
Deep groundwater flow systems and their characterization in single-well settings by “push-pull” tracer tests

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"If I have seen further it is by standing on the shoulders of giants"

Sir Isaac Newton, 1643 – 1727

(Letter to Robert Hooke,

5th February 1676)

Abstract

Deep groundwater resources were not in the research focus for most time in the past. This is due to the negligible relevance for daily drinking water supply and high access costs. In the last approximately two decades this changed due to rising demands for deep geological repositories for radioactive waste, CO₂ storage, geothermal energy supply, or aquifer storage and recovery systems (*ASR*). As a consequence, the fast growing demand on knowledge and understanding of these systems has spurred the research on deep groundwater systems. The development of suitable methods for investigating these resources became the main target. Currently available methods show considerable limitations. Accordingly, comprehensive methods for the hydraulic and hydrochemical characterization of deeper aquifers with single-well access are needed.

The objective of this research was to gain information about the groundwater transport characteristics of the Upper Sarabetsu aquifer at the Hamasato test site in Horonobe (Hokkaido, Japan). The aquifer is part of a sedimentary coastal basin. In Japan, coastal basins are potential host rocks for future disposal of radioactive waste. Therefore, the Japan Atomic Energy Agency (*JAEA*) is operating an underground research laboratory (*URL Horonobe*) near the city of Horonobe. Within this framework, various research projects with different scopes are conducted in the surrounding region of Horonobe. At Hamasato, the Geological Survey of Japan (*GSJ*) and the National Institute of Advanced Industrial Science and Technology (*AIST*) are developing techniques for deep (down to ~1,200 m below ground level surface) aquifer and groundwater flow characterization. Within the research scope are groundwater or porewater age dating (using stable isotope ratios), porewater analysis, and various methods for hydraulic testing. The goal of this PhD thesis was to identify, test, and enhance potentially suitable single-well methods for characterization of groundwater flow and solute transport in this setting.

Transport characterization in single-well settings, as at the Hamasato test site, is challenging. Therefore, the first step of the project was to provide an extensive literature study, in which an overview about deep groundwater flow and research methods based on six case studies in Germany and Central Europe is presented.

In a second step two Single-Well Injection-Withdrawal (“*push-pull*”) tracer tests, which were identified as a potentially suitable method, were applied at the Hamasato field site in a ~100 m deep groundwater monitoring well. During this test a known amount of selected solutes as conservative and reactive tracers were injected into the aquifer (“*push*”) and afterwards extracted (“*pull*”). The main objective of this test was to investigate the groundwater flow and transport under changing fluid characteristics. A second objective was to test, improve, and standardize the push-pull tracer test setup. As the Sarabetsu formation is located in a coastal basin, potential consequences of a rising or falling saltwater-freshwater interface, caused by sea level rise or marine regression in the future, is within the scope of research. In a first field campaign, two push-pull tracer tests were conducted: a brackish water (*Electric conductivity* $EC = 3,800 \mu\text{S/cm}$, higher density than the original groundwater with an $EC = 1,083 \mu\text{S/cm}$) and a deionized water ($EC = 25 \mu\text{S/cm}$, lower density) test. Results reveal the hydrochemical and hydraulic response of the Sarabetsu formation, i.e. ion exchange or sorption capacity, and redox conditions. The injection of brackish water leads to the expected conservative mixing with the origin groundwater. Sufficient mass balances for the dissolved species could be calculated. By using curve fitting of the conservative breakthrough curve an effective porosity of 5% was determined in the brackish water test. Compared to the first experiment, the deionized water showed a significant different behavior in the test. The injection of very low mineralized water causes complex reactions within the aquifer, as ion exchange, dissolution of some species, redox, and sorption-desorption reactions. Also, curve fitting results in a very low effective porosity. Whether this is caused by changes of the hydraulic properties of the aquifer (e.g. by clay swelling or clay dispersion) remains unclear.

Based on the experiences of the first methodological test, a second field campaign was conducted. This campaign focused on a systematic evaluation of the push-pull tracer test method for the first time at all. Therefore, an extensive study was conducted at the Hamasato site, including 12 push-pull tracer tests. In the first experiment – which are not further described in this thesis –, six large push-pull tests were conducted. In a first step the reproducibility of the push-pull tracer test method was demonstrated (identical test setup provides identical results). In every of the following tests

only one parameter (injection/pumping rate, mineralization of test fluid) was varied at a time to identify the respective influence of the aquifer, the gravel pack, and the test setup on the resulting tracer breakthrough curves. In a second experiment, another six push-pull tests were conducted to investigate specific parts of the method. The experiments aimed at investigating the role of the “*chaser*” on the test results. The chaser is often applied in push-pull tracer tests. The chaser consists of natural groundwater without any added solutes and is injected directly after the test solution. Its objective is to push the test solution out of the borehole into the aquifer and by this to minimize the influence of the gravel pack on the shape of the breakthrough curve. However, the influence of the chaser on the tracer breakthrough curves was unknown so far. Also the determination of the right chaser volume was a difficult task, as the actual effective porosity of the gravel pack is usually unknown.

It was shown that the application of a chaser lowers the main peak concentration, but neither alters the tailing of the breakthrough curve nor does it have a negative impact on the tracer mass recovery itself. Accordingly, this work shows under which conditions the use of a chaser should be avoided in a push-pull tracer test (when the hydraulic characteristics are within the focus), and under which conditions the use of a chaser may help to improve the quality (when hydrochemical reactions of the aquifer are investigated). Furthermore, a new and fast method was developed for determination of the required chaser injection by using the temporal moment analysis.

This thesis demonstrates the growing importance of deep groundwater research and the increasing demand for the development of suitable single-well test methods. At the forefront of the research on groundwater in the deep underground in Germany, radioactive waste disposal is on the agenda. Furthermore, contributions to the application of push-pull tests in deep aquifers are presented. In the focus was a specific design for the saltwater-freshwater interface. The application on the behavior of different fluids within the same system, e.g. different mineralized fluids (saltwater-freshwater-interface, ASR) or temperatures (geothermal research), are promising future approaches for this method. Finally, the results of a systematic evaluation of the push-pull tracer test are presented for the first time. By adaption of the temporal mo-

ment analysis an easy method was developed for a wider application of the push-pull tracer test method.

Zusammenfassung

Aufgrund der geringen Bedeutung tieferer Grundwasserleiter für die Trinkwasserversorgung und der hohen Kosten für deren Erschließung waren diese in der Vergangenheit nicht im Fokus der Forschung. Erst mit steigenden Anforderungen an die Nutzung des tieferen Untergrundes, etwa als geologische Tiefenendlager für radioaktive Abfälle, zur CO₂-Speicherung, für die geothermische Energie- und Wärmeversorgung, oder als Grundwasserleiter-Speicher-Systeme (aquifer storage and recovery system – *ASR*) hat sich die Bedeutung des tieferen Untergrunds für die hydrogeologische Forschung in den letzten zwei Jahrzehnten geändert. Der schnell wachsende Bedarf zum Verständnis dieser Systeme hat in den letzten Jahren zur intensiveren Erforschung tiefer Grundwassersysteme und entsprechend zur Entwicklung geeigneter Testmethoden geführt, die allerdings in der praktischen Anwendung oft erheblichen Einschränkungen unterliegen. Folglich werden weiterhin experimentelle Methoden zur hydraulischen und hydrochemischen Charakterisierung tieferer Grundwasserleiter benötigt.

Das Ziel dieser Arbeit war die Charakterisierung des Stofftransports im Grundwasser der Oberen Sarabetsu-Formation am Forschungsstandort Hamasato (Hokkaido, Japan). Die Sarabetsu-Formation ist Teil eines sedimentären Küstenbeckens. In Japan sind diese Becken potentielle Wirtsgesteine für eine mögliche Endlagerung von radioaktiven Abfällen, weshalb in der Nähe von Horonobe durch die Japanische Atomenergiebehörde (Japan Atomic Energy Agency – *JAEA*) ein entsprechender Forschungsstandort (Untergrundlabor Horonobe) betrieben wird. Innerhalb dieses Rahmens werden in der Region unterschiedliche Forschungsprojekte von verschiedenen Forschungsinstituten durchgeführt. In Hamasato entwickeln der Geologische Dienst von Japan (Geological Survey of Japan – *GSJ*) und das Nationale Institut für Industrielle Wissenschaft und Technologie (National Institute of Advanced Industrial Science and Technology – *AIST*) Methoden und standardisierte Arbeitsabläufe für die Charakterisierung tiefer (bis ~1.200 m unter der Oberfläche) Grundwasserleiter. Forschungsgebiete sind z.B. Altersdatierung von Grund- oder Porenwasser (mittels Isotopenverhältnissen), Porenwasseranalytik und die hydraulische Charakterisierung. Das Ziel der vorliegenden Arbeit innerhalb dieses Projektes war die Identifikation möglicher geeigneter

Ein-Bohrloch-Versuche, sowie deren Untersuchung und Weiterentwicklung für die Charakterisierung von Grundwasserströmung und Stofftransport in einen solchen Rahmen.

Die Ermittlung des Transportverhaltens unter Bedingungen wie in Hamasato, in denen nur ein Bohrloch bzw. eine Grundwassermessstelle zur Verfügung steht, ist eine Herausforderung. Daher umfasste die erste Phase des Projektes eine umfangreiche Literaturstudie, in der ein Überblick über den Stand der Erforschung tiefer Grundwässer und deren Methoden, basierend auf sechs Fallstudien aus Deutschland und Mitteleuropa, erstellt wurde.

Im zweiten Schritt wurde die als geeignet identifizierte sogenannte "Single-Well Injection-Withdrawal"-Methode (Ein-Bohrloch-Injektions-Extraktionstest – "Push-Pull"-Tracertest) in einer ~100 m tiefen Grundwassermessstelle in Hamasato angewendet. Bei dieser Methode wird eine bekannte Menge verschiedener gelöster Stoffe (reaktiv oder konservativ) in den Grundwasserleiter injiziert ("push") und anschließend extrahiert ("pull"). Ziel des Versuchs war die Untersuchung von Grundwasserströmung und Stofftransport unter wechselnden Fluidcharakteristika. Da der Sarabetsu-Grundwasserleiter Teil eines Küstenbeckens ist, sind mögliche Auswirkungen einer sich verlagernden Salzwasser-Süßwasser-Grenzschicht ("Interface") im Zuge von zukünftigen Meeresspiegelanstiegen oder -absenkungen relevante wissenschaftliche und technische Fragestellungen. In einer ersten Feldkampagne wurden deshalb zwei verschiedene Push-Pull-Versuche durchgeführt: Mit Brackwasser (Elektrische Leitfähigkeit $L_f = 3.800 \mu\text{S/cm}$, höhere Dichte als das ursprüngliche Grundwasser mit $L_f = 1.083 \mu\text{S/cm}$) und mit entionisiertem Wasser ($L_f = 25 \mu\text{S/cm}$, geringere Dichte). Es konnten wichtige Erkenntnisse sowohl über die hydrochemische und hydraulische Reaktion des Sarabetsu-Grundwasserleiters (z.B. Ionenaustausch, Sorptionskapazität, Redoxbedingungen), als auch über die Leistungsfähigkeit des Push-Pull-Verfahrens in einer derart tiefen Messstelle gesammelt werden. Das injizierte Brackwasser hat sich wie erwartet mit dem Grundwasser konservativ gemischt. Massenbilanzen haben gute Wiederfindungen der injizierten Stoffe gezeigt. Mittels Kurvenanpassung der konservativen Durchbruchkurve wurde eine effektive Porosität von 5% ermittelt. Im Vergleich zum Brackwassertest wurde im zweiten Experiment, bei dem entionisiertes Wasser als Injektionslösung verwendet wurde, eine signifikant unterschiedliche Reaktion

des Grundwasserleiters beobachtet. Die Injektion von sehr niedrig mineralisiertem Wasser hat zu komplexen Reaktionen, wie Ionenaustausch, Lösung einiger Spezies, Redoxreaktionen und Sorptions-Desorptions-Prozessen, geführt. Auch bei der Kurvenanpassung der konservativen Durchbruchskurve wurden eine deutlich niedrigere effektive Porosität ermittelt. Ob diese beobachteten Effekte ursächlich an Veränderungen der hydraulischen Eigenschaften des Grundwasserleiters durch die Durchströmung mit sehr niedrig mineralisiertem Wasser zurückzuführen sind (durch quellende Tonminerale oder Tondispersion), bleibt aber unklar.

Mit den Erfahrungen und Erkenntnissen aus dem ersten Methodentest wurde eine zweite umfangreiche Feldkampagne in Hamasato durchgeführt. Ziel dieses Großversuchs war die erstmalige systematische Untersuchung der Push-Pull-Methode überhaupt. Insgesamt wurden 12 Push-Pull-Versuche durchgeführt. Im ersten Experiment – die nicht Teil dieser Arbeit sind und deshalb nicht weiter beschrieben werden – wurden sechs Push-Pull-Tests durchgeführt. Zuerst wurde die Reproduzierbarkeit der Methode nachgewiesen (identischer Versuchsaufbau liefert identische Ergebnisse). In jedem folgenden Versuch wurde nur ein Parameter (Injektion/Pumprate, Ionengehalt der Testflüssigkeit) verändert, um die verschiedenen Einflüsse von Grundwasserleiter, Kiesschüttung und Versuchsaufbau auf die resultierenden Durchbruchskurven zu identifizieren. Im zweiten Experiment wurden weitere sechs Push-Pull-Versuche mit geringeren Injektionsvolumina durchgeführt, um einen spezifischen Teil des Versuchsaufbaus zu untersuchen. Dieses Experiment hatte das Ziel, den Einfluss des sogenannten „*chaser*“ auf die Testergebnisse eines Push-Pull-Versuchs zu identifizieren und zu charakterisieren. Ein Chaser wird oft während eines Push-Pull-Versuches eingesetzt und besteht im Allgemeinen aus natürlichem Grundwasser ohne zusätzliche gelöste Stoffe. Er wird direkt nach der Injektion der eigentlichen Testlösung injiziert und soll diese möglichst vollständig aus dem Bohrloch (also Filter und Kiesschüttung) heraus- und in den Grundwasserleiter hineindrücken. Dadurch soll der Einfluss des Versuchsaufbaus (Schläuche, Rohre) und der Kiesschüttung auf die Form der Durchbruchskurven minimiert werden. Allerdings sind mögliche Auswirkungen des Chasers auf die Durchbruchskurven bisher nicht untersucht worden. Auch ist die Bestimmung des optimalen Chaser-Volumens (also technische Einrichtungen plus effektives Porenvolu-

men der Kiesschüttung) schwierig, da im Allgemeinen die effektive Porosität der Kiespackung nicht bekannt ist.

Im Rahmen der Versuche konnte gezeigt werden, dass der Chaser die maximale Konzentration des Tracerdurchgangs zwar senkt, aber nicht das sogenannte *“tailing”* (also den langsamen Abfall der Konzentrationen verursacht durch Dispersion und Mischung innerhalb des Aquifers) verändert und auch keinen signifikanten Einfluss auf die Massenbilanzen hat. Dementsprechend konnte in dieser Arbeit gezeigt werden, unter welchen Voraussetzungen der Einsatz eines Chasers in einem Push-Pull-Versuch vermieden werden sollte (bei Versuchen zum hydraulischen Verhalten des Grundwasserleiters) und unter welchen Bedingungen der Einsatz eines Chasers zu einer Verbesserung der Versuchsergebnisse beiträgt (bei Versuchen zu hydrochemischen Reaktionen). Zudem wurde eine sehr einfache und schnelle Methode entwickelt, mit der das erforderliche Injektionsvolumen des Chasers mit Hilfe der *“temporal moment analysis”* bestimmt werden kann.

Diese Arbeit zeigt die wachsende Bedeutung des tieferen Untergrundes für die Hydrogeologie und den gesteigerten Bedarf an geeigneten Erkundungsmethoden. In Deutschland ist aktuell die Suche nach einem Tiefenlager für radioaktiven Abfall eines der Forschungsfelder, das sich mit tiefen Grundwassersystemen beschäftigt. Weiterhin konnten Beiträge zur Anwendung von Push-Pull-Versuchen in tiefen Grundwasserleitern vorgestellt werden. Im Fokus war ein spezieller Versuchsaufbau zur Klärung von Fragen bezüglich der Salzwasser-Süßwasser-Grenze. Der Push-Pull-Tracertest ist eine vielversprechende Methode bei allen Fragestellungen, die sich mit unterschiedlichen Fluiden innerhalb eines Systems beschäftigen, z.B. verschiedene Salzgehalte (Salzwasser-Süßwasser-Grenze, ASR) oder verschiedene Temperaturen (Geothermie). Schließlich werden die Ergebnisse einer erstmalig durchgeführten systematischen Evaluation der Push-Pull-Tracertestmethode vorgestellt. Durch die Anpassung der *“temporal moment analysis”* wurde eine einfache Methode entwickelt, die die Push-Pull-Methode einer weiteren Anwendung zugänglich macht.

Contents

Abstract	i
Zusammenfassung	v
1 Introduction	1
1.1 Deep groundwater flow and its characterization	1
1.2 Single-well methods in deep groundwater research	5
1.3 The Single-Well Injection-Withdrawal (“push-pull”) tracer test	8
1.4 Outline of the thesis	12
1.5 References	17
2 Review: Deep groundwater research with focus on Germany	23
2.1 Abstract	24
2.2 Introduction	24
2.3 A short history of deep groundwater concepts	27
2.4 What are the reasons for deep groundwater research?	31
2.5 Deep groundwater flow in different geological units	32
2.5.1 Sedimentary basins	33
2.5.2 Igneous and metamorphic rocks	34
2.5.3 Rock salt	35
2.5.4 Argil/argillaceous rocks	36
2.6 Selected case studies of deep groundwater research	38
2.6.1 Sedimentary basins: the Sellafield Test Site	38
2.6.2 Sedimentary basins: geothermal research in the North German Plain	41
2.6.3 Metamorphic rocks: the German Continental Deep Drilling Program (<i>KTB</i>)	45
2.6.4 Rock salt: the Gorleben Test Site	46
2.6.5 Rock salt: the final repository for radioactive waste at Morsleben (<i>ERAM</i>)	49

2.6.6	Argillaceous rocks: the Bure Test Site (France)	51
2.7	Conclusions	55
2.8	Acknowledgements	57
2.9	References	57
3	Performance of single-well push-pull tracer tests to characterize transport processes: a case study in a sedimentary coastal basin	67
3.1	Abstract	68
3.2	Introduction	69
3.3	Push-pull tracer tests	70
3.4	Study area	73
3.5	Experimental methods	74
3.5.1	Test fluids	74
3.5.2	Experimental setup	75
3.5.3	Sampling and analysis	76
3.5.4	Modeling for transport parameter estimation	78
3.6	Results and discussion	79
3.6.1	Chemical reactions	79
3.6.2	Hydraulic characterization and modeling	87
3.7	Conclusions	93
3.8	Acknowledgments	94
3.9	References	95
4	Study of the effects of the chaser in push-pull tracer tests by using temporal moment analysis	99
4.1	Abstract	100
4.2	Introduction	101
4.3	Study area	104
4.4	Experimental methods	106
4.4.1	Influence of the chaser on a push-pull tracer test BTC	106
4.4.2	Estimation of the optimal chaser volume	108
4.4.3	Temporal moment analysis	110
4.5	Results and Discussion	112
4.5.1	Influence of the chaser on a push-pull tracer test BTC	112
4.5.2	Estimation of the optimal chaser volume	116

4.6	Conclusions	120
4.7	Acknowledgments	122
4.8	References	122
5	Synthesis	127
5.1	Summary and discussion of the main findings	128
5.2	Open questions and outlook	137
5.3	References	140
6	List of Figures	143
7	List of Tables	149
8	Appendix	I
8.1	Eidesstattliche Versicherung (Declaration of academic integrity)	I
8.2	Angaben zum Eigentanteil (Outline of the author's contribution)	II
8.3	Acknowledgments	IV
8.4	List of publications	V
8.5	Curriculum vitae	X

1 Introduction

1.1 Deep groundwater flow and its characterization

“While Internet searching and .pdf versions of more recent published material make ‘keeping up’ easier, there is a body of important early work that is often ignored by young researchers. As a result, we stand at the beginning of the 21st century in danger of memory loss of our young sciences.”

Jeffrey J. McDonnell

Foreword to the Benchmark Papers in Hydrology Sciences
(Anderson, 2008)

Groundwater research used to be focused mainly on the intensively used shallow aquifers, because of their crucial importance providing drinking and irrigation water. Due to its negligible relevance for daily usage and the great efforts and high costs associated with its access, only little research was performed on deeper groundwater. Only in the last few decades, new arising demands on the deep underground, like final disposal of heat generating radioactive waste, CO₂ storage, production of potable water as an alternative to the geogenic or anthropogenic contaminated shallow aquifers, and – last but not least – the use of geothermal energy, lead to significant efforts for the investigation and characterization of deeplying aquifers, the related fluid movements, and solute transport.

Due to the long lasting disregard of deeper aquifers in hydrogeological sciences research, little is known about their characteristics. Even the term “deep groundwater” is not clearly defined. Its evolution is strongly related

to the development of the early groundwater sciences in the middle of the nineteenth century. Its meaning has changed from the more speculative and static image as “deep stagnant water” (Weithofer, 1936) to a more dynamic understanding. More recently, deep groundwater is not only defined by its depth, but by its genesis, age, chemical composition, etc. (Einsele et al., 1983). It is widely accepted that deeper aquifers are dynamic systems (Fig. 1.1), which are influenced by both, surface processes (from the meteoric cycle) and crustal processes (from the lithosphere). Great efforts by hydrogeologists have led to a thorough understanding of regional groundwater systems, their driving forces, and their hydrochemical dynamics (e.g. Back, 1960; Freeze and Witherspoon, 1967; Hubbert, 1940; Tóth, 1962, 1963).

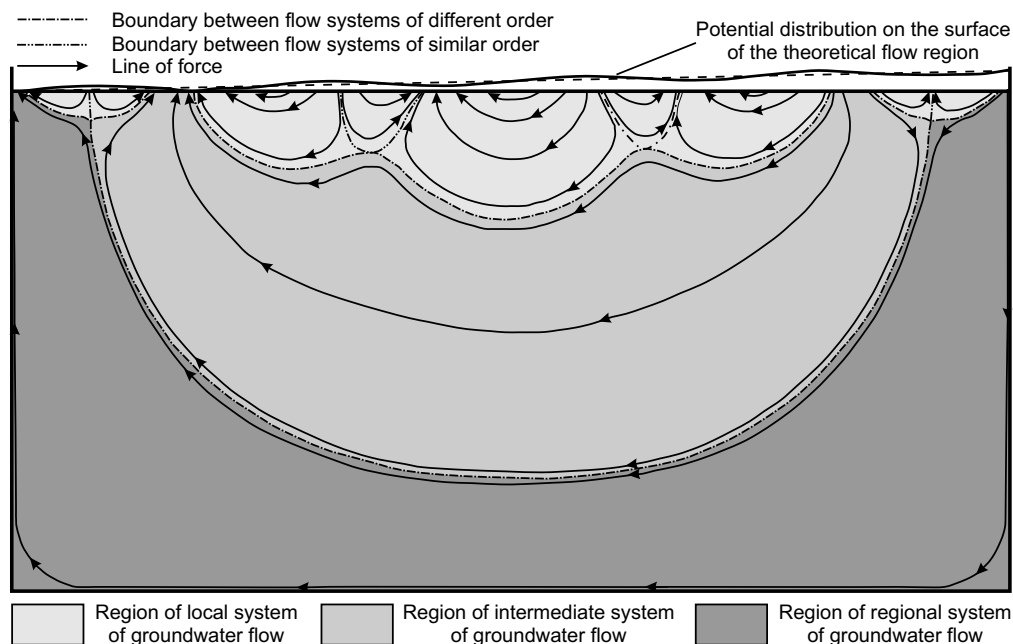


Figure 1.1: Theoretical flow pattern and boundaries between different flow systems in the regional scale (modified from Tóth, 1963)

Interest in the deeper underground and groundwater has increased only with respect to resources since the beginning of industrialization and especially at the end of the nineteenth century. In addition to the generally increasing scientific interest in evolution of Earth at that time, the main interest in Central Europe concentrated on understanding the origins of mineral resources, ore dikes, and mineralized springs (e.g. Cotta, 1850), or weathering deposits, which may be accumulated by *Petrophaga lorioti* (Pohl et al., 1992). Since that time, the need to understand the “system earth”, and

accordingly regional groundwater systems, has increased (e.g. Freeze and Witherspoon, 1967; Hubbert, 1940; Tóth, 1963). The driving forces were always the prospection and exploration of resources. One of the most important research fields is the use of geothermal energy, which often requires large amounts of hot groundwater. As part of the investigation of potential host rocks for the final repository of toxic, dangerous, or radioactive waste, research on associated deep aquifers is a crucial aspect of safety assessment, which is often require least amount of water and little flow. The deposition of brines in deep aquifers (as practiced for some time in central Germany) can affect the groundwater systems and may lead to contamination even of shallower aquifers. An important field of research on deep groundwater is the storage of CO₂ in deep aquifers. For that, deep groundwater itself should act as the supporting medium for safe and long-term storage. Now, in some regions, deeper aquifers are considered as potential alternatives to shallower, contaminated aquifers. For example, Shibasaki et al. (2007) and Michael and Voss (2008) investigated the potential use of an underlying aquifer for drinking-water supply instead of the arsenic-contaminated shallow aquifer in Bangladesh.

Research activities cover a wide range from regional-scale basin modeling down to micro-scale laboratory experiments. Complex processes in deep groundwater systems have been intensively examined (e.g. Back, 1960; Bethke et al., 2000; Grenthe et al., 1992; Hölting, 1969; Magri et al., 2005; Stober, 1986). The basic groundwater flow concepts in basins are widely accepted, the importance of redox reactions on groundwater quality is well-known, and recently it has become common to compile numerical flow and mass transport models for the future development of catchment areas influenced by changing boundary conditions caused by climate change. The aim of research projects is to present integrated concepts about the past and the future evolution of deep groundwater systems (Einsele et al., 1983). However, many questions regarding the transport behavior of deep groundwater and the physical laws of its movement have not been answered so far, which is due to the sometimes very specific conditions (e.g. low hydraulic gradients, saltwater-freshwater interface, gas migration). Therefore, the objectives of deep groundwater research studies are often different from shallower “conventional” projects, as well as the suitable experimental methods. Depending

on the specific questions, research is directed to aquifers that contain large amounts of hot water, or formations with as little groundwater movement as possible. Deep groundwater research is often challenging: high demands on the technical equipment, highly saline fluids, low permeabilities and low sample volumes. Many well-established methods for hydraulic characterization of shallow aquifers are not or hardly applicable because of the generally small number of deeper monitoring wells (e.g. tracer tests), slow groundwater velocities (e.g. fluid logging), and low hydraulic conductivities, often combined with local zones of high conductivities from fissures (Seiler, 1983). Also hydrochemical and isotopic characterization of the fluids is often technically limited because of contamination by drilling mud, which is used for stabilization of the boreholes during excavation. Möller et al. (1997) reported contamination by the drilling mud even after a 4-month pumping test. Also analysis for rare earth metals was affected by the drilling mud, as heavy metals, which originated from the abrasion of the drilling equipment, were enriched over time due to recycling of the drilling mud (Möller et al., 1997). The duration of pumping until the samples are delivered hundreds of meters to some kilometres up to the ground surface is causing oversaturation due to depressurizing, temperature decrease, and degassing (Stober and Bucher, 2005). By the degassing, species elemental fractionation of noble gases may occur (Lippmann et al., 2005). It seems that, at least in some settings (e.g. argillaceous rocks), the boreholes themselves affect the chemical characteristics of the fluids within the formation, e.g. by redox reactions of SO_4^- with dissolved organic carbon, and accordingly a significant change of isotopic compositions and related ^{14}C age (Beaucaire et al., 2008). Another difficulty for most in-situ tests is that processes for reaching equilibrium are very slow at those depths (caused by the low flow velocities). Accordingly, chemical equilibrium between drilling and testing or sampling is often not reached. Additionally, the tests often cannot be conducted before the aquifer reached equilibrium again (which may take years; Appelo et al., 2008). Although numerical modeling became a fully developed state-of-the-art technology for all kinds of shallow-groundwater projects in the last decade, this method is difficult to apply to deep groundwater systems not only because of the lack of data and the resulting uncertainties of parameter estimation. Also the groundwater conditions in deeper aquifers (high temperatures, pressures, and salinities) are challenging for numerical flow and transport modeling.

Altogether, both the heterogeneity of the deeper subsurface and the differing goals of research projects lead to differing strategies and methods between the individual projects. The search for final repositories, development of deep geothermal energy techniques, or storage of CO₂ are the driving forces for development of methods for deep groundwater research. Thus, they contribute to a better understanding of these systems. Due to different goals of both research and commercial projects, the gained knowledge and experiences are widely spread, the access to the studies need a high effort and is time consuming. A general overview about the knowledge and experiences about deep groundwater research is missing so far. To fill this gap, an extensive review of peer reviewed literature, project reports, and historical hard copy publications was conducted to summarize the current state of the research on deep groundwater.

1.2 Single-well methods in deep groundwater research

“Ideally, what is needed is an in-situ method that is rapid, relatively inexpensive, and has direct theoretical connection to hydraulic conductivity.”

Carl D. Palmer
in Palmer (1993)

For groundwater research in shallow aquifers a wide range of fully developed techniques are available for aquifer characterization and estimation of transport behavior, e.g. pumping tests, slug-and-bail tests, or tracer tests (Fig. 1.2a). For the investigation of the deeper underground, however, these methods are generally more difficult and costly. Potential obstacles are the limited access, often low hydraulic conductivities and the resulting slow groundwater flow, which would result in very long travel times during application of well-established test methods using a tracer input and several monitoring wells. Hence, in deeper aquifers one have to deal with single-well settings (Fig. 1.2b).

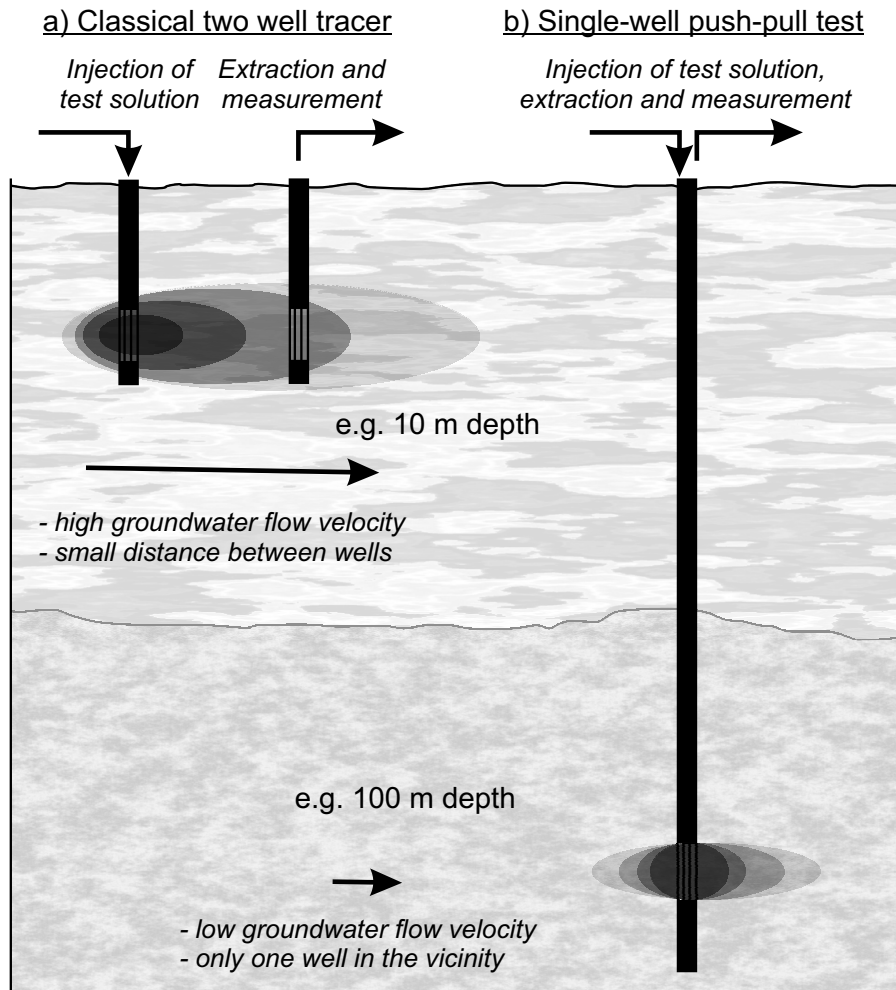


Figure 1.2: Comparison of a) multi-well setting and b) single-well setting (modified from Zeilfelder et al., 2014)

Various single-well methods for estimation of hydraulic parameters are described in the literature. An often reported approach is to test excavated cores from the drilling works ex-situ in the laboratory for their permeability by flow through experiments (Huenges and Zimmermann, 1999; Michie, 1996; Reeves et al., 1975). The fluid-solid interface and the tortuosity of migration channels – as measure for the porosity and permeability – can also be determined from core samples by Nuclear Magnetic Resonance (NMR; Frosch et al., 2000). The validity of these laboratory methods is limited due to scale effects. Differences from more than one magnitude are reported between measured field and laboratory permeabilities from the identical site, as measurements from core samples cannot consider large fractures, in which the main flow may occur (Michie, 1996). The

field permeability can be determined in single-well settings by production or borehole pumping tests, or by slug-and-pulse tests (rapid increase of the water level and observation of its decline). Especially for estimation of parameters like porosity also some geophysical well logging methods are available for single-well settings (e.g. electrical resistivity, NMR). However, most of the well logging methods can only be applied when no casing is constructed. Furthermore, these indirect methods bear some uncertainties in interpretation. The determination of groundwater flow dynamics, like dispersion, or solute transport, is not possible.

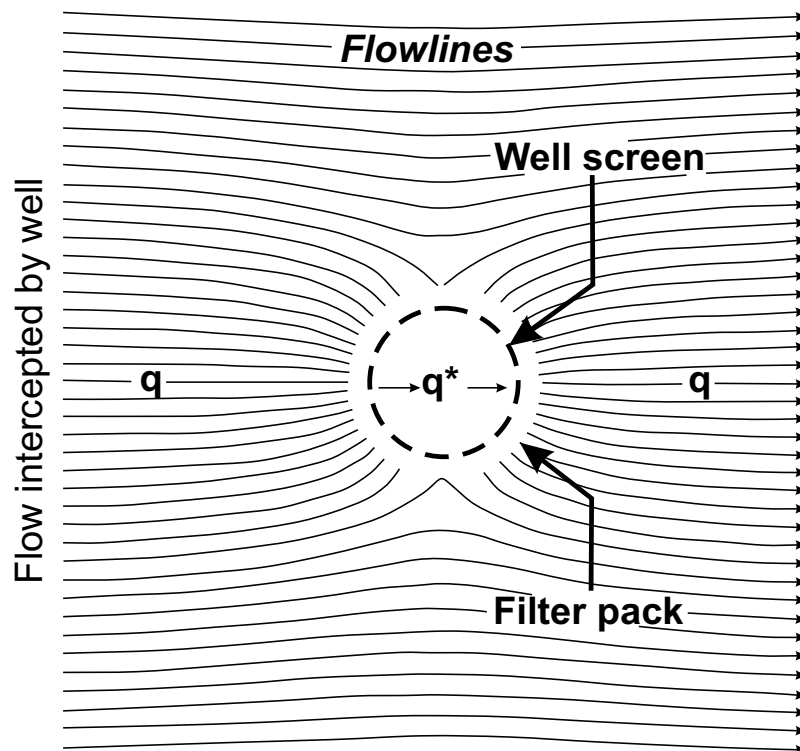


Figure 1.3: Disturbance of the natural groundwater flowfield (from the left to the right) caused by the high hydraulic conductivity contrast of an open well or borehole. The flux through the borehole or well, q^* , differs from the flux through the aquifer, q . Here: $q < q^*$ (modified from Palmer, 1993)

An established in-situ method for estimation of groundwater flow velocity in a single borehole are dilution tests (Butler et al., 2009; Delakowitz, 1996; Langkutsch et al., 1998; Williams et al., 2006), in which the concentration decrease of an adapted tracer is measured within the borehole. In this test it is assumed that all the concentration decrease is caused by dilution due to groundwater flow through the borehole. When radioactive tracers are used,

even the flow direction beyond the casing can be determined (Delakowitz, 1996). However, due to molecular diffusion of the tracer there is a lower detection limit for this method for very low flow velocities ($<0.005 \text{ m day}^{-1}$; Delakowitz, 1996), or highly porous but low permeable fractured zones (Bernstein et al., 2007). In zones of significant groundwater flow (like fractures or preferential flowpaths) spinner, temperature, and *EC* (electrical conductivity) logging can also be used for measurement of velocity (Chaplow, 1996). Results obtained from these passive methods overestimate groundwater flow velocities, because of the high conductivity contrast between aquifer and borehole, which forces the naturally parallel groundwater flowlines towards the well (convergent flow; Fig. 1.3).

