miniRUEDI Symposium

21–23 November 2023

Eawag, Überlandstrasse 133, 8600 Dübendorf, Switzerland

Tuesday, 21 Nov 2023

9:00 – 9:30	Coffee and snacks
9:30 – 9:40	Welcome
9:40 – 10:00	Introduction
10:00 – 10:40	Presentations
10:40 – 11:10	Break
11:10 – 12:10	Presentations
12:10 – 14:00	Lunch at Eawag
14:00 – 15:00	Presentations
15:00 – 15:30	Break
15:30 – 16:30	Presentations

Wednesday, 22 Nov 2023

9:00 – 9:30	Coffee and snacks
9:30 – 10:30	Presentations
10:30 – 11:00	Break
11:00 – 12:00	Presentations
12:00 – 14:00	Lunch at Eawag
14:00 – 15:00	Presentations
15:00 – 15:30	Break
15:30 – 16:30	Presentations
18:00	Group dinner (open end)

Thursday, 23 Nov 2023

9:00 – 9:30	Coffee and snacks
9:30 – 10:30	Presentations
10:30 – 11:00	Break
11:00 – 11:40	Presentations
12:00 – 14:00	Lunch at Eawag
14:00 – 15:00	miniRUEDI hands-on, lab tour

21 Nov 2023, 10:00–10:40

Taking the miniRuedi to the (shaking) spa

presented by Sebastien Giroud

Eawag, Swiss Federal Institute of Aquatic Science and Technology

The relationship between seismic activity and dissolved gas concentrations in geological fluids remains a contentious issue and is hotly debated. Although some correlations between changes in gas composition and seismicity have been identified, these often rely on observations of occasional events rather than long-term time series. Due to the lack of systematic assessments, it is difficult and complex to establish a causal connection between changing gas dynamics and earthquakes [1].

Incorporating a custom-built heating box into the miniRuedi setup has introduced new possibilities for addressing this question [2]. The primary aim of this heating box is to provide an optimal analytical environment to the membrane module, allowing the miniRuedi to continuously monitor dissolved gases in (hot) thermal fluids. This enabled the deployment of the miniRuedi in a seismically active region of Switzerland, with the aim of investigating the potential link between gas dynamics in terrestrial fluids and active seismicity. There, the Lavey-les-Bains hot springs discharge geothermal fluids with temperatures ranging between 50 °C and 65 °C. The instrument recorded dissolved gas concentrations for over a year at high-frequency intervals of approx. 6 minutes, providing quasi-continuous measurements of He, Ar, Kr, N_2, O_2, H_2, CH_4, and CO_2 data. The extensive dataset (>200'000 gas measurements) represents a robust experimental basis to critically evaluate the possible causal link between gas evolution in geological fluids and seismicity.

1. Toutain et Baubron (1999), Tectonophysics, 304, 1-27
2. Giroud et al. (2023), Front. Water, Vol. 4

21 Nov 2023, 11:10–11:30

Joint use of ^{3}H/^{3}He apparent age and on-site helium analysis to identify groundwater flow dynamics and transport of PCE in an urban area

presented by Christian Moeck[1], Andrea Popp[1,2], Matthias S. Brennwald[1], Mario Schirmer[1,3,4], Rolf Kipfer[1,2]

1 Swiss Federal Insitute of Aquatic Science and Technology (Eawag), 2 Swiss Federal Insitute of Science and Technology (ETH), 3 University of Neuchâtel Switzerland, 4 Université Laval, Canada

For our urban study site in Northern Switzerland, we used stable water isotopes, chlorinated solvents, dissolved gas concentrations, and ^{3}H and tritiogenic ^{3}He concentrations to assess water flow paths and mixing between artificially infiltrated surface water and groundwater. Especially, the recent developments of portable field-operated gas equilibrium membrane inlet mass spectrometer (GE-MIMS) systems provide a unique opportunity to measure dissolved gas concentrations, such as ^{4}He with a high temporal resolution at relatively low costs. Although the GE-MIMS are not capable of providing apparent water ages, ^{4}He accumulation rates are often obtained from ^{3}H/^{3}He ages and it has been shown that non-atmospheric ^{4}He concentrations determined in the laboratory (e.g., by static (noble gas) mass spectrometry) and by field-based (GE-MIMS) methods closely agree. This agreement allowed us to establishing an inter-relationship between ^{3}H/^{3}He apparent water ages and the non-atmospheric ^{4}He excess (e.g., calibrating the ^{4}He excess in terms of residence time). We demonstrate that the 4He excess concentrations derived from the GE-MIMS system serve as an adequate proxy for the experimentally demanding laboratory-based analyses. We combined the obtained water ages with hydrochemical data, water isotopes (δ^{18}O and δ^2H), and PCE concentrations to understand water flow dynamics. Moreover, we explain the origin and spatial distribution of PCE contamination found at our study site with our multi-tracer approach.

21 Nov 2023, 11:30–11:50

In situ observation of helium and argon release during fluid-pressure-triggered rock deformation

presented by Clément Roques

University of Neuchatel, Switzerland

Temporal changes in groundwater chemistry can reveal information about the evolution of flow path connectivity during crustal deformation. Here, we report transient helium and argon concentration anomalies monitored during a series of hydraulic reservoir stimulation experiments measured with an in situ gas equilibrium membrane inlet mass spectrometer. Geodetic and seismic analyses revealed that the applied stimulation treatments led to the formation of new fractures (hydraulic fracturing) and the reactivation of natural fractures (hydraulic shearing), both of which remobilized (He, Ar)-enriched fluids trapped in the rock mass. Our results demonstrate that integrating geochemical information with geodetic and seismic data provides critical insights to understanding dynamic changes in fracture network connectivity during reservoir stimulation. The results of this study also shed light on the linkages between fluid migration, rock deformation and seismicity at the decameter scale.

