at regular intervals for each analytical batch (Soil V, n: 10; Soil VII, n: 10; GXR-2, n: 11; GXR-5, n: 10; Sco-1, n: 7; SDO-1, n: 7). The average accuracy with these reference materials was found to be of 1.04% (Neidhardt et al., 2013a).

Samples for stable isotope analysis (δ^2H and δ^{18}O) were measured from the anion sample aliquots. Stable isotope compositions were determined by Gasbench-IRMS (Delta V Advantage, Thermo SCIENTIFIC) and standardised to the Vienna Standard Mean Ocean Water (VSMOW) reference material. Analysis quality was regularly checked with 3 certified reference solutions. Accuracy of the measurements was regularly checked with three certified reference solutions (Table 3.1).

Table 3.1. Precision for isotopic reference materials, measured by IRMS against VSMOW (Vienna Standard Mean Ocean Water) during in-situ experiment sample analyses (reference values by IAEA 1993).

Parameter	Reference Material	n	Reference value	Analysis
δ^{18}O	GISP*	3	-24.78	-24.72 ± 0.08
	SLAP**	3	-55.50	-55.53 ± 0.03
	VSMOW***	3	0	-0.04 ± 0.04
δ^2H	GISP	7	-189.73	-189.9 ± 1.2
	SLAP	7	-428.00	-427.80 ± 0.54
	VSMOW	7	0	0.23 ± 0.68

* GISP: Greenland Ice Sheet Precipitation; * SLAP: Standard Light Antarctic Precipitation;

** VSMOW: Vienna Standard Mean Ocean Water

Paired t test was carried out by using SPSS 16 to compare the significance of the analyzed PRM and PSTM samples (Table 3.2a and b).

Table 3.2. a) Sample statistical summary; b) Paired samples correlations, c) Paired samples test.

a)

Area	Sample type	Mean	SD
Flood Plain	As(T) (Post-monsoon)	115.87	88.39
	As(T) (Pre-monsoon)	105.56	82.57
	As(III) (Post-monsoon)	98.96	80.91
	As(III) (Pre-monsoon)	29.89	25.47
Natural Levee	As(T) (Post-monsoon)	17.36	13.35
	As(T) (Pre-monsoon)	18.56	17.67
	As(III) (Post-monsoon)	14.98	10.87
	As(III) (Pre-monsoon)	4.03	4.4

b)

Area	Sample Type	N	Correlation	P VALUE
Flood Plain	As(T) (Post-monsoon) and As(T) (Pre-monsoon)	21	0.563	0.008
	As(III) (Post-monsoon) and As(III) (Pre-monsoon)	21	0.444	0.044
Natural Levee	As(T) (Post-monsoon) and As(T) (Pre-monsoon)	10	-0.016	0.965
	As(III) (Post-monsoon) and As(III) (Pre-monsoon)	10	-0.008	0.982

c)

Area	**Sample type**	**Std. error mean**	**95% confidence interval of the difference**		**t**	**df**	**p value**
			Lower	**Upper**			
Flood Plain	As(T) (PSTM-PRM)	17.47	-26.13	46.75	0.59	20	**0.562**
	As(III) (PSTM-PRM)	15.98	35.73	102.41	4.32	20	**<0.001**
Natural Levee	As(T) (PSTM-PRM)	7.06	-17.16	14.77	-0.17	9	**0.869**
	As(III) (PSTM-PRM)	3.72	2.54	19.36	2.94	9	**0.016**

PSTM – Post-monsoon; PRM – Pre-monsoon.

3.4. Results

3.4.1. Groundwater composition

The groundwater is reducing in nature (negative Eh values), especially during the PSTM season (Table 3.3). The pH values are overall in a circumneutral range. Only the flood plain wells show slightly alkaline nature, especially during the PSTM season (mean = 7.55). The major cation is represented by Ca^{2+}, followed by Mg^{2+}, Na^{+}, K^{+}, Mn^{2+} and Al^{3+}. The concentrations of Ca^{2+}, Mg^{2+}, Mn^{2+} and Al^{3+} decrease steadily in passing from PRM to PSTM period in case of flood plain wells. However, this trend is not clear with the natural levee samples (the decrease in Ca^{2+}, Mg^{2+} and Al^{3+} is not so significant and concentration of Mn^{2+} actually increased after the monsoon). The major anion is HCO_3^-, followed by Cl^-, SO_4^{2-}, NO_3^- and PO_4^{3-} (Table 3.3). The As_T concentration is generally higher in the flood plain samples than the natural levee samples (Figure 3.2a). The concentration further increases after the monsoon. Interestingly the As(III) concentration increases drastically in the PSTM season (Figure 3.2b), whereas very little increase is observed in As_T concentration (Figure 3.2a). The specific observations regarding the water chemistry from both sites are discussed below (shown in Figure 3.2):

i) Dissolved Organic Carbon (DOC): Increase in DOC observed (Figure 3.2c) in going from PRM to PSTM flood plain samples (from <3 mg/L to ~12.5 mg/L).

ii) HCO_3^-: Along with DOC, HCO_3^- concentrations in flood plain samples increase from PRM to PSTM season (Figure 3.2d). In natural levee, no such trend is visible.

iii) Eh: Redox potentials decline in flood plain PSTM samples (from ~ +50 to –250 mV). In contrast, natural levee samples throughout remain within similar ranges (+40 to -65 mV) in PRM flood plain groundwater (Table 3.3 and Figure 3.2e).

iv) Fe^{2+} and Fe_T: Similar to As(III), there is a significant increase in Fe^{2+} proportions in PSTM samples in both flood plain and natural levee groundwater (Figure 3.2f). In addition, increase in Fe_T concentration in PSTM flood plain samples mimics increase in DOC (Figure 3.2g).

v) Mn: Natural levee samples are generally characterized by higher Mn concentration (>300 µg/L). Here, 12 samples exceed the former WHO guideline value of 400 µg/L Mn in drinking water (WHO, 2004), as compared to the flood plain samples (Figure 3.2h).

vi) SO_4^{2-}: In both locations, a strong variation in SO_4^{2-} concentrations seen in PRM and PSTM samples whereas a majority of PSTM samples show depletion in SO_4^{2-} in going from pre- to post-monsoon season (Figure 3.2i).

vii) NO_3^-: Generally, groundwater in the study area is characterized by very low NO_3^- concentrations (<3 mg/L). There is little increase in PRM samples from both locations, with a few exceptions where concentrations strongly increase in PRM samples (Figure 3.2j).

viii) Isotopic compositions: Isotopic composition of water from flood plain wells differs from the natural levee, with lower $\delta^{18}O$ and $\delta^{2}H$ values (Figures 3.2k and 3.2l). In addition, isotopic composition of PSTM flood plain groundwaters show pronounced changes as compared to PRM samples. This is similar to changes in DOC, HCO_3^-, Fe_T, As(III) and Fe^{2+}. Furthermore, insignificant decrease in $\delta^{18}O$ and δ^2H values is also visible in natural levee PSTM samples.

Table 3.3. Statistical summary of the groundwater chemistry.

Parameters	Site ID	n	Min	Max	Mean	Median	SD (±)
pH	FP (PRM)	21	5.87	7.99	6.95	6.98	0.73
	FP (PSTM)	22	6.53	8.10	7.55	7.88	0.57
	NL (PRM)	10	5.88	7.45	6.62	6.91	0.59
	NL (PSTM)	13	5.96	7.63	6.66	6.56	0.53
Eh	FP (PRM)	21	-114	42.0	-47.1	-56.0	41.5
(mv)	FP (PSTM)	22	-248	8.00	-150	-181	79.2
	NL (PRM)	10	-49.0	40.0	1.20	3.00	32.2
	NL (PSTM)	13	-65.0	14.0	-27.0	-29.0	23.1
Conductivity	FP (PRM)	21	824	978	856	844	49.7
(µs/cm)	FP (PSTM)	22	837	1098	879	859	57.6
	NL (PRM)	10	547	820	718	725	61.7
	NL (PSTM)	13	561	836	723	722	49.7
Temperature	FP (PRM)	21	25.2	27.4	26.7	27.0	0.79
(°C)	FP (PSTM)	22	25.1	28.1	27.0	27.6	1.00
	NL (PRM)	10	25.4	27.6	26.8	26.8	1.06
	NL (PSTM)	13	25.4	27.9	26.9	27.0	0.97

Parameters	Site ID	n	Min	Max	Mean	Median	SD (±)
HCO_3^- (mg/L)	FP (PRM)	21	230	590	367	332	93.7
	FP (PSTM)	22	380	670	482	485	80.5
	NL (PRM)	10	242	520	362	350	93.6
	NL (PSTM)	13	260	550	396	400	89.5
Cl^- (mg/L)	FP (PRM)	21	5.65	31.5	15.9	15.4	6.71
	FP (PSTM)	22	3.65	33.8	16.3	15.0	7.93
	NL (PRM)	10	3.00	34.2	13.5	11.1	9.59
	NL (PSTM)	13	6.90	22.6	13.8	11.6	5.92
Br^- (mg/L)	FP (PRM)	21	0.16	1.66	0.57	0.50	0.32
	FP (PSTM)	22	0.10	1.41	0.55	0.52	0.31
	NL (PRM)	10	0.38	1.98	0.79	0.67	0.48
	NL (PSTM)	13	0.30	1.45	0.88	0.90	0.34
NO_3^- (mg/L)	FP (PRM)	21	0.59	20.7	4.83	2.14	6.58
	FP (PSTM)	22	0.27	6.65	1.30	0.63	1.74
	NL (PRM)	10	0.33	4.94	1.84	0.95	1.73
	NL (PSTM)	13	0.18	3.01	0.70	0.36	0.83
SO_4^{2-} (mg/L)	FP (PRM)	21	0.00	15.3	4.86	2.29	5.01
	FP (PSTM)	22	0.00	9.83	1.96	0.37	2.86
	NL (PRM)	10	1.76	15.8	6.52	5.55	4.36
	NL (PSTM)	13	0.17	6.97	3.29	3.41	2.77

Parameters	**Site ID**	**n**	**Min**	**Max**	**Mean**	**Median**	**SD (±)**
PO_4^{3-} (mg/L)	FP (PSTM)	22	0.14	1.47	0.31	0.21	0.31
	NL (PRM)	10	0.09	0.90	0.42	0.32	0.27
	NL (PSTM)	13	0.04	1.36	0.32	0.21	0.35
Na^+ (mg/L)	FP (PRM)	21	18.6	41.9	30.3	30.2	6.25
	FP (PSTM)	22	8.61	28.9	17.7	17.6	4.86
	NL (PRM)	10	10.6	27.8	20.7	20.0	5.92
	NL (PSTM)	13	2.12	23.4	14.9	14.2	5.59
K^+ (mg/L)	FP (PRM)	21	1.36	82.6	11.6	2.81	19.7
	FP (PSTM)	22	1.68	37.8	5.97	3.05	9.66
	NL (PRM)	10	1.21	14.4	3.98	2.88	3.80
	NL (PSTM)	13	2.33	15.6	4.67	3.99	3.48
Mg^{2+} (mg/L)	FP (PRM)	21	12.8	36.1	26.5	26.8	6.16
	FP (PSTM)	22	11.5	23.2	17.7	17.4	3.47
	NL (PRM)	10	12.2	28.6	19.1	16.8	5.40
	NL (PSTM)	13	10.0	28.9	18.7	20.3	3.99
Ca^{2+} (mg/L)	FP (PRM)	21	57.8	147	96.9	80.3	30.1
	FP (PSTM)	22	61.4	98.7	77.7	77.6	9.26
	NL (PRM)	10	23.6	97.1	71.5	78.4	20.2
	NL (PSTM)	13	53.1	104	79.4	79.6	13.2

Parameters	**Site ID**	**n**	**Min**	**Max**	**Mean**	**Median**	**SD (±)**
As_T	FP (PRM)	21	6.90	290	106	80.4	82.6
(µg/L)	FP (PSTM)	22	12.6	319	113	81.8	87.3
	NL (PRM)	10	1.12	61.3	18.6	11.4	17.7
	NL (PSTM)	13	0.95	43.0	12.8	11.2	10.5
As(III)	FP (PRM)	21	2.00	80.3	29.9	22.8	25.5
(µg/L)	FP (PSTM)	22	11.0	318	96.6	68.9	79.7
	NL (PRM)	10	0.34	14.7	4.03	2.70	4.40
	NL (PSTM)	13	0.25	43.0	12.8	11.2	10.5
Fe_T	FP (PRM)	21	0.01	6.22	2.06	1.24	2.13
(mg/L)	FP (PSTM)	22	1.74	7.95	4.19	4.24	1.59
	NL (PRM)	10	0.01	6.25	2.27	2.18	2.20
	NL (PSTM)	13	0.10	8.28	2.71	2.60	2.21
Fe(II)	FP (PRM)	21	0.00	3.98	1.02	0.47	1.21
(mg/L)	FP (PSTM)	22	1.22	5.91	3.23	2.84	1.40
	NL (PRM)	10	0.01	3.21	1.15	0.53	1.29
	NL (PSTM)	13	0.00	4.70	1.53	1.38	1.31
Mn^{2+}	FP (PRM)	21	41.9	798	244	195	197
(µg/L)	FP (PSTM)	22	50.0	524	211	144	157
	NL (PRM)	10	33.2	694	394	367	172
	NL (PSTM)	13	47.1	754	448	461	188

Parameters	Site ID	n	Min	Max	Mean	Median	SD (±)
Al^{3+} (μg/L)	FP (PRM)	21	13.0	53.8	26.9	25.2	11.3
	FP (PSTM)	22	7.63	35.0	14.4	12.1	6.76
	NL (PRM)	10	16.3	31.4	22.4	22.2	4.86
	NL (PSTM)	13	10.7	40.5	18.5	17.6	7.34
DOC (mg/L)	FP (PRM)	21	0.07	2.62	1.33	1.35	0.86
	FP (PSTM)	22	0.21	12.5	6.29	7.36	3.80
	NL (PRM)	10	0.03	0.62	0.23	0.18	0.18
	NL (PSTM)	13	0.02	1.12	0.59	0.57	0.31

FP (PRM) – Flood plain (Pre-monsoon)

FP (PSTM) – Flood plain (Post-monsoon)

NL (PRM) – Natural levee (Pre-monsoon)

NL (PSTM) – Natural levee (Pre-monsoon)

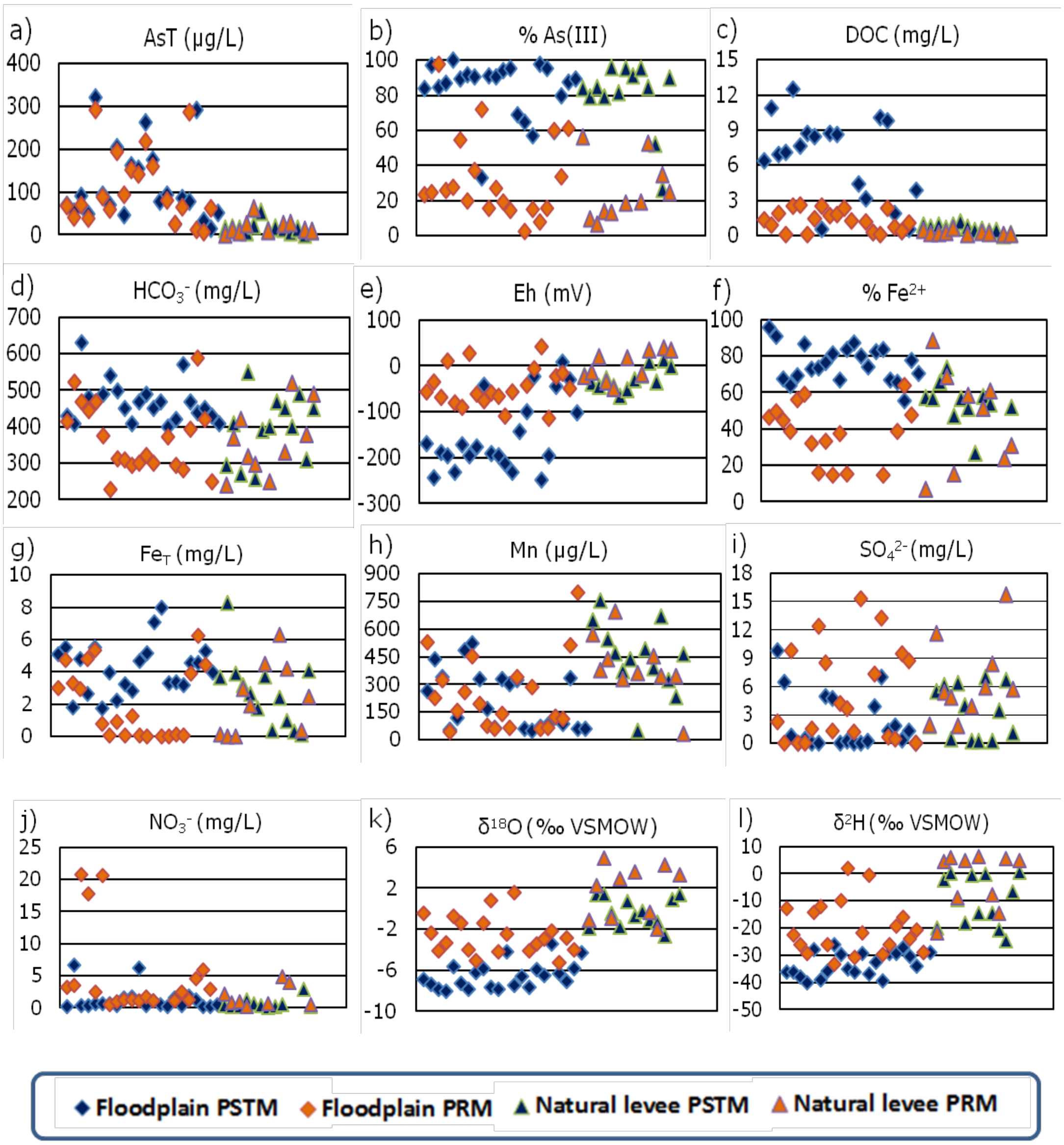


Figure 3.2. Spatio-temporal variation of various hydrochemical parameters in flood plain and natural levee wells during pre- and post- monsoon times. The percentage of As(III) and Fe^{2+} here represents the their respective proportions in As_T and Fe_T.

3.4.2. Spatio-temporal variaion of As_T and As(III)

Total arsenic (As_T) concentrations are generally higher in flood plain samples than in natural levee (Table 3.3 and Figsures 3.2a and b). In nearly all PSTM flood plain samples As_T concentrations slightly increase, while in natural levee samples, concentration changes are rather insignificant. Despite slight changes in the total concentrations, there are pronounced changes in the As species of almost all samples – As(III) ratios strongly increase during monsoon. In both flood plain and natural levee samples, mean As_T concentration do not show any significant change from PRM to PSTM season (p value >0.05). However, As(III) concentration show a significant increase (p value <0.05) in PSTM compared to PRM seasons. The extent of this significant increase is much greater for flood plain (P value <0.001) compared to natural levee wells (see Table 3.2). Mean As_T concentration increases by 6.6% in the flood plain wells during PSTM seasons, while decreases by 17.7% in the natural levee wells (Table 3.4 and Figure 3.2a). In case of flood plain wells, the As(III) concentration increases by 223% on passing into PSTM periods. Similar increase of As(III) concentration (217%) is observed in the natural levee wells (Table 3.4 and Figure 3.2b).

Table 3.4. Percentage increase in As concentration [both As(III) and As_T] on passing from pre- to post-monsoon season.

Site	As(III)	As_T
Flood plain	223	6.60
Natural levee	217	-17.7

More As contaminated wells are seen in the depth range of 15-20 m (Figures 3.3a and b). Depth distribution of As_T concentration shows that natural levee wells are mostly low (<50 μg/L), whereas high concentrations (>50 μg/L) are observed for flood plain wells. The similar distribution patterns are also observed for As(III) concentrations in both areas.

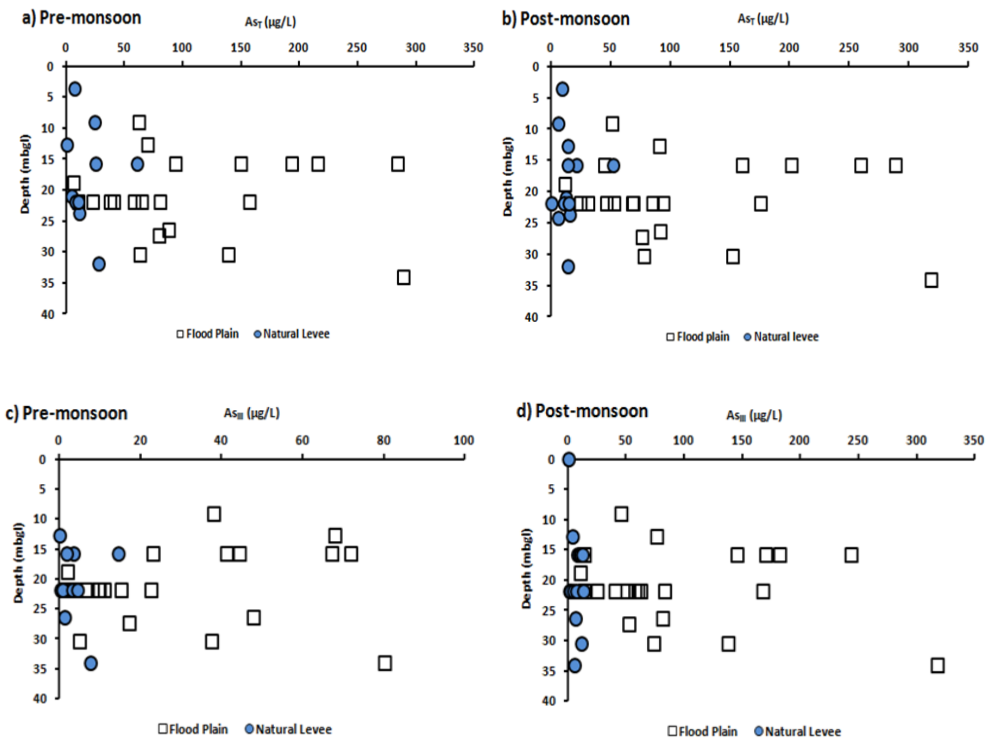


Figure 3.3. Depth profile of As_T a) pre-monsoon; b) post-monsoon and As(III) c) pre-monsoon; d) post-monsoon.

3.4.3. Link between lithology of sediments and groundwater arsenic

Sub-surface sediment samples have been collected from drilled boreholes up to 45 m depth to capture the lithological variation in natural levee (Chakudanga) and flood plain (Sahispur) sites. The general lithology portrays a fining upward sequence and units are of variable thickness. The natural levee is dominated by fine to medium sands throughout indicating a strong fluvial influence, while the flood plain is dominated by muds and finer sands at depth indicating a tidal estuarine influence. At the shallow depths (15-25 m), color of the sediments within the flood plain is blackish gray (reducing sediments) where maximum groundwater As concentration is upto 300 µg/L. On the contrary, the color of the sediments in natural levee boreholes between 5 and 35 m depth is off-white where maximum groundwater As concentration is upto 60 µg/L. The grain size analysis also shows a change in between natural levee and flood plain (Figures 3.4a and b). In the flood plain area, medium sand (approximately 40-50%) and fine sand are equally present at the depth 15-25 m, where groundwater As concentration is maximum, whereas, in case of natural levee sediment, fine sand is dominating (~70%) with medium sand

and silty clay coverage where As concentration is relatively low. The grain size and sedimentary packages indicate fluvial origin of the sediments. A repetitive, vertical stacking of the packs pronounced in natural levee (Figure 3.4a) indicates river migration and consequently superimposition of overbank deposits. The repetitive flood plain sequence is commonly pronounced in sandy lithofacies with occasional channel filled deposits. Finer overbank levee deposits are also noticed during lithological strata change (Figure 3.4b).

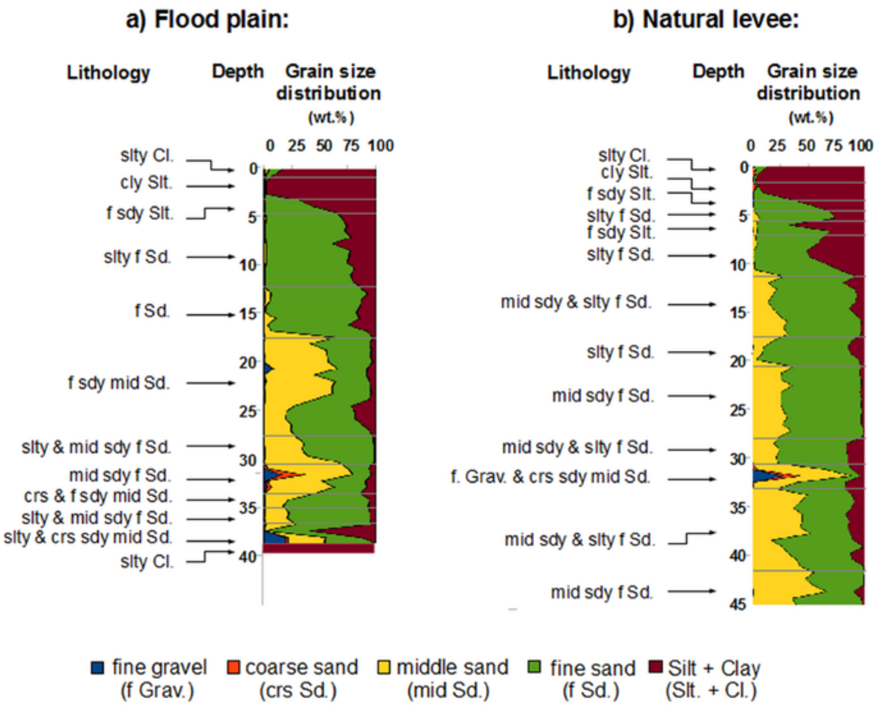


Figure 3.4. Lithologs from the study are a) flood plain (Sahispur litholog), b) natural levee (Chakudanga litholog) (modified after Neidhardt et al., 2013b).

The lithology is controlled by channel filled and overbank deposits, thereby controlling the geometry of the aquifers (3D). This part of the Bengal delta is a tectonically active depositional environment composed of unconsolidated muds and sands constructed by channel migration, avulsion, and overbank processes. These riverine sediments define the channels, flood plains, and terraces that make up the surface morphology of the upper delta plain. The stratigraphy and land surface are consequences of controls on the system and reflect channel behavior over time.

3.4.4. Cl/Br molar ratio and the isotope composition of groundwater

The relationship between Cl^- concentration and the Cl/Br molar ratio (Table 3.3 and Fig. 3.5a) shows two different trends: 1) no significant change in the Cl/Br ratio with increasing Cl^- concentration and 2) sharp increase in Cl/Br ratio with little variation in the Cl^- concentrations.

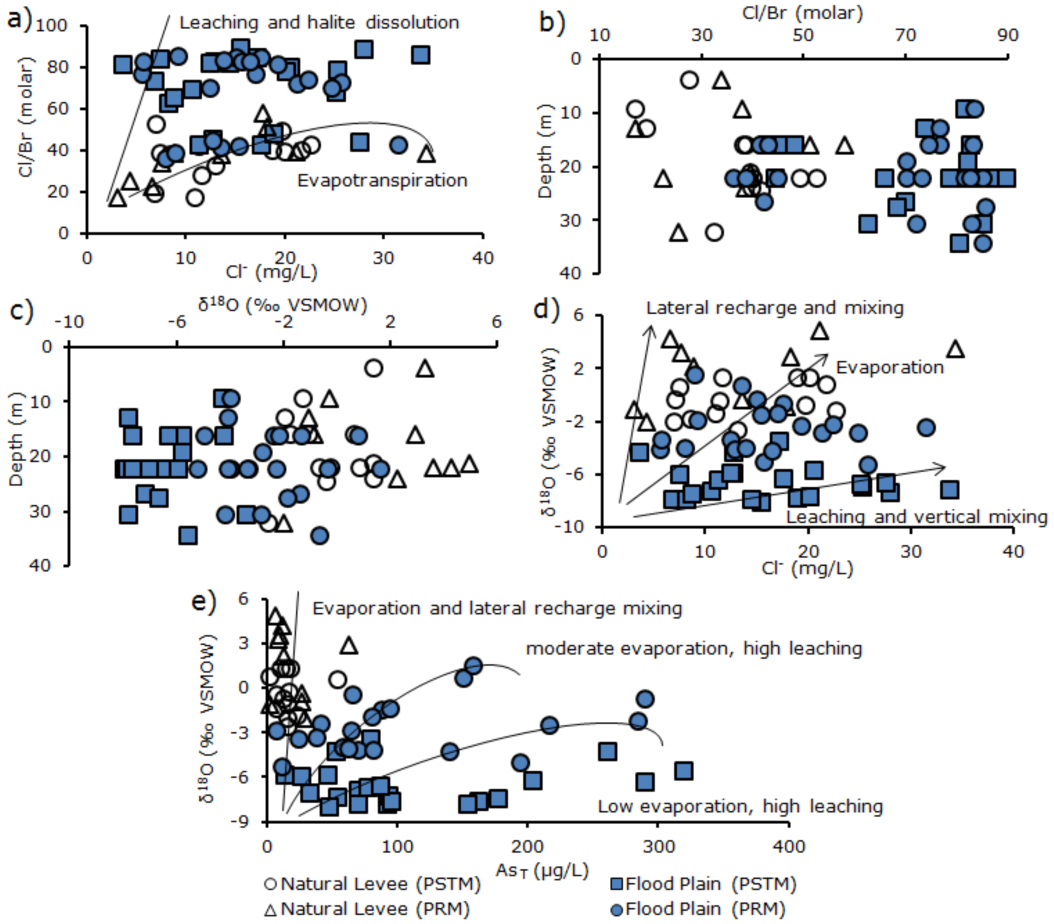


Figure 3.5. a) Relationship of Cl^- concentration and Cl/Br molar ratio, b) vertical distribution of Cl/Br molar ratio, c) Depth distribution of $\delta^{18}O$, d) relationship of Cl^- concentration and $\delta^{18}O$, and e) relationship of As_T and $\delta^{18}O$ (modified after Xie et al., 2012).

Figure 3.5b shows Cl/Br molar ratio is much higher and inconsistent in shallower depths when compared to deeper depths. Figure 3.5c illustrates irregular distribution in terms of $\delta^{18}O$ in the shallow wells (<40 m). Higher values of $\delta^{18}O$ in the natural levee wells are obtained within 25 m. The relationship of Cl^- and $\delta^{18}O$ values (Figure 3.5d) depicts three situations: 1) steep increase in the Cl^- concentration with little variation in the $\delta^{18}O$ values, 2) moderate variation both in

Cl^- concentration and $\delta^{18}O$ values, and 3) pronounced changes in the $\delta^{18}O$ values with no significant change in the Cl^- content. Samples from the first group are mainly flood plain PSTM samples along with a few PRM counterparts. The second group mostly contains the flood plain PRM samples, along with some flood plain PSTM and natural levee samples. Most of the natural levee PRM samples (along with a few PSTM samples and a very few flood plain PRM samples) fall into the third category. Figure 3.5e shows three scenarios: 1) samples containing high As_T concentration with little change in $\delta^{18}O$ value, 2) samples containing moderate As_T concentration and $\delta^{18}O$ value, and 3) samples with increase in $\delta^{18}O$ value with little change in As_T concentration. Here again, the flood plain PSTM samples mostly belong to the first group, whereas the flood plain PRM samples mostly dominate the second group. The third group primarily consists of samples originating from the natural levee wells comprising both, PRM and PSTM seasons.

The stable isotopic signature of groundwater samples taken during the PRM season is characterized by heavier $\delta^{18}O$ values compared to the PSTM samples (flood plain PSTM $\delta^{18}O$ mean -6.5, whereas PRM $\delta^{18}O$ mean -2.5; natural levee PSTM $\delta^{18}O$ mean -0.3, whereas PRM $\delta^{18}O$ mean 1.7) (Figure 3.6a). Although, a few PSTM samples from the natural levee area ($n = 5$) also show higher values of $\delta^{18}O$. Stable isotopic compositions of PSTM samples plot closely to those of surface water. In contrast to natural levee groundwater, $\delta^{18}O$ values of flood plain samples are generally lower (Figure 3.6b) and plot close to the range of surface water isotopic values. There is no notable distinction observed between the PRM and PSTM pond waters. Some of the PRM waters fall close to the Global Meteoric Water Line (GMWL) and close enough to the pond waters, which may indicate possible recharge pathway. Other PRM waters fall on a mixing line with heavier isotopes which indicate evaporative enrichments but not necessarily being fed by pond or other surface waters. Many of the PSTM samples (from the flood plain areas) fall closer to the pond water samples. The Local Evaporation Line (LEL) of the present study shows trend similar to that of the LEL proposed by Lawson et al. (2008).

