
Arsenic in Groundwater

- A World Problem

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Production

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Proceedings
Seminar
Utrecht
29 November 2006

Organised by the Netherlands National Committee of the International Association of Hydrogeologists (NNC-IAH) in cooperation with the Netherlands Hydrological Society (NHV) and with financial support of:

- **UNESCO's Division of Water Sciences**
- **WMO**
- **Deltares**
- **International Groundwater Resources Assessment Centre (IGRAC)**

Cover photo

Testing the color of the sand during drilling of a tube well in Sonargaon Bangladesh (Photo Martijn Jansen).

To guarantee arsenic-free groundwater, drillers in Sonargaon, Bangladesh, base well screen depth on sand color, a relation discovered after a series of wells had been analyzed for arsenic. Arsenic-free water correlated with iron free water, which is easily recognized on site by the driller. (Bart Fugers, Martijn Jansen, Sebastiaan Kiemel (2008) Sustainability of targeting shallow arsenic-free layers: An indigenous developed process to find arsenic-free water in Bangladesh. Traineeship report TU-Delft, 2008).

Colophon

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Seminar Utrecht 29 November 2006

ISBN/EAN : 978-90-808258-2-6

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Secretariat Netherlands National Committee IAH: Deltares, P.O. Box 80015, 3508 TA Utrecht, The Netherlands

Cover: courtesy Martijn Jansen

Arsenic in Groundwater - A World Problem

Preface

During the past two decennia it has become apparent that arsenic poisoning (As) via groundwater has become a worldwide problem. Some of the best-documented and most severe cases of arsenic contaminated groundwater have been found in aquifers in Asia (e.g. parts of Bangladesh, China, India, Nepal) and South America (e.g. Argentina, Mexico). High levels of arsenic in groundwater not only cause significant problems in the provision of safe drinking water, but lately have also raised concern regarding food safety: in the case of long-term use of groundwater for irrigation purposes – whereby crops become contaminated due to the accumulation of arsenic. Long-term exposure to arsenic has been associated with cancer of the skin, lungs, urinary tract, kidneys and liver, and can also produce various other non-cancerous effects. Recent studies also indicate the adverse effects of arsenic exposure on reproduction and child development. Arsenic not only effects public health, but it may also have certain social implications for those affected by skin diseases caused by exposure to this pollutant.

Arsenic can be produced and mobilised naturally in water and soils via the weathering processes and microbial activity. Contamination can also be caused by anthropogenic activities such as metal mining and groundwater abstraction, and in some cases through the use of arsenic-based pesticides in agriculture and forest preservation. In most cases, however, it is the natural biogeochemical processes that play a dominant role in the mobilisation of arsenic in water.

The WHO provisional guideline limit-value for arsenic in drinking water has been reduced from 50 µg/l in 1993 to 10 µg/l at present. Most industrialised countries also take 10 µg/l as a statutory limit but most developing nations continue to use the pre-1993 WHO guideline value as a national standard because of difficulties with analytical detection and compliance.

A significant amount of research carried out over the last decade has focused on characterising the occurrence and distribution of arsenic in water and solid phases in affected regions across the world and on investigating the processes controlling arsenic mobility in groundwater and aquifers. Today, environmental arsenic problems have been recognised and documented in numerous countries across the world, within a range of geological and climatic settings. The International Groundwater Resources Assessment Centre (IGRAC) plays a significant role in this process. IGRAC is an initiative of UNESCO and WMO, financially supported by the Dutch Government through the “Partners for Water Programme” and hosted by the *Geological Survey of the Netherlands-TNO*.

Internationally recognised institutes and universities, among others, the British Geological Survey (BGS), the Karolinska Institute and the Amsterdam Vrije Universiteit, various UN organisations, namely the WHO, WMO, FAO and UNESCO, have also been involved in this research and knowledge dissemination. UNESCO therefore very much appreciates the initiative of the Netherlands National Committee of the Dutch Chapter of the International Association of Hydrogeologists (IAH) to organize a symposium on Arsenic in Groundwater and encourages the decision to publish the contributions of the internationally recognised experts on arsenic participating in this symposium.

The various contributions dealing with, among others, occurrence and causes of arsenic contamination and its effects on health and food production, give a clear and broad insight into the state-of-the-art knowledge of all aspects of arsenic in groundwater. The publication No. 5 *Arsenic in Groundwater – a World Problem* presents the arsenic problem in such way that it becomes accessible to a broad and involved public that normally might not have easy access to scientific literature; giving this publication a rather unique status among the extensive list of existing literature on this subject.

Publication No. 5 *Arsenic in Groundwater – a World Problem*, as well as the arsenic symposium are valuable contributions to the VIth Phase of the International Hydrological Programme (IHP) of UNESCO (2002-2007).



Dr Alice Aureli
Groundwater coordinator
International Hydrological Programme (IHP) - Groundwater Resources Programme
UNESCO

Other publications in this series of proceedings are:

1. Netherlands Hydrogeological Research in International Co-operation (March 1994)
2. Netherlands Experiences with Integrated Water Management, considerations for International Co-operation (October 1995)
3. Evaluation and Protection of Groundwater Resources, from Vision to Action (September 2000)
4. Management of Aquifer Recharge and Subsurface Storage – *Making Better Use of Our Largest Reservoir* (September 2003)

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by *Alice Aureli*

IHP Groundwater Resources Programme, UNESCO

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1 Introduction and summary

Authors: Albert Tuinhof, Jan Piet Heederik, Theo Olsthoorn,
Michael van der Valk and Co de Vries

Arsenic in groundwater in various parts of the world – most notably the Ganges Delta of Bangladesh and West Bengal, India – is poisoning large numbers of people. In the Ganges Delta, a naturally occurring high concentration of arsenic in groundwater has become a high-profile problem due to the expanding use of tube wells for drinking water during the last three decades. Parts of Thailand, Taiwan, Argentina, Chile and China have also been affected. Tens of millions of people are affected, the majority of which live in Southeast Asia.

Research on the occurrence and effects of arsenic in groundwater and drinking water is ongoing. Current research questions include the following:

- In what concentrations does arsenic become a health threat?
- How does arsenic behave in different environments?
- Under what conditions will arsenic be mobilised?
- What are the threats of arsenic poisoning to humanity?

In the Dutch subsoil, locations with relatively elevated concentrations of arsenic have been found, yet these gave rise to research into its origin and behaviour in order to quantify and minimize risk.

To address the global dimension of arsenic contamination and importance of research results, the IAH's Dutch Chapter and the Netherlands' Hydrological Society organised a one day symposium in Utrecht, the Netherlands, on 29 November 2006, under the title '**Arsenic in Groundwater – A World Problem**'.

The Netherlands' situation was addressed in the morning session while the global dimension of arsenic in groundwater and drinking water was the subject of the afternoon session. The chairman of the day was Dr. Tony Appelo.

Morning session

Dr. Tony Appelo, well known for his contribution to arsenic research, introduced the other speakers and discussed concentration patterns of arsenic in groundwater in the Netherlands. He introduced a new model for the release of arsenic for the Dutch case: Pleistocene iron-hydroxide formed in groundwater discharge zones and sorbed arsenic. During the Holocene transgressions, the deposits were covered with peat and the iron-hydroxide transformed by sulphur from seawater to pyrite (FeS_2). During the cutting of the peat bogs since the Middle Ages, the pyrite became exposed to air, thus releasing the arsenic.

Sophie Vermooten (**Chapter 7**, 'Arsenic in the Dutch coastal Provinces'), discussed a national project in which policy-makers are to be advised about the use of soil, sediments and groundwater in areas affected by relatively high arsenic concentration levels in the Netherlands. She explained that one of the two processes leading to higher concentrations of Arsenic is when Arsenic is mobilized and taken up by anaerobic groundwater flowing from higher Pleistocene deposits like the Dutch ice pushed ridges

towards lower lying seepage areas like the polders. The outcome of the project would be the drawing up of risk maps and a soil management map.

Professor Pieter Stuyfzand (**Chapter 8**, 'Regional occurrence with relation to drinking water production in the Netherlands') explained the role of arsenic in the production of Dutch drinking water. At a few locations, the arsenic level is above the WHO norm of 10 µg/l, but the situation appears to be stable. While there is no large-scale problem, individual wells have been more closely examined, indicating that at the local level a few problematic cases might arise in the future, due to changes in the chemical composition of the infiltrating water (e.g., gases like CH₄ may give rise to the mobilisation of arsenic, which might lead to rather high arsenic levels locally, up to 1000 µg/l).

In his presentation, Slavek Vasak (**Chapter 6**, 'Mapping of hazardous substances in groundwater on a global scale'), explained the role of IGRAC (International Groundwater Resources Assessment Centre) in the production of an inventory of hazardous substances in groundwater at a global scale. For many countries adequate information is lacking, especially quantitative data. He called for more active sharing of information, as this may lead to better management of hazardous substances in groundwater.

Afternoon session

In the afternoon, Dr. Tony Appelo introduced the global dimensions of arsenic in groundwater and drinking water, thereby touching upon the problems of arsenic poisoning in Bangladesh and India.

Dr. Pauline Smedley (British Geological Survey, Wallingford, UK) discussed 'Arsenic in groundwater – natural sources and/or human interferences?' (**Chapter 2**, 'Sources and distribution of arsenic in groundwater and aquifers') She explained that arsenic occurs in different minerals, and that it can be mobilised under different conditions. Countries with arsenic levels above 50 µg/l (that is, five times the WHO norm) are Argentina, Chile, Bangladesh and the Southwest of the US. Arsenic problems are mostly related to one of three situations: geothermal, mines (e.g. in Obuasi, Ghana, where by oxidation of sulphide minerals large amounts of arsenic come into the water), and large water reservoirs (e.g., La Pampa in Argentina, and California in the USA, where arsenic collects in topographically low reservoirs). The first two situations are sources of high arsenic concentrations, while in the latter case the problem is the mobilisation of arsenic by changing geochemical conditions.

'Arsenic in drinking water: threatening the health of millions?' was discussed by Professor Marie Vahter (Karolinska Institute, Stockholm, Sweden), whose answer was 'yes': measured concentrations of thousands of µg/l (WHO norm is 10 µg/l) at different places of the world, in combination with the effects on human health, make arsenic a global problem (**Chapter 5**, 'Health effects in inorganic arsenic'). More than 50 million people in Bangladesh are currently exposed to the risk of being poisoned. When consumed in very high doses, arsenic may lead to acute gastro-intestinal or paralytic symptoms. The lethal dose is probably around a few mg per kg of body weight. Chronic effects are due to adverse effect on enzyme reactions. The most important chronic effect of arsenic poisoning is cancer (skin, lung, bladder, and kidney). Not all forms of arsenic

are as dangerous, but it is clear that arsenic in drinking water is a serious threat to human health.

The last speaker treated the question ‘Do we understand the origin of high arsenic concentrations in groundwater? Can we quantify it?’ (**Chapter 3**, ‘Geochemical experimentation and modelling are tools for understanding the origin of As in groundwater in Bangladesh and elsewhere’). Dr. Tony Appelo looked into three chemical theories to explain high concentrations of arsenic in groundwater. Even after experiments, no general conclusive answers can presently be given. Groundwater mixing often makes correlations vague. Possibly, there are different systems that give rise to the mobilisation of arsenic in groundwater in different situations. While superficial aquifers become poor in arsenic, the deeper aquifers remain rich in arsenic due to the connection with iron hydroxide that inhibits mobilisation.

One aspect our symposium could not cover was the threat of arsenic in the food chain due to arsenic-contaminated irrigation water. However, we are very pleased that we found Alex Heikens willing to write a paper about the results of his research on arsenic contamination of irrigation water, soils and crops in Bangladesh (**Chapter 4**, ‘Review of arsenic behaviour from groundwater and soils to crops and potential impacts on agriculture and food supply’). This paper provides an overview of arsenic behaviour in food and agriculture, and evaluates the available knowledge of the effects of irrigating with arsenic-contaminated water on crop production and food safety in Asia.

The present publication contains the papers of the symposium in order to bring the most relevant aspects of arsenic in groundwater to the attention of a broader public.

Our thanks go to Dr. Tony Appelo who chaired the symposium. We also thank all the speakers for their valuable contributions and their efforts made to prepare the papers for this publication. Dr Tony Appelo read all the contributions and gave valuable suggestions for improvements, especially due to his effort this publication gives a balanced overview of the various aspects of arsenic in groundwater –a world problem.

Our special thanks go to TNO for hosting the symposium and to the sponsors UNESCO-IHP, IGRAC and WMO and the advertisers for their financial support to make this publication possible.

We sincerely hope that this publication no.5 will contribute to a better understanding of the arsenic problem and that it will stimulate further research and development in finding effective mitigation measures in regions where the arsenic contamination poses hazards to the communities and the economy.

The Netherlands National Committee of the IAH

Utrecht, February 2008

Ir Albert Tuinhof	Chairman
Ir Jan Piet Heederik	Secretary/treasurer
Prof. Dr Ir Theo Olsthoorn	Member
Drs Michael van der Valk	Member
Prof. Dr Jacobus de Vries	Advisor

2 Sources and distribution of arsenic in groundwater and aquifers

Author: Pauline L. Smedley

2.1 Introduction

A rapid growth in research on arsenic occurrence and behaviour in the environment has occurred over the last decade or so. Today, environmental arsenic problems have been recognised and documented in numerous countries across the world, in a range of geological and climatic settings. Arsenic can be mobilised naturally in water and soils through weathering reactions and microbiological activity. Its mobilisation can also be initiated or exacerbated through anthropogenic activities such as metal mining and groundwater abstraction, and in some cases through the use of arsenical pesticides in agriculture and wood preservation. The relative roles of these processes vary from region to region although most workers would accept the dominant role played by natural biogeochemical processes in the mobilisation of As in waters from the areas of the world that have been worst affected.

Drinking water constitutes a major, and possibly dominant, pathway of exposure to As in humans. The WHO provisional guideline value for As in drinking water is 10 µg/L, having reduced from 50 µg/L in 1993. Most industrialised countries also take 10 µg/L as a statutory limit although most developing nations continue to use the pre-1993 WHO guideline value as a national standard because of difficulties with analytical detection and compliance.

Although the concentrations of As in drinking water are usually low, in some circumstances they can reach far in excess of these statutory drinking-water limits and thus cause a potentially severe threat to health. Groundwaters are generally more vulnerable to As contamination than surface waters because of the interaction of groundwater with aquifer minerals and the increased potential in aquifers for the generation of the physicochemical conditions favourable for As release. Indeed, the majority of the world's recognised As-related health problems are linked with long-term use of groundwater for drinking. Some of the best-documented and most severe cases of As-contaminated groundwater occur in aquifers from Asia (e.g. parts of Bangladesh, China, India, Nepal) and South America (e.g. Argentina, Mexico).

A significant amount of the research carried out over the last decade has focused on characterising the occurrence and speciation of As in affected regions across the world and investigating the processes controlling As mobility in groundwaters and aquifers. This chapter describes the key features of high-As groundwater provinces with examples taken from a range of geological and climatic settings, and outlines some of the main biogeochemical processes involved.

2.2 Arsenic occurrence in groundwater

2.2.1 Aqueous speciation

Arsenic occurs in the environment in several oxidation states but in water is mostly found as the inorganic forms, arsenite (+3) and arsenate (+5). Organic forms of As are

rarely significant in groundwaters but may become more important in waters affected by industrial pollution.

Under oxic conditions at thermodynamic equilibrium, aqueous As is dominated by arsenate oxyanions ($\text{H}_2\text{As}(\text{V})\text{O}_4^-$ or $\text{HAs}(\text{V})\text{O}_4^{2-}$ depending on pH conditions). Under reducing conditions and over a wide range of pH values, the uncharged arsenite species

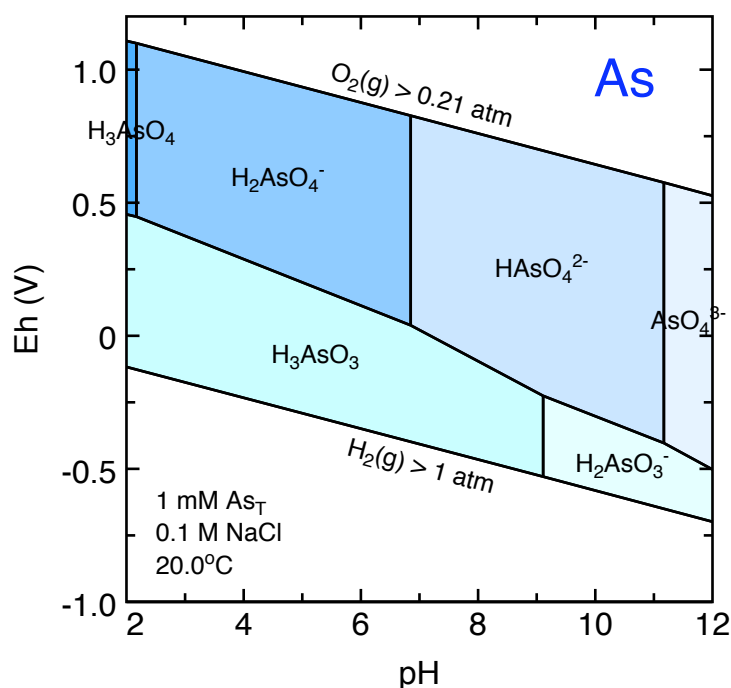


Figure 2.1 Eh-pH diagram of aqueous As species in a system containing As and NaCl at 20°C and 1 bar total pressure. The speciation calculations were performed using PHREEQC (Parkhurst and Appelo, 1999; Kinniburgh and Cooper, 2004).

H_3AsO_3^0 predominates (Figure 2.1). However, in natural systems thermodynamic equilibrium is often not achieved because of slow As redox kinetics (e.g. Eary and Schramke, 1990). Much recent evidence suggests that redox kinetics can be significantly accelerated by microbial activity which has been implicated in both the oxidation of arsenite (Wilkie and Hering, 1998; Hering and Kneebone, 2002; Katsoyiannis et al., 2004) and the dissimilatory reduction of arsenate (Oremland and Stolz, 2003). Oxidation of As(III) is also well known to be catalysed by Mn oxides (Oscarson et al., 1981; Driehaus et al., 1995; Katsoyiannis et al., 2004; Amirbahman et al., 2006). Arsenite oxidation rates are pH-dependent, the reaction being slowest in acidic conditions (Eary and Schramke, 1990; Amirbahman et al., 2006). Dissolved As-S species can occur in strongly reducing environments although precipitation of As sulphide minerals limits the concentrations of dissolved As in conditions where sulphide concentrations are high.

Sorption plays an important role in As speciation. Amorphous iron oxides in particular are well-known to have strong sorption capacities for As and therefore exert a strong influence on As mobility (Dzombak and Morel, 1990). Figure 2.2 shows the predominant species in the system As-Fe- H_2O where sorption of As species onto hydrous ferric oxide (Hfo) is taken into consideration. The diagram is subject to the deficiencies of current As thermodynamic databases but illustrates the strong adsorptive capacity of Hfo for As (especially arsenate) at near-neutral pH under oxic to mildly reducing conditions. Under oxic conditions, aqueous As species have increased

importance at both high and low pH, the former related to electrostatic repulsion from negatively charged oxide surfaces and the latter to Hfo instability and dissolution. Under strongly reducing conditions, aqueous arsenite is a predominant species over a wide pH range, again linked to Hfo instability. The system illustrated in Figure 2.2 does not consider sulphide species. The strong tendency for sorption to iron oxides at near-neutral pH in oxic conditions is a significant factor in defining the low-As status of most natural groundwaters. The distribution of predominant species shown in Figure 2.2 also goes some way to explaining the high As concentrations observed in some groundwaters under strongly reducing conditions and at extremes of pH.

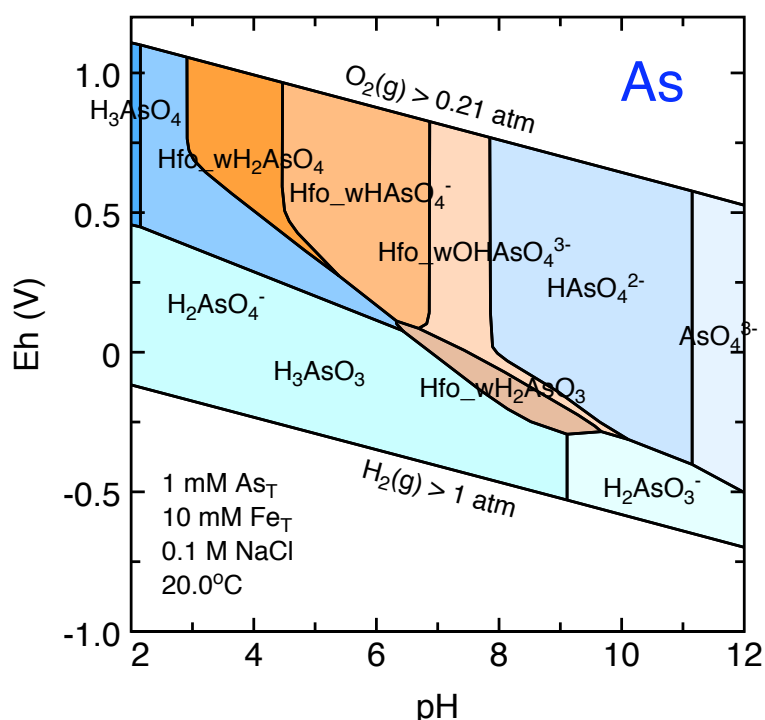


Figure 2.2 Eh-pH diagram for an As-Fe system in which hydrous ferric oxide (Hfo: $(\text{Fe}(\text{OH})_3(\text{a}))$) precipitates and adsorbs As(V) and As(III) species. Under strongly reducing conditions, Hfo does not precipitate and so cannot adsorb As. The speciation calculations were performed using PHREEQC (Parkhurst and Appelo, 1999; Kinniburgh and Cooper, 2004) and the Diffuse-Double-Layer model of Dzombak and Morel (Dzombak and Morel, 1990).

2.2.2 World distribution of high-As groundwaters

Although the occurrence of several cases of high As concentrations in groundwaters have by now been well-documented, it should be stressed that the concentrations of As in groundwater are usually low or very low. Most groundwaters have concentrations below the WHO provisional guideline value for drinking water of $10 \mu\text{g/L}$ and many have concentrations below analytical detection limits. In an investigation of some 20,000 groundwater samples from public-supply wells in the USA, Focazio et al. (2000) found that 11% exceeded $10 \mu\text{g/L}$ and 2% exceeded $50 \mu\text{g/L}$, while 55% contained $1 \mu\text{g/L}$ or less (the detection limit of the method used). Similarly, from some 1200 groundwater analyses from various aquifers in England & Wales reported by Shand et al. (2007), 6% had concentrations exceeding $10 \mu\text{g/L}$ and 1% had more than $50 \mu\text{g/L}$ while 68% had concentrations of $1 \mu\text{g/L}$ or less. This distribution is largely because of the normally strong partitioning of As to solid minerals, especially iron oxides, under the pH and redox conditions of most groundwaters.

Exceedances of As above drinking-water limits can and do occur in groundwaters from many aquifers of varying lithology. Indeed, the toxicity of As is such that only very small mass transfers of As to water are required for this to be achieved. Increased testing of groundwaters for As in recent years has resulted in the recognition of many examples. However, the occurrence of very high aqueous As concentrations, perhaps one to two orders of magnitude higher than the WHO guideline value, or high concentrations occurring on a regional scale, tend to be associated with a small number of specific geological and hydrogeochemical environments.

Areas of sulphide mineralisation have long been associated with environmental As problems. Sulphide minerals can contain very high concentrations of As and oxidation of the minerals during weathering can lead to As release. Rates of mineral dissolution in such mineralised areas may be enhanced by mining activity and As contamination can be particularly severe in water associated with mine wastes and mine drainage. Geothermal environments may be regarded as the precursors of mineralised areas and geothermal fluids can also contain very high concentrations of As.



Figure 2.3 Summary of the world distribution of documented problems with As in groundwater (>50 µg/L) and the environment (updated from Smedley and Kinniburgh, 2002).

A map of the distribution of documented cases of As contamination in groundwater and the environment is given in Figure 2.3 (updated from Smedley and Kinniburgh, 2002). Many of these cases are related to areas of mineralisation and associated mining activity. Examples include several parts of the USA and Canada, northern Burkina Faso, the Lavrion area of Greece, Chattisgarh in India, the Zimapán region of Mexico, Ron Phibun District of Thailand, and parts of south-west England (Thornton, 1994; Komnitsas et al., 1995; Williams et al., 1996; Chakraborti et al., 1999; Pandey et al., 2002; Armienta et al., 2005; Smedley et al., 2007). Some high-As areas are also associated with the occurrence of geothermal fluids. Examples include parts of the USA (Wilkie and Hering, 1998), central America (Criaud and Fouillac, 1989), Japan and New

Zealand (Swedlund and Webster, 1998). Contamination of local soils and waters can be severe in such mineralised or geothermal areas, at least locally. Some, though not all, have had an adverse effect on human health through contamination of drinking water.

Other areas with recognised high-As groundwaters are not associated with obvious mineralisation or geothermal activity. Some of these occur in regionally extensive aquifers which can be a major source of drinking water for large populations. Such affected aquifers are found in parts of Argentina, Chile, Mexico, USA, Hungary, Romania, Bangladesh, India, Nepal, Burma, Cambodia, Pakistan, China and Vietnam (Figure 2.3). In several of these aquifers, high As concentrations have only been discovered through the identification of health problems. Some have been identified relatively recently as a result of randomised groundwater testing programmes.

Many differences exist in hydrogeological and geochemical conditions between these regions, but some notable similarities are also apparent. The majority of the recognised high-As groundwater provinces are in young unconsolidated sediments, usually of Quaternary, and often of Holocene, age (<12,000 years). The affected aquifers tend to be in inland closed basins in arid or semi-arid settings (e.g. Argentina, Mexico, south-west USA) (Robertson, 1989; Rosas et al., 1999; Smedley et al., 2002) or large alluvial and deltaic plains (e.g. Bengal delta, Yellow River Plain, Irrawaddy delta, Red River delta, Mekong valley) (e.g. Chatterjee et al., 1995; Berg et al., 2001; Smedley et al., 2003; van Geen et al., 2003; Polya et al., 2005). The groundwaters with high As concentrations tend to occur under oxic, high pH conditions or under strongly reducing conditions. Some documented case studies from these terrains are described below.

2.3 Arsenic in mining and mineralised areas

Arsenic occurs as a major constituent in more than 200 minerals, most of them ore minerals or their weathering products. They include elemental arsenic, arsenides, sulphides, oxides, arsenates and arsenites. These As minerals are relatively rare in nature but are concentrated in some ore zones. The most abundant As ore minerals are arsenopyrite (FeAsS) and arsenian pyrite ($\text{Fe}(\text{S},\text{As})_2$). Other As-bearing sulphides in mineralised areas include realgar (AsS) and orpiment (As_2S_3). Arsenic is also present at high concentrations in the more common sulphide minerals, the most abundant of which is pyrite (FeS_2). Concentrations in pyrite, chalcopyrite, galena and marcasite can be very variable but potentially reach several weight % (Table 2.1). High concentrations of As, up to several weight %, can also be found in many oxide minerals and hydrous metal oxides (Table 2.1), especially when formed as weathering products of primary sulphide minerals. Iron sulphides and iron oxides together constitute the most important mineral sources of As in groundwaters and it follows that environmental As problems can arise in mineralised areas where these are particularly concentrated.

Arsenic-related health problems in mineralised areas can arise through exposure to high-As soils and waste piles, release of As to the atmosphere through intensive coal burning (e.g. Ding et al., 2001), or contamination of drinking water.

2.3.1 Ron Phibun District, Thailand

Health problems linked to As in drinking water were first recognised in residents of Ron Phibun District, Nakhon Si Thammarat Province in Thailand (Figure 2.1) in 1987. Over 1000 people in the area were diagnosed with As-related skin disorders, including

keratosis and melanosis, particularly in and close to Ron Phibun town (Williams, 1997). At the time of first recognition of the problems, some 15,000 people were thought to be drinking water with more than 50 µg/L As (Fordyce et al., 1995).

Table 2.1 Ranges of arsenic concentrations in various minerals (data sources: Stewart, 1963; Baur and Onishi, 1969; Boyle and Jonasson, 1973; Dudas, 1984; Arehart et al., 1993; Fleet and Mumin, 1997; Pichler et al., 1999; Paktunc et al., 2006).

Mineral	Arsenic concentration range (mg/kg)
<i>Sulphide minerals</i>	
Pyrite	100–120,000
Pyrrhotite	5–100
Marcasite	20–276,000
Galena	5–10,000
Sphalerite	5–17,000
Chalcopyrite	10–5000
<i>Oxide minerals</i>	
Haematite	up to 29,000
Iron(III) oxyhydroxide	up to 76,000
Magnetite	2.7–41
Maghemite	up to 186,000
<i>Silicate minerals</i>	
Quartz	0.4–1.3
Feldspar	<0.1–2.1
Biotite	1.4
Amphibole	1.1–2.3
Olivine	0.08–0.17
Pyroxene	0.05–0.8
<i>Carbonate minerals</i>	
Calcite	1–8
Dolomite	<3
Siderite	<3
<i>Sulphate minerals</i>	
Gypsum/anhydrite	<1–6
Barite	<1–12
Jarosite	34–1000
<i>Others</i>	
Apatite	<1–1000
Halite	<3–30
Fluorite	<2

The affected area lies within the South-East Asian Tin Belt where primary Sn-W-As mineralisation and alluvial placer tin deposits were mined for over 100 years. Legacies of the mining operations included arsenopyrite and pyrite-rich waste piles, and waste from ore dressing plants and panning. Waste piles from former bedrock mining contained up to 30% As (Williams et al., 1996). Alluvial soils also contain up to 0.5% As (Fordyce et al., 1995).

High As concentrations have been found in both surface waters and shallow groundwaters from the area around the mining activity as a result of natural oxidation of arsenopyrite, mining activity and release following post-mining groundwater rebound (Figure 2.4) (Williams, 1997). Williams et al. (1996) reported concentrations of As in the surface waters reaching up to 580 $\mu\text{g/L}$. Shallow groundwaters (<15 m deep) from alluvial and colluvial deposits were reported to have extremely high As concentrations, reaching up to 5100 $\mu\text{g/L}$ with 39% of samples having more than 50 $\mu\text{g/L}$. Conditions in the shallow aquifer were noted to be generally oxic with nitrate concentrations (as N) up to 8.9 mg/L, low Fe concentrations (<0.4 mg/L) and dissolved As being present dominantly as As(V).

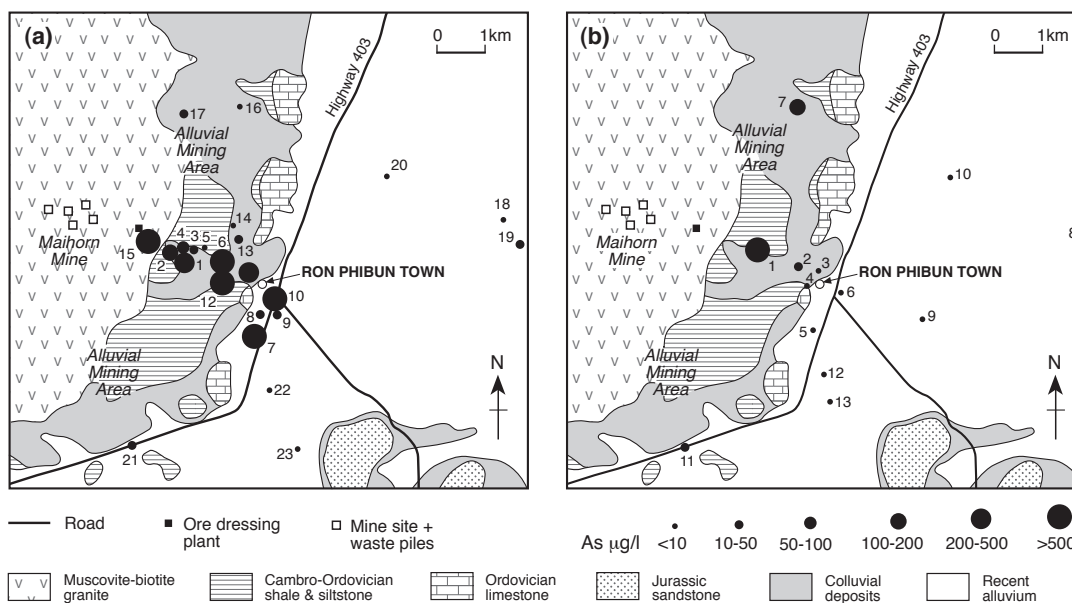


Figure 2.4 Simplified geological map of Ron Phibun area, peninsular Thailand, showing the distribution of As in groundwaters (from Williams et al., 1996). The distributions are (a) As in groundwaters from shallow boreholes in an alluvial aquifer (<15 m depth), (b) As in groundwaters from deeper boreholes (>15 m) in a carbonate aquifer. Sample numbers refer to data given in Williams et al. (1996).

Deeper groundwaters from an underlying carbonate aquifer (well depth >15 m) had generally lower As concentrations, although 15% of samples exceeded 50 $\mu\text{g/L}$ (Williams et al., 1996). The presence of more reducing conditions may be responsible for the observed high As concentrations in some of the deeper groundwaters, though leakage of high-As groundwater from the overlying aquifer is also possible.

As a result of the severe health and environmental problems, mining activity in the area has ceased and remediation measures have included transportation of mine waste to confined local landfill (Wattanasen et al., 2006).

2.3.2 Burkina Faso

Although investigations in the 1970s revealed the occurrence of high As concentrations in groundwater from three boreholes from one village in central Burkina Faso (de Jong and Kikietta, 1981), little investigation of As concentrations in groundwater has taken place in the country until relatively recently. Over the last few years, surveys have

revealed the presence of high concentrations of As in some groundwaters from northern Burkina Faso and more extensive testing programmes are ongoing.

High groundwater As concentrations have been found in the provinces of Yatenga and Zondoma, close to the town of Ouahigouya in northern Burkina Faso (COWI, 2004; Smedley et al., 2007) (Figure 2.5). Skin disorders (melanosis, keratosis and skin tumours) have also been reported in the region (Ouedraogo, 2006). The As is found in groundwater from Lower Proterozoic (Birimian) volcano-sedimentary rocks which host gold and associated sulphide mineralisation. Gold mining has expanded significantly in Burkina Faso since the 1980s, although production is artisanal. The sulphide minerals present in the mineral veins include pyrite, arsenian pyrite and chalcopyrite which are highly altered, as are the host schists. A prominent mineralised zone runs with a NE–SW orientation in the Mogombouli–Nongfaere–Margo–Tanlili area (Figure 2.5).

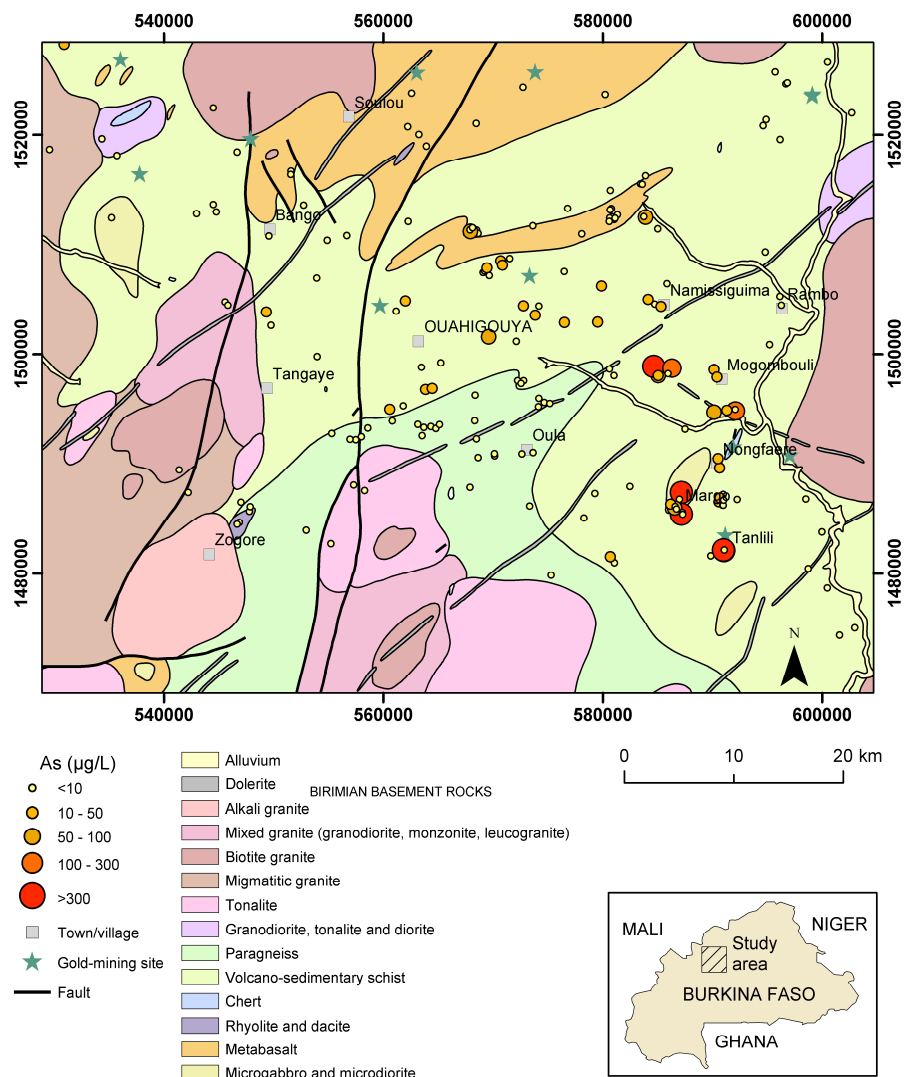


Figure 2.5 Geological map of the Ouahigouya area, northern Burkina Faso, showing the concentrations of As in sampled boreholes and dug wells (data from COWI, 2004; Smedley et al., 2007).

Groundwater in the Ouahigouya area is abstracted from hand-pumped boreholes, typically 50–120 m deep, or from more traditional shallow dug wells. Smedley et al.

(2007) reported from a study of 45 groundwater samples from the area that most had As concentrations of less than the WHO guideline value of 10 $\mu\text{g/L}$, although a large range from <0.5 to 1630 $\mu\text{g/L}$ was observed. The high concentrations were found exclusively in borehole waters, concentrations in sampled dug wells being less than 10 $\mu\text{g/L}$. High concentrations of As in the groundwater appear to be strongly associated with this mineralised zone.

From available data, the groundwater appears to be mainly oxic, with dissolved oxygen present in most samples and median nitrate concentrations of 2.1 and 1.1 mg/L (as N) in groundwater from dug wells and boreholes respectively (Table 2.2). As with the Ron Phibun shallow groundwaters, dissolved As occurs dominantly as As(V) (Figure 2.6). The source of the As in the Ouahigouya area is most likely to be the oxidised sulphide minerals and secondary iron oxides in the mineralised zones.

Table 2.2 Summary statistical data for selected chemical constituents in groundwater from the Ouahigouya area of Burkina Faso (after Smedley et al., 2007).

Parameter	Units	Range (n=9)	Median	Range (n=36)	Median
		Wells		Boreholes	
pH		5.2–7.0	5.7	5.8–7.8	7.1
DO	mg/L	1.4–4.5	3.3	<0.1–5.8	0.8
SEC	$\mu\text{S/cm}$	40–201	65	54–1770	369
SO ₄	mg/L	<0.2–33	0.38	<0.2–657	6.8
NO ₃ -N	mg/L	<0.05–5.5	2.1	<0.05–22	1.05
Fe	mg/L	0.009–0.11	0.03	0.005–0.69	0.008
Mn	$\mu\text{g/L}$	1.5–1450	18	0.2–99	1.1
As	$\mu\text{g/L}$	<0.5 – 6.1	1.5	<0.5 – 1630	15

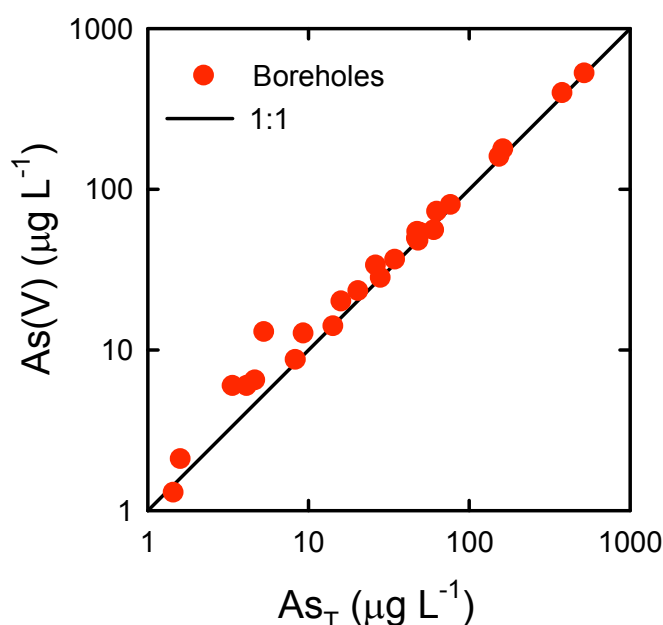


Figure 2.6 Relationship between As(V) and total As in waters from boreholes in the Ouahigouya area of Burkina Faso (after Smedley et al., 2007).

2.4 Arsenic in geothermal waters

High concentrations of As have also long been associated with some geothermal fluids. Geothermal systems are found in diverse tectonic settings including active plate margins (e.g. the Pacific Rim), continental and oceanic hot spots (e.g. Yellowstone, Hawaii respectively) and within-plate rift zones (e.g. the East African Rift) (Webster and Nordstrom, 2003). High As concentrations have been found in geothermal fluids from continental plate margins (e.g. Alaska, Japan, Kamchatka, New Zealand, Philippines) and some continental hotspots (e.g. Yellowstone) but are generally not associated with oceanic hotspots or within-plate rift zones. Stauffer and Thomson (1984) found As concentrations up to 10,000 $\mu\text{g/L}$ and Thompson and Demonge (1996) found concentrations up to 7800 $\mu\text{g/L}$ in hot springs and geysers from Yellowstone National Park. Geothermal brines from the Wairakei geothermal field in New Zealand have As concentrations up to 3800 $\mu\text{g/L}$ (Robinson et al., 1995). White et al. (1963) reported concentrations up to 5900 $\mu\text{g/L}$ in thermal waters from Kamchatka. In contrast, concentrations in the range $<0.03\text{--}10$ $\mu\text{g/L}$ were found in geothermal waters from Iceland (Arnorsson, 2003) and $<10\text{--}70$ $\mu\text{g L}^{-1}$ in geothermal waters from Hawaii (Webster and Nordstrom, 2003). The reasons for the differences in As concentrations in geothermal fluids between these tectonic settings are not fully understood. They may be partially related to the fact that basaltic rocks, which constitute the likely As sources in oceanic settings, have comparatively low As concentrations (ca. 0.05–0.2 mg/kg compared to around 1 mg/kg for more evolved rhyolites, Arnorsson, 2003). Potentially more importantly, increased loads of dissolved As can be derived by leaching from continental crustal material which is present in convergent plate margin and continental hotspot settings.