21 Nov 2023, 11:50–12:10

Continuous Measurements of Radon and Other Dissolved Gas Species in Groundwater: A Crucial Step in Earthquake Precursor Research?

presented by Alexandra K. Lightfoot

Swiss Seismological Service (SED) at ETH Zurich, Switzerland

The ArtEmis project represents a new approach within the discipline of earthquake precursor research, focused on elucidating the relationship between radon (Rn) concentration fluctuations in groundwater and seismic events. The initial phase of the project entails measuring Rn concentrations at selected study sites by employing already available techniques, while in parallel developing a new Rn sensor, with increased sensitivity and at low-cost. In order to measure Rn concentrations at a high spatial resolution, further development and deployment of over 100 sensors is needed. Additional observables, such as groundwater temperature and acidity levels and other dissolved gas species will also be analysed. In preparation and to validate data to be obtained from the newly developed sensors, Rn analysis will be performed in advance and later in parallel utilising the currently available standard for analysing continuous Rn gas concentrations in groundwater (i.e., the Rad8). One location for pilot testing such continuous Rn analysis will be at the Bedretto tunnel and laboratory in Ticino, Switzerland, where groundwater channels are connected to existing fault lines. The Bedretto tunnel is located specifically around 1.5 km below the Swiss Alps, extending 5 km in length between Bedretto (Ticino) and the Furkapass in Switzerland. Due to its well-documented geological, seismotectonic and geochemical properties, and the fact that experiments on induced seismicity are conducted, the Bedretto site is ideal for real time monitoring of Rn concentrations. In addition to Rn, other dissolved noble and reactive gas species will simultaneously be analysed with a portable mass spectrometer, which is preceded by a gas permeable membrane-inlet system. Such initiatives are being pursued, given recent observations between seismic events and corresponding changes in dissolved noble and reactive gas concentration ratios in groundwater analysed in the Valais, Switzerland (Giroud, S. et al., 2022, doi: 10.46427/gold2022.8935).

21 Nov 2023, 14:00–14:20

Gas monitoring while Drilling the Ivrea-Verbano zonE (DIVE) with miniRUEDI

presented by Hugo Dutoit

ISTerre, France

MiniRUEDI is a versatile QMS allowing dissolved gas analysis with quick results directly on the field. However, with proper calibrations this mass spectrometer also enables in situ free gas analysis. In order to experiment long time running free gases measurement with the miniRUEDI, the latter was implemented to an On-Line Gas Analysis set up (OLGA) for mud-gas monitoring while drilling. The ICDP project "Drilling the Ivrea Verbano zonE (DIVE)" explores the Ivrea Verbano Zone in the Southern Alps of Italy, the probably most complete pre-Permian lower crust–upper mantle transition worldwide, by deep scientific drilling. A first borehole has been completed near the city of Ornavasso in mid-December 2022, reaching a final depth of 578.5 m, with excellent drill core recovery (100%). The drilling was accompanied by various scientific experiments, including the continuous extraction, measurement and sampling of gases from the circulating drilling fluid (OLGA). The gas phase was continuously measured with two quadrupole gas mass spectrometers (miniRUEDI © and Pfeiffer Omnistar ©) for Ar, H2, He, N2, O2, CH4 and CO2, a gas chromatograph for hydrocarbons (CH4, C2H6, C3H8 and i/n C4H10), and a radon detector for 222Rn. Initial results show a correlation between formation gases in drilling mud and the drilled fault and fracture zones. In addition to the unavoidable input of atmospheric gases in drilling mud, the most non-atmospheric gases extracted from drilling mud are hydrogen (up to 1.2 vol.-%) and methane (up to 0.3 vol.-%). Likewise, helium content was sometimes found to be higher than atmospheric. MiniRUEDI appeared to be a very efficient and robust tool facing the many issues occurring during the drilling period. Moreover, the obtained results were in good agreement with the initial OLGA set-up.

21 Nov 2023, 14:20–14:40

Results of gas measurements during a pump test in Cornwall

presented by Bettina Strauch and Martin Zimmer

GFZ Potsdam, Germany

Within the EU funded project "CRM geothermal", that aims to establish an overview of the potential of geothermal fluids for raw material extraction, a pump test was conducted at a drill site in Cornwall, UK to assess the composition of the produced geothermal liquid. The borehole was drilled in 2019 to 1100m depth by Cornish Lithium Company in United Downs, Cornwall, UK for lithium exploration. The well crosses two permeable structures at approximately 600 m and 1011 m where low-salinity geothermal waters are hosted in natural fractures of granite and a metamorphic aureole. The water has an elevated lithium concentration due to the dissolution of lithium-enriched minerals in the granite. During a test campaign in summer 2023, a production test was conducted from 19/06/2023 to 22/06/2023. Beside the dissolved ions, also the gas composition was monitored during pumping operation. The focus was here on Helium which is of economic importance and, in view of emerging digital applications, assumed to become critical (high demand, low availability). An elevated helium content in the produced gas was expected, as the host granite contains large amounts of radionuclides, such as Uranium and Thorium, that results in Helium production upon decay. The sampling campaign was accompanied by an online gas monitoring of the headspace gas using the MiniRuedi. Furthermore, the GMIMS was used for gas-water separation. In addition, experiments addressing the option of online-helium extraction using an alternative membrane-based gas extraction method, were performed. A conventional gas sampling for lab-based analyses was completed as well. The data showed up to 1 vol.% Helium and a good agreement between different extraction and measurement techniques. can be attested. The data evaluation is still ongoing and preliminary results will be presented.

