



## **Arsenic removal from water using naturally occurring iron, and the associated benefits on health in affected regions**

**Sharma, Anitha Kumari**

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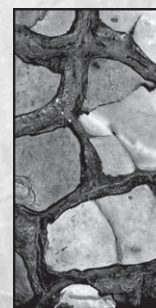
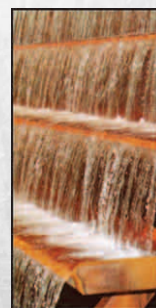
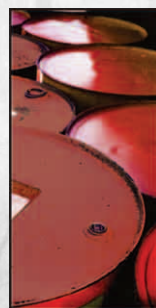
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# Arsenic Removal from Water using naturally occurring Iron, and the Associated Benefits on Health in Affected Regions

Anitha Kumari Sharma

INSTITUTE OF ENVIRONMENT & RESOURCES





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Ph.D. Thesis, April 2006

Institute of Environment & Resources  
Technical University of Denmark

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Institute of Environment & Resources

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# Preface

The present thesis is submitted as a partial requirement for the attainment of the Ph.D. degree. The research was conducted during September 2001 to January 2006 in the form of laboratory investigations at the Institute of Environment & Resources (E&R), Technical University of Denmark (DTU) and field investigation in West Bengal, India. The work was supervised by Professor Jens Christian Tjell, Associate Professor Hans Mosbæk and Professor Dieke Postma all from the E&R, DTU. The project was funded by a Ph.D. grant awarded by the DTU.

This dissertation is composed of a summary of the subject “Arsenic Removal from Water using naturally occurring Iron, and the Associated Benefits on Health in Affected Regions”, as well as 5 accepted research papers (3 published with Peer review in special issues, 1 published in international Peer reviewed journal, and 1 accepted and presented as conference paper) and 3 manuscripts submitted to international Peer reviewed journals. The in-text references and the titles of the papers are:

(**I:** Sharma et al., 2003; **II:** Sharma et al. 2004; **III:** Sharma et al. 2005; **IV:** Sharma et al. 2006; **V:** Sharma et al. 2006 (accepted and presented as conference paper); **VI:** Sharma & Tjell (submitted); **VII:** Sharma et al. (submitted) **VIII:** Sharma & Tjell (submitted).

- I.** **Sharma, A. K.**, Tjell, J. C., and Mosbæk, H. (2003). Removal of arsenic using naturally occurring iron. *Journal de Physique IV*, 107, pp:1223-1226.
- II.** **Sharma, A. K.**, Sarmani, S., and Tjell, J. C. (2004). Arsenic concentration in hair as an indicator of exposure. *Malaysian Journal of Science*, 23, pp:227-234.
- III.** **Sharma, A. K.**, Tjell, J. C., and Mosbæk, H. (2005). Optimisation of iron removal units to include arsenic removal. *In Natural arsenic in groundwater. Occurrence, remediation and management. Proceedings of the Pre-congress Workshop Natural arsenic in groundwater (BWO6), 32nd International Geological Congress, Florence, Italy, August 18-19, 2004.* pp:263-271. Leiden, NL: A.A. Balkema.
- IV.** **Sharma A.K.**, Tjell, J.C., and Mosbæk, H. (March 2006). Health effects from arsenic in groundwater of Bengal delta: Effects of iron and water storage practices. *Environmental Geosciences*. 13(1), pp:17-30.
- V.** **Sharma, A. K.** Tjell, J. C. & Bregnhøj H. Exploiting natural iron precipitation against arsenicosis. *IGC-2006*, held in New Delhi February 1-4, 2006.
- VI.** **Sharma, A.K.** & Tjell, J.C. Simple Arsenic removal from drinking water in rural settings (submitted to Water Research)
- VII.** **Sharma, A.K.**, Tjell, J.C., & Mosbæk H. Understanding oxidation of arsenite with iron. (submitted to Environmental Science & Technology)
- VIII.** **Sharma, A.K.** & Tjell, J.C. Effects of interfering ions on As(III) and As(V) removals with Fe from water. (submitted to Environmental Science & Technology)

The papers are not included in this www-version but can be obtained from the Library at the Institute of Environment & Resources, Bygningstorvet, Building 115, Technical University of Denmark, DK-2800 Kgs. Lyngby (library@er.dtu.dk).

Two other contributions are published during the study but not included in this thesis:

**Sharma A.K.**, and Tjell, J.C. (2003). Can water storage habits influence the cancer risk of drinking arsenic contaminated water? *In: Fate of Arsenic in the Environment*. A compilation of papers presented at the International Symposium, 5-6 February, 2003, Dhaka, pp. 37-56. Bangladesh University of Engineering & Technology Dhaka, Bangladesh & The United Nations University, Tokyo.

**Sharma A.K.**, Tjell, J.C., Genc-Fuhrman, Bregnhøj, H. and Mosbæk, H. (2005). Arsen, et drikkevandsproblem med flere løsninger. (Arsenic, a drinking water problem with several answers, in Danish). *Vand og Jord*. 12, pp:150-154.

I would like to thank my supervisors Jens Christian Tjell, Hans Mosbæk and Dieke Postma for their support throughout the study. I would further like to thank all from the E&R fort their help, especially Anders Torp Gundersen, Susanne Cruse, Camilla Hedberg, Monica Refstrup Pedersen, Nina Maria Gram and Sinh Hy Nguyen for their assistance in the laboratory; Grete Hansen and Helle Offenbergs for their support in acquiring the relevant literature and Torben Dolin for the graphical work in this thesis. I would further like to thank Henrik Bregnhøj and all the people working for the three NGO organisations (BSSKS (Bharpara Srijani Samaj Kalyan Samiti); KTT (Kishalaya Tarun Tirtha), SPREAD (Society for Participatory Research, Environment and Development) & RCS (Red Crescent Society)) from West Bengal (India) in helping me in collecting the field data. I would also like to thank DUCED-I&UA and Otto Mønstedsfond for their financial support to attend conferences.

I am very grateful to my family and friends, especially my parents and my husband Anoop for their support and understanding and last but not the least to my children Vivek and Nikhil for their understanding during my very hectic working hours.

Fredensborg, February 2006

Anitha Kumari Sharma

## Abstract

This thesis presents the results of a detailed study on ‘‘Arsenic Removal from Water using naturally occurring Iron, and the Associated Benefits on Health in Affected Regions’’. The details of the experimental work carried out in the laboratory and field as part of the Ph.D. work are presented and discussed in the 8 accompanied papers.

Arsenic (As) intake with drinking water is a very severe problem in the South East Asia with the Bengal delta being the worst affected area. The occurrence of As in ground water in the Bengal delta is of natural origin and microbial mediated reductive dissolution of Fe hydroxides with adsorbed As and phosphate (P) is the most accepted theory for the release of As to the groundwater. In 1993 WHO lowered the guideline value for As in drinking water from 50  $\mu\text{g/l}$  to 10  $\mu\text{g/l}$ . However only during the past 5 years many industrial countries adopted this lowered guideline value as maximum contaminant level (MCL). On the other hand many developing countries including India and Bangladesh still have 50  $\mu\text{g/l}$  as MCL. As is a documented human carcinogen and the estimated excess life time risk of getting skin cancer even at 10  $\mu\text{g/l}$  level is  $6 \times 10^{-4}$ . The risk estimates for population of Bengal delta would even be higher because of the lower average body weight of the person, higher water intakes and lower nutrient intake. However, the reported arsenicosis cases in Bengal delta are lower than expected compared to other parts of the world, despite the relatively higher As concentrations in hair. This Ph.D. study points to shorter duration of exposure to and co-occurrence of iron (Fe) as the two main factors responsible for the observed lower arsenicosis prevalence.

Presence of Fe renders colour to water upon exposure to air and hence people would either leave the water to stand for a couple of hours, to remove Fe, leading to indirect As removals due to co-precipitation with Fe, or, they would not use the water. Both these practices would lead to reduced As exposure. However, the development of colour in the water depends on the concentration and oxidation rate of  $\text{Fe}^{2+}$ . The oxidation rate of  $\text{Fe}^{2+}$  depends on many factors. At lower dissolved oxygen and/or high P concentrations the colour development is slow. Further the colour of the precipitates in presence of phosphate (P) is pale yellow compared to red-brown in the absence of P. Hence the presence of Fe may not be detected if the distance to tube well is short and people do not store the water. The BGS study and the study by Technical University of Denmark (DTU) showed that the installation of the tube wells increased exponentially in the beginning of 1990's. This led to usage of drinking water without prior storage due to shorter distance to the tube well. Based on the higher As concentrations in hair and the recent exposure to direct consumption of tube well water, the study indicated that the disaster is yet to be seen and there is a need for immediate measures/action.

Based on the available literature this study identified removal of arsenic using naturally occurring Fe as the most appropriate and accessible mitigation option for the rural setting prevailing in India and Bangladesh. The field results showed that an Fe/As ratio above 80 (M/M) is necessary to achieve As concentrations below 50  $\mu\text{g/l}$  using iron removal units (IRU) and based on the British Geological Survey (BGS) survey this method can be applied at 25% of the tube wells. The field results also showed that



simple sedimentation of water with elevated Fe and As concentrations would lead to removal of As and an Fe/As ratio of above 120 (M/M) is required to attain residual As concentrations below 50 µg/l.

Insight into the mechanisms responsible for removal of As with Fe is important to optimise As removals. As occurs mainly in the form of inorganic arsenite (As(III)) in the ground waters of the Bengal delta. As(III) is neutrally charged and is difficult to remove compared to the negatively charged arsenate (As(V)) in the near neutral pH range. The possibility to differentiate between arsenite (As(III)), and arsenate (As(V)), is important to understand the As removal mechanisms involving Fe. Investigations on preservation of samples showed that neither acidification nor acidification and storage at 4°C were appropriate for preservation of samples. Storage in the dark also did not prove to be sufficient for preservation of samples. Hence, a method based on continuous hydride generation and measuring As using AAS was developed for immediate and continuous measurement of both As(III) and total As. The results were verified using on-line separation of As species with an anion exchange resin.

Extensive investigations were carried out to understand the removal mechanisms responsible for As removal in presence of Fe. The results showed that oxidation of As is an important factor furthering the removal of As with Fe and the results indicate that the oxidation is most probably due to heterogeneous oxidation on the surface of Fe-hydroxides. The properties of the Fe-hydroxides vary greatly depending on the initial oxidation state of Fe and the presence of ions. The results in the present study showed higher As oxidation and removal with Fe initially present as  $Fe^{3+}$  compared to  $Fe^{2+}$ . However, the presence of P had a stronger negative effect on oxidation and removal in presence of  $Fe^{3+}$  compared to  $Fe^{2+}$ . At very high P concentrations both oxidation and removals were completely inhibited with initial  $Fe^{3+}$ , whereas both oxidation and removal of As(III) occurred though decreased with initial  $Fe^{2+}$ . Similarly presence of silicate (Si) also had a negative effect on oxidation of As(III). Lower  $O_2$  concentrations also had a negative effect on As(III) oxidation in presence of  $Fe^{2+}$  and higher pH had a positive effect on As(III) oxidation. The results indicated that maximum oxidation of As(III) occurred within the first 30 minutes of the experiments and similarly maximum As removals also occurred during this time. However, in presence of P and Si prolonged sedimentation of up to 24 hours was required to achieve maximum As removals. Slightly lower As removals were observed in the field compared to the laboratory and could be due to lower  $O_2$  concentration in the field. These results indicate that high Fe/As ratios are necessary if As removal is based on Fe alone.

Since oxidation of As(III) is an important factor controlling the As removal capacity of Fe, addition of simple oxidising agents would reduce the required Fe/As ratio. Fe-citrate complex in presence of UV-light as well as  $KMnO_4$  were investigated for their oxidation capability. Citrate could be added as lime and sunlight can be used as UV-light. The results with Fe-citrate complex in presence of UV-light showed that both oxygen and UV-light is necessary for As(III) oxidation. The results further showed that if the citrate/Fe ratio is above 1 then As removals could not be achieved as Fe will not precipitate. Based on these results the method is not suitable for practical applications.  $KMnO_4$  was found to be an appropriate oxidising agent and the results showed that sufficient amount of  $KMnO_4$  necessary for oxidation of both As(III) and  $Fe^{2+}$  should be

added immediately after pumping the groundwater to achieve satisfactory results. Attaining sufficient surplus can be verified in the field by the development of pale pink colour. The calculations showed that application of sufficient  $\text{KMnO}_4$  in presence of high Fe concentrations would alone be enough at 60% of the existing tube wells. The monthly cost of this treatment would be 4 INR (~8 Eurocent) assuming a daily requirement for treated water for a family to be 50 litres. For the rest of the tube wells an extra addition of coagulant is required and could be either in the form of Fe or Al. Even though lower amount of Fe would be required compared to Al, the cost of Fe is higher than Al and hence to reduce the costs an extra amount of Al could be added. To achieve better As removal efficiencies, Al should either be added in very fine powdered or soluble form. The laboratory investigations showed that an aqueous mixture of  $\text{Al}_2(\text{SO}_4)_3$  and  $\text{KMnO}_4$  is stable at pH 11 adjusted with NaOH. The application of chemicals in solution would result in better mixing and the results showed that this mixture would have great potential for treatment of As. However, verification is required in the field.

In all cases the daily generation of As contaminated sludge is very low, however care should be taken in avoiding disposal of the sludge near children's playing area or edible crops. A suitable way of disposal of this sludge would be to bury it.

Instead of waiting for an expensive solution based on construction of deep tube wells, taking years and reaching few, removal of As based on naturally occurring Fe along with application of  $\text{KMnO}_4$  supplemented with Fe/Al could be recommended as a mitigating option for the affected rural areas of the Bengal delta.



## Dansk Resumé

Denne afhandling omhandler resultaterne af et detaljeret studie over ”Arsenfjernelse fra vand ved hjælp af naturligt forekommende jern, og betydning for helbred”. Det eksperimentelle arbejde samt feltarbejde er rapporteret og diskuteret i de 8 vedlagte artikler.

Problemer med for høj indtagelse af giftigt Arsen (As) gennem drikkevand i det Bengalske delta er anset for de mest alvorlige, selvom As i drikkevand også forekommer i andre lande i Sydøstasien. As i grundvandet i det Bengalske delta er af naturlig oprindelse. Den mest accepterede teori for tilstedeværelsen af de høje As koncentrationer i drikkevandet er reduktiv opløsning af jernhydroxider i dybereliggende sediment, hvilket skyldes mikrobiel nedbrydning af organisk stof. Gennem opløsning af jernhydroxider sker frigivelse af adsorberet arsen, mest som As(V) der dog ofte reduceres til As(III), samt fosfat (P). WHO nedsatte den anbefalede grænseværdi for As i drikkevand i 1993 fra 50 til 10  $\mu\text{gL}^{-1}$ . Det er dog først i de sidste par år, at flere industrialiserede lande har indført 10  $\mu\text{gL}^{-1}$  som værende den maksimalt tilladte værdi (MCL) i drikkevand. Flere udviklingslande, inklusive Indien og Bangladesh, har stadig 50  $\mu\text{gL}^{-1}$  som den maksimalt tilladte værdi. Arsen er et dokumenteret kræftfremkaldende kemikalie og den estimerede livstidsrisiko for at få hudkræft er  $6 \cdot 10^{-4}$  ved 10  $\mu\text{gL}^{-1}$ . Estimeret risiko for befolkningen i Bangladesh vil blive endnu højere pga. lav gennemsnitlig kropsvægt, stor indtagelse af drikkevand og lav fødeindtagelse. Et litteratur studie foretaget i dette ph.d. studie har vist, at de observerede tilfælde af arsenikose i Bengaldeltaet er lavere end beregnet og sammenlignet med andre områder i verden. Dette på trods af at der er fundet højere As koncentrationer i hår i det Bengalske delta. Dette ph.d. studie udpeger hovedårsagerne til den øjensynlige lave forekomst af arsenikose til at være den relativt korte tid hvor befolkningen har været eksponeret til As-holdigt vand, samt på den beskyttende forekomst af opløst jern sammen med As i oppumpet vand.