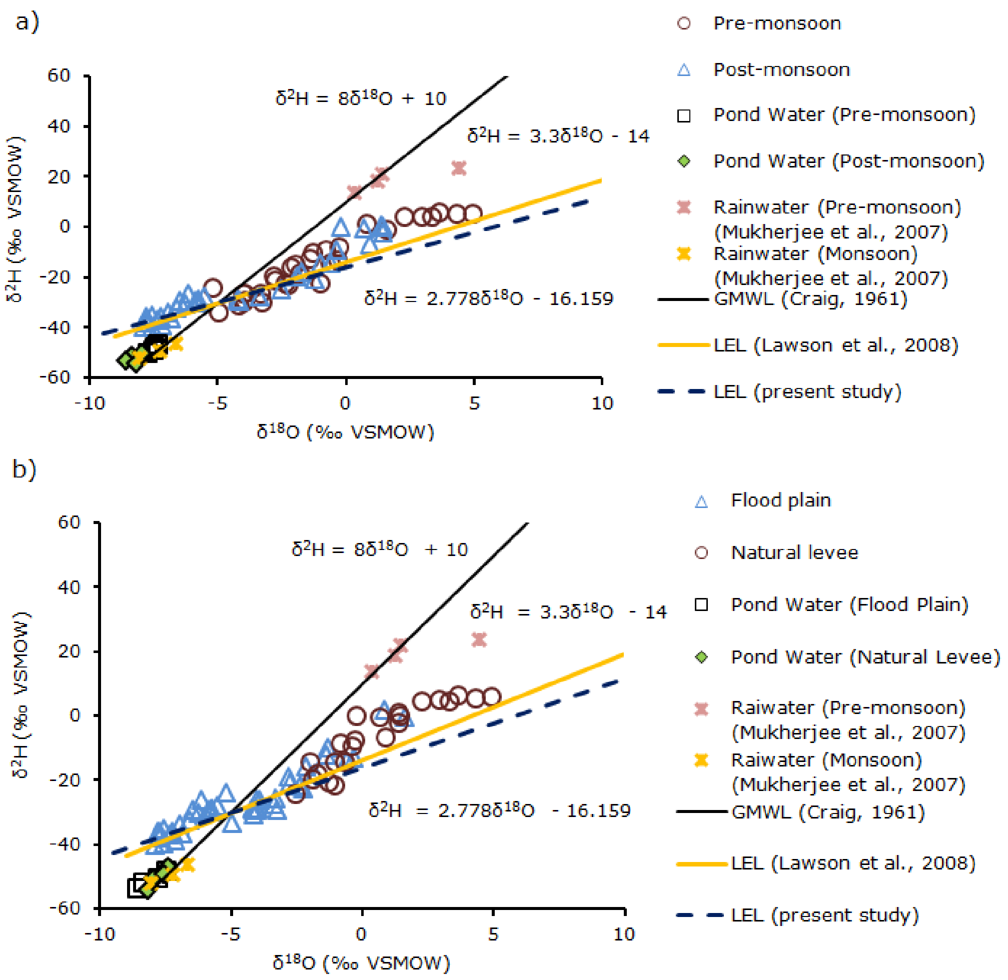


Figure 3.6. Stable isotope plot: a) monsoonal variation, b) spatial variation.

3.5. Discussion

3.5.1. Monsoonal influence on arsenic speciation – the redox control

There are three major observations from the results mentioned above - a) seasonal influence on As speciation (mainly in case of the flood plain wells), b) correlation between As(III) and DOC in the flood plain PSTM samples and c) pronounced difference in As concentration of flood plain and natural levee groundwater. In the natural levee, the prevailing redox potential is obviously less reducing as compared to the flood plain. The redox potential (Eh), DOC, Fe^{2+}, NO$_3^-$, SO$_4^{2-}$, and even the Mn^{2+} concentrations supports the above behavior (Figure 3.2). In the flood plain area, the DOC (the redox driver) is also higher and further increases during the PSTM along with HCO$_3^-$. As a result, microbial processes may get activated (Harvey et al., 2002; Neumann et al., 2009; Sutton et al., 2009) and we see a decrease in the redox potential, which goes along with an increase in As(III) proportions. At the same time, other potential terminal electron acceptor (TEA) substances like NO_3^-, SO_4^{2-} (used for microbial respiration) decrease – supporting microbial activity during increase in DOC following fresh recharge in the PSTM season. As described earlier, the increase in DOC may be connected to the monsoon rain. This indication is in the Cl/Br ratio and $\delta^{18}O$ plots also (Figures 3.5 and 3.6).

DOC holds a consistent, linear relationship with $As(III)/As_T$ in case of the flood plain wells during the PSTM period (Figure 3.7a). Moreover, HCO_3^- concentration in the flood plain wells during the PSTM season shows a similar trend with the $As(III)/As_T$ (Figure 3.7a), reinforcing the idea of possible influence of DOC in these wells as it is expected that if DOC is degraded, HCO_3^- should also be released as end-product and the resulting increase should also correlate positively with the increase in the As(III) concentration. This may also trigger microbial activity. DOC concentrations in the natural levee wells increases with increasing As, however, no clear trend is observed (Figure 3.7b). This may be due to the lower amount of DOC available in the natural levee samples as compared to the flood plain. A close observation of the two sampling areas reveals that flood plain wells are associated with densely populated natural ponds. According to some reports, wetlands, ponds and fields are known to serve as potential sources of infiltrating organic matter, especially during monsoon rains, when the surface recharge drastically increases (Kocar et al., 2008; Nath et al., 2008a; Polizotto et al., 2008). However, the potential influence of ponds is still a matter of intensive debate (e.g, Harvey et al., 2006; Sengupta et al., 2008; Neumann et al., 2009; Farooq et al., 2010; Datta et al., 2011).

The important question is why As is enriched in groundwater and why are concentrations in the flood plain area higher? Arsenic release is very likely to be caused by microbe mediated reduction of Fe(III)-(oxyhydr)oxides during anaerobic decomposition of organic matter and this organic matter could be sediment-bound organic matter in these shallow aquifers. This assumption is also suitable to explain why As concentrations in the flood plain area are generally higher than in the natural levee, where Fe concentrations are lower and the redox potential is less reducing according to the measured Eh and redox sensitive elements. According to concentrations of redox sensitive NO_3^-, Mn, Fe and SO_4^{2-}, all samples were classified in respective redox states (Figure 3.8) according to Jurgens et al. (2009). One can see that most flood plain PSTM samples plot in a more reducing state as in the case of PRM samples. Since most samples still hold NO_3^- concentrations exceeding the applied threshold value (0.5 mg/L), these samples from the natural levee are classified as mixed type, somewhere between NO_3^- reduction and Fe/ SO_4^{2-} reduction (Figure 3.8).

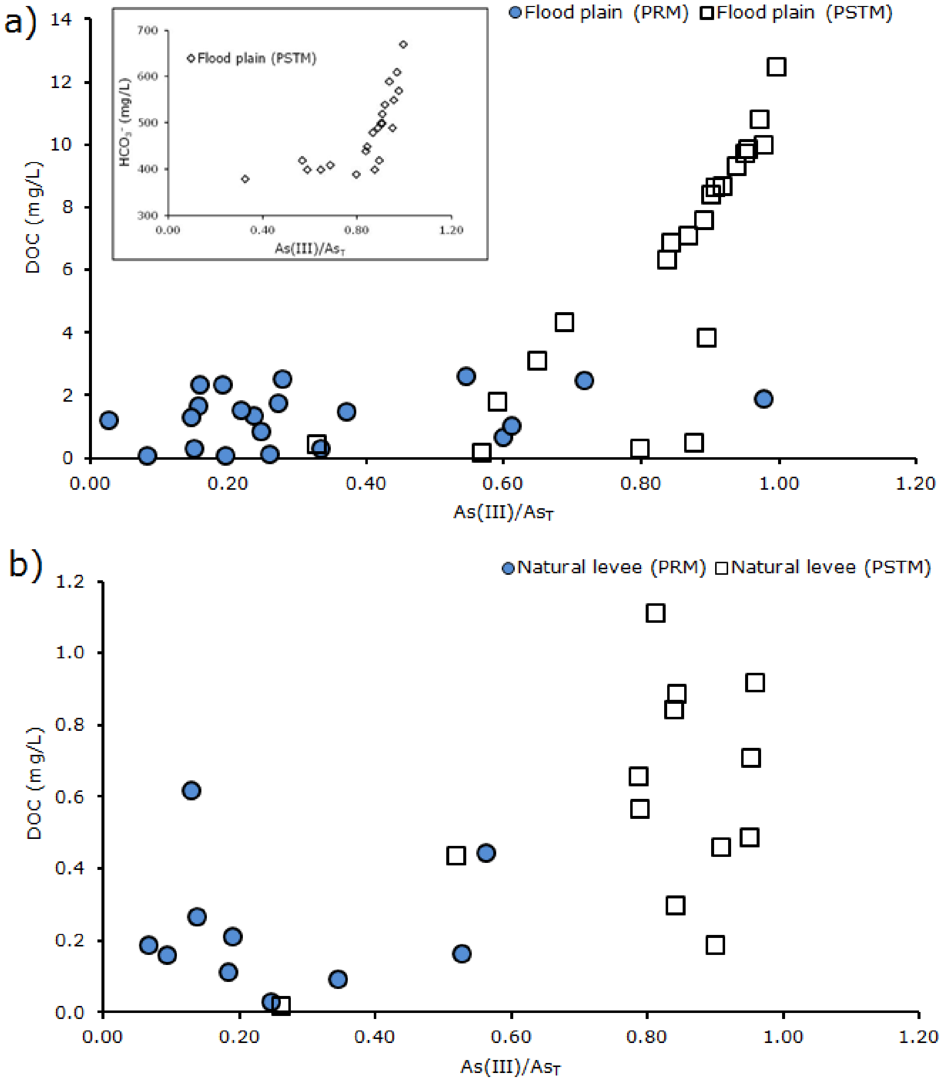


Figure 3.7. Spatio-temporal variation of $As(III)/As_T$ in relation with DOC a) flood plain (inset: relation of HCO_3^- with $As(III)/As_T$ in the flood plain wells during the post-monsoon season), b) natural levee.

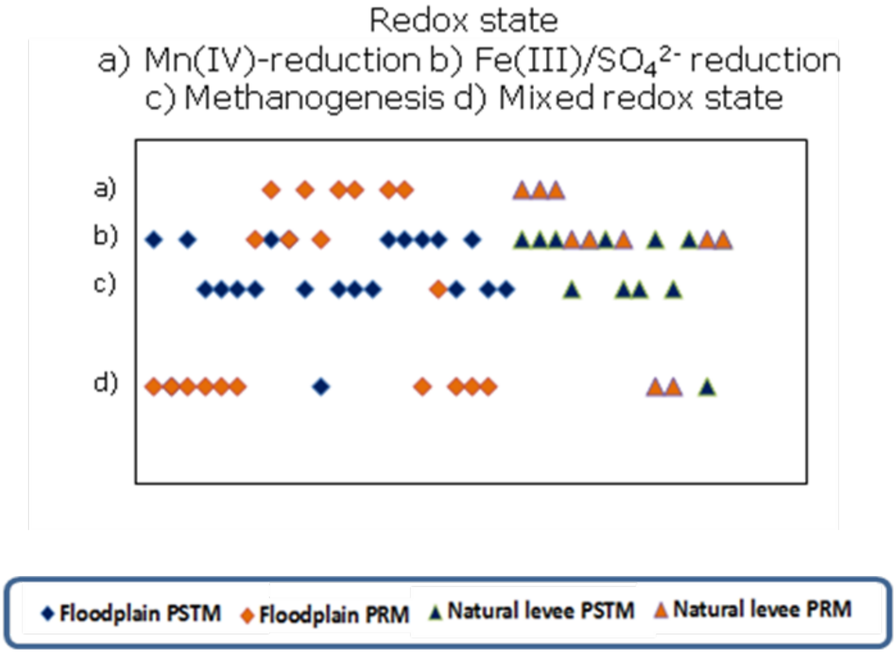


Figure 3.8. Redox state scenario of the groundwaters in flood plain and natural levee wells during pre- and post- monsoon times. All samples were classified in respective redox states (see Table 3.4) according to Jurgens et al. (2009).

Interestingly, Fe^{2+} proportions are much lower in PRM flood plain samples as compared to the Fe_T concentration. Based on the prevailing pH and Eh, Fe^{2+} should generally represent the dominating Fe species in local groundwater. The reason for this discrepancy remains unknown. Most interestingly, increase in DOC and concomitant decline in the redox state, increase in Fe^{2+} concentrations and As(III) of PSTM flood plain samples follow changes in the isotopic composition of local groundwater. Isotopic signatures (Figures 3.6a and b) indicate an increased influence of water which plots left of the LEL after the monsoon season. This indicates possible mixing with water that is closer to the composition of rainwater. The observed changes can best be explained assuming that the monsoon rain may cause changes in the local hydrogeological system of the flood plain, resulting in possible mixing of water with different hydrochemical compositions. As the DOC concentrations increased, this may influence the microbe mediated decomposition of organic matter, coupled to the reduction of Fe(III) and As(V), resulting a drop in the local redox potential. This assumption is supported by the strong positive correlation between DOC and As(III) (Figure 3.7a).

On the other hand, local aquifers of the natural levee area appear to be disconnected from infiltrating groundwater with increased DOC, possibly resulting in comparatively invariant groundwater compositions before (PRM samples) and after (PSTM samples) the monsoon season. Here available sources of organic matter (especially DOC) are likely to be depleted, causing microbe mediated redox reactions to restrict in a less reducing state as compared to the flood plain area.

3.5.2. Cl/Br ratio, the stable isotope signature and recharge processes

It seems that during the monsoon season, possibly wells around the flood plain are flushed with sub-surface monsoonal recharge from adjacent ponds. The increased mean Cl^- concentration in pond water during the PSTM season (pond FP1 16.8 mg/L and pond FP2 16.4 mg/L, Table 3.5) is very similar to the PSTM flood plain wells (mean – 16.3 mg/L), which further suggests possible flushing of the shallow aquifer which is notably effective in these areas during the PSTM period.

Most of the PSTM flood plain wells seem to have been influenced by vertical mixing (Fig. 3.5d) with the irrigation return flow or the anthropogenic inflows (high Cl^- concentration and lower isotopic values) after the monsoon (Xie et al., 2012). This is also consistent with the results from Figure 5e, as these wells are also high in As_T concentration with lighter isotopic composition, which in turn, indicates that a vertical recharge is plausible and transporting As in to these wells. The second set of samples both in Figures 3.5d and e are the samples principally from the flood plain PRM samples (with a small number of PSTM samples). The moderate Cl^- concentration (flood plain PRM Cl^- concentration 15.9 mg/L and for flood plain PSTM Cl^- concentration 16.3 mg/L) and isotopic composition ($\delta^{18}O$ values for flood plain PRM -2.5 and for flood plain PSTM -6.5) indicates moderate evaporation in these samples as evaporation can be responsible for heavier isotopic composition. On the other hand moderate As_T concentration (Figure 3.5e) reflects the influence of evaporation as evaporation can increase As_T concentration in pore waters, and aided by the vertical mixing, it can ultimately cause high As concentration in the groundwater (Xie et al., 2012). The third set of samples, mostly consisting of natural levee samples, show the potential effect of strong evaporation and weak vertical leaching as the concentration of Cl^- do not increases notably, but the isotopic composition gets heavier (Figure 3.5d). This is also possible due to some lateral mixing at deeper aquifer depths as both of them are low in Cl^-, but the isotopic compositions are different. The low As_T concentration in these wells also emphasizes this fact (Figure 3.5e). This argument is also important to explain observed changes in total As(III)/As_T ratio between PRM and PSTM samples of the flood plain area.

Table 3.5. Chemistry of pond waters.

	Flood plain			
	Pre-monsoon		**Post-monsoon**	
	Pond FP1	Pond FP2	Pond FP1	Pond FP2
pH	7.20	7.40	7.40	7.7
HCO_3^- (mg/L)	189	156	230	180
Cl^- (mg/L)	14.8	15.1	16.8	16.4
Fe (mg/L)	0.11	0.15	0.36	0.40
As_T (mg/L)	> 0.01	> 0.01	0.02	> 0.01
NO_3^- (mg/L)	0.89	0.93	0.57	0.64
PO_4^{3} (mg/L)	0.22	0.18	0.19	0.18
	Natural levee			
	Pre-monsoon		**Post-monsoon**	
	Pond NL1	Pond NL2	Pond NL1	Pond NL2
pH	6.70	6.90	7.10	7.60
HCO_3^- (mg/L)	167	145	177	161
Cl^- (mg/L)	13.0	12.8	13.5	13.8
Fe (mg/L)	0.09	0.12	0.10	0.12
As_T (mg/L)	> 0.01	> 0.01	> 0.01	> 0.01
NO_3^- (mg/L)	0.93	0.94	0.90	0.87
PO_4^{3-} (mg/L)	0.28	0.32	0.19	0.23

Hence, it can be concluded that the flood plain samples are possibly recharged through vertical inflow or mixing due to post-irrigational activities especially after the monsoon. The wells in the flood plain area, during the PRM season, are also shown to have influenced by moderate evaporation and high leaching. On the contrary, the groundwater of natural levee wells indicate influence of strong evaporation and less mixing, although lateral mixing cannot be discounted.

Highly soluble Cl^- and Br^- shows very conservative behavior and the various water-rock interactions like adsorption, ion-exchange, redox changes could not affect its hydrochemical behavior. This makes Cl/Br molar ratio as an indicator of groundwater flow and solute origination (Catwright et al., 2006; Xie et al., 2012). Any groundwater Cl/Br ratio lower than 650 generally indicates an evaporite origin (Richer and Kreitler, 1993) and the lowest Cl/Br ratio should represent the rainfall in the area (Xie et al., 2012).

The wide variation of Cl/Br ratio in shallow depths (Figure 3.5b) may reflects varying degrees of halite dissolution or anthropogenic and waste-water pollution (McArthur et al., 2012; Xie et al., 2012) and consequent vertical inflow into the shallow aquifer. Halite dissolution can rapidly increase the Cl/Br ratio with increase in Cl^- concentration whereas evapotranspiration do not allow a notable change in the Cl/Br ratio. Although, a few samples from both the flood plain and natural levee area shows the control of evapotranspiration (Figure 3.5a).

The stable isotope composition of the groundwater samples (Figures 3.6a and b) fall sub-parallel to the Global Meteoric Water Line (GMWL) (Craig, 1961). This indicates that evaporated surface water could be recharging the shallow groundwater, with ponds and infiltrating irrigation water as possible sources. Extensive groundwater withdrawal for agriculture in these areas may contribute to the drawdown of these evaporated surface waters (Nath et al., 2008a). Precipitation and subsequent evaporation seem to be the main controls on the water isotopic composition in the study area.

The heavier isotopic composition during the PRM season could be due to greater mixing of isotopically heavier water sources (e.g., evaporation influenced surface water) (Mukherjee et al., 2007). The isotopic closeness to the nearby pond water samples (Figure 3.6a) after the monsoon indicates a possible inflow of pond water into the aquifer. The increase in DOC concentration following the monsoon season supports this assumption (Figures 3.7a and b). Métral et al. (2008) even highlighted that there are sometimes sandy gaps in the normally clayey surface-near sediments (around the area of Chakdaha city), where rainwater can easily infiltrate into the aquifer sediments below, which is why, in these specific parts researchers find a higher redox potential and consequently less As, more SO_4^{2-} and NO_3^- in the groundwater.

3.5.3. Increase in As(III) concentrations after monsoon

The most important observation in this study is the significant increase in As(III) concentrations than As_T concentrations in both the flood plain and natural levee wells (223 over 6.6% and 217 over -17.6% respectively) on passing from the PRM to PSTM season (Table 3.4). Arsenic is omnipresent in soils and sediments. Apart from that, irrigation with high As groundwater is another source of As storage in the surface soils and sediments (Norra et al., 2005). However, during waterlogged field conditions, reductive dissolution of stored As in Fe-(oxyhydr)oxides enhances mobility of As. Therefore irrigation return fluxes containing significant amount of organic matter and dissolved As may make way to the shallow aquifer (Harvey et al., 2002). Arsenic in groundwater is possibly resulted from the reduction and concomitant dissolution of As-rich Fe-/Mn-oxides/hydroxides promoted by organic matter (Bhattacharya et al., 1997; Swartz et al., Nickson et al., 2000; Swartz et al., 2004), such as buried peat (McArthur et al., 2001) or by dissolved organics in recharging waters (Harvey et al., 2002). Many of these redox processes are coupled with the mineralization of natural organic matter (NOM) and their distribution may control to a large extent the mobilization of As in a sedimentary environment (Lovley, 1993; McArthur et al., 2004).

Ferrous iron (Fe^{2+}) and As(III) concentrations are increased in the flood plain area during the PSTM season (Figure 3.2). The Eh of the samples are more negative during the PSTM season (especially for the flood plain samples) (Figure 3.2) indicating an increase in reducing environment. The increase in the As(III), Fe^{2+} and

HCO_3^- concentrations in the aquifer after monsoon could be attributed to the reductive dissolution of As-rich Fe/Mn-(oxyhydr)oxides by the natural organic molecules (McArthur et al., 2001). The HCO_3^- enhancement could also be due to microbial oxidation of the organic compounds. It looks like that we probably have a combination of groundwater flow/transport during the monsoon season, which induces an import of DOC, resulting microbial redox reactions that possibly cause again a decrease in the redox state and a change in the As(III)/As(V) water chemistry. However, another important question is why does As(III) changes to As(V) in the PRM season? This is really interesting. Several studies report that As(III)/As(V) can react differently with DOC to form complexes, which is even more favorable in presence of few cations (Thanabalasingam and Pickering, 1986; Warwick et al., 2005; Buschmann et al., 2006). As(III) and As(V) may both compete with DOC for the binding sites on the available host mineral phases in groundwater (Grafe et al., 2001; Redman et al., 2002; Bauer and Blodau, 2006). Microbial reactions can also change the relative abundance of As(III) or As(V) depending on the aquifer redox changes (Lovley et al., 1996; Oremland and Stolz, 2005). All these together could possibly be a plausible reason for the selective increase of As(III) over As(V) during the PSTM season and the reverse during the PRM season. However, further laboratory scale investigations are required to probe into these assumptions.

3.6. Implications

The increase in As(III) concentration in groundwater is significant compared to the overall increase in As_T concentration during PRM and PSTM periods. The increase of As(III) in the flood plain wells as compared to the natural levee wells is also very significant. The correlation of DOC with As(III) after the monsoon indicates a possibility of microbe induced release of As. The decreasing Eh also supports such behavior. The stable isotopic composition of shallow groundwater suggests a contribution of evaporated water, which may be derived from various surface water bodies. In case of flood plain wells, the stable isotope signature and Cl/Br molar ratio has shown that vertical mixing could be the major recharge process, especially during the PSTM season. However, evaporation of surface waters is controlling the recharge in case of natural levee wells. The relationship between As_T concentration and the isotope profile shows a combined effect of both mixing and evaporation.

The increase in the As(III), Fe^{2+} and HCO_3^- concentrations during the post-monsoon season could be an indication of reductive dissolution of As-rich Fe/Mn-(oxyhydr)oxides by the natural organic molecules (possibly by the microbial activity). Probably due to the monsoon rain, a combined groundwater flow/transport induces an import of DOC, which may result in microbial redox reactions that can cause a decrease in the redox state, subsequently changing the As(III)/As(V) water chemistry. However, further studies are needed to track and characterize the interaction between organic carbon and As in both water and sediment-water interface to understand As mobility.

References

Bauer M., Blodau C. (2006) Mobilization of arsenic by dissolved organic matter from iron oxides, soils and sediments. *Sci. Total Environ.* **354**, 179–190.

Bauer, M., Blodau C. (2009) Arsenic distribution in the dissolved, colloidal and particulate size fraction of experimental solutions rich in dissolved organic matter and ferric iron. *Geochim. Cosmochim. Acta* **73**, 529–542.

Bhattacharya P., Chatterjee D., Jacks G. (1997) Occurrence of arsenic-contaminated groundwater in alluvial aquifers from delta plains, Eastern India: Options for safe drinking water supply. *Water Res. Develop.* **13**, 79–92.

Bhattacharya R. (2001) Removal of Arsenic from groundwater and safe drinking water supply. Unpublished doctoral thesis, University of Kalyani, Nadia, West Bengal, India.

Bhattacharyya R., Chatterjee D., Nath B., Jana J., Jacks G., Vahter M. (2003) High arsenic groundwater: Mobilization, metabolism and mitigation – An overview in the Bengal Delta Plain. *Mol. Cell. Biochem.* **253**, 347–355.

Buschmann J., Kappeler A., Lindauer U., Kistler D., Berg M., Sigg L. (2006) Arsenite and arsenate binding to dissolved humic acids: Influence of pH, type of humic acid, and aluminum. *Environ. Sci. Technol.* **40**, 6015–6020.

Cartwright I., Weaver T. R. (2005) Hydrochemistry of the Goulburn Valley region of the Murray Basin, Australia: implications for flow paths and resource vulnerability. *Hydrogeol. J.* **13**, 752–770.

Cartwright I., Weaver T. R., Fifield L. K. (2006) Cl/Br ratios and environmental isotopes indicators of recharge variability and groundwater flow: An example from the southeast Murray Basin, Australia. *Chem. Geol.* **231**, 38–56.

Chatterjee D., Chakraborty S., Nath B., Jana J., Bhattacharya R., Basu Mallik S., Charlet L. (2003) Mobilization of arsenic in sedimentary aquifer vis-à-vis subsurface iron reduction processes. *Journal de Physique IV* **107**, 293–296.

Chatterjee D., Halder D., Majumder S., Biswas A., Nath B., Bhattacharya P., Bhowmick S., Mukherjee-Goswami A., Saha D., Maity P. B., Chatterjee D. Mukherjee A., Bundschuh J. (2010) Assessment of arsenic exposure from groundwater and rice in Bengal Delta Region, West Bengal, India. *Water Res.* **44**, 5803–5812.

Chen Z., Nie Z., Zhang G., Wan L., Shen J. (2006) Environmental isotopic study on the recharge and residence time of groundwater in the Heihe River Basin, northwestern China. *Hydrogeol. J.* **14**, 1635–1651.

Craig H. (1961) Isotopic variations in meteoric water. *Science* **133**, 1702–1703.

Das D., Samanta G., Mandal B. K., Chowdhury T. R., Chanda C. R., Chowdhury P. P., Basu G. K., Chakraborti, D. (1996) Arsenic in groundwater in six districts of West Bengal, India. *Environ. Geochem. Health.* **18**, 5–15.

Datta S., Neal A. W., Mohajerin T. J., Ocheltree T., Rosenheim B. E., White C. D., Johanesson K. H. (2011) Perennial ponds are not an important source of water or dissolved organic matter to groundwaters with high arsenic concentrations in West Bengal, India. *Geophys. Res. Lett.* **38**, 1–5.

Farooq S. H., Chandrasekharam D., Berner Z., Norra S., Stüben D. (2010) Influence of traditional agricultural practices on mobilization of arsenic from sediments to groundwater in Bengal delta. *Water. Res.* **44**, 5575–5588.

Fendorf S., Michael H. A., van Geen A. (2010) Spatial and temporal variations of groundwater arsenic in south and southeast Asia. *Science* **328**, 1123–1127.

Grafe M., Eick M. J., Grossl. P. R. (2001) Adsorption of arsenate(V) and arsenite(III) on goethite in the presence and absence of dissolved organic carbon. *Soil Sci. Soc. Am. J.* **65**, 1680–1687.

Harvey C. F., Ashfaque K. N., Yu W., Badruzzaman A. B. M., Ali M. A., Oates P. M., Michael H. A., Neumann R. B., Beckie R., Islam S., Ahmed M. F. (2006) Groundwater dynamics and arsenic contamination in Bangladesh. *Chem. Geol.* **228**, 112–136.

Harvey C. F., Swartz C. H., Badruzzaman A. B. M., Keon-Blute N., Yu W., Ali M. A., Jay J., Beckie R., Niedan V., Brabander D., Oates P. M., Ashfaque K. N., Islam S., Hemond H. F., Ahmed M. F. (2002) Arsenic mobility and groundwater extraction in Bangladesh. *Science* **298**, 1602–1606.

Islam F. S., Gault A. G., Boothman C., Polya D. A., Charnock J. M., Chatterjee D., Lloyd J. R. (2004) Role of metal reducing bacteria in arsenic release from Bengal delta sediments. *Nature* **430**, 68–71.

Jurgens B. C., McMahon P. B., Chapelle F. H., Eberts S. (2009) M. An Excel® workbook for identifying redox processes in groundwater: U.S. Geological Survey Open-File Report, 2009-1004. Available from: http://pubs.usgs.gov/of/2009/ b1004/ofr_2009-1004.pdf.

Kanematsu M., Young T. M., Fukushi K., Green P. G., Darby J. L. (2013) Arsenic (III, V) adsorption on a goethite based adsorbent in the presence of major co-existing ions: Modeling competitive adsorption consistent with spectroscopic and molecular evidence. *Geochim. Cosmochim. Acta* **106**, 404–428.

Kocar B. D., Polizzotto M. L., Bebber S. G., Ying S. C., Ung M., Ouch K., Samreth S., Suy B., Phan K., Sampson M., Fendorf S. (2008) Integrated biogeochemical and hydrologic processes driving arsenic release from shallow sediments to groundwaters of the Mekong delta. *Appl. Geochem.* **23**, 3059–3071.

Lawson M., Ballentine C. J., Polya D. A., Boyce A. J., Mondal D., Chatterjee D., Majumder S., Biswas A. (2008) The geochemical and isotopic composition of groundwaters in West Bengal: tracing ground-surface water interaction and its role in arsenic release. *Min. Mag.* **72**, 107–110.

Lovley D. R. (1993) Dissimilatory metal reduction. *Annual Review of Microbiology* **47**, 263–290.

Lovley D. R., Coates J. D., Bluny-Harris E. L., Phillips E. J. P., Woodward J. C. (1996) Humic substances as electron acceptors for microbial respiration. *Nature* **382**, 445–448.

Majumder S., Chatterjee D., Biswas A., Berner Z., Neidhardt H. (2010) Characterization of factors affecting arsenic distribution in groundwater. In: P. Birkle & I.S. Torres-Alvarado (eds.) *Proceedings of the 13th Water-Rock Interaction Symposium, WRI-13, Guanajuato, Mexico, 16–20 August, 2010*. Balkema, CRC Press/Taylor & Francis, pp. 403-406.

Majumder S., Nath B., Sarkar S., Islam S. M., Bundschuh J., Chatterjee D., Hidalgo M. (2013) Application of natural citric acid sources and their role on removal of arsenic from drinking water: a green chemistry approach. *J. Hazard. Mater.* Just accepted, doi:10.1016/j.jhazmat.2012.09.007.

McArthur J. M., Banerjee D. M., Hudson-Edwards K. A., Mishra R., Purohit R., Ravenscroft P., Cronin A., Howarth R. J., Chatterjee A., Talukder T., Lowry D., Houghton S., Chadha D. K. (2004) Natural organic matter in sedimentary basins and its relation to arsenic in anoxic groundwater: the example of West Bengal and its worldwide implications. *Appl. Geochem.* **19**, 1255–1293.

McArthur J. M., Ravenscroft P., Safiulla S., Thirlwall M. F. (2001) Arsenic in groundwater: Testing pollution mechanisms for sedimentary aquifers in Bangladesh. *Water Resour. Res.* **37**, 109–117.

McArthur J. M., Sikdar P. K., Hoque M. A., Ghosal U. (2012) Waste-water impacts om groundwater: Cl/Br ratios and implications for arsenic pollution of groundwater in the Bengal Basin and Red River Basin, Vietnam. *Sci. Total Environ.* **437**, 390–402.

Metral J., Charlet L., Bureau S., Basu Mallik S., Chakraborty S., Ahmed K. M., Rahman M. W., Cheng Z., van Geen A. (2008) Comparison of dissolved and particulate arsenic distributions in shallow aquifers of Chakdaha, India, and Araihazar, Bangladesh. *Geochem. Trans.* 9, DOI:10.1186/1467-4866-9-1.

Mukherjee A., Fryar A. E., Rowe H. D. (2007) Regional scale stable isotopic signature and recharge of the deep water of the arsenic affected areas of West Bengal, India. *J. Hydrol.* **334**, 151–161.

Nath B., Sahu S. J., Jana J., Mukherjee-Goswami A., Roy S., Sarkar M. J., Chatterjee D. (2008a) Hydrochemistry of arsenic-enriched aquifer from rural West Bengal, India: a study of the arsenic exposure and mitigation option. *Water, Air and Soil Pollut.* **190**, 95–113.

Nath B., Stüben D., Basu Mallik S., Chatterjee D., Charlet L. (2008b) Mobility of arsenic in West Bengal aquifers conducting low and high groundwater arsenic. Part I: Comparative hydrochemical and hydrogeological characteristics. *Appl. Geochem.* **23**, 977–995.

Neidhardt H., Berner Z., Freikowski D., Biswas A., Winter J., Chatterjee D., Norra S. (2013b) Influence of groundwater extraction on the distribution of dissolved As in shallow aquifers of West Bengal, India. *J. Hazard. Mater.* Just accepted, doi:10.1016/j.jhazmat.2013.01.044.

Neidhardt H., Biswas A., Freikowski D., Majumder S., Chatterjee D., Berner Z. (2013a) Reconstructing the sedimentation history of the Bengal Delta Plain by means of geochemical and stable isotopic data. *Appl. Geochem.* **36**, 70–82.

Neumann R. B., Ashfaque K. N., Badruzzaman A. B. M., Shoemaker J. K., Harvey C. H. (2009) Anthropogenic influences on groundwater arsenic concentrations in Bangladesh. *Nature Geosci.* **3**, 46–52.

Nickson R. T., McArthur J. M., Ravenscroft P., Burgess W. G., Ahmed K. M. (2000) Mechanism of arsenic release to groundwater, Bangladesh and West Bengal. *Appl. Geochem.* **15,** 403–413.

