29. Doktoranden-Treffen

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Organisatoren:

Die Doktoranden des Lehrstuhls für Hydrogeologie der Technischen Universität München

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Das 29. Doktoranden-Treffen der Hydrogeologie fand vom 31.07. bis zum 02.08.2019 an der Technischen Universität München (TUM) statt.
Der erste Tag stand im Zeichen der erneuerbaren Energien und startete mit einer Key-Note von Dr. Kai Zosseder (TUM) über die geologischen Besonderheiten des Süddeutschen Molassebeckens und dessen geothermischer Nutzung. Vor allem der Einfluss des globalen Klimawandels auf die Themengebiete der Hydrogeologie sowie die Chancen und Möglichkeiten des Berufes als Hydrogeologe bei der Bewältigung der Energiewende waren ein zentrales Thema. Im Anschluss wurde die Bohrbaustelle eines der größten europäischen Geothermieprojekte der Stadtwerken München (SWM) in der Schäftlarnstraße in Sendling besucht. Dort wurden unter anderem die geologischen und bohrtechnischen Aspekte des innerstädtischen Großprojektes mit sechs Tiefenbohrungen erläutert und vorgestellt.
Am Workshop-Tag wurden die Forschungsprojekte aller Teilnehmer in Form von Vorträgen und Postern in den Räumlichkeiten der TU München präsentiert und diskutiert. Insgesamt stellten sich 24 Teilnehmer von über acht unterschiedlichen Instituten und Universitäten dem wissenschaftlichen Diskurs mit spannenden Themen zu Gasspeichern, über Scalingsreduktion in Geothermieanlagen mithilfe von CO_2 Einspeisung, reaktive Reservoirsysteme, kombinierte Grundwassersanierungs- und Wärmetauschersysteme sowie Themen rund um den Gewässerschutz mit Methoden zur Nitratreduktion, Ermittlung von Schadstoffquellen und Prozessenverständnissen im Grundwasser oder Grundwasser-Oberflächenwasser-Interaktionen. Im Rahmen des Workshop-Tages wurde so ein breites Spektrum der Themengebiete in der Hydrogeologie abgedeckt und die Möglichkeit geschaffen, einen regen Austausch über das eigene, persönliche Forschungsthema hinaus zu führen.

Impressionen von der Key-Note von Dr. Kai Zosseder und der Besichtigung der Geothermiebohrung Sendling der Stadtwerke München. ©F. Konrad

Am letzten Tag wurde mit dem Fahrrad entlang des M-Wasserweges im idyllischen Mangfalltal die Grundwassergewinnungsanlage für München der SWM besucht. Dort wurden die wichtigsten Aspekte der Gewinnung und Aufbereitung sowie nachhaltigen Bewirtschaftung der Ressource Grundwasser in München erläutert und unter anderem die berühmte Grundwasserfassung in Reisach besichtigt.
Das Treffen stellte auch in diesem Jahr wieder eine schöne und wertvolle Plattform für alle teilnehmenden Doktoranden dar, sich wissenschaftlich auszutauschen und auch die Themengebiete

und Arbeitsweisen anderer Arbeitsgruppen kennen zu lernen. Da es bei allen Teilnehmern großen Anklang gefunden hat, haben bereits die Planungen für das kommende 30. Doktoranden-Treffen 2020 an der CAU Kiel begonnen.

Das 29. Doktoranden-Treffen wurde freundlicherweise durch die Fachsektion Hydrogeologie in der DGGV (FH-DGGV), International Association of Hydrogeologists (IAH), Geothermie-Allianz Bayern sowie TUM-Graduate School finanziell unterstützt. Auch sei vor allem den Stadtwerken München (SWM) gedankt, die die Durchführung der Exkursionen zur Schäftlarnstraße und ins Mangfalltal ermöglicht haben.

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Abstractverzeichnis

1 Using CO_2 for enhancing permeability in deep geothermal carbonate aquifers

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In geothermal energy production, adequate permeability and favorable fluid pathways are vital aspects. Scaling and precipitation of carbonates poses a great challenge, as it worsens the permeability, heat exchange, and pumping of thermal fluids. Therefore, preventing precipitation, preserving and improving these pathways during long term operation is a key task in deep geothermal energy production. With the aim of maintaining and enhancing the permeability of the aquifer, we investigated the feasibility of adding CO_2 to the geothermal water in laboratory and pilot plant experiments. Kinetic batch experiments were performed to examine the interactions between carbonate reservoir rock (from the Malm strata in Kirchweidach, Germany) with water and CO_2 under reservoir conditions. Additionally, casing material and borehole cementation which come into contact with CO_2 saturated water were tested under the same conditions.
Chemical analysis of the water samples was achieved by ICP-MS (metals and cations), IC (anions) and TIC (inorganic carbon). In addition, SEM analysis was used to see surface and morphological changes of casing material, borehole cementation, precipitates and rock cuttings.
Laboratory experiments showed that rock material underwent a preferred dissolution of major rock forming minerals caused by increased pCO_2. Casing material showed a weight loss of 1.7 % during the test period of 28 days and no indications of passivation on the casing surface were found. As for the concrete samples, results demonstrated that there is a weight gain of 5-10 wt. %, which is associated with carbonation of the cement. In the pilot plant, cooled geothermal CO_2 enriched water passed through rock filled columns which were sequentially heated up to reservoir temperature. During the 6 months operational period, redox potential, EC, pH, flow and temperature in the inlet and outlet of the columns were monitored. Water was sampled continuously and analyzed for main cations, DOC, and acid / base capacity.
The pilot plant system which was used in this research allowed for flexible simulations of boundary conditions and tracking of the corresponding reactions during the reinjection of geothermal thermal water back into the aquifer. Overall results showed, that the adding of CO_2 to geothermal water leads to a favored dissolution of carbonate rock which could be used to enhance the permeability in low permeable carbonate reservoirs by using this natural gas. Additionally, precipitation of carbonate minerals and the formation of scales which deteriorate the transmissivity of reservoir pathways can be prevented due to under-saturation with respect to carbonates. Furthermore, this suggested approach could eventually become a safer and resource-conserving alternative to current techniques especially due to the fact that above ground energy production is not interrupted while CO_2 is being added. This and the positive CO_2 storage as by-effect (Carbon Capture, Utilization and Storage) can be important factors for policymakers.

