Tracer compounds in geothermal reservoirs: Improving the outcome quality of a tracer test

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To my family

Short summary

In a tracer test, applied tracers are introduced and transported with a working fluid so that the tracer response signals can be used to determine the target parameters of the aquatic system, such as temperatures, flow paths and residence times. Implementing a tracer test requires adherence to a series of specified steps, and a failure in one step can attribute to an unreliable tracer response. The presented work focuses on ameliorating tracer test results with regard to selecting a proper tracer compound, preserving the tracer test samples, and expanding the number of thermo-sensitive tracers.

The application of reactive tracers can provide specific information about a system, such as temperature distribution. Reactive tracers have become important as they have been extensively developed during the past decades for a wide spectrum of field applications. Amongst numerous reactive tracer compounds, selecting suitable tracers for a specific system is challenging due to the lack of knowledge of their physicochemical properties while satisfying the large number of requirements each tracer must fulfill. In this thesis, a complete overview of the current state of reactive tracers is provided. Thorough understanding of tracer properties assists not only the selection of proper reactive traces, but also the synthesis of a future tailor-made tracer. Furthermore, the potential research directions of reactive tracers are suggested.

Sample preservation is prerequisite to achieve reliable results, especially for complex water samples like geothermal fluids. However, there is a lack of proper sample preservation methods in tracer testing. In this thesis, a preservation method for the most commonly applied conservative tracers, namely uranine, eosin, 1-naphthalene sulfonate, 1,5-naphthalene disulfonate, 2,6-naphthalene disulfonate, 4-amino-1-naphthalene sulfonate, 6-hydroxy-2-naphthalene sulfonate, 1,3,6-naphthalene

trisulfonate, and 1,3,6,8-pyrene tetrasulfonate, is provided. A simple but effective preservation method is proposed to ensure the quality of the analytical results for conservative tracers.

In addition, a new class of thermo-sensitive tracers is investigated that brings more options for researchers involved with characterizing geothermal reservoir performance. Carbamates are hydrolysable compounds susceptible to a well-defined thermo-sensitive hydrolysis reaction. In this study, the kinetic parameters of structurally different carbamates (eight primary and one secondary carbamate(s)) are investigated by isothermal batch experiments. The influences of compound structure, temperature, and pH/pOH on hydrolysis kinetics are estimated. The results demonstrate the possible application of carbamates within a broad range of temperatures (up to 200 °C).

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Chapter 1

1   Introduction

1.1   Background and motivation

1.1.1 Geothermal energy: Potential and challenges

Replacing fossil-based energy with more environmentally friendly energy sources has been gaining importance worldwide. Fossil fuels are considered the largest source of energy, with over 80% of global final energy consumption since 1971 (IEA, 2017). However, use of this source of energy will decrease because of resource depletion and environmental impacts (Sovacool, 2014). Renewable energy comes from resources which can be naturally replenished and have low environmental impacts, such as sunlight, wind or geothermal heat. Therefore, renewable energy enhances energy security and assists in creating a sustainable energy future. Great efforts have been made to foster the contribution of renewable energy in the total global energy consumption, which is estimated to contribute nearly 50% by 2040 (Panwar et al., 2011).

In the context of clean energy, attention has been primarily focused on wind and solar energy, with each accounting for roughly 47% of total investment in 2016 (REN21, 2017). Geothermal, however, has not gained as much recognition as it deserves. Despite the fact that this thermal energy is distributed unevenly and is challenging to

exploit, it is an inexhaustible resource in the Earth's crust. Currently, a small percent of the identified geothermal potential has been utilized by humankind, around 74 TWh/a in 2015 compared to a potential of 11,000 TWh/a (Bertani, 2016; Fridleifsson, 2001). However, advances in reservoir characterization techniques may offer a new perspective in geothermal energy by enhancing the estimates of the system geometries and temperatures. Greater geothermal energy exploitation will be supported by innovative drilling technologies, which lower initial investment; and better management practices, which lowers operational costs (e.g, Soldo and Alimonti, 2015). Along with expanded public awareness of geothermal benefits, this energy source is coming into widespread practice in the renewable energy industry. Geothermal is the only renewable energy source that experienced an increase in new investment in 2016 (up 17% compared to 2015) (REN21, 2017).

Geothermal is the energy source stored in the natural fluids and host rock within the Earth's crust. In general, the geothermal temperature increases with depth as indicated by the geothermal gradient. The average geothermal gradient is $2.5 - 3\,°C/100\,m$, however it varies widely depending on the physicochemical and geological properties of a specific system (Dickson and Fanelli, 2006). Geothermal resources can therefore be categorized as low enthalpy systems for regions with normal geothermal gradients ($T < 150\,°C$) and high enthalpy systems for significantly high geothermal gradients ($T > 150\,°C$). Low enthalpy systems are commonly found in shallow reservoirs with a depth up to 400 m and are mainly used for direct application or heat pumps. In contrast, high enthalpy reservoirs that can be utilized for electric energy production are mostly located at depths too challenging to be exploited. The first commercial geothermal power plant was built in Larderello, Italy, in 1913 (Bertani, 2005).

Geothermal has primarily been developed in regions along continental plate boundaries such as the USA, Indonesia, and Iceland. Traditionally, naturally occurring

geothermal systems are located in easily assessable regions, where hot rock and open water-filled fractures can be accessed at shallow depths. However, some systems lack either the necessary permeable rock or natural fluids to provide sufficient energy. Enhanced Geothermal Systems (EGS) is a new method that could dramatically increase and extend the use of potential sites into working geothermal wells. Fundamentally, EGS involves drilling an injection well several kilometers into hot rock, where the injection of water will result in the stimulation of existing natural fractures, creating enormous pathways in which water can flow and be heated. A production well is drilled near the injection well, allowing the heated water to move to the surface to power a turbine, generating electricity. The cooled water is then reinjected back into the hot rock to complete the water circulation loop. EGS is considered a reliable form of energy with effectively unlimited sources. It can furnish base load continuous power supply with high availability. Moreover, EGS is an essentially environmentally friendly energy source as it is emissions free.

High initial investment is currently one of the main drawbacks to developing EGS, with drilling costs contributing from 42 % to 90 % of overall capital costs (Breede et al., 2013). Simultaneously increasing productivity and decreasing drilling costs could make the overall technology much more attractive. Once geothermal energy is implemented on a larger scale, the costs will come down naturally.

Other main concerns for successful EGS development are proper site characteristics (Lu, 2018) and sustainable management of geothermal resources, of which reinjection is considered an essential technology (Axelsson, 2013). The limitation of reinjection, however, is having thermal breakthrough and reservoir cooling (Kaya et al., 2011). In order to consider geothermal a renewable energy resource, heat extraction must not exceed the reservoir replenishment rate (Barbier, 2002; O'Sullivan et al., 2010). Therefore, proper reservoir evaluation and monitoring is required to mitigate the

potential threat of cooling. Tracer tests are commonly applied in geothermal research, development and resource management for this purpose.

1.1.2 Tracer testing: History of tracers and their application in geothermal reservoirs

Tracer testing is considered an efficient tool for characterizing aquatic systems, in which tracer compounds are intentionally introduced to provide information. Traditional targets of the conservative tracer technique are basic hydraulic transport properties such as conductivity or flow rates. The application of this type of tracer in water research has a long history. Dyes and salts have been used to study water movement since the late nineteenth century (Dole, 1906). In the 1950s, radioactive tracers were introduced allowing extremely precise and selective tracer measurement (Fox, 1952; Rogers, 1958). During this time, the noble gas helium was also introduced as a groundwater tracer by Carter et al. (1959). In the 1980s, fluorinated organic acids (Bowman and Gibbens, 1992; Stetzenbach et al., 1982) and halocarbons (Fogelqvist et al., 1982) were presented as tracers with high sensitivity. In general, conservative tracers should be non-reactive, safe for humans and the environment, detectable at low concentrations, and inexpensive.

The demand for investigating unique information of geometric system properties and/or water chemistry beyond the capability of conservative tracers led to the emergence of reactive tracers. Reactive tracers are compounds that undergo a chemical reaction or physicochemical interaction process in a predicable way under specific hydrogeological conditions. The interpretation of reactive tracers relies on their known properties, physicochemical or chemical behavior during transport. The first reactive tracer was likely introduced by Cooke (1971) by applying isobutyl alcohol for the determination of fluid saturation in reservoirs. Since then, numerous types of

reactive tracers have been developed for investigating a wide spectrum of field possibilities such as residual saturation in oil fields (Rhee et al., 2011; Silva et al., 2017), microbial activity in karst (Hillebrand et al., 2015; Knapp et al., 2017) and temperature distribution in geothermal reservoirs (Leecaster et al., 2012; Maier et al., 2015a; Rose and Clausen, 2014; Schaffer et al., 2016). With the increasing number of advanced reservoir applications (e.g., geothermal power generation or carbon capture and storage (CCS)), the demand for development of existing reactive tracers as well as new optimal reactive tracers is still rising.

Site characteristics are vital for the success of EGS development (Lu, 2018). By providing important insights into system characterization, tracer technique has been established as an important method for sustainable geothermal reservoir research and management. Tracer testing can be used for evaluation and monitoring of cooling due to reinjection during the operation of EGS. During the past several decades, extensive research has been conducted to study the application of existing tracers and to discover new tracers for a wide spectrum of geothermal fields (Adams and Davis, 1991; Kruger et al., 1977; Maier et al., 2015a, 2015b; McCabe et al., 1983; Nottebohm et al., 2012; Rose et al., 2001; Schaffer et al., 2016; Upstill-Goddard and Wilkins, 1995). The application of tracers with thermo-sensitive properties has been established as a useful method for tracking the thermal state of a geothermal system. One approach is to use established tracers like naphthalene sulfonates, Amino G and rhodamine WT as thermo-sensitive tracers (Rose and Clausen, 2017, 2014; Rose and Adams, 1994). This approach, however, is limited to high temperature systems (from 150 to 350 °C). Another approach applying to low enthalpy systems (below 150 °C) is based on compounds with chemical groups susceptible to hydrolysis (a temperature-dependent reaction), leading to defined reaction products (Maier et al., 2015a, 2015b; Nottebohm et al., 2012; Robinson and Tester, 1990; Schaffer et al., 2016). These tracer compounds

are water-soluble and have different fluorescent properties than their hydrolysis products, which allows for the detection of tracers on site.

1.2   Scope, objectives and further outline

To improve georeservoir management strategies, the results of a tracer test needs to be reliable through adherence to a series of specified steps. Selection of the optimal tracer is essential to avoid failure in testing. A thorough understanding of the physicochemical properties of tracers and their chemically reactive behavior is prerequisite. Although previous introductory review papers provide excellent coverage of conservative tracers, there is no systematic information on reactive tracers yet, which have been extensively developed over the past decades. Furthermore, poor sampling methodology is considered the main reason for tracer test failure (Du and Guan, 2005), therefore the preservation method should receive more attention. This is especially true for complex water samples (e.g., high salinity), which are usually be encountered in geothermal reservoirs. In the geothermal industry, thermo-sensitive tracers could be used to monitor the spatial and temporal temperature distribution in a reservoir during active production and reinjection. With a substantial lack of candidate tracers for determining the temperature along a flow path (U.S. DOE, 2008), the demand for a new group of thermo-sensitive compounds is still rising.

It is obviously impossible for a single study to focus upon all aspects for achieving ideal tracer test results. Therefore, this work can be recognized as a successful work for improving the overall quality of tracer test results. Moreover, the obtained information is useful for the development of future tailor-made reactive tracers for specific studies.

In the beginning, systematic review of reactive tracers was provided with a focus on their development over the past decades. Furthermore, preservation methods for

samples in complex were proposed to guarantee a successful sampling strategy. In addition, a new thermo-sensitive tracer group was investigated and the first results gained from controlled laboratory experiments were presented. A more detailed outline is presented in the following.

In one tracer test, a combination of non-reactive tracers and at least one reactive tracer is commonly applied. Reactive tracers are compounds which can provide unique information about chemical, physical and biological properties of aquatic systems. The development of new reactive tracers has become a focus of attention due to their promising application in different advanced technologies such as geothermal power generation and CCS. Reactive tracers undergo chemical reactions or physicochemical interaction processes under particular hydrogeological conditions to determine the unique characteristics of the aquatic environment. It is necessary to know the physicochemical properties and the chemical behavior of reactive tracers to select a suitable tracer for a specific problem. **Chapter 2** summarizes the recent development in compounds and compound classes that are exploitable and/or have been used as reactive tracers, including their systematization based on the process to be investigated. Reactive tracers are categorized in three groups, namely (1) partitioning tracers, (2) kinetic tracers and (3) reactive tracers for partitioning. This contribution also highlights the potential for future research directions. Recent advances from the development of new tailor-made tracers could overcome existing limitations.

As mentioned above, sample preservation and pre-treatment are vital procedures to guarantee accurate and reproducible results from tracer tests, particularly for samples from complex water matrices such as geothermal reservoirs and acid mine drainage sites. Specifically, induced changes in redox conditions, temperature, and pH during sampling (e.g., due to degassing, cooling) will lead to the ineluctably present of the precipitates iron and calcium. Within this framework, many common conservative

tracer compounds having carboxyl groups (e.g., uranine, eosin) or sulfonic groups (e.g., naphthalene sulfonates) may suffer a substantial mass loss during storage due to sorptive (electrostatic) interactions to certain precipitates or be prone to co-precipitation. **Chapter 3** addresses the preservation of commonly applied conservative tracers in complex water matrices prior to fluorescence analysis. In this study, the interference of abundant iron and calcium contents with nine commonly applied conservative tracers is investigated in batch experiments. The results observed are influenced by precipitates. A technique consisting of pH adjustment and centrifugation is described for preserving samples and avoiding the impact of these precipitates on observed results.

The utilization of reinjection requires a detailed monitoring of spatial and temporal temperature distribution of the studied field location, as the application of this technique may lead to the risk of early thermal breakthrough. The use of thermo-sensitive tracers has shown to be a practical method for tracking the thermal state of a geothermal reservoir. In this regard, hydrolysable compounds with known kinetic properties (e.g., esters and amides) have been promoted as promising thermo-sensitive tracers. In **Chapter 4** a new thermo-sensitive tracer is investigated for tracing the thermal state of geothermal reservoirs. The kinetic parameters of eight primary and one secondary carbamate(s) are studied by means of isothermal batch experiments. The influence of the compound structure, temperature and pH/pOH on hydrolysis kinetics was investigated. The results demonstrate the possible application of these tracers within a broad range of temperatures (up to 200 °C).

Chapter 5 summarizes the conclusions with respect to the focus of the thesis and gives an outlook for future research activities.

Appendix A presents additional information regarding to Chapter 3.

Appendix B lists publications from the author relating to the presented work (including journal articles and conference contributions).

This thesis follows a cumulative dissertation. Therefore, literature cited is listed at the end of each individual chapter.

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Chapter 2

2 Solute reactive tracers for hydrogeological applications:

a short review and future prospects

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Abstract

Tracer testing is a mature technology used for characterizing aquatic flow systems. To gain more insights from tracer tests a combination of conservative (non-reactive) tracers together with at least one reactive tracer is commonly applied. The reactive tracers can provide unique information about physical, chemical, and/or biological properties of aquatic systems. Although, previous review papers provide a wide coverage on conservative tracer compounds there is no systematic review on reactive tracers yet, although they were extensively developed during the past decades. This review paper summarizes the recent development in compounds and compound classes that are exploitable and/or have been used as reactive tracers, including their systematization based on the underlying process types to be investigated. Reactive tracers can generally be categorized into three groups: (1) equilibrium tracers, (2) kinetic tracers, and (3) reactive tracers for partitioning. The work also highlights the potential for future research directions. The recent advances from the development of new tailor-made tracers might overcome existing limitations.

Key words: Reactive tracer, Tailor-made tracer design, Hydrogeological tracer test, Kinetics, Partitioning

Graphical abstract
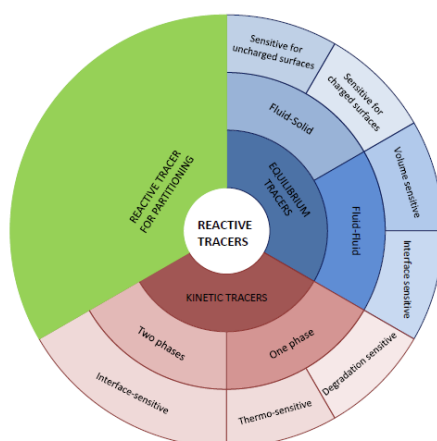
2.1 Introduction

Tracer tests are one of the most well established techniques for site and process characterizations in the aquatic environment (i.e., in hydrology or hydrogeology). Various additives (e.g., particles, solids, solutes, and gases) and physical quantities (e.g., temperature and pressure) can be applied as tracers for interpreting hydraulic transport properties and/or reactive processes in the aquatic environment (e.g., Abbott et al., 2016; Chrysikopoulos, 1993; Flury and Wai, 2003; Serres-Piole et al., 2012). Some basic hydraulic properties, such as flow velocity or porosity, can be obtained by tracer tests using conservative (non-reactive) tracer compounds. The combination of a conservative tracer with at least one reactive tracer is commonly applied in order to assess additional system parameters, such as residual saturation (Rhee et al., 2011; Silva et al., 2017), microbial activity (Hillebrand et al., 2015b; Knapp et al., 2017), or temperature distribution (Maier et al., 2015a; Schaffer et al., 2016). The unique features of reactive tracers could provide valuable information on physical, chemical, and/or biological properties of the hydrological system which surpasses the capability of conservative tracers.

The application potential for tracers within the scope of advanced reservoir management, such as geothermal power generation or carbon capture and storage, has triggered the development of new tracers and tracer techniques in the past decades (e.g., Myers et al., 2012; Schaffer et al., 2013). Reactive tracers used to detect specific properties and processes in the aquatic environment must generally either have distinctive physicochemical properties (e.g., sorption) or undergo specific reactions such as hydrolysis. To identify the most suitable tracer compounds for a specific system or problem, a thorough understanding of the physicochemical properties and their chemically reactive behavior in the probed system is a prerequisite.

The main objective of this overview article is to present a systematic review of existing and proposed reactive solute tracers based on current research advances conducted in different scientific fields. For each subclass of tracer, the underlying process, their key properties, and possible target parameters/applications are described. Furthermore, the potential areas for the future development and exploitation of new reactive tracers are elaborated. Hereby, the new approach of producing tailor-made reactive tracers may break down currently existing limitations on the investigation potential of commercially available compounds.

2.2 Definition and theoretical background

2.2.1 Definition

A tracer is defined herein as a distinguishable chemical compound which is deliberately added to an aquatic system having a temporally and spatially well-known input function (e.g., pulse injection). The respective system property or information of interest is derived based on the relation of the input function to the observed response function (breakthrough curve) within the investigated system.

Two general tracer types can be defined based on the degree of interaction with the systems. First, conservative tracers show virtually no interaction with the reservoir materials, and thus they flow passively with the carrier fluids at their velocity. Furthermore, they do not suffer any chemical or biological processes. This implies that these tracers are inert under reservoir conditions. The second type of tracers can be summarized as reactive tracers. The interpretation of reactive tracers relies on their known properties, physicochemical or chemical behavior during the transport. Reactive tracers are compounds that undergo a chemical reaction or physicochemical interaction processes in a predicable way under specific boundary conditions existing in the investigated system. Consequently, using the particular features of reactive

tracers could provide unique information on physicochemical properties and/or water chemistry of the hydrological system far beyond the capability of conservative tracers.