22 Nov 2023, 14:40–15:00

Quantifying Carbon Cycling across the Groundwater-Stream-Atmosphere Continuum Using High-Resolution Time Series of Multiple Dissolved Gases

presented by Chuan Wang

Eawag, Swiss Federal Institute of Aquatic Science and Technology

The quantification of carbon cycling across the groundwater-stream-atmosphere continuum (GSAC) is crucial for understanding regional and global carbon cycling. However, this quantification remains challenging due to highly coupled carbon exchange and turnover in the GSAC. Here, we disentangled carbon cycling processes in a representative groundwater-stream-atmosphere transect by obtaining and numerically simulating high-resolution time series of dissolved He, Ar, Kr, O2, CO2, and CH4 concentrations. The results revealed that groundwater contributed ∼60% of CO2 and ∼30% of CH4 inputs to the stream, supporting stream CO2 and CH4 emissions to the atmosphere. Furthermore, diurnal variations in stream metabolism (-0.6 to 0.6 mol O2 m-2 day-1) induced pronounced carbonate precipitation during the day and dissolution at night. The significant diurnal variability of biogeochemical processes emphasizes the importance of high-resolution time series investigations of carbon dynamics. This study shows that dissolved gases are promising environmental tracers for discerning and quantifying carbon cycling across the GSAC with high spatiotemporal resolution. Our high-resolution carbon exchange and turnover quantification provides a processoriented and mechanistic understanding of carbon cycling across the GSAC.

21 Nov 2023, 15:30–15:50

Real time on-site gas analysis – a ballad of (noble) gases, arsenic, fracking and CO_2 sequestration

presented by Rolf Kipfer

Eawag, Swiss Federal Institute of Aquatic Science and Technology

Water and other terrestrial fluids crucially impact processes in the deep surface and in the environment, including some that have significant social implications: fracking, nuclear waste disposal, geological CO2 sequestration, natural gas and heat production.

However, our current understanding of (geological) fluid dynamics is rather limited as traditional techniques for gas analysis are time-consuming and involve the laborious analysis of very few samples in high-specialized laboratories. To conclude, available experimental methods fall short in tracking fluid dynamics in real time and under field conditions. To address these technical limitations that impede real-time gas analysis in environmental and geological systems in the last few years analytical methods were developed to quantify (noble) gas concentrations in terrestrial fluids under real-world conditions [1]. Our second-generation self-contained and portable mass spectrometer [2] can be operated in the field permitting the quasi-continuous quantification of He, Ne, Ar, Kr, N2, O2, CH4, CO2 and H2 at high temporal resolution (seconds (gases) - minutes (liquids)). Recent tailored technical adjustments empower the instrument to be operated even under harsh conditions such as high temperatures and high water vapor pressures [3] and enable for targeted sampling of rare species for later laboratory analysis.

Our contribution discusses results of on-site gas measurements identifying gas production to modulate geogenic Arsenic mobilization [4] and allowing the fluid migration to be investigated during fracking and experiments targeting CO2 sequestration and geothermal heat [5].

1. ES&T 2012, 46, 8288-8296; ES&T 2016, 50, 13455-13463; ES&T 2017, 51, 846-854
2. www.gasometrix.com
3. Front. Water 4, 1032094
4. Water Res. 214, 118199
5. Sci. Rep. 2020, 10, 6949

21 Nov 2023, 15:50–16:10

Long term monitoring of noble gas and water isotope tracers in a localised MAR scheme to assess recharge and regional groundwater mixing dynamics

presented by Jared van Rooyen

Eawag, Swiss Federal Institute of Aquatic Science and Technology

Managed aquifer recharge (MAR) has become increasingly popular in Central Europe as a sustainable, clean, and efficient method for managing domestic water supply. In these schemes, river water is artificially infiltrated into shallow aquifers for storage and natural purification of domestic water supply, while the resulting groundwater mound can simultaneously be designed such that it suppresses inflow of regional groundwater from contaminated areas. MAR schemes are typically not managed based on automated optimization algorithms, especially in complex urban and geological settings. However, such automated managing procedures are critical to guarantee safe drinking water. With (seasonal) water scarcity predicted to increase in Central Europe, improving the efficiency of MAR schemes will contribute to achieving several of the UN SDGs and EU agendas. Physico-chemical and isotope data has been collected over the last 3-4 decades around Switzerland's largest MAR scheme in Basel, Switzerland, where 100 km3/d of Rhine river water are infiltrated and 40 km3/d are extracted for drinking water. The other 60 km3/d are used to maintain the groundwater mound that keeps locally contaminated groundwater from industrial heritage sites out of the drinking water. The hydrochemical/isotope data from past and ongoing studies were consolidated to contextualize all the contributing water sources of the scheme before online noble gas and regular tritium monitoring commenced in the region. The historical and the new continuous tracer monitoring data is now used to inform new sampling protocols and create tracer enabled/assimilated groundwater-surface water flow models, vastly helping algorithm-supported MAR optimization.

21 Nov 2023, 16:10–16:30

Demonstration of Solexperts high-pressure membrane module coupled to miniRUEDI

presented by Jocelyn Gisiger

Solexperts, Switzerland

Demonstration of a new membrane module for dissolved-gas analysis with the miniRUEDI in fluids at high pressure.

