PARIS LODRON UNIVERSITÄT SALZBURG

Dr. Giorgio Höfer Ziviltechniker GmbH

SINA 2023

19th Stable Isotope Network Austria Meeting

17th & 18th November 2023

Paris Lodron University Salzburg (PLUS)

Department Environment and Biodiversity
Dekanatsaal
Hellbrunner Str. 34
5020 Salzburg

PROGRAM AND ABSTRACTS

Book of Abstracts - Proceedings of the 19th Stable Isotope Network Austria Meeting 2023 / S. Hilberg, G. Höfer-Öllinger, A. Leis (Ed.) Paris Lodron University Salzburg, Salzburg. 41p.

PROGRAM

Friday, 17th November 2023

9:45 – 10:45 Registration

10:45 – 10:55 Opening

Session 1: Stable Isotope Methods (Chair: G. Höfer and S. Hilberg)

10:55 – 11:15 **Manfred Groening**
Recent challenges for consistent $\delta^{13}C$ scale value reporting

11:15 - 11:35 **Kathiravan Meeran**
Vienna Urban Carbon Laboratory: Investigating urban CO_2 emissions through Isotope Analysis from Tall Tower Observations

11:35 – 11:55 **Kathrin Rosenthal**
Analysis of dissolved nitrate stable isotopes using the one-step Ti (III) reduction method and Elementar EnvirovisION System

11:55 – 12:15 **Johannes Friedl**
A synthesis of ^{15}N isotope methods to inform measurement, scaling and modelling of N_2O and N_2 emissions from agricultural soils

12:15 - 12:35 **Patric Simões Pereira**
Acquisition of a new generation multicollector ICP-MS at the Institute of Geology, University of Innsbruck

12:35 - 14:00 ***Lunch Break***

Session 2: Stable Isotopes in Geology and Biogeochemistry (Chair: A. Leis)

14:00 – 14:40 *Keynote:* **Michael Böttcher**
Multi isotope biogeochemistry of a temperate coastal peatland under impact by submarine groundwater discharge and storm-induced flooding

14:40 – 15:00 **Patricia Roeser**
Carbon(ate) diagenesis in Lake Constance: A stable isotope geochemical perspective

15:00 - 15:20 **Ana-Voica Bojar**
Monitoring multi-decadal temperature changes in the Eastern Alps: a tunnel stable isotope archive

15:20 - 15:50 ***Coffee Break***

Session 3: Stable Isotopes in Lifesciences (Chair: A. Watzinger)

15:50 – 16:10 **Kathiravan Meeran**
Effects of Tree Size and Site Characteristics on the Intraspecific Variability of Sessile Oak Growth and Water-Use-Efficiency Response Under Wet-Dry Years

16:10 - 16:30 **Sabrina Santos Pires**
Sugar Beet Water Uptake Studies Through Water Stable Isotopes

16:30 - 16:50 **Magdalena Blanz**
Stable isotope ratios to identify seaweed-consumption and fertilisation in archaeology

17:00 – 18:00 **Poster Session** (including 3 min oral presentation in front of poster)

starting 19:30 **Conference Dinner**
Stiegl-Keller, Festungsgasse 10; 5020 Salzburg (traditional restaurant)

Saturday, 18th November 2023

Session 4: Stable Isotopes in Hydrogeology (Chair Stefan Wyhlidal)

9:30 - 9:50 **Giorgio Höfer-Öllinger**
The potential of Stable Isotopes to identify Permafrost degradation, Sattelkar Landslide, Obersulzbachtal, Salzburg

9:50 - 10:10 **Julien Farlin**
Using isotopes to estimate groundwater recovery times from diffuse pollution

10:10 - 10:30 **Michael Stockinger**
Lessons learned from the spatiotemporal analysis of long-term and time-variable young water fractions of large Central European catchments

10:30 - 10:50 **Selma Hajric**
Investigating the impact of land use, slope position, and soil heterogeneity on soil water fluxes in a small agricultural catchment

10:50 -11:10 **Eva Kaminsky**
Identification of recharge processes in the shallow aquifer of Vienna

11:10 – 11:30 ***Coffee Break***

starting 11:30 **General Assembly** – Stable Isotope Network Austria (SINA)

POSTERS

Michael Böttcher[a]	Stable isotopes indicate sources and fate of sulfur in a modern analogue for the Baltic Sea freshwater stage
Michael Böttcher[b]	Biogeochemistry and hydrology of a tidal basin with the northern-most German submarine ground water discharge: A water and carbon isotope perspective
Michael Böttcher[c]	Seasonal and spatial multi-isotope hydrobiogeochemistry of a managed river draining into the southern Baltic Sea
Monis Nolitha Gcakasi	Establishment and application of the Ti (III) reduction method for analysis of nitrogen isotopes in water samples
Sven Gindorf	Acquiring photosynthesis of cryoflora at remote field sites using stable isotopes (^{13}C)
Linee Goswami	The status of ecosystem functions of polluted lands assessed in situ using plant, soil, and microbial indicators
Micha Horacek	The search for the GSSP for the Spathian-Anisian Boundary - a long story slowly approaching its end?
Rebecca Hood-Nowotny	A trans-European decomposition index study in arable soils, focusing on the impact of different depths and plant diversity using a common ^{13}C-labelled litter.
Martin Kralik	Timing of an Alpine water cycle unraveled by water isotopes and age-dating tracers (^{3}H, ^{3}He, ^{14}C, CFCs, SF_6 and ^{222}Rn), Eastern Alps, Austria
Tereza Kunkelova	NAWI Graz Core Facility: Stable Isotopes
Albrecht Leis	Regionalization of stable isotope data (oxygen-18 and deuterium) in Swiss precipitation for hydrological studies
Katharina Schott[a]	Detection of climate change induced drought stress at Rosalia forest using stable isotope methods (^{13}C, ^{18}O)
Katharina Schott[b]	Influence of alpine ranges on the isotope signature in precipitation in Austria
Elisabeth Schwaiger	Traceability of fruit and vegetables
Vera Winde	Method for determining the origin of water damage
Paul Zemann	Characterization of the flow regime in a karst aquifer using stable water isotopes (Hochschwab, Austria)

Book of Abstracts

Scientific Organizing Committee

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Book of Abstracts - Proceedings of the 19th Stable Isotope Network Austria Meeting 2023 / S. Hilberg, G. Höfer-Öllinger, A. Leis (Ed.) Paris Lodron University Salzburg, Salzburg. 41 p

Recent challenges for consistent $\delta^{13}C$ scale value reporting

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The reporting of $\delta^{13}C$ data was performed on the PDB scale since 1957 using the reference material PDB. After the depletion of its stocks, in 1982 the reference material NBS19 was used for the same purpose, and the scale renamed as VPDB to indicate the changed reference to NBS19. In 2006, a further change to the scale was recommended to create a two-point scale by adding a second anchor material LSVEC, thus introducing the VPDB-LSVEC scale (also called VPDB2006). Ten years later, severe problems were discovered with LSVEC, making it unsuitable as carbon isotope reference material due to isotopic heterogeneity of more than 0.3‰ between individual units of LSVEC. For climate research measurements on CH_4, the WMO aimed for consistent $\delta^{13}C$ measurements within 0.02‰. This was clearly not achievable based on such an instable second reference point.

At this time, IAEA was already producing a new carbonate reference material IAEA-603, carefully calibrated versus NBS19, to replace that exhausting NBS19 reference material. Due to the severe LSVEC problem, a suite of three additional carbonate reference materials was produced in the following years (IAEA-610, IAEA-611, IAEA-612) to span most of the natural $\delta^{13}C$ range, independent of the unsuitable LSVEC. Their isotopic values were based on one-point calibration versus NBS19 with careful memory correction. Thus, this practically re-established the VPDB scale, while it was renamed VPDB2020 scale to indicate the change of materials used for calibration. This scale is intended to be used as two-point calibration scale to harvest its advantages for routine users.

A lot of reference materials (RM) were produced since 2006 using previously calibrated reference materials - partially using the VPDB-LSVEC scale. Their newly determined isotopic values are variable by up to 0.3‰, depending on the used reference materials and their calibration history (versus VPDB or VPDB-LSVEC or a mix of both…). The reported values thus are fully depending on the origin of calibration values of used reference materials.

