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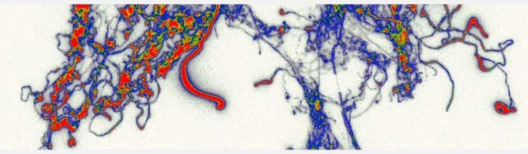
BayCenSI

GASIR

42. Meeting of the German Association for Stable Isotope Research 2023

27.-29. September 2023



Book of Abstracts

Bayreuth Center of Ecology
and Environmental Research
BayCEER

DFG
Deutsche
Forschungsgemeinschaft

Welcome to Bayreuth!

Dear Esteemed Colleagues and Participants,

On behalf of the Local Scientific Committee and as hosts of the GASIR 2023 annual meeting in Bayreuth, Bavaria, we are delighted to extend to you a warm and enthusiastic welcome.

This year holds special significance as we return to Bayreuth for the third time, reinforcing the city's reputation as a hub of expertise in Isotope Biogeochemistry. The establishment of the DFG Core Facility BayCenSI (Bayreuth Center for Stable Isotope Research in Ecology and Biogeochemistry) at the University of Bayreuth (UBT) and within the Center for Environmental and Ecosystem Research (BayCEER) has further solidified our commitment to advancing stable isotope research.

Bayreuth's scientific community has a rich history, with a strong focus on Soil and Plant interactions and a renowned Geo-Ecology program. The introduction of stable isotopes into research areas such as limnology and microbial ecology represents a significant expansion of our capabilities. As hosts, we are proud to facilitate the convergence of expertise from various fields within the realm of stable isotope research.

With over 115 participants representing more than 20 Universities, 18 research institutes, and nine companies from 10 countries within and beyond the European Union, we have assembled a diverse and dynamic group of experts. This diversity promises to create a fertile ground for exchanging ideas, establishing collaborations, and initiating fruitful discussions that will advance the frontiers of stable isotope research.

As we convene in Bayreuth, we invite you to immerse yourself in this unique gathering. Take advantage of this opportunity to share your knowledge, connect with colleagues, and explore the ever-evolving landscape of stable isotope research. Together, we can celebrate our past achievements while charting new paths toward a deeper understanding of the natural world.

Our heartfelt thanks go to the DFG for their funding, the BayCEER for their support in organizing, our sponsors, and our international selection of keynote lecturers. Finally, we want to thank each of you for contributing to the success of GASIR 2023. Your presence enriches our community, and your contributions are invaluable.

We are excited to welcome you to Bayreuth and anticipate stimulating conversations and exciting discoveries presented during our time together. May this meeting be enlightening and enjoyable, leaving you with valuable memories and meaningful professional relationships.

With warm regards,
The Local Scientific Committee

Scientific Committee and Conference Organization

The Local Scientific Committee of the GASIR 2023 Meeting consists of:

- Susanne Baldermann
- Alexander H. Frank
- Gerhard Gebauer
- Eva Lehndorff
- Tillmann Lüders
- Johanna Pausch

The organization and logistics of the conference are managed by:

- Alexander H. Frank
- Verena Faßold
- Birgit Thies
- Stefan Holzheu
- Gerhard Müller

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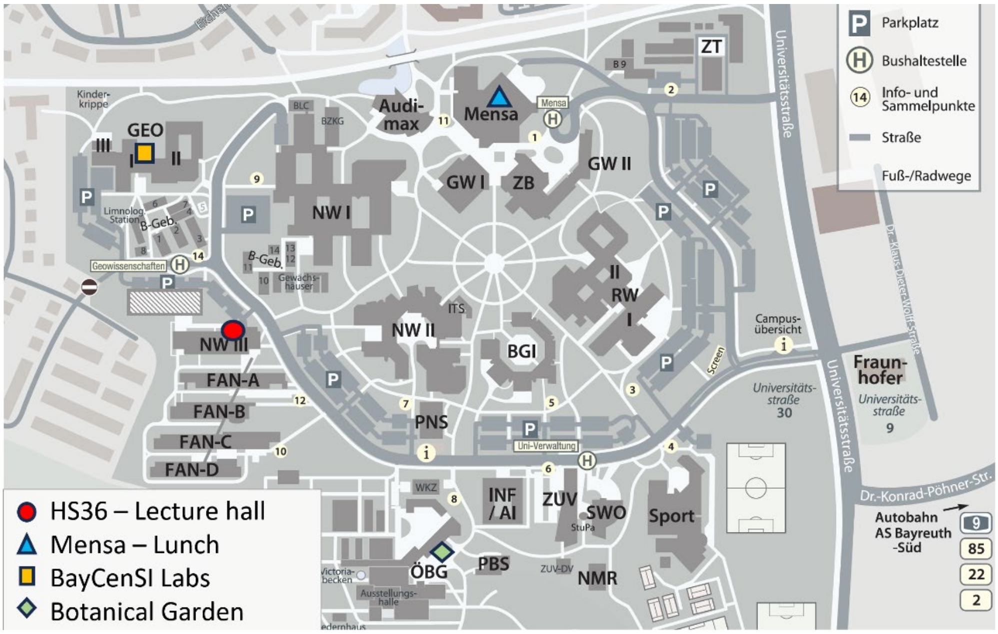
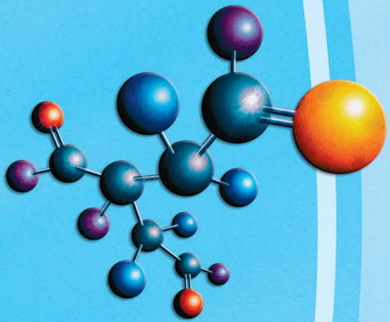
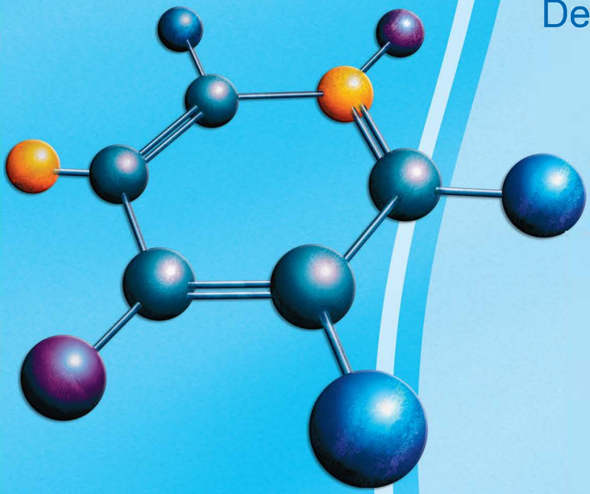
Directions



