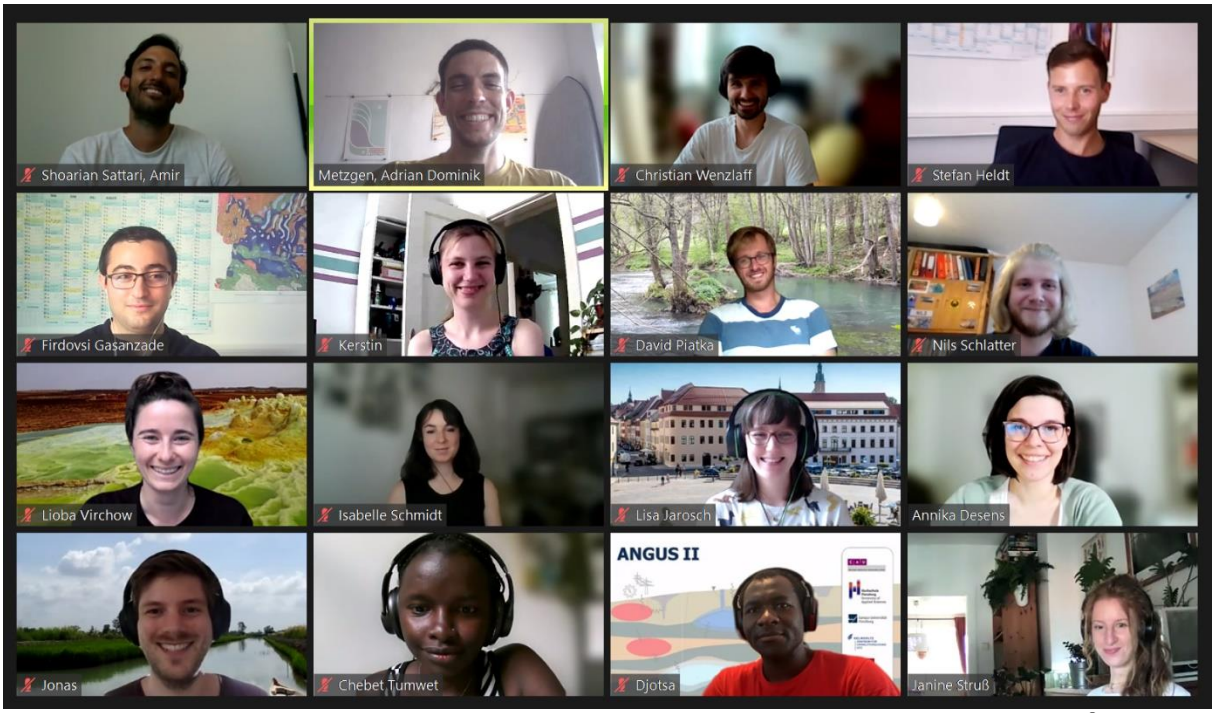
30. Doktorand*innentreffen der Hydrogeologie

Kiel

14. und 15. Juli 2021



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Organisation:

Die Doktoranden der Arbeitsgruppen für Angewandte Geowissenschaften – Aquatische Geochemie und Hydrogeologie, Geohydromodellierung sowie der marinen und terrestrischen Geomechanik und Geotechnik vom Institut für Geowissenschaften der Christian-Albrechts-Universität zu Kiel.

Adrian Metzgen, Janine Struss, Kerstin Meier zu Beerentrup, Firdovsi Gasanzade, Amir Shoarian Sattari, Stefan Heldt, Victorien Djotsa und Falko Vehling

Das 30. Doktorand*innentreffen der Hydrogeologie fand vom 14.07. bis zum 15.07.2021 aufgrund der Einschränkungen durch die COVID 19 Pandemie im Unterschied zu den vorherigen Jahren als Onlineveranstaltung statt. Gastgeber waren in diesem Jahr die Doktorand*innen der Arbeitsgruppen der Angewandten Geologie der Christian Albrechts Universität (CAU) zu Kiel.

Der erste Tag des Doktorand*innentreffens startete mit einer Key Note von Prof. Dr. Andreas Dahmke, Leiter der Arbeitsgruppe für aquatische Geochemie und Hydrogeologie am Institut für Geowissenschaften in Kiel. Prof. Dr. Andreas Dahmke legte insbesondere einen Fokus auf zukünftige Arbeitsfelder von Hydrogeologen insbesondere in Bezug auf die Herausforderungen des globalen Klimawandels sowie die Umstellung der Energieversorgung auf erneuerbare Energien. Vor allem die Nutzung des Untergrundes als saisonalen Wärmespeicher war Thema seines Vortrages.

Im Anschluss folgte ein Vortrag des Gastredners Mathias Foot zu der öffentlichkeitswirksamen Darstellung wissenschaftlicher Daten. Im Anschluss an den Vortrag diskutierte er mit den teilnehmenden Doktorand*innen über die Möglichkeiten ihre Forschungsergebnisse verständlich für Interessierte außerhalb des eigenen Fachbereichs aufzubereiten.

Im weiteren Verlauf folgten neun Beiträge der teilnehmenden Doktorand*innen von der TU Freiberg, dem Karlsruher Institut für Technologie, der FU Berlin, der FAU Erlangen, dem Geozentrum Hannover, dem GFZ Potsdam und der CAU Kiel in Form von Vorträgen zu den Themen Wasser bzw. Grundwassermanagement und -Monitoring sowie zu der Hydrochemie von Untergrundwärmespeichern. Im Anschluss an die Vorträge folgten spannende Diskussionen zu roboterunterstützten Wasserprobenahmen in Seen, (Grund-)wassermanagement in Vietnam und Indien, gelöstem Sauerstoff in aquatischen Ökosystemen, Methodiken zur Bestimmung des Grundwasseralters, dem Transport von Mikroplastik in Böden sowie zu hydrochemischen Auswirkungen der Nutzung des Untergrundes als Wärmespeicher.

Der zweite Tag stand ebenfalls im Zeichen der erneuerbaren Energien und startete mit einem Gastvortrag von Dr. Klaus Wortmann (EKSH) zu Szenarien-Modellen der Energiewende sowie Energielandschaften in Schleswig-Holstein. Dabei wurden Zukunftsvisionen zur Klimaneutralität in urbanen Räumen aber auch länderübergreifend diskutiert und die Frage aufgegriffen, welche Aufgaben künftig die Hydrogeologie zur Bewältigung der Energiewende beschäftigen werden. Weiterhin wurde in Verbindung zum Gastvortrag des 1. Tages das Thema

Wissenschaftskommunikation aufgegriffen und eine Diskussion darüber geführt, wie man Ergebnisse aus Forschung und Wissenschaft, wie beispielsweise Zukunftsszenarien zur Klimaneutralität, an die weite Bevölkerung bringen kann und wie die Resonanz zu solchen Projekten ist.