Når anoxisk jernholdigt vand ved neutralt pH kommer i kontakt med ilt efter oppumpning, dannes der rødfarvede jernhydroxider, hvilket ofte medfører at vandet står i et par timer for at fjerne farven ved bundfældning, eller det fravælges som drikkevand. Hvis vandet henstår i et stykke tid fjernes en god del af As ved bundfældning sammen med jernhydroxiderne. Forekomsten af farve i vandet afhænger dog af koncentrationen samt oxidationsraten af  $\text{Fe}^{2+}$  som afhænger af flere faktorer. Ved lavere opløst ilt og/eller høj P koncentrationer farves vandet langsomt og mindre intenst. Desuden er farven af bundfaldet svagt gul, hvis der er P tilstede i modsætning til en stærk rødbrun farve hvis der ikke er P tilstede i vandet. Derfor er det ikke i alle tilfælde at forekomsten af jern i vandet vil erkendes, hvis f.eks. afstanden til brønden er kort og folk undlader at lade vandet henstå før det indtages. Både opgørelser foretaget af British Geological Survey (BGS) i Bangladesh og af Danmarks Tekniske Universitet (DTU) i Vest-Bengalen (Indien) viser at antallet af borer steg eksponentielt siden starten af 1990'erne. Dette har medført direkte indtagelse af oppumpet drikkevand uden henstand i spand på grund af kortere afstand til borerne. Baseret på målte højere koncentrationer af arsen i hår og den seneste udvikling i indtagelsen af oppumpet vand

uden henstand, indikerer denne afhandling at de fulde konsekvenser endnu ikke er set, men at der er behov for snarlig handling.

Baseret på en litteraturgennemgang er der i dette ph.d. studie identificeret fjernelse af arsen fra vand med det naturligt forekommende jern som værende en god tilpasset løsning til nedsættelse af eksponeringen. Afhængigt af forholdene kan fjernelse af As i praksis foretages på jernfjernelsesanlæg for landsbyer (IRU), eller ved henstand af vand i en spand i passende tid i husholdningerne. Felt undersøgelser fra de eksisterende jernfjernelsesanlæg har vist, at et Fe/As forhold over 80 (M/M) er nødvendige for at opnå As koncentrationer under 50 µg/l. Endvidere har felt undersøgelserne vist, at et Fe/As forhold > 120 (M/M) er nødvendige for at opnå As koncentrationer på under 50 µg/l ved henstand af vand i en spand. Udregninger baseret på BGS data viser at Fe/As forholdet er > 80 ved 25% af borerne og > 120 ved 14% af borerne i berørte områder i Bangladesh.

Forståelsen af mekanismerne bag As fjernelse ved hjælp af jern er vigtig for at optimere As fjernelsen. As forekommer primært som As(III) i grundvandet i det Bengalske delta. As(III) er neutralt ladet og er svært at fjerne i forhold til de negativt ladede As(V)-ioner i nær neutral pH område. For at forstå mekanismerne bag As-fjernelsen er det vigtigt at kunne analysere både As(III) og As(V) i vandprøver. Undersøgelser i denne afhandling af opbevaring af prøver har vist, at oxidation af As(III) forekommer i syretilsatte prøver. Ligeledes er syretilsætning samt opbevaring i mørke og/eller ved 4°C ikke nok til at stoppe oxidation af As(III) i opbevarede prøver. Derfor blev en metode baseret på kontinuert As-hydrid dannelse og måling af As med AAS udviklet for kontinuerede målinger af As(III) og for total As. Denne metode blev verificeret ved en ligeledes anvendt on-line separering af As-komponenter ved anionbytning.

Undersøgelserne af mekanismerne bag fjernelsen af As med Fe viste at oxidation af As med atmosfærisk ilt er vigtig for at fremme As fjernelsen ved udfældning/adsorption på Fe-hydroxider. Oxidationen af As(III) sker sandsynligvis ved heterogen reaktion på Fe-hydroxidoverflader, hvor flere faktorer påvirker egenskaberne som initialt iltningstrin for tilsat Fe, og tilstedeværelsen af andre ioner. Der er generelt vist højere oxidation og fjernelse af As med initialt tilsat  $\text{Fe}^{3+}$  i forhold til  $\text{Fe}^{2+}$ . Ejendommeligt nok er initialt tilsat  $\text{Fe}^{2+}$  bedre til at oxidere As(III) i forhold til  $\text{Fe}^{3+}$  i tilstedeværelse af P, som dermed har negativ effekt på både oxidation og fjernelse af As. Ved høje P koncentrationer stoppede oxidation og fjernelse af As(III) totalt med initialt tilsat  $\text{Fe}^{3+}$ . Derimod forekom både oxidation og fjernelse af As(III) med  $\text{Fe}^{2+}$  selv ved høje P koncentrationer, dog med betydelig negativ effekt på fjernelsen og mindre effekt på oxidationen af As(III). Si viste også negativ effekt på oxidation af As(III) med  $\text{Fe}^{2+}$ . Ligeledes havde en lav opløst  $\text{O}_2$  koncentration negativ effekt på As(III) oxidationen med  $\text{Fe}^{2+}$ . Endvidere blev det vist at højere pH har en positiv effekt på As(III) oxidation med  $\text{Fe}^{2+}$  og at den maksimale oxidation og fjernelse af As forekom i de første 30 minutter. Derimod krævede tilstedeværelsen af P og Si en sedimentationstid på op til 24 timer til opnåelse af maksimal fjernelse. Den opnåede As fjernelse i feltundersøgelser var lavere end i laboratorieforsøgene, hvilket kan skyldes lav  $\text{O}_2$  koncentration i oppumpet vand i felten. Og endelig er det generelt vist at høje Fe/As forhold er nødvendige for at opnå tilstrækkelig As fjernelse baseret på Fe alene.

Da oxidation af As(III) er et vigtigt kontrollerende led i fjernelsen af As med Fe, vil tilsætning af simple oxidationsmidler kunne formindske det nødvendige Fe/As forhold. Fotokemisk oxidation med Fe-citrat og uv-lys, samt kemisk oxidation med  $\text{KMnO}_4$  blev undersøgt for oxidationen af As(III). Citrat kan tilsættes i form af citronsaft og uv-lys gennem eksponering til sollys. Det vistest at tilstedeværelsen af både ilt og uv-lys var nødvendige for fotokemisk oxidation med Fe-citrat. Desuden blev det konstateret, at ved citrat/As forhold over 1 kan As fjernelsen ikke ske da det kompleksbundne Fe ikke kan udfælde. Baseret på disse resultater er denne metode ikke velegnet til implementering i praksis.

Derimod viste  $\text{KMnO}_4$  sig velegnet til oxidation af As(III), med maksimal As fjernelse når mængden af tilsat  $\text{KMnO}_4$  kan oxidere både  $\text{Fe}^{2+}$  og As(III) lige efter oppumpning af grundvandet. Dette kan let kontrolleres i felten, idet et lille overskud af  $\text{KMnO}_4$  giver en svag, men tydelig lyserød farve. Beregningerne viste at tilsætning af  $\text{KMnO}_4$  alene er nok til at nedbringe As koncentration under  $50 \mu\text{gL}^{-1}$  ved 60 % af boringerne. De månedlige udgifter vil da være 4 INR (~8 Eurocent) for en familie med et dagligt vandforbrug på 50 liter. Det vil være nødvendigt at tilsætte enten Fe eller Al salte til vandet for at opnå As koncentration under  $50 \mu\text{gL}^{-1}$  for de resterende boringer med lavere Fe koncentrationer. Selv om en relativt større mængde Al-salt end Fe-salt skal tilsættes for at opnå samme fjernelse af As, er det billigst at tilsætte Al. For at opnå optimal As fjernelse kan Al enten tilsættes som fint pulver eller som flydende kemikalieblanding. Laboratorieforsøgene viste at en vandig opløsning af  $\text{Al}_2(\text{SO}_4)_3$  og  $\text{KMnO}_4$  var langtidsstabil ved pH 11 efter justering med NaOH. Tilsætningen af kemikalierne i væskeform er let at administrere og vil medføre en bedre indblanding, og dermed har dette blandingsprodukt et stort potentiale til fjernelse af As. En grundig efterprøvning af den foreslåede metode i felten er nødvendig for at undersøge metodens egnethed i praksis.

Bortskaffelsen af Fe-slam med udfældet As bør ikke være et stort problem, da den daglige mængde af As er ganske ubetydelig. Dog bør deponeringen ikke foregå i køkkenhaver eller nær legeområder. Den bedste måde til bortskaffelse af slammet vil være nedgravning.

Alternativet til fjernelse af As ved simple metoder er installation af dybe boringer (150-300m), hvilket vil tage mange år at implementere for at dække behovet for rent vand, og som relativt få mennesker vil få glæde af grundet ekstreme omkostninger. En fjernelse af As som foreslået her baseret på naturligt forekommende Fe med tilsætning af  $\text{KMnO}_4$  eventuel suppleret med Fe/Al kan anses som værende den bedste løsning for de arsenramte landsbyer i det Bengalske delta.



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# 1 Introduction

Discovery of Arsenic (As) in the ground waters of alluvial deposits of West Bengal (India) and Bangladesh referred to as the Bengal delta with up to 97% of domestic water supply in rural areas based on tube wells, threatens millions of people to be exposed to high As concentrations. Recent studies indicate additional contamination of the food chain due to irrigation with As contaminated water<sup>(1,2,3,4,5,6,7,8,9,10)</sup>. In 1993, WHO lowered the guideline value for As in drinking water from 50 µg/l to 10 µg/l<sup>(11)</sup>. In the past 5 years many countries adopted 10 µg/l as the maximum contamination level (MCL) in drinking water. However, India and Bangladesh still adopt 50 µg/l as the MCL for As in drinking water.

Reported incidences of health effects due to exposure to elevated As concentrations from drinking water are available from Argentina<sup>(12,13)</sup>, Bangladesh<sup>(14,15,16,17,18)</sup>, Chile<sup>(19,20,21)</sup>, PR China ((Inner Mongolia, Xinjiang, Shanxi)<sup>(22,23,24,25,26,27)</sup>, Taiwan<sup>(28)</sup>, Cambodia<sup>(29)</sup>, Finland<sup>(30,31)</sup>, Hungary<sup>(32)</sup>, India<sup>(33,34,35,36,37,38,39)</sup>, Japan<sup>(40)</sup>, Mexico<sup>(41,42,43)</sup>, Nepal<sup>(44,45)</sup>, USA<sup>(43,46,47,48)</sup>, Thailand<sup>(49,50)</sup> and Vietnam<sup>(51,52)</sup>. One of the well documented exposures to As through groundwater originates from Taiwan, where people for many years consumed As contaminated drinking water and suffered from characteristics symptoms of arsenicosis referred as Black foot disease<sup>(28,53,54)</sup>. The first cases of arsenicosis from the Bengal delta were reported from West Bengal in 1980's<sup>(55)</sup>, however the dimension of the problem was unknown at that time. A study<sup>(56)</sup> published in 2004 showed that the As contaminated area of Bengal delta covers an area of around 160 000 km<sup>2</sup> populated with approximately 147 million people. More than 40 million people are estimated to be exposed to As concentrations above 50 µg/l. The percentage of tube wells contaminated with As varies from place to place and is mostly in the range of 20-50%<sup>(56)</sup>. High As concentrations in the Bengal delta usually occur in the anoxic shallow ground waters, with reported maximum concentrations at 20-50 m depth. Rivers, ponds and dug wells are usually free from As. The deep aquifers which are free from As are presumably separated from shallow aquifers with a clay layer and the depth to this aquifer can vary from 80 m to > 200m<sup>(57)</sup>.

Since As is tasteless, colourless and odourless, the detection of As is only possible through chemical Analysis. Similarly exposure to low levels of As can not be detected visually since it takes more than 10 years for the common As related dermal symptoms to develop<sup>(55)</sup>. Other symptoms due to As exposure like diabetes<sup>(58)</sup>, anaemia<sup>(59)</sup>, adverse pregnancy outcomes<sup>(60)</sup> are not specifically related to As alone. The most direct way of determining recent As exposure is measuring As content in urine, while the chronic As exposure can be detected by measuring As concentration in hair and nails<sup>(61)</sup>. The difficulties in detecting As in water due to its properties like colourless, odourless and tasteless along with long latency period in development of As related symptoms at low concentrations are may be the main reasons why, despite the discovery of As in ground waters of Bengal delta more than a decade ago, general population is unaware of the presence of As in water and the related health effects due to consumption of high As contaminated water. The available data shows that exploration of ground water increased exponentially until 2000 in the form of drilling of private tube wells (data from BGS survey<sup>(62)</sup>). My visit during 2002 and literature<sup>(63)</sup>

also proved that people were unaware of As contamination and were consuming As contaminated drinking water.

As is a documented human carcinogen with no substantial evidence from animal studies at low exposures<sup>(64)</sup> and the mechanisms behind As carcinogenesis in humans is not fully understood yet<sup>(65,66)</sup>. Non-occupational exposure to As commonly occur through contaminated food and water<sup>(11)</sup>. Burning of As contaminated coal for cooking and heating purpose would also lead to exposure to airborne As in non-occupational exposure<sup>(67)</sup>. The largest contribution to total As exposure is generally through food with daily As intakes in the range of 5-1000 µg. But this exposure has not caught much attention since most of As in food is in the organic form and is considered to be rather non-toxic. Recent literature from Taiwan<sup>(3)</sup>, Bangladesh<sup>(6,1,4)</sup>, and West Bengal<sup>(2,68)</sup> shows high As concentrations in food grown on As contaminated soils compared to food grown in other areas. However, in case of the Bengal delta the major contributor to total As intake is As contaminated ground water with concentrations up to 4000 µg/l<sup>(57)</sup>. The daily water intake in Bengal delta is also very high (4-6 l<sup>(68)</sup>) compared to the WHO's assumption of 2 l<sup>(11)</sup>, because of the hot climate and consumption of food items like rice and lentils prepared with ample water<sup>(69)</sup>.

The early symptoms of arsenicosis can be treated with selenium supplementation as a short term solution<sup>(70)</sup>. However, the long term sustainable remedy against As exposure is access to As free water and food with low As concentration<sup>(71)</sup>. One of the ways of obtaining As free water at the household level is treatment of As contaminated water. As can be removed upon coagulation with iron (Fe) salts and the ground waters of Bengal delta contain high concentrations of Fe. Therefore the objectives of this study are:

Objectives: To explore the possibility of utilising the naturally occurring Fe in removal of As and to investigate the possibilities of improving the As removal process. The other objective is to investigate whether the occurrence of Fe has any indirect effect on exposure to As in the form of discarding the water for drinking and cooking purposes due to the development of red colour and/or passive sedimentation for removal of Fe along with As.