2 Evaluation of petrophysical rock parameters of the "Malm" aquifer for classification of the aquifer system in the central Bavarian Molasse basin

Daniel Bohnsack, Martin Potten und Kai Zosseder

Technische Universität München

The exploration and use of geothermal resources in the central area of the Bavarian Molasse Basin has increased strongly in recent years. The focus in the area around Munich is on the "Malm" aquifer. This fractured and partly strongly karstified aquifer represents one of the most promising reservoirs for hydrothermal projects in the widespread carbonate sequences of the Upper Jurassic ("Weißer Jura", "Malm") in Europe. A good knowledge of the aquifer is a prerequisite for successful development of the reservoir at various locations and for productivity and long-term forecasts of the aquifer's behavior. The rock-physical, hydraulic and geomechanical properties form the basis for thermal mining models and thermal-hydraulic-mechanical simulations (THM). Due to the very heterogeneous formation of the aquifer, the different parameters vary particularly depending on lithology, facies, diagenesis and depth of the aquifer and must therefore be investigated and correlated across different sites.

Within the framework of the Geothermal Alliance Bavaria (GAB) detailed parameter studies were carried out on drill cores from the Upper Jurassic of the Bavarian Molasse Basin (Moosburg SC4, Dingolfing FB and oil exploration wells). The porosity, permeability, thermal parameters and elastic behavior of the aquifer rock were determined on more than 400 samples from rare rock cores. The results were put together in a holistic context regarding lithology and facies as well as their stratigraphic distribution in order to develop a statistical and lithofacially oriented database for the rocks of the "Malm" aquifer. Regional transfer will be carried out by correlation with geophysical borehole measurements of surrounding boreholes and by a newly developed sequence stratigraphy in the Bavarian Molasse Basin. In order to consider the influence of different rock pressures, depending on the depth of the aquifer, the hydraulic parameters are also investigated under varying pressure conditions in hydrostatic pressure tests.

The investigations so far show a good differentiability of the different parameters according to their lithology and facies. For a transfer to other areas of the reservoir, the data were divided into groups with distinctive properties, each as a bandwidth. The correlation of the rock properties with each other shows a clear dependence of the thermal and elastic properties on the porosity, which has a considerable effect on the heat conduction and strength of the rock matrix. Porosity and permeability, in turn, are significantly influenced by varying ambient pressures. A pressure increase of 25 MPa can already cause a 25 % reduction in permeability, with elastic and partly irreversible deformation of the rock structure playing a role.

The aim of the work is thus a characteristic classification of hydraulically active aquifer intervals and their transferability to new locations with reference to the depth of the aquifer. The newly developed and extensive data base thus forms a significantly improved basis for site characterization and forecasts in numerical models.

3 A holistic method to integrate the potential of thermal groundwater use in spatial energy planning

Fabian Böttcher und Kai Zosseder

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4 Bending of the concentration discharge relationship potentially explains dominant controls of in-stream nitrate removal

Joni Dehaspe

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Nutrient excess in rivers leads to ecosystem harm and can induce detrimental algae growths in coastal areas. In Germany and Europe, the management of riverine systems is complicated by the lack of understanding of nutrient pathways from application to export. In-stream processing (e.g. temporal fixation by assimilatory uptake or permanent denitrification) is thought to be a relevant process, affecting exported nitrate concentrations and loads. Nevertheless, quantification based on field-evidence is limited to lower order streams and hardly take larger catchments into account. In this work, we hypothesize that uptake effects are observable from concentration-discharge (C-Q) relationships. To explore the effect of in-stream nitrate removal on C-Q behavior in a realistic stream network setting, the Holtemme catchment in central Germany was modelled as a test-case. For this, a parsimonious catchment wide network model is used (1x1km^2). Here, the land-to-stream transfer of nitrate is assumed to follow a power law dependence from $Q(C = a * Q^b)$, resulting in different nutrient loading according to the contributing area of each grid cell in the network. In-stream load uptake follows $L_i = L_{in} * exp(-v_f * w * L/Q)$, with v_f the uptake rate and w and L respectively the width and length of the river section. We test the impact of different average nitrate concentrations and uptake velocities on the C-Q relationship. Based on the modeling exercise we can decide on a suitable metric to characterize and potentially quantify instream uptake from observed C-Q relationships across Germany. This metric needs to be explored further by connections to catchment characteristics (such as topography, land-use, potential for stream shading, potential for fine sediments) and biogeochemical conditions (nutrient stoichiometry). This will allow us to argue if the observed C-Q bending can be indeed related to instream uptake and not to other processes (e.g. denitrification along the subsurface flow path) and to derive the dominant processes shaping the uptake (light availability, just instream travel time, nutrient stoichiometry, impact of fine sediments...). On a longer run we aim at transferable parameters allowing to quantify instream removal of nitrate in meso-scale water quality models.