1.3 The Single-Well Injection-Withdrawal (“push-pull”) tracer test

“Push-pull tests represent a solid approach for gathering information on aquifer characteristics, and testing these techniques in more challenging settings is a worthy objective”

Anonymous Reviewer

The Single-Well Injection-Withdrawal test (“push-pull” tracer test) is a suitable tracer test method for characterization of an aquifer in a single-well setting (Fig. 1.2b) as will be demonstrated in the following. A known amount of selected solutes as conservative and reactive tracers is injected into the aquifer (“push”) and afterwards extracted (“pull”). Often a so-called “chaser”, which is just natural groundwater without any added solutes, is injected directly after the test solution. In few publications the use of tap water as chaser fluid instead of untreated groundwater was reported (Istok et al., 1997, 1999). Its objective is to push the test solution out of the borehole into the aquifer and therefore to minimize the influence of the gravel pack on the shapes of the breakthrough curves (*BTCs*). The application of a so-called “reaction” or “drift” time before start of extraction is also often reported (Leap and Kaplan, 1988). Its aim is to allow a reaction of the injected solutes

with the groundwater and the aquifer material in case of hydrochemical experiments (Kim et al., 2004), or to let the injected conservative tracers drift with the natural groundwater flow velocity to gain information about hydraulic parameters (Hall et al., 1991; Leap and Kaplan, 1988). In general, it is common to perform push-pull tracer tests in the following steps:

1. Injection (“push”) of the test solution,
2. Injection of a chaser (optional),
3. Drift/reaction phase (optional), and
4. Extraction (“pull”) of the test solution.

The push-pull tracer test method was developed initially by Tomich et al. (1973) for the estimation of the residual oil saturation within reservoirs by the partitioning behavior of a reactant. The injected ethyl acetate hydrolyzes into ethanol as product. While ethyl acetate is soluble in both, water and oil phase, ethanol is only soluble in the water phase. Therefore, the retardation of ethyl acetate with respect to ethanol during extraction from the formation can be used to determinate the residual oil saturation (Tomich et al., 1973). In hydrogeology, the push-pull method is often used to detect and to quantify organic pollutants at contaminated sites, in situ determination of microbial activity, transformation and degradation rates, denitrification rates, and simulation of large recharge events in shallow (<20 meters depth) wells by partitioning push-pull tests (e.g. Addy et al., 2002; Cunningham et al., 2001; Haggerty et al., 1998; Istok et al., 1997; Kleikemper et al., 2002; McGuire et al., 2002). For that, reactive solutes are injected into the aquifer and after a certain reaction time within the aquifer re-extracted by pumping from the same well. As a result, the conservative tracer, the remaining reactant, and the reaction product are recovered. The gained concentration breakthrough curves (BTCs) during the pumping back phase then can be analyzed for transport and reaction parameters (Fig. 1.4). The shape of the BTCs and the mass recoveries of the solutes can be used to characterize sorption, degradation, ion-exchange, or precipitation-dissolution reactions within the aquifer. Common reactive solutes are nitrate (Azizian et al., 2005; Istok et al., 1997), 1-hexanol, 1-heptanol, 2-ethyl-1-hexanol (Istok et al., 2002), linear alkylbenzene sulfonate (Istok et al., 1999), sulfate, $H_{2,gas}$, CO_3^{2-} (Istok et al., 1997), propane gas, ethylene gas, propylene gas, $O_{2,gas}$ (Kim et al., 2004), and ^{85}Sr (Schroth et al., 2001). Additionally, physical parameters like the

fluid temperature (Vandenbohede et al., 2009) can be used as a reactive tracer. The most common conservative tracer is bromide (Addy et al., 2002; Azizian et al., 2005; Davis et al., 2002; Hall et al., 1991; Istok et al., 1999; Kim et al., 2004; Vandenbohede et al., 2009). Further conservative tracers are 2-butanol (Istok et al., 2002), chloride (Kim et al., 2004), and iodide (Meigs and Beauheim, 2001; Schroth et al., 2001). A more unconventional tracer is radon, which is produced in-situ within the aquifer during the reaction time between push and pull phases (Davis et al., 2002).

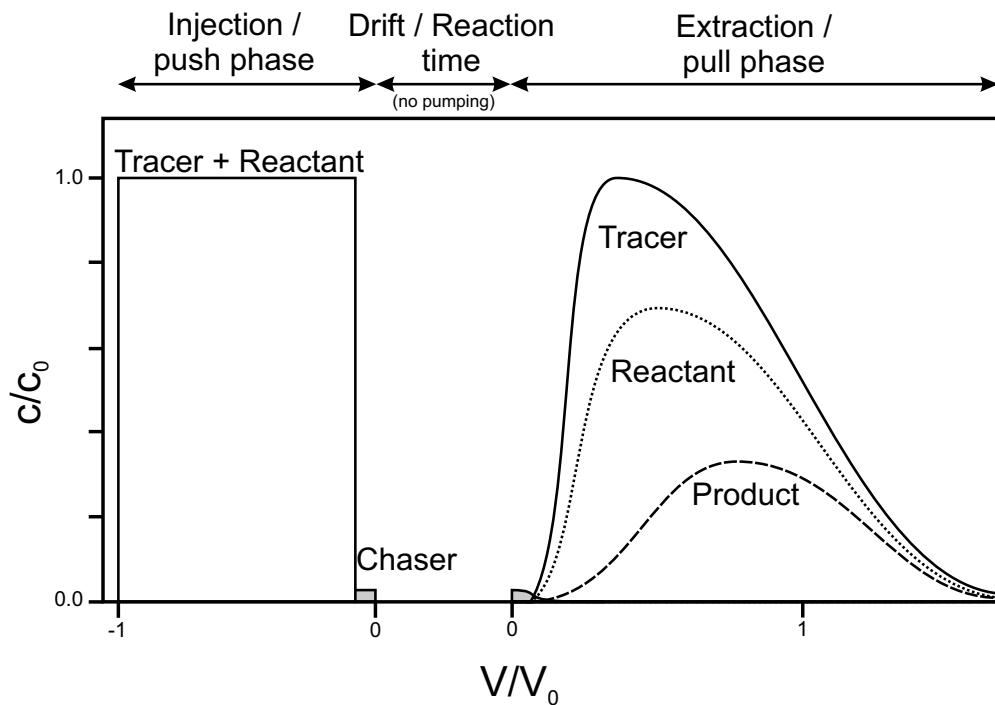


Figure 1.4: Schema of idealized BTCs during injection (-V) and extraction (+V) phase of a push-pull test (modified from Istok et al., 1997)

Several research groups adapted the push-pull method to characterize hydraulic behavior in shallow single-well settings, e.g. for estimation of transport parameters as flow velocities, dispersion/dispersivities, and matrix or effective porosities (e.g. Hall et al., 1991; Leap and Kaplan, 1988; Novakowski et al., 1998; Riemann et al., 2002). Also the investigation of mixing, cation exchange, and oxidation-reduction reactions caused by the change of salinization by using push-pull tests was reported for deeper aquifers (Vandenbohede et al., 2008).

Novakowski et al. (1998) estimated the velocity, dispersivity, and matrix porosity by manually fitting the BTC with a numerical model. The BTC was obtained from a test in a discrete horizontal fracture. Guven et al. (1985), Molz et al. (1985), Pickens and Grisak (1981a,b), and Pickens et al. (1981) were able to determine the dispersion from push-pull tests and even the depth dependent dispersion in a stratified aquifer. However, for this approach additional observation wells in the surrounding of the injection-withdrawal well are needed. Push-pull tests were also reported as appropriate method to estimate regional advective groundwater flow velocities in porous materials (Leap and Kaplan, 1988). Rieman et al. (2002) also used the Leap and Kaplan (1988) method and combined it with a point dilution test to estimate the groundwater flow velocity in a fractured aquifer. Hall et al. (1991) enhanced the method to determine the effective porosity. However, for most of these approaches at least one additional observation well is required. As the travel distance of the injected and afterwards extracted tracer plume, as well as the pristine groundwater gradient will always remain unknown in single-well settings, the reliability of the published approaches for the hydraulic analysis of push-pull tests remains limited.

Only few applications of push-pull tests in deeper aquifers were reported so far. In Belgium, Vandenbohede et al. (2008) used the push-pull method for estimating the suitability of the about 150 m deep Tienen Formation as an aquifer storage and recovery (ASR) system for potable water. By injecting freshwater into the brackish aquifer conclusions about the influence of the natural brackish groundwater on the quality of the stored and afterwards recovered freshwater could be drawn. Therefore, the BTCs of the pull-phase were analyzed with respect to mixing, cation exchange, and oxidation-reduction reactions. Radloff et al. (2011) injected arsenic-bearing groundwater into a well screened at 60 m depth within the arsenic-free brown sand aquifer in central Bangladesh. In this experiment the pull-phase was conducted stepwise. By analyzing the BTCs, the adsorption of arsenic within the brown sands could be estimated. Moreover, the risk of arsenic breakthrough from the shallower contaminated aquifer into the deeper brown sand aquifer, induced by deep pumping (150 – 200 m), was assessed.

As the goal of the research in the coastal sedimentary basin of Horonobe is the characterization of deep groundwater flow under the influence of

the saltwater-freshwater interface, two push-pull tests – one simulating an intruding fluid with higher mineralization than groundwater and one test with a lower mineralization – were conducted in a first field campaign in 2010.

Despite its often reported application, no systematic evaluation of the push-pull test method has been performed so far. The repeatability of this method, the effect of changes of its setup on the resulting BTCs, and the influence of the chaser on the tracer BTCs are unknown so far. Potential effects may be dilution of the test solution (in the worst case below the detection limit), pushing the tracer plume too far into the aquifer (e.g. beyond the radius of the cone of influence and accordingly the loss of the tracer), or any other kind of shifting or alteration of the BTC. The injection of a chaser directly after the injection of the tracer test fluid will disturb the idealized cylindrical tracer plume and therefore change its shape into a more “*donut*” form (Hall et al., 1991), which could make (hydraulic) interpretation more challenging. Otherwise, the application of a chaser helps to obtain a complete recovery BTC (Nordqvist et al., 2012). Also, the determination of the right chaser volume is a difficult task. The volume of the chaser should be enough to fill the whole well and gravel pack volume, but should not penetrate the aquifer. For this, the volume of all used tubes, pipes, the tested well, and its gravel pack has to be known. However, in most cases the effective porosity of the gravel pack and accordingly its volume is unknown and has to be estimated, which may result in insufficient results. To fill this gap, a second field campaign was conducted and described within this thesis in 2012.

1.4 Outline of the thesis

This cumulative thesis comprises three manuscripts. The first paper is already published, the other two papers are currently under review:

1. Hebig, K.H., Ito, N., Scheytt, T. & Marui, A. (2012) Review: Deep groundwater research with focus on Germany. *Hydrogeology Journal*, 20 (2), 227 – 243 (*Chapter 2*);
2. Hebig, K.H., Ito, N., Tecklenburg, J. Machida, I., Marui, A. & Scheytt, T. (submitted) Performance of single-well push-pull tracer tests to char-

acterize transport processes: a case study in a sedimentary coastal basin (*Chapter 3*);

3. Hebig, K.H., Zeilfelder, S., Ito, N., Machida, I., Marui, A. & Scheytt, T. (in press) Study of the effects of the chaser in push-pull tracer tests by using temporal moment analysis (*Chapter 4*).

The first paper reviews the state of the science for deep groundwater systems, the history of research on this topic, and provides an overview about different deep aquifer types. Furthermore, six different case studies about deep groundwater research projects are presented, with the focus on Germany and Central Europe. In the second paper the results of a single-well push-pull test in about 100 m depth at the field site in Horonobe, Japan, are presented and discussed. Aim of this pilot study was to test the performance of this method in a deep sedimentary coastal basin with freshwater-saltwater interface and single-well setting. The third paper presents partial results of an integrated systematic method evaluation, in which the push-pull method was tested for its reproducibility. Furthermore, the influence of specific changes of the test setup was investigated. Here, the results of a specific part of the experiment – the influence of the chaser solution on the overall test results and the determination of the optimal chaser volume – are presented and discussed. The results of the overall experiment are presented in Zeilfelder et al. (2014) and thus not part of this thesis. A more detailed outline is presented in the following.

Chapter 2: “Review: Deep groundwater research with focus on Germany”

In this review study, the results of a fundamental literature research are presented. Aim was the first systematic compilation of the past and the recent concepts and theories concerning deep groundwater movement and characteristics. For this purpose, many difficult to access reports and rare hard copy publications were collected, analyzed, and summarized. For a better understanding, a short introduction on the groundwater flow in different hydrogeological main units (sedimentary basins, igneous and metamorphic rocks, rock salt, and argil/argillaceous rocks) is presented. Case studies of

large scientific or industrial projects are presented for the main hydrogeological units to show the significance of deep groundwater research nowadays. Furthermore, the specific methods and experiments of each project are described and evaluated:

- The Sellafield Test Site in England (2.6.1),
- Geothermal research and applications in the North German Plain (2.6.2),
- The German Continental Deep Drilling Program – KTB (2.6.3),
- The Gorleben Test Site (2.6.4),
- The Final Repository for Radioactive Waste at Morsleben – ERAM (2.6.5),
- The Bure Test Site in France (2.6.6).

This review paper demonstrates the significance of deep groundwater research for urgent issues, like radioactive waste management in deep geological repositories, potential CO₂ storage, or supply with renewable geothermal energy. There are no common, generally accepted, and easily applicable technical or scientific standard solutions or test methods available to characterize deep groundwater. However, the fast growing demand for knowledge and understanding of these dynamic systems have spurred the research on deep groundwater systems. Accordingly, test methods are being developed, which still show considerable limitations.

Chapter 3: “Performance of single-well push-pull tracer tests to characterize transport processes: a case study in a sedimentary coastal basin”

The objective of this study was to gain information on the groundwater transport characteristics of the 100 m deep Sarabetsu aquifer at the Hamasato test site in Horonobe (Hokkaido, Japan). The Hamasato test site is part of an integrated research project within the framework of the research for the Japanese final repository for radioactive waste, in which the Japanese Atomic Energy Agency (*JAEA*) operates the Horonobe Underground Research Laboratory in the inland Teshio Mountains. In our project, the National Institute of Advanced Industrial Science and Technology (*AIST*) develops methods and techniques to characterize a coastal sedimentary basin including the continental shelf. The shelf would be the natural discharge area of the slowly

flowing groundwater originating from a possible final repository in the Teshio mountains. Potential aquifer characterization in deeper sedimentary basins is bound to single-well settings, due to the expected low groundwater flow velocities in the target depths (between 100 and 1,200 m below ground level surface) and the potentially large area of interest (with the according large distances between boreholes). The Upper Sarabetsu aquifer is composed of heterogeneous porous sediments (fine sand matrix, coarse to fine gravel channels, and clay lenses). Therefore, transport characterization in the single-well setting at the Hamasato test site is challenging.

One aim of the project was to investigate the saltwater-freshwater interface. An additional objective was to evaluate the performance of the push-pull method for groundwater transport and aquifer characterization (e.g. ion exchange or sorption capacity, redox conditions, hydraulic properties). To investigate the influence of fluctuations of the saltwater-freshwater interface (induced, e.g. by sea level fluctuations or change of groundwater recharge) on the transport characteristics of the system, two tests were conducted: a brackish water ($EC = 3,800 \mu S/cm$, higher density than the original groundwater with an $EC = 1,083 \mu S/cm$) and a deionized water ($EC = 25 \mu S/cm$, lower density) test. A strong fluid dependent hydrochemical behavior of the injected tracers was observed in the experiment. By fitting the breakthrough curves of Li^+ and Cl^- , the hydraulic parameters effective porosity n_f and dispersion coefficient (in the longitudinal direction) α_L could be estimated. It was shown that the push-pull method is a suitable single-well technique for hydrochemical characterization of dynamic deep coastal aquifers. It was demonstrated that the push-pull method can be considered as a relatively fast and cheap test method. However, the method has limitations and needs a more confident theoretical fundament, as analysis and interpretation are difficult and deliver ambiguous results.

Chapter 4: “Study of the effects of the chaser in push-pull tracer tests by using temporal moment analysis”

Although the push-pull tracer test method is widely known, the method was not be systematic evaluated. An extensive experiment was conducted at

the Hamasato test site (Horonobe, Japan) to evaluate the influence of the experimental setup of a push-pull test on the resulting tracer BTCs. The repeatability of this method, the effect of variations of its setup, and the influence of the chaser on the tracer BTCs were tested. In the third paper of this thesis, a specific part of the comprehensive field campaign is presented: the evaluation of the role of the chaser in push-pull tests.

The chaser, which is natural groundwater without any added solutes, is injected directly after the test solution. Its objective is to push the test solution out of the borehole into the aquifer and therefore to minimize the influence of the gravel pack on the shapes of the BTCs. Indeed, the application of a chaser was reported in nearly half of the publications on push-pull tests. However, the reasons or considerations for applying a chaser remain unclear. Moreover, the influence of the chaser on the tracer BTC is unknown so far. Also the determination of the right chaser volume is a difficult task.

To address this issue, two experiments were conducted: in a first step three push-pull tests with similar injection volumes were compared, two tests with and one test without chaser. In a second step the optimal chaser volume was determined by testing seven different chaser injection volumes. In the first experiment it was shown that the application of a chaser lowers the main peak concentration, but does not alter the tailing of the BTC and also has no negative effect on the tracer mass recovery. It can be concluded that the application of a chaser is recommended, when reactions of injected solutes within the open well or the gravel pack should be avoided. On the contrary, the application of a chaser should be avoided, when more hydraulic issues are within the research focus, because of its effects on the BTCs (dilution, dispersion). Based on the second experiment, a simple and fast method for the determination of the optimal chaser volume was developed. The presented method is also suitable for the determination of the effective porosity of the gravel pack, which is often unknown. For analytical interpretation of the both experiments temporal moment analysis was used.

Due to the cumulative structure of the thesis, references are indicated at the end of every chapter.

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2 Review: Deep groundwater research with focus on Germany

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2.1 Abstract

While research focuses mainly on the intensively used shallower aquifers, only a little research has addressed groundwater movement in deeper aquifers. This is mainly because of the negligible relevance of deep groundwater for daily usage and the great efforts and high costs associated with its access. In the last few decades, the discussion about deep geological final repositories for radioactive waste has generated strong demand for the investigation and characterization of deeplying aquifers. Other utilizations of the deeper underground have been added to the discussion: the use of geothermal energy, potential CO₂ storage, and sources of potable water as an alternative to the geogenic or anthropogenic contaminated shallow aquifers. As a consequence, the fast growing requirement for knowledge and understanding of these dynamic systems has spurred the research on deep groundwater systems and accordingly the development of suitable test methods, which currently show considerable limitations. This review provides an overview of the history of deep groundwater research. Deep groundwater flow and research in the main hydrogeological units is presented based on six projects and the methods used. The study focuses on Germany and two other locations in Europe.

Keywords

History of hydrogeology · Groundwater flow · Radioactive waste repositories · Equipment/field techniques · Germany

2.2 Introduction

Deep groundwater has been underrepresented in hydrogeological sciences research for a long time and accordingly little is known about its behavior. Evolution of the term “*deep groundwater*” is strongly related to the development of the early groundwater sciences in the middle of the nineteenth century. Its meaning has changed from the more speculative and static image as “*deep stagnant water*” (Weithofer, 1936) to a more dynamic un-

derstanding. Now, deep groundwater is not only defined by its depth, but by its genesis, age, chemical composition, etc. (Einsele et al., 1983). It is now widely accepted that deeper aquifers are dynamic systems, which are influenced by both surface processes (from the meteoric cycle) and crustal processes (from the lithosphere). Intensive research has mainly focused on characterization of the commonly used shallower aquifers. Great efforts by hydrogeologists have led to a thorough understanding of regional groundwater systems, their driving forces and their hydrochemical dynamics (e.g. Back, 1960; Freeze and Witherspoon, 1967; Hubbert, 1940; Tóth, 1962, 1963). The range of research activities is extending from regional-scale basin modeling down to micro-scale laboratory experiments. Complex processes in groundwater systems have been intensively examined in the past and more recently (e.g. Back, 1960; Bethke et al., 2000; Grenthe et al., 1992; Hölting, 1969; Magri et al., 2005; Stober, 1986). The basic groundwater flow concepts in basins are widely accepted, the importance of redox reactions on groundwater quality is well-known, and recently it has become common to compile numerical flow and mass transfer models for the future development of catchment areas influenced by changing boundary conditions caused by climate change. The appearance of new emerging contaminants of concern, the remediation of polluted sites, and the development of new mathematical approaches to describe mass transfer of organic substances in groundwater has been the aim of recent and past hydrogeological sciences. There has been less focus on deep aquifers because of their very complex nature, expensive access and negligible importance for supply with respect to potable and irrigation uses.

Except for some deep drilling projects, which have mainly focused on crustal processes, very little research has been performed in the field of deep groundwater flow. However, already these few previous experiments have revealed that the traditional image of stagnant or very slow flowing groundwater with poor hydraulic connection at greater depths seems to be obsolete, e.g. *KTB* (Kontinentales Tiefbohrprogramm der Bundesrepublik Deutschland [The German Continental Deep Drilling Program]; see Fig. 2.1c), and Kola superdeep well in Russia. Simultaneously, interest in deep groundwater research has increased for economic reasons in the last few years. Deep-lying aquifers have become important resources (e.g. for

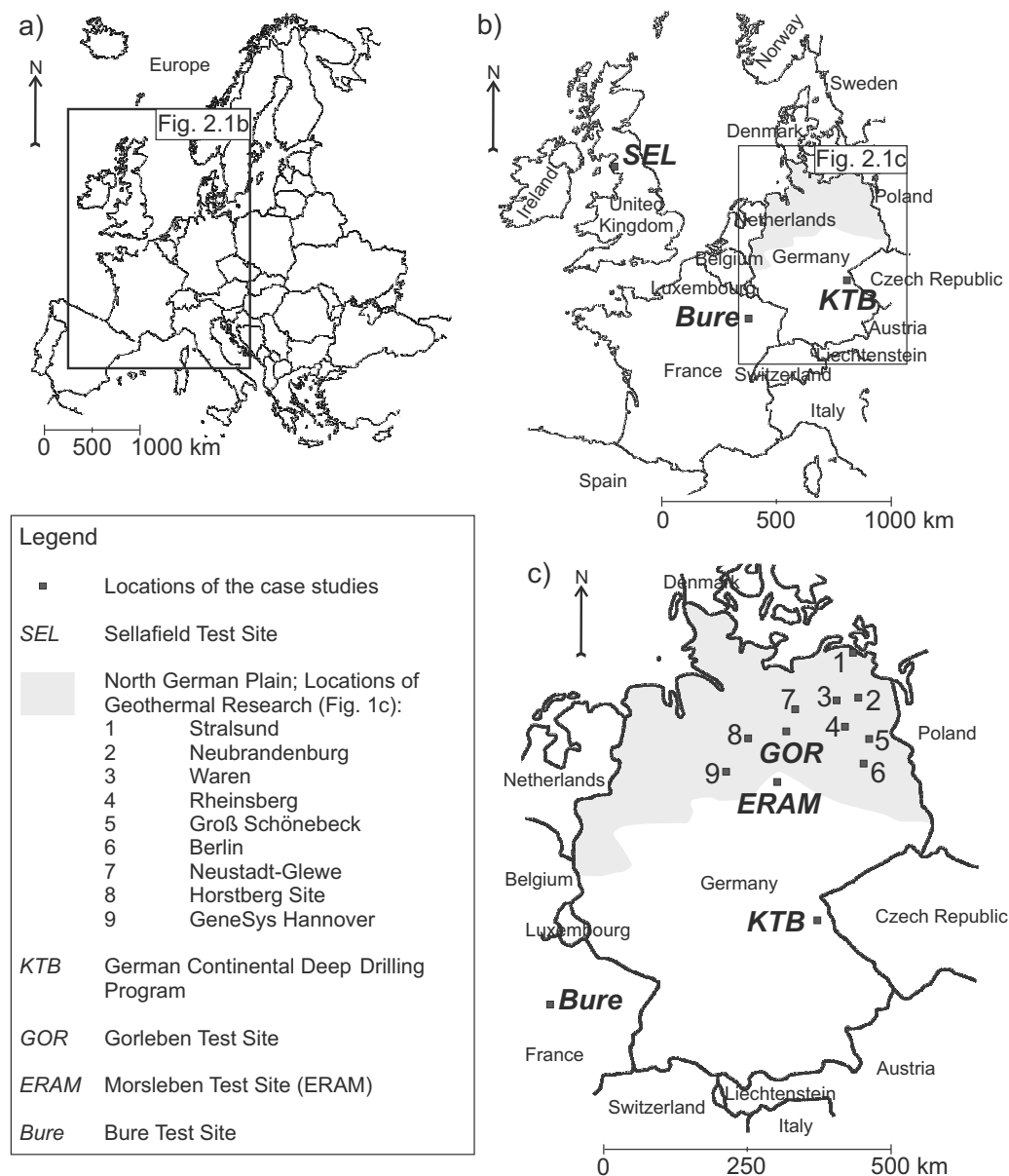


Figure 2.1: Locations of the case studies in Central Europe and the UK

the production of geothermal energy or as an alternative potable water source), or are intended as a medium for final repository (e.g. CO₂ storage). The behavior of deep groundwater as a transport medium for dissolved substances is an important factor in risk assessment for the worldwide planned or projected final geological repositories for toxic or radioactive waste. A thorough understanding of deep groundwater systems is crucial in the supply of engineered solutions for these modern society requirements. Nevertheless, the knowledge about deep groundwater is relatively poor. Due

to their different intentions, the knowledge and experiences acquired during the few experiments that have been conducted so far are widely spread and access to the studies have been time consuming. Research using adapted or newly developed methods shows some limitations caused by the conditions in the deeper underground. The evolution of deep groundwater, its movement, and its chemical behavior are unclear. In this paper, previous deep groundwater flow concepts, knowledge about deep groundwater flow in different hydrogeological units, methods, and examples of past and recent research projects (with the main focus on Central Europe and especially Germany; see Fig. 2.1) are outlined. The aim of this review is to provide a general overview of the history of deep groundwater research and state-of-the-art techniques.

2.3 A short history of deep groundwater concepts

Interest in deep groundwater increased in the nineteenth century. One of the main questions was (and still is): Is deep groundwater in motion or stagnant? At that time several authors published their ideas regarding the origin of mineral resources in dike outcrops and in highly mineralized springs. They imagined convection cells forced by gravity-driven descent and heat-driven ascension with the accumulation of mineral resources in dikes (e.g. Beaumont, 1850; Cotta, 1850; Daubrée and Gurlt, 1880; Müller, 1860). Other authors believed that the deeper groundwater is connate (from sedimentation), juvenile (from magmatic segregation), or a mix of both (e.g. Behrend and Berg, 1927; Weithofer, 1936). According to these rules deep stagnant groundwater would prevent the penetration of younger, meteoric water from the surface because of its greater density. Weithofer (1936) introduced a term translatable as “*deep stagnant water*” (*Tiefenstandwasser*). The deep stagnant water is located below the deepest possible discharge area (which is the ocean). He postulated that due to the friction of moving water within an aquifer, motion of groundwater against gravitation is impossible without outer forces. Above this deep stagnant water, he defines the shallow “*flowing water*” (*Fließwasser*), which is moving as a part of the meteoric water cycle from

its recharge to its discharge area forced by gravitation (accordingly always downgradient). Due to the lack of data from deep wells, the early research was more speculation than interpretation. With the increasing worldwide demand for mineral resources and hydrocarbons during the first half of the twentieth century knowledge of the deeper underground increased. Important contributions to the understanding of regional groundwater flow were given by Hubbert (1940), who introduced modern physics to groundwater sciences. He discussed several existing concepts of groundwater flow from his point of view as a geologist and as a physicist (Anderson, 2008). Important for the understanding of groundwater flow was his negation of the concept of deep stagnant groundwater caused by friction. He showed that the amount of work required to drive a unit of mass of the fluid from one equipotential surface to another is always the same, independent from the flowpath. The consequences for the analytical solution of groundwater flow systems were crucial. One of them is that in a homogeneous aquifer a zone of stagnant groundwater cannot exist (except for groundwater with a considerably different density). Tóth (1962, 1963) applied these essential findings in his analysis of groundwater flow in small basins in Alberta, Canada, by defining boundary conditions like an impermeable lower layer and varying the ratio of basin depth to its lateral extent. The results of his analytical solution were the differentiation of (1) a homogeneous aquifer in shallow zones (local flow systems) with high groundwater flow velocities and relatively large recharge areas, and (2) deep zones (regional flow systems) with very low groundwater flow velocities and relatively small recharge areas. Important conclusions of this work were: (1) regional groundwater flow systems are always dynamic systems with changing local flow systems; (2) the vertical extension of local flow systems depends on the topography; (3) the groundwater flow velocities become lower with depth; and (4) the mineralization of groundwater increases with its depth (according to its velocity within the aquifer). Freeze and Witherspoon (1967) improved and enhanced the analytical model of Tóth (1963) by including different cases of heterogeneity and anisotropy in a finite difference model. They provided useful schemata for different groundwater flow systems and demonstrated the growing prospects and significance of numeric modeling for the solution of hydraulic problems.

In the 1960s the hydrochemical description of groundwater flow systems became more and more important: Back (1960) applied trilinear Piper diagrams to describe different types of groundwater from a coastal basin in the eastern USA. By using the distribution of the different ion concentrations within the Piper diagram, it became possible to describe the genesis of a regional groundwater system. Therefore, he linked the geochemical observations to regional groundwater flow and defined the hydrochemical facies concept (Glynn and Plummer, 2005). Hölting (1969) presented a summary of definitions of the term deep groundwater with a focus on the special situation in the North German Basin. He defined deep groundwater, besides its absence from the meteoric water cycle, by chemical attributes. He differentiated the groundwater in northern Germany by its mineralization (deep groundwater shows high salinization) and by its anion ratios. According to Hölting (1969) shallow groundwater is characterized by a high content of hydrogen carbonate and is part of the active meteoric water cycle. He set the depth of this zone at approximately 300 m below the ground surface in the North German Basin. Beneath the shallow groundwater zone he defined a transition zone with increasing sulfate and chloride contents. At depths below about 600 m, a zone of very low groundwater exchange is expected (which he called the “*zone of stagnant water with strongly decelerated groundwater motion*”). This zone is characterized by high mineralization and high contents of calcium chloride and sodium chloride.

Einsele et al. (1983) presented a comprehensive compilation about the field of deep groundwater research published by DVWK (Deutscher Verband für Wasserwirtschaft und Kulturbau e.V. [The German Association for Water Management and Land Improvement]). In these guidelines, the generally accepted characteristics of deep groundwater were summarized. According to that compilation, the term deep groundwater is not bound to a defined depth below the surface, but to specific characteristics: “*‘Deep groundwater’ in Central Europe is defined as water which originates from slowly-circulating, deep-lying, subsurface aquifers, although in discharge areas it can occur at relatively shallow depths. It is usually devoid of ^3H and has low ^{14}C values.*” (Einsele et al., 1983, p. XIII). The guidelines suggest use of the hydrochemical facies concept (e.g. Back, 1960; Hölting, 1969) to describe and classify groundwater and its evolution. The increasing impact of isotope dating (by

radioactive isotopes) and the evaluation of the paleoclimatic conditions (by stable isotopes) at that time were described. The challenges related to the geothermic gradient (change of density, change of viscosity, heat driven convection) were outlined.

In the second part of the twentieth century an integrated approach for the analysis of specific basins was established, which used all the different fundamental findings and methods for the deep groundwater flow analysis: the development of a regional groundwater flow concept, hydrochemical interpretation, modeling of paleoclimatic with isotopic analysis, and numerical modeling of hydraulic behavior, mass transport, and heat transport. Today, it is accepted that in regional basins, deep groundwater is never stagnant, but moving with very slow velocity towards its discharge area. Certainly stagnant groundwater appears in small isolated aquifers comparable to hydrocarbon traps.

Recently, groundwater research has been in the phase of application, enhancement, and adaptation of the models and methods for the investigation and description of specific basins and deep groundwater flow systems. Seiler (1983) examined the influence of pumping tests on deep groundwater flow. He pointed out that the higher density and temperature of deeper groundwater can lead to inconsistent results. Additionally, he reported on the extreme periods (months to years) needed to reach steady-state conditions during and after pumping tests. Grenthe et al. (1992) investigated the accuracy of redox measurements in deep boreholes. Bethke et al. (2000) compared different transport models (velocity after Darcy's Law, piston flow, transport of atmospheric ^{36}Cl , transport of geogenic ^4He) for deep groundwater flow in sedimentary basins and emphasized the uncertainties of the term groundwater "age". The modeling results of an area in the eastern part of the North German Basin by Magri et al. (2005) suggest a slow (1 – 2 km per 10,000 years) thermally induced free convection, which causes saline springs at the surface. Deep groundwater circulation in crystalline rocks has had more research focus since the 1980s. Research projects about the origin and behavior of groundwater in the deep crystalline rock basement of southern Germany were published by Lippmann et al. (2005), Lodemann (1993), Lodemann et al. (1998), Stober (1986), and Stober and Bucher (1999a,b, 2005, 2007). These authors investigated deep groundwater movement in

the Black Forrest region (about 1,000 m to maximum 3,500 m depth) and in the Oberpfalz region (KTB: 2 – 9 km depth). Further examples of deep groundwater research in basins in Germany include Hofmann (1990; Lower Franconia), Schubert (1996; Molasse Basin), and both Naumann (2000) and Magri et al. (2009b) about salty groundwater flow in the North German Basin.

2.4 What are the reasons for deep groundwater research?

Considering the wide variety of (mostly ambiguous) definitions of the term deep groundwater in history it becomes clear that the main feature of deep groundwater is its uselessness for daily human consumption and utilization. Interest in the deeper underground and groundwater has increased only with respect to resources, since the beginning of industrialization and especially at the end of the nineteenth century. In addition to the generally increasing scientific interest in evolution of Earth at that time, the main interest in Central Europe concentrated on understanding the origins of mineral resources, ore dikes, and mineralized springs. Since that time, the need to understand the “*system earth*”, and accordingly regional groundwater systems, has increased significantly. The driving forces were always the prospection and exploration of resources. One of the most important research fields is the use of geothermal energy, which requires large amounts of hot groundwater. As part of the investigation of potential host rocks for the final repository of toxic, dangerous, or radioactive waste, research on associated deep aquifers is a crucial aspect of safety assessment. The deposition of brines in deep aquifers (as practised for some time in central Germany) strongly affects the groundwater systems and leads to contamination even of the shallow aquifers. An important field of research of deep groundwater is the storage of CO₂ in deep aquifers. For that, utilization of deep groundwater itself should act as the supporting medium for safe and long-term storage. Now, in some regions, deeper aquifers are considered as potential alternatives to shallower, contaminated aquifers. For example, Shibasaki et al. (2007) and Michael and Voss (2008) investigated the potential use of an underlying aquifer for

drinking-water supply instead of the arsenic-contaminated shallow aquifer of Bangladesh.