## 2 History and Chemistry of Arsenic

### 2.1 History and uses of Arsenic

As is the 20<sup>th</sup> most abundant element in the earth's crust and 12<sup>th</sup> most abundant element in the human body<sup>(11,72)</sup>. It has been used as a homicide since the middle Ages. However, As is also known as a therapeutic agent as early as 400 BC. For example, Fowler solution (arsenite solution containing  $7.6 \times 10^6 \mu\text{g As/l}$ ) has been used since the 19<sup>th</sup> century for the treatment of leukaemia, psoriasis, chronic bronchial asthma and also as a tonic. The daily dosage was often as high as 3000  $\mu\text{g}$ . As has also extensively been used as pesticides, herbicides, wood preservatives, manufacture of dyestuffs, chemical warfare gases, glass industry, electronics, and growth promoting agent<sup>(59)</sup>. The discovery of adverse health effects due to As exposure led to decreased usage of As. For example, the use of As salts in the agriculture went down drastically since 1970's with 70% of the worldwide production As trioxide applied in the agriculture in 1970 to only 45% in 1980<sup>(73)</sup>. The usage of As in the glass manufacturing industry is also reduced<sup>(74)</sup>. The current uses of As compounds are as clarifier in the glass industry, as wood preservative, in semiconductors, as a desiccant and defoliant in agriculture<sup>(75,76)</sup>. One of the present usages of As as therapeutic agent is in Cancer treatment. Recently in 2000 randomized clinical trials in the US led the Food and Drug Administration (FDA) to approve As trioxide for treatment against leukaemia<sup>(77)</sup>.

### 2.2 Arsenic Chemistry of relevance

As in the environment can occur in several oxidation states (-3, 0, +3, +5) and as both organic and inorganic As. However, in natural waters inorganic As is predominant and is found as oxyanions of trivalent arsenite ( $\text{H}_3\text{As(III)O}_3$ ) or pentavalent arsenate (e.g.  $\text{H}_2\text{As(V)O}_4^-$ ). In surface waters organic As compounds may be produced by biological activity, but are rarely important quantitatively. Figure 1 shows structures of some of the As compounds referred in the text. Redox potential and pH are the most important controlling factors in As speciation. As(V) is more predominant under oxidising conditions and As(III) is more predominant under reducing conditions. The rate of oxidation of As(III) to As(V) or reduction of As(V) to As(III) depends on many factors like pH, Eh, the presence of micro-organisms, the presence of other oxidizing agents like manganese, Fe, etc., exposure to light and temperature<sup>(57,78,79,80,81,82)</sup>. Generally the rate of oxidation of As(III) to As(V) is very low<sup>(83)</sup> in natural waters, but can proceed measurably in several days in strongly alkaline or acid solutions. The speciation of As is important in controlling the mobility, bioavailability and toxicity. As(V) with  $\text{pK}_1$  and  $\text{pK}_2$  values of 2.2 and 7.1 is present in the anionic form, whereas As(III) with  $\text{pK}_1$  value of 9.2 is present in neutral form in natural waters. The mobility of As is mainly controlled by the presence of metal (hydr)oxides and since at the pH of natural water As(III) is present as a neutral species and As(V) is present in anionic form the sorption of As(V) is strongly favoured. Therefore As(III) is more mobile compared to As(V) in neutral to slightly acidic pH range. The presence of other competing ions also have an effect on the mobility of As<sup>(84,85)</sup>. For example high concentrations of P can desorb both As(V) and As(III). Similarly in the absence of other ions and abundance of available surface sites sorption of As(III) can also take place<sup>(86,87)</sup>. Under extremely reducing conditions and acidic pH with high concentration of reduced S precipitation of orpiment

(As<sub>2</sub>S<sub>3</sub>), realgar (AsS), FeAsS or other sulphide minerals is favoured leading to lower As concentrations<sup>(57,88)</sup>.

Arsenic is readily absorbed when ingested in dissolved form (80-90%) or inhaled (30-85%). As(V), whether organic or inorganic, is better absorbed from the gastrointestinal tract compared to As(III). In contrast to inorganic arsenic, neither mono- methyl arsenic nor di-methyl arsenic binds strongly to biological molecules in humans<sup>(61)</sup>.

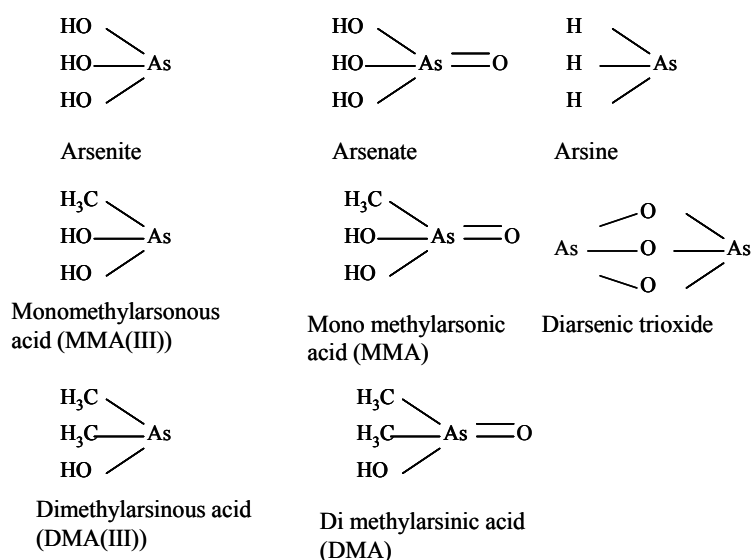


Figure 1: Structures of some of the As compounds referred in the text (after<sup>(89)</sup>)

### 2.3 Health effects and risk Assessment

As toxicity depends on many factors like species, amount of exposure, duration of exposure, nutritional status, methylation capacity, genetic conditions, bioavailability, selenium intake and presence of co-carcinogenic factors like exposure to sunlight, cigarette smoking<sup>(90,65,91,12,92,93,94,95)</sup>. As methylation is considered to be a detoxification path, because the pentavalent organic As metabolites (DMA and MMA) were the most common forms found in urine samples of exposed humans. These forms are readily excreted and less toxic than inorganic As. However, some recent studies identified trivalent metabolites of organic As, DMA(As(III)) and MMA (As(III)), in urine samples of human exposed to As (sited in<sup>(96)</sup>). Laboratory studies have shown that these organic As(III) metabolites are more toxic than inorganic As(III)<sup>(97,98,99)</sup>. Some of the early clinical symptoms of acute effects include abdominal pain, vomiting, diarrhoea, muscular pain, and weakness<sup>(100)</sup>. Organic As is considered to be less toxic than inorganic As and the toxicity decreases in the order of AsH<sub>3</sub> > As(III) > As(V) > organic arsenic compounds. The lethal dosage of As range from 1.5 mg/kg body weight for As<sub>2</sub>O<sub>3</sub> to 500 mg/kg of body weight for DMA<sup>(11)</sup>. Chronic exposure to low concentrations of As can cause dermal changes like skin pigmentation, hyperkeratosis and ulceration. Other chronic non dermal effects of As are diabetes<sup>(101)</sup>, effects on cardiovascular system<sup>(102)</sup>, hypertension<sup>(103)</sup>, respiratory effects<sup>(104)</sup>, adverse pregnancy outcomes<sup>(16)</sup> etc<sup>(61)</sup>. Chronic exposure to As is also documented to be carcinogenic in

humans<sup>(11)</sup> at high exposures. However, discussion is still going on about the threshold limit for carcinogenic action of As, since both US and non-US-based studies showed only positive correlation between exposure to As and occurrence of cancer at As concentrations above 100 µg/l<sup>(105,106,107,108,65,93,109,110)</sup>.

Exposure to As can occur through food, water and air and table 1 shows general exposure level through these various routes<sup>(11)</sup>. According to the values in table 1, the major route of exposure to total As is through food. However, the exposure through food did not receive much attention, since more than 90% of As in food is in the form of organic As. Water is the second major route of exposure to total As, and As is mainly present as inorganic As in natural waters. However, in areas with elevated As concentrations exposure of As through water becomes the major route. The first study related to exposure to As through drinking water and prevalence of skin cancer was reported from Taiwan<sup>(28)</sup>. Based on this study WHO lowered the maximum permissible level from 50 µg/l to 10 µg/l<sup>(11)</sup>. Table 2 depicts the acknowledgement of As in drinking water as a cause for adverse health effects in the form of lowered guideline values through years<sup>(111)</sup>. In later years more studies also reported prevalence of internal cancers like bladder, liver, kidney and lung due to As exposure through drinking water<sup>(12,108,54,19,112,113)</sup>. The latency period for development of skin and internal cancers are reported to be 6->40 years and depends on many factors like exposure level, duration of exposure, smoking habits, nutritional status, gender, sunlight and genetic conditions<sup>(114,11,115)</sup>. The estimated life time excess risk of getting skin cancer in the US population at 50 µg/l is 3/1000<sup>(61)</sup> and for the sum of internal cancers it is 1/100<sup>(116)</sup>. This risk estimate would be even higher for general population in Bengal delta with a body weight of 50 kg, consuming 4-6 litres of water and nutrient deficient food. For more information see (IV).

Table 1: Intake of inorganic and organic Arsenic compounds in the general population<sup>(117)</sup>.

Source	Inorganic Arsenic (µg/d,p)	Organic Arsenic compounds (µg/d)
Air	0.05	-
Food	5-20	5-1000
Water	<1-10	-
Smoking	1-20	-

Tabel 2. Developments in the WHO's guideline value for arsenic in drinking water<sup>(111)</sup>.

Year	Guideline value	Reasons for the change in the guideline value
1958	200 µg L <sup>-1</sup>	Possible risk for adverse health effects
1963	50 µg L <sup>-1</sup>	No reason was mentioned
1971	50 µg L <sup>-1</sup>	It is wise to have a guideline value as low as possible
1984	50 µg L <sup>-1</sup>	No health effects were observed at this level
1993	10 µg L <sup>-1</sup>	Estimated risk of excess skin cancer $6 * 10^{-4}$ . It was practically impossible to measure at levels below this value at that time. <i>If the guideline value is based on the tolerance of an excess life time risk of <math>10^{-6}</math> as is the case for pesticides and other carcinogenic matter, As concentration in drinking water should be 0.017 µg/L.</i>



## 3 Arsenic in the Bengal Delta

### 3.1 Occurrence of Arsenic

The As contamination in the Bengal delta was first discovered in 1980's in West Bengal (India) followed by Bangladesh in 1993<sup>(56)</sup>. The As contaminated area is mainly situated in the flood plains of the rivers Ganges, Brahmaputra and Meghna emerging from Himalayas. The drinking water in the Bengal delta is mainly extracted using tube wells from 10-150 m depth (also called as shallow tube wells) and elevated As concentrations mainly occur at these depths. The very shallow wells (< 10 m depth), ponds, and river water are basically free from As. Deep tube wells (> 150 m) are also generally free from As, however, some studies show that the As concentration in the deep tube wells increases with age due to reasons like absence of impermeable layer or improper tube well casing<sup>(57)</sup>.

The ground water in shallow tube wells with elevated As is of typically Ca(Mg)HCO<sub>3</sub> type and positive correlation exists between As and HCO<sub>3</sub><sup>-</sup>. Dissolved Ca<sup>2+</sup> follows dissolved As profile. The pH is near neutral with low dissolved oxygen. As is predominantly present as inorganic As(III). High phosphate (P) and silicate (Si) occur along with As. Elevated Fe concentrations also occur and in some areas a positive correlation exists between elevated As and Fe. Although, the Fe and As are not strongly correlated in other areas elevated As concentrations usually occur with elevated Fe concentrations<sup>(118,119)</sup>.

The recent studies show that the As contaminated area is more widespread than the Bengal delta and occur along the courses of Himalayan Rivers covering Nepal<sup>(44,120)</sup> and other districts of India upstream of the Bengal delta<sup>(33,121,122)</sup>, and Pakistan<sup>(123,124)</sup>. Figure 2 shows the 4 major rivers along which elevated As concentrations occur, with the Bengal delta being the most studied area for the reasons behind occurrence of As.





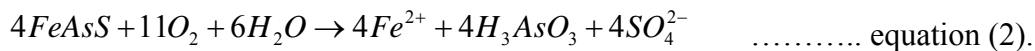
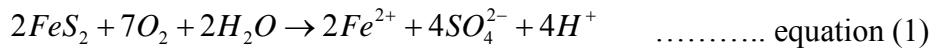
Figure 2: Extent of As contamination in the Indian subcontinent.

### 3.2 Origin of As

At the initial stages of As discovery in the Bengal delta the contamination was thought to be of anthropogenic origin due to reasons like burial of light poles coated with chromate copper arsenates (CCA), application of pesticides and phosphatic fertilizers rich in As, or other industrial contamination<sup>(125)</sup>. In 1993 a study was also published from Behala, West Bengal on elevated As concentrations in ground water due to discharge from insecticide (Paris Green (copper acetoarsenite)) manufacturing industry<sup>(126)</sup>. However, the theory of anthropogenic sources for As contamination in the Bengal delta was later discarded due to the extent and nature of the problem and it was established that the As occurrence is natural in origin. It is believed that the rivers like Ganges, Meghna and Brahmaputra carry As bearing primary minerals like pyrite, arsenopyrite and other sulfides from various sources like Himalayas, Subhimalayas (Siwalik mountains), Rajmahal, ChotNagpur, Darjeeling Himalayas, Shillong hills and later deposited along their courses<sup>(57,127,128,129)</sup>.

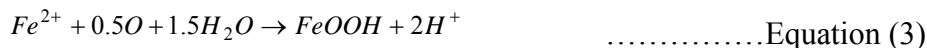
### 3.3 Causes for release of As

Three different hypotheses on release of naturally occurring As were put forward to explain the mobilization of As into ground water. 1) Desorption due to P from fertilizers 2) Pyrite-oxidation theory 3) Oxi-hydroxide reduction theory. The hypothesis of As release due to displacement with P from phosphatic fertilizers was based on the fact that the ground waters in the Bengal delta contain high concentrations of P along with As<sup>(130,131,127)</sup>. Studies are also available from other parts of the world where elevated As concentrations in groundwater resulted due to application of phosphatic fertilizers<sup>(84,132,133,134)</sup>. However, this theory did not get any support in the Bengal delta context due to inadequate and contradictory evidence. The pyrite oxidation theory also called oxidation theory was put forward due to the discovery of pyrite grains in the sediments both in West Bengal (India) and Bangladesh. The supporters of this theory believe that As is present as pyrite in the sediments and is released due to heavy withdrawal of groundwater<sup>(135,127)</sup>. The lowering of groundwater table due to heavy water withdrawal would result in penetration of oxygen into the deeper sediments resulting in oxidation of pyrites rich in As as shown in equations 1 & 2.