5 Germany-wide analysis of dominant controls on nutrient export dynamics at catchment scale

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Nutrient inputs from human activities resulting in fertilizer applications and wastewater inputs have increased pressures on aquatic ecosystems. The health of these ecosystems and eutrophication are linked to levels and temporal variability of nutrient concentrations in the streams. Moreover, temporal dynamics of nutrient concentrations and discharge control the nutrient loads exported from catchments to the oceans. Catchments are the spatial unit at which water quality management is implemented. However, catchments are complex units within which multiple biogeochemical and physical processes interact at different scales. Here, top-down approaches addressing the integrated response of concentration and discharge at the catchment outlet can provide valuable insights into the hierarchy and dominance of processes. Previous studies have found evidence that nitrate export dynamics in many agricultural catchments exhibit a chemostatic export regime with low concentration variability at high concentration levels, which may hamper mitigation measures to reduce exported nutrient loads to improve water quality. The chemostatic regime is attributed to homogenization of source areas due to the legacy of high inputs in the past, while chemodynamic regimes are hypothesized to be related to heterogeneous source areas and variable discharge generating zones. It remains insufficiently understood for which type of agricultural catchments and how widespread chemostatic nutrient export can be observed. Therefore, we investigated dominant controls of nutrient export dynamics over a wide range of catchments with varying characteristics such as climatic, geologic, topographic and land cover conditions. To this end, we analyzed integrated catchment responses of nitrate and phosphate concentrations and discharge using a Germany-wide dataset of about 800 stations with biweekly to monthly samples and the catchments covering an area of about 80 % of Germany. Mean concentrations and metrics of concentration-discharge (C-Q) relationships were linked to catchment characteristics as descriptors in a partial least squares regression analysis. The Germany-wide analysis shows clear spatial patterns in mean nitrate levels, but also in C-Q-metrics, which we assume are related to spatial patterns in catchment characteristics. The analysis revealed that (1) Mean nitrate concentrations are positively but heteroscedastically related to the fraction of agricultural land use and (2) Several but not all highly managed, agricultural catchments exhibit a chemostatic nitrate export behavior. Chemodynamic accretion patterns for nitrate have been found, suggesting that processes related source heterogeneity, connectivity and reactivity can play a dominant role. Relating the export regime to catchment characteristics, such as the drainage density, land cover distribution and aquifer type, will shed more light at the controls of nutrient export regime at national scale.

6 Reaktive Reservoirsysteme - Kristallkeimbildung und Filterprozesse in geothermischen Systemen

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Die Rückführung von abgekühlten Fluiden nach der Energieausbeute in Geothermieanlagen in das hydrothermale Reservoir kann zur Übersättigung und damit zur Fällung von Mineralphasen führen. Grund dafür sind sich ändernde Druck- und Temperaturbedingungen (Gunnlaugsson 1989, Demir et al. 2014) durch den Wärmeentzug. Dies führt bezüglich diverser Mineralphasen zu einer Gleichgewichtsverschiebung, damit zu einer Übersättigung des Reservoirfluids und schlussendlich zu Ausfällungen, wodurch Wegsamkeiten im Reservoir allmählich verschlossen werden, sollten diese sich im Reservoir absetzen. Dieser Effekt wird als Scaling bezeichnet und limitiert nachhaltig die Nutzung geothermischer Ressourcen. Solche Scalingprozesse werden häufig mittels hydrogeochemischer Modellierungsprogramme nachgebildet, die vor allem auf der Temperatur- und Druckabhängigkeit von Lösungs- und Reaktionsgleichgewichten im Reservoir basieren (Bozau & van Berk 2013, Bozau et al. 2015).

Bisher ist noch unklar, welchen Einfluss dabei Kristallkeime haben, die sich durch die Abkühlung nahezu gesättigter Fluide während der Energiegewinnung an der Oberfläche bilden. Neben gut belegten kristallinen Ablagerungen an Rohrwänden können strömungsbedingt auch freischwimmende spontan gebildete Kristallkeime in das Reservoir reinjiziert werden. Dort können sich die Kristallkeime dann durch Filtereffekte kumulieren und als Kristallisationszentren für Zementationsprozesse fungieren.

Mit Hilfe einer Hochdruck-Hochtemperatur-Säulenapparatur, die einer Geothermieanlage nachempfunden ist (Knuth et al. 2016), soll ein besseres Verständnis von Bildung und Wachstum von Kristallkeimen in gesättigten geothermischen Lösungen bei thermischer Entspannung untersucht werden. Die Apparatur ermöglicht zum einen die Einstellung von Druck- und Temperaturverteilungen, wie sie innerhalb tiefer geothermischer Reservoire vorliegen, zum anderen können mit unabhängig voneinander betriebenen Heizspiralen und einem Wärmeübertrager Abkühlungsprozesse nachgestellt werden. Über ein Hilfsgas (z.B. Helium) und die Heizthermostate sind Drücke von bis zu 300 bar und Temperaturen bis zu 100 °C möglich.

In experimentellen Ansätzen sollen zunächst die hydraulische Durchlässigkeit von geklüfteten Proben bestimmt und anschließend Ausfällungsexperimente durch die Abkühlung von Fluiden durchgeführt werden. Nach den Ausfällungsexperimenten werden erneut die hydraulischen Parameter untersucht und mit den vorangegangenen Ergebnissen verglichen. Anhand der Ergebnisse soll die Entwicklung von Ansätzen zur Kontrolle der Kristallkeimbildung bzw. Minimierung der Filterprozesse im Reservoir durchgeführt werden.

