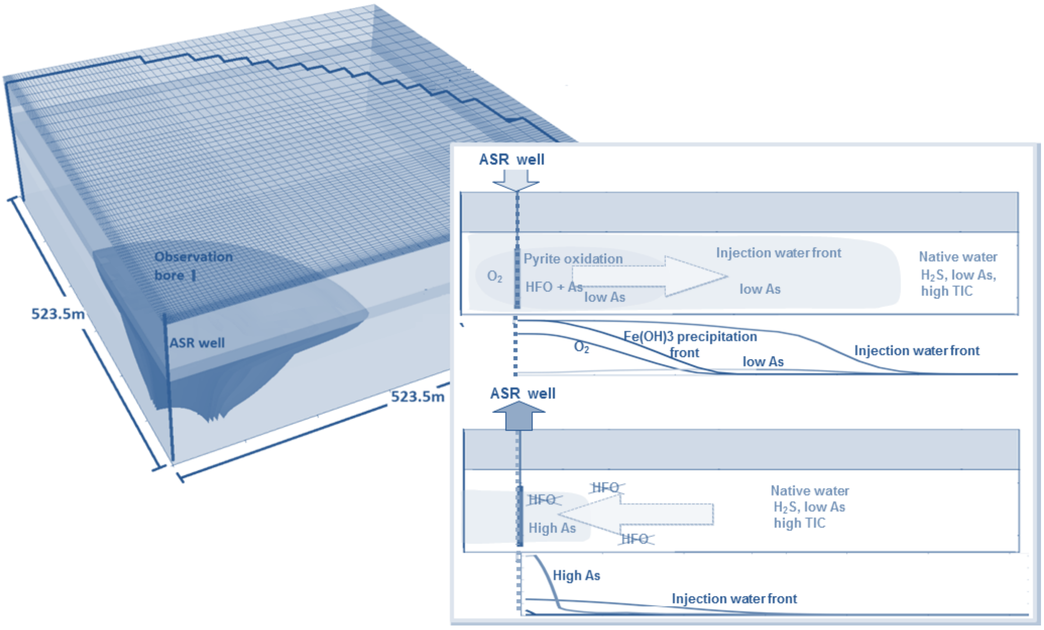
QUANTIFICATION OF ARSENIC MOBILISATION AND ATTENUATION BY COUPLED FLOW AND MULTI-COMPONENT REACTIVE TRANSPORT MODELLING



SUBMITTED BY

ILKA WALLIS

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SUMMARY

Knowledge about the human toxicity of arsenic (As), combined with widespread naturally and anthropogenically-induced elevated As concentration in groundwaters in many parts of the world (e.g. Argentina, Bangladesh, India and Vietnam), have sparked an increasing interest in the factors controlling the distribution of As and the mechanisms that influence the fate of As in groundwater systems.

Several common naturally-occurring geochemical processes can play an important role in controlling the distribution of As. However, in natural systems, it is often difficult to discern which chemical or biochemical processes take the lead in controlling the fate of arsenic, or whether its fate might be predominantly controlled by physical transport processes. In such cases integrated flow and reactive transport modelling can provide an important and consistent quantitative framework for advancing our understanding of the complex and often non-intuitive field-scale behaviour of arsenic.

This thesis describes the development and evaluation of detailed process-based simulation capabilities for two selected managed aquifer recharge (MAR) operations in Langerak, the Netherlands and Bradenton, Florida. At both field sites, injection of potable, oxygenated water into anoxic aquifers for storage and later withdrawal resulted in the mobilisation of arsenic. Both sites were well-characterised and benefited from the controlled hydraulic flow conditions that were induced by the MAR operations and from the availability of comprehensive data describing the geochemical evolution of the aquifer.

The simulators used for the studies were the USGS flow model MODFLOW in conjunction with the reactive multi-component transport model PHT3D (Prommer et al. 2003). PHT3D couples the three-dimensional transport simulator MT3DMS (Zheng and Wang, 1999) with the geochemical model PHREEQC-2 (Parkhurst and Appelo, 1999).