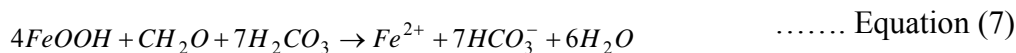
Reported incidences of elevated As concentrations in ground water due to oxidation of pyrite and other arsenic-bearing rocks are available from other parts of the world<sup>(136,57)</sup>. However, in the Bengal delta context, this theory did not either get wider acceptance due to the widespread absence of arsenopyrite in the sediments<sup>(127,137)</sup>. There are many other opposing facts to the oxidation theory as the cause of As occurrence. Instead of positive correlation between  $SO_4^{2-}$  and As concentrations as expected due to pyrite oxidation, negative correlation exists between  $SO_4^{2-}$  and As concentrations. The presence of pyrite shows that it has not been oxidised, but was formed in situ and hence it is sink and not source for As. The intensity of As problem has no direct relation with groundwater fluctuations. Hence the oxidation theory is not being considered as main mechanism for As release<sup>(138,139)</sup>.

The oxy-hydroxide reduction hypothesis assumes that the As bearing minerals carried by the rivers were oxidized during transportation (as shown in equation 1- 4) and metals and As in solution (mainly as As(V) species) were co-precipitated or adsorbed on the flocculating particulate matter and on the surface of grains coated with Mn- and Fe-oxyhydroxides (Equation 5 & 6) and deposited<sup>(138,118)</sup>.



where Me denotes metal ions like Mn, Fe.

Adsorbed As and P from metal hydroxides were later released due to reductive dissolution as shown in equations 7-8 leading to ground waters with elevated As(III) and  $Fe^{2+}$  concentrations.



Reported incidences of elevated As concentrations in ground water under reducing conditions are also available from other parts of the world <sup>(57,140)</sup>. Both anthropogenic and natural causes for prevalence of reducing conditions have been suggested <sup>(141,138,142)</sup>. According to Nickson et al. <sup>(138)</sup> the reducing environments were always there and also when the first tube well was sunk. Nickson et al. <sup>(138)</sup> and Acharya et al. <sup>(130)</sup> explained the origin of organic matter in the sediments based on the changes in the sea level. During the past 18000 years the sea level was both above and below the present level. The As contaminated layer was deposited around 10000 to 7500 years before present (b.p.). Sea level rose rapidly between 7000 to 5500 years b.p. to reach levels higher than present level. This caused flooding of the partly sedimented valleys, resulting in formation of marshes, lagoons and estuaries with organic rich matter. They observed a positive correlation between the location of As-bearing zones with deltaic environment and organic rich deposition during this sea level rise. Another hypothesis for the prevalence of reducing conditions is intensive rice irrigation <sup>(143)</sup>. Cultivation of two crops per year of wetland rice would result in water standing on the fields for about 200-300 days. This would result in reduced diffusion of oxygen into the subsoil. A joint study conducted by Bangladesh University of Engineering and Technology (BUET), Massachusetts Institute of Technology, (MIT) and University of Cincinnati the proposed that release of As is due to introduction of nutrients for the microorganisms <sup>(125)</sup>. Laboratory investigations also <sup>(144)</sup> showed that addition of nutrients, glucose and polypepton to sediments from Bangladesh resulted in enhanced bacterial activity with rapid drop in Eh values and increase in As concentration. Infiltration of young water rich in organic matter due to heavy withdrawal of ground water was also one of the hypothesis for prevalence of reducing conditions <sup>(145)</sup>. A study <sup>(146)</sup> conducted in Hat Yai, Thailand also showed that infiltration of water with high organic content containing urban recharge caused reducing conditions and release of As to ground water. Though there are many theories explaining the reasons behind prevalence of reducing conditions, the microbial mediated reductive dissolution of As contained Fe-hydroxides is now the most widely accepted hypothesis. However, the possibility of application of other theories can not be ruled out as a possible cause of As release in some areas of the vast As contaminated Bengal delta.

## 4 As mitigation options

The As calamity in the Bengal delta has emerged as the biggest ever known drinking water problem. The only sustainable solution in the long term is to supply As free potable water. The various options available for supplying As free drinking and cooking water are finding a new source free from As and/or treating the As contaminated tube wells.

### 4.1 Changing water source

The various options for As free water source are surface water, rain water harvesting, As free ground water sources in the form of deep tube wells, shallow tube wells and dug wells, centralized piped water supply, and bottled water supply. Table 3 shows advantages, disadvantages and costs of implementation and maintenance of these solutions.

#### 4.1.1 Supply from surface waters:

The Bengal delta has abundance of surface water in the form of ponds, lakes and rivers free from As and until the introduction of ground water, surface water was used as the main source for all domestic purposes. However, the consumption of often bacteriological contaminated surface water without any treatment lead to diseases like diarrhoea, dysentery, typhoid, cholera and hepatitis. This was the main cause for replacing surface water with ground water since late 1960's. Reintroduction of surface water as a safe water source would require hygienisation and treatment of surface water and the available options are pond sand filters (PSF)<sup>(147)</sup> and combined surface treatment units. The withdrawal of surface water could be improved by installation of infiltration galleries or wells with sanitary protection<sup>(148)</sup>. However, literature reports that the treatment of surface water using PSF has not gained popularity due to aesthetic and safety reason, but is accepted for cooking. The other drawback of this option is that most of the ponds are used for fish culture; therefore the community has to be motivated to reserve a pond exclusively for drinking purpose.

#### 4.1.2 Rain water harvesting:

Since ancient times rain water harvesting has been widely used throughout the world as a method of utilising rain water for domestic and agricultural purposes and is still widely used in some of the East-Asian countries with some success. However, this technology has never been widely used in Bangladesh and West Bengal. The reported experiences of using rain water harvesting in the Bengal delta until so far are not satisfactory. The rainfall in Bengal delta varies spatially and is restricted during the months of April to September. This would require a huge storage tank. The implementation of this technology in rural areas would require changes in the roofing since the houses are mostly with thatched roofs and are not good for rainwater harvesting<sup>(148)</sup>.

### **4.1.3 Supply from ground water**

#### *4.1.3.1 Dug well*

Dug wells are open wells without protection. Studies show that As concentration in most of the dug wells is very low probably due to continuous oxidizing conditions and Fe precipitation or due to recharge of the dug wells with rain water. However, there are some dug wells where As concentration is above the MCL. Before the installation of tube wells dug wells have been used as drinking water source<sup>(148)</sup>. However, the acceptance of dug well water for drinking purpose is not high anymore<sup>(149)</sup>. Some improvements have been suggested to prevent the bacterial contamination of dug well water in the form of closed dug wells with an hand tube well attached to withdraw the water<sup>(150)</sup>. A study<sup>(149)</sup> showed that the acceptance of the use of dug well water for drinking purpose was improved, but people complained about the smell of chlorine due to chlorination of dug well water.

#### *4.1.3.2 As free Shallow tube well*

Even though exposure to As in Bengal delta is due to the water extracted through shallow tube wells, studies indicate that the percentage of As contaminated tube wells is usually in the range of 20- >50%<sup>(56,62)</sup>. Therefore the cheapest solution would be switching to the uncontaminated tube wells. However, the applicability of this solution would depend on the availability of As safe tubewells and the distance to the safe water source. A study<sup>(151)</sup> showed that even though 82% of the investigated tube wells were found to be contaminated with As, 89% of the people lived within 200 m to the nearest safe tube well<sup>(148)</sup>. Apart from the distance to the nearest As safe tube wells, the other factors influencing this solution could be socio-economic barriers. One of the barriers could be that women (the traditional water providers) are traditionally not expected to leave their Bari (a cluster of related households)<sup>(151)</sup>. The other barrier could be that the tube well owner would not permit others to use the water. Well switching as a long term solution would require continuous monitoring for As concentration. There are studies showing that the As concentration in the tube wells changes over time, with high concentrations during summer compared to winter<sup>(152)</sup>.

#### *4.1.3.3 Deep tube well water*

The ground water extracted from deeper aquifers is usually free from As, however, it is difficult to give an exact depth where this will dominate. Usually water extraction below 150/200m deep is considered as deep aquifer, but in many cases this can be below 200m<sup>(153)</sup>. The study by BGS showed that only 5% of the deep tube well waters had an As concentration above 10 µg/l and 1% exceeded 50 µg/l<sup>(62)</sup>. But if the deeper aquifer is not separated geologically from the upper aquifer the As concentration can increase with time due to leaching. Monitoring of As concentration is also required for this solution.

## **4.2 Overview of methods for treatment of Arsenic contaminated water**

The available conventional technologies on As removal from pumped ground water can be divided into 4 categories: Coagulation/Coprecipitation, Adsorption onto surfaces,

Membrane technologies and Ion exchange methods<sup>(154,155,156)</sup>. Apart from these 4 categories Microbial treatment processes have also been suggested in the literature as a possibility for removal of As.

#### 4.2.1 Coagulation/co-precipitation

The processes involved in As removal by coagulation are addition of metal salts, sedimentation and filtration. The common coagulants added in the pH range of 4-8 are Fe<sup>(157,158,159,160,161,162,154,163,164,165)</sup> and Aluminium salts<sup>(166,167,162,154,163,166)</sup> and Ca(OH)<sub>2</sub><sup>(168,169,170)</sup> is added at pH above 10. The removal efficiency for As(V) is usually much better than for As(III), therefore pre-oxidation of As(III) is necessary to increase the As removal efficiency<sup>(157,171,172,173)</sup>. Presence of competing ions like P and Si, and bicarbonate would have negative effect on As removal efficiency<sup>(174,175,176,87)</sup>, whereas Ca<sup>2+</sup> and Mg<sup>2+</sup> would have positive effect<sup>(173)</sup>.

#### 4.2.2 Adsorption on activated/coated surfaces

The principle behind removal of As using activated/coated surfaces is sorption. Several adsorbents have been investigated in the literature and the most widely investigated adsorbents are Activated Alumina<sup>(177,178,165)</sup>, and various Fe (hydr)oxide<sup>(179,180,181,182,183,184)</sup>. Similar to coagulation the removal of As depends on As species with better As(V) sorption compared to As(III) at pH lower than 7<sup>(173,185,182)</sup>. The adsorption capacity would also depend on pH, presence of other ions like P, Si, HCO<sub>3</sub><sup>-</sup>, Ca<sup>2+</sup><sup>(186,187,177,178,173,185,181,188,189)</sup>. The possibility of regeneration of these kinds of adsorbents varies widely.

#### 4.2.3 Ion exchange:

The principle of Ion exchange is that As is adsorbed on to anion-exchange resins in exchange of other ions that are less strongly adsorbed compared to As. Various resins have been tested for removal of As from water<sup>(190,191,192,193,194,165)</sup>. Pre-oxidation of As(III) is necessary to achieve removal of As from water since As(III) is present in neutral form and As(V) is present as an anion at neutral pH. The regeneration of the spent ion exchange resin can be carried out.

#### 4.2.4 Membrane processes

The principle of a membrane process is that water is allowed to pass through special filter media, which physically retain the impurities, present in the water. Reverse Osmosis, Electrodialysis, Nanofiltration and Colloidal floatation are some of the membrane processes studied, and some results show that removal of As(V) is better than As(III)<sup>(195,196,197,198,199,200,201,202,203)</sup>.

The advantages and disadvantages of these 4 principles are listed in table 4. Based on these 4 principles various treatment units are available in the market. Table 5 lists the costs of installation and O&M costs of these treatment units. This table further contains a category called indigenous methods. Most of the indigenous methods act on the combined principle of coagulation-coprecipitation and adsorption. For example in Sono 3 kolshi method the Fe filings present comes in contact with oxygenated water and Fe

gets oxidized to  $\text{Fe}^{3+}$  and hence the process acts as coagulation and coprecipitation. The release of Fe to water from Fe filings will continue so long there are Fe filings. Therefore the advantages and disadvantages of these methods can be compared with the adsorption onto activated/coated surfaces and ion exchange method, except that the material is locally made and can be bought locally without the need for regeneration as in case of Adsorption onto activated surfaces.

### **4.3 Appropriate solution in context to the rural areas of the Bengal delta**

Selection of a suitable method to supply As free drinking water depends on several factors. In the rural Bengal delta context where centralized water supply is not available, the factors to be taken into consideration for selecting an appropriate solution for the supply of potable water are:

- Simple
- Low-cost
- Able to function without electricity
- Based on local resources and skills
- Accessible to community and women's group
- Include provisions for a safe method of disposal of As rich-sludge

Apart from the above, decision should also be made on whether the As free water supply should be based on the community level or household level. This decision would vary from place to place depending on the people who are supposed to use the system. Problems could arise in the long run if the water supply is based on the community level, where a local community committee is formed only for As mitigation. The reported experiences in literature on the water supply at community level showed that if the formation of a local committee is only for procurement of As treatment technology, the committee may dissolve after procuring the unit. There is no one to take the responsibility to maintain the unit. In some cases the landowner where the unit is installed denies others to use the unit or individual members of the community deny paying the maintenance cost. Literature review shows that the affordability of majority of the population in the rural areas of Bengal delta is in the range of INR 250-500 (4.8-9.5 EUR)<sup>(204)</sup> per household.

Comparison of these criteria with the results from Table 3, 4 and 5 shows that well switching and/or treatment using the coagulation and indigenous principle are the only solutions that are appropriate on the individual basis for the majority of population in the rural villages of the Bengal delta.

Since the ground waters of the Bengal delta contain high concentrations of Fe the costs of the treatment could further be lowered if the naturally occurring high concentrations of Fe can be utilized for removal of As. However, field studies show that rather high Fe concentrations are necessary for removal of As. The overview of mechanisms involved in removal of As with naturally occurring Fe is important in understanding the removal of As in presence of Fe and the simple measures necessary for improving the removal method.

Table 3. Advantages and disadvantages of changing water source.

Solution	Installation cost (EUR)		O & M cost/HH/y (EUR)	Number of people	Advantages	Disadvantages
	Total	/HH				
Surface water sand filters)	440	8.8	0.05-1.3	250	<ul style="list-style-type: none"> <li>• Free from As</li> <li>• Locally available materials</li> <li>• No use of electricity</li> </ul>	<ul style="list-style-type: none"> <li>• could be dry during the dry season</li> <li>• Low discharge</li> <li>• Difficulty in washing filter beds</li> <li>• May not remove 100% of the pathogens</li> <li>• Longer distance lead to usage of STW</li> </ul>
Combined surface water treatment unit	9400	9.4	1.2	5000	<ul style="list-style-type: none"> <li>• Free from As</li> <li>• Locally available materials</li> <li>• No use of electricity</li> <li>• Easy maintenance</li> </ul>	<ul style="list-style-type: none"> <li>• could be dry during the dry season</li> <li>• Low discharge</li> <li>• Longer distance lead to usage of STW</li> </ul>
Rain water Harvesting	80	80	0.25	5	<ul style="list-style-type: none"> <li>• Free from As</li> <li>• Locally available materials</li> <li>• No use of electricity</li> <li>• Easy maintenance</li> <li>• Shorter distance</li> </ul>	<ul style="list-style-type: none"> <li>• Depends on rainfall and roof area</li> <li>• Can not be used on thatched roofs.</li> <li>• Possibility of bacterial contamination</li> <li>• Require big storage tanks and disinfection</li> </ul>
Dug wells	440	17.6		125	<ul style="list-style-type: none"> <li>• Low As concentrations</li> <li>• Locally available materials</li> <li>• No use of electricity</li> <li>• Easy maintenance</li> </ul>	<ul style="list-style-type: none"> <li>• Longer distance lead to usage of STW</li> <li>• Risk of bacterial and other contamination</li> <li>• Monitoring is necessary</li> <li>• Risk of well collapsing</li> </ul>
Deep tube wells	570	11.4		250	<ul style="list-style-type: none"> <li>• Free from As</li> <li>• No treatment required</li> <li>• Locally available materials</li> <li>• No use of electricity</li> </ul>	<ul style="list-style-type: none"> <li>• Longer distance lead to usage shallow tube wells</li> <li>• Monitoring for As is necessary</li> </ul>
Well switching	0	0			<ul style="list-style-type: none"> <li>• No additional instalments</li> </ul>	<ul style="list-style-type: none"> <li>• Depends on the availability of As free STW</li> <li>• Longer distance lead to usage of As contaminated STW</li> <li>• Monitoring is necessary</li> </ul>
Piped water supply	23180	23.8	0.25	5000	<ul style="list-style-type: none"> <li>• Water quality can be controlled at one place</li> </ul>	<ul style="list-style-type: none"> <li>• Needs proper infrastructure</li> <li>• Is a long term solution</li> </ul>

HH denotes household and a typical household is with 5 persons. STW (Shallow Tube Wells) The costs are from year 2003<sup>(148)</sup>.