High concentrations of As in geothermal areas are more commonly reported in surface waters than groundwaters (e.g. Nimick et al., 1998; Wilkie and Hering, 1998), although some groundwaters have been affected (Welch et al., 2000).

High-As geothermal waters are often associated with a characteristic suite of other trace constituents, including Li, B, F, Hg, Sb, Se, Th, and H_2S . Positive correlations with Cl and salinity have also often been reported (Webster and Nordstrom, 2003).

2.5 Arsenic in young sedimentary aquifers

In recent years it has become increasingly apparent that some of the most extensive and serious groundwater As problems occur not in areas influenced by metalliferous mineralisation or geothermal activity, but in seemingly ordinary sedimentary aquifers. Indeed, this is one of the most significant reasons why As problems in regions such as the Bengal Basin were not recognised earlier. An important discovery of recent years has been that the sediments composing these aquifers do not tend to contain unusually high As concentrations. Average As concentrations in soils and sediments are in the approximate range 5–10 mg/kg. This compares for example with concentrations of 1–15 mg/kg found in sediments of the Bengal Basin (BGS and DPHE, 2001), 3–29 mg/kg found in the Huhhot Basin of China (Smedley et al., 2003) and 0.6–33 mg/kg in the Red River Basin of Vietnam (Berg et al., 2001). All of these areas are characterised by high groundwater As concentrations. Arsenic release to groundwater in such areas must therefore occur by a combination of special geochemical and hydrogeological conditions rather than extraordinary As-rich sources.

Many minerals may be involved in the release of As to groundwater and it is often very difficult in a given aquifer to distinguish the principal As mineral sources. There is also a problem in distinguishing between primary and secondary sources. However, it is widely recognised that metal oxides, particularly iron oxides, can and do play an important role in the cycling of As in sedimentary aquifers. The release of As from iron oxides under reducing conditions has been widely documented (e.g. Deuel and Swoboda, 1972; de Vitre et al., 1991; Widerlund and Ingri, 1995). It is also recognised that many of As problems in young sedimentary aquifers occur under strongly reducing conditions. Recent investigations have shown that release of significant concentrations of As can occur under oxidising conditions in aquifers where pH values rise sufficiently high to promote desorption of As(V) from metal-oxide surfaces, or at least inhibit sorption to such surfaces. Some well-documented case studies from both reducing and oxic high-pH aquifer settings are outlined below.

2.5.1 Aquifers in reducing conditions

Bangladesh

The most serious of the world's recognised groundwater As problems without doubt occurs in Bangladesh. The region has been the subject of intensive water testing, hydrogeological and epidemiological investigation, patient identification and treatment and mitigation effort since the groundwater As problem was first recognised by the national government and others in 1993.

The high-As groundwaters of the region are mainly from aquifers of Holocene age which comprise unconsolidated grey micaceous sands, silts and clays deposited as alluvial and deltaic sediments associated with the Ganges, Brahmaputra and Meghna rivers. The sediments are derived from the upland Himalayan catchments and from basement complexes of the northern and western parts of West Bengal. Many studies have observed that the highest concentrations of As in the shallow Holocene aquifer of Bangladesh occur at depths typically around 15–50 m (BGS and DPHE, 2001; Harvey et al., 2002; Klump et al., 2006). Concentrations of As in excess of 1000 µg/L have been found in some shallow groundwaters from the region, although these are relatively rare.

A random national survey of As in groundwater (BGS and DPHE, 2001), using laboratory data for 3208 groundwater samples from the shallow Holocene aquifer (<150 m depth), found that 27% of samples had As concentrations greater than the national standard for As in drinking water of 50 µg/L; 46% exceeded 10 µg/L. A map of smoothed groundwater As distributions is given in Figure 2.7. More recent data from the Bangladesh Arsenic Mitigation and Water Supply Program (BAMWSP, 2005) showed that of almost 5 million boreholes tested nationally using field-test kits, some 30%, had As concentrations greater than 50 µg/L. Each dataset produced for Bangladesh groundwaters demonstrates a very variable distribution of As regionally across the country, with the greatest proportion of exceedances in groundwaters from the south and south-east (Figure 2.7).

In some parts of southern Bangladesh, the majority of boreholes have concentrations greater than 50 µg/L. A recent UNICEF/DPHE survey of groundwaters from 15 upazilas in southern Bangladesh (Rosenboom, 2004) found that of 316,951 boreholes tested, 66% had As concentrations greater than 50 µg/L. In 574 villages tested in the survey, groundwater from every single borehole had concentrations exceeding 50 µg/L.

Van Geen et al. (2003) also found, from a survey of 6000 boreholes in Araihaazar upazila of central Bangladesh, that some 75% of the shallow boreholes deriving water from Holocene sediments (depth range 15–30 m) had As concentrations above 50 $\mu\text{g/L}$. The BGS and DPHE (2001) survey also found some villages in southern Bangladesh where more than 90% of the boreholes had As concentrations greater than 50 $\mu\text{g/L}$.

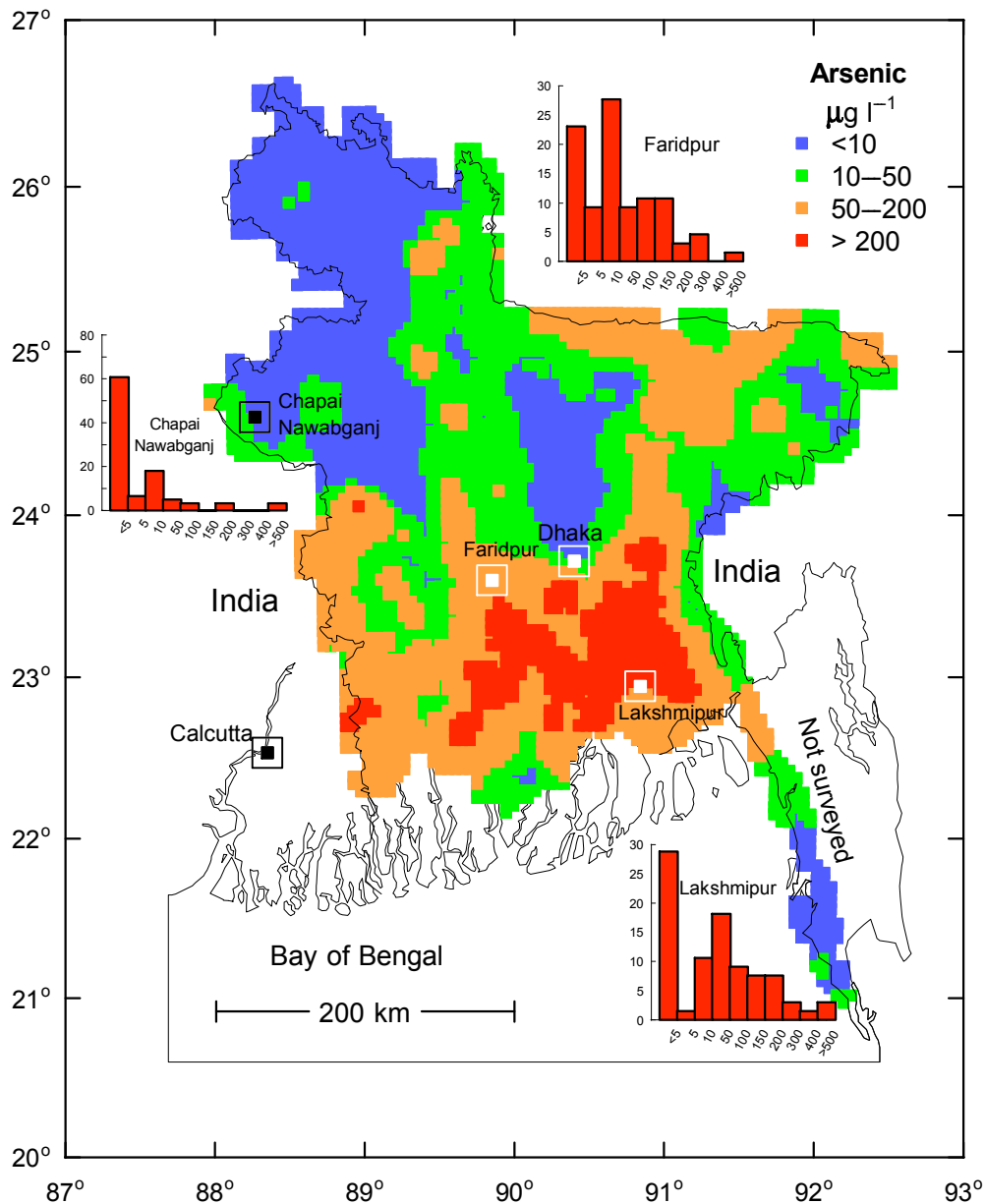


Figure 2.7 Smoothed map of As distributions in groundwater in Bangladesh showing the locations of special study areas described in detail by BGS and DPHE (2001) and histograms of As concentrations in each area. Arsenic distributions based on 3208 groundwater samples from the shallow aquifer (<150 m depth).

The results clearly indicate a problem that is very large. BGS and DPHE (2001) estimated, on the basis of the population at the time, that up to 35 million people were drinking groundwater with As concentrations above 50 $\mu\text{g/L}$ and up to 57 millions were drinking water with greater than 10 $\mu\text{g/L}$. Mitigation efforts have gone some way to

reducing the exposure, although this is offset somewhat by the rapid population growth rate and the continuing installation of new boreholes. Many millions of people in the country still remain without access to low-As water.

Table 2.3 Statistical summary of chemistry of groundwater from shallow boreholes (<100 m) in Faridpur, central Bangladesh (see Figure 2.7 for location) (after BGS and DPHE, 2001).

Parameter	Units	Range (n=59)	Median
pH		6.4–7.4	6.9
DO	mg/L	<0.1–1.4	<0.1
SEC	μS/cm	344–1400	749
SO ₄	mg/L	<0.2–64	<0.2
HCO ₃	mg/L	200–848	536
NO ₃ -N	mg/L	<0.3–4.9	<0.3
NH ₄ -N	mg/L	<0.06–17.6	1.02
DOC	mg/L	0.1–13.0	1.9
Fe	mg/L	0.05–20	5.6
Mn	mg/L	0.04–4.2	0.69
P	mg/L	<0.2–5	1.5
As	μg/L	<0.5–1460	39

A combination of the presence of poorly-permeable sediment horizons, particularly as overbank deposits in the upper part of the Holocene sequence and a relative abundance of co-deposited fresh organic matter leads to often poor hydraulic circulation and the generation of strongly reducing conditions in many parts of the aquifers. The groundwaters of the region typically have high concentrations of Fe, Mn and HCO₃ and often high NH₄-N and DOC concentrations, as well as low concentrations of SO₄ and NO₃-N (Table 2.3) (BGS and DPHE, 2001; Harvey et al., 2002; van Geen et al., 2003). In some areas, conditions are even sufficiently reducing for methane generation and ‘flaring’ wells have been recognised (Ahmed et al., 1998). Such reducing conditions favour the mobilisation of As.

Arsenic speciation studies suggest that a large range in the relative proportions of dissolved As(V) and As(III) exists in the groundwaters of Bangladesh (Acharyya, 1997; Ohno et al., 2005; Bhattacharya et al., 2006a). BGS and DPHE (2001) found the modal proportion of As(III) to be between 50% and 60% of the total As (Figure 2.8). However, detailed studies of groundwaters with high As concentrations have generally shown a strong dominance of As(III) (≥70%) (e.g. Zheng et al., 2005).

Arsenic has been found in the sediments in association with mixed Fe(II)-Fe(III) oxides (Bhattacharya et al., 1997; BGS and DPHE, 2001; Harvey et al., 2002; Horneman et al., 2004; Swartz et al., 2004), phyllosilicate minerals (Breit et al., 2001) and sulphide minerals (e.g. Nickson et al., 2000; Polizzotto et al., 2006). There is as yet little overall consensus on the detailed mechanisms involved in As mobilisation in the Bangladesh aquifers, although most workers would agree that the iron oxides exert a significant control in the process. Under the ambient strongly reducing conditions, dissolution of sulphide minerals is unlikely to be a major release mechanism on a regional scale.

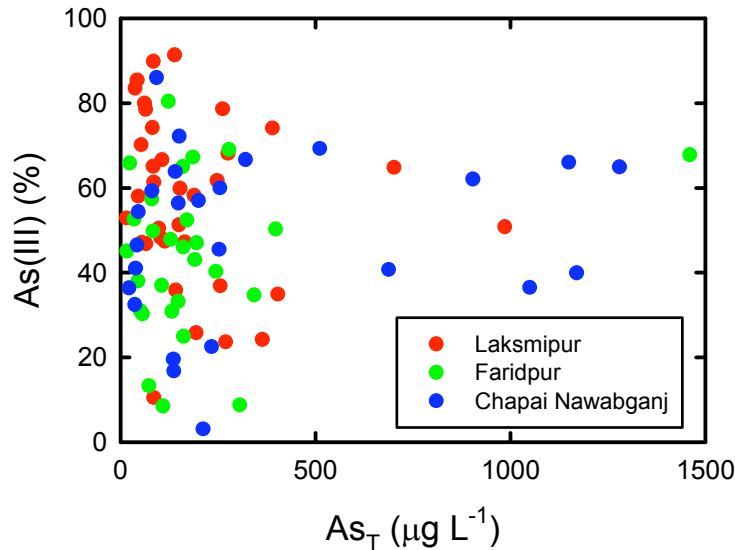


Figure 2.8 Percentage of As present as As(III) in groundwaters from three special study areas in Bangladesh.

Huhhot Basin, Inner Mongolia, China

Drinking-water related As problems have been recognised in several parts of northern China and a number of studies have documented arsenicosis symptoms among resident populations (Ma et al., 1999; Yu et al., 2007). In Inner Mongolia, high As concentrations have been found in groundwaters from the Ba Men region and Tumet Plain, part of which includes the Huhhot Basin (Luo et al., 1997; Ning et al., 2007).

The Huhhot Basin (area around 80 x 60 km, Figure 2.9) lies on the southern edge of the Gobi Desert and experiences an arid climate with average annual precipitation of around 440 mm. The basin inclines gently south-westwards and is composed of up to 1500 m of poorly-consolidated sediments, a large thickness of which are Quaternary (Smedley et al., 2003). The Quaternary sediments consist largely of coarse-grained alluvial-fan deposits on the basin margins, but with finer-grained lacustrine deposits in the lower-lying parts of the basin further south-west.

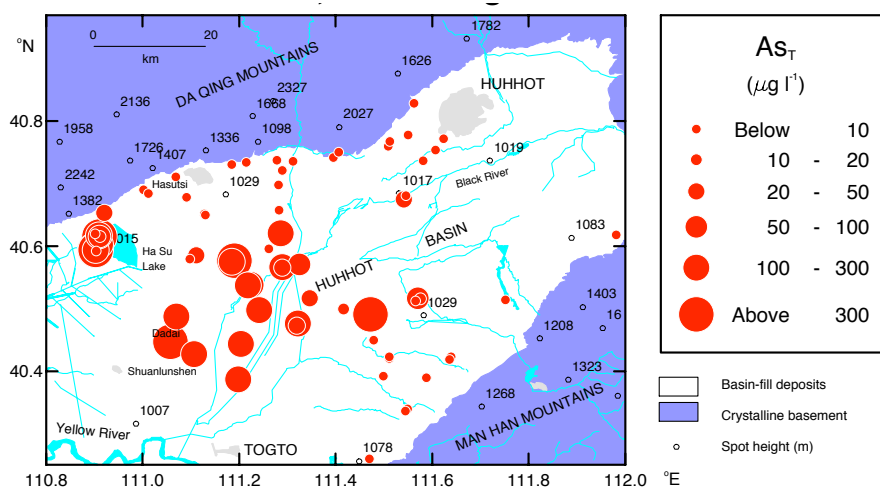


Figure 2.9 Distribution of total As in groundwaters from the Huhhot Basin of Inner Mongolia (after Smedley et al., 2003).

Residents in the region depend heavily on groundwater for domestic supply and agriculture. In recent years, traditional dug wells have largely been replaced as drinking-water sources by hand-pumped boreholes which mainly abstract groundwater at shallow levels (typically <30 m). Groundwater is also present within a discrete, deeper aquifer (typically >100 m depth) which is separated from the shallow aquifer by clay layers. Boreholes tapping this deeper aquifer are often artesian in the central parts of the basin.

Table 2.4 Statistical summary of groundwater chemistry (boreholes and wells) in the Huhhot Basin, China (Smedley et al., 2003).

Parameter	Units	Range (n=73)	Median
pH		7.0–8.6	7.8
DO	mg/L	<0.1–9.8	0.4
SEC	µS/cm	463–4350	841
SO ₄	mg/L	<0.2–1007	34.6
HCO ₃	mg/L	182–1150	389
NO ₃ -N	mg/L	<0.01–34.3	1.13
NH ₄ -N	mg/L	<0.01–18	0.02
DOC	mg/L	0.3–30.6	3.6
Fe	mg/L	<0.01–4.51	0.07
Mn	mg/L	<0.001–1.29	0.026
P	mg/L	<0.05–3.10	0.18
As	µg/L	<1–1480	5.4

Smedley et al. (2003) found from a study of 73 samples taken from the Huhhot Basin that groundwaters have a large range of As concentrations: <1–1480 µg/L in the shallow aquifer and <1–308 µg/L in the deep aquifer. They reported that 25% of shallow sources and 57% of deep sources had As concentrations greater than 50 µg/L. Unlike Bangladesh, the deep aquifer is actually more severely affected than the shallow aquifer. The regional distributions of As in the groundwaters from the shallow and deep aquifers combined are shown in Figure 2.9. Groundwaters from the basin margins within the coarser-grained deposits are oxic and have universally low dissolved As concentrations. High As concentrations are generally restricted to the low-lying part of the basin where the sediments are finer-grained and the groundwaters strongly reducing (Smedley et al., 2003). As with Bangladesh, these high-As groundwaters also typically have high concentrations of dissolved Fe, Mn, NH₄-N, P and DOC and low concentrations of SO₄ and NO₃-N (Table 2.4). The aquifer characteristics of the Huhhot Basin clearly have many similarities with those of Bangladesh although high DOC concentrations (often with discoloured waters reflecting an abundance of humic substances) are a particular feature of this region.

The sediments in the Huhhot Basin have been less well studied than those of Bangladesh, but available evidence suggests that here too, iron oxides are likely to have played an important role in the cycling of As in the aquifers. Positive correlations between sediment As and Fe concentrations and the presence of a relatively high proportion of oxalate-extractable As in the aquifer sediments (Smedley et al., 2003) supports this conclusion. The generation of high alkalinity values, as well as depleted δ¹³C ratios (to -21 ‰) in some of the high-As groundwaters also suggests that organic matter has been an important factor in the development of the strongly reducing

conditions found in the aquifers (Smedley et al., 2003). The high concentrations of dissolved organic matter may also have played a role in maintaining As in soluble form.

2.5.3 Aquifers in alkaline oxidizing conditions

Chaco-Pampean Plain, Argentina

The Chaco-Pampean Plain covers a vast area of around 1 million square kilometres in central Argentina and represents perhaps the largest high-As groundwater province known. The region experiences a temperate climate with aridity increasing towards the west. Average annual rainfall in La Pampa province in central Argentina is around 600 mm. High-As groundwaters in the region are from shallow aquifers formed in Quaternary deposits of loess (mainly silt) with intermixed rhyolitic or dacitic volcanic ash. These often occur within closed basins (Nicolli et al., 1989; Smedley et al., 2002; Smedley et al., 2005; Bhattacharya et al., 2006b). Investigations carried out in the provinces of Córdoba, La Pampa and Santiago del Estero have shown that many groundwaters from the loess aquifers not only contain high concentrations of As, but also a number of other potentially toxic trace elements including F, V, B, U, Se and Mo. Groundwater salinity is also often high in many of the groundwaters of the region (Nicolli et al., 1989; Smedley et al., 2002; Bhattacharya et al., 2006b).

Table 2.5 Statistical summary of selected chemical constituents in groundwater from La Pampa, Argentina (after Smedley et al., 2002).

<i>Parameter</i>	<i>Units</i>	<i>Range (n=108)</i>	<i>Median</i>
<i>pH</i>		7.0–8.7	7.9
<i>SEC</i>	$\mu\text{S/cm}$	773–17500	2610
<i>DO</i>	<i>mg/L</i>	0.8–9.9	6.1
<i>Cl</i>	<i>mg/L</i>	8.5–4580	192
<i>HCO₃</i>	<i>mg/L</i>	195–1440	653
<i>SO₄</i>	<i>mg/L</i>	6.8–3200	290
<i>As_T</i>	$\mu\text{g/L}$	<4–5300	150
<i>As(III)</i>	$\mu\text{g/L}$	<3–110	4.2
<i>Fe</i>	<i>mg/L</i>	<0.006–1.1	0.055
<i>Mn</i>	$\mu\text{g/L}$	<1–79	2
<i>B</i>	<i>mg/L</i>	0.46–13.8	3.0
<i>F</i>	<i>mg/L</i>	0.03–29	3.8
<i>Mo</i>	$\mu\text{g/L}$	2.7–990	62
<i>U</i>	$\mu\text{g/L}$	6.2–250	31
<i>V</i>	<i>mg/L</i>	0.02–5.4	0.56

Groundwaters from La Pampa province are oxic and have neutral to alkaline pH (pH around 7.0–8.7; Table 2.5) (Smedley et al., 2002). The high-As waters are typically of Na-HCO₃ type. Dissolved As is dominated by As(V) (Figure 2.10). Arsenic correlates positively with pH, alkalinity (HCO₃), F and V and weaker positive correlations have been observed with Be, B and U. High salinity is related to evaporation in the semi-arid climatic conditions and high pH and alkalinity are derived dominantly by silicate-weathering reactions. Bhattacharya et al. (2006b) found a more varied range of redox conditions in groundwaters from Santiago del Estero province although conditions there were also mostly oxic with dissolved As being dominated by As(V). The median groundwater As concentration in their study was 54 µg/L (40 samples).

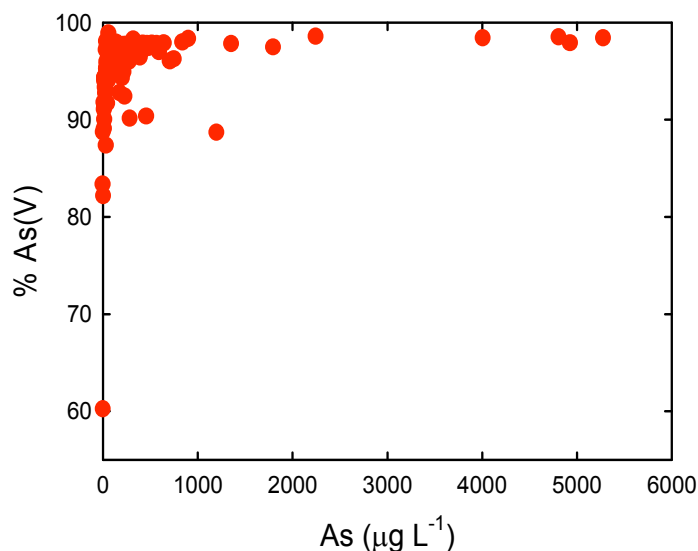


Figure 2.10 Relationship between As(V) and total As in groundwaters from La Pampa province of Argentina (after Smedley et al., 2002).

Concentrations of arsenic in the loess sediments of Córdoba were found in the range 5.51–37.3 mg/kg (Nicolli et al., 1989) and those from La Pampa were in the range 3–18 mg/kg (Smedley et al., 2005). Similarly, 7M HNO₃ extracts of Quaternary sediments from Santiago del Estero province were in the range 2.5–7.3 mg/kg (Bhattacharya et al., 2006b). Rhyolitic ash present in the loess deposits may constitute a significant primary source of the As and associated trace elements in the groundwaters (Nicolli et al., 1989), but Fe and Mn oxides in the loess sediments are also likely to play a role in controlling the concentrations of As in the groundwaters. Adsorption of As(V) and other oxyanion species to Fe oxides is likely to be important at neutral pH but less strong under alkaline (pH>8) conditions (Smedley et al., 2002). Therefore, an increase in pH can lead to the release of As, and other co-adsorbed anions, to groundwater.

2.6 Mechanisms of arsenic release

2.6.1 Oxidation of sulphide minerals

Numerous primary sulphide minerals occur in association with gold and base-metal deposits in mineralised zones. These minerals include Fe sulphides such as pyrite and arsenopyrite, complex copper sulphides such as enargite and tennantite, as well as the As sulphides orpiment and realgar. Dissolution of these minerals, particularly the more abundant Fe sulphides, has been recognised as a cause of high concentrations of aqueous As in many mineralised areas of the world. All these minerals oxidise readily in

contact with the atmosphere and release As and other potentially toxic trace elements. The As released is repartitioned between water and secondary minerals, including schwertmannite, scorodite and the iron oxides. The oxidation reactions can lead to severe degradation of water quality, particularly in areas strongly affected by mining activity. However, aqueous As is strongly attenuated by adsorption to iron oxides, especially under the acidic and oxidising conditions prevalent in the vicinity of the mineral transformations. High As concentrations in surface waters and groundwaters are therefore typically of localised occurrence.

2.6.2 Release from iron oxides under reducing conditions

In many of the world's recognised high-As aquifers, the generation of reducing conditions appears to have played a critical role in triggering the release of As to groundwater. The presence of organic matter in the system drives a complex series of redox reactions, involving progressive and sequential loss of dissolved oxygen, production of CO₂ from the oxidation of organic carbon, reduction of nitrate, Mn(IV) and Fe(III) and subsequently reduction of SO₄ and possibly production of CH₄. The reductive dissolution of Fe oxides during this process can be responsible for release of As to water. As part of the redox reaction sequence, As(V) is also reduced to As(III). This species is normally less strongly adsorbed to Fe oxides and may therefore trigger a further net release of As from adsorption sites as reduction proceeds (Figure 2.2). The importance of microbial activity in catalysing As release in aquifers has been increasingly recognised in recent years (Oremland et al., 2002; Islam et al., 2004). Several species of microbes have been found to be capable of dissimilatory arsenate reduction and a number of others use arsenate reduction as a detoxification mechanism (Hoeft et al., 2002).

Another potentially important process in the sediments is diagenesis of the iron oxides themselves. This may involve a change in oxide structure (bulk and surface) and oxidation state, which can affect the affinity of the minerals concerned for As binding. A change under reducing conditions from Fe(III) forms to mixed Fe(II)/Fe(III) oxides such as magnetite or green rust has been recognised in Bangladesh and elsewhere (Lovley et al., 1990; BGS and DPHE, 2001; Benner et al., 2002; Horneman et al., 2004).

The role of competitive sorption has been stressed by many studies. Phosphate is a well-known competitor for arsenate on Fe-oxide binding sites (Manning and Goldberg, 1996) and is often present at relatively high concentrations in reducing high-As groundwaters such as those in Bangladesh (BGS and DPHE, 2001), West Bengal (McArthur et al., 2004) and China (Smedley et al., 2003). Phosphate concentrations are sometimes in excess of 1 mg/L and almost always in excess of the concentrations of dissolved As. Bicarbonate, also often present at very high concentrations in high-As groundwaters, has likewise been implicated as a potential competitor for As (Appelo et al., 2002; Charlet et al., 2007). Silica may exert a control on the sorption of As(V) and As(III) (Swedlund and Webster, 1998; Rochette et al., 2000) although its effect was considered less significant for groundwaters in West Bengal by Charlet et al. (2007). The competitive impact of dissolved organic carbon species such as fulvic and humic acids is unclear at present.

The nature and origin of the organic carbon that acts as a driver for redox reactions in high-As aquifers has been much debated. Peat deposits (McArthur et al., 2001) and peaty strata marginal to peat basins (McArthur et al., 2004) have been implicated.

Alternatively, disseminated organic matter in the sediments and water have been cited as likely carbon sources (BGS and DPHE, 2001). The introduction of anthropogenic organic carbon through drawdown induced by groundwater pumping has also been proposed as a driver for As release (Harvey et al., 2002; Harvey et al., 2006).

2.6.3 Release of arsenic at high pH

As noted above, under aerobic and near-neutral pH conditions characteristic of many aquifers, adsorption of arsenic to Fe oxides as arsenate is normally strong. Aqueous As concentrations in aquifers are therefore usually low. However, at high pH the adsorption capacity for As(V) is reduced. There are a number of reasons why groundwater pH might increase, but among the most important are uptake of protons by mineral-weathering and ion-exchange reactions, evaporation and inputs from geothermal sources. Uptake of protons during mineral weathering and evaporation can be significant processes in arid and semi-arid regions. Observed pH increases in such environments are commonly associated with the development of groundwater and soil salinity. Inputs of high-pH geothermal waters may be important in maintaining high As concentrations in some alkaline lakes.

The generation of high groundwater pH, especially above pH 8.5, is thought to be an important criterion for the mobilisation of As(V) since sorption to Fe oxides is less favourable under such conditions (Figure 2.2). Such processes are likely to have been responsible for maintaining high groundwater As concentrations in oxidising Quaternary sedimentary aquifers in the semi-arid inland basins of Argentina (Smedley et al., 2002), south-western USA (Robertson, 1989) and Mexico (Rosas et al., 1999) for example. As such a pH increase induces the desorption of a wide variety of oxyanions, other solute oxyanions such as vanadate, uranyl, phosphate and molybdate may also accumulate, as has been observed in some areas (Smedley et al., 2002; Bhattacharya et al., 2006b). As with reducing high-As groundwaters, specific adsorption of these anionic species to oxide binding sites can reduce the load of sorbed As(V). Vanadate has been proposed as a particularly important competitor for As in the oxic Pampean aquifer of Argentina (Smedley et al., 2005). By contrast, some cations, because of their positive charge, may promote the adsorption of negatively charged arsenate (Wilkie and Hering, 1996). Calcium is likely to be the most important cation in this respect because of its abundance in most natural waters and its +2 charge. Aluminium and manganese oxides can also adsorb As to some extent and although less well studied in high-As groundwater contexts, these may be additional sources of or sinks for As in some aquifers.

2.6.4 Variations in groundwater flow

A high degree of spatial variability in arsenic concentrations both areally and with depth has been noted in many of the recognised high-As groundwaters (BGS and DPHE, 2001; Smedley et al., 2002; van Geen et al., 2003; Charlet et al., 2007). Variations in groundwater flow are likely to have been a factor in generating the chemical variations observed. Considerable heterogeneity in sediment texture and composition on a scale of centimetres to metres has been observed in Holocene Bangladesh sediments for instance (BGS and DPHE, 2001) and can be responsible for large variations in permeability and flow. Low-flow horizons occur in low-lying parts of deltas and the insides of river meanders. These have often been associated with occurrences of localised As 'hotspots'. The accumulation of fine-grained, iron-oxide rich deposits may also be favoured in such low-flow zones.

Lack of aquifer flushing has been considered important in maintaining high groundwater As concentrations in both reducing aquifers and oxic, high-pH aquifers. In the latter case, arid climatic conditions enable high pH values to be maintained as well as restricting groundwater flow. High As concentrations are less likely to occur in well-flushed aquifers.

2.6.5 Impact of man's activities

One question that has not been fully answered by the various studies on As in groundwater carried out to date is the extent to which man's activities have contributed to the As problems in different aquifers. In some sulphide mining areas, man has clearly had a major impact by excavating ore minerals, accumulating and redistributing waste piles and pumping mine effluent. This is particularly the case where mining activity is large-scale and long-term. However, in areas where mining activity is small-scale (e.g. artisanal) and/or initiated relatively recently, the impact is likely to be much smaller. Such is the case in northern Burkina Faso where Smedley et al. (2007) concluded that there was no evidence for the high groundwater As concentrations observed being affected significantly by human activity.

In sedimentary high-As aquifers the impacts of anthropogenic activity are also poorly-defined. Groundwater pumping will have an inevitable effect on groundwater flow and mixing both within and between aquifers and will mean that some changes to the aquifer systems can be expected in the medium to long term. Other potential impacts include inputs of anthropogenic organic carbon and phosphorus to the land surface and seasonal waterlogging of soils due to rice production. The significance of such processes is difficult to quantify for any given region.

Studies in the Bengal Basin during the 1990s concluded that high-As groundwaters there were the result of recent over-pumping of groundwater for rice irrigation which were considered to cause dewatering of the sediments and resultant oxidation of sulphide minerals (e.g. Das et al., 1996). Subsequent studies in the region have dismissed this as a significant mechanism as strongly reducing conditions prevail in the affected parts of the aquifers. Many workers have attributed the redox transformations in the Bengal aquifers to reactions with naturally-occurring organic carbon in a natural process which may have been going on for many thousands of years (BGS and DPHE, 2001; McArthur et al., 2001; McArthur et al., 2004). Harvey et al. (2002) attributed the process to more recent introductions of anthropogenic carbon from the land surface from pollutants, although the evidence for this has been disputed (e.g. Klump et al., 2006).

A number of retrospective studies have suggested that groundwater As concentrations in Bangladesh are higher in older boreholes. DPHE/BGS/MML (1999) suggested that an increase in the percentage of boreholes exceeding 50 µg/L occurred as a function of well age, although possible causes of such changes were not discussed. Variations with well age could occur for example as a result of time-varied changes in spatial or depth distribution of boreholes, which may have responded to increased intelligence on As spatial distributions since the mid 1990s. However, in Bangladesh, no obvious spatial or depth relationship is discernible from available groundwater-quality data (dataset of BGS and DPHE, 2001).

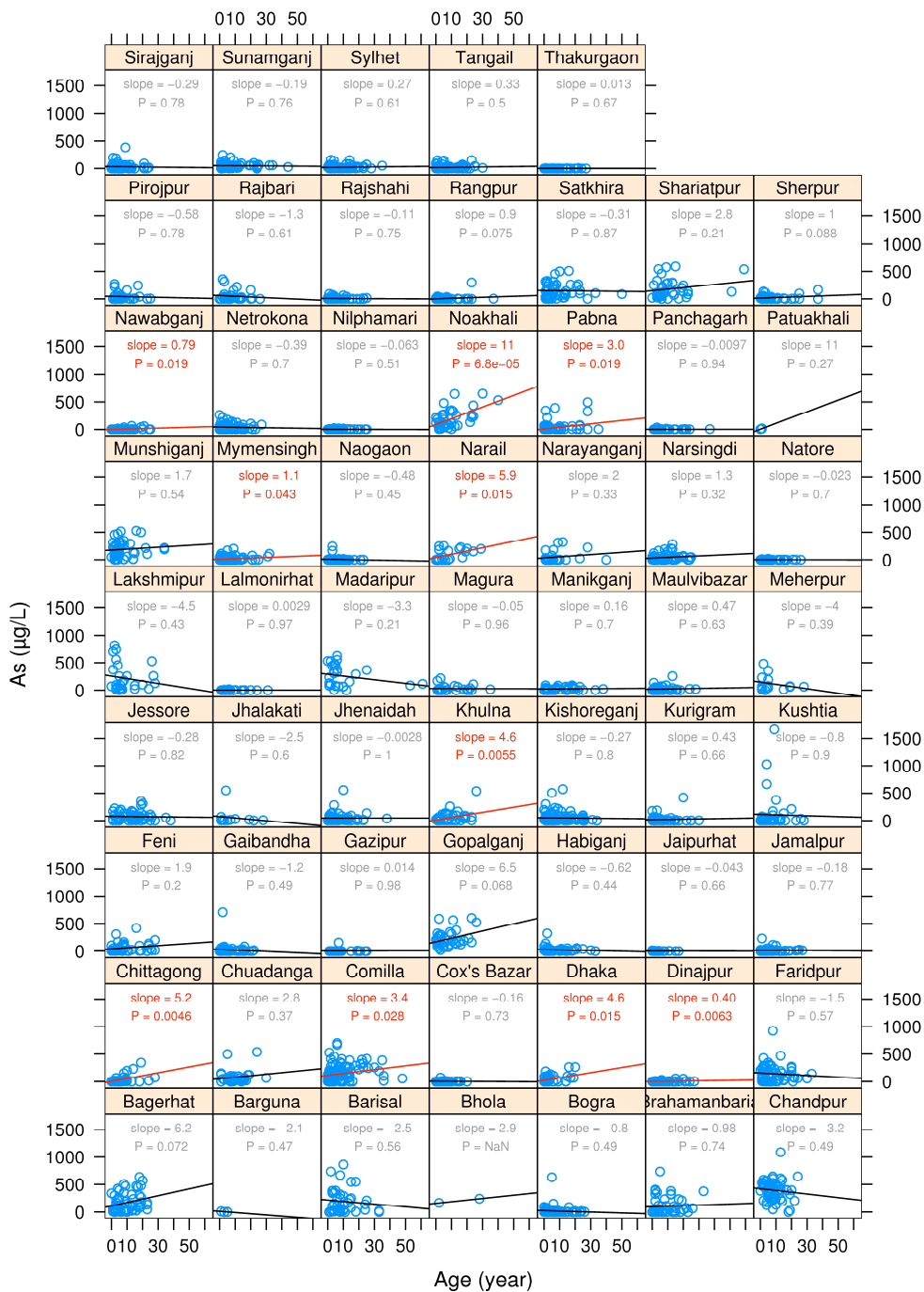


Figure 2.11 Relationship between groundwater As concentration and borehole age in Bangladesh, divided by district. Linear regression has been performed on each data subset and values of slope are given for each district. Statistically significant trends ($p < 0.01$) are highlighted in red. Dataset from BGS and DPHE (2001) (3173 samples, borehole depth <150 m).

Van Geen et al. (2003) suggested on the basis of regression of As concentrations as a function of year of borehole installation that small increases occurred with well age over all depth intervals investigated in Araihaazar upazila of central Bangladesh. Rosenboom (2004) also found that median As concentrations in boreholes from southern Bangladesh were higher where well age was >25 years old than those of <25 years. They found no significant change in spatial distribution of wells with time, although deep (low-As)

tubewells were not present among the older wells in the dataset and shallow dug wells constituted a larger proportion of the old wells.

The results of these studies do not provide strong evidence that groundwater As concentrations in Bengal Basin boreholes have increased with time. However, they do raise some interesting questions about temporal variability and reiterate the need for detailed long-term monitoring. The analysis of survey-type data in this way often involves large numbers of samples and invariably explains only a small proportion of the total variance. A critical analysis needs to be undertaken to ensure that any so-called ‘statistically significant’ trends are indeed truly significant. Division of the Bangladesh groundwater As data from the BGS and DPHE (2001) database into districts (Figure 2.11) suggests that As concentrations in most districts do not show significant trends as a function of well age, although a few exceptions occur. A closer examination of the local circumstances is needed to establish whether a real temporal variation exists at these sites.

2.7 Conclusions

The concentrations of As in natural waters, including groundwater, are usually low. Most are below the WHO provisional guideline value for As in drinking water of 10 µg/L and many below 1 µg/L. Investigations in the last few years have shown that As mobilisation can occur in many aquifers and concentrations can exceed the low drinking-water thresholds in diverse hydrogeological conditions. However, very high As concentrations in groundwater, potentially orders of magnitude greater than threshold values, and extensive areas affected by high-As groundwater tend to be found in a rather limited number of settings.

This chapter has described some of the key features of these settings. They include areas of metalliferous mineralisation and mining, particularly in connection with gold occurrence, areas of geothermal activity, and major alluvial/deltaic plains and inland basins composed of young (Quaternary) sediments. High-As groundwaters in young sedimentary aquifers occur in response to the generation of specific geochemical conditions, among the most important of which appear to be the development of conditions which are either strongly reducing or oxidic and high-pH. Although these two cases are geochemically very different, they each favour As mobility in part through the reduced capacity of metal oxides to adsorb As under such conditions. Lack of flushing of groundwater from an aquifer can also be a factor in maintaining high groundwater As concentrations. Low-lying sedimentary basins and delta plains are typically areas of such slow groundwater movement.

The extent to which anthropogenic activity has affected the distributions of As in groundwater in sedimentary aquifers is not well-established although the evidence for a significant deleterious effect on As concentrations is not compelling. Impacts are potentially diverse and include modification of groundwater flow regimes and inputs of chemical pollutants that can affect As speciation. Pumping-induced groundwater mixing will inevitably modify the chemistry of groundwater in a given aquifer over time but such changes could feasibly lead to decreased As concentrations in places as well as increased ones. Further investigations are required for any given aquifer to establish the magnitude of any impacts.

Although the most important triggers for As release in aquifers have become increasingly well-established in recent years, newly discovered areas of contamination are still emerging as a result of increased groundwater testing. Fortunately, new examples on the scale of Bangladesh As contamination have not emerged. However, the discovery of high As concentrations in groundwaters and associated health problems in a mineralised area of Burkina Faso as recently as 2004 reiterates the need for continued reconnaissance testing, especially in areas that are recognised to be potentially at risk.

2.8 Acknowledgements

I am grateful to David Kinniburgh for producing Figures 4.1 and 4.2 using PhreePlot (Kinniburgh and Cooper, 2004) and for a critical review of this chapter. The chapter is published with the permission of the Executive Director, BGS.

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3 Geochemical experimentation and modeling are tools for understanding the origin of As in groundwater in Bangladesh and elsewhere

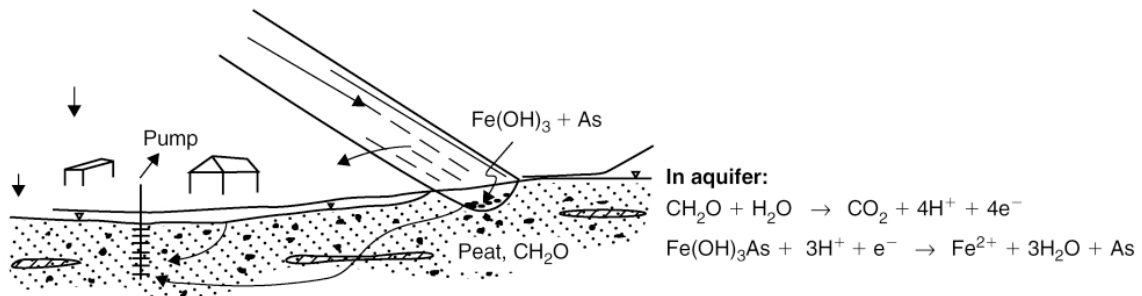
Author: C.A.J. Appelo

3.1 Introduction

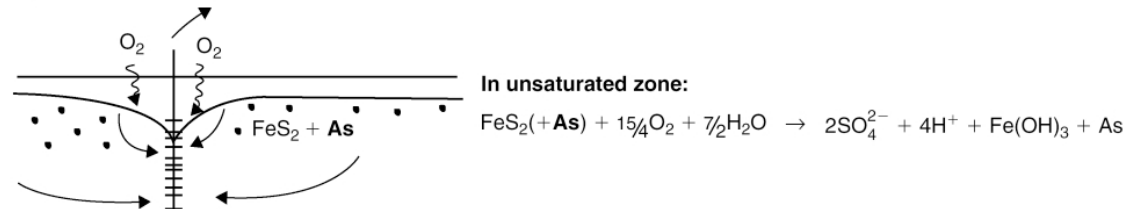
Three chemical reactions have been invoked to explain the high concentrations of arsenic in Bangladesh and West-Bengal groundwater (DPHE/BGS, 2001; Appelo et al., 2002; Smedley and Kinniburgh, 2002; Kinniburgh et al., 2003; Nath et al., 2005; Ravenscroft et al., 2005):

- A) reductive dissolution of iron-oxyhydroxides which releases sorbed As;
- B) oxidative dissolution of As-pyrite;
- C) displacement of sorbed As by increasing PO_4^{3-} or HCO_3^- concentrations.