This creates a major risk for $\delta^{13}C$ data consistency. Three possible solutions for that problem are feasible and will be briefly discussed (keep the VPDB2006 scale and re-calculate all RM values accordingly; move to the VPDB2020 scale and re-calculate all RM values accordingly; fully report all isotopic values of reference materials used for calibration of results).

Vienna Urban Carbon Laboratory: Investigating urban CO_2 emissions through Isotope Analysis from Tall Tower Observations

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Understanding the extent of cities' contribution to global carbon dioxide (CO_2) emissions is essential for effective climate change mitigation, emphasizing the need to monitor these emissions accurately. Uncertainties in emission inventories become pronounced when applied at the scale of individual cities, due to a lack of adequately resolved activity and/or emission factors. Measurement methods involving atmospheric CO_2 mole fraction and the corresponding stable carbon isotope ratio ($\delta^{13}C$) of CO_2 can help overcome these challenges and provide independent insights into urban emissions. At the Vienna Urban Carbon Laboratory (VUCL), we are testing an analysis framework to best utilize such measurements to identify and quantify local sources of CO_2 emissions in Vienna. In May 2022, a isotope analyzer (G2201-i, Picarro Inc., USA) was installed on top of the Arsenal Tower in Vienna at 144 meters above the surface to continuously measure the mole fraction and $\delta^{13}C$ value of CO_2. Our results show that, in summer, nocturnal increases and daytime decreases in CO_2 concentration align with its stable carbon isotope ratio, indicating increased influence from photosynthesis and natural respiration. During Autumn, increased CO_2 levels with a temporal shift suggest a stronger flux from respiration. In winter, though not exceeding autumn CO_2 levels, it shows lower $\delta^{13}C$ values, indicating a significant contribution from natural gas combustion. Spatial analysis using polar plots highlights elevated CO_2 mole fraction with winds from the east and southeast, accompanied by decreased $\delta^{13}C$, and these correspond to the location of nearby large point sources of CO_2. In winter, overall CO_2 concentration is high, particularly in eastern regions, with a decrease in isotopic values from east and northwest directions, pointing to contributions from gas combustion in buildings and power stations for heating purposes. Additionally, we will present results from our ongoing footprint analysis, enabling us to better understand the spatial influences on our measurements, in particular the enhancements caused by local emissions.

Analysis of dissolved nitrate stable isotopes using the one-step Ti (III) reduction method and Elementar EnvirovisION System

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Identifying and quantifying sources and cycling of nitrogen is important for understanding not only aquatic ecosystems but also planning water resource management, mitigating urban and agricultural pollution, and optimizing government policy. Stable isotopes of dissolved nitrate and nitrite ($\delta^{15}N$, $\delta^{18}O$ and $\delta^{17}O$) have been useful in distinguishing between the diverse nitrogen sources and sinks and help understand large scale global ocean processes as well as revealing major changes in agricultural land use and urbanization.

Despite the strength of dissolved nitrate and nitrite stable isotope analysis, the strong barrier for uptake using the favoured contemporary methods (bacterial denitrifier and Cd-azide reaction) due to the laborious multi-step methods, maintenance of anerobic bacterial cultures and use of highly toxic chemicals has limited the analysis to highly specialized laboratories. We evaluate the performance of the Elementar EnvirovisION using the new Titanium (III) reduction method (Altabet *et al*., 2019) for one step conversion of nitrate into N_2O for IRMS analysis.

The EnvirovisION has been developed for high performance analysis of CO_2, N_2O and CH_4 and dissolved nitrate. The system has the capacity to be rapidly customized for specific needs with options for dual GC columns supporting the Weigand 'heart-cut' N_2O method (Weigand et al., 2016) and sequential N_2 and N_2O analysis from a single atmospheric sample.

A synthesis of ^{15}N isotope methods to inform measurement, scaling and modelling of N_2O and N_2 emissions from agricultural soils

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Magnitude and sources of nitrous oxide (N_2O) and dinitrogen (N_2) emission from agricultural soils remain a major uncertainty for the nitrogen (N) budget of agro-ecosystems. Their high spatial and temporal variability, and measuring N_2 against a high atmospheric background makes monitoring, temporal and spatial scaling and modelling of these emissions challenging. Here we show development and deployment of innovative approaches to constrain drivers, pathways and magnitude of N_2O and N_2 production at different scales across a series of field and laboratory based studies in Australian sugarcane systems. The development of a novel incubation system enabled to monitor real-time $^{15}N_2O$ and $^{15}N_2$ fluxes at subdiel resolution providing new insights into different production pathways of N_2O and N_2. The system couples continuous flow IRMS system with a fully automated chamber system via a sampling box. The setup was also deployed in the field, monitoring in-situ fluxes of N_2O and N_2 using the ^{15}N gas flux method. To capture the temporal and spatial variability of N_2O and N_2 emissions over the whole cropping season, we combined a) high temporal resolution N_2O measurements b) in-situ N_2O and N_2 quantification via the ^{15}N gas flux method and c) fertiliser ^{15}N recoveries at the end of the season with d) statistical models. This novel approach enabled us to upscale high temporal resolution N_2O data to daily N_2 emissions over the season, accounting for spatial differences of N availability between N fertiliser band and non-fertilised furrow. These approaches can serve as a blueprint to constrain drivers and pathways of N_2O and N_2 under controlled conditions, but also to estimate N_2O and N_2 losses based on in-situ measurements for a wide range of agroecosystems. The current implementation of refined estimates of the $N_2O/(N_2O+N_2)$ ratio in biogeochemical models will help to advance our quantitative understanding of N cycling across scales, and help to identify best management practice for agronomic and environmental benefits

Acquisition of a new generation multicollector ICP-MS at the Institute of Geology, University of Innsbruck

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Multicollector inductively coupled mass spectrometry (MC-ICP-MS) has proven an essential technique to analyse isotopic systems, making it an indispensable tool for investigating the geologic history of the Earth, origin of the solar system, past climates, nuclear safeguards, and natural and anthropogenic processes in the environment. With the installation of a new high-class clean laboratory and acquisition of the NEOMA™ [1], the next generation mass spectrometer developed by Thermo Scientific™, the Institute of Geology recently established a state-of-the-art analytical facility for isotope and geochronological analysis at the University of Innsbruck, Austria. Here, we report on the technical specification and analytical capabilities of our new clean laboratory and mass spectrometer. The power of the NEOMA™ lies in that it provides enhanced sensitivity, large mass dispersion and enhanced mass resolving power compared to its predecessor. The primary focus of the laboratory is directed to the production of high-resolution U and Th isotope measurements in carbonate systems. The development of U/Th dating protocols will provide invaluable support to ongoing and future projects at the institute, and foster sustained scientific collaboration across scientific disciplines and institutions, by delivering high-resolution geochronological information in the broad field of earth, and more specifically on the continually expanding field of speleothem-based paleoclimate research [2,3].

[1] Thermo Fisher Scientific (2020) BR30600-EN 0520C: Neoma Multicollector ICP-MS [pdf]
[2] Henderson (2006) Science 313, 620-622
[3] Wendt et al. (2021) Elements 17, 87–92

Multi isotope biogeochemistry of a temperate coastal peatland under impact by submarine groundwater discharge and storm-induced flooding

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Land-ocean interactions in the coastal zone are of particular interest regarding the exchange of substances, like nutrients, carbon, sulfur, metals, and water. The rising sea level is and will further increase the influence of seawater on previously freshwater systems. Currently, coastal areas in the NE of Germany are increasingly being rewetted by water from the Baltic Sea. Furthermore, the role of submarine groundwater discharge (SGD) on the coastal balance of water, elements, and the associated biogeochemical processes is still lacking fundamental knowledge requiring the investigation by multi-isotope approaches.
Here, we present multi-isotope results on the biogeochemistry of recent rewetted coastal wetland, at the southern coast of the Baltic Sea, the Huetelmoor. Huetelmoor is impacted by event-type flooding from the Baltic Sea sediment cores on transects within the wetland were investigated for the pore water and soil composition, together with selected groundwater wells and surface waters from the channeling system. Different fractions of the peat were analyzed for the elemental composition, mineral micro-textures, and the composition of different stable isotopes, especially the stable sulfur- (and oxygen-) isotope composition of different sulfur fractions. The flooding events lead to an increase of sulfate availability for microbial carbon transformations. The addition of sulfate by rewetting pulses creates space for mineral authigenesis and organic matter sulfurization. The peatland is impacted by different intensities in sulfur cycling as reflected by isotope and textural signals. In addition, up to 5 m deep permanent pore water lances in the coastal sediments allow for the identification and quantification of fresh SGD draining from the aquifer below the peatland towards the coast. This enabled the characterization of the benthic biogeochemical implications of SGD originating from a sulfur rich system. The results can be transferred as proxy information to other modern and past coastal organic-rich peatlands.