Table 4. Advantages and Disadvantages of the different As removal Principles.

Removal Technology	Advantages	Disadvantages
Coagulation	<ul style="list-style-type: none"> <li>• Low capital Costs</li> <li>• Locally available chemicals</li> <li>• Simple in operation</li> <li>• Simple in maintenance</li> <li>• Already exists at many treatment plants</li> <li>• No use of electricity</li> </ul>	<ul style="list-style-type: none"> <li>• Care is necessary for dosage of chemicals</li> <li>• Problems with Sludge disposal</li> <li>• Frequent filter maintenance</li> <li>• Longer treatment time required</li> </ul>
Adsorption on Activated/Coated Surfaces	<ul style="list-style-type: none"> <li>• No daily sludge problem</li> <li>• Easy operation</li> <li>• No use of electricity</li> </ul>	<ul style="list-style-type: none"> <li>• High Capital cost</li> <li>• Requires trained person for maintenance</li> <li>• Requires monitoring of breakthrough</li> <li>• Readjustment of pH</li> <li>• Toxic Liquid Waste from regeneration</li> <li>• Regeneration required</li> <li>• Solid waste in the form of spent adsorbent</li> </ul>
Ion-Exchange Methods	<ul style="list-style-type: none"> <li>• High removal efficiency</li> <li>• No solid Waste</li> <li>• No chemical requirements</li> </ul>	<ul style="list-style-type: none"> <li>• Toxic liquid waste</li> <li>• High Capital Cost</li> <li>• Qualified persons for maintenance</li> </ul>
Membrane Processes	<ul style="list-style-type: none"> <li>• High removal efficiency</li> <li>• No Solid waste</li> <li>• No chemical requirements</li> </ul>	<ul style="list-style-type: none"> <li>• High Capital Cost</li> <li>• High Running Costs</li> <li>• Qualified persons for maintenance</li> <li>• Toxic Liquid Waste</li> <li>• Re-adjustment of water quality is required</li> </ul>

Table 5. Some of the tested treatment technologies at the household basis in the Bengal delta (204,148)

Principle	Name of the Unit	Chemicals used	Installation cost (EUR)	Running cost/year (EUR)
Coagulation/Coprecipitation	DPHE-DANIDA Bucket Treatment Unit	Alum + KMnO <sub>4</sub>	3.8-5	3.2-4.4
	Steven's Institute Technology	Fe + Ca(OCl) <sub>2</sub>	6.3	1.8
	Garnet Filter	Fe	5	
	AIHH & PH	Alum+ KMnO <sub>4</sub>	2.5	
	SOES	Fe <sup>3+</sup> salt+oxidizing agent+charcoal	3.13	
	Adsorption onto Activated/Coated surfaces	Alcan (MAGC)	Activated Alumina	315
BUET Activated Alumina Filter		Activated Alumina	12.5	
BUET Fe coated Sand		Fe coated sand	??	
ARU of Project Earth Industries inc., USA		Activated Alumina and Composite metal oxide		
PAL TROCKNER		Granular ferric hydroxide	38	
Tetrahedron		Resin	150	
MRT-1000		Reverse osmosis		
Reid System		Reverse osmosis		
Techno-food		Nano filtration		
Techno-food.		Reverse osmosis by bicycle pump		
Indigenous:	Sono 3-kolshi Filter:	Fe filings	3.2-3.8	2.5-3.2
	Shapla filter:	Fe coated dust	3.8	6.3
	Chari filter	Brick chips	3.8-5.1	3.2-4.4
	SAFI Filter	Filter media	25.1	3.8



## 5 Arsenic analysis

As is colourless, odourless and tasteless and hence difficult to detect. The methods available for determination of As analysis could be categorized into colorimetric techniques, spectrometric techniques, inductively coupled plasma techniques, neutron activation analysis, and electrochemical methods<sup>(205)</sup>. The molybdenum blue method and the silver diethyldithiocarbamate were the first reasonably good quantitative methods developed based on the colorimetric technique in 1950's<sup>(59)</sup>. The spectrometric techniques with hydride generation (hydride generation atomic absorption spectrometry (HGAAS), hydride generation atomic absorption fluorescence spectrometry (HGAFS)) or without hydride generation (Graphite furnace atomic absorption spectrometry (GFAAS)) are the most popular techniques for measuring As<sup>(205)</sup>. For this study a method based on HGAAS was developed for As analysis in water and both HGAAS and GFAAS were used for As analysis in hair, since the other techniques were not feasible or available.

### 5.1 Sample preservation

The speciation of inorganic As in this study was very important since one of the objectives of this study was to investigate the mechanisms involved in As(III) removals in presence of Fe. Oxidation of As(III) in presence of Fe depends on many factors as indicated in (VII) and in the absence of proper preservation oxidation of As(III) can occur during sample preservation<sup>(206,207,208,209)</sup>. The effect of type of preservative, (0.2% v/v) HCl, (0.2% v/v) HNO<sub>3</sub><sup>(34)</sup>, (0.2% v/v) H<sub>2</sub>SO<sub>4</sub><sup>(210,211)</sup>, EDTA<sup>(212)</sup>, temperature (4°C and room temperature) and light (dark and room light) on oxidation of As(III) during sample preservation were investigated in distilled water and tap water and the obtained results are shown in figure 3a and 3b respectively. The experiments were conducted by adding the required amounts of As to the water followed by simultaneous addition of Fe and preservative. The investigated As(III) and Fe<sup>2+</sup> (FeCl<sub>2</sub>) concentrations were 1 and 10 mg/l. The obtained results showed that oxidation of As occurred in all the investigated conditions. Though highest oxidation occurred upon addition of EDTA, there was no increase in oxidation of As(III) upon preservation of the samples. The results further showed that in case of distilled water similar results were obtained in presence of acid compared to in the absence of acid. This is due to the fact that Fe was added from an acidic solution and hence the resulting pH upon addition of Fe would be in the acidic range. The results further showed that preservation at 4°C did not inhibit oxidation of As(III). Similarly storage in dark did not inhibit As(III) oxidation. Oxidation of As(III) increased with time and at the end of 8 days, 30-40% oxidation occurred even in presence of acid. These results indicate that none of the investigated methods were appropriate for sample preservation. The samples were analysed for total As (pH 2 using HCl) and As(III) (pH 5.5 using acetate buffer) using HGAAS (MHS-20) in batch system. Since the results from sample preservation showed that none of the investigated methods were suitable for preservation of As a method was developed in this study based on online generation system which is described below.

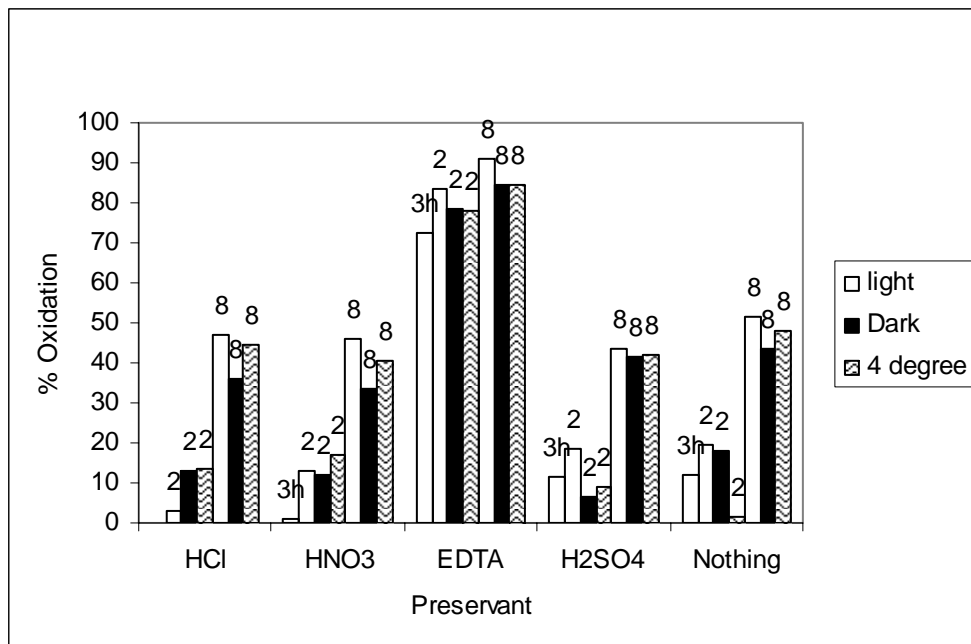


Figure 3a: Effect of preserving agent on oxidation of As(III) in distilled water. Legends: 3h = 3hours, 2 = 2 days and 8 = 8days.

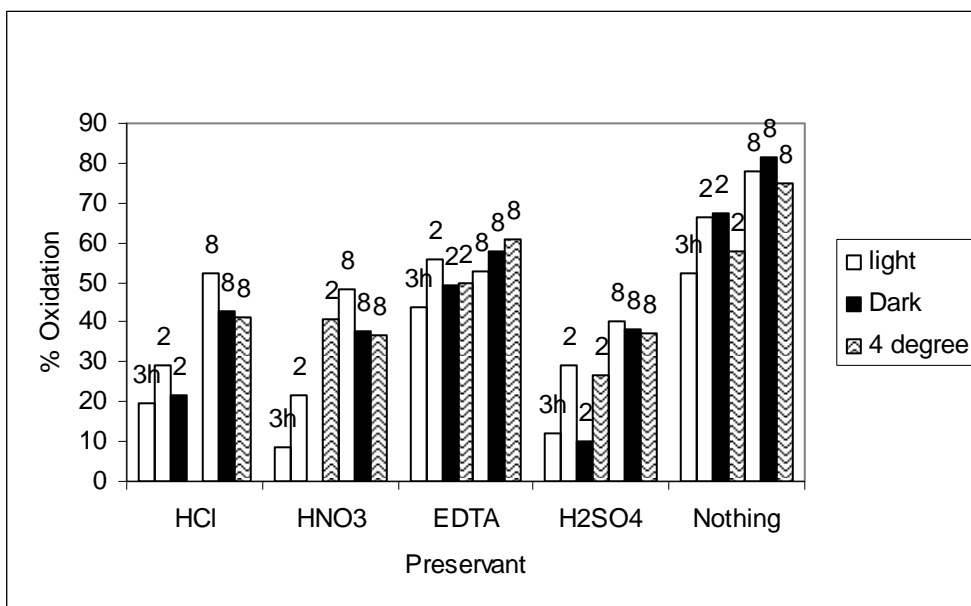


Figure 3b: Effect of preserving agent on oxidation of As(III) in tap water. Legends: 3h = 3hours, 2 = 2 days and 8 = 8days.

## 5.2 Continuous hydride generation system

The continuous hydride generation system has many advantages like simple in operation, excellent reproducibility and low detection limit. The schematic representation of the continuous system used in this study is shown in figure 4. A peristaltic pump was used to transport the solutions. Sample and acid were mixed together and transported to the reaction chamber (RC) where  $\text{NaBH}_4$  is added. Nitrogen

is used as a carrier gas to strip and carry the produced  $\text{AsH}_3$  into the electrically heated quartz tube. The spent liquid is drained to a waste container.

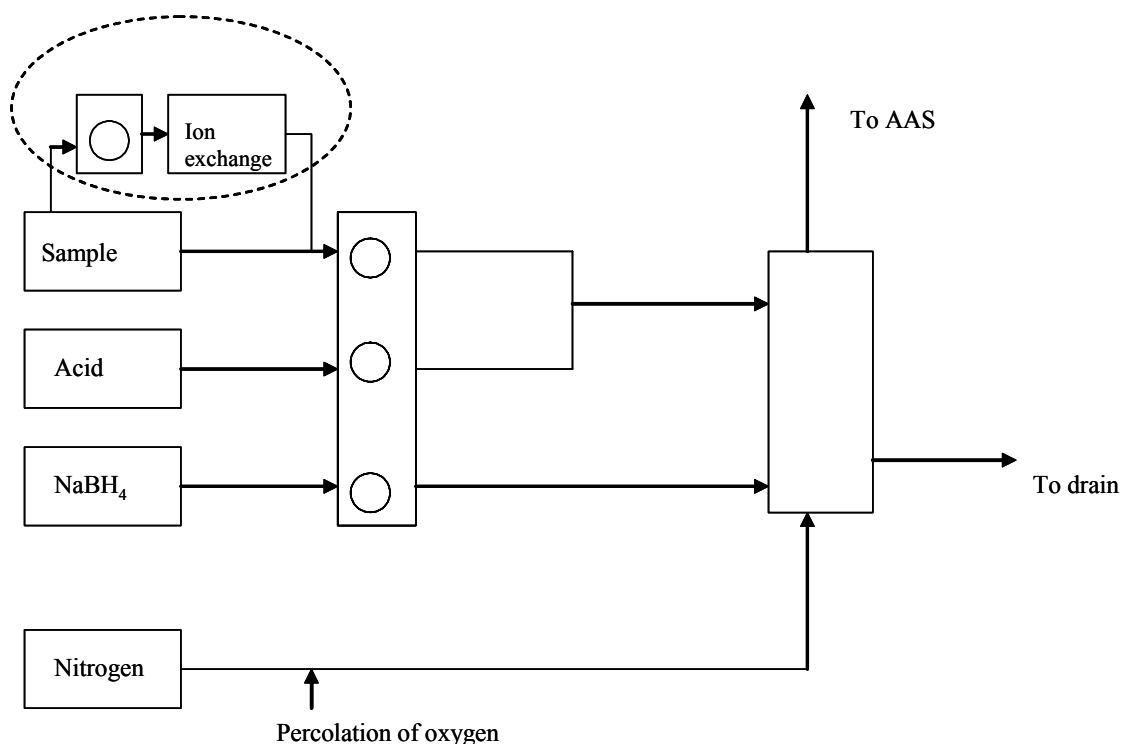
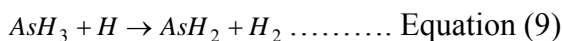


Figure 4. Schematic representation of continuous hydride generation used for As analysis in this study.