22 Nov 2023, 9:30–9:50

Measuring diffusion of gas in partly saturated clay

presented by Elke Jacops

SCK CEN, Belgium

Within a deep geological repository (DGR) for nuclear waste, generation of gas is unavoidable. The main, initial transport mechanism is diffusion as dissolved species. In order to calculate a correct balance between gas generation and gas dissipation by diffusion, accurate knowledge of gas diffusion coefficients is essential. Currently, a large database is available for diffusion coefficients of different gases and different clay-based materials – but all tested samples were fully saturated. As desaturation of engineered barriers and host rock can occur in a DGR, diffusion has to be studied also under unsaturated conditions. Therefore, SCK CEN developed a new set-up and methodology to study diffusion of gases in unsaturated clay-based materials. The concept uses the double through-diffusion technique, with 2 gases diffusing in counter directions. In order to allow only diffusive transport, gas pressure is equal at both sides. The diffusion coefficient is calculated from the concentration increase of each gas in its downstream compartment. As the gas volume is limited, the amount of gas, used for sample analysis should be as small as possible. The most suitable analyser to measure the gas composition in the set-up is Mini-Ruedi. Initial experiments were performed using He and CH4 at one side, and Xe and C2H6 at the other side. Because of peak interference between CH4 and C2H6 and the extreme prices for Xe, it was decided to switch to He and Ar for the rest of the experimental matrix. The m/z ratios of 4 and 40 were obtained from the scans and used as base peaks for the measurement of helium and argon respectively. The standards used were of the composition 0.1% (or 1000 ppm) He/Ar in 99.9% Ar/He. Since the peak intensity from the argon peak is quite small relative to the helium peak in a standard gas of 99.9% Helium and 0.1% Argon and no other detectable peak in the spectrum was identified from the scans, the M detector was used for the tuning of the m/z scale. The base peaks have been used for all quantification and tuning. This method has proven to be quite efficient as the errors estimated from the sample gases are often under the 5% margin from the analyses done so far.

22 Nov 2023, 9:50–10:10

miniRUEDI as handy tool for onsite monitoring of gas injection tests in the frame of GAST experiment

presented by Yama Tomonaga[1], Emiliano Stopelli[2], Jocelyn Gisiger[3], Bill Lanyon [4]and Thomas Spillmann[2]

1: Entracers GmbH, Switzerland, 2: Nagra, Switzerland, 3: Solexperts AG, Switzerland, 4: Fracture Systems Ltd, United Kingdom

In radioactive waste repositories gas generation is expected from the degradation of organic substances and metal components. To manage gas generation while ensuring the containment of radionuclides, concepts for gas-permeable plugs and seals have been developed.

The Gas permeable Seal Test (GAST) at Grimsel Test Site is an international project (ANDRA, NAGRA, NWMO, NWS) aimed at demonstrating the feasibility and functionality of a gas-permeable seal made of a sand/bentonite mixture, at 1:1 scale and realistic boundary conditions. After progressive seal saturation, gas injection tests were conducted between May 2022 and August 2023, using noble gases as tracers of gas transport through the seal section of the experiment. The miniRUEDI portable mass spectrometer system has been shown to be a very versatile and reliable instrument for the mid- to long-term assessment of gas dynamics both in engineered and natural environments. Thus, it was deployed onsite at the GAST experiment to:

- detect any potential gas leaks from the experimental set-up
- qualitatively monitor the changes in gas composition at the outflow line of the experiment, via coupling with a semi-permeable membrane module
- allow real-time support for the operational decisions throughout all gas injections phases
- be compared for quality check with off-site analyses (e.g., to infer equipment biases)

In this contribution we present and discuss observations related to the first phase of GAST experiment using a 2% He-spiked N_2 gas.

22 Nov 2023, 10:10–10:30

Application of noble gases to urnaium deposite sites and net-zero

presented by Ye Ji Kim

University, Republic of Korea

Isolation of spent nuclear fuel (SNF) disposed underground from people and the environment is crucial. Even in the cases where the nuclide species escape through the engineering barriers, these have to be slowly transported through the natural barrier for over 10 million years until they decay to low hazardous materials. Hence, understanding whether geological structure can adequately control the movement of nuclides and what changes occur in the migration processes are crucial. These kinds of long-term observations and analyses can be conducted by analyzing cases that have been in progress for a long time. Therefore, this project aims to establish the basis for natural analogue research by securing a uranium mineral research site in Korea. Along with this project goal, one of our goals is to characterize the transport of uranium (U) and its daughter product, helium (He), within the groundwater of our study site, Boeun. Samples from the dry season and wet season were each collected with copper tubes and the miniREUDI respectively. Dry season samples showed radiogenic 4He at a depth of 80 m, which coincided with the natural gamma ray peak at this depth. Whereas for the wet season samples, while argon (Ar) showed similar trends to the dry season, He showed hardly any variation between the wells. Summer samples were also characteristic of varying tritium values, while carbon-14 values were consistent. In addition to the aforementioned individual sampling campaigns, an event of continuous extraction of groundwater with the analyzation of helium and other parameters (O2, CO2, CH4) that are related to the mobilization of uranium, is anticipated to provide a wider understanding of the transport relation between uranium and helium.

22 Nov 2023, 11:00–11:20

The search for microbial activity

presented by Anneleen Vanleeuw

SCK CEN, Belgium

Safe geological disposal of radioactive waste necessitates understanding the geochemical dynamics and microbial activities that show an interplay with these dynamics. A seven-year in situ monitoring study on Boom Clay pore water revealed significant fluctuations in dissolved CO2 concentrations, in combination with a progressive increase in dissolved methane concentrations over time. The latter phenomenon was observed in correlation with increasing pH levels. The empirical finding of the rising methane concentrations complicates the further development of geochemical models for Boom Clay pore water, thereby underscoring the need for a better understanding of contributing factors that influence pore water composition, including microbial activities such as methanogenesis. The bentonite buffer of the multi-barrier concept is expected to play an important role in precluding microbial activity for the purpose of limiting any negative microbial impact on corrosion rates. Not only the underlying mechanism constraining microbial activity in high density bentonite but also to what extend microbial activity in such high density bentonite can affect corrosion remains unclear. Therefore, an oedometer based experimental setup developed at SCK CEN was used to study microbial corrosion of carbon steel at a bentonite dry density of 1.6 g/cm^3. Bentonite powder (MX-80) was added to the oedometers and 4 carbon steel coupons were placed in the MX-80 such that all coupons were completely covered with bentonite. Afterwards, the oedometers were closed and percolation was initiated with sterile synthetic Opalinus Clay water with or without 1.5 bar of a H2:CO2 (80:20 v/v) mixture. After full saturation, water and gasses are being collected and monitored for their microbial and chemical composition As the presence and concentration of gas is a very important indicator for several microbial processes, accurate analysis of the CO2, CH4 and H2 concentration in the gas phase is essential. Given its low detection limits, small gas volume consumption and the possibility for in-line analysis, Mini-Ruedi is considered to be an appropriate solution for the gas analysis in microbial experiments.