Traditionally, tracer tests were conducted using conservative tracers. These tracers can provide general physical and hydraulic parameters of the system (e.g., porosity, dispersivity, or arrival time). In order to derive these parameters with great accuracy, the compounds are desired to behave ideally. The properties of an ideal tracer are well established (e.g., Flury and Wai, 2003); they (1) behave conservatively (e.g., are transported with water velocity, not degradable), (2) have a low background concentration in the system, (3) are detectable in very low concentrations, and (4) have low or no toxicological environmental impact. Nevertheless, all solute tracers are influenced to some degree by physical, chemical, and/or biological processes. This means that completely ideal tracers do not exist in reality. Therefore, some knowledge of the investigated system is required beforehand to verify the practically ideal tracer behavior and thus to avoid test failure.

2.2.2 Conservative tracer transport versus reactive tracer transport

The transport behavior of a tracer compound in the aquatic environment is affected by several physical and chemical processes. These processes result in spatial and/or temporal concentration changes of the introduced tracer during its transport, which are reflected in the system response function (e.g., breakthrough curve $c(t)$). Tracer transport is commonly described based on the principle of mass conservation by means of the advection-dispersion-reaction model in the three-dimensional form as follows:

①   ②   ③   ④

$$R\frac{\partial c}{\partial t} = -\bar{V}\cdot\nabla c \; + \; \nabla(D_H\nabla c) + \; S \qquad\qquad (2.1)$$

where R is the retardation factor, c is the tracer concentration, t is the time, $\bar{V}$ is the average pore water velocity, D_H is the hydrodynamic dispersion tensor (including mechanical dispersion and molecular diffusion), and S is the source/sink term accounting for the tracer transformation (degradation/generation).

As described above, tracer transport in water can be classified as conservative or reactive according to its interaction within the system to be studied. A conservative tracer does not interact or alter during the transport, and thus the concentration is not changed by processes other than dilution, dispersion and partial redirection. As such, conservative tracers are expected to mimic the transport of water without retardation and transformation. Thus, they underlie only the purely hydrodynamic transport processes: advection, diffusion, and dispersion (as terms 2 and 3 in Eq. 2.1). Therefore, conservative tracers are generally used to investigate hydraulic properties (e.g., tracking connectivities, flow pathways), analyzing travel times and flow velocities, determining recharge and discharge, and estimating hydromechanical properties (e.g., dispersivity, porosity). Common examples of conservative tracers under ambient temperatures are major anions such as bromide (e.g., Reimus et al., 2003; Yakirevich et al., 2017), stable isotopes such as ^{2}H and ^{18}O (e.g., Abbott et al., 2016; Moeck et al., 2017), dye tracers such as uranine (e.g., Field et al., 1995; Hillebrand et al., 2012; Wolkersdorfer et al., 2016), and rhodamine WT (e.g., Battaglia et al., 2016; Guo et al., 2017; Olson et al., 2017; Shih et al., 2017; Zhu et al., 2017).

Apart from hydrodynamic transport processes, reactive tracers additionally underlie physical, chemical, and/or biological processes during their transport (terms 1 and 4 in Eq. 2.1). The implementation of reactive tracers with identical and well understood interactions or reactions could implicitly provide unique information on physicochemical aquifer properties (e.g., sorption capacity), water chemistry (e.g., redox condition, pH, ion concentrations), and other influencing parameters (e.g.,

temperatures, microbial activity) (Divine and McDonnell, 2005; Luhmann et al., 2012; Ptak et al., 2004).

In order to benefit from the selective and process specific nature of reactive tracers, it is a prerequisite to combine them with at least one conservative reference tracer by performing a multitracer experiment to account for the purely hydrodynamic transport processes that affect both tracer types in the same way. Consequently, the reactive processes can be identified and quantified. The intended information from the tracers is gained by comparing the concentration versus time curves (breakthrough curves) of the reactive tracers with the conservative tracers (reference). This can be illustrated by the schematic breakthrough curves for a simulated tracer test having a pulse input function (Fig. 1). The time shift and/or the reduction of the peak area (tracer mass) of the breakthrough curves indicate retardation and/or degradation, respectively. Measured breakthrough curves can be inversely interpreted using analytical or numerical models to estimate the values of controlling parameters, such as the distribution coefficient for the sorption process or the decay rate for the sorption process or the decay rate for the biodegradation process.
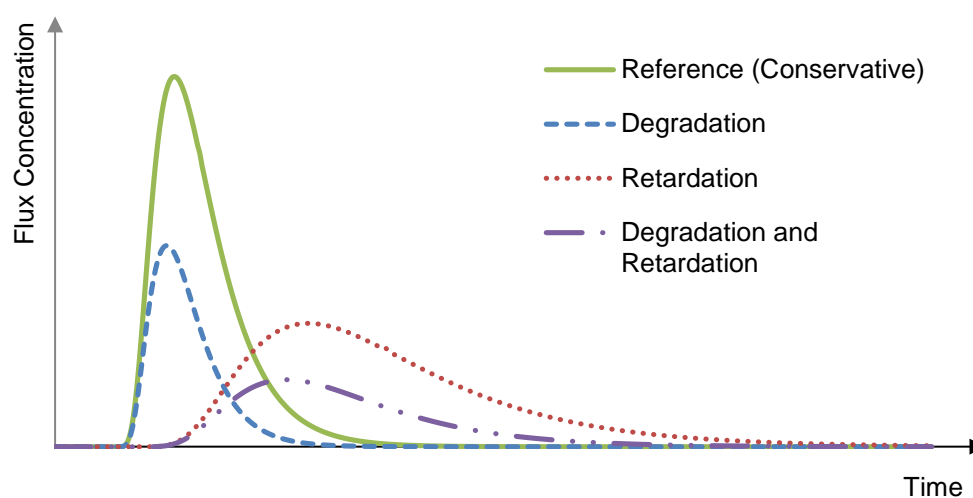
Fig. 2.1 Schematic breakthrough curves for conservative tracer and reactive tracers after a pulse injection.

2.3 Types of reactive tracers

A generalized classification of currently existing reactive tracers and proposed reactive tracer concepts, including their required properties, possible applications, and processes is provided. Depending on their physical, chemical, and/or biological behavior, three major subgroups are distinguished (Table 1):

- Equilibrium tracers: These types are based on the partitioning equilibrium between two immiscible phases or at their interfaces (fluid-solid, fluid-fluid) leading to a retardation relative to the conservative tracer remaining in (one) fluid phase.

- Kinetic tracers: These types are non-equilibrium tracers in which only the reaction kinetics are used for the parameter determination. As a result of the tracer reaction, the tracer signals are decreasing (parent compound) or increasing (daughter compound) with time (degradation). These tracers usually do not show retardation (no partitioning).

- Reactive tracers for partitioning: These tracers are a hybrid form of the preceding tracers, containing features of both: chemical reaction (degradation) of the parent compound and subsequent partitioning (retardation) of the daughter products.

Table 2.1 Classification of reactive tracers.

	Equilibrium tracers (partitioning tracers)				Reactive tracer for partitioning (volume or interface sensitive after degradation)	Kinetic tracers (decaying tracers)		
	Fluid-Solid		Fluid-Fluid			One phase		Two phases
	Sensitive for uncharged surfaces	Sensitive for charged surfaces	Volume sensitive	Interface sensitive		Degradation sensitive	Thermo-sensitive	Interface-sensitive
Determining properties of tracer molecules	Uncharged but still soluble (moderately polar) organic compounds	Organic and inorganic ions with opposite charge compared to the surface	Compounds with quantifiable partitioning between two phases (soluble in both phases)	Amphiphilic compounds (surface active agents- surfactants)	Hydrophilic compounds, susceptible to decay leading to daughter compounds with different partitioning properties (coefficients)	Degradable compounds under applied conditions	Hydrolysable and hydrophilic compounds with known kinetic parameters and decay mechanisms	Hydrophobic and hydrolysable compounds
Possible target parameters / Application	Organic carbon content, surface area to volume ratio A/V (of uncharged surfaces)	Surface charge (surface charge density, exchange capacity), Surface area to volume ratio A/V (of charged surface)	Residual saturation	Residual distribution, contact area	Residual saturation or residual distribution, contact area	Attenuation capacity, other reaction relevant boundary conditions (e.g., redox conditions, pH)	Temperature and temperature distribution (cooling fractions)	Interfacial area (development with time)
Underlying (reactive) process	Sorption due to hydrophobic interactions	Sorption due to electrostatic interactions (e.g, ion exchange, hydrogen bonding)	Phase partitioning	Interfacial adsorption (partitioning between bulk phase and interface)	In-situ decay with subsequent partitioning	Chemical and biological reactions	Hydrolysis reaction, substitution	Hydrolysis reaction leading to inter-phase mass transfer

Reactive tracers (non-conservative tracers)

2.3.1 Equilibrium tracers

2.3.1.1 Fluid-Solid (sorbing tracers)

Sensitive for uncharged surfaces

A tracer compound sensitive for uncharged surfaces undergoes hydrophobic sorption onto uncharged sites of the sorbent (e.g., soil, aquifer material), particularly organic matter. Hydrophobic sorption is the result from a weak solute-solvent interaction coming from a decrease in entropy of the solution and can be explained by general interactions between sorbate and sorbent, e.g., van-der-Waals forces (dipole and/or induced-dipole interactions) (Hassett et al., 1980). The organic carbon content (f_{OC}) of the aquifer material generally correlates with the sorptivity and thus the retardation of a neutral (uncharged) organic compound (Maeng et al., 2011; Schaffer and Licha, 2015; Schwarzenbach et al., 1983). Therefore, it is conceivable that substances, which are sensitive to uncharged surfaces, have the potential to determine the f_{OC} of a system from their observed retardation factor (R_{unc}) assuming a linear sorption isotherm:

$$R_{unc} = 1 + \frac{\rho}{n_e} K_{unc} \tag{2.2}$$

where ρ is bulk density, n_e is effective porosity, and K_{unc} is the sorption coefficient. K_{unc} depends primarily on the hydrophobicity of the tracer molecules, typically characterized by the *n*-octanol-water partition coefficient ($\log K_{OW}$) and the f_{OC} of the geological materials. From $\log K_{OW}$ of the tracer compound, K_{unc} for a particular system can be estimated. According to the literature (e.g., Karickhoff et al., 1979; Sabljic et al., 1995; Schwarzenbach et al., 2002) $\log K_{OW}$ can empirically be related to the organic carbon normalized sorption coefficient (K_{OC}) in the form:

$$\log K_{OC} = a \log K_{OW} + b \qquad\qquad (2.3)$$

$$K_{OC} = \frac{K_{unc}}{f_{oc}} \qquad\qquad (2.4)$$

where a and b are empirical parameters.

Thus, from known $\log K_{OW}$ and determined R_{unc}, the average f_{OC} between the injection and observation points can be estimated. By selecting non-ionic compounds with moderate $\log K_{OW}$ values between 1 and 3 (1H-benzotriazole, carbamazepine, diazepam, and isoproturon) from formerly published column experiments by Schaffer et al. (2015a, 2012) using correlation factors for non-hydrophobic compounds after Sabljic et al. (1995), the observed f_{OC} values of the columns agree very well with the independently measured ones from the bulk using total organic carbon measurements. Despite the relatively large uncertainty regarding the chosen $\log K_{OW}$ values, all deviations of the absolute values between the measured and calculated f_{OC} are within one order of magnitude (less than factor 5).

To the extent of our knowledge, this tracer type has not yet been explicitly proposed, and therefore their potential could be further investigated. Some promising examples include 8:2 fluorotelomer alcohol (Liu and Lee, 2005), short-chained alkyl phenols (Fischer et al., 2014), or pharmaceutical compounds (e.g., Burke et al., 2013; Hebig et al., 2017; Nham et al., 2015).

Sensitive for charged and hydrophilic surfaces

A tracer compound sensitive for charged surfaces undergoes ionic sorption between a charged moiety of a tracer molecule and an oppositely charged surface of the sorbent (e.g., soil, aquifer material). In this case, there is a strong electrostatic interaction (e.g.,

ion exchange, hydrogen bonding, or surface complexation) between tracer sorbate and sorbent.

Retardation of a solute due to ion sorption on natural solids (R_c) can be related either to a sorbent mass (Eq. 2.2) or to its surface sensitivity to the surface area (A) to volume (V) ratio if the sorption coefficient (K_c) is known (Freeze and Cherry, 1979):

$$R_c = 1 + \frac{A}{V} K_c \qquad\qquad (2.5)$$

These tracers are required to be water soluble, ionized (electrically charged), and can be organic or inorganic substances. The selection of tracers for this application is based on the surface charge of the sorbents. Further, the pH condition strongly influences the charge states of organic compounds (e.g., bases, acids, and ampholytes) and the sorbent's surface (Schaffer and Licha, 2015); thus, pH and the point of zero charge of the surface should be considered before selecting a tracer compound.

Many laboratory tests have been conducted to demonstrate the feasibility of charged surface tracers to interrogate the surface area, e.g., using safranin (Leecaster et al., 2012), lithium (Dean et al., 2015, 2012; Reimus et al., 2012), and monoamines (Schaffer et al., 2017). A couple of field tests have also demonstrated the potential use of charged surface tracers for investigating the surface area, e.g., using safranin (Rose et al., 2012) and caesium (Hawkins et al., 2015; Neretnieks, 2002). Furthermore, this tracer type has the potential to estimate the ion exchange capacity of sediments (Wilson, 2010).

2.3.1.2 Fluid-Fluid

The fluid-fluid tracers summarize liquid-liquid tracers and liquid-gas tracers due to the similarity in the underlying processes and applications.

Volume sensitive tracers

A volume sensitive tracer is a compound that partitions between two immiscible fluid phases (liquid-liquid or liquid-gas). A different solubility in the two fluid phases leads to the specific phase distribution and results in a retardation of the tracer. Volume sensitive tracers are very useful in estimating the volume of the immobile phase (residual saturation). For example, one common application of this type of tracer is to characterize the source zone of non-aqueous phase liquids (NAPLs) for contaminated sites. Another popular use is to evaluate the effectiveness of treatment techniques before and after the remediation of NAPLs, thereby obtaining independent estimates on the performance of the cleanup. This tracer can also be used to identify residual gas or supercritical fluid phases, such as in carbon capture and storage applications. When sorption onto solids is negligible, the retardation factor (R_{vs}) is a function of the average residual saturation (S_r) within the tracer flow field (Annable et al., 1998b; Jin et al., 1995):

$$R_{vs} = 1 + \frac{S_r}{(1 - S_r)} K_{vs} \qquad (2.6)$$

where K_{vs} is the partition coefficient between two fluid phases.

A large number of laboratory experiments and field-scale tests have been conducted to detect NAPL contaminations since the 1990's. The most commonly applied volume sensitive tracers are alcohols of varying chain length, such as 1-hexanol (Cápiro et al., 2011; Imhoff et al., 2003; Jawitz et al., 2000; Johnston et al., 2013), 1-pentanol and 1-heptanol (Brooks et al., 2002; Jin et al., 1997; Young et al., 1999), 2-ethyl-1-butanol (Divine et al., 2004; Jin et al., 1997; Rhee et al., 2011), 6-methyl-2-heptanol (Cain et al., 2000; Jawitz et al., 2002), 2,2-dimethyl-3-pentanol (Annable et al., 1998b; Cain et al., 2000; Jawitz et al., 2002), 2,4-dimethyl-3-pentanol (Annable et al., 2005; Brooks et al., 2002; Divine et al., 2004; Hartog et al., 2010; Jawitz et al., 2000; Noordman et al.,

2000; Wang et al., 2014), substituted benzyl alcohols (Jessheim et al., 2013; Silva et al., 2017) and fluorotelomer alcohols (Dean et al., 2016). Additionally, sulfur hexafluoride (SF_6) (Davis et al., 2002; Reid and Jaffé, 2013; Vulava et al., 2002; Werner and Höhener, 2002; Wilson and Mackay, 1995), perfluorocarbons (Deeds et al., 1999; Jin et al., 1997), radon-222 (Hunkerler et al., 1997; Ponsin et al., 2015; Schubert et al., 2007), fluorescent dyes (e.g., rhodamine WT, sulforhodamine B, and eosin) (Ghanem et al., 2003) have also been suggested for use as volume sensitive tracers. Recently, the noble gases krypton and xenon were applied successfully in the determination of the residual CO_2 saturation (LaForce et al., 2014; Rasmusson et al., 2014; Roberts et al., 2017; Stalker et al., 2015; Zhang et al., 2011).

Interface sensitive tracers

An interface sensitive tracer is a compound that undergoes the accumulation (adsorption) at the interface between two immiscible fluids, typically liquid-liquid or liquid-gas, leading to the retardation of the tracer. The magnitude of adsorption at the interface is controlled by the physicochemical properties of tracer compounds and by the interfacial area, particularly the size of the specific fluid-fluid interfacial area (a_{nw}) and the interfacial adsorption coefficient (K_{if}). The retardation factor (R_{if}) defined through porous media follows (Saripalli et al., 1998, 1997):

$$R_{if} = 1 + \frac{a_{if}}{\theta_w} K_{if} \tag{2.7}$$

$$K_{if} = \frac{G_{eq}}{C_{eq}} \tag{2.8}$$

where a_{if} is the specific interfacial area, θ_w is the volumetric water content, and K_{if} is the interfacial adsorption coefficient (ratio between the interfacial tracer

concentration in the sorbed phase at the interface (G_{eq}) and the fluid (C_{eq}) at equilibrium).

The desired compounds for this tracer class are amphiphilic molecules (containing both hydrophobic and hydrophilic groups). Information on fluid-fluid interfacial areas, along with residual saturation (assessed by volume sensitive tracers) assists the understanding of the fate and transport of contamination in the systems.

One of the most popular interface sensitive tracers that have been successfully tested in laboratory and field scales is the anionic surfactant sodium dodecylbenzene sulfonate (Annable et al., 1998a; Anwar et al., 2000; Araujo et al., 2015; Brusseau et al., 2010; Mark L Brusseau et al., 2007; Hartog et al., 2010; Jain et al., 2003; Kim et al., 1999, 1997; Narter and Brusseau, 2010; Noordman et al., 2000; Saripalli et al., 1997; Schaefer et al., 2000; Zhong et al., 2016). Further potential arises for other ionic and non-ionic surfactants (e.g., marlinat (Setarge et al., 1999), 1-tetradecanol (Karkare and Fort, 1996; Silverstein and Fort, 1997), sodium dihexylsulfosuccinate (Dobson et al., 2006)) and for cosurfactants (e.g.,*n*-octanol and *n*-nonanol (Kim et al., 1998)).

2.3.2 Kinetic tracers

2.3.2.1 One phase

Degradation sensitive tracers

Degradation sensitive tracers are compounds that undergo biotic and/or abiotic transformations. Depending upon the nature of the tracer specific chemical and/or biological characteristics (reaction controlling boundary conditions) of the flow system can be investigated. Information on the decay mechanism and the equivalent kinetic parameters is a prerequisite for their successful application. The decay mechanism is usually desired to follow a (pseudo) first order reaction to limit the number of required

kinetic parameters and to avoid ambiguity. In addition, other influencing factors on kinetics should be considered before application (e.g., pH, light, and temperature). The reaction rate constant (k_{DS}) can be estimated by measuring the extent of tracer loss of the mother compound or the associated increase of a transformation product along the flow path.