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7 Numerical study on influence of local thermal non equilibrium on heat transport in conditions of porous aquifers

Manuel Gossler

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8 Lessons learned: Experience from hydro- and isotope chemical sampling and analysis of geothermal waters in the Bavarian Molasse Basin

Florian Heine, Kai Zosseder und Florian Einsiedl

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The deep Upper Jurassic aquifer in the Bavarian Molasse Basin has a great potential for hydrogeothermal energy supply. The geothermally used water from more than 23 wells has a temperature up to 150 °C. The hydrochemistry and several environmental isotopes were measured in a multi parameter approach and analysed using statistical factor and cluster analyses within the research projects IsoMol and Geothermal-Alliance of Bavaria. It was possible to characterise the occurring deep groundwater and define different water types in the Upper Jurassic aquifer. During the construction of a geothermal well, large quantities of controlled circulating fluids such as drilling fluid or acid and tap water are usually injected into the reservoir during chemical stimulation. Therefore, regular investigations of the hydrochemical composition of the thermal water take place during the cleaning work of the borehole in order to evaluate the success of the cleaning work and to derive first indications of the geogenic hydrochemical signature of the thermal water. These investigation measures are required in so-called water rights notices, whose catalogue of requirements in the past was generally based on the parameter lists in Büttner & Kolmer (2012). Depending on the phase in the production process and operation of the well, a difference is made between basic and operational investigations.

This contribution presents and discusses the ßensitive parametersöf the influences during construction of the well (drilling mud, chemical stimulation) and their impact on the basic investigations. In a long-term pump test (approx. 108 hours) on a geothermal doublet, the hydro- and isotope chemistry at an interval of two hours was measured. Its evaluation showed that various parameters (e.g. content of dissolved organic carbon (DOC) as well as chloride, calcium and magnesium concentrations, etc.) were significantly influenced depending on the sampling time after drilling, which is related to the input of the drilling mud and fluids during the chemical stimulation work. In addition, the results of that long-term pump test will be put into context of existing data sets from basic and operational investigations of other geothermal wells in the Bavarian Molasse Basin and their significance in terms of reservoir characterisation will be discussed.

9 Reducing nitrate contamination in electron-donor limited groundwater

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Groundwater is the main source of drinking water in Germany [1]. As a result of intensive agricultural land use, 28 % of regularly monitored groundwater wells in Germany exceed the drinking water limit for nitrate (NO_3^-) of 50 mg/l [2]. A need exists for technologies to remove nitrate from such highly polluted aquifers.
Therefore, our project aims to develop a new remediation technology that stimulates in situ hydrogenotrophic denitrification in groundwater. As the solubility of H_2 is limited in groundwater the reaction pathway from nitrite (NO_2^-) to nitrous oxide (N_2O) is also linked with an abiotic reaction using a Fe(II)-mineral.
Here we present some results of our batch experiments including the microbial community distribution that show the potential of hydrogenotrophic denitrification in a nitrate polluted aquifer. Our data serve as the basis for small-scale remediation studies.

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10 DEEPWATER CE Interreg Project

Anne Imig

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In Central Europe groundwater is the dominant drinking water source. Climate change causes negative effects on availabilities of groundwater resources. The ERDF Interreg Central Europe project DEEPWATER-CE aims at developing solutions to these challenges by exploring the possibilities of Managed Aquifer Recharge (MAR). MAR is a viable approach of collecting excess surface water and precipitation in periods characterized with water abundance and storing it for dry times in aquifers. Building on results of relevant previous FP7 and H2020 projects, 8 Partners from 5 CE countries, will work together. In the framework of the project, an integrated environmental management approach for water resources and adoption of MAR is developed. Four pilot sites in porous aquifers will be selected to investigate different applications and environmental stresses on MAR, e.g. water usage for irrigation or drinking water supply and the hazard of contaminant intrusion or salinization of the aquifer. The team at the Chair of Hydrogeology is work package leader for the pilot feasibility studies. Research tasks will focus on characterizing water flow and contaminant transport in the unsaturated and saturated zone at the different pilot sites by stable water isotope techniques and modelling. The models will be calibrated and validated with field data from the four pilot experiments.

11 Hydraulic behavior of fault zones in pump tests of geothermal wells - a parametric analysis using numerical simulations for the Upper Jurassic aquifer of the North Alpine Foreland Basin

Florian Konrad

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Fault zones in the Upper Jurassic aquifer of the North Alpine Foreland Basin are generally regions with possibly increased hydraulic properties. They are consequently often part of the geothermal exploration concepts in this area and a primary target for the drilling operation. Data from this aquifer, gathered in pump tests, however shows that only four out of 41 successful wells exhibit hydraulic proof for the presence of such a fault zone in terms of a bi-/linear flow regime. Besides technical effects, also the contrast in hydraulic properties itself, between fault zone and surrounding host rock, can prevent the detection of a fault zone in pump test data. This means a certain threshold has to be surpassed until its effects become clearly visible.

A simplified realistic numerical model was constructed and calibrated with pressure data from an exploration site in the south of Munich. This model was then used to observe the presence of linear and bilinear flow in dependence of the Malm aquifers parameter space. Sampling the possible hydraulic property-combinations with the help of an HPC (high performance computing) cluster and automating the detection of the corresponding main flow type allowed to quantify the areas in parameter space where the fault zone-related flow regimes of interest are present. Through the investigation of more than 30000 combinations between fault zone permeability, matrix permeability, fault zone storage, matrix storage and fault zone thickness, it was found that, in the parameter space of the Malm aquifer, a bilinear flow can be observed for the first time only if the matrix permeability is lower than 2.0 x 10^{-13} m², and a linear flow for matrix permeability values below 6.0 x 10^{-14} m². Additionally, it was shown that fault zones, which have better hydraulic properties than the surrounding matrix, can indeed be hidden in pumping tests due to the parameter setting.