Time	Wednesday, 27.09.2023, HS 36:
11:00	**Registry and Coffee**
12:30	**Conference Opening**
13:00	**"Trophic Interactions, Organic Matter, and Nutrient Cycling"** Keynote 1: **Liliane Rueß**: Stable isotopes in trophic ecology
13:30	O 1.1: **Claudia Guidi et al.**: Tracing sources and turnover of soil organic matter in a long-term irrigated dry forest using a novel hydrogen isotope approach
13:45	O 1.2: **Guido Wiesenberg et al.**: Combination of molecular markers and isotopes for improved assessment of the impact of warming on organic matter cycling in plant-soil systems
14:00	O 1.3: **Xiaolei Sun et al.**: Depth distribution of phosphate ^{18}O isotope values along the Paposo transect
14:15	O 1.4: **Franziska Zahn et al.**: Do common shade-tolerant tropical tree and shrub saplings exhibit a partially mycoheterotrophic form of nutrition?
14:30	**Coffee break**
15:00	**Climate Change and Physiology** O 2.1: **Christiane Werner et al.**: Whole ecosystem $^{13}CO_2$ and $^{2}H_2O$ and metabolite labeling to trace drought response from leaf/roots to ecosystem scale and investigate the role of deep-water reserves during drought recovery
15:15	O 2.2: **Laura Kinzinger et al.**: Continuous in-situ water stable isotopes show the effect of species identity on water use after precipitation events
15:30	O 2.3: **Angelika Kübert et al.**: Plant water relations during drought and recovery in an experimental rainforest
15:45	O 2.4: **Matthias Beyer et al.**: Vegetation controls spatial patterns of soil water isotopes in a tropical dry forest and UAV can help to predict demand
16:00	O 2.5: **Lars Erik Daber**: Position-specific isotope labelling gives new insights into chiral monoterpene synthesis of Norway spruce (*Picea abies* L.)
16:15	O 2.6: **Ruth-Kristina Magh et al.**: Practical measurements of water stable isotopes in tree stems and soils using conservative water vapor storage
16:30	**Poster Session A** with poster numbers P1.1 - P3.7
18:00	
19:00	**Conference Dinner at the Lohmühle restaurant**

Time	
08:30	**Morning Coffee**
09:00	**Earth System Science and Reconstruction** Keynote 2: **Hagit Affek et al.**: ^{17}Oexcess in Soreq Cave speleothems
09:30	O 3.1: **Marika Stutzriemer et al.**: Ongoing paleoenvironmental research in the Fotsch Valley – first oxygen isotope records derived from hemicellulose sugars of two subalpine mires
09:45	O 3.2: **Michael Zech et al.**: A late glacial and Holocene ^{18}O paleoclimate record form the afro-alpine Wulf Lake, Bale Mountains, Ethiopia
10:00	O 3.3: **Michael E. Böttcher et al.**: An isotope view on hydrology and carbon cycling in a tidal basin under impact by submarine groundwater discharge
10:15	O 3.4: **Rhodelyn Saban et al.**: Isotope biogeochemical dynamics of pore waters under impact by submarine ground water discharge after removal of coastal protection
10:30	O 3.5: **Cátia Milene Ehlert von Ahn et al.**: Benthic processes in tidal basins release isotopically light DIC to the southern North Sea
10:45	O 3.6: **Diana Burghardt et al.**: Investigations on the origin of mineral waters by analysis of stable isotopes of water and sulfate
11:00	**Poster Session B** **with poster numbers P4.1 - P6.2**
12:30	**ELEMENTAR Lunch & Learn (30')**
13:30	**Isotope Award Session**
14:30	**Coffee break**
15:00	**Environment and Pollution** Keynote 3: **Martin Elsner et al.**: Isotope fractionation reveals limitations and microbial regulation of pollutant biodegradation at low concentrations
15:30	O 4.1: **Arno Rein et al.**: Characterization of pesticide fate in the unsaturated zone using numerical transport modeling and stable carbon isotopes
15:45	O 4.2: **Tobias Goldhammer et al.**: Phosphate oxygen isotope insights into lacustrine phosphorus cycling
16:00	O 4.3: **Jonas Hädeler et al.**: Natural abiotic iron-oxido-mediated formation of C1 and C2 compounds from environmentally important methyl-substituted substrates
16:15	O 4.4: **Moritz Schroll et al.**: Methane accumulation and its potential precursor compounds in the oxic surface water layer of two contrasting stratified lakes
16:30	**ASI general meeting**
19:00	**THERMO User Meeting**





Time	Friday, 29.09.2023: H 36
08:30	**Morning Coffee**
09:00	**Methods, Models, Standards** Keynote 4: **Sergey Assonov**: Towards compatibility of stable isotope datasets: Progress with new reference materials and related concepts.
09:30	O 5.1: **Andreas Hilkert et al.**: ESI-Orbitrap IRMS: A revolutionary tool with pros and cons
09:45	O 5.2: **Sarah P. Rockel et al.**: Two dimensional LC-IRMS – The future of CSIA?
10:00	O 5.3: **Markus Greule et al.**: Accurate and comparable site-specific stable carbon isotope ratio measurement of vanillin methoxy group by IRMS and ^{13}C-qNMR
10:15	O 5.4: **Sam Barker et al.**: Analysis of dissolved nitrate stable isotopes using the one-step Ti (III) reduction method and Elementar EnvirovisION System
10:30	**Extended Coffee Break**
11:15	O 5.5: **Montana Puscas et al.**: Laser ablation IRMS – the minimally destructive alternative for in-situ δ^{13}C analyses of solid or liquid matrices
11:30	O 5.6: **Lucas Bittner et al.**: A new oxygen-free HTC pyrolysis reactor – first insights and results
11:45	O 5.7: **Joachim Mohn et al.**: Clumped isotope laser spectroscopy of non-CO_2 GHGs
12:00	**Life Science, Forensics and Medicine** O 6.1: **Nils Kuhlbusch et al.**: Isotopologue ratio analysis in organic compounds using ESI-FTMS: origin of caffeine in foods
12:15	O 6.2: **Frank Hülsemann et al.**: IRMS of urinary norandrosterone in doping control analysis
12:30	O 6.3: **Helena Engel et al.**: Assessment of energy expenditure using doubly labelled water during an altitude training camp in elite alpine skiers
12:45	O 6.4: **Frank Keppler et al.**: Radical-driven methane formation in humans evidenced by stable isotope studies
13:00	**Announcements & Conclusions** Poster & Talk Prizes
13:30	
14:30	**Guided Tour Ecological-Botanical Garden**