Norra S., Berner Z. A., Agarwala P., Wagner F., Chandrasekharam D., Stüben D. (2005) Impact of irrigation with As rich groundwater on soil and crops: a geochemical case study in West Bengal Delta Plain, India. *Appl. Geochem.* **20**, 1890–1906.

Nriagu J. O., Bhattacharya P., Mukherjee A. B., Bundschuh J., Zevenhoven R., Loeppert R. H. (2007) Arsenic in soil and groundwater: an overview. In *Arsenic in Soil and Groundwater Environment*; Bhattacharya P., Mukherjee A. B., Bundschuh J., Zevenhoven R. and Loeppert R. H. Eds.; Elsevier: Amsterdam; 2007, *Trace Metals and other Contaminants in the Environment* **9**, 3-60.

Oremland R.S., Stolz J.F. (2005) Arsenic, microbes and contaminated aquifers. *Trends Microbiol.* **13**, 45–49.

Polizzotto M. L., Kocar B. D., Benner S. G., Sampson M., Fendorf S. (2008) Near-surface wetland sediments as a source of arsenic release to groundwater in Asia. *Nature* **454**, 505–508.

Rahman M. M., Chowdhury U. K., Mukherjee S. C., Mondal B. K., Paul K., Lodh D., Biswas B. K., Chanda C. R., Basu G. K., Saha K. C., Roy S., Das R., Palit S. K., Quamruzzaman Q., Charaborti D. (2001) Chronic arsenic toxicity in Bangladdesh and West Bengal, India – a review and commentary. *Clin. Toxicol.* **39**, 683–700.

Redman A. D., Macalady D. L., Ahmann D. (2002) Natural organic matter affects arsenic speciation and sorption onto hematite. *Environ. Sci. Technol.* **36**, 2889–2896.

Richer B. C., Kreitler C. W. (1993) Geochemical techniques for indentifying sources of groundwater salinization. CRC Press, Boca Raton.

Sengupta S., McArthur J. M., Sarkar A., Leng M. J., Ravenscroft P., Howarth R. J., Banerjee D. M. (2008) Do ponds cause arsenic-pollution of groundwater in the Bengal basin? An answer from West Bengal. *Environ. Sci. Technol.* **42**, 5156–5164.

Smith A. H., Lingas E. O., Rahaman M. (2000) Contamination of drinking water by arsenic in Bangladesh: A public health emergency. *Bulletin of World Health Organization* **78**, 1093–1103.

Sutton N. B., van der Kraan G. M., van Loosdrecht M. C., Muyzer G., Bruining J., Schotting R. J. (2009) Characterisation of geochemical constituents and bacterial populations associated with As mobilization in deep and shallow tube wells in Bangladesh. *Water Res.* **43**, 1720–1730.

Swartz C. H., Blute N. K., Badruzzman B., Ali A., Brabander D., Jay J., Besancon J., Islam S. A., Hemond H. F. (2004) Mobility of arsenic in a Bangladesh aquifer: inferences from geochemical profiles, leaching data and mineralogical characterization. *Geochim. Cosmochim. Acta* **68**, 4539–4557.

Thanabalasingam P., Pickering W. F. (1986) Arsenic sorption by humic acids. *Environ. Pollut. Ser. B* **12**, 233–246.

van Geen A., Zheng Y., Goodbred Jr., S., Horneman A., Aziz Z., Cheng Z., Stute M., Mailloux B., Weinmen B., Hoque M. A., Seddique A. A., Hossain M. S., Chowdhury S. H., Ahmed K. M. (2008) Flushing history as a hydrogeological control on the regional distribution of arsenic in shallow groundwater of the Bengal Basin. *Environ. Sci. Technol.* **42**, 2283–2288.

Warwick P., Inam E., Evans N. (2005) Arsenic's interaction with humic acid. *Environ. Chem.* **2**, 119–224.

WHO (2004) Guidelines for Drinking-water Quality, 4th ed.; World Health Organization: Geneva.

WHO (2011) Guideline For Drinking Water Quality, 4th ed.; *World Health Organization*: Singapore.

Xie X., Wang Y., Su C., Li J., Li M. (2012) Influence of irrigation practices on arsenic mobilization: Evidence from isotope composition and Cl/Br ratios in groundwater from Datong basin, northern China. *J. Hydrol.* **424–425**, 37–47.

Yu W. H., Harvey, C. M., Harvey C. F. (2003) Arsenic in groundwater in Bangladesh: a geostatistical and epidemiological framework for evaluating health effects, and potential remedies. *Water Resour. Res.* **39**, 1146.

Zhu G. F., Li Z. Z., Su Y. H., Ma J. Z., Zhang Y. Y. (2007) Hydrogeochemical and isotope evidence of groundwater evolution and recharge in Minqin Basin, Northwest China. *J. Hydrol.* **333**, 239–251.

CHAPTER 4: COLLOIDAL PARTICLES AS SCAVENGERS OF GROUNDWATER ARSENIC AND ITS TRANSPORT

Colloidal distribution of groundwater arsenic (As) has been investigated for the first time in the aquifers of Bengal basin. Most of the groundwater As (83-94%) was found to be in the dissolved phases. Iron (Fe) correlated strongly with As in the larger pore-sized fractions indicating association between As and Fe-rich inorganic colloids. On the other hand, DOC and As correlated strongly in the smaller pore-sized fractions highlighting the interaction of organic colloids and As. As(III) species mostly associated with larger colloidal fractions (0.45-0.22 µm), while As(V) species mostly associated with smaller pore-sized organic/organometallic colloids (0.22-0.05 µm). SEM-EDX and ATR-FTIR studies confirm the formation of As-Fe-NOM organometallic colloids

4.1. Introduction

Naturally occurring carcinogenic arsenic (As) is ubiquitous in the environment and commonly observed in high concentrations in the alluvial groundwaters of south-east Asia (Bhattacharya et al., 1997; Nickson et al., 1998; Charlet and Polya, 2006; Mukherjee et al., 2008; Nath et al., 2011). In south-east Asia, the use of As-enriched groundwater as the primary source of drinking and other household activities has led to an unprecedented human health problems, creating a major concern for the environmental and public health experts (Smedley and Kinniburgh, 2002). The human health problem is particularly alarming in the rural Bengal Delta Plain (BDP), i.e., in West Bengal, India and Bangladesh, yet there is no sustainable alternatives of drinking water sources available (Mukherjee et al., 2011).

Previous studies have suggested the role of dissolved organic carbon (DOC) and dissolved Fe on As mobility in groundwater (e.g., Charlet and Polya, 2006). Dissolved organic carbon or natural organic matter (NOM) can compete with As for binding sites on mineral surfaces and influence As redox processes (Redman et al., 2002; Dixit and Hering, 2003; Bauer and Blodau, 2006; Buschmann et al., 2006). Arsenic can sorbed onto organic matter (especially humic components) through covalent bonding (Buschmann et al., 2006). On the other hand Fe-(oxyhydr)oxides binds As more efficiently in presence of organic matter (Ritter et al., 2006). However, the inorganic As species [i.e., As(III) and As(V)] react differently in presence of organic matter depending on As/DOC ratios (Buschmann et al., 2006).

The competition for the sorption sites between As and NOM can notably influence As mobility in groundwater (Redman et al., 2002; Warwick et al., 2005; Bauer and Boldau, 2006; Ritter et al., 2006). The formation of As-NOM complexes was reported to change the course of As redox reactions in aqueous phase (Thanbalasingham and Pickering, 1986; Lin et al., 2004; Wang and Mulligan, 2006; Buschmann et al., 2006). These complexes mostly belong to the colloidal size fraction generally ranging between 2 and 300 nm or higher (Mueller, 1996; Sharma et al., 2010). Both inorganic and organic colloids can control the fate of trace metals in aqueous medium due to adsorption (Pokrovsky and Scott, 2002; Pourret et al., 2007). Laboratory studies demonstrated that 94% of As was associated with colloidal Fe-NOM fractions (Sharma et al., 2010). Some field studies have reported that As can be scavenged by colloidal Fe and dissolved organic matter (DOM) in river waters (Astrom and Corin, 2000).

There is a very little information available in the literature on the formation of As-bearing colloids in groundwater (Bauer and Blodau, 2009; Sharma et al., 2010). Additionally, limited information is available on the control of dissolved or colloidal DOC and Fe phases on As mobility in groundwater (Guo et al., 2011). There is no data available on the colloidal distribution of As in different size fractions in the alluvial aquifers of West Bengal, the major drinking water source to millions of inhabitants. Therefore this study has been aimed to investigate the fractional distribution of As (and other metals/metalloids) through different size fractions (i.e., particulate, colloidal and dissolved phases) of groundwater and subsequent characterization of organic/inorganic colloids potentially responsible for As mobility.

4.2. Materials and methods

4.2.1. Study area

The study area (latitude 23°00/20//–23°05/20//N; longitude 88°31/40//–88°49/00//E) is located in Chakdaha block, Nadia district, West Bengal, India. The study area was previously characterized and reported as one of the worst As affected areas of West Bengal, India (Pal et al., 2002; Nath et al., 2009).

In the study area, the tube wells were mostly (>70%) installed at the shallow depths (10–50 m) which is used for groundwater abstraction for domestic purposes. In addition to that, a large number of shallow 'irrigation' wells (10–20 m; pumped: diesel/electrically operated) are used for agricultural purposes. Deep wells (>100 m depth) are mainly used for community water supply schemes.

4.2.2. Groundwater sampling

Groundwater samples were collected from 6 hand operated domestic shallow tube wells (sample no #1, 3, 4, 5, 7, 8) and 2 deep public wells (sample no #2 and 6) in December, 2011 (Table 4.1). The tube wells were pumped for about 15 minutes prior to sampling to ensure removal of standing water. The samples were microfiltered through a 0.45 μm cellulose nitrate filters (Millipore Isopore Membrane filters). Then the microfiltered samples were divided into three groups. The first group was unacidified for anion analysis, while second group was used for sequential ultrafiltration using 0.22 μm, 0.10 μm and 0.05 μm (Millipore Isopore Membrane filters) cellulose nitrate membranes. These samples including the third group were acidified (HNO_3 0.2% v/v) for the analysis of major cations, trace and ultra-trace elements. All these filtration steps were performed under N_2 atmosphere to ensure a stable redox state of the analytes in water. Elements passing through 0.05 μm microfilter were assumed to be 'truly dissolved' in nature. Disposable As speciation cartridges (MetalSoft Center, USA) were used during sampling (i.e., micro- and ultra- filtered samples) for As speciation [i.e., As(III) and As(V)]. All these samples were collected in polyethylene bottles. Simultaneous duplicates for each sample throughout the sampling steps were done. The duplicates were within ± 5% for all measured parameters, which suggests good reproducibility.

Temperature, pH, and Eh were measured on-site before filtration steps using a WTW multimeter (WTW, Germany). Alkalinity (reported as HCO_3^-) was quantified on-site by titration with 0.2 M H_2SO_4. The samples for DOC measurement were collected in 100 mL amber glass bottles. The colloid containing membranes were put in acid-washed Petri dishes and then kept in N_2 sealed plastic bags (Guo et al., 2011). All the samples were stored at 4 ^oC until analysis.

4.2.3. Groundwater analysis

The concentrations of major cations were measured by inductively coupled plasma-atomic emission spectroscopy, ICP-AES (Liberty RL. Varian, Australia), while for the determination of As and metals at μg/L level, inductively coupled plasma-quadrapole mass spectrometry (Agilent 7500C ICP-QMS) was used (sample dilution 1:1 with 1% HNO_3 Suprapur, Merck). The concentrations of major anions were measured with the help of 761 compact ion chromatography equipped with an 813 compact autosampler and a conductivity detector (Metrohm, Switzerland). The concentration of dissolved organic carbon (DOC) was determined with a TOC analyzer (AnaLYTIK JENA TOC Analyzer 2100).

Table 4.1. Physico-chemical characteristics of groundwater samples filtered through 0.45 μm filters.

SN	X	Y	pH	Eh (mV)	Cl^- (mg/L)	PO_4^{3-} (mg/L)	SO_4^{2-} (mg/L)	HCO_3^- (mg/L)
1	23.0786	88.6134	7.09	-169	25	0.17	9.8	440
2	23.0632	88.6510	7.88	-171	11	0.33	bdl	490
3	23.0835	88.6378	7.88	-194	8.3	0.19	0.21	500
4	23.0894	88.6309	6.53	-22	7.5	0.15	7.0	420
5	23.0714	88.6092	6.67	-29	12	0.14	bdl	400
6	23.0676	88.6040	5.87	12	12	0.07	bdl	444
7	23.0479	88.6311	6.99	-76	17	0.25	1.2	310
8	23.0654	88.6210	6.70	-70	9.3	0.24	2.2	332

Note: na – not available; bdl – below detection limit.
SN – Sample number; X – Latitude (in degrees); Y – Longitude (in degrees)

Water samples were concentrated by centrifugation at 1500 rpm prior to spectroscopic studies (Sharma et al., 2010) to observe the formation of As-Fe-NOM complexes with the help of attenuated total reflectance-Fourier transform infrared spectroscopy, ATR-FTIR (Nicolet 380, Thermo Scientific).

4.2.4. Solid phase analysis

Morphological and elemental analysis of the colloids adsorbed on the membrane ultrafilters was performed by Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) analysis (Microanalysis separation energy EDX and Quantax with detector spectrometer Bruker-AXS Microanalysis XFlash, Berlin, Germany).

4.3. Results and discussion

4.3.1. Water chemistry and arsenic distribution

Most of the sampled wells are shallow in depth (~ mean – 22 m) with the deepest and shallowest being screened at 122 m and 16 m respectively. The overall groundwater chemical composition is summarized in Table 4.1 and 4.2. Groundwater is highly reducing in nature with pH values in the circumneutral range. The groundwater temperature is within the range of 25-27 °C. The major cations being Ca^{2+} followed by Mg^{2+}, Na^{+}, and K^{+}. The major anions are HCO_3^- followed by Cl^-, SO_4^{2-}, and PO_4^{3-}. The NO_3^-, Br^- and F^- concentrations are very low. The alkali (Na, K) and alkaline earth (Mg, Ca) metals do not show any significant variation throughout the sequential filtration steps (Table 4.2). This suggests that these metals are mostly in 'truly dissolved phases' (Pokrovsky and Schott, 2002). Similarly, trace elements such as Cd, Pb and Mn do not show much variation, except for some negligible variations in the larger pore-sized fractions. Zn concentration is variable throughout the filtration steps, especially in the smaller size fractions indicating its presence in the colloidal phases. U and V concentrations are also variable along the sequential filtration steps.

The variation in Fe, DOC and Al concentrations are quite noticeable (Table 4.2). Apart from sample 1, all the wells have As_T (total) concentration > 50 µg/L, which is the current national drinking water standard in India. In all the samples, As_T concentration gradually decreased after each filtration steps (Table 4.2) and thus indicating the role of both particulate and colloidal phases in scavenging As from the aqueous media. However, apart from sample 5, 83-94% of the total As (i.e., relative to As concentrations in unfiltered samples) has remained after ultrafiltration (0.05 µm filters) steps (Table 4.3 and Figure 4.1). This indicates that the bulk of the total As remained in the 'truly dissolved' phases (Bauer and Blodau, 2009; Balzer et al., 2012).

Table 4.2. Summary of groundwater chemistry of samples after different filtration steps. The As_T data presented in the table below was already published in a conference procedia (Majumder et al., 2013).

SN	FS	Na (mg/L)	K (mg/L)	Mg (mg/L)	Ca (mg/L)	DOC (mg/L)	As_T (µg/L)	As(III) (µg/L)	As(V) (µg/L)
1	U	21.5	5.29	17.1	83.9	6.35	39.2	28	11.2
	0.45 µm	21.4	5.22	16.9	83.6	5.24	38.7	21.4	17.3
	0.22 µm	21.1	4.94	16.3	83.6	4.53	37.3	20.2	17.2
	0.10 µm	20.8	4.87	15.9	83.2	3.79	36.8	20	16.7
	0.05 µm	20	4.27	15.6	82.8	2.11	35	20	15
2	U	18.2	3.85	16.4	93	10	74	64.5	9.48
	0.45 µm	18	3.6	16	92.5	8.98	73.7	58.3	15.4
	0.22 µm	17.9	3.1	15.7	92.2	7.97	73.1	53.1	20
	0.10 µm	17.5	3.04	15	92	5.92	71.1	50.1	21
	0.05 µm	17.1	2.91	15	91.5	5.18	69.3	49.8	19.5
3	U	22.6	3.15	22.4	87.6	8.65	69.7	58.4	11.3
	0.45 µm	22.1	2.85	22	87.3	7.63	65.3	54.1	11.2
	0.22 µm	21.9	2.52	21.9	87	7.6	61.3	52.9	8.43
	0.10 µm	21.5	2.29	21.7	86.9	5.54	60.2	52.7	7.52
	0.05 µm	21.3	1.99	21.6	86.7	3.98	60.2	52.4	7.72
4	U	18.2	3.68	19.5	67.5	21	129	104	24.4
	0.45 µm	18	3.37	19.4	67.1	18	119	93.5	25.3
	0.22 µm	17.6	3.15	19.2	67	17	116	89.3	26.5
	0.10 µm	17.6	2.93	18.9	66.7	11.9	111	88.7	22.3
	0.05 µm	17.4	2.81	18.5	66.4	9.34	108	88	19.9
5	U	12.8	3.64	17.7	149	38.8	215	191	24.3
	0.45 µm	12.2	3.52	17.5	149	36.7	74	66.3	7.74
	0.22 µm	12.1	3.36	17.1	149	34.6	73.2	63.4	9.79
	0.10 µm	11.9	2.96	16.9	149	25.6	66.8	59.1	7.65
	0.05 µm	11.7	2.46	16.8	148	10	52.1	51.9	0.18
6	U	24.3	4.81	36.1	73.4	12.1	71	59.8	11.2
	0.45 µm	24	4.59	35.9	73	10.5	69.1	50.3	18.8
	0.22 µm	24	4.33	35.6	73	8.62	63.5	48	15.5
	0.10 µm	23.5	3.93	35.3	72.8	5.07	61.6	46.4	15.2
	0.05 µm	23.1	3.46	35	72.5	4.46	60.3	46	14.4
7	U	41.9	2.9	29.6	141	40	259	227	31.9
	0.45 µm	41.8	2.66	29.3	141	37.9	233	223	9.65
	0.22 µm	41	2.31	29	141	35	230	213	17.5
	0.10 µm	40.3	2.08	28.9	141	26.1	222	207	14.9
	0.05 µm	40	1.95	28.6	140	19.9	217	207	10.1
8	U	33.9	3.47	38.6	130	39.2	260	220	40.6
	0.45 µm	33.6	3.09	38.3	130	37	259	211	48.2
	0.22 µm	33.5	2.72	38.1	130	35.7	259	204	55.3
	0.10 µm	32.9	2.59	38	129	29.2	252	199	53.1
	0.05 µm	32.5	2.17	37.6	129	17.1	245	198	47.0

SN – Sample number; FS – Filtration steps; U - Unfiltered

Table 4.2. continued.

SN	FS	Fe (mg/L)	Al (μg/L)	Cd (μg/L)	Pb (μg/L)	Mn (μg/L)	Zn (μg/L)	U (μg/L)	V (μg/L)
1	U	3.31	8.97	0.06	0.84	264	12.8	0.02	0.22
	0.45 μm	2.22	4.87	0.04	0.6	264	10.9	0.02	0.13
	0.22 μm	2.06	2.1	0.03	0.17	264	7.23	0.02	0.1
	0.10 μm	1.98	1.96	0.03	0.12	263	4.51	0.02	0.09
	0.05 μm	0.97	1.78	0.02	0.06	263	3.67	0.01	0.09
2	U	6.87	21.8	0.08	3.8	482	66.2	0.27	0.25
	0.45 μm	4.14	16	0.05	3.11	482	60.1	0.19	0.2
	0.22 μm	3.01	7.23	0.04	2.25	482	53.1	0.12	0.14
	0.10 μm	2.78	6.89	0.03	0.81	482	39.2	0.05	0.1
	0.05 μm	1.21	1.03	0.03	0.74	481	22.2	0.05	0.08
3	U	6.79	15.4	0.05	1.07	326	34.1	0.05	0.19
	0.45 μm	3.78	11	0.05	0.92	326	32	0.04	0.17
	0.22 μm	1.98	7.67	0.03	0.43	325	30.6	0.02	0.11
	0.10 μm	0.96	6.54	0.02	0.4	325	28.8	0.02	0.06
	0.05 μm	0.07	1.98	0.02	0.25	325	22.4	0.02	0.06
4	U	10.3	29.1	0.08	1.29	70.8	12.4	0.03	0.13
	0.45 μm	7.47	16	0.07	1.02	70.8	9.22	0.03	0.08
	0.22 μm	4.23	11.9	0.05	0.64	70.1	7.1	0.03	0.08
	0.10 μm	1.98	9.2	0.05	0.44	69.4	5.43	0.03	0.08
	0.05 μm	0.86	1.74	0.03	0.24	69	3.12	0.02	0.07

SN	FS	Fe (mg/L)	Al (µg/L)	Cd (µg/L)	Pb (µg/L)	Mn (µg/L)	Zn (µg/L)	U (µg/L)	V (µg/L)
5	U	20.3	44.5	0.04	0.23	58	36.1	0.03	0.13
	0.45 µm	7.92	30.1	0.03	0.18	57	32.3	0.02	0.07
	0.22 µm	6.77	15.3	0.03	0.1	56.5	29.1	0.02	0.07
	0.10 µm	2.08	4.7	0.02	0.08	56.1	28.2	0.02	0.06
	0.05 µm	0.37	1.03	0.02	0.08	56	23.9	0.02	0.06
6	U	7.91	19.6	0.08	0.19	41.9	32.9	0.05	0.13
	0.45 µm	6.7	9.97	0.07	0.16	41.4	29.8	0.04	0.12
	0.22 µm	4.11	6.34	0.04	0.13	41.1	18.9	0.04	0.12
	0.10 µm	2.01	5.15	0.02	0.12	41	10.9	0.02	0.11
	0.05 µm	0.93	4.86	0.02	0.12	40.5	8.56	0.02	0.11
7	U	23.7	53.4	0.16	3.31	74.9	58.5	0.05	0.12
	0.45 µm	16	31	0.12	2.89	74.6	47.1	0.03	0.08
	0.22 µm	13.4	20	0.05	1.99	74.1	30.3	0.03	0.05
	0.10 µm	8.02	18	0.02	1.15	73.9	29.1	0.02	0.05
	0.05 µm	6.75	4.43	0.02	0.98	73.2	27.8	0.01	0.05
8	U	22.6	56.1	0.09	3.9	319	11.7	0.07	0.16
	0.45 µm	17.1	29.9	0.07	2.85	318	10.1	0.06	0.16
	0.22 µm	16.2	14.7	0.06	1.45	318	5.12	0.06	0.11
	0.10 µm	8.12	14.2	0.03	1.34	317	4.67	0.03	0.09
	0.05 µm	2.99	7	0.03	0.83	317	3.89	0.02	0.07

SN – Sample number; FS – Filtration steps; U - Unfiltered

4.3.2. Arsenic distribution in tandem with Fe, DOC and Al

In almost all the samples, large proportions of Al are associated with the particulate phases owing to their large decrease in concentration on passing through the 0.45 µm filter. In contrast,

Table 4.3. Percentage of As remaining after each sequential filtration steps.

Sample no.	Filtration steps	% As remained
1	0.45 µm	98.67
	0.22 µm	95.18
	0.10 µm	93.75
	0.05 µm	89.19
2	0.45 µm	99.67
	0.22 µm	98.85
	0.10 µm	96.15
	0.05 µm	93.61
3	0.45 µm	93.69
	0.22 µm	87.98
	0.10 µm	86.39
	0.05 µm	86.30
4	0.45 µm	92.21
	0.22 µm	89.96
	0.10 µm	86.20
	0.05 µm	83.78
5	0.45 µm	34.37
	0.22 µm	34.00
	0.10 µm	31.00
	0.05 µm	24.20
6	0.45 µm	97.30
	0.22 µm	89.39
	0.10 µm	86.67
	0.05 µm	84.92
7	0.45 µm	89.79
	0.22 µm	88.79
	0.10 µm	85.70
	0.05 µm	83.62
8	0.45 µm	99.63
	0.22 µm	99.50
	0.10 µm	96.95
	0.05 µm	94.03

large variation in DOC has mostly observed in 0.22-0.05 μm fractions, indicating its association with smaller colloidal phases. However, Fe has behaved in an interesting manner showing variations both in larger as well as in smaller colloidal fractions. Apart from sample 1, 2 and 8, large amount of As has been swept away by the particulate phases through filtration with 0.45 μm (Figure 4.1).

In sample 1, large variations in As concentration is observed in 0.45-0.22 μm and then in 0.10-0.05 μm fractions. In 0.45-0.22 μm fractions, there is no significant change in Fe and DOC concentrations. However, a notable change in Al concentration is observed which suggests the association of As with the larger Al colloidal phases (i.e., >0.22 μm). On the other hand, large variations in Fe and DOC concentrations highlight the interaction of As with smaller Fe and organic colloids, i.e., <0.10 μm sizes (Figure 4.1). In sample 2, the most notable variation in As concentration is observed in 0.22-0.05 μm fractions, which coincides with a significant drop in Fe and Al concentrations, indicating the influence of smaller Fe-Al colloids. Similar trend is also observed in sample 8. In these samples, a sharp decrease in Fe and Al content is observed in the higher pore-sized fractions (0.45-0.22 μm) but do not show significant change in As concentrations. This indicates that the larger inorganic colloid is not always playing a crucial role in As mobility (Figure 4.1). In sample 3, large variations in As content is observed in 0.45-0.22 μm size fractions, however, almost steady concentration is observed in 0.22-0.05 μm size fractions, even though there is a decline in DOC, Al and Fe contents. Hence, it can be considered that the large variations in As concentrations is controlled by the larger inorganic colloidal phases. Similar trends are also observed in sample 6 and 7 (Figure 4.1). In sample 4, As concentrations decreased consistently through all the sequential filtration steps. Similarly, Fe, Al and DOC content dropped consistently with As indicating the influence of both larger inorganic colloids and smaller inorganic/organic colloids in scavenging As. Sample 5 is quite interesting considering that most of the As, Fe, and Al are associated with the particulate phases, which shows large variations in unfiltered to 0.45 μm filtered samples. Arsenic concentration is not affected by the colloidal phases, except only a slight decrease in concentrations in the 0.10-0.05 μm size ranges (Figure 4.1).

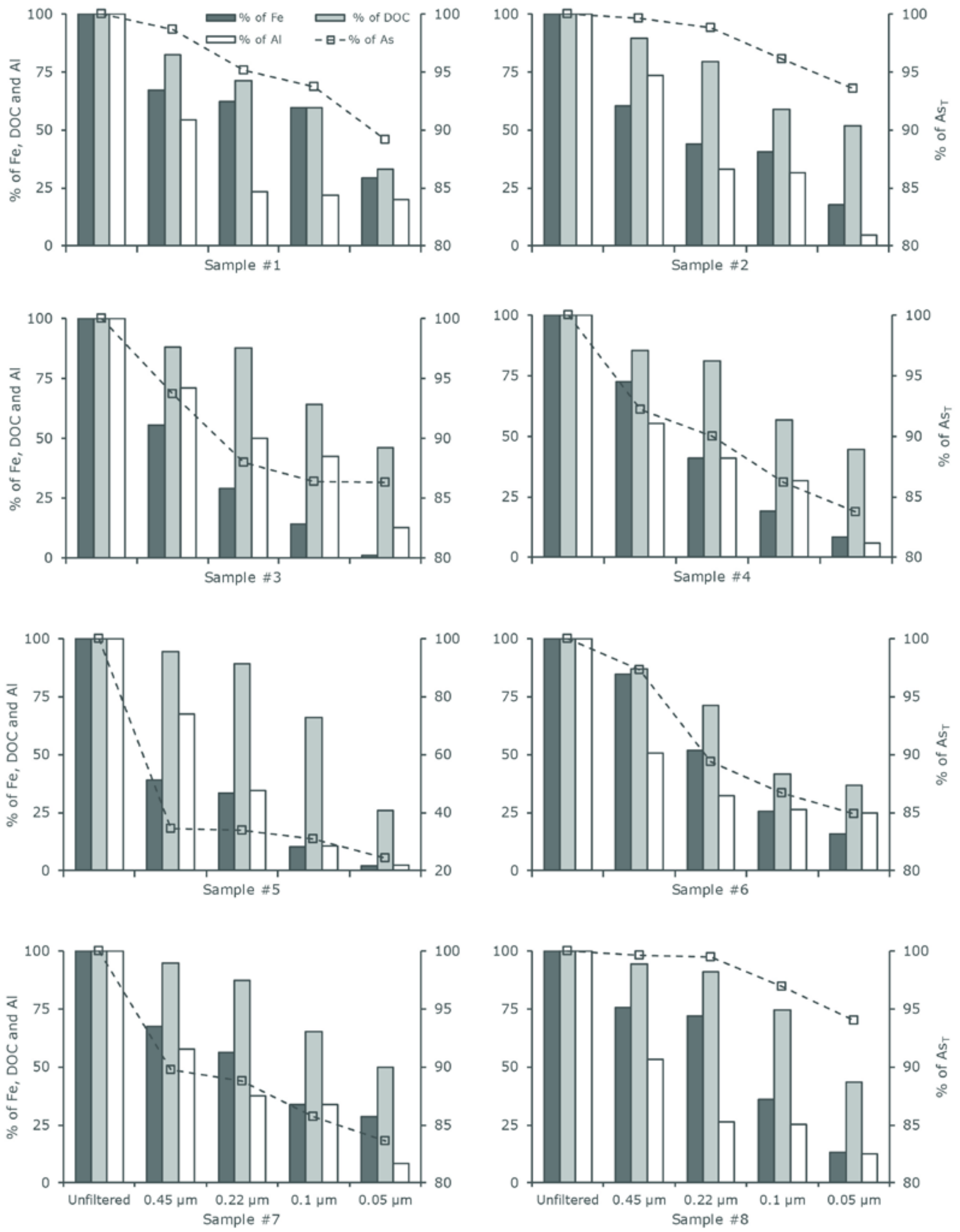


Figure 4.1. Variation in Fe, DOC, Al and As_T concentrations in groundwater samples (both unfiltered and after sequential filtration).

In 0.45 µm filtered samples, As correlates strongly with Fe ($r^2 = 0.94$) while relatively poorly with DOC ($r^2 = 0.59$) and Al ($r^2 = 0.57$) (Figure 4.2a). This is expected as the larger Fe-rich inorganic mineral phases are abundant in the greater pore-sized fractions (Guo et al., 2011). This is also consistent with the understanding that NOM can undergo co-precipitation and adsorption on Fe-oxides (Chan et al., 2009; Fritzsche et al., 2011). In 0.22 and 0.10 µm size fractions, the correlation between As and Fe is stronger (r^2 = 0.91 in both fractions) than DOC (r^2 = 0.60 and 0.63, respectively) and Al (r^2 = 0.60 and 0.88, respectively) (Figures 4.2b, c). This

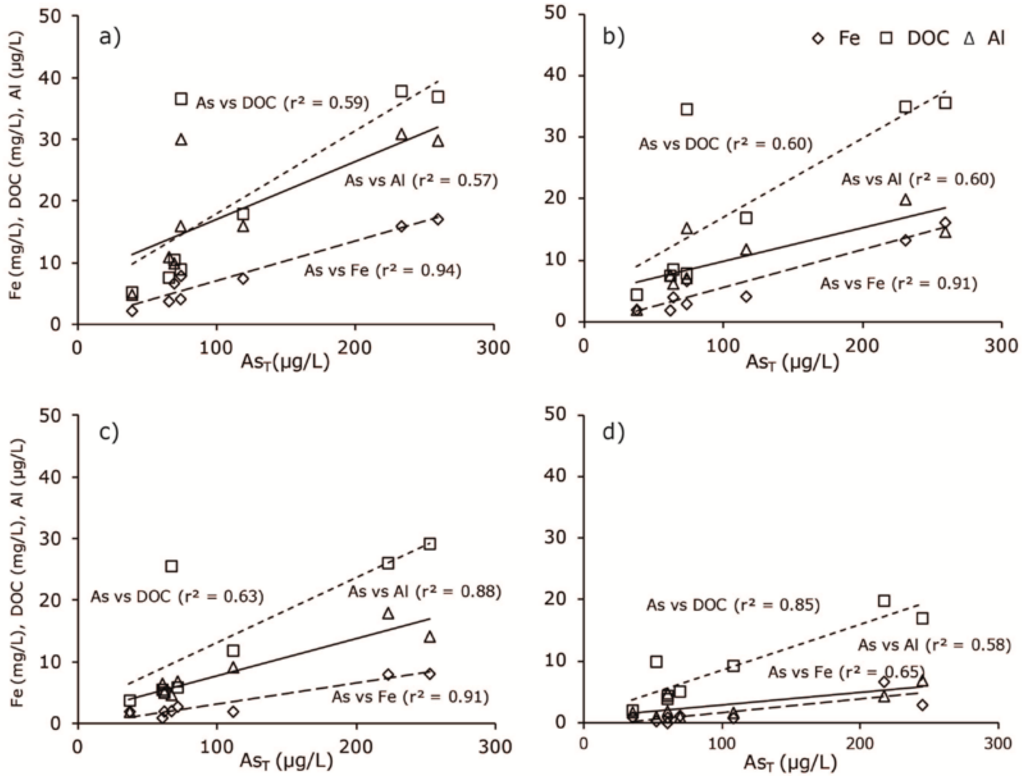


Figure 4.2. Correlation of As_T with Fe, DOC and Al in a) 0.45 µm, b) 0.22 µm, c) 0.10 µm, and d) 0.05 µm filtrates.

suggests that the Fe-rich colloids are possibly the major controlling factor for As distribution in groundwater for different colloidal size fractions (Bauer and Blodau, 2009). Although, in the smallest size fraction (i.e., 0.05 µm), the correlation of As with Fe and Al decreases considerably, whereas, with DOC shows a strong correlation (r^2 = 0.85) (Figure 4.2d). Therefore, variation in As concentrations in the larger sized fraction is attributed to Fe-Al rich inorganic colloids, while smaller sized fraction to organic colloids (Guo et al., 2011). High concentrations of DOC and moderate concentrations of Fe in the smallest size fractions indicate the formation of colloidal organo-metallic complexes that can strip off dissolved As from groundwater (Thanabalasingam and Pickering, 1986; Tipping et al., 2002; Warwick et al., 2005; Buschmann et al., 2006; Sharma et al., 2010).