A) Reductive dissolution of $\text{Fe}(\text{OH})_3$



B) Oxidation of pyrite



C) Displacement of As by HCO_3^-

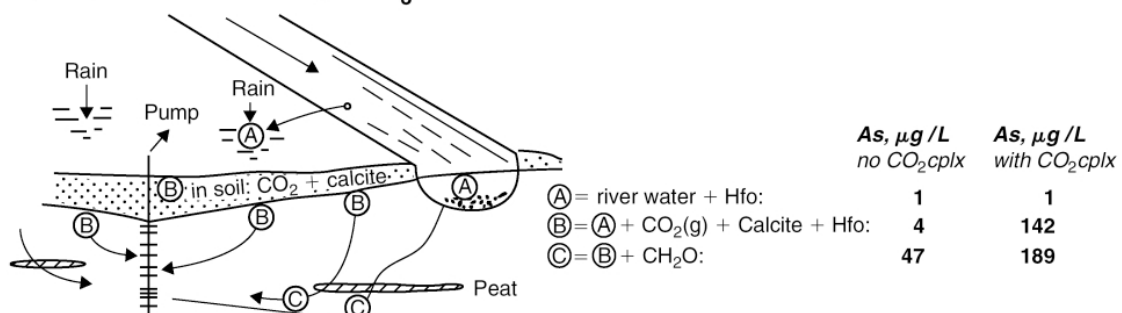


Figure 3.1 Mechanisms to explain the release of As from sediment into groundwater in Bangladesh. (A) iron-oxyhydroxide is reduced by organic matter and releases sorbed As. (B) groundwater drawdown facilitates access of oxygen to pyrite which contains As and dissolves. (C) higher HCO_3^- concentrations in groundwater than in surface water displace As from iron-oxyhydroxide that was deposited with river-sediments. From: Appelo and Postma, 2005.

Figure 3.1 shows where the processes can be located in the field and defies the chemical reactions.

Correlations of arsenic and the major solutes produced by reactions A-B-C might show which process is dominant. The first reaction is triggered by organic carbon, suggesting that As is linked with dissolved organic carbon (DOC) and Fe^{2+} . For the second process, oxidation and dissolution of FeS_2 -(As), a correlation is anticipated among As and Fe^{2+} and SO_4^{2-} . In the third reaction, the As concentration would increase with *a.o.* PO_4^{3-} and HCO_3^- . Figure 3.2 shows the correlation plots using the database in DPHE/BGS, 2001.

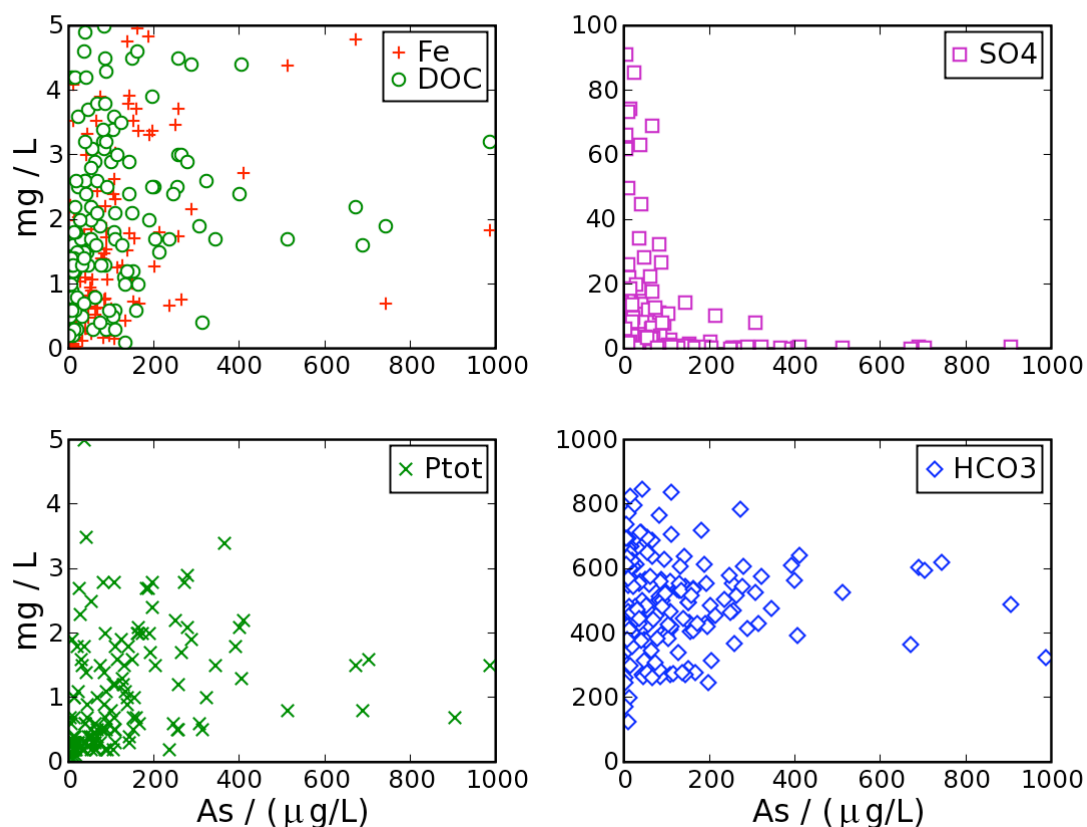


Figure 3.2 Concentrations of major ions plotted vs. As in Bangladesh groundwater. Reactions (A), (B) and (C) from Figure 1 are associated with Fe^{2+} and DOC, Fe^{2+} and SO_4^{2-} , and, among others, P_{tot} and HCO_3^- , respectively. Data from DPHE/BGS (2001).

The relations are weak or absent as noted by DPHE/BGS, 2001; Ahmed et al., 2004; Nath et al. 2005; Ravenscroft et al., 2005; Van Geen et al., 2006. Would it mean then, that none of the theories is applicable? No one seems to argue so. Rather, it is accepted that the relations among solutes in groundwater can be complicated by a plethora of chemical reactions, and further confused by transport and dispersion or by mixing through pumping and irrigation return flow. And, although it is generally realized that arsenic is important for drinking water quality with a small maximal admissible concentration of 10 – 50 $\mu\text{g/L}$, it is only a minor constituent of groundwater that is readily affected by changes in the concentrations of the major solutes.

One way forward is to test the theories by experimenting and computer-modeling, a route that is explored here. It is rather essential to use the combination of modeling and experimenting. The results of experiments may depend on intricate details that are difficult to take in at a glance without a model that shows the interdependencies. For example, Radu et al. (2005) carried out column experiments to test the effectiveness of dissolved carbonate as displacer of sorbed arsenic and noted “these results indicate that dissolved carbonate, even at extremely high concentrations, is not an effective competitive anion with As”. It will be shown that their column results can be modeled well when HCO_3^- is included in the surface complexation model of Dzombak and Morel (1991) for sorption on ferrihydrite, a weakly crystalline iron-hydroxide. The column experiments and the model parameters are essential for constructing a model that can reproduce the depth-concentration profiles for As that have been found in many investigations (Kinniburgh et al., 2003; Van Geen et al., 2003; Swartz et al., 2004; Nath et al., 2005; Zheng et al., 2005). Similarly, before starting calculations, the existence of the chemical reactants should be checked or sediments should be analyzed. In the Ganges delta, the three processes listed above can all be operative since the reactants are all present in the subsoil.

In the following, the three processes will be discussed in detail and available experiments will be modeled to show how far our understanding has come. The modeling provides chemical parameters that can be used for calculating the development of the As-concentration in a hypothetical cross section of a Bangladesh aquifer. Finally, the understanding gained allows to make predictions about geographical locations where As-concentrations are expected to be lowest.

3.2 Chemical reaction

3.2.1 Reductive dissolution of iron-oxyhydroxides

The sediments in Bangladesh show a strong correlation among Fe and As (Nickson et al., 2000; DPHE/BGS, 2001; Ahmed et al., 2004; Swartz et al., 2004; Meharg et al., 2006), and extractions indicate that about half of the As is sorbed on iron oxides (Kinniburgh et al., 2003; Swartz et al., 2004). Islam et al. (2004) added acetate to a sediment-groundwater slurry, and observed that the concentrations of Fe^{2+} and As increased with time (Figure 3.3). Acetate acts as the electron-donor and iron oxide is the electron acceptor according to the reactions shown in Figure 3.1A. If the sediment slurry

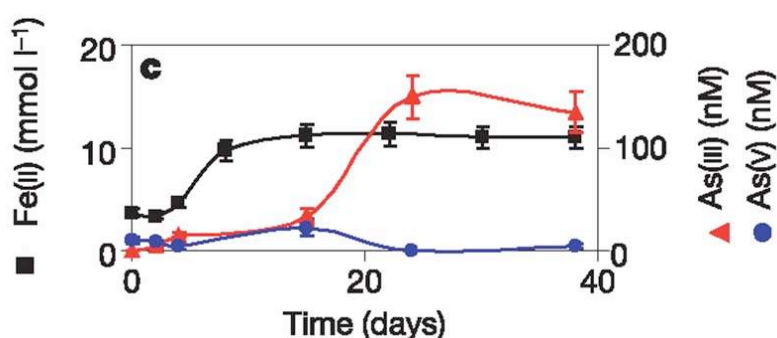


Figure 3.3 Dissolved Fe^{2+} and As concentrations vs. time in an experiment with Bengal sediment incubated with acetate. Fe^{2+} increases by microbial reduction of iron-oxyhydroxide and As is released with a time-lag of 15 days. Adapted from Islam et al., 2004.

was sterilized first before acetate was added, the Fe^{2+} concentration remained constant at the groundwater concentration, and the As-concentration was near-zero throughout the experiment. Apparently, the reaction is catalyzed by Fe(3)-reducing bacteria that harvest the reaction-energy. Harvey et al. (2002) injected a solution with molasses in an aquifer in Bangladesh, and also observed increasing As concentrations when the well was back-pumped.

In the experiment shown in Figure 3.3, the Fe^{2+} concentration starts to rise after about 7 days, because the iron-reducing bacteria need to grow first before the reaction becomes notable. Furthermore, the As concentration increases later than Fe^{2+} . It appears that As, when released from the dissolving iron-oxyhydroxide, is sorbing again on the remaining surface, or that it needs to be reduced from As(5) to As(3) before it is transferred into the solution.

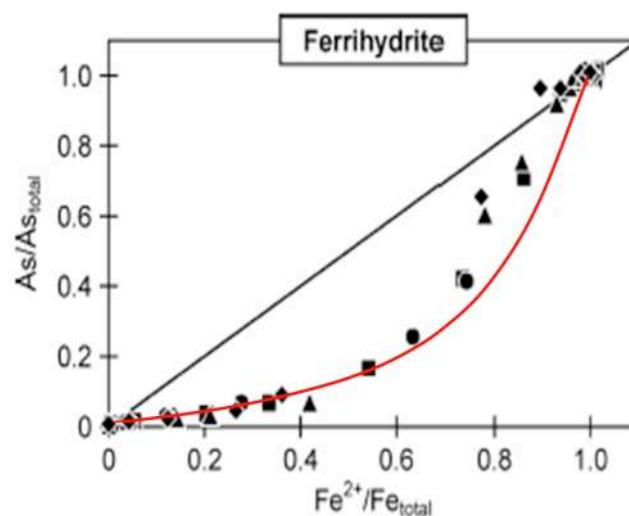


Figure 3.4 The fractions of dissolved Fe and As in an experiment in which ferrihydrite, precipitated with As(5), is reducing and dissolving in ascorbic acid solution. The data show that As is released in relatively smaller amounts than Fe since it resorbs partly on the remaining surface. The red line is modeled with PHREEQC as described in the text. Adapted from Pedersen et al., 2006.

A similar effect was noted by Pedersen et al. (2006), who used ascorbic acid to reduce ferrihydrite doped with As(5). Ascorbic acid can reduce iron-oxyhydroxide abiotically, in contrast to acetate which needs bacterial catalysis to do so. Figure 3.4 plots the fraction of Fe vs. the fraction of As in solution in the experiments of Pedersen. The 1:1 line would result if both chemicals dissolve in the stoichiometric ratio of the solid, but the actual data illustrate that the release of As is delayed relative to Fe. Apparently, As is resorbing on the remaining surface, and we can try to model that with PHREEQC (Parkhurst and Appelo, 1999). PHREEQC uses the database of Dzombak and Morel (1991), which assembles the results from many experiments and allows computing competitive sorption of inorganic solute species for the sorption sites on ferrihydrite. In the database, the number of sorption sites amounts to 0.2 moles per mol ferrihydrite, but with that number, all As resorbs as long as 1% of the original surface is present. However, ascorbic acid, which is the major solute in the experiment, can be expected to be sorbed as well, thus reducing the available sites for As. When the available sites are reduced to 0.015 moles per mol ferrihydrite (7.5% of the total sorption sites), the model calculates the red line shown in Figure 3.4, which follows the data well.

PHREEQC allows simulating the water composition when Ganges water passes a peat layer and is charged with organic carbon that can reduce iron oxides according to the process of Figure 3.1(A). This case is also described in Appelo and Postma, 2005, and the PHREEQC input file can be found there as well. Briefly, Ganges water with 1 ppb As is defined as the solution, and is in equilibrium with ferrihydrite that is part of the sedimentary load of the river and the sediments that make up the aquifer. ferrihydrite sorbs all the elements in solution in conformity with the database. In the simulation, organic carbon is added stepwise as reductant of ferrihydrite, and the resulting water compositions are shown in Figure 3.5. Alkalinity is produced in the reaction and is used as the master variable on the x-axis. Clearly, the concentration of As increases, similarly as in Figures 3 and 4, and it could be concluded that the increase of As in Bangladesh groundwater has been explained. Instead of peat, which seems to be scarce, organic carbon that is closely associated with sedimentary iron can be the reductor (Meharg et al., 2006). However, the alkalinity in the model is about 300 mg HCO_3^- /L which is lower than observed (Figure 3.2), and the pH is calculated to be 8.5, while it is 7 in groundwater. So far, the discrepancy in pH has not been explained by the advocates of the reduction theory, but it may be accounted for by the higher CO_2 pressure of groundwater. Also, the concentration of iron-oxyhydroxides is almost invariant with depth in the aquifer (Swartz et al., 2004), which suggests that depletion by reduction and dissolution is, overall, not an important reaction. On the other hand, some reduction by organic matter does occur as evidenced by the the presence of acid volatile sulfides in the sediment and the dominance of As(3) in groundwater.

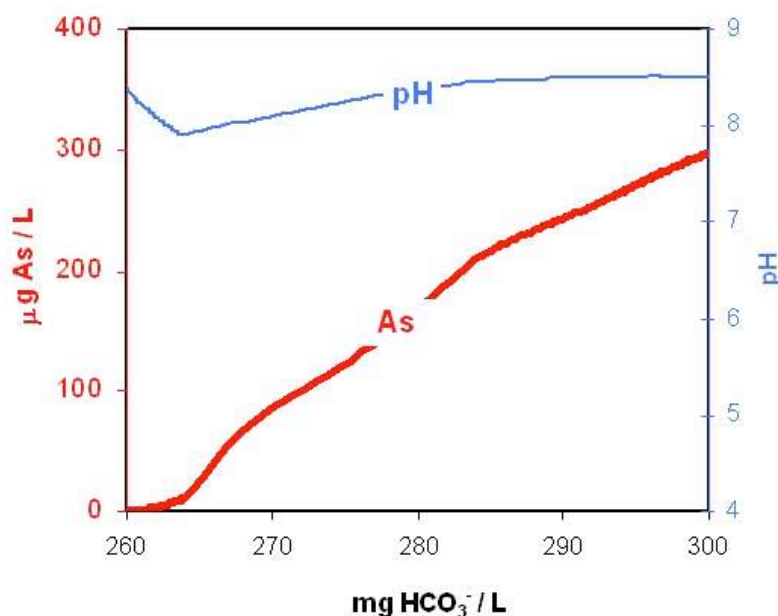


Figure 3.5 Concentration of As and pH during reductive dissolution of iron-oxyhydroxide (Appelo and Postma, 2005).

3.2.2 Pyrite oxidation

Pyrite oxidation has been refuted to be a major process in Bangladesh aquifers by the scarcity of pyrite in the sediments, the framboidal form of pyrite and the omnipresence of acid volatile sulfides which suggest formation rather than dissolution, and the inverse correlation of SO_4^{2-} and As (Nickson et al., 2000; DPHE/BGS, 2001; Kinniburgh et al., 2003; Akai et al., 2004; Swartz et al., 2004; Polizotto et al., 2006). Moreover, if pyrite oxidizes completely, part or all of As will be occluded in the resulting iron oxides (Szramek et al., 2004). To illustrate the reactions, results from a laboratory experiment are presented in Figure 3.6. In the experiment, a pyrite containing sediment from Vierlingsbeek (NL) was oxidized with oxygen (Van Helvoort, 1998). During oxidation, the SO_4^{2-} concentration increases and the pH decreases (Figure 3.6). Initially, Fe^{2+} does

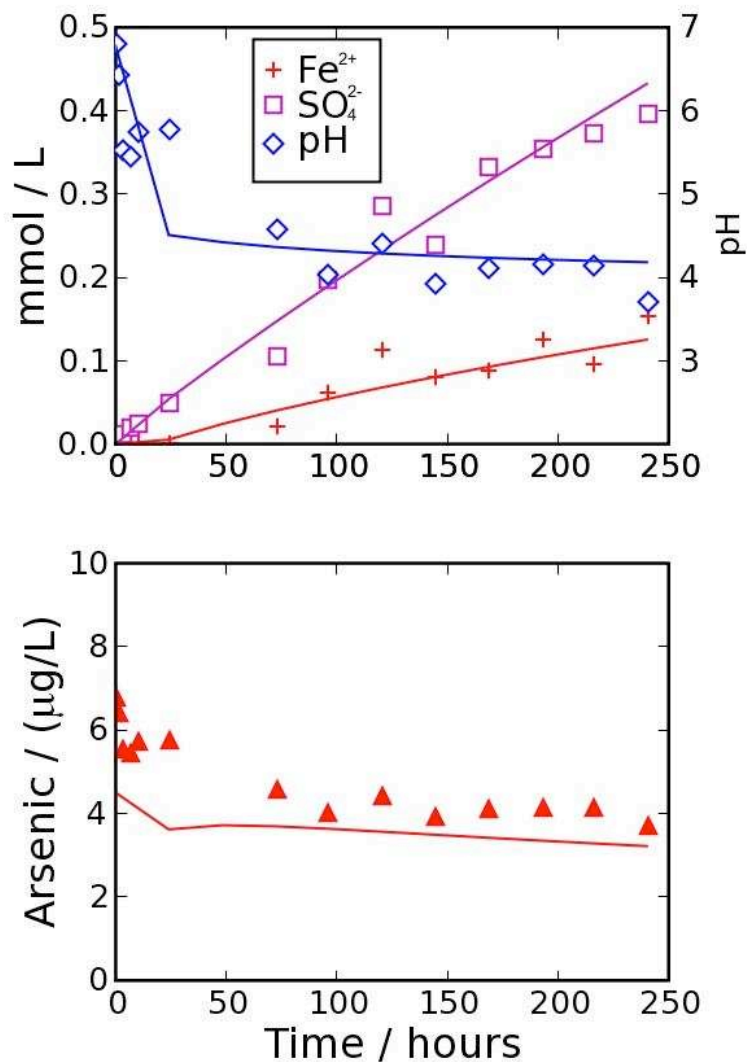


Figure 3.6 Concentrations of SO_4^{2-} , Fe^{2+} , As, and pH (data points) in an oxidation experiment with a pyrite containing sediment from Vierlingsbeek (NL) by Van Helvoort (1998). Model-lines are calculated with PHREEQC.

not appear in solution since it is oxidized to Fe^{3+} and precipitates (or forms $\text{Fe}(\text{OH})_3$ complexes in solution). However, the oxidation rate diminishes with decreasing pH and becomes quite low when pH is below 5, resulting in buildup of Fe^{2+} in solution after 25

hours. The ratio $\text{SO}_4^{2-}/\text{Fe}^{2+}$ in solution is smaller than 2 (the ratio resulting from pyrite oxidation) since part of Fe^{2+} is taken up by cation exchange on the sediment. The lines in Figure 3.6 are simulations with PHREEQC and include the pyrite oxidation rate of Williamson and Rimstidt (1994), the pH dependent, kinetic oxidation of Fe^{2+} (Singer and Stumm, 1970), cation exchange, and sorption on ferrihydrite. Also shown in Figure 3.6 is the concentration of As. Evidently, As does not increase at all. Actually, the model calculates a slight decrease in the first 25 hours when ferrihydrite forms and sorbs a small part of As that goes in solution at the start of the experiment as a result of desorption.

Although the evidence for pyrite oxidation appears to be small, Polizotto et al. (2006) have invoked the reaction since they found sedimentary As to be closely associated with sulfides, and the highest solute concentrations at depths where iron oxides were smallest, which would exclude them from acting as a source for As. Solute As would be released by a combination of pyrite oxidation and reduction of the produced iron oxide during seasonal cycling of aerobic/anaerobic conditions with water table fluctuations. Subsequently, the released As is transported into the aquifer. The water table fluctuations are the result of groundwater pumping for irrigation. The theory was discussed at large by Meharg et al. (2006) and dismissed, major counter-arguments being 1) that arsenic concentrations in groundwater are highest (in south-central Bangladesh) where irrigation rates are lowest, and concentrations are lowest (in north-west Bangladesh) where irrigation rates are highest and 2) that the increased concentrations of As in shallow groundwater have nowhere been found. If the high concentrations have been transported deeper-down in the aquifer, the high source concentrations of As have disappeared with time.

3.2.3 Displacement by HCO_3^- and other solutes

Figure 3.7 shows sorption edges of oxyanions on ferrihydrite, calculated with the Dzombak and Morel database. The calculations were done with $1 \mu\text{mol}$ anion/L and 1 mmol ferrihydrite/L, in 0.1 M NaNO_3 as background electrolyte. The surface of ferrihydrite is neutral at $\text{pH} = 8.1$, the point of zero charge (PZC). At lower pH, the surface becomes positively charged by sorbed protons, and at higher pH the surface is negatively charged. As expected, sorption of anions is enhanced when the surface turns positive with decreasing pH. However, as shown in Figure 3.7, some anions bind

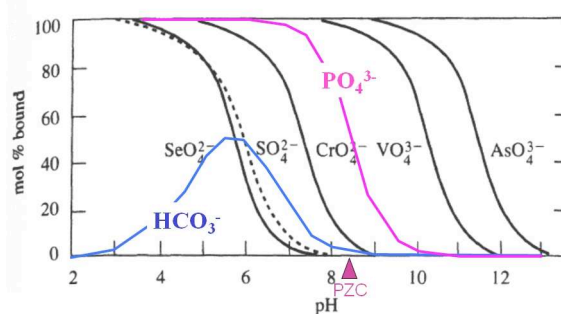


Figure 3.7 Sorption edges of oxyanions on ferrihydrite, showing the percentage bound to the surface as a function of pH.

already at the surface above the PZC, where it is negatively charged. AsO_4^{3-} binds most strongly of all, 50 % of total moles being sorbed at the highest pH of 11.5. Thus, if the anions are all at $1 \mu\text{mol/L}$ concentrations at $\text{pH} = 7$, the surface of ferrihydrite will be

covered predominantly by AsO_4^{3-} . However, if the concentrations of SO_4^{2-} and HCO_3^- would increase 1000-fold to their normal concentrations in groundwater, they will also take a larger share of the surface sites and displace AsO_4^{3-} . This was the major argument to include HCO_3^- in the sorption database (Appelo et al., 2002). Other solutes not included in Figure 3.7, but which are known to be sorbed by iron-oxyhydroxides, are H_4SiO_4 and DOC. For DOC, surface complexation constants are lacking. The concentrations of H_4SiO_4 are equal in surface water and groundwater (average 0.58 mmol/L, DPHE/BGS, 2001), and unless a geochemical process is invoked that alters the concentrations, the effect of H_4SiO_4 is similar to a reduction of the amount of sorption sites.

Sorption of HCO_3^- on ferrihydrite was measured by Zachara et al., 1987, on Goethite by Van Geen et al., 1994 and Villalobos and Leckie, 2000, and displacement of As by NaHCO_3 from Bangladesh sediment was demonstrated by Anawar et al., 2004. Clearly, in batch experiments, carbonate is sorbing on iron oxides, and with increasing concentrations it displaces As. On the other hand, Radu et al. (2005) studied the competition of As and HCO_3^- in column experiments with iron-oxide coated quartz grains, and noted that increasing carbonate concentrations had relatively little effect on As(5) adsorption. This conclusion is important since HCO_3^- could act as a displacer of As from iron oxides that once formed part of the river-load, were sedimented and buried, and still coat the sediment grains that constitute the aquifers from which groundwater is pumped. In the river, the iron oxides sorbed As from water with a low HCO_3^- concentration. In the aquifer, HCO_3^- is much higher. The experiments of Radu et al. are unique and encompass both the low and the high HCO_3^- concentrations found in surface- and groundwater in Bangladesh.

Briefly, Radu et al. coated quartz grains with iron oxide, poured them in a 2.5 cm long column, and percolated the column sequentially with solutions containing (a) both carbonate and As, (d1) only carbonate at the same concentration, (d2) a high carbonate concentration without As, and finally (d3) phosphate, also without As. The iron oxide coating consisted for about 10% of ferrihydrite and 90% more crystalline iron oxides, and the Dzombak and Morel database will only approximately be applicable. Also, the flow velocity of 45000 m/yr in the experiment is extremely high (compared with flow velocities in aquifers), and physical and chemical equilibrium cannot be expected in the experiment. Radu noted indeed that not all As, sorbed during phase (a) was recovered in desorption stages (d1)-(d3). Still, if this experiment can be modeled in acceptable manner, it will inspire confidence in simulations of the behavior of As in Bangladesh aquifers.

The results are shown in Figure 3.8. First note the adsorption stage, in which the As concentration in the effluent from the column crawls slowly up to the concentration in the injected solution with increasing number of injected pore volumes. Three datasets are plotted for solutions with different HCO_3^- concentrations, each in equilibrium with different CO_2 pressures. The CO_2 pressure of $10^{-3.5}$ atm corresponds to the pressure in the earth's air and gives 0.06 mmol HCO_3^- /L at pH 7, $10^{-1.8}$ atm CO_2 pressure gives 3 mmol HCO_3^- /L, and 10^{-1} atm CO_2 (which is about the maximum found in Bangladesh groundwater) yields 19 mmol HCO_3^- /L at pH 7. Figure 3.8 shows that the As concentration in the effluent increases quicker when the CO_2 pressure and the associated HCO_3^- concentration are higher, because then more sorption sites are occupied by carbonate, and fewer are left over for As. Second, follow the desorption steps (d2) and (d3), in which increasing HCO_3^- or PO_4^{3-} concentrations result in desorption peaks of

As. Unmistakably, adsorption and desorption of As are affected by the concentrations of HCO_3^- and PO_4^{3-} .

For the model, it was assumed that sorption on the iron oxide coating could be simulated with the database for ferrihydrite. The 0.391 mol Fe/ L porewater in the experiments had a surface area of 237 m^2/g which translates to 0.15 mol ferrihydrite / L porewater and 0.03 mol sorption sites / L (Ferrihydrite has a surface area of 600 m^2/g). Calculations with these parameters in PHREEQC showed an earlier arrival of the influent As-concentration than observed, and a much steeper rise when equilibrium was assumed. Apparently, equilibrium was not reached in the 18 seconds contact time in the column, and sorption was introduced as a first order kinetic process (the model calculates, for a

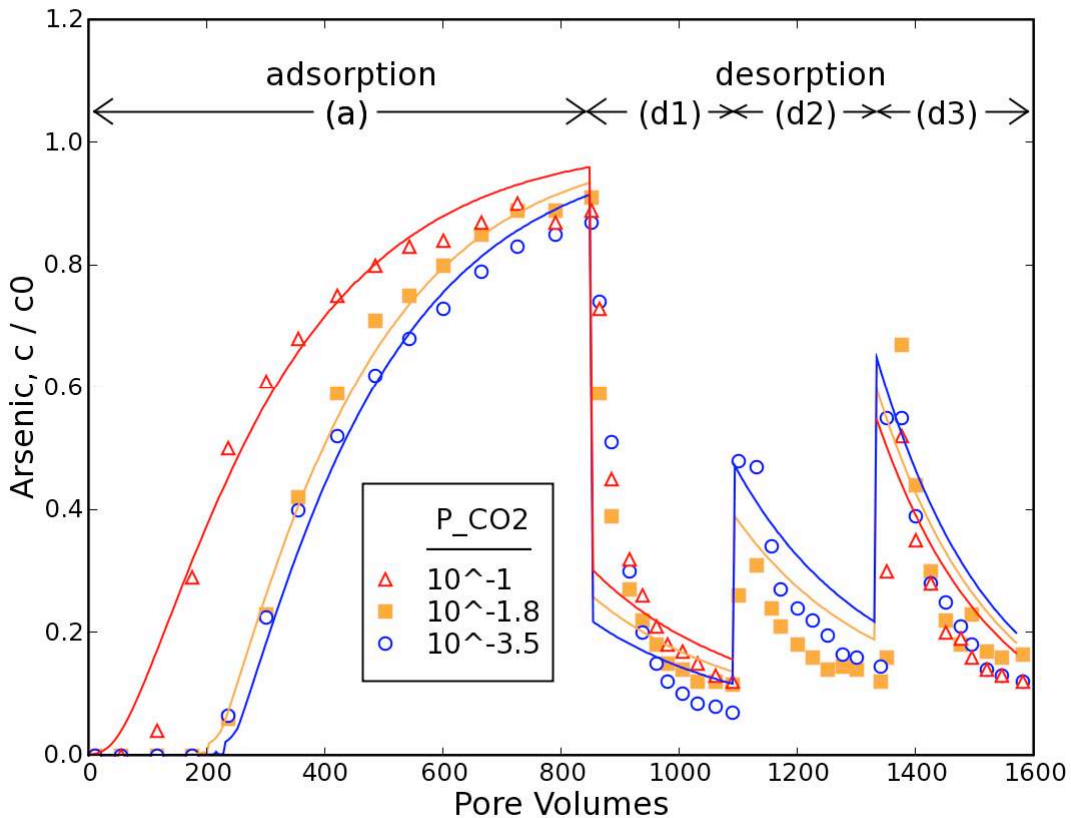


Figure 3.8 Arsenic concentrations in the effluent of column experiments by Radu et al., 2005. The Arsenic concentration is normalized to the concentration in the influent during the adsorption stage ($c_0 = 1000 \mu\text{g As/L}$), and plotted as a function of the pore volumes injected. Desorption is achieved in three steps with (d1) the same carbonate concentration as was used during adsorption, (d2) water in equilibrium with 0.1 atm CO_2 , and (d3) 0.25 mmol $\text{PO}_4^{3-}/\text{L}$. Model lines are calculated with PHREEQC, as explained in the text.

very small amount of ferrihydrite surface, the sorbed concentration at equilibrium, and uses the difference with the amount actually sorbed as the driving force which is multiplied with the timestep and a rate constant; a rate constant of 0.3 ms was used for all three adsorption curves shown in Figure 3.8). The calculated early arrival suggested that sorption sites were too few. But, if the sorption sites were doubled (assuming that a larger part of the Fe-coating had the properties of ferrihydrite), almost all As was

desorbed with the high HCO_3^- concentration in step (d2) and the desorption peak in step (d3) with PO_4^{3-} disappeared altogether. This suggested that carbonate sorption was too strong. The sorption sites were halved again (set to 0.03 mol/L) and the sorption constants for the 2 carbonate species found by Appelo et al. (2002) were reduced by 10. This gives a good fit for the adsorption stages shown in Figure 3.8.

In the experiment, not all As was recovered during desorption. With some trial and error, the desorption rate constant for half of the sites was reduced 100-fold, which produces the desorption curves shown in Figure 3.8. The model might be further improved by adapting the fractions of sorption sites that adsorb and desorb with the same rate, and by introducing a fraction that reacts with full equilibrium. However, it is also possible that the delayed desorption is the result of physical disequilibrium due to the high flow velocity in the column, or of recrystallization of the iron oxide coating and occlusion of sorbed As; it is difficult to determine the correct factor(s) without additional experiments. Nevertheless, the column results show that the release of sorbed As by displacement is sluggish for part of the iron oxide.

Radu's column experiments show that transport of As is very strongly retarded by sorption: about 400 pore volumes are necessary before the As concentration is midway with the intermediate HCO_3^- concentrations. The actual retardation (R , no dimension)

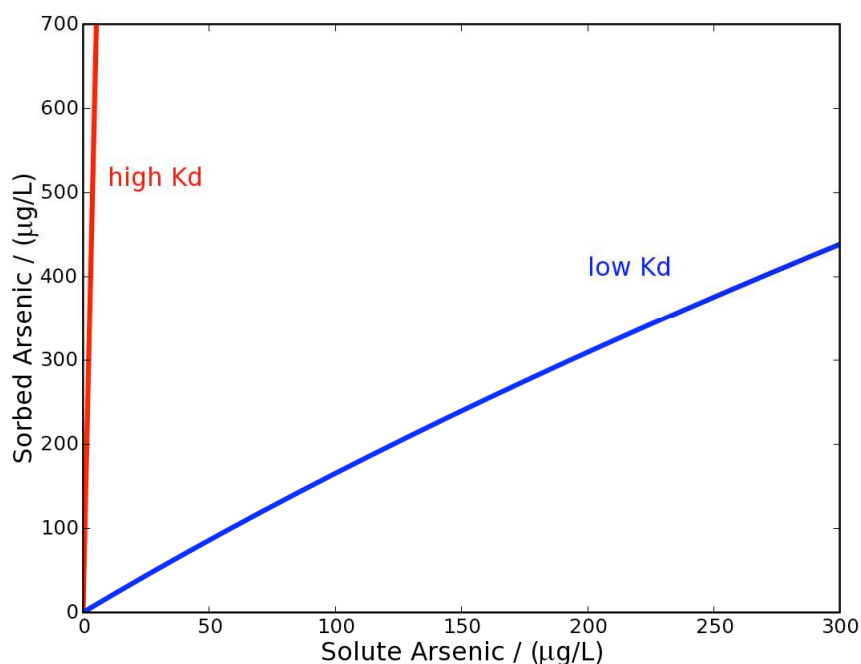


Figure 3.9 Calculated sorption isotherms for As in a Bangladesh aquifer. Curve “high Kd” is for 0.2 g ferrihydrite/L and with reduced surface complexation constants for HCO_3^- . Curve “low Kd” is for 10 times less ferrihydrite and 10 times higher surface complexation constants for HCO_3^- and has about 100 times smaller slope.

and the distribution coefficient ($K_d = R - 1$) are even higher because not all the sorption sites in the column are filled by kinetics. The distribution coefficient is directly related to the amount of ferrihydrite, and it depends in a complicated manner on other solutes

that compete for sorption sites. However, that can be calculated easily with PHREEQC and transferred to the possible conditions in a Bangladesh aquifer. Taking 0.2 g ferrihydrite/kg sediment (Swartz et al., 2004), which translates to 2 mmol sorption sites/L porewater, the surface complexation constants for HCO_3^- found from Radu's experiments, and the groundwater composition given in Appelo and Postma with 500 mg HCO_3^-/L , results in the sorption isotherm shown in Figure 3.9 marked as "high K_d ". The sorption isotherm has a nearly straight slope of 130, and consequently, the retardation $R = 131$. On the other hand, Appelo and Postma used a 10 times smaller amount of ferrihydrite and 10 times higher surface complexation constants for HCO_3^- . This produces the curve marked as "low K_d " in Figure 3.9. This sorption isotherm is slightly curved, and results in a concentration dependent retardation of approximately 1.5. Probably, the actual value in a Bangladesh aquifer will have some intermediate value; column experiments as done by Radu are essential for obtaining the correct value.

Appelo and Postma (2005) showed that the difference of HCO_3^- concentrations in surface water and groundwater could give rise to the observed high As concentrations in Bangladesh groundwater by desorption (*cf.* Figure 3.5: 1 $\mu\text{g As/L}$ and 260 mg HCO_3^- in river water; if the HCO_3^- concentration increases 3 times, As will increase to 700 $\mu\text{g/L}$). However, they used the high surface complexation constants for HCO_3^- . If the constants are 10 times smaller, the concentration of As increases about 3 times less, and does not exceed 150 $\mu\text{g/L}$. On the other hand, if the initial concentration of As is 10 times higher (10 $\mu\text{g/L}$), the concentrations surge up again on desorption.

3.2.4 Summarizing

The three theories are summarized with arguments pro and contra in Table 3.1. From the previous discussions it will have emerged that the various arguments are not unequivocal. Thus, the weak correlations among various elements and As (Figure 3.2) may result from a high retardation of As, which causes the major solutes and As to become separated along flowlines. The lack of comprehensive sorption models is perhaps not so much a counter-argument for theory (C) but rather indicates the difficulties that must be handled when concentrations and transport of trace-elements are modeled in groundwater.

One item, not discussed so far, is why the very high As concentrations of more than 100 $\mu\text{g/L}$ occur so frequently in Bangladesh groundwater, while they are rare in other sedimentary basins in which the sediments have otherwise similar iron-oxyhydroxide and arsenic concentrations. The explanation by the displacement theory is that the high soil temperature and a lush vegetation result in relatively high soil- CO_2 pressures which give, when calcite dissolves, much higher HCO_3^- concentrations in groundwater than found in other locations where the temperature is lower. Another possibility is that indigenous mangrove forests have accumulated As in iron-oxyhydroxides around the tree roots, thus forming localized concentrates which are incorporated in the sediments (Meharg et al., 2006).

Table 3.1 Summary of pro's and contra's of three theories for explaining high As concentrations in Bangladesh groundwater.

	Pro	Contra
A) Iron reduction	<ul style="list-style-type: none"> As and Fe are highly correlated in the sediments experiments show the expected reaction experiments can be modeled dissolved As is mainly present in the reduced form, as As(3) 	<ul style="list-style-type: none"> weak correlation of As and Fe in groundwater model pH is higher than observed reaction seems to stop at a given depth for unknown reasons (<i>cf.</i> Section 3)
B) Pyrite oxidation	<ul style="list-style-type: none"> none in Bangladesh, but enrichment is possible by a combination of oxidation and reduction 	<ul style="list-style-type: none"> pyrite is authigenic, it <i>forms</i> As and SO_4^{2-} are uncorrelated in groundwater As, if released, sorbs on iron-oxyhydroxide
C) Displacement by HCO_3^- and PO_4^{3-}	<ul style="list-style-type: none"> experiments show it models predict it groundwater quality (pH, HCO_3^-) is correct 	<ul style="list-style-type: none"> weak correlations of As with HCO_3^- and PO_4^{3-} sorption processes are much more complicated: the database is incomplete, surface complexation constants for HCO_3^- are uncertain, other surfaces are present, more solutes compete, desorption may be sluggish or inhibited altogether

3.3 A model for Bangladesh groundwater

Figure 3.10 shows As concentrations and tritium from a borehole in a typical profile for Bangladesh (Klump et al., 2006). The As concentration reaches a peak below the depth where tritium is highest, and then decreases to give a “bell-shape” profile. It indicates that water with the high As concentration has infiltrated before 1963, a time when pumping of the aquifers was uncommon. Thus, As at the highest concentration has a natural origin and is released from the sediments (Klump et al., 2006). If theory (A) holds (*cf.* Figure 3.1), the reaction is triggered by decay of organic matter that is associated with the iron oxides (Meharg et al., 2006). Now, the reactivity of organic matter slows down with age, but it does not stop reacting altogether if it is present. Consequently, since iron oxides, organic matter and As are present in the sediments at all depths, the As concentration would increase with depth and increasing water age, and not show the “bell-shape” profile if only reaction (A) takes place. Recently, Lowers et al. (2007) suggested that recrystallization of framboidal pyrite into the massive form of the mineral, which takes up more As, may explain the decreasing As concentrations at larger depths.

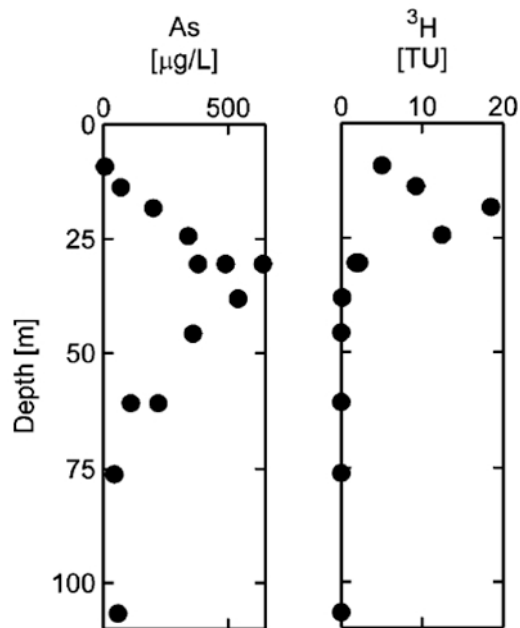


Figure 3.10 Concentrations of As and Tritium with depth in a borehole in Bangladesh (Klump et al., 2006).

The reaction of pyrite in the unsaturated soil (theory B) is generated by water level fluctuations (Harvey et al., 2006; Van Geen et al., 2006), but these are small when the aquifer is not pumped. Moreover, the retardation of As is at least 15, because the concentration of ferrihydrite in the area (Swartz et al., 2004) is 10 times higher than the value used by Appelo and Postma (2005). Thus, even if As were released at the time that Tritium infiltrated, it still cannot not have reached the depth of the concentration-peak. Rather, the high retardation suggests that As is released close to the depth where the high concentrations are sampled.

Displacement by HCO_3^- (theory C) as a source of As is unlikely as well, because the HCO_3^- concentrations decrease in the top of the profile (Swartz et al., 2004) and are not highest at the highest As concentration. One explanation is that iron-oxyhydroxides at the depth of the As-peak were once in equilibrium with water with a high As concentration, and are able to maintain that concentration in water since they act as a large buffer. Concentration changes in the aquifer may result from a combination of changing concentrations of HCO_3^- and other anions (theory C) and reduction of iron-oxyhydroxides (theory A).