Timing of Sessions

1 Trophic Interactions, Organic matter, and Nutrient Cycling
Wed.27.09.2023 13:00-14:30, H 36 & Wed. 16:30-18:00 (PSA)

2 Climate Change and Physiology
Wed 27.09.2023 15:00-16:30, H 36 & Wed. 16:30-18:00 (PSA)

3 Earth System Science and Reconstruction
Thu 28.09.2023 09:00-11:00, H 36 & Wed. 16:30-18:00 (PSA)

4 Environment and Pollution
Thu 28.09.2023 15:00-16:30, H 36 & Thu. 11:00 -12:30 (PSB)

5 Methods, Models, Standards
Fri 29.09.2023 09:00-12:00, H 36 & Thu. 11:00 -12:30 (PSB)

6 Life Science, Forensics, and Medicine
Fri 29.09.2023 12:00-13:00, H 36 & Thu. 11:00 -12:30 (PSB)

Oral Presentations

1 Trophic Interactions, Organic Matter, and Nutrient Cycling

Keynote 1: H 36, 27.09.2023, 13:00-13:30

Stable isotopes in trophic ecology

LILIANE RUEß[1]
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Stable isotope ratios of plant and animal tissue are a useful tool for reconstructing dietary habits, describing trophic relationships, and constructing food webs. As a result, the number of studies using carbon (d^{13}C), nitrogen (d^{15}N), and hydrogen (d^{2}H) in trophic ecology has increased strongly over the past decade. To understand consumer dietary needs and resource use, researchers have employed a variety of methods, including bulk stable isotope analysis (SIA) as well as compound specific stable isotope analysis (CSIA) of fatty acids and amino acids. This presentation will give an overview of these methods and provide recommendations for method selection. The different approaches are illustrated using studies at the natural abundance level as well as enriched physiological tracers, with a focus on soil food webs. In addition, the innovative methods of fatty acid isotopomer and isotopologue profiling are presented, which are not yet widely used in ecological studies, but have the potential to overcome some of the limitations of current techniques. Combining the different isotope-based applications with further empirical studies of individual dietary habits, promises to greatly advance food web ecology.

O.1 Trophic Interactions, Organic Matter, and Nutrient Cycling

O 1.1: H 36, 27.09.2023, 13:30-13:45

Tracing sources and turnover of soil organic matter in a long-term irrigated dry forest using a novel hydrogen isotope approach

CLAUDIA GUIDI[1], MARCO M. LEHMANN[1], KATRIN MEUSBURGER[1], MATTHIAS SAURER[1], VALENTINA VITALI[1], MARTINA PETER[1], IVANO BRUNNER[1], FRANK HAGEDORN[1]
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The contribution from foliage, roots, and fungi to soil organic matter (SOM) is still largely unknown. Since stable hydrogen isotope ratios (δ^2H_n) can differ among sources, we explored δ^2H_n to elucidate sources contribution to SOM. We also assessed whether addition of ^2H-depleted water allows tracing new organic H incorporation into SOM.

In a 17-year-long irrigation experiment in a dry forest, we measured δ^2H_n and stable carbon and nitrogen isotope ratios ($\delta^{13}C$, $\delta^{15}N$) in sources, bulk SOM and fractions, and estimated source contribution to SOM by Bayesian mixing models.

The δ^2H_n increased from foliar litter (-153‰) to fine roots (-118‰) and fungal mycelia (-81‰). Mixing models indicated that foliar litter dominated organic layers (69±15%) and coarse particulate organic matter (POM) at 0-5 cm (65±12%). In contrast, roots dominated fine POM at 2-5 cm (58±12%). Fungal mycelia contributed only to 1-5% of POM, but to 5-25% of mineral associated organic matter (MOM).

The soil water ^2H-depletion with irrigation was paralleled by 11‰ lower δ^2H_n in coarse POM of irrigated vs dry plots, indicating organic H turnover of less than 17 years. In contrast, δ^2H_n in fine POM and MOM decreased only by 3‰ with irrigation, implying organic H turnover of about 30 years.

Our study showed that δ^2H_n allowed a clear differentiation among SOM sources. Long-term ^2H-labelling by irrigation indicated higher organic H turnover in coarse vs fine fractions, offering a novel tool to identify SOM cycling.

O.1 Trophic Interactions, Organic Matter, and Nutrient Cycling

O 1.2: H 36, 27.09.2023, 13:45-14:00

Combination of molecular markers and isotopes for improved assessment of the impact of warming on organic matter cycling in plant-soil systems

GUIDO WIESENBERG[1], TATJANA SPECKERT[1], DARIO PÜNTENER[1], NICHOLAS OFITI[1], CYRILL ZOSSO[1], MARGARET TORN[2], JENNIFER SOONG[2], ELAINE PEGORARO[2], MICHAEL SCHMIDT[1]
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Global warming has severe impacts on plant-soil systems. However, the assessment of climate change-driven impacts on organic matter (OM) cycling and storage in plant-soil systems remain largely unknown. Consequently, several warming experiments at field scales like the SPRUCE open-top chamber experiment (Minnesota, USA) and the Blodgett Forest warming experiment (California, USA) were initiated. We combined findings from both sites with laboratory experiments and applied molecular markers as well as bulk and compound-specific isotopes. In peat, the active acrothelm got deeper with warming and thus enabled improved root growth and consequently OM input and cycling. In contrast, lower moisture in deep oxic soils resulted in unfavorable conditions for root growth and therefore less OM input. In-situ decomposition experiments of ^{13}C-labeled root litter highlighted that warming has a strong impact on the microbial community composition and degradation of OM, while spatial variability and accessibility of OM in subsoils can have an even higher impact on decomposition of organic matter than warming. Further, laboratory experiments using ^{13}C-labeled litter showed that soil microbial communities seem to have a certain temperature optimum, beyond which decomposition of OM might get reduced, again. The chosen combination of different experiments using molecular markers, stable isotopes and isotope-labeling experiments enabled an improved assessment of the impact of future warming on OM cycling in plant-soil systems.