This type of tracer has been studied and tested in field-scale experiments over the past 20 years. Their main purpose is to determine microbial metabolic activity (natural attenuation processes) and/or to assess redox conditions. Numerous redox-sensitive tracers have been applied for laboratory and field scale investigations, such as inorganic electron acceptors (e.g., O_2, NO_3^-, SO_4^{2-}, CO_3^{2-}) (Addy et al., 2002; Burbery et al., 2013; Cho et al., 2013; Goldhammer et al., 2008; Henson et al., 2017; Istok et al., 1997; Kleikemper et al., 2002; Michalsen et al., 2013; Schroth et al., 2001, 1998; Urmann et al., 2005), organic electron donors (e.g., low-molecular weight alcohols and sugars (Rao et al., 2000) and benzoate (Alter et al., 2003; M. L. Brusseau et al., 2007; Sandrin et al., 2004)), or the organic electron acceptor resazurin (González-Pinzón et al., 2016, 2015, 2012, Haggerty et al., 2014, 2009, 2008; Knapp et al., 2017; Lemke et al., 2014; Stanaway et al., 2012).

Thermo-sensitive tracers

Thermo-sensitive tracers are compounds undergoing chemical reactions that are well-defined and temperature driven, such as hydrolysis (Cao et al., 2018; Nottebohm et al., 2012, 2010) or thermal decay (e.g., Rose and Clausen, 2017, 2014). Prior knowledge on their reaction mechanisms is required for each specific thermo-sensitive tracer. To avoid ambiguity, reactions following (pseudo) first order reaction are desired, and the reaction speed (expressed by the reaction rate constant (k_{TS})) is preferred to be solely controlled by temperature. For these reactions, the dependence of temperature (T) on

k_{TS} is the essential factor for estimating the thermo-sensitivity expressed by Arrhenius law:

$$k_{TS} = Ae^{-\frac{E_a}{RT}} \tag{2.9}$$

where A is the pre-exponential factor, E_a is the activation energy, and R is the ideal gas constant. By knowing the corresponding kinetic parameters, the equivalent temperature (T_{eq}) and the cooling fraction (χ) can be obtained (Maier et al., 2015b). T_{eq} references the thermal state of a probed reservoir relative to an equivalent system having isothermal conditions, whereas χ has the potential to further estimate a spatial temperature distribution of the investigated system.

A typical application of these tracers is to investigate the temperature distribution of a georeservoir. The first field experiments using ester compounds (ethyl acetate and isopentyl acetate), however, were unable to determine a reservoir temperature (Batchelor, 1986; Kwakwa, 1988; Tester et al., 1986). The failure of the studies was attributed to the poor determination of pH dependence and the lower boiling point of the tracer compounds compared to the reservoir temperature leading to vaporization. New attempts demonstrated the successful application in the laboratory (Maier et al., 2015a) and in the field (Hawkins et al., 2017). Other studies using classical tracers like fluorescein (Adams and Davis, 1991) or Amino G (Rose and Clausen, 2017, 2014) were able to identify the reservoir temperatures. Currently, extensive research has been conducted to study structure-related kinetics of defined thermo-sensitive reactions with promising results (Cao et al., 2018; Maier et al., 2015a, 2015b; Nottebohm et al., 2012; Schaffer et al., 2016).

2.3.2.2 Two phases

Kinetic interface sensitive (KIS)

KIS tracers are intended to be dissolved or mixed with a non-aqueous carrier fluid (e.g., supercritical CO_2 (Schaffer et al., 2013)) and injected into the reservoir. The underlying process is an interface-sensitive hydrolysis reaction at the interface between the aqueous and the non-aqueous phase. Here, the tracer saturates the interface of the evolving plume due to interfacial adsorption and reacts irreversibly with water (hydrolysis with first-order kinetics). Due to the constant (adsorbed) concentration of the reactant at the interface, the reaction kinetics is simplified to (pseudo) zero order kinetics. The formed reaction products are monitored in the water phase.

In order to have minimal partitioning into the polar water phase, the potential tracers have to be non-polar in conjunction with high $\log K_{OW}$ values. Furthermore, the KIS tracer reaction kinetics has to be adapted to the characteristics of the reservoir (T, pH) and the interfacial area dynamics in order to resolve the plume development. In contrast to the parent compound, at least one of the reaction products has to be highly water soluble resulting in low or even negative $\log K_{OW}$ values. Thus, back-partitioning into the non-aqueous phase can be avoided.

This class of reactive tracers was originally intended to characterize the fluid-fluid interfacial area (e.g., between supercritical CO_2 and formation brine during CO_2 storage experiments (Tatomir et al., 2015)). Currently, only limited laboratory experiments with the supercritical CO_2 analogue fluid *n*-octane are available (Schaffer et al., 2013).

2.3.3 Reactive tracers for partitioning

A reactive tracer for partitioning is a compound comprising the features of both equilibrium tracers and kinetic tracers. This type of tracer undergoes in-situ decay of

the parent tracer compounds with subsequent partitioning of the daughter compounds. The concentration of both parent and daughter compounds are determined. The separation of the arrival times of the two tracers indicates the residual saturation similar to volume sensitive tracers (see section 3.1.2). The tracer compounds are hydrophilic and must be susceptible to decay leading to daughter compounds with different partitioning coefficients. Kinetic parameters should be evaluated in order to acquire suitable compounds for specific conditions of tracer tests (e.g., types and time scales). In contrast to kinetic tracers, the kinetic parameters are not used in the evaluation of the breakthrough curves for these tracers.

The most common fields for the application of these types of tracers are oilfields and carbon capture and storage. Esters like ethyl acetate have been proposed to determine the residual oil saturation according to Cooke (1971). By 1990 they have been successfully applied to oilfields (Tang and Harker, 1990; Tang and Zhang, 2001) and are continued to be implemented today (Khaledialidusti et al., 2015; Pathak et al., 2012). Myers et al. (2012) demonstrate the feasibility of using reactive ester tracers (i.e. triacetin, propylene glycol diacetate and tripropionin) to quantify the amount of residually trapped CO_2 through an integrated program of laboratory experiments and computer simulations. Later, the research was also demonstrated successfully in field experiments (Myers et al., 2015).

2.4 Exploitation potential and further challenges of developing reactive tracers

2.4.1 The necessity for new tracers – Tracer design approach

The use of tracers for hydrogeological applications has a long history. The first reported tracer application was around 10 A.D. to track the connection between the spring source of the Jordan River and a nearby pond (Käss, 1998). Since then, the

development of technology and the advances of tracer testing with a wide selection of tracer compounds have brought effective tools for investigating different properties of the aquatic environment. In general, tracer tests could be applied to any kind of natural and engineered systems. It is especially advantageous for not directly accessible systems compared to other techniques. Nevertheless, there are still many systems in which the potential of using reactive tracers is not yet fully exploited and more attention should be paid to these, including:

- The hyporheic zone, a transition zone between surface water and subsurface water, has been recognized as hotspot for biogeochemical reactions, making the exchange of water, nutrients, and organic matter important parameters. This zone is a mixing zone which has a complex hydrological situation and heterogeneity containing dissolved gasses, oxidized and reduced species, temperature patterns, flow rates, etc. Due to the large number of variables, the quantification of processes in the hyporheic zone is still a challenge (Palmer, 1993; Sophocleous, 2002).

- Hydraulic fracturing (fracking) in shale/tight gas reservoirs has gained growing interests in the oil and gas industry during the last decade (Kissinger et al., 2013). However, fracking may pose environmental risks (Taherdangkoo et al., 2017; Vengosh et al., 2014). During the stimulation process, fracking fluid is injected into the reservoir to create additional flow paths for the transport of hydrocarbons. Hydraulically induced fractures may connect pre-existing natural fractures and faults leading to the creation of multiple permeable pathways which may cause groundwater contamination (King, 2012). Therefore, there is a high demand for the application of tracers to predict the risk or to track the contamination (i.e. fracking fluid) (Kurose, 2014).

- Other fields may include karst aquifer characterization (due to the strong system heterogeneity and variability), geothermal fluids and acid-mine-drainage (due to complex water chemistry and temperature).

The design of new innovative reactive tracers requires new strategies. Molecular design has been successfully established as a methodology for producing tailor-made molecules with desired properties or effects in several scientific disciplines, especially in life sciences, such as pharmacology, biochemistry, medicine (Kuntz et al., 1994), and material sciences (Kang and Zhang, 2000). The target-oriented combination of well-studied structural elements and molecular features (e.g., functional groups, substructures, homologues, etc.) allows the creation of novel compounds with desired structures and properties. Almost an unlimited number of compounds is imaginable and can be synthesized individually for a magnitude of applications. However, molecular target design of tracer substances for studying the aquatic environment has yet to be widely considered.

2.4.2 Strategy for designing novel reactive tracers

Creating tracer molecules, which react in a predictable way under given physicochemical conditions, is a relatively new and very innovative concept. By knowing exactly how certain reservoir conditions drive the tracer reaction, new insights into the controlling variables may be gained. In the following, the exemplary molecular target design of thermo-sensitive and interface-sensitive tracers is described. The prerequisite for the design (selection and modification) of molecules that are able to act as thermo-sensitive and interface-sensitive tracers in reservoir studies, respectively, is a thorough understanding of their reactive behavior. In particular, it is vital to understand the role and the influence of each structural element in the molecule on its reaction kinetics and its physicochemical tracer properties (e.g.,

detection, acidity, solubility, sorption, etc.). In Fig. 2 the main steps for a successful theoretical and practical molecular target tracer design are shown schematically.

Based on available literature and experiences from laboratory and field tests, a promising base molecule for both tracer types is believed to be the class of naphthalenesulfonates, into which thermo- and interface-sensitive groups can be incorporated (Fig. 3). Several physicochemical attributes make them convenient for the selection as the backbone structure. Naphthalenesulfonates are strong acids with corresponding low logarithmic acidity constants (pK_a) of <1. Therefore, this compound class forms anions even at very low pH values and is highly water-soluble (>1000 g L^{-1}). The resulting pH-dependent $\log K_{OW}$ of −2.87 at pH > 5 (SciFinder, ACD/Labs) is also very low, which implies a non-sorptive behavior and, thus, a high mobility in aquatic systems. Additionally, naphthalenesulfonates are stable under oxygen-free conditions and temperatures up to 250 °C (Nottebohm et al., 2010; Rose et al., 2001a). The molecule's good fluorescence with a direct detection limit in the low μg L^{-1} range is another important feature of naphthalenesulfonates. Hence, their detection in field tests by online determination simplifies the experimental effort needed. Furthermore, (high-pressure liquid) ion pair chromatography combined with solid phase extraction and fluorescence detection (SPE-IPC-FLD) lowers the detection limit by around one order of magnitude (<1 μg L^{-1}) even in highly saline matrices, such as brines from deep reservoirs (Nottebohm and Licha, 2012; Rose et al., 2001b). The chromatographic separation even allows the simultaneous analysis of several compounds and, therefore, the use of different isomers, derivates, and homologues. Finally, naphthalenesulfonates are non-toxic (Greim et al., 1994), their use in groundwater studies is administratively non-restricted, and they are established conservative tracers for the characterization of geothermal reservoirs (e.g., Rose et al., 2001b; Sanjuan et al., 2006).
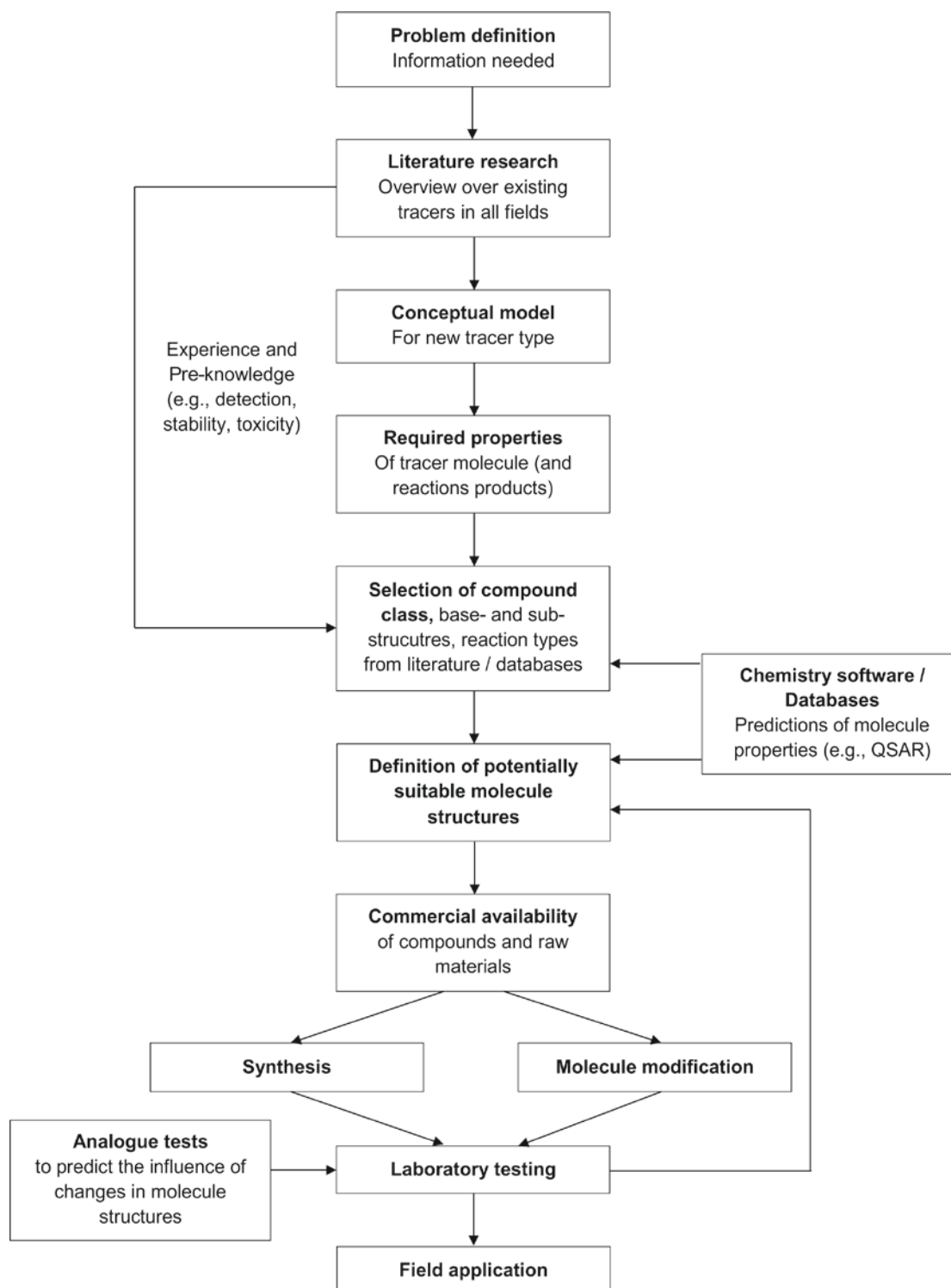
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                        │    Problem definition    │
                        │    Information needed     │
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                        ┌─────────────────────────┐
                        │   Literature research    │
                        │   Overview over existing │
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                        │    Conceptual model      │
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   Experience and       │   Required properties    │
   Pre-knowledge        │   Of tracer molecule (and│
   (e.g., detection,    │   reactions products)    │
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                        │ strucutres, reaction types│   │
                        │ from literature / databases│  │
                        └─────────────────────────┘   │
                                    │          ┌─────────────────────────┐
                                    ▼          │ Chemistry software /     │
                        ┌─────────────────────────┐ │ Databases              │
                        │ Definition of potentially│◄┤ Predictions of molecule│
                        │   suitable molecule      │ │ properties (e.g., QSAR) │
                        │      structures          │◄┐└─────────────────────────┘
                        └─────────────────────────┘ │
                                    │               │
                                    ▼               │
                        ┌─────────────────────────┐ │
                        │  Commercial availability │ │
                        │  of compounds and raw    │ │
                        │       materials          │ │
                        └─────────────────────────┘ │
                            ╱            ╲           │
                           ▼              ▼          │
              ┌──────────────┐    ┌──────────────────┐ │
              │  Synthesis   │    │ Molecule modification│ │
              └──────────────┘    └──────────────────┘ │
                           ╲            ╱               │
  ┌────────────────────┐    ▼          ▼                │
  │   Analogue tests    │  ┌─────────────────────────┐  │
  │ to predict the influence│ │  Laboratory testing  │──┘
  │ of changes in molecule  │→│                      │
  │     structures          │ └─────────────────────────┘
  └────────────────────┘            │
                                    ▼
                        ┌─────────────────────────┐
                        │    Field application     │
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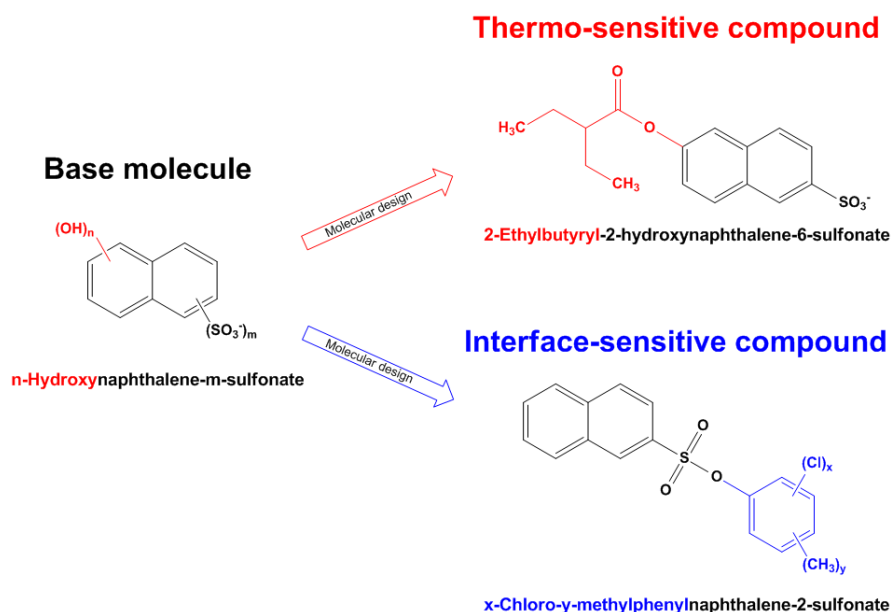**Fig. 2.2** Schematic overview for the design of reservoir tracers.

Fig. 2.3 Design of two different types of potential reservoir tracers based on naphthalenesulfonate as common structural element.

2.5 References

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Chapter 3

3 Preservation of commonly applied fluorescent tracers in complex water samples

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Abstract

Water sample preservation and pre-treatment are important steps for achieving accurate and reproductive results from tracer tests. However, this is particularly challenging for complex water matrices prior to fluorescence analysis. In this study, the interference of iron and calcium precipitation with nine commonly applied conservative tracers, uranine, eosin, 1-naphthalene sulfonate, 1,5-naphthalene disulfonate, 2,6-naphthalene disulfonate, 4-amino-1-naphthalene sulfonate, 6-hydroxy-2-naphthalene sulfonate, 1,3,6-naphthalene trisulfonate, and 1,3,6,8-pyrene tetrasulfonate, was investigated in batch experiments. In general, the observed results are influenced by precipitates. A technique consisting of pH adjustment and centrifugation is described for preserving samples and avoiding the impact of these precipitates on obtained results.

