Reactive transport processes in artificially recharged aquifers
-Field and modelling studies-

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Preface

The following work was conducted as part of the NASRI (Natural and Artificial Systems for Recharge and Infiltration) Project of the KompetenzZentrum Wasser Berlin, funded by the Berliner Wasser Betriebe and Veolia Water. The general aim of the Project was to gain a better understanding of the interacting physical, chemical and biological processes that affect the water quality changes during subsurface passage in riverbank filtration and ponded infiltration systems in the City of Berlin, Germany. The project was a cooperation of the Berliner Wasser Betriebe, Free University Berlin, Technical University Berlin, German Federal Environmental Agency and the Leibniz Institute of Freshwater Ecology and Inland Fisheries, Berlin. The research described in this thesis was carried out at the Leibniz Institute of Freshwater Ecology and Inland Fisheries in close collaboration with the Free University Berlin, CSIRO Land and Water, South Australia and the University of Utrecht, The Netherlands.

Abstract

Managed aquifer recharge is becoming increasingly popular to secure and enhance water resources through a variety of techniques such as riverbank filtration, aquifer storage and recovery (ASR) or ponded infiltration. In this thesis, three major studies were carried out in order to understand the key factors controlling the water quality changes that occurred during an ASR experiment at Bolivar, South Australia and during ponded infiltration in Berlin, Germany.

In the first study, multi-component reactive transport modelling was used to provide a consistent process-based interpretation of the observed hydrochemical changes that occurred during a reclaimed water ASR experiment at Bolivar. The major geochemical processes considered in the model were microbially mediated redox-reactions driven by the mineralisation of organic carbon, mineral dissolution/precipitation and ion exchange. The results suggest that during the storage phase, dynamic changes in bacterial mass have a significant influence on the local geochemistry in the vicinity of the injection well. Water quality changes further away from the injection well were mainly driven by ion exchange and calcite dissolution.

The aim of the second study was to identify the spatial and temporal distribution of the redox zones directly below an artificial recharge pond in Berlin, Germany. The system is characterised by regular hydraulic changes between saturated and unsaturated conditions due to the periodic formation of a clogging layer at the pond's bottom. Geochemical and hydraulic measurements showed that during summer nitrate and manganese reducing conditions generally dominated below the pond as long as water saturated conditions prevailed. Iron and sulphate reduction occurred only locally due to chemical and physical heterogeneity of the aquifer sediment. During unsaturated conditions, atmospheric oxygen penetrated from the pond margins to the centre below the pond, leading to (i) a sudden re-oxidation of the previously formed sulphide minerals and (ii) an enhanced mineralisation of sedimentary particulate organic carbon. During the entire winter period, the redox environment below the pond remains aerobic despite variable hydraulic conditions.

In the third study, multi-component reactive transport modelling was carried out to evaluate and quantify the processes controlling the redox dynamics and the related fate of the pharmaceutically active compound phenazone within the aquifer that surrounds the recharge pond. The simulation results showed that seasonal temperature changes of the infiltration water are the key control for the observed temporal and spatial redox dynamics. Variable residence times resulting from varying recharge rates appeared to be less important. It could also be shown that the phenazone's attenuation behaviour solely depends on the distribution of dissolved oxygen concentration within the aquifer.

Overall this thesis shows that a sound understanding and analysis of the key processes affecting the water quality changes during artificial recharge of groundwater could only be achieved when flow, transport and reactive processes are considered simultaneously, both in the field and during modelling.

Zusammenfassung

Künstliche Grundwasseranreicherung (GWA) gewährleistet zunehmend die Sicherung von Wasserressourcen. Techniken der künstlichen GWA umfassen dabei die Uferfiltration, Anreicherung über Injektionsbrunnen (engl.: Aquifer Storage and Recovery (ASR)) und Versickerung über so genannte Grundwasseranreichungsbecken. In der vorliegenden Dissertation sollten die hydrogeochemischen Prozesse herausgearbeitet werden, die für die Wasserqualitätsänderung während eines ASR Experiments in Bolivar, Südaustralien und während der Versickerung in einem künstlichen Grundwasseranreicherungsbecken in Berlin von Bedeutung waren.

Im Rahmen einer ersten Studie wurde eine reaktive Stofftransportmodellierung durchgeführt, mit dem Ziel, die im Bolivar ASR Experiment beobachteten hydrochemischen Veränderungen im Aquifer zu interpretieren. Die Modellierung zeigte, dass die hydrochemischen Veränderungen in der direkten Umgebung des Injektionsbrunnens während der Speicherphase nur durch rapide Konzentrationsänderungen der Sauerstoff- und Nitrat reduzierenden Bakterien erklärt werden können. Die hydrochemischen Veränderungen in größerer Distanz zum Injektionsbrunnen wurden überwiegend durch Ionenaustauschprozesse und Kalzitlösung verursacht.

In einer zweiten Studie sollte im Wesentlichen die räumliche und zeitliche Verteilung von Redoxzonen direkt unter einem Sickerbecken in Berlin untersucht werden. Hydraulisch ist das betrachtete System durch wechselnde gesättigte und ungesättigte Bedingungen charakterisiert, verursacht durch die natürliche Bildung einer Kolmationsschicht am Beckenboden. Geochemische und hydraulische Messungen zeigten, dass im Sommer Nitrat- und Manganreduzierende Bedingungen vorherrschend sind, solange das Sediment unter dem Becken voll wassergesättigt ist. Eisen- und Sulfatreduktion findet nur marginal in einigen anaeroben Mikrozonen statt. Während der nachfolgenden ungesättigten Phase wird Luft unter das Becken gezogen und führt zur plötzlichen Reoxidierung von zuvor gebildeten Eisensulfiden und zur beschleunigten Mineralisation von sedimentärem organischem Kohlenstoff. Im Winter bleibt das Sediment unter dem Becken trotz der variablen gesättigt/ungesättigen hydraulischen Bedingungen im aeroben Zustand.

In der letzten Studie wurde eine reaktive Stofftransportmodellierung durchgeführt, um zu untersuchen welche Prozesse in welchem Maße die Dynamik von Redoxzonen und das Abbauverhalten der Arzneimittelsubstanz Phenazon in dem Sickerbecken umgebenden Aquifer steuern. Die Modellierung zeigte, dass allein die saisonalen Temperaturunterschiede im Infiltrationswasser für die beobachtete zeitliche und räumliche Dynamik der Redoxzonen verantwortlich sind. Des Weiteren konnte gezeigt werden, dass der Phenazonabbau ausschließlich von der Verteilung der Sauerstoffkonzentration im Aquifer abhängt.

In der vorliegenden Arbeit wird deutlich, dass ein adäquates und umfassendes Verständniss der wasserqualitätsändernden Prozesse in künstlichen Grundwasseranreicherungsystemen nur dann erreicht werden kann wenn Strömung, Transport und reaktive Prozesse, im Feld als auch in der Modellierung, simultan betrachtet werden.

Contents

1 General introduction

1.1 Artificial recharge of groundwater

Within the last 50 years, the world's annual production of organic chemicals, such as pesticides, solvents, cleansing agents and drugs has increased from 7.5 Megatons to 300 Megatons, and more and more of these compounds are detected at trace concentrations in the aquatic environment, including the groundwater (Scheffer and Schachtschabel, 2002). This demonstrates that anthropogenic pollution of freshwater resources is one of the most challenging problems of the modern world, which has to be faced by the human race in the coming decades (UNEP, 2002).

Since groundwater is a major source for drinking water and also compensates agricultural and industrial water demands, artificial groundwater recharge will be increasingly important for effective water resource management, safety and continuity in water supply (Martijn, 1998). Artificial recharge of groundwater includes a variety of techniques, such as riverbank filtration (e.g., Sontheimer, 1980; Kühn and Müller, 2000; Ray et al., 2002), aquifer storage and recovery (ASR, Pyne, 1995; Herczeg et al., 2004; Dillon et al., 2005), deep well injection (e.g., Stuyfzand, 1998) and infiltration ponds (Asano, 1992; Bouwer, 2002). All over the world, numerous artificial recharge applications already exist or are currently under investigation. The following list gives a brief overview of the broad range of environmental and technical problems for which artificial recharge of groundwater has already been applied or planned:

- Artificial recharge of pre-treated Rhine water in the coastal dune area west of Amsterdam prevents further sea water upconing that resulted from excessive groundwater extraction for drinking water supply (van Breukelen et al., 1998).

- ASR of treated imported water is considered to avoid further land subsidence in the city of Lancaster (California), which was induced by excessive groundwater production since the 1920s, causing increased erosion, flooding and structural damages (Phillips et al., 2002).

- Storm and reclaimed water ASR in South Australia is intended to store excess water in the wet season for the supply of irrigation water in the dry season (Dillon et al., 1999; Vanderzalm, 2004).

- Deep well injection of surface water in the Netherlands is proposed to recharge confined aquifers in order to compensate the drawdown of groundwater tables due to increasing drinking water demands (Stuyfzand, 1998).

- So-called soil-aquifer treatment (SAT), i.e., quality improvement of pre-treated wastewater by infiltration in recharge ponds and its subsequent downgradient recovery through extraction wells is very popular in many dry regions of the world (e.g., Idelovitch and Michail, 1984;

Fox, 2002). The feasibility of this wastewater reuse technique was demonstrated in the prominent Flushing Meadows Project installed west of Phoenix, USA in 1967 (Bouwer et al., 1980).

- Riverbank filtration and ponded infiltration has been used for pre-treatment of surface water for more than hundred years in Europe (Kühn and Müller, 2000; Hiscock and Grischek, 2002). For instance, about 16% of the drinking water in Germany is provided by riverbank filtration and ponded infiltration (Kühn and Müller, 2000), which is applied mainly in densely populated urban areas, e.g., the City of Berlin, where about 70% of the drinking water production depends on these techniques (Massmann et al., 2004a).