4.3.3. Arsenic species variations in sequential filtration steps

Figure 3 shows the changes in As_T and As(III) concentrations in sequential filtration steps. The changes in As_T and As(III) concentrations do not respond in similar fashion in all samples (except for samples 3, 4 and 5). This observation is somewhat different from the study in Hetao Basin, Inner Mongolia, reported by Guo et al. (2011). This is expected considering differences in groundwater systems. The groundwater system in Inner Mongolia was colder with slightly higher pH. Additionally Na^+, Cl^- and DOC concentrations were much higher while Ca^{2+} concentrations were much lower in the Inner Mongolia study site (Guo et al., 2011) compared to our study area (Tables 4.1 and 4.2).

In sample 1 and 2, As_T decreases notably in the smaller pore-sized filtration steps (i.e., 0.22-0.10 μm). However, As(III) concentration dropped initially, i.e., in the larger pore-sized filtration steps, while little decrease in concentrations in smaller pore-sized filtration steps (Figure 4.3). In sample 3 and 4, both As_T and As(III) concentration dropped notably during larger pore-sized filtration steps (i.e., 0.45-0.22 μm). In sample 5, the trend observed for both As_T and As(III) are identical and most of the As are associated with particulate phases. In sample 6 and 8, As_T concentration remains stable during larger filtration steps, whereas As(III) decreases considerably during smaller filtration steps. Sample 7 shows a different behavior in the larger filtration steps (i.e., unfiltered to 0.45 μm). In this sample the % change in As_T concentration is greater than the % change in As(III) concentration, indicating a greater association of As(V) in particulate phases rather than As(III) (Figure 4.3).

In BDP, the concentration of organic As is very low or negligible (Sharim et al., 2002; Gault et al., 2003). As(III) and As(V), i.e., inorganic species, are the most abundant forms of As in groundwater. In most cases, large differences in As_T concentration is observed in the smaller pore-sized fractions (i.e., 0.22-0.05 μm), whereas, large differences in As(III) concentration is observed in the larger pore-sized fractions (i.e., 0.45-0.22 μm) (Figure 4.3). The variations in As_T concentration in the smaller pore-sized filtrate could be due to differences in As(V) concentration. This suggests that As(V) may primarily be scavenged by the smaller sized organic colloids, while As(III) is scavenged by the larger sized Fe-Al rich inorganic colloids.

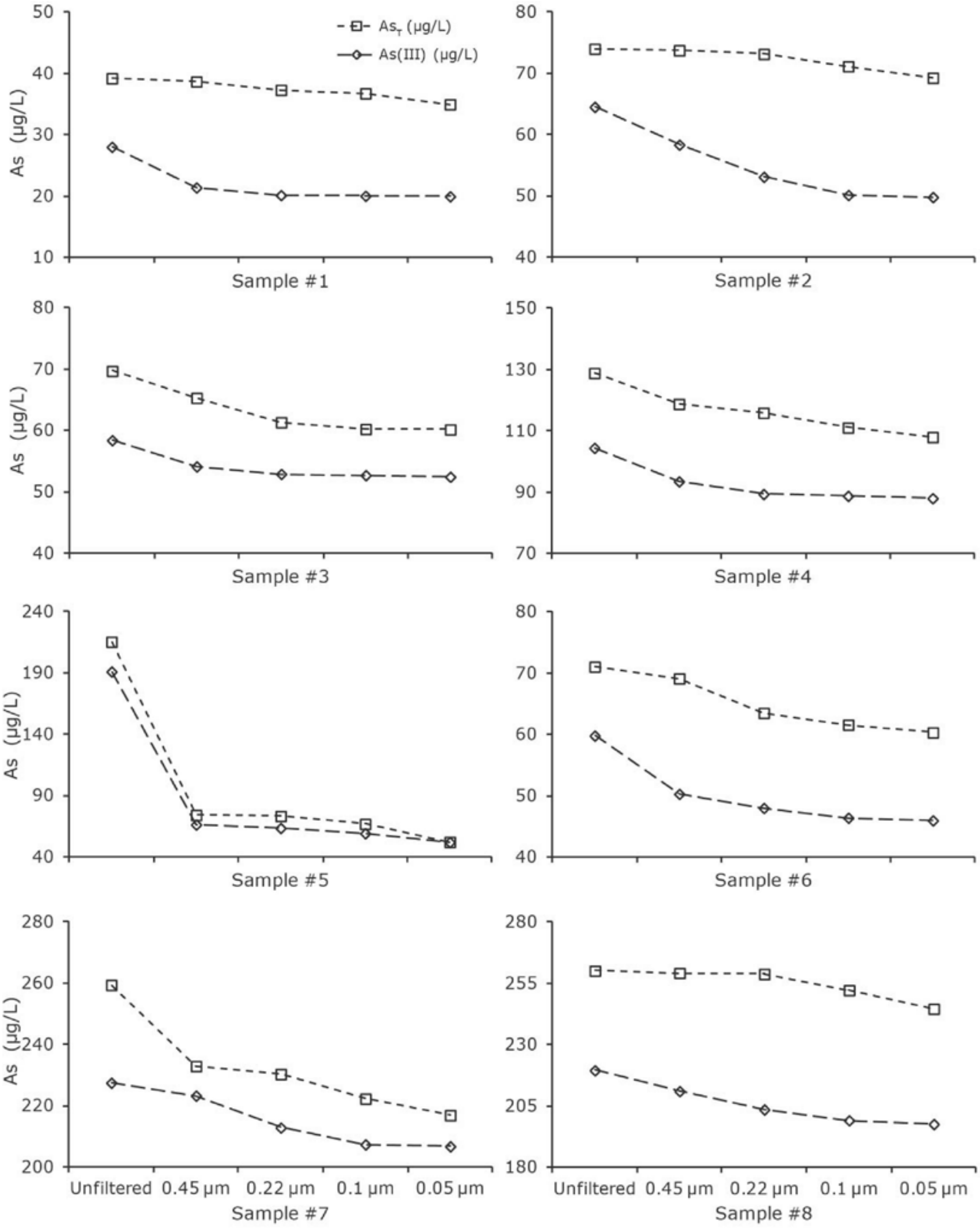


Figure 4.3. Variation in As_T and As(III) concentrations in groundwater samples after sequential filtration.

4.3.4. Colloidal fractionation of arsenic – inorganic vs. organic control

The stability and transport mechanism of colloids are controlled by various hydrochemical parameters, such as pH, Eh, alkalinity, and the presence of DOC (O'Melia and Tiller, 1993; Degueldre et al., 2000). These parameters can also influence As mobility in groundwater and its chemical speciation. Therefore, any changes in physico-chemical properties of the aquifer may effectively control colloidal (either inorganic and/or organic) As transport.

To investigate further, SEM analysis was performed on 0.05 µm ultrafilters to acquire morphological and elemental information (Figure 4.4a). The EDX analysis shows noticeable presence of C, O, Fe and As (Figure 4.4b). This indicates the presence of organic colloidal particles with Fe phases bound to it. The presence of Fe in the smaller colloidal fraction could be due to the formation of NOM complexes through carboxyl or phenolic groups (Tipping et al., 2002; Sharma et al., 2010). The association of As in these colloidal phases demonstrate the formation of organometallic complexes smaller than 0.05 µm. However, Guo et al. (2011) found purely organic colloids associated with As.

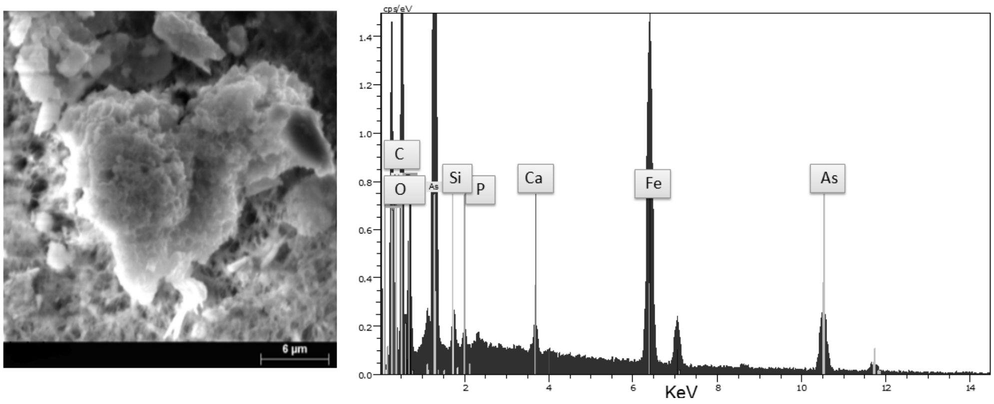


Figure 4.4. a) SEM photomicrographs showing the structure of colloidal organo-metallic particles, and b) EDX spectra of the same colloidal particles (after Majumder et al., 2013).

The ATR-FTIR spectra (Figure 4.5) shows a broad range of v(O-H) vibrations (3000-3700 cm^{-1}) due to predominance of water molecules along with a number of asymmetric v(COO^-) vibrations (~1400-1700 cm^{-1}) (Sharma et al., 2010). The observation of such spectral signature indicates the presence of organic components. The presence of absorption peak at 1624.1 cm^{-1} and 1636.7 cm^{-1} indicates the presence of As-Fe-NOM colloidal complex (Myneni et al., 1998; Sharma et al., 2010). However, more detailed spectroscopic investigations are required to get a consolidated proof of the formation of these organometallic complexes.

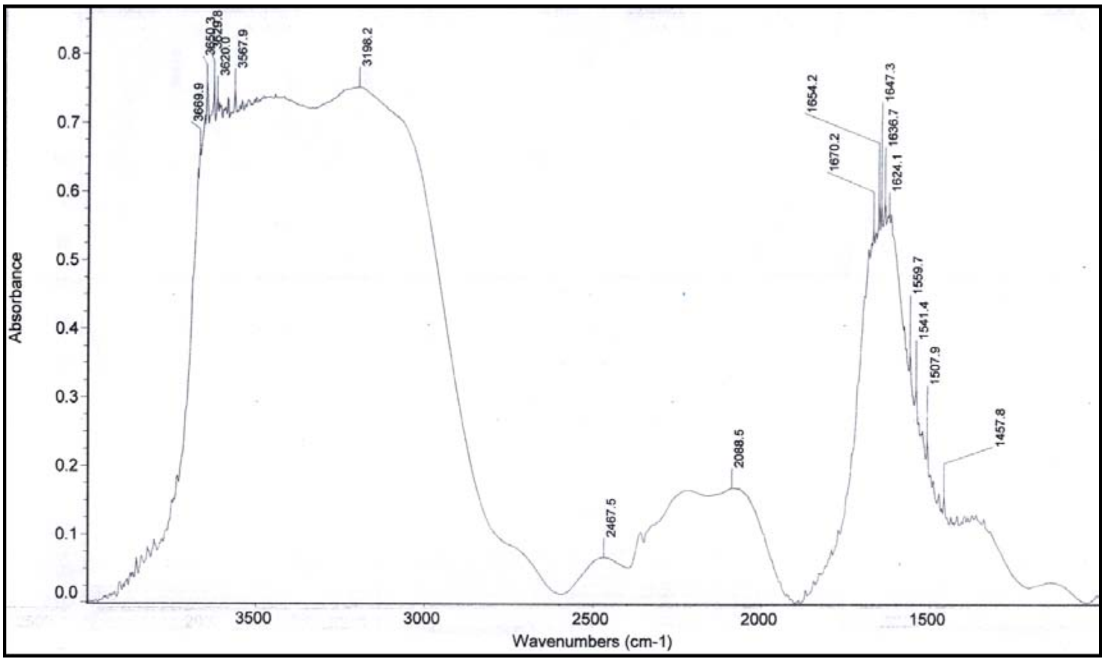


Figure 4.5. ATR-FTIR spectra of the colloidal particle showing the formation of As-Fe-NOM complexes.

4.4.4. Environmental implication and public health

In West Bengal, local public health regulatory agencies use 0.45 μm filter membrane during sample collection for the groundwater As monitoring purpose. However, this study showed large association of As in the particulate phase (especially in sample 5). Therefore, it is important to consider unfiltered samples for laboratory determination of As during monitoring program, as the rural inhabitant consumes raw (unfiltered) groundwater. The presence of 83-94% of As_T in the 'truly dissolved' phase (Table 4.3) suggests that the As removal technology based on ultrafiltration technique is unlikely to remove As from these groundwaters. This is similar to what observed by Guo et al. (2011) in Hetao Basin, Inner Mongolia. It will be more effective to oxidize Fe(II) to Fe(III) to form Fe-(oxyhydr)oxides and subsequently adsorption of both As(III) and As(V) (Leupin and Hug, 2005; Jang and Dempsey, 2008; Guo et al., 2011).

In addition to that analysis of different As species in groundwater should be a requirement before opting for a mitigation effort as different sized colloidal particles have different effect on the As species [i.e., As(III) and As(V)] in groundwater. Both larger sized Fe-Al rich inorganic colloids and smaller sized organic or organometallic colloids can act as a crucial host in scavenging As species from groundwater. Colloids can travel over a substantial distance in the aquifer and quickly mobilize due to their smaller sizes (Degueldre et al., 2000). This implies the importance of colloidal bound As in groundwater before implementation of sustainable As-safe drinking water extraction strategies.

4.5. Conclusion

This study determines that large proportions (83-94%) of As_T remain in the 'truly dissolved' phase. The strong correlation between Fe and As in the larger pore-sized fractions indicate the association between As and Fe-rich inorganic colloids. The strong correlation between DOC and As in the smaller pore-sized fractions highlight the interaction between organic colloids and As. As(III) species mostly associated with larger pore-sized inorganic colloids, while As(V) species mostly associated with smaller pore-sized organic/organometallic colloids. SEM and EDX confirms an association of As with DOC and Fe mineral phases which potentially indicate the involvement of dissolved organo-Fe complexes or colloidal organo-Fe oxide phases in scavenging dissolved As from groundwater. ATR-FTIR spectra further confirm the formation of As-Fe-NOM organometallic colloids. This study invokes wider consideration of dissolved and colloidal particles while assessing its mobility and/or mitigation effort due to potential scavenging behaviour of colloidal particles in groundwater.

References

Astrom M, Corin N. (2000) Abundance, Sources and speciation of trace elements in humus-rich streams affected by acid sulphate soils. *Aquat. Geochem.* **6**, 367–383.

Balzer W., Boehler E., Tang X., Ren J., Zhang J., Wang D. (2012) Arsenic in solution, colloidal and particulate phases of East-Haina estuaries. *Cont. Shelf. Res.* **57**, 73–81.

Bauer M., Blodau C. (2006) Mobilization of arsenic by dissolved organic matter from iron oxides, soils, and sediments. *Environ. Sci. Technol.* **354**, 179–190.

Bauer M., Blodau C. (2009) Arsenic distribution in the dissolved, colloidal and particulate size fraction of experimental solutions rich in dissolved organic matter and ferric iron. *Geochim. Cosmochim. Acta* **73**, 529–542.

Bhattacharya P., Chatterjee D., Jacks G. (1997) Occurrence of arsenic-contaminated groundwater in alluvial aquifers from delta plains, Eastern India: Options for safe drinking water supply. *Int. J. Water. Res. Dev.* **13**, 79–92.

Buschmann J., Kappeler A., Lindauer U., Kistler D., Berg M., Sigg L. (2006) Arsenite and arsenate binding to dissolved humic acids: Influence of pH, type of humic acid, and aluminum.. *Environ. Sci. Technol.* **40**, 6015–6020.

Chan C. S., Fakra S. C., Edwards D. C., Emerson D., Banfield J. F. (2009) Iron (oxyhydr)oxide mineralization on microbial extracellular polysaccharides. *Geochim. Cosmochim. Acta* **73**, 3807–3818.

Charlet L., Polya D. (2006) Arsenic in shallow, reducing groundwaters in Southern Asia: an environmental health disaster. *Elements* **2**, 91–96.

Degueldre C., Triay I., Kim J., Vilks P., Laaksoharju M., Miekeley N. (2000) Groundwater colloid properties: a global approach. *Appl. Geochem.* **15**, 1043–1051.

Dixit S., Hering J. G. (2003) Comparison of arsenic(V) and arsenic(III) sorption onto iron oxide minerals: Implications for arsenic mobility. *Environ. Sci. Technol.* **37**, 4182–4189.

Fritzsche A., Rennert T., Totsche K. U. (2011) Arsenic strongly associates with ferrihydrite colloids formed in a soil effluent. *Environ. Pollut.* **159**, 1398–1405.

Gault A. G., Davidson L. E., Lythgoe P. R., Polya D. A., Abou-Shakra F. R., Walker H. J., Chatterjee D. (2003) Iron and arsenic speciation in groundwater from West Bengal, India by coupled HPLC-ICPMS utilizing a hexapole collision cell in plasma source mass spectrophotometer: application and emerging technologies. Roy. Soc. Chem. Spec. Publ. 288, 112–126.

Guo H., Zhang B., Zhang Y. (2011) Control of organic and iron colloids on arsenic partition and transport in high arsenic groundwaters in the Hetao basin, Inner Mongolia. *Appl. Geochem.* **26**, 360–370.

Jang J. H., Dempsey B. A. (2008) Co-adsorption of arsenic(III) and arsenic(V) onto hydrous ferric oxide: effects on abiotic oxidation of arsenic(III), extraction efficiency, and model accuracy. *Environ. Sci. Technol.* **42**, 2893–2898.

Leupin O. X., Hug S. J. (2005) Oxidation and removal of arsenic (III) from aerated groundwater by filtration through sand and zero-valent iron. *Water Res.* **39**, 1729–1740.

Lin H. T., Wang M. C., Li G. C. (2004) Complexation of arsenate with humic substance in water extract of compost. *Chemosphere* **56**, 1105–1112.

Majumder S., Sarkar S., Chatterjee D., Roman-Ross G., Hidalgo M. (2013) Role of colloidal particles as scavengers of groundwater arsenic: a case study from rural Bengal. *Procedia Earth Planet. Sci.* **7**, 546–549.

Mueller F. L. L. (1996) Measurement of electrokinetic and size characteristics of estuarine colloids by dynamic light scattering spectroscopy. *Anal. Chim. Acta* **331**, 1–15.

Mukherjee A., Fryar A. E., Scanlon B. R., Bhattacharya P., Bhattacharya A. (2011) Elevated arsenic in deeper groundwater of the western Bengal basin, India: Extent and controls from regional to local scale. *Appl. Geochem.* **26**, 600–613.

Mukherjee A., von Bromssen M., Scanlon B. R., Bhattacharya P., Fryar A. E., Hasan M. A., Ahmed K. M., Chatterjee D., Jacks G., Sracek O. (2008)

Hydrogeochemical comparison and effects of overlapping redox zones on groundwater arsenic near the western (Bhagirathi sub-basin, India) and eastern (Meghna sub-basin, Bangladesh) margins of the Bengal Basin. *J. Contam. Hydrol.* **99**, 31–48.

Myneni S. C. B., Traina S. J., Waychunas J. A., Logan T. J. (1998) Experimental and theoretical vibrational spectroscopic evaluation of arsenate coordination in aqueous solutions, solids, and at mineral-water interfaces. *Geochim. Cosmochim. Acta* **62**, 3285–300.

Nath B., Chakraborty S., Burnol A., Stüben D., Chatterjee D., Charlet L. (2009) Mobility of arsenic in the sub-surface environment: An integrated hydrogeochemical study and sorption model of the sandy aquifer materials. *J. Hydrol.* **364**, 236–248.

Nath B., Maity J. P., Jean J-S., Birch G., Kar S., Yang H-J., Lee, M-K., Hazra R., Chatterjee D. (2011) Geochemical characterization of arsenic-affected alluvial aquifers of the Bengal Delta (West Bengal and Bangladesh) and Chianan Plains (SW Taiwan): Implications for human health. *Appl. Geochem.* **26**, 705–713.

Nickson R. T., McArthur J. M., Burgess W. G., Ahmed K. M., Ravenscroft P., Rahman M. (1998) Arsenic poisoning of Bangladesh groundwater. *Nature* **395**, 338.

O'Melia C., Tiller C. (1993) Physicochemical aggregation and deposition in aquatic environments. In: Characterisation of Environmental Particles, II. Lewis Publishers, Chelsea MI; p. 353-86.

Pal T., Mukherjee P. K., Sengupta S., Bhattacharya A. K., Shome S. (2002) Arsenic pollution in groundwater of West Bengal, India – an insight into the problem by sub-surface sediment analysis. *Gondwana Res.* **5**, 501–502.

Pokrovsky O. S., Schott J. (2002) Iron colloids/organic matter associated transport of major and trace elements in small boreal rivers and their estuaries (NW Russia). *Chem. Geol.* **190**, 141–179.

Pourret O., Dia A., Davranche M., Gruau G., Hénin O., Angée M. (2007) Organocolloidal control on major- and trace-element partitioning in shallow groundwaters: confronting ultrafiltration and modeling. *Appl. Geochem.* **22**, 1568–1582.

Redman A. D., Macalady D., Ahmann D. (2002) Natural organic matter affects arsenic speciation and sorption onto hematite. *Environ. Sci. Technol.* **36**, 2889–2896.

Ritter K., Aiken G. R., Ranville J., Bauer M., Macalady D. L. (2006) Evidence for the aquatic binding of arsenate by natural organic matter (NOM)-suspended Fe(III). *Environ. Sci. Technol.* **40**, 5380–5387.

Sharim A., Shekharan N. C., Anuradha C. D., Hirano S. (2002) Speciation of arsenic in tube-well water samples collected from West Bengal, India, by high-performance liquid chromatography-inductively coupled plasma mass spectrometry. *Appl. Organomet. Chem.* **16**, 202–206.

Sharma P., Ofner J., Kappler A. (2010) Formation of binary and ternary colloids and dissolved complexes of organic matter, Fe and As. *Environ. Sci. Technol.* **44**, 4479–4485.

Smedley P. L., Kinniburgh D. G. (2002) A review of the source, behaviour and distribution of arsenic in natural waters. *Appl. Geochem.* **17**, 517–568.

Thanabalasingam P., Pickering W. F. (1986) Arsenic sorption by humic acids. *Environ. Pollut.* **12**, 233–246.

Tipping E., Rey-Castro C., Bryan S. E., Hamilton-Raylor J. (2002) Al(III) and Fe(III) binding by humic substances in freshwaters, and implications for trace metal speciation. *Geochim. Cosmochim. Acta* **66**, 3211–3224.

Wang S., Mulligan C. N. (2006) Effect of natural organic matter on arsenic release from soils and sediments into groundwater. *Environ. Geochem. Health* **28**, 197–214.

Warwick P., Inam E., Evans N. (2005) Arsenic's interaction with humic acid. *Environ. Chem.* **2**, 119–224.

CHAPTER 5: NATURAL CITRATE SOURCES TO REMOVE ARSENIC FROM GROUNDWATER

This study report for the first time that the citrate source from tomato can effectively remove arsenic (As) from groundwater at the household level, compared to lemon and lime that are usually used for the Solar Oxidation and Removal of Arsenic (SORAS). The removal efficiency was mainly controlled by varying As/Fe molar ratios and citrate doses, which showed an 'optimized central tendency'. Tomato, containing hydroxycinnamate as the key anti-oxidants, would probably form Fe(III)-hydroxycinnamate complex and thus favored for the SORAS photochemical cycle. The market survey highlights tomato as the cheapest, eco-friendly, frequently available and efficient citrate source compare to lemon and lime for the SORAS treatment at the household level.

5.1. Introduction

Groundwater is the main source of drinking water in most part of the Bengal Delta Plain (BDP), the world's largest deltaic alluvium. The easy accessibility of groundwater makes it a vital resource for the rural people living in this region. Groundwater is widely used for agricultural irrigation and crop production (Bhattacharya et al., 1997; Smedley and Kinniburgh, 2002; Nath et al., 2008; van Geen et al., 2008). Though the aquifer is generally free from bacterial contamination, the large-scale exploitation of groundwater has resulted in severe water quality problems, the most threatening of which is the hydroarsenicosis (Guha Mazumder et al., 1988; Smith et al., 2000, 2009; Bhattacharyya et al., 2003; Kapaj et al., 2006; Mukherjee et al., 2007; Chatterjee et al., 2010; Nath et al., 2011).

There have been a number of technologies available for the removal of As from groundwater. For example, iron and alum coagulation (Shen, 1973), lime softening (McNeill and Edwards, 1995), reverse osmosis (Schneiter and Middlebrooks, 1983), zero-valent iron and nano-particulate zero-valent iron (Lien and Wikin, 2005; Morgada et al., 2009), natural/synthetic metal oxides (Guo et al., 2007; Chang et al., 2009), iron doped activated carbons (Fierro et al., 2009), granular TiO_2 adsorbent (Bang et al., 2005), hybrid materials (Mandal et al., 2011) are some of the many proposed removal techniques. Among these, some are efficient but expensive whereas others are cheaper but not efficient. The success of these technologies depends on several factors such as input water quality and composition, operation and maintenance problem, cost and user awareness level and education. Nevertheless, treated surface water was recommended as an alternative option for the community drinking water supply to the affected population. However, this is a costly and time-consuming solution and require distribution network for water supply. The field experience revealed that installation time for surface water treatment plant was between 2 and 3 years (Mukherjee et al., 2007). Therefore, a method is required which should be readily available and affordable to poor, affected rural villagers and at the same time highly efficient to remove As from drinking water without producing any hazardous wastes.

Solar Oxidation and Removal of Arsenic (SORAS) is a simple, cost effective and efficient technique for the removal of As from drinking water at the household level

(Hug, 2001; Hug et al., 2001). The method uses naturally available citric acid (as lemon juice) as the major complexing agent during irradiation with natural UV-A light (315 to 400 nm) to catalyze the photochemical oxidation. Similar to other oxidative removal methods, the dissolved As(III) oxidizes to As(V) in order to get adsorbed onto Fe-(oxyhydr)oxide surfaces at circumneutral pH (Impellitteri and Scheckel, 2006). The citric acid from lemon generally maintains a larger fraction of Fe(III) in the dissolved phase at circumneutral pH. The dissolved Fe(III) then reacts with citrates producing superoxide ($O_2^{\cdot -}$) and some intermediate oxygen free radicals (like $OH^{\cdot}$). Then, through a cyclic photochemical reaction, equilibrium concentrations of these oxidizing species and Fe(II) is maintained. It has been postulated that a Fenton type reaction is possibly responsible for further oxidation of As(III) and Fe(II), producing As(V) with stronger adsorption affinity for Fe-(oxyhydr)oxide surfaces formed in-situ and thereby ensuing removal of As (Hug, 2001; Hug et al., 2001; Hug and Leupin, 2003).

In this chapter, we reported for the first time the applicability and affordability of low-cost natural citrate sources from tomato and lime (locally known as ‘kagzi lebu’) in order to remove As from drinking water following SORAS technique. We have also critically evaluated the effect of As/Fe molar ratios and citrate doses on removal efficiency using synthetic test solutions to determine the optimal condition necessary for the SORAS technique. We have compared removal efficiencies posed by juices of tomato and lime with that of lemon for the recommendation of best available natural citrate sources.

5.2. Experimental

5.2.1. Preparation of synthetic test solutions

Synthetic test solutions were prepared in the laboratory in such a way that the solution represents the composition of groundwater (Table 5.1). The As concentration in the test solutions varied between 0.1 and 0.5 mg/L, while Fe concentrations varied between 2 and 6 mg/L (Figure 5.1a). The test solutions were prepared by volumetric dilution procedure (micro-pipette, Merck) in acid clean, dry, pre-weighed volumetric flasks. Arsenic stock solution was prepared by dissolving 1.302 g of arsenic trioxide (As_2O_3, Aldrich & Fluka) in high purity water

(HPW, Millipore, 18MΩ) containing 0.4 g of NaOH (Merck) and 20 mL of concentrated HCl (supra pure, Merck). The stock solution was diluted to 1 L with HPW to attain 1000 mg/L of As. The Fe stock solutions (1000 mg/L) were prepared by dissolving $FeSO_4.7H_2O$ (Merck) in HPW. The reagents used were only of analytical grade.

5.2.2. Collection of groundwater samples

Groundwater samples for solar radiation experiments (Figure 5.1b) were collected from the domestic hand-operated tube wells located in the rural villages of Chakdaha block, Nadia district (65 km north of Kolkata). The selection of tube wells was done based on the results of a previous survey on As contamination status of the region (Pal et al., 2002; Nath et al., 2009). The groundwater samples were collected in plastic bottles. Prior to sampling, the tube wells were pumped for several minutes to flush the standing volume of water to get fresh water from the aquifer. Water samples were filtered (0.45 µm cellulose nitrate membrane filter) on-site and divided into two groups. The first group was acidified (HNO_3 0.2% v/v) for the analysis of cations and As, while the second group was left un-acidified for anion analysis. Prior to sample collection, the groundwater samples were also measured for pH, Eh, alkalinity, temperature and electrical conductivity at the well-head (Table 5.1). All the samples were stored under normal refrigerated condition at 4^{o}C until the analysis.

Table 5.1. Physico-chemical characteristics and composition of major ions of synthetic solutions and groundwater (S-1 to S-3) samples.

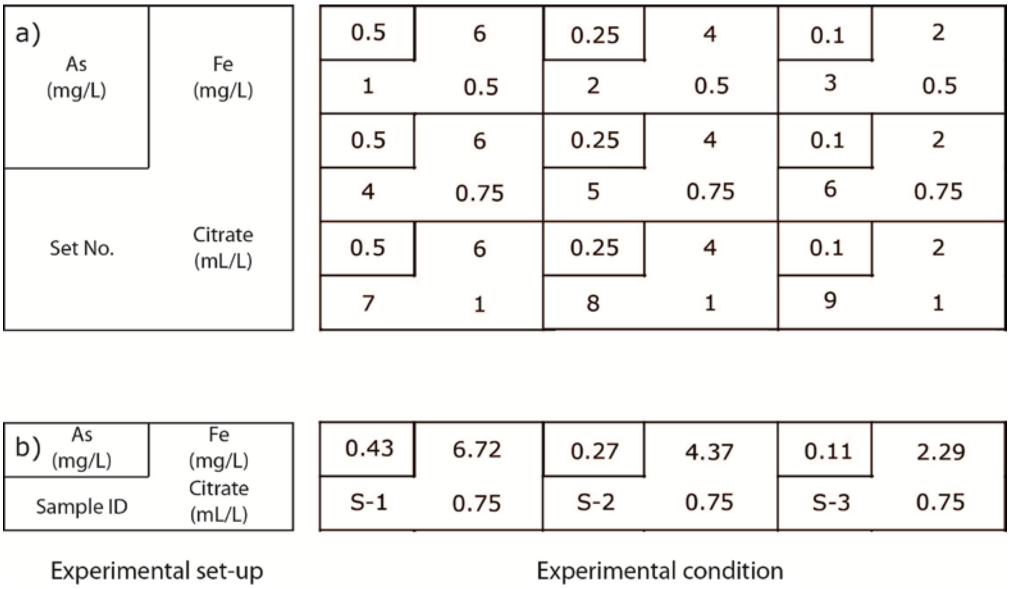
SN	**pH**	**Eh (mV)**	**EC (µS/cm)**	**HCO_3^- (mg/L)**	**Cl^- (mg/L)**	**PO_4^{3-} (mg/L)**
SS	6.5-7.4	na	680-1100	450-650	10-100	0.01-5.2
S-1	7.11	-130	991	512	88	2.8
S-2	7.08	-127	826	607	80	2.0
S-3	7.24	-105	739	457	48	3.7

SN – Sample number; SS- Synthetic solutions; na – not available; Electrical conductivity

Table 5.1. continues

SN	**Depth (m)**	**Temp (°C)**	**Ca^{2+} (mg/L)**	**Mg^{2+} (mg/L)**	**Na^+ (mg/L)**
SS	na	na	90-130	21-30	16-40
S-1	27	28.2	124	27	35
S-2	24	28.9	113	23	21
S-3	29	29.1	109	27	24

SN – Sample number; SS- Synthetic solutions; na – not available



a)

Set No.	As (mg/L)	Fe (mg/L)	Citrate (mL/L)
1	0.5	6	0.5
2	0.25	4	0.5
3	0.1	2	0.5
4	0.5	6	0.75
5	0.25	4	0.75
6	0.1	2	0.75
7	0.5	6	1
8	0.25	4	1
9	0.1	2	1

b)

Sample ID	As (mg/L)	Fe (mg/L)	Citrate (mL/L)
S-1	0.43	6.72	0.75
S-2	0.27	4.37	0.75
S-3	0.11	2.29	0.75

Figure 5.1. Experimental set-up and condition of a) treatment of synthetic solutions, and b) treatment of groundwater samples exposed to natural solar radiation for the removal of arsenic. Blank samples were also run during each set of experiments

5.2.3. Solar radiation experiments

Locally available lemon, tomato and lime were used as a citrate source for SORAS photochemical reaction (Figure 5.2a). The raw fruit juices were extracted with the help of a grinder and then filtered through a pre-cleaned (with distilled water) domestic fine mesh tea-strainer. The citrate doses were set to 0.5, 0.75 and 1 mL/L. The reported citrate concentrations of lemon and lime were 48 and 45.8 g/L, respectively (Penniston et al., 2008). The citrate concentration in tomato usually ranges between 34 and 50 g/L (http://www.resultsnowtests.biz/Titratable%20Acidity%20Tests.html).