Keywords: Conservative fluorescent tracers; Precipitates; Geothermal fluids, Acid mine drainage; Sample preservation; Storage

3.1 Introduction

Conservative fluorescent tracers are widely used for the assessment of hydrogeological parameters and flow properties of aquifer systems (Flury and Wai, 2003) and also as reference tracers in multi-tracer tests conducted using reactive (non-conservative) tracers (e.g., Luhmann et al. 2012; Hillebrand et al. 2015). Appropriate water sample preservation and pre-treatment are important steps for achieving accurate and reproducible results from tracer tests. However, sample preservation in complex water matrices is challenging, particularly in samples from highly mineralized geothermal reservoirs and acid mine drainage sites. Specifically, precipitates in the form of oxyhydroxides, sulfates and carbonates from, e.g., iron and calcium, will inevitably be present due to induced changes in the redox conditions, temperature, and pH during sampling (e.g., due to degassing, cooling) (e.g., Klepetsanis and Koutsoukos 1991; He et al. 1999; Akcil and Koldas 2006). In this context, many common conservative tracer compounds that contain carboxyl groups (e.g., uranine, eosin) or sulfonic groups (e.g., naphthalene sulfonates) are anionic in the usually encountered pH range of natural groundwater (pH = 5–8). They may therefore suffer from sorptive (electrostatic) interactions (e.g., anion exchange) to certain precipitates (Pirillo et al., 2008; Saha et al., 2011) or be prone to co-precipitation (Noubactep, 2008). These processes may lead to a substantial mass loss of the fluorescent tracers in solution during storage. Moreover, increasing the pH in order to analyze tracers with pH-dependent fluorescence properties, such as uranine and eosin (Käss, 1998), may lead to additional problems due to increased precipitation. To the authors' knowledge, no systematic study for sample preservation for these compounds is available for water matrices to date.
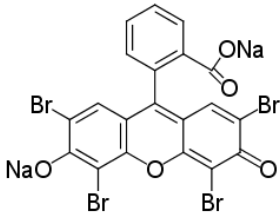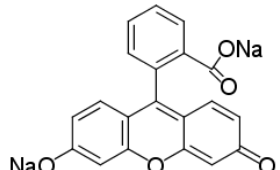
The objective of this work is to test the influence of iron and calcium precipitates on the analytical recovery of commonly used fluorescent tracers during storage. Ultimately, a practical preservation method is suggested to avoid misinterpretations in tracer test evaluations.
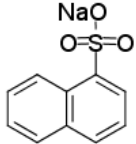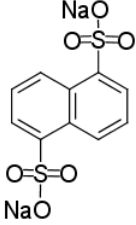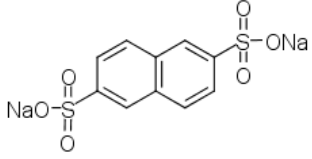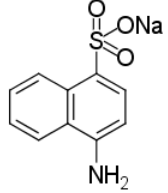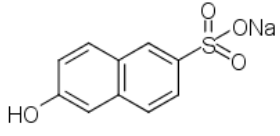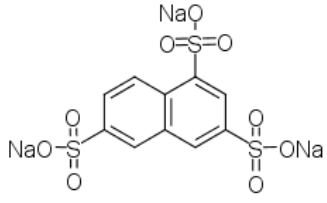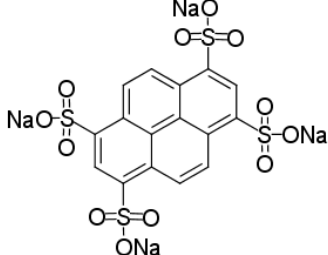
3.2 Materials and methods

3.2.1 Chemicals

The nine investigated tracer compounds with their excitation and emission wavelengths, CAS registry number, and their logarithmic acid dissociation constants, pK_a, are listed in Table 3.1. 1-Naphthalene sulfonate (1NS, >95%), 1,5-naphthalene disulfonate (15NDS, >98%), 2,6-naphthalene disulfonate (26NDS, >98%), and 1,3,6-naphthalene trisulfonate (136NTS, >98%), were purchased as sodium salts from TCI Europe. 6-Hydroxy-2-naphthalene sulfonate (6H2NS, >98%) was obtained from TCI Japan. 4-Amino-1-naphthalene sulfonate (4A1NS, >98%), 1,3,6,8-pyrene tetrasulfonate (1368PTS, >85%), and eosin (Eo) were purchased from Acros Organics. Uranine (Ur) was purchased from Fluka.

Table 3.1 Summary of the properties of investigated fluorescent compounds

Compound names	Structure	CAS number	pK_a[a]	Excitation wavelength (nm)	Emission wavelength (nm)
Eosin (Eo)		17372-87-1	2.02[b]; 3.80[b]	518	538
Uranine (Ur)		518-47-8	2.08[c]; 4.31[c]; 6.43[c]	490	511

Compound	Structure	CAS	pK_a[a]	Ex (nm)	Em (nm)
1-Naphthalene sulfonate (1NS)		130-14-3	0.17[d]	220	332
1,5-Naphthalene disulfonate (15NDS)		1655-29-4	-0.60[d]	224	335
2,6-Naphthalene disulfonate (26NDS)		1655-45-4	-0.41[d]	230	345
4-Amino-1-naphthalene sulfonate (4A1NS)		123333-48-2	-0.37[d]	220	423
6-Hydroxy-2-naphthalene sulfonate (6H2NS)		825652-02-6	0.41[d]	232	429
1,3,6-Naphthalene trisulfonate (136NTS)		5182-30-9	-0.76[d]	232	345
1,3,6,8-Pyrene tetrasulfonate (1368PTS)		59572-10-0	-1.71[d]	242	385

[a] Logarithmic acid dissociation constant pK_a refers to the free acid form of the dissolved tracers

[b] (Batistela et al., 2011)

[c] (Sjöback et al., 1995)

[d] Sci Finder (https://scifinder.cas.org/scifinder) predicted values, calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (1994-2016 ACD/Labs)

All other (inorganic) chemicals were of high purity (>98%, analytical grade). $NaHCO_3$ and KCl were purchased from Applichem; $NaSO_4$, $FeCl_3$ and $MgCl_2$ from Merck; $FeCl_2$, $CaCl_2$ and NaCl from Acros Organics. Ultrapure water, prepared by a combined water purification system consisting of Elix 5 and Milli-Q Gradient A10 (both from Merck Millipore), was used for all experiments.

To simulate a complex water matrix, an artificial background water of high salinity was prepared based on the chemical composition of a natural water from a deep saline aquifer. The artificial background water used consisted of 15,640 mg/L Cl^-, 856 mg/L SO_4^{2-}, 404 mg/L Ca^{2+}, 732 mg/L K^+, 259 mg/L Mg^{2+}, and 8,720 mg/L Na^+ with a pH of 7.5. Due to the high mineralization (high salinity), this water is representative for other complex and frequently encountered water matrices, such as geothermal brines After adding different amounts of ferrous and ferric iron to this background water there was a subsequent drop of pH. The solution may therefore be representative of acid mine drainage waters. Consequently, the obtained results are generally transferable.

3.2.2 Influences of pH and turbidity on fluorescence intensity

The pH dependence of the fluorescence intensity (Käss, 1998) was considered by measuring the relative signal recovery for the investigated compounds for different pH values. As a result, pH-dependent charts were obtained in ultrapure water within the pH range 1–11. The fluorescence measurements (Cary Eclipse, Agilent) were performed following the addition of the respective amounts of HCl and NaOH to the solutions with constant concentrations of Eo (100 µg/L), Ur (1000 µg/L), and 15NDS (1000 µg/L) at a room temperature of 20±1 °C.

Turbidity often influences the fluorescence intensity due to light scattering or absorption, which may lead to large analytical errors and false results. Centrifugation is an efficient and reproducible way to separate suspended particles from the water

phases and, thus avoid turbidity effects. In order to find the optimal conditions for centrifugation, the artificial solutions were divided into three parts and separately centrifuged with three different set-ups (3000 rpm in 5min, 5000 rpm in 5min, 5000 rpm in 10min, Centrifuge 5804, Eppendorf AG) before analysis by fluorescence spectrophotometry (Cary Eclipse, Agilent). Furthermore, the scattering due to turbidity was characterized at an excitation wavelength of 800 nm and an emission wavelength of 800 nm.

3.2.3 Influence of precipitates on signal recovery

A first set of batch experiments was prepared with the aim of testing the influence of different concentrations (0–200 mg/L) and valences (Fe^{2+} and Fe^{3+}) of iron. The pH was not adjusted and, therefore, the final pH values are a direct result of different iron ion concentrations (acidic reaction in water) in these experiments. This means that increasing iron concentrations lead to lower pH values. The addition of Fe^{3+} results in even lower pH values than for Fe^{2+} when comparing identical concentrations. Batches were prepared in 15 mL polypropylene centrifugation tubes. For each tracer compound, a separate set of batch experiments was performed containing 10 mL of the background water, a constant concentration of the respective tracer (100 µg/L for Ur; 250 µg/L for 6H2NS; 500 µg/L for 4A1NS and 1368PTS; 1000 µg/L for Eo, 1NS, 15NDS, 26NDS, and 136NTS), and varying amounts of iron. The added amounts of Fe^{2+} and Fe^{3+} (as $FeCl_2$ and $FeCl_3$) were equivalent to concentrations of 10, 50, and 200 mg/L. The tubes were stored and shaken on a horizontal shaker with 300 rpm (KS 501D, IKA) in a climatic chamber (dark) at a temperature of 10±1 °C for 12 h, 24 h, and 120 h, respectively. All samples in this and the following experiment were centrifuged for 5 min at 5000 rpm (the optimum centrifugation setup) prior to analysis with the fluorescence spectrophotometer. The analytical error in this study was around 5% for

all compounds in the considered concentration range. The pH values were measured using a Sentix 91 pH electrode (WTW).

In a second set of experiments, the influence of added iron was tested for adjusted pH values of 7.5 for 15NDS, Eo and of 9.0 for Ur by adding predefined amounts of NaOH (according to the amount of added iron). The batch experiments were prepared for the same iron concentrations as mentioned before. In contrast to the previous experiment, the pH value was kept constant and only Eo, Ur and 15NDS (exemplary compound for naphthalene sulfonates) were tested. The samples were shaken for 12 hours at a temperature of $10\pm1\,^{\circ}C$.

In the last (third) set of experiments, the influence of calcite ($CaCO_3$) and calcium sulfate ($CaSO_4$) precipitates was investigated. Here, the pH values were also kept constant (pH = 7.5 for 15NDS, Eo and pH = 9.0 for Ur) by adding predefined amounts of NaOH. The precipitates were prepared by mixing 5 mL $CaCl_2$ (20.0 g/L) with 5 mL $NaHCO_3$ (10.0 g/L) and 5 mL $CaCl_2$ (20.0 g/L) with 5 mL Na_2SO_4 (20.0 g/L), respectively. All batch experiments were conducted as triplicates and, in total, approximately 650 experiments were carried out.

3.3 Results and discussion

3.3.1 Influences of pH and turbidity on fluorescence intensity
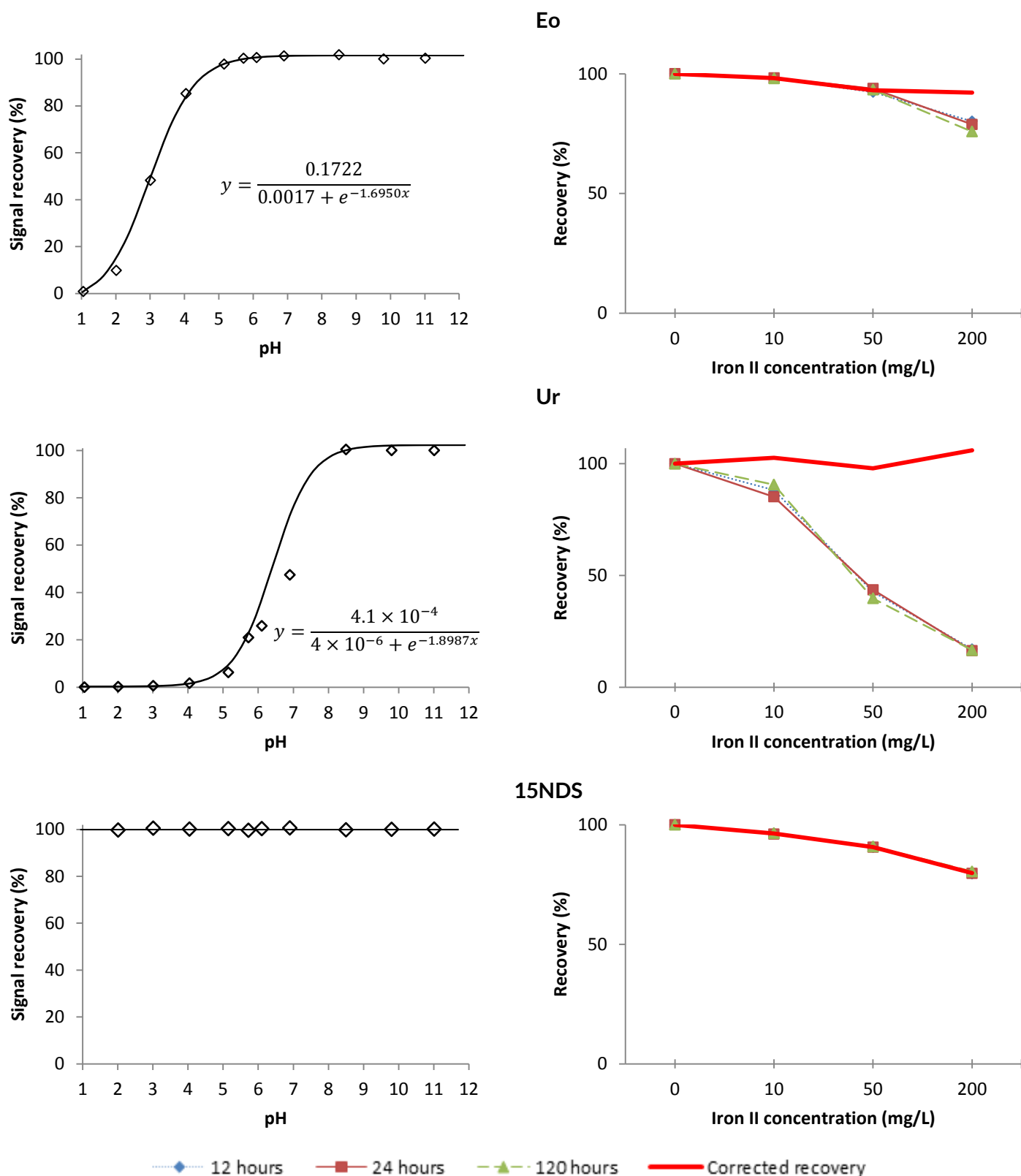
Fig. 3.1 Influence of pH on fluorescence signal recovery of Eo, Ur, and 15NDS (left). The corrected recovery of Eo, Ur, and 15NDS for deviations of the pH and Fe^{2+} concentration (right) (0 mg/L (pH = 7.5), 10 mg/L (pH = 7.1), 50 mg/L (pH = 6.4) 200 mg/L (pH = 5)).

Fig. 3.1 (left) shows the influence of pH on the fluorescence intensity of Eo, Ur, and 15NDS. The fluorescence intensity of Eo, here expressed as relative signal recovery, increased between pH 1.0 and 6.0 from 0 to 100%. At higher pH values, the fluorescence intensity remained constant. A similar but shifted curve was observed for Ur, where the fluorescence intensity increased between pH 4.0 and 9.0 and remained constant at higher pH values. The curves reflect one pK_a value of each tracer, as the changing pH leads to different species of Eo ($pK_{a,2}$ = 3.80) and Ur ($pK_{a,3}$ = 6.43) in solution. Hereby, only the anionic (de-protonated) species show fluorescence. In contrast to Eo and Ur, the fluorescence intensity of 15NDS showed no variation within the investigated pH range. This is in accordance with the generally very low pK_a values of naphthalene sulfonates of less than 1. Therefore, their fluorescence intensities are stable, as only their anionic form exists in the applied pH range (fully de-protonated).

In this study, a centrifugation at 5000 rpm for 5 min was clearly sufficient to avoid any turbidity effects caused by iron and calcium precipitates on all tested tracer compounds during fluorescence analysis (see Fig. S1).

3.3.2 Influence of precipitates on signal recovery

Experiments with iron precipitation without pH adjustment

In the first set of batch experiments (without adjusting the pH), the amount of precipitates clearly increased (visually) with increasing amounts of added iron. The ferric iron precipitates consist most likely of α-FeO(OH) and Fe_2O_3, which were predicted with PHREEQC using the *phreeqc.dat* database for solution with Fe^{3+} (Table S1). Solution with Fe^{2+} was not modelled because $Fe(OH)_{2(s)}$ is not defined in *phreeqc.dat*.

The results of Eo showed that the signal recoveries were close to 100% in the batches with the added Fe^{2+} and Fe^{3+} concentrations ranging from 0 to 50 mg/L (pH resulting pH between 6 and 7.5) (Fig. S2). In contrast, much lower recoveries were obtained for 200 mg/L of Fe^{2+} (pH = 5) and for 200 mg/L of Fe^{3+} (pH = 3).

A slightly different pattern was observed for Ur (Fig. S3). The recoveries showed a sharper decline compared to Eo within the investigated Fe^{2+} and Fe^{3+} concentration range. These results are expected and can be explained by the different pH dependence of the fluorescence signal for Eo and Ur. After applying the correction factors (reciprocal recoveries) derived from the pH-dependent charts, the corrected analyte recoveries of Eo and Ur were around 100% (Fig. 3.1, right). This means that the reduced (measured) fluorescence intensities are solely caused by the pH dependence of the Eo and Ur signals.

The results for 15NDS showed that the signal recoveries decreased steadily with increasing Fe^{2+} and Fe^{3+} concentrations; the signal of 15NDS even drops down to zero for Fe^{3+} concentrations of 200mg/L (pH = 3) (Fig. S4). The observed pattern was very similar for all tested naphthalene sulfonates (Fig. S4–S10). Therefore, only 15NDS was chosen as an exemplary compound for the whole class of naphthalene sulfonates in all further investigations. In contrast to Eo and Ur, the low recoveries cannot be explained by a pH dependence of the fluorescence signal and must be a result of a concentration decrease (mass loss) in solution (Fig. 3.1). Sorption onto Fe^{2+} and Fe^{3+} precipitates likely explains the observed low analyte recoveries. This is because the point of zero charge, pH_{pzc}, of Fe-oxides can range between 3 to 6 (Sadowski et al. 2001, Kosmulski 2011). At pH values lower than the pH_{pzc}, the precipitate surface is predominantly positively charged. Thus, anions like sulfonates ($pK_a < 1$) may sorb due to electrostatic sorption mechanisms (e.g., ion exchange (Schaffer et al., 2017)). High pH values should therefore considerably reduce the sorption of naphthalene sulfonates onto iron surfaces.

Furthermore, similar values were measured for different time steps of 12 hours, 24 hours and 120 hours, respectively (Fig. S4-S10). This indicates that equilibrium conditions were reached after 12 hours. Hence, for practical application, samples should be treated immediately after being collected by increasing their pH.