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Carbon(ate) diagenesis in Lake Constance: A stable isotope geochemical perspective

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Lacustrine carbonates are excellent archives for past environment and climate conditions, due to the climate sensitivity in their formation either as erosional sources of suspended matter or through lake internal processes. At the same time, their reactivity makes them susceptible to diagenetic overprints. Lake Constance, placed in a carbonate-rich catchment at the northern foot of the Alps, is one of the largest lakes in Central Europe, and has been intensively investigated in the past. The lake water chemistry makes it a natural laboratory to investigate carbonate formation, preservation, and the influence of detrital carbonate fractions in detail. Up to 24 m long cores were recovered from Lake Constance, covering the (post-)glacial sedimentary record. To investigate the benthic carbon cycle and mineral sources and transformations, porewaters and sedimentary solid phases were analysed for their stable isotope signatures (CHOS), and major- and trace element compositions.

The water isotope signatures display a trend towards lighter data with depth, indicating the development in the lake water composition with time, superimposed by diffusion processes in the sediments. The dissolved inorganic carbon (DIC) concentrations increase below the sediment-water interface and are generally higher in the postglacial sediments, indicating that mineralization rates followed the enhancement of lake productivity under milder climate conditions. The δ^{13}C-DIC shows the lightest values in the glacial sediments and displays an enrichment in Holocene sediments, together with pore water hydrochemistry, indicative of organic matter (OM) oxidation, carbonate dissolution, and potential involvement of methane. The sulfur isotope record indicates that minor dissimilatory sulfate reduction is involved in

OM degradation. Bulk carbonate C and O isotope signatures show strong variations partly induced by non-authigenic dolomite. Vertical variations in the composition of porewaters, bulk, and acid-soluble phases, in combination with SEM investigations, allow insights about the (trans)formation of authigenic mineral phases and the destruction of allochthonous carbonates, as possible modifiers of the sedimentary record.

Monitoring multi-decadal temperature changes in the Eastern Alps: a tunnel stable isotope archive

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Speleothems are formed by precipitation of calcium carbonate from surface aqueous solutions, which further seep into subterranean cavities that are generally made of limestones. Speleothems, especially stalagmites represent excellent archives for high-resolution reconstruction of climatic fluctuations at different time scales, going even to sub-annual resolutions.

According to the Köppen-Geigen climate classification system, the Graz region belongs to a temperate climate with no dry season (Rubel et al., 2017). During years 1800 to 2100, the shift of the climate zones for the European Alps was investigated, and it was documented that the Graz region climate shifted from a boreal climate (Dfb) at the beginning of the 20th century to a warm temperate with no dry season (Cfb) in the second half of the 20th century. For the next 50 years the prediction is toward a Cfa type climate, with warm summer and no dry season. According to scenario, 80% of the ice cover will be reduced in the Alps (Zemp et al., 2006).

In the present study, we investigate speleothems collected from a tunnel that was built as underground hospital and shelter between 1943 to January 1945 (Stelzl-Marx, werkstadt.mur.at/schlossbergstollen/arbeit.html) across the Schlossberg hill. The hill is situated in the centre of Graz and consists of dolostones belonging to the so-called Paleozoic of Graz (Flügel and Neubauer, 1984).

High temporal resolution isotopic profiles were sampled on stalagmites from the above described tunnel. The isotopic profiles are correlated with outside mean annual temperature (MAT), mean annual precipitation (MAP), and the weighted mean annual oxygen isotope compositions of meteoric waters. The database built from the continuous monitoring of meteorological variables as well as isotopic data is displayed at monthly to decadal time scale. The resulting Time Series (TS) reveal long- and short-term fluctuations that correspond to regional climate forcing, converging to increasing regional MAT (Bojar et al., 2020).

References

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Cycle and Terrestrial Environments", Eds. Bojar, A.-V., Pelc, A., Lécuyer, C., Geological Society, London, Special Publications, Lyell Collection, 507, doi.org/10.1144/SP507-2019-154.
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Effects of Tree Size and Site Characteristics on the Intraspecific Variability of Sessile Oak Growth and Water-Use-Efficiency Response Under Wet-Dry Years

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Drought is a significant global environmental stressor, known to impact tree growth and survival, and even leading to a substantial die-off of temperate forests. Contemporary forest management strategies aim increasingly to transition from spruce-dominated to oak-dominated forests, driven by both ecological and human factors. Sessile oak (*Quercus petraea* (Matt.) Liebl.), a key forest tree species, is widespread across central Europe, but its response to climate extremes, especially individual intraspecific variability, remains poorly understood. As part of the TERZ (Thayataler Eichen- genetische Ressource für die Zukunft) project, we examined 404 Sessile oak trees in Thayatal National Park, using tree-ring width to assess radial growth and $\delta^{13}C$ in tree-rings from wet (1987) and dry (1994) years, to assess tree intrinsic water-use efficiency (iWUE). We investigated the effects of site conditions, specifically the light and water availability as inferred from photoperiod duration and the topographic wetness index, on key tree characteristics such as diameter at breast high (DBH), height, and the height-to-diameter ratio (HDR) . We then examined how these factors influenced tree iWUE and tree resilience, which is the ability of individual trees to resist and recover from drought. Our findings highlight that tree age and size exert the most significant effects: large, older trees exhibit higher growth during dry year but recover more slowly compared to small, young trees. While water availability contributes to increased tree height and diameter, it does not affect growth or iWUE during the extreme years. Increased daylight positively influenced tree height, while during dry year, it enhanced iWUE, decreased growth, but supported recovery. Furthermore, both tree age and size contributed to increased iWUE. The trees that become more water-use-efficient during dry years displayed increased growth and greater resistance to drought. In summary, our study underscores the pivotal roles of tree age and size, daylight and water availability, and iWUE in influencing growth, resilience, and recovery. It provides valuable insights into the adaptive strategies of trees in the face of climate change.

Sugar Beet Water Uptake Studies Through Water Stable Isotopes

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Sugar beet farming holds immense importance in Austria, especially in the eastern region, where limited water supply constrains crop production. Here, climate change poses additional challenges to sugar beet production, particularly due to increased drought and heat stress, which reduce agricultural productivity. To ensure long-term sugar beet production, strategies enhancing water resource utilization and plant resilience against drought are essential. Therefore, this study investigates if sugar beets adapt their water uptake in response to dry topsoil conditions and variations in root depth, water uptake, and drought response among sugar beet cultivars. Controlled rhizobox laboratory experiments with individual sugar beet varieties were conducted and combined with water-stable isotope analysis to provide insights into the relationship between sugar beet root development and water uptake. To locate root water uptake, water with different stable isotope labelling was applied from upper and lower soil layers separated by a water-repellent barrier, and the transpired water on live plants was analyzed. Therefore, leaves were placed in Ziploc bags, inflated with dry air, and allowed to stabilize for at least 16 hours. After equilibration, the bag was punctured, and the equilibrated air and transpired vapor were directed to a laser spectrometer for stable water isotope analysis (2H, 18O). These isotopic ratios provided insights into the depth of root water uptake, aiding in the selection of crop varieties with effective water extraction from deep soil layers. Results revealed that sugar beets develop long roots capable of taking up water from deeper soil layers and adjusting their water uptake mechanisms when topsoil water availability is limited. The findings will inform more efficient agricultural practices, enhance crop resilience, and support sustainable water resource management.

Stable isotope ratios to identify seaweed-consumption and fertilisation in archaeology

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Despite plentiful historical and ecological evidence of the voluntary consumption of seaweeds by wild and domesticated animals (e.g. deer, coyotes, sheep, cattle) and humans, seaweed is often neglected as a potential food source in archaeological interpretations. For domesticated animals in particular, the study of seaweed consumption offers a unique opportunity to investigate the development of local adaptations to the coastal environment, and to study past land use and access.