22 Nov 2023, 11:20–11:40

Tracing and quantifying microbes in riverbank filtration sites combining online flow cytometry and noble gas analysis

presented by Friederike Currle

University of Basel, Switzerland

Understanding microbial transport in surface water – groundwater systems is crucial for drinking water management. Particularly in the context of climate change, the quality of groundwater pumped near streams might be affected by high microbial loads after heavy rain, peak flow and spring snowmelt events. Dissolved noble gases have been shown to be conservative tracers and provide information on pathways and travel times of groundwater. Although it is known that due to size exclusion, microbes appear to travel faster than solutes, most hydrological tracer methods target groundwater movement and solute transport, while specific tracers for microbial transport are not yet considered for protection zone delineation of drinking water supply wells. Recently, online flow cytometry (FCM) has been shown to be a promising tool to track on site, continuously and in near-real time the movement of microbes in riverbank filtration settings (Besmer et al., 2016). Beyond direct cell counting, advanced computational tools enable to extract automatically relevant features from the multivariate FCM data describing the phenotypic diversity of the microbial community.

Aiming to understand microbial transport behavior in surface water – groundwater systems and develop tracer methods to track their movement, we combined online FCM with online (noble) gas analysis at a riverbank filtration site in the Emme valley, Switzerland (Schilling et al., 2022). Dissolved gas concentrations and microbial community patterns (measured using the gas equilibrium-membrane inlet portable mass spectrometer miniRUEDI (Brennwald et al. (2016), Gasometrix GmbH), the electronic radon detector Rad7 (DURRIDGE), and the online flow cytometer BactoSense (bNovate Technologies SA)) were monitored continuously over a period of several months of river restoration activity inside the river, a piezometer next to the river, and nearby riverbank filtration wells. Systematic changes in the microbial and dissolved gas patterns could be observed in reaction to a 2-year peak flow event, river restoration activities, and spring snowmelt events.

In summary, this combination of state-of-the-art analytical techniques allows to track and quantify microbial pathways from surface water into and through an alluvial aquifer. Furthermore, the setup increases understanding of reactive microbial transport compared to the transport of conservative dissolved gases and, highlights the potential of environmental DNA as a hydrological tracer technique.

21 Nov 2023, 11:40–12:00

Exploring the Potential of On-Site Gas Analysis in Aquatic Systems

presented by David C. Finger

Reykjavik University, Iceland

The study of aquatic ecosystems plays a pivotal role in understanding and mitigating the impacts of environmental changes on water quality, biodiversity, and ecosystem health. The application of on-site gas analysis techniques provide a more profound insights into the dynamic biogeochemical processes that govern aquatic environments. Icelandic hydropower reservoirs are fed by millennial old glacial melt water that has a preindustrial CO2 content. When the carbon dioxide (CO2) concentration in the water of hydropower reservoirs is lower than in the atmosphere, CO2 uptake can occur. The lower CO2 concentration in the reservoir water compared to the atmosphere can lead to the dissolution of CO2 from the air into the water.

Geothermal energy production produces emissions of Carbon Dioxide (CO2), Sulfur Compounds (H2S), Volatile Organic Compounds (VOCs), Hydrogen and Methane (CH4), to name the most important ones. The assessment of emissions and monitoring is essential to reduce GHG emissions and identify the potential for a circular use of these natural emissions [1]. On-site gas analysis plays a crucial role in identifying the origin of runoff water from glaciers, snow, and rain by examining the isotopic composition of gases dissolved in the water. The isotopic Signatures can reveal the ratio of snow-, ice and rain runoff, helping hydropower operators manage water resources and adapt to climate change [2]. This presentation will conclude with a call for international research cooperation on on-Site Gas Analysis in Aquatic Systems in Iceland.

1. Finger, D.C., Saevarsdottir, G., Svavarsson, H.G. et al. (2021) Improved Value Generation from Residual Resources in Iceland: the First Step Towards a Circular Economy. Circ.Econ.Sust. 1, 525–543. DOI 10.1007/s43615-021-00010-7

2. Finger, D., Hugentobler, A., Huss, M., Voinesco, A., Wernli, H., Fischer, D., Weber, E., Jeannin, P.-Y., Kauzlaric, M., Wirz, A., Vennemann, T., Hüsler, F., Schädler, B., and Weingartner, R. (2013) Identification of glacial meltwater runoff in a karstic environment and its implication for present and future water availability, Hydrol. Earth Syst. Sci., 17, 3261–3277, DOI 10.5194/hess-17-3261-2013

22 Nov 2023, 14:00–14:20

Quantifying Groundwater Recharge Dynamics and Unsaturated Zone Processes in Snow-Dominated Catchments via On-Site Dissolved (Noble) Gas Analysis

presented by Schilling, O.S.[1,2,3], Parajuli, A.[3], Tremblay Otis, C.[4], Müller, T.U.[3], Antolinez Quijano, W.[3], Tremblay Y.[3], Brennwald, M.S.[2], Nadeau D.F.[3], Jutras, S.[3], Kipfer, R.[2], Therrien, R.[3]

1 University of Basel, Switzerland, 2 Swiss Federal Institute of Aquatic Science and Technology (Eawag), 3 Universite Laval, Canada, 4 Universite de Neuchatel, Switzerland