Experiments with iron precipitation and pH adjustment

In the experiments conducted at a constant pH, the measured intensities of all tracers (after centrifugation) were generally identical for all tested iron concentrations, indicating no mass loss in the solutions (full recovery >90%) (Table S2). The obtained analyte recoveries of Eo, Ur and 15NDS were in the range of 94–101%; 93–100%; and 97–100%, respectively.

Experiments with calcium precipitation and pH adjustment

Based on the solution chemistry, the calcium precipitates ($CaCO_3$ and $CaSO_4$) consisted most likely of aragonite and calcite for $CaCO_3$, and anhydrite and gypsum for $CaSO_4$ (predicted with PHREEQC using *phreeqc.dat* database) (Table S1). After centrifugation, neither the carbonate nor the sulfate precipitate revealed some influence on the measured fluorescence signals of Eo, Ur and 15NDS , thus, full analyte recoveries were obtained (Table S3).

3.4 Recommendations

In conclusion, the influence of the pH on the fluorescence signal of Eo and Ur can significantly be reduced if measurements of the samples are conducted at alkaline pH values. Furthermore, turbidity effects caused by the precipitates can be prevented by proper centrifugation prior to analysis.

Consequently, the following recommendations for sample preparation and conservation can be given to avoid interferences of precipitates with tracer compounds. This applies for many aquifer systems, especially for water with a complex matrix, such as samples from highly mineralized geothermal reservoirs, saline aquifers, or acid mine drainage sites.

- The pH values have to be adjusted (increased) immediately after sampling, for example, to at least pH > 9 for Ur, pH > 7.5 for Eo and naphthalene sulfonates. Even though the increase of pH induces more precipitation, no mass loss is expected due to the low points of zero charge of the minerals in the precipitates.

- One suitable treatment could be the addition of NaOH pellets (with caution from releasing heat), which are more stable than its solutions (formation of carbonates by reaction with atmospheric CO_2) and do not cause dilution of the samples.

- Prior to analysis, a proper sample centrifugation (of at least 5 min at 5000 rpm) is vital to avoid turbidity effects during the fluorescence analysis.

3.5 Acknowledgments

3.6 Supplementary material

Supplementary material to this article can be found in Appendix A.

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Chapter 4

4 The feasibility of using carbamates to track the thermal state in geothermal reservoirs

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Abstract

Organic compounds with functional groups susceptible to hydrolysis hold the potential to become thermo-sensitive tracers. To broaden the range of available compound classes for typical temperatures encountered in low enthalpy geothermal reservoirs, the group of carbamates was investigated. The kinetic parameters of eight primary and one secondary carbamate(s) were studied by means of isothermal batch experiments. The influence of several parameters on hydrolysis kinetics was investigated, which included the compound structure, temperature, and pH/pOH. The results demonstrate the possible application of these tracers within a broad range of temperatures.

Keywords: Thermo-sensitive tracer; Carbamates; Hydrolysis; Kinetics; Reservoir temperature; Molecular design

Graphical abstract
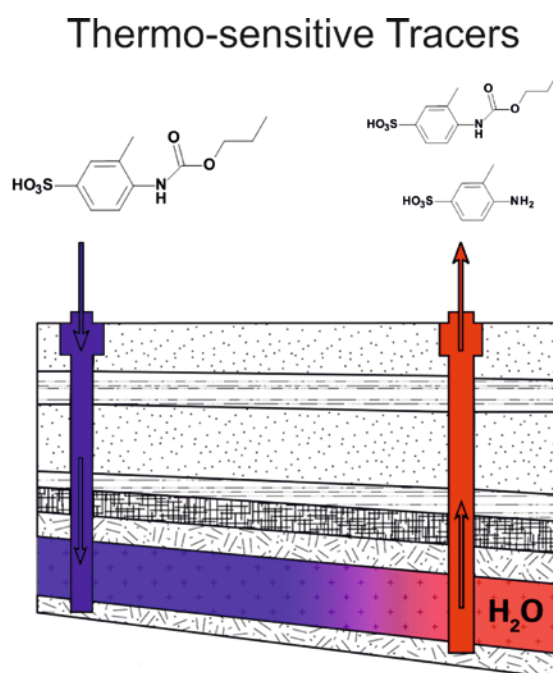
4.1 Introduction

An important aspect of sustainable development is the availability of renewable energy resources (Dincer, 2000), and among these resources, geothermal energy carries a significant potential in the near future (Fridleifsson, 2001; Lund and Boyd, 2016). To optimize the long-term operation of geothermal reservoirs, proper exploitation strategies must be applied. Reinjection is a common technique in geothermal reservoir management that plays an important role in influencing the success of a geothermal reservoir (Kaya et al., 2011). However, the utilization of this method may lead to the risk of early thermal breakthrough (Stefansson, 1997); therefore, it generally requires the monitoring of the reservoir's spatial and temporal temperature distribution. In the past decades, the application of tracers with thermo-sensitive properties to track the thermal state of a geothermal reservoir has been demonstrated as a promising tool in both laboratory (Maier et al., 2015a, 2015b) and field scale research (Adams and Davis, 1991; Hawkins et al., 2017; Rose and Clausen, 2014). A recent promoted approach to track the thermal distribution involves the use of hydrolysable compounds with known kinetic properties, such as esters and amides (Maier et al., 2015a; Nottebohm et al., 2012; Schaffer et al., 2016). These compounds are derived from common conservative dye tracers (e.g., naphthalene sulfonates) in which a reactive group susceptible to a well-defined thermo-sensitive hydrolysis reaction is incorporated.

Depending on the underlying decay mechanism, thermo-sensitive tracer compounds potentially cover a wide range of temperatures (e.g., Adams and Davis, 1991; Nottebohm et al., 2012; Rose et al., 1999; Schaffer et al., 2016). In particular, amides hold great potential for exploitation within the temperature range of 100–200 °C. Furthermore, the hydrolysis reaction of amides is rather independent from environmental pH/pOH conditions, and the reaction products have a high thermal

stability (Schaffer et al., 2016). For temperatures lower than 100 °C, esters are proposed as good tracers to track thermal changes (Nottebohm et al., 2012). However, esters are likely to be unstable in a reservoir in which the hydrolysis reaction may be catalyzed (e.g., by microbial activity (Gianfreda and Rao, 2004; Hawkins et al., 2017)) and consequently accelerated, making these compounds unfavorable for field applications. On the contrary, carbamates are more stable due to the donation of the nitrogen's free electron pair to the carbonyl group (resonance stabilization) (Larson and Weber, 1994). Additionally, carbamates are more electrophilic than amides due to the presence of an additional electronegative oxygen atom, which may facilitate faster hydrolysis for carbamates than amides.

To extend the number of applicable compounds for tracking geothermal temperatures, various carbamates (eight primary and one secondary) were investigated. A similar approach to that of Schaffer et al. (2016) was applied to examine the influence of the molecule structure, temperature, and pH/pOH on the hydrolysis kinetics of carbamates. The aim of this study is to widen the current knowledge of thermo-sensitive tracers and to progress towards the designing of tracers for the specific boundary conditions in various reservoirs.

4.2 Theoretical background

4.2.1 Reaction mechanism

Depending on the molecular structure of the carbamate, the hydrolysis reactions may proceed via two mechanisms: the elimination reaction (E1cb) or the acyl-oxygen bond cleavage ($B_{AC}2$) (Drossman et al., 1988; Hegarty and Frost, 1973). Primary carbamates (R_1 = alkyl/aryl, R_2 = H, Fig. 1a) follow the E1cb mechanism in which the N-H group is deprotonated, resulting in the subsequent formation of isocyanate. This isocyanate

intermediate is quickly hydrolyzed to form the carboxylated amine, which loses carbon dioxide spontaneously to yield the free amine.

An alternative mechanism ($B_{AC}2$) is available to secondary carbamates (R_1, R_2 = alkyl/aryl, Fig. 1b) in which a tetrahedral intermediate is formed by the nucleophilic attack of a hydroxide anion on the carbonyl carbon. The alkoxide (R_3O^-) is subsequently expelled to produce the carboxylated amine, which then decomposes to carbon dioxide and the amines. An alcohol/phenol, carbon dioxide, and amine are formed as reaction products in the reaction shown in Fig. 4.1.
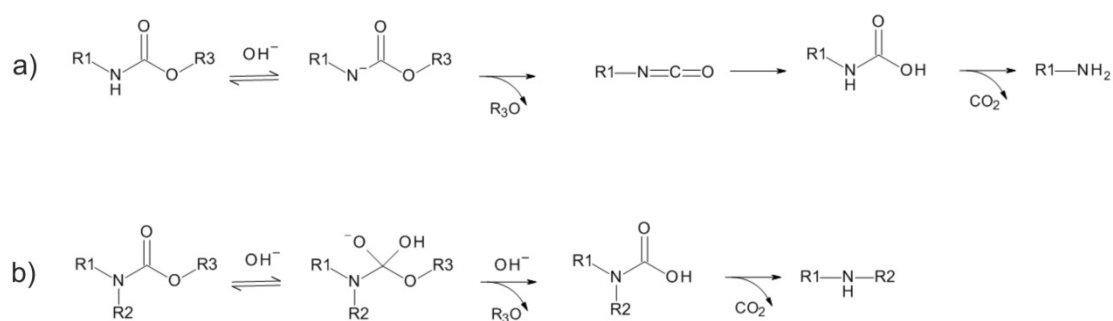
Fig. 4.1 Carbamates hydrolysis mechanism, including a) E1cb (primary carbamates) and b) BAC2 (secondary carbamates).

4.2.2 Reaction kinetics and thermo-sensitivity

The hydrolysis of a carbamate can proceed via three distinct bimolecular mechanisms, including acid, neutral, and base catalyzed.

$$Acid\ catalyzed\ rate = -k_A \,.\, [H^+][Carbamate] \tag{4.1}$$

$$Neutral\ catalyzed\ rate = -k_{H_2O} \,.\, [H_2O][Carbamate] \tag{4.2}$$

$$Base\ catalyzed\ rate = -k_B \,.\, [OH^-][Carbamate] \tag{4.3}$$

where k_A, k_{H2O}, and k_B are second order rate constants; $[H^+]$, $[H_2O]$, and $[OH^-]$ are the concentrations of the catalysts; and $[Carbamate]$ is the concentration of the reactant (thermo-sensitive tracer).

The overall hydrolysis rate is equal to the sum of all individual mechanisms. Hence, the combined rate constant k_h is defined by:

$$k_h = k_A \cdot [H^+] + k_{H_2O} \cdot [H_2O] + k_B \cdot [OH^-] \tag{4.4}$$

According to Larson and Weber (1994), the base catalyzed hydrolysis of carbamates tends to be more dominant in common natural systems than acid catalyzed and neutral catalyzed hydrolysis. As a result, k_h simplifies to:

$$k_h = k_B \cdot [OH^-] \tag{4.5}$$

Consequently, the kinetics of carbamate hydrolysis at constant pH/pOH exhibits pseudo-first-order kinetics similar to those of amides (Schaffer et al., 2016) and is expressed by:

$$-\frac{d[Carbamate]}{dt} = -k_h \cdot [Carbamate] \tag{4.6}$$

The kinetics of carbamate hydrolysis may also be determined by monitoring the concentration of the reaction product $[Amine]$:

$$\frac{d[Amine]}{dt} = k_h \cdot [Amine] \tag{4.7}$$

The temperature dependence of the reaction rate constant k_h is an essential factor for estimating the thermo-sensitivity of carbamate hydrolysis, and it follows Arrhenius' law:
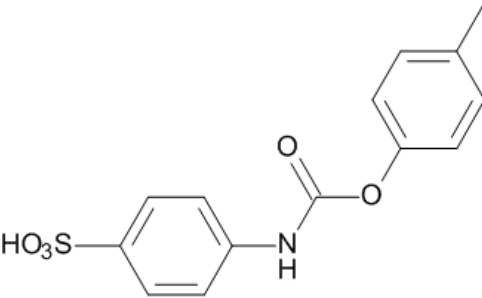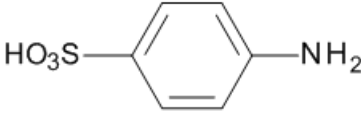
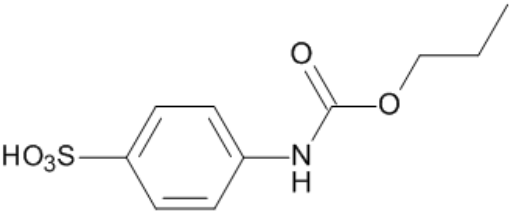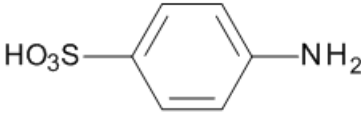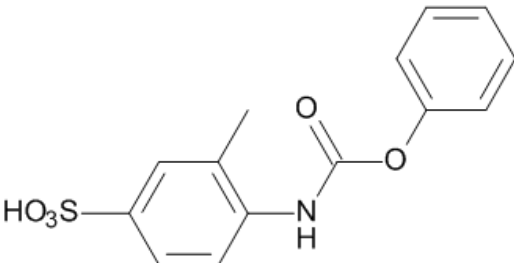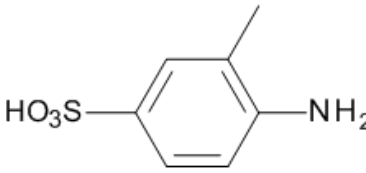$$T = -\ln\frac{A}{k_h} \cdot \frac{E_a}{R} \tag{4.8}$$
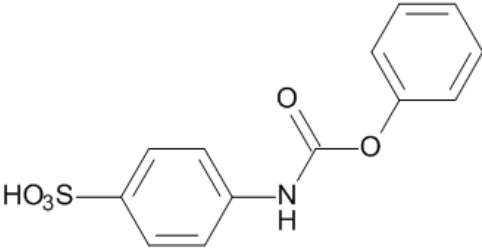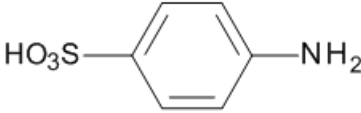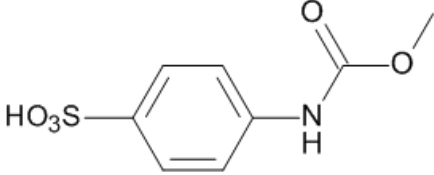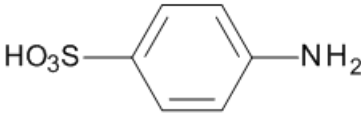
where A is the pre-exponential factor, E_a represents the activation energy for the reaction, R is the ideal gas constant, and T is the equivalent temperature of the reservoir. Therefore, by knowing the Arrhenius parameters E_a and A, k_h can be determined for various T values and vice versa. This is important for the determination of the degree of cooling of the reservoir (Maier et al., 2015a, 2015b).

4.3 Materials and methods

4.3.1 Carbamates and other chemicals

Eight structurally different primary carbamates were synthesized based on the acylation of primary amines (Idzik et al., 2015). These carbamates are highly soluble, and thus a non-sorbing behavior is probable due to the anionic sulfonic group attached to the molecules (Schaffer and Licha, 2014). One secondary carbamate (dimethyl-carbamic acid phenyl ester, 98%) was purchased from abcr GmbH. The carbamates investigated (C1–C9) in this systematic laboratory study, in which the focus lies on the relationship between the molecular structure and the hydrolysis speed, are deliberately designed based on stability and detectability. For the latter, the carbamates do not show fluorescence while one product (H1–H3) does to ease investigation efforts (Table 4.1).

Table 4.1 List of carbamates (C1–C9) investigated and their corresponding hydrolysis products (H1–H3).

Carbamate structure	Fluorescent hydrolysis products

C1 H1

C2 H1

C3 H1

C4 H1

C5 H2

C6

H2

C7

H2

C8

H2

C9

H3
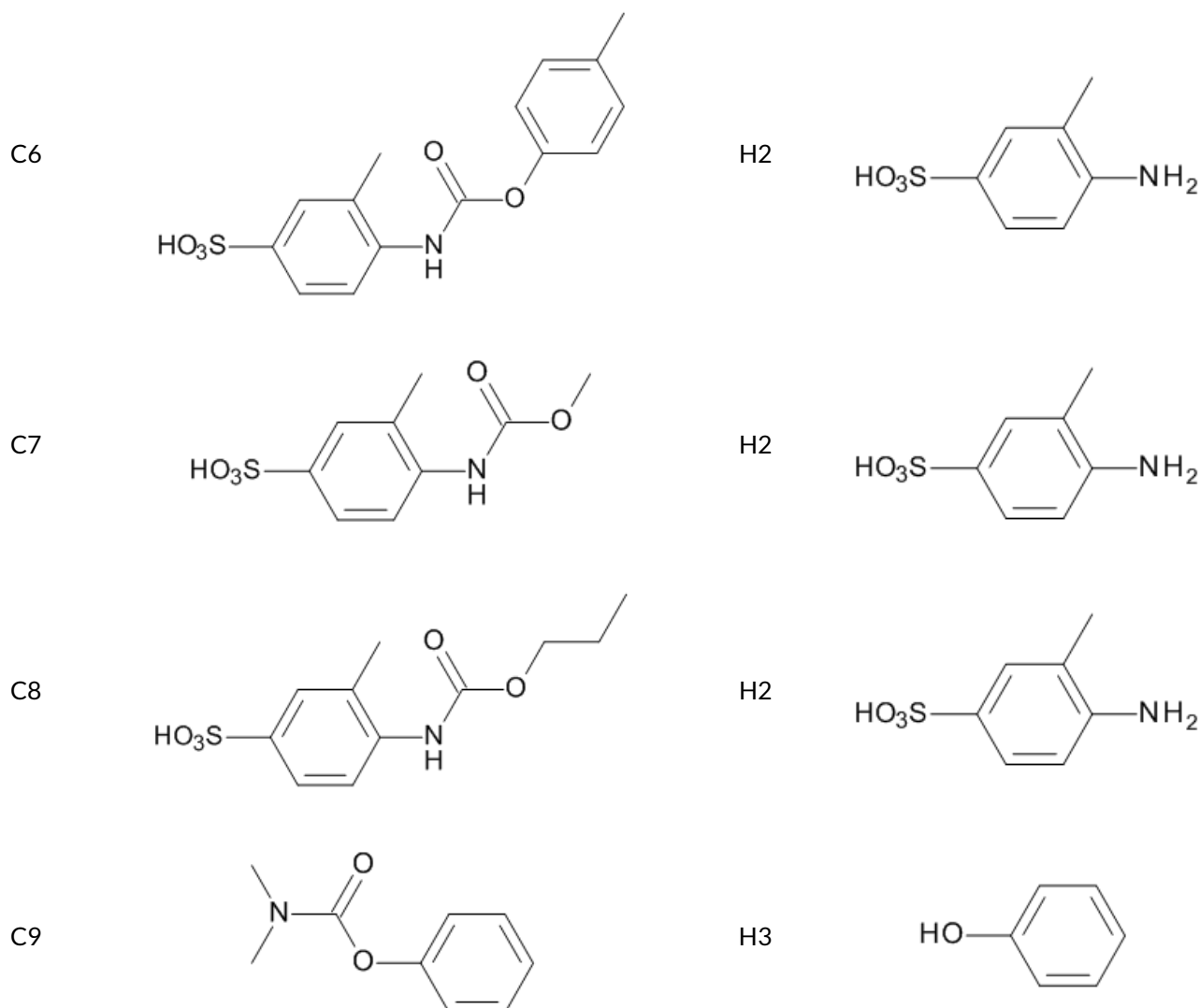
The corresponding hydrolysis products 4-aminobenzenesulfonic acid (H1) from carbamates C1–C4 and 4-amino-3-methyl-benzenesulfonic acid (H2) from carbamates C5–C8 were obtained from Sigma-Aldrich, while phenol (H3) from carbamate C9 was provided by Merck. The phosphate salts (di-sodium hydrogen phosphate dihydrate and potassium dihydrogen phosphate) with analytical reagent grade employed for preparing the buffer solutions were purchased from Fischer Scientific. Ultrapure water used in all experiments was obtained from a combined water purification system consisting of Elix 5 and Milli-Q Gradient A10 (both from Merck Millipore). Individual stock solutions of the carbamates with $c = 1\,\mathrm{g\,L^{-1}}$ were prepared in dry dimethyl sulfoxide (DMSO) from AppliChem and stored in glass vials at 4 °C.