1.2 Processes and water quality issues

During infiltration and subsurface flow, the artificially recharged water usually undergoes quality changes. In general, they result from the interaction of physical (filtration, advection and dispersion), chemical (sorption, precipitation/dissolution) and biological (biodegradation) processes (e.g., Jacobs et al., 1988; von Gunten et al., 1991; Bourg and Bertin, 1993, 1994; von Gunten and Zobrist, 1993; Hiscock and Grischek, 2002). The geochemical changes in a hydrogeological system are often to a large extent triggered and determined by microbial mediated redox reactions (e.g., Eckert and Appelo, 2002; Massmann et al, 2004b). These redox reactions are driven by the biodegradation of dissolved and/or sediment-bound organic matter and involve the consumption of so-called terminal electron acceptors (TEA), such as O_2, NO_3^-, manganese- and iron-(hydro)oxides, SO_4^{2-} and dissolved inorganic carbon (e.g., Lovley and Phillips, 1988; McMahon and Chapelle, 1991; Chapelle and Lovley, 1992; Lovley et al., 1994; Chapelle et al., 1995). Typically, the consumption of the TEA occurs in a sequential order constrained by thermodynamic principles (e.g., Champ et al., 1979; Stumm and Morgan, 1996; Postma and Jakobsen, 1996; Christensen et al., 2000). With decreasing of Gibbs free energy, this redox sequence theoretically starts with aerobic respiration and is subsequently followed by denitrification, manganese-, iron- and sulphate reduction and finally methanogenesis (Figure 1.1a). In a groundwater flow system, this leads to the formation of spatially distinct redox zones along the flow direction (Champ et al., 1979; Matsunaga et al., 1993; von Gunten and Zobrist, 1993; Bjerg et al., 1995; Amirbahman et al., 2003). This is schematically shown in Figure 1.1b.
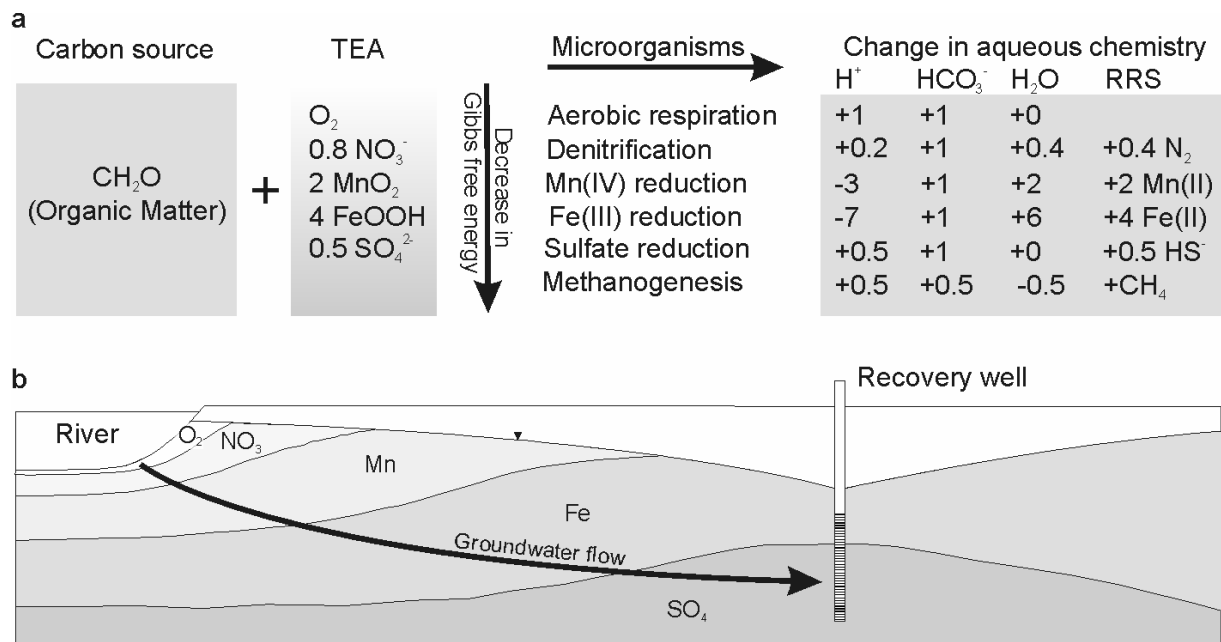
a

Carbon source	TEA	Microorganisms	Change in aqueous chemistry			
			H^+	HCO_3^-	H_2O	RRS
	O_2	Aerobic respiration	+1	+1	+0	
	$0.8\ NO_3^-$	Denitrification	+0.2	+1	+0.4	$+0.4\ N_2$
CH_2O $+$ (Organic Matter)	$2\ MnO_2$	Mn(IV) reduction	-3	+1	+2	$+2\ Mn(II)$
	$4\ FeOOH$	Fe(III) reduction	-7	+1	+6	$+4\ Fe(II)$
	$0.5\ SO_4^{2-}$	Sulfate reduction	+0.5	+1	+0	$+0.5\ HS^-$
		Methanogenesis	+0.5	+0.5	-0.5	$+CH_4$

Decrease in Gibbs free energy

b

Figure 1 a. (adapted from van Breukelen (2003)): Theoretical sequence of terminal electron acceptor (TEA) processes related to the biodegradation of organic matter in hydrogeochemical systems. RRS = reduced redox species. **b.** Schematic illustration of spatially distinct redox zones (O_2=aerobic-, NO_3=denitrifying-, Mn=Mn-reducing- , Fe=Fe-reducing- and SO_4=sulfate reducing conditions) along the ground water flow direction during riverbank filtration.

The redox reactions often induce additional reactions such as precipitation and dissolution of minerals, ion exchange or surface complexion reactions due to the consumption and production of protons and other reactants (e.g., Eckert and Appelo, 2002). Besides water quality changes, these reactions can also change the hydrogeological properties of the aquifer such as porosity and hydraulic conductivity (Vandevivere and Baveye, 1992; Rinck-Pfeiffer et al., 2000) as well as the geochemical properties such as mineral reactivity (Postma and Jakobsen, 1996; Larsen and Postma, 2001) and sorption capacity (Dzombak and Morel, 1990, Stumm and Morgan, 1995). Thereby, the latter is of high importance, since it can affect the mobility of trace metals such as Cd, Ni, Zn or As (e.g., Jacobs et al., 1988; Appelo and de Vet, 2002).

Natural degradation processes (i.e., biodegradation and sorption) can help to remove dissolved (trace) organic compounds as well as pathogenic bacteria and viruses, and thus are of importance for the protection of ground- and drinking water quality in artificial recharge systems (Bosma et al., 1996). However, the nature and reaction rates of these processes are strongly determined by physical and chemical conditions. For instance, the biodegradability of many organic micropollutants, such as pharmaceutically-active compounds (PhAC's, Holm et al., 1995; Khan and Rorije, 2002; Ternes et al., 2004 and references therein), pesticides (Agertved et al. 1992; Tuxen et al., 2000; Broholm et al., 2001a,b) or adsorbing organic halogens (AOX, Ziegler et al., 2002) and other halogenated organic compounds (Bouwer and McCarty, 1983; Gupta et al., 1996; Bosma et al., 1996) is affected by locally prevailing redox conditions. Moreover, the fate of pathogenic microorganisms is often influenced by water quality parameters such as pH, redox state, ionic strength and divalent cation concentration (Schijven, et al., 2000; Zhuang et al., 2003).

1.3 Scientific problems

A major aim of the research on artificial recharge of groundwater is to understand the potential key factors that control the water quality changes occurring between recharge/infiltration and recovery. The influence of those factors can be very different, depending on field site characteristics such as recharge water quality, composition of aquifer matrix, subsurface residence time or hydraulic conditions. In order to assess these factors and quantify their influence on the water quality changes at a specific field site, a complex understanding of the interactions of hydraulic, hydrogeochemical and microbial processes is necessary. Since these (non-linear) interactions are generally not intuitive (Amos et al., 2004), the identification and quantification of key processes by interpreting collected field data is difficult and often cannot be clarified with confidence. Interpretation is even trickier when the hydraulic and hydrochemical boundary conditions such as recharge/recovery rate and recharge water quality are highly transient. Unfortunately, such conditions are the rule rather than the exception in artificial recharge systems (e.g., von Gunten et al., 1991, 1994; Bourg and Bertin, 1994; Bouwer, 2002; Vanderzalm, 2004). Thus, for a thorough analysis of such complex hydrogeochemical systems, simultaneous high-resolution monitoring of both hydraulic and hydrochemical parameters in space and time is fundamental.

Typically, the acquisition of spatially and temporally dense information, especially in the field, is quite expensive and so records are generally sparse. Integrated mathematical modelling is becoming increasingly popular to (i) fill the gaps between the measured data and (ii) assist in analysing and understanding complex environmental systems (Prommer and Barry, 2005). In the past decade, multi-component reactive transport modelling has been used to support the identification of the relevant hydrogeochemical processes in artificial recharge systems both at laboratory (Matsunaga et al., 1993; Amirbahman et al., 2003) and field scale (Valocchi et al., 1981; Lensing et al., 1994; Doussan et al., 1997; Parkhurst and Petkewich, 2002; Appelo and de Vet; 2002; Prommer and Stuyfzand, 2005). However, most of these modelling studies only regarded steady-state hydraulic and/or hydrogeochemical boundary conditions and also only addressed a sparse set of possible hydrogeochemical interactions. It appears that there is still a lack of reactive transport models applied to more complicated field situations, which, as already pointed out, are the rule rather than the exception.

Moreover, the importance of redox conditions for the fate of organic micropollutants was highlighted in a number of field site investigations (e.g., Holm et al., 1995; Agertved et al. 1992; Broholm et al., 2001a,b; Bosma et al., 1996; Grünheid et al., 2005; Massmann et al., 2005a,b). Studies incorporating this knowledge into process-based, field scale modelling frameworks would be extremely helpful in supporting these findings and evaluating their importance also in relation to the transient hydraulic and hydrochemical boundary conditions. To date, such mechanistic modelling studies do not seem to exist in the literature.

Conclusively, for a sound understanding of how the interacting processes, especially under transient boundary conditions, affect the water quality changes during artificial recharge of groundwater, there is an urgent need for more detailed field site and modelling investigations.

1.4 Scope of this work

In this work, two specific artificial recharge sites were investigated for the relevant hydraulic and hydrogeochemical processes. The research was conducted by three separate studies described in Chapter 2, 3 and 4. The specific objectives were as follows:

- Providing a process-based modelling framework that integrates and interprets the hydrogeochemical data colleted during a reclaimed water ASR experiment at Bolivar, South Australia. Thereby, the focus was to understand the fate of the various forms of organic and inorganic carbon, and the role of biomass dynamics.

- Understanding the impact of transient saturated and unsaturated conditions directly below an artificial recharge pond on the dynamics of hydrogeochemical changes during infiltration. This field site investigation was carried out at a recharge pond in Berlin, Germany.

- Providing a process-based modelling framework to clarify the seasonal degradation behaviour of the redox-dependent pharmaceutical residue phenazone within the aquifer surrounding the investigated recharge pond.

- Exploring the capabilities of multi-component reactive transport modelling to interpret field observations in artificial recharge systems, and to reveal and quantify the complex non-intuitive interactions of the controlling processes in those systems.

The different studies of this work were carried out with the help of (i) field site methods, i.e., monitoring of hydraulic and hydrochemical data as well as measurements of the aquifer properties and (ii) modelling methods, i.e., hydraulic and multi-component reactive transport modelling of the investigated hydrogeochemical systems. The specific methods used in this thesis are described in detail in the following chapters.

1.5 Structure of this thesis

This thesis comprises this introduction, three separate pieces of research work, synthesis and appendices. The general introduction (Chapter 1) gives a brief overview of artificial groundwater recharge, fundamental processes that occur in these systems, the state-of-the-art research background, remaining problems and the scope 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. They are as follows:

Chapter 2 is published as:

Greskowiak, J., Prommer, H., Vanderzalm, J., Pavelic, P., Dillon, P. (2005), Modelling of carbon cycling and biogeochemical changes during injection and recovery of reclaimed water at Bolivar, South Australia, *Water Resources Research*, 41(10), W10418, doi:10.1029/2005WR004095.

Chapter 3 is published as:

Greskowiak, J., Prommer H., Massmann, G., Johnston, C. D., Nützmann, G., Pekdeger, A. (2005), The Impact of variably saturated conditions on hydrogeochemical changes during artificial recharge of groundwater, *Applied Geochemistry,* 20(7), 1409-1426.

Chapter 4 is published as:

Greskowiak, J., Prommer H., Massmann, G., Nützmann, G. (2006), Modeling seasonal redox dynamics and the corresponding fate of the pharmaceutical residue phenazone during artificial recharge of groundwater, *Environmental Science and Technology,* doi: 10.1021/es052506t.