Snowmelt contributes a significant fraction of groundwater recharge in snow-dominated regions, making its accurate quantification crucial for sustainable water resources management. While several components of the hydrological cycle can be measured directly, catchment-scale recharge can only be quantified indirectly. Stable water isotopes are often used as tracers to estimate snowmelt recharge, even though estimates based on stable water isotopes are biased due to the large variations of δ^2H and δ^{18}O in snow and the difficulty to measure snowmelt directly. To overcome this gap, a new tracer method based on on-site measurements of dissolved He, ^{40}Ar, ^{84}Kr, N_2, O_2, and CO_2 is presented. The new method was developed alongside classical tracer methods (stable water isotopes, ^{222}Rn, ^{3}H/^{3}He) in a highly instrumented boreal catchment. By revealing (noble gas) recharge temperatures and excess air, dissolved gases allow (i) the contribution of snowmelt to recharge, (ii) the temporal recharge dynamics, and (iii) the primary recharge pathways to be identified. In contrast to stable water isotopes, which produced highly inconsistent snowmelt recharge estimates for the experimental catchment, dissolved gases produced consistent estimates even when the temperature of snowmelt during recharge was not precisely known. As dissolved gases are not controlled by the same processes as stable water isotopes, they are not prone to the same biases and represent a highly complementary tracer method for the quantification of snowmelt recharge dynamics in snow-dominated regions. Furthermore, an observed systematic depletion of N_2 in groundwater provides new evidence for the pathways of biological N-fixation in boreal forest soils.

22 Nov 2023, 14:20–14:40

River rafting with the miniRUEDI

presented by Connor P. Newman[1], Eric C Humphrey[1], Matthias S Brennwald[2], W. Payton Gardner[3], Kelli M Palko[1] and Michael N Gooseff[4]

1: U.S. Geological Survey, 2: Eawag, Swiss Federal Institute of Aquatic Science and Technology, 3: University of Montana USA, 4: University of Colorado USA

Saline geothermal systems in the western United States are major sources of solutes that negatively affect downstream water use. Discharge from these systems is commonly manifested as both discrete springs and diffuse outfow along the riverbed. Discrete discharges may be quantified using physical measurements, but large diffuse discharges are difficult to quantify. To quantify total discharge from several large saline geothermal systems in the Upper Colorado River Basin high-resolution noble gas measurements were made from a boat-mounted portable gas equilibrium membrane-inlet mass spectrometer (miniRUEDI) in two locations in the western United States: the Colorado River near Glenwood Canyon and the Virgin River near Pah Tempe springs. Geothermal discharge in both locations has distinctive noble gas signatures, with He concentrations in springs enriched three orders of magnitude above atmospheric equilibrium (about 10^{-5} ccSTP/g). We hypothesize that the enriched He concentrations of discrete (springs) and diffuse (riverbed) discharge from these systems will have an influence on the noble gas composition of river water, allowing for the total geothermal discharge in each location to be quantified by helium mass balance. Continuous noble gas measurements also allow for direct estimation of the air/water He gas transfer rate), which commonly requires time-consuming gas injections. Results from the Glenwood Canyon area indicate that He concentrations in the river undergo an order of magnitude increase (to about 10^{-7} ccSTP/g). Elevated helium concentrations in the river extend kilometers downstream from mapped inflows and indicate substantial diffuse inflows or slow degassing of geothermal He. Mass balance modeling accounting for helium inflow and degassing indicates a total geothermal discharge of 425 to 850 L/s, compared to a previous estimate of 300 L/s from discrete springs. Results from the Pah Tempe area indicate He concentration in the river enriched two orders of magnitude above atmospheric equilibrium (up to about 10^{-6} ccSTP/g). Geothermal discharge to the Virgin River in this reach is estimated at approximately 250 L/s, similar to the flux measured by differential gaging. Data allow for estimation of the He gas transfer rate in the Colorado River (40 m/d) and Virgin River (80 m/d), illustrating the utility of the high-resolution measurements in quantifying this important parameter.

22 Nov 2023, 14:40–15:00

Gases as artificial tracers to study SW-GW interactions

presented by Théo Blanc

University of Neuchatel, Switzerland, and Eawag, Swiss Federal Institute of Aquatic Science and Technology

Understanding the interaction between groundwater (GW) and surface water (SW) is crucial for effective drinking water management and the well-being of ecosystems. However, comprehending these interactions can be quite challenging due to the subsurface heterogeneity, which causes preferential groundwater flow. Tracers are commonly used to study GW-SW interactions. Traditional artificial tracers like dyes are difficult to handle. Moreover, the coloring of rivers may cause negative public perception. Recent advances in portable mass spectrometry facilitate their direct and continuous measurement in the field [1], enabling their operational use in GW [2]. Nevertheless, there are technical and economic barriers that hinder the routine application of gas tracers for studying SW-GW interactions, particularly the substantial volumes of gas (especially noble gases) required for injection into rivers, which can be cost-prohibitive.

We present a cost-effective method for diffusive gas injection into rivers using easily available materials. We tested our approach with the noble gas helium (He) in a pre-alpine river connected to an alluvial aquifer (Emmental, Switzerland). We present a cost-effective method for diffusive gas injection into rivers using easily available materials. We tested our approach with the noble gas helium (He) in a pre-alpine river connected to an alluvial aquifer (Emmental, Switzerland). Gas injection was sustained for 35 days and oversaturated the river water with He by one order of magnitude compared to natural conditions. Dissolved gas concentrations (He, O2, N2, Ar, and Kr) were monitored in the river, a drinking water well, and several piezometers Gas measurements provided quantitative information on connectivity and river infiltration dynamics. The results demonstrated a direct hydraulic connection between the infiltrating river and the drinking water well. Moreover, results from a pulse gas tracer test, conducted by injecting Krypton directly into the aquifer, highlighted the existence of preferential groundwater flow paths in the aquifer, with measured groundwater velocities above 3 mm/s (13 m/h).