The atomization of  $\text{AsH}_3$  in a quartz tube depends on factors like temperature, acid concentration, flow rate of carrier gas, presence of oxygen, surface of the quartz tube etc<sup>(213,214,215,216,217,218,219,220,221,214,222,223)</sup>. Literature indicates that temperatures of 800-900<sup>0</sup>C are adequate in a quartz tube atomizer to obtain optimum sensitivity. Literature also indicates that addition of small amount of air or oxygen to the purge gas enhances the sensitivity substantially and complete atomization is possible even at temperatures of around 700<sup>0</sup>C<sup>(213,224,225)</sup>. The quartz surface has also a considerable influence on the atomization signal and the atomizer attains a final sensitivity after a prolonged period of use. <sup>(213,215)</sup> proposed a three step mechanism for the atomization of As (equations 9 – 11) and later on the mechanism was confirmed by many others<sup>(215)</sup>. The production of H radicals depends on the oxygen supply to the atomizer. Silicone rubber tubes were used for transportation of Nitrogen to allow penetrations of air and the amount of air needed was optimized by changing the length of the tube.



Hydride generation can be carried out either using a batch system or flow system. The main principle behind the batch system is that acidic solution is present and the alkaline  $\text{NaBH}_4$  solution is added simultaneously with carrier gas over a period of time, whereas

in flow system carrier gas is added after the continuous addition of NaBH<sub>4</sub>. The principle used in the present method is a combination of batch and flow system.

### 5.2.1 Total As analysis:

The generation of AsH<sub>3</sub> depends on the As species, pH, type of system, and interference of other ions. Formation of AsH<sub>3</sub> is more rapid with As(III) compared to As(V). At pH  $\leq 1$  and in batch systems AsH<sub>3</sub> is formed more slowly from As(V) compared to As(III) resulting in peak height that is 25-30% lower in As(V) compared to As(III). Whereas in flow systems the slower reduction of As(V) leads to greater differences in sensitivity with decrease in signal height by 80-90% in case of As(V) compared to As(III)<sup>(59)</sup>. However, using the present system the difference between As(III) and As(V) signal is less than 10% when measured at pH  $\leq 1$ . And hence to simplify the measurement the pre-reduction of As(V) to As(III) as recommended for flow injection system can be omitted. The presence of concomitants can interfere by changing the effectiveness of hydride generation or the release of the hydride from solution<sup>(215)</sup>. In the present system the presence of ions in tap water or Fe (0-30 mg/l), P (0-3 mg/l), Si (0-20 mg/l) did not have an effect on total As measurements.

### 5.2.2 As(III) analysis

As(III) analysis in the batch system can easily be performed at pH values  $> 5$ , whereas for flow systems species have to be separated before the addition of NaBH<sub>4</sub><sup>(215)</sup>. The pK<sub>1</sub> value for As(V) is 2.3 whereas the pK<sub>1</sub> value for As(III) is 9.2. In natural waters with pH values around 6.5-8 As(III) would be neutral and As(V) would be negatively charged. Due to this difference in the surface charge As(III) can be easily separated from As(V) with the help of an anion exchange resin.

Since the present system acted as a batch system the possibility of As(III) analysis at pH values above 5 was investigated. Acetate buffer was used similar to the batch system to attain a pH of 5.5. However, the results showed that even at pH 5.5 the presence of As(V) produced a signal similar to As(III). Various combinations of acetate, HCl and NaBH<sub>4</sub> were investigated and it was found that at pH around 8.5-9 the interference due to As(V) on As(III) measurements was insignificant as shown in figure 5. However, in presence of Fe a black precipitate was formed and was deposited on the bottom of the reaction chamber. This interfered with the signals of the subsequent analysis. The interference due to precipitates formed has been reported in the literature. The elimination of the interference required frequent washing of the reaction chamber.

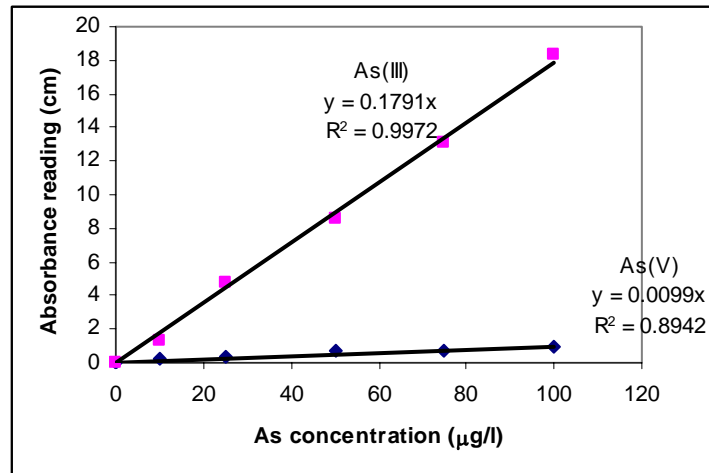


Figure 5: Speciation of As(III) at pH 9.

### 5.2.3 Speciation of As using mini ion exchange column

To avoid frequent washing of the reaction chamber separation of the As(V) species was carried out using a mini column containing dowex anion exchange resin (standard grade of Dowex 1-X8(Cl) from BGH chemicals Ltd. Poole England). The mini column was attached prior to the addition of acid. Figure 6 shows continuous measurements of As(III) concentrations in water between using direct (speciation at pH 8.5-9) and ion exchange method. Figure shows 5% error bars and the obtained results show that the difference between these two methods was within the 5% error.

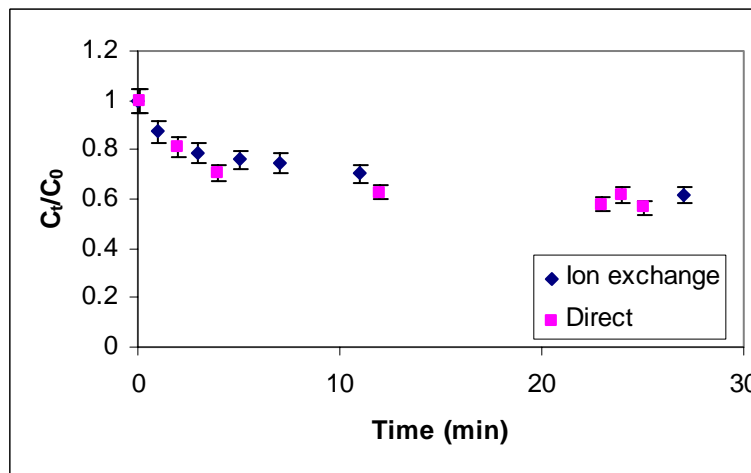


Figure 6. Comparison of As(III) measurements using pH difference (direct) and speciation (Ion exchange)

The different conditions used in the analysis of As are summarized in table 6.



Table 6. Various conditions used in the analysis of As with HGAAS.

Parameters	Batch flow (MHS-20 <sup>*</sup> )		Continuous flow		
	Total As	As(III)	Total As	As(III)	As(III)
Principle	pH < 2	P = 5.5	pH < 2	pH ~ 9	pH < 2 and speciation with mini ion exchange column.
Buffer	2 M HCl	0.5 mM acetate	2 M HCl	0.2 M HCl	2 M HCl
NaBH <sub>4</sub> concentration, % (m/v) in 1% NaOH	4	4	3	1	3
Lamp current, EDL (wt)	8	8	8	8	8
Wavelength (nm)	194.2	194.2	194.2	194.2	194.2
Slit width(nm)	0.7	0.7	0.7	0.7	0.7
Slit height	Low	Low	Low	Low	Low
Back ground correction	Yes	Yes	Yes	Yes	Yes

\* is the Mercury-hydride system used for hydride generation.

## 6 Co-occurrence of Fe & its effects on Health

The ground waters of the Bengal delta contain high concentrations of Fe and the presence of Fe may affect people's water usage habits. Fe renders colour to the water upon storage and stains rice and for aesthetic reasons people would either store the water to remove the Fe or find another water source with low Fe<sup>(226)</sup>. High As concentrations usually occur along with high Fe concentrations in the Bengal delta and the changes in water usage habits due to high Fe would indirectly lead to reduced exposure to As, as reported in (V). My field visit during 1997 and 2002 indicated that the prevalence of arsenicosis in Bangladesh and West Bengal was lower than expected. Therefore both literature and risk analysis was carried out to investigate whether the population in the Bengal delta apparently are protected in one way or the other. The obtained results can be seen in (IV) and (V). The literature survey confirmed the findings of the field visit that the prevalence rate of hyperpigmentation and keratosis were lower in West Bengal and Bangladesh compared to China and Chile. The identified factors responsible for the lower observed prevalence rates in this study were shorter duration of exposure, and indirect effect of Fe in the form of reduced water intakes and removal of As upon storage. The results (V) further indicated that intake of high phosphate would lead to lower prevalence of arsenicosis.

The drinking water supply in the rural areas of Bengal delta is mostly based on shallow tube wells, where more than 10 million tube wells were installed. In rural Bangladesh > 97% of water supply is based on shallow tubewells<sup>(125)</sup>. The first installation of these tube wells started in the late 60's. However, the data from BGS survey conducted in Bangladesh showed that the installation of tube wells increased exponentially in 90's (See figure 7). Figure 7 also shows the cumulative percentage of tube wells present at a given year in village Gazna situated in North 24-Parganas (the data is taken from<sup>(227)</sup>), West Bengal, and shows similar installation statistics as in Bangladesh.

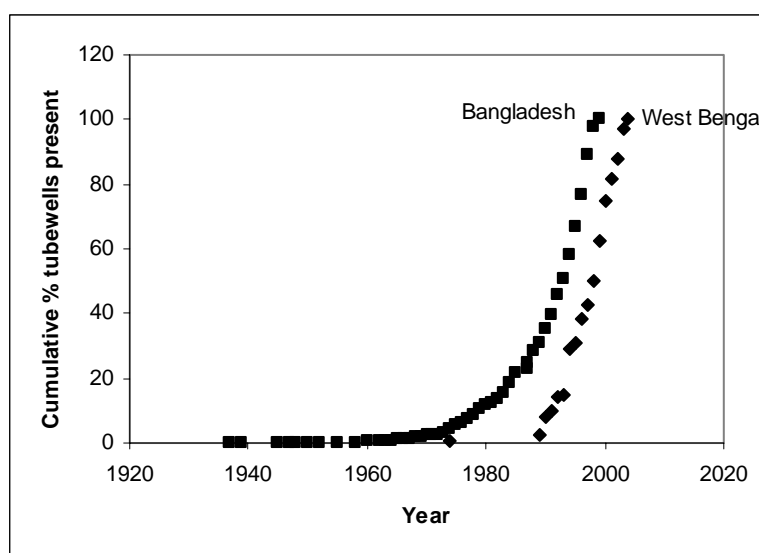


Figure 7. Cumulative percentage of tube wells present at a given year in Bangladesh and village Gazna in West Bengal.

In the absence of own tube well and longer distance to a tube well would lead people to store the fetched water in containers. The calculations (V) showed that the actual excess risk of arsenicosis was reduced by 35% due to these storage habits. However, the findings (V) indicated that the indirect effect of Fe is diminishing due to increased installation of tube wells leading to changes in water storage habits. The longer distance to tube wells before the increased installation of tube wells forced people to store the water, whereas the shorter distance now lead to direct consumption of water without prior storage. However, in the villages with surface water availability, the presence of high Fe concentrations still lead to usage of surface water for cooking purpose due to discoloration of rice cooked with high Fe content. This would result in lower risk of arsenicosis.

Chronic exposure to As can be detected by measuring As in hair and was used in this study as an indicator of exposure. The methods used for digestion and analysis of As are explained in II. The results (II) showed that even though the prevalence rate of arsenicosis in the areas studied is lower than expected the As concentrations in hair samples collected from West Bengal were rather high. Figure 8 shows some newer results along with the results published in II. Here the As content in 83% of the hair samples exceeded 1 mg/kg, which is the generally accepted limit for excessive exposure. The line literature in the figure is derived based on the studies from Inner Mongolia and indicates the As concentrations to be expected in hair corresponding to As concentrations in drinking water<sup>(26)</sup>. Compared to these values the obtained hair arsenic concentrations from West Bengal were far above the expected values. Literature review<sup>(228,229,230)</sup> indicates that elevated As concentrations in hair occur not only due to consumption of water but also due to washing of hair with As contaminated water would increase the As concentration in hair. According to a study from Fairbanks, Alaska<sup>(229)</sup> washing hair with 345 µg/l and 10 µg/l resulted in respective hair As concentrations of 5.7 µg/g and 0.4 µg/g. Using these results the resulting hair As concentrations from washing alone were calculated and are shown in figure 8 as Washing. The results showed that calculated contribution of As through washing hair with As contaminated water in West Bengal alone is higher than the actual As concentration in hair reported in the literature. Even after subtracting these high values due to washing, the As concentrations were higher than the literature values. The higher observed As concentrations in hair in West Bengal compared to literature at similar exposure levels through drinking water could also be due to higher water consumption and higher As intake through food. As shown in (II), the As concentration in Malaysian population living in cities was higher than in rural villages and the possible reason for this difference could be that city population consume high amount of fish containing elevated As concentrations. Literature shows that the average water consumption in the Bengal delta is in the range of 4-6 l/d<sup>(68)</sup>, whereas the water consumption in Inner Mongolia is supposed to be 2l<sup>(26)</sup>. The reported As concentrations in hair in Bangladesh<sup>(231,232)</sup> and other parts of West Bengal<sup>(233,234)</sup> are similar to the present study (V).

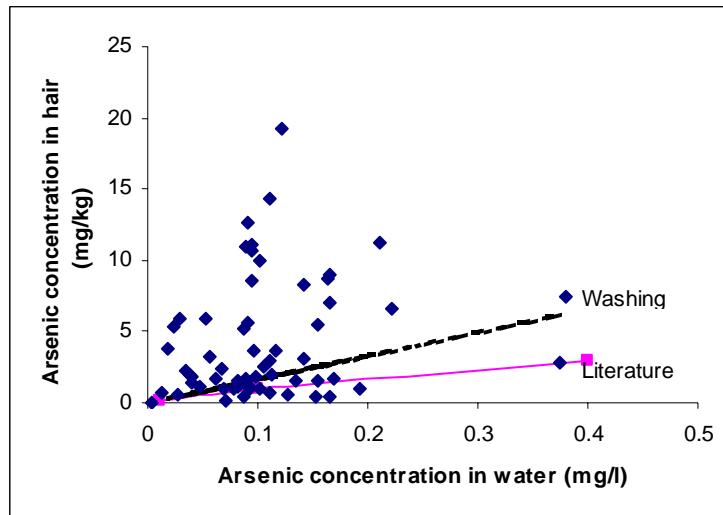


Figure 8: Comparison of As concentration in hair with As concentration in water.

Although the observed prevalence rates of arsenicosis until now seem lower than expected, the presence of high As concentrations in drinking water and hair and the recent changes in the water storage habits to direct consumption of water without prior storage indicates that the disaster due to arsenicosis is yet to be seen. The field study in 2001, the installation statistics from Gazna village and literature<sup>(63)</sup> showed that there are still many people unaware of As contamination and more tube wells are being installed leading to increased direct consumption of tubewell water. The only effective way of mitigation against As is to make public aware of the problem and supply As free drinking and cooking water.