12 Geochemische Effekte von H_2-Intrusionen in oberflächennahe Aquifere – denkbares Störfallszenario eines unterirdischen Gasspeichers

Louisa Lagmöller, Markus Ebert, Adrian Metzgen, Dirk Schäfer und Frank Dethlefsen

CAU Kiel

13 Anwendung von drainierter Zentrifugation zur experimentellen Bestimmung temperaturabhängiger Veränderungen der Porenwasserchemie in geringdurchlässigen Sedimenten

Kerstin Meier zu Beerentrup

CAU Kiel

14 Kombinierte Grundwassersanierungs- und Wärmetauschersysteme zum Einsatz in Untergrundwärmespeichern

Adrian Metzgen und Markus Ebert

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Bedingt durch Veränderungen im Energiesektor im Zuge der Energiewende, sowie durch das Wachstum urbaner Infrastruktur kommt es zum Anstieg der Temperaturen im urbanen Untergrund. Daher sind heute bereits Grundwassertemperaturen über 20 °C möglich, wobei Untergrundwärmespeicher (UTES) als Mittel zur Effizienzsteigerung Erneuerbarer Energien zu Grundwassertemperaturen von bis zu ca. 90 °C führen können. Da Altlasten, wie z.B. Kontaminationen durch chlorierte Kohlenwasserstoffe (CKWs) insbesondere in urbanen Aquiferen auftreten können, ist es von besonderer Bedeutung, Sanierungssysteme zu entwickeln, die im Bereich erhöhter Grundwassertemperaturen eingesetzt werden können. Der Fokus der hier vorgestellten Arbeit liegt auf der Nutzung von nullwertigem, reaktivem Eisen (ZVI) als Hybridsystem zur Grundwassersanierung und als Wärmetauschermaterial in UTES. Drei in permeablen, reaktiven Barrieren (PRBs) zur Grundwassersanierung eingesetzte ZVIs (Gotthart-Maier-Roheisengranulat, Peerless-Roheisengranulat und ISPAT-Schwammeisen) wurden hinsichtlich ihrer Temperaturabhängigkeit in Bezug auf Schadstoffabbau, anaerobe Eisenkorrosion, Aktivierungsenergien sowie die Wärmeleitfähigkeit untersucht.

Untersuchungen zum anaeroben Korrosionsverhalten von ZVIs in Standversuchen bei 25 °C, 40 °C, 55 °C und 70 °C zeigten temperaturabhängige initiale Korrosionsraten (R_{ini}) und größtenteils temperaturunabhängige Langzeitkorrosionsraten (R_{lt}). R_{ini} nahm bei einer Temperatursteigerung von 25 °C auf 70 °C um den Faktor 40 (ISPAT-Schwammeisen), 90 (Gotthart-Maier-Roheisengranulat) und 140 (Peerless-Roheisengranulat) zu. Mittels REM Aufnahmen konnten dabei passivierende Oberflächenpräzipitate festgestellt werden, die als Grund für weitestgehend temperaturunabhängige R_{lt} angenommen werden. Aktivierungsenergien der initialen Eisenkorrosion lagen bei 69.1 kJ mol-1 (ISPAT-Schwammeisen), 87.1 kJ mol-1 (Gotthart-Maier-Roheisengranulat) sowie 96.1 kJ mol-1 (Peerless-Roheisengranulat).

In Säulenexperimenten mit PCE-haltigen Zulauflösungen (10 mg/l) konnte ein beschleunigter Schadstoffabbau bei einer Temperaturerhöhung von 25 °C auf 40 °C festgestellt werden. PCE-Halbwertszeiten nahmen dabei um 43 % (Gotthart-Maier-Roheisengranulat), 30 % (Peerless-Roheisengranulat) und 23 % (ISPAT-Schwammeisen) ab. An Gotthart-Maier- und Peerless-Roheisengranulat konnte sowohl bei 25 °C als auch bei 40 °C ein vollständiger PCE-Abbau über die Aufenthaltszeit im Säulenexperiment (ca. 40 h) beobachtet werden, wohingegen an ISPAT-Schwammeisen ein unvollständiger PCE-Abbau, mit temperaturabhängigen Restkonzentrationen am Säulenablauf vorlag. Weitere Daten zum Abbauverhalten bei 55 °C und 70 °C sowie zum Einfluss gelöster Grundwasserinhaltsstoffe auf den PCE-Abbau bei erhöhten Temperaturen werden aktuell erhoben. Die Bestimmung der Wärmeleitfähigkeit granularer, wassergesättigter ZVI-Schüttungen zeigte ähnliche bis leicht erhöhte Werte im Vergleich zur Wärmeleitfähigkeit von Sanden und Kiesen. Daher wird davon ausgegangen, dass ZVIs hinsichtlich der Wärmeausbreitung in UTES analog zum sonstigen Aquifermaterial behandelt werden können.

Die erhobenen Daten sollen in einem Model zur Simulation der Wechselwirkungen innerhalb von PRB Systemen bei erhöhten Temperaturen zur Anwendung kommen.

15 Steigerung der Nitratreduktion durch Zugabe organischer Substanzen

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Der Eintrag von Nitrat ist eine der häufigsten Ursachen für die Belastung des Grundwassers. Diese Belastung ergibt sich hauptsächlich durch die über viele Jahre ausgebrachten Stickstoffdünger der Landwirtschaft, welche zur Ertrags- und Produktionssteigerung verwendet werden [DWA, 2015]. Der Stickstoffdünger wird folglich als Nitrat (NO_3^-) in großen Mengen ins Grundwasser transportiert, so dass in vielen Bereichen Deutschlands bereits heute der Grenzwert der aktuellen Trinkwasserverordnung von 50 mg/l überschritten wird. Im Grundwasserleiter kann jedoch durch reduzierende Schwefelverbindungen und organischen Kohlenstoff eine Nitratabbaukapazität vorhanden sein, durch die bisher noch ein Teil des Nitrates reduziert wird. Da dieses Abbauvermögen immer weiter abnimmt und endlich ist, werden in Zukunft erhebliche Zunahmen der Nitratkonzentrationen erwartet [DVGW, 2016].
Um diese Nitratbelastungen im Grundwasser und vor allem auch im Trinkwasser zu senken, wird in dieser Forschungsreihe eine mögliche Steigerung der Nitratreduktion erforscht. Hierfür werden Säulenversuche durchgeführt, bei denen der Nitratabbau im Wasser durch Zugabe von Glucose, Ascorbinsäure oder Ethanol hervorgerufen und gesteigert wird. Bei der Auswahl dieser Reduktionsmittel wurde besonders darauf geachtet, dass von diesen Substanzen grundsätzlich keine Gefahren ausgehen oder Umweltschäden zu befürchten sind. Weiterhin wird erforscht, wie sich die Temperatur auf die Nitratreduktion mit Zugabe eines nitratabbaufördernden Stoffes auswirkt. Bisher liegen noch wenige Erkenntnisse über die Auswirkung der Grundwassertemperatur auf die Abbauprozesse vor. Da die mittlere Grundwasserjahrestemperatur in Deutschland etwa 10 °C beträgt, werden die Säulenversuche auf diese Temperatur heruntergekühlt. Somit können Aussagen über die Nitratreduktion unter Zugabe eines Reduktionsmittels bei Raumtemperatur im Vergleich zur Temperatur im realen Grundwasserleiter erhalten werden.