The effect of different surface complexation constants of HCO_3^- in theories (A) and (C) was further explored in a model aquifer. A 100 m thick phreatic aquifer of 5000 m length was defined with horizontal and vertical hydraulic conductivities of 20 and 1 m/day, respectively (Klump et al., 2006), porosity of 0.3, horizontal and vertical dispersivities of 10 and 0.1 m, respectively, and diffusion coefficient of $3 \times 10^{-10} \text{ m}^2/\text{s}$. The aquifer is closed along the left, bottom and right sides and discharges to a river (Figure 3.11).

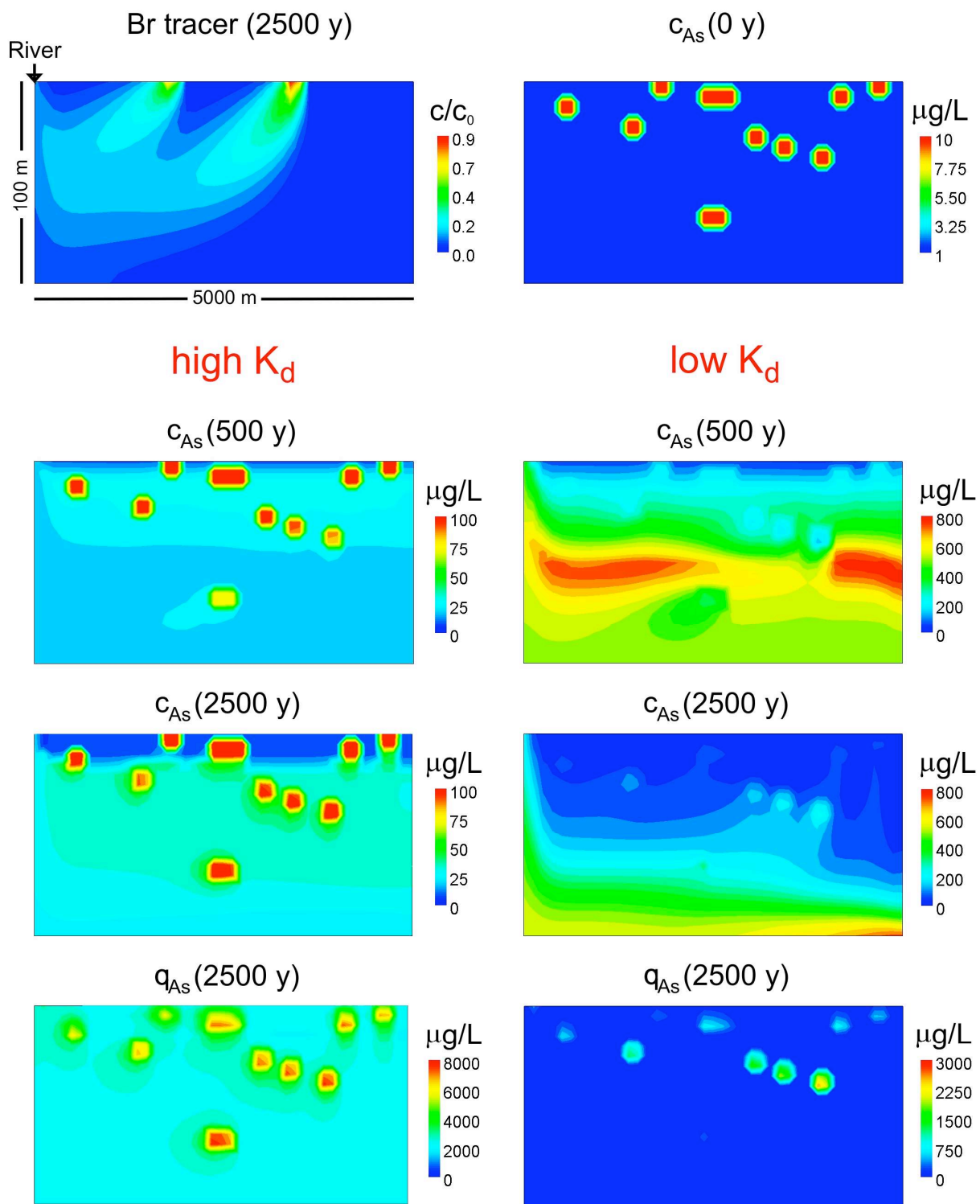


Figure 3.11 Arsenic concentrations in a cross-section of a hypothetical aquifer in Bangladesh. The left top-row panel shows the aquifer outline and the steady-state concentration-pattern of a conservative tracer infiltrating from 2 points at the phreatic surface. The right top-row panel gives the distribution of the initial concentration of As. “Hotspots” indicate the presence of $10 \mu\text{g As/L}$. The other panels illustrate how concentrations develop with time when water with a high HCO_3^- concentration infiltrates and organic Carbon in the aquifer reacts. The two columns demonstrate the effect of different retardations as a result of different surface complexation constants for HCO_3^- . c_{As} and q_{As} indicate solute and sorbed concentrations of As, respectively.

The pristine condition is sediment with calcite, 5 mM kinetic reacting organic carbon and 10 mM ferrihydrite, in equilibrium with Ganges-river water with 1 $\mu\text{g As/L}$. Local concentrates in the cross section have 10 $\mu\text{g As/L}$, 100 mM ferrihydrite and 50 mM organic carbon. Ganges-river water with increased HCO_3^- due to calcite dissolution in the soil (cf. Appelo and Postma) infiltrates at a constant rate of 0.03 m/yr (this gives a hydraulic head of 0.55 m at the divide, in line with the low relief in the area). The surface complexation constants for HCO_3^- from Radu's experiments and the values from Appelo result in panels in the two columns headed by "high K_d " and "low K_d ", respectively. The calculations were done with PHAST (Parkhurst et al., 2004).

The snapshots at 500 years in Figure 3.11 show that the As concentrations increase quickly with the "low K_d " option (they become highest at the HCO_3^- front, where displacement is most effective). With the "high K_d " option, the concentrations only increase to higher than 100 $\mu\text{g/L}$ in the concentrates, and remain below 50 $\mu\text{g/L}$ elsewhere. After 2500 years, As is flushed from the upper part of the aquifer with "low K_d ", but remains high at the bottom. The concentration pattern with "high K_d " shows some leaching from the hotspots, but keeps the same overall form. The differences are corroborated by the sorbed concentrations, which are high, almost unaltered when K_d is high, but very much reduced after 2500 years when K_d is low.

The results indicate that the sediments will be leached free of As in a few thousand years when K_d is low, while about the whole Holocene period is needed when K_d is high. With increasing age of the sediments of the aquifer and amounts of water that have percolated, the As-concentration decreases. Comparison with the published concentration-depth profiles suggests that the "high K_d " option is more applicable to the Bangladesh aquifers (concentrations are highest at 30 - 50 m, decreasing upwards and towards greater depths where sediments are older). The high retardation also explains why such largely different As concentrations can be found in wells at quite close distance; the panels with a low K_d show much more spreading when the HCO_3^- wave has passed. However, the modeled concentrations with the high K_d option are smaller than observed. It may be that the surface complexation constants for HCO_3^- have a somewhat higher value (intermediate between the values used for the calculations), or that higher initial concentrations are present in the concentrates in the field. Column experiments with native sediments should be done and will be helpful for deciding on the dominant factors.

3.4 Conclusions and a perspective

Of the three explanations for the high As-concentrations in Bangladesh groundwater, the reduction and the displacement theories are applicable. Reduction by organic carbon takes place in the aquifers, it explains the presence of reduced As(3), of methane and Fe^{2+} . However, it does not account for the lower As concentrations at greater depths. Displacement of sorbed As by HCO_3^- and possibly other solutes is found in batch and column experiments, and hydrochemical reasoning suggests that it must be operative. However, sorption and desorption is a complicated process that is difficult to model precisely with the now available data. Comparison of model calculations and concentration-depth profiles suggests that local concentrates of As and iron-oxides are the sources of the extremely high As concentrations in groundwater. Such concentrates could form in mangrove forests or in effluent reaches of rivers where iron-oxyhydroxide precipitates and sorbs As. These are the (paleo-)environments that should be avoided

when installing groundwater wells for irrigation and drinking water. However, it is probably difficult to recognize and map these places in the field. On the other hand, influent reaches of rivers are the sites where flushing can be most effective and where As has been desorbed and flushed most with time. An influent reach is characterized by a relatively low HCO_3^- concentration similar to river water (about 240 mg/L). Finally, since As is being washed out with groundwater flow, and since shallow groundwater has been flushed most, it is probable that the shallow wells at a given locality will be the ones with the lowest As-concentrations.

3.5 Acknowledgement

Comments of David Kinniburgh on a draft version are gratefully acknowledged.

3.6 References

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4 The risks of arsenic contaminated irrigation water to food safety and crop production¹

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¹ Modified from Heikens (2006) Arsenic contamination of irrigation water, soil and crops in Bangladesh: Risk implications for sustainable agriculture and food safety in Asia. FAO-RAP Publication 2006/20.

<http://www.fao.org/docrep/009/ag105e/ag105e00.htm>

Abstract

During the last few years, concern is growing about the possible risks of irrigating with arsenic-contaminated groundwater resources. This review paper will provide an overview of arsenic behaviour in food and agriculture, and evaluates available knowledge of the effects of irrigating with arsenic-contaminated water on crop production and food safety in Asia. The focus is on Bangladesh, where most studies on arsenic contaminated irrigation water have been carried out. It is also the country with the most serious arsenic contamination crisis in the drinking water sector. Specific attention is given to rice because it is the most important staple crop in Asia, and it is one of the crops most sensitive to arsenic contamination.

This paper will conclude that As in irrigation water can result in soil pollution that in turn affects food safety and crop production. A number of reports have found evidence that irrigating with As-contaminated water, causes accumulation of As in the soil and that this is reflected in higher levels of As in the edible parts of crops. Major gaps in our knowledge still need to be filled and these currently hamper a comprehensive risk assessment and the development of mitigation options.

4.1 Background

Over the last three decades, millions of shallow tube wells (STWs) have been installed throughout Asia. This has significantly contributed to the reduction of diarrhoea and has saved many lives, and access to groundwater resources has been a major contributor to the green revolution in Asia.

Since the 1980s however, evidence has gradually unfolded that As is naturally present in elevated levels in part of tapped groundwater resources. At present, twelve countries in the region have reported high levels of As in part of their groundwater resources: Afghanistan, Bangladesh, Cambodia, China, India, Lao PDR, Mongolia, Myanmar, Nepal, Pakistan, Thailand and Viet Nam.

To date, only limited attention has been paid to the risks of using contaminated groundwater for irrigation. Irrigation water with high levels of As may result food chain contamination and loss of crop yield. Long-term use of As-contaminated irrigation water could result in As accumulation in the soil. If absorbed by the crops, this may add substantially to the dietary As intake, thus posing additional human health risks. Over time, As accumulation in the soil could reach soil concentrations toxic to crops, thus reducing yields (Figure 4.1).

Reliable and representative data are therefore needed to assess and manage the risks of As- contaminated irrigation water. With millions of irrigation STWs tapping water from the same As- contaminated aquifer as the STWs for drinking water, the extent of possible risks can be substantial.

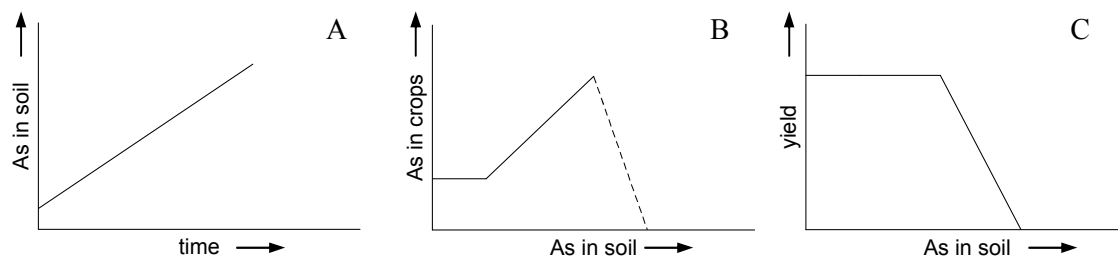


Figure 4.1 The possible risks of using As-contaminated irrigation water over time.

Note: A: input of As via irrigation water can lead to accumulation of As in the soil over time. B: depending on bioavailability, uptake and transport within the plants, higher soil concentrations may be reflected in higher concentrations in crops. The dotted line indicates that at a certain level the plant growth becomes severely inhibited and As concentrations in the plants are then no longer relevant. C: with an increase in soil concentration, yields are expected to stay more or less constant until a threshold level is reached, after which yield will decline.

4.2 Arsenic in agriculture

4.2.1 Soil

Low levels of As are naturally present in the soil. The background levels are around 5 mg/kg worldwide with substantial variation depending on the origin of the soil (Mandal and Suzuki, 2002). The behaviour of As is distinctly different under flooded (anaerobic) and non-flooded (aerobic) soil conditions, with flooded conditions being likely the most hazardous in terms of uptake by plants and toxicity. Taking into consideration that rice is the staple crop in Asia, that its cultivation largely takes place under flooded conditions, and that its high demand for irrigation water, often from groundwater resources, understanding the behaviour of As under flooded soil conditions is of particular importance.

As exists in the environment in various organic and inorganic forms (species). The most important inorganic species are arsenate (AsV) and arsenite (AsIII). Monomethylarsenic acid (MMA) and dimethylarsenic acid (DMA) are the most common organic species in the soil, but their natural presence is low compared to inorganic As (Abedin et al., 2002; Fitz and Wenzel, 2002).

Speciation of inorganic As in the soil is largely controlled by reduction and oxidation processes (redox). Under aerobic (oxidizing) conditions AsV predominates, whereas AsIII predominates under anaerobic (reducing) conditions. Microbial activity can influence As speciation via various mechanisms such as redox reactions with Fe and As

and via (de)methylation of As species (Fitz and Wenzel, 2002; Mahimairaja et al., 2005; Takahashi et al., 2004).

AsV and AsIII adsorb mainly to iron hydroxides (FeOOH) present in the soil and AsV is bound strongest. The behaviour of FeOOH is highly dependent on redox conditions, making Fe redox chemistry the most important factor in regulating As behaviour. Under anaerobic conditions, FeOOH readily dissolves and As is released into the soil solution, where As will be present mainly as AsIII. Under aerobic conditions FeOOH is relatively insoluble and serves as a sink for As. Fe and As behaviour is therefore dynamic and closely related in lowland paddy fields. FeOOH is mainly present in the clay size soil fraction (< 2 µm) and clayey soils therefore generally have a higher As content compared to more sandy soils (Fitz and Wenzel, 2002; Mahimairaja et al., 2005; Masscheleyn et al., 1991; Takahashi et al., 2004).

The As concentrations in the irrigation water usually differ from those in the soil water. For example, Takahashi et al. (2004) reported that As concentrations in irrigation water were higher compared to the soil water concentrations during the non-flooded period because of sorption to FeOOH. Under flooded conditions, soil water concentrations increased because of remobilization and, important to note, became higher than the irrigation water concentrations. Under flooded conditions, plants can therefore be exposed to much higher concentrations in the soil water than would be expected based on the concentrations in the applied irrigation water.

Phosphate (PO₄) behaves very much like AsV, but not like AsIII. Both PO₄ and AsV compete for the same sorption sites on FeOOH and for uptake by plants, making PO₄ an important factor in the behaviour of As in aerobic soils. AsV adsorption decreases with increasing pH, in particular above pH 8.5, whereas the opposite occurs for AsIII. The extent to which pH influences As sorption differs between soils. As may be lost from the soil via the formation of volatile As components. The extent to which this process is relevant to flooded paddy fields with their distinct soil conditions is however still unknown (Fitz and Wenzel, 2002; Masscheleyn et al., 1991; Mahimairaja et al., 2005; Williams et al., 2003;).

4.2.2 Crops

Conditions in the rhizosphere (the micro-environment around the roots) may deviate substantially from the bulk soil. As summarized by Fitz and Wenzel (2002), plants will influence the pore water composition by uptake and excretion of substances. Micro-organisms in the rhizosphere will also influence its composition. Because Fe and As behaviours in the soil are closely related to each other, it can be expected that plant processes related to Fe uptake may also influence As bioavailability and uptake. The same is true for PO₄.

When a paddy field is flooded, the rhizosphere can still be aerobic. The main reason is that rice plants can transport oxygen from the leaves to the roots. The oxidized conditions can result in the precipitation of FeOOH around the roots, also known as Fe-plaque. Fe-plaque has been reported frequently on roots of wetland plants including rice. It may influence As speciation, bioavailability and uptake and Fe reducing and oxidizing bacteria are likely to play a major role (Fitz and Wenzel, 2002; Meharg, 2004; Weiss et al., 2003; Weiss et al., 2004).

AsIII and AsV are taken up by different mechanisms in the roots. AsV is taken up via the high affinity phosphate uptake system. PO₄ additions have therefore been suggested to reduce uptake because of competition between PO₄ and AsV for uptake. In the field however, competition both for sorption to the soil and uptake by the plants takes place. Experiments with PO₄ additions to As-contaminated soils to minimize As uptake by plants particularly under non-flooded conditions have given conflicting results (Abedin et al., 2002; Meharg, 2004; Fitz and Wenzel, 2002).

AsIII is taken up by so-called water channels (aquaporins) in the roots (Meharg and Jardine, 2003). Laboratory experiments have shown that Boro (dry season) rice cultivars take up less AsIII and AsV than Aman (rainy season) rice cultivars. However, this does not imply that Boro rice will accumulate less As than Aman rice under field conditions, because Boro rice is irrigated with As-rich groundwater whereas Aman rice is rainfed. Translocation of inorganic As from the roots to the above ground parts is generally limited. In rice plants, concentrations can be ranked as follows: root > straw > husk > grain.

4.2.3 As toxicity to plants

Although a substantial number of papers have been published on As toxicity to crops, results cannot be translated to the field. It is most likely that As toxicity to crops is related to As soil water concentrations. Based on various laboratory experiments, toxic effects might be expected if the pore water concentrations would exceed 1 mg/l.

Although irrigation water concentrations rarely reach that level, pore water concentrations have been reported up to 3 mg/l (Loeppert et al., 2005). With the elevated As levels found in various paddy fields in Bangladesh, it should be possible to study phytotoxicity at the field level. Results from such studies would by definition be representative of the field situation, but a thorough understanding of the critical parameters involved would still be necessary in order to extrapolate the data to locations with other environmental conditions.

4.3 Arsenic in food and agriculture in Bangladesh

4.3.1 Irrigation water

Bangladesh is mainly known for periods of flooding and not so much for drought. However, a lack of water during the dry season and spells of drought at the beginning and end of the rainy season are a threat to agricultural production in Bangladesh. It is also feared that more areas will become drought prone as a result of climate change.

During the last three decades, many hectares (ha) of land have been brought under Boro rice cultivation in the dry season by using STWs for irrigation. This is one of the main reasons that the country is self-sufficient in rice production. Boro rice receives the most irrigation water of all crops, with an estimated amount of 1000 mm/cycle. The total area under irrigation is 4 million ha and 75% is covered by groundwater resources: 2.4 million ha via 924 000 STWs and 0.6 million ha via 23 000 deep tube wells (DTWs). In the dry season, 3.5 million ha is used for Boro rice, 0.23 million ha for wheat and 0.27 million ha for other crops. Classifying the divisions according to the area under irrigation gives the following ranking: Rajshahi (39%) > Dhaka (27%) > Chittagong (13%) and Khulna (12%) > Sylhet (7%) and Barisal (2%). The area under Boro rice production follows the same pattern. Wheat and other crops follow a somewhat different

pattern with Rajshahi being the most important area followed by Dhaka and Khulna (BADC, 2004).

In terms of drinking water, the As-affected areas are mainly located in the south and southwest, i.e. Khulna, Dhaka and north Chittagong. With an estimated 20 % of the drinking water STWs having As concentrations above the Bangladesh drinking water standard of 0.050 mg/l, it can be expected that a substantial percentage of irrigation STWs also have high As levels. The exact percentage is unknown because the spatial distribution of irrigation STWs is not similar to that of drinking water STWs. In groundwater, only AsIII and AsV have been found and levels are within the same order of magnitude.

Based on available data on drinking water STWs, it has been estimated that 900,000 – 1,360,000 kg As per year is brought onto the arable land via groundwater extraction for irrigation (Ali, 2003). The deposition of As on the arable land is high, especially in southwest and south Bangladesh. The northwestern part of the country, which has relatively low As concentrations in the shallow aquifer but has a very high intensity of using irrigation STWs, is also extracting a considerable amount of As from the aquifer. Other sources like P-fertilizer and manure are likely to be minor sources of As, but this needs confirmation.

In a case study in West Bengal (India), data on As in irrigation water and the paddy soil profile indicated a yearly As input of 1.1 mg/kg to the top soil (Norra et al., 2005). Duxbury and Zavala (2005) estimated that ten years of irrigating paddy fields with As-contaminated water would add 5–10 mg/kg soil to 41% of their 456 study sites. Based on existing national data for As in STWs used for drinking water and the distribution of Boro rice production, Ross et al. (2005) estimated that 76% of the Boro rice is grown in areas where STWs usually contain less than 0.050 mg/l, 17% in areas with 0.050–0.100 mg/l, and 7% in areas with more than 0.100 mg/l.

4.3.2 Soil and crops

Meharg and Rahman (2003) carried out a preliminary survey of As in rice and soil from Bangladesh. The highest measured soil concentration was 46 mg/kg, whereas less than 10 mg/kg was found in areas with low As in irrigation water. The western part of Bangladesh seems to have the highest soil concentrations (> 30 mg/kg), followed by the central belt, which is in agreement with groundwater concentrations. At various locations with high As levels in groundwater, low concentrations were found in the soil. However, they did find a correlation between soil concentrations and irrigation water concentrations when the age of the water-well is taken into account. A positive correlation between As concentrations in rice and soil was also found. Islam et al. (2000) reported total As concentrations of 5–33 mg/kg with an average of 17 mg/kg for some soil samples from Nawabgonj, Rajarampur, Jessore, Jhenidah and Comilla.

Williams et al. (2006) did an extensive sampling of rice throughout Bangladesh and found a positive correlation between As in the groundwater and rice. This correlation was stronger for Boro rice than for Aman rice. Highest As concentrations in rice were all from districts in the southwest, namely Faridpur > Satkhira > Chuadanga > Meherpur.

Miah et al. (2005) also found that the soils in the west and southwest part of Bangladesh contained the highest As concentrations. In these parts, irrigated soils had higher levels of As compared to adjacent non-irrigated soils. In the irrigated soils, the first 0–15 cm had the highest levels of As. In other parts of the country, irrigated and non-irrigated soils did not differ in As concentrations. The differences in soil concentrations were, however, not reflected by As levels in the rice plants.

Islam et al. (2005) studied As levels in water, soil and crops at 456 locations in five upazilas. The average As concentration in the soil was 12.3 (ranging from 0.3 to 49 mg/kg) and the thanas were classified according to soil concentrations: Faridpur > Tala > Brahmanbaria > Paba > Senbag. Of all soil samples, 53 % contained less than 10 mg/kg, 26 % contained between 10.1 and 20 mg/kg, and 18 % contained more than 20 mg/kg. Concentrations both between and within thanas were highly variable. The same was observed at the command area and paddy field level. In some cases this correlated with the distance to the tubewell used, in other cases the variation seemed to be random or related to micro-elevation. They also found a high seasonal variation in As soil concentrations. At the end of the Boro (dry) season the soil concentration had increased sharply when irrigated with As-rich water. Most of it was again removed after the Aman season, i.e. after flooding. There are various explanations for this phenomenon: 1) As desorbs to the standing water and is then removed laterally; 2) the top layer may be eroded and run off during heavy rainfall; 3) volatilization of As during prolonged periods of flooding; and 4) leaching of standing water desorbing and transporting As from the topsoil to deeper layers. These different processes have not been quantified yet.

In agreement with Takahashi et al. (2004), As concentrations in soil water from flooded paddy fields increased with the duration of flooding reaching levels above 3 mg/l (Loeppert et al., 2005). During both Boro and Aman seasons, the soil water concentrations thus largely exceeded the irrigation water concentrations. This is important to realize, particularly for Aman rice, which is rainfed and contains As below the detection limit. It has been hypothesized that As uptake and toxicity to rice is much better correlated with As in the soil water than with As in irrigation water or total As in the soil.

Two studies from West Bengal have provided strong evidence for accumulation of As in topsoil because of irrigation with contaminated groundwater (Norra et al., 2005; Roychowdhury et al., 2002a). Roychowdhury et al. (2002a) reported for Domkal block that fallow lands contained 5.31 mg/kg, whereas adjacent lands irrigated with 0.082 mg/l and 0.17 mg/l contained 11.5 and 28.0 mg/kg, respectively. The calculated input of As was approximately 1.6–16.8 kg/ha/yr. The good correlations between concentrations in irrigation water and soils clearly showed the effect of the contaminated irrigation water on As concentrations in the soil. On a smaller scale, measurements of As in paddy fields with increasing distance from the tubewells also gave a good correlation, again showing that soil concentrations increased because of the application of contaminated water. The same was reported by Hossain (2005) for a number of locations in Faridpur, Bangladesh.

Norra et al. (2005) collected water, soil and plant samples from three fields in Kaliachack I block: one paddy field and one adjacent wheat field both irrigated with water containing 0.5–0.8 mg/l, and one reference paddy field not contaminated with As. The upper topsoil in the contaminated paddy field contained 38 mg/kg, the less

intensively irrigated wheat field grown with wheat contained 18 mg/kg, whereas a reference paddy field contained 7 mg/kg. The soil profiles of the contaminated paddy field and wheat field clearly showed a decreasing As level with increasing depth. Although, to a lesser extent, it is important to note that As did not only build up in the paddy field but also in the wheat field.

Hardly any work has been done on the potential risk of As in irrigation water to crop production. In the 2006 Boro season, a small but detailed pilot study was conducted in which phytotoxicity to rice was studied at the field level in a paddy field in Faridpur contaminated by twenty years of irrigation. Preliminary data indicate a clear negative correlation between As in the soil water and plant growth (G. Panaullah, personal communication, 2006). These results emphasize the need to further investigate the possible risks of As in irrigation water to crop production.

4.3.3 Arsenic in foods

It is generally recognized that inorganic As is far more toxic to humans than organic As. A well-balanced evaluation of As in foods should thus be based on inorganic As and not on total As to avoid an overestimation of the human health risks. However, the methodology to assess As speciation in plant and animal tissue is complicated. To date, the methodology is not yet standardized and certified reference materials for inorganic As are not available.

Only limited data on As speciation in rice, vegetables and spices from Bangladesh have been published. Williams et al. (2005) collected 15 samples of various rice cultivars from the wholesale market in Dhaka and analysed for total and inorganic As. The average total As concentration was 0.13 ± 0.02 mg/kg (ranging from 0.03 to 0.30 mg/kg). The average percentage of inorganic As was 80 ± 3 %. It also implies that three out of 15 samples exceeded the Chinese food safety standard of 0.15 mg/kg for inorganic As in rice.

Williams et al. (2006) analysed another 21 rice samples from Bangladesh (seven different cultivars, both Boro and Aman) for As speciation of which approximately half of the samples exceeded the Chinese food safety standard. The observed As speciation pattern was similar to Williams et al. (2005). Combining the data from Williams et al. (2005) and Williams et al. (2006) shows a strong positive correlation between total As and inorganic As in rice from Bangladesh, and indicates that 80 % of inorganic As in rice may be representative of use within the country (Figure 4.2). They also analyzed a number of vegetables and spices, and results indicated a presence of 100% inorganic As.

With only two studies published on inorganic As in rice and vegetables from Bangladesh, some data on total As in foods from Bangladesh and its neighbour West Bengal, India are presented here as well. Williams et al. (2006) collected a large number of samples (rice, vegetables, pulses and spices) throughout the country. For rice, the results clearly showed that the highest levels of As were found in the southwestern part of the country, and there was a positive relationship between As levels in rice and As levels in groundwater. Concentrations in Boro rice were in the range of 0.04 to 0.91 mg/kg, whereas Aman rice contained < 0.04 to 0.92 mg/kg. Assuming that 80 % of the total As was in the inorganic form, a substantial number of samples exceeded the Chinese food safety standard. Other data on total As in rice from Bangladesh indicate levels between 0.01 and 2 mg/kg, with most data around 0.2 mg/kg.

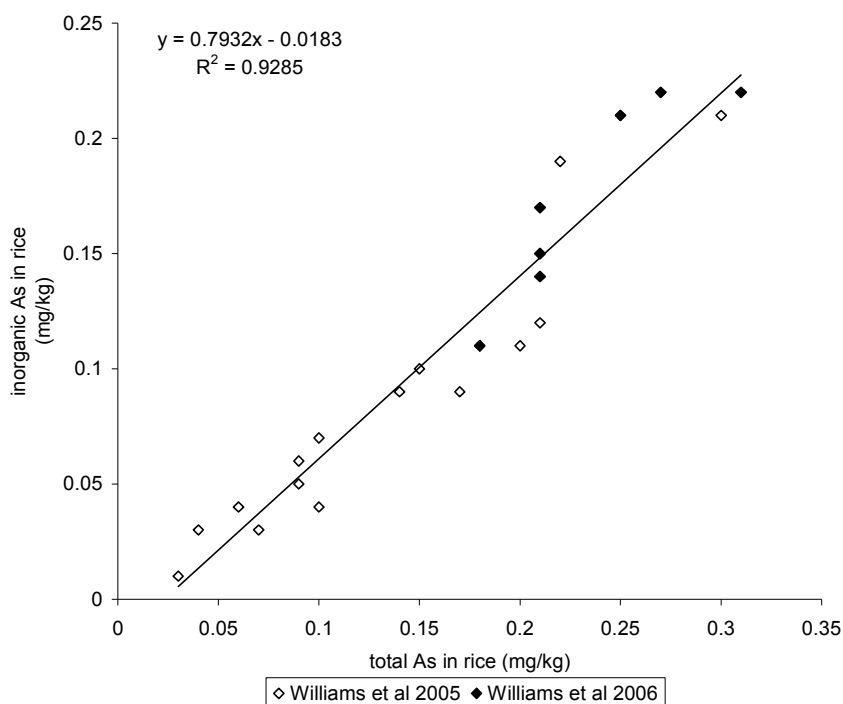


Figure 4.2 The correlation between total As and inorganic As in rice from Bangladesh

Williams et al. (2006) found that most of the non-rice samples contained between 0.1 and 0.8 mg/kg dry weight (dw), which is around 0.02 – 0.16 mg/kg ww. It indicates that a number of samples exceed the Chinese food safety standard 0.05 mg/kg ww for vegetables. Three other papers were found on total As in vegetables from Bangladesh and West Bengal with most samples having less than 0.5 mg/kg dw, (Alam et al. 2003, Das et al. 2004, Roychowdhury et al. 2002b). Most samples were collected from a few locations known for high As in the shallow aquifer. Concentrations in vegetables, fruits, spices, and fresh water fish ranged from less than 0.04 mg/kg dw to 3.99 mg/kg dw, with most samples having less than 0.5 mg/kg dw.

4.3.4 Food and water consumption in Bangladesh

Only one in-depth study reported food consumption on a gram/capita/day basis in Bangladesh (Hels et al., 2003). The average consumption reported from two villages, Falshatia (Manikganj) and Jorbaria (Mymensingh) was rice 450 g/day, vegetables 200 g/day, roots/tubers 60 g/day, fish 40 g/day, and meat 30 g/day. Drinking water consumption in Bangladesh is around 3 l/day and an additional 1 l/day through food preparation (Watanabe et al. (2004; Mandal et al.1998).

4.3.5 Dietary exposure to arsenic

Williams et al. (2006) concluded that rice is the predominant source of inorganic As from foods. This was based on a daily consumption of 500 g rice, 130 g vegetables, 12 g pulses and 5 g spices and data on inorganic As and total As in a range of food items from Bangladesh. Most of the Boro rice samples collected contributed at least 50 % to the provisional maximum tolerable daily intake (PMTDI) for inorganic As (0.126 mg/day for a 60 kg person). Food items other than rice only make a minor contribution. Even for a worst case scenario (consumption of 130 g/day of a vegetable with the highest As level on a wet weight basis, which in this study is potato with 0.23 mg/kg ww), the contribution is only 0.03 mg/day (25 % to the PMTDI). In a number of cases,

arum stolon has been receiving particular attention because of the reportedly high levels of As. The data show that high levels of As in arum stolon (in this study 1.93 mg/kg dw, i.e. 0.193 mg/kg wet weight (ww)) would only contribute 0.025 mg/day. This emphasizes the need to consider As concentrations in food items from the perspective of the overall dietary intake of inorganic As. Also the important nutritional value of vegetables like arum should be taken into account before conclusions are drawn on the risks of As in such food items.

Roychowdhury et al. (2002b) estimated the daily intake of total As via water and food for two locations in West Bengal. The intake via foods was approximately 180 and 97 µg/day for adults and children (10 years old) respectively. Adults and children were exposed to approximately 400 and 200 µg/day via drinking water. Drinking water counted for ~70 % of the exposure whereas rice contributed ~30 %. Watanabe et al. (2004) estimated that the daily intake of total As by adults was approximately 600 µg/day (male: 674 µg/day, female: 515 µg/day) with 70 % via drinking water and 10 % via rice.

Duxbury et al. (2003) analysed 150 rice samples from Bangladesh. Assuming a rice consumption of 400 g/day with 0.250 mg/kg and a water intake of 4 l/day with 0.050 mg/l As (drinking water standard Bangladesh), the total daily intake would be 0.3 mg/day. Rice would contribute 33 %. Fourteen % of their rice samples contained \geq 0.250. Meharg and Rahman (2003) assumed a rice consumption of 420 g/day with 0.5 mg/kg and a water intake of 2 l/day (the WHO default value) with 0.1 mg/l. The calculated total daily intake was 0.41 mg/day and rice contributed 50 %. However, taking into account the climate in Bangladesh and the high consumption of rice, 2 l/day is likely to be an underestimation (Watanabe et al., 2004).

When evaluating risks to human health associated with As in foods, other sources of exposure such as drinking water have to be taken into account as well. The WHO guideline value is 0.010 mg/l and the Bangladesh drinking water standard is 0.050 mg/l (Duxbury and Zavala, 2005; Williams et al., 2005). Assuming a body weight of 60 kg, the PMTDI is 0.126 mg/day. A water consumption of 3 l/day with 0.050 mg/l would already exceed the PMTDI, regardless the levels of As in foods. This suggests that the PMTDI and the Bangladesh drinking water standard need to be evaluated so that a proper assessment of As in foods can be made.

4.3.6 Agricultural management options

Even though the risks to food safety and, in particular, to crop production are not yet fully understood, it can be stated that the input of contaminants to the environment should be avoided or, at least, minimized, and that natural resources such as groundwater should be used in a sustainable way. From this perspective, there are various topics that can be explored to address management options. For example, i) irrigation water use can be reduced in rice cultivation, which will reduce As input and extraction of groundwater resources, ii) alternative, less water demanding cropping patterns can be introduced, iii) Select/breed rice cultivars that are tolerant to As and have a limited uptake of As. Phytoremediation has been suggested as a means to remove As from soil. There are two main reasons why this is an unlikely option. First, there may be no need to remove As actively from the soil. Second, phytoremediation is a very slow process and thus not a practical approach for agriculture.

4.4 Conclusions and recommendations

This paper has shown that As in irrigation water can result soil pollution and food chain contamination. The continuous contamination of soil is a growing threat to crop production itself, and thus to sustainable agriculture, because As in soils will become toxic to plants and other organisms at a certain level. This would result in reduced crop yields and thus pose a risk to incomes and the nutritional status of rural farming communities. To date, the risks of using As-contaminated groundwater resources for irrigation have not received sufficient attention. An overview of the fact and gaps in our knowledge that need to be filled is given below. It should be remembered that a number of points are based on results from Bangladesh only. These need to be validated in other countries, taking into account differences in agricultural practices, environmental conditions, food habits and other factors.

The facts: Twelve countries in the region have reported high levels of As in parts of their groundwater resources. All these countries use groundwater resources for irrigation, but the extent differs substantially between and within countries. Depending on local conditions, irrigation with As-contaminated water can result soil pollution which can be reflected in concentrations in crops, including the edible parts. Rice cultivars and other crops can differ substantially in As accumulation and in the percentage of inorganic As. The limited number of rice samples analysed for inorganic As indicates that various rice cultivars from Bangladesh, contain a high percentage of inorganic As. A substantial number of rice samples from Bangladesh contained As levels exceeding the Chinese food safety standard for inorganic As. Rice can contribute significantly to the total daily intake of inorganic As through water and foods in Bangladesh because of the high rice consumption and the relatively high levels of inorganic As in rice. Although some vegetables have been reported to have high levels of As, their contribution to the total daily intake is low because of their low consumption rate. In addition, many vegetables are only available during specific seasons.

The needs: With the continuation of uncontrolled use of contaminated water in agriculture, it is expected that the risks will increase over time. In the long run, this may offset the ongoing efforts in the drinking water sector to reduce the adverse impacts of As. Rice production systems are of particular concern because flooded soil conditions are most favourable for As uptake and rice is the most important staple food in the region. Other crops under irrigation with contaminated water need to be addressed as well as there are great uncertainties about the As mass balance under different environmental conditions.

It is important to note that once arable soils are polluted to an unacceptable level, rehabilitation is unlikely to be cost effective. Preference should thus be given to prevention and control over rehabilitation. Most importantly at this stage, the scale of the problem needs to be quantified. This should be based on scientifically justified methodologies resulting in reliable results, conclusions and recommendations.

The extent of land degradation caused by As in irrigation water needs to be quantified and weighted against other factors causing land degradation. This will require in-depth understanding of As levels in irrigation water, soil and crops, the behaviour of As in soil, uptake and toxicity in crops in the relevant agro-ecosystems, the influence of

agricultural practices including irrigation water management on As, and the establishment of standards for As in irrigation water, soil and crops. This information would result in an evaluation of the current situation and would serve as a baseline for the future.

It is generally accepted that drinking water is the main source of exposure, but foods could be an important and possibly growing source as well. To determine the risk to human health posed by As in foods a reliable and representative database on inorganic As in foods is a necessary first step. This database can then be used with data on food consumption to estimate the dietary intake of As through foods and the resulting exposure levels can be compared to health guidelines to assess the risks. Considering the high prevalence of nutrient deficiency in Asia, it will be of great importance to take the nutritional value of foods into consideration when evaluating the risks of As in foods.

4.5 Acknowledgements

Tony Appelo is thanked for reviewing the draft of this paper. Andy Meharg, Golam Panaullah, Sasha Koo-Oshima, Zhijun Chen and Thierry Facon are acknowledged for their valuable inputs to the original FAORAP publication.

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5 Health effects of inorganic arsenic

Authors: Anna-Lena Lindberg and Marie Vahter

Abstract

Exposure to inorganic arsenic (iAs), a potent human carcinogen and toxicant, occurs mainly via drinking water and industrial emissions. Long-term exposure to arsenic has been associated with cancer in skin, lungs, urinary bladder, kidney and liver, as well as various non-cancer effects. Recent studies also indicate adverse effects of arsenic exposure on reproduction and child development. There is a wide variation in susceptibility to arsenic induced health effects, which, in part, may be due to the large inter-individual variation in arsenic metabolism and nutritional status. Inorganic arsenic is metabolized in humans and most mammals via reduction and methylation reactions, using one-carbon metabolism with S-adenosylmethionine (SAM) as methyl donor. Arsenic is excreted in urine mainly as dimethylarsinate (DMA) and methylarsonate (MA) as well as some unmethylated iAs (As(V) and As(III)). The exposure level is often the strongest influencing factor on arsenic metabolism, due to inhibition of the methyltransferases involved in arsenic methylation, especially the second methylation step, at elevated exposure levels. Demographic factors such as age and gender, as well as genetic polymorphisms have also been found to influence the metabolism of arsenic. Assessment of exposure to inorganic arsenic is generally based on measurements of the concentrations of arsenic metabolites in urine (inorganic arsenic, MA and DMA) or total arsenic concentration in blood (mixture of arsenic compounds) or hair (mainly inorganic arsenic). Concentrations of arsenic metabolites in urine are preferentially measured by high performance liquid chromatography coupled to either inductively coupled plasma mass spectrometry or atomic fluorescence spectrometry via hydride generation (HPLC-HG-ICPMS and HPLC-HG-AFS).

Key words: arsenic, toxicity, exposure, metabolism, health

5.1 Occurrence of arsenic in the environment

Arsenic is a ubiquitous allotropic trace element and the 52nd most common element in the earth's crust (Ahmed 2003). It occurs naturally in many mineral ores and is the main constituent of more than 200 mineral species. Arsenopyrite, realgar and orpiment are minerals commonly found in ore zones (Selinus, Alloway et al. 2005). Arsenopyrites may under certain conditions release arsenic into the groundwater. Arsenite (As(III)) and arsenate (As(V)) are the two most important forms in water. Elevated concentrations of arsenic in groundwater used as drinking water have been found all over the world, e.g. Taiwan (Chen, Hsu et al. 2005), India (Rahman, Sengupta et al. 2005), Bangladesh (Rahman, Vahter et al. 2006), China (Pi, Yamauchi et al. 2002), Chile (Caceres, Pino et al. 2005), Mexico (Meza, Kopplin et al. 2004), Argentina (Vahter, Concha et al. 1995) and Romania (Le, Lu et al. 2000). In Bangladesh alone over 50 million people drink water containing more arsenic than the World Health Organization (WHO) guideline of 10 µg/L (WHO 2003; Chakraborti, Sengupta et al. 2004).

Surface and sea water are generally very low in arsenic, typically 1-2 µg/L (WHO 2001). Seafood and algae may contain mg/kg concentrations of arsenic, mainly in the form of organic arsenicals, such as arsenobetaine, arsenocholine and arsenosugars

(Francesconi and Kuehnelt 2002), which have low toxicity and are rapidly excreted in the urine (Vahter, Marafante et al. 1983; Marafante, Vahter et al. 1984; Sabbioni, Fischbach et al. 1991).

The main anthropogenic source of arsenic in the environment is the metal production (mining and smelting) industry. Agricultural use of arsenic containing pesticides, wood preservation and the burning of fossil fuels constitute other important anthropogenic sources (WHO 2001).