2.5 Deep groundwater flow in different geological units

In Germany and Central Europe, the regional hydrogeological formations and the resulting usability of groundwater for drinking-water supply are quite variable. Accordingly, the knowledge about shallow and deep groundwater flow is quite different depending on the different geologic formations. The most productive and consequently the best known groundwater reservoirs are porous aquifers, like the most important hydrogeological formation, the North German Basin (geographic name is North German Plain). This was formed by glaciers, which overrun northern Germany several times during the Ice Age. The North German Basin is built up by unconsolidated Quaternary sediments, which form multiaquifer formations. The several-hundred-metres-thick aquifers are intensely used for drinking-water supply. For example in the cities of Berlin and Hamburg production wells are pumping at depths between 30 and 430 m below ground surface (BWB, 2009; HWW, 2010). These deeper aquifers provide enough good quality groundwater for drinking-water supply for altogether about 5.4 million citizens in the both cities.

There are serious problems with saltwater intrusion at the coasts, near salt domes, and in deep aquifers (BGR, 2009; Henningsen and Katzung, 2002). Because of the occurrence of saltwater at relatively shallow depths, very little research on deep groundwater systems of coastal aquifers has been conducted so far.

Further important sedimentary groundwater storage units in central and southern Germany are the Molasse, the Oberrheingraben (Upper Rhine Graben), and the Niederrheinische Bucht (BGR, 2009; Henningsen and Katzung, 2002). Because of the availability of sufficient amounts of groundwater with good to excellent quality, and cost-effective pumping from shallow aquifers, it is not common to pump groundwater from deep aquifers.

In the low mountain ranges in the central and southern part of Germany, the productivity and usability of the aquifers depend on the geological setting. In the escarpments of southern Germany (Fränkischer and Schwäbischer Jura), which are built up by limestones, regional karst formations can provide very productive aquifers. In the Pfälzer Wald, Schwarzwald (Black Forest), Spessart and Solling, which are built up by thick sandstones, and in the Vogelsberg (basalt), fissured regional rock aquifers are very productive. Groundwater use in these regions is related to vulnerable karst and fissured rock aquifers, which are at risk from anthropogenic contamination caused by short flow times. Other low mountain ranges, like Harz, Rheinisches Schiefergebirge (Rhenish Slate Mountains), Thüringer Wald (Thuringian Forest), Bayrischer Wald (Bavarian Forest), Erzgebirge and Hochschwarzwald, are predominantly built up by very low permeable rocks, like argillaceous shale, and metamorphic or plutonic rocks. In these areas, only local aquifers built up by unconsolidated Quaternary sediments in river valleys are usable for drinking-water supply. There, the common source for potable water is surface water (BGR, 2009; Henningsen and Katzung, 2002).

2.5.1 Sedimentary basins

The largest and most important sedimentary basin in Germany, the North German Basin, is composed of Tertiary and Quaternary glacial sediments, which are underlain by Palaeozoic and Mesozoic sediments up to a maximum depth of about 10 km. In the basin, the shallow freshwater aquifer is separated from the underlying saltwater aquifer by the Tertiary Rupel Clay. This clay barrier lies at a depth of several tens of meters to some hundreds of meters. Due to the easy supply of large amounts of excellent quality groundwater from the shallow aquifer, only a little was known about the deeper salty aquifer and the underlying basement. This situation has changed with the beginning of deep exploration programs for hydrocarbons and geothermal research. In general, groundwater becomes more mineralized with increasing depth in the North German Basin (Hölting, 1969). The increasing mineralization is probably caused by the dissolution of evaporates from the Zechstein formations (mainly from large salt structures). Evidence for this comes from Naumann (2000), who compared the geochemical analy-

ses of five geothermal boreholes at depths between 1,250 and 3,250 m in northern Germany. Magri et al. (2005) modeled very slow but deep-reaching thermally induced convective flow, which causes transport of brine to the surface (salty springs). Highly mineralized aquifers, caused by dissolution of evaporates, are often observed.

In coastal aquifers high salinity is caused by connate seawater (as a residue from a former marine sedimentation) or by mixing of intruded seawater and evaporate-mineralized meteoric water. An example of a coastal sedimentary basin is the Sellafeld groundwater system in northwestern England (United Kingdom), which contains waters of three levels of salinity (fresh, saline, and brine; Black and Brightman, 1996). An important controlling factor of coastal basins is the location and the evolution of the saltwater-freshwater interface, which has a crucial impact on the groundwater flow system (Masterson and Garabedian, 2007; Werner and Simmons, 2009).

In general, groundwater flow systems of regional sedimentary basins are topographically driven and Darcy flow can be assumed. Nevertheless, in large sedimentary basins, isolated zones of stagnant or very old groundwater are reported (e.g. the Dogger aquifer in the Paris Basin, France; Marty et al., 2003). Therefore the Darcy flow model is, maybe, not always the best flow model for deep and slow groundwater movement (Bethke et al., 2000).

2.5.2 Igneous and metamorphic rocks

Igneous and metamorphic rocks cover wide areas of Germany. Most of these rocks were generated during the Precambrian and the Palaeozoic Age. In many regions, extensive mining was conducted in the past. The mountain range Erzgebirge, in particular, has a long mining tradition for ore, silver, uranium, and other mineral resources (Henningesen and Katzung, 2002). Only a little is known about the deep groundwater flow behavior in crystalline basement. Crystalline rocks themselves exhibit very low permeability, are nearly insoluble and highly rigid, and exhibit low sensitivity to high temperature (BGR, 2007). Larger crystalline rock formations are fissured by tectonic stress or by expansion during their ascension. Because of the enormous overburden pressure, researchers used to assume that no groundwater flows

in these fissures at great depths. These days, it is accepted that at great depths groundwater may flow and even circulates (Rybach, 1997; Smithson et al., 2000). Carlé (1975) explained mineral springs and thermal waters in the crystalline basement of the Black Forest with the mixing of different groundwater flow systems. Stober (1995) enhanced this work by adapting the model of topography-driven flow to the Black Forest region. Pumping tests show that strongly fissured granitic rocks may behave as homogeneous and isotropic aquifers. Stober and Bucher (2007) reported on hydraulic conductivities up to 10^{-6} m s^{-1} at depths of about 1 km. From the Kola well, which was drilled to about 12 km into the crystalline basement of the Kola Peninsula, fissure-related water was reported (Kremenetsky and Ovchinnikov, 1986; Popov et al., 1999). Rybach (2009) used geothermal data to evaluate the deep groundwater flow characteristics of three example sites in the Hercynian basement of Western Europe (at various depths from 1.5 km to 5 km). For all sites he found similar ranges for very slow groundwater movements of 10^{-10} to $10^{-11} \text{ m s}^{-1}$ within a depth range of groundwater circulation of ~5 – 7 km. According to the findings of a pumping test in the 4,000 m pilot hole of KTB, Stober and Bucher (2005) concluded that *“the water-saturated fracture pore space of the brittle upper crust is highly connected, hence, the continental upper crust is an aquifer”*. Accordingly, large areas without fissures and cracks were not expected to be found in the crystalline rocks of Germany. The German Federal Institute for Geosciences and Natural Resources (Bundesanstalt für Geowissenschaften und Rohstoffe, BGR) concluded that it is unlikely to find potential suitable host rocks for final repository within crystalline rocks in Germany (BGR, 2007).

2.5.3 Rock salt

Rock salt formations were mined for more than 100 years in Germany. Extensive knowledge about the behavior and properties of these formations exists (BGR, 2007). The most important salt formation in Germany is the Zechstein salt formation, which was deposited at the end of the Permian Age. The Zechstein salt formation is composed by seven evaporate cycles, each of them containing carbonates, gypsum, anhydrite, rock salt, potash salt, and argillaceous rocks. The ductile behavior of rock salt and the release

of tectonic stress lead to the ascension of the Zechstein formation through the overburden sediments at many locations. More than 200 of the resulting salt structures (salt domes, walls, and pillows) occur in the North German Basin. They accumulate very important mineral resources such as potash and rock salt, and, in traps on the structure flanks, petroleum and natural gas (Henningesen and Katzung, 2002). Rock salt is quasiimpermeable to fluids and gases (e.g. Baumann et al., 1995; BGR, 2007). Within a salt dome, only connate water from its formation during the Zechstein and pore water originating from mineral metamorphosis exist (e.g. the release of up to six water molecules from one carnallite molecule at temperatures exceeding 85°C). Although no moving groundwater is expected within a salt structure, a salt dome affects the regional groundwater flow system. By subrosion, which means the dissolution of salt by groundwater, a freshwater-saltwater system will be established. Consequentially a low permeability cap rock will be formed by the remaining residues (gypsum, anhydrite, clay minerals) at the top of salt domes. At the flanks of the salt dome a quasi-stationary equilibrium will be established. Its high mineralization and the resulting higher density causes very slow groundwater movement. Probably, gravity-driven groundwater flow can cause convection cells (Magri et al., 2009a,b). Anyway, in the overburden sediments highly mineralized groundwater has often been reported even at the surface, caused by groundwater circulation (e.g. Langkutsch et al., 1998). A further attribute of rock salt is its very good thermal conductivity. The combination of the rock salt properties (impermeability, heat conductivity, ductile behavior) lead to the recommendation, even in 1963 (BGR, 2007), of rock salt as the favoured host rock for high level radioactive waste (Röthemeyer, 1991).

2.5.4 Argil/argillaceous rocks

Argil and argillaceous rocks were deposited in many different stratigraphic formations within several sedimentary basins in Germany. The different conditions during sedimentation caused strong variations in thickness, distribution, homogeneity, and formation. The maximum thicknesses of clay formations were reached in great basins (North German Basin; Molasse Basin at the foothills of the Alps). The main clay formations were deposited

during the Jura, the Lower Cretaceous, and the Tertiary ages. The most important formation in northern Germany is the Rupel Clay (Tertiary), mentioned previously, which divides a lower saltwater aquifer from an upper freshwater aquifer in many areas. In southern Germany, the Opalinus Clay (Jura) accumulates an important argillaceous rock formation. Clay or argil will not be extracted by underground mining, but by open pit mining. There are no experiences about the behavior (e.g. mechanical strength, thermal conductivity, etc.) of deep clay formations comparable with the knowledge about salt formations in Germany (Hoth et al., 2007). Because of the impermeable properties of argil formations, they act as an aquitard. They protect an aquifer that is in use for drinking water supply, from groundwater contamination (from the surface) or groundwater salinization (from the underlying layers). At higher levels of diagenesis the sealing properties of clay decline, caused by the appearance of micro-fissures and micro-cracks. Because of the many different formations of argillaceous rocks, a general estimation about its stability at great depths is not possible (BGR, 2007; Czaikowski et al., 2005; Hoth et al., 2007). According to the experiences of the petroleum industry, argillaceous rocks reach their greatest impermeability at depths between 400 and 600m (Hoth et al., 2007). The main groundwater research related to argillaceous rock formations is focused on the aquifer formations surrounding potential host rock clay. In argil and argillaceous rocks, mass transport occurs, which is driven by thermodynamic forces as near-field transport (thermo-osmosis, thermo-diffusion; Horseman and McEwen, 1996). Clay formations can be overpressured or underpressured compared with the surrounding aquifers depending on their geological history of subsidence. This leads to groundwater flowing out of the formation or into the formation and may change the existing flow system (Houben, 2006; Raven et al., 1992). Armstrong et al. (1998) reported on the influence of clay-water ion exchange on the pore-water chemistry of the surrounding aquifers. With increasing depth, the temperature increases, which leads to clay mineral metamorphosis at temperatures higher than 100°C (BGR, 2007). Horseman and McEwen (1996) pointed out that higher temperatures (e.g. by geological sinking or by a high-level radioactive waste repository) may lead to high pore pressures in low permeability rocks. Accordingly, the permeability of argil will be increased by fissures because of shrinkage under increasing temperatures. Mazurek et al. (1998) reported variable transmissivities within

a system of faults. A further important property of clay minerals is their high sorption potential, which is an interesting attribute for the research on all kinds of final repositories (Hoth et al., 2007).

2.6 Selected case studies of deep groundwater research

A collection of six projects in different geological settings is presented, which is an overview of the various objectives and approaches in the field of deep groundwater research. Two of the six case studies are not located in Germany, but in England (UK) and France. These projects were chosen for this review because of their exemplarity with respect to deep groundwater research in their respective geological settings.

2.6.1 Sedimentary basins: the Sellafield Test Site

The Sellafield Test Site is located in north-western England near the Irish Sea (Fig. 2.1b). Starting in 1991, an extensive investigation program was conducted by *NIREX* (originally known as the Nuclear Industry Radioactive Waste Executive) to test the site as a potential final repository of radioactive waste produced by the UK. Therefore, the Sellafield area is a very well analyzed coastal basin (Bath et al., 2006). The geological investigations of the basin included the drilling of 20 deep boreholes, seismic surveys, and airborne geophysical surveys. The basin is filled with Permo-Triassic sedimentary rocks, which are underlain by Ordovician metavolcanic basement (Chaplow, 1996). The sedimentary rocks are mainly composed of sandstones (Sherwood Sandstone Group), which form a locally important aquifer with a thickness up to 500 m. The underlying basement consists of metamorphosed ignimbrite (Borrowdale Volcanic Group), which is a low permeability fractured aquifer (Bath et al., 2003; Chaplow, 1996). Because of their low permeability, the basement rocks were intended as the potential host rock for the UK's final repository (Bath et al., 2006). Therefore, the identification of hydrogeologically significant fractures is crucial in the

fracture-flow-dominated Borrowdale Volcanic Group (Chaplow, 1996). For understanding of the hydraulic behavior of the individual geological and hydrogeological formations, the geometry of all observable fractures on the different outcrops was mapped in detail and fractal concepts were applied. Therefore, for some formations (Mercia Mudstone Group) only a little direct information on the hydraulic properties is available because of the lack of outcrops in the Sellafield area (Michie, 1996). For understanding the flow of deep groundwater between sedimentary and crystalline formations and to derive a conceptual model of the regional hydraulic system, deep boreholes were drilled along profiles several kilometres long and from a maximum depth of 1,950 m (Bath et al., 2006; Black and Brightman, 1996; Metcalfe et al., 2007). Production tests were conducted over the full length of the boreholes. Due to the low flow, the zones of hydrogeologically significant fractures could not be identified by spinner logging, but only by temperature and conductivity logging (Chaplow, 1996). Permeabilities of the overlying Sherwood Sandstone Group were measured, although on core samples measured values are several orders of magnitude less than those obtained during borehole pumping tests, observed as field permeability (Michie, 1996). Using the acquired data about the fracture system from the outcrops and the borehole studies, a discrete fracture network model was established by using *NAPSAC*, the finite-element software package for groundwater flow and transport in fractured rock (Hitchmough et al., 2007). Although the fracture modeling was consistent with the observed variability of heads, the authors emphasized that more than one fracturing concept will be consistent with the observed data (Heathcote et al., 1996). Groundwater samples were taken from the boreholes, which was difficult because of the small permeabilities of the Borrowdale Volcanic Group and because of the influence of the drilling fluid on the groundwater samples. Although groundwater samples were obtained during 163 borehole tests, only 79 samples showed less than 10% contamination by drilling fluid. Even these samples could not be used to measure reliable pH, HCO_3^- , ^{14}C , and ^{13}C values. Especially the weak ^{14}C data made it very difficult to date the groundwater (Bath et al., 2006).

The gained knowledge about the fracture system was combined with the determined hydrogeological parameters and with attributes derived from cross-hole seismic tomography and vertical seismic profiles (Michie, 1996).

Three regimes were defined for the Sellafield Test Site by Black and Brightman (1996) to establish the conceptual hydrogeological model: (1) Coastal Plain Regime (freshwater system, which is topographically driven and related to present day precipitation); (2) Hills and Basement Regime (mixture of freshwater from precipitation and saline groundwater of different origins, which is mainly topographically driven and at depth driven by density variations); and (3) Irish Sea Basin Regime (basin-derived brines, which are driven by basin processes over long periods of time). The groundwater system in the sedimentary cover rocks and basement formations consists of water with different origins, ages and salinities. The oldest groundwater was detected in off-shore sedimentary rocks. It was probably meteorically recharged more than 2 million years ago. The saline water in the basement formation was recharged between 10,000 years and 2 million years ago. The stable oxygen and hydrogen isotopic compositions suggest a dominantly meteoric origin of all water types (Bath et al., 2006). Based on the conceptional hydrogeological model, several numerical models were tested with respect to various features such as porosity and fracture flow, complex geology, anisotropic formations, and the presence of dense solutes from more than one source. A two-dimensional (2D) model was set up (Heathcote et al., 1996) to identify recharge and discharge areas and to constrain the hydraulic conductivity of the sandstone (model features: porous medium, steady-state, 2D-flow, only topography-driven force); the codes used were *MODFLOW* (a modular finite-difference three-dimensional groundwater flow model) and *NAMMU* (a finite-element software package for groundwater flow and transport modeling in porous media). 2D-vertical-section density dependent models were set up (Heathcote et al., 1996; model features: included basement, anisotropy, topography-driven and density-driven flow); the code used was *SUTRA* (a saturated and/or unsaturated, constant or variable-density fluid flow model, for solute or energy transport). By establishing a 3D-model (Heathcote et al., 1996) using simplified geology, the interaction of salinity and geology, and the evolution of pressures and salinities could be demonstrated (model features: horizontal layers, faults represented simply by geometrical displacements in a vertical plane, two water layers of different density); the code used was *SWIFT* (a model to simulate groundwater flow, and heat, brine, and radionuclide transport).

Although the numerical modeling shows good comparability with the observations of salinity and head, certain details remained unexplained (Heathcote et al., 1996). By investigating the paleoclimate, Heathcote and Michie (2004) determined that the Sellafield groundwater system will be affected by major climate changes, particularly by glacial-interglacial cycles (land and sea level changes, erosion, glaciation, and permafrost). The main finding was that the potential repository would be situated in the saline groundwater zone and the flow path from the repository back to the surface environment would be long and directed to the sea (Michie, 1998). Anyway, all investigations were stopped by a political decision concerning the site of Sellafield and its scenic value in 1997. Currently, there is no research for a final repository for radioactive waste in the UK (Bath et al., 2006; Michie, 1998).

2.6.2 Sedimentary basins: geothermal research in the North German Plain

Energy and heat generation with geothermal technologies has had a sustained rise in importance in the last few decades. Geothermal research and application started early in the North German Basin because of the locally very capable geological conditions and the policy of self-sufficiency of the former German Democratic Republic (GDR, i.e. East Germany; Seibt and Kellner, 2003). The geothermal gradient is relatively low in this sedimentary basin. Accordingly, the geothermal research in northern Germany contributes a significant part to the deep groundwater research in Germany. Already in the 1980s, intensive investigations started by testing production and reinjection wells and equipment. In 1984, a geothermal heating plant for heat supply to a residential area was commissioned in Waren (hot water supply from about 1,500 m depth; Fig. 2.1c). Further sites were Neustadt-Glewe (2,200 m depth) and Neubrandenburg (1,150 and 1,250 m depth). All of them were located in the German state of Mecklenburg-Western Pomerania. In the meantime, more sites were investigated and developed successfully in the North German Basin. For example, some German Parliament buildings in Berlin such as the Reichstag and some further new buildings, are supplied with water from about 300 m depth (Seibt and Kellner, 2003). Because of the high salinities of deep groundwater in the North German Basin (Hölting,

1969), it is common to reinject the cooled brine into the aquifer (Frosch et al., 2000; Kühn et al., 2002). The interests of deep groundwater research in the field of geothermal energy supply are related to the prospects of finding widely (lateral) extended productive formations, providing high flow rates, high temperatures, low salinities, and long-term stable production and reinjection rates (Seibt and Kellner, 2003). Adequate sandstones (high effective porosity, high permeability, large net thickness, low accumulated matrix, low diagenetic changes) were found in the North German Basin at depths down to about 3,000 m (Hurter and Schellschmidt, 2003; Seibt and Kellner, 2003).

To generalize, the obtained knowledge from individual projects on geothermal energy, the origin and evolution of the deep groundwater in the North German Basin has to be understood. Naumann (2000) compared deep groundwater samples from five different geothermal boreholes in northern Germany (ranging from 1,250 to 3,250 m depth), as mentioned previously. The results suggest the same origin and evolution of all samples. According to the $\delta D-^{18}O$ ratios, the investigated samples are the mixture of a strong meteoric component with some seawater, which took place ~20 – 50 million years ago in the aquifer (according to the cumulative He-ages). The groundwater of the North German Basin is highly mineralized. The main component is NaCl (up to 200 – 300 g L⁻¹ total dissolved solids). By interpreting the Br-Cl ratios, Naumann (2000) assumed that the high salinity is probably not caused by mixing with seawater but by dissolution of Zechstein salt.

One of the aims of geothermal research is the determination of the permeability of the aquifer. The high salinity of deep groundwater in the North German Basin may cause several dissolution and precipitation reactions in the aquifer during continuous extraction and reinjection. This may have an impact on the hydraulic properties of the geothermal reservoir. Therefore, processes such as solution, dissolution, and cementation are often described with chemical models. Because of the great number of possible mineral reactions during pumping and injection within an aquifer, such models become very complex and simplifications have been postulated, e.g. Kühn et al. (2002) examined the hydrothermal sandstone reservoir of Stralsund at the Baltic Sea (Fig. 2.1c). The target formation (Buntsandstein) is located at depths of about 1,500 m. Since the reinjection of cooled brine into deep aquifers strongly affects the mass and energy flows in the reservoir, Kühn

et al. (2002) modelled the impact on the aquifer by using the subsurface flow and hydrogeothermal simulation system *SHEMAT*. For the modeling it was assumed that only calcite and anhydrite would react in the aquifer. They found that the injection of cooler and accordingly more viscous water leads to a reduction of injectivity of the aquifer. This effect will be reduced by thermally induced mineral reactions (by the dissolution of anhydrite). They refer to the difficulty of estimating changes of permeability during modeling of chemical reaction rates, as the permeability not only depends on the porosity, but also on the structure of the pore space. Accordingly, the understanding of pore space changes caused by thermally induced precipitation and dissolution reactions is crucial for the use of geothermal energy (Kühn et al., 2002).

Frosch et al. (2000) investigated the impact of reinjected cold brine on reservoir parameters of deep aquifers. They suggest that the classical reservoir parameters like porosity and permeability are not adequate for the description of the impact of reinjection on the aquifer. For that, they examined the fluid-solid interface and the tortuosity of migration channels in porous media by using nuclear magnetic resonance (*NMR*) on samples from deep drill cores of the geothermal wells of Neustadt-Glewe, Neubrandenburg, and additionally Rheinsberg (in the German state of Brandenburg). Based on these data, the transport properties of hot and cold fluids in deep aquifers may be better estimated, but laboratory measurements, like those taken during investigations of drill cores by *NMR*, are limited by scale effects. In Hannover, a research group – *GeneSys* - Generierte Geothermischen Energiesysteme (artificially generated geothermal systems) – tested the 'single borehole method' by reinjecting the cooled brine via the annulus in the same borehole into a more shallow permeable rock formation. Simultaneously the overall low permeability of these formations should be enhanced by hydraulic fracturing. A deep circulation system should be established through the extraction of water from one sandstone layer and reinjection into a shallower sandstone layer (Kehrer et al., 2007). Ghergut et al. (2009) conducted a single-well inter-layer flow path tracer test in a 4-km-deep former gas exploration well, located north-east of the city of Hannover (Horstberg site). The exploration well was used for preliminary studies for the *GeneSys* project. The test was conducted between two sandstone layers, which are separated by a few hundred metres of faulted and fractured claystone. By this test, not only the

mean residence time of the injected water as it moves towards the production horizon should be determined, but other important aquifer parameters should be determined such as residence time distribution, flow-storage repartition, and transport-effective fracture densities (Ghergut et al., 2009). However, these parameters could not be determined reliably in that test. Because of the short test duration and very low tracer recoveries, the tracer breakthrough curves could not be extrapolated for longer time periods than the test duration itself (Ghergut et al., 2009).

Another current large-scale research project, involving the utilization of deep groundwater systems for the supply of geothermal energy and heat, is located near Groß Schönebeck (German state of Brandenburg). Helmholtz-Zentrum Potsdam - Deutsches GeoForschungsZentrum (Helmholtz Centre Potsdam - German Research Centre for Geosciences) deepened a former gas exploration well down to about 4,300 m to identify suitable geological structures and to develop new methods to increase the productivity of deep geothermal reservoirs. For that, technologies to enhance the permeability of deep aquifers were tested in the well, which serves now as a geothermal in situ laboratory (Huenges and Bruhn, 2007). Zimmermann et al. (2009) reported on two different technologies tested in the target formations (Upper Rotliegend sandstones and Lower Rotliegend volcanic rocks). They used high viscous gel and proppants to stimulate the sandstone aquifer by hydraulic fracturing. High flow rate hydraulic fracturing (waterfrac) stimulation was done within the low permeability volcanic rocks. For technical reasons the waterfrac experiment had to be conducted over both formations. Accordingly, it was not possible to assign the success of the stimulation to a single formation, because fracturing occurred in both rock types. The efficiency control of such aquifer enhancement technologies is quite challenging. One simple and common method is the comparison of the water-level lowering during pumping with a specific flowrate before and after treatment (Ghergut et al., 2009). According to that test, the production rate could be increased, but is still too low for the profitable generation of geothermal electricity (Reinicke et al., 2005; Zimmermann et al., 2009). The research on geothermal resources provides some of the most important findings about deep groundwater behavior. Additionally it will probably be one of the most important utilizations of these systems in the future.

2.6.3 Metamorphic rocks: the German Continental Deep Drilling Program (*KTB*)

The KTB was a scientific drilling project conducted to study the deeper continental crust. The drilling site is located in Windischeschenbach in northeastern Bavaria, Germany (Fig. 2.1c). This location was chosen for its specific geological properties, which were: (1) its location in an important suture zone; (2) the occurrence of gravitational, magnetic, and electrical anomalies; (3) the presence of specific seismic reflectors (which were linked to fracture zones); and (4) a probably relatively low geothermal gradient. The drilling operations of *KTB-VB* (Vorbohrung; the KTB pilot borehole) started in 1987 and reached about 4,000 m depth. During this pilot phase, which was conducted to determine the technical concept for the main borehole, several important findings were obtained: (1) a higher geothermal gradient than expected; (2) a strong lithological heterogeneity; and (3) significant fluid inflow zones. Afterwards, the *KTB-HB* (Hauptbohrung; the KTB main borehole) was drilled to a depth of about 9,100 m. The operations were completed in 1994 (Emmermann and Lauterjung, 1997). The two boreholes provided samples of fluid inclusions (paleofluids) as well as free fluids in the crystalline basement (Möller et al., 1997). Indeed, hydrochemical sampling showed some limitations caused by the long pumping duration during which the sample water travelled several kilometres up to the surface. This led to oversaturation with respect to calcite, fluorite, chalcedony, and quartz of the sampled fluid (Stober and Bucher, 2005). This effect is mainly caused by the strong decrease of fluid temperature during pumping from 119°C down to 11°C at the surface (Lodemann et al., 1998). A further consequence of the long pumping time is diffusive degassing during uplift and accordingly undersaturation and elemental fractionation of noble gases (Lippmann et al., 2005). Möller et al. (1997) reported problems with hydrochemical analysis and interpretation of the samples obtained during a 4-month pumping test in the KTB-VB just after finishing the drilling operations. The borehole had to be stabilized and the used drilling mud, including several organic additives, contaminated the surrounding pore- and fissure water and affected the chemical and isotopic results. Even at the end of the pumping test for determination of several elements and gases, the samples were slightly contaminated with the organic additives. Additionally, heavy metals from

abrasion of the drilling equipment were found. The rare earth analysis was affected by the enforced release of these elements during drilling, which altered the rock and mineral surfaces. The concentration of rare earth elements in the drilling fluid further increased during the drilling operations, because of recycling of the fluid (Möller et al., 1997). Möller et al. (2005) reported of a 1-year pumping test on the KTB-VB between 3,850 and 4,000 m depth, which was conducted between 2002 and 2003. Lippmann et al. (2005) measured the concentrations of H₂, O₂, Cl₂, N₂, CH₄, and noble gases during this test. All gas concentrations and isotopic signatures, except those of ²²²Rn, remained constant during the 12 month of pumping. These data and the large fluid flow rates suggest a homogeneous and large fluid reservoir in that depth. Lippmann et al. (2005) conclude that the findings of the 1-year pumping test are more reliable compared to the 4-month test because of the much lower level of contamination by drilling mud. Stober and Bucher (2007) reported hydraulic conductivities (K) of about 10⁻⁸ m s⁻¹ resulting from the long-time pumping test in the KTB-VB. They conclude possible Darcy flow mechanisms even at great depths, which may provide advective fluid and heat transport. The isotopic and hydrochemical fingerprint suggests that the pumped water is a mixture of ascending basement brine and descending very old meteoric water. Hydraulic tests revealed a communicating system of fractures. Möller et al. (1997) and Rybach (1997) concluded that in deep-laying aquifers, slow but extensive movement of crustal fluids appears. From the findings of the long-time pumping test in the KTB-VB, Stober and Bucher (2005) summarised that the water-saturated fracture pore space of the brittle upper crust is highly connected. This leads to their conclusion that the continental upper crust is an aquifer. Despite all the technical limitations, the KTB project showed at least that Ca-Na-Cl brines associated with gases (N₂, CH₄) occur in open fracture systems at depths below 5.5 km (Lodemann et al., 1998). This is, from the view of a hydrogeologist, a crucial finding.

2.6.4 Rock salt: the Gorleben Test Site

The Gorleben Test Site (Fig. 2.1c) is located in the northeast of the German state of Lower Saxony, near the River Elbe. The test site will be investigated for its suitability as the German final repository for all kinds of radioactive

waste. These investigations are based on the recommendation for salt as the best host rock for final repository by the BGR in 1963 (Röthemeyer, 1991). Gorleben was chosen because of its location within a sparsely populated area near the border to the former GDR. Starting in 1979, the Gorleben salt dome was investigated with a geological and hydrogeological exploration program (Klinge et al., 2002). The aim of this program was the description of the regional groundwater flow system and the estimation of the prospective evolution of this system, considering a potential use as a repository. The investigation of the groundwater flow system was conducted between 1979 and 1999 and included (Klinge et al., 2007): the construction of a monitoring network (maximum depth about 450 m), long time running pumping tests, pedological field mapping (for the estimation of percolation rates), geothermal investigations (to indicate the groundwater movement by temperature anomalies), analysis of isotopes and noble gases (to estimate the groundwater age and residence time), and numerical modeling (2D with variable density, 3D with constant density). It is accepted that in a compact salt structure, like a salt dome, no groundwater moves. Therefore, the main focus of hydrogeological research on salt domes is the groundwater flow system at the periphery of the structure. In Gorleben, the most important structure for groundwater flow is the Gorleben Channel (Gorlebener Rinne). This was caused by partial glacial erosion of the Tertiary Rupel Clay and the protecting cap rock, which lead to a hydraulic window (Klinge et al., 2002). Accordingly, fresh groundwater from the upper aquifer is in contact with brines from the dome. A freshwater-saltwater system was established, which leads to slow subsidence of the salt dome by the solution of salt. Röthemeyer (1991) reported a subsidence rate of about 0.025 to 0.062 mm per year. For a better understanding of the groundwater flow system, including the freshwater-saltwater effects and the dimension of subsidence, numeric modeling was conducted. Because of the limited technical capabilities of numerical models at that time, the design of the compiled 3D-model (*GS4000*, a program code developed by the BGR to simulate 3D groundwater movement in constant-density porous media) could not take the density-dependent flow into account in the late 1980s (Klinge et al., 2007). The area northwards of the River Elbe was strongly simplified in the model because of the lack of data during the compilation of the model (this area was part of the former GDR until 1990). Bearing in mind these limitations of the numeric 3D-model, an average groundwater

velocity from the salt dome surface to the biosphere of some thousands up to 17,000 years was calculated. As the density difference between the saltwater and the freshwater zone affects the groundwater flow, a 2D-model (*SUTRA*) considering variable density was also conducted. The 2D model was started with simple and idealized geometries and parameters. Step by step, more heterogeneities were introduced leading to a more complex model (Klinge et al., 2007; Schelkes et al., 2001). Several models were constructed with different initial conditions to find a salinity distribution comparable to present day conditions. During these simulations, it became clear that steady-state conditions will not be reached but that the past density distribution (e.g. during ice ages) still affects the groundwater system today (Schelkes et al., 2001). Most input parameters for the model were derived by laboratory experiments on rock samples (porosity, permeability, adsorption capacity, and diffusion data). The hydraulic conductivity was estimated with various empirical approaches, which use the grainsize distribution. Field permeabilities, storativity values, and leakage coefficients were determined with single-well pumping tests ("*local scale*") and long-term pumping tests ("*regional permeabilities*"). The long-term pumping tests were used for identification of potential hydraulic connections between different aquifers in the sedimentary cover of the salt dome (Schelkes et al., 1998). Although no connection could be identified, Schelkes et al. (1998) emphasized that this result is no proof for the complete hydraulic isolation of the lower aquifer in terms of contaminant transport over very long periods. Caused by the limited capability of the density dependent 2D-model at that time the findings show some uncertainties. It seems that the groundwater velocity was overestimated by ignoring the density differences in the 3D-model (Klinge et al., 2007). For characterization of the groundwater system the hydrochemistry was investigated. Since the saline water originated from dissolution of the Zechstein rock salt, there are only a few variations in the saline water composition, which limits the significance of chemical and trace element analysis (Schelkes et al., 1998).

In 2000, all research activities in Gorleben were stopped by a decreed moratorium by the government, which caused stagnancy in several investigation projects. As the moratorium ended in October 2010, it has to be decided which research projects, like the numerical modeling project, have to be updated or started again.

2.6.5 Rock salt: the final repository for radioactive waste at Morsleben (*ERAM*)

ERAM (Endlager für Radioaktive Abfälle Morsleben; see Fig. 2.1c) is located in the western part of the German state of Saxony-Anhalt as a part of the Allertal salt structure. It was the first regular operating deep geological final repository for radioactive waste worldwide. ERAM also will probably be the first repository worldwide that will be regularly closed and sealed after its working phase. Morsleben was a former commercial salt mine, which was established about the year 1900 (Shaft Bartensleben and Shaft Marie). In 1970, Morsleben was chosen from 10 ancient salt mines by the government of the former GDR as the national final repository for radioactive waste. After the reunion of Germany in 1990, the low and medium radioactive waste of the Federal Republic of Germany (FRG) was stored at Morsleben. Between 1971 and 1998 a total of about 37,000 m³ of low and medium radioactive waste was stored in ERAM (BfS, 2009).

The storage of radioactive waste was stopped for legal reasons in 1998. After that, in 1999, the operator of ERAM, the Bundesamt für Strahlenschutz (Federal Office for Radiation Protection; *BfS*), resigned the further use of ERAM (Brasser and Droste, 2008). Due to the natural convergence of salt by rock pressure, selected parts of the mine will be filled by a mixture of salt and cement. By this procedure, the mine layout should be stabilized until the administrative permission for decommissioning is granted. For the final closing, the total deposit area and the shafts will be filled with the salt-cement mixture and sealed. All buildings and constructions above ground will be removed (BfS, 2009). It is assumed that the closing phase will take ~10 – 15 years after the final decommissioning permission has been granted. As part of the administrative procedure for obtaining the permission for decommissioning of a final repository (including licensing procedure, environmental impact assessments, public participation, etc.) the BfS, as the operator, has to prove its long-term safety for the biosphere. For that, an extensive research program was undertaken.