O.1 Trophic Interactions, Organic Matter, and Nutrient Cycling

O 1.3: H 36, 27.09.2023, 14:00-14:15

Depth distribution of phosphate ^{18}O isotope values along the Paposo transect

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[2] Institute of Crop Science and Resource Conservation (INRES)-Soil Science and Soil Ecology, Rheinische Friedrich-Wilhelms-University Bonn, Germany
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The extreme conditions of the Chilean Atacama Desert preserve life's fingerprints. The subsoil, in particular, offers protection for microbial communities. Our study sampled at Paposo four pits at 10 cm intervals, reaching a depth of 2 m, along a transect with increasing distances from the coast and thus aridity. The oxygen isotope composition of HCl-extractable phosphate ($\delta^{18}O_{HCl\text{-}Pi}$) analysis was conducted to explore the biological P cycling. None of the measured values of $\delta^{18}O_{HCl\text{-}Pi}$ fell within the equilibrium range, indicating that soil phosphate had only undergone partially biological cycling. However, variations were observed at different depths. In the fog-nourished zone near the coast (3.5 km), the highest $\delta^{18}O_{HCl\text{-}Pi}$ value of 16.6 ‰ was found at the surface, gradually decreasing with depth. However, a relatively higher value of 15.8 ‰ was detected at a depth of 80–90 cm, pointing to wetter period in the past. At a location 13.4 km from the coast with rare rainfall, both profiles had lower average $\delta^{18}O_{HCl\text{-}Pi}$ values of 8.9 and 7.7 ‰ at the surface, in an active and abandoned section respectively. Interestingly, in the abandoned section, the value increased to 13.1‰ in the second layer (10–20 cm), while it remained stable in the active section. This suggests that topography plays a role in detecting past signs of life. Our investigation sheds new light on the historical presence and variability of (microbial) life in relation to changes in soil wetness due to climate fluctuations.

O.1 Trophic Interactions, Organic Matter, and Nutrient Cycling

O 1.4: H 36, 27.09.2023, 14:15-14:30

Do common shade-tolerant tropical tree and shrub saplings exhibit a partially mycoheterotrophic form of nutrition?

FRANZISKA ZAHN[1], BETTINA ENGELBRECHT[2], GERHARD GEBAUER[1]

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Some chlorophyllous understory species with Paris-type arbuscular mycorrhiza in temperate forests are capable to gain carbon (C) from their mycorrhizal fungi, suggesting that partial mycoheterotrophy – where plants gain C from fungal partners additionally to own photosynthesis – might be globally much more common than previously thought (Giesemann et al., 2020, 2021). Paris-type morphology is considered a requirement for fungus-to-plant C transfer (Imhof, 2009). Tree and shrub saplings in tropical forests are candidates for partial mycoheterotrophy based on mycorrhizal morphotypes (Dickson et al., 2007) and due to their severely light-limited habitat.

Using stable isotope and microscopic techniques, we examined whether common shade-tolerant tropical tree and shrub species are partially mycoheterotrophic as saplings. Own observations of fungal morphology within plant species (n=40) disagreed somewhat with the literature (Dickson et al., 2007), indicating the demand for in situ determination. Enrichment occurring only in few Paris-type target species in the heavy isotopes ^{13}C, ^{2}H and ^{15}N relative to surrounding plants (but detected in mycoheterotrophic Voyria) did not support fungi as a prevalent C source. Yet, differences in stomatal regulation and transpiration of plants probably led to underestimation of a heterotrophic part of nutrition based on ^{13}C enrichment and could explain even the depletion in ^{2}H.

O 2.1: H 36, 27.09.2023, 15:00-15:15

Whole ecosystem $^{13}CO_2$ and ^2H_2O and metabolite labeling to trace drought response from leaf/roots to ecosystem scale and investigate the role of deep-water reserves during drought recovery

CHRISTIANE WERNER[1], LAURA MEREDITH[2], S. NEMIAH LADD[3], ANGELIKA KÜBERT[4], JOHANNES INGRISCH[5], JOOST V.HAREN[2], TEAM B2WALD[1]
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Severe droughts endanger forest worldwide, but how plant responses drive ecosystem water, carbon and volatile organic compound (VOC) fluxes remains poorly understood. To disentangle complex ecosystem dynamics, we imposed a 9.5-week drought on the Biosphere 2 tropical rainforest (B2WALD experiment [1]). We continuously measured isofluxes of ecosystem exchange, soil and leaf H_2O, CO_2 and BVOCs, over 5 months and applied an ecosystem $^{13}CO_2$-pulse during pre-drought and drought. Leaves and roots of different species were labelled with position-specific pyruvate. Finally, a ^2H-labelled deep-water labelling provided a unique opportunity to evaluate legacy effects during recovery.

Ecosystem $^{13}CO_2$-pulse-labeling showed enhanced mean residence times of freshly assimilated carbon during drought and down-regulation of carbon transport to trunk and roots. Plants continued to allocate a similar proportion of fresh carbon to de novo VOC synthesis, demonstrating the fundamental role of VOC in protecting plants from heat stress and photooxidative damage. Soil VOC uptake increased immediately upon rain rewetting. Interestingly, all canopy trees taped into deep water, but spared deep-water reserves until severe drought and exhibited long transit times before transpiring d^2H-labelled water. These data highlight the importance of taking dynamics ecophydrological regulations and soil-plant-atmosphere interactions into account.

[1] Werner et al. 2021, Science 374, DOI: 10.1126/science.abj6789

O.2 Climate Change and Physiology

O 2.2: H 36, 27.09.2023, 15:15-15:30

Continuous in-situ water stable isotopes show the effect of species identity on water use after precipitation events

Laura Kinzinger[1], Judith Mach[2], Simon Haberstroh[1], Markus Weiler[2], Natalie Orlowski[2], Christiane Werner[1]
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The need to understand species identity and interaction effects on their water use strategies becomes more urgent considering the eco- and hydrological impacts of climate change. Especially the characteristic timescales and pathways of water movement potentially provide important information on drought resilience of different forest ecosystems. This study investigated the temporal and spatial distribution of precipitation and their effect on the water uptake dynamics of different forest types. Isotope labelling experiments of throughfall and stemflow using continuous in-situ isotope measurements were used in a mixed forest with European beech (*Fagus sylvatica*, n=18) and Norway spruce (*Picea abies*, n=18). Our central hypothesis is that species identity and water competition between tree species are major drivers for ecohydrological flux dynamics. The analyses of the labelled irrigation during a drought revealed an immediate increase in water use and resulting fast use of recent irrigated water in *F. sylvatica*. *P. abies* saved water over a longer period increasing water use only slowly. The conifer species consequently showed negative competition effects during drought when co-existing with *F. sylvatica* contrary to the broadleaf species. Consequently, species identity is determining the plant reaction after a precipitation event especially during drought but interspecific interaction can influence the water use uptake species dependent.