[1] ES&T, 2016, 50, 13455-13463; ES&T, 2017, 51, 846-854; [2] Front. Water, 2022, 4, 925294.

22 Nov 2023, 15:30–15:50

Using (noble) gases as tracers to assess hydrology and gas dynamics in trees

presented by Capucine Marion

Eawag, Swiss Federal Institute of Aquatic Science and Technology

Plants are a major control of the water exchange between the geosphere and the atmosphere. Despite the fact that plants annually transpire within a factor of 5 as much water as rivers discharge to the ocean, fluid and gas transport and other (tracer) hydrological aspects in plants are barely known. As roots take up water and gases from the soil and transport the fluids upward in the xylem, the supersaturation of dissolved atmospheric (noble) gases in soil and groundwater (excess air) might be used as a natural tracer to study the dynamics of water and gases in trees. By modifying techniques to determine (noble) gases in porous media we are developing an experimental method for real-time, in-situ and in-vivo analysis of dissolved gases in tree sap. The technique allows to continuously track fluid dynamics from the soil, through trees and other plants, into the atmosphere. Semipermeable membrane probes were installed in the soil and at different heights in the stem of a small fir tree to sample the dissolved gases in the soil and in the xylem sap. Each probe was connected to a portable mass spectrometer (miniRUEDI) to analyze He, Ar, Kr, N2, O2, CO2, CH4 over weeks. Even the current experimental set up is not yet optimal we observed modulations in CO2 (and O2) abundance in response to plant-physiological processes within the tree. We also carried out artificial tracer experiments by watering the tree with He or Ar labelled water enabling to monitor the water uptake and transport in the tree. In our contribution we will discuss these experiments and the potential of the developed methodology as new analytical tool assess the mutual relation between fluid dynamics and physiological processes in plants (e.g., drought induced cavitation in the vascular system).

22 Nov 2023, 15:50–16:10

Analyse of discrete (ground)water dissolved gases samples using the miniRUEDI: The tricks of a simplified protocol and tests for passive gas samplers

presented by Antoine Picard, Matéo Lacheux, Christin Müller, Florent Barbecot, and José Corcho

UQAM-Geotop, Montreal, Canada

While the miniRUEDI is widely used for continuous measurements, some projects in our laboratory imply to measure gases in discrete samples. To test the feasibility of such measurements, an in-house made system was built to connect the miniRUEDI to stainless steel tubes of determined volumes. Numerous protocols and tests have been performed to enhance a methodology for the analysis of such finite-volume samples such as long-term analyses, short-term analyses, and signal integration as well as diffusion effects within the miniRUEDI line system, filament lightning duration and gas leaks testing. The final protocol allows for a precise simultaneous determination of gases concentration (typically: He, N2, O2, Ar and Kr) within two hours of analysis. This new discrete measurement protocol has been tested on gas tracing experiment and for passive samplers equilibrated with atmosphere and surface water. The results are very promising as the practical implication of this work is to give a simple access to discrete sampling analyses of noble gases. Then, scientific projects such as groundwater influx quantification to rivers, investigation of vertical stratification in boreholes/aquifers/lakes, mapping of artificial tracing experiments, excess air, degassing and groundwater dating will find a great support from the miniRUEDI community.

22 Nov 2023, 16:10–16:30

Presenting the Omnistar

presented by Edith Engelhardt and Emma Fiedler

Institute of Environmental Physics, University Heidelberg, Germany

We present data from gas measurements in air and water conducted with the Omnistar, a commercially available mobile mass spectrometer by Pfeiffer Vacuum. Over the years, several MiniRuedi-inspired changes and improvements were made to the system by our group to make the Omnistar available for measurements in water as a GE-MIMS and to reduce fractionation processes. We would be happy to discuss potential and limitations of the Omnistar and receive input for improvements from more experienced GE-MIMS users.

23 Nov 2023, 9:30–9:50

Online monitoring to shed light on mixing dynamics in the aquifers of Mt. Fuji (Japan)

presented by Stephanie Musy

University of Basel, Switzerland

Mt. Fuji is the iconic centerpiece of a large, tectonically active volcanic watershed (100 km2) which plays a vital role in supplying safe drinking water to millions of people through groundwater and numerous freshwater springs. Situated at the top of the sole known continental triple-trench junction, the Fuji watershed experiences significant tectonic instability and pictures complex geology. Recently, the conventional understanding of Mt. Fuji catchment being a conceptually simple, laminar groundwater flow system with three isolated aquifers was challenged: the combined use of noble gases, vanadium, and microbial eDNA as measured in different waters around Fuji revealed the presence of substantial deep groundwater water upwelling along Japan's tectonically most active fault system, the Fujikawa Kako Fault Zone (FKFZ) [1].

These findings call for even deeper investigations of the hydrogeology and the mixing dynamics within large-scale volcanic watersheds, which are typically characterized by complex geologies and extensive networks of fractures and faults. In our current study, we approach these questions by integrating existing and emerging methodologies, such as continuous monitoring of dissolved gases (GE-MIMS; e.g. [2]) and microbes [3], combined with discrete samplings of eDNA, trace elements, and environmental isotopes. The continuous monitoring is installed in a 100-m-deep pumping well hitting directly the FKFZ, where other tracers revealed a mixing between deep He-rich groundwater with freshly infiltrated water. The results are used to assess the response of the system to seismic activity and hydraulic forcings in the area.