4.3.2 Evaluation of hydrolysis reaction kinetics

To investigate the hydrolysis reaction kinetics, the methods of Guggenheim and initial rates were applied. The selection of each method was based on the experiment's duration.

The method of Guggenheim was applied to determine the reaction rate for fast reacting compounds. This method is suitable for a pseudo-first-order reaction in which the initial and infinite reaction times, as well as the purity of the substances, are unknown. According to Guggenheim (1926), if c_t is the concentration of carbamate at time t, c_0 and c_∞ is the initial ($t = 0$) and final ($t = \infty$) concentration of carbamate, and Δt is a fixed time increment, the following equations hold true:

$$c_t = c_\infty + (c_0 - c_\infty)e^{-k_h t} \tag{4.9}$$

$$c_{t+\Delta t} = c_\infty + (c_0 - c_\infty)e^{-k_h(t+\Delta t)} \tag{4.10}$$

The following equations are derived from equation (9) and (10):

$$c_{t+\Delta t} - c_t = (c_\infty - c_t)e^{-k_h t}(1 - e^t) \tag{4.11}$$

$$\ln(c_{t+\Delta t} - c_t) = -k_h t + \ln[(c_\infty - c_t)(1 - e^t)] \tag{4.12}$$

The resulting k_h is derived from the slope of the linearized equation (12). In order to achieve accuracy, a significant decrease in the concentration of reactants must be assured (i.e. above 50%).

The method of initial rates was applied for slow reaction kinetics. The slope of initial concentration c_0 versus time t plot at $t = 0$ is the initial rate of the reaction v_0, and the rate equation for a sufficiently short time step Δt can be expressed as:

$$v_0 = -\left(\frac{dc}{dt}\right)_{t=0} = -\frac{c_0 - c(\Delta t)}{\Delta t} = k_h . c_0^{\,n} \tag{4.13}$$

$$\ln v_0 = \ln k_h + n \ln c_0 \tag{4.14}$$

The k_h values were obtained for different c_0 from the intercept of the linearized equation (14) with a slope equal to the reaction order n = 1 (nearest integer). The concentration change must be significant but not greater than 10% in order to ensure the accuracy of the method.

The Arrhenius parameters E_a and A of the carbamates can be derived from the linearized Arrhenius equation:

$$\ln k_{h\,T} = \ln A - \frac{E_a}{R} . \frac{1}{T} \tag{4.15}$$

In some circumstances, both the method of Guggenheim and that of initial rates were applicable, and the results showed a high consistency between the two methods.

4.3.3 Carbamate hydrolysis at different temperatures

A set of batch experiments was prepared to measure the k_h values for all nine carbamates at 95±0.5 °C. The method of Guggenheim was applied for four carbamates: C1, C2, C5, and C6. For each of these carbamates, a separate batch experiment was performed with 10 mg L^{-1} c_0 in buffer solution. Carbamates C3, C4, C7, C8, and C9 were investigated using the method of initial rates, in which five buffered solutions with c_0 between 0.4 and 20 mg L^{-1} were prepared. The phosphate buffer (10 mM) was prepared to a stable pOH of 7 for all target temperatures by mixing predefined amounts of $Na_2HPO_4{}^{.}2H_2O$ and KH_2PO_4. The chemical modeling software PHREEQC (Version 3.3.2.10335) with the *phreeqc.dat* was used to calculate the related pH value

of the buffer solution at room temperature (T = 20 °C) and the required amounts of phosphate salts. All batch experiments were prepared in 20 mL glass vials sealed with a polypropylene screw cap with a polytetrafluoroethylene liner. The vials were incubated in a temperature-controlled water batch or isothermal GC oven for different time steps (from 1 minute to 60 days). Before each measurement, the samples were stored in a cooled water bath with a maximum temperature of 5 °C to hinder significant hydrolysis. The concentration of the hydrolysis products of the carbamates were determined with a Cary Eclipse fluorescence spectrophotometer (Agilent Technologies) with a Peltier temperature controller using an excitation wavelength of 250 nm (H1, H2) and 270 nm (H3) and an emission wavelength of 342 nm (H1, H2) and 296 nm (H3).

To evaluate the influence of temperature and to determine the Arrhenius parameters, similar experiments were performed with carbamates C1–C8 using the same instrumentation and experimental set-up at temperatures of 55±0.5 °C and 75±0.5 °C. An additional experiment was conducted with C8 as an representative compound at 95±0.5 °C and pOH = 6 to identify a possible pOH/pH dependence of carbamate hydrolysis in the pH range encountered in low enthalpy reservoirs.
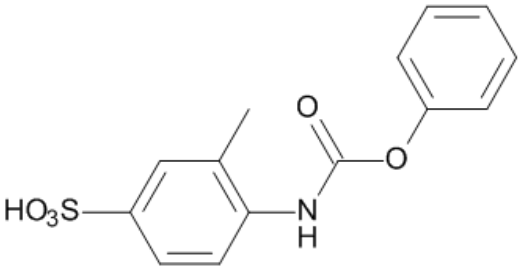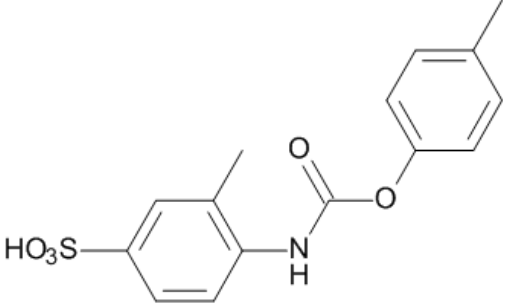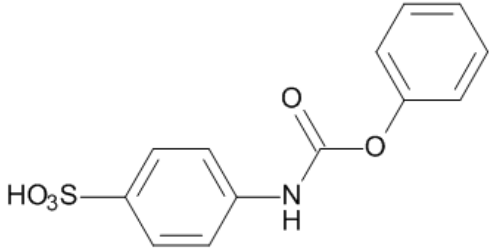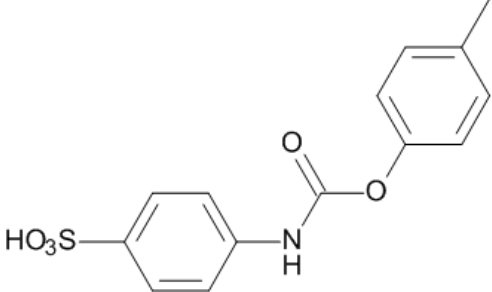
4.4 Results and discussion
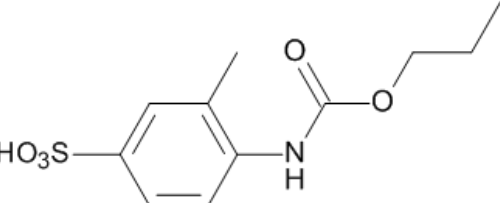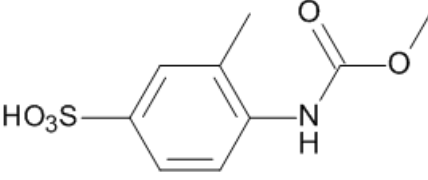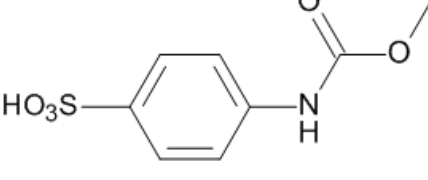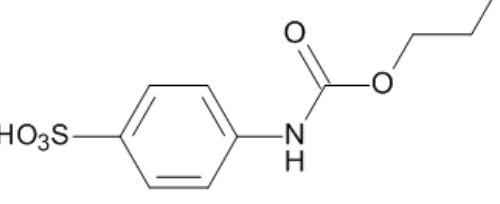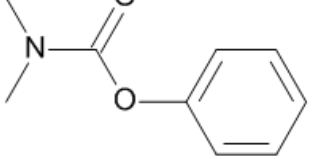
4.4.1 Influence of molecular structure on hydrolysis kinetics

The basic understanding and the relationship between molecular structure and hydrolysis kinetics is of special interest for suggesting carbamates as thermo-sensitive tracers for different reservoir conditions. The relative k_h values (normalized to $k_{h,max}$) and half-lives $t_{1/2}$ of the nine carbamates investigated at 95±0.5 °C are shown in Table 4.2. The carbamate reaction kinetics observed revealed a wide range of reaction

rates for primary and secondary carbamates. Hydrolysis half-lives dramatically span from minutes to years at the temperature of 95±0.5 °C, and the greatest differences are observed between primary and secondary carbamates. This can be attributed to the considerably different hydrolysis mechanisms of carbamates of different orders. Primary carbamates tend to follow the E1cb pathway which is relatively rapid, whereas secondary carbamates follow the slow $B_{AC}2$ hydrolysis (Hegarty and Frost, 1973). The high variation in the half-lives of around six orders of magnitude (minutes to years) makes it highly promising for using carbamate tracer molecules for different temperatures. For example, this could be applied to low enthalpy systems, such as with esters (Nottebohm et al., 2012), and intermediate enthalpy systems, such as with amides (Schaffer et al., 2016).

Table 4.2 Comparison of relative hydrolysis constant and half-life of the investigated carbamates at 95 °C.

Carbamate structure		$k_h/k_{h,max}$	$t_{1/2}\ [h]$
C5		1.00000	0.04
C6		0.77002	0.05

C1		0.46723	0.08
C2		0.18599	0.20
C8		0.00007	556
C7		0.00005	712
C3		0.00002	2132
C4		0.00002	2138
C9		0.000001	28,751

For primary carbamates, the structure of the leaving group R$_3$ (CH$_3$, C$_3$H$_7$, C$_6$H$_5$, p-CH$_3$-C$_6$H$_4$) controls the speed of hydrolysis. The benzene ring attached to the acid part will increase reaction speeds in comparison to the attached alkyl chain. The number of compounds tested is restrained due to two characteristics of the tracer: a) the different fluorescence properties of the tracer and reaction product, and b) the water solubility, which limits the modification of the amine part. However, modification of the acid part demonstrates the potential of modifying the reaction speeds by changing the carbamate structure. The result obtained is consistent with the previous result from Schaffer et al. (2016). Therefore, the chemical modification is favorable for customizing suitable tracer molecules for various experimental conditions.

4.4.2 Dependence of reaction rate constant on temperature

To evaluate the temperature dependence of k_h, Arrhenius parameters of C1–C8 were obtained from data sets with at least two temperatures at a constant pOH of 7. In the Arrhenius plot (Fig. 4.2), the linear and comparable relationship between $\ln k_h$ and inverse temperature 1/T indicates the high quality of the results. The hydrolysis rate constants obtained (Table 4.3) and Arrhenius parameters (Table 4.4) show a wide range. The activation energy E_a is between 55–95 kJ mol^{-1}, and the pre-exponential factor $\ln A$ is between 15–30 ln(h^{-1}), which confirms the typical values for hydrolysis reactions of other compound classes tested in previous studies (Nottebohm et al., 2012; Robinson and Tester, 1990; Schaffer et al., 2016).

From experimentally obtained Arrhenius parameters (Table 4.4) the reaction rates at higher temperatures can be calculated using Eq. (4.8). The respective half-lives $t_{1/2}$ calculated (Table 4.5) show a good agreement with esters at 110 °C from Nottebohm et al. (2012) and amides at 190 °C from Schaffer et al. (2016). Moreover, $E_a / \ln A$ ratios are between 2–5, which cover the ratios observed for esters and amides (Jin et al.,

2017). This again proves that carbamates cover a broad range of reaction speeds for these compounds. Therefore, carbamates are likely the ideal molecules for investigating the wide span of subsurface reservoir temperatures without switching compound classes (Schaffer et al., 2015b).
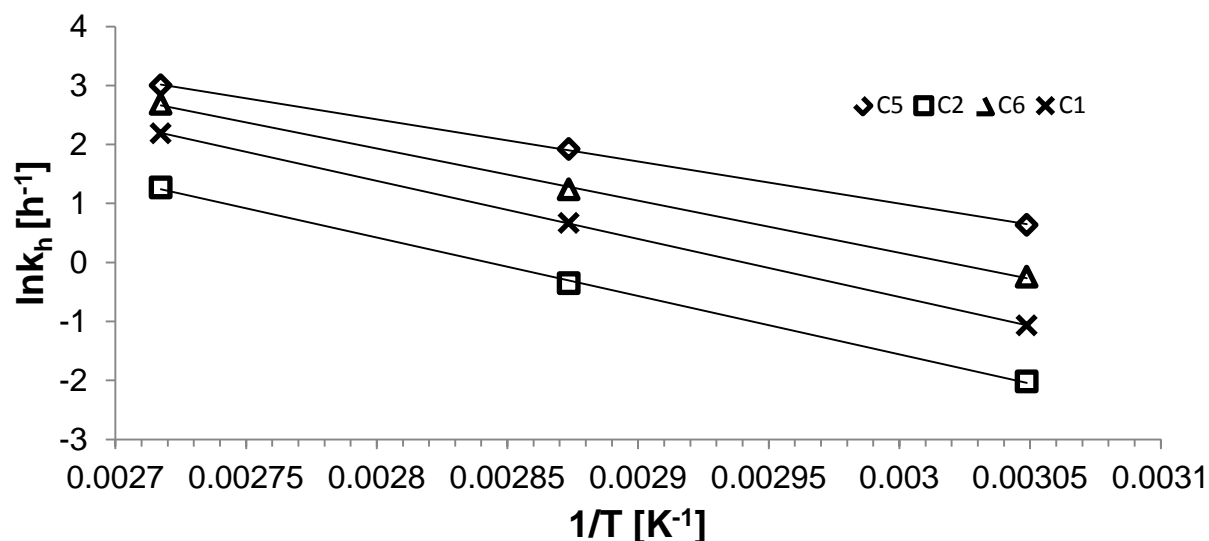
Fig. 4.2 Arrhenius plots for the hydrolysis of selected carbamates at pOH = 7.

4.4.3 Influence of pOH/pH on the reaction rate constant

It is apparent from Equation 4 (Section 3.2) that the overall reaction rate constant for hydrolysis k_h depends on pH/pOH. However, the relation between hydrolysis kinetics and pH is dependent on the nature of the hydrolysable functional group (Larson and Weber, 1994). For instance, in typical geothermal systems with pH values from 2–7.5 (DiPippo, 2016), the hydrolysis of ester is generally pH-dependent (Bender, 1960; Kirby, 1972; Maier et al., 2015a), whereas amides are pH independent (Duan et al., 2010; Schaffer et al., 2016) in the relevant range encountered in geothermal fields. Therefore, the pH dependence of carbamates is investigated to ensure minimal obscuring factors in the experimental results.

Table 4.3 Hydrolysis rate constants k_h [h-1] for the carbamates C1–C8 between 55 and 95 °C at a constant pOH = 7.

T [°C]	C1	C2	C3	C4	C5	C6	C7	C8
55	0.34	0.13	-	-	1.89	0.78	-	-
75	1.95	0.70	7.50E-05	7.97E-05	6.83	3.45	1.66E-04	2.49E-04
95	8.93	3.56	3.25E-04	3.24E-04	19.12	14.72	9.74E-04	1.25E-03

Table 4.4 Arrhenius parameters for the carbamates C1–C8 at pOH = 7.

	C1	C2	C3	C4	C5	C6	C7	C8
E_a [kJ mol^{-1}]	81.70	82.35	78.07	74.67	59.38	73.51	94.29	85.67
lnA [ln(h^{-1})]	28.90	28.16	17.48	16.37	22.42	26.69	23.88	21.32
E_a/lnA	2.83	2.92	4.47	4.56	2.65	2.75	3.95	4.02

Table 4.5 Half-lives $t_{1/2}$ [h] calculated for the carbamates C1–C8 for 110 and 190 °C, respectively, at a constant pOH = 7.

T [°C]	C1	C2	C3	C4	C5	C6	C7	C8
110	0.03	0.07	785	822	0.02	0.02	213	186
190	-	-	11.4	14.3	-	-	1.28	1.79

Due to different mechanisms, a secondary carbamate (following $B_{AC}2$) tends to be less pH dependent than a primary carbamate (following E1cb). Nevertheless, the hydrolysis of carbamates shows pH independence between 0–7 and 2–9 for primary and secondary carbamates, respectively (Vontor et al., 1972). This is again confirmed in our experiment for the primary carbamate C8 at 95 °C, which is expected to be base catalyzed. Despite an alteration in $[OH^-]$ by one order of magnitude, almost identical values of $k_h = 1.25 \times 10^{-3}\,h^{-1}$ (for pOH = 7; pH = 5.3) and $k_h = 1.28 \times 10^{-3}\,h^{-1}$ (for pOH = 6, pH = 6.3) were observed. Therefore, the use of carbamates is promising in geothermal systems with pH values from 2–7.5.

4.5 Conclusions

Recently, there has been an increase in demand for tracers with thermo-sensitive properties to better predict thermal breakthrough in the context of geothermal reservoir management. To extend the number of applicable compounds as practical thermo-sensitive tracers, the hydrolysis kinetics of nine carbamates (eight primary and one secondary) were investigated in batch experiments. The results demonstrate that the molecular structure and the temperature have a significant influence on the reaction rate as well as its underlying mechanism. It was also demonstrated that the effect of pH/pOH values observed in typical geothermal environments is not a significant factor influencing reaction kinetics.

With molecular design the fluorescence properties of both reactants and products can be preselected (Schaffer et al., 2013), which allow the online detection of both compounds on site. This further allows a mass balance and, thus, enhances the interpretation of a tracer experiment significantly and opens the opportunity of a tracer test design without an additional conservative tracer. The extent of measured reaction speeds from structurally different carbamate compounds supports the idea of

designing molecules for specific target temperatures and reservoir conditions. Overall, primary carbamates have faster reaction kinetics than secondary carbamates. The modification with alkyl groups in the acid part (CH_3, $n\text{-}C_3H_7$, C_6H_5, $p\text{-}CH_3\text{-}C_6H_4$) shows the potential of modifying the reaction speeds by changing the structure of the carbamates.