5.2 Use of arsenic

Arsenic is one of the most notorious poisons of all times. The presence of arsenic (in form of As_2O_3) in lethal doses in food, water, or air are not noticeable to human senses of sight, smell and taste, which makes it a perfect homicidal and suicidal agent. For example, the death of the French emperor Napoleon Bonaparte in 1821 is believed to be due to arsenic poisoning, as high arsenic concentrations have been found in hair samples taken from his head (Kintz, Ginet et al. 2006), but this is still a controversial issue (Keynes 2004). Because of As_2O_3 being taste-, odor- and colorless a lot of accidental arsenic poisonings have occurred throughout history. Arsenic poisoning was a problem in the Victorian-era England, mainly because arsenic was used as dyes and pigments in several consumer products, including wallpaper, toys, food wrappers and clothing made from dyed fabrics. The most frequently used arsenic compound was copper arsenite, also known as Scheele's Green. Copper arsenite was, under humid conditions, converted into gaseous di- and tri-methylated arsines by mold living in wallpaper paste and caused chronic poisoning and even fatalities (Meharg 2005). In Manchester in 1900-1901 around 6,000 people, with 80 fatalities, were poisoned from drinking arsenic contaminated beer. It was found that the sugar used in the production of the beer was prepared by hydrolyzing starch with arsenic-contaminated sulfuric acid. Accidental mass poisonings have also occurred in modern times. In 1955, over 12,000 Japanese infants were poisoned by dried milk made with arsenic-contaminated sodium phosphate as a stabilizer (Dakeishi, Murata et al. 2006).

The therapeutic use of arsenic dates back to 400 B.C. with Hippocrates recommending arsenic for treatment of ulcers. Most commonly used were simple compounds such as the two sulfides, realgar and orpiment. The peak of the use as a therapeutic agent took place during the 19th century after the introduction of "Liquor Mineralis", consisting of 1% potassium arsenite, in 1786 by Thomas Fowler. It was widely prescribed for various dermatoses such as psoriasis and syphilis, infectious diseases, epilepsy and asthma (Meharg 2005). Almost a century ago the Nobel Prize winner Paul Ehrlich together with Sakahiro Hata discovered the effectiveness of arsphenamine, also known as Salvarsan, in the treatment of syphilis. Arsphenamine was soon followed by neoarsphenamine, which was water soluble and therefore easier to administer. These drugs remained the main treatment against syphilis for forty years, until penicillin rendered them obsolete (Thorburn 1983).

The use of arsenic as a pharmaceutical has been resumed in the past years. Arsenic trioxide (As_2O_3) has been shown to be effective in the treatment of acute promyelocytic leukemia (APL) with its ability to induce apoptosis of the cancer cells at rather high concentrations (Zhu, Chen et al. 2002; Lallemand-Breitenbach, Zhu et al. 2005). The standard dosage for human patients with APL is about 0.16 mg As/kg body weight and

day over a period of six weeks (Niu, Yan et al. 1999; Shen, Shi et al. 2004). Further research on anti-cancer activity of arsenic and its combination with other treatments, e.g. retinoic acid, is ongoing.

The largest part of the world's arsenic production is used in timber treatment as copper chrome arsenate (CCA, almost 70%) and the second largest part is used as agricultural chemicals (WHO 2001). Glass industries in many countries still use arsenic trioxide as a clarifier (Peters, McCurdy et al. 1996). While the use of arsenic in those applications is decreasing, mainly due to the toxicity of arsenic, there is an increasing use of arsenic compounds such as gallium and indium arsenides in the electronics industry (Liao, Yu et al. 2004).

5.3 Uptake and biotransformation of arsenic

Both trivalent and pentavalent inorganic arsenic are readily absorbed in the gastrointestinal tract (Pomroy, Charbonneau et al. 1980; Vahter and Norin 1980). Arsenic is also absorbed in the lungs following inhalation, as indicated by increased urinary arsenic concentrations after respiratory exposure in workers, although some of the inhaled arsenic may be absorbed in the intestine after clearance from the upper respiratory tract (Vahter, Friberg et al. 1986; Yamauchi, Takahashi et al. 1989; Offergelt, Roels et al. 1992; Hakala and Pyy 1995; Yager, Hicks et al. 1997). The dermal absorption of arsenic is generally very low (Wester, Maibach et al. 1993).

The absorbed inorganic arsenic is biotransformed in most mammals, including humans, by reduction and methylation reactions, (Challenger 1945; Vahter and Envall 1983; Cullen, McBride et al. 1984; Marafante, Vahter et al. 1985; Buchet and Lauwerys 1988; Vahter and Marafante 1988; Hirata, Tanaka et al. 1990; Thompson 1993). The reduction reactions seem to occur already in the blood, using thiols as electron donors (Vahter and Envall 1983; Marafante, Vahter et al. 1985; Vahter and Marafante 1985). The main arsenic reductase identified in humans is glutathione-S-transferase omega, GSTO1 (Zakharyan, Sampayo-Reyes et al. 2001). The valence state is of great importance for the cellular uptake of arsenic (Gebel 2002). As(V) is a charged molecule at physiological pH 7.4 and is an analog to phosphate, thus, it probably enters the cell through non-specific anion transporters and other phosphate transporters (Gonzalez, Aguilar et al. 1995). As(III), however, is neutral and mimics glycerol and uses the aquaglyceroporin channels (Liu, Shen et al. 2002; Liu, Carbrey et al. 2004). Only As(III) is taken up by the liver, where the main biotransformation occurs before inorganic arsenic and its methylated metabolites are distributed throughout the body. As(V) has been shown to be taken up by e.g. kidney or skeleton (Lindgren, Vahter et al. 1982; Lerman, Clarkson et al. 1983).

The methylation of arsenic takes place mainly in the liver, where the blood from the intestine passes through before being distributed to other organs. Other tissues have also been shown to have methylating ability, but to a lesser extent (Charbonneau, Tam et al. 1979; Vahter 1981; Lerman, Clarkson et al. 1983; Buchet, Geubel et al. 1984; Buchet and Lauwerys 1985; Geubel, Mairlot et al. 1988; Healy, Casarez et al. 1998). The methylating activity is localized in the cytosol via the one-carbon metabolism (Figure 5.1) with S-adenosyl methionine (SAM) as the main methyl donor (Marafante and Vahter 1984; Buchet and Lauwerys 1985; Zakharyan, Wu et al. 1995; Styblo and Thomas 1997). One methyltransferase, that catalyze the methylation reactions, has been

identified in humans, i.e. arsenic (III) methyltransferase (AS3MT) (Lin, Shi et al. 2002). The main arsenic metabolites excreted in urine are methylarsonate (MA) and dimethylarsinate (DMA), besides some remaining unmethylated inorganic As(III) and As(V).

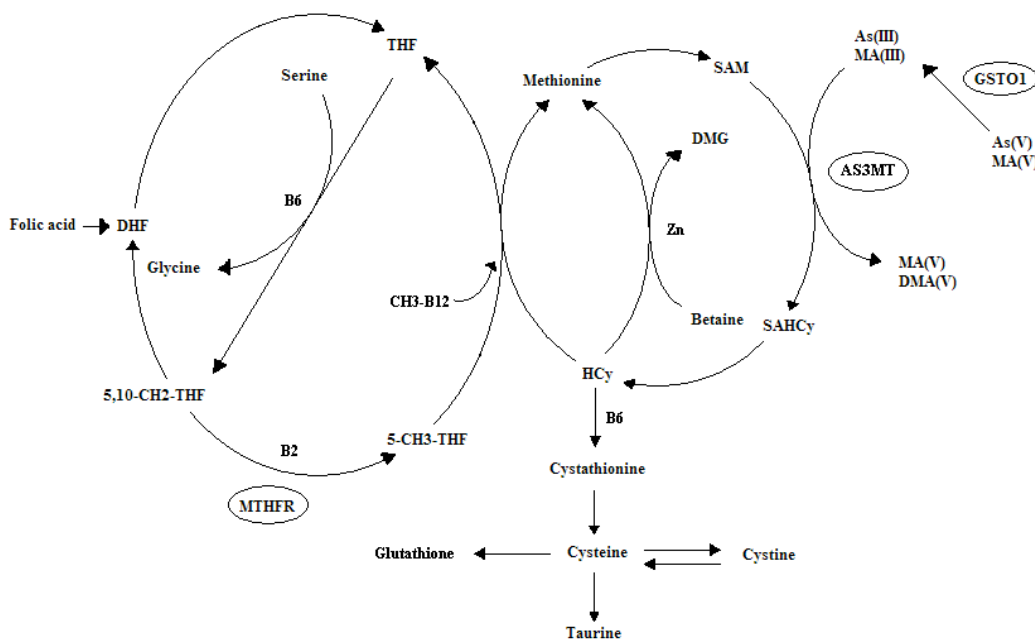


Figure 5.1 The one carbon metabolism and the metabolic pathway of arsenic. As(III), arsenite; As(V), arsenate; MA(III), methylarsonite; MA(V), methylarsonate; DMA(III), dimethylarsinite; DMA(V), dimethylarsinate; SAM, S-adenosyl methionine; SAHCy, S-adenosyl homocysteine; HcY, homocysteine; DMG, dimethylglycine; 5-CH₃-THF, methyl tetrahydrofolate; 5,10-CH₂-THF, methylene tetrahydrofolate; DHF, dihydrofolate; THF, tetrahydrofolate; *GSTO1*, glutathione-S-transferase omega; *As3MT*, arsenic (III) methyltransferase; *MTHFR*, methylene tetrahydrofolate reductase; B₂, vitamin B₂ (Riboflavin); B₆, vitamin B₆; CH₃-B₁₂, methylated vitamin B₁₂; Zn, zinc.

Variation in arsenic metabolism seems to be one explanation for the marked variation in susceptibility to arsenic-induced toxicity. The methylation efficiency is generally measured as the percentage of the metabolites in urine. In general, urine consists of 10-30% inorganic arsenic, 10-20% MA and 60-80% DMA (Hopenhayn-Rich, Smith et al. 1993; Vahter 2002). However, indigenous people in the north of Argentina only have a few percent of MA in urine (Vahter, Concha et al. 1995), while people in Taiwan have 20-30% (Chiou, Hsueh et al. 1997; Hsueh, Huang et al. 1998). A higher proportion of MA in urine seems to be a risk factor as it has been associated with a higher prevalence of urothelial carcinomas (Chen, Su et al. 2003; Chen, Su et al. 2005; Steinmaus, Bates et al. 2006; Pu, Yang et al. 2007), skin effects, including cancer (Del Razo, Garcia-Vargas et al. 1997; Hsueh, Chiou et al. 1997; Yu, Hsu et al. 2000; Chen, Guo et al. 2003; Ahsan, Chen et al. 2007), chromosomal aberrations (Maki-Paakkanen, Kurttio et al. 1998) and cardio-vascular effects (Tseng, Huang et al. 2005; Tseng 2007). A higher fraction of urinary MA is associated with higher retention of arsenic (Vahter 2002).

Probably, a higher proportion of MA in urine indicates a lower methylating capacity and probably also a higher concentration of the highly reactive MA(III) in tissue leading to a higher retention and toxicity.

Considerable differences in arsenic metabolism have also been observed between different mammalian species (Vahter 1999). Most of the commonly used experimental animals are more efficient in methylating inorganic arsenic to DMA than are humans, with the exception of the chimpanzee and the marmoset monkey which have been shown not to methylate arsenic at all (Vahter, Marafante et al. 1982; Vahter and Marafante 1985; Vahter, Couch et al. 1995). Also, the guinea pig seems to be a poor methylator of arsenic (Healy, Zakharyan et al. 1997). Most experimental animals excrete very little MA in urine as compared to humans. The rat differs from most mammalian species by accumulating DMA in erythrocytes (Vahter 1981), probably by binding to a cysteine component in the hemoglobin (Lu, Wang et al. 2007).

As a large variation is seen in arsenic metabolism between individuals and population groups, genetic polymorphisms in genes coding for enzymes directly or indirectly involved in the methylation of arsenic have been suggested to be one of the main factors influencing the metabolism and thereby also the susceptibility to arsenic toxicity (Vahter 2000). Genetic polymorphisms in the AS3MT gene has been shown to affect the pattern of arsenic metabolites in urine differently in different populations. The wild type showed a higher %MA in urine in indigenous people in the Argentinean Andes (Engstrom, Broberg et al. 2007), but a lower %MA in central Europe (Lindberg, Kumar et al. 2007). However, the AS3MT polymorphism did not account for the major part of the variation in arsenic metabolism and additional studies are needed.

The methylation of arsenic is also likely to be dependent on the nutritional status, as several nutrients are involved in the strictly regulated one-carbon metabolism (Figure 5.1). Availability of methyl groups is crucial for the maintenance of the methylation reactions, which are essential for numerous important cellular functions. Experimental studies have shown that rabbits with low intake of protein, choline or methionine decrease the ability to methylate arsenic (Vahter and Marafante 1987). Some epidemiologic studies in Bangladesh and USA have shown associations between arsenic methylation ability and folate and B vitamins involved in the one-carbon metabolism (Gamble, Liu et al. 2005; Steinmaus, Carrigan et al. 2005). Furthermore, it has been indicated that a low selenium intake can lead to reduced arsenic methylation and prolonged retention in the body (Chen, Hsueh et al. 1995; Hsueh, Ko et al. 2003). However, in studies carried out in central Europe and Bangladesh, nutrition was found to play a minor role in the inter-individual variation in arsenic methylation (Lindberg, Ekström et al. 2007; Lindberg, Kumar et al. 2007). In both of the latter studies, women were found to have a more efficient methylation of arsenic to DMA than men, in accordance with previous studies (Hopenhayn-Rich, Biggs et al. 1996; Loffredo, Aposhian et al. 2003; Gamble, Liu et al. 2005). However, the more efficient methylation capacity in women was only noticeable before menopause, indicating hormonal regulation of arsenic methylation (Lindberg, Ekström et al. 2007; Lindberg, Kumar et al. 2007). Also, before menopause women were less affected by various modifying factors, e.g. nutrition, compared to men.

Children and adolescents seem to be more efficient in methylating arsenic to DMA than adults, and had lower %MA and %iAs than the adults (Lindberg, Ekström et al. 2007;

Sun, Xu et al. 2007). It may be speculated that this could be due to increased overall methylation in the body during the period of major growth. Indeed, the expression of genes coding for methyltransferases involved in DNA methylation decreases significantly with age in humans (Zhang, Deng et al. 2002). Furthermore, other inhibitory factors such as smoking, alcohol consumption (Hopenhayn-Rich, Biggs et al. 1996; Steinmaus, Carrigan et al. 2005; Steinmaus, Bates et al. 2006; Pu, Yang et al. 2007) and exposure to other environmental pollutants all increase with age and could also contribute to the decreasing methylating capacity with age.

5.4 Distribution and excretion of arsenic

Once inside the cell As(III), which is the more reactive form of inorganic arsenic, has a preference for SH-groups found in thiols such as glutathione (GSH) and thiol-containing proteins (Vahter and Marafante 1983; Lin, Del Razo et al. 2001; Cui, Wakai et al. 2006; Zhou, Zhu et al. 2006). Indeed, tissues high in SH-groups, e.g. keratin rich tissues such as hair, nails and skin showed a strong tendency to accumulate arsenic after intravenously administered radio labeled As(III) and As(V) in mice (Lindgren, Vahter et al. 1982). Other tissues with high arsenic levels were liver, kidney and gallbladder. The results also revealed that the distribution of arsenic was dependent on the valence state of arsenic. After As(V) administration at fairly high concentrations the concentrations were lower in all organs than after As(III) administration, except in kidney and skeleton (Lindgren, Vahter et al. 1982). At low doses these differences were small or non-existent, because most of the absorbed As(V) was reduced to As(III). The higher AsV concentrations in skeleton were probably due to that As(V) substitutes phosphate in hydroxyapatite, which is the main mineral component of bone. In most tissues taking up As(V), it competes with phosphate and interferes with cellular metabolism, e.g. respiration.

The variation in distribution of the different metabolites of inorganic arsenic has only recently been studied. It has been suggested that the distribution of inorganic arsenic and its metabolites differ both with tissue and animal species. In mice, the highest distribution of MA, DMA and iAs were seen in blood, bladder and kidney, respectively (Hughes, Kenyon et al. 2003). In hamsters, exposed to 5.0 mg As(III)/kg body weight, the liver contained mainly iAs, while the kidney and erythrocytes contained mostly MA (Naranmandura, Suzuki et al. 2007). In a study on mice administered an acute oral dose (0, 10 or 100 μmol As(V)/kg body weight) it was demonstrated that blood, liver and kidney contain mainly iAs and MA and less DMA, while the opposite is true for urine (Kenyon, Del Razo et al. 2005).

Arsenic is able to cross the blood-brain barrier, but the concentrations in brain are considerably lower than in other tissues (Lindgren, Vahter et al. 1982). Further, Concha and coworkers (Concha, Vogler et al. 1998) reported approximately equal levels of arsenic in cord blood as in maternal blood, showing that arsenic is also readily transferred across the placenta barrier in humans.

The major route of excretion is via the urine. When exposed to a single dose of inorganic arsenic the over all half-time is about four days and fits a three-component exponential function with 66% having a half time of about two days, 30% with a half time of about 10 days and 4% with a half time of about 38 days (Tam, Charbonneau et

al. 1979; Pomroy, Charbonneau et al. 1980). However, this could well be different after chronic exposure with saturated binding sites.

Approximately 60% of the dose is excreted in urine and only about 6% in feces within a few days after oral administration (Pomroy, Charbonneau et al. 1980). Experimental animals that have a more efficient methylation also have a more rapid excretion (Vahter and Marafante 1983), which could explain the fact that arsenic is less toxic in most animals compared to humans. There are other routes of excretion for arsenic, e.g. hair, skin, nails, sweat and breast milk, however, the amounts excreted by those routes are insignificant in comparison with urine.

A number of studies have reported substantial amounts of the trivalent forms of the methylated arsenic metabolites (MA(III) and DMA(III)) in urine (Aposhian, Gurzau et al. 2000; Le, Lu et al. 2000; Mandal, Ogra et al. 2001; Valenzuela, Borja-Aburto et al. 2005). However, the high reactivity of these metabolites render them to bind in tissue and the rate of oxidation to the pentavalent forms are very high (Vahter 2002; Nakayama, Edmonds et al. 2006). Recent work has suggested that DMA(III) may at times have been misidentified because its chromatographic properties can be similar to those of thio-dimethylarsinate (thio-DMA) (Hansen, Raab et al. 2004). Analysis by HPLC-ICPMS (inductively coupled plasma mass spectrometry) of urine samples from arsenic-exposed women from Bangladesh with total arsenic concentrations ranging from 8 to 1,000 $\mu\text{g As/L}$ showed that thio-DMA was present in 44% of the samples at concentrations ranging mostly from trace amounts to 123 $\mu\text{g As/L}$ (Raml, Rumpler et al. 2007).

5.5 Toxic effects of arsenic

Chronic exposure to arsenic causes cancer as well as a wide range of non-cancer effects. Carcinogenic effects of arsenic compounds were recognized more than 100 years ago by Hutchinson (Hutchinson 1887). The International Agency for Research on Cancer (IARC) first evaluated the carcinogenic effect of arsenic in 1973 and concluded that arsenic causes skin cancer in people exposed to inorganic arsenic both in the working environment and via drugs, drinking water and pesticides, while there was not sufficient evidence that inorganic arsenic was carcinogenic in experimental animals (IARC 1973). The same conclusions were drawn in the second evaluation performed in 1980 (IARC 1980). In the most recent evaluation, inorganic arsenic was classified to be carcinogenic to humans (Group 1) and causes cancer of the urinary bladder, lung, skin and possibly also kidney and liver (IARC 2004). Evidence that inorganic arsenic is carcinogenic in animals have been lacking for a long time. However, recently several studies in experimental animals have demonstrated the carcinogenic effect of arsenic species in the same organs as in humans (Kitchin 2001; Wang, Qi et al. 2002; Waalkes, Liu et al. 2006; Waalkes, Liu et al. 2007). The lack of positive carcinogenic data in animal studies in the past could be due to the opposing effects of inorganic arsenic at different doses. While low doses of arsenic increase cell proliferation, higher doses induce apoptosis and even necrosis of the cells (Liu, Pan et al. 2006). Another reason for species differences in susceptibility is the extensive metabolism to DMA by most experimental animals, which in turn is rapidly excreted (Vahter 1999).

The National Research Council (NRC) has recently performed risk assessment of arsenic in drinking water (NRC 2001) and concluded that the cancer risk at water

concentrations of 10 µg/L, the guideline recommended by the WHO (WHO 2003), far exceed the tolerable limit of 1 extra cancer case per 100,000 individuals. For bladder cancer the excess lifetime risk was calculated to be 12 for women and 23 for men per 10,000 individuals and for lung cancer the risk was calculated to be 18 and 14 per 10,000 individuals for men and women, respectively.

The earliest signs of toxicity from chronic exposure to inorganic arsenic in humans are pigmentation changes. However, the latency period is normally about 5-10 years (NRC 1999; NRC 2001). Hyperkeratosis usually follows the initial pigmentation changes and could proceed to skin cancer. Two different types of arsenic induced skin cancers are seen, basal cell carcinoma, which is usually only locally invasive and squamous cell carcinoma, which may have distant metastases. The arsenic induced skin cancers differ from those induced by ultraviolet light by generally occurring on areas of the body not exposed to sunlight, e.g. soles and palms (Mazumder, Haque et al. 1998; NRC 1999; NRC 2001; Rahman, Vahter et al. 2006). Other non-carcinogenic effects induced by arsenic include vascular diseases, liver- and neurotoxicity, chronic cough and diabetes mellitus (Mazumder, Haque et al. 2000; WHO 2001). Recent studies have also seen associations between arsenic exposure and adverse pregnancy outcomes and impaired child development (Rahman, Vahter et al. 2007; Wasserman, Liu et al. 2007). However, more studies are needed for evaluation of dose-response relationships and susceptibility factors.

5.6 Mechanisms of toxicity

Although a large amount of research has been performed on the mechanism of arsenic toxicity, the exact nature of the carcinogenic effect of arsenic is not yet clear. The valence state and form of arsenic are of great importance for the toxicity. The trivalent forms of arsenic are the principal toxic forms, which react with e.g. enzymes and transcription factors (Hughes and Kenyon 1998; Petrick, Ayala-Fierro et al. 2000; Styblo, Del Razo et al. 2000; Petrick, Jagadish et al. 2001; Vega, Styblo et al. 2001; Styblo, Drobna et al. 2002; Kligerman, Doerr et al. 2003; Schwerdtle, Walter et al. 2003; Schwerdtle, Walter et al. 2003).

Several modes of action of the carcinogenic effect of arsenic have been proposed, e.g. genotoxicity, altered DNA repair, induction of oxidative stress, altered DNA methylation, altered cell proliferation and altered cell signaling. Arsenic can induce chromosomal aberrations, micronuclei, aneuploidy, endoreduplication and gene amplification (Huang, Ho et al. 1995; Gebel 2001; Mahata, Basu et al. 2003; Chakraborty, Das et al. 2006). Arsenic has been seen to inhibit several DNA-repair enzymes, especially zinc-finger proteins (Li and Rossman 1989; Schwerdtle, Walter et al. 2003; Andrew, Burgess et al. 2006; Witkiewicz-Kucharczyk and Bal 2006). Arsenic exposure results in the formation of reactive oxygen species (ROS) that could lead to DNA adduct formation like 8-hydroxy-2'-deoxyguanosine (8-OHdG), which is used as a common marker of oxidative DNA damage (Matsui, Nishigori et al. 1999; Kessel, Liu et al. 2002; Ding, Hudson et al. 2005; Fujino, Guo et al. 2005; Kubota, Kunito et al. 2006). The alteration of DNA methylation may also be involved in arsenic carcinogenesis. Arsenic can cause hypo-methylation of DNA leading to altered gene expression, probably due to the inhibition of DNA methyltransferases (Sciandrello, Caradonna et al. 2004; Chanda, Dasgupta et al. 2006; Cui, Wakai et al. 2006; Reichard, Schneidenburger et al. 2007). Signal transduction pathways have also been demonstrated

to be a target for arsenic interaction. Mitogen-activated protein kinases (MAPKs) like extracellular signal-regulated kinases (ERKs) have been shown to be induced at low arsenic levels leading to uncontrolled cell proliferation and transformation (Bode and Dong 2002; Qian, Castranova et al. 2003).

5.7 Assessment of exposure and analytical methods

Assessment of human exposure to inorganic arsenic is often based on the concentrations of arsenic in exposure media such as water or food, which need to be combined with estimates of the ingested amounts of water and food (Calderon, Hudgens et al. 1999). More precise estimates of the absorbed amounts of arsenic on the individual basis are obtained by measurements of concentrations of arsenic in biomarkers such as blood, hair and urine. Urine is the most commonly used biomarker for evaluation of recent arsenic exposure as urine is the major route of excretion and samples are easy and non-invasive to collect. A problem, however, is that the concentration of arsenic in spot urine samples (single voided urine), which are often used as complete 24-hour urine is very difficult to collect, vary considerably by the dilution of the urine, which, in turn, is dependent on the intake of fluids, physical activity, temperature etc. Therefore, it is essential to adjust for this variation in dilution when comparing concentrations between individuals and populations, either by the specific gravity of the urine or the urinary creatinine excretion, which is fairly constant in healthy individuals, but may vary by muscle mass and protein intake (Suwazono, Akesson et al. 2005; Nermell, Lindberg et al. 2007).

Because of the frequently occurring elevated concentrations of organic arsenic compounds in various seafood a single meal containing such food even in small amounts may markedly increase the arsenic concentrations in blood and urine (Vahter 1994). Therefore, it is essential to distinguish between species derived from exposure to inorganic arsenic and species derived from organic arsenic exposure, e.g. arsenobetaine and arsenocholine. Exposure to inorganic arsenic is often assessed by measuring either the separate metabolites in urine, i.e. As(III), As(V), MA(V) and DMA(V), or the sum of these species in urine (hereinafter referred to as SumAs). Speciation of different forms of arsenic in blood is more difficult due to binding of arsenic to the red blood cells and plasma proteins.

Several commercial field test kits are available on the market. They are commonly used when analyzing arsenic in drinking water, due to its simplicity and low costs (Van Geen, Cheng et al. 2005; Steinmaus, George et al. 2006; Jakariya, Vahter et al. 2007). However, these have been shown to only be semi-quantitative. The most frequently used laboratory method for determination of arsenic in drinking water is atomic absorption spectrometry (AAS), with its low detection limits and high accuracy (Wahed, Chowdhury et al. 2006). For determination of inorganic arsenic and its metabolites in urine some commonly used analytical methods include speciation analysis with high performance liquid chromatography (HPLC), with or without hydride generation (HG), coupled to inductively coupled plasma mass spectrometry (ICPMS) or atomic fluorescence spectrometry (AFS) (Lindberg, Goessler et al. 2007). Determination of SumAs with AAS coupled to HG is also a frequently used method (Norin and Vahter 1981; Francesconi and Kuehnelt 2004). Hydride generation is commonly coupled to the detector to discriminate for the organic arsenic species AB and AC as these do not form volatile arsines like inorganic arsenic and its metabolites do.

5.8 References

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6 Mapping of hazardous substances in groundwater on a global scale

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6.1 Introduction

Some of the substances found in groundwater are dangerous to human health and/or ecosystems. The hazardous substances have both natural and anthropogenic origins. The distribution of these substances from their sources is affected by many factors which are related to transport of water and bio-geochemical reactions.

Information on spatial and temporal distribution of hazardous substances is essential for any water resources management. Extensive hydrogeological surveys and monitoring programmes are required to obtain such information. Some countries have national monitoring programmes, but in many countries the occurrence of hazardous compounds is reported on an incidental basis only in various projects. Such projects have usually limited areal extent and duration, reflecting the needs of specific groundwater users (public health, agricultural). Even for monitored regions, different set-up and monitoring densities, combined with different hydrogeological conditions complicate the comparison of distribution patterns.

In order to manage the hazardous substances in groundwater adequately, information on their occurrence should be easily available and presented in an accessible format. Maps are extremely helpful in this respect. The patterns they show allow the information to be understood easily in its spatial context.

The International Groundwater Resources Assessment Centre (IGRAC)¹ produces thematic maps for a large number of groundwater-related attributes, using either a world map of countries or a map of global groundwater regions. This paper summarizes IGRAC's efforts to open up information and knowledge on worldwide occurrence and distribution of hazardous substances in groundwater.

6.2 Global inventory of groundwater quality

Within the framework of IGRAC's Global Groundwater Information System (GGIS) a global country-wise inventory of general groundwater quality has been carried out. The methodology applied and results of this global overview are described by Griffioen et al (2005). Publicly available information from internet, publications, technical reports and map has been collected for the attributes related to:

- Occurrence of no fresh water
- High fluoride
- High arsenic
- High nitrate
- Pollution from various sources

Information gathered so far varies from statements like "there are high concentrations found at some places" (without any other specification of location) to maps displaying

¹ The International Groundwater Resources Centre is an initiative of UNESCO and WMO. It is financially supported by the Dutch Government through "Partners for Water Programme" and hosted by *Geological Survey of the Netherlands-TNO*.

spatial distribution in detail. An example of a map showing detailed distribution of a specific hazardous compound on a country scale is shown in Figure 6.1.

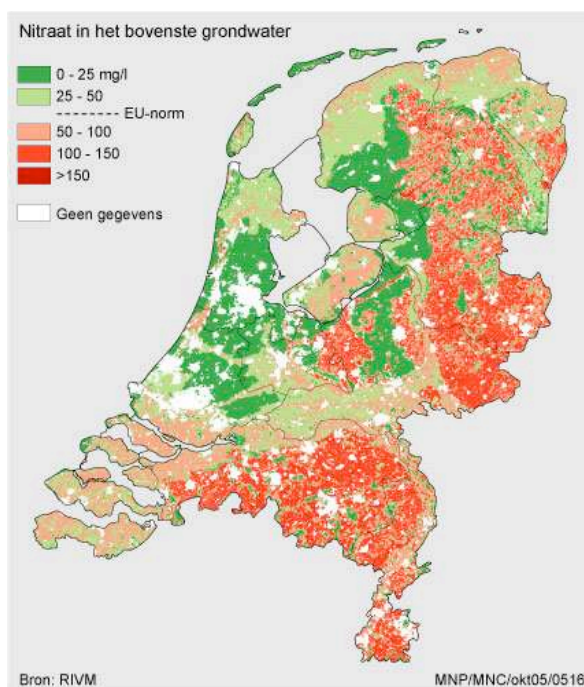


Figure 6.1 Nitrate in upper groundwater in the Netherlands round 2000 (The Netherlands Environmental Agency, 2007).

Unfortunately, detailed maps as shown in Figure 6.1 are available only for very few countries.

In order to provide a global overview of hazardous compounds, IGRAC used a simple approach, based on qualitative estimates of number of locations or zones with concentrations in excess of certain limit. Limits used are listed in Table 6.1 for single variables.

Table 6.1 Limits for some hazardous compounds.

Compound	Limit	Based on
TDS	1000 mg/l	Upper limit for fresh water
Fluoride	1.5 mg/l	WHO (2004) guideline values drinking water
Arsenic	0.05 mg/l	WHO (2004) guideline value drinking water*)
Nitrate	50 mg/l	WHO (2004) guideline value drinking water

*) The actual guideline value for As is 0.01 mg/l. However, many affected countries still operate 0.05 mg/l standard due to lack of adequate testing facilities.

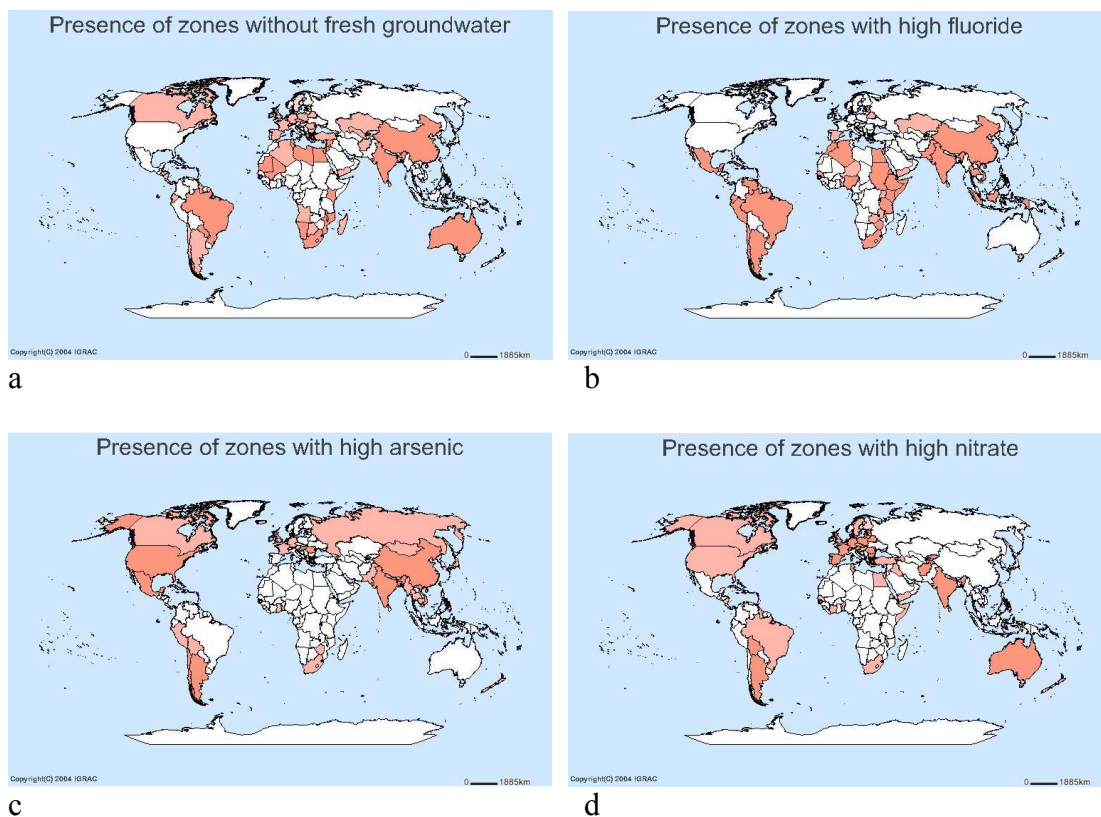
Four classes were distinguished to compare between individual countries:

- No cases reported. This class refers to country reports or other literature in which no occurrence of a specific compound is explicitly mentioned. There were investigations carried out, but the compound is not found.

- Few cases reported. The occurrence of a specific compound is reported only for a few locations. Or there is “assumed risk” of excessive concentrations on basis of other indicators (health problems, environmental changes).
- Many cases reported. Country has many locations with excessive concentrations. The cases are well documented and the seriousness of the contamination is explicitly stressed.
- Information not available. During the inventory, no information at all has been obtained from publicly available sources for these countries.

During IGRAC’s inventory, anthropogenic influence on groundwater quality has been mapped on the basis of reported pollution from domestic sewage, agriculture and industry. Each sector is responsible for a large number of organic and inorganic pollutants (e.g. pathogenic bacteria, chlorinated hydrocarbons, metals, pesticides). Similarly to the single variables described above, only qualitative estimates have been made in terms of “few”, “many” and “none”.

Using the Global Overview of the Global Groundwater Information System (GGIS) (www.igrac.nl), global thematic maps can be generated. Those maps relevant to hazardous substances are shown in Figure 6.2.



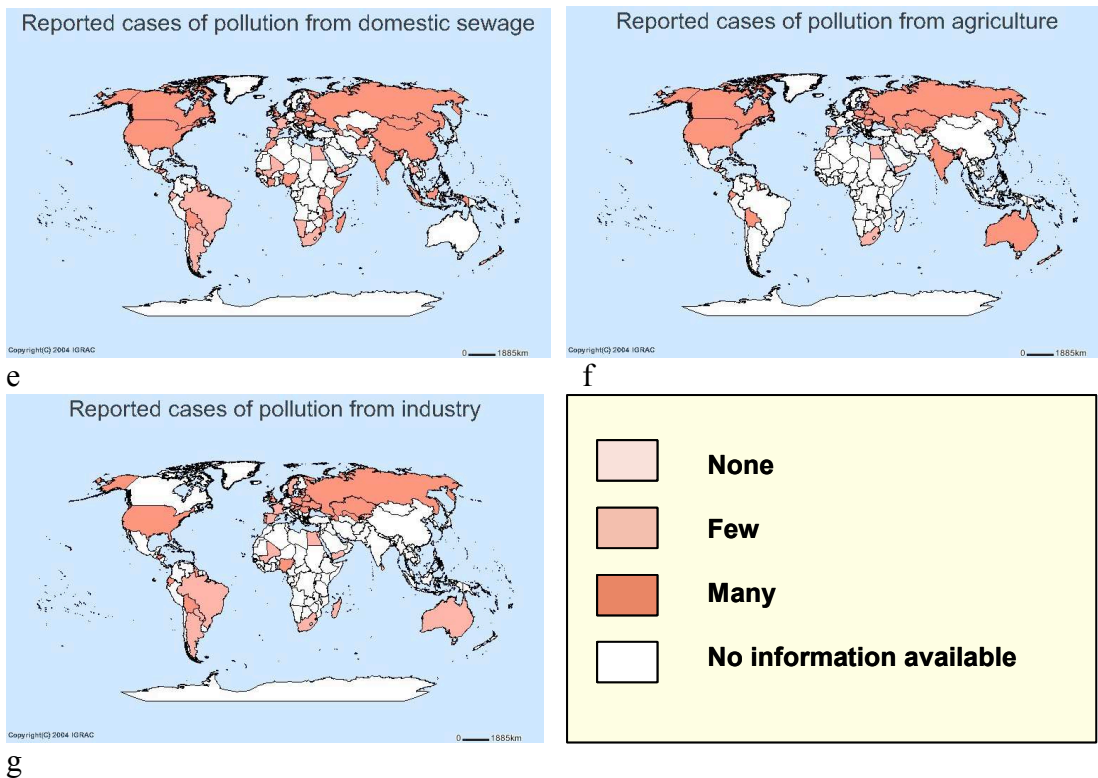


Figure 6.2 Maps indicating the groundwater quality at national level (IGRAC, 2007): Total dissolved solids (a); fluoride (b); arsenic (c); nitrate (d); domestic sewage pollution (e); agricultural pollution (f); industrial pollution (g).

6.3 Advantages and limitations of the GIS maps

From the information management point of view, the maps shown in Figure 6.2 provide overview about information gaps (the white-marked countries). However, the reasons for the gaps could not be indicated, because no differentiation can be made between the availability (there are no data at all) and accessibility (data available at sources unknown to persons carrying out an inventory).

The global maps allow for a comparison among the countries. They provide a first insight in the (potential) problem areas. However, as the information is aggregated over the whole country, possible spatial variations in occurrence can not be indicated. The reported cases vary in size from a small domestic water supply to large regional monitoring networks covering an extensive area. Some countries falling into the category “many” cases may have problems with hazardous compounds concentrated in only a small part of the total area. In the USA, occurrence of excessive concentrations of arsenic is reported only in a few states, but many cases are connected with mining activities in California, and justify the country-wide category label.

The information sources available during the inventory have variable reference years. This implies that information shown on the map for the neighbouring countries might compare relatively old data with recent ones. The differences can reach several decades.

6.4 From general indication to refined spatial distribution

IGRAC maps from the GGIS-Global Overview provide a general indication of occurrence of hazardous compounds on a global scale. National level maps allow for intercomparison, but are not well suited to small-scale water resources management. Therefore, IGRAC studied possibilities of how to map the spatial variations of hazardous compounds at a more detailed scale taken into account geo-scientific instead of administrative boundaries. Two special projects regarding the probability of occurrence of excessive concentrations of respectively arsenic and fluoride were initiated (Brunt et al., 2004a,b). The approach used for these two projects included the following steps:

1. *Determination of locations for reported country cases*
In some case, exact geographical coordinates could be obtained from maps or descriptions included in publications or reports. In other cases indicated administrative units like “Ashanti region” in Ghana or “Xinjiang Province” in China were used.
2. *Gaining knowledge on sources and geochemical behaviour*
The main sources for both arsenic and fluoride are known. Sources of arsenic are described in detail in Chapter 4 of this publication. Fluoride-bearing minerals and volcanic gases are the natural sources of fluoride. The anthropogenic sources are related to use of phosphatic fertilizers, processing of phosphatic raw materials, ceramic industry and burning of coal (Vasak, 1992). The geochemical behaviour of arsenic is complex and still poorly understood. The mobilization of arsenic may occur under various conditions (see Chapter 4 in this publication). Redox conditions play the dominant role in this process. These conditions can vary over very short distances within the same geological environment. Therefore a relation between different lithologies and dissolved arsenic in groundwater is very difficult to establish. The geochemical behaviour of fluoride is well understood and is strongly directly related to (hydro)geological and climatologic conditions.
3. *Selection of proxy information as an indicator of probability of occurrence*
In absence of direct information on spatial distribution of hazardous substances, proxy information can be used to assess the probability of occurrence of high concentrations. Proxy information results from the combination of various data relevant to the processes that affect the behaviour of a selected compound. Geological and climatologic data were identified as possible sources of proxy information (see above). This step included also a search for publicly available digital sources at the appropriate scale from which spatial distribution of proxy information can be obtained. Geological map of the World at 1:25.000.000 scale (CGMW/UNESCO, 2000) was used for geological information. Digital files based on Meig’s classification of aridity (Milich, 1997) and global climatologic data (CRU, 2003) were used for delineation of climatic zones.

6.5 Global arsenic map (Brunt et al, 2004a)

The approach outlined above was used to map probability of occurrence of excessive arsenic concentrations in groundwater on global scale.

Locations of reported country cases on excessive arsenic concentrations

Information on areas contaminated by arsenic was obtained for 42 countries. Most references were obtained from a review by Smedley and Kinniburgh (2002).

Knowledge on sources and geochemical behaviour

The origin of contamination is known for most of the sites. Excessive concentrations are associated with unconsolidated alluvial and deltaic sediments, geothermal fields and mining activities. As outlined above, the abundance of arsenic in groundwater is controlled by complex processes. To predict possible distribution of arsenic outside the reported cases, detailed information on hydrogeological and geochemical conditions of aquifers is required. Often it is not clear from the case descriptions, which techniques are used by extrapolating data from discrete points to larger areas.

Proxy information

Existing digital geological map of the world (CGMW/UNESCO, 2000) has not enough detail to be used as proxy information. There is no differentiation of sedimentary formation in terms of their lithologies because the map legend is based on chronostratigraphy. Also there is no description of geochemical characteristics of these formations.

Three classes of probability of occurrence were distinguished:

- High: Location of contaminated area is well defined
- Low: Precise location is not known
- Uncertain: Country mentioned as having problem with arsenic, but no areas specified

Figure 6.3 shows a world map with probability of occurrence of excessive arsenic concentrations in groundwater.