As rock salt is impermeable to water and gas, no groundwater motion within the salt structure is expected at Morsleben. Therefore, the main interest of hydrogeological research at Morsleben is the groundwater flow system

at the periphery of the salt structure. Accordingly, the research program focused on the description and quantification of the regional-scale groundwater flow system around the salt dome. For that, a conceptual regional groundwater model was developed, which was used as the base for numeric modeling of groundwater flow and potential dispersion of radionuclides in the cap rock of the repository. To estimate the model parameters, an extensive hydrogeological research program was conducted. It included several geophysical surveys (e.g. seismic reflection and high-resolution seismic methods). For the estimation of the hydraulic system parameters, pumping tests and core analyses were conducted, along with slug and pulse tests (rapid increasing of the water level and observation of its decline). These tests are relatively cheap, fast, and no water is pumped (which has to be disposed of). As a result, the transmissivity for the whole test interval (varied between 10 – 150 m within the borehole) is obtained. The resulting permeability (transmissivity divided by length of test interval) represents a mean value and may be of no relevance if the main groundwater flow contribution is from single fractures or fracture zones (Langkutsch et al., 1998). The identification of hydraulically relevant fissures was conducted by fluid logging. The drilling fluid was replaced by fresh water and the water level was decreased by pumping. The low hydraulic conductivity of many investigated formations leads to an often underestimated fracture flow, especially if the water level drop is too small to stimulate flow in the very small fractures (Langkutsch et al., 1998).

A campaign for the estimation of groundwater movement in single boreholes (groundwater monitoring wells) was conducted (radiohydrometric single-borehole method using a radioactive tracer for tracking the groundwater flow direction and velocity in single boreholes; Delakowitz, 1996). In these tests, a radioactive substance (^{83}Br) was injected and mixed into packered test intervals of 50 cm within selected groundwater monitoring wells. The decline of the concentration and the direction of the radioactive tracer movement can be measured and was used for estimation of groundwater flow velocity and direction (Langkutsch et al., 1998). A low detection limit ($<0.005 \text{ m day}^{-1}$) was achieved, and explained (Delakowitz, 1996) by the impact of molecular diffusion on mass transport at lower groundwater flow velocities. This method, as with all passive single-borehole methods, overestimates the hydraulic parameters (velocity and hydraulic conductivity) of the

aquifer. The very high hydraulic conductivity of the borehole compared to the hydraulic conductivity of the aquifer forces the naturally parallel groundwater flowlines towards the well. Accordingly, the velocities obtained by this method overestimate the natural groundwater flow velocities (Delakowitz, 1996).

The high-density differences in the groundwater system of Morsleben are relevant for its hydraulic behavior. Therefore, analysis of the hydrochemical and isotopic parameters in groundwater and pore-water samples from drilling cores was conducted; this aided the determination of salinity, description of the groundwater genesis, dating by noble gases analysis, and estimation of the mass transfer. Since the acquisition of enough groundwater for noble gas analysis was not possible in most of the boreholes because of the very low hydraulic conductivities of some Keuper claystones, Osenbrück et al. (1998) used porewater extracted from freshly drilled rock cores.

In building the model for ERAM, the groundwater recharge was estimated by comparison of several common calculation methods; also, a pedological field mapping campaign was undertaken, the surface run-off was determined for estimation of the water balance, and the surface-water quality was monitored to draw salinity and salt load balances (Langkutsch et al., 1998). With these observed data and estimations, a model (incorporating hydrogeological knowledge of 1997) was conducted in 3D (freshwater conditions) and in 2D-vertical (cross-section with variable density; Langkutsch et al., 1998). In regions of the modeled area of Morsleben where the model did not fit the measurements (water levels in observation wells) or showed unrealistic high or low values (drawdown in production wells), the initial parameters (recharge, hydraulic conductivities) were adjusted. Thus, the mean deviation between the water levels of the model and those observed in the wells, which represents the mean error of the model, could be reduced from 2.95 to 1.77 m (Klemenz et al., 2001).

2.6.6 Argillaceous rocks: the Bure Test Site (France)

The Bure Test Site (Fig. 2.1c) is located within the Parisian Basin, on the border of the districts Meuse and Haute-Marne in north-eastern France. The test site will not be used as a final repository, but only as an underground

research laboratory (*URL*) for Agence Nationale pour la Gestion des Déchets Radioactifs (The National Radioactive Waste Management Agency; *ANDRA*, 2007). The layout of the facility is designed in accordance with French government policy, which requires a reversible final repository for at least 100 – 300 years. Thus, future generations should be able to modify the procedure for the repository closure (*ANDRA*, 2006a, 2009).

One of the most important required criteria for deep geological repositories is the proof of no groundwater circulation within the repository (*ANDRA*, 2007). The host rock of the *URL* is the Callovo-Oxfordian clay, which is surrounded by two aquifers: the Oxfordian limestone on top and the Dogger limestone below (Teles et al., 2007). The marine clay of the Callovo-Oxfordian formation was deposited about 155 million years ago, has a thickness of about 130 m, is regular in shape, provides a remarkable horizontal homogeneity, and shows a very low permeability of about 10^{-6} m a^{-1} . There is only slow and very slight water circulation within the surrounding formations (*ANDRA*, 2007). To exclude the potential of later conflict of interests, a 2,000 m deep borehole was drilled in 2008. By the determined geothermal gradient (66°C in 2,000 m) and its low productivity, a potential future use of the regional aquifers as a geothermal resource could be excluded (*ANDRA*, 2006a). Its permeability is the fundamental physical property of the investigated host rock formation of interest. The groundwater research of *ANDRA* is focused on the behavior of pore water and the permeability of the host rock under overburden pressure. The sorption and retention behavior of the clay is another of the main research interests at the Bure Test Site.

The investigations at Bure started in 1999 with a 3D-seismic survey over 4 km². Afterwards (between 2000 and 2004), scientific drilling programs over an area of about 2,000 km² were conducted to characterize the regional geology, the hydrogeology and the structural features of the Callovo-Oxfordian argillites and of the Dogger limestones (Rebours et al., 2006). During the specific hydrogeological drilling program (2003 and 2004), nine deep boreholes (down to a maximum depth of about 920 m) were constructed (Delay, 2006). The hydraulic data related to the argillite were determined by short-term hydraulic packer tests (24 – 72 h at about 10 regular intervals) and long-term monitoring of formation pressures by electromagnetic pressure gauge (*EPG*; Distinguin and Lavanchy, 2007). For the long-term investigations, about

130 boreholes were equipped with sensors, which record deformation by overburden pressure and the pore-water pressures. The pressure equivalent to a 400-m water column in the overburden limestone and marly rock leads to a strong compaction of the Callovo-Oxfordian argillite and the reduction of its porosity. Because of the lower quantity of contained water in the clay, its mechanical strength is enhanced, compared with argillaceous rock found at the ground surface. The displacement of the walls of a repository structure would amount to less than a few centimetres after 1,000 years (ANDRA, 2006b, 2007). The Callovo-Oxfordian formation is overpressured, which can be explained in part by osmotic processes (Gueutin et al., 2007). The stability of the host rock during the excavation of the test site facilities (shaft and drifts) and the according change of the stress field distribution (causing micro-cracking and alteration of the mechanical and hydraulic properties of the host rock) were investigated and modelled (Fabian et al., 2007). The behavior of hydromechanical stability of argillaceous rock during dissolution, which increases the porosity, was investigated (Haxaire and Djeran-Maigre, 2009).

An important transport mechanism of contaminants in argillaceous rocks is mass transfer by diffusion in addition to transport in fractures. Therefore, the main focus of the geochemistry research program at the Bure site is on the behavior of the interstitial fluids and on the diffusion and retention capabilities of the radionuclides. For determination of diffusion of radionuclides in clay, Cormenzana et al. (2008) conducted laboratory studies on samples from boreholes drilled vertically through the clay bedding. The tracers (tritium and ^{85}Sr) were injected into the center of the cylindrical core sample. After a certain time, the core was sampled by drilling small bores in three concentric circles around the center. The so obtained small cores were cut in slices, which were then analyzed for the tracers. By this procedure, the 3D distribution of the tracers could be investigated. By the orthogonal bedding of the cores in these studies, the modeling of transport was simplified. In addition to the scale-dependent uncertainties of laboratory observations, which should deliver conclusions on the field scale, it cannot be ruled out that the used samples were disturbed by the core drilling. Drilling may produce artificial fissures within the argillaceous rock and may affect the observed mass transport. To exclude these uncertainties, several in-situ diffusion experiments

were conducted (Appelo et al., 2008; Samper et al., 2008). The changes of solute concentration within a borehole by reactions and transport between porewater and borehole solution were monitored for 1 year and modeled with the program *PHREEQC* (used for modeling geochemical reactions and aqueous equilibria; Appelo et al., 2008). By this approach, the in-situ porewater composition can be determined without subsampling from rock samples, which affects the quality of the data with many uncertainties (contact with air, loss of CO_2 , change of chemistry by leaching with pure water, and sequential compositional changes during squeezing or centrifuging). Because the equilibrium in the borehole was not reached after 1 year, the authors intended to verify the model-porewater concentrations after some 3 – 4 years (Appelo et al., 2008).

Samper et al. (2008) pointed out that interpretation of results from in-situ borehole studies was very complicated because of various non-ideal effects. They tried to estimate the influence of these effects on the observed diffusion. It was found that the filter, the gap between filter and borehole wall, and the by the excavation disturbed rock significantly affect diffusion processes between aquifer and borehole and therefore have to be taken into account for interpretation of in-situ borehole studies. In general, for all borehole tests for in-situ determination of parameters (permeability, diffusion) in argillaceous formations, the very long periods (months to years) for re-equilibration of the system, after the disturbances induced by drilling and testing, have to be taken into account (Distinguin and Lavanchy, 2007). Though diffusion is probably the most important transport mechanism at the Bure test site, Beaucaire et al. (2008) showed at another site (Tournemire, France) that fracture-related relatively fast groundwater-flow velocities in argillaceous rock are also relevant. Beaucaire et al. (2008) also reported on chemical alterations of fluids in boreholes at that site. Since the boreholes were drilled at Tournemire, reduction of SO_4^{2-} and oxidation of dissolved organic carbon have changed the isotopic composition of the fluids within the surrounding aquifers and influenced the ^{14}C groundwater ages. For proof of safety, the impact of the repository on man and the environment was evaluated for the following 1 million years. The probable future development of the land surface was estimated by topographic analysis of the past 2 million years in the region. In those scenarios, the Callovo-Oxfordian clay formation plays a major role

for immobilizing, delaying, and limiting the migration of the radionuclides. Currently, the regional groundwater flow system is from the recharge areas in the south and east of the Bure Test Site towards the centre of the Parisian Basin. The general flow direction is expected to undergo relatively few changes. However, the repository disturbs the natural hydraulic equilibrium within the Callovo-Oxfordian. It will need about 100,000 to 200,000 years to establish a new equilibrium (ANDRA, 2006b). Some river valleys will reach the Oxfordian limestone aquifer during that time by erosion. This will probably cause changes in the upper aquifer, but will not strongly impact the host rock during the next million years (Teles et al., 2007). The prospective investigation program (until 2015) includes pore-water characterization, the study of hydrothermal coupled phenomena, and further research on diffusion. This is required for quantifying the safety margins during the modeling of flow-migration of water-gas systems and of reactive migration in a desaturated environment more precisely (Delay, 2006).

2.7 Conclusions

Deep groundwater research was underrepresented in the hydrogeological sciences for a long time and accordingly little is known about its behavior. Recently, deep groundwater is not only defined by its depth, but by its genesis, age, chemical composition, etc. (Einsele et al., 1983). It is now widely accepted that deeper aquifers are dynamic systems, which are influenced by both surface processes (from the meteoric cycle) and crustal processes (from the lithosphere). The aim of recent research projects is to present integrated concepts about the past and the future evolution of deep groundwater systems. Questions as to the transport behavior of deep groundwater and the physical laws of its movement have not been answered so far. This is caused by the lack of interest of the research community in the past, and by the difficult and expensive access to deep aquifers. As shown in the selected case studies, the aims of deep groundwater research studies are fundamentally different from shallower “conventional” projects. Depending on the specific questions, research is directed to aquifers that contain large amounts of hot water, or formations with as little groundwater movement as

possible. Deep groundwater research is often challenging: high demands on the technical equipment, highly saline fluids, low permeabilities and low sample volumes. Many well-established methods for hydraulic characterization are not or hardly applicable because of the generally small number of monitoring wells (e.g. tracer tests), slow groundwater velocities (e.g. fluid logging), and low hydraulic conductivities, often combined with local zones of high conductivities from fissures. Some single-well methods for estimation of groundwater flow velocity have been established in the last few years using the dilution characteristics. They promise advances in determination of groundwater velocity and even flow direction. However, these methods may overestimate velocities due to the impact of the borehole on the flow field. Hydrochemical and isotopic characterization of the fluids is often technically limited because of contamination with drilling mud (which is necessary during excavation of boreholes), and very long duration of pumping until the samples are delivered hundreds of meters to some kilometres up to the ground surface (causing degassing, change of temperature, and accordingly change of chemical equilibriums). It seems that, at least in some settings (e.g. argillaceous rocks), the boreholes themselves affect the chemical characteristics of the fluids within the formation. Another difficulty for most in-situ tests is that processes for reaching equilibrium are very slow at those depths (caused by the low flow velocities). Accordingly, often chemical equilibrium is not reached between drilling and testing or sampling. Additionally, the tests often cannot be conducted before the aquifer reached equilibrium again (which may take years). Although numerical modeling became a fully developed state-of-the-art technology for all kinds of shallow-groundwater projects in the last decade, this method is difficult to apply to deep groundwater systems because of the lack of data and the uncertainties of parameter estimation.

Altogether, both the heterogeneity of the deeper subsurface and the differing goals of research projects lead to very different strategies and methods. The search for final repositories, development of deep geothermal energy techniques, or storage of CO₂ are the driving forces for development of methods for deep groundwater research and therefore for a better understanding of these systems.

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3 Performance of single-well push-pull tracer tests to characterize transport processes: a case study in a sedimentary coastal basin

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3.1 Abstract

The groundwater system in the area of Horonobe (island of Hokkaido, Japan) is a deep coastal basin, which is composed of heterogeneous porous sediments (Upper Sarabetsu aquifer). The aim of the project was to investigate the impact of a dynamic saltwater-freshwater interface on the aquifer, induced e.g. by sea level fluctuations, change of groundwater recharge, or the operation of man-made aquifer storage and recovery systems. Comparable to many deeper settings, access to the Upper Sarabetsu aquifer is bound to single-well settings. Hydraulic and hydrochemical characterization in single-well settings is challenging, because many well established test methods require more than one access point to the aquifer. Therefore, single-well tracer injection-withdrawal ("*push-pull*") tests were conducted. First, a solution with a significant higher mineralization ($EC = 3,800 \mu S/cm$, *brackish water test*) compared to the original groundwater composition ($EC = 1,080 \mu S/cm$) was injected and recovered. In the second push-pull test, the aquifer was flushed by water containing a significant lower mineralization ($EC = 25 \mu S/cm$, *deionized water test*) than the natural groundwater at that site. An additional aim was to evaluate the performance of the push-pull method for groundwater transport and aquifer characterization (e.g. ion exchange or sorption capacity, redox conditions, hydraulic properties). The injection of brackish water leads to the expected conservative mixing with the origin groundwater. The mass balance reveal complete recovery of the dissolved species. Curve fitting of the conservative breakthrough curve lead to a low effective porosity of ~5%. Compared to the first experiment, the deionized water showed a significant different behavior. The injection of very low mineralized water caused complex reactions within the aquifer, which could be identified as ion exchange, dissolution of some species, redox, and sorption-desorption reactions. Curve fitting reveal in a very low effective porosity. However, while clay swelling may be affect the effective porosity during the experiment, other results show that clay dispersion can be excluded as a major process.

Keywords

Groundwater characterization · porous aquifer · saltwater-freshwater interface · field study · Japan

3.2 Introduction

Japan, as well as many other industrialized countries, faces various challenges such as the safe disposal of radioactive waste, longtime storage of CO₂, and the use of groundwater as potential source for drinking water supply. Particularly in Japan, but also in many other Asian countries, coastal basins consisting of unconsolidated Quaternary deposits are major aquifers and important settlement areas. The knowledge and the understanding of the history and the evolution of these systems, including the groundwater flow and solute transport behavior, are crucial. Groundwater systems in coastal areas are characterized by some special features such as saltwater-freshwater interfaces and significant discharge zones of groundwater into the sea. Therefore, examples for research questions regarding coastal sedimentary basins are, e.g. groundwater flow behavior related to the saltwater-freshwater interface, the evolution of the interface depending on different sea levels or changing groundwater recharge, mass transport properties depending on different mineralization and density, and hydrochemical or hydraulic reactions caused by the intrusion of high or low mineralized fluids into the aquifer.

The aim of this study was to gain hydrogeological information about the groundwater system of the coastal sedimentary basin of Horonobe (Hokkaido, Japan). The Sarabetsu aquifer reaches down to more than 1,200 m depth below ground level (bgl). Access is provided via three groundwater monitoring wells and boreholes (100 m, 160 m, and 1,200 m depth). For groundwater research in shallow aquifers a wide range of fully developed techniques are available for aquifer characterization and estimation of transport behavior (e.g. pumping tests, slug-and-bail tests, tracer tests, etc.). For the investigation of the deeper underground these methods are generally more difficult and costly due to limited access, often low hydraulic conductivities and the resulting slow groundwater flow, which would result in very long travel times

during application of well-established test methods using a tracer input and several monitoring wells (Hebig et al., 2012). Considering this, we applied the presented single-well push-pull test method, which may be a potential alternative to gain information about such aquifers. Therefore, one aim was to obtain information about chemical and hydraulic properties of the aquifer.

Two single-well push-pull tests were conducted in the 100 m deep well (DD-2). The aims of these experiments were:

- a) to gain information about hydrochemical and hydraulic properties of the specific groundwater system of the Sarabetsu formation in Horonobe.
- b) to test the response of the system on different intruding fluids, and
- c) to test the setup and the (technical) applicability of the push-pull method in deeper aquifers.

3.3 Push-pull tracer tests

The push-pull method was developed initially for the estimation of the residual oil saturation within reservoirs (Tomich et al., 1973). In hydrogeology, the push-pull method is often used to proof and to quantify organic pollutants at contaminated sites, in situ determination of microbial activity, transformation and degradation rates, denitrification rates, and simulation of large recharge events in shallow (<20 meters depth) wells by partitioning push-pull tests (e.g. Addy et al., 2002; Cunningham et al., 2001; Haggerty et al., 1998; Istok et al., 1997; Kleikemper et al., 2002; McGuire et al., 2002). For that, a known amount of different solutes including a conservative tracer is injected into the aquifer (“*push*”) and afterwards extracted (“*pull*”) by pumping. After a specific reaction time, the tracer, the remaining reactant, and the reaction product are recovered. The gained breakthrough curves (*BTCs*) during the pumping back phase can be analyzed for transport and reaction parameters. The shape of the *BTCs* and the mass recoveries of the solutes can be used as indicators for their chemical reactions, such as sorption, degradation, ion exchange, or precipitation-dissolution reactions within the aquifer. Reactive solutes commonly reported are nitrate (Azizian et al., 2005; Istok et al., 1997), 1-hexanol, 1-heptanol, 2-ethyl-1-hexanol (Istok et al., 2002), linear

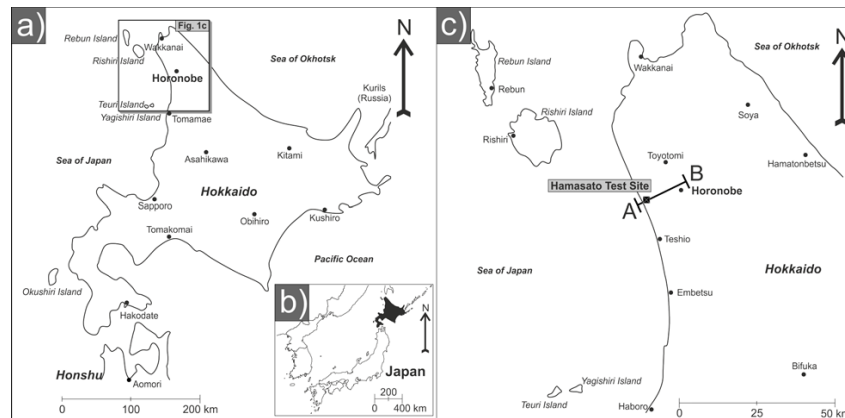


Figure 3.1: Location of the Hamasato test site on the north-western part of the Japanese main island of Hokkaido (a), Japan (b). The test site is located within the municipality of Horonobe (c). The distance to the shoreline of the Sea of Japan is approx. 250 m. The cross section of Fig. 3.2 is marked with AB.

alkylbenzene sulfonate (Istok et al., 1999), sulfate, $H_{2,gas}$, CO_3^{2-} (Istok et al., 1997), propane gas, ethylene gas, propylene gas, $O_{2,gas}$ (Kim et al., 2004), and ^{85}Sr (Schroth et al., 2001). Additionally, physical parameters like the fluid temperature (Vandenbohede et al., 2009) can be used as a reactive tracer. Conservative tracers reported in literature are bromide (Addy et al., 2002; Azizian et al., 2005; Davis et al., 2002; Hall et al., 1991; Istok et al., 1999; Kim et al., 2004; Vandenbohede et al., 2009), 2-butanol (Istok et al., 2002), chloride (Kim et al., 2004), and iodide (Meigs and Beauheim, 2001; Schroth et al., 2001). A more exotic tracer is radon, which is produced in-situ within the aquifer during the reaction time between push- and pull-phases (Davis et al., 2002).

Several research groups adapted the push-pull method to estimate transport parameters. Novakowski et al. (1998) estimated the velocity, dispersivity, and matrix porosity by manually fitting the BTC with a numerical model. The BTC was obtained from a test in a discrete horizontal fracture. Guven et al. (1985), Molz et al. (1985), Pickens and Grisak (1981a,b), and Pickens et al. (1981) were able to determine the dispersion from push-pull tests and even the depth dependent dispersion in a stratified aquifer. However, for this approach additional observation wells in the surrounding of the injection-withdrawal well were needed. Push-pull tests were also reported as appropriate method to estimate regional advective groundwater flow velocities in porous materials (Leap and Kaplan, 1988). Riemann et al. (2002) used

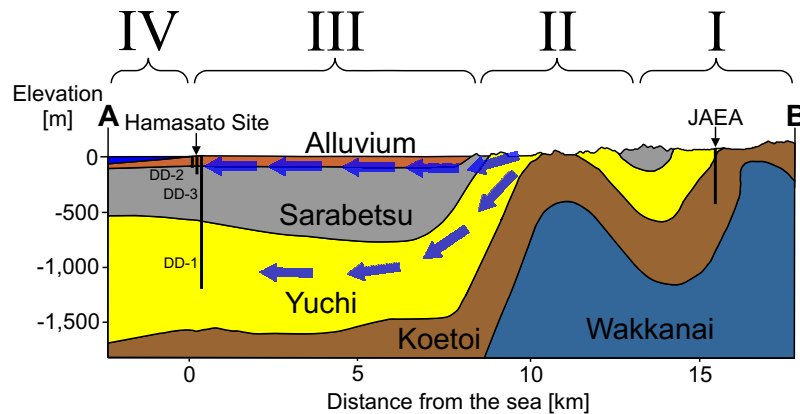


Figure 3.2: Schematic cross section (A – B in Fig. 3.1c) of the coastal basin of Horonobe. The blue arrows represent the regional groundwater flow model. “JAEA” represents the location of the Underground Research Laboratory Horonobe, which is operated by the Japan Atomic Energy Agency (JAEA). I – Teshio Mountains; II – Horonobe Anticline (groundwater recharge area); III – The wetlands of the Rishiri-Rebun-Sarobetsu National Park (groundwater discharge area); IV – Sea of Japan (groundwater discharge area). Modified after H-Rise Institute Horonobe, oral presentation, September 29, 2010

the Leap and Kaplan (1988) method and combined it with a point dilution test to estimate the groundwater flow velocity in a fractured aquifer. Hall et al. (1991) enhanced the method to determine the effective porosity. However, for most of these approaches at least one additional observation well is required.

Only few experiences for the application of push-pull tests in deeper aquifers were reported, so far. In Belgium, Vandenbohede et al. (2008) used the push-pull method for estimation of the suitability of the about 150 m deep Tienen Formation as an aquifer storage and recovery (ASR) system for potable water. By injection of freshwater into the brackish aquifer and analysis of the BTCs of the pull-phase for mixing, cation exchange, and oxidation-reduction reactions, conclusions about the influence of the origin brackish groundwater on the quality of the stored and afterwards recovered freshwater could be drawn. Radloff et al. (2011) injected arsenic-bearing groundwater into a well screened at 60 m depth within the arsenic-free brown sand aquifer in central Bangladesh. In this experiment the pull-phase was conducted stepwise. By analysis of the BTCs the adsorption of arsenic within the brown sands could be estimated. In this way, the risk of arsenic

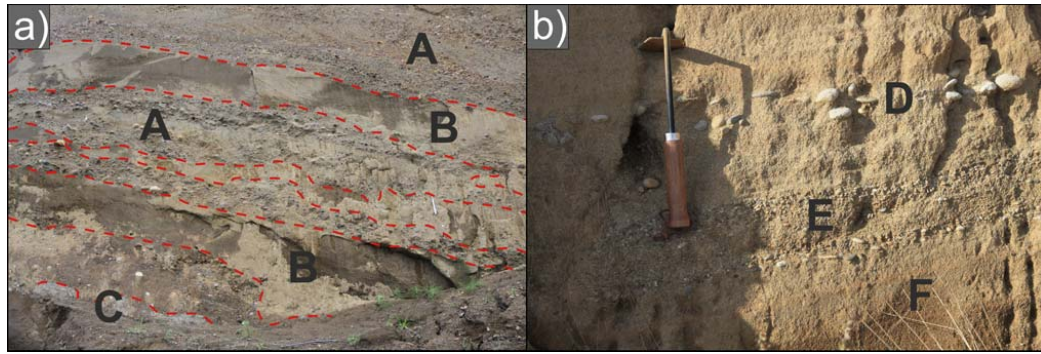


Figure 3.3: Sarabetsu Formation built up by poorly compacted quaternary alluvial deposits with interbedded strata from channeling. (a) A: Coarse sand and fine gravel channels; B: Fine sand matrix; C: Clay lens; (b) D: Fluvial pebble gravel; E: Coarse and fine gravel channels; F: Fine sand matrix. Both outcrops are located near the city of Horonobe.

breakthrough from the shallower contaminated aquifer into the deeper brown sand aquifer, induced by deep pumping (150 – 200 m) could be assessed.

3.4 Study area

The *Hamasato test site* is part of the municipality of Horonobe, at the north-western coast of the northern Japanese main island of Hokkaido (Fig. 3.1a – c). Horonobe is located within a sedimentary coastal basin, which is composed of poorly compacted Neozoic sand-, silt- and mudrocks. The central plain consists mainly of the wetland Rishiri-Rebun-Sarobetsu National Park and partly of farmland (livestock farming). Next to the shoreline are dunes.

At the test site there are three boreholes: DD-1 (1,200 m depth), DD-2 (100 m depth), and DD-3 (160 m depth). The distance to the shoreline of the Sea of Japan is approx. 250 meters (Fig. 3.1c, Fig. 3.2). The push-pull test was conducted in DD-2, a 2" (5.08 cm) well, screened between 90.7 to 99.7 meters bgl within the Sarabetsu Formation. The Sarabetsu Formation consists of poorly compacted quaternary alluvial deposits with interbedded strata by channeling of coarse sand and fine gravel channels, fine sand matrix, and clay lenses (Fig. 3.3). In the uppermost part of the Sarabetsu Formation, which is screened by DD-2, the main aquifer is composed of sand and gravel. The aquifer is located between 91.4 and 99.0 m bgl. At the top

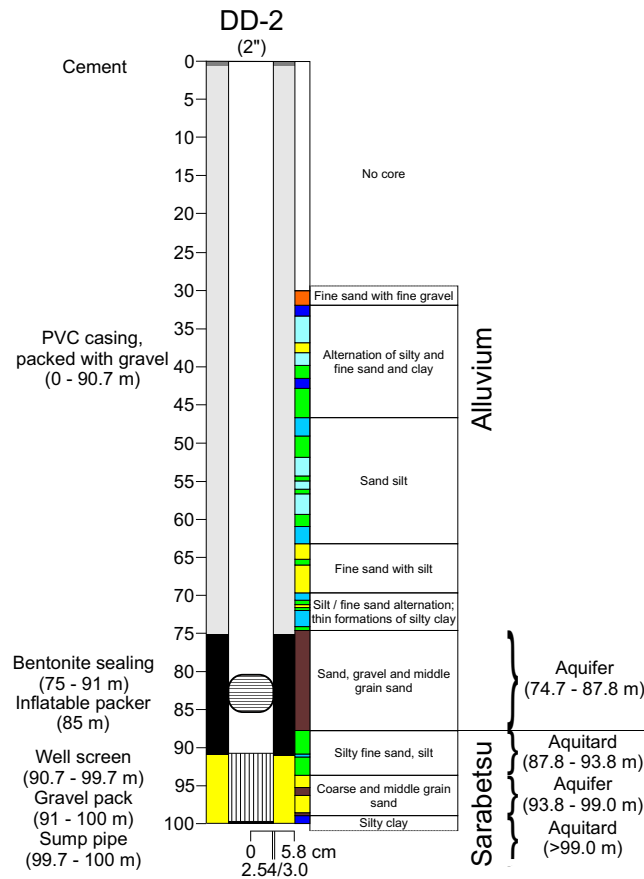


Figure 3.4: Profile of the upper Sarabetsu aquifer in the area of the well screen of DD-2.

the aquifer is bordered by an alternation of silt and clay, and at the bottom by silty clay (Fig. 3.4). More detailed information about the Sarabetsu coastal aquifer system at Horonobe is given by Ikawa et al. (2014).

3.5 Experimental methods

3.5.1 Test fluids

The aim of the push-pull test in DD 2 (100 m depth) was the hydraulic and chemical characterization of the Sarabetsu Formation (Fig. 3.3). The research focus in the coastal basin of Horonobe is to locate the saltwater-freshwater interface (including related hydraulic and chemical interactions)

and to study the mass transport related to that interface. Therefore, two tests were conducted: a *brackish water* and a *deionized water* test.

In the brackish water test, a fluid including several dissolved ions with different sorption properties and the dye tracer uranine (Kishida Chemical, Osaka, Japan) was injected into the aquifer and afterwards pumped back. Uranine is assumed to have conservative transport behavior. The aim of this test was the simulation of higher mineralized, higher density water movement within the Sarabetsu Formation. The test fluid for the saltwater test was produced by spiking natural groundwater from DD-2 with the salts potassium iodide (Nacalai Tesque, Kyoto, Japan), potassium bromide, lithium chloride, calcium chloride, sodium sulfate, and magnesium sulfate (all purchased from Wako Pure Chemical Industries, Osaka, Japan). The test fluids were stored in containers until injection.

The second push-pull test was conducted as deionized water test. The injected fluid consisted of onsite produced deionized groundwater from DD-2 (G-70B deionizer from Organo Corporation, Tokyo, Japan) and the added dye tracer uranine (Kishida Chemical, Osaka, Japan). The aim of this test was the simulation of lower mineralized, lower density water movement in the Sarabetsu Formation and to gain additional information about its sorption-desorption behavior.

The composition of both the untreated groundwater and the artificial produced test solutions is shown in Table 3.1.

3.5.2 Experimental setup

Before the start of the brackish water test, groundwater was pumped from DD-2 by a submersible pump (MP-1, Grundfos, Bjerringbro, Denmark) and stored for the production of the test fluids as described above. After a resting phase of some days the well was sealed by an inflatable packer (ToyoShoji Co., Tokyo, Japan) in the same depth as the bentonite barrier layer (85 m bgl) and 7 m³ of the brackish test fluid were injected at an injection rate of ~28.5 L min⁻¹ into the aquifer by an injection pump (Maruyama MFG, Tokyo, Japan). Following Hall et al. (1991), 100 L of untreated groundwater (*“chaser”*) were injected at the same injection rate afterwards. Its aim was to force the test

fluid out of the pipe and the annulus from DD-2 and into the aquifer. The test solution then should penetrate the aquifer in an approximately cylindrical form. Generally, due to heterogeneities within the aquifer the exact shape of the penetration zone remains unknown (Haggerty et al., 1998). By injecting high volumes of 7 to 8 m³ of the test solution and 100 L of chaser it was assured that the test solution penetrates a comparable large radial distance into the aquifer. The estimated penetration depths, which are computed using an estimated effective porosity of 30%, were between 0.90 to 1.00 m beyond the outer edge of the sand pack. In former experiments, penetration depths of about 0.25 m were reached (e.g. Istok et al., 1997). After a resting phase of about 15 to 19 hours the injected water was pumped back with a pumping rate of ~15 to 16 L min⁻¹. Between both tests a resting phase of one day was kept to allow the aquifer to restore. The pumped and injected volumes and rates are shown in Table 3.2.

3.5.3 Sampling and analysis

Ions were sampled using PET-sample bottles, which were filled with approx. 100 mL of 0.45 µm filtered water. The samples were stored at a temperature of approx. 7 °C. All cation and anion samples were analyzed by ion chromatography (DX320J, Dionex, Osaka, Japan) at the laboratories of AIST in Tsukuba, Japan. Calibration curves were determined by four standard solutions. Alkalinity was determined by 0.02N H₂SO₄ titration using three point calibration (at pH = 4, 7, and 9). Seven samples were from the original groundwater to gain the natural background concentrations. During the first experiment, water was sampled four times during injection, and 46 times during the pumping back phase. In the second experiment, three samples were taken during injection phase, and 67 samples were taken during the pumping back phase. Field parameters (temperature T, electric conductivity EC, total dissolved solute TDS, pH, oxidation-reduction-potential ORP) were measured continuously (measurement intervals between 10 seconds and 10 minutes) by a Horiba Multi sensor (Horiba, Kyoto, Japan). The concentrations of the uranine dye tracer were measured continuously (every 10 seconds) and in real time both during injection and pumping back phase by a flow-through field fluorometer (GGUN-FL30, Albillia, University of Neuchâtel,

Table 3.1: Compositions of the test solutions; EC = Electric conductivity, TDS = Total dissolved solutes, ORP = Oxidation reduction potential

Fluid	pH	EC [$\mu\text{S}/\text{cm}$]	T [$^{\circ}\text{C}$]	TDS [g/L]	ORP [mV]	Cl^-	SO_4^{2-}	HCO_3^-	Br^-	I^-	NO_3^-	NO_2^- [mg/L]	F^-	Ca^{2+}	Mg^{2+}	Na^+	K^+	Li^+	NH_4^+
Origin groundwater	7.3	1,080	11.4	0.69	-150	164	0.0	449	1.6	0.5	0.0	0.0	0.0	42.1	40.8	149	22.0	0.0	4.0
Brackish water	7.7	3,800	17.5	2.56	+146	920	588	442	118	135	0.0	0.0	0.0	156	145	245	128	116	4.4
Deionized water	8.9	25	17.9	0.02	+215	0.7	0.4	14.1	0.0	0.0	0.0	0.0	0.0	5.1	0.3	0.8	0.2	0.0	0.0

Table 3.2: Injected and extracted volumes during the push-pull tests (PPT)

Experiment	Aquifer thickness [m]	Estimated effective porosity [-]	Injected volume push-phase [m^3]	According aquifer penetration depth [m]	Injected volume of chaser [m^3]	Injection rate [L/min]	Resting time [h]	Extracted volume pull-phase [m^3]	Extraction rate [L/min]
Brackish water	7.6	0.3	7.0	~0.93	0.1	28.5	15.8	26.4	15.4
Deionized water			7.9	~1.00	0.1	32.0	18.5	24.6	16.2

Neuchâtel, Switzerland). Thus, it was possible to adjust the frequency of ion sampling from about every 2 minutes during the first hour until several hours at the end of the test. In both tests, water was pumped back until the uranine concentration reached the background value.