In all three cases I have carried out the research work described and authored the paper manuscripts. The co-authors have played advisory or supervisory roles. In chapters 2-4 a limited amount of repetition of introductory information can be found, which was necessary for the autonomy of the papers.

Chapter 5 summarises the conclusions of this thesis and provides recommendations for future research.

Appendix A: Conference paper supporting the findings of Chapter 2:

Greskowiak J., Prommer H., Vanderzalm J. L., Pavelic P., Dillon P. J. (2005), Quantifying Biogeochemical Changes during ASR of Reclaimed Water at Bolivar, South Australia, *Proceedings of 5th International Symposium on Management of Aquifer Recharge, Berlin, June 2005*, in press.

Appendix B: Conference paper extending the results found in Chapter 3:

Greskowiak J., Massmann G., Nützmann G., Prommer H. (2005), Hydrogeochemical Changes of Seepage Water during Artificial Recharge of Groundwater in Berlin, Germany, *Proceedings of 5th International Symposium on Management of Aquifer Recharge, Berlin, June 2005*, in press.

Appendix C: Additional Figures and Tables, which in the original manuscripts (Chapters 2-4) were declared as *not shown*.

2 Modelling of carbon cycling and biogeochemical changes during injection and recovery of reclaimed water at Bolivar, South Austalia

Published as:

3 The impact of variably saturated conditions on hydrogeochemical changes during artificial recharge of groundwater

Published as:

Greskowiak, J., Prommer H., Massmann, G., Johnston, C. D., Nützmann, G., Pekdeger, A. (2005), The Impact of variably saturated conditions on hydrogeochemical changes during artificial recharge of groundwater, *Applied Geochemistry,* 20(7), 1409-1426.

4 Modeling seasonal redox dynamics and the corresponding fate of the pharmaceutical residue phenazone during artificial recharge of groundwater

Published as:

5 Synthesis

The overall aim of this thesis was the identification and quantification of the hydraulic and hydrogeochemical key processes controlling the water quality changes during a reclaimed water ASR experiment in Bolivar and during artificial recharge at an infiltration pond in Berlin. This aim was successfully met with a variety of field and modelling methods. Based on the results of Chapters 2, 3 and 4, this chapter summarises the major conclusions of this research and gives prospects for future research on the investigated artificial recharge systems and reactive transport modelling of such systems in general.

5.1 Major conclusions

Since in this thesis two different artificial recharge schemes in completely different field situations were investigated, the conclusions are predominantly site-specific, and thus are presented here separately for each field site. Conclusions relating to the reactive transport modelling issues are given thereafter.

5.1.1 Bolivar site

A quantitative process-based modelling framework was developed and applied to an ASR experiment at Bolivar, Australia, in order to simulate the geochemical response during injection, storage and recovery. The developed modelling framework is capable of providing a very good quantitative description of the physical and biogeochemical processes that occurred during the injection, storage and recovery periods. The modelling study in particular demonstrates that the explicit incorporation of bacterial mass is essential to describe the local hydrogeochemical effects occurring in the vicinity of the injection/extraction well during the storage phase. Without a detailed microbial growth and decay model, these hydrogeochemical observations could not be reproduced at all (see Appendix A). The model shows that hydrogeochemical changes further away from the injection/extraction well were mainly driven by ion exchange and calcite dissolution. Microbial mass dynamics have no relevance for the hydrochemical changes further away from the injection/extraction well. In summary, the model provides a consistent interpretation of how different biogeochemical processes affect the injected plume on its full scale. Besides the advanced process understanding, a practical aspect of this study lies in the preliminary evaluation of how much the aquifer properties might by altered by physical, chemical and biological clogging processes. The model simulations affirm that significant local conductivity reduction did not occur during the field study.

5.1.2 Berlin site

The artificial recharge pond in Berlin was investigated in Chapter 3 and 4 of this thesis with the aims of (i) identifying the hydraulic regime and its impact on the dynamics of the hydrogeochemical environment immediately below the pond, and (ii) providing a quantitative process-based modelling framework for simulating the fate of the redox-sensitive PhAC phenazone within the surrounding aquifer of the pond.

Directly below the recharge pond, the hydrogeochemical environment is predominantly impacted by transient hydraulic conditions and seasonal temperature variations. Thereby, the entire hydraulic system is controlled by the formation of a clogging layer at the bottom of the pond resulting in alternating saturated/unsaturated conditions below the pond. During summer, when the infiltrated water is relatively warm (about 20-25°C), the spatial and temporal distribution of different redox conditions is strongly determined by the prevailing hydraulic conditions and their dynamics below the pond. When the sediment below the pond is fully water saturated in the earlier part of the operational recharge cycle, nitrate reducing and manganese reducing conditions are dominant. Iron and sulphate reducing conditions develop only in anaerobic micro-sites due to chemical and/or physical heterogeneity. When the hydraulic conditions change from water saturated to water unsaturated conditions, which is approximately in the middle of the recharge period, remarkable changes of the local hydrogeochemistry below the pond can be observed. They result from the temporal re-oxidation of previously formed iron-sulphides due to the lateral intrusion of atmospheric oxygen penetrating from the pond margins into the centre below the pond. During the following unsaturated period, the availability of atmospheric oxygen enhances the mineralisation of particulate organic carbon, which in turn promotes the dissolution of calcite. Whereas in summer the dynamics and the character of the hydrochemical system are strongly affected by the hydraulic situation below the pond, hydrogeochemical changes are relatively independent from the hydraulic conditions in winter. During the entire winter period, the redox status below the pond remains aerobic due to decreased biodegradation rates at lower temperatures (see Appendix B). Since the redox system does not shift to nitrate reducing conditions during winter, nitrification of sedimentary bound nitrogen can be observed as elevated nitrate concentrations in the groundwater. This could indicate that nitrification below the pond is less affected by temperature changes than nitrate reduction.

The modelling study for this site showed that at larger scale, the hydrogeochemical processes, in particular the redox processes, are predominantly controlled by seasonal temperature changes rather than transient groundwater flow due to varying recharge rates. The influence of transient saturated/unsaturated conditions appeared not to be important for the behaviour of the hydrogeochemical system on that scale. It could be clearly demonstrated that solely the redox dependency of the degradation rate of phenazone controls the fate of phenazone in the subsurface of this artificial recharge site.

5.1.3 Reactive transport modelling

Throughout the modelling procedures in Chapter 2 and 4, the capabilities of mechanistic multi-component reactive transport modelling for interpreting field observations and understanding and quantifying the non-intuitive interactions of processes in artificial recharge systems were intensively tested. Both modelling studies clearly illustrate the suitability of multi-component reactive transport modelling as a fundamental tool for analysing the complex hydrogeochemical processes occurring in artificial recharge systems. It was demonstrated that such models could be used to successfully evaluate the underlying physical, chemical and biological processes separately, which in reality are highly co-dependent. This allows a systematic development and verification of new hypotheses of how these processes interact. Furthermore, the application of the model independent parameter estimation program PEST to the Bolivar reactive transport model was found to be particular useful, since the automatically generated calibration statistics helped to evaluate the selected conceptual model and its parameterisation. However, the processes and the respective parameters that were identified for both artificial recharge systems are, of course, subject to the ever-present uncertainty problem. Thus, it's clear that there might be other conceptual models, which describe the field observations equally well. An extensive predictive capability of the developed models at this stage is therefore unrealistic, especially for other field sites with different recharge water and site characteristics. However, future studies for other sites or long-term data of the Bolivar and Berlin site will provide additional constrains to test the present and potential alternative conceptual models. Fortunately, the flexible nature of sophisticated and user-friendly modelling tools such as PHT3D allow a quick and steady improvement and adoption of conceptual models rather than to focus on a single conceptual model where pre-defined parameters are fitted.

5.2 Prospects

As outlined in the previous section, for a further verification of the present conceptual models developed in Chapter 2 and 4, it would be necessary to extend the simulation periods where data is available. This is especially needed for the Bolivar site, as it has not been tested yet if the model is able to adequately reproduce the geochemical evolution of the injected plume, the recovered water and the groundwater for more than the one ASR-cycle. After an extension of the simulation period and a possible re-calibration of the reactive transport model for the Bolivar site, the incorporation of disinfection-by-products as components into the modelling framework might be of interest, since it has been found that the fate of some of these compounds are highly dependent on the local geochemical environment (Pavelic et al., 2005). Analogue to the investigation of the fate of phenazone at the recharge site in Berlin, such an extended model can help to find and quantify the key processes of the attenuation behaviour of these compounds during ASR.

Since the monitoring of hydrogeochemical changes within the unsaturated zone below the recharge pond at the Berlin site was restricted to the fringe area (Chapter 3), the magnitude of

hydrochemical changes of the seepage water in the centre area of the pond is still unclear. In order to fill this gap, future investigations on that site are recommended including (i) an extended field campaign monitoring the relevant hydraulic and hydrochemical parameters in the entire cross-sectional area below the pond, and (ii) the development of a two-dimensional multi-component reactive transport model for this cross section, considering advective-dispersive transport of O_2 and CO_2 in the gas phase and major ions in the water phase during the unsaturated stage.

With the successful simulation of the redox dynamics and the fate of phenazone at the Berlin site, one can expect that it is also possible to model the fate of other phenazone-type pharmaceuticals such as 1-acetyl-1-methyl-2-dimethyloxamoyl-2-phenylhydrazide (AMDOPH), 1-acetyl-1-methyl-2-phenylhydrazid (AMPH), Acetoaminoantipyrin (AAA), formylaminoantipyrin (FAA), 1,5-dimethyl-1,2-dehydro-3-pyrazolone (DP) and 4-(2-methylethyl)-1,5-dimethyl-1,2-dehydro-3-pyrazole (PDP) that were detected at the artificial recharge site in Berlin (Massmann et al., 2005b).

An appealing option for the site operator (BWB) might be the ability to simulate the quality of the water extracted by the surrounding production well field, because the extraction water quality is likely to be altered by operational changes of the pumping regime or recharge rates. The development of a three-dimensional reactive transport model for a larger model domain capturing the production well field is undoubtedly possible, since a calibrated site-specific reaction module for the aquifer now exists (Chapter 4).

More general, for future investigations on artificial recharge systems I would strongly recommend the integration of mechanistic reactive transport modelling into the working program. This would be especially beneficial when looking at potential harmful compounds or pathogens, as multi-component reactive transport models intrinsically determine the local geochemical environment such as major ion concentration, ionic strength, pH and redox potential, which the fate of these contaminants often depends on. Moreover, as exemplarily demonstrated in Chapter 2, using automatic calibration procedures in conjunction with the development of conceptual reaction models can give valuable insights into the suitability of the chosen parameterisation. This means, for a systematic evaluation of the developed conceptual models, there is an urgent need for integrating automatic parameter estimation into the field of reactive transport modelling.

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Appendix A: Conference Paper 1 (supplement to Chapter 2)

Quantifying biogeochemical changes during ASR of reclaimed water at Bolivar, South Australia

Abstract

A modelling study was carried out to provide a process-based quantitative interpretation of the biogeochemical changes that were observed during an ASR experiment in which reclaimed water was injected into a limestone aquifer at a field-site near Bolivar, South Australia. A site-specific conceptual model for the interacting hydrodynamic and biogeochemical processes that occur during reclaimed water ASR was developed and incorporated into an existing reactive multi-component transport model. The major reactive processes considered in the model were microbially mediated redox reactions, driven by the mineralisation of organic carbon, mineral precipitation/dissolution and ion exchange. The study showed that the geochemical changes observed in the vicinity of the ASR well could only be adequately described by a model that explicitly considers microbial growth and decay processes, while an alternative, simpler model formulation based on the assumption of steady state biomass concentration failed to reproduce the observed hydrochemical changes. However, both, the simpler and the more complex model approach were able to reproduce the geochemical changes further away from the injection/extraction well. These changes were interpreted as a result of the combined effect of ion exchange, calcite dissolution and mineralisation of dissolved organic carbon.