Im weiteren Tagesverlauf folgten Beiträge der teilnehmenden Doktoranden in Form von Vorträgen zum Schwerpunkt numerische Modellierung, sowie analytische Methoden im Feld von insgesamt sieben Teilnehmern von der CAU Kiel, dem GFZ Potsdam und der RWTH Aachen. Insgesamt konnte an diesem Tag ein spannender wissenschaftlicher Diskurs zu Themen wie die Verwendung erneuerbarer Energien zur saisonalen Wärmespeicherung mithilfe von Aquifer- und Erdwärmesondenspeichern und zur Druckluftenergiespeicherung, die geomechanische Beschaffenheit geologischer Reservoir- und Barrierestrukturen, sowie ein Einblick in die laserinduzierte Plasmaspektroskopie als Analysemethode im Feld abgehalten werden.

Das 30. Doktorand*innentreffen der Hydrogeologie stellte auch in diesem Jahr trotz pandemiebedingter Online-Veranstaltung wieder eine schöne und wertvolle Plattform für alle teilnehmenden Doktorand*innen dar, sich wissenschaftlich über die eigenen Forschungsthemen hinaus auszutauschen und damit auch die Themengebiete und Arbeitsweisen anderer Arbeitsgruppen kennen zu lernen. Da es bei allen Teilnehmern großen Anklang gefunden hat, wurde beschlossen das kommende 31. Doktoranden-Treffen 2022 unter dem Zusammenschluss des GFZ Potsdam und der TU Berlin in Berlin stattfinden zu lassen.

Das 30. Doktoranden-Treffen wurde freundlicherweise vom Kompetenzzentrum Geo-Energie, der Fachsektion Hydrogeologie in der DGGV (FH-DGGV), der Gesellschaft für Energie und Klimaschutz Schleswig-Holstein (EKSH), sowie der International Association of Hydrogeologists (IAH) unterstützt. Wir danken herzlich den Gastrednern Mathias Foot und Dr. Klaus Wortmann für Ihre großartigen Beiträge. Ein besonderer Dank gilt auch dem Key-Note Speaker Prof. Dr. Andreas Dahmke, der vor ca. 30 Jahren die Tradition der hydrogeologischen Doktorand*innentreffen ins Leben gerufen hat.

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Abstractverzeichnis

1. RoBiMo- Robot-assisted inland water monitoring

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Research on hydrochemical stratification of lakes, groundwater-surface water interaction and degassing into lake water is based on detailed hydrochemical investigations. However, until now high temporal and spatial resolution of hydochemical parameters in lakes are rare even in Saxony with its challenges regarding acidity, contamination with metal ions and sulfate, and high content of organic carbon and nutrients. The research project RoBiMo aims at setting up diverse automated modular swimming platforms which are measuring various chemical parameters at different depths in the lake along self-determined routes.

The swimming platforms will be developed within a just recently launched interdisciplinary research project RoBiMo at TU Bergakademie Freiberg. The partners included in this research project are from sensor development, scientific diving, geoecology, hydrogeology, and robotics. The swimming platforms are controlled autonomously from a shore station and transmits the data via a network-independent connection. A measuring chain with multi-sensors will be developed to record the relevant parameters. These parameters include pH, electrical conductivity, as well as content of phosphate and nitrate. Furthermore, respiration processes will be investigated by using the gas chamber SE(M)ACH-FG developed at TU Bergakademie Freiberg. These processes will be studied at selected drinking water reservoirs of LTV (Landestalsperrenverwaltung) in Saxony as well as in opencast mining lakes. Additionally, another platform will be equipped with an underwater sonar and tool for LiDAR mapping to provide high-resolution data of the subsurface. The created 3D point clouds from the sonar will be used for the classification of structures, obstacles and objects through machine learning analysis. Scientific divers of the Scientific Diving Center will collect "Ground Truth" data to validate the functionality of the individual multi-sensors in situ and to sample water and sediment for further hydrochemical and geochemical analyses in the laboratory.

The measurement results will be presented in 3-dimensions by the means of artificial intelligence and virtual reality to provide new insights into the spatial distribution of hydrogeological processes in inland waters.

2. Evolution and dynamics of groundwater resources in the context of salinization and freshening in the most southern Mekong Delta, Vietnam

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Availability of freshwater resources is a major challenge in fast growing deltas around the world. In the Vietnamese Mekong Delta (MD) in South-East Asia, groundwater is the major source of freshwater and unregulated overexploitation in the last decades led to various negative environmental impacts, such as salinization and severe land subsidence. In combination with additive processes, e.g. sea-level rise, the low-lying MD is threatened in its very existence. Overall, the problems can be summarized as a progressive "loss of land and fresh water", which might eventually lead to inundation of large parts of the delta by the end of the century. Therefore, a comprehensive large-scale environmental study focusing on groundwater dynamics and evolution in the context of salinization and freshening in the confined, around 350 m deep, multi-layer aquifer system was conducted in the southernmost and most vulnerable province Ca Mau. Groundwater samples from private household wells, schools and public institutions, drinking water production facilities and smaller businesses were taken between 2017 and 2019 and analyzed for their geochemical and stable isotopic composition. In addition, a hydrogeological model was constructed. As peoples acceptance to new water utilization concepts is a key factor, questionnaires and group interviews were conducted while sampling to get insights of people's water use habits as well as their awareness of consequences related to groundwater overexploitation and land subsidence. The evaluation of 190 groundwater samples showed that Na-HCO3 is the dominant water type in the Pleistocene and Pliocene aquifers down to > 300 m, which indicates significant freshening due to freshwater infiltration, probably during the last glacial maximum. However, freshwater intrusion seems to decrease from Pleistocene to Miocene aquifers, as Na+ (%) indicates. Conversely, extensive salinization in the following marine transgression did not occur due to the formation of impermeable Holocene clay layers and only a few samples show distinct salinization signatures, like element ratios and water type, which might have originated more recently by mixing with saline water of unknown origin, which will be determined in a future study. Past marine transgression and regression cycles, water-rock interactions and reductive processes mainly control geochemical

water composition. Although seawater infiltration is a major concern for Vietnamese water management authorities, no recent seawater intrusion has been detected in Ca Mau province so far. Elevated total dissolved solid concentrations near the coast are attributed to additional HCO3- generation in organic rich marine sediments rather than an increase in Cl-. Aquifers seem to be connected, at least partly, as geochemical signatures show a distinct spatial pattern, which is not correlated to depth or aquifer. Groundwater recharge is limited and extensive pumping might enhance severe local land subsidence. Insights gained in this study are used to develop integrated counter measures to mitigate negative environmental impacts in the project region.