The model-based data interpretation provided conceptual insight into the predominating reaction patterns, their spatial variability and their dependence on the flow regime under a variety of MAR operating conditions. The integrated flow and reactive transport modelling illustrated that arsenic was initially released/mobilised following pyrite oxidation triggered by the injection of oxygenated water into the anoxic aquifers. Dissolved concentrations were controlled by complexation to neo-formed hydrous ferric oxides during injection. Modelling suggested this to be an effective arsenic attenuation mechanism, albeit a temporary one. During recovery arsenic was remobilized as a result of both dissolution of hydrous ferric oxides and displacement from sorption sites by competing anions.

The numerical framework allowed detailed assessments of arsenic partitioning among mineral phases, surface complexes and aqueous phases during injection, storage and recovery and the evaluation of the temporal and areal extent of arsenic mobility and capture within the aquifer.

During the model development and applications it became clear that computational efficiency and accuracy consideration can play an important role for the simulation of arsenic fate at field scale. This motivated additional and more systematic investigations on the efficiency and accuracy of the numerical modelling approaches for multi-dimensional field-scale reactive transport.

Taken collectively, this thesis creates a depth of knowledge on the science and simulation capabilities of field-scale As behaviour. The work demonstrates, that a clear understanding of the fundamental geochemical processes affecting the mobility of arsenic and their interaction with physical transport can only be achieved, if flow, transport and reactive processes are considered simultaneously. A contribution to understanding the complete cycling of arsenic in complex field-scale groundwater systems as a coupled process of hydraulic and geo(bio)chemical controls is made.

The practical aspect of the work is the provision of a tool to assess the suitability of different MAR sites and techniques in relation to As mobility, to optimize operational conditions as well as to evaluate proposed engineering solutions that could mitigate the As problem at affected MAR sites.

DECLARATION OF ORIGINALITY

I certify that this thesis does not incorporate, without acknowledgment, any material previously submitted for a degree or diploma in any other university; and that to the best of my knowledge and belief it does not contain any material previously published or written by another person except where due reference is made in the text.

Ilka Wallis

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I would like to express my gratitude to a number of people who have shared their ideas, gave their time and comments. These include Andy Love, Carlos Descourvieres, Janek Greskowiak, Simone Seibert, Evelien Martens, David Kinniburgh, Pieter Stuyfzand and Thomas Pichler.

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Chapter 1. INTRODUCTION

1.1 THE RESEARCH PROBLEM

Naturally and anthropogenically induced elevated As concentrations in groundwaters are reported from a wide range of hydrogeological and geochemical settings in many parts of the world (e.g. Argentina, Bangladesh, India and Vietnam). Arsenic is both a toxin and a carcinogen and is recognised as one of the most serious inorganic threats to drinking water on a global scale (Smedley and Kinniburgh 2002). Pathways of arsenic into and within groundwater systems are still not fully understood. However, several common naturally-occurring geochemical processes are confirmed to play an important role in controlling the distribution of As at the near-neutral pH range that is typical for many groundwaters. The oxidation of As-bearing sulphides (e.g. pyrite) under aerobic conditions (Jones and Pichler 2007) and the reductive dissolution of Fe-oxides under reducing groundwater conditions were shown to be important release mechanism for As (Smedley and Kinniburgh 2002, Burnol 2007, Dixit and Hering 2003) and played a key role in many studies that investigated naturally high As groundwaters. Major processes mitigating the mobilisation of arsenic are adsorption, i.e., surface complexation and (co)-precipitation. Minerals such as ferrihydrite, Al-oxides or Mn-oxides are known to be effective scavengers for As under oxic conditions, while precipitation of As-bearing sulphides may reduce dissolved concentrations under reducing conditions (Stollenwerk 2003, Saunders et al. 2008, Wolthers et al. 2008). Other processes such as competitive displacement of sorbed As by increasing carbonate and phosphate concentrations (Smedley and Kinniburgh 2002, Welch et al. 2000, Stollenwerk 2007), adsorption of As on carbonates and clay minerals (Goldberg 2002, Charlet et al. 2007) or biochemical processes (Oremland and Stolz 2003, Islam et al. 2004, He et al. 2009) may also be important components of As cycling in groundwaters and sediments.