Considering the above range of citric acid concentrations, the respective citrate level in case of lemon added to the experimental solutions were 0.024, 0.036 and 0.048 g/L. In case of lime the added citrate concentrations were 0.0229, 0.03435 and 0.0458 g/L. The added citrate concentrations as tomato juices were 0.017-0.025, 0.0255-0.0375 and 0.034-0.05 g/L.

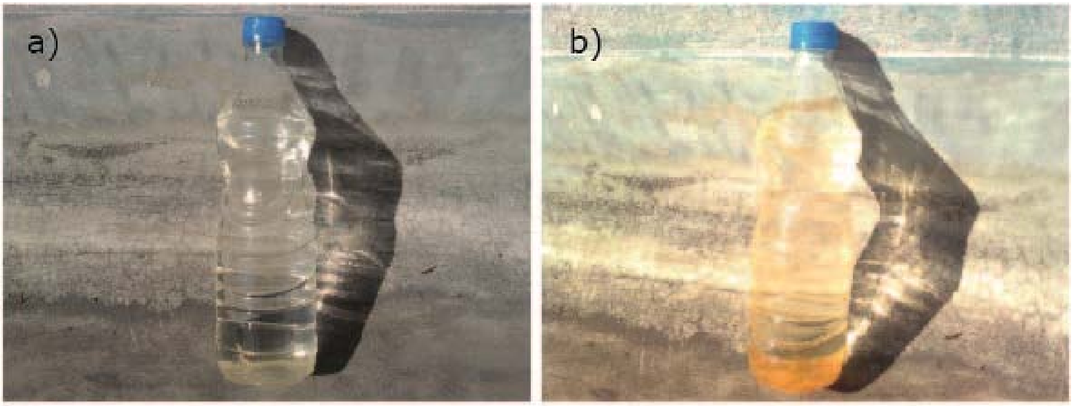


Figure 5.2. Solar radiation experiment: a) water samples in PET bottles before irradiation, b) after 2 h of irradiation (brown coloration of Fe-oxyhydroxides), and c) after 4 h of irradiation (precipitations of Fe-oxyhydroxide at the bottom).

One liter of synthetic solution containing range of As and Fe concentrations (set no. 1 to 9, Figure 5.1a) were transferred to transparent polyethylene-terpthalate (PET, volume 1.2 L) bottles. The solutions were then subjected to different doses of citric acids, i.e. juices from lemon, tomato and lime as mentioned above. The mixture was then shaken vigorously (~1 to 2 min) to ensure saturation of mixed liquid with the air. This provides sufficient oxygen to oxidize fraction of the dissolved Fe(II) into Fe(III). The experimental PET bottles were then tightly capped and exposed to sunlight for 4 h. The experiment was conducted in March 2010 between 10 am and 2 pm. The PET bottles were set at 45 degree inclined position supported by a tin sheet on the wall of an open roof with free access to sunlight (Figure 5.2a). During initial phase of the experiment, the visual inspection confirms precipitation of Fe(III)-(oxyhydr)oxides (Figure 5.2b). After complete irradiation (4 h), no significant visual change in color was observed (Figure 5.2c). Samples were collected twice during the experiments (i.e. after 2 and 4 h) which were preserved with HNO_3 (0.2% v/v) and stored in the refrigerator at 4^{o}C until analyzed for As and Fe concentrations. Blank samples (i.e. distilled water with no reported As concentrations) were prepared and run during each experimental stage to ensure that the system returns to a clean condition and allow establishment of the baseline with respect to noise.

Groundwater samples (S-1, S-2 and S-3) were treated in the similar fashion (Figure 5.1b). In groundwater samples, the solar radiation experiment was conducted with an optimal citrate dose of 0.75 mL/L which is based on the results of synthetic solutions. Separate control samples (i.e. groundwater with no reported As concentrations) were tested simultaneously alongside groundwater samples, without adding any citric acids.

5.2.4. Analytical procedures

The concentrations of Ca^{2+}, Mg^{2+}, Na^{+} and As were measured using double focusing High Resolution Inductively Coupled Plasma Mass Spectrometer (HR-ICP-MS VG AXIOM, VG Elemental) in a clean room (sample dilution 1:1 with 1% HNO_3 of sub-boiled quality). The concentrations of Cl^{-}, SO_4^{2-} and PO_4^{3-} were measured using Ion Chromatograph (IC, DIONEX ICS 1000) with a separating column (DIONEX AS 4 SC). Electrical Conductivity (EC), pH, Eh, temperature was measured using WTW multimeters. Alkalinity (reported as HCO_3^{-}) was quantified by titration with 0.2 M H_2SO_4 following the standard protocols. In case of groundwater samples, EC, pH, Eh, temperature and alkalinity were measured at the well head (Table 5.1). The concentration of citrate acid was measured following the method detailed in Ranganathan et al. (1985).

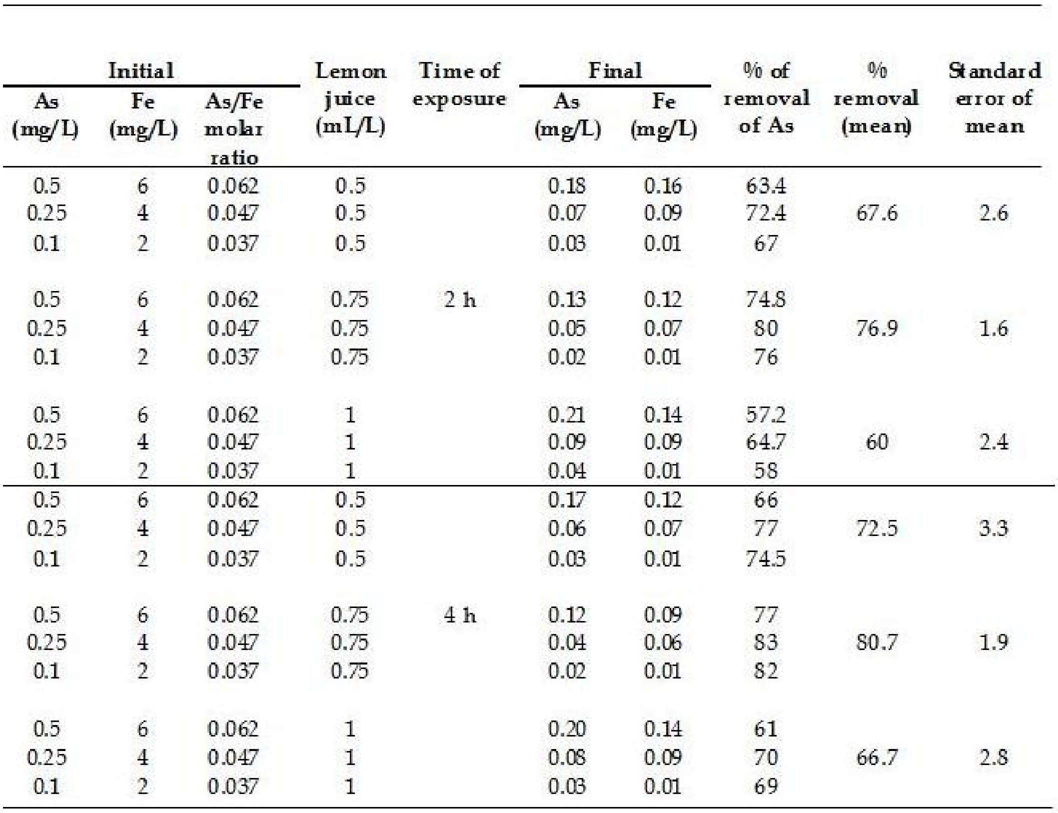
5.3. Results and Discussion

5.3.1. Arsenic removal efficiency in synthetic test solutions

Arsenic removal efficiency showed differential behavior with different citrate sources during SORAS photochemical cycle. Overall, the citric acid from tomato juices showed highest removal efficiency (range: 78-98%, mean: 88%) compared to lemon (range: 61-83%, mean: 73%) and lime (range: 39-69%, mean: 50%) juices (Tables 5.2a-c). This suggests tomato as the efficient natural citrate source for the removal of As from groundwater through solar irradiation. In general, high removal rate was observed during the first half (ie. within 2 hrs) of the experiment compared to the last half (Tables 2a-c) which suggests fast adsorption of As onto precipitated

Fe(III)-complexes. This is consistent with the findings of earlier studies (Gabriela Garcia et al., 2004; Majumder and Chaudhuri, 2005; Lara et al., 2006). Low reaction rates during second half of the experiment might be associated with decrease in dissolved As and Fe(III) concentrations in the solution and thereby less likely to form Fe(III)-complex.

Table 5.2a. SORAS experimental result showing removal efficiency of As in synthetic solutions dosed with lemon juice as a natural citrate source.



Initial			Lemon juice (mL/L)	Time of exposure	Final		% of removal of As	% removal (mean)	Standard error of mean
As (mg/L)	Fe (mg/L)	As/Fe molar ratio			As (mg/L)	Fe (mg/L)			
0.5	6	0.062	0.5	2 h	0.18	0.16	63.4	67.6	2.6
0.25	4	0.047	0.5		0.07	0.09	72.4		
0.1	2	0.037	0.5		0.03	0.01	67		
0.5	6	0.062	0.75		0.13	0.12	74.8	76.9	1.6
0.25	4	0.047	0.75		0.05	0.07	80		
0.1	2	0.037	0.75		0.02	0.01	76		
0.5	6	0.062	1		0.21	0.14	57.2	60	2.4
0.25	4	0.047	1		0.09	0.09	64.7		
0.1	2	0.037	1		0.04	0.01	58		
0.5	6	0.062	0.5	4 h	0.17	0.12	66	72.5	3.3
0.25	4	0.047	0.5		0.06	0.07	77		
0.1	2	0.037	0.5		0.03	0.01	74.5		
0.5	6	0.062	0.75		0.12	0.09	77	80.7	1.9
0.25	4	0.047	0.75		0.04	0.06	83		
0.1	2	0.037	0.75		0.02	0.01	82		
0.5	6	0.062	1		0.20	0.14	61	66.7	2.8
0.25	4	0.047	1		0.08	0.09	70		
0.1	2	0.037	1		0.03	0.01	69		

Table 5.2b. SORAS experimental result showing removal efficiency of As in synthetic solutions dosed with tomato juice as a natural citrate source.

Initial			Tomato juice (mL/L)	Time of exposure	Final		% of removal of As	% removal (mean)	Standard error of mean
As (mg/L)	Fe (mg/L)	As/Fe molar ratio			As (mg/L)	Fe (mg/L)			
0.5	6	0.062	0.5	2 h	0.10	0.07	80	86.7	3.5
0.25	4	0.047	0.5		0.02	0.02	91.6		
0.1	2	0.037	0.5		0.01	0.01	88.6		
0.5	6	0.062	0.75		0.09	0.06	82	89.6	4.2
0.25	4	0.047	0.75		0.02	0.01	96.3		
0.1	2	0.037	0.75		0.01	0.01	90.5		
0.5	6	0.062	1		0.15	0.11	69.4	77.5	4.3
0.25	4	0.047	1		0.03	0.03	84		
0.1	2	0.037	1		0.02	0.01	79		
0.5	6	0.062	0.5	4 h	0.09	0.07	82	88.3	3.3
0.25	4	0.047	0.5		0.02	0.02	93.2		
0.1	2	0.037	0.5		0.01	0.01	89.7		
0.5	6	0.062	0.75		0.08	0.05	84	91.4	4.1
0.25	4	0.047	0.75		0.02	0.01	98.2		
0.1	2	0.037	0.75		0.01	0.01	92		
0.5	6	0.062	1		0.11	0.10	78	84	3.1
0.25	4	0.047	1		0.03	0.02	88		
0.1	2	0.037	1		0.01	0.01	86		

Table 5.2c. SORAS experimental result showing removal efficiency of As in synthetic solutions with lime juice as a natural citrate source.

Initial			Lime juice (mL/L)	Time of exposure	Final		% of removal of As	% removal (mean)	Standard error of mean
As (mg/L)	Fe (mg/L)	As/Fe molar ratio			As (mg/L)	Fe (mg/L)			
0.5	6	0.062	0.5	2 h	0.33	0.27	33.4	42.9	5.0
0.25	4	0.047	0.5		0.13	0.19	50.2		
0.1	2	0.037	0.5		0.05	0.22	45		
0.5	6	0.062	0.75		0.30	0.28	40	52	7.4
0.25	4	0.047	0.75		0.09	0.19	65.6		
0.1	2	0.037	0.75		0.03	0.11	50.5		
0.5	6	0.062	1		0.34	0.25	32.2	39.8	3.9
0.25	4	0.047	1		0.14	0.21	45.2		
0.1	2	0.037	1		0.06	0.20	42		
0.5	6	0.062	0.5	4 h	0.3	0.17	41	47.3	3.8
0.25	4	0.047	0.5		0.11	0.16	54		
0.1	2	0.037	0.5		0.05	0.17	47		
0.5	6	0.062	0.75		0.28	0.19	44	56.4	7.3
0.25	4	0.047	0.75		0.08	0.16	69.2		
0.1	2	0.037	0.75		0.03	0.09	56		
0.5	6	0.062	1		0.31	0.21	39	46.7	3.9
0.25	4	0.047	1		0.12	0.18	52		
0.1	2	0.037	1		0.05	0.18	49		

5.3.2. The effect of As/Fe molar ratio

The As/Fe molar ratios showed an 'optimized central tendency' during the removal of As for all citrate sources (Tables 5.2a-c). The removal efficiency was higher for the solutions with molar ratio of 0.047 (set no. 2, 5, 8) compared to the solutions with molar ratio of 0.037 (set no. 3, 6, 9). However, the solution (set no. 1, 4, 7) with higher molar ratio (0.062), the removal efficiency was the lowest for all citrate sources. Therefore, the initial As and Fe concentrations in the treated water are important for better removal efficiency. Lara et al. (2006) suggested that the ratio of As, Fe and the citrate content are important for better removal efficiency. The low removal efficiency at low As/Fe molar ratio indicates that species like Fe(IV), $O_2^{\cdot-}$ or $OH^{\cdot}$ (Hug, 2001; Hug et al., 2001) may not be the only oxidizing agent for As(III). There may be a possible interference from other potential oxidizing agents like HCO_3^- taking part in the cyclic reaction, which could regulate the course of the SORAS photochemical reaction (Hug, 2001; Hug et al., 2001; Gabriel Garcia et al., 2004). Another possibility could be the acceleration of some intermediate reactions (Hug et al., 2001) in the photochemical cycles due to presence of excess Fe in the samples. Consequently, the concentration of free radicals is diminished, thereby reducing the removal efficiency. In contrast, with higher molar ratio, the removal efficiency might have lowered due to scarcity of sufficient dissolved Fe concentrations and subsequent generation of photocatalysts.

5.3.3. The effect of citrate dose

The 'optimized central tendency' was also observed for different citrate doses. The removal efficiency was higher for the 0.75 mL/L of citrate juices compared to 0.50 mL/L (Tables 5.2a-c). The removal efficiency was the lowest for 1.0 mL/L of citrate juices. At low citrate doses (i.e. 0.50 mL/L of juices), the cyclic photochemical reaction (Hug, 2001) might not able to generate intermediate reaction products (e.g., free radicals and Fe(III)-citrate complex) in order to provide necessary conditions for the efficient removal of As from the solution. This is mainly due to scarcity of citrates during photochemical reactions and thus unable to trigger Fenton type reactions. On the other hand, at higher citrate doses, the low removal efficiency was probably due to interference of the Fe(III)-citrate complex during the formation of Fe(III)-(oxyhydr)oxide solids (Majumder and Chaudhuri, 2005). Additionally antioxidant composition of different citrate sources could influence the removal efficiency detailed in later section.

5.3.4. Arsenic removal efficiency in groundwater samples

Being the most efficient citrate level to remove As from the synthetic solutions, optimum citrate dose of 0.75 mL/L were only maintained for the experiment with the groundwater samples. The data showed that tomato juice was more efficient to remove As from groundwater samples compared to juices of lemon and lime. The sample, S-1 with As/Fe molar ratio of 0.048 has the highest removal efficiency, followed by S-3 (molar ratio of 0.036) and S-2 (molar ratio of 0.046) (Table 5.3). Although S-1 and S-2 has similar molar ratios, the removal percentage of As was quite different. This suggests that Fe concentrations are also critical for better removal efficiency. Additionally, high HCO_3^- concentrations of S-2 groundwater samples (607 mg/L, Table 5.1) might have controlled the SORAS photochemical reaction. In all the samples, the consumption of citrate was almost similar (range: 92-96%) after the radiation exposure (Table 5.3). This indicates possible controlling factors other than the photochemical cycle of Fe(III)-citrate complex, that are promoting the citric acid from tomato juices over lemon and lime for the efficient removal of As from groundwater.

Table 5.3. SORAS experimental result showing removal efficiency of As in groundwater samples dosed with lemon, tomato and lime juices as a natural citrate source.

CS	SN	Initial (mg/L)		ICJ (mL/L)	FCJ (mL/L)	T	Final (mg/L)		% of removal of As	% X	SE_m
		As	Fe				As	Fe			
Lemon	S-1	0.43	6.72	0.75	0.03	4 h	0.03	0.35	85	82.2	1.7
	S-2	0.27	4.37	0.75	0.05		0.07	0.44	79		
	S-3	0.11	2.29	0.75	0.06		0.03	0.35	82.5		
Tomato	S-1	0.43	6.72	0.75	0.03		0.01	0.29	97	93.9	2.0
	S-2	0.27	4.37	0.75	0.03		0.03	0.45	90.2		
	S-3	0.11	2.29	0.75	0.05		0.01	0.43	94.5		
Lime	S-1	0.43	6.72	0.75	0.05		0.06	0.29	70.2	67	2.1
	S-2	0.27	4.37	0.75	0.06		0.12	0.37	63		
	S-3	0.11	2.29	0.75	0.03		0.05	0.36	67.8		

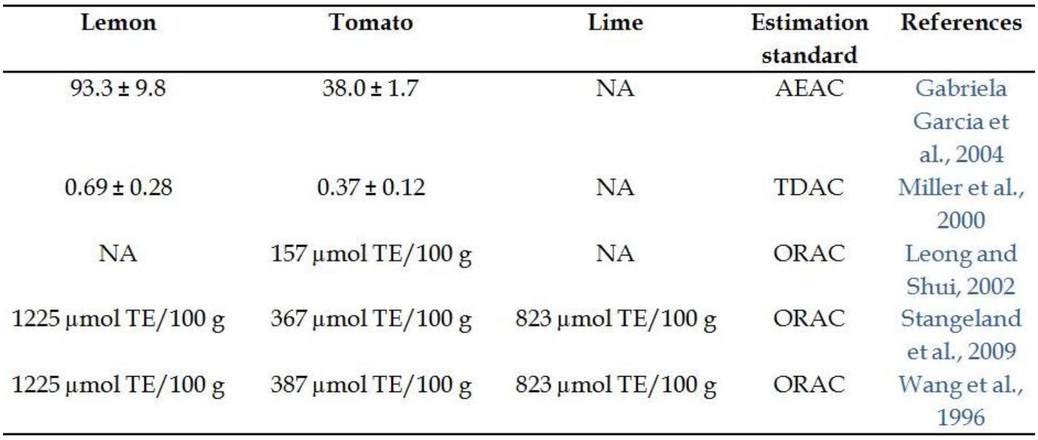
CS – Citrate source; SN – Sample number; ICJ – Initial citrate juice; FCJ – Final citrate juice; T – Time of exposure; % X – percentage of removal (mean); SE_m – Standard error of mean

Note – Control samples (i.e. with no added citrate juices) were run simultaneously during this experiment. The removal efficiency of control samples were 49%, 37% and 43%, respectively.

5.3.5. Antioxidant activity of the citrate juices

The citrate juices discussed here have the quantitative amount of polyphenolic anti-oxidants (Wang et al., 1996; Miller et al., 2000; Leong and Shui, 2002; USDA, 2007; Stangeland et al., 2009; Haytowitz and Bhagwat, 2010). Table 5.4 shows that anti-oxidant activity is much lower in the case of citrate sources from tomato than lemon and lime.

Table 5.4. Antioxidant activity of different citrate sources.



Lemon	Tomato	Lime	Estimation standard	References
93.3 ± 9.8	38.0 ± 1.7	NA	AEAC	Gabriela Garcia et al., 2004
0.69 ± 0.28	0.37 ± 0.12	NA	TDAC	Miller et al., 2000
NA	157 µmol TE/100 g	NA	ORAC	Leong and Shui, 2002
1225 µmol TE/100 g	367 µmol TE/100 g	823 µmol TE/100 g	ORAC	Stangeland et al., 2009
1225 µmol TE/100 g	387 µmol TE/100 g	823 µmol TE/100 g	ORAC	Wang et al., 1996

NA – Not Available

AEAC – L-Ascorbic Acid Equivalent Antioxidant Capacity

TDAC – Total Anti-oxidant Capacity

TE – Trolox Equivalent

ORAC – Oxygen Radical Absorbance Capacity

Therefore, the citric acids from lemon and lime juices are susceptible to oxygen radical (like superoxides or $OH_{\cdot}$) absorption and less conducive towards photochemical oxidation, the basic requirement for the effective execution of SORAS. Hence, the reaction step 4 and the subsequent photochemical cycle (shown below) might get hindered after certain period of time that was also proposed by Hug (2001). Consequently, due to insufficient formation of superoxides (or other oxygen radicals, $OH_{\cdot}$), the reaction step 5 could not able to re-produce enough Fe(III) which could again involve in the reaction with organic acids to form Fe(III)-organic complex (reaction 2) in order to continue the cyclic reaction:

$$Fe(II) + O_2 \rightarrow Fe(III) \text{ ---------------------- (1)}$$

$$Fe(III) + \text{Organic acid} \rightarrow Fe(III)\text{-Organic complex} \text{ --------------- (2)}$$

$$Fe(III)\text{-Organic complex (on irradiation with UV-A light)} \rightarrow \text{Organic radical} + CO_2 + Fe(II) \text{ ------------------- (3)}$$

$$\text{Organic radical} + O_2 \rightarrow O_2^{\cdot -} + \text{Oxidized organic species} \text{ ----------------- (4)}$$

$$O_2^{\cdot -} + Fe(II) \rightarrow Fe(III) + H_2O_2 \text{ ------------------ (5)}$$

Additionally, flavanones (e.g. taxifolin, naringenin, and narirutin) were the major anti-oxidants found in citrus fruits like lemon and lime, whereas, hydroxycinnamic acids (e.g. p-Coumaric acid and ferulic acid) were the major anti-oxidants in tomato (Figure 3) (Rice-Evans et al., 1996, 1997). Therefore, the carboxylate ($R–COO^-$) group of hydroxycinnamates could promote SORAS photochemical cycle, forming Fe(III)-hydroxycinnamate complex and generating additional oxidizing radicals. On the contrary, flavanones have no such groups to form complexes with Fe(III). Therefore, tomato juices can act as a better promoter for the SORAS technique because of its ability to generate hydroxycinnamate complexes for the efficient removal of As from groundwater.

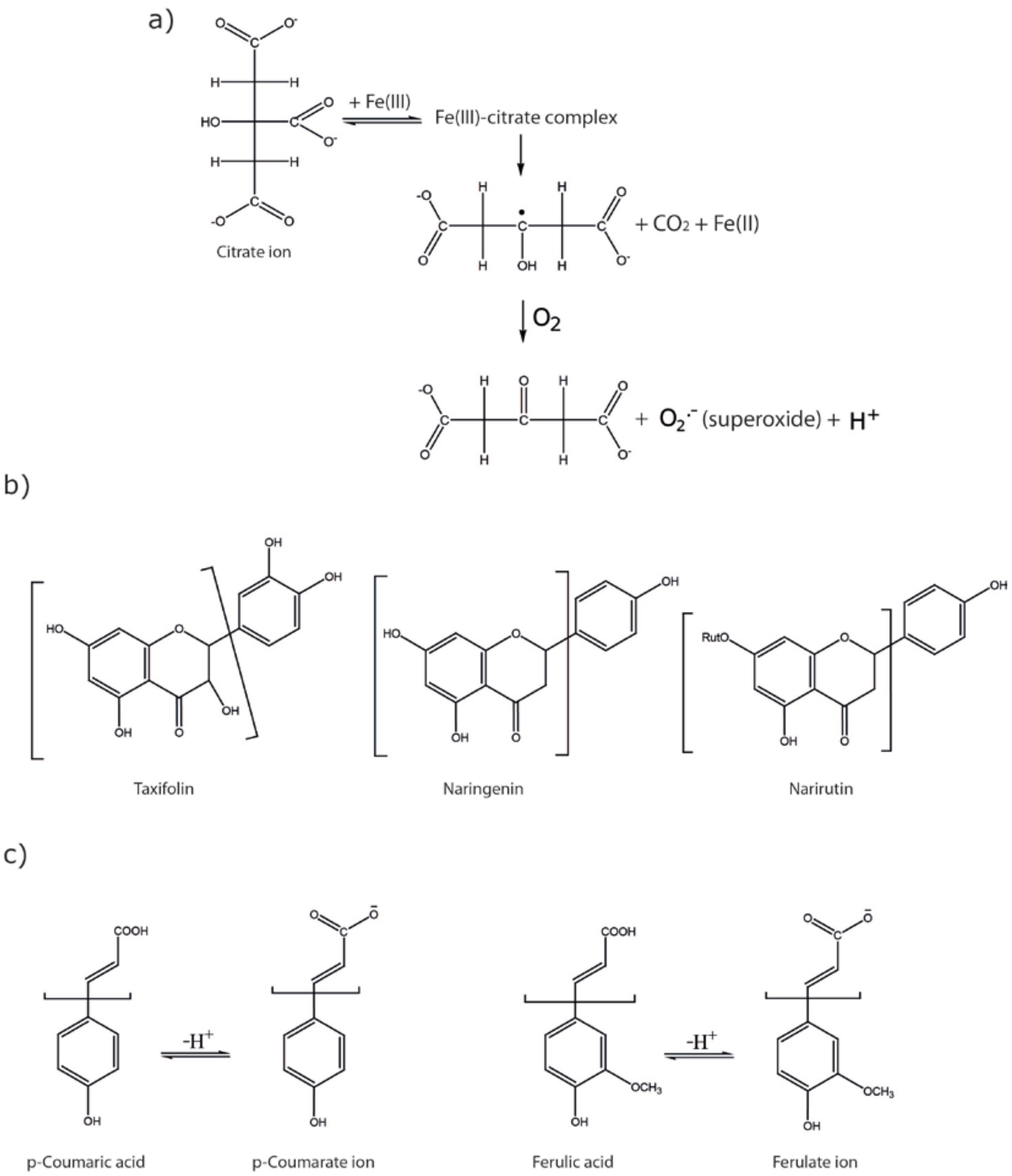


Fig. 5.3. a) SORAS reaction steps (modified after Hug et al., 2001), b) major anti-oxidants found in lemon and lime, and c) major anti-oxidants found in tomato.

5.3.6. Cost analysis, availability and affordability of citrate sources

A survey was carried out in the local market of As contaminated regions in West Bengal, India for the cost analysis of different citrate sources (Table 5.5). The average cost of lemon and tomato (100 g in weight) is INR 4.00 whereas a lime costs INR 3.00. The average extractable juice from tomato and lime is 90 mL whereas from lemon is 70 mL (Table 5.5). The reported citrate concentrations in lemon is 48 g/L, 45.8 g/L in lime and 42 g/L in tomato (Penniston et al., 2008;

http://www.resultsnowtests.biz/Titratable%20Acidity%20Tests.html). Therefore total citrate content of 3.36, 3.78 and 4.12 g can be extracted from lemon, tomato and lime weighing 100 g, respectively. Thus, apart from the effective removal of As, 100 g of tomato can produce greater volume of juices and citrate concentrations for the treatment of large volume of As contaminated drinking water compared to lemon.

Table 5.5. Cost-estimate of different citrate sources based on the market survey[a].

Citrate sources	Availability	Price / 100 g (INR)[b]	Extractable juices / 100 g (mL)	Treatable volume of water / 100 g of citrate sources (L)	Citrate content[d] (g)	Arsenic removal (%)
Lemon	All seasons	4.00 (0.072 USD)	70	93	3.36	82
Tomato	All seasons[c]	4.00 (0.072 USD)	90	120	3.78	94
Lime	Specific seasons	3.00 (0.054 USD)	90	120	4.12	67

[a] The survey has been carried out in the local market of the study area (i.e. Chakdaha block, West Bengal, India).

[b] Average weight of a lemon is ~25 g, cost INR 1/-; whereas, average weight of a tomato and lime is 100 g, cost INR 4/- and 3/-, respectively. The USD value in the parenthesis is as on 29.08.2012, 1 USD = 55.6807 INR (www.xe.com).

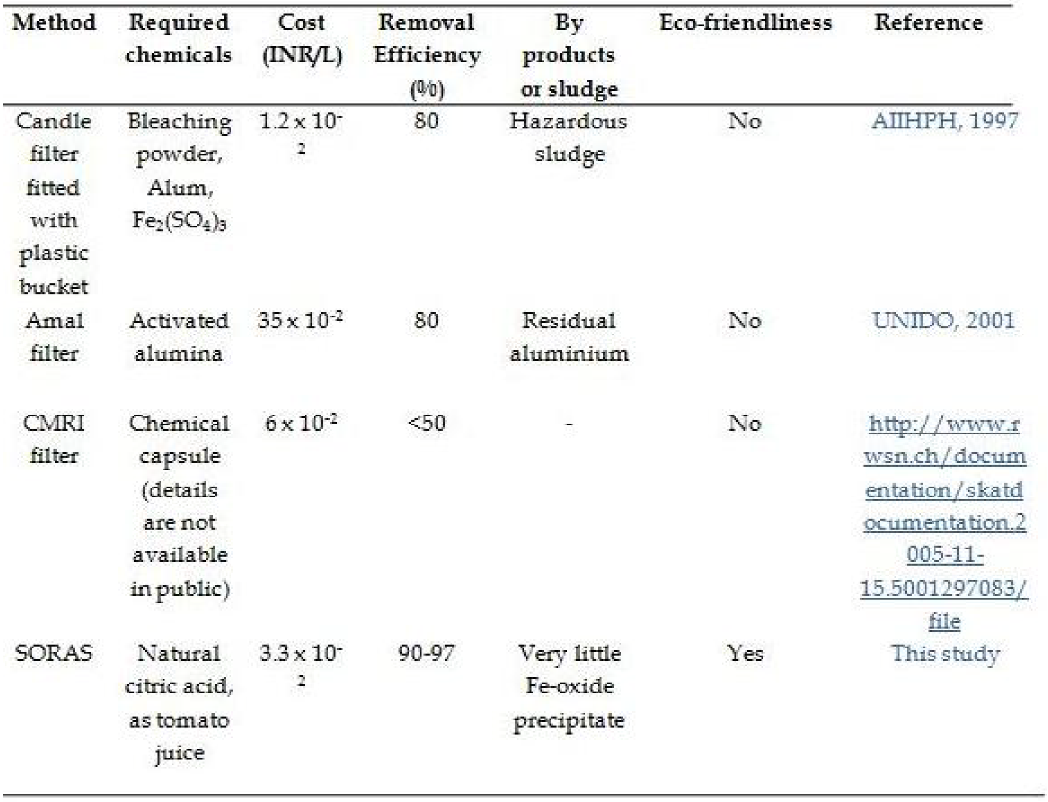
[c] Modified varieties during some seasons.

[d] Considering citrate concentrations of 48 g/L in lemon and 45.8 g/L in lime [29] and 42 g/L in tomato (http://www.resultsnowtests.biz/Titratable%20Acidity%20Tests.html).

Using tomato, the average removal efficiency was 93.9% in case of the groundwater samples and the concentration of As in the treated water was ~ 0.1-0.5 mg/L (Table 5.3). Therefore, by adopting this method the concentration of As could be brought down below the WHO guideline value (0.01 mg/L) or the national safe limit of India (0.05 mg/L). We expect that this method should work for low or high As groundwater and this require further investigations. However, the removal efficiency would depend on the initial As and Fe concentration (i.e. molar ratios of As and Fe) in the treated water.

