miniRUEDI Symposium 2023

Eawag, 8600 Dübendorf, Switzerland

Tuesday, 21 Nov 2023

9:30 – 10:00	Welcome coffee and snacks
10:00 – 10:10	Introduction
10:10 – 11:10	Presentations
11:10 – 11:30	Break
11:30 – 12:30	Presentations
12:30 – 14:00	Lunch at Eawag
14:00 – 15:00	Presentations
15:00 – 15:20	Break
15:20 – 17:20	Presentations

Wednesday, 22 Nov 2023

9:30 – 10:00	Coffee and snacks
10:00 – 11:00	Presentations
11:00 – 11:20	Break
11:20 – 12:20	Presentations
12:20 – 14:00	Lunch at Eawag
14:00 – 15:00	Presentations
15:00 – 15:20	Break
15:20 – 17:20	Presentations
19:00	Group dinner in Zürich (open end)

Thursday, 23 Nov 2023

9:30 – 10:00	Coffee and snacks
10:00 – 11:00	Presentations
11:00 – 11:20	Break
11:20 – 12:20	Presentations
12:20 – 14:00	Lunch at Eawag
14:00 – 15:00	miniRUEDI hands-on, lab tour

21 Nov 2023, 10:10–10:30

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

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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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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

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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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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.

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Application of noble gases to the study of the natural analogy of geologically disposed spent nuclear wastes

presented by Ye Ji Kim[1], Won-Tak Joun[2], Dugin Kaown[1], Jaeyeon Kim[1], Kang-Kun Lee[1]

1: School of Earth and Environmental Sciences, Seoul National University, Republic of Korea, 2: Disposal Safety Evaluation Research Division, Korea Atomic Energy Research Institute

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.

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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.

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The search for microbial activity

presented by Anneleen Vanleeuw

SCK CEN, Belguium

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.

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Combining and comparing systematic and continuous gas monitoring techniques at the Hartoušov mofette, Czech Republic

presented by Kyriaki Daskalopoulou[1,2], Martin Zimmer[2], Heiko Woith[2], Samuel Niedermann[2], Andrea Vieth-Hillebrand[2], Walter D´Alessandro[3], Fausto Grassa[4], Josef Vlček[4]

1 University of Potsdam Germany, 2 GFZ Potsdam Germany, 3 INGV-sezione di Palermo Italy, 4 Charles University Prague Czechia

The Cheb Basin (Czech Republic) is an intraplate region without active volcanism that is characterised by emanations of magma-derived gases and the occurrence of mid-crustal earthquake swarms. Associated intense mantle degassing occurs at the Hartoušov mofette field, a representative site for the Cheb Basin. Gases ascending from two boreholes (F1, ~28m depth and F2, ~108m depth) and two bubbling ponds (surface expressions) have been sampled systematically since 2019. Samples were analysed for their chemical (CO2, N2, O2, Ar, He, CH4, and H2) and isotopic contents (noble gases and CO2). CO2 is the dominant gas species (concentrations >99.3%), while the remaining gases are present in minor amounts. The He isotopic composition is typical for the subcontinental lithospheric mantle (~5.4 to 5.9RA), and the δ13CCO2 data reflect mantle-like CO2 (-2.4 to -1.3‰vs. V-PDB). Variations in the chemical composition are mainly mirrored in the minor components and, similar to the δ13CCO2 shifts, are often related to changes in water temperature, water/gas ratio, solubility differences, and the impact of microbial activity. To better document these changes, a multidisciplinary observatory was built at the Hartoušov mofette. There, gas composition from F2 is continuously analysed in-situ through a quadrupole mass spectrometer. Radon concentration and fluid parameters (water temperature, water level/pressure, gas pressure) are continuously measured at 3 different depth levels. In addition to the fluid monitoring equipment, a weather station records meteorological standard parameters, and a seismometer documents earthquake activity. This work will present data from the systematic and continuous gas monitoring and will discuss the problematics of continuous monitoring that may occur in systems characterised by extreme conditions.