In natural systems, it is often difficult to discern which of these chemical or biochemical processes take the lead in controlling the fate of arsenic, or if its fate might even be controlled predominantly by physical transport processes. The underlying causes of elevated arsenic concentrations will vary from site to site and are affected by the composition of the aquifer matrix, the composition of the ambient groundwater and recharge water and the hydrogeological conditions of the site. Since these interactions are generally highly nonlinear and non-intuitive, integrated coupled flow and reactive transport simulations can greatly assist in the analysis of field data and can provide a useful framework for advancing our understanding of field-scale arsenic behaviour in hydrogeologically and geochemically complex aquifer systems. Conceptual models can be formulated and their applicability tested, with the results eventually providing constraints for the interpretation of measured geochemical data.

Transport behaviour of As under controlled laboratory conditions was previously successfully quantified by numerical modelling (e.g. Dzombak and Morel 1990; Appelo et al. 2002, Jang and Dempsey 2008, Saunders 2008, Jeppu et al., 2010). Recent modeling efforts have built on these studies and quantified As behavior under the simplifying assumption of 1D flow conditions; e.g. Appelo and de Vet (2003), Moldovan and Hendry (2005), Postma, et al. (2007) and Stollenwerk et al. (2007). An early example at using a comprehensive three-dimensional transport model (PHAST, Parkhurst et al. 2010) to simulate arsenic behavior on a regional scale was provided by Parkhurst et al . (1996, 1999). The evolution of naturally high arsenic concentrations present in the Central Oklahoma aquifer was simulated over geological times. A 2D reactive transport model study on arsenic attenuation under field conditions was reported by Jung et al. in 2009. However, a wider range of studies which demonstrate the ability of laboratory-derived conceptual models to capture the processes that influence and control As distribution at the field scale is still lacking.

The research presented in this thesis investigates conceptual and numerical models to provide an integrated, process-based quantification of mechanisms that control As mobility at two hydrogeologically and geochemically heterogeneous “field-laboratory” sites. These well-characterised sites, both at which managed aquifer recharge (MAR) operations were closely studied, benefit from strictly controlled hydraulic flow conditions that are induced through the MAR operations and from the availability of detailed temporal and spatial data describing the geochemical evolution at the study sites. This provided effective constraints for the development of plausible conceptual and numerical models and offered the opportunity to investigate field-scale As behaviour under otherwise rarely found, well-controlled and characterised conditions. This is a significant advantage over most other sites, where high As groundwaters were studied, and where factors such as unknown source history, uncertain flow rates and a general scarcity of hydrogeological and hydrogeochemical data together with the associated parameter uncertainties may limit the robustness of any proposed conceptual and/or numerical model.

The two managed aquifer recharge operations analysed in this PhD study were (i) a deepwell injection experiment in the Netherlands and (ii) an aquifer storage and recovery operation in Florida. At both sites, injection of potable, oxygenated water into anoxic aquifers for storage and later withdrawal has resulted in the mobilisation of arsenic.

Chapter 2 describes the first of the two cases, where flow and reactive transport modelling was undertaken to provide a consistent interpretation of the observed spatial and temporal hydrochemical changes that were documented during an aquifer storage transfer and recovery (ASTR) experiment in a siliclastic pyritic aquifer at Langerak, the Netherlands. Following injection of aerated water into the anoxic target aquifer, arsenic mobilisation was detected close to the injection well, but elevated concentrations diminished to background levels with increasing travel distance. Pyrite oxidation and the formation of amorphous iron-oxides (HFO) in the progressively expanding oxic conditions of the aquifer were shown to be the key chemical processes for water quality changes, which in turn controlled the observed fate of arsenic during the experiment. In the model that best reproduced field observations the fate of arsenic could be explained by (i) release/mobilisation via co-dissolution of arsenopyrite, stoichiometrically linked to pyrite oxidation (ii) kinetically controlled oxidation of dissolved As(III) to As(V) and (iii) adsorption via surface complexation of As on neo-precipitated amorphous iron oxides. The adsorption of As on HFOs was simulated using the generalized two-layer surface complexation model (SCM) of Dzombak and Morel (1990) for sorption on ferrihydrite, extended by reactions for Fe^{2+} and HCO_3^- to allow competitive sorption between arsenic and other ions. The model assumes that sorption sites on the solid HFO surface can be described by average surface site characteristics with no specific correlation to the actual solid surface structure. The model was chosen over the more recently developed charge distribution multi-site complexation model CD-MUSIC (Hiemstra and van Riemsdijk, 1996), which distinguishes between different surface site types based on the crystal structure of the mineral. At field scale, where there is no experimental evidence to determine the exact nature and surface structure of the surface complexes, the use of the chemically more simplistic Dzombak and Morel model with a smaller number of adjustable parameters was regarded preferable over highly parameterised SCMs.