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16 Dynamics of anaerobic methane oxidation coupled to denitrification and bacterial sulfate reduction in the water column of an oligotrophic lake

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17 Hydrogeology of the Laacher See area (East Eifel Volcanic Field)

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The Laacher See (LS) Volcano is the youngest volcanic eruption center (12.900 years BP) in the East Eifel Volcanic Field (EEVF, West Germany) (Schmincke et al., 1999). The eruptions later formed a volcanic lake with a diameter of approximately 2.1 km in length and 1.6 km in width and two crater basins. The LS lake has an artificial tunnel in the south (hydraulic outflow), which was built in 1844 and lowering the water level of the lake about 5 m (Grewe, 1979). Scharf & Menn (1992) calculated the retention time for the LS of 66 years (for the time after 1844). In particular, wet and dry (CO_2-)mofettes occur on the northwestern and eastern shoreline and within the northwestern located crater basin in a circular shape (Goepel et al., 2015; Stoffels & Thein, 2000). The Variscan Siegen Main Thrust separates the Devonian sandy Siegen normal facies in the north from the Lower Devonian Hunsrückschiefer facies in the south. Main tectonic faults are oriented NW-SE (for example the (active) Ochtendung Fault Zone (Hentsch et al., 2019)) and perpendicular NE-SW due to Variscan orogeny. Additionally, younger faults striking NNW-SSE are present due to tertiary and quaternary uplift of the Rhenish Massif (Meyer & Stets, 1996). The Neuwied basin, south of the LS, was mainly covered with pumice deposits because of large eruptions of the LS Volcano (Frechen, 1976; Ahrens, 1928).

Additionally, besides the two crater basins of the LS Volcano, quaternary cinder cones are located around the LS Volcano. The volcanic deposits of these cinder cones and the emerged lava flows (basalts) are the main groundwater aquifers in the LS area, which are important drinking water resources. For fractured and weathered basalts Singhal & Gupta (2010) specify hydraulic conductivity of 10^{-9} to 10^{-2} m/s and porosity of 10-17 %. For pumice (pyroclastics and tuffs) only the porosity is specified with 87 %. The Devonian fractured rocks are aquitards with lower hydraulic conductivity (10^{-10} to 10^{-9} m/s for Devonian Sandstones (Heitfeld, 1965)). Solely, at intersections of (active) faults hydraulic conductivity can be expected to be enhanced. At two locations in the south and in the west (mineral) waters (so called „Säuerlinge“) are located, probably due to these intersections and degassing of volcanic CO_2.

To quantify the in- and outflow of the LS lake, groundwater level registrations at the southwest part of the crater and nearby the cinder cones, as well as flow investigations at the artificial tunnel have been in function since October 2017. With this dataset spanning 2 years until the end of 2019 a water balance will be calculated. To identify groundwater flow directions and possible areas of (mineral) waters, a conceptual, hydrogeological model of the LS area will be developed. Therefore, detailed geological field mapping, hydrochemical measurement campaigns (ion balance and trace elements) are arranged. These findings will be merged with underground data from boreholes and planar and linear data from geophysical measurements.

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18 Oyxgen as an indicator for groundwater surface water interactions

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Dissolved oxygen (DO) is crucial for most aquatic organisms in stream ecosystem and can be used as a proxy for its health. Due to climate change higher temperatures, altered fine sediment input, flood and dry conditions and potentially altered groundwater inputs can severely influence oxygen cycles in the stream waters and associated hyporheic zones (HZ, i.e. the interfaces between streams and groundwaters). However, identifying the sources and sinks of DO in the stream, the sediment water and the groundwater remains challenging. We apply a newly developed method of measuring stable oxygen isotopes ($\delta^{18}O_{DO}$) in combination with stable carbon isotopes ($\delta^{13}C$) and water isotopes ($\delta^{2}H$ and $\delta^{18}O_{H2O}$) in order to quantify photosynthesis and respiration in the various water compartments. For this study, three streams (Wiesent, southern Regnitz, Moosach) in the non-Alpine region of Bavaria were selected to investigate stable isotopes and the water chemistry of the stream water and the HZ. In combination with measuring stable isotopes in flume experiments, which allow a direct control of parameters like temperature, flow velocity, groundwater and sediment input, the outcome can be compared with the results of the natural streams. With this study we can assess the current health of streams and outline future trends regarding DO.