By analysing stable carbon isotope ratios ($\delta^{13}C$) of skeletal material, direct evidence of seaweed consumption may be gained, as seaweed has higher $\delta^{13}C$ values than terrestrial C_3 plants. By analysing carbonate $\delta^{13}C$ and $\delta^{18}O$ values in sequential samples of teeth, detailed seasonal dietary information can be revealed. However, mixed diets of terrestrial C_3 and C_4 plants, as well as other marine foods, may result in similar $\delta^{13}C$ values as seaweed consumption, limiting the usefulness of bulk $\delta^{13}C$ analysis in this context.

In a field trial, fertilisation with seaweed showed elevated $\delta^{15}N$ values in barley crops, but $\delta^{13}C$ values appeared not to be affected. However, fertilisation with animal dung also leads to similar results.

This presentation will give an overview of the latest stable isotope ratio results with respect to seaweed use in archaeology, as well as future plans.

Fig. 1: Seaweed-eating sheep (Image: Ingrid Mainland)

The potential of Stable Isotopes to identify Permafrost degradation, Sattelkar Landslide, Obersulzbachtal, Salzburg

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The remote Sattelkar cirque and its neighbouring cirques are located in the Obersulzbachtal, Hohe Tauern Range, in an elevation range between approximately 2.100-2.800 m above sea level (asl). Strong surface displacements have been observed in the Sattelkar since 2005. The initial displacements triggered massive degradation of the vegetation cover and the exposure and enhanced mobilization of the debris cover. Terrain analysis revealed that a deep-seated, retrogressive movement in the debris cover of the cirque had been initiated. Heavy precipitation is assumed to cause spreading and sliding of the glacial and periglacial debris cover on the underlying, smooth bedrock cirque floor. Detailed aerial photo analyses, witness reports and damage documentations demonstrated that local mass movement and debris flow activity has steadily increased over the last decade. During this period, debris flows from the Sattelkar blocked the Obersulzbach river, and, in combination with the general flooding situation in the catchment, caused substantial destruction in the middle and lower reaches of the Obersulzbach river.

Since 2019, September, in the Sattelkar cirque creeks and springs between appr 2.200 and 2.600 m asl were sampled and analyzed for oxygen 18, oxygen 17 and deuterium against SMOW. To date, five field campaigns have been conducted to clarify the role of potential permafrost degradation regarding slope instability. In situ parameters like temperature and electrical conductivity were plotted and combined with stable isotopes analyses and compared with the observations of satellite imaging.

Preliminary results show clusters of (1) young precipitation, (2) precipitation, delayed by infiltration in the landslide and (3) melting out of formerly frozen soil (rock glaciers, moraines) can be distinguished.

These results support further investigations. The Sattelkar has three neighbouring cirques with nearly identical properties that follow at upper locations of the valley: the Ofenkar, Mitterkar and Steinkar. Despite similar topographical, climatological and hydrological conditions, no significant debris flow activity has been observed so far. Currently, it is not clear, why the Sattelkar is active and its neighbours are not. A mobilization of those cirques would endanger significantly the valley and the risk of further blocking of the Obersulzbach river. The preliminary results show the potential of stable isotopes to investigate permafrost conditions as a prerequisite to better understand the role of permafrost degradation as driving force destabilizing high alpine slopes.

Using isotopes to estimate groundwater recovery times from diffuse pollution

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The isotopes deuterium and oxygen-18 can be simple, yet powerful groundwater dating tools, especially if combined with tritium. In cases of diffuse pollution by agrochemicals in water protection zones, water managers (water providers or environmental agencies) will typically need to estimate the recovery times after the contaminants of interest have been banned or their input reduced. Such recovery times can be easily calculated using lumped parameter models calibrated from isotope measurements, and used effectively for planning purposes (for example will natural attenuation be quick enough, or should a treatment plant removing the contaminant be built?) and a factual analysis of long-term trends (for instance, how long will an upward trend continue after banning the contaminant?).
In this contribution, we will explain how to calculate recovery times from calibrated lumped parameter models as shown exemplarily in Figure 1, and present case studies drawn from the experience of the Luxembourg Water Agency in the management of groundwater protection zones.

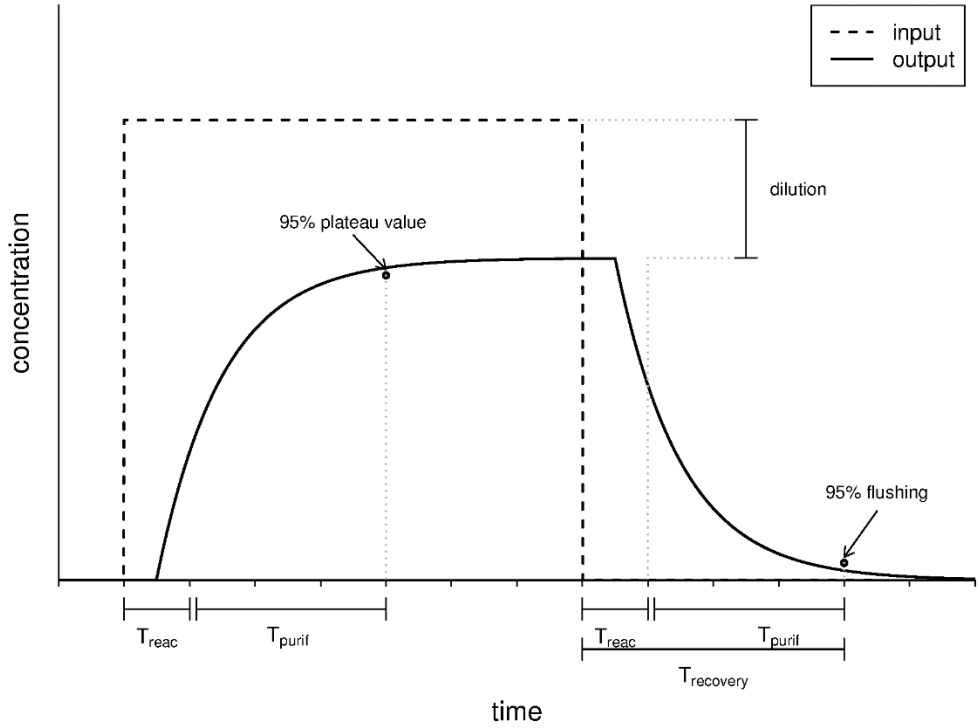

Fig. 1: Relationship between input, output and recovery times for a typical contaminant breakthrough curve.

Lessons learned from the spatiotemporal analysis of long-term and time-variable young water fractions of large Central European catchments

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The transit time of precipitation entering a catchment and leaving it as streamflow varies in space and time according to the flow paths that precipitation takes. However, investigating influences of hydrometeorological variables and catchment characteristics on time-variable transit times is challenging due to the complex water flow through heterogeneous landscapes. Recent studies investigated the fraction of streamflow younger than approximately three months (Fyw) using multi-year data (long-term Fyw) or one-year calculation windows to investigate its time-variability (time-variable Fyw). Nonetheless, it is still unclear if the inter-annual variability of one-year Fyw is due to hydrological influences or uncertainty, and no minimum time series length for the long-term Fyw was defined yet. Here, we investigated the impact of catchment characteristics and hydrometeorological variables on long-term Fyw, the time-variable Fyw, and the Fyw depending on discharge (discharge-sensitive Fyw) of nine major river basins in Central Europe. Additional to investigating hydrological processes, one- to eight-year calculation windows were used and their impact on the variability of the time-variable Fyw was investigated. All methods of estimating Fyw except for the discharge-sensitive Fyw led to similar results, with discharge-sensitive Fyw deemed unreliable most likely due to the monthly sampling interval of streamflow isotopes. The obtained results showed that Danube and Rhine had the lowest Fyw, medium Fyw were found in eastern basins (e.g., Oder), and the western ones (e.g., Mosel) had the highest Fyw. Further spatial analysis indicated a negative relationship between Fyw and altitude. Contradicting or lacking spatiotemporal relationships to other variables pointed to unknown influential factors controlling the runoff process. Using flow duration curves, it was found that basins with a low flow variability had low Fyw, indicating that the old water of their runoff stems from large subsurface storage. With increasing calculation window size, the within-basin variability of time-variable Fyw decreased. Long-term Fyw depended on the method used to define “long-term” and time series related factors such as its length and start and end date. We thus recommend future studies to calculate long-term Fyw using all data and one- to several-year time-variable Fyw to facilitate comparability between different catchments, and to account for this source of uncertainty. Further, more studies are needed in diverse catchments to investigate the hydrometeorological impacts on long-term, time-variable, and discharge-sensitive Fyw and thus on runoff generation processes.