Introduction

Aquifer Storage and Recovery (ASR, Pyne, 1995) is an increasingly popular technique to augment groundwater resources and secure and enhance water supplies. During ASR, physical, chemical and biogeochemical processes modify the water quality within the target aquifer. For instance, the injection of both oxic potable water and oxic nutrient-rich reclaimed water into an anaerobic aquifer can lead to a number of microbially mediated redox reactions (Stuyfzand, 1998; Vanderzalm et al., 2002), which in turn may trigger further geochemical reactions that have a considerable effect on the water quality and the composition of the aquifer matrix. (Eckert and Appelo, 2002). In order to design and operate efficient, sustainable and safe ASR schemes, a qualitative and quantitative understanding of those processes is important. Therefore, several field-scale investigations have been carried out over the past years, some of them specifically investigating the geochemical response to the injection of high quality water (e.g., Stuyfzand, 1998; Mirecki et al., 1998) but also of reclaimed wastewater (e.g., Valocci et al., 1981; Vanderzalm et al., 2002). However, numerical models which investigate the interacting hydrodynamic and biogeochemical processes during ASR (e.g., Valocchi et al., 1981, Saaltink et al., 2003; Prommer and Stuyfzand, 2005) and assist in the analysis and interpretation of observed field data are rather scarce to date.

As part of a larger-scale study (Dillon et al., 2005), Greskowiak et al., (2005, Chapter 2) developed a site-specific modelling framework that provides a process-based interpretation of the

biogeochemical changes that occurred during a field experiment in which pre-treated, nutrient-rich reclaimed water was injected into a limestone aquifer at Bolivar, South Australia.

The present paper addresses the ubiquitous question of selecting an appropriate level of model complexity under such circumstances. To illustrate this issue we compare and discuss two alternative conceptual biogeochemical models and their numerical implementation in relation to their respective capability of describing the observed field data.

Background

The Bolivar ASR site is located in the Northern Adelaide Plains, South Australia and used to investigate the viability of storage and recovery of reclaimed water intended to compensate the greater demand of irrigation water during summer (Vanderzalm *et al.*, 2002). During the experiment, the reclaimed water was injected into a brackish limestone aquifer, which is separated from the overlying fresh water aquifer by a 7.5 m thick confining clay layer. Discontinuous injection of 250 ML took place between October 1999 and April 2000, followed by a storage period of 110 days. Subsequently, about 150 ML were recovered within the following 130 days (Figure A.1). The injection took place over the entire depths of the target aquifer, i.e., from 103 m to 160 m below the ground surface. Several multilevel wells have been installed at various radial distances from the ASR well, monitoring the geochemical evolution of the groundwater during injection, storage and recovery.
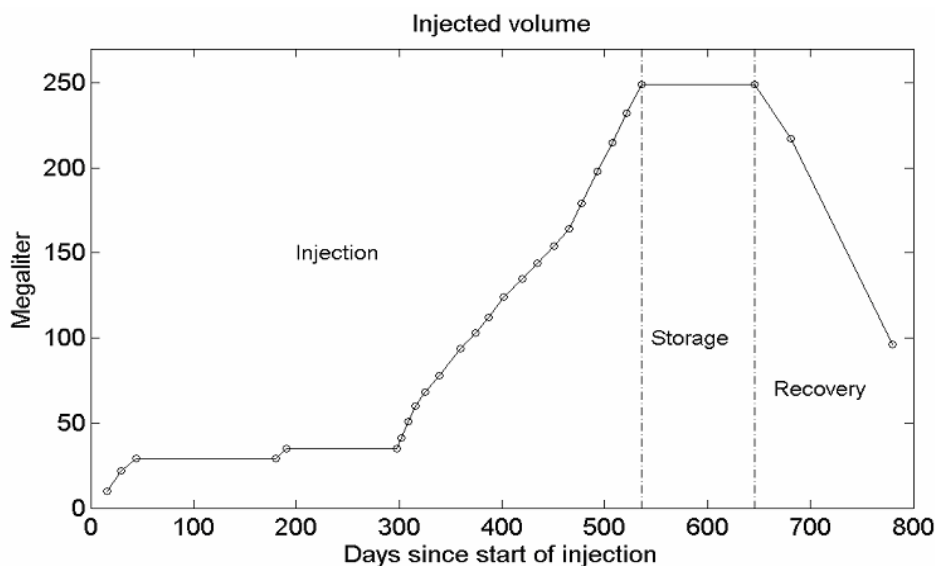

Figure A.1: Cumulative volume of injected water

The hydrogeochemistry of the target aquifer is characterised by anoxic conditions and the aquifer matrix is composed of about 74 % calcite, 18 % quartz and small amounts of ankerite and hematite (Vanderzalm *et al.*, 2002). The average total cation exchange capacity (CEC) is 20 meq/kg.

Pumping tests, flowmeter, temperature and anisotropy measurements revealed that the target aquifer could be classified into four stratified zones of similar thickness but of distinctly different permeability with an average horizontal hydraulic conductivity of about 3 m/d (Pavelic et al., 2001). Thereby, lateral flow occurs preferentially in two layers, referred to as Layer 1 and Layer 3. Throughout the trial period, the quality of the injectant varied significantly with time. For example, oxygen and nitrate concentrations ranged between <0.02 and 0.32 mmol/L and <0.0004 and 0.34 mmol/L, respectively. Correspondingly, ammonium concentrations varied between <0.02 and 2 mmol/L. However, dissolved organic carbon concentrations (DOC) were relatively constant with an average concentration of 1.40 mmol/L. The average total organic carbon concentration (TOC) was slightly higher (~1.51 mmol/L) and it is assumed that organic matter in particulate form (POC) compensated the concentration difference between DOC and TOC. The injection water is generally under-saturated with respect to calcite ($SI_{Calcite}$ = -1.44 to 0.13). As the chloride concentration of the injectant is approximately 50 % of the ambient groundwater concentration, chloride was thought to be a suitable tracer for the identification of physical transport. More details on the monitored hydrochemistry are given in Vanderzalm *et al.* (2002).

Groundwater flow and reactive transport model

In a first step a three-dimensional flow and conservative transport model of the ASR trial was set up and calibrated. In a second step the results were used to determine the groundwater flow within the most permeable layer (Layer 3) and to construct a computationally more efficient quasi-radial flow and transport model for this particular layer. The quasi-radial flow model formed the basis for the subsequent simulations with the reactive multi-component transport model PHT3D (Prommer *et al.*, 2003). The reaction network considered in those simulations included all major ions, oxygen, one type of ion exchanger site, two forms of mobile organic carbon (i.e., DOC, POC), immobile organic carbon, four minerals (i.e., calcite, hematite, siderite and amorphous iron sulphide) and two microbial groups. The two microbial groups were defined as facultative aerobic/denitrifying bacteria and facultative iron/sulphate-reducing bacteria, respectively. The reaction stoichiometry of the redox reactions, which incorporate microbial growth and decay were adapted from Prommer *et al.* 2002 and linked to a standard Monod-type microbial growth model (e.g., Barry *et al.*, 2002). The POC contained in the injectant was expected to rapidly become immobile in the close vicinity of the ASR well due to filtration (Skjemstad *et al.*, 2002) and attachment was simulated using first order kinetics. From there it was assumed to solubilise and to form a continuous source of DOC. The solubilisation was simulated by a kinetic approach adapted from Kinzelbach *et al.*, 1991. More details are given in Greskowiak *et al.* (2005, Chapter 2). For the present study two alternative conceptual biogeochemical models of differing complexity were investigated:

In alternative (A), the simplifying assumption of a steady state microbial concentration was incorporated and the mineralisation of DOC releases ammonia (Jacobs et al., 1988)

In alternative (B), microbial growth and decay were explicitly modelled and the release of ammonium was assumed not to be associated with the solubilisation of the filtered POC. Instead, ammonium was cycled through the occurrence of biomass growth and decay. That is, ammonium was included as a nitrogen source during biomass formation while biomass decay was assumed to release ammonium back into the aqueous phase.

For both alternatives, adjustable model parameters, i.e., the rate constants of the kinetic reactions were fitted such that the residual between simulated and observed concentrations was minimised. For this process the model-independent nonlinear parameter estimation program PEST (Doherty, 2002) was coupled to PHT3D.

Results and discussion

The simulation results of both calibrated alternatives (A) and (B) were compared with the hydrogeochemical data collected at the ASR well and the 50m well. The simulation results indicated that both alternatives were capable of reproducing the key features of the hydrochemical changes which occurred at the 50 m well during injection, storage and recovery. In the model, the degradation of DOC is accompanied by the consumption of oxygen (not shown), nitrate (Figure A.2) and sulphate (Figure A.2), as measured in the field. Furthermore, the observed retarded ammonium breakthrough at the 50m well can be decribed accurately by the simulated ion exchange reactions (Figure A.2), while the increased concentrations of calcium (relative to nonreactive transport, see Figure A.2) result from the dissolution of calcite.

However, alternative (A) was unable to account for some of the highly dynamic changes of the local geochemistry observed in the close vicinity of the ASR well during the storage period. While the observed rapid increase of DOC was well matched by the simulations (Figure A.2), the increase of ammonia (Figure A.2), alkalinity (Figure A.2), calcium (Figure A.2) and dissolved iron (not shown) as well as the drastic decrease of sulphate (Figure A.2) and pH (Figure A.2) was not reproduced by alternative (A).