This study is carried out in the frame of the project “ViWaT – Engineering: Water, Energy and Construction Technologies” (viwat.info, BMBF funding reference: WTCL02047517).

3. Water related adaptation strategies for small-scale farming in India to climate sensitive factors

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Climate change and its impact on water resources are currently one of the major threats to livelihood of humans. Although mitigation strategies are in place on an international level, countries have to be prepared to further shifts in regional temperature and precipitation (FAO 2011). Globally, various regions are facing groundwater depletion and deterioration which lead to negative outcomes for local communities (Jia et al. 2020).

In India, groundwater is one of the most important sources of fresh water. It is not only used for irrigation but also for domestic purposes, like drinking, cooking and hygiene. Only a small percentage is used in industry (Suhag 2016). Thus, many stakeholders are involved in regulating the process of groundwater withdrawal and use. To tackle the issues threatening the water resources, joint approaches involving stakeholders, their perspectives (Chen et al. 2020; Suhag 2016) as well as considering all influencing factors like structural and economic issues, governance, and ecosystem services is required (Katyaina 2021).

Important factors influencing water needs in food production are described in the water-food nexus, which correlates food production and the amount of water used. Due to a constant population growth in India, the need for food is increasing and therefore water extraction is intensified. But as groundwater is already under stress, specific strategies and regulations for efficient irrigation to deliver the amount of food needed should be applied (Barik et al. 2017)

India already has to deal with the effects of changing climate, especially shortage of water in an appropriate quality for usage. Although varying artificial recharge methods to enrich aquifers have been established in the past, it is still difficult to assess their effectiveness (Jacob, Jaryal, and Gurunathan 2016). Methods of Managed Aquifer Recharge (MAR) are applied in several parts of India to store water from times with increased rainfall. Especially the use of Bank Filtration, a subset of MAR to treat surface water, is effective to reduce contaminations. Recharging groundwater through e.g. ponds and tanks, also leads to reduced salinity in groundwater (Wintgens et al. 2016). But in order to guarantee safe water free from pathogens and other hazards, data on water quality is needed (Dillon et al. 2020). Besides that,

clogging impedes the percolation of the stored rainwater in the underground (Wintgens et al. 2016), which makes regular maintenance of the structures inevitable.

Additionally, various conflicts of use jeopardize the traditional recharge methods, that provide water safety for rural population. Specific land cover is needed to apply groundwater recharge techniques (Malekmohammadi et al. 2012). Furthermore, catchment protection zones to protect unconfined aquifers from ingress of pathogens would also require special restrictions for land use (Wintgens et al. 2016). This can collide with different land cover, e.g. agricultural use or building development (Malekmohammadi et al. 2012). An alternative approach to protect water resources are adaptations of agricultural and irrigation techniques, which in turn demands changings in policies, alternate sources of water and further research (Hochman et al. 2017)

The issue of lacking water resources in both quality and quantity is different in rural and urban areas (WHO; and UNICEF 2017). Factors influencing these differences are important to know, to efficiently address the problem of water scarcity in a broader sense, adapted to the individual setting on a local level (Figure 1). Thus, initial needs of the population and social challenges should be identified to develop sustainable strategies (Castelli et al. 2021).

In the same way, knowledge about the actual problems of farmers is needed to improve the situation and living conditions at present. It is important to be aware of how the main problems and risks people have to tackle daily look like (Deivalatha and Ambujam 2011). Besides this, future aspects e.g. climate change, demographic change, land cover and economic growth influencing the availability of water must also be included in each strategy (Katyaina 2021).

Research approach. To develop a strategy for supporting water security in rural areas, especially for small-scale farming, research will focus on two scales (regional and local level Figure 1) to combine governance with local practice. Thus, the effect of often superordinate governance approaches is considered when investigating watershed programs and vice versa.

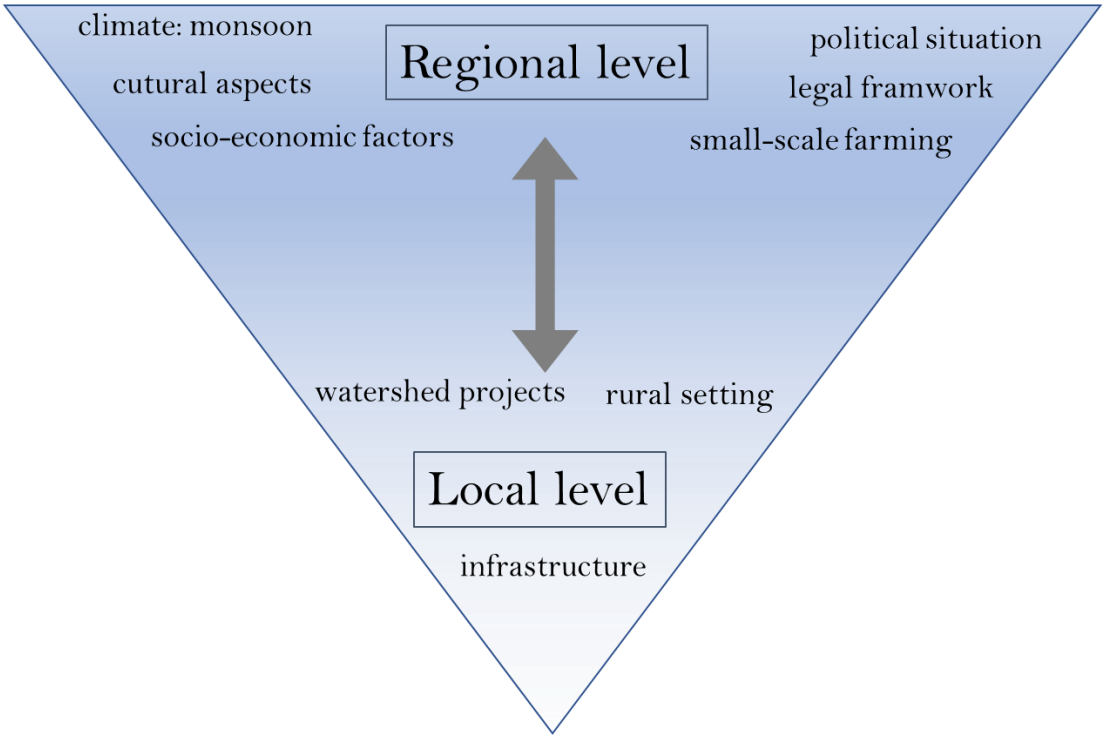

Figure 1: *Establishing a research approach to develop strategies and techniques which tackle water related challenges on various levels.*

Regional level. In the first phase, a literature research on watershed development in rural areas, regarding methods and the history of their development will be conducted. As challenges in developing nations are unique, this research gathers known problems and deficiencies of water management systems in this particular context. Also, current research of the influence of climate change on groundwater resources as well as hydrogeological processes will be gathered. In addition, research regarding the legal background and the structure of the public authorities will be conducted to determine contacts points for participatory approaches. Furthermore, cultural and gender related aspects will be investigated to picture their influences on water stress.