19 Temperaturauswirkung auf die Verflüchtigung organischer Grundwasserkontaminanten unter Berücksichtigung von Mehrkomponentenverunreinigungen und gelösten natürlichen Gasen

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Hochtemperatur-Wärmespeicher (HT-UTES) haben besonders in urbanen Gebieten, in denen häufig auftretende organische Grundwasserkontaminationen aufgrund befürchteter Umweltauswirkungen als Ausschlusskriterium für die thermische Nutzung angesehen werden ein großes Potenzial, die Nut-zung erneuerbarer Energien zu erhöhen. Die Auswirkungen des bestehenden und zukünftig zuneh-menden anthropogenen Temperaturanstiegs in Aquiferen unter Städten (z. B. urbane Wärmeinseln und UTES) auf Kontaminationen sind weitgehend unbekannt. Ein Temperaturanstieg führt z. B. zu ei-ner Steigerung der Volatilisierungstendenz von Schadstoffen, was zu einer unerwünschten Migration der Schadstoffe führen kann. Andererseits ist die Schadstoff-Volatilisierung einer der effektivsten ther-mischen Sanierungsprozesse, so dass Synergien zwischen Wärmespeicherung und Sanierung denkbar sind. Die Volatilisierung wird hauptsächlich durch die temperaturabhängigen Henry Koeffizienten (H) beschrieben; daher liegen die Ziele der laufenden Studie, die sich auf Temperaturen zwischen 5 und 90 °C fokussiert, (1) in der Beurteilung, ob die derzeit verfügbaren H für adäquate Prognosen zur Gas-phasenbildung ausreichend sind, und (2) in der Bewertung des Einflusses von gelösten natürlichen Gasen wie N_2, O_2, CO_2 und der Zusammensetzung von Mehrkomponentenschadstoffen.
Um die Qualität der verfügbaren H zu bewerten, wurden publizierte Daten verschiedener Schadstoffe zusammengestellt und zunächst mit PHREEQC-Gleichgewichtsberechnungen zur Gasphasenbildung durchgeführt. Die Berechnungen basieren auf einem geschlossenen System mit festgelegtem Druck (1 atm) und einer Starttemperatur von 10 °C. Die Zieltemperatur, die Zusammensetzung der gelösten natürlichen Gase und die NAPL-Zusammensetzung wurden variiert. Zur Verifizierung der Berechnun-gen wurden Laborversuche in einer gasdichten Edelstahlsäule durchgeführt, bei denen ein NAPL-Was-ser-Gemisch (TCE/Wasser und PCE/TCE/Wasser je 0,05 M) von 10 °C auf bis zu 70 °C erhitzt und die resultierende Gasphase quantifiziert wurde. Unterhalb der Gemischsiedetemperatur (z. B. 74 °C für TCE/Wasser) haben die Partialdrücke von N_2 ($\leq$ 1 atm) & CO_2 ($\leq$ 0,2 atm) einen großen Einfluss auf die Schadstoffvolatilisierung und führen zu einer Vervielfachung der verdampften Schadstoffe (z. B. Faktor 2 bei einer TCE-Kontamination bei 40 °C). Die Berechnungen der Gasphasenbildung von Wasser mit Mehrkomponenten-NAPL zeigten, dass kleine Anteile eines sekundären NAPL (z. B. 10 % PCE bei einer Dichlormethan-Kontamination) zu Erhöhun-gen der Gemischsiedetemperatur um $>$ 20 °C führen können. Bei den TCE/Wasser-Laborversuchen wurde ein Gasvolumen von 205 mL für 70 °C gemessen, das im berechneten Erwartungsbereich von 170-720 mL liegt, der auf der Unsicherheit der verfügbaren H bei Temperaturen $\geq$ 70 °C basiert. Die PCE/TCE/Wasser-Versuche bestätigten die berechneten Gasvolumen mit einer Abweichung von $<$ 8 %, bei einer Erwärmung auf 55 & 65 °C, was darauf hindeutet, dass die aktuelle H-Datengrundlage bei Temperaturen weit unterhalb der jeweiligen Gemischsiedetemperatur prinzipiell gut für die Prognose

der Gasphasenbildung bei der Erwärmung von verunreinigtem Wasser geeignet sind.
Die begrenzte Verfügbarkeit von H in Siedepunktnähe führt zu erhöhten Unsicherheiten bei Verflüchtigungsprognosen in diesem Temperaturbereich und spiegelt den Bedarf an weiteren H-Bestimmungen für die Planung von HT-UTES in kontaminierten Bereichen und Sanierungsprojekten wider. Dar-über hinaus zeigen die PHREEQC-Simulationen die Notwendigkeit, die Zusammensetzung der gelösten natürlichen Gase im Grundwasser und die Schadstoffzusammensetzung im Rahmen von Voruntersu-chungen für Wärmespeicherprojekte in kontaminierten Gebieten zu analysieren, um Umweltrisiken durch die Ausgasung von Schadstoffen abzuschätzen oder die Sanierungseffizienz zu bewerten. Die vorliegende Studie ist Teil des Projekts ANGUS II (gefördert durch das BMWi; 03ET6122A).

20 Development of a hydrofacies model to identify hydraulic relevant variations in highly permeable, fluvioglacial sediments of the Munich Gravel Plain

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21 Geochemical Modelling of Barite Scalings in Geothermal Systems

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Deep geothermal systems in fractured media are a promising way for extracting energy from renewable sources. However, there are certain limitations in order to have a resilient and sustainable plant operation. One of these are due to hydrothermal fluids often being highly saline. If their state temperature and pressure are altered during production, mineral scalings may form in the system or even in the fractured host rock as a consequence of perturbing equilibrium, deteriorating the overall productivity of the plant. Barite stands out as one of the most common scaling agents in this context and, in addition, is exceptionally hard to remove once accumulated. It is therefore of highest interest to assess the factors controlling its precipitation behaviour. These factors, however, are manifold, have complex interactions and are therefore challenging to quantify experimentally. This makes it imperative to investigate them by means of hydro-geochemical modelling and numerical simulations.

A Python-interface for the geochemical modelling software PHREEQC was developed, which introduces great flexibility for parameter optimisation routines and sensitivity analyses, as well as speeding up calculations through multiprocessing. Moreover, it enables geochemical calculations to be tightly coupled with transport codes and other process algorithms.