The second study (Chapter 3) allowed for significant expansion of the work described in Chapter 2 with an emphasis on the understanding of the remobilisation of arsenic which was observed during the recovery phases of an aquifer storage and recovery (ASR) trial. ASR operations involve the cyclic injection of a water source into a target aquifer and its later withdrawal from the aquifer through the same well. In this study conservative and reactive transport modelling was used to analyse the multi-cycle hydrochemical and hydrogeological data from a site in south-west Florida, where As mobilisation was detected in response to the cyclic injection of oxygenated potable water into anaerobic sections of a pyrite-containing limestone target aquifer. The coupled simulation of the highly transient flow field and geochemical conditions was used to evaluate and quantify the processes controlling the redox dynamics and the related fate of arsenic within the aquifer that surrounds the ASR well under a variety of operating conditions. The numerical modelling illustrated that pyrite oxidation and the precipitation/dissolution of amorphous iron-oxides together with competitive displacement of As from sorption sites on HFO by competing anions were the key chemical processes that controlled the mobility of arsenic.

The third study (Chapter 4) was motivated by the significant computational costs that were associated with the multi-dimensional field scale MAR model applications discussed in Chapters 2 and 3. The work described in Chapter 4 therefore focused on exploring suitable numerical modelling techniques to allow for computationally more efficient simulation of reactive transport problems around point sources/sinks. Several options of simulating radial-symmetric conservative and reactive solute transport were investigated and their applicability, accuracy and computational cost was evaluated.

1.2 OBJECTIVES

In this work coupled flow and reactive transport modelling of two well-characterised managed aquifer recharge field sites was utilized to advance our understanding of arsenics' complex and often non-intuitive field-scale behaviour. The studies were underpinned by work into numerical modelling techniques, which allow for computationally more efficient simulation of reactive transport problems around point sources/sinks. The specific objectives were as follows:

- to develop conceptual models of arsenic release and attenuation at two well characterised MAR field sites,
- to develop a numerical modelling framework that provides a process-based description of the coupled flow, solute transport and reaction mechanisms controlling the fate of arsenic during MAR
- Testing the developed quantification framework for two comprehensive field data sets collected from a deepwell injection experiment in the Netherlands and an aquifer storage and recovery operation in Florida to investigate its applicability to simulate As behaviour in natural systems, where flow, transport and reactive processes need to be considered simultaneously.

- Test computationally efficient modelling approaches for simulating multi-dimensional field scale reactive transport, applicable to MAR operations.

1.3 SUMMARY OF THE RESEARCH CONTRIBUTION

Previous numerical studies that have investigated arsenic fate and transport have mostly focused on the identification of hydrogeochemical processes affecting its mobility under controlled laboratory conditions or in simplified 1-D field situations, while detailed quantitative assessment frameworks of As behaviour in more complex groundwater systems were generally not established. The work presented in this thesis aimed to fill this gap. The well-controlled and characterised conditions at two managed aquifer recharge (MAR) sites offered the unique opportunity to up-scale and advance our understanding and simulation capabilities of field-scale As behaviour of groundwater systems, where geological, hydrogeological, and geo(bio)chemical aspects have to be considered simultaneously.

Reactive transport modelling allowed integrated consideration of the dynamics between physical (e.g. flow, mixing) and reactive processes at different spatial and temporal scales. As a consequence a deepened understanding of the subsurface processes governing the fate of As has emerged and the research makes a contribution to understanding the complete cycling of arsenic in complex field-scale groundwater systems as a coupled process of hydraulic and geo(bio)chemical controls. It also extends our process-based quantification capabilities of water quality changes in complex groundwater systems.