The establishment of contacts to relevant stakeholders from public authorities, rural population and agriculture as well as Non-Governmental Organizations and helpful experts is focused. Within this network, valuable knowledge about the living conditions of the rural population will be gathered. Also, insights on how climate change is already affecting people's lives will be gained. Furthermore, public authorities and politics are also involved in the process of groundwater extraction and use. Especially with regard to laws and legislation as well as to economic factors, data in this context will be gathered. This will be done by

questionnaires in the beginning. Depending on the situation, cooperative approaches like workshops can be useful, to gain various perspectives.

Local level. To narrow down the scale, common living conditions of people in rural areas and farmers need to be delineated. Their differing perspectives will be captured through qualitative approaches, e.g. workshops or interviews. To better understand the local conditions, explorative field trips to the study area will be conducted in the beginning. During these trips, data regarding social-economic conditions as well as knowledge about watershed projects in rural areas will be collected. This includes collecting information about the techniques which are applied as well as their effectiveness to provide water in both adequate quality and quantity. Based on the initial analysis of the situation, three individual projects will be investigated in further detail with regard to their current adaption methods. Additional data to evaluate the watershed projects will be collected during two field trips per year.

A watershed programme could be the operation and maintenance of percolation tanks, implemented in the district of Madurai. These tanks collect rainwater during seasons of high rainfall which increases recharge to the aquifer. The water is available for usage in dry seasons, but its quality is varying throughout the extraction wells (Jacob et al 2016).

Developing a strategy. Based on this analysis of the current situation on both scales, including all aspects that are influencing the situation in India, a strategy to tackle the issue of water scarcity, especially focusing the groundwater demand and supply for small-scale farming systems will be developed and evaluated within the further research phases. This strategy implies a wide approach, considering the past, current and future conditions. Also, results and approaches will be discussed within the network of stakeholders and experts, to include all perspectives and to adapt the strategy continuously.

Expected targets and outcomes. This research targets to an increased understanding of the factors influencing water stress in India and regarding water-food Nexus. The approach is focusing on a regional scale considering the socio-economic situation and narrowing down to local scale to delineate the picture of daily issues of small-scale farmers. During the research phases, data will be analyzed, and first research insights will be published.

This knowledge should lead to the development of integrated strategies and methods to improve the situation for farmers, their adaption to future scenarios and thus the rural population in India by safeguarding their livelihood.

This superior goal will be achieved by

- Outlining the impact of the current legal, societal and political situation on water stress
- Identifying correlations between socio-economic, cultural and technical factors
- characterizing climate effects on water resources and hydrogeological processes
- evaluating the impact of watershed projects on small-scale farming
- identifying effective management of water resources to guarantee safe use in rural areas
- estimating the impact of activities and behaviors on utilization of water resources
- provision of sustainable, multi-disciplinary strategies to improve present and future scenarios

A guideline for the efficient and sustainable management of water resources in the region will result from this work, which describes elements like feasible monitoring, behavioral adaption, and application of techniques.

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4. Dissolved oxygen and its stable isotopes as process indicators of aquatic ecosystems

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Dissolved oxygen (DO) is crucial for aquatic ecosystems and is a key parameter to define their health. In streams, downstream shifts of photosynthetic and respiratory activity can be result from natural and anthropogenic influences and lead to distinct DO patterns. However, identifying sources and sinks of DO remain challenging. In this study we performed seasonal sampling campaigns in three Bavarian streams (Mähringsbach, Wiesent and Moosach) and measured the downstream evolution of DO and its stable isotopes ($\delta^{18}O_{DO}$). This served as a basis to calculate photosynthesis (P) to respiration (R) ratios with the goal to show seasonal and spatial DO trends. Throughout the seasons DO saturations and $\delta^{18}O_{DO}$ deviated from expected values for atmospheric equilibrium and indicated photosynthetic DO and its consumption by respiration further downstream. During warmer and more light-intensive periods photosynthetic DO input was generally higher than during cooler periods as marked by DO oversaturation and corresponding $\delta^{18}O_{DO}$ values that approached those of water. A comparison of calculated P/R ratios of the three streams allowed to group them according to their ranges that were between 0.1 and 5.2. Differences in seasonal and downstream behaviour of DO and P/R ratios in all streams can be attributed to the high heterogeneity of the river landscapes with varying anthropogenic inputs, effects of shading by tree canopy, solar radiation, water temperature, nutrient availability and influence by tributaries. This study proves $\delta^{18}O_{DO}$ and P/R ratios as a promising tools for metabolism of stream ecosystems to disentangle DO sources and sinks.

5. Nation-wide collection and interpretation of groundwater ages from Germany

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The Federal Institute for Geosciences and Natural Resources (BGR) is currently collecting all available groundwater age data on the territory of the Federal Republic of Germany. The data will be archived in a publicly accessible database. The background to this is that the German Site Selection Act for radioactive waste disposal sites defines groundwater age as an exclusion criterion. If young groundwater is detected in the vicinity of potential host formations, these sites must be excluded as a potential repository for high-level radioactive waste. In the by-laws tritium (3H) and carbon-14 (14C) are mentioned as indicators for young groundwater.

Groundwater ages also can be used for many other scientific questions, e.g. for studies on the transport of pollutants, such as nitrate and pesticides, for groundwater recharge estimations and as for the calibration of regional groundwater models.

In addition to data collection, the dissertation will include investigations of the influence of various parameters on the determination of groundwater age and interpretations of the depth of young groundwater in the various hydrogeological units.

In the presentation, the terminology of groundwater age will be explained, what role (radioactive) isotopes play in this and how the age is calculated. There will also be a short introduction to the database and the first results on the Germany-wide distribution, and the first statistical evaluations on the depth distribution of young groundwater in the North German Basin will be presented.

6. Development of methods for the detection, elimination and immobilization of microplastics in soils, compost and plants

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The aim of the study is to develop a method for the detection, characterization and elimination or immobilization of microplastics in the soil matrices. In order to gain more precise knowledge about the transport paths of microplastics in soils, the process is tracked using a simulation and a forecast model generated through a comprehensive analysis of the material flows developed from Elution tests and Column tests, by means of fluorescence-labelled microplastics and targeted contamination, designed to investigate the behaviour of microplastics in the soil matrix. An addition aim is to investigate the influence of microplastics on crop plants, with the focus on the soil-plant-human transmission path. In order to identify exposure hotspots, monitoring is planned on potentially endangered areas. Finally, a process engineering concept is to be developed for the purification of contaminated soils and composts.