References:

1. Schilling et al., 2023, Nat. Water, 1:60-73. DOI: 10.1038/s44221-022-00001-4
2. Giroud et al., 2023, Front. Water, 4:1032094. DOI: 10.3389/frwa.2022.1032094
3. Besmer et al., 2016, Sci. Rep., 6:38462. DOI: 10.1038/srep38462

23 Nov 2023, 9:50–10:10

Monitoring a fault reactivation experiment with the miniruedi: results from the FSC experiment at the Mont Terri Rock Laboratory

presented by Antonio P. Rinaldi

Swiss Seismological Service, ETH Zurich

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23 Nov 2023, 10:10–10:30

On-site measurement of excess N2 "under pressure"

presented by Jens Gröger-Trampe

State Authority for Mining, Energy and Geology (LBEG), Germany

Nitrate pollution of aquifers in several parts of Germany is a matter of rising concern. Recent changes to the German Groundwater Ordinance therefore require all federal German states to provide data to quantify denitrification in relevant aquifers by the end of 2025, additionally to nitrate concentrations. The method of choice is the calculation of excess N2 from N2/Ar-measurements. To address potential analytical issues, the State Authority for Mining, Energy and Geology (LBEG) and the Lower Saxony Water Management, Coastal Defence and Nature Conservation Agency (NLWKN) are regularly hosting the nationwide interlaboratory tests for N2/Ar-measurements of groundwater. To assure data quality and to assess a variety of effects, LBEG developed a quality control tool (N2ArCheck, unreleased beta version).

miniRUEDI measurements are used in this context to address several aspects: The on-site measurement is an independent method for comparison with lab data, helps to get a more precise picture of excess air formation than measurements of solely N2 and Ar and is used to evaluate degassing effects. While measurements at several sites are in good agreement with lab data, tests on other sites show some issues. Some of these on-site measurements reveal major gas losses compared to lab measurements. This effect occurs at groundwater wells with elevated concentrations of dissolved gasses (total dissolved gas pressure (TDGP) up to 1.5 atm). Thus, a series of tests was set up to address this problem and explore the limits of miniRUEDI measurements in groundwater wells with elevated TDGPs.

23 Nov 2023, 11:00–11:20

Development of an Equilibrator-Inlet Mass Spectrometer (EIMS) for continuous N2, O2 and Ar measurements to quantify nitrogen fixation in the Baltic Sea

presented by Sören Iwe

Leibniz-Institute for Baltic Sea research (IOW) Warnemünde, Germany

The contribution of nitrogen fixation by cyanobacteria to the N budget of the Baltic Sea equals the total sum of DIN input from riverine and airborne sources, varying between 300 kt-N/yr and 800 kt-N/yr. The vast range is due to interannual fluctuations and significant uncertainties in the various techniques used to determine N2 fixation and in extrapolating local study to entire basins. To overcome some of the limitations, we introduce a new approach based on large-scale records of surface water N2 depletion during summer.

To determine the concentration of N2 in surface water, a membrane contactor (Liquicel) is utilized to establish gas phase equilibrium for atmospheric gases dissolved in seawater. The mole fractions for N2, O2 and Ar in the gas phase are determined by mass spectrometry and yield the concentration of these gases by multiplication with the total pressure and the respective solubility constants.

After thorough laboratory tests concerning the precision and accuracy, the measurement system, an Equilibrator-Inlet Mass Spectrometer (EIMS), was deployed on a voluntary observing ship (VOS, "Finnmaid") during June/July of summer 2023. By conducting repeated transects 2-3 times per week over a distance of approximately 1000 km between the Mecklenburg Bight and the Gulf of Finland, the results offer a high-resolution time series of N2 concentration changes induced by nitrogen fixation. Additionally, Ar measurements are used to account for the air-sea N2 gas exchange. Furthermore, the biological oxygen saturation $\Delta O2/Ar$ can be utilized to characterize the production phase.

In connection with these measurements, further investigations of nitrogen fixation and its vertical distribution were undertaken during a research cruise with a similar measurement setup. The initial results appear promising, though a final analysis and evaluation of the data is still pending. Our objectives are to identify various factors that initiate and potentially limit the growth of cyanobacteria.

23 Nov 2023, 11:20–11:40

Relative partial pressures in seawater of nitrogen, oxygen and argon; MiniRUEDI measurements in support of in-situ open ocean primary production and CO_2 flux determinations

presented by Hans A. Slagter[1], Maria Ll. Calleja[1,2], Hedy M. Aardema[1,3], Ralf Schiebel[1], Antonis Dragoneas[1], Lena Heins[1], Isabella Hrabe de Angelis[1], Gerald Haug[1,3]

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Marine primary production and microbial respiration are cornerstone global processes and integral to our understanding of climate and biogeochemical cycling. Despite long-time recognition, there remains a paucity of high temporal and spatial resolution data for both the elucidation and decoupling of seasonal and latitudinal variability. Modern approaches such as the collection of high-throughput data from miniaturised instrumentation allow for applications of such measurements in novel platforms. To this end, net community production, that is the debit of gross production and respiration, is derived from and studied in relation to a multitude of properties measured on the blue water research sailing yacht Eugen Seibold. The ratio between oxygen and argon in particular, derived from a miniRUEDI GE-MIMS and set-up in combination with pCO2 data and microbial community standing stock information, helps to inform carbon cycling. In addition, nitrogen cycling processes may be further informed by the same set-up. The miniRUEDI instrument on S/Y Eugen Seibold measures from a GE membrane integrated in our FerryBox system, which continually samples from a keel inlet at a depth of 3.2 m. Here we present our implementation and preliminary results along a North-South transect in the Atlantic Ocean, stretching from the polar circle to the equator roughly along the 20° W meridian, collected during expeditions in 2020 and 2021. This transect crosses from the mesotrophic high North Atlantic into the oligotrophic subtropical Atlantic, crossing several areas of nutrient upwelling. Transects crossing the Atlantic into the Pacific extend this data going forward.