O.2 Climate Change and Physiology

O 2.3: H 36, 27.09.2023, 15:30-15:45

Plant water relations during drought and recovery in an experimental rainforest

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Increasing drought in the tropics poses a major threat to rainforests. Therefore it is crucial to understand how individual plant species utilize water. In a large-scale drought experiment in a model rainforest (Biosphere 2, USA), we investigated the role of above- and belowground physiological responses to drought and recovery. Severe drought was concluded with a deep-water pulse highly enriched in 2H. This pulse allowed us to distinguish between deep and shallow rooted plants. Our study comprised five species, three canopy and two understory species. We assessed physiological responses using leaf water potential, sap flow, and high-resolution monitoring of leaf gas exchange, including concentrations and stable isotopes of H_2O and CO_2. We derived plant water uptake and leaf water use efficiency (WUE_{leaf}) at high temporal resolution. The observed water use of species and plants was highly variable, resulting in varying trends of decreasing, relatively constant, or increasing WUE_{leaf} across plant individuals. We hypothesize that these different responses were strongly related to the individual plants' water access. We propose that individuals with constant WUE_{leaf} were able to sustain their leaf gas exchange due to deep soil water access. Plants with increasing or decreasing WUE_{leaf} depended primarily on surface soil water and had limited or no access to deep water. Our findings highlight the plasticity of water use strategies beyond species-specific strategies.

O.2 Climate Change and Physiology

O 2.4: H 36, 27.09.2023, 15:45-16:00

Vegetation controls spatial patterns of soil water isotopes in a tropical dry forest and UAV can help to predict demand

MATTHIAS BEYER[1], MALKIN GERCHOW[1], ALBERTO IRAHETA[1], KATHI KÜHNHAMMER[1], PAUL KÖNIGER[2], RICARDO SANCHEZ-MURILLO[3], DAVID DUBBERT[4], MAREN DUBBERT[4], ANA CALLAU-BEYER[5], CHRISTIAN BIRKEL[6]
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The spatial representation in studies of water stable isotopes in soils and plants is often limited. Only few studies have investigated the spatial variability of soil water isotopes. We combined spatial sampling of ten soil water isotope profiles (up to 1.5m soil depth) with an analysis of UAV (Unmanned aerial vehicle, drone)-derived vegetation indices and thermal imaging in order to investigate the relationships between spatial patterns of soil water isotopes and vegetation characteristics. We postulate and test the hypothesis that the isotopic enrichment of soil water isotopes under steady-state dry conditions is controlled by vegetation. Finally, we interpolated (external drift kriging) the soil water isotope values using the highest correlated vegetation indices in order to provide a spatially distributed map of soil water isotope depth profiles (Isoscape).

We find that i.) soil water isotopes are (highly) spatially heterogeneous, even under steady-state conditions; ii.) this heterogeneity is particularly pronounced for the near-surface soil and diminishes with soil depth; iii.) there is a significant correlation between soil water isotopes and multiple vegetation indices. Therefore, we could prove the above-stated hypothesis. Results provide opportunities for a upscaling of soil and plant water isotope data to larger area and is highly relevant for a spatially better representation of water isotope data.

O 2.5: H 36, 27.09.2023, 16:00-16:15

Position-specific isotope labelling gives new insights into chiral monoterpene synthesis of Norway spruce (*Picea abies* L.)

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Chiral forms of monoterpenes and their enantiomeric composition are of ecological significance, e.g. for plant-insect interactions. However, biosynthetic pathways and drought-induced changes of enantiomeric monoterpene emissions are barely understood. We analyzed, for the first time, drought effects on the enantiomeric composition of de novo vs. storage emitted monoterpenes from Norway spruce saplings by position-specific ^{13}C-pyruvate (^{13}C2- and ^{13}C1-labelled) feeding and $^{13}CO_2$ fumigation. Drought reduced total monoterpene emissions already during its early stages, strongly linked to net photosynthesis, and lead to a decline in de novo synthesis of monoterpenes. Our results suggest that (-)-enantiomers were emitted mainly from storage pools while emissions of (+)-enantiomers rather depended on de novo biosynthesis. Even though biosynthesis of different monoterpenes derives from the same precursor pool, isotopic label incorporation revealed three groups among monoterpenes: storage derived, dominantly labelled via ^{13}C2-pyruvate, and dominantly labelled via $^{13}CO_2$-fumigation. Our results contribute to a growing amount of evidence of high flexibility in metabolic pathways of monoterpene biosynthesis in plant cells. The observed changes in monoterpene composition have important implications for secondary aerosol formation potential of Norway spruce. Additionally, changes in chiral monoterpene composition could play an important role, e.g. in bark beetle attraction and their ecological role merits further investigations.

O.2 Climate Change and Physiology

O 2.6: H 36, 27.09.2023, 16:15-16:30

Practical measurements of water stable isotopes in tree stems and soils using conservative water vapor storage

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The interest of inferring plant water uptake patterns grew in recent years and studies have shown the use of *in-situ* measurements based on laser absorption spectroscopy making plant water stable isotope datasets available on-site and in real-time. However useful, *in-situ* systems are limited to sites with power supply and require constant care.

We tested, first in the lab and then in the field, a method for equilibrating, collecting, storing, and finally analysing water vapour for its isotopic composition. We used a vapour storage vial system (VSVS) that relies on *in-situ* sampling, and measuring the samples in a laboratory. We tested the utility of the sampling method and the reliability of the VSVS to faithfully store the isotopic composition of its content by sampling a range of water vapour of known isotopic compositions and measuring the isotopic signature after the storage period. Samples for the field trial were taken in a boreal forest.

We were able to prove the utility of the sampling method within defined uncertainties (0.6 to 4.4‰ δ^2H; 0.6 to 0.8‰ $\delta^{18}O$) for natural abundance. We detected a small change in the isotopic composition of the sample after a longer storage period, which was consistently greater for oxygen but correctable by linear models.

Our method combines the best of two worlds: sampling *in-situ* in high spatial or temporal resolution while measuring in the laboratory, giving the community a tool that is not only cost-efficient but also easy to use while all components are commercially available.

3 Earth System Science and Reconstruction

Keynote 2: H 36, 28.09.2023, 09:00-09:30

$^{17}O_{excess}$ in Soreq Cave Speleothems

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$^{17}O_{excess}$ is the deviation of d^{17}O from the generally accepted ^{17}O-^{18}O mass dependent reference line. In carbonates, it records mostly the $^{17}O_{excess}$ of the parent water. In rainfall, $^{17}O_{excess}$ allows to reconstruct the relative humidity moisture source region, with lower relative humidity corresponding to higher $^{17}O_{excess}$. In some cases, however, partial re-evaporation of the raindrops may result in lower $^{17}O_{excess}$.