## **7 Understanding Arsenic removals using naturally occurring Fe**

Since coagulation of As with Fe is one of the suitable methods for removal of As in rural areas of Bengal delta and elevated concentrations of Fe are present along with As, removal of As using passive sedimentation with naturally occurring Fe has a great potential. The removal of As depends on many factors and in the Bengal delta context the important factors are presence of As in the form of As(III) and co-occurrence of high concentrations of P and Si.

### **7.1 Field experience on As and Fe removals in the Bengal delta**

During the Masters Degree study and the present Ph.D. study, field investigations were carried out on removal of As using naturally occurring Fe in Bangladesh and West Bengal. In some parts of Bangladesh Fe removal units (IRU) are constructed to remove Fe and the effectiveness of these Fe removal units on As removals were investigated. The results and findings are published in (III). Comparison of As removals in IRU with As removals in plain sedimentation in buckets indicated slightly better As removals in IRU compared to plain sedimentation. In case of plain sedimentation care has to be taken to remove the As laden  $\text{Fe}(\text{OH})_3$  particles. The experiments in West Bengal further showed that a sedimentation time of at least one day is necessary to attain maximum possible As removals. Since different types of containers are used for water storage, the field experiments in West Bengal also focused on whether the type of container used to store the water could have an effect on As removals (see I). Positive effect was observed in case of metal containers (aluminum & brass) compared to clay and plastic containers. The possible reasons for the observed increase in As removal capacity in case of aluminum could be due to release of aluminum from container and/or the container surface may act as an adsorbent. In case of brass the increase in % removal was uniform in all the containers and one of the reasons for this increase could be catalytic effect of Cu on oxidation of As(III) <sup>(235)</sup>. The results further showed that even after a sedimentation period of 8 hours the settling of the particles did not take place and no As and Fe removals were obtained in the unfiltered water. However, after a settling period of 24 hours slightly lower As removals were obtained in the unfiltered water compared to filtered water. The results further showed that the presence of P had a negative effect on As removals.

### **7.2 Laboratory investigations on mechanisms behind As removals**

Investigations were carried out in the laboratory to understand the mechanisms behind As removals in presence of Fe and the effect of presence of P, Si, oxidation state of Fe & As on As oxidation and removals were studied.

The results obtained on mechanisms behind As oxidation can be seen in VII. VIII shows the results on the effect of ions and time of sedimentation on As removals. The results obtained on effect of Fe on As(III) oxidation and removals showed that As oxidation and removals depends on initial Fe and As concentrations. The results further showed that As(III) removals also depends on oxidation state of Fe, with higher removals with Fe initially present as  $\text{Fe}^{3+}$  compared to  $\text{Fe}^{2+}$ . The reason behind this

observed higher removals in presence of  $\text{Fe}^{3+}$  compared to  $\text{Fe}^{2+}$  is probably higher surface area of  $\text{Fe}(\text{OH})_3$  formed with  $\text{Fe}^{3+}$  compared to  $\text{Fe}^{2+}$ . Formation of  $\text{Fe}(\text{OH})_3$  is also faster with  $\text{Fe}^{3+}$  compared to  $\text{Fe}^{2+}$ <sup>(236)</sup>. Comparison of the results on oxidation and removal of As(III) with Fe showed that the amount of As(III) oxidized was equal to the amount of As(III) removed.

Literature indicates controversial results on oxidation of As(III) in presence of Fe at neutral pH and can be categorized in 3 groups: 1. Oxidation due to intermediates formed during oxidation of  $\text{Fe}^{2+}$ <sup>(237,238,87)</sup>. 2. Oxidation in presence of  $\text{Fe}^{3+}$ <sup>(239,212)</sup>. 3. Heterogeneous oxidation in presence of Fe (hydr)oxides<sup>(240,241,242,243)</sup>. For more information see **VII**. Experiments were conducted using both the analytical methods, at pH 8.5-9 (direct), and separation using the mini ionexchange columns, to investigate the oxidation of As(III) with initial  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ . Apart from the difference in pH in the reaction chamber the other main difference between these two measurement methods is the way of injection of sample. In the direct method the sample is injected directly from the experiments and mixed with 0.2 M HCl of acid before injection into the reaction chamber. That is the sample contains both dissolved and particulate As. It takes 2 minutes and 30 sec from the time of addition of acid to time of addition of  $\text{NaBH}_4$  and during this time the added acid would partly dissolve the particles and hence adsorbed As(III) would also be measured. One of the drawbacks of this method is that the volume of the sample may be reduced due to the presence of particles. However, particles were not observed in the transparent tubes carrying the samples. In the ion exchange method sample was passed through a small cotton filter followed by a mini anion exchange column and hence only As(III) in solution was measured. Comparison of As(III) oxidation using these two methods showed (figure 8) similar results irrespective of the analytical method used. The results further showed that As(III) in the filtered samples was equal to the As(III) in the unfiltered sample. This indicate that the sorbed As on the particles is in the form of As(V). The rapid oxidation of As(III) in presence  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  was complete within the first 15 minutes and the measurements for Fe concentration shows that the residual Fe concentration was below detection limit at the end of 15 minutes. These results strongly indicate that the oxidation of As(III) is due to the heterogeneous oxidation in presence of  $\text{Fe}(\text{OH})_3$  particles.

In case of heterogeneous oxidation presence of competing ions for the available surface sites would reduce the oxidation rate of As<sup>(244,245)</sup>, and, hence, experiments were also conducted to investigate the effect of P on oxidation of As(III). These results are shown in **(VII)**. The results obtained showed that the presence of P completely hindered the oxidation of As(III) with  $\text{Fe}^{3+}$ , and had negative effect in presence of  $\text{Fe}^{2+}$ . These result support the findings of<sup>(237,87)</sup> that oxidation of As(III) in presence of  $\text{Fe}^{2+}$  is due to the intermediates formed during oxidation of  $\text{Fe}^{2+}$  with oxygen. The observed difference in oxidation capability of hydroxides formed upon addition of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  could also be explained based on the differential properties of Fe hydroxides formed from  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  addition<sup>(236,246,247)</sup>.  $\text{Fe}(\text{OH})_3$  particles have higher affinity for P compared to neutrally charged As(III) and since the formation of  $\text{Fe}(\text{OH})_3$  upon addition of  $\text{Fe}^{3+}$  is an immediate process taking less than 5 secs, P would be sorbed immediately onto the formed particles compared to As(III). In contrast the formation of  $\text{Fe}(\text{OH})_3$  in presence of  $\text{Fe}^{2+}$  would depend on the rate of oxidation of  $\text{Fe}^{2+}$ , which at constant pH would depend on  $\text{O}_2$ , initial Fe concentration and presence of other ions like P and

Si<sup>(245,248,249,250)</sup>. This may go on for hours. Further the properties of Fe(OH)<sub>3</sub> formed would be different depending on the oxidation state of Fe and presence of other ions<sup>(246,251,252,253,236,254)</sup>. Ageing and degree of crystallisation would also have an effect on oxidation properties of Fe hydroxides<sup>(255)</sup>. The speciation calculations made using PHREEQ C in solution showed that more than 99% of Fe added as Fe<sup>3+</sup> was present as Fe(OH)<sub>3</sub> and Fe(OH)<sub>2</sub><sup>+</sup>, whereas only 70% of added Fe<sup>2+</sup> under anoxic conditions was present as coupled with OH and the rest is either in the form of P or HCO<sub>3</sub><sup>-</sup> complexes. Some recent literature indicates that As(III) forms complexes with carbonate<sup>(256,257)</sup>. Literature shows that the presence of HCO<sub>3</sub><sup>-</sup> has a positive effect on the oxidation of pyrite and the positive effect was due to the formation of a pyrite-surface Fe(II)CO<sub>3</sub> complex<sup>(258,259)</sup>.<sup>(238)</sup> also showed that the presence of HCO<sub>3</sub><sup>-</sup> had a positive effect on oxidation of As(III) with Fe<sup>2+</sup> and H<sub>2</sub>O<sub>2</sub>. It could be possible that complexation of Fe<sup>2+</sup> with HCO<sub>3</sub><sup>-</sup> and adsorption of this complex onto the formed Fe(OH)<sub>3</sub> results in specific adsorption sites for As(III). The measurement for total As in presence of P and with initial Fe<sup>2+</sup> showed that approximately 15% of As was removed and was constant during the 24 hours of experiment, where as with initial Fe<sup>3+</sup> no removals took place even at the end of 24 hours. Removal of As with initial Fe<sup>2+</sup> also suggests the possibility of such surface sites. However, further study is necessary to understand the exact mechanisms behind oxidation of As(III) in presence of Fe.

### 7.3 Comparison of laboratory and field results on As(III) removals.

To understand the observed results in the field, experiments were conducted in the laboratory at similar Fe/(As+P) as observed in the field. The results obtained can be seen in VIII. The results in the laboratory showed that approximately 55% of As removals were obtained in the absence of P and Si, whereas the presence of P and Si reduced the removals to 45%.

If the results obtained in the laboratory are compared with those in the plastic containers in the field, lower As removals were obtained in the field and were in the range of 19-30%.

The results in the laboratory showed that the proportion of As removed was equal to the proportion of As oxidized. The presence of ions in the tap water did not have a significant effect on oxidation of As(III) (figure 9). However, higher As removals in tap water compared to distilled water upon prolonged storage indicated the importance of presence of other ions like Ca<sup>2+</sup> and Mg<sup>2+</sup> in destabilizing the colloids and increasing the particles size. The experiments on effect of P and Si on oxidation and removal of As showed that both P and Si had a negative effect on oxidation and removal of As. The effect of Si is not only due to competition for adsorption sites, but Si also changes particle characteristics. Literature indicates that Si reduces the particle size to around 100 nm, which leads to increased specific surface area, but also reduced removal efficiency due to difficulty in filtering smaller particles.



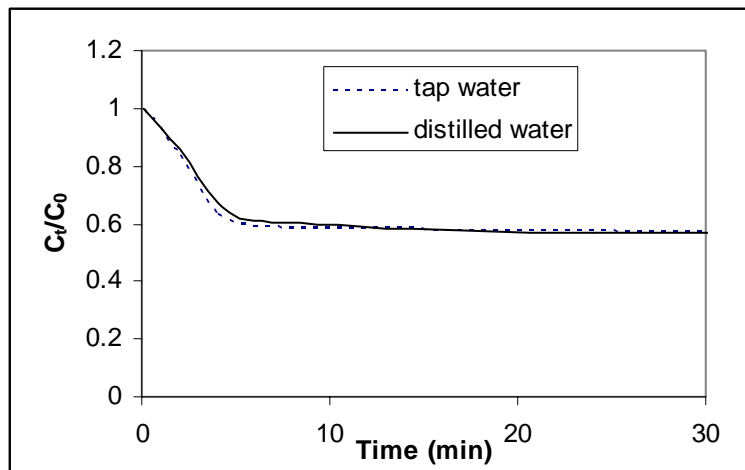


Figure 9: Effect of ions in the tap water on oxidation of As(III) with time in oxygenated water upon addition of  $\text{Fe}^{2+}$ .

The results in the laboratory also showed that the presence of high concentrations of P delayed the development of colour and the colour developed was pale yellow compared to red-brown in the absence of P. P concentrations are usually high in the ground waters of Bengal delta and hence the development of colour due to formation of Fe-hydroxides takes more than 5-10 minutes. Hence the presence of Fe may not be detected if the distance to tubewell is short and people do not store the water and thus water may be consumed directly.

Other factors differing between the laboratory tests and the field study are temperature, dissolved oxygen, light, pH and presence of other unknown ions. Low  $\text{O}_2$  concentrations had a slightly negative effect in the beginning of the experiments however after 30 minutes the effect was diminished. These experiments were only conducted in distilled water and in the absence of other ions. This negative effect on As(III) oxidation could result in reduced As removals in presence of P and Si. The effect of room light and UV-light was studied by either introduction of UV-light or by conducting the experiments in the dark. No difference was observed between these three experiments. The effect of temperature and presence of ions other than P, Si and the major ions of tap water was not studied since the laboratory investigations showed that oxidation of As(III) can not be changed by simple means like prolonging the sedimentation time to 1 day or exposing it to light without addition of any chemicals.

#### 7.4 Effect of ions on As(V) removals

The effect of ions on As(V) removals is shown in (VIII). The obtained results showed that As(V) and P competes equally for adsorption sites and literature<sup>(87,260)</sup> also indicates similar results. The negative effect of Si due to competition for adsorption appeared only in the beginning of the experiments. Desorption of Si was observed upon prolonged sedimentation and in presence of high P and As(V) concentrations. The presence of Si resulted in reduced particle sizes, and this reduced particle size had a positive effect on adsorption capacity but negative effect on removal efficiency. The negative effect on removal efficiency could be decreased by prolonging the

sedimentation time. The presence of ions like  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in ground water would destabilize the colloids resulting increased removal efficiency. Based on the results from the present study and literature a simple equation (equation 12) can be used for estimating % As removal to expected in presence of P and after a sedimentation period of 30 minutes. All the concentrations are in M.

$$\text{As}_{\text{ads}} = (0.39 \cdot \text{Fe}) / (1 + \text{P}_{\text{initial}} / \text{As}_{\text{initial}}) \dots\dots\dots \text{Equation (12)}$$

Where;  $\text{As}_{\text{ads}}$  = amount of As adsorbed (M); Fe = Fe concentration (M);  $\text{P}_{\text{initial}}$  = initial P concentration (M) and  $\text{As}_{\text{initial}}$  = initial As(V) concentration (M)



## 8 Improving As removal efficiency in presence of naturally occurring Fe

The As removal efficiency in presence of naturally occurring Fe can be increased by addition of an extra adsorbent like Fe or Al and/or an active oxidation of As(III).

### 8.1 Addition of Fe

Fe can be added from acidic solution or powdered form. Experiments were conducted to see whether there was any difference in the oxidation and removal capacity of Fe added in the form of solution or powder. The obtained results showed no difference in the oxidation capacity depending on the form of Fe added. The results further showed that in the absence of P and Si and at As concentrations of 1 mg/l an Fe/As ratio above 40 was required to achieve residual As concentrations below 50 µg/l. The amount of Fe required could be reduced if Fe addition is carried over several smaller additions as shown in figure 10. Serial addition of 2 mg/l of Fe with 10 minutes interval equal to 14 mg/l resulted in higher oxidation and removal of As(III) than one addition of 20 mg/l Fe. Similar results were also reported by Hug and Leupin. However, this kind of addition in practice is not possible.