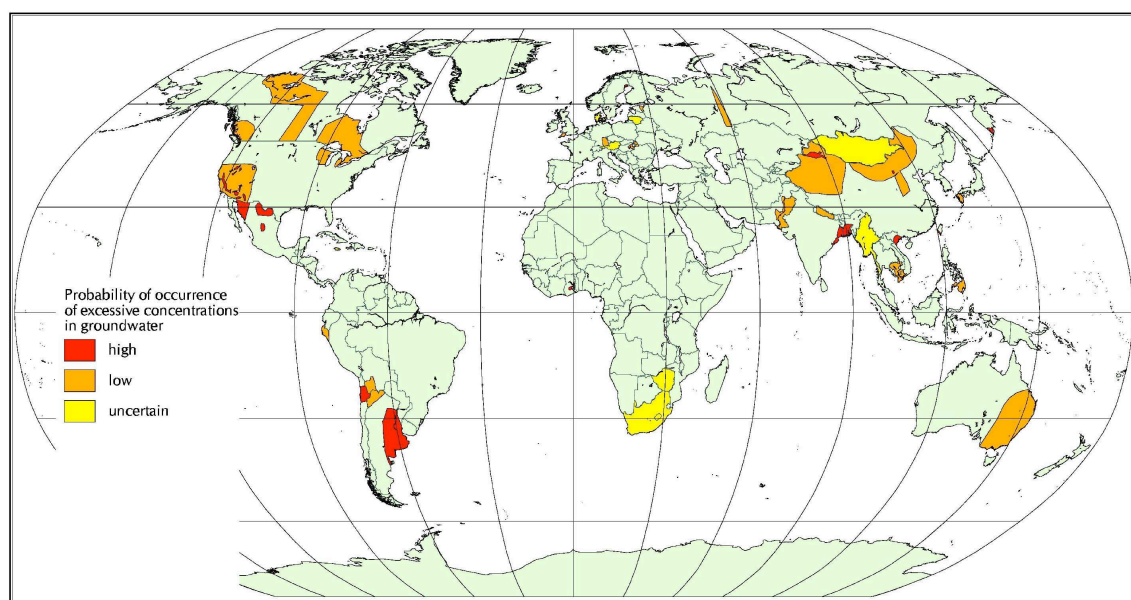


Figure 6.3 Probability of occurrence of excessive arsenic concentrations in groundwater

The map shown in Figure 6.3 provides more details on arsenic occurrence than the general GIS map shown in Figure 6.2c. Demarcation of affected areas is refined from a national level to a sub-national level (state, province) or even to a local level (delta, plain etc.).

6.6 Global fluoride map (Brunt et al, 2004b)

Locations of reported country cases on excessive fluoride concentrations

Information on sites contaminated by fluoride was obtained for 44 countries. Next to the hydrogeological references, medical references on endemic fluorosis were useful (e.g. Frencken et al., 1996).

Knowledge on sources and geochemical behaviour

Similar to arsenic, the origin of fluoride contamination is known for most of the areas. High F-concentrations are generally associated with sodium-bicarbonate water that is found in weathered alkaline igneous or metamorphic rocks, coastal aquifers affected by a cation-exchange or aquifers affected by evaporation (Griffioen et al., 2005). Climate influences the concentrations in terms of groundwater flow and evaporative concentration. In dry (arid conditions) groundwater flow is slow and the reaction time with the rock is long and evaporation high. In humid areas diluting effect on groundwater composition is high.

Proxy information

There is a clear relation between high concentrations of fluoride, lithology and climate. Therefore, knowledge on spatial extension of geological formations and climatic zones can provide good indication for fluoride risk. The geological map of the world (CGMW/UNESCO, 2000) provides enough details to differentiate between endogenous rocks, extrusive volcanic rocks, consolidated and unconsolidated sediments. The precipitation/potential evaporation ratios showed on the climate map allow for a differentiation of aridity at the regional scale.

Figure 6.4 shows a world map with probability of occurrence of excessive fluoride concentrations in groundwater. Five probability classes are distinguished. Description of these classes is given in Table 6.2. Regions falling into medium to high probability classes are abundant in South America (*Andes and Western Brazil*), Asia (*North-western China, North-western and Southern Provinces in India*) and Africa (*Rift Valley zone*). Similar to the arsenic map, the new fluoride map refines boundaries of reported risk areas. In addition it shows new areas vulnerable to excessive concentrations based on their (hydro)geological conditions and climate.

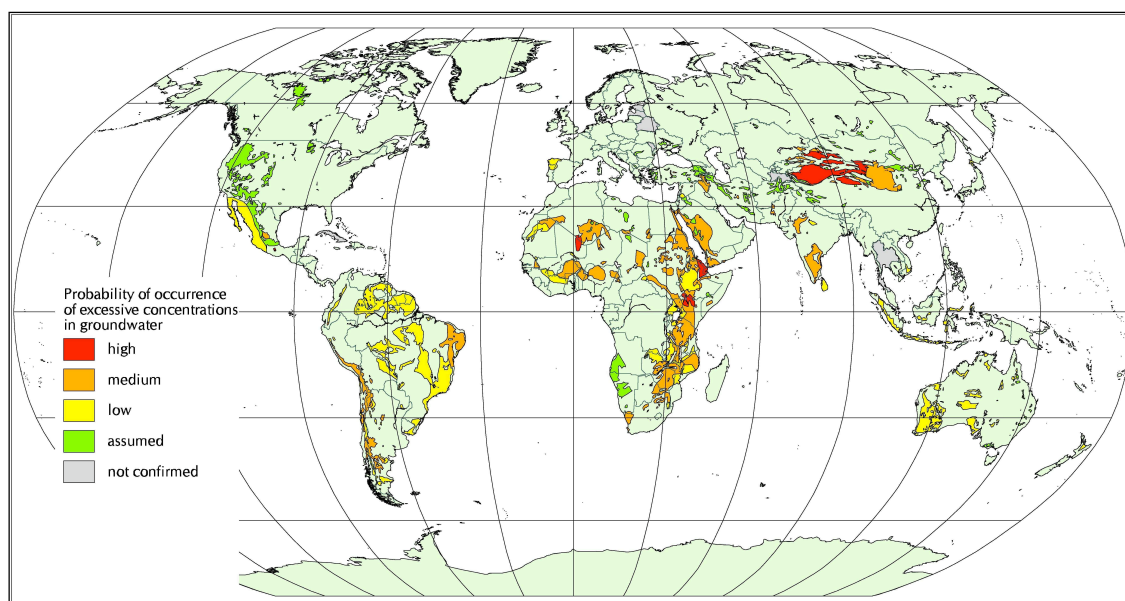


Figure 6.4 Probability of occurrence of excessive fluoride concentrations in groundwater

Table 6.2 Probability classes of occurrence of excessive fluoride concentrations (Brunt et al., 2004)

Probability	Hydrogeology	Climate	Additional references
High	Formation with F-rich groundwater	Hyper-arid/arid	yes
Medium	Formation with F-rich groundwater	Semi-arid/dry-subhumid	yes
	Potential F-rich + known fluoride-problem country (or adjoined)	Hyper- to semi-arid	no
Low	Formation with F-rich groundwater	Moist-subhumid/humid	yes
	Potential F-rich in known fluoride-problem country (or adjoined)	Dry subhumid to humid	no
Assumed Risk	Potential F-rich <i>not</i> in known fluoride-problem country	Hyper-arid/dry-subhumid	no
Not Confirmed	Not known	Not known	no

The mapping process of excessive fluoride concentration in groundwater is summarized in Figure 6.5.

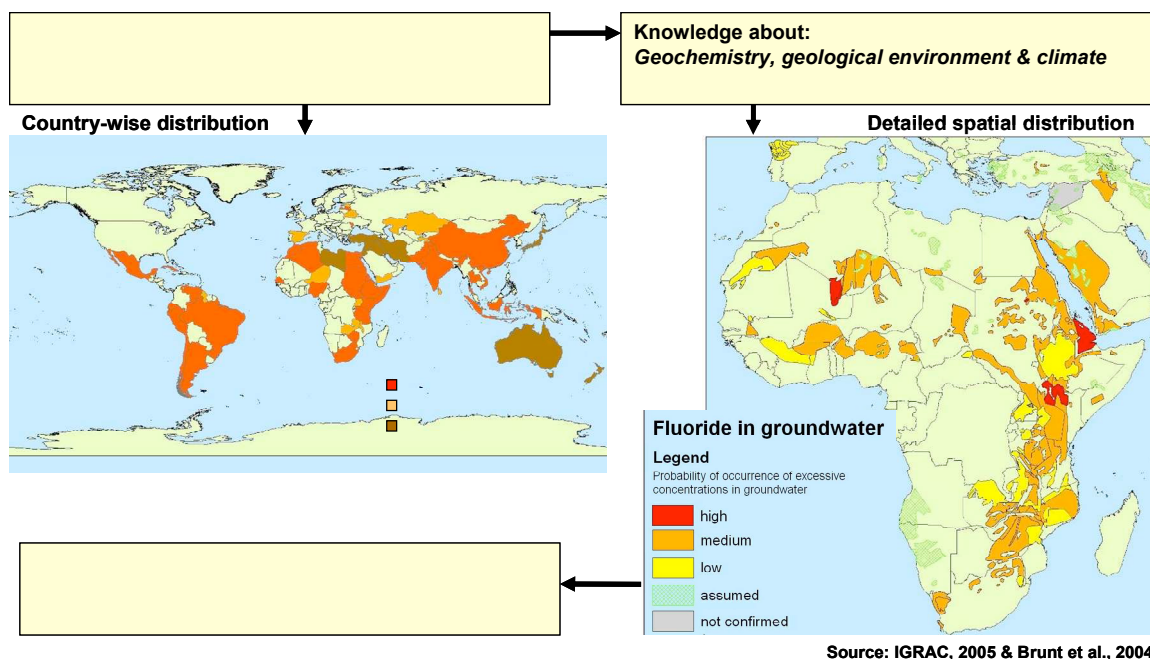


Figure 6.5 Mapping processes of excessive fluoride concentrations in groundwater (Vasak and Van der Gun, 2007).

6.7 From diagnosis to a treatment

Maps showing the distribution of hazardous compounds provide valuable information for various water users. However, pinpointing the location and assessing the risk do not solve the contamination problems. In many areas, contaminated groundwater is the only water resource available. This implies that the local population has no choice but using this water. It is very important that once the occurrence of contaminated water is assessed, suitable removal techniques are determined and applied as soon as possible. Most removal techniques are complex and/or expensive. Moreover, they often require a certain level of technical skills. An urgent need exists for a comprehensive overview of removal methods in which the suitability of each method is evaluated in terms of efficiency, costs and required technology.

The Massachusetts Institute of Technology (2001) developed an online information database about arsenic remediation technologies. IGRAC is currently preparing fact sheets and decision trees for fluoride and arsenic removal methods which will be included in the centre's on-line services. These products aim to provide low threshold guidelines, easily understandable to a "problem owner" seeking a practical solution for improvement of his groundwater resources.

6.8 Conclusions

The knowledge of occurrence and distribution of hazardous substances in groundwater is uneven among countries. For many countries, only qualitative information (observed problems; assumed risks) is publicly available while information on concentrations and their distribution in space and time is lacking. Nevertheless this qualitative information, when presented in simple maps, provides a first insight in the (potential) problem areas.

Proxy information appears to be useful for mapping of individual substances in groundwater if direct information from groundwater quality investigations is lacking. Geological patterns and climatic zones provide indications for probability of occurrence of excessive fluoride concentrations. Using proxy information, more detailed maps can be produced providing geochemical knowledge is sufficient and properly applied. Such maps can support the decision makers in regional water management (e.g. planning of new water supplies). They might be also helpful during the design and/or optimizing of monitoring networks.

Standardized and up-to-date information on occurrence of hazardous substances should be made easily accessible from the national assessments, if available. Only in this way, consistent maps on global distribution of hazardous substances can be produced and the severity of groundwater contamination can be intercompared.

Global groundwater information centres play an important role in sharing of information on the occurrence of hazardous substances. Shared information and knowledge can reveal analogies on distribution patterns in similar hydrogeological environments. Understanding these patterns will in turn contribute to proper measures for mitigation of negative effects associated with these substances. In the context of mitigation, information on hazardous substances should include not only the current environmental status but also guidelines for remediation.

6.9 References

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7 Arsenic in the Dutch coastal provinces

Authors: Sophie Vermooten and Jan Gunnink

7.1 Introduction

The sediments in the sub-surface of the Netherlands contain arsenic in low abundance. The average concentration in the Pleistocene sands is 3.7 mg / kg dry matter (90-percentile 7.4 mg / kg); the average concentration of arsenic in groundwater between 5 and 25 meter below surface level is 1.3 ug /L (90-perventile 2.2 ug/L); data derived from the DINO-database at TNO. The differences in arsenic concentration between the sediments from different geological Formations in the Pleistocene are small.

However, certain areas in the Netherlands contain high concentrations of arsenic from natural origin. Accumulation of arsenic in these areas is caused by a combination of geological, hydrological and geochemical processes, sometimes resulting in arsenic concentrations over 800 mg / kg in sediments and several thousands ppb in groundwater.

The environmental guidelines in the Netherlands do not differentiate between chemical substances from natural origin and chemicals that are introduced by human activities, like industry or agriculture. Arsenic is occurring naturally in high concentrations in parts of the Netherlands and is sometimes treated as environmental pollution. The measures that are prescribed in the Dutch legislation to deal with pollution are not suitable for natural occurring substances. Often, the source of arsenic is widespread and available in such amounts that technical measures are not feasible to get rid of the arsenic. Knowledge about the genesis of areas with natural increased levels of arsenic and the way arsenic is released in the environment can lead to more appropriate measures to deal with high arsenic concentrations. In the case of arsenic, the proposition is made to focus on minimizing the risks of arsenic for humans.

The regulatory values regarding arsenic are given in Table 7.1. The background value is based on a dataset that contains samples from areas that are presumed not influenced by human activity. The intervention value is based on the combined ecological and human risk evaluation. Legislation in the Netherlands states that, whenever the Intervention value is exceeded, an analysis of the size of the area involved and possible risks needs to be undertaken.

Tabel 7.1 Regulatory values for soil and groundwater (Guidelines values for Soil remediation strategies, Department of Housing and Environment).

	Soil	Groundwater
Intervention value (NL)	55 mg/kg d.s.	60 µg/l
Guideline value (WMO)	29 mg/kg d.s.	10 µg/l

7.2.1 Arsenic in the solid phase and in groundwater

Arsenic in pyrite

High concentrations of arsenic in the Netherlands occur both in the solid phase and in groundwater. In the solid phase arsenic occurs in pyrite or in combination with ironhydroxides.

Pyrite (FeS_2) consists of iron and sulphate and is formed under the following specific circumstances:

- organic matter needs to be available as “fuel”
- anaerobic circumstances
- abundance of iron and sulphate

Pyrite can contain high concentrations of arsenic due to the fact that sulphate is being replaced by arsenic. In the past, pyrite is formed in areas where the above mentioned circumstances were favorable; in the Holocene this was mainly in the western parts of the Netherlands.

Arsenic in ironhydroxides

Ironhydroxides (FeOOH) are formed when dissolved Fe precipitates upon oxygenation. In the case of arsenic being present in the groundwater it will be adsorbed to or incorporated into the crystal structure of FeOOH .

When groundwater, enriched with iron and in an anaerobic state, is oxygenated, iron will precipitate. In due course this may lead to thick, iron-enriched layers. In these layers arsenic can reach high concentrations.

7.2.2 Origin of areas with natural high arsenic concentrations

Processes that have caused the development of areas of high concentration of natural arsenic can be summarized according to Figure 7.1.

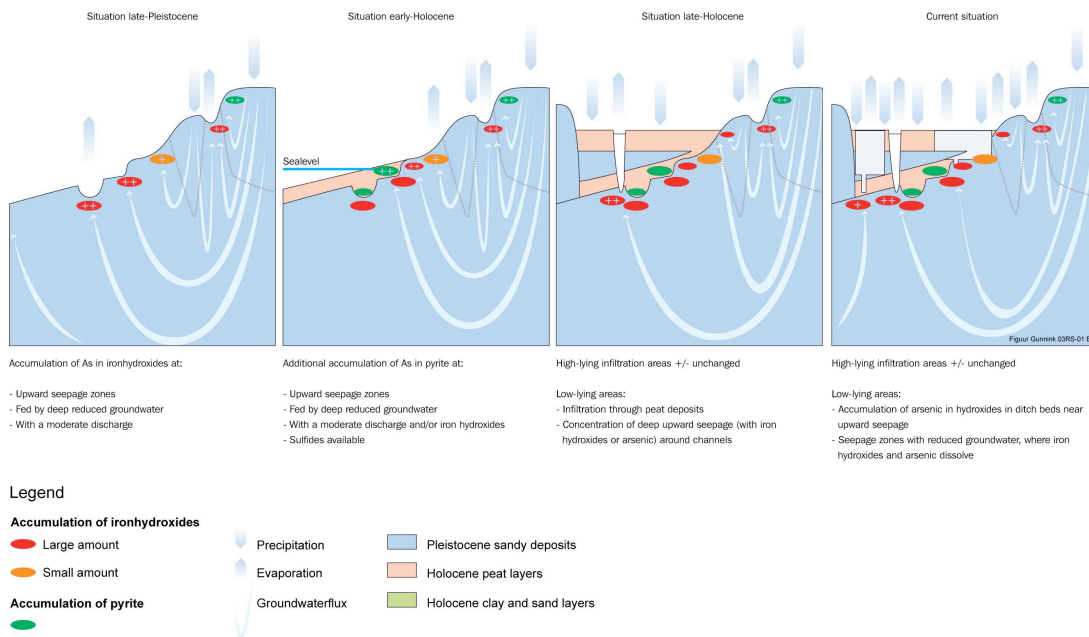


Figure 7.1 Processes causing high concentration of natural arsenic.

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1. Iron and arsenic, naturally occurring in the sandy Pleistocene sediments, are mobilized in anaerobic groundwater. The initial concentrations are low. As soon as the groundwater comes near the surface, iron will precipitate upon oxygenation, sometimes into thick, duripan-like layers. Due to the topography, groundwater will exfiltrate at specific sites and there, concentration of iron will occur in conjunction with arsenic. The favorable environmental conditions for enrichment of iron are: 1) a large hinterland in which infiltration can take place, 2) specific areas where groundwater can surface, 3) a sandy subsurface and 4) a stable situation for a long period of time. These circumstances occurred in specific areas in the Netherlands, around ice-pushed ridges and along the edges of a plateau in the Northern part of the Netherlands.
 2. Due to sea level rise in the early Holocene, large areas of the western part of the Netherlands became covered with peat. Peat that is formed directly on top of the sandy Pleistocene sediments is called “Basal Peat”. Circumstances for the formation of pyrite were favorable where groundwater – enriched with iron – came in contact with seawater or river water that contains sulphate. All the ingredients for the formation of pyrite are available: anaerobic conditions due to the “drowning” of the peat by sea level rise, iron from groundwater, sulphate from seawater and Peat as “fuel”. In large areas of the western part of the Netherlands enrichment of iron was not occurring at a large scale due to lack of relief. However, the general conditions were favorable for pyrite formation. In specific areas, where relief was present, accumulation of iron and arsenic occurred at a rate that led to high concentrations of arsenic in pyrite.
 3. In the Mid-Holocene, rivers and the sea caused erosion of the peat cover, leaving behind new relief elements that acted as pathways for groundwater. This led to new sites where accumulation of iron and arsenic took place. Due to the ongoing sea level rise, large areas of the western part of the Netherlands became covered with alternating sand/clay layers and peat, causing the basal peat to become buried and permanently anaerobic. The sandy sediments underlying the basal peat layer were anaerobic and the iron enriched layers dissolved, resulting in increased iron and arsenic concentrations in the groundwater.
 4. In modern times, the landscape is completely changed by human activity. One of the effects is that the groundwater flow has changed dramatically compared to the natural situations, sometimes the groundwater flow direction is even reversed. One of the effects is that iron and arsenic, occurring in the sandy, anaerobic Pleistocene sediments, can sometimes surface in polders in the western part of the Netherlands, causing high concentrations of arsenic in stream bed sediments. Another effect is that the anaerobic conditions in groundwater are sometimes changed into aerobic, leading to oxidation of pyrite and release of arsenic.

A typical example of the vertical distribution of arsenic concentration in sediment and groundwater is given in Figure 7.2. This figure pertains to a drilling south of Amsterdam, in which an ice-pushed ridge in the subsurface acted as a local pathway for groundwater in the early Holocene. The arsenic concentrations in the sediment are in general low; at 10m depth a large increase of arsenic concentrations occurs, associated with basal peat. It is anticipated that pyrite in the basal peat is the main contributor for the arsenic. Below the basal peat the arsenic concentrations in the sediment are slightly elevated.

In groundwater, a slight increase in arsenic concentrations occurs in the basal peat, but the largest increase is found in the Pleistocene sediments just below the basal peat. This

large concentration is associated with an iron-enriched layer, formed during the late Pleistocene / early Holocene period.

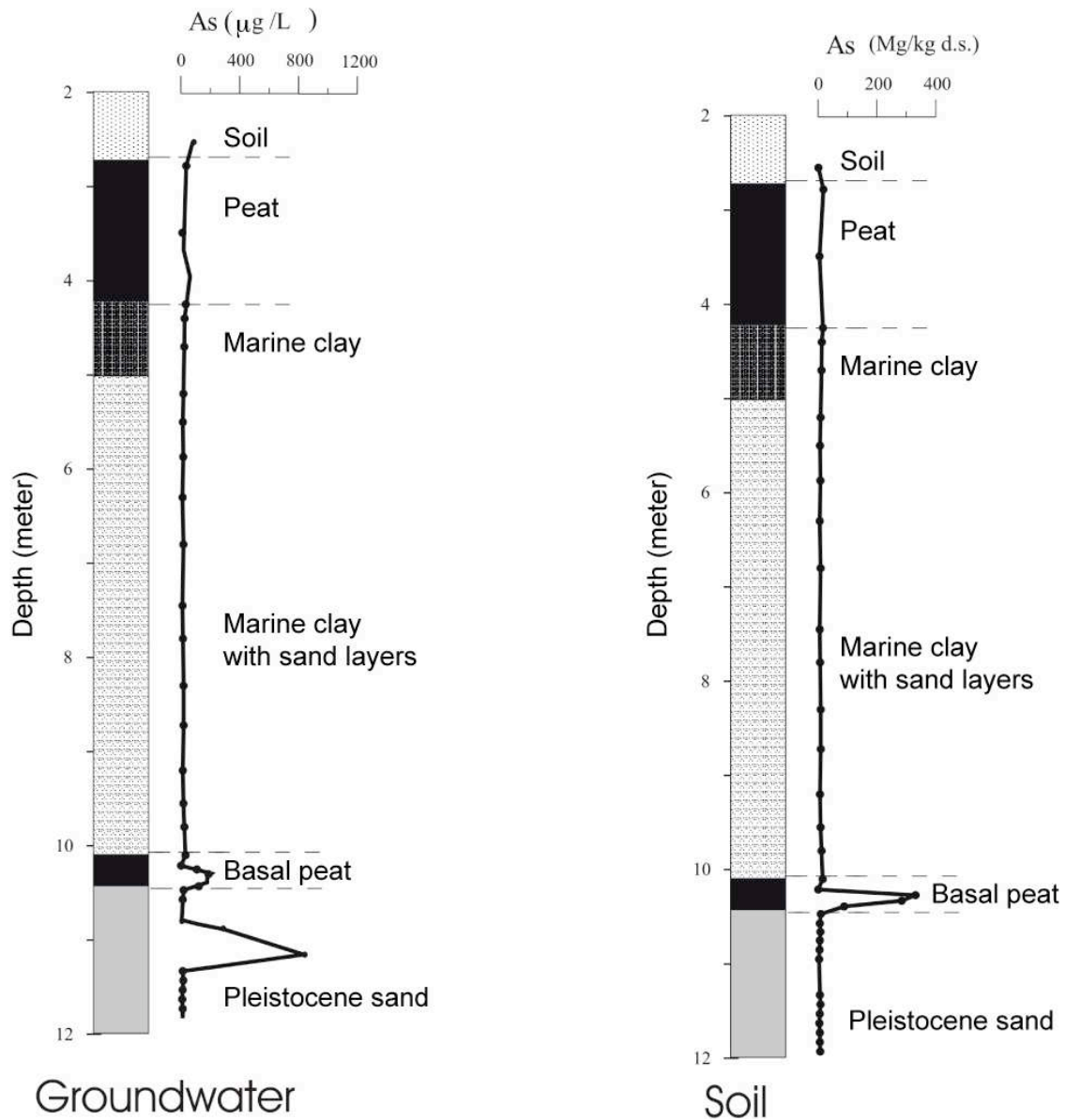


Figure 7.2 Vertical distribution with depth of arsenic concentration in sediment and groundwater.

7.2.3 Release of arsenic

Oxidation of pyrite

Pyrite will dissolve in the presence of oxygen or nitrate causing arsenic – that may be present – to be released in groundwater. The rate of oxidation of pyrite is dependent of Eh and pH; anyway, small amounts of dissolved pyrite can cause high concentrations of arsenic, up to 1500 ppb. The released iron can form ironhydroxide, in which arsenic can be incorporated.

Reduction of ironhydroxides

Arsenic in ironhydroxides is released when the environmental conditions become anaerobic (Smedley & Kinniburgh 2002). This may occur in areas where deep anaerobic groundwater comes at the surface, like deep polders in the western part of the Netherlands. Also, areas with a fluctuating groundwater level may develop anaerobic conditions when the groundwater level is high. As a consequence, ironhydroxides can dissolve, releasing arsenic in the groundwater. Arsenic concentrations may reach levels up to 700 µg/L, while the concentrations in the solid phase are low (< 10 mg / kg).

In deep groundwater, high arsenic concentrations are encountered where ironhydroxides were accumulated in the past. In permanently anaerobic conditions, ironhydroxides dissolves, releasing the associated arsenic. Due to the large amount of ironhydroxides, there is a large source available of arsenic, resulting in is a permanent situation that can not be alleviated by human measures.

The relation between the level of arsenic in the solid phase and the concentrations in the groundwater is complex. Low concentrations in the solid phase can lead to high concentrations in the groundwater, especially since solid phase concentrations are measured in ppm and groundwater concentrations in ppb.

Besides the anaerobic/aerobic conditions for releasing arsenic from ironhydroxides / pyrite, there is also the effect of pH, in which pH values > 8.5 or < 3 cause ironhydroxides to dissolve and arsenic become mobile (Sigg & Stumm, 1991).

7.3 Spatial distribution of natural arsenic concentration

7.3.1 Introduction

The spatial distribution of the areas with a higher risk of increased arsenic levels in the soils and the groundwater is mainly based on the knowledge of the processes described above. This knowledge is used to obtain a regional picture of the areas with a higher risk of natural arsenic.

7.3.2 Arsenic associated to iron hydroxides in soils and phreatic groundwater

In phreatic groundwater, the risk of higher arsenic is increased in specific areas. The location of these areas is related to the geological setting and geohydrological conditions, especially the upward seepage zones are important. In these areas, in the phreatic groundwater, the guideline values of arsenic are regularly exceeded whereas the concentrations of arsenic in the soil are often not exceeded. If the environmental conditions are favorable, a little amount of arsenic in the soil (far below the guideline value) can cause very high concentrations in the phreatic groundwater. Concentrations up to 700 µg/l are then possible.

Raised levels of arsenic in the soil (in the first meter below surface level) do not occur frequently. If raised concentrations in the soil are present in the coastal provinces, these are usually caused by processes taking place in deeper layers. The enrichment of arsenic is then related to bog iron or iron concretions.

An exception has to be made for upward seepage areas that are fed by deep arsenic enriched groundwater. In these areas the risk of arsenic enrichment in the stream bed

sediments is increased. When in these areas, dredged sediment is deposited on the surface, the soil will have high risk of increased concentrations of arsenic.

7.3.3 Arsenic associated to pyrite in the solid phase

Basal peat is present in the deeper subsurface of large areas of the coastal provinces. In a ‘corridor’ south of Amsterdam and in the eastern part of the province Zeeland (Figure 7.3, red encircled), the risk of high concentration of arsenic in the basal peat is increased because geological history and the local geohydrological situation in the past have contributed to the upward seepage of arsenic rich groundwater. In the remaining areas, higher concentrations of arsenic are hardly encountered in the basal peat because the conditions for regional enrichment of arsenic were not favorable. Figure 7.3 shows the regional distribution and depth of basal peat in the province of Zeeland and is based on available geological information. The basal peat was deposited directly on top of the Pleistocene deposits as a result of sea level rise as described in paragraph 1.3. For most of Zeeland, the basal peat was eroded. Most of the remaining basal peat is located at a depth of more than 5 m below surface level.

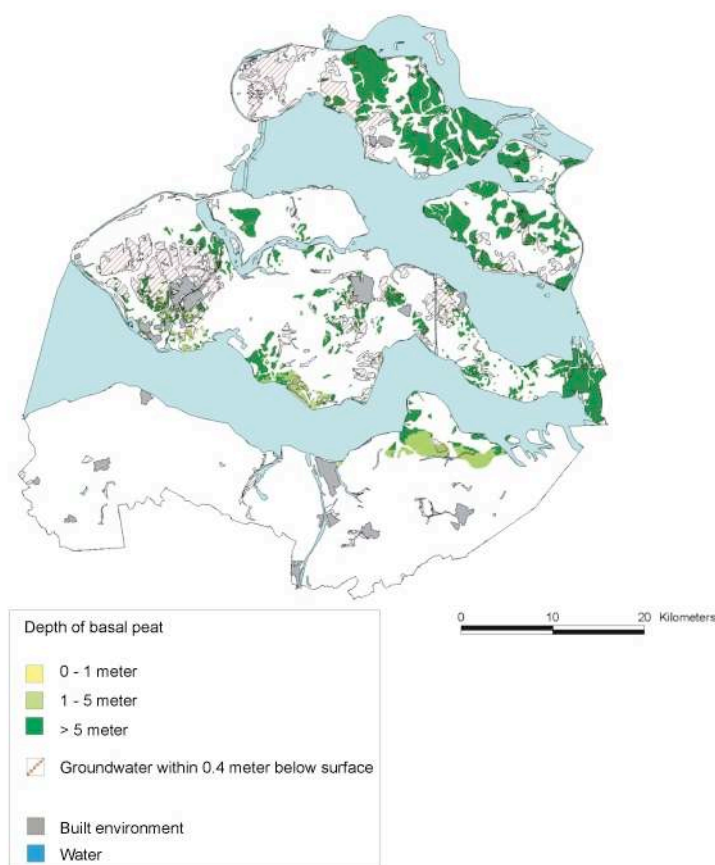


Figure 7.3 Regional distribution and depth of basal peat in Zeeland.

Where the basal peat is close to the surface, arsenic can be released by oxidation of pyrite. As a result high concentrations can be present in the groundwater (higher than the intervention value). The oxidation of pyrite is such that higher concentrations of arsenic can be encountered in groundwater for a long time (months to years). Fortunately, basal peat is present at shallow depth in only few areas.

In areas where the basal peat is excavated and oxygenated by rainwater or gets in contact with nitrate, the risk is high that increased concentrations of arsenic are encountered.

7.3.4 Arsenic associated to ironhydroxide in deep groundwater

In deeper groundwater, arsenic can be found that is associated to ironhydroxides. In locations where the conditions during the geological history were favorable for the accumulation of bog iron (Righi & Meunier, 1995), increased concentrations of arsenic are found in the deeper groundwater. South of Amsterdam, for example, these conditions were favorable for the accumulation of bog iron ores in the ice pushed ridges that were later buried by more recent deposits. These layers of bog iron ore are a constant source of arsenic. (See Figure 7.4)

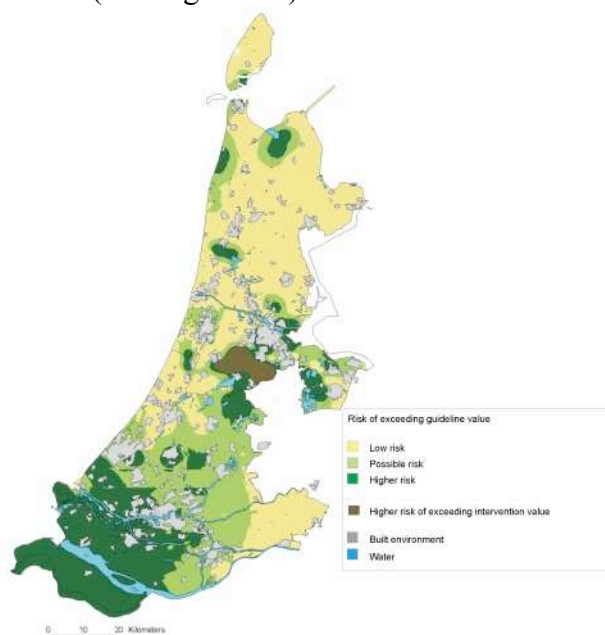


Figure 7.4 Areas with risk of exceeding guideline values of arsenic in groundwater at a depth of 5 to 15 meters below surface level.

In the interval of 5 to 15 m below surface level, the risk of exceeding the guideline value is increased in large areas. This is related to the fact that groundwater on this depth in these areas is often anaerobic. A small amount of arsenic in the solid phase, for example as coating of ironhydroxides of the sediment or as natural background value, can cause increased concentrations of arsenic in the groundwater. The risk of exceeding guidelines values was determined with a geostatistical interpolation routine (indicator kriging, Goovaerts, 1997). The geological setting was used to stratify the area into zones of comparable mechanisms for accumulation of arsenic. The resulting map gives the probability of exceeding guideline values. Areas with a probability more than 0.5 to exceed the guideline values were coded as being at high risk, while areas with probability of exceeding guideline values between 0.25 and 0.5 were coded “possible at risk”.

7.4 Effects of measures

From the above knowledge on processes, the most important mechanisms causing increased concentrations in soil and groundwater were defined. The most important

mechanism is the change of redox condition: the change from aerobic to anaerobic conditions and vice-versa. Depending on how the arsenic is fixed (associated to pyrite or iron hydroxides) changing redox conditions will release the arsenic to the groundwater.

7.4.1 Measures in areas with arsenic associated to pyrite

Pyrite is stable in anaerobic conditions, whereas it will become unstable in aerobic conditions, arsenic is then dissolved to the groundwater. Except for a delimited area south of Amsterdam and in the eastern part of the province Zeeland, the concentration of arsenic in the solid phase are low with respect to the guideline value. However if oxygen or nitrate is present, pyrite will be dissolved and arsenic released to the groundwater causing concentrations to exceed the guideline or intervention values. For this reason it is important when intervening in an area to verify if basal peat will be exposed to aerobic conditions, for example when basal peat is moved above the groundwater table (see Figure 7.5) or if the basal peat is getting in contact with nitrate rich water. In addition if the groundwater table is lowered in areas where basal peat is present near the surface, this might result in arsenic being released to the groundwater. The released arsenic can then directly get adsorbed to new formed iron hydroxides.

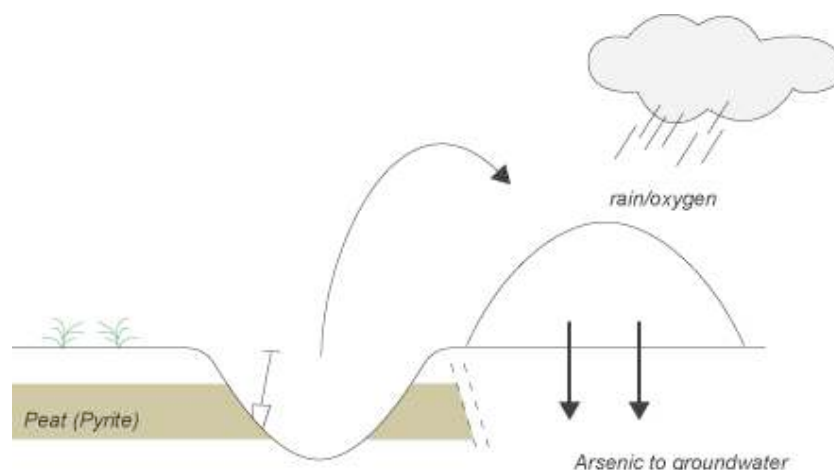


Figure 7.5 Effect of moving basal peat above the groundwater table.

7.4.2 Measures in areas with arsenic associated to iron hydroxide

Arsenic associated to iron hydroxides is released in anaerobic conditions. Concentrations of arsenic in the soil are often lower than the guideline values whereas in anaerobic conditions, the iron hydroxides dissolve with the arsenic attached to it. This happens for example when the groundwater level is raised. In phreatic groundwater, because of natural fluctuations of the groundwater level, iron hydroxides can dissolve and release arsenic, higher concentrations being measured with a higher groundwater level and lower concentrations with a lower groundwater level.

Deeper groundwater with very high concentrations of arsenic is mostly present in areas where iron and arsenic accumulated in the past. If this water is pumped and the reduced groundwater gets in contact with oxygen, iron and arsenic will rapidly precipitate to form iron hydroxides.

At locations where pumping rates are significant and initial arsenic concentrations in groundwater low, groundwater can be attracted from areas with higher arsenic concentrations depending on the local groundwater flow system.

Figure 7.6 summarizes the effect groundwater level changes on the arsenic concentration associated to pyrite or ironhydroxides in groundwater.

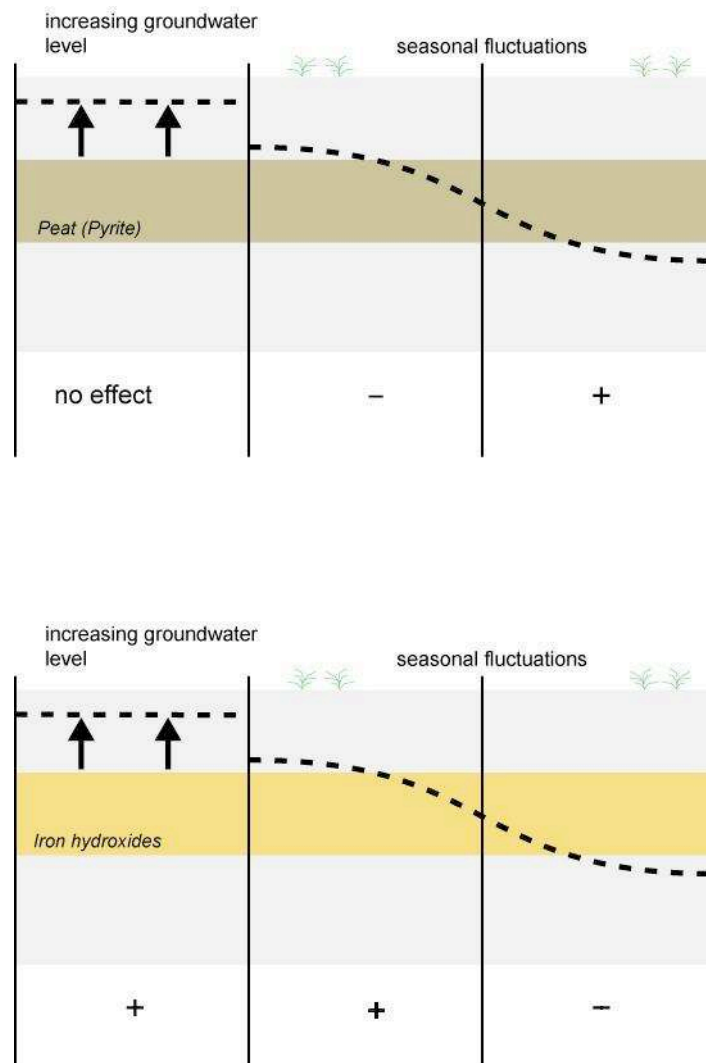


Figure 7.6 Effect of groundwater level changes on the arsenic concentration.

7.5 References

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8 Does arsenic, in groundwaters of the compound Rhine-Meuse-Scheldt-Ems delta, menace drinking water supply in the Netherlands?

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Abstract

Total arsenic concentrations of raw groundwater in the Netherlands, pumped for public drinking water supply, range from 0.1-70 µg/L. In drinking water prepared from them they range from 0.1-7 µg/L, which is below the maximum permissible concentration of 10 µg/L. In general, As is well removed by aeration and rapid sand filtration largely thanks to high natural Fe²⁺ concentrations. The arsenic content of water treatment sludges, however, frequently poses a disposal problem as the As levels classify the material as chemical waste.

Although the current situation, at the scale of well fields, is indicating that As does not menace drinking water supply, there are several situations, on a smaller scale, that are clearly pointing at a strong As mobilization (up to 1,500 µg/L) that may affect drinking water or its treatment on the long term. This field evidence derives from detailed studies of the following young hydrological systems in sandy aquifers of Quaternary age: (i) a partly decalcified, pumped aquifer system with strong agricultural inputs; (ii) artificial recharge using basins, (iii) artificial recharge using injection wells, (iv) river bank filtration, and (v) a polder system composed of a reclaimed lake surrounded by an influent eutrophic river, and underlain by Holocene peat. In a relatively 'undisturbed' coastal dune aquifer system with natural recharge in a nature reserve, As is shown to be only moderately mobilized where iron(hydr)oxides dissolve by reduction.

The most probable As mobilizing processes in systems i-v are: raised NO₃ inputs on agricultural plots underlain by a pyritiferous aquifer (i); the introduction of O₂ and NO₃ containing surface water into deep anoxic aquifers containing pyrite (ii-iii); (sub)recent changes in quality of infiltrating river water (ii, iv), especially regarding rises of PO₄, SO₄, HCO₃, DOC, F and temperature (which all contribute to desorption of As); (sub)recent sludge accumulations in infiltrating parts of lakes, rivers and recharge basins (ii, iv) where the oxidation of fresh organic matter is producing a lot of CH₄ which may reduce iron(hydr)oxides and arsenate (to arsenite), and also a lot of PO₄, HCO₃ and DOC which compete for sorption sites with As; and the reductive dissolution of iron(hydr)oxides plus desorption in peat rich polder areas (v) where the oxidation of peat is also producing elevated quantities of CH₄, PO₄, HCO₃ and DOC.

The release of sorbed As upon ageing of well incrustations from hydrous ferric oxide to goethite, suggests that this process could be significant in specific environments as well.

Key words: Arsenic, groundwater, redox environment, artificial recharge, river bank filtration, pyrite oxidation, ironhydroxide reduction, desorption, methane.

8.1 Introduction

Arsenic from natural sources, like iron minerals, can dissolve in non-thermal groundwaters in concentrations superating drinking water standards (10 µg/L) up to several thousands of µg/L. This groundwater is well known to pose serious health hazards to drinking water consumers when treatment is insufficient (Vahter, 2007). Notorious areas with problematic As concentrations in non-thermal groundwater unaffected by direct mining activities and point sources, are delta's like the ones in Bangladesh, West Bengal and Vietnam (Smedley & Kinniburgh, 2002). These areas combine several hydrogeochemical triggers to mobilize As, with a (past) hydrogeological regime to keep the As within the system. The main triggers there are: reductive desorption from and reductive dissolution of iron(hydr)oxides, desorption under oxidizing conditions, and pyrite oxidation. A favourable (past) hydrogeological regime consists of young fluvial, deltaic or estuarine sedimentary deposits containing abundant iron(hydr)oxides, pyrite and unstabilized organic material, without previous extensive periods of leaching.