Investigating the impact of land use, slope position, and soil heterogeneity on soil water fluxes in a small agricultural catchment

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For sustainable groundwater and land management, it is important to understand topsoil and vadose zone processes since they determine the fate of water and solutes and affect groundwater availability. Soil water fluxes and transit times are useful measures to describe soil water movement with implications for soil water quantity and quality. However, assessing the impact of different factors such as land cover, topography, and soil heterogeneity on spatial variability of soil water fluxes and transit times is laborious and costly. The objective of this study was to combine water stable isotopes with water content measurements to estimate average transit times and potential water fluxes under different land uses (winter wheat and grass) and slope positions (bottom, middle, and top). The results indicated shorter transit time (higher infiltration rate) and greater potential fluxes in grass profiles at the bottom of the slope compared to the top and in wheat profiles at the bottom compared to the middle slope position. However, it was not possible to confirm significant differences due to variability found inside the investigated groups. Transit times and fluxes varied among the replicates of wheat profiles within the same range at all slope positions and inside the range found in grass profiles. There was no clear difference between the land uses. Variability inside compared groups suggested the presence of soil structural heterogeneity, possibly affecting the infiltration mechanisms.

Identification of recharge processes in the shallow aquifer of Vienna

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The hydrogeology of aquifers in urban environments are often complex and not well-understood. We lack information about water and pollutant sources and recharge processes. This study therefore applied environmental tracers to identify recharge processes of the urban aquifer of Vienna (Austria). In two high-spatial resolution sampling campaigns (autumn 2021/ spring 2022) groundwater in 150 wells was collected and analysed for major ions, water stable isotope, nitrate isotopes and selected nutrients and pollutants.
A combined interpretation of conservative tracers (electrical conductivity and water stable isotopes) indicated zones influenced by surface water - groundwater interactions. These zones are close to the Danube river, local streams, and stagnant surface water bodies. Nitrate concentrations and stable isotopes, as well as waste water indicators (emerging contaminants) identified wastewater recharge areas. Nitrate concentrations exceeding the national limit (45 mg/L) at 26% of all analysed wells (spring 2022) and are predominant in the city centre and third district. It`s source was identified as manure and septic based on the isotopic fingerprint of nitrate (nitrate concentration > 45 mg/L: $\delta^{18}O_{NO3}$ between -3 and 15‰ and $\delta^{15}N_{NO3}$ between 5 and 19 ‰). The same spatial pattern is observed for emerging contaminants with additional local contamination across the city.
These findings highlight the complex and spatially variable flowpaths in the urban aquifer of Vienna and contribute to an improved understanding of its hydrological and geochemical processes.

Stable isotopes indicate sources and fate of sulfur in a modern analogue for the Baltic Sea freshwater stage

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Sulfur cycling in lakes is typically characterized by low concentrations in dissolved sulfate. This electron acceptor, on the other hand, is the major driver for the anaerobic mineralization of organic matter in brackish-marine systems. Post-glacial development in marginal seas like the Baltic or Black Sea is characterized by a transition from fresh to brackish water conditions, and sulfur isotope signatures of lacustrine sediments may be superimposed by diagenesis. To better understand the link between sulfate sources and the developing sedimentary sulfur isotope signatures in Lake Constance, the main inflows, the vertical water column profiles and sediment samples were isotopically (S, O) characterized.

It is found, that dissolved sulfate concentrations and stable isotope signatures for the two major riverine contributors, Alpenrhein and Bregenzer Aach, differ substantially in their isotopic composition and that the impact of the Alpenrhein dominates the sulfate contribution into the lake system. This contribution can be traced throughout the lake with some indication for potential minor sulfur cycling within the water column. The Bregenzer Aach loses water to an underground passage towards Lake Constance - as demonstrated by wells - water-rock interactions adding minor further sulfate to the groundwater.

The upper 10 cm of surface sediments indicate fast net dissimilatory sulfate reduction and the formation of iron sulfides that are isotopically close to water column sulfate, but depleted in the heavier isotope at further depth, indicating lower sulfate reduction rates in the past.

Biogeochemistry and hydrology of a tidal basin with the northern-most German submarine ground water discharge: A water and carbon isotope perspective

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The impact of fresh water sources like surface river and submarine groundwater discharge on the coastal water balance, element balances, and associated biogeochemical processes is currently a matter of intense debate and investigation. The measures of fresh water mixing in coastal areas has been found to be challenging, but stable water isotopes (O-16, O-17, O-18), best in combination with further hydrochemical tracers, provide a valuable tool to identify different fresh water sources, which are furthermore linked to different biogeochemical processes, e.g. impacting the benthic and pelagic carbon cycle.

In the present communication we report on combined investigations measurements in pore and surface waters of Königshafen Bay (North Frisian island Sylt), a tidal area in the eastern North Sea. Results are compared to investigations of potential surface and subterrestrial fresh water endmembers and the open North Sea, as well as the Elbe river estuary. Pore water results are furthermore compared to investigations in the backbarrier tidal area of Spiekeroog island. Besides dissolved major and minor elements, the stable water isotope composition is used to characterize the temporal and spatial distribution of different water sources for the bay and the seasonal dynamics in the water column. Besides vertical pore water profiles, also tidal cycles at the tidal outlet and transects through the pelagial of the bay were sampled. Porewater gradients indicate different degrees of freshening, locally already in the top 50 cmbf with spatial heterogeneity. Different fresh water endmembers are indicated both by the water isotope and hydrochemical signatures. It turns that at least two fresh water sources can be identified for sediments under impact by SGD, that differs in its composition from rivers and small inlets draining into the southern North Sea. Further work is on the way to investigate the dynamics in the (sub)surface fresh water sources for the tidal basin and the link to other geochemical tracers, as well as the coupling to the dissolved carbon system on different temporal and spatial scales.

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Seasonal and spatial multi-isotope hydrobiogeochemistry of a managed river draining into the southern Baltic Sea

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The composition of the Warnow draining fresh water into the coastal waters of the southern Baltic Sea (Germany) was investigated between years 2017 and 2022. A spatial study was carried out in April 2019 to follow the variations from the source to the estuary. A temporal study during a 6 years period was carried out at a site just before the river reaches the estuary. Surface water was sampled to analyze major and tracer elements, stable (H, C, O, S), and unstable (Ra) isotopes. The composition is controlled not only by its tributaries, but by a complex interplay between tributaries, in situ processes, exchange with the atmosphere, and diffuse groundwater. The river is impounded in a narrow lake-like system which increases the residence time of the water. This leads to increased evaporation and interaction with the surrounding sediments/soils. The river is a source of dissolved inorganic carbon to the estuary, which may further impact the Baltic coastal waters. The calculated CO_2 partial pressure was always found to be higher than the modern atmospheric value in north-western Europe, indicating that the Warnow River is a source of CO_2 to the atmosphere. In addition, due to CO_2 degassing and the photosynthetic activity, calcium carbonate can be formed in some parts of the river, which also causes a decrease in dissolved Ca concentrations. On a temporal scale, pH, nutrient, and redox sensitive trace element concentrations are strongly impacted by pelagic primary production in spring. During summer and autumn, influences occurred by benthic microbial activity, associated diffusive release from soils/sediments, and surface water inlets. The results of the present study highlight the need for a more detailed investigation of the surface water system discharging into coastal areas in order to better understand the coastal carbon cycle.