Table 5.6 showed a comparative estimate of the available low-cost household methods for As removal from groundwater. Most of the low-cost methods involve additional use of potentially hazardous chemicals and making them environmentally unacceptable due to generation of toxic wastes.

Table 5.6. Cost comparison of different low-cost arsenic treatment techniques at the household levels.



Method	Required chemicals	Cost (INR/L)	Removal Efficiency (%)	By products or sludge	Eco-friendliness	Reference
Candle filter fitted with plastic bucket	Bleaching powder, Alum, $Fe_2(SO_4)_3$	1.2×10^{-2}	80	Hazardous sludge	No	AIIHPH, 1997
Amal filter	Activated alumina	35×10^{-2}	80	Residual aluminium	No	UNIDO, 2001
CMRI filter	Chemical capsule (details are not available in public)	6×10^{-2}	<50	-	No	http://www.rwsn.ch/documentation/skatdocumentation.2005-11-15.5001297083/file
SORAS	Natural citric acid, as tomato juice	3.3×10^{-2}	90-97	Very little Fe-oxide precipitate	Yes	This study

On the other hand, SORAS technique with the addition of natural citric acid (as tomato juices, non-toxic) is comparatively more efficient in removing As from groundwater at the household level without producing any hazardous wastes. Additionally, in rural villages tomato can be found abundantly due to its high demand and greater earnings. Hence, it would be convenient and beneficial for the rural people to cultivate tomato in their backyard and use it for the SORAS treatment. Therefore, the citrate source from tomato should be considered for the effective functioning of SORAS technique for the removal of As from drinking groundwater. The method described here is also highly cost-effective compared with the other conventional treatment methods currently available at the market (Table 5.6). Most importantly, this method does not produce any hazardous chemicals, therefore, can be considered as a green chemistry approach for the effective removal of As from groundwater at household levels for drinking and cooking purposes.

5.4. Conclusion

This study reported for the first time that the citrate source from tomato can effectively remove As from groundwater compared to lemon and lime. The removal efficiency was mainly controlled by the varying As/Fe molar ratios and citrate doses, which showed an 'optimized central tendency'. The analogous citrate removal from experimental solutions indicate possible interference of anti-oxidants during Fe(III)-citrate photochemical cycle. Tomato, containing hydroxycinnamate as major anti-oxidants, would probably form Fe(III)-hydroxycinnamate complex and thus favored for the SORAS photochemical cycle. The market survey highlights tomato as the most cost-effective, eco-friendly, affordable, available and efficient citrate source compare to lemon and lime for the SORAS treatment at the household level.

References

All India Institute for Hygiene and Public Health (AIIHPH) (1997) Comprehensive capacity building, training and awareness generation programme to tackle the arsenic problem in West Bengal, India, Kolkata.

Bang S., Patel M., Lippincott L., Meng X. (2005) Removal of arsenic from groundwater by granular titanium dioxide adsorbent. *Chemosphere* **60**, 389–397.

Bhattacharya P., Chatterjee D., Jacks G. (1997) Occurrence of arsenic-contaminated groundwater in alluvial aquifers from delta plains, Eastern India: Options for safe drinking water supply. *J. Water Resour. Dev.* **13**, 79–92.

Bhattacharyya R., Chatterjee D., Nath B., Jana J., Jacks G., Vahter M. (2003) High arsenic groundwater: Mobilization, metabolism and mitigation – An overview in the Bengal Delta Plain. *Mol. Cell. Biochem.* **253**, 347–355.

Chang Y. Y., Lee S. M., Yang J. K. (2009) Removal of As(III) and As(V) by natural and synthetic metal oxides. *Colloid Surf. A-Physicochem. Eng. Asp.* **346**, 202–207.

Chatterjee D., Halder D., Majumder S., Biswas A., Nath B., Bhattacharya P., Bhowmick S., Mukherjee-Goswami A., Saha D., Hazra R., Maity P. B., Chatterjee D., Mukherjee A., Bundschuh J. (2010) Assessment of arsenic exposure from groundwater and rice in Bengal Delta Region, West Bengal, India. *Water Res.* **44**, 5803–5812.

Fierro V., Muniz G., Gonzalez-Sánchez G., Ballinas M. L., Celzard A. (2009) Arsenic removal by iron-doped activated carbons prepared by ferric chloride forced hydrolysis. *J. Hazard. Mater.* **168**, 430–437.

Gabriela Garcia M., d'Hiriart J., Jiullitti J., Lin H., Custo G., Hidalgo M. D. V., Litter M. I., Blesa M. A. (2004) Solar light induced removal of arsenic from contaminated groundwater: the interplay of solar energy and chemical variables. *Sol. Energy* **77**, 601–613.

Guha Mazumder D. N., Chakraborty A. K., Ghosh A., Gupta J. D., Chakraborty D. P., Dey S. B., N. Chattopadhyay N. (1988) Chronic arsenic toxicity from drinking tubewell water in rural West Bengal. *Bull. WHO* **66**, 499–506.

Guo H., Stüben D., Berner Z. (2007) Removal of arsenic from aqueous solution by natural siderite and hematite. *Appl. Geochem.* **22**, 1039–1051.

Haytowitz D. B., Bhagwat S. (2010) USDA database for the Oxygen Radical Absorbance Capacity of selected foods, release 2, Nutrient Data Laboratory, Beltsville Human Nutrition, Research Center, Agricultural Research Service, U.S. Department of Agriculture (May 2010).

http://www.resultsnowtests.biz/Titratable%20Acidity%20Tests.html (last accssed on 12th October, 2012)

http://www.rwsn.ch/documentation/skatdocumentation.2005-11-15.5001297083/file (last accssed on 29th November, 2012)

Hug S. J. (2001) An adapted water treatment option in Bangladesh: Solar Oxidation and Removal of Arsenic (SORAS). *Environ. Sci.* **5**, 467–479.

Hug S. J., Canonica L., Wegelin M., Gechter D., von Gunten U. (2001) Solar oxidation and removal of arsenic at circumneutral pH in iron containing waters. *Environ. Sci. Technol.* **35**, 2114–2121.

Hug S. J., Leupin O. (2003) Iron-catalyzed oxidation of arsenic(III) by oxygen and by hydrogen peroxide: pH dependent formation of oxidants in the Fenton reaction. *Environ. Sci. Technol.* **37**, 2734–2742.

Impellitteri C. A., Scheckel K. G. (2006) The distribution, solid-phase speciation, and desorption/dissolution of As in waste iron-based drinking water treatment residuals. *Chemosphere* **64**, 875–880.

Kapaj S., Peterson H., Liber K., Bhattacharya P. (2006) Human health effects from chronic arsenic poisoning – a review. *J. Environ. Sci. Health Part A* **41**, 2399–2428.

Lara F., Cornejo L., Yanez J., Freer J., Mansilla H. D. (2006) Solar-light assisted removal of arsenic from natural waters: effect of iron and citrate concentrations. *J. Chem. Technol. Biotechnol.* **81**, 1282–1287.

Leong L. P., Shui G. (2002) An investigation of antioxidant capacity of fruits in Singapore markets. *Food Chem.* **76**, 69–75.

Lien H. L., Wilkin R. T. (2005) High-level arsenite removal from groundwater by zero-valent iron. *Chemosphere* **59**, 377–386.

Majumder A., Chaudhuri M. (2005) Solar photocatalytic oxidation and removal of arsenic from groundwater. *Indian J. Eng. Mat. Sci.* **12**, 122–128.

Mandal S., Padhi T., Patel R. K. (2011) Studies on the removal of arsenic (III) from water by a novel hybrid material. *J. Hazard. Mater.* **192**, 899–908.

McNeill L. S., Edwards M. A. (1995) Soluble Arsenic Removal at Water Treatment Plants. *J. Am. Water Works Assoc.* **87**, 105–113.

Miller H. E., Rigelhof F., Marquart L., Prakash A., Kanter M. (2000) Antioxidant content of whole grain breakfast cereals, fruits and vegetables. *J. Am. Coll. Nutr.* **19**, 312S–319S.

Morgada M. E., Levy I. K., Salomone V., Farias S. S., Lopez G., Litter M. I. (2009) Arsenic (V) removal with nanoparticulate zerovalent iron: Effect of UV light and humic acids. *Catal. Today* **143**, 261–268.

Mukherjee P., Chatterjee D., Jana J., Maity P. B., Goswami A., Saha H., Sen M., Nath B., Shome D., Sarkar M. J., Bagchi D. (2007) In: P. Bhattacharya, A.B. Mukherjee, J. Bundschuh, R. Zevenhoven, R.H. Loeppert (Eds.), Household water treatment option: removal of arsenic in presence of natural Fe-containing groundwater by solar oxidation. Arsenic in Soil and Groundwater Environment: Biogeochemical Interactions, Health Effects and Remediation, Trace Metals and other Contaminants in the Environment, vol. 9. Elsevier B.V., Amsterdam, The Netherlands, pp. 603–622.

Nath B., Chakraborty S., Burnol A., Stüben D., Chatterjee D., Charlet L. (2009) Mobility of arsenic in the sub-surface environment: An integrated hydrogeochemical study and sorption model of the sandy aquifer materials. *J. Hydrol.* **364**, 236–248.

Nath B., Maity J. P., Jean J-S., Birch G., Kar S., Yang H-J., Lee M-K., Hazra R., Chatterjee D. (2011) Geochemical characterization of arsenic-affected alluvial aquifers of the Bengal Delta (West Bengal and Bangladesh) and Chianan Plains (SW Taiwan): Implications for human health. *Appl. Geochem.* **26**, 705–711.

Nath B., Stüben D., Basu Mallik S., Chatterjee D., Charlet L. (2008) Mobility of arsenic in West Bengal aquifers conducting low and high groundwater arsenic. Part I: Comparative hydrochemical and hydrogeological characteristics. *Appl. Geochem.* **23**, 977–995.

Pal T., Mukherjee P. K., Sengupta S., Bhattacharya A. K., Shome S. (2002) Arsenic pollution in groundwater of West Bengal, India – an insight into the problem by sub-surface sediment analysis. *Gondwana Res.* **5**, 501–502.

Penniston K. L., Nakada S. Y., Holmes R. P., Assimos D. G. (2008) Quantitative assessment of citric acid in lemon juice, lime juice, and commercially available fruit juice products. *J. Endourol.* **22**, 567–570.

Ranganathan S. (1985) Manual of food analysis, Central Food and Technological Research Institute (CFTRI), CSRI, Mysore, 3rd edition.

Rice-Evans C. A., Miller N. J., Paganga G. (1996) Structure-antioxidant activity relationships of flavanoids and phenolic acids. *Free Radic. Biol. Med.* **20**, 933–956.

Rice-Evans C. A., Miller N. J., Paganga G. (1997) Antioxidant properties of phenolic compounds. *Trends Plant Sci.* **2**, 152–159.

Schneiter R. W., Middlebrooks E. J. (1983) Arsenic and Fluoride Removal from Groundwater by Reverse Osmosis. *Environ. Int.* **9**, 289–291.

Shen Y. S. (1973) Study of arsenic removal from drinking water. *J. Am. Water Works Assoc.* **65**, 543–547.

Smedley P. L., Kinniburgh D. G. (2002) A review of the source, behaviour and distribution of arsenic in natural waters. *Appl. Geochem.* **17**, 517–568.

Smith A. H., Lingas E. O., Rahaman M. (2000) Contamination of drinking water by arsenic in Bangladesh: A public health emergency. *Bull. WHO* **78**, 1093–1103.

Smith A. H., Steinmans M. C. (2009) Health effects of arsenic and chromium in drinking water: recent human findings. *Annu. Rev. Public Health* **30**, 1–16.

Stangeland T., Remberg S. F., Lye K. A. (2009) Total antioxidant activity in 35 Ugandan fruits and vegetables. *Food Chem.* **113**, 85–91.

United Nations Industrial and Developmental Organization (UNIDO) (2001) Action on elimination-reduction of arsenic in groundwater of West Bengal, India, Vol. I, New Delhi, India.

USDA (2007) USDA database for the Oxygen Radical Absorbance Capacity of selected foods, Nutrient Data Laboratory, Beltsville Human Nutrition Research Center, in collaboration with Arkansas Children's Nutrition Centre, Agricultural Research Service, U.S. Department of Agriculture (November 2007).

van Geen A., Zheng Y., Goodbred J. S., Horneman A., Aziz Z., Cheng Z., Stute M., Mailloux B., Weinmen B., Hoque M. A., Seddique A. A., Hossain M. S., Chowdhury S. H., Ahmed K. M. (2008) Flushing history as a hydrogeological control on the regional distribution of arsenic in shallow groundwater of the BDP. *Environ. Sci. Technol.* **42**, 2283–2288.

Wang H., Cao G., Prior R. L. (1996) Total antioxidant capacity of fruits. *J. Agric. Food Chem.* **44**, 701–705.

CHAPTER 6: HOLLOW FIBER LIQUID-PHASE MICROEXTRACTION (HF-LPME) COMBINED WITH TOTAL REFLECTION X-RAY SPECTROMETRY (TXRF) FOR THE DETERMINATION OF TRACE LEVEL INORGANIC ARSENIC IN WATERS

A microextraction technique in combination with TXRF has been studied and found to be very effective for the determination of As(III) and As(V) in water samples. The method was found to be a less time consuming, low-cost, simple process to measure low concentrations of As in water. Aliquat 336 in 1-octanol was found to be the most appropriate extractant for the determination of inorganic As species. The 3-phase system was found to be the more efficient than the 2-phase system for As extraction as solvent evaporation was less, sample deposition was easier and the pre-concentration was better than with the 2-phase system. For As(III), the optimum pH for best extraction seems to be 13, whereas, for As(V), this is 8.5. The method was also employed to different spiked natural water samples and the results were satisfactory, especially for As(V).

6.1. Introduction

Natural Arsenic (As) contamination of drinking water resources is a serious threat to human health around the globe, specially, in south and south-east Asia (Smedley and Kinniburgh, 2002). During the eighties, several parts of the Bengal Delta Plain (BDP) population were identified as sporadically affected with “Arsenicosis” (IPCS, 2001; Bhattacharyya et al., 2003a). Since mid-nineties, the issue has emerged as a major international concern about the mass poisoning from the continuous and long-lasting As exposure. Millions of the shallow contaminated wells have been identified in BDP for such As menace (Bhattacharyya et al., 2003b). Latin America, especially Argentina, is another area where naturally occurring groundwater As is a widespread phenomenon (Bundschuh et al., 2012). Drinking water has always been considered as the major ingestion route of As to human system (NRC, 2001). The international standard for maximum permissible level of As in drinking water is 10 µg/L recommended by the World Health Organization (WHO) (WHO, 2004).

The inorganic As species, trivalent aresnite [As(III)] and pentavalent arsenate [As(V)], are reported to be more toxic than the organic forms such as monomethylarsonic acid (MMA), dimethylarsinic acid (DMA) and arsenobetaine (AsB) (Sharma and Sohn, 2009; An et al., 2013). Numerous discussions are going around the world to reduce the drinking water standard of As. However, it is still not reduced mostly due to economic and infrastructural deficiencies. Recent report depicts that even if the current standard is lowered to 3 µg/L, which is considered as the Practical Quantitation Level (Mushak, 2000; Rabieh et al., 2013), the risk of cancer will still be quite high. This triggers the requirement for analytical techniques that can determine As at sub µg/L range and less time consuming and very cost-effective at the same time. Very few analytical techniques are available (e.g., inductively coupled plasma-mass spectrometry) that can measure As directly. Arsenic speciation experiments can carried out by hyphenated techniques like liquid chormatography-inductively coupled plasma-mass spectrometry (LC-ICP-MS) (Radke et al., 2012). However, this is very expensive and suffers from matrix effects. On the other side, separation/preconcentration techniques like liquid-liquid extraction and solid-phase microextraction (Mester et al., 2001) can be used. Recently, the use of methods based on liquid-phase microextraction like cloud point extraction (Shemirani et al., 2005), dispersive liquid-liquid microextraction (Rabieh et al., 2013; Basiri et al., 2011) and single-drop microextraction (Fragueiro et al., 2004) has increased to improve sensitivity while reducing interferences.

Liquid-phase microextraction (LPME) is a solvent-minimized, sample pretreatment procedure that needs only a few µL of organic solvents to preconcentrate the analyte from the sample solutions, rather than using several mL of organic solvents in some other existing conventional LLE techniques (Margui et al., 2013a). In general, LPME is used in combination with the various atomic techniques like electrothermal atomic absorption spectrometry (ETAAS), electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) etc. In recent times, another technique, namely total reflection X-ray fluorescence (TXRF) has been used in conjunction with the LPME for the determination of some metals and metalloids (Margui et al., 2013a). Total reflection X-ray fluorescence (TXRF) is a multi-elemental technique specially used for liquids and powdered samples. To analyze samples with TXRF samples has to be provided as thin films on a reflective carrier. However, at present, there is no information available on using the LPME and TXRF together to determine As species in water samples.

In this study, for the first time to the best of our knowledge, we investigate the application of hollow fiber liquid phase microextraction (HF-LPME) technique combined with TXRF for the determination of inorganic As species in water samples. Various factors affecting the microextraction/preconcentration process and the experimental conditions for TXRF measurement has been evaluated in detail. The capability of the method to analyze real environmental samples has been validated by applying it to bottled mineral water, river water and different groundwaters.

6.2. Experimental

6.2.1. Reagents and solutions

The extractants used namely tricaprylmethylammonium chloride (Aliquat 336) was supplied by Sigma-Aldrich, Germany; Tributyl Phosphate (TBP) was from Merck, Germany. Tridodecyl ammonium chloride (TLA.HCl from Merck, Germany) and Tri-isobutyl phosphine sulfide (Cyanex 471 from Cyanamide, Spain) were also used.

The organic solvents used were Cumene, doedecane with 4% dodecanol (all supplied by Merck, Germany) and 1-octanol (Sigma-Aldrich, Spain). All of them were of analytical grade. Stock solutions of 0.1 mg/L As(III) and As(V) were prepared from sodium metaarsenite (Fluka) and di-sodium hydrogen arsenate heptahydrate (Merck, Germany) respectively and were used for the preparation of standards and the spiked solutions. The pH of the solutions was fixed using 0.1 M sodium hydroxide (Panreac, Spain). To prepare the stripping phase, 0.1 M hydrochloric acid (Panreac, Spain) was used. For the interference study, sodium bicarbonate, tri-sodium phosphate 12-hydrate, sodium nitrate (Panreac, Spain), sodium chloride (Fisher chemicals, UK) and sodium sulphate (Merck, Germany) were used. All the solutions were prepared using high purity water obtained from Milli-Q system operating at 18 MΩ (Millipore Corp., Bedford, MA). Two different kind of hollow fiber polypropylene membranes (Membrana, Germany) were used – Q3/2 (pore size 0.2 µm, wall thickness 200 µm, inner diameter 600 µm) and S6/2 (pore size 0.2 µm, wall thickness 450 µm, inner diameter 1800 µm). For all the experiments 3 replicates were used.

6.2.2. Liquid-liquid extraction experiments

In stoppered glass tubes, 5 ml each of the aqueous phase (10 mg/L) containing the analyte and the organic solvent containing the extractants at a concentration of 0.2 M was mixed together and equilibrated for 24 h on a rack rotator (Dinko, Spain) at 40 rpm (Figure 6.1). Then the mixtures were centrifuged (Mixtasel, Selecta, Spain) for 30 minutes at 300 rpm to separate two phases. An inductively coupled plasma atomic emission spectrometer (ICP-AES) (Liberty RL, Varian, Mulgrave, Vic., Australia) and an inductively coupled plasma-quadrapole mass spec-

Figure 6.1. Liquid-Liquid Extraction (LLE) Selection of Extractant and Solvent for arsenic.

-spectrometry (Agilent 7500C ICP-QMS) were used to determine the As(III and V) concentrations (depending on the quantitative concentration range to be determined) remained in the aqueous phase. The pH was determined with a Crison Model GLP 22 pH meter.

6.2.3. Hollow fiber liquid phase microextraction (HF-LPME) experiments

The HF-LPME experiments were carried out using two polypropylene capillary commercial membranes, Q3/2 and S6/2 both with the same pore size (0.2 µm) but different wall thickness (200 µm and 400 µm respectively) and inner diameter (600µm and 1800 µm respectively) . In case of the 2-phase system both types of fibers were tested. For S6/2 membrane (Figure 6.2a), 100 mL of 0.5 mg/L As(III/V) feeding solutions were used keeping the fiber length to 5 cm (rod-shaped with one holder) and the organic solution (0.01 M Aliquat 336 in 1-octanol) was injected inside the lumen and the pores of the fiber. Then the fibers were hanged with a plastic holding cap inside the feeding samples solution and stirred. For the 2-phase system with the Q3/2 fibers, the sample lengths were increased to 10 cm (U-shaped using two holders). In case of the 3-phase system, only S6/2 fibers were used (10 cm fiber length) (Figure 6.2b). The membrane phase (0.2 M Aliquat 336 in 1-octanol) was injected first to impregnate the pores of the hollow fiber membranes. Then the stripping phase (0.1 M HCl) was injected into the fiber lumens in excess in order to ensure that only the aqueous stripping phase remains inside. Thereafter the whole membrane system is hanged into the feeding solution of 180 mL of 0.1 mg/L of As(III/V). The whole system was then left for stirring for the desired time on a magnetic stirrer (Multistirrer 15, Fisher scientific) for equilibration.

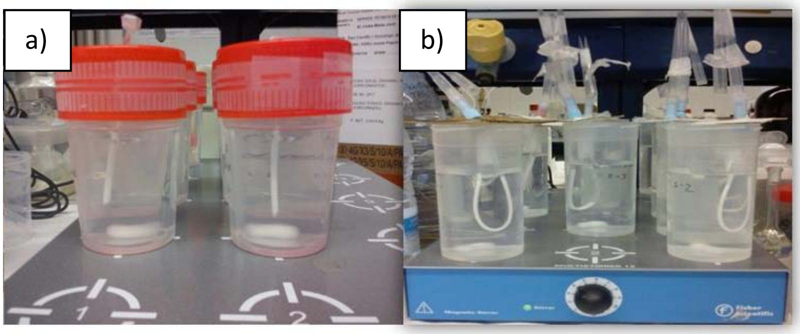


Figure 6.2. a) 2-phase HF-LPME with S6/2 fibers, b) 3-phase HF-LPME with S6/2 fibers.

After equilibration, the receiving phase (organic phase in case of 2-phase and aqueous phase in case of the 3-phase system) was collected from the hollow fiber lumens. Then these preconcentrated samples were analyzed using TXRF (the detail of this technique is discussed in the following section).

6.2.4. Total reflection X-ray fluorescence (TXRF) analysis

A benchtop spectrometer "S2 PICOFOX" (Bruker AXS Microanalysis GmbH, Berlin, Germany) was employed to anlyze the preconcentrated samples and standards (Figure 6.3). The spectrometer specifications and operating conditions are summarized in Table 6.1. To get the best instrumental sensitivity, the operating conditions for the TXRF measurements are also very important. The X-ray tube was selected to work under conditions of maximum efficiency of excitation (50 kV, 1 mA, max. power 50 W). A measuring time of 2000 s was selected as a trade-off between an acceptable instrumental sensitivity, repeatability of measurements and total analysis time. The use of W-target X-ray tube allows the TXRF analysis of high atomic number elements such as As using the K-lines (Margui et al., 2013a). No cooling media is needed as it is equipped with air-cooled low-power X-ray tube and a Peltier cooled silicon drift detector and thus gives an additional advantage over other available techniques. Spectra Plus 5.3 (Bruker AXS Microanalysis GmbH, Berlin, Germany) software was used to evaluate the analyte peak area in the spectra.

Table 6.1. Summary of TXRF spectrophotometer operating condition.

Features	**Specification**
X-ray tube	W
Rating	50kV, 1 mA
Detector	Si drift detector, 10 mm2, <160 eV, Resolution Mn-K_α
Working environment	Air
Optics	Multilayer Ni/C, 17.5 KeV, 80% reflectivity
Size	600 x 300 x 450 mm
Weight	37 kg
Sample platform	Cassette changer for 25 samples
Time needed to analyze each reflector	2000 s

Sample deposition is a very important aspect to obtain satisfactory analytical results in TXRF. In this study, we have used quartz reflectors (diameter 30 mm and a thickness of 3 mm ± 0.1 mm) (Bruker-AXS, Germany) as sample holders. For the analysis of the extracts from the HF-LPME 2-phase system, the organic analyte solution was directly deposited on the reflectors and subsequently dried at 100 ºC to facilitate the generation of a small sample spot at the center of the reflector for complete exposition of the X-ray beam. In case of the 3-phase system, the reflector surface was coated with 10 µL of silicon solution in isopropanol (Serva Eltrophoresis GmbH, Germany) prior to the deposition of the aqueous analyte solution to confine the drop at the center of the reflector and then measured in the same way as the 2-phase system. Then 10 µL of preconcentrated sample or standard solutions were deposited at the centre of the pre-heated reflector followed by drying on a hot plate at ~ 80 ºC and subsequent analysis with TXRF spectrometer (Figure 6.3).

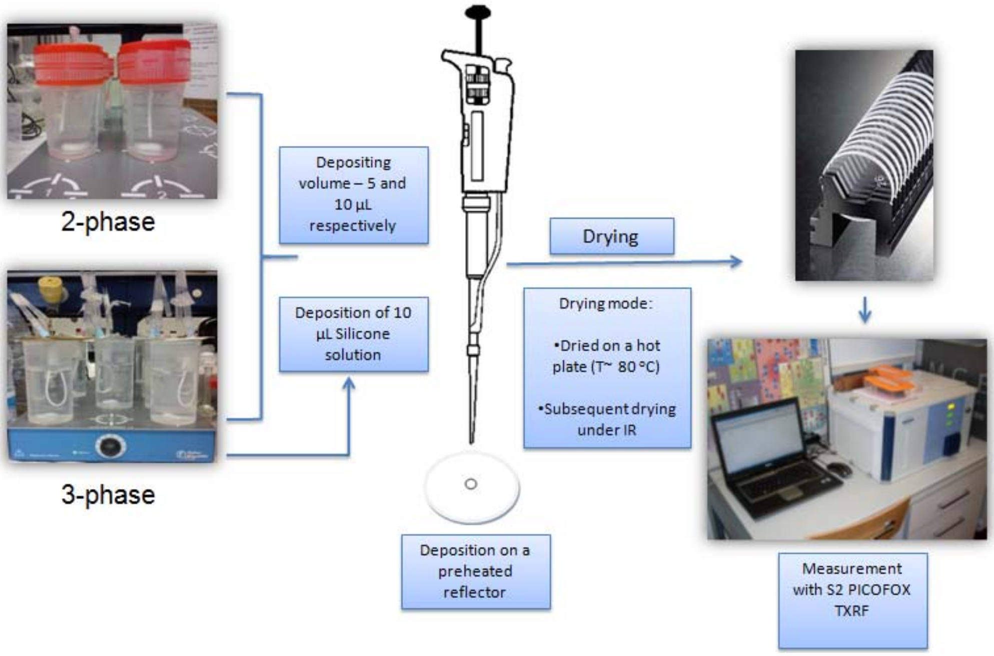


Figure 6.3. Schematic set up for TXRF experiment.

6.3. Results and discussion

6.3.1. Selection of extractant and organic phase

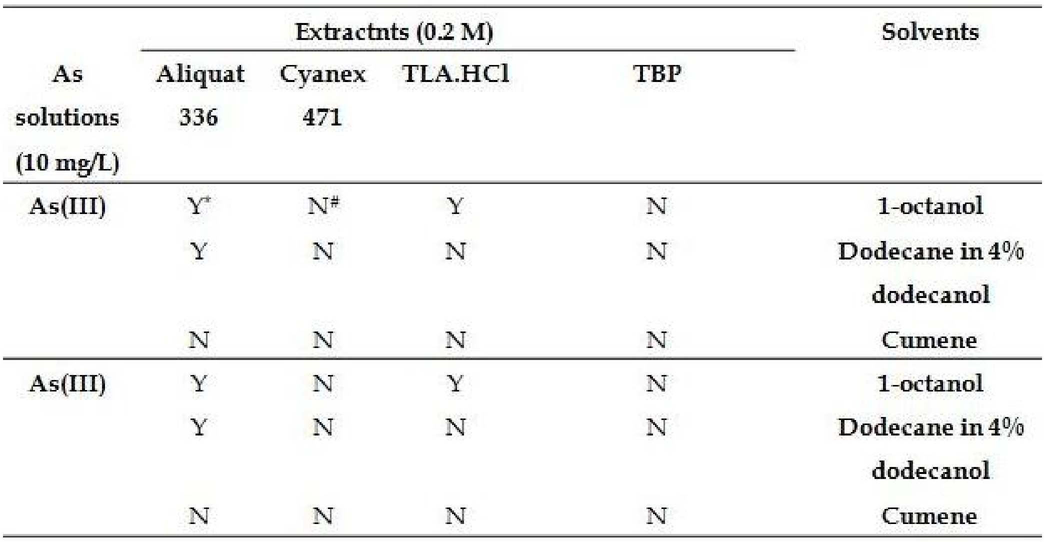
Preliminary liquid-liquid extraction experiments were performed to establish the most effective extractant and organic phase for the HF-LPME procedure for As(III) and As(V), through trial experiments with different extractants and organic solvents. The experimental conditions and obtained results are summarized in Table 6.2a. Only those organic solvents that have low solubility in water, low volatility and polarity that matches with the polypropylene fibres were selected, as these are the essential requirement for the HF-LPME methods (Dadfarnia and Haji Shabani, 2010; Luciano et al., 2010; Pena-Pereira et al., 2010; Han and Row, 2012; Zeng et al., 2011; Margui et al., 2013b).

5 mL organic phase containing 0.2 M concentration of each extractant individually with another 5 mL of aqueous phase containing 10 mg/L of As(III) and As(V) was mixed. The solutions were equilibrated for 24 h and then centrifuged at 300 rpm to separate the phases prior to analysis of the As content in aqueous solution with ICP-AES and ICP-QMS.

Among the different combinations, Cyanex 471 and TBP has been found to form third phase in all the solvents (1-octanol, dodecane with 4% dodecanol and cumene) and therefore abandoned. Aliquat 336 in cumene and TLA.HCl has been found to be non-effective to extract As(III) or As(V). TLA.HCl in dodecane with 4% dodecanol has not found to extract As efficiently either. Therefore, only three combinations (Aliquat 336 in 1-octanol and in dodecane with 4% dodecanol along with TLA.HCl in 1-octanol) were shown as the most effective solutions to extract As(III) and As(V) from the aqueous phase (Table 6.2b). Although, the problem of third phase formation remained (very slightly) in case of the TLA.HCL in 1-octanol solution. We have tried to reduce the extractant concentration from 0.2 M to 0.01 M to avoid any third phase formation with TLA.HCl in 1-octanol system, but failed. Therefore, Aliquat 336 in 1-octanol has been selected as the most appropriate option for further microextraction experiments.

Table 6.2. Combinations for initial liquid-liquid extraction experiments – a) phase 1 and b) phase 2 (experiments were done only with the positive combinations of phase a, and extractant concentration diluted).

a)

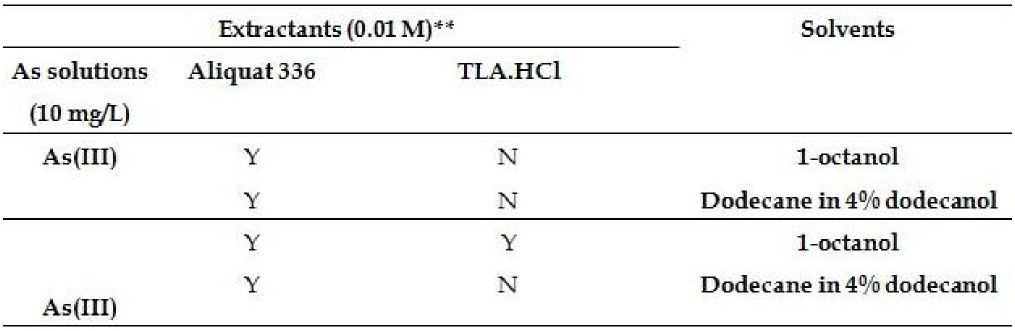


As solutions (10 mg/L)	Extractnts (0.2 M)				Solvents
	Aliquat 336	Cyanex 471	TLA.HCl	TBP	
As(III)	Y[*]	N[#]	Y	N	1-octanol
	Y	N	N	N	Dodecane in 4% dodecanol
	N	N	N	N	Cumene
As(III)	Y	N	Y	N	1-octanol
	Y	N	N	N	Dodecane in 4% dodecanol
	N	N	N	N	Cumene

Note – 5 mL aqueous phase + 5 mL organic phase; equilibration time – 24 h; Centrifugation – 30 m at 300 rpm

[*] Y = positive result for extraction; [#] N = negative result for extraction

b)



As solutions (10 mg/L)	Extractants (0.01 M)**		Solvents
	Aliquat 336	TLA.HCl	
As(III)	Y	N	1-octanol
	Y	N	Dodecane in 4% dodecanol
As(III)	Y	Y	1-octanol
	Y	N	Dodecane in 4% dodecanol

**This time the extractant was diluted to avoid chance of 3rd phase formation, if any.

6.3.2. 2-phase hollow fiber liquid phase microextraction (HF-LPME) system

For the 2-phase HF-LPME experiments, we tried two different set of fibers using equilibration time of 24 h. In case of the larger diameter fibers (S6/2) fibers, fiber length was kept to 5 cm. The experiment was carried out using 0.01 M of Aliquat

336 in 1-octanol as the organic phase inside the lumen of the fiber and 100 mL aqueous phase containing 0.5 mg/L of As(III) or As(V) solutions at pH 13 and 8.5 respectively. The reproducibility was very poor and hence we shifted to the smaller diameter fibers (Q3/2) with the same system. In this case, the fiber length was increased to 10 cm to have better reproducibility. However, again the results were not satisfactory as the reproducibility could not be improved possibly due to loss of organic acceptor phase during the process. Another problem with the 2-phase system (for both S6/2 and Q3/2 fibers) was the difficulty in depositing and stabilizing the organic acceptor phase at the center of the reflector during the TXRF analysis.