On the other hand, all of the geochemical changes observed at the ASR well could be adequately simulated by alternative (B), providing evidence that the observed hydrochemistry is strongly affected by the dynamics of microbial growth and decay. The model results suggest that in particular during the storage period, microbial decay, i.e., the mineralisation of highly degradable biomass, plays a key role and consumes considerable amounts of oxidation capacity, as discussed in Prommer *et al.* (2002). Correspondingly, inorganic carbon and protons are produced during decay, as was observed in the field. In the model this effect was caused by the decay of facultative aerobic/denitrifying bacteria (Figure A.2), which reduced sulphate (Figure A.2) and hematite (not shown) during the storage period.
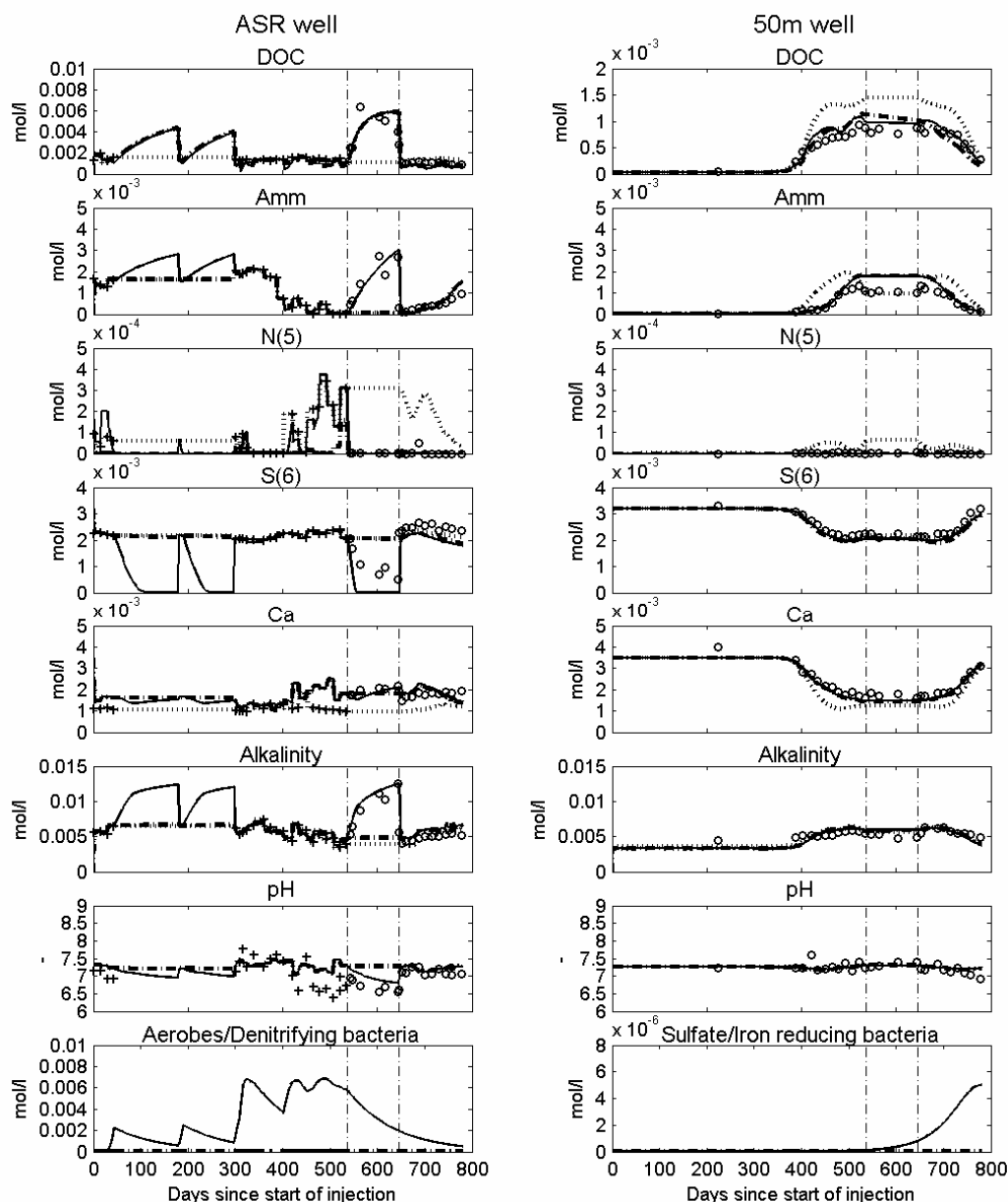
Figure A.2: Concentrations of DOC, ammonia/ammonium, nitrate, sulphate, calcium, alkalinity, pH and bacteria at the ASR and the 50m well. Concentrations of the injectant (crosses), observations (circles), alternative A (dash-dot lines), alternative B (solid lines) and non-reactive simulations (dotted lines) are shown.

Conclusions

The present study investigated two alternative conceptual biogeochemical models with respect to their capability of providing a quantitative and consistent description of the biogeochemical processes at a reclaimed water ASR research site in South Australia. The results indicate that an adequate simulation of the geochemical changes in the vicinity of the ASR well could be achieved by a more complex conceptual biogeochemical model, while geochemical changes at larger distances were well-described by both models. This suggests that dynamic changes in bacterial mass may be important in interpreting near-well hydrochemical data from reclaimed water ASR

schemes and should at least be considered during formulation of conceptual and numerical models. However, the identified processes and their respective parameters are highly nonlinear and may be subject to non-uniqueness. Thus, the possibility cannot be excluded that other conceptual models might describe the data equally well (Reichert and Omlin, 1997). Generally, the benefit of mechanistic multi-component reactive transport models is seen primarily in their capacity to constrain or reject hypotheses on interactions of physical, chemical and biological processes and to a lesser extent in their predictive capabilities.

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Appendix B: Conference Paper 2 (supplement to Chapter 3)

Hydrogeochemical changes of seepage water during artificial recharge of groundwater in Berlin, Germany

Abstract

The spatial and temporal evolution of the seepage water chemistry below an artificial recharge pond was investigated to identify the impact of dynamic changes in water saturation and seasonal temperature variations. Geochemical analysis of the pond water, suction cup water and groundwater showed that during summer, nitrate and manganese reducing conditions dominate as long as saturated conditions prevail. Iron and sulphate reduction occur only locally. When the sediment below the pond becomes unsaturated, atmospheric oxygen penetrates from the pond margins leading to re-oxidation of previously formed sulphide minerals and enhanced mineralisation of sedimentary particulate organic carbon. The latter promotes the dissolution of calcite. During winter, both the saturated and the unsaturated stage were characterised by aerobic conditions. Thereby, nitrification of sedimentary bound nitrogen could now be observed because nitrate is not immediately consumed, as is the case during summer. This suggests that nitrification below the pond might be less affected by seasonal temperature changes than nitrate reduction.

Introduction

Increasing water demands and pollution of water resources are some of the most serious challenges of the modern world. Facing these problems, techniques of artificial groundwater recharge such as river bank filtration (e.g., Ray *et al.*, 2004), aquifer storage and recovery (ASR, e.g., Pyne, 1995), deep well injection (e.g., Stuyfzand *et al.,* 2002) and infiltration ponds (e.g., Bouwer, 2002) are becoming increasingly popular. Like other recharging techniques, infiltration ponds are commonly used either to enhance the quality of surface water or to purify partially treated sewage effluent (Bouwer 1991; Asano, 1992). While the fate of specific organic substances during surface water infiltration into unsaturated porous media has been investigated intensively (e.g., Fujita *et al.*, 1998; Lindroos *et al.*, 2002; Långmark *et al.*, 2004), only a few studies exist which simultaneously give attention to the prevailing inorganic chemistry, including redox conditions (e.g., Brun and Broholm, 2001). However, as the local redox state is known to affect the fate of various organic pollutants such as pharmaceutically active compounds (PhAC's, e.g., Holm *et al.*, 1995, Massmann *et al.*, 2005), pesticides (e.g., Tuxen *et al.*, 2000), or halogenated organic compounds (e.g., Bouwer and McCarty, 1983), it is important to understand the development of redox zones and their constraints in artificial recharge systems.

The aim of this study was to characterise and understand the dynamics of the hydrogeochemical evolution of the seepage water below an artificial recharge pond, which result from transient hydraulic conditions and from seasonal temperature variations of the surface water.

Field site

The study site is one of three recharge ponds surrounded by 44 production wells located near Lake Tegel, Berlin, Germany. Its infiltration surface extends over an area of approximately 8700 m^2 and has an elevation of 3 m below the adjacent ground surface. Surface water of Lake Tegel is discharged into the pond after it has passed a microstrainer. With time, clogging processes at the pond's floor lead to a continuous decrease of infiltration rates i.e. from 3 m/d to as low as 0.3 m/d. As soon as the infiltration rate decreases to below 0.3 m/d the site operator Berliner Wasserbetriebe (BWB) abrades the clogging layer to restore the original hydraulic conductivity of the bottom sediments. This operational cycle is repeated every 3-4 months.

The sediments in the adjacent area of the pond are of Quaternary age and consist of fluvial and glacio-fluvial, medium sized sand deposits. Fragments of an up to 5m thick till layer are locally found in depths of approximately 15 m below the ground surface (Pekdeger *et al.*, 2002). The hydraulic conductivities of the aquifer sediment are about 10 -100 m/d. A more detailed description of the sediment hydraulic properties is given in Pekdeger *et al.* (2002).

The organic carbon content of the sediment below the pond is highly variable and ranges from 0.2 g/kg to 20 g/kg. Reducible forms of iron and manganese minerals are found in concentrations of 0.2 - 1.2 g/kg and 0.01 - 0.1 g/kg, respectively. Total sulphur concentrations are in the range of 0.1 - 2.1 g/kg and are highest in organic-rich layers. A more detailed description of the geochemical composition of the sediment below the pond can be found in Greskowiak *et al.* (2005, Chapter 3).

Methods

A detailed monitoring program was carried out over a period of more than one year. As part of this program (i) the pond water, (ii) groundwater at a depth of 7 m below the pond and (iii) water extracted from four ceramic suction cups located at depths of 50 cm, 100 cm, 150 cm and 200 cm below the pond were analysed for major ions and dissolved organic carbon (DOC) every week. Anions and cations were measured by ion chromatography (IC, DX 100) and atomic adsorption spectrometry (AAS, Perkin Elmer 5000), respectively. DOC was measured photometrically with a Technicon autoanalyser. Dissolved oxygen (DO) was measured by optical oxygen sensors (Hecht and Kölling, 2001) placed next to the suction cups. Water contents and pressure heads at 50 cm and 150 cm depths below the pond were recorded continuously by TDR (Time Domain Reflectometry) probes and pressure transducers respectively. The temperature of the pond water and the groundwater as well as the piezometric head at 8 m below the pond were continuously measured daily with data loggers. The location of the measurement devices are schematically shown in Figure B.1.
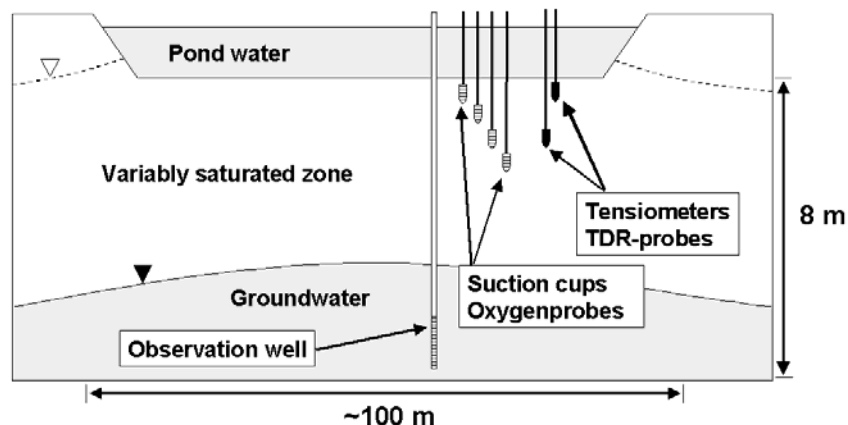
Figure B.1: Schematic cross-sectional view of study area and locations of measurement devices.