This method was applied to a modelling example case of a single fracture on the laboratory scale, flowed through by a brine supersaturated with respect to barite. Advective flow, heterogeneous nucleation and precipitation kinetics were implemented to study temporal alterations. The fracture permeability was approximated using the cubic law. A sensitivity analysis was carried out to approximate the impact of the following parameters with regards to permeability change over time due to mineral precipitation: temperature, initial fracture aperture, flow velocity, barite supersaturation and salinity (Na^+ and Cl^-). The initial fracture aperture showed to have the greatest effect, though it should be noted that all mentioned parameters had an impact. Based on the parameter set used, the time for permeability to decrease by one order of magnitude spanned multiple scales ranging from hours to years. In addition, the saturation length scale was used to estimate the potential range of influence within a fracture, which similarly spanned multiple scales ranging from metres to kilometres. Flow velocity and fracture aperture emerged as the determining factors.

22 Design of a lab-scale experiment to investigate thermal convection by high temperature BTES in water saturated porous median

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23 Saving the embankments – verifying the water balance through experiments and modelling

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Earth dam embankments function as noise protection on highways, landfill covers or recultivation layers. Meteorological processes like rainfall, draughts and frost influence the stability of the embankments, leaving them open to structural changes like localized structural failures and vegetation deficits. These changes depend on soil material, water storage capacity, composition of the embankment and type of vegetation. To increase the stability and safety of these structures, a combined analysis of the hydrological, geotechnical and pedological parameters is required.
In this work, we tried to verify if the soil water balance software (BOWAHALD) could be used to model and simulate the water balance of embankments with different soil covers and if it delivers the same results as pilot plant size experiments. To do this, we selected three different soil covers (humus, non-humus and mixed) with depths of 10 to 15 cm, planted with grass and herbs to investigate the impact of plant growth and roots on the embankment under different hydrologic conditions. Two synthetic irrigation data sets were used: one data set adapted to realistic conditions (mean value 770 mm/a) and the second one represents irrigation values for dryer conditions (545 mm/a) in the future due to climate change.
For a period of two years, daily values for surface runoff, water content in different soil depths (10, 20, 30, 50 and 90 cm) and residual leakage were collected to calculate the water balance for each embankment. After one and two growth seasons, respectively, the vegetation and roots were recorded. The results show that surface runoff in the case with the non-humus layer was highest followed by the mixed layer and the humus layer being the lowest. The high surface runoff has a negative impact on the surface cover of the embankment resulting in the transport of fine sediment downwards the embankment. While the embankment with the humus layer has the lowest surface runoff, it had the highest amount of percolating water which can cause instability. To improve stability, a compromise between surface runoff and percolating water has to be found, which could be achieved by the use of a right combination of plant cover and natural and artificial soils. The BOWAHALD software seems to be a promising tool to simulate the impact of different mixtures of soils and vegetation on the surface runoff and percolation water.
Future experiments with different mixtures of soils will be tested to optimize the stability of the embankment and to minimize the risk of landslides.

24 Contrasting long-term trends of nitrate concentrations, loads and concentration-discharge relationships after drastic fertilizer-input changes in three nested catchments

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Excessive application of nitrogen fertilizers to agricultural fields leads to increased nitrate concentrations in groundwater and surface water, threatening drinking water quality and the integrity of aquatic ecosystems. The effectiveness of measures that aim to reduce nitrate pollution is, however, still difficult to quantify because of heterogeneous catchments characteristics and the long time lags between application and concentration changes (legacy effects). Therefore, the analysis of long-term trends in heterogeneous catchments is an important step forward to better understand transport and mobilization processes that drive nitrate concentrations and loads.
After the peaceful reunification of Germany in 1989/90, agriculture, and with it fertilizer application, drastically decreased and only slowly reestablished. Thirty years later, this gives a unique chance to study the long-term changes in nitrate storage, transport and mobilization (Ehrhardt et al. 2018). Our study side is the Selke catchment, a mesoscale catchment (456 km²) located in Saxony-Anhalt, Germany. Data on discharge and nitrate concentrations have been collected on a regular basis since 1983 at three gauges: two at the upper Selke in the Harz Mountains, dominated by shallow flow paths, forest and sparse agriculture; and one gauge located downstream in the lowlands where deeper groundwater flow paths and agricultural land use dominate (Dupas et al. 2017).
We analyzed long-term trends of nitrate concentrations and loads, using Weighted Regression on Time, Discharge and Season (WRTDS, Hirsch et al. 2010) at the three stream gauges. Furthermore, we analyzed long-term changes in the relationship between nitrate concentrations and discharge (i.e., the slope of the CQ-relationship), obtained from WRTDS (Zhang et al. 2018).
Results indicate a strong decrease of nitrate concentrations and loads shortly after 1990 in the upper Selke and a constant increase thereafter, in close agreement with agricultural nitrogen input. The concurrent decrease in the lower Selke, however, seems to be mainly driven by the concentration decrease in the upper Selke, while decreasing inputs from the lower Selke watershed only become visible with a delay of two decades. This delayed response likely results from long travel times due to the dominance of groundwater in the lowlands, which will be further analyzed using effective transit time distributions calculated from long-term nitrogen inputs and outputs.
CQ-slopes show that nitrate mobilization and transport processes change over time and are fundamentally different between the upper and the lower Selke. For example, around the time of the peaceful reunification, the CQ-slope in the upper Selke reaches its absolute maximum, while the CQ-slope in the lower Selke reaches its absolute minimum.
The results demonstrate that not only concentrations and loads, but also mobilization and transport patterns in catchments can vary with time, depending on catchment characteristics and input loads. This knowledge is important for the prediction of nitrate pollution and the implementation of effective reduction measures.

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