6.3.3. Using 3-phase hollow fiber liquid phase microextraction (HF-LPME)

In case of the 3-phase HF-LPME, we have used the S6/2 larger diameter fibers with a fiber length of 10 cm. The feeding phase concentration and volume was kept at 0.1 mg/L and 180 mL respectively. 0.1 M HCl was used as the stripping phase as some of the previous studies found it effectively working for As extraction using supported liquid membranes (SLM's) (Guell et al., 2010). The membrane phase was Aliquat 336 in 1-octanol. The 3-phase system has few advantages over the 2-phase system as the problem of solvent evaporation was less (in this it is the aqueous phase that needed to be deposited on the sample carriers/reflectors), sample deposition was easier and the pre-concentration was better than in the 2-phase system. To optimize the most effective operating condition for the 3-phase HF-LPME technique to get high pre-concentration rate of As, different controlling parameters (e.g., concentration of the extractant, kinetics, effect of pH, distribution of inorganic As species, competing anions) were carefully investigated. We have examined each affecting variable individually at a time to establish the optimum experimental working condition with this method.

6.3.3.1. Effect of extractant concentration

Three different Aliquat 336 concentrations (0.01 M, 0.1 M and 0.2 M) in 1-octanol were tested in the 3-phase HF-LPME system, keeping the pH of the As(III) and As(V) feeding solutions at 13 and 8.5 respectively. It is clearly visible from Figure. 6.4, that Aliquat 336 concentration of 0.2 M was found to be most efficiently extracting both As(III) and As(V) from the feeding phase than 0.01 or 0.1 M. However, the extraction efficiency is slightly higher in case of As(V). Therefore, for all the other experiments, 0.2 M Aliquat 336 in 1-octanol were used as the membrane phase.

To make the extraction process faster, usually the samples are vigorously stirred or agitated. The speed of the extraction process is controlled by the kinetics of the reactions and the stirring rate of the HF-LPME system (Dadfarnia and Haji Shabani, 2010; Han and Row, 2012; Margui et al., 2013b). Therefore, these parameters were evaluated using 180 mL of 0.1 mg/L As(III/V) feeding phase, 0.2 M Aliquat 336 in 1-octanol as membrane phase and 0.1M HCl as stripping phase.

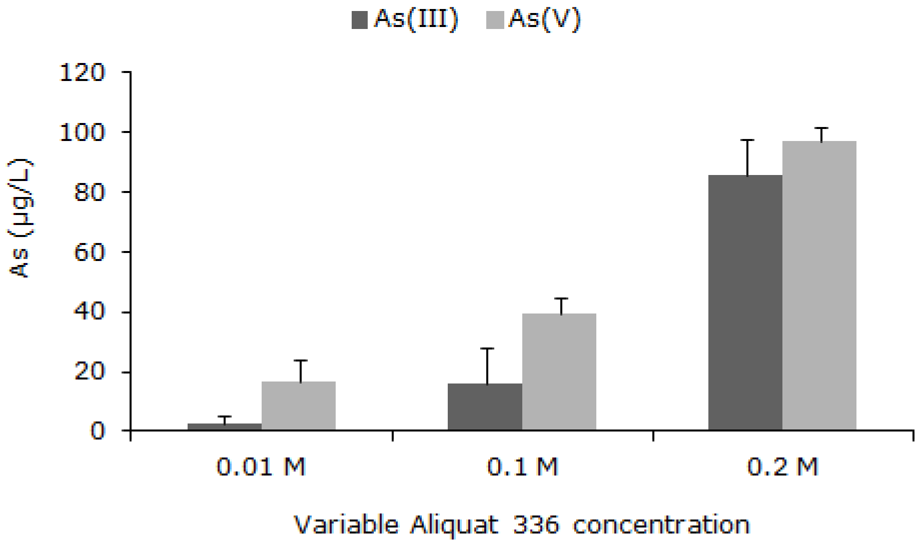


Figure 6.4. Effect of Aliquat 336 (in 1-octanol) concentration on the extraction efficiency (n=3).

6.3.3.2. Effect of extraction time

For the kinetic study, samples were collected at 1, 2, 3, 4, 6, 8 and 24 h. It is evident from Figures 6.5a and b that for both As(III) and As(V), the extraction reached a maxima at 4 h and then again decrease with time. Here again though, the extraction efficiency was better in case of As(V) than As(III). Hence, an equilibration time of 4 h was fixed to examine the effect of agitation speed in other subsequent experiments.

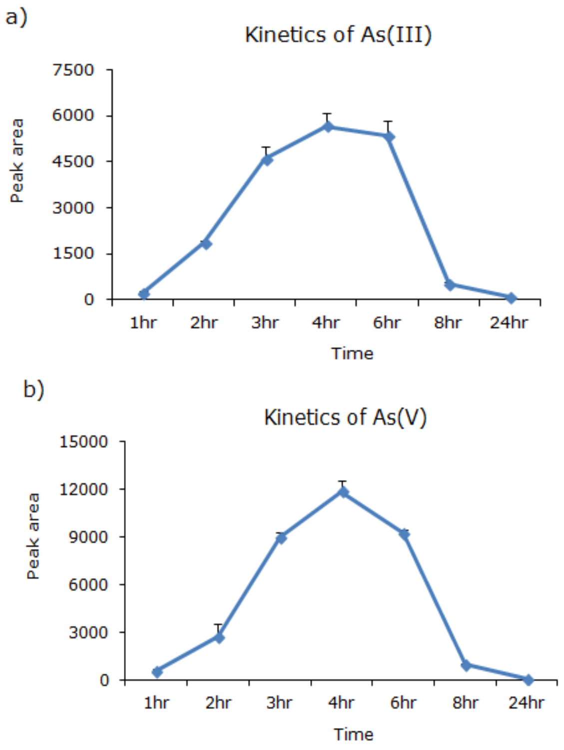


Figure 6.5. Kinetics of a) As(III) and b) As(V) extraction (n=3).

6.3.3.3. Effect of stirring rate

In case of both As(III) and As(V), the extraction efficiency was almost similar at 440 and 660 rpm (Figure 6.6). In fact, it was very slightly higher in case of 660 rpm. However, at 660 rpm, it was difficult to hold the hollow fibers consistently affecting the stability of the 3-phase system and subsequent reproducibility of the system. In addition, a notable vortex was generated at the top-surface of the sample solution that can also hamper the extraction process (Margui et al., 2013b).

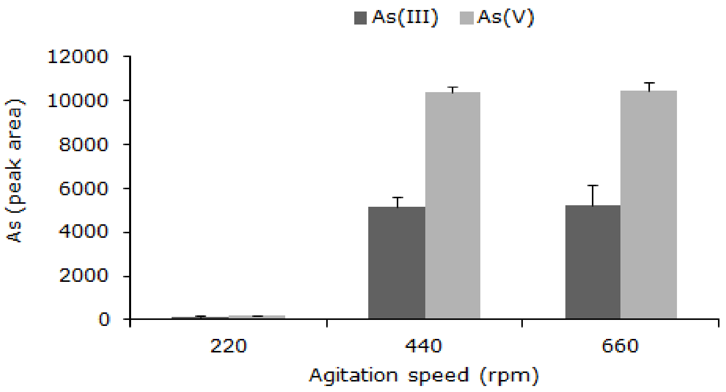


Figure 6.6. Effect of agitation speed on extraction (n=3).

Therefore, an agitation speed of 440 rpm was set to carry out the subsequent experiments.

6.3.3.4. Effect of pH

The effect of pH on the extraction of As was investigated within the range of 5.5-13 using the same experimental conditions. In case of As(III), the extraction efficiency increased and reached the maxima in the high alkaline range at pH 13 (Figure 6.7). On the contrary, for As(V), the high extraction was found at pH 8.5 (Figure 6.6). The extraction efficiency of As(III) at this pH is very negligible, likewise the extraction of As(V) at pH 13 is not much (Figure 6.7).

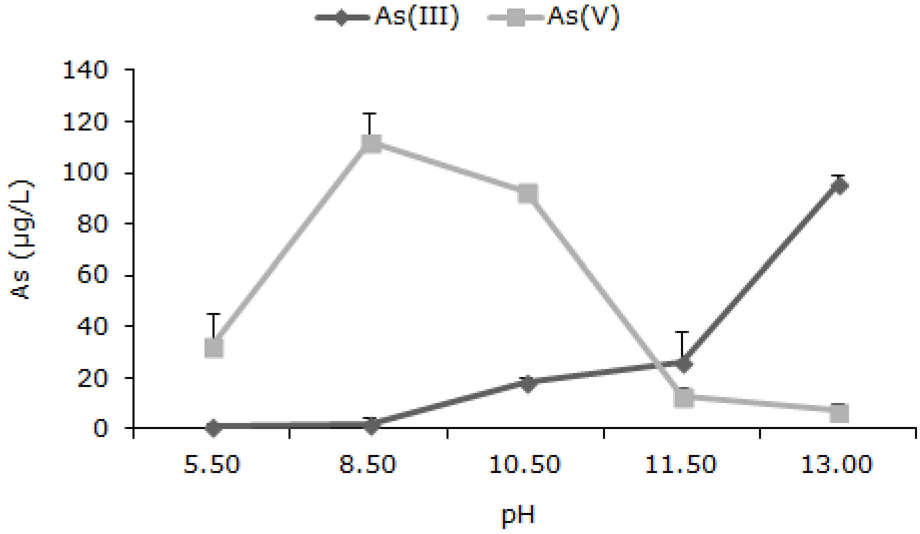


Figure 6.7. Effect of pH on extraction efficiency (n=3).

At around pH 13, the major dominating species of As(III) is the anions $HAsO_3^{2-}$ and AsO_3^{3-}. On the other hand, at pH 8.5, the major dominating species of As(V) is the anionic $HAsO_4^{2-}$ (Figures 6.8a and b).

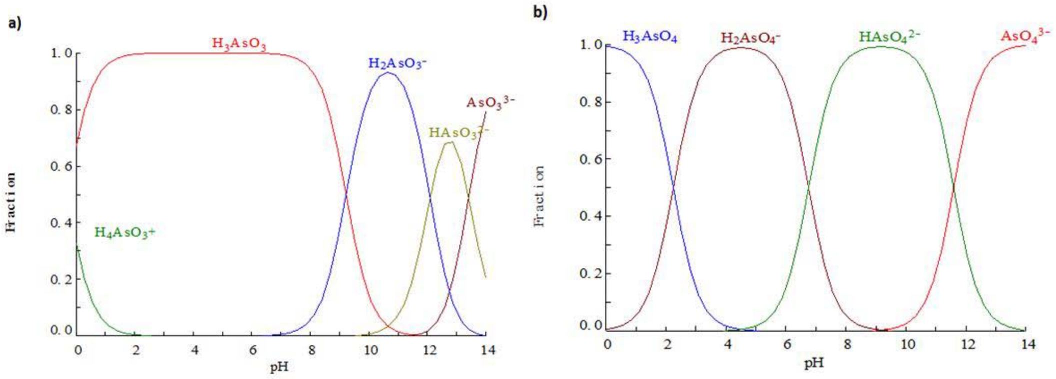


Figure 6.8. Arsenic speciation (molar fraction) at different pH a) As(III), b) As(V).

6.3.3.5. Effect of inorganic arsenic species distribution

The concentration ratios of As(III) and As(V) in different type of environmental waters vary from one to another (Radke et al., 2012). This could significantly affect the extraction efficiency of inorganic As. Experiments were designed to investigate the effect of variable concentrations [As(III)/As(V)] on the extraction by the HF-LPME method. Experiments were carried out at both pH values 13 and 8.5, which are most favourable for As(III) and As(V) respectively (Figure 6.9). Three different ratios, 70/30, 50/50 and 30/70 were examined, keeping the total As concentration to 100 µg/L and considering that at pH 13, only As(III) was extracted and at pH 8.5, only As(V) was extracted exclusively.

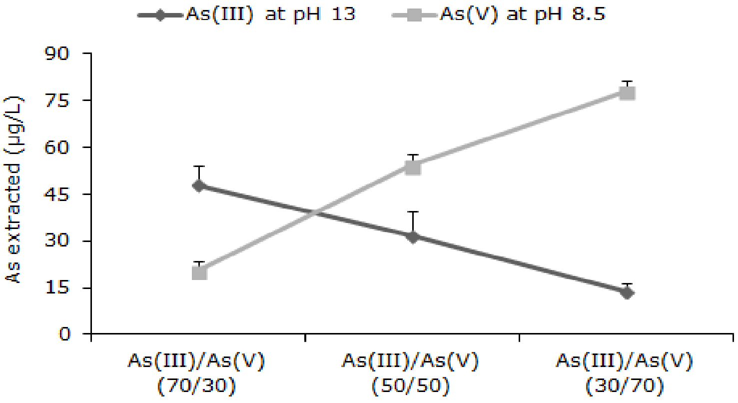


Figure 6.9. Influence of As species ratio at corresponding favourable pH's of As(III) and As(V) (n=3).

As(III) was preferentially extracted at pH 13, whereas, As(V) was strongly extracted at pH 8.5 (Table 6.3). At pH 8.5, it is clear that extraction of As(V) enhanced proportionally with the decreased As(III)/As(V) ratio. In contrast, at pH 13, As(III) extraction was decreased with the decrease in As(III)/As(V) ratio. The overall extraction was still better for As(V) though. The extraction of As(V) was found slightly higher than 100% in some cases, this may be due to possible oxidation of some As(III) during the equilibration. This indirectly shows that complete speciation is possible at two different pH's, especially at pH 8.5, where there is almost exclusively As(V) had been extracted.

Table 6.3. Effect of species distribution on As transport through the membrane and subsequent extraction considering exclusive extraction of As(III) and As(V) at pH 13 and 8.5 respectively (n=3).

	Added As(III) (µg/L)	**Added As(V) (µg/L)**	**Total As measured = As(V) extracted (µg/L)**
At pH 8.5	70	30	20.36 ± 0.41
	50	50	54.3 ± 0.53
	30	70	77.9 ± 0.76
	Added As(III) (µg/L)	**Added As(V) (µg/L)**	**Total As measured = As(III) extracted (µg/L)**
At pH 13	70	30	47.93 ± 0.98
	50	50	31.61 ± 1.08
	30	70	14.01 ± 0.94

6.3.3.6. Effect of competing anions and humic acids

In case of different environmental waters, various competing, interfering ions (especially anions) and the dissolved organic compounds can influence the extraction of As in form of oxy-anions in the HF-LPME operating conditions. Therefore, the effect of these ions together along with humic acids was studied using synthetic water samples containing 0.1 mg/L As (both III and V) at their respective favourable pH mentioned above) along with specified concentrations of different salts and humic acids (Table 6.4).

Table 6.4. Summary of anions and humic acid concentrations to examine the salt effect on extraction.

	HCO_3^-	SO_4^{2-}	Cl^-	NO_3^-	PO_4^{3-}	Humic acids
Concentration (mg/L)	100	1.8	10	1	3	8

Figure 6.10 shows that in case of As(III) both interfering ions and humic acids had some effect on the extraction efficiency. However, in case of As(V), the effect was similar only with the anions. The humic acids do not hinder the extraction efficiency of As(V) at all.

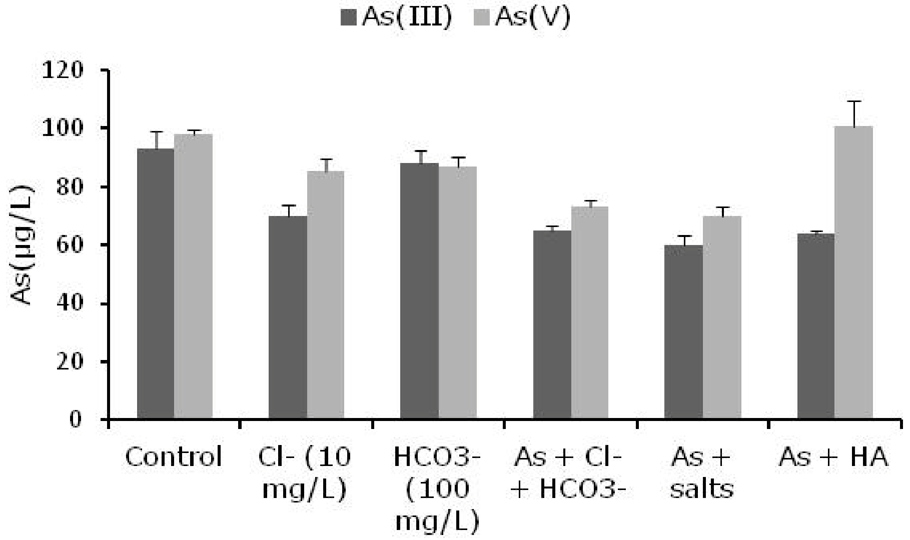


Figure 6.10. Effect of interfering anions and humic acids on extraction efficiency of As(III) and As(V).

Among the anions used in the above experiment, the concentration of HCO_3^- and Cl^- was higher than the rest and as these two anions can significantly influence the extraction of As, we further examined the influence of these two anions more in detail. To do that, we added HCO_3^- and Cl^- individually and together fixing concentrations at 100 mg/L of HCO_3^- and 10 mg/L of Cl^-, both for As(III) and As(V)

(Figure 6.10). The effect of HCO_3^- was not much both in case of As(III) and As(V), however, the effect of Cl^- was notable for As(III) (Figure 6.10).

6.3.4. Optimization of the total reflection X-ray fluorescence (TXRF) experimental conditions

The principle goal of sample preparation in TXRF is to obtain the target sample as a thin layer (<100 µm) on a carrier with high reflectivity sample support. Therefore, in order to get total reflectance the sample deposition volume is important. In addition, only a few microliters of sample should be deposited on the reflector as the diameter of the sample droplet should be within the beam size so that the drop could get completely exposed to the illuminating X-ray (Margui et al., 2013a). Experiments were carried out to examine the effect of sample deposition volume on the As peak area to analyze preconcentrated standard solution of 0.1 mg/L As(III and V) solution (Figure 6.11). It is clear that the analyte response were much higher using a double deposition of (5+5) µL or 10 µL of sample volume on the reflectors than a single deposition of 5 µL. However, as it can be seen that the element sensitivity was the highest with the 10 µL single deposition. Therefore, a sample deposition volume of 10 µL was used to analyze the peak area for all the preconcentrated samples generated through the HF-LPME experiments to have a centered thin film on the reflectors and higher element sensitivity.

After the sample deposition, it is important to fix a suitable process to dry the sample droplet for a simple and cost-effective sample preparation method prior to the analysis with TXRF. Among the available heating techniques (e.g., using laminar flow hood at room temperature, IR-lamp, drying in an oven), pre-heated (on a hot plate, ~ 80 ^oC) quartz reflectors were used for the sample deposition, as already reported for the HF-LPME systems analyzing metals (Margui et al., 2013b). Another additional heating was done using the hot plate (T ~ 80 ^oC) after the aqueous droplet was deposited.

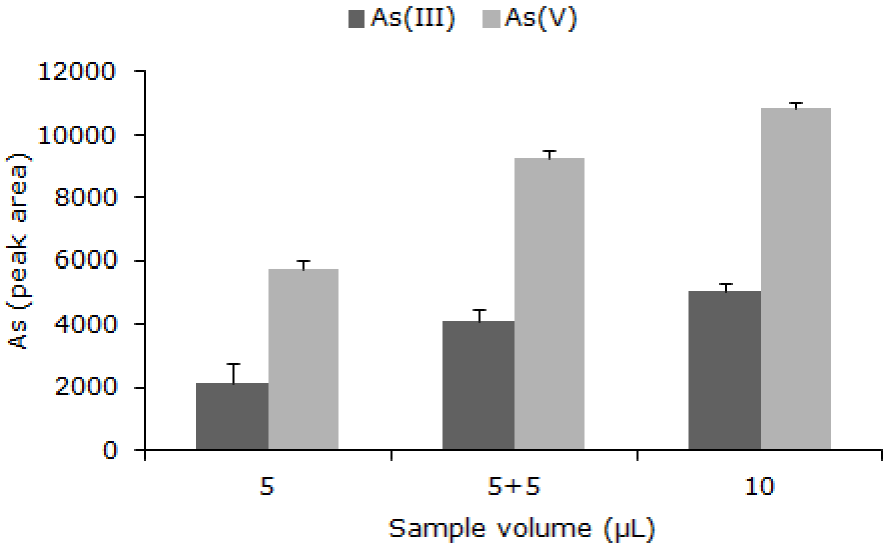


Figure 6.11. Influence of sample volume deposited on the quartz reflectors during measurement with TXRF.

6.3.5. Analytical figures of merit

This study was conducted to evaluate the advantages of using HF-LPME preconcentration method to determine inorganic As species in water samples. In this context, 10 µL solution of As standard solution containing 100 mg/L and a preconcentrated solution of 5 µg/L solution were analyzed with TXRF (Figure 6.12). It is very clear from the spectra that the absolute element sensitivity of the preconcentrated sample was much higher than the one without preconcentration. To estimate limit of detection (LOD) net intensity and background of the spectra was used according to the 3σ approach (Klockenkamper, 1997). The detection limits calculated by this method were found to be around 5 µg/L and 0.03 µg/L for the solutions without and after preconcentration respectively. The limit of detection calculated for the HF-LPME-TXRF system is more than 100 times lower than the maximum permissible As concentration in drinking water, which proves that the method under investigation is appropriate for the determination of As in water.

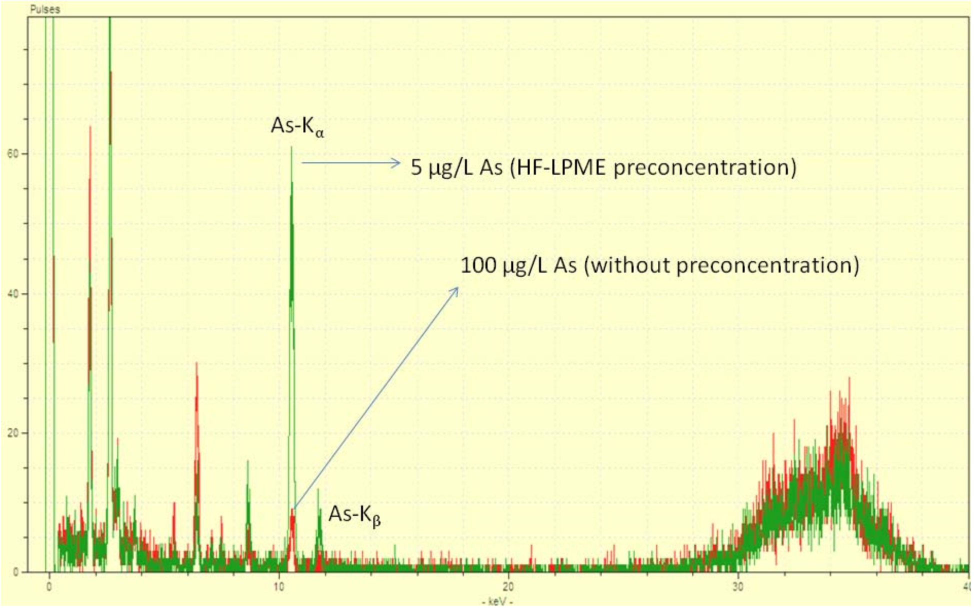


Figure 6.12. TXRF spectra showing the As-K_α and As-K_β lines and the comparative element peaks for preconcentrated solution of 5 µg/L As through HF-LPME method and a 100 µg/L As solution without preconcentration.

The preconcentration and measurement procedure was applied to aqueous standard solutions in the range of 0.5-200 µg/L. As peak areas were plotted against the known As concentrations in the aqueous solutions. It was found that the calibration curve was linear in the range of 0.5-200 µg/L for both As(III) and As(V) with determination coefficients (R^2) of 0.9882 and 0.9976 respectively (Figures 6.13a and b).

Intra-day (with 2 h interval) and inter-day experiments were carried out to investigate the precision of the proposed method both for As(III) and As(V) (Table 6.5). It is evident that both intra-day and inter-day results are very reproducible and it is even better in case of As(V).

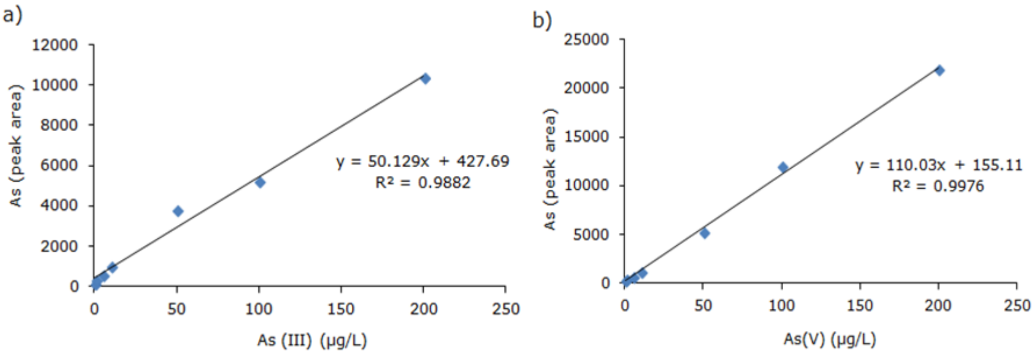


Figure 6.13. Calibration plots for a) As(III) and b) As(V) for preconcentrated standards in the range of 0.05-200 μg/L As(III and V) using the HF-LPME microextraction followed by determination with TXRF.

Table 6.5. Precision results for Intra-day and Inter-day experiments with preconcentrated 100 μg/L solutions, at pH 8.5 [for As(III)] and 13 [for As(V)] using the HF-LPME microextraction followed by determination with TXRF (n=3 for each of the experiments).

		1st run	**2nd run**	**3rd run**
Intra-day	As(III)	75.67 ± 1.37	79.83 ± 0.98	85.59 ± 1.26
	As(V)	97.26 ± 0.38	95.52 ± 0.70	94.17 ± 0.58
		Day 1	**Day 2**	**Day 3**
Inter-day	As(III)	75.45 ± 1.04	76.12 ± 1.12	90.12 ± 0.98
	As(V)	92.99 ± 0.40	94.56 ± 0.84	97.10 ± 0.79

6.3.6. Application to natural water samples

To test the capability of the proposed preconcentration and determination method for analysis of real samples, it is applied to different natural water samples having different hydrochemical matrices (Table 6.6).

Table 6.6. Hydrochemical summary of the natural water samples.

Sample	Cl^- (mg/L)	SO_4^{2-} (mg/L)	NO_3^- (mg/L)	PO_4^{3-} (mg/L)	NO_3^{2-} (mg/L)	PO_4^{3-} (mg/L)	HCO_3^- (mg/L)
GW I	563.36	13.23	bdl	0.08	bdl	0.08	3959
GW II	71.05	0.73	bdl	0.08	bdl	0.08	3673
GW III	71.21	30.66	1.26	0.03	1.26	0.03	336
GW IV	13.00	5.49	0.16	0.01	0.16	0.01	420
Mineral water	6.72	4.41	0.80	bdl	0.80	bdl	na
River water	39.62	26.59	1.57	0.08	1.57	0.08	na

Limit; na – not available; bdl – below detection limit

Table 6.6. continues

Sample	Conductivity (mS/cm)	pH	Fe (mg/L)	Mn (mg/L)
GW I	4620	6.55	bdl	bdl
GW II	4750	6.47	12.7	0.006
GW III	813	6.43	bdl	bdl
GW IV	521	7.1	bdl	bdl
Mineral water	na	na	na	na
River water	na	na	na	na

The obtained results are shown in Table 6.7. As none of the samples were known to have any history of inherent As concentration, thus all the samples were spiked with 0.1 mg/L As(III or V) prior to the preconcentration experiments. In case of As(III), the extraction efficiency was not that high except for the mineral water, river water and one groundwater sample (GW III).

Table 6.7. Results with spiked environmental waters using the HF-LPME-TXRF combined method. MW – bottled mineral water; RW – river water; GW I, GW II, GW III and GW III – groundwater I, II, III and IV respectivel (n=3 for each of the samples). The spiked concentration was 0.1 mg/L of As(III) and As(V).

	Control	Mineral water	River water	GW I	GW II	GW III	GW IV
As(III)	81.99 (± 1.87)	77.63 (± 1.61)	71.56 (± 1.31)	54.00 (± 1.67)	35.41 (± 1.81)	67.07 (± 1.43)	49.63 (± 1.38)
As(V)	92.62 (± 0.45)	92.50 (± 0.61)	91.03 (± 0.88)	72.77 (± 0.32)	51.55 (± 0.78)	84.44 (± 0.70)	75.40 (± 0.39)

However, in case of As(V), the system were found to work very fine as recovery in the range of ~ 72-93 % was observed, except for one groundwater sample (GW II) possibly because it was very high in Fe content (Tables 6.6 and 6.7). This suggests that the method has worked, however, available As species might have co-precipitated with Fe.

6.4. Conclusion

A new microextraction technique in combination with TXRF technique was studied and found to be very effective for the determination of As(III) and As(V) in water samples. The method was found to be a less time consuming, low-cost, simple process to measure low concentrations of As in water. The results of the present study show that the combined HF-LPME-TXRF system is a powerful methodology. Aliquat 336 in 1-octanol was found to be the most appropriate extractant for the determination of As. Sample deposition was difficult with the 2-phase system and the precision was also not satisfactory. The 3-phase system was found to be the more efficient than the 2-phase system for Arsenic extraction. The 3-phase system has few advantages over the 2-phase system as the problem of solvent evaporation was less, sample deposition was easier and the pre-concentration was better than the 2-phase system. For both As(III) and As(V) the optimized equilibration time was 4 h. For As(III), the optimum pH seems to be 13, whereas, for As(V), this is 8.5. The low operating and maintenance costs of the TXRF benchtop system (cooling media and gas consumption are not needed) makes it a interesting analytical tool together with the HF-LPME method for the determination of As in environmental water samples even though the sensitivity could be comparatively lower than some of the other methods. However, the LOD's were improved by more than ten folds in magnitude after the preconcentration through HF-LPME when compared to the direct measurements without preconcentration. The method was also employed to different spiked environmental water samples and the results were satisfactory, especially with As(V).

References

An J., Kim K-H., Kim J-A., Jung H., Yoon H-O., Seo J. (2013) A simplified analysis of dimethylarsinic acid by wavelength dispersive X-ray fluorescence spectrometry combined with a strong cation exchange resin. *J. Hazard. Mater.* **260**, 24–31.

Basiri S., Moinfar S., Hosseini M. R. M. (2011) Determination of As(III) using developed dispersive liquid–liquid microextraction and flame atomic absorption spectrometry, *Intern. J. Environ. Anal. Chem.* **91**, 1453–1465.

Bhattacharyya R., Chatterjee D., Nath B., Jana J., Jacks G., Vahter M. (2003a) High arsenic groundwater: Mobilization, metabolism and mitigation – An overview in the Bengal Delta Plain. *Mol. Cell. Biochem.* **253**, 347–355.

Bhattacharyya R., Jana J., Nath B., Sahu S. J., Chatterjee D., Jacks G. (2003b) Groundwater As mobilization in the Bengal Delta Plain, the use of ferralite as a possible remedial measure – A case study. *Appl. Geochem.* **18**, 1435–1451.

Bundschuh J., Litter M. I., Parvez F., Román-Ross G., Nicoli H. B., Jean J-S., Liu C-W., Lopez D., Armienta M. A., Guilherme L. R. G., Cuevas A. G., Cornejo L., Cumbal L., Toujaguez R. (2012) One century of arsenic exposure in Latin America: A review of history and occurrence from 14 countries. *Sci. Total Environ.* **429**, 2-35.

Dadfarnia S., Haji Shabani A. M. (2010) Recent development in liquid phase microextraction for determination of trace level concentration of metals – A review. *Anal. Chim. Acta* **658**, 107–119.

Fragueiro S., Lavilla I., Bendicho C. (2004) Headspace sequestration of arsine onto a Pd(II)-containing aqueous drop as a preconcentration method for electrothermal atomic absorption spectrometry. *Spectrochim. Acta B* **59**, 851–855.

Güell R., Fontàs C., Salvadó V., Anticó E. (2010) Modelling of liquid–liquid extraction and liquid membrane separation of arsenic species in environmental matrices. *Sep. Purif. Technol.* **72**, 319–325.

Han D., Row K. H. (2012) Trends in liquid-phase microextraction, and its application to environmental and biological samples. *Microchim. Acta* **176**, 1–22.

International Programme on Chemical Safety (IPCS) (2001) Arsenic and arsenic compounds (2nd ed.) English and Bengali version. Geneva, Switzerland: WHO and WHO-WBVA.

Klockenkamper R. (1997) Total X-ray Fluorescence Analysis, ed. J. D., Winefordner, John Wiley & Sons, New York.