3.5.4 Modeling for transport parameter estimation

Rock can be considered as a heterogeneous porous media. When water is injected, the flow takes place in zones with high hydraulic conductivity. Otherwise there is little or no flow in zones with low hydraulic conductivity. Advective solute transport is dominant in the mobile zones. Solutes can also be transported to the immobile zone with negligible flow by diffusion, slow advection or sorption. To consider these transport processes, the solute transport during injection and withdrawal is modeled by a mobile-immobile model (Haggerty and Gorelick, 1995; Carrera et al., 1998). The solute transport in the mobile zone is described as

$$R_m n_{f,m} \frac{\partial c_m}{\partial t} + R_{im} n_{f,im} \frac{\partial c_{im}}{\partial t} = \nabla \cdot (n_{f,m} \alpha_L |v_m| \nabla c_m - n_{f,m} v_m c_m) \quad (3.1)$$

where c (M/L³) is the concentration of the solute, R (-) is the retardation coefficient, n_f (-) is the porosity, α_L (1/L) is the dispersivity in the longitudinal direction and v (L/T) is the pore water velocity. The indices $_m$ and $_{im}$ are used for the mobile and immobile zone respectively. Introducing the effective volume ratio $a_V = (R_{im} n_{f,im}) / (R_m n_{f,m})$ and radial coordinates the equation for solute transport becomes

$$\frac{\partial c_m}{\partial t} + a_V \frac{\partial c_{im}}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\alpha_L |v|}{R} \frac{\partial c_m}{\partial r} \right) - \frac{v}{R} \frac{\partial c_m}{\partial r} \quad (3.2)$$

where r (L) is the distance from the center of the borehole. Without defining the physical transfer process the solute transfer between mobile and immobile zone can be modeled by first-order mass transfer

$$\frac{\partial c_{im}}{\partial t} = k(c_m - c_{im}) \quad (3.3)$$

where k (1/T) is a first-order mass transfer rate coefficient. In Haggerty et al. (2000) the pore water velocity in the mobile zone for a push-pull tracer test is

$$v_m = \frac{Q}{2\pi r n_{f,m} b} \quad (3.4)$$

Here Q (L³/T) is the flow or pumping rate and b (L) is the thickness of the aquifer. The flow rate Q is different for the injection, the resting, and the withdrawal period.

The parameters describing the porous media – the mobile porosity, the dispersivity, the effective volume ratio and the mass transfer rate – are unknown, while all other parameters are given by the experimental setup. These unknown parameters are estimated from the modeled and the measured BTCs for the withdrawal period using a nonlinear least square Nelder-Mead algorithm.

An analytical method to find the modeled BTC from the transport model described above can be found in Haggerty et al. (2000). Equations in the Laplace domain are transformed to the time domain using the numerical method from den Iseger (2006).

3.6 Results and discussion

3.6.1 Chemical reactions

Fig. 3.5 shows a piper plot of all samples obtained during the brackish water test. Background groundwater composition is freshwater (TDS = 0.69 g/L, EC = 1,083 μ S/cm) of (Na,K)HCO₃-type. A higher sodium content (in relation to calcium and magnesium) indicates that the groundwater was subject to mixing processes between fresh and seawater, probably caused by seawater intrusion and ion exchange processes. The injected water is a brackish

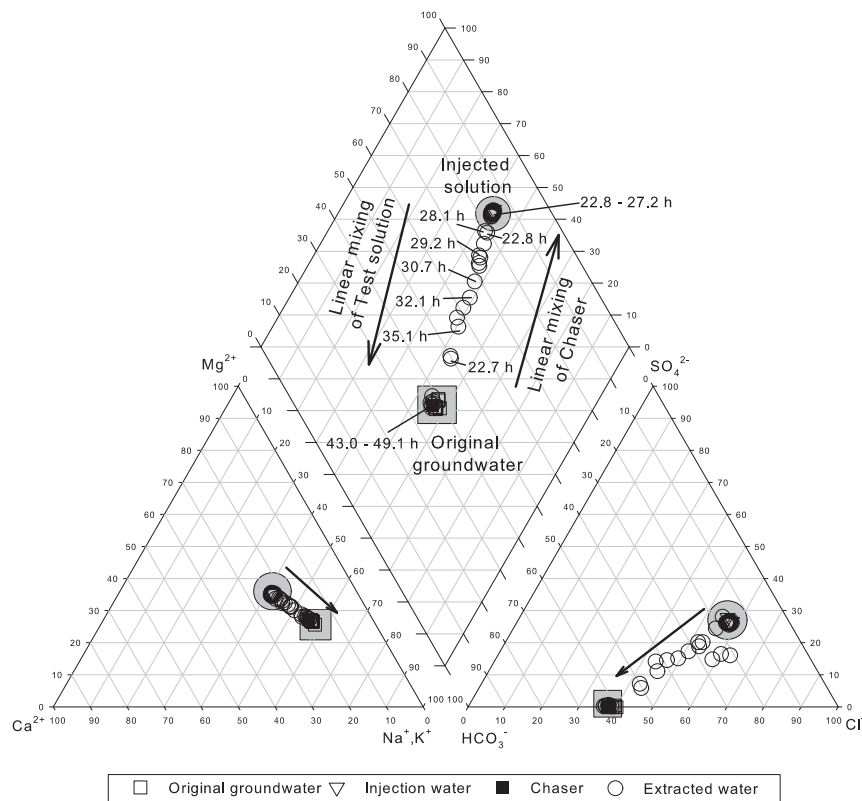


Figure 3.5: Piper plot of the brackish water push-pull test. The arrows track the chemical evolution of the pumped water from the first to the last sample. The reaction times are noted for selected samples. One linear path (reaction time between 22.7 h and 22.8 h) is conservative end-member mixing of the chaser (=natural groundwater) with the prior injected test solution. Second linear path is conservative end-member mixing of the injected test solution with the pristine groundwater.

water (TDS = 2.56 g/L, EC = 3,800 μ S/cm) with a (Na,K,Ca,Mg)Cl-type composition. The evolution of the sample chemistry during the extraction can be separated in two parts: reaction times <22.8 h represent samples from the extracted chaser, which was injected at last. Samples with reaction times between 22.8 and 50 h represent the test fluid. Both fluids show contrary evolutions: the chaser fluid composition moves from groundwater composition to brackish water composition with longer reaction time. This is an indicator for simple conservative mixing between the end-members. The test fluid composition shows a linear trend from injection brackish composition to groundwater composition. This is also an indicator for simple conservative

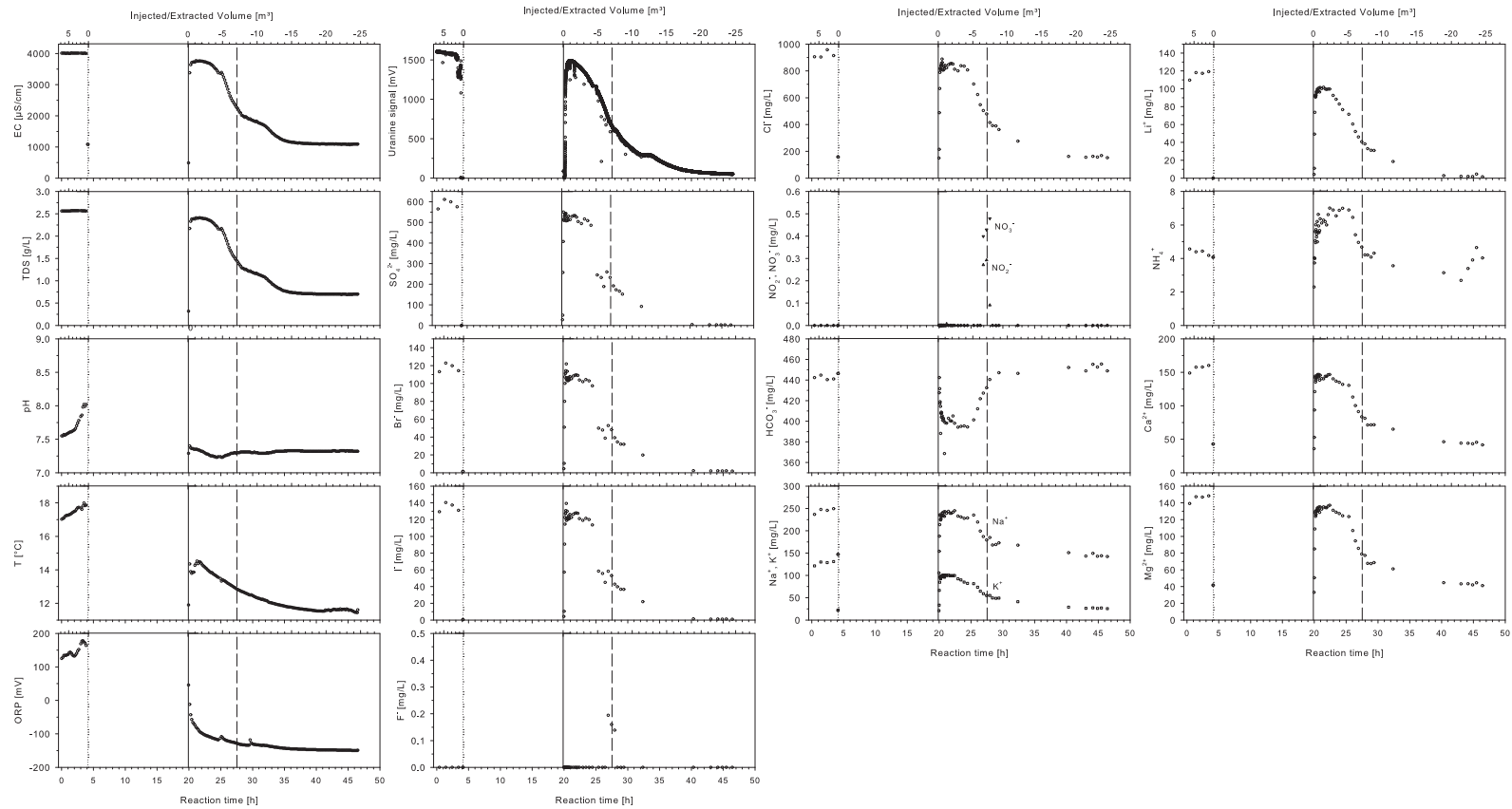


Figure 3.6: BTCs of uranine dye tracer, field parameters, and ions during the injection (“push”) and the extraction (“pull”) phase of the brackish water push-pull test. Reaction time is represented by the lower x-axis and starts at the beginning of injection of the test solution. The injected or pumped water volume is represented by the upper x-axis, which is not linear due to the varying flow rates during injection and extraction. The dotted line marks the end of injection of the chaser (and therefore the beginning of the drift phase). The solid line marks the start of the extraction phase. The dashed line marks the moment, when pumped and injected volume is equal.

Table 3.3: Concentrations, recoveries, and mass balances during the brackish water test. Injected volume was 6,980 L.

	Cl ⁻	Br ⁻	I ⁻	SO ₄ ²⁻	HCO ₃ ⁻	F ⁻	NO ₃ ⁻	NO ₂ ⁻	Na ⁺	Ca ²⁺	Mg ²⁺	K ⁺	NH ₄ ⁺	Li ⁺
Natural groundwater concentration [mg/L]	164	1.6	0.5	0.4	449	0.0	0.0	0.0	149	42.1	40.8	22.0	4.0	0.0
Injected concentrations [mg/L]	920	118	135	588	442	0.0	0.0	0.0	245	156	145	128	4.4	116
Injected net concentration [mg/L]	756	116	134	588	-7	0.0	0.0	0.0	96	114	104	106	0.4	116
Injected net mass [g]	5,280	810	935	4,100	-48.9	0.0	0.0	0.0	670	796	726	740	2.79	810
Recovered net mass [g]	5,250	776	913	3,890	-173	0.2	0.6	0.3	692	843	777	677	7.8	775
Mass recovery [%]	99.4	95.8	97.6	94.9	-362	-	-	-	103	106	107	91.5	280	95.7

Table 3.4: Concentrations, recoveries, and mass balances during the deionized water test. Injected volume was 7,900 L.

	Cl ⁻	Br ⁻	I ⁻	SO ₄ ²⁻	HCO ₃ ⁻	F ⁻	NO ₃ ⁻	NO ₂ ⁻	Na ⁺	Ca ²⁺	Mg ²⁺	K ⁺	NH ₄ ⁺	Li ⁺
Natural groundwater concentration [mg/L]	164	1.6	0.5	0.4	449	0.0	0.0	0.0	149	42.1	40.8	22.0	4.0	0.0
Injected concentrations [mg/L]	0.7	0.0	0.0	0.4	14.1	0.0	0.0	0.0	0.8	5.1	0.3	0.2	0.0	0.0
Injected net deficit concentration [mg/L]	-163	-1.6	-0.5	0.0	-435	0.0	0.0	0.0	-148	-37.0	-40.5	-21.8	-4.0	0.0
Injected net deficit mass [g]	-1,290	-12.6	-3.9	0.0	-3,440	0.0	0.0	0.0	-1,170	-292	-320	-172	-31.6	0.0
Recovered net deficit [g]	-1,164	-6.0	8.3	15.5	-2,900	0.9	0.2	0.1	-1,130	-155	-343	-62.5	-2.4	16.7
Deficit Recovery [%]	89.8	46.9	-213	-2,380	84.3	-	-	-	96.6	53.1	107	36.3	7.5	-

mixing between the two fluids or reversible sorption-desorption and/or ion exchange processes.

The logged BTCs of the dye tracer uranine, the field parameters, and ions are shown in Fig. 3.6. The BTC of the uranine dye tracer will be discussed in detail in section 3.6.2 (Hydraulic characterization and modeling).

A “negative” breakthrough was observed for the HCO_3^- concentrations, which decreased from 440 mg/L (injection = background concentration) down to 400 mg/L and increased again back to the natural background concentration within one re-pumped injection volume. This effect may indicate precipitation of calcite due to oversaturation by exchange of sodium to calcium. However, for Calcium a positive BTC was observed and more than 100% of the injected mass was recovered (Table 3.3). So, this may be a reversible process during the experiment. Also within the first pumped injection volume the concentrations of NH_4^+ increased from 4.5 mg/L (injection = background concentration) up to 7 mg/L and decrease again back to the natural background concentrations. F^- , NO_2^- , and NO_3^- , which all are neither artificially injected into the aquifer nor present in the pristine groundwater, were detected in three samples in the moment, when injected and pumped volume is equal ($V/V_0 = 1$). It is not obvious, which processes cause the observed ammonium excess or the detected peaks of F^- , NO_2^- , and NO_3^- . However, an indicator for the significant hydrochemical processes is the rapid decrease of the ORP during the test, which follows strong oxygen consumption and the mass recoveries (Table 3.3). The recoveries of most of the injected anions approximates 100% (exception was HCO_3^- with -360% recovery). Also the recoveries of most of the cations approximate or even exceed 100%.

In Fig. 3.7 a piper plot of all samples obtained during the deionized water test is shown. The original groundwater is the same freshwater (TDS = 0.69 g/L, EC = 1,083 $\mu\text{S}/\text{cm}$) as in the first test, which has a (Na,K) HCO_3 -type composition. The injected water is a very low mineralized fresh water (TDS = 0.02 g/L, EC = 25 $\mu\text{S}/\text{cm}$) with a $\text{Ca}(\text{HCO}_3)$ -type composition. The evolution of the sample chemistry during the extraction is more complex than the conservative mixing of the brackish water test. The path of chemical evolution is split in three parts: The youngest samples originate from the chaser, which

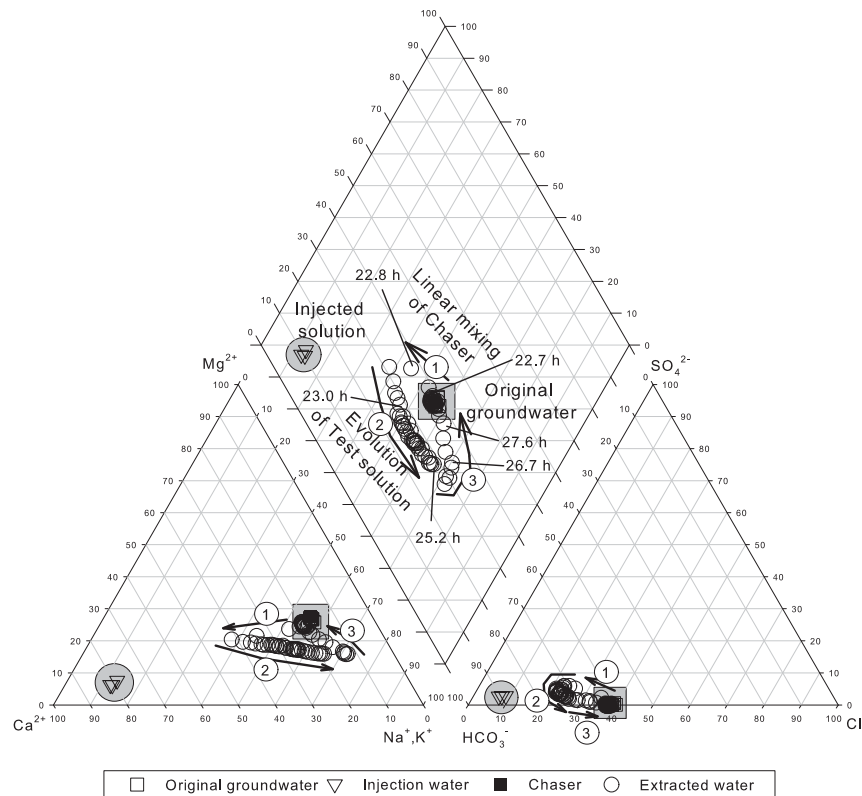


Figure 3.7: Piper plot of the deionized water push-pull test. The arrows track the chemical evolution of the pumped water from the first to the last sample. The reaction times are marked for selected samples.

was injected last. They represent conservative mixing between the chaser (= origin groundwater composition) and the test fluid injected before. The ratios of Ca^{2+} and HCO_3^- increase (first arrow). The samples, which represent the injected test solution, showed a more complicate chemical evolution. In contrast to the brackish water test, where all samples are located on a linear path between injection water and original groundwater composition, here even the samples with the shortest reaction time in the aquifer did not preserve the injection composition. The evolution path begins with a composition somewhere between both “start” compositions, which indicates a very fast and strong chemical response (ion exchange, desorption) of the aquifer to the injection of deionized water. The water becomes richer in Na^+ , K^+ , and Cl^- . The ratio of Na^+ and K^+ becomes even larger than in the original groundwater samples (second arrow). This indicates strong cation exchange of Ca^{2+} to Na^+ in the aquifer (with resulting desorption of

Na^+). In the last phase the ratio of Ca^{2+} increases again and accordingly the chemical composition of the samples moves back to the original groundwater composition (third arrow). That is the part when most of the injected volume is pumped back and a significant amount of the natural groundwater is mixed with the pumped water.

The logged BTCs of the dye tracer uranine, the field parameters, and ions are shown in Fig. 3.8. The BTC of the uranine dye tracer will be discussed in detail in section 3.6.2 (Hydraulic characterization and modeling).

The ions Cl^- , Br^- , HCO_3^- , Ca^{2+} , Mg^{2+} , Na^+ , and K^+ showed almost similar negative BTC as EC and TDS. In the shapes of most of these BTCs, the three phases indicated in the piper plot (Fig. 3.7) can also be identified: The conservative mixing of the chaser with the test solution (first arrow in the piper plot), the plateau phase (second arrow) and an increase to background concentrations (third arrow). However, for some ions an unexpected behavior was observed: Though NH_4^+ showed the expected negative BTC, at the end of the experiment the concentration exceeded the natural background concentration. Although the absolute difference was not large (<1 mg/L), the relative difference is remarkable as the background concentration is about 4 to 5 mg/L. It is not clear if this small effect is due to some mobilization effects caused by the injection of the deionized water, or to the accuracy of measurement. For the ions Li^+ , I^- , F^- , and SO_4^{2-} , which occur not or only with negligible concentrations in the original groundwater, positive BTCs were observed. The BTCs of Li^+ and I^- are divided in a minimum and a maximum peak. In the case of these two ions, the breakthrough may be caused by mobilization of injected but not completely recovered Li^+ and I^- from the prior brackish water test. The BTC of SO_4^{2-} shows a peak at the beginning of pumping back and then decreases to the background concentration. The unexpected occurrence of these ions led to negative mass balances (as less “deficit” was recovered than injected; Table 3.4). F^- neither was injected in both tests nor found in the original groundwater. Therefore, its breakthrough may be induced by dissolution of some fluoride containing mineral phases caused by the very low mineralization of the injected water. The observed breakthrough curves are clearly to identify, but the concentrations are very low (< 3.0 mg/L). NO_2^- and NO_3^- , which all are neither artificially injected into the aquifer nor are present in the pristine groundwater, were detected

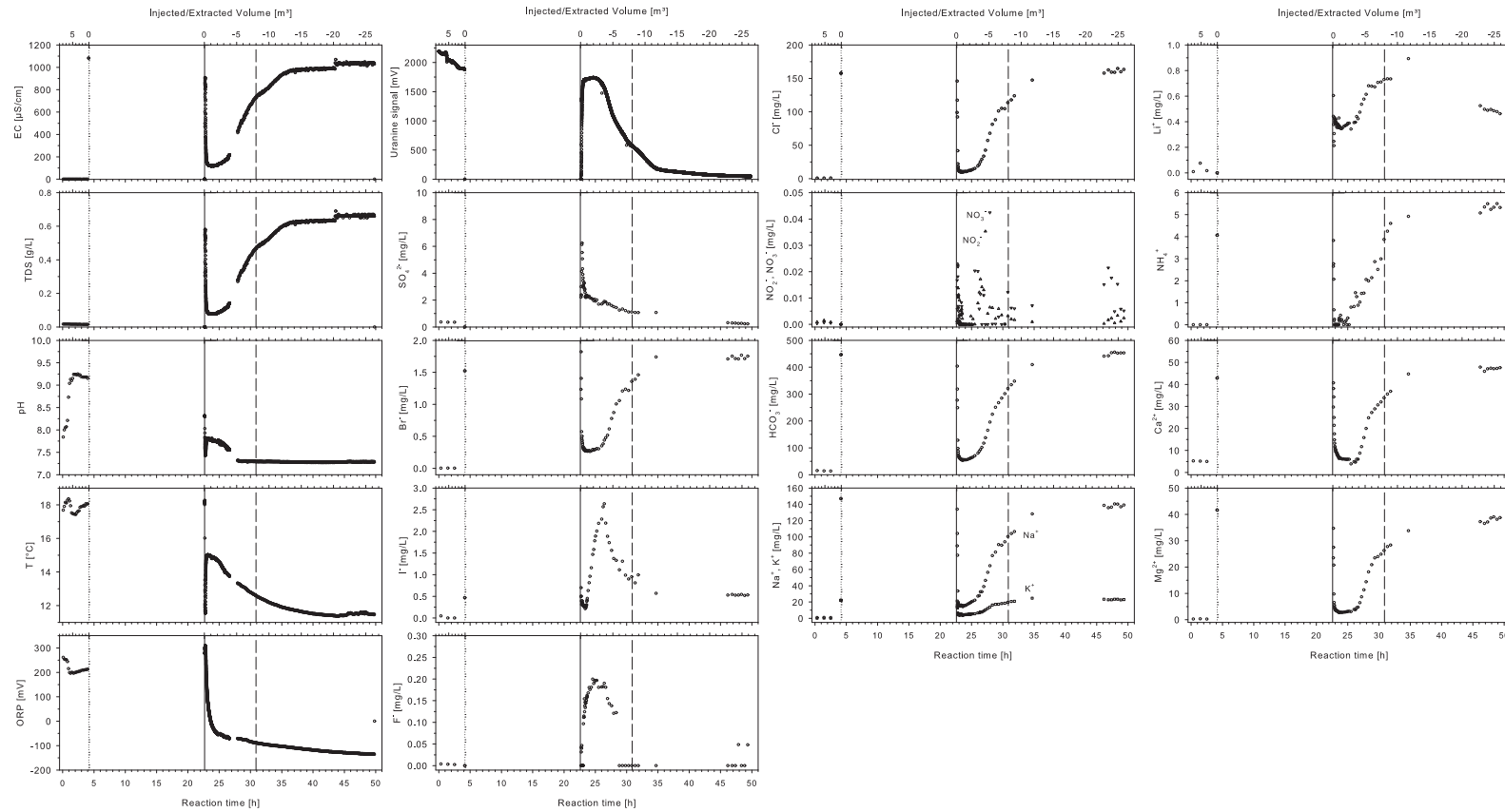


Figure 3.8: BTCs of uranine dye tracer, field parameters, and ions during the injection ("push") and the extraction ("pull") phase of the deionized water push-pull test. Reaction time is represented by the lower x-axis and starts at the beginning of injection of the test solution. The injected or pumped water volume is represented by the upper x-axis, which is not linear due to the varying flow rates during injection and extraction. The dotted line marks the end of injection of the chaser (and therefore the beginning of the drift phase). The solid line marks the start of the extraction phase. The dashed line marks the moment, when pumped and injected volume is equal.

frequently during the extraction phase, but no clear trend or BTC could be identified. The injection of the deionized water caused several hydrochemical reactions for redox sensitive nitrogen species. Comparable to the brackish water test, the ORP decreased rapidly during the deionized water test.

3.6.2 Hydraulic characterization and modeling

During extraction of the groundwater, intense gas release of very small gas bubbles was observed in both tests. The gas bubbles caused a strong turbidity signal (Fig. 3.9). As the previously injected test fluid was already in equilibrium with the surface pressure, the turbidity increased during extraction. Only negligible turbidity was detected at the start of the pull-phase. The larger the ratio of groundwater to the injected fluid became during extraction, the stronger the turbidity became due to the gas release in both experiments. In the deionized water test a small peak in turbidity was observed already at the start of the extraction (Fig. 3.9b). The dynamic turbidity signal may overprint the actual uranine fluorescence signal and may cause an over- or underestimation of the uranine concentrations.

Also, the pH values behaved more dynamic than expected prior to the test. The pH values in the injected fluids were higher than in natural groundwater (~7.3), which is most likely caused by the storage of water in open tanks and therefore equilibration with surface pressure by gas release of CO₂. The difference was larger in the deionized water test (7.7 – 9.3), than in the brackish water test (7.5 – 8.0), which may be a consequence of the deionization process and the longer storage time of the deionized water in contact with air. These high injection values even caused a small pH breakthrough at the beginning of extraction in the deionized water test (Fig. 3.10b). The difference of the pH values between injected fluid and natural groundwater will cause differing fluorescence intensities even at identical concentrations. The relation between fluorescence signal of uranine and pH is well known, its maximum is around pH 8.8 (Käss, 2004). Therefore it was possible to calculate a correction factor for every single pH value and draw a corrected uranine fluorescence signal plot (Fig. 3.10a – brackish water test; Fig. 3.10b – deionized water test).

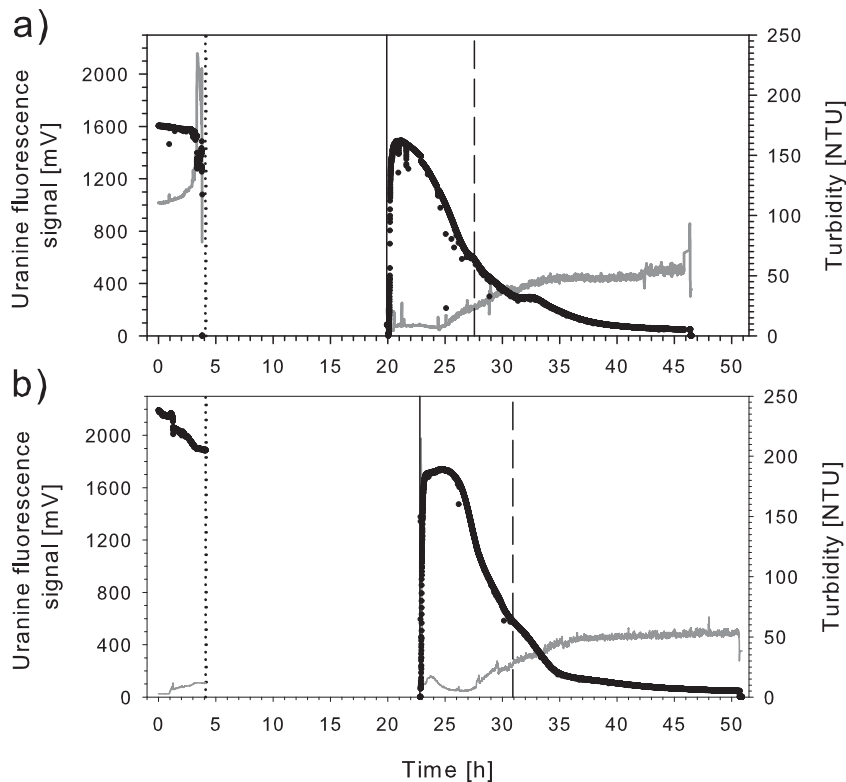


Figure 3.9: Uranine fluorescence signal (black circles) and observed turbidity (gray lines) in the brackish water test (a) and in the deionized water test (b). The dotted line marks the end of injection of the chaser (and therefore the beginning of the drift phase). The solid line marks the start of the extraction phase. The dashed line marks the moment, when pumped and injected volume is equal.

The different shapes of the tailing of the both uranine BTCs could be caused by different hydraulic behavior of groundwater due to the different densities dependent on the salinization. But also hydrochemical effects may be causing the different tailing. Flushing of a brackish aquifer with fresh water may lead to increased dispersion and decreased hydraulic conductivity by swelling clay particles and clay dispersion (Mehnert and Jennings, 1985). Clay dispersion may be a partially irreversible process, but can be avoided by flushing the aquifer with a calcium-chloride solution which causes a calcium-chloride exchange at the surface of the clay particles. However, in presence of montmorillonite the permeability of an aquifer decreases with decreasing chloride content, e.g. during flushing with freshwater (Konikow et al., 2001). Magal et al. (2008) reported on sorption of uranine to bentonite or other clay minerals, when high chloride concentrations are present. Bentonite is used

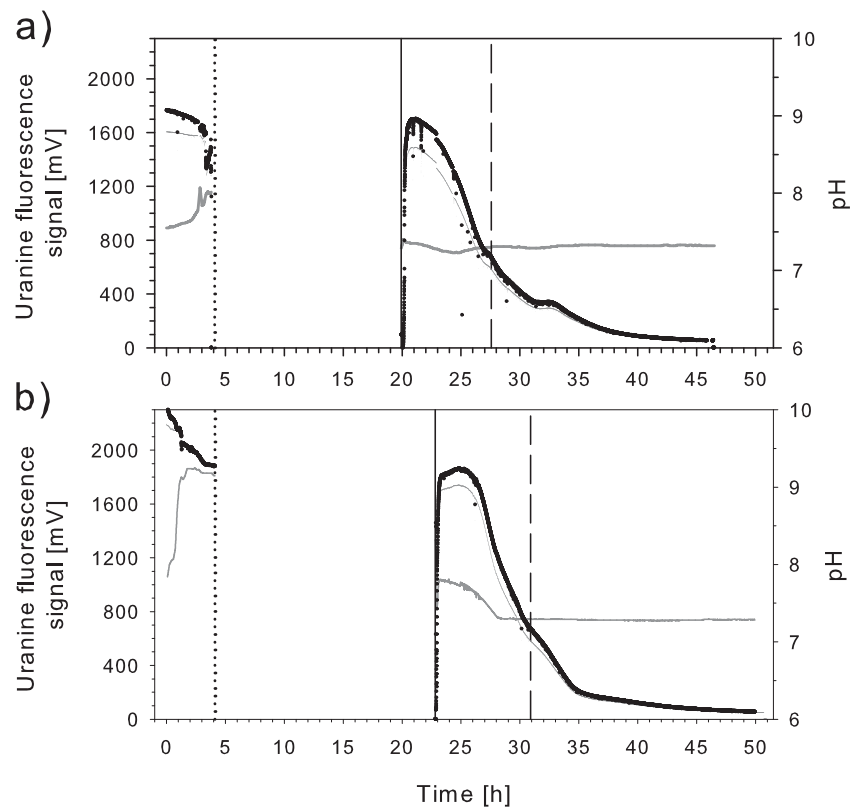


Figure 3.10: Corrected uranine fluorescence signal [mV] in the brackish water test (a) and in the deionized water test (b). The gray dots represent the measured uranine fluorescence signal, the thin gray line represent the observed pH values, and the black circles represent the for the pH value corrected uranine fluorescence signal. The dotted line marks the end of injection of the chaser (and therefore the beginning of the drift phase). The solid line marks the start of the extraction phase. The dashed line marks the moment, when pumped and injected volume is equal.

as sealing material at the top of the gravel pack (Fig. 3.4 Profile of DD-2). Hence, chloride dependent sorption on bentonite would have different effects on the BTCs of the two tests.

However, insufficient uranine concentration measurements and poor mass balances are the consequence of the observed turbidity and fluctuations of the pH value. Also the observed differences in the shape of the uranine breakthrough curves (plateau in the deionized water test) are probably caused by the influence of the increased pH (Fig. 3.10b) and turbidity (Fig. 3.9b) on the fluorescence intensity at that time. Due to the uncertainties of the determination of the correct concentrations it was decided to plot just

the fluorescence signals of uranine [mV]. Therefore, uranine was not used for further analysis and interpretation in this experiment. Instead, lithium concentrations are used for the modeling of the brackish water curve. For the modeling of the deionized water test the concentrations breakthrough curves of chloride are used. These ions are known as conservative tracers and analysis is independent of pH and turbidity fluctuations.

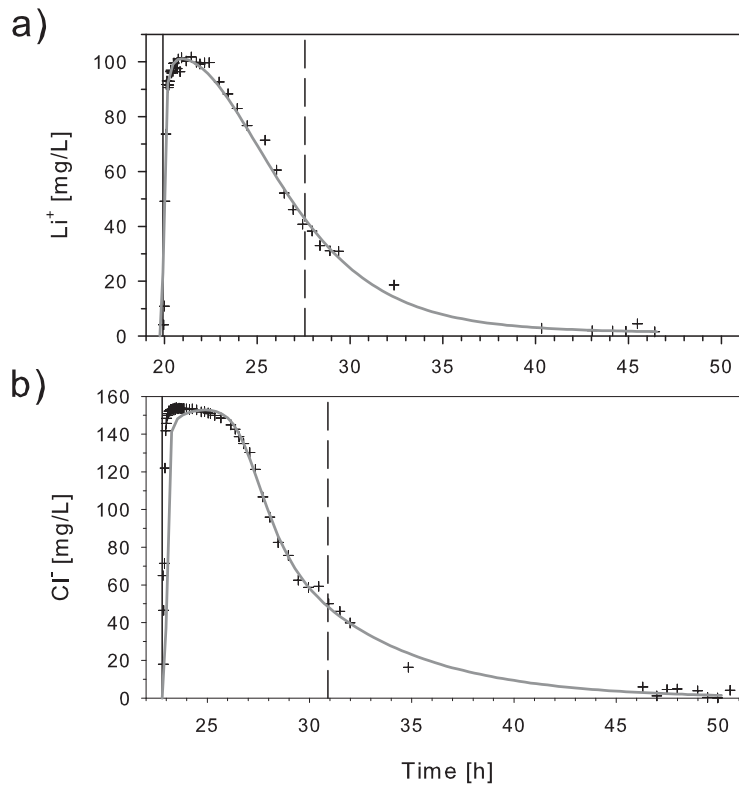


Figure 3.11: Fitted lithium BTC of the brackish water test (a) and chloride BTC of the deionized water test (b). Best fit (gray solid line) was obtained assuming conservative transport and mass loss due to mass transfer between mobile and immobile zones (single rate mass transfer). The black crosses represent the measured concentration values of chloride (a) and lithium (b). The solid line marks the start of the extraction phase. The dashed line marks the moment, when pumped and injected volume is equal.