We measure $^{17}O_{excess}$ in rain and cave water, as well as in speleothems from Soreq cave. $^{17}O_{excess}$ of 50 per meg obtained in the weighted mean modern rainfall is consistent with the relative humidity at the moisture source region of the Eastern Mediterranean Sea. In small rain events $^{17}O_{excess}$ is affected by raindrop partial evaporation.

$^{17}O_{excess}$ values of paleo water was reconstructed from $^{17}O_{excess}$ in Soreq cave speleothems, at an age range of 0 - 160 ka, and compared to fluid inclusions d-excess. Water $^{17}O_{excess}$ reconstruction was based on the ^{17}O carbonate-water fractionation in modern Soreq stalagmites and cave water, which we found to be consistent with that in biogenic and synthetic carbonates, using previously measured clumped isotopes temperatures. The results show that $^{17}O_{excess}$ and d-excess in paleo cave water vary together in some time periods but behave differently in other times, with variations in $^{17}O_{excess}$ that likely reflect a combination of increase in normalized relative humidity in the moisture source region and local evaporation.

O 3.1: H 36, 28.09.2023, 09:30-09:45

Ongoing paleoenvironmental research in the Fotsch Valley – first oxygen isotope records derived from hemicellulose sugars of two subalpine mires

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Within the "Ullafelsen" project, our working group focused on geoarchaeological research in the Fotsch Valley (Stubai Alps, Austria) (Zech et al., 2021). Besides soil profiles at the Ullafelsen itself, two peat archives, the "Potsdamer Hütte Mire" (1970 m a.s.l.) and the "Schwarzmoos" (2010 m a.s.l.), offer great potential for paleoenvironment- and climate reconstruction, as their peat formation started during the Early Holocene. Focusing mainly on geoarchaeology and human settlement history of the Fotsch Valley, Lerch et al. (2023) presented the first results of elemental, biomarker, palynological and stable isotope analyses for the "Potsdamer Hütte Mire". Ongoing paleoenvironmental research focusses on reconstructing the paleoclimate using the stable oxygen isotopic composition of hemicellulose-derived sugar biomarkers ($\delta^{18}O_{sugars}$).

Reference

Lerch et al., 2023. Holocene landscape evolution, palaeoclimate and human impact in the Fotsch Valley, Stubai Alps, Austria: interrogating biomarkers, stable isotopes, macrofossils and palynological indicators from a subalpine mire archive. The Holocene, 0(0). https://doi.org/10.1177/09596836231176485.

Zech et al., 2021. Revisiting the subalpine Mesolithic site Ullafelsen in the Fotsch Valley, Stubai Alps, Austria – new insights into pedogenesis and landscape evolution from leaf-wax-derived n-alkanes, black carbon and radiocarbon dating. E&G Quaternary Sci. J., 70(2), 171-186. https://doi.org/10.5194/egqsj-70-171-2021.

O.3 Earth System Science and Reconstruction

O 3.2: H 36, 28.09.2023, 09:45-10:00

A Late Glacial and Holocene ^{18}O paleoclimate record form the afro-alpine Wulf Lake, Bale Mountains, Ethiopia

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The Bale Mountains in the Southeastern Ethiopian Highlands are one of the few mountain ranges of Africa that were glaciated during the last glacial maximum. As a result of glacial retreat, numerous depressions started to be filled with lacustrine sediments and thus represent excellent environmental and climate archives for this fragile afro-alpine ecosystem. During a field campaign in 2017, a 4.8 m long sediment core was retrieved from the shorelines of Wulf Lake on the Sanetti Plateau at more than 4000 m altitude. Twelve radiocarbon data allow establishing a robust Late Glacial and Holocene chronostratigraphy covering the last 17,000 years. Apart from classical sedimentological parameters, we investigated and established a $\delta^{18}O_{sugar}$ biomarker record. As demonstrated in previous studies, an unambiguous aquatic source identification is possible especially for the sugar biomarker fucose in our study area and allows reconstructing lake evaporation histories. We will compare our Late Glacial and Holocene $\delta^{18}O_{sugar}$ record from Wulf Lake with the Holocene $\delta^{18}O_{sugar}$ record from Garba Guracha (Bittner et al., 2022), as well as with other paleoclimate records, in order to contribute to the regional and over-regional paleoclimate reconstruction of Eastern Africa.

Reference

Bittner et al., 2022. The Holocene lake-evaporation history of the afro-alpine Lake Garba Guracha in the Bale Mountains, Ethiopia, based on $\delta^{18}O$ records of sugar biomarker and diatoms. Quaternary Research 105, 23-36.

O.3 Earth System Science and Reconstruction

O 3.3: H 36, 28.09.2023, 10:00-10:15

An isotope view on hydrology and carbon cycling in a tidal basin under impact by submarine groundwater discharge

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The role that of fresh surface and ground water sources play on the coastal water and element balances, and the associated biogeochemical processes is still a matter of debate. Fresh and saline water mixing in coastal areas is allowed by stable water isotopes and further hydrochemical tracers. Here, we report on investigations of surface, pore and ground waters from Königshafen Bay (Sylt) and potential mixing endmembers. Besides dissolved major and minor elements, the stable water isotope composition is used to characterize the temporal and spatial distribution of different water sources to the bay and the seasonal dynamics in the water column. Porewater gradients indicate different degrees of freshening, locally already in the top 50 cmbsf 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 SGD impact, that differ in composition from surface water sources 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.

Acknowledgement:

DFG (KiSNet), BMBF (COOLSTYLE/CARBOSTORE), DAAD, DFG Baltic Transcoast, and Leibniz IOW.

O.3 Earth System Science and Reconstruction

O 3.4: H 36, 28.09.2023, 10:15-10:30

Isotope biogeochemical dynamics of pore waters under impact by submarine ground water discharge after removal of coastal protection

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Seasonal isotope biogeochemical dynamics of coastal pore waters adjacent to Hütelmoor peatland, Germany were investigated for coastal changes influence. SGD influenced the sediments at maximum discharge zone 2-3 mbsf. Groyne removal may impact the surface sediment transport and pore water dynamics. These influence the sediment-water interface, the biogeochemical processes intensity and kinetics and DIC production. Overall the hydrology of freshwater intrusion below from adjacent peatland area and brackish water intrusion from offshore may be impacted by the hydrographic regime. Collected pore waters from two permanent lances before and after groyne removal were measured for physical in-situ parameters, major, nutrient, trace elements, stable water isotopes and C isotope composition of DOC and DIC, and dissolved sulfate and sulfide S and O isotope composition. Results showed mixture of at least two different water sources, dominant DOC source and DIC sources and sinks. Both brackish and freshwater signatures were indicated in the water stable isotopes. A coupled δ^{13}C-DIC evaluation show DIC from seawater-derived DIC, carbonate dissolution, DOC mineralization and soil CO_2. δ^{13}C-DOC evaluation indicates terrestrial and marine organic matter mixture. Metal and major ion concentrations demonstrate system stability and reestablishment though long-term changes may still occur. This study shows anthropogenic activity influences on coastal water biogeochemistry and hydrological water cycle.