Results and Diskussion

Hydraulic characteristics

The hydraulic regime immediately below the pond was characterised by cyclic changes between saturated and unsaturated conditions, as indicated by (i) the varying piezometric head resembling the approximate groundwater table (Figure B.2) and (ii) the varying water contents and pressure heads below the pond (data not shown). These changes, which occurred during each operational cycle, resulted from the repeated formation of a clogging layer at the pond bottom (Greskowiak *et al.*, 2005, Chapter 3). Each operational cycle was hydraulically classified into four different stages (Figure B.2). Stage 1 was characterised by a rising groundwater table resulting from the refilling of the recharge pond. During Stage 2 the groundwater table rose to the bottom of the pond and saturated conditions were established. As soon as the hydraulic resistance of the clogging layer became too high (around day 60 and day 200 after start of the monitoring program), air penetrated from the pond margins beneath the clogging layer, which resulted in a sudden drop of water contents (not shown) and piezometric head (Figure B.2). Thus, unsaturated conditions established below the pond (Stage 3). During Stage 3 the groundwater level continuously declined to approximately 4 - 5m below the pond (Figure B.2). Note that infiltration still took place during Stage 3, but continuously decreases to approximately 0.3 m/d (Figure B.2). During Stage 4 the pond was dry and the site operator abraded the clogging layer. During this Stage, the groundwater level was at its minimum.
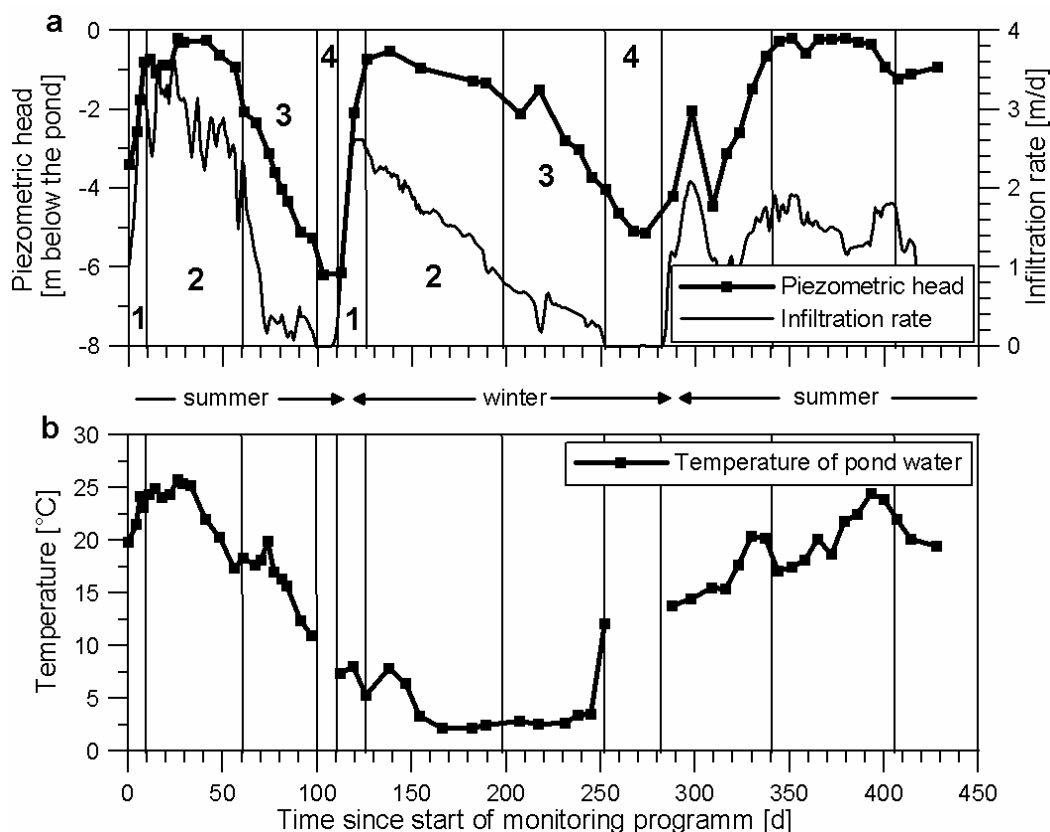
Figure B.2: a. Infiltration rate and piezometric head; **b.** temperature of the pond water; the numbers 1-4 refer to Stages 1-4.

Geochemistry

Surface water composition

Throughout the entire observation period, the pond water typically contained 7 - 16 mg/l of DO. Nitrate concentrations were highly variable and ranged from 0 - 12 mg/l. The lowest concentrations were attributed to nitrogen uptake by algae blooms during summer. With a few exceptions, dissolved iron (data not shown) and manganese were typically below detection limit. Sulphate concentrations were relatively high (~140 mg/l, data not shown). With calcium concentrations of 80 - 90 mg/l and total dissolved inorganic carbon (DIC) concentrations of 30 - 37 mg/l, the pond water was oversaturated with respect to calcite ($SI_{Calcite}$= 0.4 - 1.2). Dissolved organic carbon was rather low with concentrations of about 5 -11 mg/l. The pH was relatively stable and generally in the range of 8 - 8.5.

Summer cycle

As soon as saturated conditions established below the pond in summer (stage 2), DO became entirely depleted at all observed depths below the pond (Figure B.3). Nitrate and manganese reducing conditions were dominant beneath the pond as long as saturated conditions prevailed. This was indicated by the total depletion of nitrate and the subsequent increase of dissolved manganese at several observation points (Figures B.3 and B.4). Iron and sulphate reduction and subsequent formation of iron sulphides occurred locally as a result of the sediment's chemical

heterogeneity and non-uniform flow (Greskowiak *et al.*, 2005, Chapter 3). At the beginning of Stage 3, when the sediment below the pond became unsaturated, atmospheric oxygen entered the region leading to an increase of DO (Figure B.3) and subsequent cessation of nitrate and manganese reduction (Figure B.4). The iron sulphides that had formed during saturated conditions immediately became re-oxidised and led to a short peak of elevated sulphate concentrations at various depths below the pond. During Stage 3, nitrate concentrations at some observation points below the pond were considerably lower than the concentrations in the pond water and groundwater (Figure B.3). However, throughout the entire Stage 3, the presence of atmospheric oxygen greatly enhanced the mineralisation of labile particulate organic carbon (POC) below the pond originating from seasonal algae blooms, which promoted the dissolution of calcite (Greskowiak *et al.*, 2005, Chapter 3). As a result, DIC concentrations of the groundwater steadily increased relative to the surface water concentrations until the end of Stage 3 (Figure B.4).
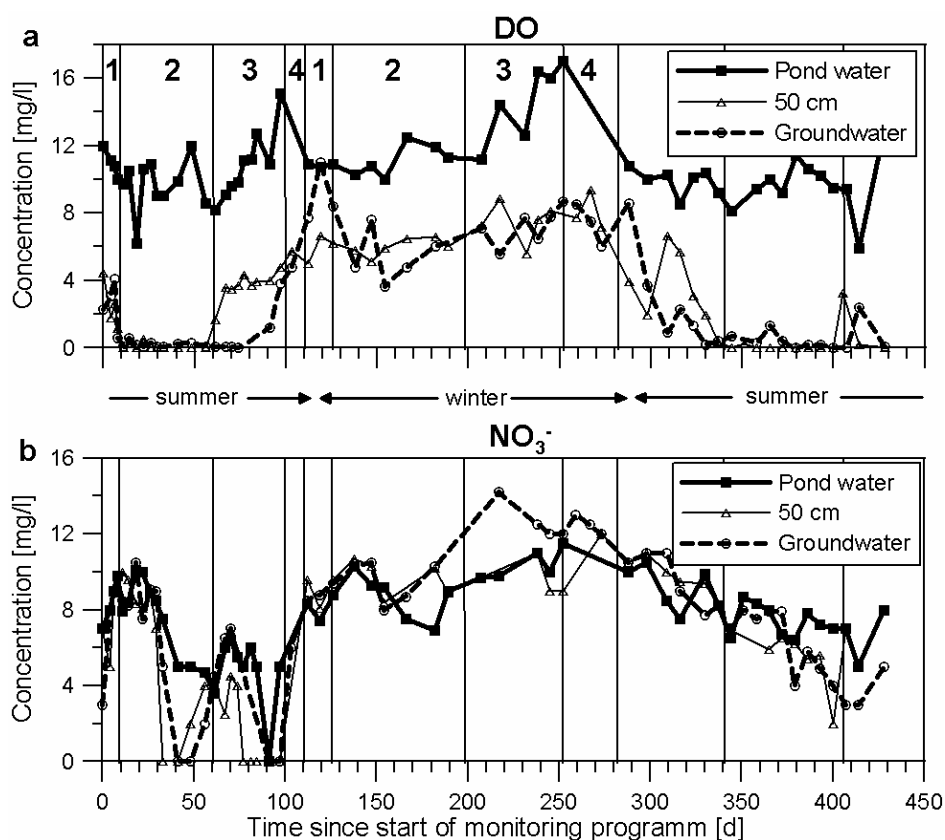
Figure B.3: Concentrations of **a.** dissolved oxygen (DO), **b.** nitrate (NO3-) in the pond water, groundwater and at depths of 50 cm; the numbers 1-4 refer to Stages 1-4.

Winter cycle

During winter, DO was not entirely consumed in the presence of fully saturated conditions (Figure B.3), presumably because very low surface water temperatures (Figure B.2) caused a reduction in microbial activity. Therefore the consumption of electron acceptors such as oxygen and nitrate proceeded at much lower rates (see also, e.g., Prommer and Stuyfzand, 2005). Unlike

in summer, aerobic conditions prevailed throughout the entire Stage 2 as a result of the lower water temperatures during winter (Figure B.2). Neither consumption of nitrate nor production of dissolved manganese occurred. Instead, during Stage 2 and Stage 3, nitrate concentration increased by 1 - 5 mg/l within the seepage water on its path from the pond bottom to the groundwater monitoring well (Figure B.3). Since ammonium concentrations within the pond water are generally small and range from 0 mg/l to 0.2 mg/l (unpublished data of BWB), additional sediment bound nitrogen might be oxidised under the prevailing aerobic conditions. The nitrogen source could either be exchangeable ammonium that was oxidised, as previously observed for other recharge basins (e.g., Bouwer *et al.*, 1980), or it might also be organic nitrogen that was oxidised during breakdown of POC (e.g., von Gunten *et al.*, 1991). The production of nitrate below the pond was only observable during winter when nitrate was not consumed simultaneously. During Stage 3, an enhanced production of inorganic carbon is observed, though not as intense as during the summer period (Figure B.4).
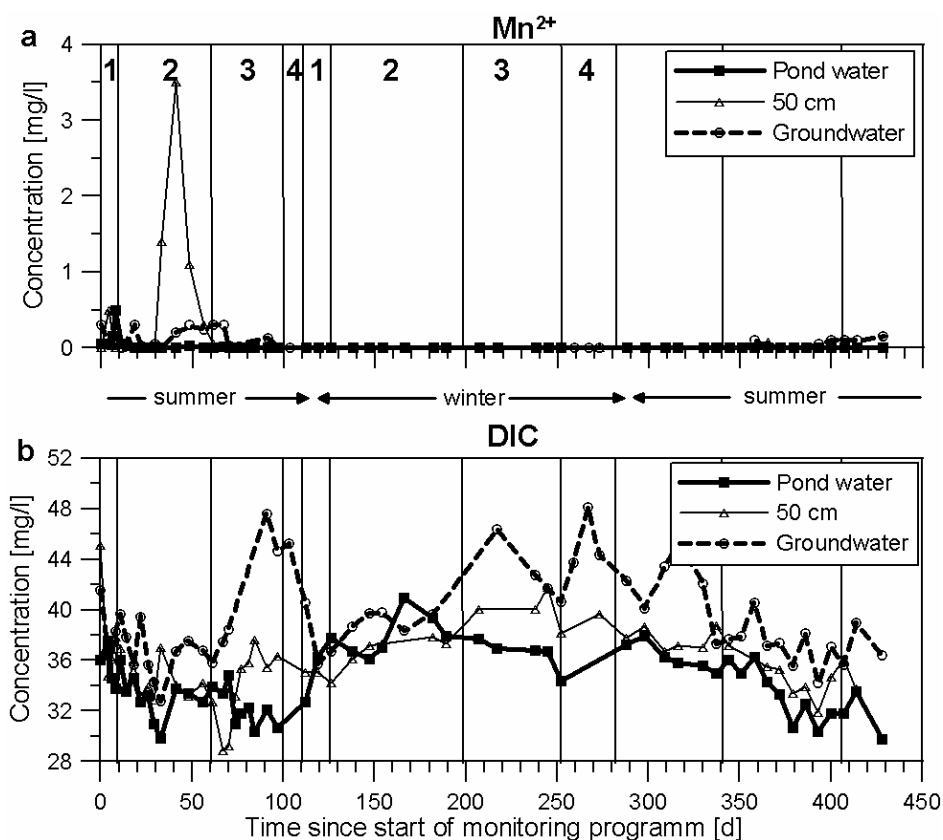

Figure B.4: Concentrations of **a.** dissolved manganese (Mn^{2+}), **b.** total dissolved inorganic carbon (DIC) in the pond water, groundwater and at depths of 50 cm; the numbers 1-4 refer to Stages 1-4.