In Table 3.5 the results of the modeling of the BTCs of lithium (brackish water test) and chloride (deionized water test) are shown. In general, for both tests sufficient fits of the BTCs could be performed (Fig. 3.11). The best fits were obtained assuming conservative transport and mass loss due to mass transfer between mobile and immobile zones (single rate mass transfer) in

both tests. However, the estimated aquifer parameters, as effective porosity and longitudinal dispersion coefficient, differ between the both tests, which was unexpected prior to the test. An effective porosity of ~5% in the brackish water test is a low value, but may be realistic due to the silty fine sand matrix. However, a value of 0.02% in the deionized water test seems to be far too low for this aquifer. In previous pumping tests, hydraulic conductivities of $5 \cdot 10^{-6} \text{ m s}^{-1}$ were determined, a value typical for permeable aquifers. The low effective porosity of the deionized water test compared to the brackish water test could be caused by clogging. While a higher dispersion coefficient would be expected in this case, we only found a lower dispersion coefficient, which leads to the conclusion that clay dispersion is only of minor importance. However, due to the insufficient uranine measurements, the “deficit” BTC of chloride was inverted and then fitted. This may be also a source for uncertainties during the fitting and therefore for the very low effective porosity.

Table 3.5: Fitted parameters from modeling of the BTC of lithium (brackish water test) and chloride (deionized water test)

	Mobile porosity $n_{f,m}$ [-]	Dispersion coefficient a_L [m]	Mass transfer rate k [1/s]	Effective volume ratio α_V [-]
Brackish water test (Li^+)	5.07	0.1464	$8.4 \cdot 10^{-6}$	0.1711
Deionized water test (Cl^-)	0.02	0.0692	$1.3 \cdot 10^{-4}$	0.4162

Further observations are local maxima or “*shoulders*” during the decrease of concentrations, which are observed in some BTCs: In the brackish water test, uranine shows two local maxima, the first maximum is very small, but distinct, and occurred after the injected volume was extracted one time (7 m^3). The second maximum is more distinct and occurred after extraction of $\sim 10 - 12 \text{ m}^3$. While the first maximum was only observed for the uranine BTC in the brackish water test, the second maximum or shoulder can be seen clearly in the BTCs of EC and TDS in both, the brackish and the deionized water test. The uranine BTC of the deionized water test shows also only the second maximum as a broad shoulder. The local maxima/minima are not observed in the ion BTCs, which may be caused by the lower sample frequency.

It is obvious that the first local maximum has to be an anomaly of the uranine fluorescence, as no other BTC showed this effect. A possible explanation may be the lower solubility of gas in higher mineralized fluids in general

and under higher chloride concentrations in particular (Rumpf et al., 1994). By dispersive mixing at the interface between the injected brackish test fluid and the natural lower mineralized groundwater, dissolved compounds were transported into the gas-bearing groundwater. Thus, the gas solubility of the groundwater becomes reduced. This would result in an increased gas release and accordingly an increase of the fluorescence signal of uranine, when this interface is extracted to the surface. In Fig. 3.9 some local maxima can be detected within the turbidity plot. However, the correlation of individual maxima observed in the uranine BTC to maxima in the turbidity BTC is challenging.

The second small maxima/shoulders were observed also in the BTCs of EC and TDS. These effects may be an indicator for zones of different hydraulic conductivity (preferential flowpaths or low-flow/stagnant zones), as it occurred in different BTCs and in both tests. Therefore, this effect can be discussed as an aquifer property. This is also confirmed by Lessoff and Konikow (1997), who noticed that heterogeneities of the aquifer may affect the reversibility of the flow during pumping back of the tracers (particularly if applying a drift phase between injection and pumping back phase) and therefore cause inconsistent results. The local maxima in the decline of the uranine and the electric conductivity breakthrough curves may represent preferential flow paths within the aquifer. Those are probably derived from coarse sand and fine gravel channels like the ones observed at the outcrop in Fig. 3.3. These channels within the Sarabetsu Formation are potential flow paths for rapid solute transport.

There are also some reports indicating an upward flow component within the groundwater system of Horonobe (Ioka, 2010), which caused several artesian wells near the Hamasato site. This implies that the discharge area of the Horonobe basin is not only the Sea of Japan but additionally the wetlands of the Rishiri-Rebun-Sarobetsu National Park (No. III in Fig. 3.2). An upward flow component may have a density-dependent influence to the shape of the BTCs of the both fluids.

3.7 Conclusions

The special setup of the both push-pull tests, which were conducted using a brackish and a deionized injection fluid, generated unique insights into the chemical and hydraulic processes of the deep coastal aquifer of Horonobe.

The flow and transport behavior within the aquifer seems to be different between freshwater and saltwater. This implies that the hydraulic system of the coastal Sarabetsu aquifer is significantly driven by the grade of mineralization of the circulating fluid. Freshwater may be highly mobile within the Sarabetsu aquifer. This may be caused by floating and runoff on the saltwater-freshwater interface by the density driven flow. Groundwater and its solutes potentially are transported through preferential flow paths (channels) within the Sarabetsu aquifer. This would cause higher transport velocities and distances. The aquifer chemistry reacts highly sensitive to pumping or injection of water. Redox reactions occur very fast. Probably further redox-sensitive ions and dissolved gases, which were not analyzed in this experiment (e.g. iron, manganese, hydrogen sulfide, nitrogen, methane, and carbon dioxide), are affected. Also, dissolution and precipitation reactions were induced by injecting and pumping water. These reactions may change the hydraulic behavior of the Sarabetsu aquifer (by closing or opening of pore spaces and flow paths). These findings imply that the behavior of ions during solute transport is dependent on the density and the composition of the fluid. Intrusion of freshwater may induce strong mobilization of ions within a coastal aquifer and simultaneously closing of pore spaces.

The push-pull method also shows some limitations during our experiments, which make a distinct interpretation difficult. The effect of the “drift” or “reaction” phase on the BTCs is not fully understood. It may be more suitable to avoid such a break between injection and extraction phase in future experiments. The role of the chaser is unknown. Its injection may disturb the flow field and produce a “spot” within the previously injected plume. Also, the influence of the volume is not investigated sufficiently. There are no criteria defined to choose an appropriate volume for chaser, if the exact effective pore volume of the gravel pack surrounding the well is unknown. A wrong design may cause further difficulties for BTC interpretation. What is a reasonable and practicable test volume to test as much aquifer volume as possible? The

amount necessary to penetrate the aquifer increases with square value (if a symmetrical cylinder is assumed for tracer plume spreading during injection).

The presented push-pull method is a suitable technique for single-well testing, if both the advantages and the limitations are considered. While the hydraulic interpretation remains challenging due to the unknown travel distance and hydraulic gradient, and the often complex flow field due to heterogeneous aquifers, the push-pull tracer test method is well established for investigation of hydrochemical studies (as redox behavior, biodegradation, etc.). Further potential applications for this single-well technique may be geothermal research, e.g. using temperature as a tracer or to determine possible precipitation-dissolution reactions during the production of geothermal heat or energy. In other cases related to the deeper underground and to higher mineralized groundwater, e.g. CO₂ long-term storage, heat storage, or aquifer storage and recovery systems, may benefit from the simple push-pull test design.

In future work, significant effort has to be invested to standardize the test setup and the reproducibility. Also the post-processing of hydraulic analysis has to become more standardized. For that, a deeper understanding of the processes during all phases of a push-pull test, e.g. the influence of heterogeneity or preferential flowpaths, or density driven flow may be necessary.

3.8 Acknowledgments

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4 Study of the effects of the chaser in push-pull tracer tests by using temporal moment analysis

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4.1 Abstract

“Push-pull” tracer tests are a suitable tracer test method for hydrochemical characterization of an aquifer in a single-well setting. A known amount of selected solutes as conservative and reactive tracers is injected into the aquifer (“push”) and afterwards extracted (“pull”). In many cases, a so-called “chaser”, which is just original groundwater without any added solutes, is injected directly after the injection of the test solution. Its objective is to push the test solution out of the borehole into the aquifer and therefore to minimize the influence of the gravel pack on the shape of the breakthrough curve. The influence of the chaser on the tracer breakthrough curve is unknown so far. Also, the determination of the appropriate volume for the chaser is a difficult task if at all applied. A first experiment was conducted with the objective to compare three push-pull tests with similar injection volumes, two tests with and one without a chaser. Results show that the application of a chaser lowers the main peak concentration. However, it does not alter the tailing of the breakthrough curve nor does it have a negative influence on tracer mass recovery. In a second experiment, a new method was developed to determine the optimal chaser volume by testing seven different chaser injection volumes combined with temporal moment analysis. As a result, the application of a chaser is recommended, when reactions of injected solutes within the open well or the gravel pack should be avoided. If a chaser is used, the new method mentioned above can easily be used to determine the required chaser injection volume. The experiments were conducted at the Hamasato test site in Horonobe (Hokkaido, Japan).

Keywords

Gravel pack · porosity · tracer test · single-well test · aquifer characterization · Japan

4.2 Introduction

In single-well settings, fully developed techniques used in hydrogeology for aquifer characterization, like multiple-well tracer tests, are impossible to apply (Hebig et al., 2012). The single-well injection-withdrawal “*push-pull*” tracer test method may be a suitable alternative to gain information about aquifers with only single-well access. In a push-pull test, tracer spiked water is injected and afterwards withdrawn from the same well.

Push-pull tracer tests have a great potential for application in geothermal studies especially to determine in-situ geochemical reactions and aquifer characteristics. Push-pull tests are already reported for being used in geothermal energy research, especially in single-well settings applying the hot-dry rock method (Herfort et al., 2003). Pauwels (1997) and Pauwels et al. (1992) used push-pull tests during the explorations phase of geothermal heat to study energy reservoirs. Various approaches are dealing with analytical solutions for thermal push-pull tests regarding reservoir lifetime, heat recoveries, diffusion coefficients, and fluid residence times (Gringarten, 1978; Herfort et al., 2003; Ghergut et al., 2007; Kehrer et al., 2007; Jung and Pruess, 2012).

Further applications of this method are often reported for hydrochemical aquifer characterization. It is used to proof and to quantify processes regarding organic pollutants at contaminated sites, like in situ determination of microbial activity, transformation and degradation rates, denitrification rates, and simulation of large recharge events in shallow (<20 meters depth) wells using so-called partitioning push-pull tests (e.g. Addy et al., 2002; Cunningham et al., 2001; Haggerty et al., 1998; Istok et al., 1997; Kleikemper et al., 2002; McGuire et al., 2002). In deeper settings, the application of the push-pull test method was reported for the investigation of mixing, cation exchange, and oxidation-reduction reactions caused by the change of salinization (Vandenbohede et al., 2008). For the investigation of the deeper subsurface, push-pull tests may also be a suitable test method for the characterization of groundwater flow velocity dispersion or dispersion coefficients, and matrix or effective porosities (e.g. Hall et al., 1991; Leap and Kaplan, 1988; Novakowski et al., 1998; Riemann et al., 2002). Though, the travel distance of the injected and afterwards extracted tracer plume, as

well as the original groundwater gradient will remain unknown in single-well settings and therefore the reliability of the published approaches for the hydraulic analysis of push-pull tests to determine groundwater flow velocity and effective porosity is limited.

A general push-pull tracer test includes the following steps:

1. Injection (“push”) of the test solution,
2. Injection of a *chaser* (optional),
3. Drift/reaction phase (optional), and
4. Extraction (“pull”) of the test solution.

No systematic evaluation of the push-pull method regarding its reproducibility and influence of the test setup on the results has been published so far. Therefore, the repeatability of this method and the influence of changes of its setup on the resulting breakthrough curves (*BTCs*) are unknown. To fill this gap, a large-scale experiment was conducted at the Hamasato site in Horonobe (Hokkaido, Japan). Various tests were conducted in a groundwater monitoring well to investigate the influence of individual setup parameters on the test results. As part of this method evaluation, also the role and influence of the so-called chaser was evaluated in two individual experiments. The aim of the injection of a chaser, usually groundwater or tap water without any added solutes or tracers, is to push the test solution out of the well and gravel pack into the formation of interest. The volume of the chaser should be large enough to fill the whole well and gravel pack volume and should push the test solution completely out into the aquifer. For this, the volume of all used tubes, pipes, the tested well, and its gravel pack has to be known. However, in most cases the effective porosity of the gravel pack and accordingly its volume is unknown and has to be estimated, which may result in ambiguous results. An approach for the determination of the optimal chaser volume was not available so far.

Also, the influence of a chaser on the *BTC* of the prior injected tracer is not known. Expected effects may be dilution of the test solution (in the worst case below the detection limit), pushing the tracer plume too far into the aquifer, e.g. beyond the radius of the cone influence (means the cone of elevation in the push phase or cone of depression in the pull phase), or any other kind of shifting or alteration of the *BTC*. The injection of a chaser directly after

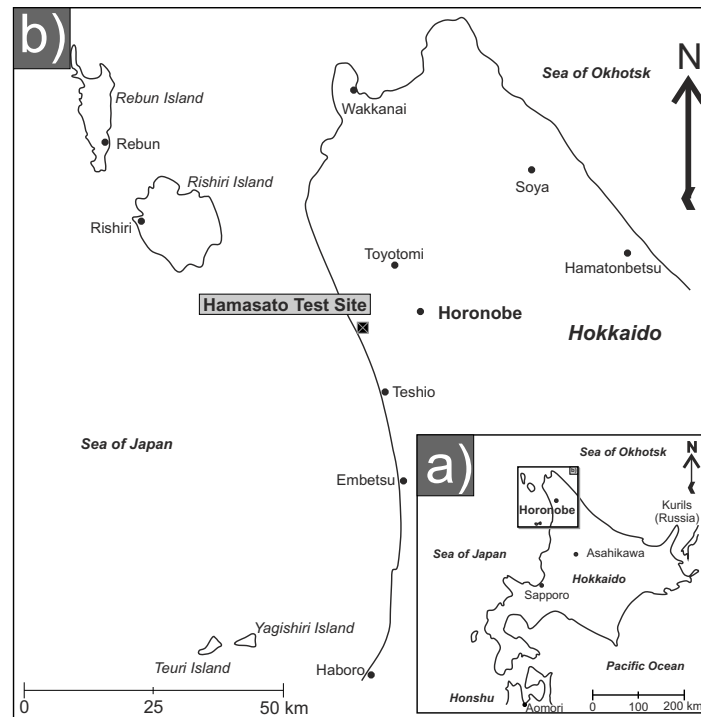


Figure 4.1: Location of the Hamasato test site on the north-western part of the Japanese main island of Hokkaido (a). The test site is located within the municipality of Horonobe (b). The distance to the shoreline of the Sea of Japan is approx. 250 m (modified from Hebig et al., 2014).

the injection of the tracer test solution will disturb the idealized cylindrical tracer plume and therefore change its shape into a more “*donut*” form (Hall et al., 1991), which could make hydraulic interpretation (e.g. estimation of groundwater flow velocity) even more challenging. The application of a chaser was reported from Hall et al. (1991), Istok et al. (1997, 1999), Luthy et al. (2000), McGuire et al. (2002), Meigs and Beauheim (2001), Molz et al. (1985), Nordqvist et al. (2012), and Tomich et al. (1973). There are many experiments reported with no application of a chaser, among them are Addy et al. (2002), Azizian et al. (2005), Davis et al. (2002), Hellerich et al. (2003), Kim et al. (2004), Schroth et al. (2001), and Vandenbohede et al. (2008).

However, it is not always clear how the decision in favor or against a chaser was made in published experiments. There is no evaluation of the positive or negative effects of the application of a chaser on the BTC of the actual test solution reported. We focus on the role of the chaser during push-pull tests and its potential influence on the BTC of the actual test solution. We

discuss the influence of the chaser and give suggestions for its application. Furthermore, we present a new method for estimation of the optimal chaser volume (which means the volume needed to fill the well and the gravel pack), when the effective porosity of the gravel pack is unknown. This new approach can help to avoid poor results from under- or overestimated chaser volumes during push-pull tests.

4.3 Study area

The Hamasato test site is part of the municipality of Horonobe, at the north-western coast of the northern Japanese main island of Hokkaido (Fig. 4.1). Horonobe is located within a sedimentary coastal basin, which is composed of poorly compacted Neozoic sand-, silt- and mudrocks. The distance of the well field to the shoreline of the Sea of Japan is approx. 250 meters and the elevation of the site is approx. 5 m above mean sea level. The experiments were performed in the groundwater monitoring well DD-2, which is screened within the upper aquifer of the Sarabetsu Formation (Fig. 4.2). The Sarabetsu Formation consists of poorly compacted quaternary alluvial deposits with interbedded strata by channeling of coarse sand and fine gravel channels, fine sand matrix, and clay lenses (Fig. 4.3).

In the uppermost part of the Sarabetsu Formation the aquifer is composed of sand and gravel. This aquifer is located between 93.8 and 99.0 m below ground level surface (bgl). At the top, the aquifer is confined by an alternation of silty fine sand and silt, and at the bottom by clay. No detailed information on hydraulic gradient and average groundwater flow velocity at the groundwater monitoring well are available, but the overall groundwater flow is directed from the recharge area located about 10 km in the north-east (Horonobe Anticline) towards the Sea of Japan in the south-west. From analysis of isotopic data from samples obtained from the Upper Sarabetsu aquifer and numeric steady-state groundwater flow simulation, groundwater ages range between 8,000 and 18,000 a (Ikawa et al., 2014). From the distance of the recharge area to the well and the groundwater ages an average groundwater flow velocity within the basin of about $0.56 - 1.25 \text{ m a}^{-1}$ can be derived. The diameter of the drilling is 11.6 cm and the depth is 100 m bgl. The inner

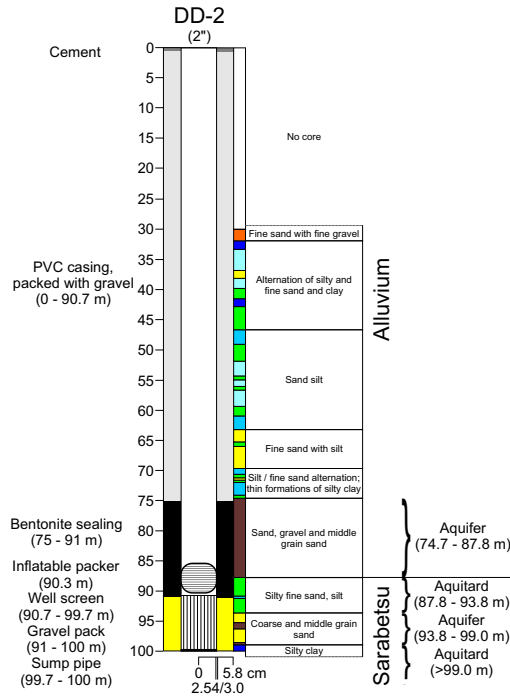


Figure 4.2: Profile of the Upper Sarabetsu aquifer and the construction of DD-2. Modified from Hebig et al. (2014)

diameter of the pipes and well screen of DD-2 is 5.08 cm (2") and the outer diameter is 6 cm. Therefore, the thickness of the gravel pack should be 2.8 cm and is constructed of pea gravel (5 – 10 mm). However, uncased air rotary drilling ("*mist drilling*") was used for the construction of DD-2 and it cannot be excluded that the excavated diameter may be larger than the size originally planned (11.6 cm). The screened section is located between 90.7 to 99.7 meters bgl and the gravel pack is constructed between 91 and 100 m bgl. An inflatable packer was used during injection and extraction. The bottom of the packer was installed in a depth of 90.3 m bgl. For the experiments it was necessary to estimate the volume of the pipes and of the gravel pack. The volume of the pipe V_{pipe} was calculated as the volume of a cylinder:

$$V_{pipe} = (r_{i_pipe})^2 \cdot \pi \cdot L_{pipe} + V_{dead} \quad (4.1)$$

in which r_{i_pipe} is the inner radius of the pipe and L_{pipe} is the length of the open pipe from the bottom of the packer down to the end of the well screen

and sump pipe (9.7 m). The term $V_{dead} = 5.7$ L and is the measured volume of the used pipes and tubes at the surface. The resulting volume of the pipe is 25.4 L. The gravel pack volume V_{gravel} was calculated as the volume of a hollow cylinder:

$$V_{gravel} = \left[(r_{borehole})^2 \cdot \pi \cdot L_{gravelpack} - (r_{o_pipe})^2 \cdot \pi \cdot L_{gravelpack} \right] \cdot n_{eff} \quad (4.2)$$

in which $r_{borehole}$ is the radius of the borehole, $L_{gravelpack}$ is the vertical thickness of the gravel pack (9 m), r_{o_pipe} is the outer radius of the pipe, and n_{eff} is the effective porosity of the gravel pack. As the effective porosity is unknown it was assumed as 0.4 during the calculations. Therefore the gravel pack volume is just a rough estimation. The calculated volume of the gravel pack is 27.9 L. The resulting chaser volume (which is composed of the volume of the pipes and the gravel pack) would then be:

$$V_{chaser} = V_{pipe} + V_{gravel} = 53.3 \text{ L} \quad (4.3)$$

The calculated volume was used as reference volume for the determination of the injection volumes of the experiments.

4.4 Experimental methods

4.4.1 Influence of the chaser on a push-pull tracer test BTC

The effect of a chaser on push-pull tracer test (PPT) BTC was studied with three PPT: two standard tests (PPT 1 and 2) using a chaser, and one test without using a chaser (PPT 6). The injection and extraction rate was set to 5 L min^{-1} in all tests. The injected volume in the no-chaser test was higher to compensate the missing chaser volume and therefore to ensure the same aquifer penetration depth as in the standard PPTs. The injected and extracted volumes are shown in Table 4.1 and were high enough to penetrate the aquifer. For the test solution and the chaser fluid, a solution

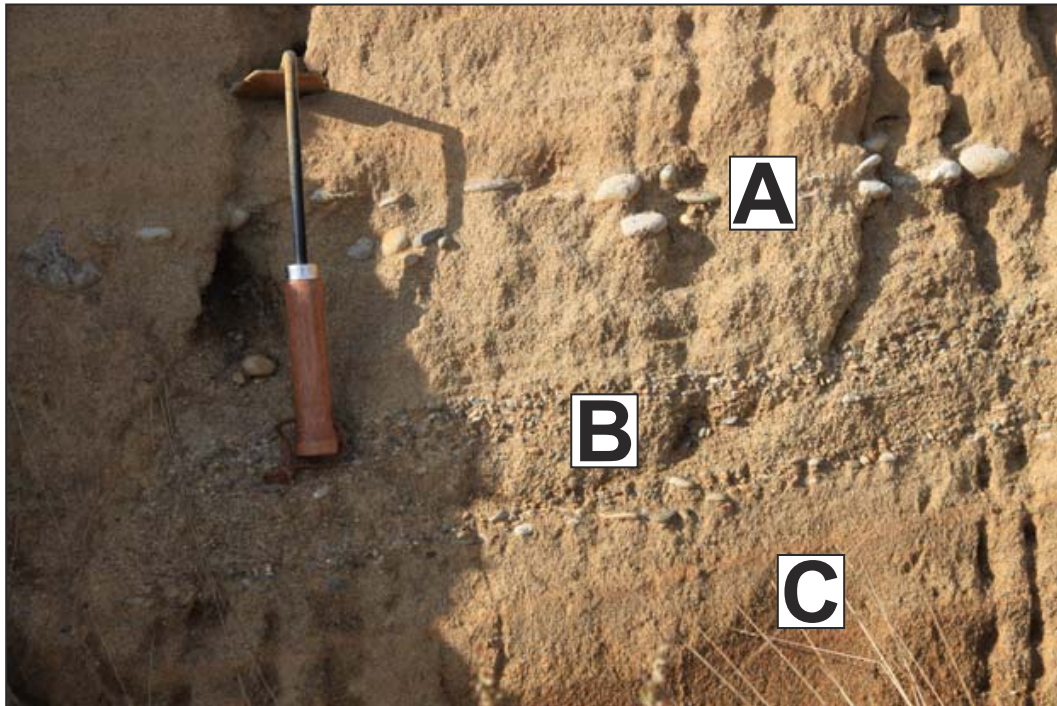


Figure 4.3: Sarabetsu Formation built up by poorly compacted quaternary alluvial deposits with interbedded strata from channeling. A – Fluvial pebble gravel; B – Coarse and fine gravel channels; C – Fine sand matrix. The outcrop is located near the city of Horonobe.

with groundwater composition was used. Prior to the injection the test solution was spiked with a 0.2% w/v uranine dye tracer solution (Wako chemicals, Osaka, Japan). The well was sealed by an inflatable packer (NEWJEC Inc., Tokyo, Japan) in the target depth (88 m bgl) before injection of the test solution using a submersible Nemo Pump 2NY30 (Heishin Ltd., Kobe, Japan). In the two standard tests PPT 1 and PPT 2, the two different solutions (uranine spiked test solution and uranine free chaser solution) were injected consecutively without any break or time delay and with the same flow rate. Immediately after injection, the test solution was extracted from DD-2 by pumping back using the same submersible Nemo Pump as for the injection. The time between the injection and extraction phase was some seconds. The extracted water was analyzed onsite in real-time for uranine concentrations by using a flow-through field fluorometer GGUN-FL30 (Albillia, University of Neuchâtel, Switzerland) and for the field parameters by a Horiba Multi Sensor W22XD (Horiba, Kyoto, Japan). In all tests, water was pumped back until the uranine concentration reached the background value.

4.4.2 Estimation of the optimal chaser volume

For estimation of the optimal chaser volume, six chaser tests (CTs) were performed. The CTs 1 – 6 were conducted with the identical procedure as the PPT 6. Only the injection volume was varied. The available basic parameters (length of well screen, diameter of well and borehole, Fig. 4.2) were used to estimate a theoretical chaser volume. For that, the effective porosity of the gravel pack was assumed as 0.4. With these input parameters a chaser volume of ~53.3 L was calculated. This calculation has been the only method for estimation of the optimal chaser volume so far. However, as the real effective porosity of the gravel pack remains unknown, this estimation may be inaccurate. Due to the expected high hydraulic contrasts between the three individual units (open pipe, gravel pack, and aquifer), different hydraulic behavior of the injected tracer plumes was expected. Therefore, six individual chaser tests (CTs 1 – 6) were conducted. A certain volume of chaser test solution, which was spiked with uranine, was injected and immediately pumped back. The injection and extraction rate was fixed at approx. 5 L min^{-1} in each test, but the injected volume was varied as shown in Table 4.2.

The smallest target injection volume of ~25 L (CT 1) was chosen according to the determination of the pipe volume presented above. The other injection volumes were just below (CT 2 ~40 L) and just above (CT 3 ~65 L) of estimated chaser volume (pipe + gravel pack) of ~55 L. All other injection volumes (CTs 4 – 6) were chosen randomly larger than these volumes. As the test setup of PPT 6 (from the first experiment) was similar to CTs 1 to 6 (similar flow rates, only one injected fluid), but with a larger injection volume of more than 1 m^3 , the results of PPT 6 were also used for the analysis of the chaser volume experiment. From the volume estimations above, it was expected that the tracer plume of CT 1 does not exit the pipe and well screen of the well. In CT 2 and 3 the tracer plume was expected to stay within the gravel pack or just exit the borehole. CTs 4 – 6 and PPT 6 represent the deeper penetration of the injected tracer plume into the Sarabetsu aquifer. As the flow behavior of the injected plume should differ between the three hydraulic units (open pipe, gravel pack, and aquifer), different BTC characteristics were expected between the individual tests.

Table 4.1: Injected and extracted volumes during the push-pull tracer tests (PPTs)

Test No.	Name	Injected volume test solution [L]	Injected volume chaser [L]	Overall injected volume [L]	Extracted volume [L]
PPT 1	Standard test 1	918	122	1,040	10,404
PPT 2	Standard test 2	916	122	1,038	10,367
PPT 6	No-chaser test	1,045	0	1,045	10,424

Table 4.2: Injected and extracted volumes during the chaser tests (CTs) and additionally of PPT 6 as very large chaser test

Test No.	Assumed location of the tracer front	Target injection volume [L]	Measured injection volume [L]	Target extraction volume [L]	Measured extraction volume [L]
CT 1	Approx. volume of pipes	25	25.5	290	255
CT 2	Somewhere within the gravel pack	40	41.0	410	410
CT 3	Just exit the gravel pack	65	66.6	666	666.0
CT 4	Extension into aquifer	90	90.8	916	916.2
CT 5	Extension into aquifer	120	123	1,228	1,228
CT 6	Extension into aquifer	155	148	1,584	1,584
PPT 6	Penetration deep into the aquifer	1,000	1,045	10,000	10,424

4.4.3 Temporal moment analysis

Temporal moment analysis was performed to identify potential trends or relations between the injection volume of a chaser and the resulting BTC. The method presented by Cunningham and Roberts (1998) was used, in which the n th temporal moment at a fixed observation point x was defined as

$$m'_n(x) = \int_0^\infty t^n C(x, t) dt \quad (4.4)$$

The zeroth temporal moment ($n = 0$) represents the mass recovery (area below the concentration curve). The n th *normalized* moment at a point x was defined as

$$M'_n(x) = \frac{m'_n(x)}{m'_0(x)} \quad (4.5)$$

The first normalized temporal moment then represents the mean recovery time at the observation point x . The mean recovery time provides a better measure than the first occurrence or the maximum breakthrough time, as this method considers also the late-time behavior of the tracer BTC (e.g. a long tailing induced by strong sorption-desorption processes). During flow within a homogeneous and isotropic unit a linear relationship between injection volume and mean recovery time is expected: larger tracer plumes should result in longer pumping times (Fig. 4.4: diamonds and solid line).

The influence of the injection volume can be eliminated by normalizing the mean recovery time to the injection volume:

$$M_v(x) = \frac{M'_n(x)}{v_{injection}} \quad (4.6)$$

Here the mean recovery time is dependent only on the hydraulic properties of the flow-through units (e.g. gravel pack, aquifer). In an idealized homogeneous and isotropic aquifer dispersion would produce a symmetric bell-shaped BTC and the resulting mean recovery time would be located in the center of the BTC. The normalized mean recovery time would be constant and independent from the injected volume, because in all parts of the model

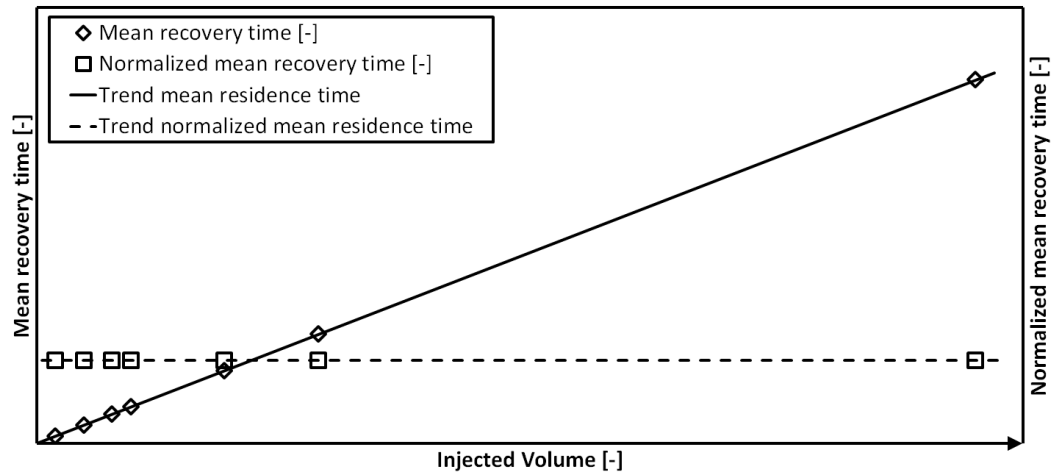


Figure 4.4: Theoretical mean recovery times and normalized mean recovery time vs. the injected volume under idealized conditions (homogeneous and isotropic aquifer, no dispersion or same dispersion in all spatial directions).

aquifer the identical hydraulic properties affect the tracer flow-through (Fig. 4.4: squares and dashed line). Consequently, there should be no significant difference or trend between the three push-pull tests (PPTs 1, 2, and 6) of the first experiment, if the use of a chaser did not alter the tailing of the BTC (as the usage of a chaser is the only difference between the three tests). In reverse, there should be some trend or changing behavior of the normalized mean recovery times of the CTs 1 – 6 and PPT 6, as the hydraulic characteristics of the flow-through units changed significantly at the interfaces between pipe, gravel pack, and aquifer. Accordingly, effects as dilution and dispersion, which determine the shape of the BTC, may be different in the different units.

To exclude potential effects of the experimental setup on the temporal moment analysis (e.g. tracer free dead volumes at the start of pumping), the main tracer breakthrough peak was set as starting point (0 s) for the calculation of the mean resident times.

4.5 Results and Discussion

4.5.1 Influence of the chaser on a push-pull tracer test BTC

In Fig. 4.5 the BTCs of the both standard tests PPT 1 and PPT 2, and the no-chaser test PPT 6 are shown as uranine concentration [ppb] vs. extracted volume [L] diagrams. In Fig. 4.6 the BTCs are normalized for the input concentration (c/c_0) and the injection volume (V/V_0).

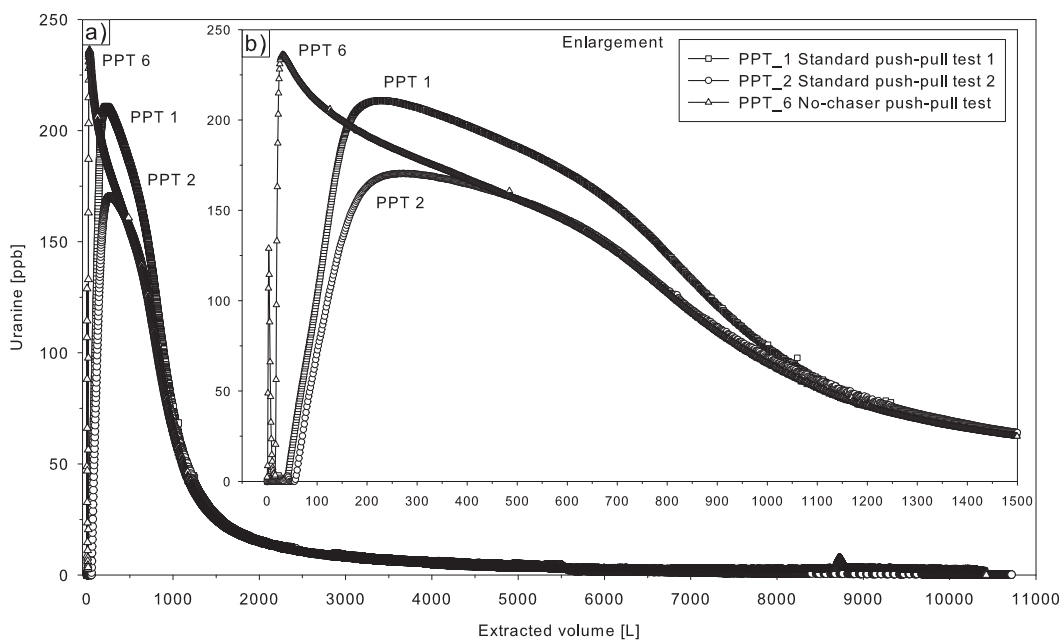


Figure 4.5: a) BTCs of the uranine dye tracer during the extraction phase of the standard push-pull tracer tests (PPT 1 and PPT 2) and the no-chaser push-pull test (PPT 6); b) Enlargement.