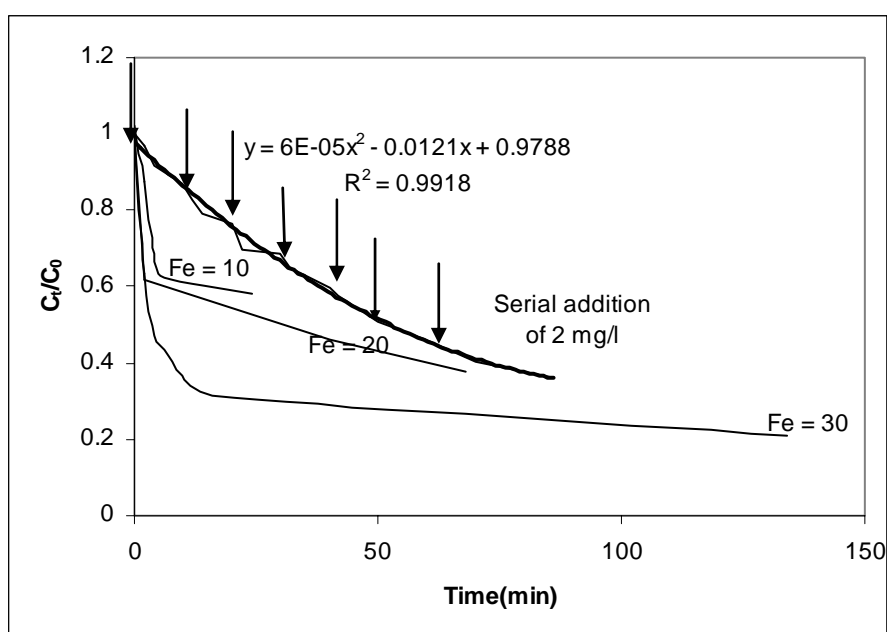


Figure 10. Effect of Fe concentrations and way of Fe addition on As(III) oxidation at initial As concentrations of 1 mg/l.

$C_t/C_0$  represents ratio of As concentration at time  $t$  to initial As concentration.

### 8.2 Photochemical oxidation of As(III)

Literature review indicates that photochemical oxidation in presence of Fe-citrate complex (lime juice can be substituted for citrate and sunlight can be used instead of artificial UV-light) would improve oxidation and removal of As(III)<sup>(237,261)</sup>. The hug and

Leupin study<sup>(237)</sup> conducted in the laboratory indicated a required Fe/As ratio of 13 at respective Fe, As, P and Si concentrations of 5, 0.5, 1 and 20 mg/l to achieve As concentrations below 50 µg/l. However, their field results gave only 45-70% removals even in presence of higher Fe/As and exposure to sunlight for 5-6 hours. Since this method looks simple, experiments were carried out in the laboratory to investigate the different factors affecting the oxidation and removal of As(III). The results are shown in (VI). Figure 11 shows the effect of oxygen, citrate and UV-light on oxidation of As(III) in presence of Fe<sup>2+</sup>. The obtained results showed that the catalytic effect was only observed when both oxygen and UV-light were present along with citrate. The observed rate of oxidation in the present study was half of what Hug and Leupin observed and the difference could be due to the difference in surface area exposed to UV-light. The results on As removals showed that at citrate/Fe ratios above 1 neither As nor Fe were removed. The application of this method in the field is not always suitable since the method depends on availability of sunlight. Further the oxidation and removals depend on the citrate concentration and the wrong dosage could either lead to lower oxidation and hence lower removals or higher oxidation, but lower As removals due to decreased Fe removals because of the formation of Fe-citrate complex.

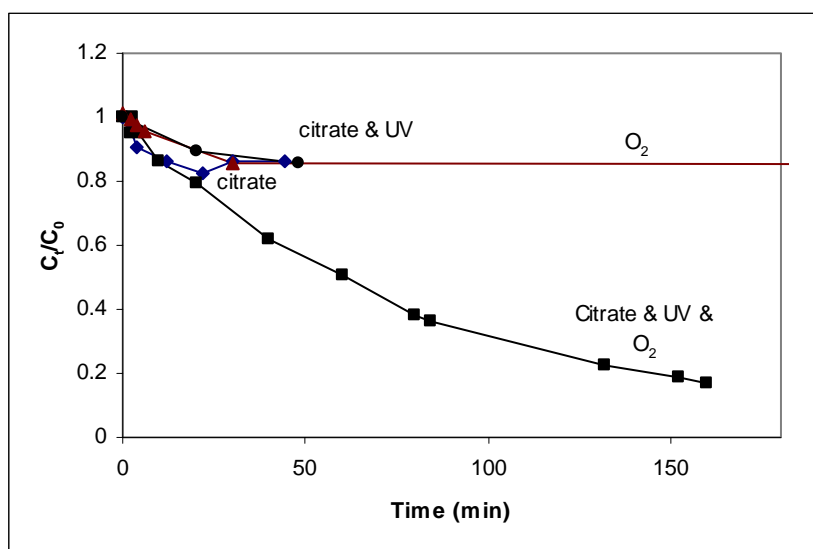


Figure 11. Effect of citrate, UV, and O<sub>2</sub> on As(III) oxidation in presence of Fe<sup>2+</sup>.

### 8.3 Chemical oxidation of As(III)

The other ways of obtaining oxidation of As(III) is the addition of simple oxidising agents like KMnO<sub>4</sub>, Ca(OCl)<sub>2</sub>, and NaOCl. Only KMnO<sub>4</sub> has been investigated here, as high dosages of Ca(OCl)<sub>2</sub> and NaOCl could lead to adverse health effects. Further these chemicals are not preferred by the people since they attribute odour and taste to water. KMnO<sub>4</sub> is a known chemical among the villagers due to its application in controlling fish pathogens and as disinfectant. Further the dosage administration can be controlled by the development of pale pink colour. KMnO<sub>4</sub> has been used as oxidising agent in the DPHE-DANIDA 2 bucket system for removal of As, but no literature to my knowledge reports the efficiency of KMnO<sub>4</sub> in oxidation of As(III) and the interfering effect of other ions especially Fe<sup>2+</sup> on the required KMnO<sub>4</sub> concentrations. Oxidation and

removal experiments were carried out in the laboratory to study the effect of  $\text{KMnO}_4$  added and the interfering effect of  $\text{Fe}^{2+}$  on oxidation of As(III). The obtained results are shown in (VI). The results showed that the presence of  $\text{Fe}^{2+}$  had a negative effect on oxidation of As(III) and to achieve complete As(III) oxidation in presence of  $\text{Fe}^{2+}$  the amount of  $\text{KMnO}_4$  added should be equal to the stoichiometric requirements for oxidation of both  $\text{Fe}^{2+}$  and As(III). Slower oxidation of As(III) occurred when the amount of added  $\text{KMnO}_4$  was lower than the required amount. The As(III) oxidation and removals also depend on the timing of  $\text{KMnO}_4$  addition. If oxidation of  $\text{Fe}^{2+}$  is completed before the addition of  $\text{KMnO}_4$  the added  $\text{KMnO}_4$  would be utilized for oxidation of As(III) alone and hence higher As(III) oxidation was achieved. However, As removals achieved in this case were lower. If  $\text{KMnO}_4$  is added before complete oxidation of  $\text{Fe}^{2+}$  the amount of As(III) oxidised would be lower, because  $\text{KMnO}_4$  would also be used for oxidation of  $\text{Fe}^{2+}$ , but higher removals would be obtained. As mentioned earlier the oxidation of  $\text{Fe}^{2+}$  in presence of oxygen depends on factors like pH, Fe concentrations,  $\text{O}_2$  concentration, temperature, and presence of other ions and hence difficult to predict. Therefore to obtain better As removals it is suggested that  $\text{KMnO}_4$  should be added just after collecting the water. Calculations based on the BGS showed that the addition of  $\text{KMnO}_4$  could be applied at 60% of the tube wells with good result ( $< 50 \mu\text{g/l}$ ) and the maximum cost of  $\text{KMnO}_4$  would be 4 INR/month ( $\sim 8$  Eurocent) per household. However, to apply this method at all the existing tube wells an extra addition of coagulant in the form of Al or Fe is required. The results from the present study also show that the amount of  $\text{KMnO}_4$  added in the DPHE-DANIDA 2 bucket system apparently was not sufficient to achieve complete oxidation of As(III).

#### 8.4 Addition of $\text{KMnO}_4 + \text{Al}_2(\text{SO}_4)_3$

Field investigations were carried out in West Bengal by students from the Technical University of Denmark (DTU), where the applicability of alum and Fe as coagulants was investigated. They used  $\text{KMnO}_4$  as an oxidising agent. Similar to the literature<sup>(167,202,159,162)</sup>, they also obtained better As removals with Fe addition compared to Al. They further reported better sedimentation of particles upon Fe addition compared to Al leading to satisfactory As removals in presence of Fe even before filtration. However, they did not consider  $\text{FeCl}_3$  as a coagulant for implementation in the field, because they found that handling and administration of  $\text{FeCl}_3$  in the field was not easy due to the hydrophilic nature  $\text{FeCl}_3$ . Based on their field experience the calculated yearly expenditure on usage of chemicals for a family consuming 50 L/day using Fe and Al coagulation were INR 180 (3.4 EUR) and INR 60 (1.1 EUR) respectively, at initial As concentrations up to 500  $\mu\text{g/l}$ . These cost estimates indicate that despite of the lower removal efficiency of Al, the cost of As treated with Al is lower than with Fe. The field results further showed that lower amounts of Al was needed to treat the water when added as smaller particles compared to bigger particles. The main disadvantage of using Al as a coagulant is that high residual Al concentrations might lead to adverse health effects. One of the reasons for the higher residual concentrations could be the decrease in pH upon formation of  $\text{Al}(\text{OH})_3$ . Investigations were carried out in the laboratory to investigate the possibility of addition of Al and  $\text{KMnO}_4$  in one solution to achieve better As removals and the obtained results are described in (VI). The preliminary investigations showed that a combined solution of  $\text{Al}_2(\text{SO}_4)_3$  and  $\text{KMnO}_4$  is stable at pH 11 and that this solution can be added to achieve better As removals. One of the advantages of this solution is that addition of Al from a

basic solution would neutralize the acid formed and would probably result in lower residual Al concentrations. The other advantage of addition of Al is formation of bigger particles which would enable easy settlement of the particles. The third advantage of addition of Al in the soluble form compared to powdered form is that mixing would be easier and higher adsorption capacity can be obtained. However, further research is necessary to investigate the applicability of this solution in the field.

The daily generation of As contaminated sludge is very low, however care should be taken in disposal of the sludge and should not be near the children's playing area or edible crops. A suitable way of disposal of this sludge would be to bury it in a hole.

## 9 Conclusions and recommendations

The As problem in Bengal delta is very severe and the problem is also spreading to other parts of the Indian subcontinent. The occurrence of As in the Bengal delta is of natural origin and microbially mediated reductive dissolution of Fe hydroxides with adsorbed As and P is the most accepted theory for the elevated As concentrations. Literature indicates lower prevalence of arsenicosis in the Bengal delta compared to other parts of the world despite the higher As in hair of the exposed population of Bengal delta. The main reasons identified for this observed lower arsenicosis prevalence rate in this study were duration of relatively short human exposure, and presence of  $\text{Fe}^{2+}$  in the ground waters. The study further showed that the installation of tube wells intensified in the 1990's favouring direct consumption of water instead of prolonged storage. The storage with higher Fe concentrations would result in oxidation and removal of As and Fe and hence people were indirectly protected against As exposure. However, the observed new trend of direct consumption together with the higher As concentrations in hair warns that the disaster is yet to be seen.

Removal of As using naturally occurring Fe appears to be an appropriate method for As mitigation. This study investigated the mechanisms responsible for As removal in presence of Fe and simple ways of improving the removals. The results showed that oxidation of As in presence of Fe plays a key role in As removals. The oxidation of As(III) is most probably due to the heterogeneous oxidation on the surface of Fe hydroxide flocs and depends on the properties of Fe hydroxides. Oxidation of As(III) further depends on initial oxidation state of added Fe with higher oxidation and removals with  $\text{Fe}^{3+}$  compared to  $\text{Fe}^{2+}$ .

The presence of P and Si has a negative effect on the oxidation of As(III). However, the effect of P varies depending on the oxidation state of Fe. P at high concentrations inhibits As(III) oxidation with initial  $\text{Fe}^{3+}$ , whereas with initial  $\text{Fe}^{2+}$  the presence of P has negative effects on As(III) oxidation. Oxidation of As(III) with  $\text{Fe}^{2+}$  also depends on  $\text{O}_2$  and pH with lower oxidation at lower  $\text{O}_2$  and pH.

P and Si also have negative effect on As(V) removals and the negative effect is due to the competition for adsorption sites. The negative effect of Si on As(V) removals is further due to the decrease in particle size resulting in difficulty in filtering the particles. Prolonged sedimentation would result in increased coagulation and hence the effect of Si would be diminished. The field results showed that Fe/As ratios of above 120 are required to achieve satisfactory As removals and even extension of sedimentation period to 24 hours would not reduce the required Fe/As ratios. Based on the BGS survey As removals with naturally occurring  $\text{Fe}^{2+}$  could only be effective at 25% of the tube wells. Addition of an oxidising agent or extra coagulant is necessary for the method to be applied at the majority of the tubewells. The results on addition of citrate and exposing to UV-light to increase As(III) oxidation and hence higher As removals showed that the oxidation of As(III) increased with an increase in citrate/Fe ratio. However at citrate/Fe ratios  $> 1$  As and Fe removals were not achieved.



KMnO<sub>4</sub> was found to be an effective oxidising agent for As(III). In presence of high Fe<sup>2+</sup> concentrations as encountered in the ground waters of Bengal delta the required KMnO<sub>4</sub> dosage is equal to a stoichiometric requirement for oxidation of both Fe<sup>2+</sup> and As(III). At this dosage both oxidation and removal of As is immediate. As concentrations lower than 50 µg/l could be achieved within 5 minutes at an Fe/As ratio of 10 with average P and Si concentrations of 1 and 20 mg/l and Fe concentrations above 5 mg/l. The calculations based on BGS showed that application of KMnO<sub>4</sub> alone in presence of naturally occurring Fe could be applied at 60% of the tube wells. Maximum cost of application of KMnO<sub>4</sub> alone would be INR 4 (~8 Eurocent) per household per month assuming a daily water consumption of 50 L for a family. Therefore application of KMnO<sub>4</sub> could be promoted in the villages for removal of As. The results further showed that a solution of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and KMnO<sub>4</sub> at pH 11 adjusted with NaOH is stable and could be applied in the field for As removals. However, further research both in the laboratory and field is required to find a proper dose of Al for As removal. The daily generation of As contaminated sludge is very low, however care should be taken for disposal of the sludge and it should not be disposed near the children's playing area or edible crops. A suitable way of disposal of this sludge would be to bury it.

Instead of waiting for an expensive mitigation through drilling deep tube wells for arsenic free water, which may take years and yet reach only few, the readily achievable As removal based on naturally occurring Fe<sup>2+</sup> in the ground waters along with application of KMnO<sub>4</sub> supplemented with Fe/Al could be recommended as a mitigating option in the rural areas of the Bengal delta.

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The background of the entire page is a microscopic image of plant cells, showing cell walls and large central vacuoles. A prominent red horizontal line runs across the middle of the image, separating the top and bottom halves.

**Institute of Environment & Resources**

Technical University of Denmark  
Bygningstorvet, Building 115  
DK-2800 Kgs. Lyngby

Phone: +45 4525 1600  
Fax: +45 4593 2850  
e-mail: [reception@er.dtu.dk](mailto:reception@er.dtu.dk)

Please visit our website [www.er.dtu.dk](http://www.er.dtu.dk)

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