O.3 Earth System Science and Reconstruction

O 3.5: H 36, 28.09.2023, 10:30-10:45

Benthic processes in tidal basins release isotopically light DIC to the southern North Sea

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The Wadden Sea is a highly dynamic system that acts as an important driver for the North Sea carbonate system. Here, we focus on understanding the pelagic and benthic processes that control the production and release of DIC into the Wadden Sea surface waters. Surface and pore water samples were collected for major and trace elements, nutrients, and the stable isotope (H, C, O) composition measurements. Sediment samples were taken for organic and inorganic carbon contents, as well as C isotopes analyses. Among the different processes impacting the DIC of the Wadden Sea surface waters, the contribution from anoxic porewater is one of the most prominent. Downcore variations of pore water variables in sediments demonstrate the role of different mineralization processes in the release of DIC and the resulting of isotopic light fluxes of DIC across the sediment-water interface. Further work is needed to understand and quantify the net production of DIC and the resulting fluxes in and out of Wadden Sea sediments and further evaluate their role for the North Sea carbon system at different temporal and spatial scales.

The investigations belong to the BMBF project COOLSTYLE/CARBOSTORE, parts to BIOACID, and are further supported by Leibniz IOW.

O.3 Earth System Science and Reconstruction

O 3.6: H 36, 28.09.2023, 10:45-11:00

Investigations on the origin of mineral waters by analysis of stable isotopes of water and sulfate

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Stable isotope analyses of more than 70 mineral water samples, mainly from Germany, were used to investigate their composition and genesis. An influence of water of meteoric origin (precipitation) was indicated by an altitude and latitude effect. Assuming the altitude of the bottling sites (m a.s.l.) and their distance from the North Sea (km), corresponding correlations with regression coefficients of 0.34 - 0.42 and 0.50 -0.64 were determined for d18O and d2H, respectively. In comparison with long-term mean values of annual precipitation of selected German GNIP stations, the percentage of young groundwater as well as groundwater recharge levels could also be estimated for the mineral waters. The origin of sulfate was assessed by d18O-/d34S sulfate isotope analyses. Additionally, chloride, sulfate and silicon concentrations of the mineral waters were evaluated.

4 Environment and Pollution

Keynote 3: H 36, 28.09.2023, 15:00-15:30

Isotope Fractionation Reveals Limitations and Microbial Regulation of Pollutant Biodegradation at Low Concentrations

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Compound-specific isotope fractionation analysis (CSIA) of chemical trace contaminants (“micropollutants”) revealed bottlenecks of degradation at low, relevant (mg/L) concentrations. Isotope fractionation was pronounced at high concentrations, but masked at trace levels providing evidence that mass transfer into and out of the cell became limiting for biodegradation specifically at low concentrations. An onset of masking was observed for atrazine when degraded by Arthrobacter aurescens TC1 at concentrations below 60 mg/L in chemostat with complete rate control at 10 mg/L in retentostat . Proteomics revealed that such mass transfer limitation served as trigger for physiological adaptation, where catabolic enzymes remained highly expressed, whereas other cellular functions were downregulated.

CSIA also demonstrated mass transfer limitations in a quasi-two dimensional sediment tank system mimicking realistic conditions of natural aquifers. High, unmasked isotope fractionation in the center of the plume indicated that 2,6-dichlorobenzamide degradation by Aminobacter sp. MSH1 was not limited by substrate availability, but rather by oxygen supply. In contrast, masked isotope fractionation pinpointed rate-limiting mass transfer during cellular uptake towards the lower end of the concentration profile. For Isotope Biogeochemistry these findings imply that, based on isotopic evidence, turnover of substances at low concentrations may be widely underestimated.

O.4 Environment and Pollution

O 4.1: H 36, 28.09.2023, 15:30-15:45

Characterization of pesticide fate in the unsaturated zone using numerical transport modeling and stable carbon isotopes

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Agrochemicals including nitrate and pesticides pose threats to ecosystems and groundwater. A field study was conducted at two lysimeters located in Wielenbach, Germany, with different soil textures within the soil cores (sandy gravel and clayey sandy silt). The lysimeters were vegetated with maize, and four different herbicides were applied according to common agricultural practice. Over a period of 4.5 years, concentrations of the herbicides and some of their metabolites were monitored in lysimeter discharge. Stable carbon isotopes ($\delta^{13}C$) were analyzed for investigating biodegradation influences. Numerical modeling with HYDRUS-1D was carried out for describing unsaturated flow and reactive transport of the herbicides, and simulations were interpreted in combination with measured $\delta^{13}C$.

At the end of the observations, 0.9 to 15.9% of the applied herbicides (up to 20.9% for herbicides plus metabolites) were recovered in lysimeter drainage. Metabolites were observed to accumulate, and biodegradation was indicated by small changes in $\delta^{13}C$ between applied herbicide solution and leached herbicides. Results point towards a higher biodegradation activity when infiltrated (herbicide-contaminated) water was residing a longer time in the unsaturated zone. Herbicide dynamics in lysimeter discharge could be covered well by modeling. Compound-specific isotope analysis using $\delta^{13}C$ provided valuable hints for microbial degradation of herbicides in the unsaturated zone.

O.4 Environment and Pollution

O 4.2: H 36, 28.09.2023, 15:45-16:00

Phosphate oxygen isotope insights into lacustrine phosphorus cycling

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The biogeochemistry of phosphorus (P) is key to the health of our freshwaters, and perturbations of the lacustrine P cycle entail severe ecological complications associated with eutrophication: harmful algae blooms, oxygen deficits, fish kills, and decline of water quality. Despite decades of eutrophication research, critical controls in the lake phosphorus cycle are not conclusively understood.

The stable oxygen isotope signature in phosphate ($\delta^{18}O_P$) has been used to detect reactions associated with biological phosphate turnover and utilization, and to track the contribution of isotopically different sources to lacustrine phosphate stocks. Many studies have evaluated $\delta^{18}O_P$ isotope effects in the lab, but it remains to be seen how these findings relate to the growing number of environmental measurements of this signature.