The shape of the two standard push-pull tests (PPT 1 and PPT 2) is similar. The uranine mass recovery is nearly the same, but the maximum concentration (both in absolute $\mu\text{g/L}$ and normalized c/c_0) is higher in PPT 1 than in PPT 2 (Table 4.3). Accordingly, the shape of PPT 1 is shifted upwards on the y-axis compared to PPT 2, but the curves meet after approx. one extracted injection volume (approx. 1,000 L in Fig. 4.5, or $V/V_0 = 1$ in Fig. 4.6). The shape of both BTCs and their mass recoveries are a strong indication for similar behavior of the uranine dye tracer in both tests and for reproducibility of the push-pull method. Slight differences between PPT 1

and PPT 2 might be induced by turbidity. To exclude these effects we used temporal moment analysis (see below), with which the behavior of the tailing can be characterized (independently of the absolute concentrations).

The BTC of the no-chaser test increases rapidly to $c/c_0 \approx 1.0$. After reaching its maximum the decrease of uranine concentration starts immediately. The decrease is relatively sharp at the beginning and becomes smoother with an inflexion point around 60 to 100 L. After the inflexion point the BTC of PPT6 is approximating to the BTCs of PPT 1 and PPT 2. Similar shape of tailing indicated similar flow behavior. This is an indicator that all the tracer solution, which was extracted after this point, experienced the similar hydraulic conditions during its transport (the aquifer). Given that no setup changes have occurred, the inflexion point between 60 to 100 L in the PPT 6 marks a significant change of hydraulic conditions and therefore allows a first visual estimation of the approx. location of the boundary between gravel pack and aquifer. The change of decrease at the assumed boundary between gravel pack and aquifer also shows that the gravel pack has indeed an effect on uranine transport.

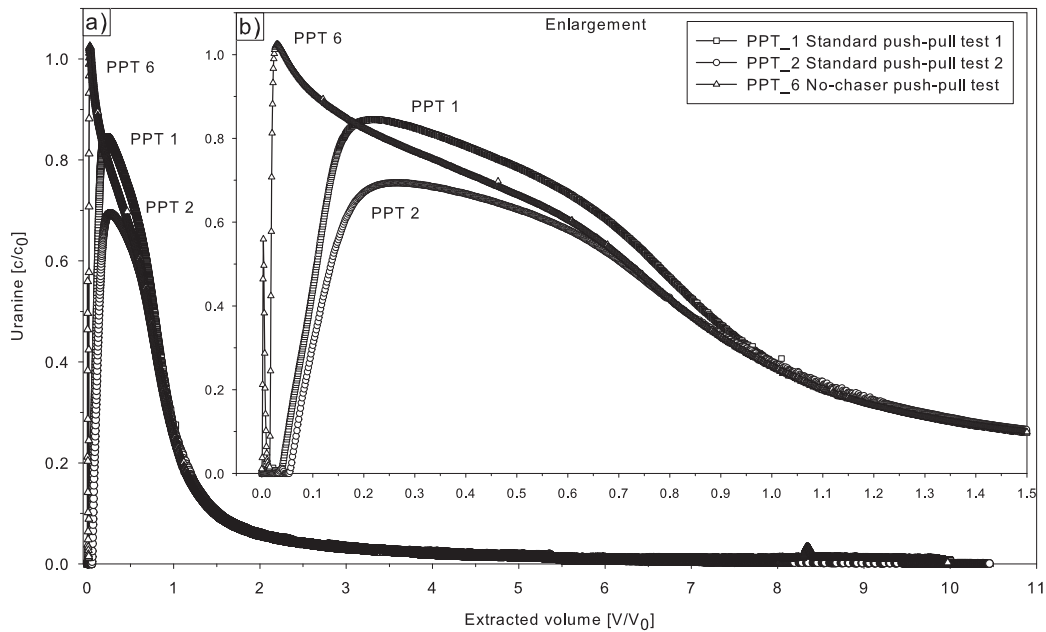


Figure 4.6: a) Normalized BTCs of the uranine dye tracer during the extraction phase of the standard push-pull tracer tests (PPT 1 and PPT 2) and the no-chaser push-pull test (PPT 6). Concentrations are normalized to input concentration $[c/c_0]$, extracted volumes are normalized to injected volume $[V/V_0]$; b) Enlargement.

Table 4.3: Maximum recovered normalized concentrations (c/c_0) = Normalized main peak concentration and uranine mass balances for the BTCs of PPT 1, 2 and 6

Test No.	Injected mass [mg]	Injected c_0 [$\mu\text{g/L}$]	Maximum extracted c/c_0	Mass recovery [mg]	Difference [mg]	Mass recovery [%]
PPT 1	227.32	249.43	0.84	195.30	32.02	85.91
PPT 2	210.17	232.18	0.76	167.40	64.78	79.65
PPT 6	238.30	230.43	1.02	187.11	51.19	78.52

Table 4.4: Maximum recovered normalized concentrations (c/c_0) = Normalized main peak concentration and uranine mass balances for the complete BTCs and the individual main and pre-peak

Test No.	Injected mass [mg]	Maximum c/c_0	Complete BTC			Main peak		Pre-peak	
			Mass recovery [mg]	Difference [mg]	Mass recovery [%]	Mass recovery [mg]	Mass recovery [%]	Mass recovery [mg]	Mass recovery [%]
CT 1	2.1	0.50	0.5	-1.6	24	0.4	18	0.1	5
CT 2	3.3	0.90	2.9	-0.4	88	2.5	77	0.4	12
CT 3	5.6	1.08	6.5	+0.9	116	6.0	107	0.5	9
CT 4	8.1	1.02	7.0	-1.1	86	6.8	82	0.2	2
CT 5	11.6	0.99	8.1	-3.5	70	8.0	69	0.1	1
CT 6	15.6	0.97	13.3	-2.3	85	13.2	85	0.1	0.6

In Fig. 4.7 the results of the temporal moment analysis are shown. In the no-chaser test PPT 6 a significant tracer mass was recovered very early during extraction of the amount of tracer which stayed within the gravel pack. For consideration of the resulting shift of the tracer breakthrough by using a chaser in PPT 1 and 2, the calculation of the first temporal moment and of the first normalized temporal moment of PPT 6 were corrected by excluding the first 122 L ($\approx 1,430$ s) from the calculation. This corresponds to the volume of the chaser used in the other two tests. The temporal moment analysis shows no obvious differences of the normalized mean recovery time between the three tests. Accordingly, the application of a chaser did not affect the tailing of the tracer BTC.

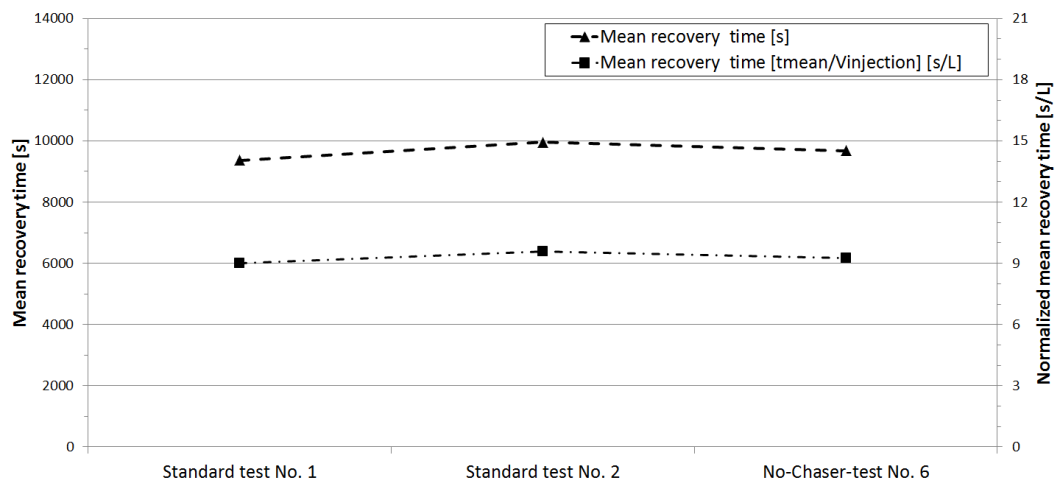


Figure 4.7: Mean recovery times of the three tracer plumes of PPT 1, 2, and 6 (triangles). The second graph (squares) shows the results of normalization of the mean recovery times to the injection volume for elimination of potential influences caused by the slightly different injection volumes between the three tests. The mean recovery time of PPT 6 (no-chaser push-pull test) was computed by skipping the first 122 L from the calculation, which represents the injected chaser volumes in the both standard tests.

The application of a chaser in PPT 1 and PPT 2 causes significant spreading of the BTC and decrease of the main peaks compared to PPT 6. The main mechanisms are probably dilution and dispersion of the actual test solution by the chaser. Otherwise, the mass recoveries do not vary significantly between the three tests. The shapes of the BTCs are comparable after approx. 100 to 150 L. From this volume on only test solution is extracted which completely penetrated the aquifer. Temporal moment analysis showed that the mean recovery time of the tracer plume is independent from the

application of a chaser. The application of a chaser has no negative influence on the tailing of the BTC, which is important for analysis (Becker and Shapiro, 2003; Schroth and Istok, 2005). Having in mind experiments with reactive tracers a chaser can help to separate the reactive tracer from the borehole.

4.5.2 Estimation of the optimal chaser volume

In Fig. 4.8 all uranine dye tracer BTCs of the chaser tests CT 1 – 6 are shown as absolute plots (ppb vs. extracted volume [L]) and in Fig. 4.9 as normalized plots of input concentration (c/c_0) vs. the injected volume (V/V_0). Additionally to the CT 1 – 6 also the no-chaser test PPT 6 from the first experiment is plotted in the both diagrams, as this setup can be handled like a very large chaser test with 1,045 L injection volume.

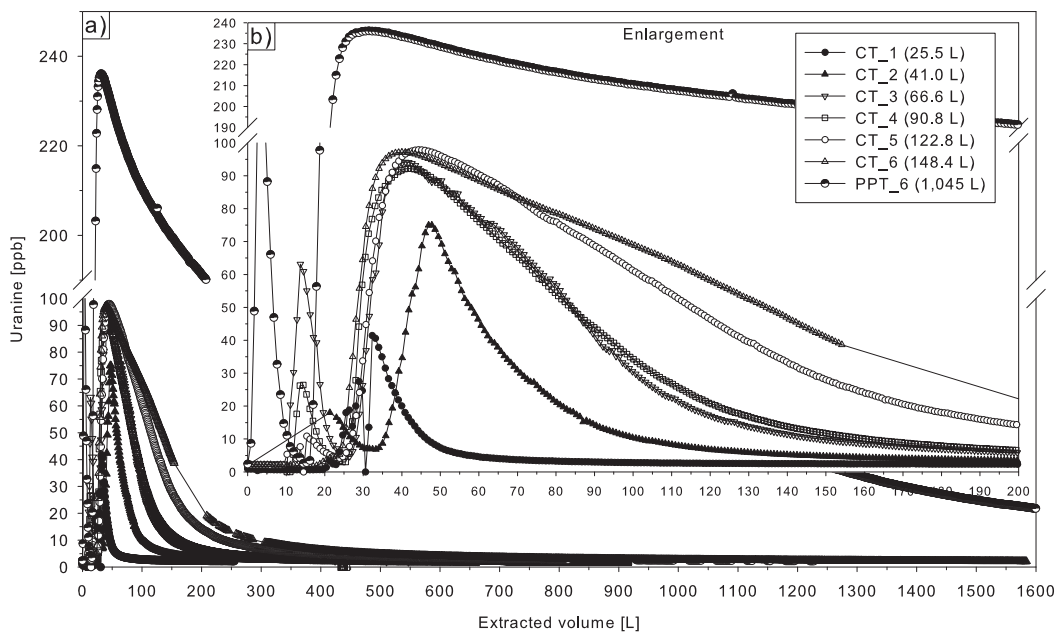


Figure 4.8: a) Absolute plots of the BTCs of the uranine dye tracer during the extraction phase of the chaser tests CT 1 – 6. The BTC of PPT 6 is shown for comparison only. The whole curve can be seen in Fig. 4.5; b) Enlargement.

All chaser BTCs follow the same trend: immediately after the start of the extraction a phase of no uranine recovery is observed (uranine concentration = background concentration). This is caused by the tracer free part of the experimental setup, which is located between uranine field fluorometer and

the injection/extraction switching valve. Its volume is approx. 6 L. The BTCs of the tracer are characterized by a smaller “pre-peak” and the actual main peak. Due to the repeated appearance in all tests, these pre-peaks are probably caused by some dead volume within the experimental setup. It can be assumed that this is some tracer free volume between packer and well screen. The larger the injected volume (from CT 1 to 6), the smaller was the ratio of the pre-peak to the overall mass breakthrough (Fig. 4.9).

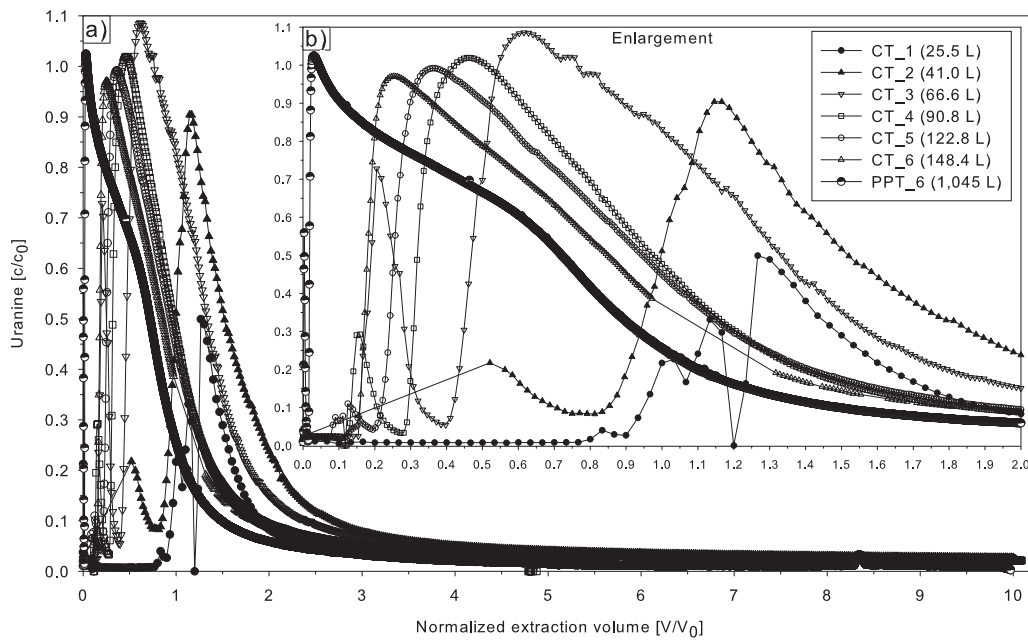


Figure 4.9: a) Normalized plots of the BTCs of the uranine dye tracer during the extraction phase of the chaser tests CT 1 – 6 and of PPT 6. Concentrations are normalized to input concentration $[c/c_0]$, extracted volumes are normalized to the injected volume $[V/V_0]$; b) Enlargement.

In both tests with the smallest injected volumes (CT 1 and CT 2) a very late peak and a very strong curve spreading (broad peak, slow increase and decrease of concentrations) was observed in the normalized plot (Fig. 4.9). The shape of both BTCs is nearly symmetric. In CT 1, the injection volume of approx. 25 L was intended to completely fill the pipes of DD-2 (Table 4.2). Obviously, this led to a strong dilution within the open pipe and accordingly to the observed low c/c_0 and poor mass balance (Table 4.4). In CT 2 the injected volume of approx. 40 L was chosen in order to fill a certain volume of the gravel pack (Table 4.2). The BTC exhibit a higher mass recovery and higher normalized peak. However, the increase of the main peak starts also

very late and shows a less pronounced increase as it would be expected. The BTC of CT 2 is still influenced by the mixing and dispersion between the injected uranine plume and the pristine tracer free water in the open well and in the large pores of the gravel pack.

The higher the injection volume, the earlier the breakthrough and the steeper the BTC. Also, the pre-peaks become steeper and narrower with increasing injection volumes. In the last chaser test (CT 6) with an injection volume of ~150 L the pre-peak nearly vanishes (Fig. 4.8 and 4.9). The behavior of the pre-peak in the test with the largest injection volume of 1,045 L (PPT 6) did not fit exactly in this trend. This may be caused by the significantly higher injected uranine concentration in the test compared to the CTs.

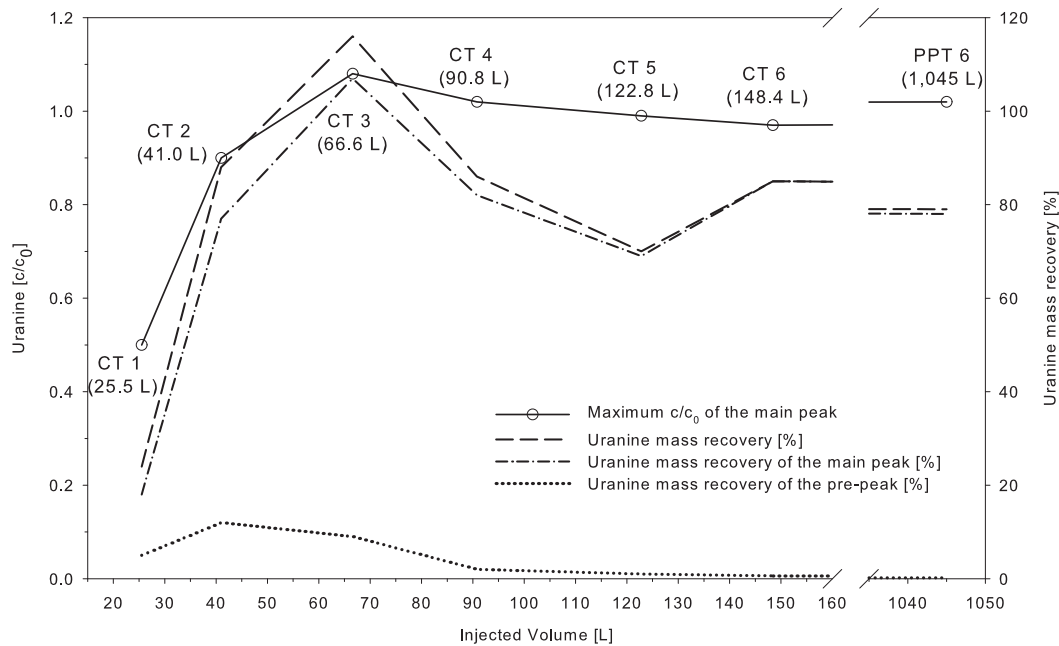


Figure 4.10: Relation of the main peak of every single chaser test to the respective injected test volume; It is assumed that the boundary between gravel pack and aquifer is represented by the moment, where the increase of c/c_0 -peak concentration and mass recovery reaches ~1 or 100%, respectively.

The maximum c/c_0 values are low in the first test and then rise up to values of approx. 1 in CT 3. In tests with higher injected volumes the maximum recovered normalized concentrations remain at this level (Fig. 4.10). The uranine mass recoveries follow the same trend as the maximum c/c_0 values: from the lowest injection volume the recoveries increase until CT 3. From

CT 4 on the maximum c/c_0 values and the mass recoveries fall to just below the value of 1 (Fig. 4.10). Normalized values and mass recoveries above 1 may be caused by turbidities during injection and extraction of the test solution and therefore results in some differences for the calibration of the field fluorometer for the injected and extracted concentrations.

From the qualitative analysis of the correlation between injection volume and shape of the BTCs (Fig. 4.9) and of the c/c_0 and the mass recoveries (Fig. 4.10) it can be concluded that somewhere between the injection volumes of CT 3 (66.6 L) and of CT 4 (90.8 L) the gravel pack was completely filled with chaser fluid.

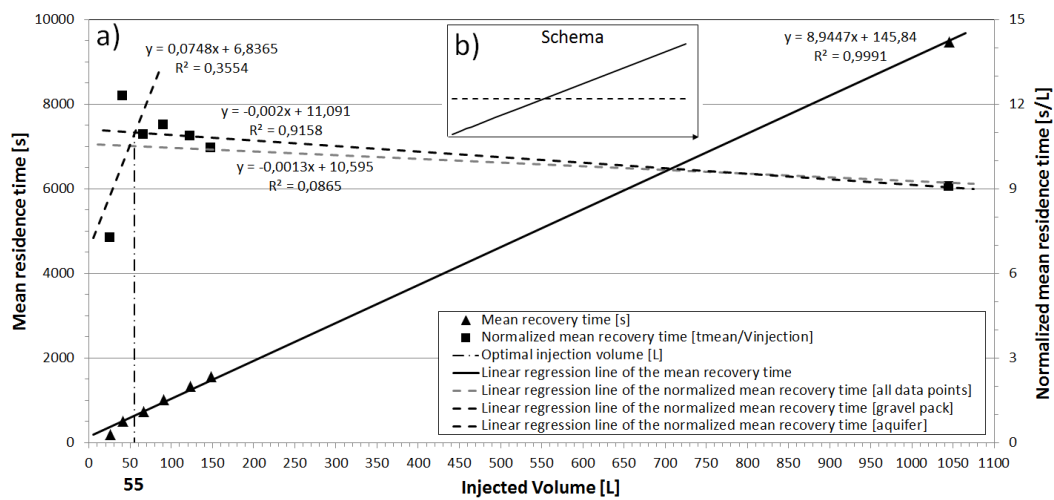


Figure 4.11: Mean residence times of the six chaser plumes of CT 1 – 6, and of the tracer plume of PPT 6 (triangles). The second graph (squares) shows the results of normalization of the mean recovery times to the injection volume to eliminate of the effects caused by the different injection volumes between the seven tests. The value of CT 1 was excluded from the calculation of the gravel pack regression line, as it represents the residence time within the pipe.

A clear linear correlation can be shown between the mean recovery time and injection volume (Fig. 4.11a). This can be expected, as a larger injected plume needs more time for recovery, if always the same pumping rates are applied. The second plot (squares) shows the same mean recovery times, but normalized to the respective injected volumes (Eq. 4.6). It is not possible to fit a linear curve with high correlation coefficient to the data points (gray dashed line in Fig. 4.11a). Best fit was achieved by separating the curves and fitting the points with two linear regression lines. The first regression line goes through the data points of CT 1 to CT 3 and is quite steep; the

second line goes through the data points of CT 3 to PPT 6 and shows a considerably lower decrease. Hence, the two regression lines with the significantly different slopes represent at least two different hydraulic units with different hydraulic transport behavior (dispersion, dilution), which cause the differences in the normalized mean recovery times. Obviously, these processes appear in an heterogeneous medium, which causes the deviation from the idealized horizontal model line (Fig. 4.11b). These findings are in accordance with the qualitative interpretation of the shape of the BTCs (Fig. 4.9) and the analytical interpretation of c/c_0 and mass recoveries (Fig. 4.10). The intersection of both lines marks the passage of the tracer volume from the gravel pack into the aquifer and accordingly the aimed chaser volume.

The resulting volume of the chaser at the intersection of the two regression lines is 55.4 L. This volume is an amount which is larger than the injected volume of CT 2 and less the injected volume CT 3. The volume is almost similar to the calculated number using geometrical assumptions which we made prior to the experiments (~53 L). Under the assumption that the other basic parameters, e.g. the gravel pack length and the borehole diameter, are correct, the chaser volume results in an effective porosity of the gravel pack of approx. 0.40, which is a realistic value.

4.6 Conclusions

From the results of our first experiment, where we compared push-pull tests with and without a chaser, we can draw the following conclusions: a push-pull test can be performed without a chaser, e.g. to provide a simple experimental setup (only one solution and therefore only one injection step), or to avoid dilution of the tracer plume and provide high maximum c/c_0 peaks in the BTC. Then, the shape of the tracer plume is not influenced by a chaser and may approximate more to the exemplary assumed cylindrical form. When a separation is required between the part of the BTC which is influenced by the aquifer hydraulics, from the experimental setup and gravel pack influenced part, the application of a chaser leads to results better accessible for interpretation. The use of a chaser in a push-pull test will cause more effort during the experiment (one additional injection step)

and will lower the main peak breakthrough due to mixing of the two fluids and dispersion/dilution among them. Also, by using a chaser the shape of the tracer plume within the aquifer becomes more like a donut (Hall et al., 1991) instead of a cylinder form. Therefore, at least hydraulic interpretation becomes more complex. But from our results, neither the shape of the tailing nor the tracer mass balance is negatively affected by the application of a chaser. Hence, it is suitable to use a chaser to obtain a complete recovery BTC (Nordqvist et al., 2012).

We conclude that the use of a chaser can be discounted, when the purpose of the push-pull test is the estimation of hydraulic characteristics of the aquifer (e.g. dispersion/dispersivity, groundwater flow velocities). Otherwise, we suggest the application of a chaser, when the chemical behavior of the aquifer is in the focus of research and reactions and mixing in the open well should be avoided (e.g. partitioning tests, estimation of first order degradation).

In our second experiment, we developed an easy and fast method to identify the required chaser volume to fill the tubes, pipes and gravel pack of the groundwater monitoring well when the actual gravel pack volume or effective porosity and/or the actual drilling diameter is unknown prior to the field experiment. The chaser test design can be realized quite fast due to low injection volumes. The additional work and expenses are manageable, as the same infrastructure is used as for the later main push-pull tests. The determination of the required chaser volume by temporal moment analysis is easy, and can be performed immediately in the field by using simple spread sheet calculations.

It is a further finding that the estimation of the chaser volume by the chaser tests led to results (55.4 L) almost identical to preliminary performed geometric calculations (53.3 L). This implies that the chaser tests may also be a suitable method to check the condition of the gravel pack and borehole. It may be an interesting future approach to use the presented chaser test method to determine the porosity of the gravel pack directly after the borehole excavation and its alteration over time. Potential applications may be to control the quality of a new well construction, or to monitor possible changes of porosity by clogging, alteration, or wash out over time.

4.7 Acknowledgments

The experiments are part of a project for the investigation of the hydraulic and hydrochemical properties of a coastal aquifer. The project is a collaboration of the Technische Universität Berlin (TUB, Germany) and the Geological Survey of Japan (GSJ) as a part of the National Institute of Advanced Industrial Science and Technology (AIST). The authors would like to thank Mr. Yuji Fujita and Mr. Shuji Daimaru (Asano Taiseikiso Engineering Co., Ltd.) and their team for the very helpful and straightforward technical support during the fieldwork.

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5 Synthesis

“Whereas it is practically impossible to observe separately all phenomena connected with a regime in groundwater flow, a correct theory discloses every feature and draws attention to the most important properties of the flow.”

József Tóth
in Tóth (1963)

In the chapters 2 to 4 the results of a literature study and two field experiments are presented. These studies are part of a PhD project and culminated in this thesis. The aim of the thesis was to summarize the current state of scientific knowledge about research on deep aquifers (chapter 2) and to suggest potential single-well methods, which may be applicable at the Hamasato field site on Horonobe, Japan. The identified single-well push-pull method was then tested for its applicability in the target depth of ~100 m, and used for the hydraulic and hydrochemical characterization of the Sarabetsu formation. The advantages and the limitations of the method, as well as potential improvements of the test setup were identified (chapter 3). In the follow-up study, the main recommendation was implemented, which was the proof of the reproducibility of the method and the evaluation of the influence of the individual parameters, like the injection/extraction rate or the chemistry/density of the test fluid on the test results (not shown in this thesis). A main purpose of the field campaign was to determinate the role of the chaser solution. Therefore, both the determination of its optimal volume and its influence on the BTCs of the test solution during a push-pull test were investigated (chapter 4).

5.1 Summary and discussion of the main findings

In the first study, which is presented in chapter 2, the increasing relevance of deep groundwater research was demonstrated by an extensive literature review, in which many hard to access publications and rare hard copy reports were assembled and analyzed. Due to the emerging requests on deeper aquifers and aquitards (e.g. for the final disposal of radioactive waste, storage of CO₂, production of geothermal energy, supply with alternative drinking water sources), an increasing number of scientific and commercial projects on the deeper underground were conducted in the recent past (Fig. 5.1). To meet the different aims of deep groundwater research, some of them are introduced as case studies in the first publication. Depending on the problem, research is directed to aquifers that contain large amounts of hot water, or formations with as little groundwater movement as possible.

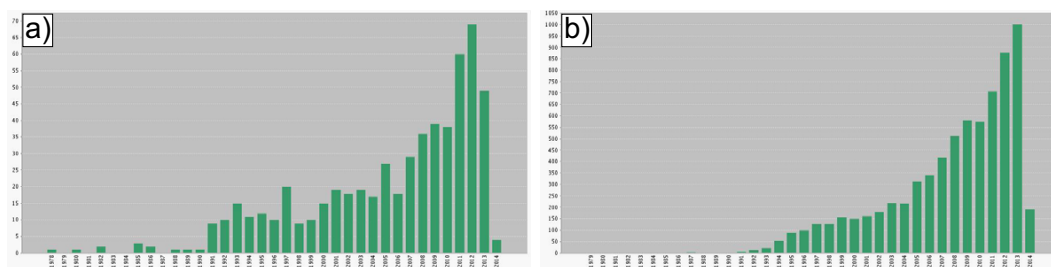


Figure 5.1: Number of peer-reviewed publications (a) and citations of these papers (b) in *Thomson Reuters Web of Science*, in which the term “deep groundwater” is included within the title, keywords, or abstract from the late 1970s to present. Retrieved 02.04.2014 from www.webofknowledge.com.

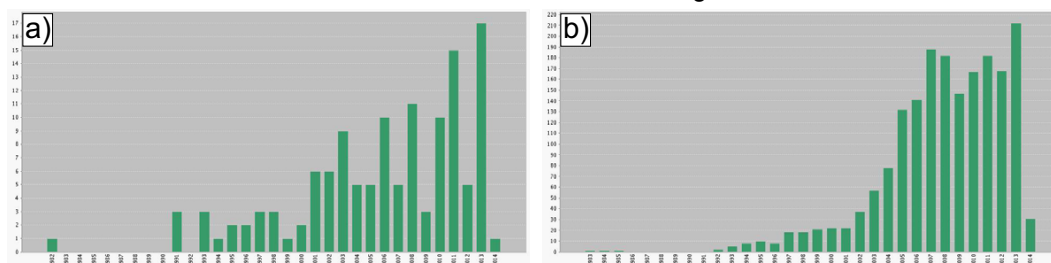


Figure 5.2: Number of peer-reviewed publications (a) and citations of these papers (b) in *Thomson Reuters Web of Science*, in which the terms “single well” and “groundwater” are included within the title, keywords, or abstract from the early 1980s to present. Retrieved 02.04.2014 from www.webofknowledge.com.

Usually, the access to the deeper underground is restricted to single-well settings (caused by the high costs and slow groundwater flow at these depths). This makes many well-established shallow aquifer methods not (e.g. multiple-well tracer tests) or only hardly (e.g. fluid logging) applicable. Accordingly, there is an increasing demand for simple and standardized test methods, by which hydraulic and hydrochemical characteristics of an aquifer in a single-well setting can be determined (Fig. 5.2).

As the Japanese research for final repositories for radioactive waste is mainly conducted in deep coastal sedimentary basins, the investigation of these groundwater systems is also bound to single-well settings. At the beginning of the project it was therefore intended to identify standardized methods by revising the published literature, which may be suitable for aquifer characterization in the case of the special needs in our project at the field site at Hamasato, Horonobe (Japan). However, the review process showed that the published methods are often only suitable for very specific conditions and therefore neither generally applicable to other settings nor in particular to the conditions at Hamasato. Also varying goals of the individual research projects are another reason why standardized procedures do not exist so far.

However, to identify a suitable test method, the Single-Well Injection-Withdrawal test (push-pull tracer test) was decided as a potential method in the second study, which is described in chapter 3. The push-pull test was already reported as a suitable single-well method to characterize chemical properties and processes (e.g. redox reactions, microbial degradation of organic contaminants) in shallow (<20 m depth) single-well settings in the past (e.g. Cunningham et al., 2001; Cunningham and Roberts, 1998; Haggerty et al., 1998; Istok et al., 1997, 1999, 2001, 2001; Kim et al., 2004, 2005; Lessoff and Konikow, 1997; McGuire et al., 2002). Furthermore, some authors presented approaches for the determination or estimation of hydraulic parameters, especially groundwater flow velocity (Leap and Kaplan, 1988), dispersivity (Hellerich et al., 2003), and effective porosity (Hall et al., 1991), by using the push-pull method. The published experiences with the push-pull method made it a promising technique to solve our questions.

In the next step, which is presented in chapter 3, this method was tested in a deeper (~100 m) single-well setting at the Hamasato site. The aim was

to gain information about the hydraulic and hydrochemical characteristics of this aquifer. Two push-pull tests were performed in a field campaign at the site near Horonobe, Japan, in 2010. The test site is located in a coastal sedimentary basin and therefore questions regarding the saltwater-freshwater interface and its movement (e.g. due to sea level change) were within the focus of the study. To simulate potential effects of a moving interface, the test solutions injected in the two tests differed in their chemical composition (artificial produced brackish water and deionized water, respectively). By analyzing the obtained conservative and reactive BTCs it was possible to describe the hydrochemical response (sorption-desorption, ion exchange, dissolution) of the aquifer on intruding fluids with different mineralizations. The flushing of an aquifer with water different from the pristine groundwater may change even the hydraulic characteristics of a formation (by closing or opening pore spaces by precipitation or dissolution reactions).

One finding was that the flushing of an aquifer with a lower mineralized fluid impacts the aquifer more than a higher mineralized fluid. This effect can cause serious problems, e.g. managed aquifer recharge (MAS) or for ASR, which are often operated in coastal areas and therefore in brackish aquifers. Intrusion of freshwater may induce strong mobilization of ions by cation exchange or desorption (Vanderzalm et al., 2010), decrease the hydraulic conductivity by clay swelling (Mehnert and Jennings, 1985) or clogging of pores (Pavelic et al., 2007), cause mineral precipitation or dissolution processes (Vanderzalm et al., 2010), and mobilization of metals (by changing the pH value of the aquifer). Due to the complexity of the various concurrent proceeding processes and the dynamic nature of saltwater-freshwater environments, these systems are not fully understood so far. Examples for such dynamic systems are not only saltwater-freshwater interfaces in coastal areas, which are dynamically moving driven by natural or man-made factors (climate change, pumping activities for irrigation or drinking water supply, ASR). Also deep final repositories may induce dynamic changes of the mineralization of the groundwater both, during the construction and operating phase (by pumping) and during the closing phase (by recovering of the groundwater table). The resulting hydrochemical processes may have a significant impact of the safety assessment on such constructions.

The intrusion of saltwater (from the sea by sea level increase) or fresh water (from the recharge areas, due to sea level decrease) and according movement of the saltwater-freshwater-interface within the coastal sedimentary basin of Horonobe is a very likely scenario for the near future (Fig. 5.3a). For this area, values of about -120 m to +5 m relative to the present day sea level are reported for the last 1.5 Ma (Fig. 5.3b). As a dynamic development of the saltwater-freshwater interface caused by sea level rise is most likely in many coastal aquifers worldwide already in the near future, the findings regarding the hydrochemical alterations of an aquifer due to saltwater intrusion or refreshing bear a high relevance for many present and future problems – e.g. safe supply with potable water in coastal areas.