The study is supported by the DFG research training group BALTIC TRANSCOAST, DAAD, the BMBF project CARBOSTORE/COOLSTYLE, and Leibniz IOW

Establishment and application of the Ti(III) reduction method for analysis of nitrogen isotopes in water samples

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Human activity has led to significant alteration of the Global Nitrogen Cycle and exponential increase in the production and accumulation of reactive nitrogen (N_r), particularly nitrate (NO_3^-). Nitrate is commonly sourced from agricultural use of synthetic N-fertilizers and from animal and human waste. This has become a global source of concern due to pervasive pollution in both surface waters and shallow groundwaters and one prominent concern is the deterioration in drinking water quality due to high NO_3^- levels in water supply. Stable isotopes of nitrogen can be used to identify NO_3^- contaminant sources as different NO_3^- sources usually have distinct N and O isotopic signatures. As such, NO_3^- isotope data can be used to trace the movement of NO_3^- contamination, constrain areas of high contamination where use of N-fertilizers can be optimized and identify areas of natural bioremediation through denitrification. At the University of Natural Resources and Life Sciences (BOKU), we have established the Ti(III) reduction method which uses Ti(III) chloride to reduce NO_3^- to N_2O gas under a one-step chemical conversion. The converted N_2O gas is then used for the stable isotope analysis of $^{15}N/^{14}N$ and $^{18}O/^{16}O$ using PT-CF-IRMS. An interlaboratory comparison exercise comprising of ten international laboratories will be set-up for method validation and in-depth comparison between the Ti(III) reduction method and other diverse methods used for analysis of NO_3^- isotopes. We will also apply this method within various studies that aim to identify NO_3^- sources and estimate denitrification potential/rates. Ultimately, we hope to increase the scientific accessibility of aqueous NO_3^- isotope analysis in Austria.

Acquiring photosynthesis of cryoflora at remote field sites using stable isotopes (^{13}C)

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Psychrophilic microalgae (cryoflora) are found worldwide in extreme environments such as melting snow fields or glaciers. Due to pigments, blooms cause macroscopic discolorations or darken the ice surface. Up to date, the significance of this photoautotrophic productivity at high alpine and polar ecosystems has been neglected, despite such phenomena effect vast regions e.g. coastal Antarctica or the Western Greenland Icecap.
All kind of field measurements are tedious in such exposed and remote habitats, with limited time at the site. Thus, our aim was to establish a robust, user-friendly protocol based on the uptake of a supersaturated isotope label. An assay inspired by Havig & Hamilton (2019) was tested with field samples from the Alps and Arctic Svalbard, whereas strains were measured in a climate chamber.
In detail, borosilicate bottles were filled with snow, ice sluh or culture. Three replicates were either darkened (control) or exposed to irradiation (light samples) at about 0.5°C. Assays were started by addition of a ^{13}C labelled sodium hydrogencarbonate ($NaH^{13}CO_3$; 10 or 20 µM) and physiological processes stopped after incubation time (~1-4 h) by adding Lugol solution (JKJ), or by flash freezing (-80°). Cells were harvested onto glass fibre filters and dried prior to analysis.
Analysis of C and N concentration and isotope signals was conducted using an Isotope Ratio Mass Spectrometer coupled to an elemental analyser (EA-IRMS), and results were reported relating to the mass of organic carbon in the incubation material.
Preliminary data indicate $\delta^{15}N$ values ranging -7.6$\pm$0.53 to 12.13$\pm$0.71 and raw carbon uptake rates ranging 507.5$\pm$17.78 to 6580.62$\pm$569.82 µg ^{13}C/ g biomass/ h. This indicated differed N sources and confirmed that cryoflora is photoautotrophically active but shows pronounced differences between species and/or environmental conditions. Organic and inorganic impurities present in snow and ice did not allow for direct balancing of the microalgal biomass. The presented uptake rates are based on assumptions that only added $NaH^{13}CO_3$ was incorporated (due to oversaturation). Future attempts have to cover DIC measurements and mass balance calculations to improve the reliability.

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The status of ecosystem functions of polluted lands assessed in situ using plant, soil, and microbial indicators.

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The present research endeavor is committed to advancing the realm of ecological risk assessment pertaining to soils contaminated with metals, with a focus on developing and evaluating site-specific methodologies that can gauge ecologically significant processes directly in their natural environment. Traditional techniques employed to assess metal pollution in soils have encountered significant challenges, primarily stemming from an incomplete understanding of how such contamination influences soil ecosystems and their vital functions. In this investigation, we are delving into the persistent impacts of metal pollution on the intricate dynamics of carbon (C) and nitrogen (N) cycling within natural mixed conifer ecosystems located in proximity to historically contaminated sites.

Our approach revolves around a comprehensive examination of the consequences of metal contamination on various aspects of this ecosystem. Specifically, we are scrutinizing alterations in C and N content, isotopic compositions, water use efficiency, and microbial activity in the ecosystem's diverse components viz. soil, plant, and microorganisms. This multifaceted exploration aims to address a pervasive knowledge gap, which frequently results in the indiscriminate removal of contaminated soils, often without consideration of their potential benefits to the soil ecosystem.

The overarching goal of this research project is to bridge the existing knowledge deficit and establish a clear and actionable link between scientific insights and the demands of society. This connection is designed to furnish stakeholders with more precise and informed tools for conducting comprehensive risk assessments in metal-contaminated soil environments. By doing so, we aspire to provide a valuable framework that not only advances the field of ecological risk assessment but also enables more effective and sustainable decision-making, ultimately promoting the well-being of both ecosystems and the communities that rely upon them.

Keywords: Stable isotopes, Nutrient cycling, Heavy metal, Polluted site

The search for the GSSP for the Spathian-Anisian Boundary – a long story slowly approaching its end?

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The Spathian-Anisian Boundary (i.e. the boundary between the Lower and Middle Triassic, with the Triassic as oldest unit of the Mesozoic) has originally been identified in Upper Austria more than 100 years ago. The Austrian section later turned out unsuitable for the exact definition, as it includes a large fossil-barren interval in the immediate boundary region. The boundary was revised in the 1970-ies, however, also the new section on Chios proved unsuitable due to condensation and a fault. Since then, several attempts have been made to define the boundary elsewhere and to agree on a GSSP (Global Stratotype Section and Point). From palaeontological viewpoint there are very precise but diverging ideas on how to define the boundary, because between scientists there are two groups, one favouring ammonoids and a second preferring conodonts as primary marker for the boundary. The conodont group suffered a heavy blow when it turned out that the conodont *Chiosella timorensis* does co-occur with late Lower Triassic ammonoids and was thereon found to be unsuitable as index fossil.

We have worked and refined the stratigraphic resolution of two (Desli Caira/Romania, Kcira/Albania) of the three sections currently proposed as GSSP candidates. Furthermore, we have investigated new additional Spathian-Anisian boundary sections. We provide a tentative recommendation for the (in our opinion) most suitable section (which is Desli Caira, under certain conditions), and we believe to have resolved the problem related to *Chiosella timorensis*. However, we see it as premature to give a recommendation concerning the fossil boundary marker as this is more a matter of convention than a scientific question.

A trans-European decomposition index study in arable soils, focusing on the impact of different depths and plant diversity using a common 13C-labelled litter.

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Root carbon has been shown to be one of the most dominant forms of soils carbon inputs in agricultural systems. New paradigms about the decomposition of soil organic matter suggest the role of root derived soil carbon may have been overlooked. Current data and knowledge do not allow for prediction of the fate of root derived SOC storage in agricultural soils, specifically in relation to soil-depth and the complexity of the standing crop or intercrop.

Mixed species systems are currently gaining traction Europe providing opportunities for sustainable intensification of agriculture and other ecosystem-service co-benefits. Agroforestry systems cover about 9% of the utilized agricultural area and integrated crop livestock systems are both historically and culturally important in European agriculture, as they include perennial forage grasses and grasslands. Intercropping and other mixed cash crop systems are currently less developed in the EU. The aim of the EU EJP-SOIL funded MIXROOT-C and MAXROOT-C projects (2021-2024) is to gain a management-oriented understanding of the effect of mixed-species root systems on carbon flow and organic matter accumulation in European agricultural soils.

As part of the project, we have conducted a pan-European in-situ field experiments across pedo-climatic conditions. Treatments include:((i) monoculture (1 species), (ii) low diversity (2-4 different plant species in the mix culture) and (iii) high diversity (≥ 5 different plant species in the mix culture)) and different soil depths. The goal is to determine the impact of increased plant diversity and soil depth on the organic matter breakdown in both the topsoil (0-15 cm) and sub soil and to develop a trans-European decomposition index. To achieve this, we monitored the decomposition of 13C-labelled maize litter in mixed agroecosystems and in the main crop monocultures across Europe. Using a hub spoke design, a common 13C-labelled maize material was supplied to each participant and was mixed in a similar manner with the local soil from the treatment plots, packed in mesh bags and buried in the treatment plots. This was then excavated after six months and returned to Vienna for analysis.