Conclusions

This study investigated the geochemical evolution below an artificial recharge pond with respect to its transient hydraulic behaviour and seasonal temperature changes. The results show that during the summer period the spatial and temporal development of different redox environments is impacted considerably by the hydraulic conditions prevailing below the pond. During the entire

winter period, the redox environment below the pond remains aerobic despite variable hydraulic conditions. As a side effect of decreased biodegradation rates, nitrification of sedimentary bound nitrogen is only observed during winter conditions. This could indicate that nitrification below the pond is less affected by temperature changes than nitrate reduction. Since local redox conditions are–the key control for the attenuation of some trace organic compounds, the study provided the base for further investigations on the fate of such compounds during artificial recharge, as demonstrated for the case of PhAC's by the companion paper by Massmann *et al.* (2005).

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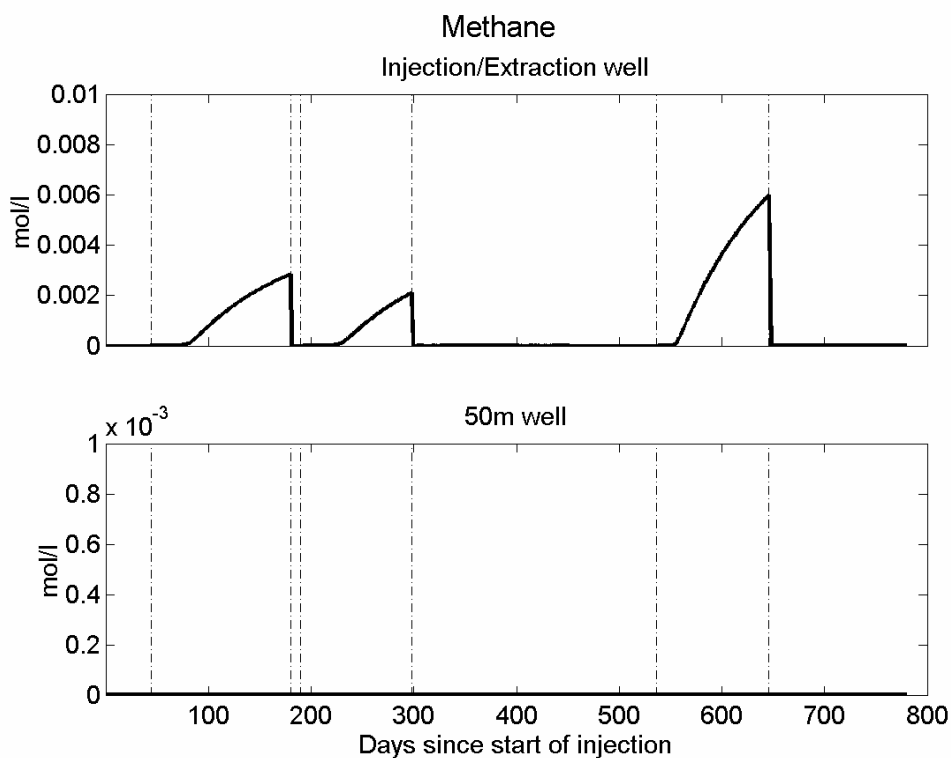
Appendix C: Additional Figures and Tables

Figure C.1: Supplement to Chapter 2: Simulated concentration of methane at the injection/extraction well and at the 50 m well.
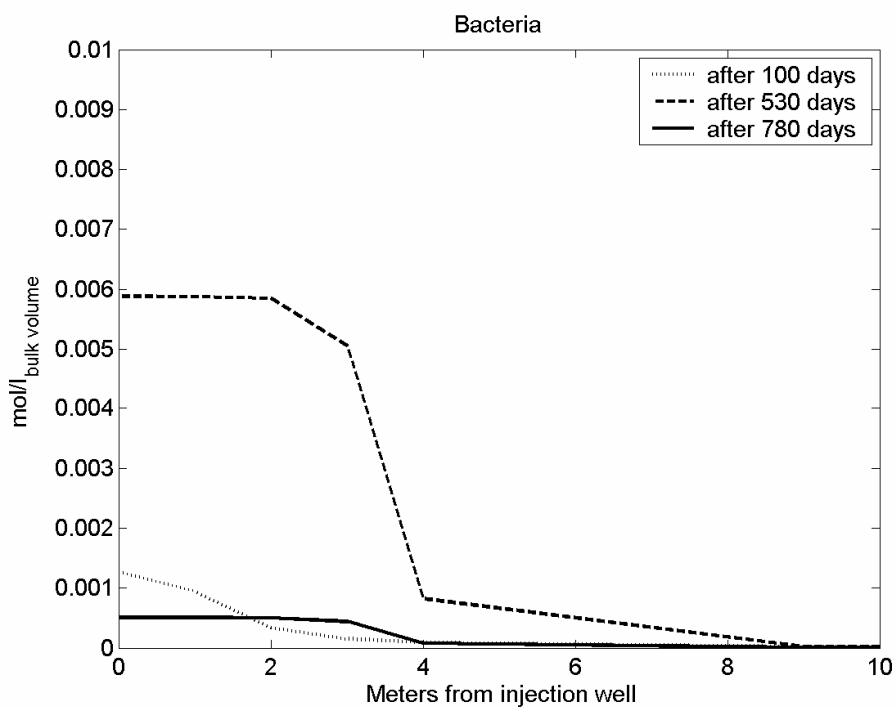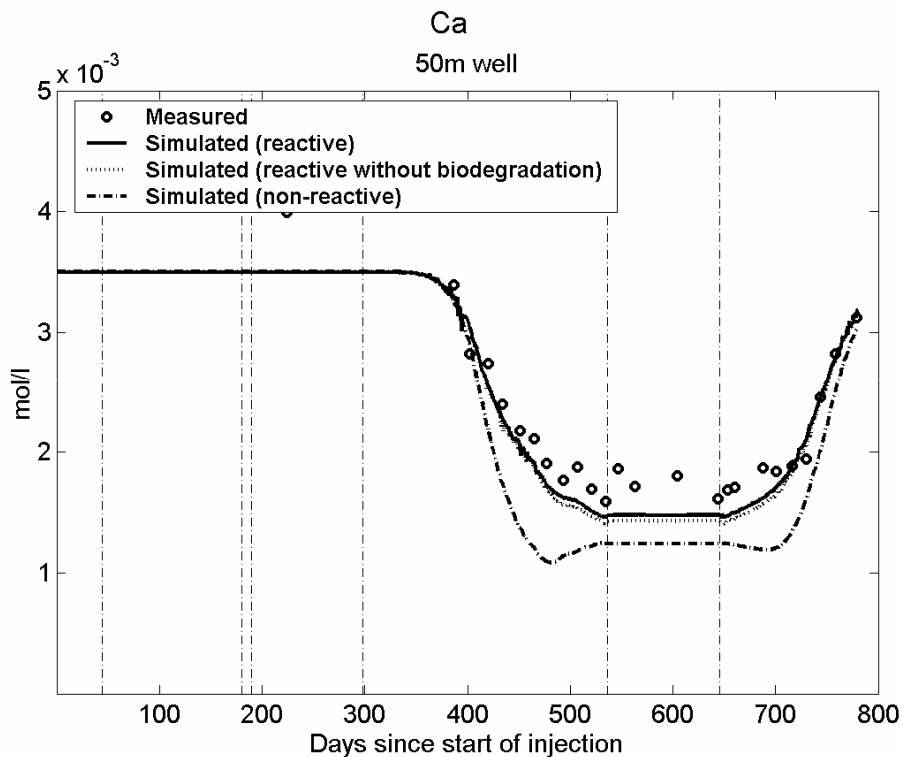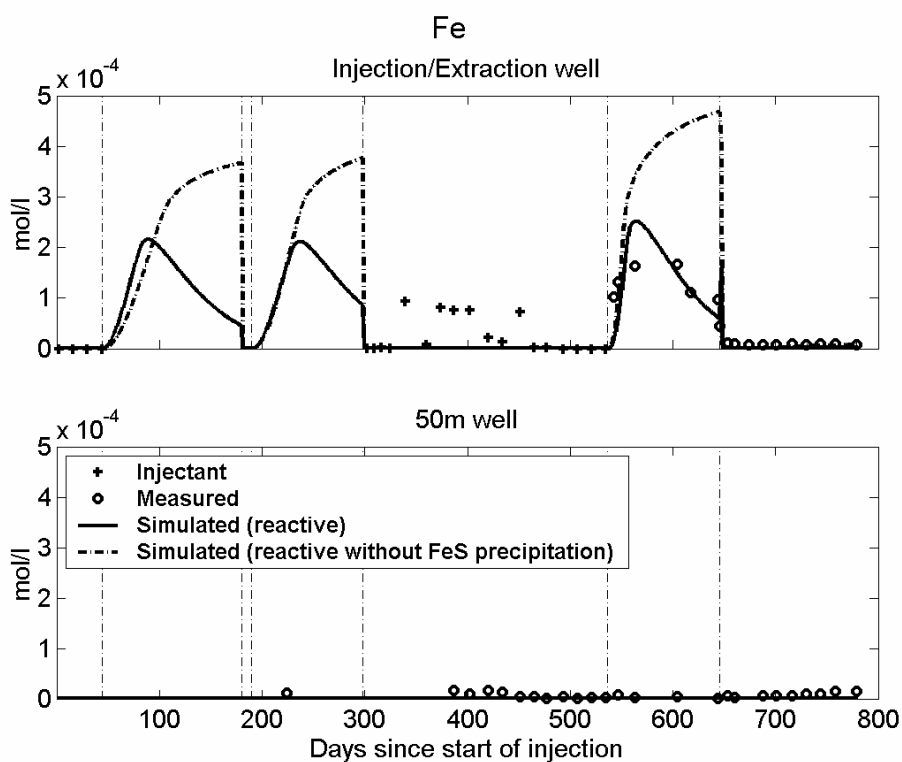

Figure C.2: Supplement to Chapter 2: Simulated concentration profile of Bacteria at 100, 530 and 780 days after the start of the trial.