The residue-free separation of the organic and inorganic fraction of the soil samples is essential for the analysis. Here, density separation and oxidative or enzymatic digestion come into question. Microscopic and FT-IR based devices are available for the qualitative analysis of the individual polymers, while various spectroscopic and thermogravimetric analyses have to be used for the quantitative determination.

When eliminating microplastics, the focus is on the two substrates, soil and compost. The microplastics should be separated from the matrix using common sorting methods, their adaptation and extension. The effectiveness of these methods and the sorting limits are examined in detail. The effects of microplastics on plants - especially cash crops - are also

evaluated. Root growth is observed in rhizotrons. The translocation within the plants is monitored by means of fluorescence-labelled microplastics in hydroponics. The influence on the soil matrix is assessed through leachate analysis and measurement of soil moisture.

7. Hydrochemical effects of high-temperature Borehole Thermal Energy Storage: Temperature-dependent changes in pore water chemistry of Glacial Tills

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-Abstract nicht zur Veröffentlichung freigegeben-

8. Einfluss von Heißwasserinjektionen auf die geochemischen und hydraulischen Eigenschaften potentieller Aquiferwärmespeicher in Berlin

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-Abstract nicht zur Veröffentlichung freigegeben-

9. Application of Elevated Temperatures (10 to 70°C) on ZVI PRBs for an Enhancement of CHC-Degradation

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Thermal remediation methods are common means of remediating contaminated sites. However, against the background of globally rising urban groundwater temperatures due to climate change and infrastructure as well as the use of the urban geological subsurface for seasonal heat storage, other established remediation methods must also be examined for their thermal coupling capability. This is of particular interest to enable the thermal use of contaminated aquifers under licensing law and thus reduce inevitable spatial limitations in the operation of underground seasonal heat storage facilities. The presented study investigates the effects of groundwater temperatures between 10°C and 70°C on permeable Fe(0) reaction walls (PRBs) for the degradation of CHCs and aims to provide an experimental database for possible hybrid management (remediation and thermal use) of contaminated urban sites. A temperature of 25°C corresponds to the thermal impact of urban heat islands, whereas temperatures of up to 70°C may occur in the future, e.g., due to active alteration of groundwater temperatures resulting from seasonal storage of heat in the geological subsurface.

Three different common ZVIs (Gotthart-Maier (GM) and Peerless (PL), and ISPAT iron sponge (ReSponge®, IS)) were investigated in column and batch experiments for their temperature-dependent behavior with respect to CHC degradation (10 mg L^{-1} PCE in solutions of different mineralization), gas formation (H_2 and fractionation of CHCs), and anaerobic corrosion. Column experiments with run times of up to 18 months showed a time-stable and strong increase in the rate of CHC degradation with increasing groundwater temperatures. The temperature range of 10°C to 70°C showed an increase in the rate of degradation with pseudo-first order kinetics by a factor of up to 80, with a decrease in the half-life of PCE degradation from 25 h to 0.3 h for GM and PL and 2.4 h to 0.3 h for IS. GM and PL completely degraded PCE as well as the metabolites TCE, cis- and 1,1 DCE during the residence time in the column experiments (11 h to 40 h), whereas IS showed incomplete degradation of PCE with residual temperature-dependent PCE concentrations up to 4000 µg L^{-1} at 10°C and up to 700 µg L^{-1} at 70°C at the column effluent. The metabolites TCE, cis-, 1,1- and trans-DCE formed during PCE

degradation at IS were not degraded. Activation energies (E_a) for PCE degradation, derived from the Arrhenius relation of first-order rate coefficients to temperature, were found to be 60 kJ mol^{-1} for GM and PL. The significantly lower E_a for PCE degradation on IS of 27 kJ mol^{-1} suggests a different dominant reaction mechanism, presumably diffusion limitation of degradation due to the higher intraparticle surface area of this material. With increased temperature, TCE occurred almost exclusively as a metabolite of PCE degradation.

Anaerobic Fe(0) corrosion showed a temperature-dependent initial corrosion behavior with an increase in corrosion rates with increasing temperatures from 25°C to 70°C from 1.5 to 65 mmol kg^{-1} d^{-1} for IS, 0.2 to 18 mmol kg^{-1} d^{-1} for GM, and 0.1 to 10 mmol kg^{-1} d^{-1} for PL . The long-term corrosion behavior (~50 d) showed a passivation-induced lower temperature dependence, with an increase in anaerobic iron corrosion rates from 25°C to 70°C from 1.5 to 6.2 mmol kg^{-1} d^{-1} for IS, 0.2 to 1.7 mmol kg^{-1} d^{-1} for GM, and 0.03 to 0.4 mmol kg^{-1} d^{-1} for PL. The activation energies for the initial corrosion process are 86 kJ mol^{-1} for GM and PL, and 71 kJ $mol^{-1}$for IS.

The laboratory results presented indicate that coupling Fe(0)-PRB for CHC remediation with thermal management of the contaminated aquifer can theoretically lead to significant reductions in Fe(0) material costs (up to ˜70%) and possibly also in heat supply costs if other processes associated with the temperature change, such as emission behavior and/or outgassing, etc., can be controlled in field systems. The next steps will be experimental studies on the temperature influence on the degradation performance of e.g. injected nano-Fe(0) particles, ISCO processes as well as Natural Enhanced Attennuation processes to provide experimental basis for hybrid management of contaminated aquifers.

10. Compressed air energy storage in deep aquifers in a 100% renewable energy supply future

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Large-scale compressed air energy storage (CAES) in aquifers is one option to mitigate fluctuating availability of weather-dependent renewable energy sources in future energy systems with share of renewables up to 100%. Mechanical energy is stored as pressurized air in a subsurface porous formation using off-peak power, and released during peak demand using a turbine for power generation. Depending on share and type of renewable energy sources in the future, different storage capacities and storage power rates will have to be satisfied to compensate fluctuating nature of the renewable power supply. Therefore, this study investigates scenarios for subsurface compressed air storage using four potential future energy system development pathways. Because for CAES subsurface processes and power generation are strongly linked via reservoir pressure and flow rates, coupled power plant and geostorage model has to be developed and employed to evaluate potential operation conditions for such a storage technique.