This experiment, which includes many sites, climates and cropping systems, will provide key information on the rate of litter decomposition and the inclusion of litter C in different soil OM pools depending on the climatic condition, soil type and management. Furthermore, the experiment will provide information on litter turnover and link this process to soil C storage. We will present data on the effect of increased crop species diversity on the rate of decomposition of litter. We will test the null hypothesis that increased plant diversity does not increase the decomposition rate in the field. Moreover, we will investigate if increased depth leads to decreased OM decomposition. Data will be used to model the fate pf belowground C inputs in single and mixed species systems at different soil depths.

Keywords* Mixed cropping, Diversity, 13C labelled, Maize litter, Monoculture, Carbon

Timing of an Alpine water cycle unraveled by water isotopes and age-dating tracers (^{3}H, ^{3}He, ^{14}C, CFCs, SF_6 and ^{222}Rn), Eastern Alps, Austria

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Alpine regions are important as "water towers" in regional water supply of clean groundwaters due to their increased precipitation rates and their unspoiled environment. However, they are often characterized by complex geology structures, covered by down-sliding glacio-fluvial sediments. Groundwater recharge conditions and mean transit times (MTTs) are fundamental components of mountain watershed hydrological systems. Here, we used measurements of stable water isotopes of precipitation, pore water, surface and groundwater. In addition, measurements of environmental age tracers (^{222}Rn, CFCs, ^{3}H, ^{3}He, ^{4}He and ^{14}C) were performed to investigate groundwater MTTs from springs in glacio-limnic sediments (<20 m) and deeper wells (>20 m) located along a mountainous hillslope (1,400-800 m) within the Subersach watershed near Sibratsgfäll, Bregenzer Wald, Austria. The near surface spring waters contain ^{3}H and CFCs in excess. The deeper artesian well samples contain ^{3}H and CFCs, in addition to elevated terrigenic ^{4}He and low ^{14}C values, suggesting a mixture of waters characterised by residence times that are modern (<70 years) and pre-modern (>70 years). We show that binary-mixing MTT models with distinct young and old fractions are needed to explain the full suite of environmental tracers, further supporting the importance of groundwater mixing processes.

The vertical unsaturated infiltration in silt/sand dominated glacio-lacustrine sediments were estimated by seasonal variation of $^{2}H/^{18}O$-isotopes in pore-water to be 1-4 m/year approximately. Precipitation in the Flysch dominated area at higher altitudes is transported partly as mountain bloc recharge and ascends into the glacial sediments, indicated by temperatures 2-3° C higher than the mean surface temperature. The MTTs of the shallow groundwater (<20 m) estimated by a combination of isotopes $^{2}H/^{18}O$, $^{3}H/^{3}He$, $^{13}C/^{14}C$ and tracer gases (CFC, SF_6) indicate ages between some months and 4 years. Radon measurements identify springs supplied by very young drainage or surface waters. Deeper (>20 m) artesian wells in the western part are dominated by MTT older than 70 years.

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NAWI Graz Core Facility: Stable Isotopes

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Stable isotope results find applications in a broad spectrum of fields, including the earth and analytical sciences, archaeology, and palaeoanthropology. The NAWI Graz Core Facility: Stable Isotopes at the Department of Earth Sciences at the University of Graz provides high-precision stable isotope analysis capabilities encompassing several research subjects. The core facility offers fast and user-friendly solid and liquid sample analysis using a state-of-the-art isotope ratio mass spectrometer (IRMS) and two peripheral preparation lines (isoFLOW and PYROcube) produced by Elementar Analysensysteme GmbH. The Elementar isoFLOW system delivers the capability for the analysis of $\delta^{13}C$ and $\delta^{18}O$ in carbonate phases as well as δD and $\delta^{18}O$ analysis in liquids (e.g., water, urine, wine, juices) measured by a single preparation line using continuous-flow isotope ratio mass spectrometry (CF-IRMS).

Our second peripheral, the Elementar PYROcube, provides combined combustion-based elemental analyser isotope ratio mass spectrometry (EA-IRMS) and high-temperature pyrolysis isotope analysis (HTP-IRMS). Thanks to the unique Advanced Purge and Trap (APT) technology of Elementar for separating and focusing post-combustion gas mixtures, this preparation line can analyse a diverse range of solid samples and deliver multi-elemental isotopic analysis on a single sample. In the EA-IRMS combustion mode, $\delta^{13}C$, $\delta^{15}N$, and $\delta^{34}S$ stable isotope ratio can be measured, while the analysis of δD and $\delta^{18}O$ is conducted in the HPT-IRMS pyrolysis mode. We can process dry bulk sample material from organic substances (plants and animal tissues) to natural soil and sediment samples and various natural and industrial mineral phases and compounds.

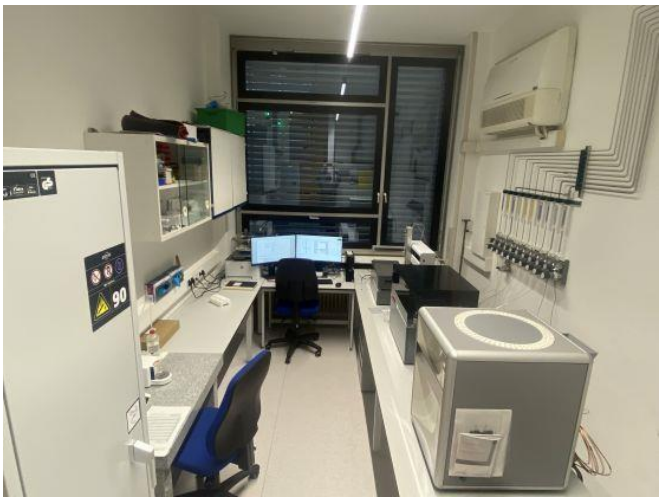

Fig. 1: NAWI Graz Core Facility Laboratory.

Regionalization of stable isotope data (oxygen-18 and deuterium) in Swiss precipitation for hydrological studies

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This study focuses on regionalizing stable isotope data (oxygen-18 and deuterium) in Swiss precipitation on a monthly basis, using data from the ISOT isotope observation network in Switzerland. The main influencing variables (e.g., topographical and climate variables) are tested in a multi-regression framework, and the residuals are interpolated by the use of ordinary kriging. The tests are performed by cross-validation, also to provide information about regional differences of the interpolation quality. The resulting monthly "Isoscapes" provide insights into the spatial variability of these isotopes, with an example shown for January 2013 in Figure 1.

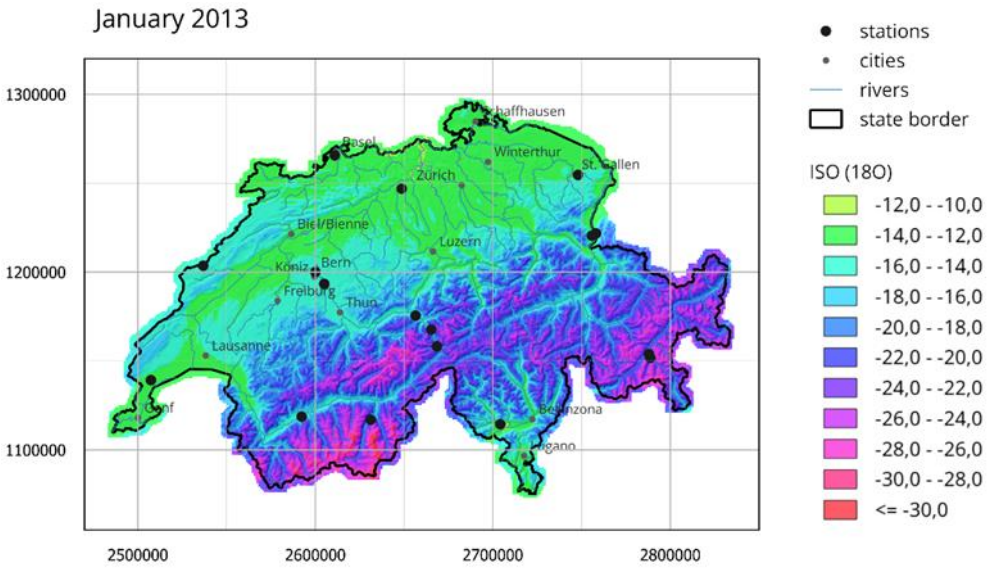

Fig. 1: Calculated pattern of oxygen-18 in precipitation in January 2013 for Switzerland in a 500m raster (Swiss reference system: CH1903+ (LV95)).