The numerical data interpretation presented in this thesis provides guidance for sampling design and analysis for other MAR operations, where As mobilisation is suspected. Possible oxidants (e.g. O_2, NO_3, SO_4), ions competing with As for sorption sites (e.g. PO_4, DOC, HCO_3), arsenic speciation (As^{3+}, As^{5+}) and analytes which characterise the redox conditions of the aquifer (e.g. Fe, Mn) are shown to be essential for a quantitative understanding of arsenic behaviour and should be part of any future routine analysis. A lack thereof induces considerable uncertainty in the determination of the key chemical process influencing arsenic mobilisation.

A practical aspect of the developed quantification framework is its use as a tool for the assessment of the suitability of different MAR sites and different MAR techniques in regards to As mobility. It also provides a basis to assess and optimize operational conditions and their impact on As mobility as well as to evaluate proposed engineering solutions that could mitigate the As problem at affected MAR sites.

1.4 STRUCTURE OF THIS THESIS

This thesis comprises this introduction, three separate pieces of research work and supplementary information included as appendices. The general introduction (Chapter 1) gives a brief overview of the fundamental processes that occur in groundwater systems in relation to arsenic mobilisation and attenuation and our current ability to quantify these using numerical modelling and details the objectives of this thesis. The main research work is described in Chapters 2, 3 and 4. Written as manuscripts for publication in peer-reviewed journals, each of these chapters can be read independently as a stand-alone piece of research, including introduction, methodology, results and discussion and conclusions. The three manuscripts included in this thesis are:

(1) WALLIS, I., PROMMER, H., SIMMONS, C., POST, V. AND STUYFZAND, P. (2010): EVALUATION OF CONCEPTUAL AND NUMERICAL MODELS FOR ARSENIC MOBILIZATION AND ATTENUATION DURING MANAGED AQUIFER RECHARGE. *ENVIRONMENTAL SCIENCE & TECHNOLOGY*, VOL. 44 (13) P. 5035-5041 [CHAPTER 2]

(2) WALLIS, I., PROMMER, H., PICHLER, T., POST, V., NORTON, S.B., ANNABLE, M. AND SIMMONS, C. (2011): A PROCESS-BASED REACTIVE TRANSPORT MODEL TO QUANTIFY ARSENIC MOBILITY DURING AQUIFER STORAGE AND RECOVERY OF POTABLE WATER. *ENVIRONMENTAL SCIENCE & TECHNOLOGY*, 45(16):6924-31 [CHAPTER 3]

(3) WALLIS, I., PROMMER, H., POST, V., VANDENBOHDE, A., AND SIMMONS, C. (2012): SIMULATING MODFLOW-BASED REACTIVE TRANSPORT UNDER RADIAL-SYMMETRIC FLOW CONDITIONS. *GROUND WATER*, (IN PRESS). [CHAPTER 4]

Supplementary information for Chapters 2 and 3 are included as an appendix at the end of the document. In Chapters 2-4 some repetition of introductory information can be found. This was necessary for the autonomy of the papers. Additionally, conference papers, which were the direct result of this work are also included as appendices. The following appendices are included:

Appendix A: Additional figures and tables and supporting findings for Chapter 2

Appendix B: Additional figures and tables and supporting findings for Chapter 3

Appendix C: Example model input data for the Geometry, Langevin and Louwyck methods

- C1: Geometry method
- C2: Langevin method
- C3: Louwyck method

Appendix D: Published conference proceedings resulting from the research work

- D1: Numerical evaluation of arsenic mobilisation during deepwell injection of aerobic groundwater into a pyritic aquifer, *Goldschmidt 2009*
- D2: Evaluation of Conceptual and Numerical Model for Arsenic Mobilisation During Managed Aquifer Recharge, *2010 Ground Water Summit*
- D3: Reactive transport modelling to quantify arsenic mobilization and capture during aquifer storage and recovery of potable water, *Goldschmidt 2011*
- D4: Modelling of Arsenic fate during ASR of potable water, *ModelCare 2011*