For the study, virtual diabatic CAES facility with three-stage compression and two-stage expansion and heat recuperator is designed. As geological storage site, an anticline structure at 1 km depth formed by Rhaetian sandstones of 20 m thickness is used. Energy load profiles with hourly resolution generated from an energy system model show that the power plant needs to provide 115 MW during withdrawal and take up 230 MW during loading. Simulations are performed using the open-source thermal engineering code TESPy and the multiphase-multicomponent ECLIPSE reservoir simulator.

Study results indicate that nine vertical storage wells are required to provide the required target mass flow rates while limiting the bottom-hole pressure to the geomechanically safe range of 80 – 130 bars and achieving a stable air-water contact level. A sensitivity analysis shows that already three vertical or two horizontal wells with three open sections each can provide the required mass flow rates and thus power during withdrawal, while power mismatches of less

than 23%. Similarly, reducing the initial cushion gas volume by 60% would still provide the annual withdrawal rates, but limit the total injected volume. Thus, our study shows that one porous media CAES site can provide all required power and balance the expected offsets between energy demand and energy supply up to the GWh scale. Balancing of the energy system at the national level can be achieved by up-scaling of the results obtained in this study.

11. Thermal energy applications and associated processes in porous and fractured aquifers

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Investigation of thermal convection in a water saturated porous medium induced by heat exchangers in high temperature borehole thermal energy storage

Borehole thermal energy storage is a well-established technology for seasonal heat storage in geological subsurface used to regulate the seasonal disparities between heat production and supply. The stored heat originates from the surplus of solar thermal installations or industrial production. However, the application of high temperature-BTES of up 90°C in the subsurface characterised by highly permeable zones or intermediate layers may allow for thermally induced fluid migration, which reduces the amount of heat store at the vicinity of the BHE and thus decreases the thermal operationality of the BTES system. Here, we present results from experimental work and subsequent numerical modelling aimed at quantifying thermally induced convection for a lab-scale BHE in a water saturated porous medium for a temperature range of 20°C to 70°C.

The heat storage unit consists of a fully water saturated sand sediment and a vertical coaxial BHE of 0.0315 m outer radius located at the centre of the system. It is constructed in polypropylene barrel of 1.23 m height and 0.6 m radius. The sidewall barrel is cooled from the outside using ventilators and laboratory air. A grid of 68 thermocouples is emplaced in the storage medium for the monitoring of the transient internal temperature distribution during the experiments. For the static charging/discharging experiment, heat is transferred to the storage unit using a supply temperature of 70°C for 6 days, followed by 3 days of heat recovery. The dynamic experiment begins with 3 days stationary heating with 70°C followed by 6 cycles of 12 hours alternate heating of 70°C and cooling of ca. 19°C until the temperature distribution remains constant.

The static experiment reveals a vertical temperature stratification, with temperatures increasing up to 48°C towards the top of the porous medium. The radial temperature gradient along the

top of the sand is stronger whereas the lower part of the barrel and the outer wall remain at the laboratory temperature of approximately 18°C. This indicates a clearly tilted thermal front and confirms the dominant contribution of the convection to overall heat transport in the sand. Additional experiments carried out at 30°C, 50°C and 90°C shows a recognizable dominance of heat transport by density driven flow at temperature of 50°C.

The experimental observations are corroborated by the numerical simulations, which reproduce the spatial and temporal temperature distribution with good accuracy. The simulations results show that conduction heat process may be explained the measured data.

A model sensitivity analysis reveals the permeability as the most relevant parameter for studied heat transport processes, followed by grout and medium thermal conductivity.

12. Experimental and numerical investigation of the geomechanical integrity of host and barrier formations

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In the conducted research work, the effect of evolution of discontinuities on integrity and tightness of geological reservoirs under varying thermo-hydro-mechanical (THM) conditions is studied. With the increase in utilization of the geological barrier or host facilities, it is essential to understand the influence of macro- and micromechanical frack developments in rock formations' long term THM behavior. The developed discontinuities in host and barrier rocks, such as salt and clay rocks, are fluid migration pathways from deep to near-surface geological strata and ultimately into the Biosphere. Both experimental and numerical studies are conducted to better understand and capture the micro-meso scale material behavior.

A series of laboratory experiments are conducted on saltstone and Opalinus claystone geomaterials to determine the material's elastic stiffness, fracture toughness and splitting strength under different temperature and humidity boundary conditions. Additionally, the anisotropy of Opalinus Claystone formations and the effect of the orientation of embedded layering on material's THM behavior is studied. The outcomes of the lab results are used also as an input data for numerical simulations. The shrinkage and swelling of the Oplainus Claystone under the thermo-hydro condition is evaluated. To do so, different saturated salt solutions are placed in a closed desiccator with a controlled temperature. The drying and wetting paths of the samples resulted in surface deformations which were recorded using the strain gauges glued on the surface of the sample. Additionally, the fluid driven percolation tests are conducted on a cubic sample with a side dimension of 43 mm. A true triaxial apparatus is used to apply different principle stresses along the axis. The pressurized fluid then is injected into the pre-drilled centered borehole with a length of 20 and diameter of 8 mm. The results indicate the effect of the anisotropy and embedded layering on the direction of the fluid pathways. The outcomes of the experimental data support the further development of continuum-discontinuum hybrid numerical models.

The in-house developed coupled THM lattice element method (LEM) is used to further investigate the micro-meso scale material behavior. The developed lattice model is based on the generation of Voronoi cells and their connectivities using the Delaunay triangulation. The simulated domain is then represented with a series of beam or spring elements. The regularization of the LEM is conducted to ensure the mesh independency of the results. A frack is initiated or propagated when the stresses within a single lattice reach its pre-defined strength threshold. The implemented hydro model is based on the conservation of mass theory, where a dual lattice is used for the simulations. The conduit elements are used to transfer the fluid, where in each virtual cavity a pore pressure can build up when a defined cavity is fully saturated. The change of hydraulic aperture and developed pore pressure under the coupled hydro-mechanical conditions are calculated and eventually the change of materials' permeability and stiffness are simulated. The conducted experimental-numerical investigations for relevant time and dimension scales and considered case studies provided more reliable and more efficient realization of geotechnical applications.

13. A methodological approach to transfer complex geological models to TH numerical simulators for HT-ATES simulations within the Lower Muschelkalk in the subsurface of Berlin

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During summer, a large amount of waste heat e.g. from industrial processes is generally dissipated to the air. High temperature aquifer thermal energy storages (HT-ATES) is an promising technology to efficiently store this heat due to its high storage capacity and possible direct integration into existing local heating networks for ed.g. residential heating during winter in urban areas.

Storage capacity and efficiency of ATES systems strongly depend on the hydrogeological setting of the target reservoirs. Often simplified homogenous layer cake models are used to present these storage systems. The fluid pathways, however, are dispersed due to a natural open fracture network or heterogeneity of rock permeability and porosity. This, in turn will impact the efficiency and, consequently, the reliability of the corresponding ATES system.