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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 ($\sim$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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Geochemical Background of Volatiles in Kyejo Area (Rungwe Volcanic Province) and Geochemical Composition of Soil Gas, Macro Seep and Gas Vent: Implication to CO_2 Prospect

presented by Karim Mtili

Department of Geosciences, School of Mines and Geosciences, University of Dar es Salaam, Tanzania

The study focuses on the geochemical investigation of volatile compounds, with a specific emphasis on carbon dioxide (CO2), in the Kyejo area, situated within the Rungwe Volcanic Province, a part of the East African Rift System (EARS). The region is recognized for hosting one of the most active hydrothermal systems, closely associated with Quaternary volcanic activity. This leads to the active and passive diffusion of gases in various geochemical compartments, including the soil matrix, cold and hot springs, and gas vents. These gases are predominantly of magmatic origin and encompass a range of gaseous species, including CO2, nitrogen (N2), argon (Ar), oxygen (O2), sulfur dioxide (SO2), hydrogen sulfide (H2S), hydrogen chloride (HCl), hydrogen fluoride (HF), and noble gases such as helium (He).

In this study, particular attention is given to CO2, the second most abundant gas emitted by magma. Due to its low solubility and high mobility, CO2 serves as an effective tracer for detecting concealed natural resources. Areas exhibiting anomalous CO2 concentrations are indicative of subsurface gas systems, structural features like faults, preferential pathways, and geological units. To address these objectives, we conducted an examination of the distribution of CO2 within the soil pore matrix around the study area, with the assumption that gases originating from the subsurface sources migrate to near-surface environments where they can be detected. Furthermore, we provide insights into the geochemical composition of macro seeps found in cold springs and gas vents within the study area.

The research approach comprises two main components: first, soil gas sampling to assess the distribution of bulk gas concentrations across the study area, and second, sampling of high-purity gas vents and macro-seeps (cold springs) to identify the sources of these emissions. Utilizing a portable quadrupole mass spectrometer (MiniRuedi), we conducted on-site bulk gas composition analysis of collected samples. This study contributes to a better understanding of the geological and geochemical characteristics of the Kyejo area, specifically in relation to CO2 emissions, and implications to the economic prospectivity of this gas and effects to climate change.

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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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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, N2, O2, H2, CH4, and CO2 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

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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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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 ΔO2/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.

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presented by Hans Slagter

MPIC, Germany

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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).

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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.

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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.

DATE / TIME HERE

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.

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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.

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Prospects for onsite gas applications in groundwater-dependent wetlands

presented by Lucia Ortega Ormaechea

IAEA

The effects of climate changes are threatening wetlands and groundwater systems, both directly and indirectly, through rising temperatures, changes of rainfall intensity and frequency, extreme climatic events like drought, flooding, and the frequency of storms. Although the impacts of climate change to water resources are yet relatively unknown, the potential impacts on surface water, particularly projected regional climate patterns and trends (i.e., climate variability and change) have been studied in some detail (Green et al., 2011). Yet, the effect of climate change on groundwater resources is poorly understood, especially how the systems will respond to climate change coupled with anthropogenic activities such as land use changes (Earman & Dettinger, 2011; Havril et al., 2018). This is because groundwater systems are complex, and a combination of processes affect groundwater recharge, discharge, and quality. Moreover, visualisation of these impacts on groundwater is difficult, driving assumptions that the resource is more resilient than it is. In contrast to groundwater systems, wetlands provide strong visualisation of how water resources are impacted by both natural and anthropogenic processes. Yet, little is known about how groundwater resources can be assessed through the lens of wetland systems.

To protect and manage groundwater resources through wetlands, it is necessary to understand the sources and sinks of water in the wetland, groundwater-surface water interactions, and the pathways of water within a catchment area at a range of spatial and temporal scales. The IAEA launched in 2022 a new Coordinated Research Project to explore the use of onsite noble gases, among other tracers, to assess groundwater resources through the lens of wetland systems for efficient water resources management in Member States. The project is still under implementation but some preliminary results of onsite noble gases have provided promising insights on recharge rates and groundwater origin.