Also the Netherlands consist for a large part of delta's, built today by, in order of decreasing surface area and river discharge, the Rhine, Meuse, Scheldt and Ems rivers (Figure 8.1). Both the hydrogeochemical triggers and the hydrogeological regime seem to be favourable to yield high As concentrations in groundwater. It is therefore interesting to understand why arsenic is not causing problems (yet) with drinking water supply, and what could be the impact of elevated As levels that have been observed in some well defined, fresh groundwater flow systems, both natural and man-made.

8.2 Material and methods

Groundwater has been analysed in samples from well fields and dedicated observation wells in the period 1980-2006, during various national, regional and local surveys.

The samples from well fields derive, in each case, from the mixed, raw water pumped by a cluster of pumping wells for local or regional drinking water supply. This raw water and the drinking water prepared from it, are monitored by each water utility on a frequent basis on a minimum set of water quality parameters, following governmental rules. The resulting data are stored in a centralized data base (KIDAP) managed by Kiwa Water Research. Most pumping wells consist of a PVC well screen, on average 10-60 m long, and a PVC riser 10-100 m long.

The samples from observation wells derive from individual PVC piezometers with a 0.2-2 m long well screen, or from PE miniscreens (0.01 m) attached to a piezometer.

As the well field is always producing groundwater, the only specific rules for its sampling consist of the right timing (when a very representative set of wells is operating) and a sufficient flushing of the sampling port on the well head or transport main. Prior to sampling an observation well, the water contents of well screen plus riser were evacuated at least 3 times and until a stable specific electrical conductivity (SEC) was attained. Temperature, pH, SEC and O₂ were normally measured in the field.

Sample conservation for cations and trace elements incl. total As consisted of filtration over 0.45 µm membrane filter, acidification by 65% HNO₃ suprapure (0.7 mL/100 mL), and storage in the dark at 4°C. Macroparameters (like major cations and anions, and DOC) were analysed using conventional, well standardized techniques by certified laboratories. Total arsenic (in solution) was analysed through either AAS hydride with

graphite furnace (limit of quantification [LOQ] 0.5-1 µg/L), or ICP-MS (LOQ 0.1-0.5 µg/L).

The redox state of each sample was determined on the basis of all redox sensitive main components of water, i.e. O₂, NO₃, SO₄, Fe, Mn, CH₄ and H₂S, following the scheme in Table 8.1. The redox clustering ((sub)oxic, anoxic and deep anoxic or mixed) in Table 8.1 is used here because of lack of sufficient data on O₂, CH₄ and H₂S. It can be assumed that in (sub)oxic environment As(V) as H₂AsO₄³⁻ or HAsO₄³⁻ will be dominant, and in deep anoxic environment As(III) as H₃AsO₃.

8.3 Arsenic from well fields in the Netherlands

8.3.1 Drinking water supply in the Netherlands

A centralized, public drinking water supply started in the Netherlands in 1853 with the pumping of phreatic dune groundwater. The increasing population and water consumption per capita raised the water demands from 70 Mm³/y in 1900 to 1,250 Mm³/y in 2000, and the connectivity to tap water from 20 to 99.9%. The 1,250 Mm³ of drinking water prepared in 2000, was composed of 6 types of water resources, in decreasing order: 440 Mm³ of (semi)confined groundwater from sandy aquifers, 335 Mm³ of phreatic groundwater from sandy aquifers, 232 Mm³ of directly purified surface water, mainly from the rivers Rhine and Meuse, 161 Mm³ of artificially recharged Rhine and Meuse river water, 55 Mm³ of Rhine bank infiltrate, and 27 Mm³ of groundwater from Cretaceous limestone.

Table 8.1 Practical criteria for determination of the redox environment of a water sample (modified after Stuyfzand, 1988). Concentrations in mg/L.

Level	Environment	Criteria						
		O ₂	NO ₃ ⁻	Mn ²⁺	Fe ²⁺	SO ₄ ²⁻	H ₂ S #	CH ₄
0	Oxic	O ₂ ≥ 0.9 (O ₂) _{sat}		< 0.1	< 0.1	≥ 0.9 (SO ₄) _o	no	< 0.1
1	Penoxic (O ₂ -reducing)	1 ≤ O ₂ < 0.9 (O ₂) _{sat}		< 0.1	< 0.1	≥ 0.9 (SO ₄) _o	no	< 0.1
2	Suboxic (NO ₃ -red)	< 1	≥ 1	< 0.1	< 0.1	≥ 0.9 (SO ₄) _o	no	< 0.1
3	Transition (Mn-red)	< 0.5	< 0.5	≥ 0.1	< 0.1	≥ 0.9 (SO ₄) _o	no	< 0.1
4	Sulphate-stable (Fe-red)	< 0.5	< 0.5		≥ 0.1	≥ 0.9 (SO ₄) _o	no	< 0.1
5	Sulphate-reducing	< 0.5	< 0.5			A	yes	< 1
6	Methanogenic	< 0.5	< 0.5			B		≥ 1
Redox clusters:		O ₂	NO ₃ ⁻	Mn ²⁺	Fe ²⁺	SO ₄ ²⁻	H ₂ S #	CH ₄
0-2	(sub)oxic	≥ 1 or	≥ 1	< 0.1	< 0.1		no	< 0.1
3-4	anoxic	< 0.5	< 0.5		≥ 0.1	≥ 0.9 (SO ₄) _o	no	< 0.5
5-6	deep anoxic	< 0.5	< 0.5			C	yes	≥ 0.5
M	mixed @	≥ 1 or	≥ 1	≥ 0.15 or	≥ 0.2 or			> 0.1

#: yes/no = yes/no H₂S-smell in field; A = 0.1{SO₄}_o < SO₄²⁻ < 0.9{SO₄}_o if Cl⁻ ≤ 300 mg/L and else 0.5{SO₄}_o ≤ SO₄²⁻ < 0.9{SO₄}_o;

B = SO₄²⁻ ≤ 0.1{SO₄}_o or SO₄²⁻ ≤ 3, if Cl⁻ ≤ 300 mg/L or SO₄²⁻ < 0.5{SO₄}_o if Cl⁻ > 300 mg/L;

C = SO₄²⁻ ≤ 0.9{SO₄}_o or SO₄²⁻ ≤ 3, if Cl⁻ ≤ 300 mg/L, with {SO₄}_o = original SO₄²⁻ concentration in mg/L.

{O₂}_{sat} = 14.594 - 0.4 t + 0.0085 t² - 97 10⁻⁶ t³ - 10⁻⁵ (16.35 + 0.008 t² - 5.32/t) Cl⁻, in which t = temp. in °C and Cl in mg/L.

@: sample composed of a mix of water from different redox environments

8.3.2 Groundwater from well fields

The 5 above mentioned groundwater types, in total ca. 1,000 Mm³ in 2000, were abstracted on 221 well fields. Total arsenic concentrations in these raw groundwaters ranged from 0.1-70 µg/L in the period 1989-2002, without clear trends. The spatial distribution of arsenic is indicated in Figure 8.1, the mean composition of the 5

groundwater resources in Table 8.2. The mean values for each groundwater type (0.3 – 3 µg/L) are quite low, but there are 6 well fields with As concentrations >10 µg/L (Figure 8.1). These higher concentrations are observed in anoxic sand aquifers and deep anoxic river bank filtration systems. The maximum value at Oostrum (Figure 8.1) is associated with pyrite oxidation through excessive manure and fertilizer applications on an agricultural catchment area (Broers & Buijs, 1997). This situation is encountered in more well fields, like in Vierlingsbeek (a phreatic well field) which is discussed in detail in section 4 ad site 2.

Relatively high As concentrations (>5 µg/L) also correlate with abstraction from glauconitic sand aquifers of Late Tertiary age. The exact mechanism behind this correlation is still unclear (Flink, 1985; Coetsiers, 2007), but seems to involve the reductive dissolution of iron. Well fields pumping from Cretaceous limestone and those with artificial recharge typically have low As concentrations (Table 8.2).

There are no clear relations between As on the one hand and PO₄, SO₄, HCO₃, Fe, Cl, Mn and DOC on the other hand (Figure 8.2; Cl, Mn and DOC not shown). Maximum concentrations correspond with pH 6-7.5 (Figure 8.2), NO₃ < 2 (Figure 8.2) and screen depths of 0-50 m-MSL (Figure 8.4, left).

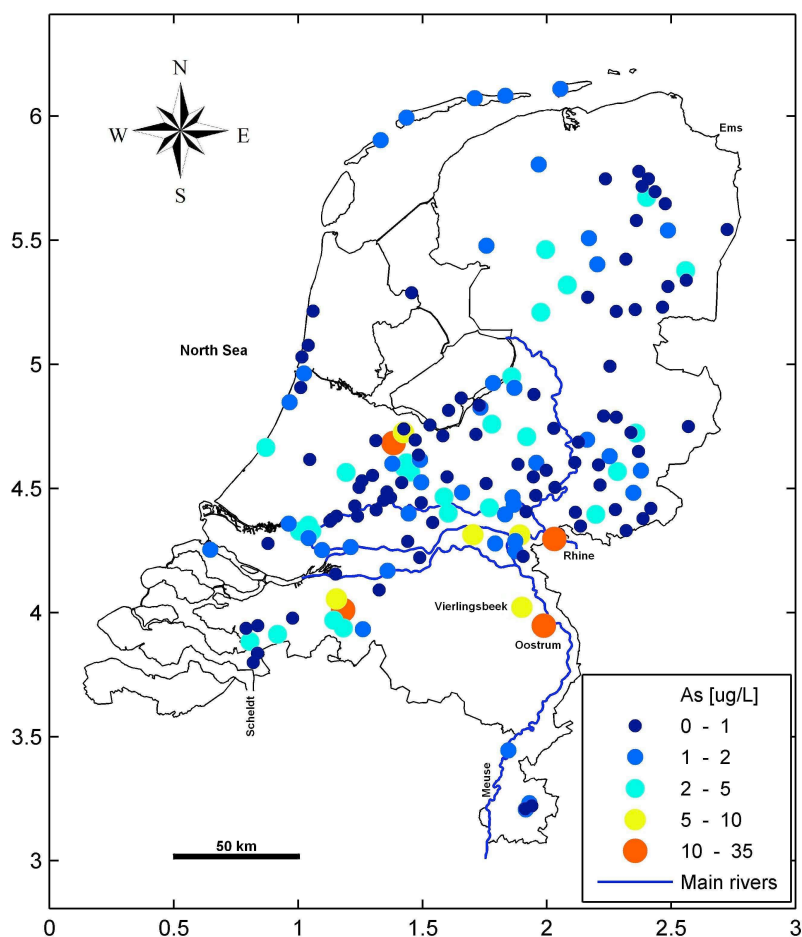


FIGURE 8.1 Mean total arsenic concentration in the raw water from 221 well fields and 16 surface water treatment plants, for public drinking water supply in the Netherlands, in the period 1989-2002. Mean = average of annual mean concentration.

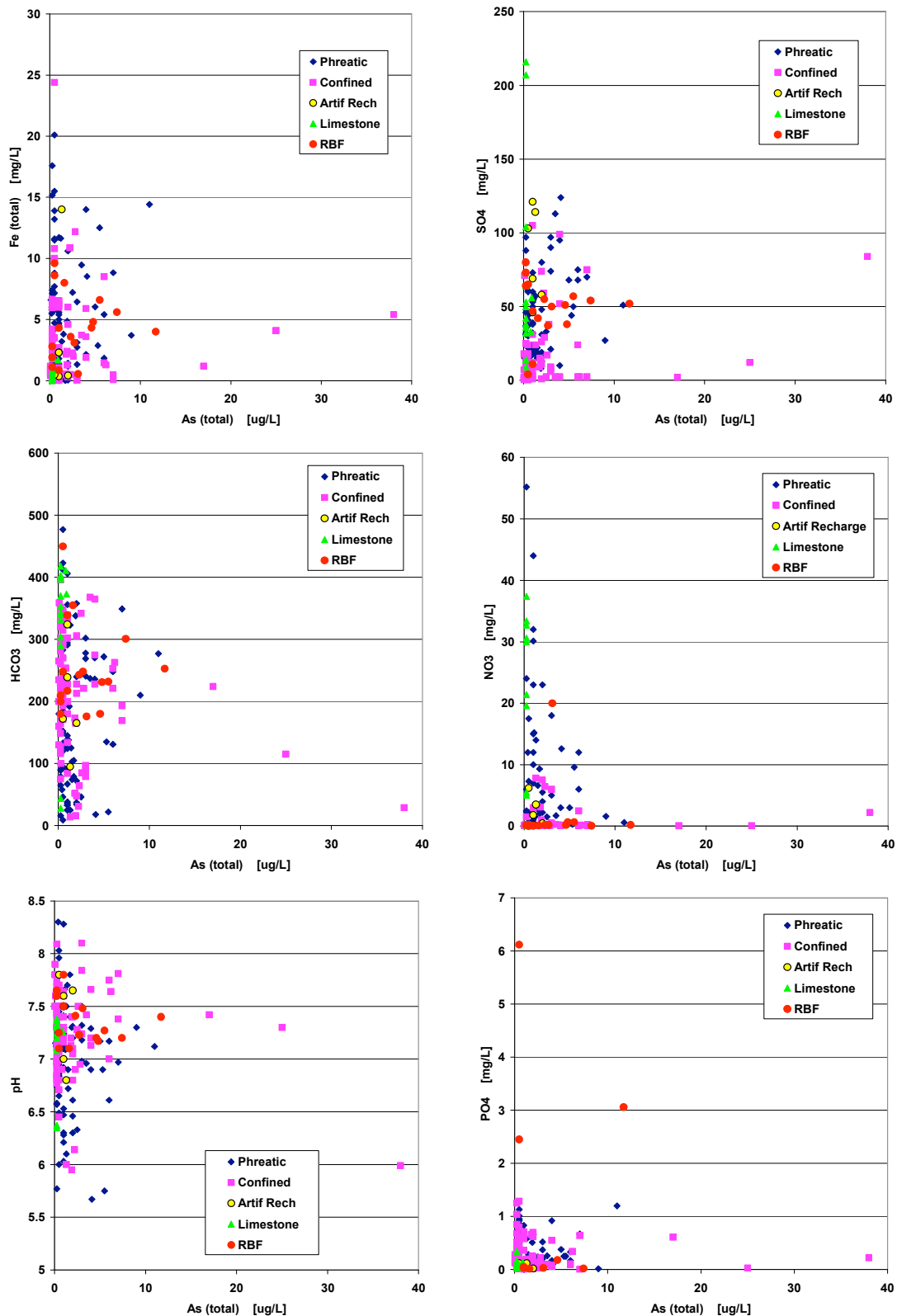


Figure 8. 2 Plots of total dissolved arsenic versus various inorganic macroparameters in raw water for all well fields in the Netherlands in 1989 (for public drinking water supply).

Table 8.2. The 5 well field types in the Netherlands (for public drinking water supply), with some characteristics and their mean chemical composition (period 1989-2002) incl. the maximum total As concentration encountered in the raw water of a well field in a specific year. In reverse video: maximum values. LS = Land Surface.

Parameter	Unit	Well field type				
		Phreatic	Confined	Artif Rech	Limestone	RBF
Number	n	98	86	6	15	16
Q (sum/type)	Mm ³ /a	335	440	161	27	55
Well screen	m - LS	32-65	63-125	8-30	23-74	28-69
SO ₄	mg/L	33.9	14.5	85.2	68.5	48.8
NO ₃	mg/L	5.2	0.8	2.1	14.4	1.4
PO ₄	mg/L	0.33	0.30	0.09	0.11	1.33
HCO ₃	mg/L	174	222	199	317	254
Fe	mg/L	4.38	3.29	3.31	0.50	4.36
As	ug/L	1.6	2.0	1.1	0.3	3.0
As-max	ug/L	11	70	2	1	12

Especially phreatic well fields, well fields with artificial recharge and those in limestone frequently show a mixed redox status (both NO₃ and Fe high; Table 8.2). The mixing of (sub)oxic with (deep) anoxic groundwater in most cases results in well clogging by precipitation of iron(hydr)oxides on the screen slots (Houben & Treskatis, 2007; Stuyfzand, 2007). These incrustations also contain As, but upon ripening to goethite As is remobilized (Figure 8.3). The coprecipitation of As leads to negligible losses of As, and the remobilization to negligible gains in the raw groundwater pumped.

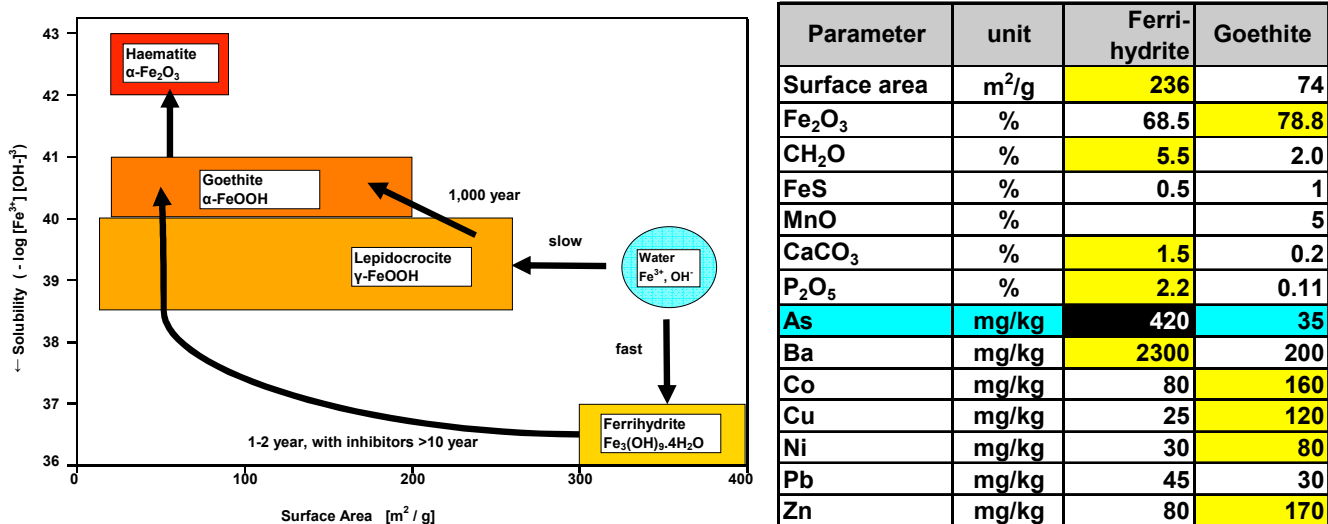


Figure 8.3 Chemical ripening (left) and composition of ferric well incrustations (right). Based on data in Houben & Treskatis (2007). Recrystallization (chemical ripening by loss of water) of fresh ferrihydrite (general) or lepidocrocite (rare) leads to the formation of goethite (general) and ultimately hematite (rare). In well incrustations, the fresh ferrihydrite shows higher As contents than goethite ripened from that ferrihydrite.

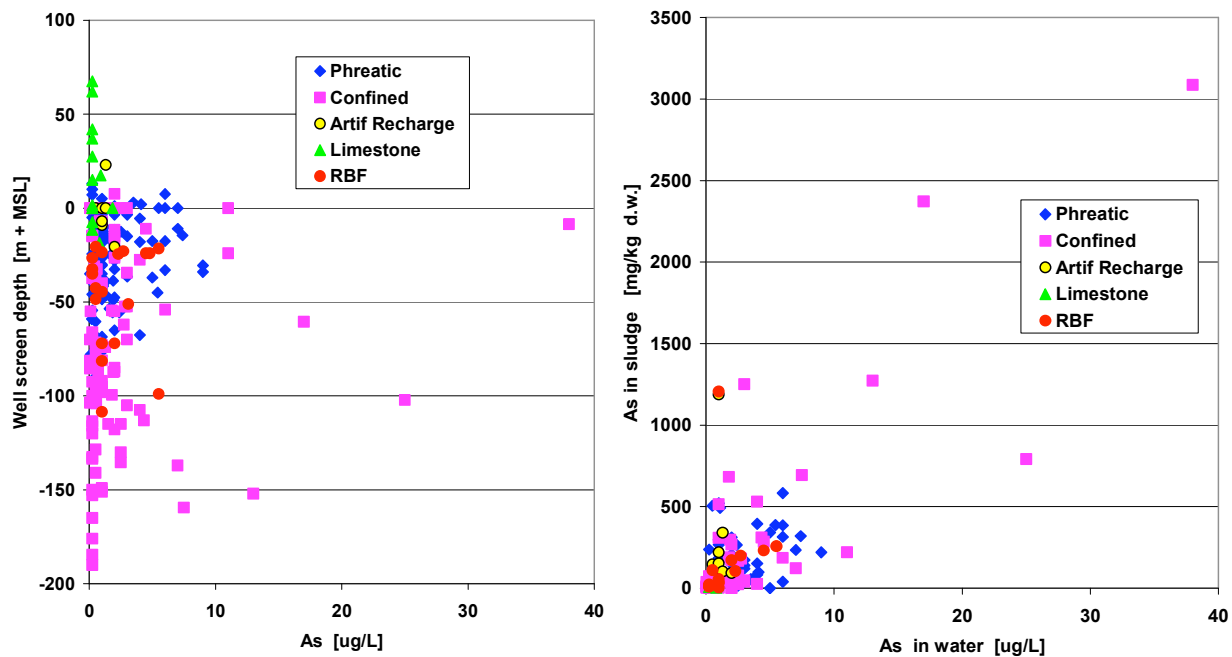


Figure 8.4 Plot of total dissolved As versus resp. depth of well screen in 1989, and As in sludge, for all well fields (for drinking water supply) in the Netherlands. Data from files Kiwa Water Research.

8.3.3 Drinking water

In drinking water arsenic concentrations range from 0.1 to 7 $\mu\text{g/L}$, which is below the maximum permissible concentration of 10 $\mu\text{g/L}$. In general, As is well removed by aeration and rapid sand filtration, largely thanks to high Fe^{2+} concentrations (0.01-25 mg/L). The arsenic content of water treatment sludges, thereby, frequently poses a disposal problem as the As levels (10-3100 mg/kg d.w.) often classify the material as chemical waste (>55 mg/kg d.w.). Arseniferous ferric sludges are, however, used for making construction bricks, thus alleviating the disposal problem. There is a weak but significant positive correlation between the As concentration in raw groundwater and the As content of water treatment sludge (Figure 8.4, right).

8.4 Arsenic behavior in selected hydrological systems

Arsenic concentrations much higher than the maximum of 70 $\mu\text{g/L}$ in the raw water of well fields, have been observed in selected parts of fresh groundwater flow systems in the Netherlands. These localized anomalies can be important for predicting future trends in the As concentration of raw groundwater from well fields, and for understanding the processes of As mobilization. In the following we therefore present the results of detailed field studies of the following fresh groundwater systems in sandy aquifers of Quaternary age: (1) a coastal dune aquifer system near Zandvoort, with natural recharge in a nature reserve, (2) a partly decalcified aquifer system near Vierlingsbeek, with high agricultural nitrate inputs, (3) anoxic river bank filtration near Opperduit, (4) deep anoxic river bank filtration in the Hollandsch Deep, (5) a shallow polder system near Amstelveen, (6) an artificial recharge system using pretreated Rhine River water and basins, near Zandvoort, (7) ditto using pretreated Meuse River water and basins near The Hague, and (8) an artificial recharge system using injection wells, near Langerak. The location of these study sites is indicated in Figure 8.5.

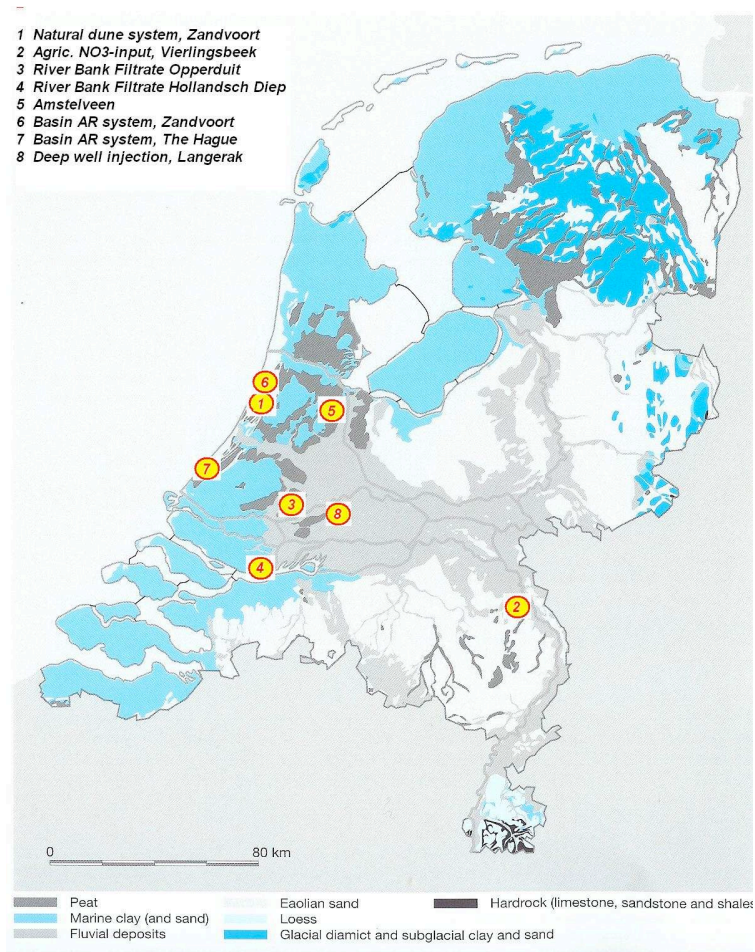


Figure 8.5 Site map showing the 8 study sites with detailed information regarding As behavior. Geological background derived from Dufour (2000).

Site 1: a natural, coastal dune aquifer system near Zandvoort

The hydrochemical evolution of dune groundwater is presented in Figure 8.6, for a flow path from its relatively undisturbed recharge area in the calcareous dunes south of the town of Zandvoort, to its exfiltration in the Haarlemmermeer polder, a former lake reclaimed in 1852. Further details about this study are given by Stuyfzand (1993a, 1993b).

It can be concluded from Figure 8.6 that As is mobilized when the water becomes anoxic (immediately after all NO₃ disappeared) and Fe²⁺ is dissolving from abundant iron(hydr)oxides in Holocene marine deposits. The lack of concomitant peaks in SO₄ or Ni indicates that pyrite oxidation is not taking place. Further downgradient, in a deep anoxic environment (with sulphate reduction) As seems to coprecipitate with neoforming pyrite. Interestingly, in this system As peaking is typically preceded by natural U peaking (Stuyfzand, 1993b).

Relatively high As concentrations (>10 µg/L) in the coastal dune area (without artificial recharge) are only observed in the upper few meters of groundwater where the groundwater table rose during the past decades by several meters, very close to land surface (0-0.3 m) in areas that were used for extensive farming in the 19th-20th century

(Stuyfzand, 1993b). In these cases the redox system changed from oxic, unsaturated to deep anoxic, saturated, and iron(hydr)oxides reductively dissolved.

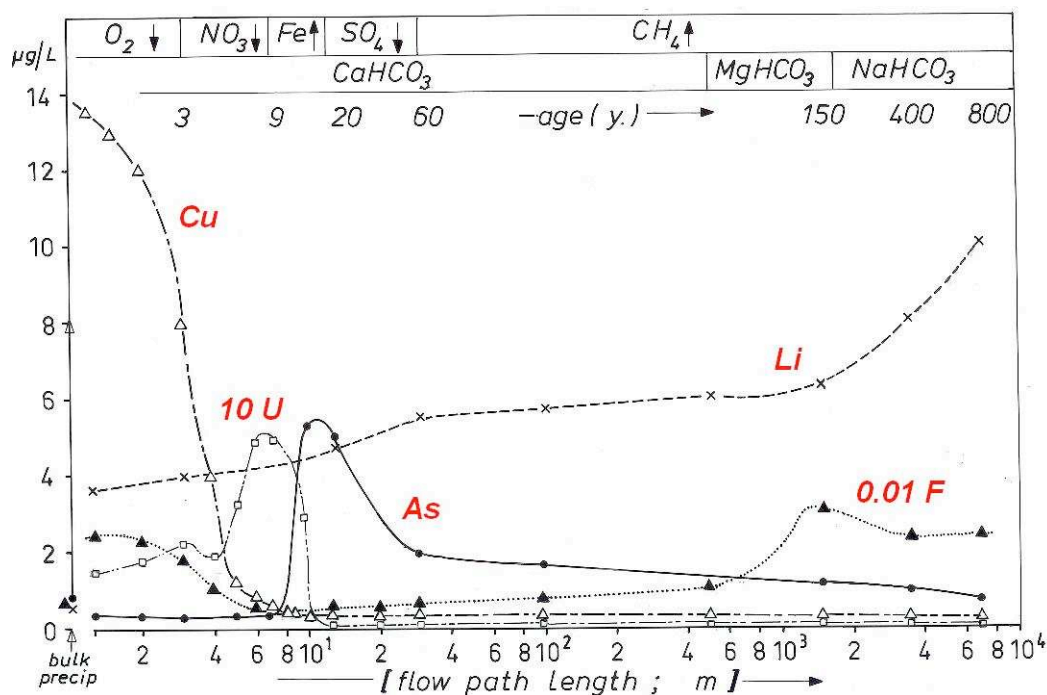


Figure 8.6 Site 1: Changes in trace elements (incl. total As) in coastal dune groundwater along a flow path from infiltration area (calcareous dunes) to exfiltration area in the reclaimed lake Haarlemmermeer (after Stuyfzand, 1993a). Redox zones, chemical watertype and groundwater age indicated at top.

Site 2: a natural aquifer system near Vierlingsbeek, with strong agricultural inputs

Near the town of Vierlingsbeek (Figure 8.5) a phreatic well field is pumping 3-5 Mm³/a of groundwater since its start in 1965. Its water catchment area is dominated by agriculture with excessive applications of manure and fertilizers. The resulting high nitrate inputs are responsible for a very significant oxidation of pyrite which is present below 1 m+MSL (Van Beek & Van der Jagt, 1996).

The spatial distribution of groundwater types (classified according to Stuyfzand, 1986), along a section across 3 miniscreened observation wells (NP.1-3) and one pumping well, is shown for 1986 in Figure 8.7 (left). We conclude that agricultural impacts are limited to the upper 20-25 meters in the sandy aquifer overlying the finer grained layer at 4-12 m-MSL. CaNO₃ water dominates in the upper 10 meters up to a distance of ca. 500 m from the pumping well. Downgradient of this high nitrate water (up to 330 mg/L) and from 10 to 20 m below the groundwater table CaSO₄ water takes over. The groundwater is (sub)oxic (NO₃ >1 mg/L) to a depth of ca 1 m+MSL and then turns anoxic mainly by reaction with pyrite. Reaction with pyrite has progressed most in observation well NP.1 where SO₄ and As reach their maximum concentrations of resp. 250 mg/L and 80 µg/L. Together with As also Co, Ni and Zn are clearly mobilized. Geochemical investigations of the pyrite confirmed that the pyrite contains significant amounts of As, Co, Ni and Zn (see Eq.2 in section 5).

The deeper, unpolluted groundwater at Vierlingsbeek, below 10 m-MSL still contains significant amounts of As but hardly Co, Ni and Zn. This As (mostly 10-20 $\mu\text{g/L}$) is associated with glauconitic sand, as discussed in section 3.

The As concentration of the mixed, raw groundwater from either pumping well 276 (9 $\mu\text{g/L}$) or the whole well field of Vierlingsbeek (5 $\mu\text{g/L}$) is relatively low thanks to mixing with shallow suboxic groundwater low in As.

The Vierlingsbeek case is quite representative for those phreatic and relatively shallow, semiconfined well fields in the Netherlands, that receive high agricultural NO_3 inputs on a pyritiferous aquifer system.

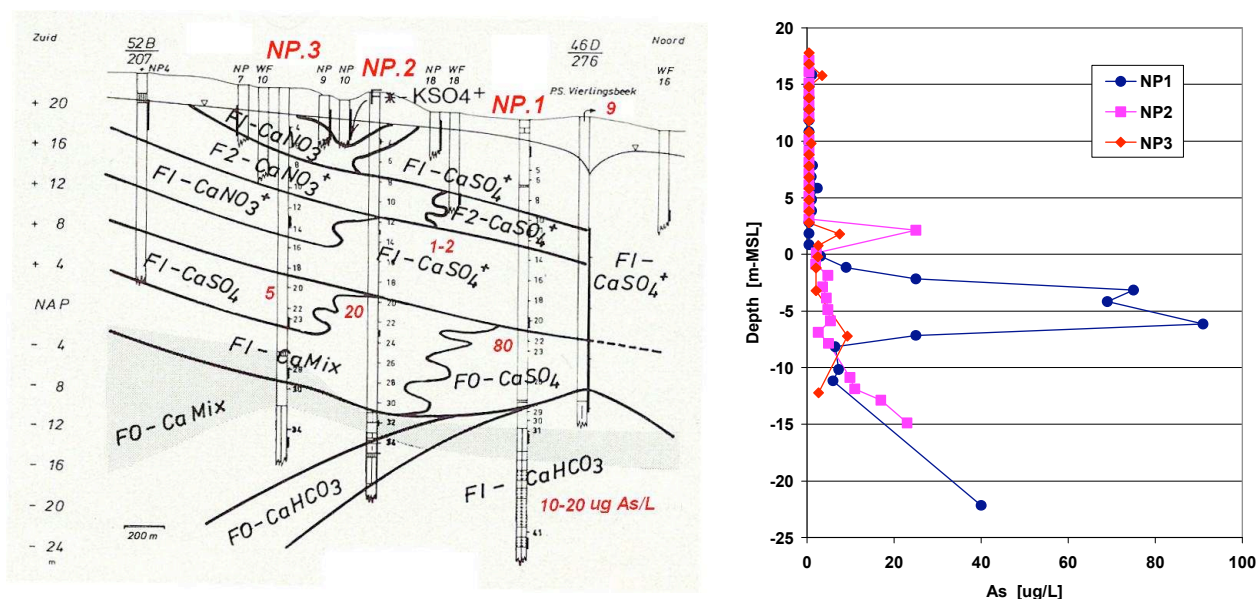


Figure 8.7 Site 2. Left: Spatial distribution of chemical watertypes and As concentrations in a section across 3 miniscreened observation wells (NP.1-3) and pumping well 276 of well field Vierlingsbeek (modified after Stuyfzand, 1986). Right: As depth log of observation wells NP.1-3 in 1988 (data obtained from Van Beek, pers. comm). NAP = Mean Sea Level (MSL).

Watertype codes: F = fresh ($\text{Cl} < 150 \text{ mg/L}$); 0-2 = total hardness, resp. 0.5-1, 1-2 and 2-4 mmol $\text{Ca}+\text{Mg/L}$; + = significant surplus of $\text{Na}+\text{K}+\text{Mg}$ with respect to atmospheric input (see Stuyfzand, 1986).

Site 3: anoxic, Rhine River bank filtrate near Opperduit

Near the town of Opperduit, along the Lek River (a tributary of the Rhine River), river bank filtration is driven already for centuries by a deep polder to the north, which is constantly drained by ditches. In the 1980s and 1990s a row of observation wells equipped with miniscreens (Figure 8.8) was sampled for extensive chemical analysis, details of which are given by Stuyfzand et al. (2006). All samples along the flow path depicted in Figure 8.8 (left) were anoxic ($\text{O}_2 = \text{NO}_3 = 0$; SO_4 unaltered), but the upper and lower parts of the main aquifer and parts below the recent sludge layer were deep anoxic (showing SO_4 -reduction and methanogenesis).

The trace elements As, Co, Cu, Ni and Pb showed breakthrough fronts, in 1983, within the first 40 m of flow (Figure 8.8, right). These fronts indicate a clear immobilization for 2 reasons: (a) the input levels of these trace elements in dissolved state was quite high in the period 1960-1980, as shown for As in the inset in Figure 8.8 (right), and (b) groundwater travel times were short (<1 year). The most probable retention mechanism is adsorption, although their precipitation as sulphides cannot be completely excluded. The SO₄ concentrations point at an anoxic redox environment (without SO₄-reduction), but low H₂S levels that hardly affect total SO₄ concentrations may already suffice for some precipitation of metal sulphides to take place. Arsenic behaves different from amongst others Co and Ni, by showing a clear mobilization peak (Figure 8.8) right below the recent fluvial sludge layer indicated in Figure 8.8 (left). This sludge layer formed in between groins that protect the town of Opperduit from river bank erosion, and is probably a very significant direct source of As, reductive solutes like DOC and CH₄, and a source of desorbents like PO₄, H₄SiO₄ and DOC.

The Opperduit case is probably representative for intergroin sedimentation areas and other accumulation areas of fluvial sludge (for instance in gravel pits and closed meanders), with anoxic conditions. The next site (4) can be considered as a more extreme situation with deeper anoxic conditions.

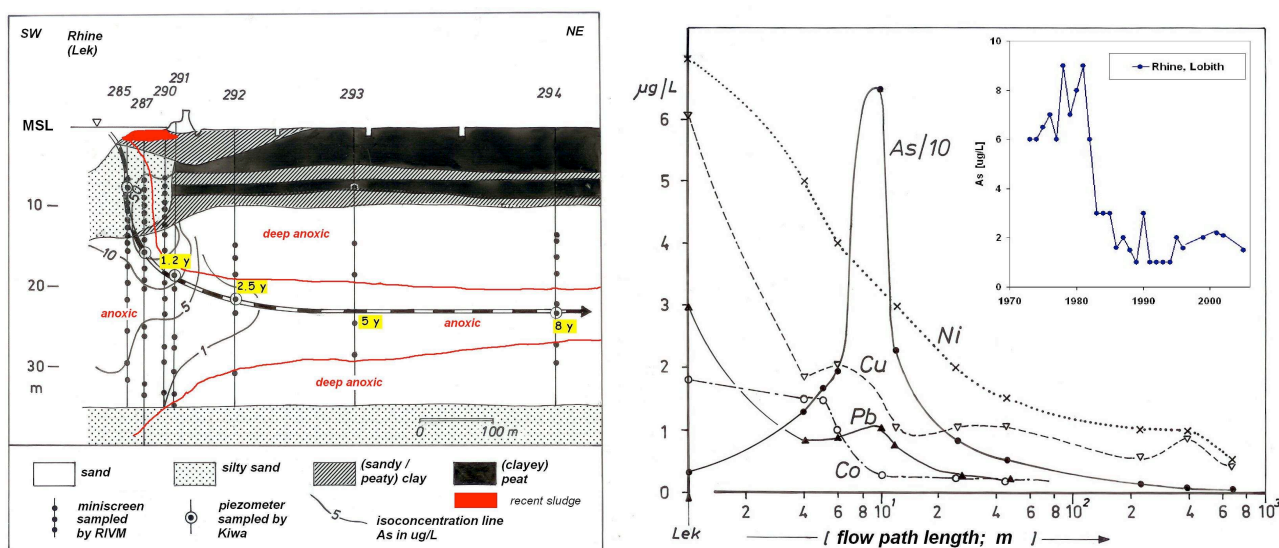


Figure 8.8 Site 3 (after Stuyfzand et al., 2006). Left: Position of the studied flow path of river bank filtrate from the Lek River to observation well 294, in a (semi)confined, Pleistocene sand aquifer, with isoconcentration lines of total As; Right: Changes of dissolved total trace element concentrations along the flow path shown left, with in the inset, As input of Rhine River (dissolved fraction).

Site 4: deep anoxic, river bank filtrate in the Hollandsch Diep

Estuarine water in the Hollandsch Diep is mainly composed of Rhine and Meuse River water (in 1997 resp. ca. 72 and 28%). At the study site (Figure 8.9, left) tidal influences were active before closure in November 1970 of the estuary outlet (Haringvliet) by a dam with sluices, as part of the famous ‘Delta Works’. In addition, the discharge of the rivers Rhine and Meuse has been partly diverted, so that the reduced dynamics since 1971 on this site provoked the deposition of a 0.2-4 m thick sludge layer on top of the sandy river bed at the northern part of the estuary (Figure 8.9, left). The presence of a

deep polder (land surface at 1.6 m-MSL), bordering the northern estuary bank beyond the strip of land shown in Figure 8.9 (left), necessitates a continued pumping of exfiltrating groundwater, and thus contributes significantly to the infiltration of the estuarine surface water since about 1600 AD.

Mainly as a result of the genesis of river bank filtration around 1600 AD, the closure of the estuary outlet in 1970 and the hydrogeological structure of the area, an intricate spatial pattern of generic groundwater types developed, as shown in Figure 8.9 (right). Further details about their genesis are given by Stuyfzand et al. (2005, 2006).

The chemical composition of 4 groundwater types is presented in Table 8.3. We conclude that they are all deep anoxic (with high CH₄ concentrations in B, C and F), and that types B and C, which had most contact with the recent sludge layer, are quite exceptional in their chemical composition, showing unusually high concentrations of a.o. Ca, HCO₃, DOC, CH₄, NH₄, Mg, K, Fe, Br, As and B. The most prominent reaction in this sludge layer is the oxidation and fermentation of labile organic matter. In this situation it is highly probable that the As derives from reducing iron(hydr)oxides in and below the sludge layer. There is no association of high As with high PO₄ concentrations (Table 8.3), because PO₄ deriving from the extensive oxidation and fermentation of labile organic matter is likely precipitating as calcium phosphate (water extremely supersaturated).

The Hollandsch Diep case is representative for many more areas in the Netherlands where rivers have been dammed and/or lakes formed, with resulting thick accumulations of deep anoxic sludges.

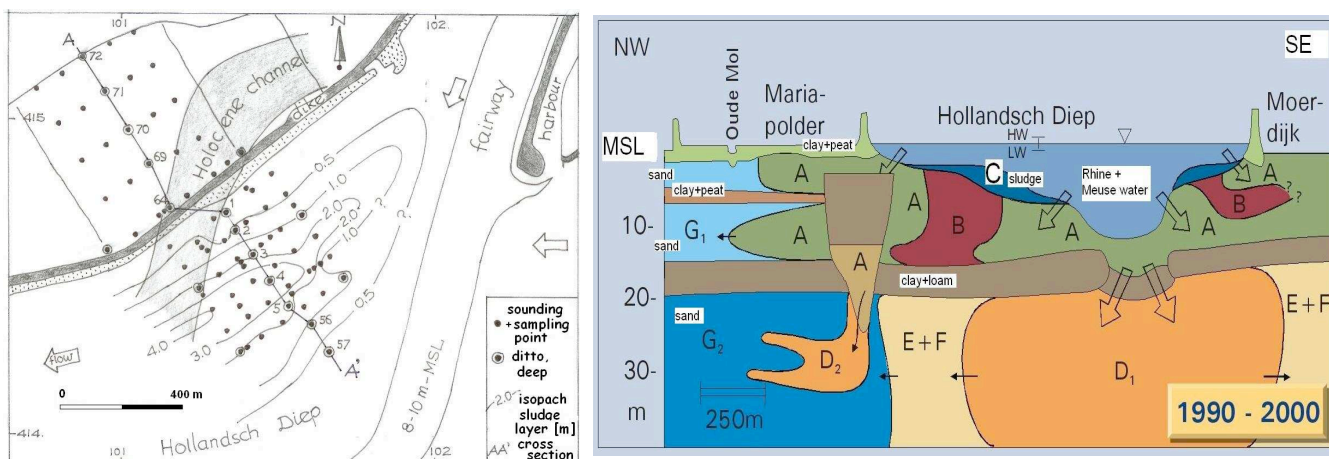


Figure 8.9 Site 4 (modified after Stuyfzand et al., 2005). Left: Situation of the study area showing all groundwater sampling points, the distribution and thickness of the recent sludge layer, the fairway which is dredged for shipping and a Holocene tidal channel fill which is clayey at the top and sandy at its base. Right: Cross section AA' over the study area extended to the opposite river bank, with the spatial distribution of generic groundwater types (A-G) anno 1997. Types B and C contacted the thick sludge layer that formed after 1970.