In this study we present an effective numerical approach to transfer a complex fractured carbonate reservoir within the Lower Muschelkalk in the subsurface of Berlin to both a commercial (FEFLOW 7.4) and an open source (GOLEM) hydro-thermal simulator for HT-ATES simulations. In comparison to a homogenous aquifer system, first results from a fractured aquifer within the Lower Muschelkalk in Rüdersdorf/Berlin show a reduction of the storage efficiency of up to 10 %.

14. Nutzung geologischer 3D-Strukturmodelle zur Simulation von Wärmespeichern

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Ziel des Vorhabens ist es, ein hinreichend aufgelöstes 3D-Strukturmodell für den Standort des Pilotversuches von CONSULAQUA Hamburg zur Aquiferwärmespeicherung im Untergrund von Hamburg zu erstellen, das langfristig als Basis für numerische Szenariensimulationen eines untertägigen Wärmemanagements dienen kann. Das Modell soll mit standortspezifischen und literaturbasierten Daten parametrisiert und anhand epignostischer Simulation des Pilotversuchs und der am Standort gemessenen Veränderungen des Wärmehaushalts kalibriert werden. Anhand des kalibrierten Modells wird eine großskalige und langfristige Wärmespeicherung an diesem Standort, u.a. unter Berücksichtigung einer heterogenen Verteilung der Permeabilität und eine Analyse von thermalen Auswirkungs- und Monitoringräumen zur Einordnung von Wärmespeichern in eine untertägige Raumplanung mithilfe von Szenariensimulationen untersucht. Ebenso werden die Möglichkeiten und Grenzen der epi- und prognostischen Modellierung und somit die Methodik für eine großskalige Raumplanung des Untergrundes erprobt.

In Hamburg wurde über einen Zeitraum von 51 Tagen ein Pilotversuch zu einer Aquiferwärmespeicherung in den Oberen Braunkohlensanden mit einer Injektion von 60-80°C heißem Wasser in drei Zyklen durchgeführt (eine Dublette, Pumprate: 20m3/h, Temperatur am kalten Brunnen: 13,5°C, Grundwassergeschwindigkeit: 0,9 m/a, Speichermächtigkeit: 100 m, Permeabilität: 1.4×10-11 m²). In Zusammenarbeit mit Projektpartnern vom UFZ-Leipzig wurde ein neuer Workflow zur Überführung geologischer Strukturdaten aus SKUA-GOCAD in ein OGS6 finite-Elemente-Modell erarbeitet, mit dem der Pilotversuch mit nur geringen Abweichungen der Rückholtemperatur nachvollzogen werden konnte. Mithilfe dieses kalibrierten Modells wurden numerische Simulationen zur Prognose einer langfristigen und großskaligen Wärmespeicherung am Standort des Pilotversuchs durchgeführt, was eine Abschätzung der Dimensionierung des Speichers in realen geologischen Strukturen ermöglichte. Das Modell einer langfristigen und großskaligen Wärmespeicherung (vier

Dubletten, Pumprate: 100 m³/h, Beladungstemperatur: 80°C) zeigte für einen Speicherbetrieb im halbjährlichen Zyklus eine Steigerung der Wärmerückgewinnung von 81,5% in der ersten Rückgewinnungsphase auf 93,1% nach fünfzehn Jahren.

Die Auswirkung der räumlich heterogenen Verteilung der Permeabilität auf die thermische Rückgewinnung eines Aquiferwärmespeichers wurde anhand des Modells zu einer großskaligen und langfristigen Wärmespeicherung untersucht. Dafür wurde eine Methodik zur Erstellung eines Zufallsfeldes der Permeabilität für jede Unterschicht des Speicherhorizontes mithilfe eines Kovarianzmodells, Konvertierung zu einer lognormalen Verteilung und Integration dieser Zufallsfelder in das finite-Elemente-Modell erarbeitet. Die Szenariensimulationen unter Berücksichtigung einer heterogenen Verteilung der Permeabilität nach Borden-Geostatistik von Sudicky (1986) zeigten nach der ersten Rückgewinnungsphase eine durchschnittlich geringe Reduktion der Wärmerückgewinnung um 0,5% und eine max. Reduktion um 0,7% im Vergleich zum homogenen Ansatz.

Die Auswirkungen der häufig auf Literaturdaten basierten thermischen Parameter auf die Wärmerückgewinnung wurden ebenfalls anhand des Modells zu einer großskaligen und langfristigen Wärmespeicherung untersucht. Dafür wurde für den Speicherhorizont die Spanne der Wärmeleitfähigkeit (2,0-3,0 W/mK) und der spezifischen Wärmekapazität (2,3-2,8 MJ/(m3K)) nach VDI4640 Blatt 1 variiert. Die Variation der thermischen Parameter zeigte, dass die Auswirkungen der thermischen Eigenschaften auf die Wärmerückgewinnung gering sind (<1%), wobei der Speicherverlust durch Wärmeleitung im Wesentlichen von der Wärmeleitfähigkeit des Speichergesteins abhängig ist.

Damit haben, wie bereits aus einfachen Modellen zu erwarten war, die thermischen Parameter und eine heterogene Verteilung der Permeabilität nur einen vergleichsweise geringen Einfluss auf die Wärmerückgewinnung. Die Speichereffizienz hängt wie in der Studie zu Umweltwirkungen und umweltverträglicher Ausbau der oberflächennahen Geothermie im Auftrag des Umweltbundesamtes gezeigt wird, somit vor allem von grundlegenden System- und Betriebsparametern wie der Grundwasserfließgeschwindigkeit, der Pumprate und der Beladungstemperatur ab.

Mithilfe dieses Modells kann eine Abschätzung der Dimensionierung von Aquiferwärmespeichern durch Simulation von thermalen Auswirkungs- und Monitoringräumen erfolgen, welche eine Einordnung in eine untertägige Raumplanung

ermöglichen können. Damit ist die Modellierung von Wärmespeichern mit den verwendeten Methoden und Workflows jetzt auch in großskaligen und heterogenen Aquiferstrukturen möglich und kann auch an anderen Standorten eingesetzt werden. Die Entwicklung und während der Projektlaufzeit stetige Verbesserung dieser Methodik hin zu einer Anwendung für großskalige und heterogene Aquiferstrukturen ist somit auch ein wichtiger Baustein für weiterführende Projekte, wie z.B. die Reallabore IW3 und NDRL in Hamburg oder WiseUP.

