

miniRUEDI Symposium 2023

Eawag, 8600 Dübendorf, Switzerland

Tuesday, 21 Nov 2023

9:30 – 10:00	Welcome coffee and snacks
10:00 – 10:50	Presentations
11:50 – 11:10	Break
11:10 – 12:00	Presentations
12:00 – 14:00	Lunch at Eawag
14:00 – 15:15	Presentations
15:15 – 15:45	Break
15:45 – 17:00	Presentations

Wednesday, 22 Nov 2023

9:30 – 10:00	Coffee and snacks
10:00 – 10:50	Presentations
11:50 – 11:10	Break
11:10 – 12:00	Presentations
12:00 – 14:00	Lunch at Eawag
14:00 – 15:15	Presentations
15:15 – 15:45	Break
15:45 – 17:00	Presentations
19:00 (open end)	Group dinner in Zürich

Thursday, 23 Nov 2023

9:30 – 10:00	Coffee and snacks
10:00 – 10:50	Presentations
11:50 – 11:10	Break
11:10 – 12:00	Presentations
12:00 – 14:00	Lunch at Eawag
14:00 – 15:15	miniRUEDI hands-on, lab tour

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Gases as artificial tracers to study SW-GW interactions

presented by Théo Blanc

University of Neuchâtel, 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.

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River rafting with the miniRUEDI

presented by Connor P. Newman¹, Eric C Humphrey¹, Matthias S Brennwald², W. Payton Gardner³, Kelli M Palko¹ and Michael N Gooseff⁴

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 outflow 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.

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

presented by Friederike Curre

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.

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presented by Kyriaki Daskalopoulou

University Potsdam, Germany

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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.

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Presenting the Omnistar

presented by Edith Engelhardt

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.

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presented by Jens Gröger-Trampe

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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

Nitrogen fixation by cyanobacteria is a common phenomenon in the Baltic Sea. Its contribution to the N budget is of the same order of magnitude as the combined sum of riverine and airborne DIN input, 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, when the probability of a cyanobacteria bloom is high. Additionally, Ar measurements are performed to account for the air-sea N₂ gas exchange. Furthermore, the biological oxygen saturation $\Delta\text{O}_2/\text{Ar}$ can be utilized to further characterize the production phase. For our studies, we developed an Equilibrator-Inlet Mass Spectrometer (EIMS) designed for deployment on a ferry line, enabling repeated transects along the same route and providing high temporal and spatial resolution data for N₂, O₂ and Ar gas concentrations in the surface water. During June/July of summer 2023, we performed surface water measurements on a voluntary observing ship (VOS, "Finnmaid") which is travelling 2-3 times per week over a distance of about 1000 km between the Mecklenburg Bight and the Gulf of Finland. In connection with these measurements, further investigations of nitrogen fixation and its vertical distribution were undertaken during a research cruise in order to identify the processes that control nitrogen fixation and the linked biomass production. The initial results appear promising, though a final analysis and evaluation of the data is still pending. In the future, we plan to use the 2023 dataset to establish a nitrogen budget for the Baltic Proper. Our objectives are to identify various factors that initiate and potentially limit the growth of cyanobacteria.

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Analyzing Unexpected Gas Seep in Mbeya, Tanzania with a Portable Mass Spectrometer (“MiniRuedi”)

presented by Clarah Kimani

University of Dar es Salaam, Tanzania

A study was conducted in Mbeya region Tanzania, to investigate unexpected gas seepage from a dry well at Harrison Uwata Girls Secondary School. Gas samples were collected and analyzed using a portable mass spectrometer (“MiniRuedi”), an analytical instrument to determine their composition. The study focused on the Rungwe Volcanic Province (RVP), situated within the East African Rift System, known for active magmatic activity, including vigorous gas and volatiles emanations. The primary gas in the seep was found to be carbon dioxide (CO₂), with trace amounts of nitrogen (N₂), argon (Ar), and helium (He). The analysis traced the sources of these gases to contributions from both the Earth’s atmosphere and the subsurface, particularly the Earth’s mantle. The concentration of CO₂ in the seep was found to vary based on proximity to volcanic centers, with closer locations having higher CO₂ concentrations (90%). This decrease in CO₂ concentration with distance was attributed to dilution by other gases from sources like the atmosphere and the Earth’s crust. The study emphasizes the importance of understanding the origin of CO₂ in these seeps and calls for further research to explore its nature, storage, and potential economic extraction and utilization as a resource.

The investigation at Harrison Uwata Girls Secondary School gas seep in the RVP has significant implications for understanding the geology, geochemistry, and geological processes in the area and the broader East African Rift System, offering opportunities for future research and resource exploration. Additionally, the study highlights the presence of different hydrothermal systems in the RVP, including cold-gassy and hot-gaseous systems, with varying characteristics and potential hazards.

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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).

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**Geochemical Background of Volatiles in Kyejo Area
(Rungwe Volcanic Province) and Geochemical
Composition of Soil Gas, Macro Seep and Gas Vent:
Implication to CO₂ Prospect**

presented by Karim Mtili

University of Dar es Salaam, Tanzania

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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

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.

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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.

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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.

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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.

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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.