Figure C.3: Supplement to Chapter 2: Simulated and observed concentration of calcium at the injection/extrac tion well and at the 50 m well. The comparison of simulations with and without biodegradation indicates that biodegradation of organic carbon only had a minor impact on calcite dissolution.

Figure C.4: Supplement to Chapter 2: Simulated and observed concentration of Fe (ferric+ferrous) at the injection/extraction well and at the 50 m well. Simulation with and without FeS precipitation allowed.
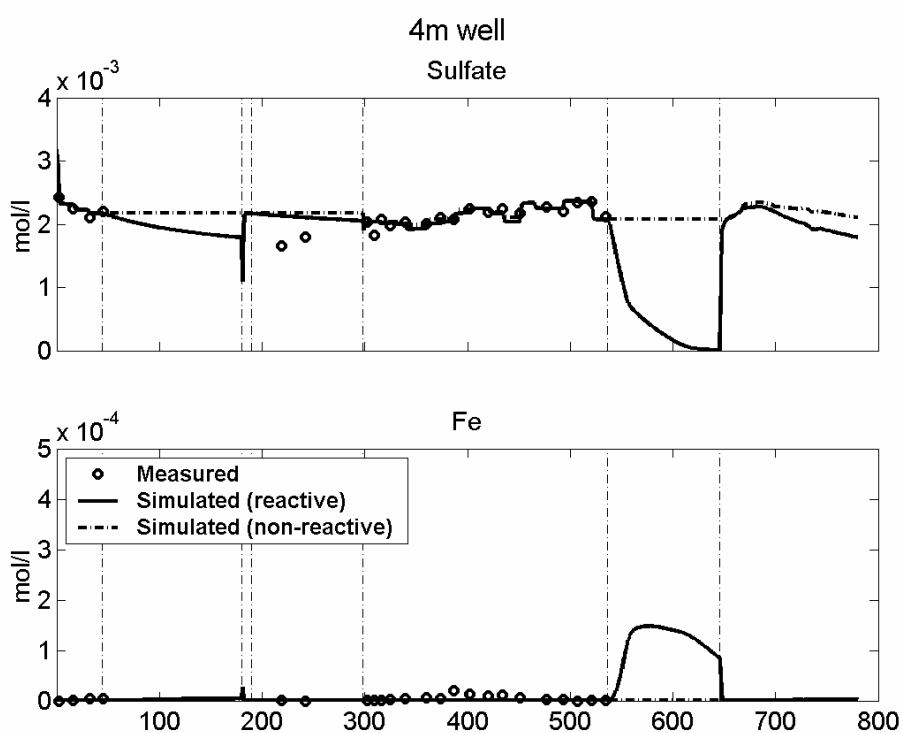
Figure C.5: Supplement to Chapter 2: Simulated and observed concentration of sulfate and Fe (ferric+ferrous) at the 4m well.
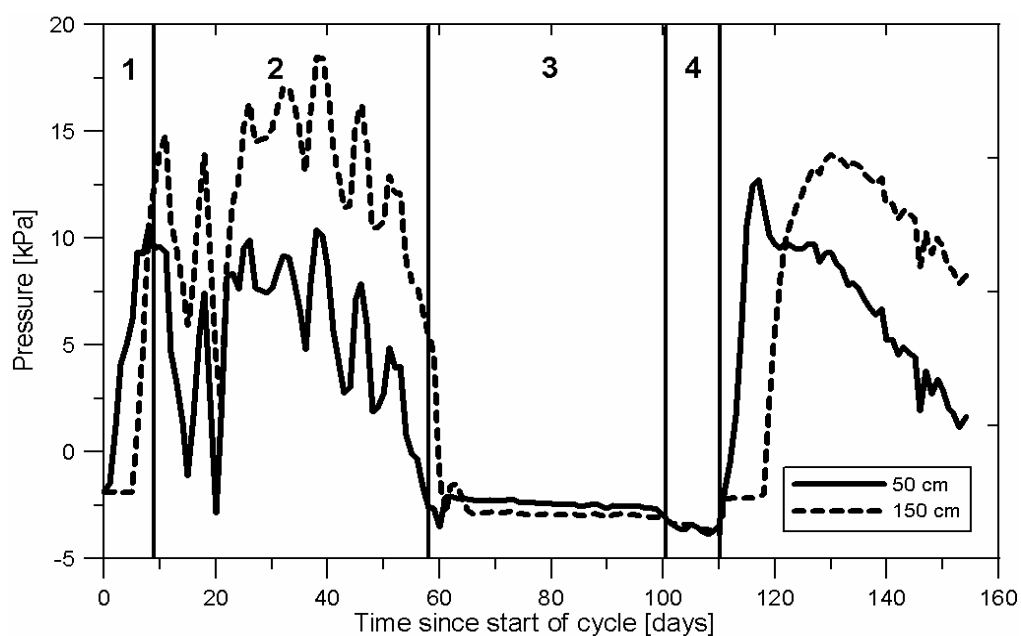

Figure C.6: Supplement to Chapter 3: Pressures at depths of 50 cm and 150 cm below the pond; the numbers 1-4 refer to the Stages 1-4 of the operational cycle. Note that the pond was dry during Stage 4.

Table C.1: Supplement to Chapter 2: Parameter correlation coefficient matrix.

	r_{attach}	C_{sat}	β	$V_{decay\_Aerobes/Denitr}$	$V_{decay\_Iron/Sulf.\ reducers}$	r_{ox}	r_{nitr}	X_{max}	$r_{hem/sulf}$	K_{inh_ox}	r_{FeS}	K_{ox}	K_{nitr}	$K_{sulfate}$	$K_{hematite}$	K_{NH4+}	K_{DOC}
r_{attach}	1.00	-0.11	0.17	-0.05	0.07	-0.18	0.28	0.18	0.24	0.47	-0.09	0.03	-0.38	0.00	-0.05	0.17	0.36
C_{sat}	-0.11	1.00	-0.09	0.07	0.06	0.14	-0.09	-0.08	0.02	-0.12	-0.05	0.01	0.15	-0.08	0.21	0.03	-0.35
β	0.17	-0.09	1.00	0.07	-0.10	0.20	0.13	-0.03	-0.07	0.19	-0.04	0.10	-0.24	-0.13	0.05	0.06	0.45
$V_{decay\_Aerobes/Denitr}$	-0.05	0.07	0.07	1.00	-0.35	0.15	0.33	-0.69	-0.28	-0.06	0.14	0.02	-0.04	-0.37	-0.22	0.16	0.07
$V_{decay\_Iron/Sulf.\ reducers}$	0.07	0.06	-0.10	-0.35	1.00	0.05	-0.14	0.09	0.60	0.01	0.09	0.20	-0.08	0.01	0.22	-0.43	-0.25
r_{ox}	-0.18	0.14	0.20	0.15	0.05	1.00	-0.12	-0.05	0.21	0.00	0.24	0.24	0.02	-0.22	0.20	0.28	-0.06
r_{nitr}	0.28	-0.09	0.13	0.33	-0.14	-0.12	1.00	0.01	0.09	-0.07	-0.04	0.01	-0.39	-0.11	-0.09	0.33	0.29
X_{max}	0.18	-0.08	-0.03	-0.69	0.09	-0.05	0.01	1.00	0.24	0.07	-0.04	-0.02	-0.14	0.22	0.17	0.18	0.04
$r_{hem/sulf}$	0.24	0.02	-0.07	-0.28	0.60	0.21	0.09	0.24	1.00	0.03	0.02	0.02	-0.29	0.05	0.23	0.29	-0.02
K_{inh_ox}	0.47	-0.12	0.19	-0.06	0.01	0.00	-0.07	0.07	0.03	1.00	-0.04	0.12	0.15	-0.01	-0.39	-0.05	0.41
r_{FeS}	-0.09	-0.05	-0.04	0.14	0.09	0.24	-0.04	-0.04	0.02	-0.04	1.00	0.09	0.19	-0.18	0.13	0.01	-0.33
K_{ox}	0.03	0.01	0.10	0.02	0.20	0.24	0.01	-0.02	0.02	0.12	0.09	1.00	-0.06	-0.05	-0.02	-0.19	-0.04
K_{nitr}	-0.38	0.15	-0.24	-0.04	-0.08	0.02	-0.39	-0.14	-0.29	0.15	0.19	-0.06	1.00	0.04	0.06	-0.33	-0.32
$K_{sulfate}$	0.00	-0.08	-0.13	-0.37	0.01	-0.22	-0.11	0.22	0.05	-0.01	-0.18	-0.05	0.04	1.00	0.15	-0.17	0.07
$K_{hematite}$	-0.05	0.21	0.05	-0.22	0.22	0.20	-0.09	0.17	0.23	-0.39	0.13	-0.02	0.06	0.15	1.00	0.00	-0.32
K_{NH4+}	0.17	0.03	0.06	0.16	-0.43	0.28	0.33	0.18	0.29	-0.05	0.01	-0.19	-0.33	-0.17	0.00	1.00	0.09
K_{DOC}	0.36	-0.35	0.45	0.07	-0.25	-0.06	0.29	0.04	-0.02	0.41	-0.33	-0.04	-0.32	0.07	-0.32	0.09	1.00

Table C.2: Supplement to Chapter 2: Confidence intervals for the estimated parameter values.

Parameter	95% percent confidence limits	
	Lower limit	Upper limit
r_{attach}	8.19	15.5
C_{sat}	4.06×10^{-03}	5.24×10^{-03}
β	2.39×10^{-03}	6.87×10^{-03}
$V_{decay\_Aerobes/Denitr}$	8.98×10^{-03}	1.16×10^{-02}
$V_{decay\_Iron/Sulf.\ reducers}$	8.68×10^{-03}	1.31×10^{-02}
r_{ox}	8.96	10.4
r_{nitr}	4.95	5.77
X_{max}	6.27×10^{-01}	7.33×10^{-01}
$r_{hem/sulf}$	4.35×10^{-01}	5.05×10^{-01}
K_{inh_ox}	7.38×10^{-06}	1.26×10^{-05}
r_{FeS}	4.56×10^{-07}	5.80×10^{-07}
K_{ox}	6.25×10^{-05}	1.17×10^{-04}
K_{nitr}	1.01×10^{-04}	1.39×10^{-04}
$K_{sulfate}$	2.97×10^{-05}	1.76×10^{-04}
$K_{hematite}$	-6.04×10^{-05}	4.40×10^{-04}
K_{NH4+}	3.68×10^{-05}	1.83×10^{-04}
K_{DOC}	1.22×10^{-04}	1.66×10^{-04}

Acknowledgements

Eidesstattliche Erklärung

Hiermit erkläre ich, dass ich die vorgelegte Doktorarbeit selbstständig und ohne fremde Hilfe verfasst habe.

Ich erkläre, dass ich keine anderen als die in der Doktorarbeit angegebenen Hilfsmittel benutzt habe.

Ich erkläre, dass ich die Arbeit erstmalig und nur an der Humboldt-Universität zu Berlin eingereicht habe und keinen entsprechenden Doktorgrad besitze.

Der Inhalt der dem Verfahren zugrunde liegenden Promotionsordnung ist mir bekannt.

Janek Greskowiak

Liste der Veröffentlichungen und Vorträge

International referierte Aufsätze

Greskowiak, J., Prommer, H., Massmann, G., Johnston, C. D., Nützmann G., Pekdeger, A. (2005), The impact of variably saturated conditions on the hydrochemistry during artificial recharge of groundwater, *Applied Geochemistry*, 20(7), 1409-1426.

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