Luciano R. M., Bedendo G. C., Carletto J. S., Carasek E. (2010) Isolation and preconcentration of Cd(II) from environmental samples using polypropylene porous membrane in a hollow fiber renewal liquid membrane extraction procedure and determination by AAS. *J. Hazard. Mater.* **177**, 567–572.

Margui E., Queralt I., Hidalgo M. (2013a) Determination of Cd at ultra-trace levels in environmental water samples by means of total reflection X-ray spectrometry after dispersive liquid-liquid microextraction. *J. Anal. At. Spectrom.* 28, 266–273.

Margui E., Sague M., Queralt I., Hidalgo M. (2013b) Liquid phase microextraction strategies combined with total reflection X-ray spectrometry for the determination of low amounts of inorganic antimony species in waters. *Anal. Chim. Acta* **786**, 8–15.

Mester Z., Sturgeon R., Pawliszyn J. (2001) Solid phase microextraction as a tool for trace element speciation. *Spectrochim. Acta B* **56**, 233–260.

Mushak P. (2000) Arsenic and old laws, a scientific and public health analysis of arsenic occurrence in drinking water, its health effects, and EPA's outdated arsenic water standard. http://www.nrdc.org/water/drinking/arsenic/chap1.as (last accssed on 24th June, 2013).

National Research Council (NRC) (2001) Arsenic in Drinking Water. National Academy of Sciences, Washington DC.

Pena-Pereira F., Lavilla I., Bendicho C. (2010) Liquid-phase microextraction approaches combined with atomic detection: A critical review. *Anal. Chim. Acta* **669**, 1–16.

Rabieh S., Bagheri M., Planer-Friedrich B. (2013) Speciation of arsenite and arsenate by electrothermal AAS following ionic liquid dispersive liquid-liquid microextraction. *Microchim. Acta* **180**, 415–421.

Radke B., Jewell L., Namiesnik J. (2012) Analysis of arsenic species in environmental samples. *Clin. Rev. Anal. Chem.* **42**, 162–183.

Sharma V. K., Sohn M. (2009) Aquatic arsenic: Toxicity, speciation, transformations, and remediation. *Environ. Int.* **35**, 743–759.

Shemirani F., Baghdadi M., Ramezani M. (2005) Preconcentration and determination of ultra trace amounts of arsenic(III) and arsenic (V) in tap water and total arsenic in biological samples by cloud point extraction and electrothermal atomic absorption spectrometry. *Talanta* **65**, 882–887.

Smedley P. L., Kinniburgh D. G. (2002) A review of the source, behaviour and distribution of arsenic in natural waters. *Appl. Geochem.* **17**, 517–568.

World Health Organization (WHO) (2004) Guidelines for Drinking-Water Quality, vol. 1, 3rd edn., Recommendations WHO, Geneva.

Zeng C., Yang F., Zhou N. (2011) Hollow fiber supported liquid membrane extraction coupled with thermospray flame furnace atomic absorption spectrometry for the speciation of Sb(III) and Sb(V) in environmental and biological samples. *Microchem. J.* **98**, 307–311.

GENERAL DISCUSSION

General Discussion

The hydrochemistry of the study area indicates that the groundwater is enriched with arsenic (As). The As contamination in many wells are relatively high (>300 µg/L). The distribution of high As wells are heterogeneous with some areas more enriched than others. High As concentrations are often found in shallow aquifers where Na and Cl^- levels are high. Cl^- in groundwater is most probably derived from the sanitary systems. In the deeper part of the aquifers, generally the Na concentrations are varying and the Cl^- concentrations remain unchanged. SO_4^{2-} concentrations are generally low. The lack of positive correlation between dissolved As and SO_4^{2-} may suggest that the removal of SO_4^{2-} from groundwater has occurred. One of the possible mechanisms is likely to be bacterial reduction of SO_4^{2-} that is possibly operating in the aquifer. SO_4^{2-} reduction further indicates that the reduction process has been accompanied by As mobilization (denitrification → Fe-reduction → SO_4^{2-} reduction). In BDP, Ca-HCO_3^- type groundwater is most common and reported by several workers. Unlike Ca, concentration of Mg is relatively low and the molar Mg/Ca ratio is also variable. This indicates dissolution of Ca and Mg from different mineral sources. Similarly, the molar K/Na ratio is also varying and suggests that Na might have occurred in groundwater from the local source (pollution) rather than conservatively mineral dissolution.

The importance of local anthropogenic influence and its possible sources (surface water body, sanitary systems, and agricultural field) may contribute on As mobilization. The hydrochemical features (normalized values) and site specific well associated features explain the importance of local anthropogenic influence on groundwater quality as well as heterogeneous As distribution. The higher concentrations of NO_3^-, SO_4^{2-} and Cl^- in groundwater are found to be associated with sanitation systems as well as sanitation coupled with surface water body. The higher concentrations of PO_4^{3-} and HCO_3^- are primarily linked with agricultural fields and surface water body. The relatively higher mean HCO_3^- value (424.53 mg/L) possibly indicates the surface input of dissolved organic material from agricultural field and surface water bodies. PO_4^{3-} input is common from agricultural (irrigated) field as wells as local infiltration from ponds into the groundwater.

Further examination of hydrochemical features has also been carried out on spatial scale to examine the pattern of spatial heterogeneity. The As distribution pattern is not equivocally following the Fe/Mn distribution pattern. This suggests that possibly single mechanism (reductive dissolution of Fe/Mn-(oxyhydr)oxides) is not sufficient to explain heterogeneous As distribution pattern. Heterogeneity of As occurrences can be further resolved by the competitive ion-exchange process (such as with PO_3^{4-}) where local anthropogenic input is regulating the system. The concentrations of NO_3^- and SO_4^{2-} are important because they act as a terminal electron acceptor in water systems. It has been observed that As concentration (mean: 17 µg/L) in groundwater is relatively low where NO_3^- is high (mean: 9 mg/L). This suggests that the groundwater chemistry of the aquifer is influenced by local anthropogenic influence to some extent and thereby gradually becoming less anoxic. The appearance and disappearance of SO_4^{2-} are also regulated by the local anthropogenic influence where microbial reduction of SO_4^{2-} may have often occurred, even though, H_2S is mostly below detection limit. Local land-use pattern possibly influences the natural cycling of As between sediment and water, ultimately releasing As in the aqueous environment. In the absence of primary sources (arsenopyrite/pyrites), secondary metal oxides/hydroxides, especially of Fe and Mn along with micas (altered aluminosilicates) are considered to be important. These are dominant sources as they are abundant in the sediments of Bengal Delta Plain (BDP). In addition, fluvial geomorphology and their physical location within land-use pattern are also influencing heterogeneity of As distribution and thereby regulating the patchiness.

The presence of saturated carbonate minerals (aragonite, calcite, dolomite, siderite, rhodochrosite) and high values of Ca, Mg, Fe, HCO_3^- in groundwater with circumneutral to slightly alkaline pH, is an indication of carbonate (CO_3^-) mineral dissolution process, in addition to the Fe-oxides/hydroxides. This often indicates that carbonate reactions are important for influencing groundwater hydrochemistry in the surveyed wells. It is pertinent to mention that SI values for dolomite fluctuate to certain extent (0.12-0.53), which might be indication of dolomitization of calcite and aragonite. Groundwater is commonly super-saturated with hematite and saturated with siderite. This suggests that the precipitation of Fe(III) phases from groundwater is thermodynamically favourable and thereby regulating As concentration in groundwater. The mean As concentration is relatively higher in wells nearby agricultural fields and surface water bodies where PO_4^{3-} (run-off from agricultural fields) and HCO_3^- (bio-indicator and end product of degraded natural organics) are high and dissolved organic carbon (DOC), NO_3^- and SO_4^{2-} are relatively low. This supports the combined release mechanism (Fe reduction and PO_4^{3-} competitive exchange process) for the occurrence of high As in groundwater. In contrast, mean As concentration is relatively low in case of wells adjacent to sanitary installations and sanitation coupled with surface water bodies, where SO_4^{2-}, NO_3^-, Cl^- and Fe are relatively high and PO_4^{3-}, HCO_3^- are relatively low. This suggests that Fe reduction is the principal process for release of As in groundwater in case of these type of wells. Several workers have already identified these minerals principally hematite in the sediment. Saturation indices of rhodochrosite and gibbsite are also important because the formation of rhodochrosite and gibbsite can regulate As concentration in groundwater. These minerals can act as a sink for As by co-precipitation with Mn(II), Al(III) ions from the anoxic groundwater.

The heterogeneous As distribution can be linked with multiple natural geochemical processes playing simultaneously and thereby enriching the groundwater with As. Nevertheless, ion exchange and ion concurrence from anthropogenic sources together with the complex deltaic environment may also have some impact on the spatio-vertical heterogeneity of As.

There are three major observations from the results mentioned in Chapter 2 - a) seasonal influence on As speciation (mainly in case of the flood plain wells), b) correlation between As(III) and DOC in the flood plain post-monsoon (PSTM) samples and c) pronounced difference in As concentration of flood plain and natural levee groundwater. In the natural levee, the prevailing redox potential is obviously less reducing as compared to the flood plain. The redox potential (Eh), DOC, Fe^{2+}, NO_3^-, SO_4^{2-}, and even the Mn^{2+} concentrations supports the above behavior. In the flood plain area, the DOC (the redox driver) is also higher and further increases during the PSTM season along with HCO_3^-. At the same time, other potential terminal electron acceptor (TEA) substances like NO_3^-, SO_4^{2-} (used for microbial respiration) decrease – supporting possibility of microbial activity during increase in DOC following fresh recharge in the PSTM season. DOC holds a consistent, linear relationship with As(III)/As_T in case of the flood plain wells during the PSTM period. Moreover, HCO_3^- concentration in the flood plain wells during the PSTM season shows a similar trend with the As(III)/As_T, reinforcing the idea of possible influence of DOC in these wells as it is expected that if DOC is degraded, HCO_3^- should also be released as end-product and the resulting increase should also correlate positively with the increase in the As(III) concentration. Arsenic release is very likely to be caused by microbe mediated reduction of Fe(III)-(oxyhydr)oxides during anaerobic decomposition of organic matter and this organic matter could be sediment-bound organic matter in these shallow aquifers. This assumption is also suitable to explain why As concentrations in the flood plain area are generally higher than in the natural levee, where Fe concentrations are lower and the redox potential is less reducing according to the measured Eh and redox sensitive elements. Interestingly, Fe^{2+} proportions are much lower in pre-monsoon (PRM) flood plain samples as compared to the Fe_T concentration. The reason for this discrepancy remains unknown. Most interestingly, increase in DOC and concomitant decline in the redox state, increase in Fe^{2+} concentrations and As(III) of PSTM flood plain samples follow changes in the isotopic composition of local groundwater.

The stable isotope composition of the groundwater samples fall sub-parallel to the global meteoric water line (GMWL) with precipitation and subsequent evaporation seems to be the major controlling factor on the water isotopic composition. This shows that evaporated surface water could be recharging the shallow groundwater, with ponds and infiltrating irrigation water as possible sources. Moreover, large-scale groundwater withdrawal helps drawdown of the evaporated surface water. Isotopic signatures indicate an increased influence of water (especially in case of the flood plain samples) which plots left of the local evaporation line (LEL) after the monsoon season. This indicates possible mixing with water that is closer to the composition of rainwater, resulting in possible mixing of water with different hydrochemical compositions. As the DOC concentrations increased, this may influence the microbe mediated decomposition of organic matter, coupled to the reduction of Fe(III) and As(V), resulting a drop in the local redox potential. This assumption is supported by the strong positive correlation between DOC and As(III). On the contrary, natural levee samples appear to be disconnected from infiltrating groundwater with increased DOC, possibly causing depletion in sources of organic matter (especially DOC) and thereby microbe mediated redox reactions are restricted in a less reducing state.

Most of the PSTM flood plain wells seem to have been influenced by vertical mixing with the irrigation return flow or the anthropogenic inflows (high Cl^- concentration and lower isotopic values) after the monsoon. Moreover, for some of the flood plain samples, moderate Cl^- concentration (PRM Cl^- concentration 15.9 mg/L and for PSTM Cl^- concentration 16.3 mg/L) and isotopic composition ($\delta^{18}O$ values for PRM -2.5 and for PSTM -6.5) indicates moderate evaporation. On the other hand moderate As_T concentration reflects the influence of evaporation as evaporation can increase As_T concentration in pore waters, and aided by the vertical mixing, it can ultimately cause high As concentration in the groundwater. Most of the natural levee samples show the potential effect of strong evaporation and weak vertical leaching as the concentration of Cl^- do not increases notably, but the isotopic composition gets heavier. This is also possible due to some lateral mixing at deeper aquifer depths as both of them are low in Cl^-, but the isotopic compositions are different. The low As_T concentration in these wells also emphasizes this fact.

Highly soluble Cl^- and Br^- shows very conservative behavior and the various water-rock interactions like adsorption, ion-exchange, redox changes could not affect its hydrochemical behavior and thus makes it as an indicator of groundwater flow and solute origination. The wide variation of Cl/Br ratio in shallow depths may reflects varying degrees of halite dissolution or anthropogenic and waste-water pollution and consequent vertical inflow into the shallow aquifer. Halite dissolution can rapidly increase the Cl/Br ratio with increase in Cl^- concentration whereas evapotranspiration do not allow a notable change in the Cl/Br ratio. Although, a few samples from both the flood plain and natural levee area shows the control of evapotranspiration.

The most important observation in this study is the significant increase in As(III) concentrations than As_T concentrations in both the flood plain and natural levee wells (223 over 6.6% and 217 over -17.6% respectively) on passing from the PRM to PSTM season. During waterlogged field conditions, reductive dissolution of stored As in Fe-(oxyhydr)oxides enhances mobility of As. Therefore irrigation return fluxes containing significant amount of organic matter and dissolved As may make way to the shallow aquifer. Arsenic in groundwater is possibly resulted from the reduction and concomitant dissolution of As-rich Fe-/Mn-oxides/hydroxides promoted by organic matter. Fe^{2+} and As(III) concentrations are increased in the flood plain area during the PSTM season. The Eh of the samples are more negative during the PSTM season (especially for the flood plain samples) indicating an increase in reducing environment. The increase in the As(III), Fe^{2+} and HCO_3^- concentrations in the aquifer after monsoon could be attributed to the reductive dissolution of As-rich Fe/Mn-(oxyhydr)oxides by the natural organic molecules. The HCO_3^- enhancement could also be due to microbial oxidation of the organic compounds. Several studies report that As(III)/As(V) can react differently with DOC to form complexes, which is even more favorable in presence of few cations. As(III) and As(V) may both compete with DOC for the binding sites on the available host mineral phases in groundwater. Microbial reactions can also change the relative abundance of As(III) or As(V) depending on the aquifer redox changes. All these together could possibly be a plausible reason for the selective increase of As(III) over As(V) during the PSTM season and the reverse during the PRM season. However, further laboratory scale investigations are required to probe into these assumptions.

Detailed investigations also highlight that the presence of large amount of As even after sequential filtration step suggests its occurrence in the 'truly dissolved' phases. However, one of the samples (sample 5) show large amount of As being swept away by the particulate phases. Large proportions of Al are associated with the particulate phases owing to their large decrease in concentration on passing through the 0.45 μm filter. On the other hand, DOC mostly associated with the smaller colloidal phases owing to their large variation in the range of 0.22-0.05 μm fractions. However, Fe has behaved in an interesting manner showing its variations both in larger as well as in smaller colloidal fractions.

Arsenic concentration correlates strongly with Fe ($r^2 = 0.94$) in 0.45 μm filtered samples, while correlate relatively poorly with DOC ($r^2 = 0.59$) and Al ($r^2 = 0.57$) possibly due to abundance of larger Fe-rich inorganic mineral phases in the greater pore-sized fractions. Stronger correlation of As with Fe ($r^2 = 0.91$ in both fractions) in 0.22 and 0.10 μm size fractions than with DOC ($r^2 = 0.60$ and 0.63, respectively) and

Al (r^2 = 0.60 and 0.88, respectively) suggests wide control of Fe-rich colloids on As distribution through different colloidal size fractions. In the smallest size fraction (i.e., 0.05 µm), the correlation of As with Fe and Al decreases steadily (r^2 = 0.65 and 0.58, respectively), whereas, with DOC shows a stronger correlation (r^2 = 0.85). Therefore, the variation in As concentrations in the larger sized fraction could be attributed to Fe-Al rich inorganic colloids, while smaller sized fraction is associated to the organic colloids. Presence of high concentrations of DOC and moderate Fe in the smallest size fractions instigate the possiblility of colloidal organo-metallic complexe formation that can influence the transport of dissolved As in groundwater.

The concentration of organic As is very low or negligible. Large differences in As_T concentration is observed in the smaller pore-sized fractions (i.e., 0.22-0.05 µm), whereas, noticeable differences in As(III) concentration is observed in the larger pore-sized fractions (i.e., 0.45-0.22 µm). The variations in As_T concentration in the smaller pore-sized filtrate could be due to differences in As(V) concentration, inorganic As [As(III) and As(V)] being almost the exclusively dominating species in BDP groundwaters. This suggests that As(V) may primarily be scavenged by the smaller sized organic colloids, while As(III) is scavenged by the larger sized Fe-Al rich inorganic colloids. Various physico-chemical parameters (such as Eh, pH, alkalinity, and the presence of DOC) controls the stability and/or transport of colloids as well as influence the As mobility in groundwater and its chemical speciation. Therefore, any changes in these physico-chemical properties of the aquifer may affect the course of the colloidal (either inorganic or organic) As transport.

For morphological and elemental information, SEM analysis was carried out on 0.05 µm ultrafilter precipitates. The EDX analysis shows the peak of C, O, Fe and As indicating the presence of organic colloidal particles together with associated Fe phases. The presence of Fe in the smaller colloidal fraction reinforces the ideo of NOM complexe formation through carboxyl or phenolic groups. The association of As in these colloidal phases demonstrate the formation of organometallic complexes smaller than 0.05 µm. The ATR-FTIR spectra shows a broad range of ν(O-H) vibrations (3000-3700 cm^{-1}) along with a number of asymmetric ν(COO^-) vibrations

(~1400-1700 cm^{-1}) indicating the presence of organic components. The presence of specific absorption peaks at 1624.1 cm^{-1} and 1636.7 cm^{-1} indicate the presence of As-Fe-NOM colloidal complex. However, further spectroscopic studies are needed to consolidate the formation of these complexes and their role to act as a scavenger of colloidal As.

Arsenic removal efficiency varied with different citrate sources during SORAS photochemical cycle. Overall, the citric acid from tomato juices showed highest removal efficiency (range: 78-98%, mean: 88%) followed by lemon (range: 61-83%, mean: 73%) and lime (range: 39-69%, mean: 50%) juices. This suggests tomato as the more efficient natural citrate source for the removal of As from groundwater through solar irradiation. Most of the As was removed during the first half (within 2 hrs) suggesting fast adsorption of As onto precipitated Fe(III)-complexes. Low reaction rates during second half of the experiment decreases dissolved As and Fe(III) concentration in the solution, prohibiting the formation of Fe(III)-complexes and subsequently the As removal.

The As/Fe molar ratios showed an 'optimized central tendency' during the removal of As for all citrate sources. The removal efficiency was higher for the solutions with molar ratio of 0.047 compared to the solutions with molar ratio of 0.037. However, the removal efficiency was the lowest for solutions with higher molar ratio (0.062) in case of all citrate sources. Therefore, the initial As and Fe concentrations in the treated water plays a crucial role for better removal efficiency. The lower removal efficiency at lower As/Fe molar ratio indicates that oxidizing agents like HCO_3^- may also catalyze the SORAS photochemical cyclic reaction in addition to Fe(IV), $O_2^{\cdot-}$ or $OH^{\cdot}$, which could regulate the course of the reaction. Moreover, some intermediate reactions could also be activated in the photochemical cycles due to presence of excess Fe in the samples reducing the concentration of free radicals and the removal efficiency. On the other hand, scarcity of required dissolved Fe concentrations and subsequent shortage of photocatalysts could be the reason for lower removal efficiency with higher molar ratio samples.

Similar 'optimized central tendency' was also noticed for different citrate doses used. The removal efficiency was higher for the 0.75 mL/L of citrate juices compared to 0.50 mL/L. The removal efficiency was lowest for the 1.0 mL/L of citrate juices. The cyclic photochemical reaction might not be able to produce intermediate reaction products (e.g., free radicals and Fe(III)-citrate complex) to provide necessary reaction conditions for the efficient removal of As from the solution with the low citrate doses (i.e. 0.50 mL/L). This could be attributed to the scarcity of citrates during photochemical reactions that trigger Fenton type reactions. In contrast, at higher citrate doses, the low removal efficiency was probably due to interference of the Fe(III)-citrate complex during the formation of Fe(III)-(oxyhydr)oxide solids.

An optimal citrate dose of 0.75 mL/L of juices was selected for the experiments with the groundwater samples. Tomato juice was again found to be more efficient to remove As from groundwater samples compared to lemon and lime juices. Interestingly for all the samples, citrate consumed was almost similar (range: 92-96%) after complete (4 h) radiation exposure. This highlights possible role of additional key factors apart from the photochemical cycle of Fe(III)-citrate complex, that are helping tomato juices over lemon and lime to efficiently remove of As from groundwater.

The better removal efficiency in case of tomato (than lemon and lime) could also be related to the respective anti-oxidant composition of the different citrate sources. All the citrate juices investigated here contain quantitative amount of polyphenolic anti-oxidants. Anti-oxidant activity is much lower in the case of citrate sources from tomato than lemon and lime and therefore, less susceptible to oxygen radical (like superoxides or $OH_{\cdot}$) absorption and more conducive towards photochemical oxidation, the basic requirement for the effective execution of SORAS. In addition, hydroxycinnamic acids (e.g. p-Coumaric acid and ferulic acid) were the major anti-oxidants in tomato. The carboxylate ($R–COO^-$) group of hydroxycinnamates could endorse SORAS photochemical cycle, forming Fe(III)-hydroxycinnamate complex and generating additional oxidizing radicals, in addition to the Fe(III)-citrate complexes. On the contrary, flavanones (e.g. taxifolin, naringenin, and narirutin), the dominant anti-oxidants present in lemon and lime, have no such groups to form complexes with Fe(III).

A local market survey of As contaminated regions in West Bengal, India shows that apart from the effective removal of As, 100 g of tomato can produce greater volume of juices and citrate concentrations for the treatment of large volume of As contaminated drinking water compared to lemon. In addition, comparative estimate of the available low-cost household methods for As removal from groundwater highlight that SORAS technique with the addition of natural citric acid (as tomato juices, non-toxic) is comparatively more efficient in removing As from groundwater at the household level without producing any hazardous wastes. Additionally, in rural villages tomato can be found abundantly due to its high demand and greater earnings. Hence, it would be convenient and beneficial for the rural people to cultivate tomato in their backyard and use it for the SORAS treatment. Therefore, the citrate source from tomato should be considered for the effective functioning of SORAS technique for the removal of As from drinking groundwater as it is also highly cost-effective compared with the other available treatment methods and most importantly, does not produce any hazardous chemicals. Hence, it can be considered as a green chemistry approach for the effective removal of As from groundwater.

Investigations on developing novel, cost-effective, environment friendly analytical techniques for the determination and speciation of As in water is also very important as some of the conventional techniques either quite expensive or consumes large volume of hazardous organic solvents. In this thesis, hollow fiber liquid phase microextraction (HF-LPME) technique combined with total reflection X-ray fluorescence (TXRF) was applied for the determination and speciation of inorganic As in water. Preliminary liquid-liquid extraction experiments were performed to establish the most effective extractant and organic phase for the HF-LPME experiments for As(III) and As(V), through trial experiments with different extractants and organic solvents.

For the 2-phase HF-LPME experiments, the reproducibility was very poor for both the smaller diameter fibers (Q3/2) and larger diameter fibers (S6/2). This could be possibly due to loss of organic acceptor phase during the process. Another problem with the 2-phase system (for both S6/2 and Q3/2 fibers) was the problem in depositing and stabilizing the organic acceptor phase at the center of the reflector during the analysis with TXRF.

In case of the 3-phase HF-LPME, we have used the S6/2 larger diameter fibers with a fiber length of 10 cm. The 3-phase system has few advantages over the 2-phase system as the problem of solvent evaporation was less (in this it is the aqueous phase that needed to be deposited on the sample carriers/reflectors), sample deposition was easier and the pre-concentration was better than the 2-phase system.

Three different Aliquat 336 concentrations (0.01 M, 0.1 M and 0.2 M) in 1-octanol were tested in the 3-phase HF-LPME system. As it is clearly visible that Aliquat 336 concentration of 0.2 M was found to be most efficiently extracting both As(III) and As(V) from the feeding phase and the extraction efficiency is slightly higher in case of As(V). For both As(III) and As(V), the extraction reached a maxima at 4 h and then again decrease with time. Here again though, the extraction efficiency was better in case of As(V) than As(III). An optimal agitation speed of 440 rpm was set to carry out the subsequent experiments. The effect of pH on the extraction of As was investigated within the range of 5.5-13 using the same experimental conditions. In case of As(III), the extraction efficiency increased and reached the maxima in the high alkaline range at pH 13. On the contrary, for As(V), the high extraction was found at pH 8.5. The extraction efficiency of As(III) at this pH is very negligible, likewise the extraction of As(V) at pH 13 is not much.

The varying concentration ratios of As(III) and As(V) in different type of environmental waters could significantly affect the extraction efficiency of inorganic As. Three different ratios, 70/30, 50/50 and 30/70 were examined, keeping the total As concentration to 100 μg/L and considering that at pH 13, only As(III) was extracted and at pH 8.5, only As(V) was extracted exclusively. As(III) was preferentially extracted at pH 13, whereas, As(V) was strongly extracted at pH 13. At pH 8.5, it is clear that extraction of As(V) enhanced proportionally with the deacreased As(III)/As(V) ratio. In contrast, at pH 13, As(III) extraction was decreased with the decrease in As(III)/As(V) ratio. The overall extraction was still better for As(V) though. The extraction of As(V) was found to be more than 100% in some cases may be due to possible oxidation of some As(III) during the equilibration. This indirectly shows that complete speciation is possible at two different pH's, especially at pH 8.5, where there is almost exclusively As(V) had been extracted.

In case of different environmental waters, various competing, interfering ions (especially anions) and the humic acids can influence the extraction of As in form of oxy-anions in the HF-LPME operating conditions. In case of As(III) both interfering ions and humic acids found to have someeffect on the extraction efficiency. However, in case of As(V), the effect was similar only with the anions. The humic acids do not hinder the extraction efficiency of As(V) at all. In case of As(III), the effect of HCO_3^- was not much until it reached the threshold value of 500 mg/L, however, the effect of Cl^- was consistent and notable. In case of As(V), the extraction was significantly affected when the concentrations of both HCO_3^- and Cl^- were maximum (i.e., 500 and 40 mg/L respectively).

The major objective of sample preparation in TXRF is to obtain the target sample as a thin layer (<100 μm) on a carrier with high reflectivity sample support. Therefore, in order to get total reflectance the sample deposition volume is important. Experiments were carried out to examine the effect of sample deposition volume on the As peak area to analyze preconcentrated standard solution of 0.1 mg/L As(III and V) solution. It is clear that the analyte response were much higher using a double deposition of (5+5) μL or 10 μL of sample volume on the reflectors than a single deposition of 5 μL. However, as it can be seen that the element sensitivity was the highest with the 10 μL single deposition. Therefore, a sample deposition volume of 10 μL was set to analyze the peak area for all the preconcentrated samples generated through the HF-LPME experiments. Among the available heating techniques (e.g., using laminar flow hood at room temperature, IR-lamp, drying in an oven), pre-heated (on a hot plate, ~ 80 ^oC) quartz reflectors were used for the sample deposition, as already reported for the HF-LPME systems analyzing metals. Another additional heating was done using the hot plate (T ~ 80 ^oC) after the aqueous droplet was deposited. The low operating and maintenance costs of the TXRF benchtop system (cooling media and gas consumption are not needed) makes it a handy, user-friendly and complementary analytical tool together with the HF-LPME method for the determination of As in environmental water samples. Although, the possibility of matrix effect with this system is much lower, however, the sensitivity might be lower than some of the conventional sophisticated methods.

It is very clear from the TXRF spectra that the absolute element sensitivity of the preconcentrated sample was much higher than the one without preconcentration. To estimate limit of detection (LOD) net intensity and background of the spectra was used according to theΩ3 approach. The detection limits calculated by this method were found to be around 5 µg/L and 0.03 µg/L for the solutions without and after preconcentration respectively, which proves that the method under investigation is appropriate for the determination of As in water. The preconcentration and measurement procedure was applied to aqueous standard solutions in the range of 0.5-200 µg/L. It was found that the calibration curve was linear in the range of 0.5-200 µg/L for both As(III) and As(V) with correlation coefficients (R^2) of 0.9882 and 0.9976 respectively. Intra-day and Inter-day experiments were also found to be highly reproducible.

The discussed method was applied to different natural water samples having different hydrochemical matrices. The extraction efficiency of As(III) was not that high except for the mineral water, river water and one groundwater sample. However, in case of As(V), the system were found to work very fine as recovery in the range of ~ 72-93 % was observed, except for one groundwater sample possibly because it was very high in Fe content resulting co-precipitation of As species

GENERAL CONCLUSION

General Conclusion

The main conclusions of the present thesis are as follows:

1. The groundwater of the study area is generally HCO_3^- type, occasionally enriched with Na and Cl^- in shallow aquifers. The groundwater composition reveals that Fe-(oxyhydr)oxide reduction and arsenic (As) mobilization may not be the only process to explain high As groundwater in Bengal Delta Plain (BDP). Altered mica (like biotite) which accommodates both Fe(II) and Fe(III) may be another potential host in BDP sediment to release As in groundwater.

2. The increase in As(III) concentration in groundwater is significant compared to the overall increase in As_T concentration during pre-monsoon (PRM) and post-monsoon (PSTM) periods. The increase of As(III) in the flood plain wells as compared to the natural levee wells is also very significant. The correlation of dissolved organic carbon (DOC) with As(III) after the monsoon indicates a possibility of microbe induced release of As.

3. The stable isotopic composition of shallow groundwater suggests a contribution of evaporated water that may be derived from various surface water bodies. The stable isotope signature and Cl/Br molar ratio of the flood plain wells have shown that vertical mixing could be the major recharge process, especially after the monsoon. The relationship between As_T concentration and the isotope profile shows a collective effect of both mixing and evaporation.

4. The increase in the As(III), Fe^{2+} and HCO_3^- concentrations during the post-monsoon season could be an indication of reductive dissolution of As-rich Fe/Mn-(oxyhydr)oxides by the natural organic molecules (possibly by the microbial activity). Probably due to the monsoon rain, a combined groundwater flow/transport induces an import of DOC, which may result in microbial redox

reactions that can cause a decrease in the redox state, subsequently changing the As(III)/As(V) water chemistry.

5. This is the first study in the Bengal Delta Plain to investigate the colloidal fractionation of groundwater arsenic. Major proportions (83-94%) of As_T remain in the 'truly dissolved' phase in the groundwater. Larger pore-sized fractions indicate the association between As and Fe-rich inorganic colloids, whereas the smaller pore-sized fractions highlight the interaction between organic colloids and As. As(III) is mostly associated with larger pore-sized inorganic colloids, while As(V) species mostly associated with smaller pore-sized organic/organometallic colloids.

6. SEM and EDX confirm involvement of dissolved organo-Fe complexes or colloidal organo-Fe oxide phases in scavenging dissolved As from groundwater. ATR-FTIR spectra further confirm the formation of As-Fe-NOM organometallic colloids. This proves that detail study of both dissolved and colloidal arsenic is needed to effectively assess the transport and/or mitigation options.

7. This study reported for the first time that the citrate source from tomato can effectively remove As from groundwater compared to lemon and lime for the application of solar oxidation and removal of arsenic (SORAS). Major controlling factors like varying As/Fe molar ratios and citrate doses showed an 'optimized central tendency'. Tomato, containing hydroxycinnamate as major anti-oxidants, would probably form Fe(III)-hydroxycinnamate complex and thus favored for the SORAS photochemical cycle. The market survey highlights tomato as the most cost-effective, eco-friendly, affordable, available and efficient citrate source compare to lemon and lime for the SORAS treatment at the household level.

8. A new hollow fiber-iquid phase microextraction (HF-LPME) based technique in combination with total reflection X-ray fluorescence (TXRF) technique was found to be very effective for the determination of As(III) and As(V) in water samples. The

method was less time consuming, cost-effective, easy-to-use process to measure low concentrations of As in water. As(V) was more successfully extracted than As(III). Aliquat 336 in 1-octanol found to be the most appropriate extractant for the determination of As. Sample deposition was difficult with the 2-phase LPME system and the reproducibility was also not satisfactory. The 3-phase system was found to be the more efficient than the 2-phase system for the extraction of arsenic. For both As(III) and As(V) the optimized equilibration time was 4 h. For As(III), the optimum pH seems to be 13, whereas, for As(V), this is 8.5.

9. The low operating and maintenance costs of the TXRF benchtop system (cooling media and gas consumption are not needed) makes it a interesting analytical tool together with the HF-LPME method for the determination of As in environmental water samples. The LOD’s were improved by more than ten folds in magnitude after the preconcentration through HF-LPME when compared to the direct measurements without preconcentration. The method was also employed to different spiked environmental water samples and the results were satisfactory, especially for As(V).