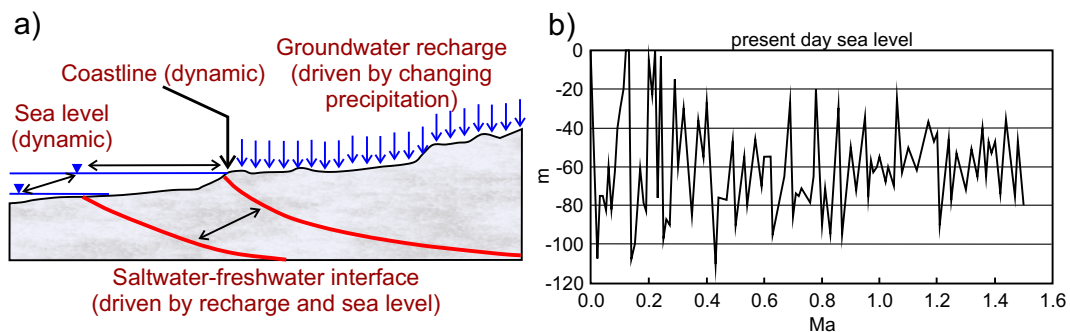


Figure 5.3: a) Dynamics of the saltwater-freshwater interface driven by changing sea level and groundwater recharge (modified from HRISE, 2010). b) Evolution of the relative sea level from 1.5 Ma until present in Horonobe (modified from JAEA, 2010).

Though, the push-pull test delivers relevant findings about the hydrochemical behavior of the aquifer, also the limitations of the method were revealed during the field campaign. By qualitative analysis of the BTCs it was shown that flow and transport within the Sarabetsu aquifer is dependent on the salinity of the fluid. Observed local peaks within the decreasing tracer BTCs may be an indicator for transport by multi-layer flow or through preferential flow paths, like channels, which would imply both higher transport velocities and distances than prior expected. Despite these interesting qualitative interpretations, a quantitative analysis of the results is desirable. It turns out that the published approaches for determination of the regional groundwater flow velocity by Leap and Kaplan (1988); Hall et al. (1991) are not feasible for more complex flow, as it was found in the heterogeneous fluvial Sarabetsu aquifer (including clay lenses, fine sand matrix, and fine to coarse gravel lenses; Fig. 3.3). The mentioned method of Leap and Kaplan (1988), which

was refined by Hall et al. (1991), uses a simplified geometric solution, in which the tracer plume movement is dominated by advective transport with the regional groundwater flow (“drift”, Fig. 5.4). For the calculation the aquifer thickness has to be known and the effective porosity has to be estimated. Furthermore, the arrival of the “center of mass” of the tracer during extraction is used in relation to the moment of injection:

$$v_a = \frac{\left[\sqrt{\left(\frac{Q}{\pi n b} \right)} \sqrt{t} \right]}{T} \quad (5.1)$$

with

$$t = t_a - t_p \quad (5.2)$$

$$T = t_a - t_i \quad (5.3)$$

and

t_i = Begin of drifting of the tracer plume (after injection)

t_p = Begin of pumping back (after drifting phase)

t_i = Return of the “center of mass” to the well (during extraction phase)

In the case of our experiment, the “Leap-&-Kaplan”-calculation led to groundwater flow velocities of $\sim 0.82 \text{ m d}^{-1}$ (brackish water) and $\sim 0.69 \text{ m d}^{-1}$ (deionized water). These values are unexpectedly high, due to the depth of the aquifer. Ikawa et al. (2014) showed by isotope analysis and groundwater flow simulations that the age of groundwater in the Upper Sarabetsu aquifer ranged between 8,000 and 18,000 ka in the area of the Hamasato field site. The recharge area is about 10 km in the north-east of Hamasato (Fig. 3.2: II – Horonobe Anticline). Therefore, the overall resulting regional groundwater flow velocity is in the order of $0.56 - 1.25 \text{ m a}^{-1}$. Additionally, Ikawa et al. (2014) pointed out that the chloride concentrations suggest the maximum groundwater flow during the last glacial age, which would imply even slower groundwater flow currently.

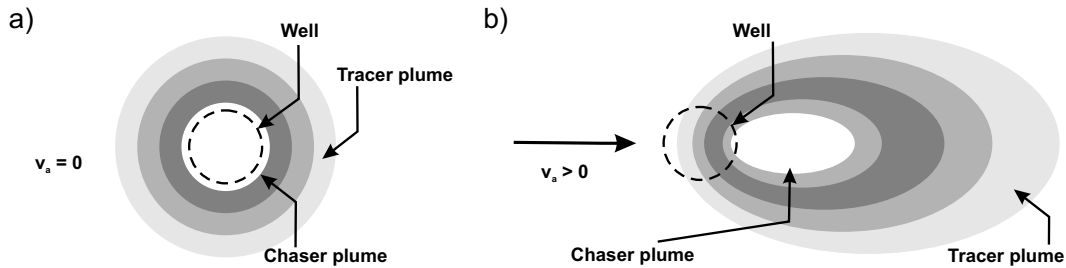


Figure 5.4: a) Schematic expansion of the injected solution during the push-phase under the assumption of homogeneous and isotropic conditions, when no regional groundwater flow is assumed (“donut shape”, Hall et al., 1991). b) Deformation of the injected solution caused by drifting forced by regional groundwater flow under the assumption of homogeneous and isotropic conditions (based of the conceptual model of Leap and Kaplan, 1988).

The simplification of a single moment of injection, the required long drifting time (to minimize the disturbing effect of the injection of the natural flow field), and – most important – the assumed homogeneity of the aquifer led to an unknown uncertainty of this analytical method in more complex field cases, like the heterogeneous (fluvial) coastal Sarabetsu aquifer. The quantitative analysis of the hydraulic behavior of the injected fluid remains challenging. Sufficient methods for hydraulic analysis, like groundwater flow velocity or dispersion/dispersivities, are not available so far. This is ultimately caused by the unknown distance, which the test fluid was transported within the aquifer during the experiment. However, by curve fitting of the chloride and the lithium breakthrough, the hydraulic parameters effective porosity and longitudinal dispersion coefficient could be estimated.

During the field work and the successive data analysis and interpretation some unexpected technical difficulties within the test setup were revealed. It turned out that the fluorescence signal of the (prior to the experiment) as conservative assumed tracer uranine is very sensitive to both turbidity (in our case caused by gas bubbles, not by particles) and changes of the pH value (Fig. 5.5). In the beginning, degassing or change of pH were not considered as they had not been reported before. Also, some compromises about the test setup, which had to be made prior to the execution of the experiment, led to difficulties during the further analysis procedure. For legal reasons it was necessary to spontaneously exclude some solutes (nitrate, strontium, fluoride) from the injection solution, which were originally intended to deliver valuable results about sorption and oxidation-reduction processes.

Furthermore, it was not possible to install downhole measurement devices (e.g. for hydraulic head, field parameter, or fluorescence tracer) within the packered interval of the well due to technical limitations. Therefore, all field parameters and the fluorescence tracer were measured after extraction from the ~100 m deep well on the ground surface, which caused the observed gas release.

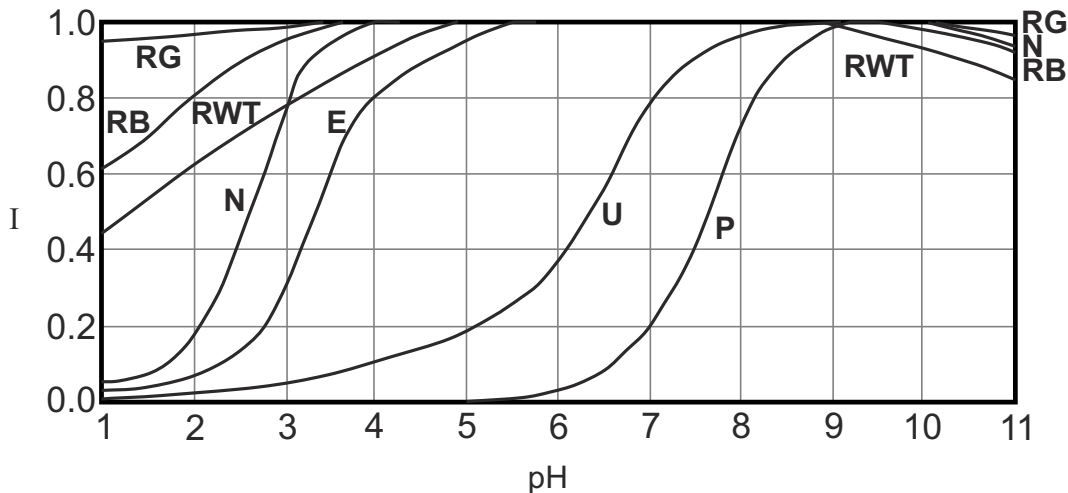


Figure 5.5: Correlation of fluorescence intensity I and pH for selected fluorescence dye tracer. U = Uranine, E = Eosin, RB = Rhodamin B, RG = Amidorhodamin G, RWT = Rhodamin WT, P = Pyranin, N = Natrium-Naphthionat (Käss, 2004).

Summarizing the results and experiences from the first field campaign, it can be concluded that the push-pull test is a seemingly easy and fast aquifer test method for single-well settings. Its main field of application is the investigation of hydrochemical questions. However, the execution of the method needs an accurate planning of the test design and a very careful preparation and performance of the experiment. Later changes of the setup may quickly lead to conflicts in data analysis and interpretation. Also, conditions specific to different aquifers may arise (e.g. gas release), which may lead to unexpected difficulties for the setup, which not may be correctable in the field.

The experiences and improvements of the single-well test setup from this study were implemented in the guideline of recommended aquifer test methods for the search and planning of the Japanese final repository for radioactive waste.

During interpretation of the results of the first experiment also the question arose, how the experimental design influences the BTCs. How to separate the influence of the aquifer on the shape of the BTCs from the characteristics of the different fluids used and from the influence of the test setup itself, respectively?

In the third paper, which is presented in chapter 4, partial results of the 2012 field campaign at the Hamasato field site in Horonobe, Japan, are shown. The whole study aimed at proving the reproducibility of the method and to evaluate the influence of the experimental setup or variations of the setup on the recovered tracer BTCs. The goal of the sub-project, which is presented in this thesis, was the investigation of the chaser and its influence on the tracer BTC. Despite its often reported application (e.g. Hall et al., 1991; Istok et al., 1997, 1999; Luthy et al., 2000; McGuire et al., 2002; Meigs and Beauheim, 2001; Molz et al., 1985; Nordqvist et al., 2012; Tomich et al., 1973), the role of the chaser was unknown so far. The injection of untreated water disturbs the flow field and produces a tracer free spot within the previously injected plume (Hall et al., 1991). Also the influence of the applied chaser volume was not yet investigated. There were no criteria defined up to date on how to choose an appropriate chaser volume, if the exact effective pore volume of the gravel pack surrounding the well is unknown. However, a too small or too large volume may cause further difficulties during BTC interpretation.

Therefore, two different experiments were conducted to answer two questions: What is the effect of a chaser on the tracer BTCs? What is the optimal chaser volume? Both experiments described in the paper delivered valuable findings for the understanding of the role of the chaser within a push-pull test setup. From the first experiment, in which the BTCs of two push-pull tests with an applied chaser were compared to the BTC of a push-pull test without a chaser, it can be concluded that the shape of the BTC during the tailing is not affected by the application of a chaser. Accordingly, the use of a chaser has no negative influence on experiments, in which the hydrochemical behavior, e.g. partitioning coefficients or degradation rates, is within the research focus. For these experiments it is more relevant that the injected reactive solutes do not react within the open borehole or groundwater monitoring well, which can be avoided by a chaser solution.

Otherwise, the use of a chaser should be avoided, when the focus is on hydraulic characterization, as we found some advantages of avoiding the use of a chaser. The maximum peak concentration is significantly higher, when no chaser is mixing with the tracer labeled test solution. The shape of the injected plume is more consistent with the model conception of a cylindric form, which makes hydraulic interpretation more easy. However, neither the shape of the tailing nor the tracer mass balance is negatively affected by the application of a chaser. Hence, it is suitable to use a chaser to obtain a complete recovery BTC (Nordqvist et al., 2012). This helps to separate the part of the BTC, which is mainly aquifer influenced, from the part, which is mainly influenced by the well constructions.

To answer the second question on the best volume of the chaser, we developed a method to identify the required chaser volume to fill the tubes, pipes, and the gravel pack of the groundwater monitoring well, but not to intrude into the aquifer. The test can be realized quite fast due to the low required injection volumes and the additional efforts are manageable, as the same infrastructure is used as for the later main push-pull test. The determination of the required chaser volume is easy, and can be performed immediately in the field (if an on-site monitoring system for tracer measurement is used) by using temporal moment analysis. The chaser volume method is planned to apply for a patent in Japan.

However, also in the second field campaign some of the technical limitations, which were already observed in the first campaign from 2010, could not be solved. While this time it was possible to install a downhole measurement device for the field parameters and the hydraulic head, no possibility was found to install the available downhole fluorometer within the packered section. Therefore, comparable to the first experiment, the uranine concentrations could be measured only at the surface by a flow-through measurement device after extraction from ~100 m. The resulting shift of the BTCs (caused by the tracer free section of the pipes at the surface) lead to difficulties in data analysis and needed additional calculations to correct this effect.

Optimal results are achieved by installing downhole equipment throughout the whole experiment. The transport of the groundwater and the test solution

from larger depths through long pipes and tubes towards the surface is a main factor for significantly increasing the methodological error.

5.2 Open questions and outlook

During the various literature studies and field experiments, as well as in many discussions with other researchers during conferences and meetings, several questions on push-pull tests as single-well method for aquifer characterization still remain open.

So far, no satisfying tool or method is available for sufficient hydraulic interpretation of the BTCs. The main reason for that is the unknown travel distance of the tracer plume within the aquifer. In addition, the flow regime and the respective flow paths make an interpretation difficult. During injection and withdrawal a radial symmetric flow field is established within one well, in the first step with positive flow direction and in the second with negative. This implies that the first amount of tracer, which is injected at the start of the test, penetrates the aquifer the furthest and also has the longest reaction time in the aquifer. Hence, the last amount of tracer penetrates much less and resides much shorter in the aquifer. All transport processes (as dispersion, sorption-desorption, etc.) affect the solutes two times – the first time during the transport into the aquifer, the second time during transport out of the aquifer (Fig 5.6). Becker and Shapiro (2003) defined the two main transport processes of a conservative tracer during a push-pull test as “*heterogeneous advection*”, which is describing mass spreading related to the separation of advective pathways, and “*hydrodynamic dispersion*”, which describes mass spreading related to local mixing. Following the model conception of radial flow (Hoopes and Harleman, 1967), it is expected that the hydrodynamic advection is a reversible process, when the flow field is reversed (in the pull-phase). In contrast, hydrodynamic dispersion will always increase the mass spreading, independently of the actual flow direction and therefore is an irreversible transport process. Becker and Shapiro (2003) conclude that the observed tailing of a BTC in a push-pull test must be caused by the tracer mass spreading from dispersion, while the tailing caused by advective transport is reversed due to the reversed flow field (Becker and Shapiro,

2003). This characteristic behavior may be a starting point for a more sufficient approach to describe and to analyze the push-pull tracer test with a numeric model.

A further challenge is the overprinting of the natural groundwater flow direction and flow velocity during the injection/extraction by using comparable high flowrates (especially in the low-flow regimes of the deeper underground). Consequently, groundwater flow velocity, hydrodynamic dispersion or dispersivities, and effective porosity cannot be easily determined with classic numerical models or curve fitting to the transport equation. As expected, simple analytical solutions do not seem to be able to reproduce the complex flow behavior.

A feasible and easy approach to avoid the effect of overprinting natural groundwater flow by high injection rates may be a combination of the push-pull method with another single-well technique: Riemann et al. (2002) suggested to conduct the injection period of the experiment (the push-phase) as a point-dilution test, in which the tracer is not injected dissolved in a large bunch of water, but is allowed to drift under natural flow conditions. Afterwards the tracer can be extracted again (the pull-phase) to recover the BTC and to investigate the hydrochemical characteristics of the aquifer. As a first step to study this promising strategy, a point dilution test was performed after completion of the field experiments of 2012 in the well of DD-2 in Horonobe. The recovery of the plume is planned for the end of 2014 or 2015 and may further improve our understanding of the effect of a push-pull test on the flow processes within the aquifer.

However, also a deeper theoretical understanding of the processes during all phases of a push-pull test, e.g. the influence of heterogeneity or preferential flow paths, density driven flow, or the hydrochemical and hydraulic impact of fluids with varying mineralizations or temperatures is necessary. We propose a bunch of systematic laboratory tests, in which the transport characteristics under the special flow field of a push-pull test can be simulated under controlled boundary conditions (e.g. sandbox experiments; Barns et al., 2012; Knecht et al., 2011) and a comparison of a push-pull test BTC with a standard well-to-well tracer breakthrough becomes possible (e.g. column studies; Huang et al., 1995).

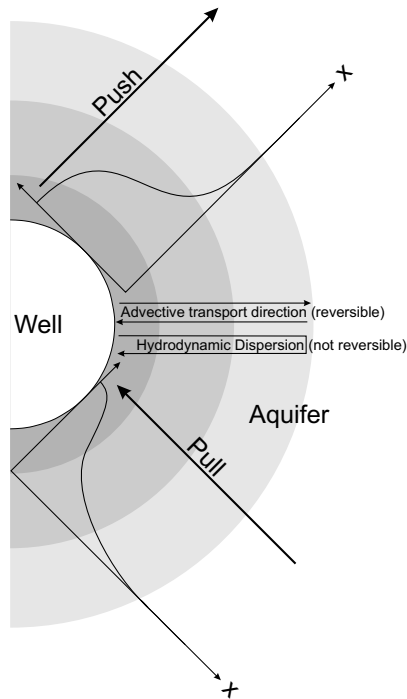


Figure 5.6: The effect of the irreversible dispersion on the tracer BTC during a push-pull test following Becker and Shapiro (2003).

Also the post-processing regarding hydraulic analysis has to become more standardized and repeatable. Though for many experiments parameter estimation by curve fitting or modeling (Haggerty et al., 1998; Hellerich et al., 2003; McGuire et al., 2002; Nordqvist et al., 2012; Phanikumar and McGuire, 2010) is reported, most of these approaches are very specific simulations, which are only applicable for the particular field study and not or only hardly transferable to other settings. Moreover, the numeric code is often not accessible (due to pay walls) or not executable for normal non-computer scientists. Therefore, the gained BTCs and experiences regarding the transport should be used for a better analytical understanding and implementation into a generally available analysis software for curve fitting procedure. That would open up the push-pull test a variety of new applications for aquifer and process characterization.

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6 List of Figures

1.1	Theoretical flow pattern and boundaries between different flow systems in the regional scale (modified from Tóth, 1963) . . .	2
1.2	Comparison of a) multi-well setting and b) single-well setting (modified from Zeilfelder et al., 2014)	6
1.3	Disturbance of the natural groundwater flowfield (from the left to the right) caused by the high hydraulic conductivity contrast of an open well or borehole. The flux through the borehole or well, q^* , differs from the flux through the aquifer, q . Here: $q < q^*$ (modified from Palmer, 1993)	7
1.4	Schema of idealized BTCs during injection (-V) and extraction (+V) phase of a push-pull test (modified from Istok et al., 1997)	10
2.1	Locations of the case studies in Central Europe and the UK .	26
3.1	Location of the Hamasato test site on the north-western part of the Japanese main island of Hokkaido (a), Japan (b). The test site is located within the municipality of Horonobe (c). The distance to the shoreline of the Sea of Japan is approx. 250 m. The cross section of Fig. 3.2 is marked with AB.	71
3.2	Schematic cross section (A – B in Fig. 3.1c) of the coastal basin of Horonobe. The blue arrows represent the regional groundwater flow model. “JAEA” represents the location of the Underground Research Laboratory Horonobe, which is operated by the Japan Atomic Energy Agency (JAEA). I – Teshio Mountains; II – Horonobe Anticline (groundwater recharge area); III – The wetlands of the Rishiri-Rebun-Sarobetsu National Park (groundwater discharge area); IV – Sea of Japan (groundwater discharge area). Modified after H-Rise Institute Horonobe, oral presentation, September 29, 2010	72

- 3.3 Sarabetsu Formation built up by poorly compacted quaternary alluvial deposits with interbedded strata from channeling. (a) A: Coarse sand and fine gravel channels; B: Fine sand matrix; C: Clay lens; (b) D: Fluvial pebble gravel; E: Coarse and fine gravel channels; F: Fine sand matrix. Both outcrops are located near the city of Horonobe. 73
- 3.4 Profile of the upper Sarabetsu aquifer in the area of the well screen of DD-2. 74
- 3.5 Piper plot of the brackish water push-pull test. The arrows track the chemical evolution of the pumped water from the first to the last sample. The reaction times are noted for selected samples. One linear path (reaction time between 22.7 h and 22.8 h) is conservative end-member mixing of the chaser (=natural groundwater) with the prior injected test solution. Second linear path is conservative end-member mixing of the injected test solution with the pristine groundwater. 80
- 3.6 BTCs of uranine dye tracer, field parameters, and ions during the injection (“push”) and the extraction (“pull”) phase of the brackish water push-pull test. Reaction time is represented by the lower x-axis and starts at the beginning of injection of the test solution. The injected or pumped water volume is represented by the upper x-axis, which is not linear due to the varying flow rates during injection and extraction. The dotted line marks the end of injection of the chaser (and therefore the beginning of the drift phase). The solid line marks the start of the extraction phase. The dashed line marks the moment, when pumped and injected volume is equal. 81
- 3.7 Piper plot of the deionized water push-pull test. The arrows track the chemical evolution of the pumped water from the first to the last sample. The reaction times are marked for selected samples. 84

- 3.8 BTCs of uranine dye tracer, field parameters, and ions during the injection (“push”) and the extraction (“pull”) phase of the deionized water push-pull test. Reaction time is represented by the lower x-axis and starts at the beginning of injection of the test solution. The injected or pumped water volume is represented by the upper x-axis, which is not linear due to the varying flow rates during injection and extraction. The dotted line marks the end of injection of the chaser (and therefore the beginning of the drift phase). The solid line marks the start of the extraction phase. The dashed line marks the moment, when pumped and injected volume is equal. 86
- 3.9 Uranine fluorescence signal (black circles) and observed turbidity (gray lines) in the brackish water test (a) and in the deionized water test (b). The dotted line marks the end of injection of the chaser (and therefore the beginning of the drift phase). The solid line marks the start of the extraction phase. The dashed line marks the moment, when pumped and injected volume is equal. 88
- 3.10 Corrected uranine fluorescence signal [mV] in the brackish water test (a) and in the deionized water test (b). The gray dots represent the measured uranine fluorescence signal, the thin gray line represent the observed pH values, and the black circles represent the for the pH value corrected uranine fluorescence signal. The dotted line marks the end of injection of the chaser (and therefore the beginning of the drift phase). The solid line marks the start of the extraction phase. The dashed line marks the moment, when pumped and injected volume is equal. 89

3.11 Fitted lithium BTC of the brackish water test (a) and chloride BTC of the deionized water test (b). Best fit (gray solid line) was obtained assuming conservative transport and mass loss due to mass transfer between mobile and immobile zones (single rate mass transfer). The black crosses represent the measured concentration values of chloride (a) and lithium (b). The solid line marks the start of the extraction phase. The dashed line marks the moment, when pumped and injected volume is equal.	90
4.1 Location of the Hamasato test site on the north-western part of the Japanese main island of Hokkaido (a). The test site is located within the municipality of Horonobe (b). The distance to the shoreline of the Sea of Japan is approx. 250 m (modified from Hebig et al., 2014).	103
4.2 Profile of the Upper Sarabetsu aquifer and the construction of DD-2. Modified from Hebig et al. (2014)	105
4.3 Sarabetsu Formation built up by poorly compacted quaternary alluvial deposits with interbedded strata from channeling. A – Fluvial pebble gravel; B – Coarse and fine gravel channels; C – Fine sand matrix. The outcrop is located near the city of Horonobe.	107
4.4 Theoretical mean recovery times and normalized mean recovery time vs. the injected volume under idealized conditions (homogeneous and isotropic aquifer, no dispersion or same dispersion in all spatial directions).	111
4.5 a) BTCs of the uranine dye tracer during the extraction phase of the standard push-pull tracer tests (PPT 1 and PPT 2) and the no-chaser push-pull test (PPT 6); b) Enlargement.	112
4.6 a) Normalized BTCs of the uranine dye tracer during the extraction phase of the standard push-pull tracer tests (PPT 1 and PPT 2) and the no-chaser push-pull test (PPT 6). Concentrations are normalized to input concentration $[c/c_0]$, extracted volumes are normalized to injected volume $[V/V_0]$; b) Enlargement.	113

4.7	Mean recovery times of the three tracer plumes of PPT 1, 2, and 6 (triangles). The second graph (squares) shows the results of normalization of the mean recovery times to the injection volume for elimination of potential influences caused by the slightly different injection volumes between the three tests. The mean recovery time of PPT 6 (no-chaser push-pull test) was computed by skipping the first 122 L from the calculation, which represents the injected chaser volumes in the both standard tests.	115
4.8	a) Absolute plots of the BTCs of the uranine dye tracer during the extraction phase of the chaser tests CT 1 – 6. The BTC of PPT 6 is shown for comparison only. The whole curve can be seen in Fig. 4.5; b) Enlargement.	116
4.9	a) Normalized plots of the BTCs of the uranine dye tracer during the extraction phase of the chaser tests CT 1 – 6 and of PPT 6. Concentrations are normalized to input concentration $[c/c_0]$, extracted volumes are normalized to the injected volume $[V/V_0]$; b) Enlargement.	117
4.10	Relation of the main peak of every single chaser test to the respective injected test volume; It is assumed that the boundary between gravel pack and aquifer is represented by the moment, where the increase of c/c_0 -peak concentration and mass recovery reaches ~1 or 100%, respectively.	118
4.11	Mean residence times of the six chaser plumes of CT 1 – 6, and of the tracer plume of PPT 6 (triangles). The second graph (squares) shows the results of normalization of the mean recovery times to the injection volume to eliminate of the effects caused by the different injection volumes between the seven tests. The value of CT 1 was excluded from the calculation of the gravel pack regression line, as it represents the residence time within the pipe.	119

5.1	Number of peer-reviewed publications (a) and citations of these papers (b) in <i>Thomson Reuters Web of Science</i> , in which the term “deep groundwater” is included within the title, keywords, or abstract from the late 1970s to present. Retrieved 02.04.2014 from www.webofknowledge.com	128
5.2	Number of peer-reviewed publications (a) and citations of these papers (b) in <i>Thomson Reuters Web of Science</i> , in which the terms “single well” and “groundwater” are included within the title, keywords, or abstract from the early 1980s to present. Retrieved 02.04.2014 from www.webofknowledge.com	128
5.3	a) Dynamics of the saltwater-freshwater interface driven by changing sea level and groundwater recharge (modified from HRISE, 2010). b) Evolution of the relative sea level from 1.5 Ma until present in Horonobe (modified from JAEA, 2010).	131
5.4	a) Schematic expansion of the injected solution during the push-phase under the assumption of homogeneous and isotropic conditions, when no regional groundwater flow is assumed (“donut shape”, Hall et al., 1991). b) Deformation of the injected solution caused by drifting forced by regional groundwater flow under the assumption of homogeneous and isotropic conditions (based of the conceptional model of Leap and Kaplan, 1988).	133
5.5	Correlation of fluorescence intensity I and pH for selected fluorescence dye tracer. U = Uranine, E = Eosin, RB = Rhodamin B, RG = Amidorhodamin G, RWT = Rhodamin WT, P = Pyranin, N = Natrium-Naphthionat (Käss, 2004).	134
5.6	The effect of the irreversible dispersion on the tracer BTC during a push-pull test following Becker and Shapiro (2003).	139

7 List of Tables

3.1	Compositions of the test solutions; EC = Electric conductivity, TDS = Total dissolved solutes, ORP = Oxidation reduction potential	77
3.2	Injected and extracted volumes during the push-pull tests (PPT)	77
3.3	Concentrations, recoveries, and mass balances during the brackish water test. Injected volume was 6,980 L.	82
3.4	Concentrations, recoveries, and mass balances during the deionized water test. Injected volume was 7,900 L.	82
3.5	Fitted parameters from modeling of the BTC of lithium (brackish water test) and chloride (deionized water test)	91
4.1	Injected and extracted volumes during the push-pull tracer tests (PPTs)	109
4.2	Injected and extracted volumes during the chaser tests (CTs) and additionally of PPT 6 as very large chaser test	109
4.3	Maximum recovered normalized concentrations (c/c_0) = Normalized main peak concentration and uranine mass balances for the BTCs of PPT 1, 2 and 6	114
4.4	Maximum recovered normalized concentrations (c/c_0) = Normalized main peak concentration and uranine mass balances for the complete BTCs and the individual main and pre-peak	114

8 Appendix

8.1 Eidesstattliche Versicherung (Declaration of academic integrity)

Hiermit versichere ich, Klaus Hebig-Schubert, an Eides statt, dass die vorliegende Dissertation in vollem Umfang von mir selbst erstellt wurde. Es wurden keine weiteren als die angegebenen Quellen verwendet.

Berlin, den 06.06.2014

Klaus Hebig-Schubert

8.2 Angaben zum Eigentanteil (Outline of the author's contribution)

The thesis comprises of three manuscripts, which are presented in chapters 2 to 4. The author's contribution to each manuscript is described below.

Chapter 2 – first author

Review: Deep groundwater research with focus on Germany

The concept of the study was developed by the author and co-authors Traugott Scheytt and Narimitsu Ito. The collection of literature for this study was done by the author. The interpretation of the results was done by the author, supported by suggestions of the co-authors Narimitsu Ito, Traugott Scheytt, and Atsunao Marui. Writing and editorial handling of the manuscript were done by the author.

Chapter 3 – first author

Performance of single-well push-pull tracer tests to characterize transport processes: a case study in a sedimentary coastal basin

The concept of the study was developed by the author and the co-author Narimitsu Ito. The application of the method to the field site was developed by the author. The field experiments and laboratory work was performed by the author and the co-authors Narimitsu Ito and Isao Machida. The modeling of the breakthrough curves was done by the co-author Jan Tecklenburg. The interpretation of the results was done by the author, supported by suggestions of the co-authors Narimitsu Ito, Jan Tecklenburg, Isao Machida, Atsunao Marui, and Traugott Scheytt. Writing and editorial handling of the manuscript were done by the author.

Chapter 4 – first author

Study of the effects of the chaser in push-pull tracer tests by using temporal moment analysis

The concept of the study was developed by the author and the co-authors Sarah Zeilfelder, Narimitsu Ito, and Isao Machida. The application of the method to the field site was developed by the author and the co-authors Sarah Zeilfelder, Narimitsu Ito, and Isao Machida. The field experiments and laboratory work was performed by the author and the co-authors Sarah Zeilfelder, Narimitsu Ito and Isao Machida. The interpretation of the results was done by the author, supported by suggestions of the co-authors Sarah Zeilfelder, Narimitsu Ito, Isao Machida, Atsunao Marui, and Traugott Scheytt. Writing and editorial handling of the manuscript were done by the author.

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8.4 List of publications

Journals (peer-reviewed)

- Hebig, K.H.**, Zeilfelder, S., Ito, N., Machida, I., Marui, A. & Scheytt, T. (in press). Study of the effects of the chaser in push-pull tracer tests by using temporal moment analysis. *Geothermics*. DOI: 10.1016/j.geothermics.2014.11.004
- Hebig, K.H.**, Nödler, K., Licha, T. & Scheytt, T. (2014). Impact of materials used in lab and field experiments on the recovery of organic micropollutants. *Science of the Total Environment* 473 – 474:125 – 131.
- Hebig, K.H.**, Ito, N., Scheytt, T. & Marui, A. (2012). Review: Deep groundwater research with focus on Germany. *Hydrogeology Journal* 20 (2):227 – 243.

Submitted or in preparation for submission to a journal (peer-reviewed)

- Hebig, K.H.**, Ito, N., Tecklenburg, J., Machida, I., Marui, A. & Scheytt, T. (2014). Performance of single-well push-pull tracer tests to characterize transport processes: a case study in a sedimentary coastal basin. Submitted to *Hydrogeology Journal*.
- Zeilfelder, S., **Hebig, K. H.**, Ito, N., Machida, I., A., M., and Scheytt, T. (2014). Reproducibility of push-pull tracer tests and influence of the setup on the test results. In preparation for submission to *Journal of Hydrology*.
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Conference abstracts

Oral presentations

- Hebig, K.H.**, Zeilfelder, S., Ito, N., Machida, I., Tecklenburg, J., Marui, A., & Scheytt, T.J. (2014). The reaction of an aquifer on a dynamic saltwater-freshwater interface: a case study in a sedimentary coastal basin. GSA Annual Meeting, 19 – 22 October 2014, Vancouver, B.C., Canada.
- Zeilfelder, S., **Hebig, K.H.**, Ito, N., Machida, I., Scheytt, T. & Marui, A. (2013). The “push-pull” tracer method: how does the test design influence the shape of the breakthrough curves? GSA Annual Meeting, 27 – 30 October 2013, Denver, USA.
- Hebig, K.**, Nödler, K., Licha, T. & Scheytt, T. (2013). Impact of storage and filter materials on the recovery of 43 organic micropollutants. GSA Annual Meeting, 27 – 30 October 2013, Denver, USA.
- Hebig, K.**, Zeilfelder, S., Ito, N., Machida, I., Scheytt, T. & Marui, A. (2013). Are single-well “push-pull” tests suitable tracer methods for aquifer characterization? Geophysical Research Abstracts, Vol. 15, EGU2013-8305-1, EGU General Assembly 2013, 8 – 12 April 2013, Vienna, Austria.
- Hebig, K.H.**, Ito, N., Scheytt, T.J. & Marui, A. (2011). Hydraulic and hydrochemical characterization of deep coastal sedimentary basins by single-well Push-Pull tests. GSA Annual Meeting, 9 – 12 October 2011, Minneapolis, USA.
- Hebig, K.**, Ito, N., Scheytt, T. & Marui, A. (2011). Parameter determination in a deep coastal sedimentary basin by single-well (“push-pull”) tests. Geophysical Research Abstracts, Vol. 13, EGU2011-1408, EGU General Assembly 2011, 3 – 8 April 2011, Vienna, Austria.
- Ptacek, C.J., Woessner, W.W., Scheytt, T.J., Blowes, D.W., Robertson, W.D., Groza, L.G., McLagan, K.L., Seibert, S., **Hebig, K.**, Sabourin, M.J. & Lynch, T. (2010). Transport of mobile trace pollutants in highly permeable sediments. GQ10: Groundwater Quality Management in a

Rapidly Changing World. Proc. 7th International Groundwater Quality Conference, 13 – 18 June 2010, Zurich, Switzerland.

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Poster presentations

Hebig, K., Zeilfelder, S., Ito, N., Machida, I., Scheytt, T. & Marui, A. (2013). The role of the “chaser” in “push-pull” tests. GSA Annual Meeting, 27 – 30 October 2013, Denver, USA.

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- Hebig, K.H.**, Ito, N., Scheytt, T.J. & Marui, A. (2011). Hydrochemical behavior of two different artificial fluids in a coastal sedimentary basin during single-well (“Push Pull”) tests. GSA Annual Meeting, 9 – 12 October 2011, Minneapolis, USA.
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- Hebig, K.** (2005). Der Ätna und die Liparischen Inseln – Ein Reisebericht Fachgruppe Mineralogie, Geologie, Paläontologie im Brandenburgischen Kulturbund e.V., 01.06.2005, Potsdam.

8.5 Curriculum vitae

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Work experience

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10/2009 – 10/2013	Research assistant at the Hydrogeology Research Group at TU Berlin
11/2008 – 11/2009	Consultant, project engineer, project manager at IUP.Ingenieure Berlin

Stays abroad

2012	1-month stay as guest researcher at the Horonobe Research Site (Hokkaido, Japan)
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2008	4-month stay as guest researcher at the Department of Earth and Environmental Sciences at the University of Waterloo (Ontario, Canada)