The findings of this study demonstrate that carbamates are highly promising thermo-sensitive tracers for low enthalpy geothermal systems, especially the ones typically encountered in the Northern German Basin. This is especially true when the cooling front has moved deep into the reservoir or for short term push-pull tests in the vicinity of the injection well. Our predicted half-lives for higher temperatures show the potential for carbamates following the mechanism $B_{AC}2$ to be further developed as tracers based on molecular design (Schaffer et al., 2013). Further temperature studies are needed to explore their full potential. Moreover, the influence of complex water samples (e.g., high salinity) (Cao et al., 2017) and the acceleration by enzymes in natural systems cannot be ruled out (Chanika et al., 2011; Kim et al., 2004) and should be considered in further investigations.

4.6 Acknowledgments

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Chapter 5

5 General conclusions and perspectives

An accurate characterization of aquatic systems is essential for geothermal reservoir development and management. This can be achieved by tracer testing in which distinguishable chemical compounds are introduced and have a temporally and spatially well-known input function. By recording tracer signals, valuable hydraulic information on the working fluid and in-situ interaction between the tracers and the system can be gained. However, conducting a proper tracer test is never simple, as it requires adherence to a series of specified steps. A failure in any step yields unreliable test results. This work provides important contributions for better evaluation of tracer response by addressing fundamental aspects in a tracer test.

5.1 Assuring quality for tracers responses

It is a common practice to combine reactive and conservative tracers to gain general hydraulic properties and specific properties or processes of a system. Here, conservative tracers are deployed for estimating transport-relevant properties and using as a reference for reactive tracers (for identifying and quantifying). To ensure the quantitative interpretation of the test, the evaluation of conservative tracer response need to be accurate, meaning that the concentration of the conservative tracer is not changed by processes other than dilution, dispersion and partial redirection. However,

ideal conservative tracers do not exist in reality. Therefore, a fundamental understanding of the investigated system and the tracer's properties are required beforehand to verify the practically tracer behavior and thus to avoid test failure. For example, the application of uranine in open systems should be careful as it is well-known for the photochemical decomposition (Gutowski et al., 2015); rhodamine WT cannot be applied as a conservative tracer in high enthalpy geothermal systems as it is decayed at temperature above 160 °C (Rose and Adams, 1994). Preliminary tests (e.g., interaction of tracers and site soils to estimate retardation, travel times) also should be performed before any real field implementation.

In addition, tracer loss due to samplings is often overlooked. This work demonstrated the influence of precipitates forming from complex water samples on observed results of commonly applied conservative tracers (uranine, eosin, 1-naphthalene sulfonate, 1,5-naphthalene disulfonate, 2,6-naphthalene disulfonate, 4-amino-1-naphthalene sulfonate, 6-hydroxy-2-naphthalene sulfonate, 1,3,6-naphthalene trisulfonate and 1,3,6,8-pyrene tetrasulfonate). The influence of the pH on the fluorescence signal of Eo and Ur can be significantly reduced if measurements of the samples are conducted at alkaline pH values. Furthermore, high pH values can considerably reduce the sorption of naphthalene sulfonates onto iron surfaces. As a recommendation, therefore, the pH values have to be adjusted (increased) immediately after sampling (i.e., to at least pH > 9 for Ur, pH > 7.5 for Eo and naphthalene sulfonates). Finally, to prevent turbidity effects by precipitates, proper centrifugation prior to analysis should be applied. The results highlight the neccessity of reliable preservation methods for tracer samples.

Although the investigated tracers cover a variety of the most common and persistent tracer compounds, the results of this study are not applicable to other tracer compounds (without further studies). An investigation to find an appropriate preservation method is required when selecting a conservative tracer, since the

method depends on the external conditions of the system (e.g., temperature, pH, water sample composition). The similar approach should be also applied for reactive tracers after samplings in order to enable quantitative interpretation.

5.2 Selecting suitable reactive tracers, future of a taylor-made tracer

The selection of optimal reactive tracer compounds is another main challenge that needs to be considered. For instance, when designing a thermo-sensitive tracer test, a tracer that decay too slowly under system's temperature lengthens test duration needlessly and thus makes observing the differences in mean residence times difficult; too fast decay makes it challenging for the test implementation. Moreover, new reactive tracer compounds have been extensively developed in the past decades due to the demand in new advanced technologies. Therefore, a complete understanding of the physicochemical properties of reactive tracers and their occurring processes is essential. Depending on the biophysicochemical behavior, three types of reactive tracers can be distinguished, namely: equilibrium tracers, kinetic tracers and reactive tracer for partitioning. Equilibrium tracers are based on the partitioning equilibrium between two immiscible phases or at their interfaces. Kinetic tracers are non-equilibrium tracers in which only the reaction kinetics are used for the parameter determination. Reactive tracers for partitioning are a hybrid form of equilibrium tracers and kinetic tracers.

The complexities of natural systems, along with the large number of requirements for the tracers, make the selection and use of reactive tracers not a simple task, but an art. Based on the knowledge of tracer properties, tailor-made tracer compounds are being developed with the required properties or effects in hydrogeology. The target-oriented combination of well-studied structural elements and molecular features (e.g.,

functional groups, substructures, homologues) allows for the creation of novel compounds with desired structures and properties. Nearly an unlimited number of compounds can be synthesized individually for specific applications. This innovative concept can expand the potential application of tracers in different fields (e.g., quantification of processes in the hyporheic zone, prediction of environmental risks of hydraulic fracturing). Molecular design assists the preselected properties (e.g., fluorescence) of both reactants and products. This allows a mass balance, and thereby opens the opportunity of a tracer test design without an additional conservative tracer.

5.3 Investigation of a new thermo-sensitive tracer class

With a substantial lack of candidate tracers for tracking the thermal state of geothermal reservoirs, the demand for new and advanced compound classes is still rising. The kinetic parameters of nine carbamate compounds are investigated for typical temperatures encountered in low enthalpy geothermal reservoirs. The two methods chosen to investigate the hydrolysis reaction kinetics are the Guggenheim and initial rates methods. The influence of several parameters on hydrolysis kinetics was investigated, including the compound structure, temperature and pH/pOH.

The results suggest the significant influence of the molecular structure and temperature on the reaction rate and its underlying mechanism. It is concluded that the pH/pOH values observed in typical geothermal environments do not have significant effects on reaction kinetics. The idea of designing molecules for specific reservoir conditions is supported by the extent of measured reaction speeds from structurally different carbamate compounds. With the wide range of $E_a / \ln A$ ratios (covering both esters and amides), carbamates can be considered the most promising thermo-sensitive tracers for low enthalpy systems to date.

Further temperature studies (for high enthalpy systems) and structure-related (e.g., branched chains in the leaving group) are required to explore carbamates full potential. To develop the applicability of carbamates, the transferability of the obtained results from static batch should be assessed by dynamic flow experiments (Maier et al., 2015a, 2015b), followed by testing in the field (e.g., push-pull test). So far, only a limited number of successful field applications has been reported (Adams and Davis, 1991; Batchelor, 1986; Hawkins et al., 2017). This is likely due to the complexities of a geothermal reservoir leading to unexpected loss of tracers. Further investigation is needed to reduce uncertainty arising from reservoir heterogeneities, such as catalytic effect of enzymes in natural systems on the hydrolysis.

Introducing a new functional group in established tracers will enable the use of hydrolysis as a temperature-driven reaction. Other hydrolysable functional groups can be further exploited to extend the number of candidate thermo-sensitive tracers, such as halogenated aliphatics. However, possible human and environmental effects should also be considered. For example, organophosphorus esters and ureas are hydrolysable groups, but should not be investigated as they are known to pose a threat to human health.

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Appendix

Appendix A

Table S1. PHREEQC prediction for artificial water samples.

| Input	Output

temp 10
pH 3
pe 4
redox pe
units mg/kgw
density 1
Na 8720
Mg 259
K 732
Ca 404
S(6) 856
Cl 16240
Fe(3) 200
water 1 # kg
	``
	------------------Saturation indices-----------------
	
	  Phase SI** log IAP log K(283 K, 1 atm)
	
	  Anhydrite -1.41 -5.53 -4.12 CaSO4
	  Fe(OH)3(a) -0.28 4.62 4.89 Fe(OH)3
	  Goethite 5.06 4.62 -0.44 FeOOH
	  Gypsum -0.96 -5.55 -4.59 CaSO4:2H2O
	  H2(g) -14.03 -17.08 -3.05 H2
	  H2O(g) -1.92 -0.01 1.91 H2O
	  Halite -2.64 -1.09 1.56 NaCl
	  Hematite 12.06 9.25 -2.81 Fe2O3
	  Jarosite-K 5.05 -2.95 -8.00
	KFe3(SO4)2(OH)6
	  O2(g) -60.56 -63.33 -2.77 O2
	  Sylvite -3.26 -2.44 0.82 KCl
	``

temp 10
pH 7.5
pe 4
redox pe
units mg/kgw
density 1
Alkalinity 3631
Ca 3604
Cl 9397
Na 1369
water 1 # kg
	``
	------------------Saturation indices-----------------
	
	Phase SI** log IAP log K(283 K, 1 atm)
	
	  Aragonite 2.23 -6.03 -8.26 CaCO3
	  Calcite 2.38 -6.03 -8.41 CaCO3
	  CO2(g) -1.15 -2.42 -1.27 CO2
	  H2(g) -23.03 -26.08 -3.05 H2
	  H2O(g) -1.91 -0.00 1.91 H2O
	  Halite -3.67 -2.11 1.56 NaCl
	  O2(g) -42.56 -45.32 -2.77 O2
	``

temp 10
pH 7.5
pe 4
redox pe
units mg/kgw
density 1
Ca 3604
Cl 6397
Na 3239
S(6) 6758
water 1 # kg
	``
	------------------Saturation indices-----------------
	
	Phase SI** log IAP log K(283 K, 1 atm)
	
	  Anhydrite 0.36 -3.76 -4.12 CaSO4
	  Gypsum 0.82 -3.77 -4.59 CaSO4:2H2O
	  H2(g) -23.03 -26.08 -3.05 H2
	  H2O(g) -1.91 -0.00 1.91 H2O
	  Halite -3.48 -1.92 1.56 NaCl
	  O2(g) -42.55 -45.32 -2.77 O2
	``
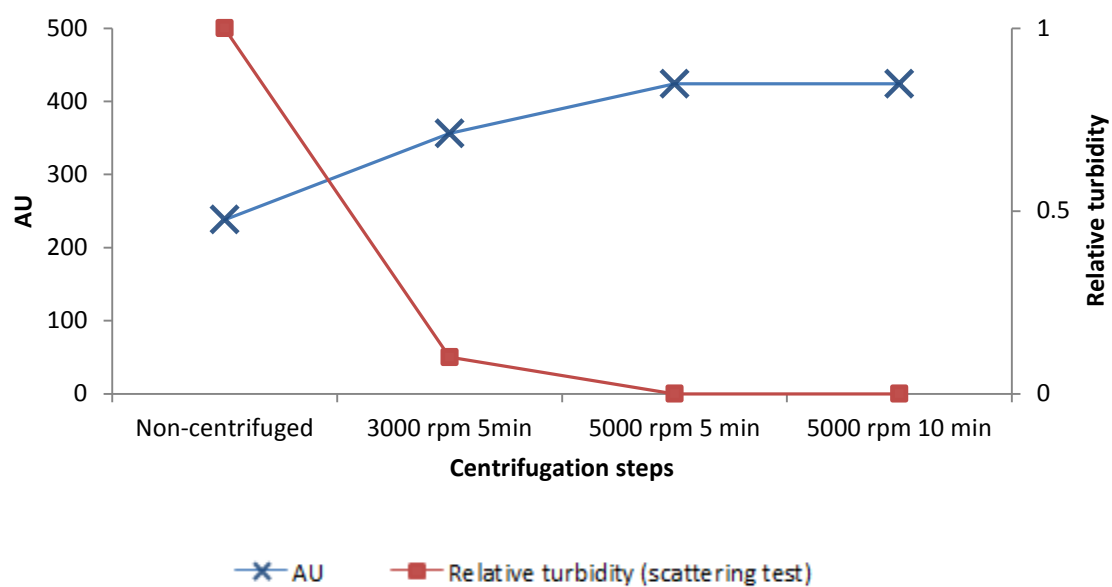
Fig. S1 Influence of different centrifugation steps on Ur.
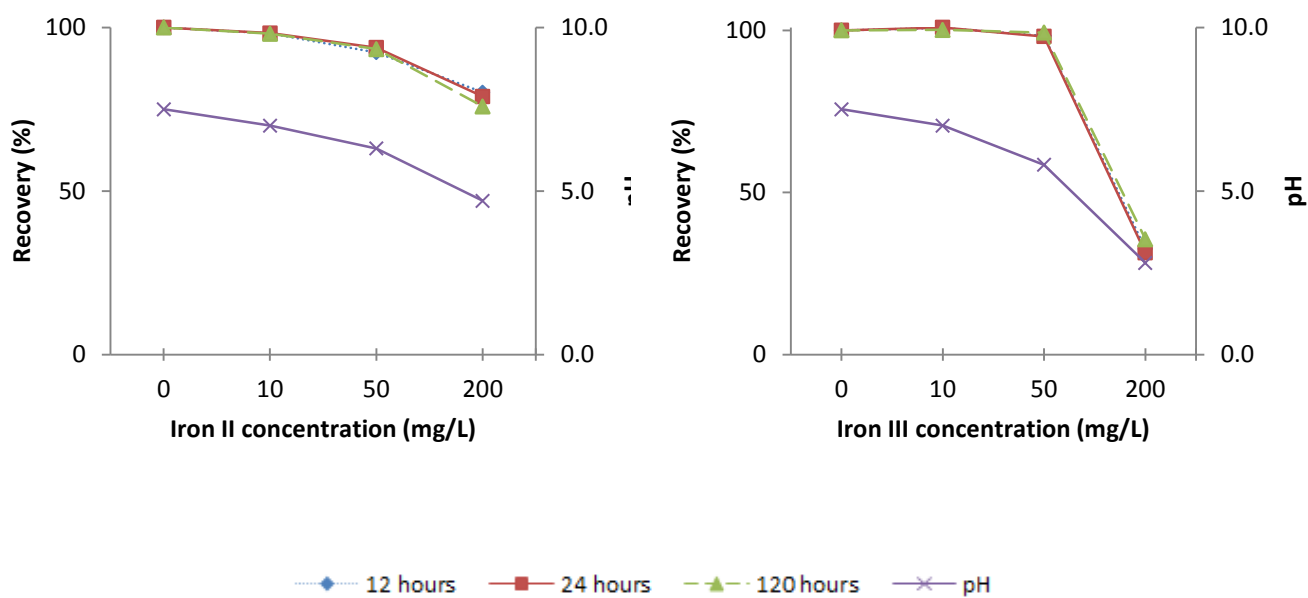
Fig. S2 Recovery for Eo with increasing Fe^{2+} (left) and Fe^{3+} (right) concentrations.
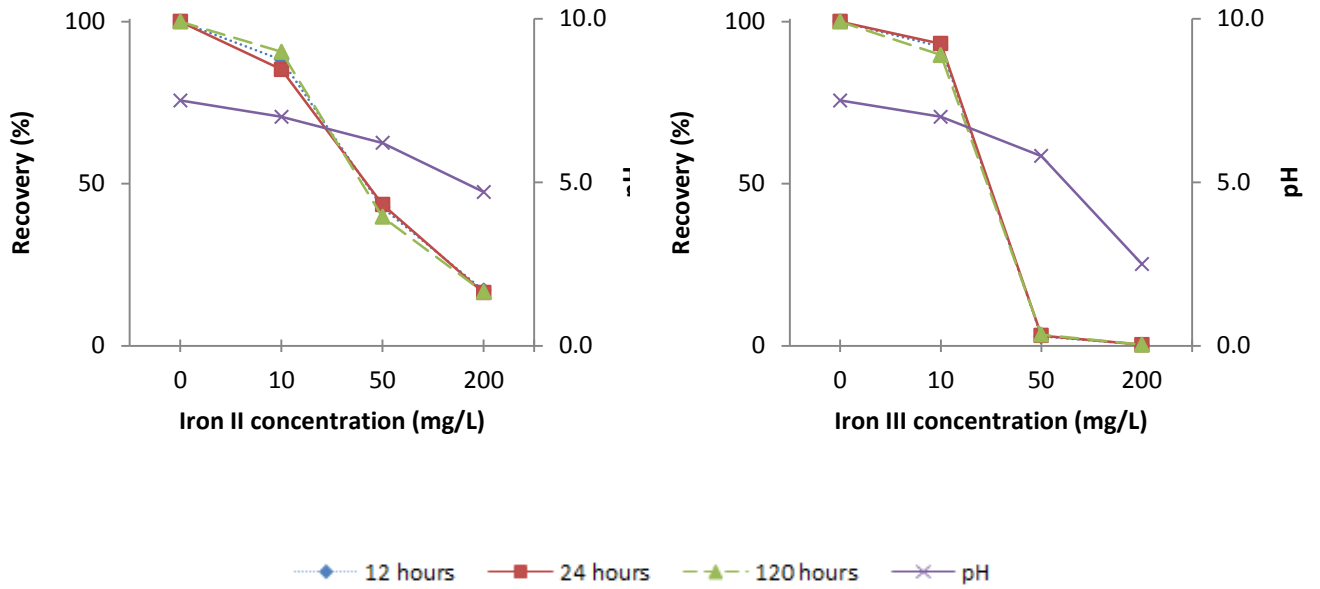
Fig. S3 Recovery for Ur with increasing Fe^{2+} (left) and Fe^{3+} (right) concentrations.
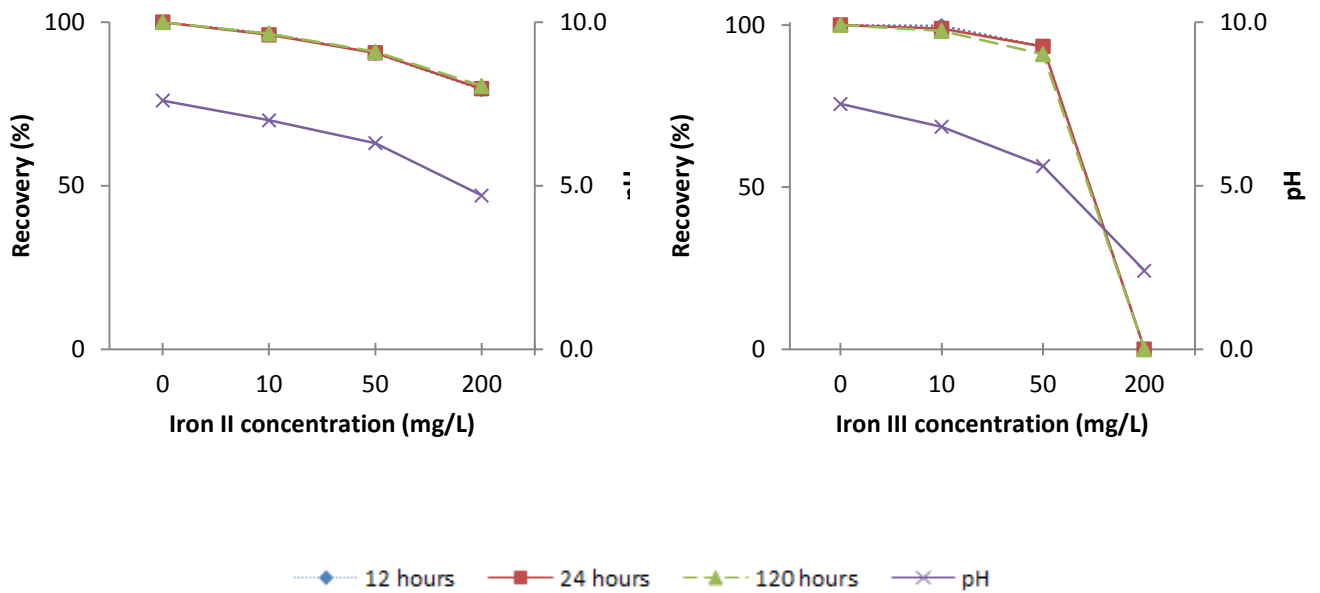