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15.Numerical Modelling of a High Temperature Heat Injection Test

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With the transition of the heating sector towards renewable energy sources technologies are needed to compensate for the seasonal mismatch between heat supply and demand. Aquifer thermal energy storage (ATES) is considered a promising candidate for that purpose. Especially high temperature ATES (HT-ATES) with temperatures up to 90 °C has the advantage of higher storage capacities and allows for the direct use of the stored heat without intermediate heat pumps. In order to improve the understanding of processes induced by HT-ATES and to validate numerical tools for the prediction of storage capacities, storage rates as well as thermal impacts, a heat injection test (HIT) with an injection temperature of 75 °C was conducted, densely monitored and numerically simulated. This work presents the prediction of the thermal impacts based on parameter estimations from the field site investigation prior to the experiment. Furthermore, it is evaluated, whether different parameter assumptions would have resulted in better predictions and the parameter sensitivities are shown.

The heat injection test took place at a shallow aquifer with a low natural groundwater flow velocity of 0.07 m/d. Hot water was injected at a borehole using flow rates of 14 l/min for 4.5 days and the resulting thermal plume was monitored by a dense arrangement of thermocouples. Previous to the experiment, the field site was thoroughly investigated for the thermal and hydraulic parameters by standard hydrogeological methods, such as pumping tests, hydraulic head measurements, Hydraulic Profiling Tool (HTP) employment, liner sampling and laboratory measurements. A coupled heat transport and fluid flow model was set up and the heat injection test was simulated using high resolution numerical modeling of the coupled thermo-hydraulic processes using the OpenGeoSys (OGS) simulation code.

The comparison of measured and simulated temperature breakthrough curves showed a good correspondence, indicating the capability of the model to predict the general thermal behavior of the heat injection test. The accuracy was higher for larger distances to the injection well and at the longer time scale, while the largest deviations occurred close to the injection well and shortly after the injection. The model was then used to estimate the sensitivity of the simulated

temperature distribution on thermal and hydraulic aquifer parameters, which were varied according to the span of measurements. The evaluation of the model fit to the measured temperatures for the different parameter scenarios showed, that the initial parameter assumptions were almost ideal, which confirmed the suitability of the applied field investigation methods. The sensitivity analysis furthermore showed, that the thermal plume development is most sensitive on the horizontal and vertical hydraulic conductivity, since these parameters influence the intensity of buoyancy driven flow and were measured in large ranges. The sensitivity to the groundwater flow velocity, the heat capacity and the thermal conductivity is less pronounced, while the result is insensitive to the specific storage. It is shown, that a heat injection test in combination with numerical simulations is suitable for identifying parameter sensitivities also on small scales, thus showing the investigation needs for HT-ATES projects.

16. Real-time elementary analysis of waters using portable LIBS technology

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Water is analysed for its chemical composition to identify and quantify selected chemical components. Such chemical characterisation is generally achieved using laboratory-based techniques as well as portable, field test methods. Standard water testing procedures involve in-situ measurements of water quality parameters like pH, temperature, redox potential, specific electrical conductivity and hydrogen carbonate content in the field, because these hydrochemical properties may change upon sample transport and storage. Subsequently, collected water samples (acidified, sealed, cooled) are transported to a laboratory for further analyses using ion-exchange chromatography (IC), atomic absorption spectroscopy (AAS) and/or inductively coupled plasma mass spectrometry (ICP-MS) techniques. Such laboratory analyses are time-consuming and cost intensive and unfortunately sometimes impossible to achieve, especially if samples are taken in remote places and cooling cannot be ensured, preventing the necessary rapid analysis of collected materials. Consequently, there is an ever-increasing array of test strips, test kits and hand-held digital instruments for in-field measurements of inorganic constituents. Yet, many of these field test methods are characterised by low accuracies and relatively high costs, or these test formats are only capable of analysing selected elements and compounds (e.g. nitrate). To date, there is no portable field method that is capable of analysing water samples quantitatively for a range of elements simultaneously and in real-time.

The aim of this PhD thesis is to evaluate how water samples may be quantitively analysed for their chemical constituents, using portable LIBS (laser induced breakdown spectroscopy). LIBS is a spectroscopic method which has been used successfully in the laboratory for quantitative water analysis down to the ppt range. As portable LIBS devices have been developed in recent times, several new promising applications have emerged (e.g. analysis of solid samples for their lithium content in the field). Yet to date, there is no application of portable LIBS to water analysis, and best practice guidelines as well as standard operating procedures for water quality analysis using LIBS are missing.

In this study, the following research questions will be pursued: (1) A literature review will be conducted on laboratory-based LIBS water quality analyses. Such work will identify those elements that are best analysed with LIBS technology rather than using other analytical tools (e.g. pXRF). The data generated by previous works will be compared with results of this study. (2) A simple testing method for on-site, in-situ measurements of waters with portable LIBS (SciAps Z300) will be established. This includes the development of a special sample holder for in-field water analysis that will be applicable to a range of target element concentrations (0.1 to 1000 ppm). (3) The developed test protocol will be evaluated and validated on bottled mineral waters, thermal brines and mine waters. (4) Finally, best practice guidelines and standard operating procedures for portable LIBS analysis of water samples will be documented, detailing competencies, health and safety considerations as well as analytical procedures. It is expected that results of this research will add to the ever-increasing array of field-testing methods of waters in real-time.

17.Benchmarking Conventional and Machine Learning Segmentation Techniques for Analysis of Digital Rock Physics Properties

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Image segmentation remains the most critical step in Digital Rock Physics (DRP) workflows, affecting modelling results and the analysis of physical rock properties. Conventional segmentation techniques struggle with numerous image artefacts and user bias, which lead to considerable uncertainty. This study evaluates the advantages of the random forest algorithm, implemented in Ilastik, to DRP problems. Images of fractured samples were acquired by X-ray computer tomography and segmented by both conventional methods (thresholding, watershed), and machine learning approachs (random forest, convolutional neural network). Porosity, permeability, flow fields, and preferred flow paths were computed. For each fracture segmentation, two skeletonized 3D images were calculated providing information about the true aperture distribution and orientation variation. Mean mechanical aperture and roughness were obtained from these aperture data. Additionally, the uncertainty of the pixel classification segmentation was calculated. A comparison with conventional segmentation methods highlight the superior capabilities of the random forest approach, which does not even need excessive amounts of training data. Instead, these data can be provided by the user directly on the images, where a constant feedback with the output of Ilastik minimizes user bias. The program is resource saving and provides for high quality segmentations and uncertainty calculations as a quantitative measure for evaluating the output. For our rock samples, the machine learning segmentation was able to handle all artefacts and complexities without prior filtering. A comparison of the described methods highlights the importance of a high-quality segmentation if considerable variations in physical rock properties are to be considered.