Table 8.3 Mean composition of 4 types of River Bank Filtrate (RBF) resulting from different interactions with recent sludge deposits in the Hollandsch Diep (Rhine-Meuse estuary at site 4). Modified after Stuyfzand et al. 2006.

Parameter	Unit	Input	RBF - watertype			
		Holl Diep	A	C	B	F
Sludge @	m	0	0.2-0.5	3.5	1-2.5	0
Depth #	m-LS	0	6	9	14	22
Recharge	period	1996	1960-1998	1972-1998	1972-1992	1920-1952
pH	-	8.2	7.45	6.8	6.99	6.99
DOC	mg/L	2.9	6	33	23	9
TIC	mmol/L	2.72	4.74	54.1	23	13.4
CH4	mg/L	<0.01	0.1	>>19	>16	20
Cl	mg/L	146	110	260	130	330
SO4	mg/L	65	18	<1	<1	<1
HCO3	mg/L	162	265	2400	1120	650
NO3	mg/L	16.1	<0.1	<0.1	<0.1	<0.1
PO4-ortho	mg/L	0.31	5.51	0.46	0.49	0.21
Ca	mg/L	75	88	230	190	87
Mg	mg/L	12.9	11	110	40	59
NH4	mg/L	0.19	3	230	53	15
Fe	mg/L		2	36	39	4
Mn	mg/L		0.6	0.5	3	0.2
SiO2	mg/L	4.7	27	16	18	24
As	ug/L	<2	6	81	413	0.6

@ = thickness of sludge layer formed after 1970, which the RBF passed; # = below river bed

Site 5: a shallow polder system south of Amsterdam

In several polder areas south of the town of Amsterdam, Van Rossum (1998) observed elevated concentrations of As especially in the upper 50 m. of groundwater (Figure 8.10, left), and high As contents of some perimarine clays and especially of the so-called basal peat (Figure 8.10, right), both of Holocene age. The high As concentrations (10-800 µg/L) are limited to anoxic high SO₄ and deep anoxic low SO₄ groundwater, and do only moderately correlate with Fe, HCO₃, PO₄ or NH₄ (CH₄ not analysed; Van Rossum, in prep.), as in case of the well fields (section 3). The high As content of the Holocene deposits seems to connect with their position in the main exfiltration area of fresh groundwater from nearby, ice pushed hills or the postglacial cover sand area (Van Rossum, 1998).

The polder flow system depicted in Figure 8.10 (right) originated around 1700 AD. The continuous drainage of the deep Bovenkerkerpolder changed groundwater flow from a semistagnant state to a rather intense flow from the Amstel River and connected lakes, and topographically higher peat lands (shallow polders) to the deep polder. The drainage water from the shallow and deep polders is very eutrophic mainly due to peat oxidation, and is discharged through pumps to the Amstel River. This influent river which is composed for a large part of eutrophic Rhine River water, is thus further enriched in nutrients.

The As mobilization in the area is probably caused by local pyrite oxidation, and a more regional, reductive dissolution of iron(hydr)oxides in the Holocene sediments and underlying Pleistocene sediments, desorption of As(V) through raised concentrations of PO₄, H₄SiO₄, HCO₃, SO₄ and DOC, and reduction of As(V) to As(III). Peat digging in

the area may have contributed to the oxidation of arseniferous pyrite (Vermooten & Gunnink, this issue).

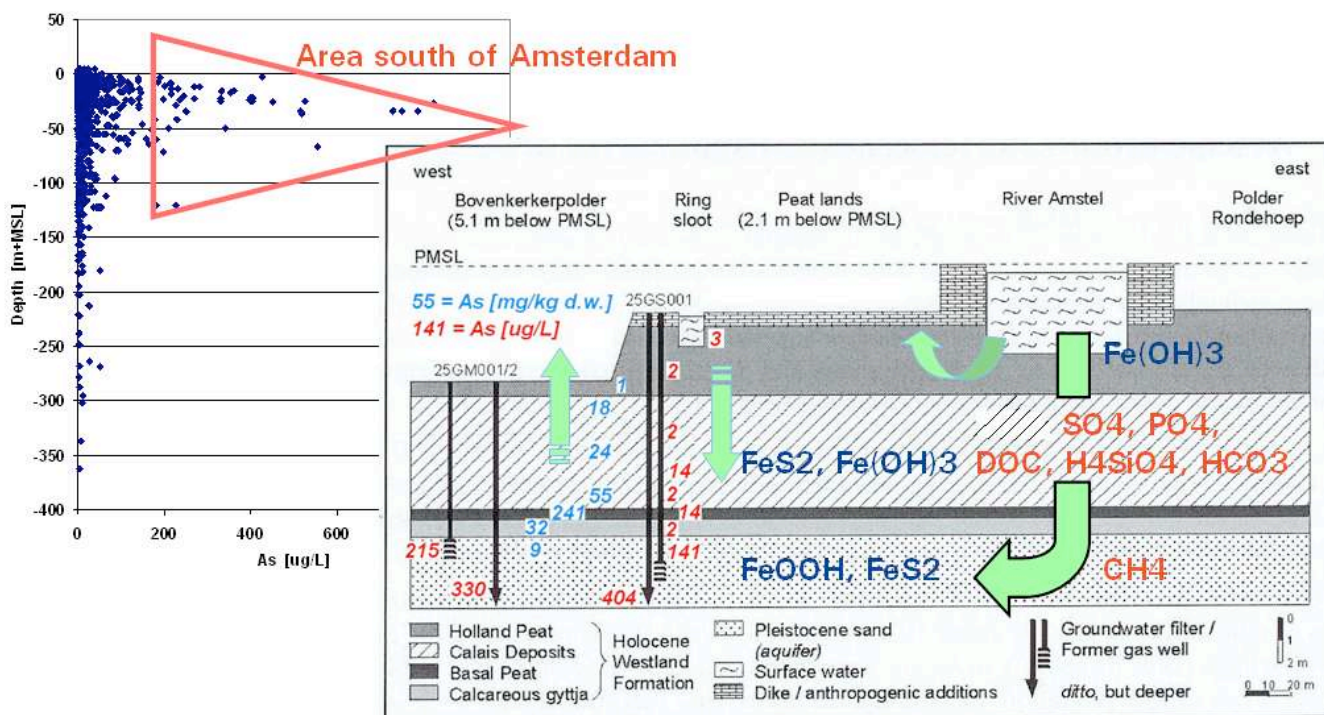


Figure 8.10 Site 5. Left: depth relation for total arsenic in groundwater in the coastal province of North Holland, with triangle showing values encountered in the high As-belt south of Amsterdam.

Right: cross section over a typical polder area in the high As-belt south of Amsterdam (modified after van Rossum, 1998). Numbers in blue = As in solid [mg/kg d.w.]; numbers in red = As in water [ug/L].

Site 6: artificial recharge using pretreated Rhine River water and basins, near Zandvoort

South of the town of Zandvoort pretreated Rhine River water (ca 60 Mm³/a) is recharging a large dune area since 1957 for the drinking water supply of the city of Amsterdam. In between an important influent supply canal for the northern recharge basins, and a 1 km distant drainage canal 8 piezometer nests equipped with miniscreens were sampled in 1980 and 1982 to study the distribution of water types and the behavior of inorganic solutes incl. trace elements (Stuyfzand, 1993b; Van Breukelen et al., 1998). The situation and flow path studied here are shown in Figure 8.11 (left), with the chemical evolution of several components and total arsenic in Figure 8.11 (right).

It can be concluded from Figure 8.11 (right) that As is peaking in between 250 and 450 m of flow, which coincides with that part of the flow path that passes the marine sands underlying the dune sand below 1 m – MSL and the marine aquitard b at 5-10 m-MSL. The start of peaking thus coincides with the change from eolian to marine deposits and with the onset of anoxic conditions (complete disappearance of NO₃ and appearance of Fe²⁺). This situation strongly resembles the natural situation in the dunes without artificial recharge (site 1), but the As levels are higher, probably due to the lack of SO₄-reduction in connection with higher flow velocities in artificial recharge systems. For further details we refer to Stuyfzand (1993b).

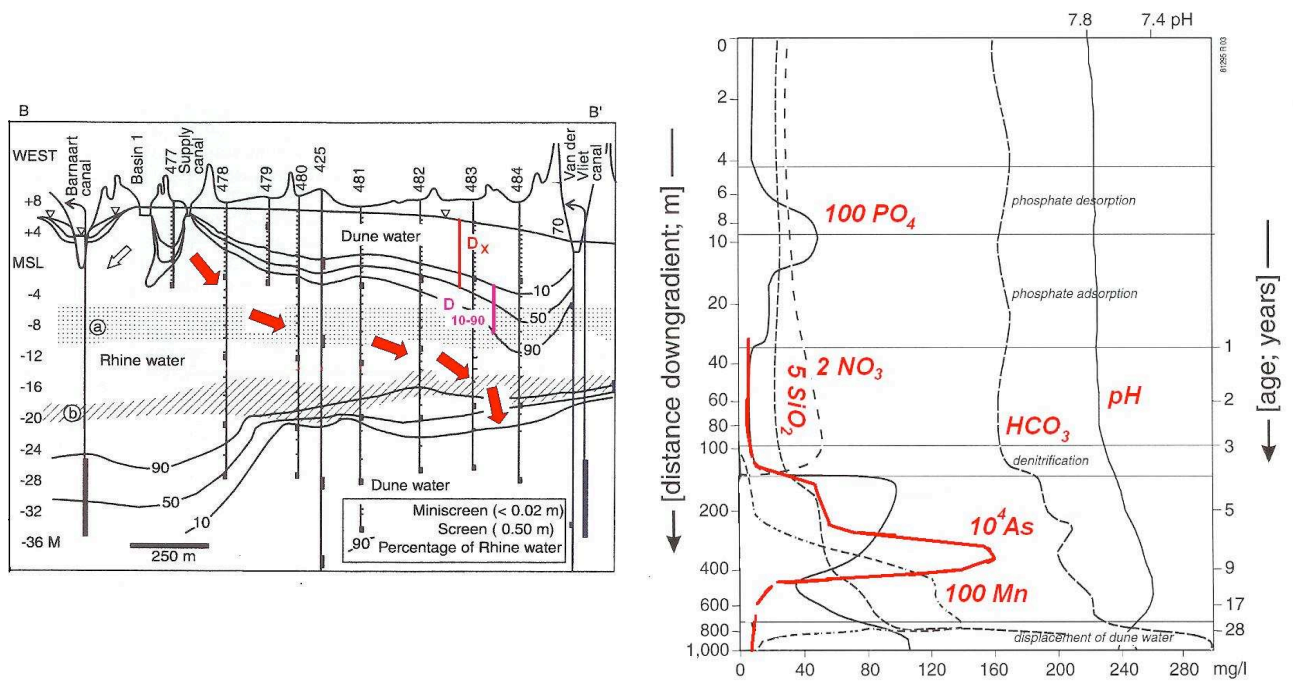


Figure 8.11 Site 6. Left: Position of the studied flow path of artificially recharge Rhine River water from the supply canal to the prograding intrusion front into deep dune groundwater. a = very fine, silty, marine Holocene sand (moderate aquitard); b = sandy, marine, Holocene clay (aquitard). Right: quality evolution anno 1981, along the flow path indicated in the cross section at the left (after Stuyfzand, 1993b).

Site 7: artificial recharge using pretreated Meuse River water and basins, near The Hague

North of the city of The Hague a large coastal dune area is artificially recharged (ca 50 Mm³/a), initially using pretreated Rhine River water (1955-1976) and subsequently pretreated Meuse River water.

The spatial distribution of As concentrations and redox environments, anno 2006, along a row of monitoring wells in between 2 infiltration ponds is shown in Figure 8.12 (left). Travel times from pond to recovery are 50-70 d in the upper aquifer, and 400-1000 d in the second aquifer. The input of As and PO₄ was high in the period 1955-1980 (resp. ca 6 µg/L and 0.4 mg/L), and since 1980 it is much lower (resp. 1-2 µg/L and 0.15 mg/L).

We conclude from Figure 8.12, (upper) that As is low in the (sub)oxic environment (≤2 µg/L), as expected, but highly variable in both the anoxic and deep anoxic environment (0.2-62 µg/L). A surprisingly good positive correlation is only observed for As and PO₄-ortho concentrations (Figure 8.12, lower). The elevated PO₄ and As levels probably derive from sludge that accumulated at the bottom of the infiltration ponds, without being frequently removed as in other dune areas with artificial replenishment. Arsenic concentrations <1 µg/L in deep anoxic environments are likely connected with coprecipitation with iron sulphides.

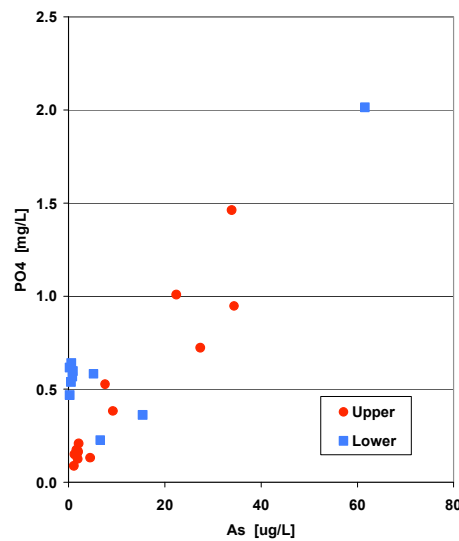
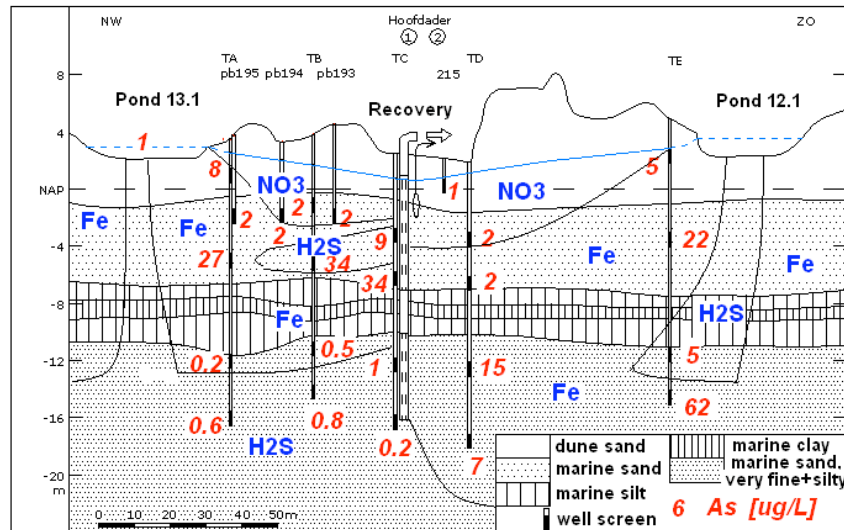


Figure 8.12 Upper: Cross section over 2 recharge basins near The Hague along a monitoring row of observation wells, with the indicated total As concentrations and redox environments in August 2006.

NO₃ = (sub)oxic; Fe = mainly anoxic; H₂S = mainly deep anoxic.

Lower: Relation between total As and PO₄-ortho in the cross section, with distinction between samples taken from the upper and lower aquifer (separated by marine silt and clay).

Site 8: artificial recharge using wells, near Langerak

Close to the Rhine River tributary Lek, near the town of Langerak, a deep well injection pilot was run for 20 months, recharging a semiconfined, deep anoxic sandy aquifer with oxic drinking water (Figure 8.13, left). Further details on the pilot study are given by Stuyfzand & Timmer (1999) and Saaltink et al.

Mass balances revealed that both O₂ and NO₃ oxidized pyrite, that contained significant amounts of As, Co, Ni and Zn. In this case As was clearly mobilized close to the injection well and largely immobilized again further downgradient, by adsorption to or coprecipitation with neoformed iron(hydr)oxides (Figure 8.13, right). Whereas pyrite oxidation continued in each observation well during the whole pilot (number of pore flushes [PFs] at 20 m >88), the As mobilization stopped after ca 10 PFs. This is explained

by the initial lack of (a) complete oxidation of the mobilized As (probably as H_3AsO_3) to better adsorbable AsO_4^{3-} and (b) sufficient sorption sites on neoforming iron(hydr)oxides.

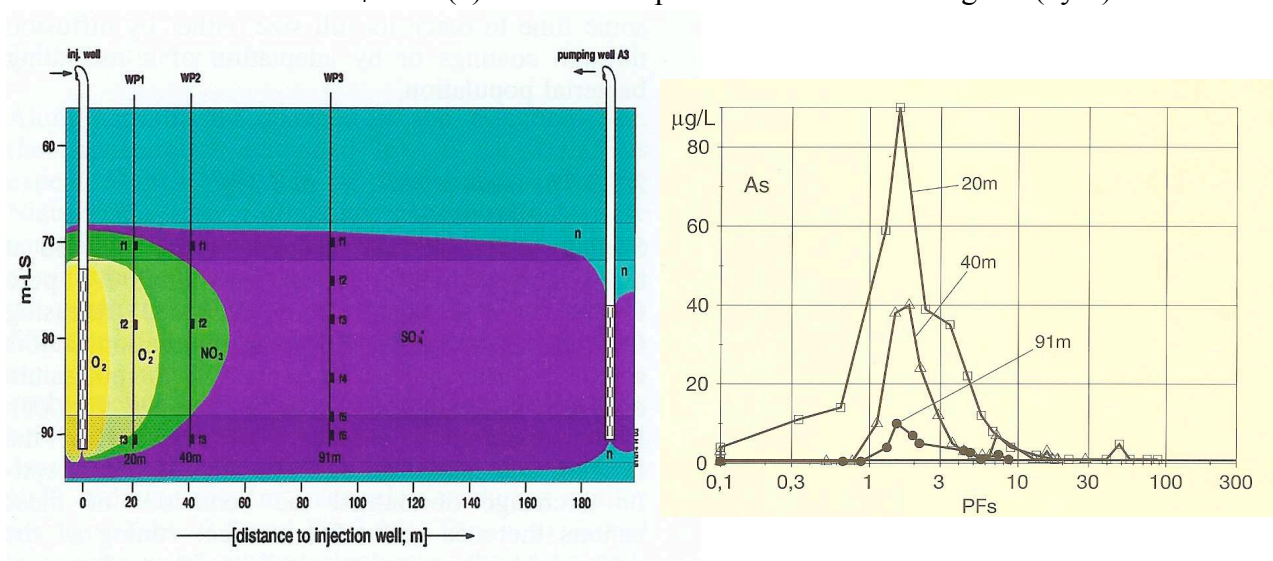


FIGURE 8.13 Site 8 (after Stuyfzand & Timmer, 1999). Left: Redox zonation in an originally deep anoxic aquifer after 1.5 years of deep well injection of oxic drinking water and distant recovery (after Stuyfzand & Timmer, 1999). O_2 = oxic (>90% O_2 saturated); O_2^* = (sub)oxic (<90% O_2 saturated); NO_3 = (sub)oxic ($O_2 < 2$ mg/L, $NO_3 > 1$ mg/L), SO_4^* = anoxic ($O_2 = NO_3 = 0$, SO_4^* above input due to pyrite oxidation); n = native, deep anoxic. Right: As mobilisation in observation wells WP1-3 at ca. 90 m-LS as a function of number of pore flushes (PFs). As as total arsenic.

8.5 Processes that mobilize arsenic in the Netherlands

The most probable As mobilizing processes in the Netherlands, with their presumed frequency of occurrence, are summarized in Table 8.4. We can discern the following groups, with between brackets the number as indicated in Table 8.4: (i) redox indifferent processes (1-4); (ii) redox reactions in an oxidizing environment (5), and (iii) redox reactions in a reducing environment (6-7).

TABLE 8.4 Overview of the most probable arsenic mobilizing processes in the Netherlands.

No.	Mobilizing process	Trigger	Freq
1	Desorption	pH-increase, temp. increase, ?clay+peat compaction?	C
2	Ripening of ironhydroxides	Time, Increase of temp.	CC
3	Anion exchange	Flushing with water high in PO_4 , HCO_3 or SO_4 (low pH)	C?
4	Dissolution of As-minerals (like As_2S_3)	Input CO_3^{2-} in reduced environment --> complexation as: $As(CO_3)_2^-$, $As(CO_3)(OH)_2^-$, $AsCO_3^+$	RR
5	Oxidation of Fe-sulphide minerals + Elimination other O_2+NO_3 -consumers + Prevention of sorption	High input of O_2 and/or NO_3 , Fe^{2+} escaping from oxidation Low input of DOC, NH_4 High input of PO_4 , H_4SiO_4 , HCO_3 , SO_4 , DOC, ?F?	CC
6	Reduction of AsO_4 to H_3AsO_3	High input of CH_4 , H_2 , labile DOC, H_2S (Fe^{2+} low),	CC
7	Reduction of iron(hydr)oxides		

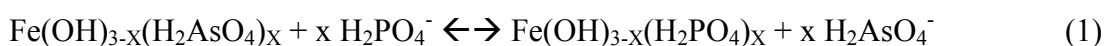
C? = probably frequent; C = frequent; CC = very frequent; RR = very rare.

8.5.1 Redox indifferent processes

This group is hard to isolate in the systems from which drinking water is abstracted in the Netherlands, because redox reactions are nearly always operating in its relatively young deposits. Yet it is highly probable that especially the ripening of ironhydroxides and anion exchange are important processes.

The ripening of hydrous ferric oxides or ferrihydrite (simplified to $\text{Fe}(\text{OH})_3$) to for instance goethite ($\alpha\text{-FeOOH}$) requires one molecule of H_2O to detach, and results in a strong decrease in surface area and desorption of anions like arsenate. This is nicely illustrated by the chemical composition of well incrustations (Figure 8.3). We presume that this process is also active in specific groundwater flow systems.

Pure anion exchange, without complications due to peat or pyrite oxidation and reduction of iron(hydr)oxides, is important in phosphate loaded agricultural soils that receive(d) excessive manure and fertilizer inputs, and in artificial recharge and river bank filtration systems that use(d) surface waters with high PO_4 concentrations due to their eutrophication. Orthophosphate is generally considered the most common competitor of arsenate (AsO_4) for sorption sites, due to its very similar molecular structure and much higher concentrations (normally 50-100 times higher). The exchange reaction can be schematized as follows, assuming the exclusive participation of the dominant species of phosphate and arsenate at pH 6.5:



Although As mobilization due to raised PO_4 inputs is to be expected (also because of concomitant high As inputs), there is no clear evidence of it in well fields to date. This is probably connected with counteracting changes or reactions in the hydrogeochemical system, like PO_4 -fixation, redox changes due to the introduction of nitrate, pH changes etc.

Also SO_4 may act as a desorbent, especially at lower pH (<5). Sulfate increased in rain water especially in the period 1950-1980 due to atmospheric pollution, but was accompanied then by a pH decrease in groundwater which on the one hand reduces the dissociation of H_2AsO_4 , but on the other raises the anion sorption capacity of the soil. The net result therefore remains unclear. The infiltration of polluted surface waters also increased SO_4 concentrations in artificial recharge and river bank filtration systems. This may have provoked As desorption, but the pH of these waters is probably too high (7-8.2) for SO_4 to be a significant As desorbent.

Hydrogen carbonate may also act as an As desorbent (Appelo et al., 2002), especially in the deep anoxic groundwaters that passed peat, clay or sludge layers in the Netherlands.

The anion sorption capacity of the aquifer system will decrease when pH or temperature increases, thus leading to As desorption. In case of arsenite, pH increases could raise the sorptive behavior of the As itself as it changes from uncharged H_3AsO_3 to H_2AsO_3^- near pH 9.3. This pH has, however, never been observed in groundwater flow systems in the Netherlands.

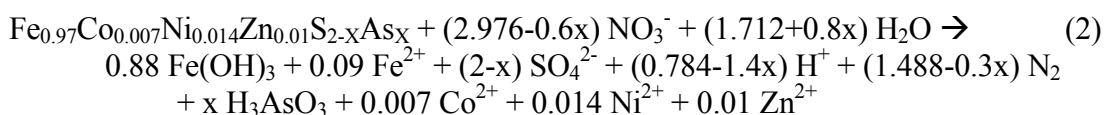
Small increases in groundwater pH have been observed where eutrophic and more mineralized surface water is replacing direct rain water recharge. Groundwater

temperature is already increasing in the upper tens of meters due to climate change (in the Netherlands ca. 1°C) and in artificial recharge and river bank filtration systems due to thermal pollution of the surface waters (in the Netherlands ca 2°C).

It is hypothesized that the compaction and alteration of clays and peat might play a role as well in reducing both the cation and anion sorption capacity of the system.

8.5.2 Redox reactions in an oxidizing environment

The most important oxidizing reaction that generates As in the Netherlands, is the oxidation of iron sulfides, mainly pyrite, especially in situations where the oxygen supply is limited. This situation is met for instance on site 2, where excessive agricultural nitrate is oxidizing a pyritiferous aquifer (Figure 8.7). The reaction there is schematized as follows, assuming congruent dissolution, about 90% oxidation of Fe²⁺ to Fe(OH)₃ (which corresponds to the observed Fe²⁺ concentrations) and no sorption of Co, Ni and Zn to neoformed Fe(OH)₃:



The composition of the pyrite derives from linear relations between the observed concentration increases of SO₄, Co, Ni and Zn in observation well NP.40 of the Vierlingsbeek well field (Van Beek & Van der Jagt, 1996). Extension with As yields x = 0.0013. This composition deviates especially regarding As, from the one of similar pyrites involved in deep well injection experiments, which were, however, analysed by extraction of the trace elements with aqua regia and linear correlation with selectively extracted pyrite. Those and other pyrites in fluvial sands had the following mean composition (Stuyfzand, 1998) with a surprisingly small range for As (0.003-0.006): Fe_{0.98}Co_{0.0037}Ni_{0.01}Zn_{0.01}S_{1.9947}As_{0.0053}.

The lower mole fraction (x) of As in pyrites at Vierlingsbeek is therefore probably biased by significant losses of As to neoformed iron(hydr)oxide, whereas the metals Co, Ni and Zn remained in solution (pH 5.4).

High O₂ concentrations, in pyritiferous systems suffering from a drawdown of the groundwater table or receiving deep well injection of (sub)oxic surface or drinking water, tend to completely oxidize the pyrite to hydrous ferric oxide which is capable of sorbing or coprecipitating the As mobilized to a large extent. During deep well injection As was mobilized close to its stoichiometric release, only in the beginning and close to the injection well when O₂ and NO₃ started their penetration into pyritiferous deposits (site 8, Figure 8.13, right). Obviously the formation of As scavenging iron(hydr)oxides takes some time and the process needs some areal extent. It is probable that the conversion of the mobilized, more mobile arsenite to less mobile arsenate is also retarded, by the initial lack of (i) sufficient O₂ or NO₃, (ii) the right microbial population to catalyze this conversion; and (iii) formation of MnO₂ to catalyze the conversion as well.

The downstream shrinking of the initial As peak (Figure 8.13, right) is probably connected with continued interaction with iron(hydr)oxides. The latter could be transported as particles over some distance and then become filtered away by the

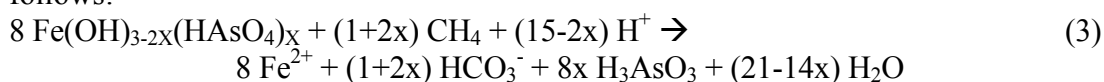
aquifer. In fact, filtration of the water samples in the field led to a remarkable removal of ferric iron flocs, as evidenced by a brownish coating of the membrane filters used. This particle transport in deep well injection systems is enhanced by relatively high groundwater flow velocities (1-3 m/d).

As compared to the Vierlingsbeek case, deep well injection resulted in higher As and lower Co, Ni and Zn concentrations. This can be attributed to the higher pH (7).

8.5.2 Redox reactions in a reducing environment

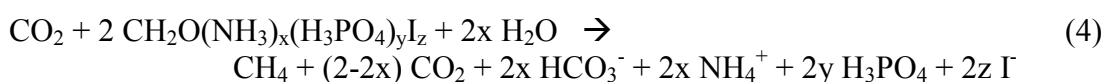
The most important reducing reactions that generate As in the Netherlands, are the reductive dissolution of iron(hydr)oxides and the reduction of arsenate to arsenite. The reduction is mainly achieved, in the Netherlands, in the upper 300 m where fresh groundwater is pumped for drinking water supply, by unstabilized soil organic matter (SOM), either directly in solid or dissolved state, or indirectly through 2 reaction products: H₂S (or HS⁻) deriving from SO₄ reduction, and methane (CH₄) produced by methanogenesis. H₂S is probably much less productive than CH₄ in mobilizing As from iron(hydr)oxides, because it will lead to the precipitation of pyrite (FeS₂) with coprecipitation of As.

The overall reaction of arseniferous iron(hydr)oxides with CH₄ is schematized as follows:



The kinetics of this reaction could be extremely slow without the presence of catalyzing micro-organisms. No data on the reaction kinetics were found in the literature, indicating that further research on the relevance of reaction 3 is needed.

Methane concentrations in deep anoxic groundwaters in the Netherlands are normally in the range of 1-50 mg/L, with occasional outliers to 100 mg/L (Stuyfzand et al., 1994; Fortuin & Willemsen 2005). The methanogenesis can be schematized as follows (Stuyfzand, 1993b):



SOM is represented here as CH₂O(NH₃)_x(H₃PO₄)_yI_z with default values x = 0.151 and y = 0.0091 in accordance with Froelich et al. (1979), or x = 0.075 and y = 0.0045 in accordance with Hartmann et al. (1973) and z = 0.0002 in accordance with Ullman & Aller (1985).

Reaction 4 shows that the presence of methane should be associated with high concentrations for HCO₃, PO₄ and I. This is indeed very often the case (Stuyfzand, 1993b, Stuyfzand et al., 1994), which also holds for dissolved organic carbon (DOC). The paragenesis of CH₄, CO₂, HCO₃, NH₄, PO₄, DOC and I implies that mobilized arsenite, if it could sorb anyway, finds a huge amount of competitors (PO₄, HCO₃ and DOC) which increases its mobility. It should be noted that the direct reduction of Fe(OH)₃ by labile organic material likewise yields elevated concentrations of at least HCO₃, NH₄ and PO₄. It can therefore be concluded that redox reactions in a reducing (anoxic to deep anoxic) environment, with the exception of SO₄ reduction, not only dissolve iron(hydr)oxides and the associated As, but also generate anions and DOC that

act as inhibitors of As sorption. In addition, high concentrations of H_4SiO_4 may develop in anoxic environments due to the dissolution of diatoms, which can be abundant in the aquitards responsible for developing the (deep) anoxic conditions. Dissolved silica was observed by Swedlund & Webster (1998) to compete with As for sorption sites.

In some cases CH_4 could be nearly completely consumed by reaction 3. In that case the above mentioned paragenesis is not conserved in the groundwater. Also, when CH_4 is reductively dissolving large amounts of iron(hydr)oxide, the Fe^{2+} concentration and pH will rise to such an extent that siderite (FeCO_3), calcite (CaCO_3) and phosphate minerals precipitate. Arsenic is not particularly sensitive to coprecipitation with these carbonates, but may coprecipitate to a significant degree in phosphate minerals like apatite and vivianite (Smedley & Kinniburgh, 2002). This situation is probably encountered in the glauconitic sand aquifers of Late Tertiary age in the southern Netherlands.

Further deviations from the above mentioned paragenesis arise when CH_4 is transported as free gas bubbles, from either below or above, to an aquifer without methanogenesis (Stuyfzand et al., in press).

8.6. Conclusions

Although the current situation in the Netherlands, at the scale of well fields, is indicating that As does not menace drinking water supply, there are several situations, on a smaller scale, that are clearly pointing at a strong As mobilization (up to 1,500 $\mu\text{g/L}$) that may affect drinking water or its treatment on the long term. In the following we focus on the 3 most important situations for water supply.

The first situation arises where sludge is forming at the bottom of low-flow, infiltrating surface water bodies, for instance in closed-off estuaries, eutrophicated lakes, canals, rivers, gravel pits and recharge basins. Here the As is delivered by reductive dissolution of iron(hydr)oxides, especially when methane is generated. The problem is, however, in a way selfregulating: when the accumulation proceeds, the infiltration of surface water with the leakage of As will diminish, or man will remove the sludge because of problems arising due to a decreased water depth for shipping or decreased groundwater recharge rates. The cure to sludge formation consists of combatting eutrophication and soil erosion, periodically admitting or creating high flows to remove sludges from the system, and in case of artificial recharge, pretreatment of the infiltration water. Combatting eutrophication and pretreatment also help to reduce PO_4 which will increase the chance of As sorption.

The second situation is related to nitrate pollution of groundwater catchment areas underlain by pyritiferous deposits, mainly due to excessive applications of fertilizers and manure. The As derives in this case from pyrite oxidation. The cure is simple: ban agricultural activities in those water catchment areas or only allow biological cultivation methods.

The last situation is connected with deep well injection. Although As in the current systems with distant recovery wells does not pose problems in pyritiferous aquifers, new systems in the Netherlands operating with only one Aquifer Storage and Recovery (ASR) well could provoke As problems. This is currently happening in Florida USA, where pyrite in limestone is oxidized by the (sub)oxic infiltration water and As seems to

be remobilized from the neoformed iron(hydr)oxides (Arthur et al., 2007; Pyne, in press). The main problem (especially regarding Fe and Mn and possibly As) with ASR application in the Netherlands is, that post-treatment of injected drinking water is undesirable, because it would undermine the economical benefits of direct delivery during peak demands.

In the first and second situation As will not pose real problems to public drinking water supply, under the following conditions: (i) the arsenic should remain accompanied by high iron concentrations requiring iron removal (to <0.2 mg/L) which normally also reduces As to the drinking water standard of 10 µg/L; and (ii) the drinking water standard should not be lowered any further. The latter is, however, not in favour of the drinking water consumer, as a lower drinking water standard seems to be highly desirable (Vather, this volume).

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Water as key to development

One of the water-related Millennium Development Goals is to halve the number of people without access to safe and reliable drinking water and hygienic sanitation by 2015. In order to contribute to this goal, the Dutch water sector (both sanitation and drinking water) has combined its means and expertise through the foundation of Aqua for All.

Based on the basic needs for water and sanitation for human living, the projects selected by Aqua for All aim for a strong impulse for self supporting economic development for the poor in the rural and peri-urban areas. We support small scale and large scale water projects, initiated by local community based organisations.

Activities:

- ▶ Water and sanitation programmes;
- ▶ Demonstration projects for innovative water en sanitation solutions;
- ▶ Water conservation programmes such as sanddams and rooftop harvesting;
- ▶ Business Development: partnerships between public and private companies and promotion of low cost Appropriate Technologies based on local available resources.

Aqua for All

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Combining forces in the Delta

Over 50% of the global population live and work in a delta. Delta areas are attractive because of their strategic location close to the sea and waterways. The ground is fertile and rich in minerals and raw materials. But delta areas are also vulnerable. Soft soil subsides, the sea level is rising, river levels are unpredictable and pressure on space and the environment is on the increase.

Integrated approach

Deltares has an integrated approach to the development of innovative solutions that make living and working in deltas safe, clean and sustainable. Four renowned Dutch knowledge institutes have combined their strengths in Deltares: WL | Delft Hydraulics, GeoDelft, a part of TNO Subsurface and Groundwater Built Environment and Geosciences, and parts of Rijkswaterstaat, RIKZ, RIZA and DWW. Deltares is a unique combination of 800 experts with vision, expertise and experience in the field of delta technology. An international authority in the area of water and the subsurface. With an area of operations that includes deltas, coastal areas, river basins and other low-lying areas throughout the world.

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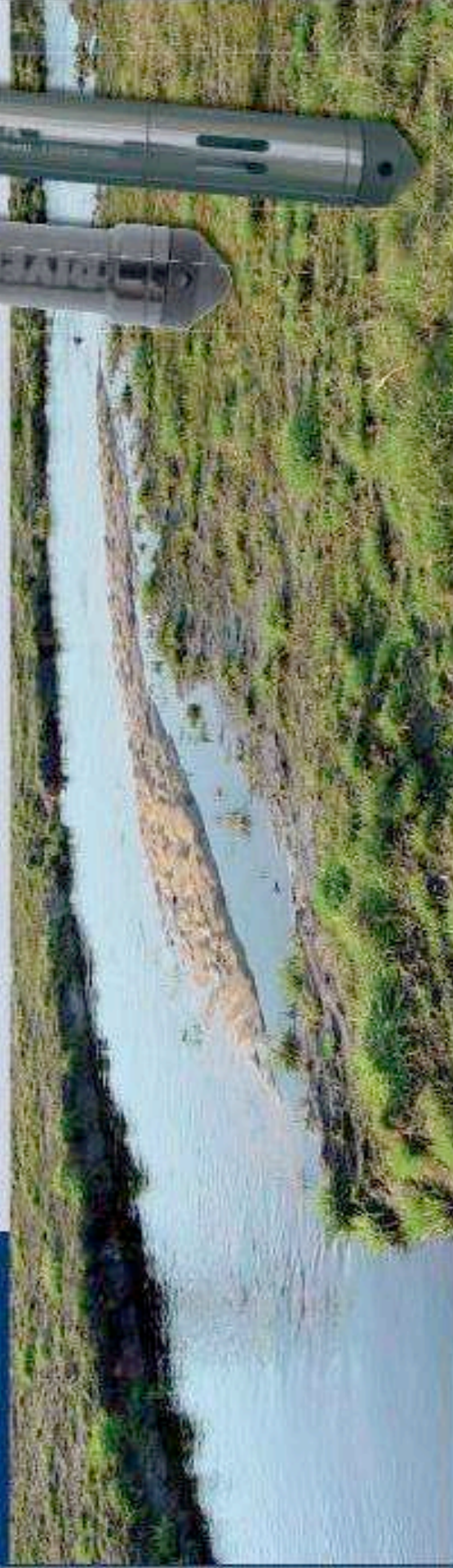
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Your portal to groundwater knowledge



Appropriate exploration, exploitation and protection of groundwater ask for substantial knowledge on groundwater and its interaction with the environment.

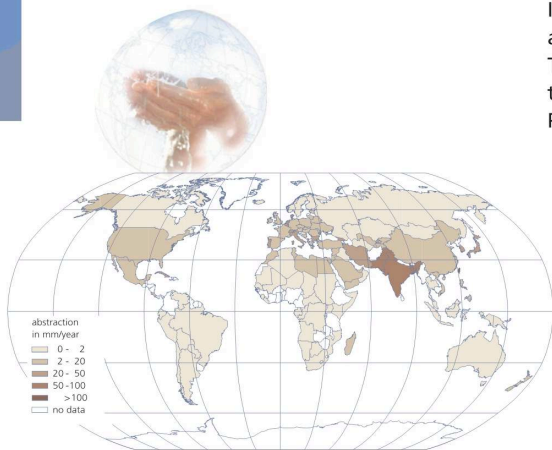
International Groundwater Resources Assessment Centre (IGRAC) is founded to facilitate and promote global sharing of information and knowledge required for sustainable groundwater resources development and management.

Accordingly, IGRAC main activities are meant to contribute to:

- management of transboundary aquifers
- internationally consistent data collection and monitoring
- identification of comparable problems already solved elsewhere
- understanding of groundwater processes and patterns on regional and global scales
- promotion of groundwater in water resources planning and management

As a non-commercial centre, IGRAC operates under auspices of UNESCO and the World Meteorological Organisation (WMO). In 2008 the centre celebrates its 5th birthday.

IGRAC is hosted by TNO Built Environment and Geosciences in Utrecht, The Netherlands. The centre receives financial support from the Dutch government (Partners for Water Programme).



Mean groundwater abstraction rates (mm/a).



Netherlands Water Partnership: Uniting Dutch Water Expertise

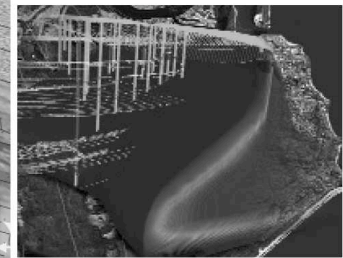
Groundwater management has for years been a priority in the Netherlands. The Dutch water sector has built up a considerable expertise in assessing and managing the sustainable development of groundwater resources. For years, this expertise is being exported abroad and enriched by the experiences gained.

The Netherlands Water Partnership (NWP) is a public-private network organisation for the Dutch water sector. 160 Dutch organisations active in water are comprised in the NWP, including knowledge institutes, private and public parties and non-governmental organisations. The principal aims of the NWP are to harmonise the activities and initiatives of the Dutch water sector abroad and to promote Dutch water expertise worldwide.

Netherlands Water Partnership
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Billions of people have no access to decent drinking water or sanitation, which are essential for health and social-economic development.

World Waternet² was founded in 2007 to bring into practice total and sustainable solutions for drinking water, sanitation, groundwater and surface water management. It does so through building long-term relationships with water operators in cooperation with governing agencies, knowledge institutions, NGO's and market parties in developing and developed countries. We believe long-term empowerment of involved parties to be corner stone for sustainable development and maintaining of water supply. As an idealistic organization, any profits will directly be recycled to water projects in developing countries.

World Waternet has a small staff provided by Waternet³ at nominal cost. World Waternet primarily uses expertise from Waternet and daughter institutions like *Het Waterlaboratorium en Waterproof* but involves external parties whenever useful.

World Waternet is working in Egypt, the Caribbean, Indonesia and Latvia but is extending its activities to other countries.

World Waternet depends on donations, sponsoring, subsidies, paid consultancy and royalty's. Customers are invited to sponsor the activities of World Waternet through their water bill and subsidies are granted by the City of Amsterdam and the Water Board Amstel Gooi and Vecht.

For further information see www.worldwaternet.nl, www.waternet.nl

Worldwaternet

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² World Waternet is a foundation of the City of Amsterdam and the Water Board Amstel Gooi and Vecht with an idealistic mission to help solve water and sanitation challenges in developing countries

³ Waternet is the organization responsible for drinking water, sanitation and water management of Amsterdam and its surroundings. Waternet is owned by the City of Amsterdam and the Water Board of Amstel Gooi and Vecht.