DATE / TIME HERE

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.

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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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Groundwater recharge and paleoclimate deduced from noble gas with miniRUEDI measurement and other methods in arid Qaidam basin, China

presented by Dan Zhao and Guangcai Wang

China University of Geosciences, Beijing

The Qaidam Basin (QB) is an extremely arid endorheic basin with high altitudes (2600 to 3000 m excluding mountainous areas) in northwest China. Huge aquifers, dozens of alluvial-lacustrine plains, as well as salt lakes and playas formed due to its hydrogeological and climatic circumstances. It's very important and interesting to discover the groundwater recharge and its connection with local paleoclimate for sustainable utilization of water resources.

Here we present a case study on the groundwater recharge and paleoclimate with multiple methods in the Golmud water system, south part of QB. Field and lab work were conducted in 2017-2018. (i) Noble gases were performed with both in-situ miniRUEDI measurement and lab analysis for noble gas temperatures (NGTs). (ii) 3H, 3H-3He and 14C dating methods were used for the recharge period identification. (iii) Hydrochemistry, stable isotopes (2H and 18O), radioactive 222Rn, and in-situ physical-chemical parameters (temperature, pH, EC, etc.) were also employed for the groundwater recharge features and groundwater-surface water interaction characterization.

The preliminary results showed that (i) miniRUEDI provided a quick and relatively accurate measurement of gases (O2, N2, CO2, 40Ar, 4He and 84Kr) in air and water. Difference with lab analysis was found in some samples, but the results were comparable. (ii) MiniRUEDI measurement helps a lot in conveniently field-distinguishing ancient groundwater with high 4He and low O2 contents. (iii) Local atmospheric air showed stable percentage of different gases, but with lower air pressure (P¡0.75 atm) and gases concentrations due to the high altitude (H from 2700 to 3700 m). Meanwhile, the air P-H relationship basically matches the equation P=e(-H/8300). (iv) Modern and late Pleistocene groundwater was identified. And NGTs result presents a gradually warming-up process of about 3°C in 17.2-14.8 ka BP (corrected 14C age) after the Last Glacial Maximum in QB.

Acknowledgments: this research was supported by the National Natural Science Foundation of China (No. 41672243). The authors greatly appreciate the help from Dr. Edith Horstmann with noble gas analysis. Wan-Jun Jiang, Liang Guo, Fu Liao, Nuan Yang are also kindly acknowledged for their fieldwork assistance.

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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

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

presented by Stephanie Musy[1], Currle Friederike[1], Nakajima Teresa[2], Tomonaga Yama[1,3] Sano Yuji[2], Schilling Oliver S.[1,4]

[1]University of Basel, Switzerland, [2]Kochi University, Japan, [3]Entracers GmbH, Switzerland, [4]Eawag–Swiss Federal Institute of Aquatic Science and Technology, Switzerland

Mt. Fuji is the iconic centerpiece of a large, tectonically active volcanic watershed (1750 km^2) 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].

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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.

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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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Laboratory Applications of the miniRUEDI for Field-Collected Samples

presented by Darren Hillegonds, Daniel Halford, Fahad Souid, Thomas Renshaw, Ruta Karolyte, and Christopher Ballentine

University of Oxford, UK

Assessment of bulk gas content in gas samples collected in copper tubes and returned to the laboratory for noble gas isotope analysis will be presented. These measurements provide insight into the performance of the miniRUEDI instrumentation where inlet pressure is low and variable, helping to establish a pathway towards wider application of a capillary inlet mass spectrometry system within a noble gas mass spectrometry laboratory.

Measurements made on gas samples returned from Yellowstone National Park will be discussed. We will also discuss the prospect of utilising the miniRUEDI to assess bulk gas content in field-collected water samples, with example analyses made with a modified version of our water extraction system.