Fig. S4 Recovery for 15NDS with increasing Fe^{2+} (left) and Fe^{3+} (right) concentrations.
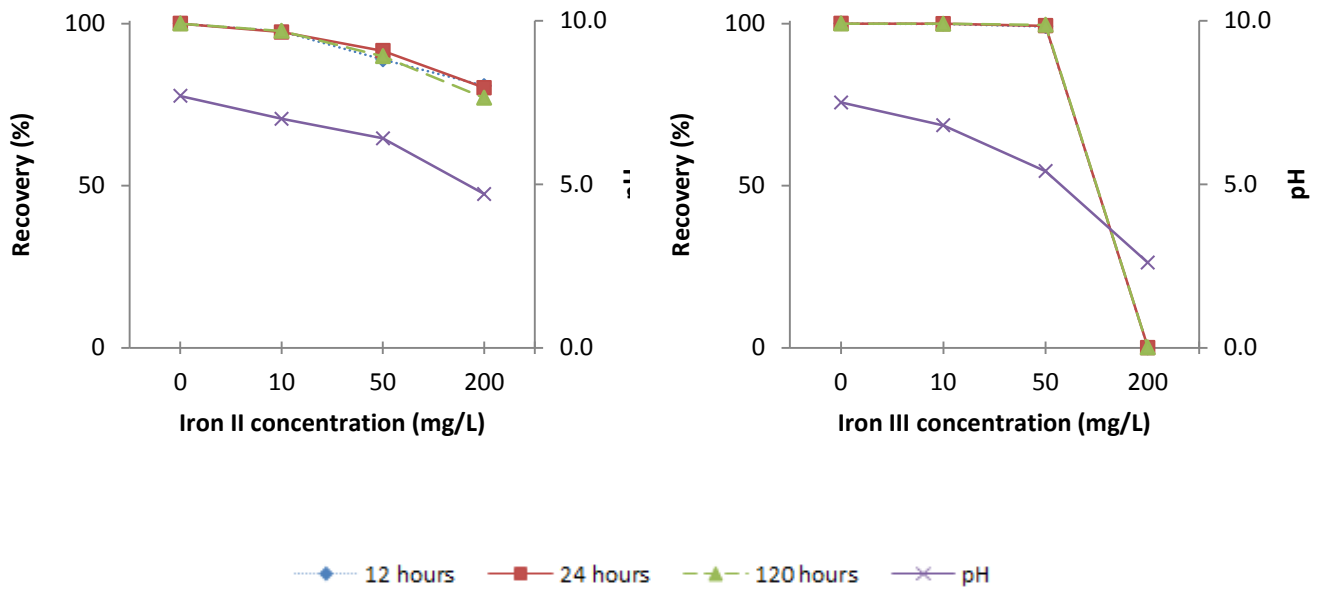
Fig. S5 Recovery for 1NS with increasing Fe^{2+} (left) and Fe^{3+} (right) concentrations.
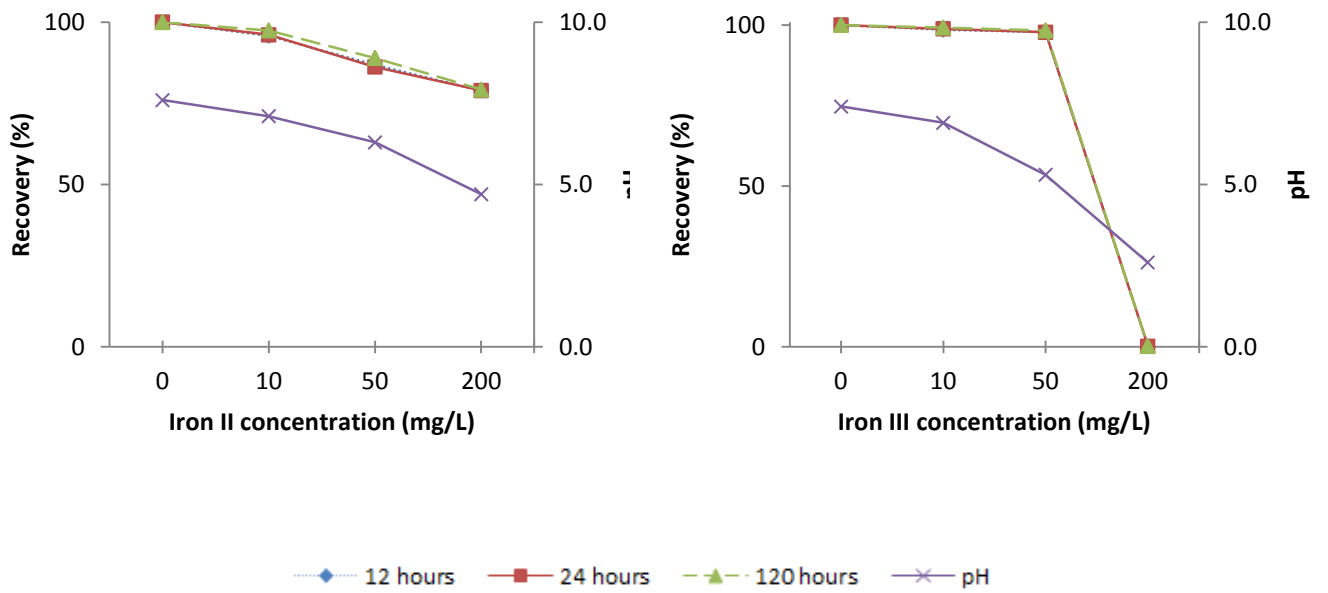

Fig. S6 Recovery for 26NDS with increasing Fe^{2+} (left) and Fe^{3+} (right) concentrations.
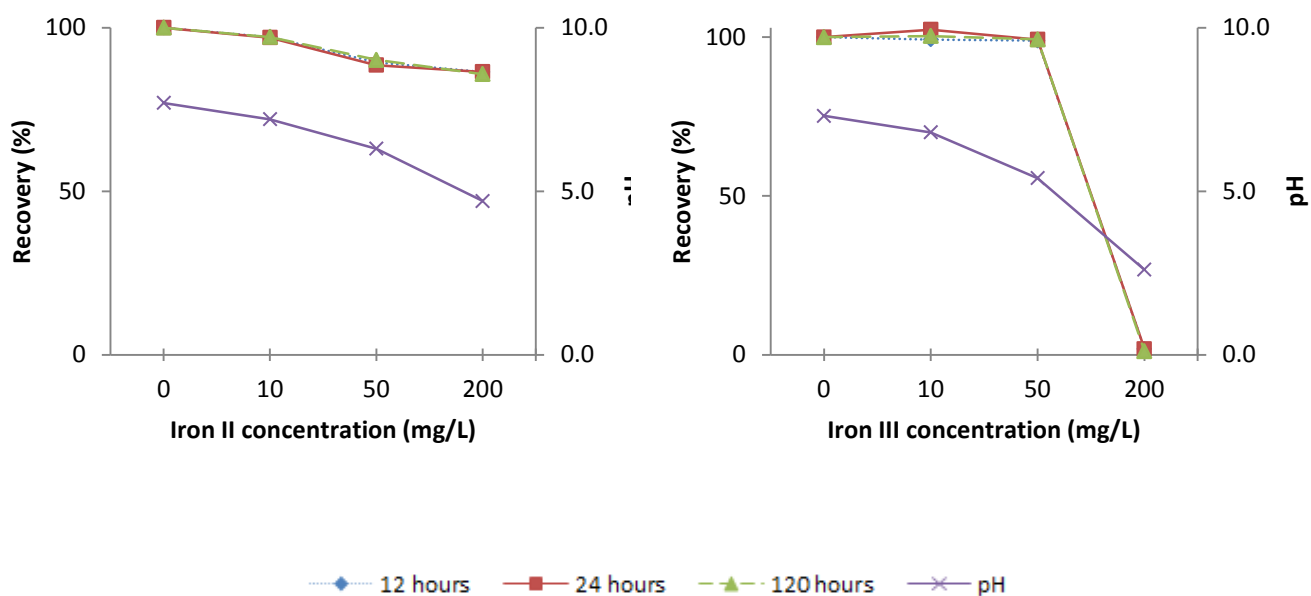
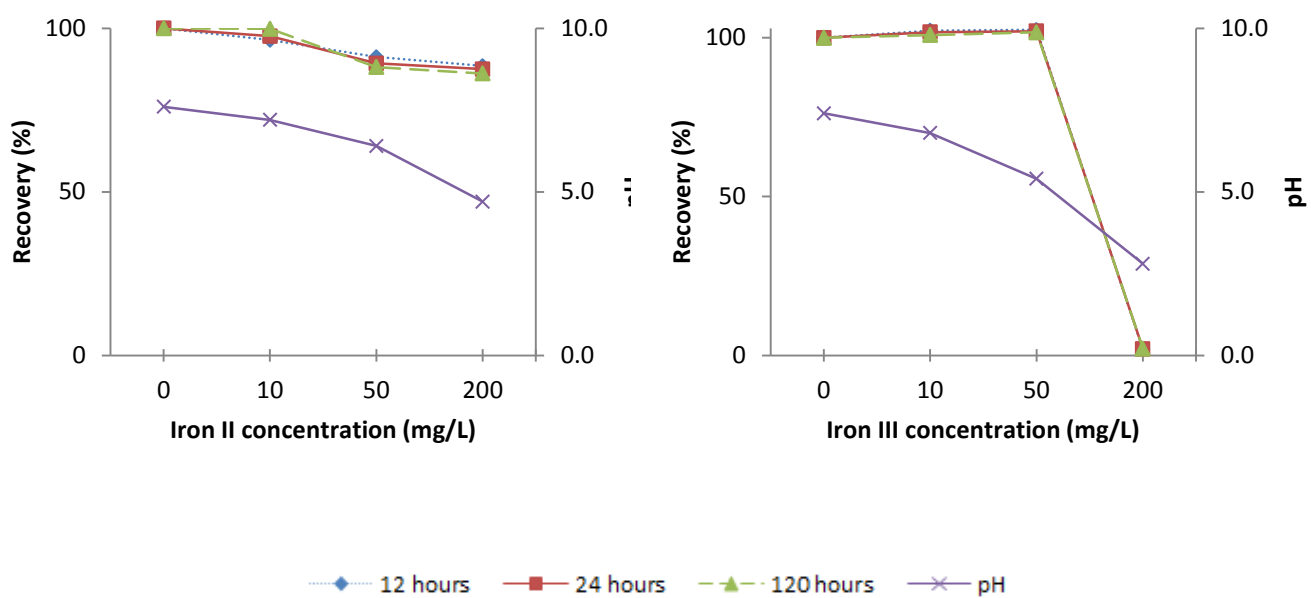**Fig. S7** Recovery for 4A1NS with increasing Fe^{2+} (left) and Fe^{3+} (right) concentrations.

Fig. S8 Recovery for 6H2NS with increasing Fe^{2+} (left) and Fe^{3+} (right) concentrations.

Fig. S9 Recovery for 136NTS with increasing Fe^{2+} (left) and Fe^{3+} (right) concentrations.

Fig. S10 Recovery for 1368PTS with increasing Fe^{2+} (left) and Fe^{3+} (right) concentrations.
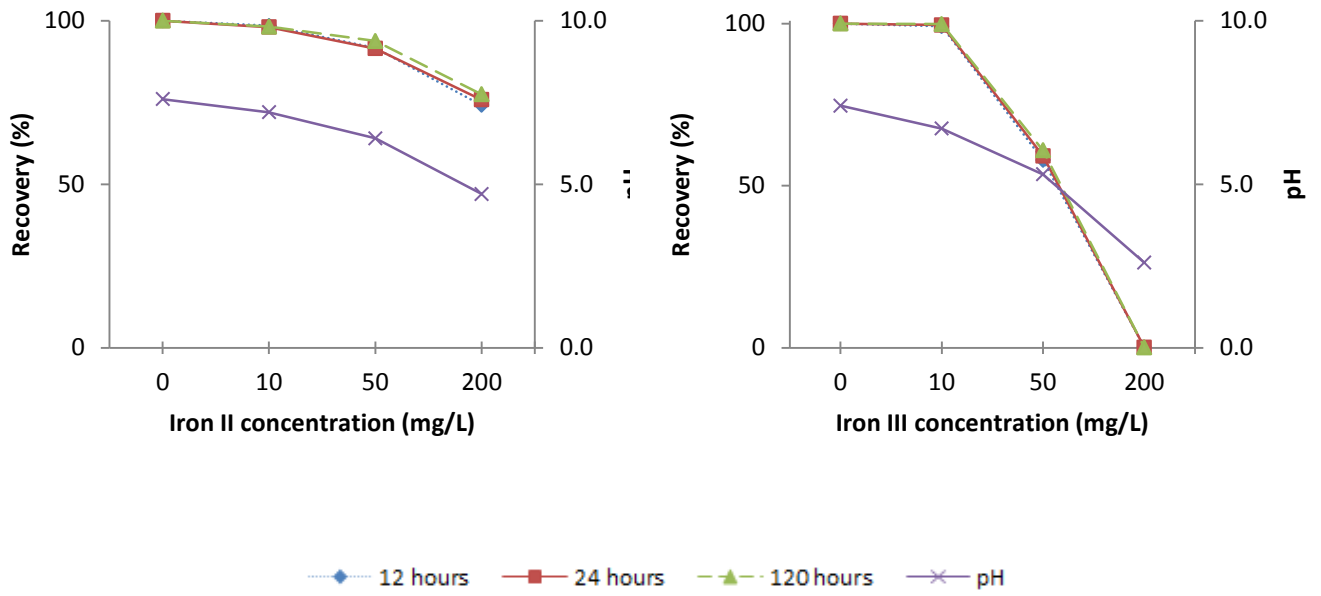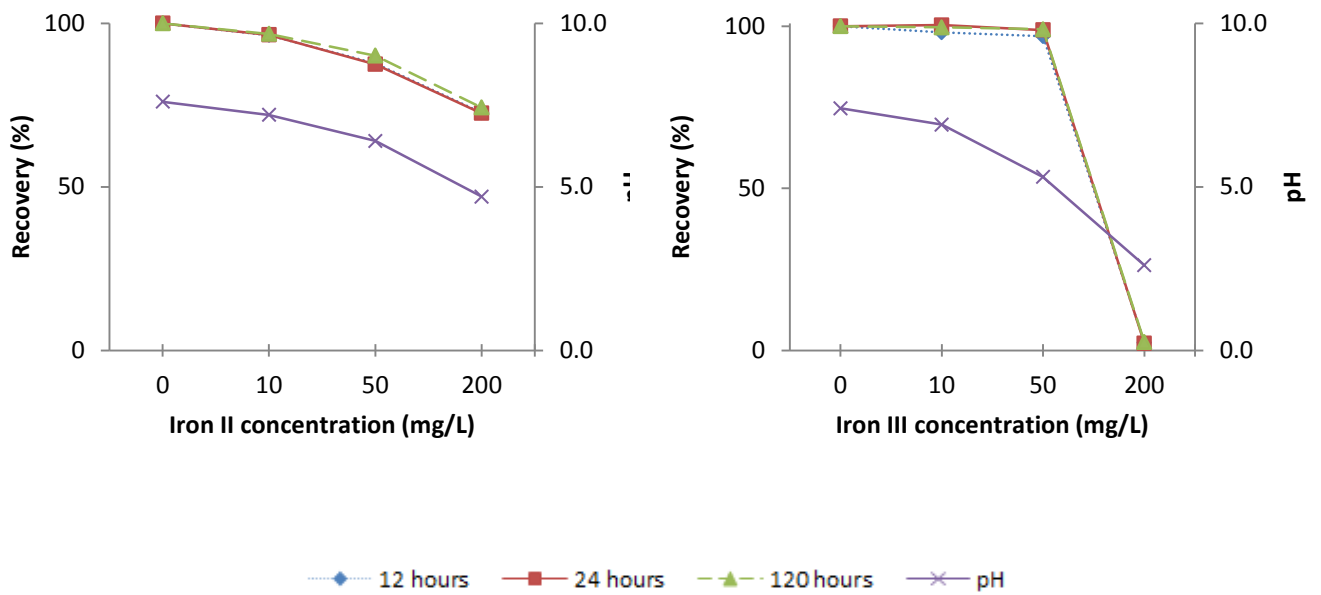
Table S2 Mean recovery and relative standard deviation (RSD) of Eo (a), Ur (b) and 15NDS (c) under increasing Fe^{2+} and Fe^{3+} concentrations at constant pH.

a. Eo

Concentration	10 mg/L		50 mg/L		100 mg/L		200 mg/L	
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Eo + Fe^{2+}	98	0.7	94	1.0	95	0.9	94	1.3
Eo +Fe^{3+}	101	0.2	99	1.0	98	2.2	96	1.3

b. Ur

Concentration	10 mg/L		50 mg/L		100 mg/L		200 mg/L	
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Ur + Fe^{2+}	97	1.2	99	1.3	97	1.6	93	3.3
Ur + Fe^{3+}	99	3.0	99	2.0	100	0.6	95	4.0

c. 15NDS

Concentration	10 mg/L		50 mg/L		100 mg/L		200 mg/L	
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
15NDS + Fe^{2+}	100	0.3	100	0.4	99	0.1	100	0.4
15NDS + Fe^{3+}	98	0.3	99	0.3	99	0.5	97	0.6

Table S3 Mean recovery and relative standard deviation (RSD) of Eo (a), Ur (b) and 15NDS (c) with $CaCO_3$ and $CaSO_4$ at a constant pH.

		Recovery (%)	RSD (%)
Eo	$CaCO_3$	100	0.3
	$CaSO_4$	99	0.4
Ur	$CaCO_3$	99	0.1
	$CaSO_4$	99	0.3
15NDS	$CaCO_3$	100	0.1
	$CaSO_4$	100	0.2

Appendix B

List of all journal articles, conference abstracts authored by me and related to presented work (last update: March 2018)

Journals (peer-reviewed)

Cao, V., Schaffer, M., Jin, Y., Licha, T., 2017. Preservation of commonly applied fluorescent tracers in complex water samples. Grundwasser 22, 127–133. doi:10.1007/s00767-017-0356-1

Cao, V., Schaffer, M., Licha, T., 2018. The feasibility of using carbamates to track the thermal state in geothermal reservoirs. Geothermics 72, 301–306. doi:10.1016/j.geothermics.2017.12.006

Cao, V., Schaffer, M., Licha, T. (under review): Solute reactive tracers for hydrogeological applications: a short review and future prospects. Journal of Hydrology

Conference contributions

Cao, V., Schaffer, M., Jin, Y., Licha, T., 2016. An evaluation of common conservative tracers in hydrogeology - Influence of sampling and storage on the recovery of some commonly applied conservative tracers. In: Book of Abstracts of the 9th GeoSymposium of Young Researchers Silesia 2016, Kroczyce, Poland, p. 68 (ISBN 978-83-934005-9-1).

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	Department Applied Geology
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