The figure illustrates the high spatial variability in this month due to the topography (e.g., differences between the Plateau and the Alps) as well as the different climate zones (e.g., higher values in the south). Monthly time series may be derived from the isoscapes for each geographical location, serving as valuable input for hydrological data analysis and modeling. This data resource presents novel opportunities in the realm of water transport and quality investigations, facilitating nuanced exploration of the associated atmospheric and hydrological mechanisms. These monthly isotope data patterns in precipitation, known as isoscapes, are accessible for specific years (2013 and 2020) through the Swiss Federal Office for the Environment (FOEN), having undergone rigorous testing and validation.

Detection of climate change induced drought stress at Rosalia forest using stable isotope methods (^{13}C,^{18}O)

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Climate change poses an enormous challenge to native forests. Spruce is high-yielding, easy to manage and has a number of economic advantages over hardwood production. As a result, it is the most economically important and common tree species in Austrian forestry. Spruce is a shallow rooter and therefore has less access to deeper soil moisture, which makes it particularly susceptible to drought stress. Trees that suffer from altered site conditions are likely to be more susceptible to disease and pest infestation than trees that are not exposed to additional site stresses. To identify sites that have suffered from drought in the past and are susceptible to pest attack, stable isotopes in tree rings are ideal: stable isotope composition in tree rings provides retrospective information about tree response to past environmental conditions. The carbon isotope signature provides reliable information about the drought stress to which the tree was exposed during extreme events, on an annual basis over decadal time periods. This can be used to assess the success of any adaptation the plant may have undergone, or whether it has exceeded its resilience and consequently reduced its resistance to insect pests.

The study area is located in the Rosalia mountains of Lower Austria at an elevation of about 700 m above sea level. It is an old spruce stand (P. abies) intermixed with beech (Fagus sylvatica), which allows us to study the effects of prolonged drought and the response of the trees in the last 5 decades. We present preliminary results of carbon isotope analyses of tree rings and attempts to visualize drought stress with drone techniques combined with stable isotope approaches.

Influence of alpine ranges on the isotope signature in precipitation in Austria

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Air masses of different origin with different isotope signatures collide in the alpine region and provide different input signals for the terrestrial part of the hydrologic cycle. They allow detailed conclusions about the origin, the subsurface path and the residence times of groundwater and surface water.
The amount of annual precipitation (400-3000 mm/a in Austria) increases towards the mountain ranges. Strong regional differences exist between the windward and the lee side of the Alpine ranges. The Alps act as a weather divide and sharply distinguish precipitation events caused by different air inflow directions (mainly from the Atlantic, but also from the Mediterranean).
The differences in the $\delta^{18}O$ values of sampling stations at similar altitudes can be explained by the origin of the air moisture. An Atlantic influence (moisture from NW) causes lower $\delta^{18}O$-values than a Mediterranean one. The main reason for these different $\delta^{18}O$ values is the longer path of the Atlantic air masses over the continent with increasing depletion in heavy isotopes due to successive rainout (continental effect). Significant variations of the deuterium excess in precipitation in the Alps (higher values at the mountains, lower values in the valleys and forelands) are mainly a consequence of the local orographic conditions and not the result of a different origin of the air masses transported into the mountainous region.
The tritium content of precipitation shows also spatial variability caused by different origin of air masses. The influence of air moisture from the Mediterranean causes lower ^3H contents in precipitation in the southern parts of Austria due to the shorter travel time of these air masses over the continent and therefore less admixture of ^3H bearing continental air. The ^3H content at the Villacher Alpe (southern Alpine region), for instance, is about 30 % lower than at the Feuerkogel (northern Alpine region).
The application of isotope methods for hydro(geo)logical and climatological investigations in the Alpine region with often local air flow systems requires a relatively dense precipitation measurement network for the determination of the isotope input data (precipitation) for the terrestrial part of the hydrologic cycle.

Traceability of fruit and vegetables

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Since 2017, the Austrian Trade Association for Fruit and Vegetables (ÖBOG) has been carrying out origin analyses on fruit and vegetables in collaboration with project partners from the sector. The aim of this project is to safeguard the Austrian origin and maintain or strengthen customer confidence, as well as to raise awareness in the industry of problems relating to origin and labelling. After market samples are gathered from all over Austria, they are analysed by Imprint Analytics GmbH. The analysis system is designed to compare reference samples with market samples. Reference samples are acquired directly from Austrian agricultural producers on the one hand and foreign producers that are located in the area of interest for the respective crop on the other. Market samples come from the food retail trade and direct marketing, where the advertised Austrian origin is checked. Over the years, origin analyses have been conducted for apples, tomatoes, cucumbers, peppers and apricots. Thanks to ÖBOG's close cooperation with the authorities, suspicious results can be investigated and the necessary steps can be taken.

Method for determining the origin of water damage

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Understanding water damage, localizing it, and determining its source pose major challenges for those concerned, for experts, and for insurance companies. Particularly in buildings, the water pathways and thus the origin of the damage water are often difficult to trace. Often, for example, the question arises as to whether the damage water is rainwater that has penetrated from the outside or tap water.
In these cases, the method of determining deuterium and oxygen-18 of the water molecule has proven to be a practicable and low-invasive method, which allows quick and cost-effective results on the origin of damage water.
Water consists of a mixture of frequently and rarely occurring hydrogen and oxygen isotopes. In the water cycle, these isotope mixtures are subject to constant change through so-called fractionation processes, which in the case of the water molecule are mainly caused by evaporation and condensation. Measurements of global precipitation have revealed an approximately stable linear relationship in the concentration of these isotopes in the seasonal course, which can be represented by the so-called global meteoric water line (GMWL). Fresh water, on the other hand, is mostly derived from groundwater, which, due to longer residence times in the subsurface, forms a stable mixed signature specific to the local climate. These differences are used for damage characterization.
Damage and reference water samples are analyzed for their deuterium and oxygen-18 signatures. Taking into account the boundary conditions, it is possible in many cases to distinguish between damage and reference waters, so that statements can be made with regard to the origin of the damage water.

Characterization of the flow regime in a karst aquifer using stable water isotopes (Hochschwab, Austria)

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About half of the drinking water consumed in Austria originates from karst springs. However, the behaviour of the water within the karst systems, such as mixing of new and old water, is not yet well understood. Stable water isotopes represent one important tool for studying flow regimes in natural systems and enable to calculate mixing ratios between infiltrated and stored water. In this study, we sample precipitation as well as drip water in a cave (Hirschgrubenhöhle) in the upper vadose zone, as well as at the Kläffer springs at the base of the Hochschwab to better understand the hydrological processes in the karst system. Water stable isotopes (δ^2H and $\delta^{18}O$) are analysed for precipitation and runoff. Additionally, discharge, electrical conductivity and water temperature measured at both runoff sites allow for comparing different karst zones. The cave drip water, with a small catchment of ~ 60 m² and a soil cover of ~ 0.3 m, as well as epikarst thickness of up to 6 m (Fig. 1), shows a reaction to the precipitation event of ~ 25 mm after ~ 18 hours while the Kläffer springs reacts later (~ 21 hours). Mean isotope values for precipitation are -11 $\delta^{18}O$ / -66 δ^2H, for cave drip water -10 / -62 and -11 / -76 at the Kläffer springs, respectively. Preferential rain-out of heavy isotopes can be observed in the precipitation. While the signal of newly infiltrated water is clear at the cave water (Hirschgrubenhöhle), there is no such effect at the Kläffer springs. This confirms the higher buffer capacity at the downstream end of the drainage system at the Kläffer springs. This approach shows that the use of multiple tracers is necessary to distinguish between old and young water and bears great potential to characterise flow regimes and storage behaviour of water in karst systems.

Fig. 1: Entrance of the cave “Hirschgrubenhöhle” and karst landscape in the background shows the catchment of the cave drip water. View towards NW.

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