We here present two case studies – Lake Arendsee and Lake Stechlin from NE Germany –where we obtained comprehensive data on phosphate oxygen isotopes in lake and ground water and interpreted these with respect to P transport via lacustrine groundwater discharge and phosphorus turnover in the water column. We address problems associated with the interpretation of $\delta^{18}O_P$ data from "open" aquatic ecosystems, postulate that integrative studies in aquatic ecosystems of reduced complexity can help identifying critical benchmarks for the $\delta^{18}O_P$ concept, and discuss how these can eventually be transferred to enhance our understanding of P cycling in large water bodies such as lakes and estuaries.

O.4 Environment and Pollution

O 4.3: H 36, 28.09.2023, 16:00-16:15

Natural abiotic iron-oxido-mediated formation of C1 and C2 compounds from environmentally important methyl-substituted substrates

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Organic and inorganic volatile compounds containing one carbon atom (C1), such as carbon dioxide, methane, methanol, formaldehyde and chloromethane are ubiquitous in the environment and play an important role in atmospheric physics and chemistry as they act as greenhouse gases, destroy ozone and control the atmospheric oxidation capacity. Up to now, most C1 compounds in the environment were associated to complex metabolic and enzymatic pathways in organisms or to combustion processes of organic matter. So far, it was not recognized that many C1 and C2 compounds might also have a common origin in methyl groups of methyl-substituted substrates that are cleaved by the iron-catalyzed formation of methyl radicals. Here, using stable isotope techniques we present a mechanism for the formation of all major C1 and various C2 compounds from methyl radicals derived from methyl-substituted substrates such as dimethyl sulfoxide (DMSO). We applied isotopic labeling experiments (^{2}H, ^{13}C and ^{18}O labeling) in order to investigate (using GC-MS and GC-IRMS) the source of the carbon, hydrogen and oxygen groups in the formed products C1 and C2 compounds. Our combined approach (experimental, computational, and based on field studies) implies that the iron-oxido-mediated process is a common abiotic source for environmentally important gases and of potential relevance for the global carbon cycling.

O.4 Environment and Pollution

O 4.4: H 36, 28.09.2023, 16:15-16:30

Methane accumulation and its potential precursor compounds in the oxic surface water layer of two contrasting stratified lakes

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Oversaturation of methane (CH_4) in oxygenated waters is a widespread phenomenon, challenging the traditional perception of strict anoxic methanogenesis. Recent findings have uncovered mechanisms that produce CH_4 in oxic environments. While some processes contributing to the accumulation of CH_4 in the oxygenated water layers of lakes have been identified, temporal variations and their drivers are still poorly understood. In this study, we investigated the accumulation of CH_4 in oxic water layers of two contrasting lakes: Lake Willersinnweiher (shallow, eutrophic) and Lake Stechlin (deep, mesotrophic) from 2019 to 2020. Strong CH_4 oversaturation was observed in the surface waters of both lakes, primarily concentrated around the thermocline. In both lakes, increases in CH_4 concentrations from the surface to the thermocline were mostly associated with an enrichment in ^{13}C-CH_4 and ^{2}H-CH_4, indicating a complex interaction of multiple processes, such as CH_4 oxidation, CH_4 transport from littoral sediments, and oxic CH_4 production, sustaining and regulating CH_4 oversaturation. Moreover, incubation experiments with ^{13}C- and ^{2}H-labelled methylated P-, N-, and C- compounds clearly demonstrated that methylphosphonate, methylamine, and methionine acted as precursors of CH_4 and partially sustained CH_4 oversaturation. This highlights the need to better understand the mechanisms underlying CH_4 accumulation by focusing on production and transport pathways of CH_4 and its precursor compounds.

5 Methods, Models, Standards

Keynote 4: H 36, 29.09.2023, 09:00-09:30

Towards compatibility of stable isotope datasets: Progress with new reference materials and related concepts.

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Commonly, datasets obtained in different laboratories and in different years have to be compared /combined. Despite reliable IRMS systems, quality of measurement results cannot be better than quality of Reference Materials (RMs) in use. Thus, to achieve the required data quality and compatibility, one must understand major aspects of RMs and associated concepts.

One of focuses in recent years has been on the $\delta^{13}C$ scale. First, the primary RM NBS19 expired in 2009, and its replacement needed to be characterized. Next, the scale-anchor, RM LSVEC, was found to have a significant drift in $\delta^{13}C$ of up to 0.35 ‰, so this RM was withdrawn from the use. Reconstruction of its "original" $\delta^{13}C$ based on available RMs or other information was not possible. As a result, new scale-anchor RMs had been developed and their value assignment principles revised. Furthermore, one has also demonstrated a compatibility in $\delta^{13}C$ obtained for NIST RMs 8562-8564 in 2003-04, 2007 (pre-LSVEC era) and 2020.

Details of developments of new RMs for $\delta^{13}C$ and their value assignment provide an example of modern approaches and quality assurance. Although the high accuracy in $\delta^{13}C$ obtained for new RMs (±0.010 to ±0.15‰, k=1) may not be necessary in many applications, these principles can be applied to achieve data compatibility in other studies.

Presentation will also discuss isotope scales, their relationships, data treatment, and a simplified scheme of uncertainty propagation. All that is relevant to the use of RMs and quality control materials.

O.5 Methods, Models, Standards

O 5.1: H 36, 29.09.2023, 09:30-09:45

ESI-Orbitrap IRMS: A Revolutionary Tool with Pros and Cons

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Electrospray ionization (ESI) with Orbitrap technology gives access to the isotopic anatomy of intact organic and inorganic molecules. Key aspects are soft ionization by ESI, target separation by quadrupole and high-resolution accurate mass (HRAM) spectrometry in the Orbitrap. For the first time we now can read natures fingerprints compounds. Orbitrap IRMS delivers isotope ratios of singly substituted isotopologs, clumped isotopes and position specific isotope analysis.

As many fields of application have started to do research with Orbitrap IRMS a discussion of its pros and cons is required to give guidance in the development of new applications. Some of the key aspects discussed in this presentation are,

- Analysis of intact molecules from liquid samples
- Simultaneous access to multiple isotopologs carrying ^{13}C,^{15}N,^{18}O, ^{34}S, and ^{2}H
- High sensitivity with concentrations down to 1 pmol/µL and sample consumptions of < 1 nmol per compound
- High specificity by HRAM removing contaminants and interferences
- Equal ESI conditions for samples and references
- Selection of target compounds by HPLC
- Peak broadening to acquire data for > 5 min to reach < 1‰ precision
- 2-point referencing and new reference compounds

We also will give insight to Orbitrap IRMS technology, sample introduction techniques, data evaluation and will highlight latest applications on oxyanions, amino acids and first steps in the deconvolution of metabolic pathways.

O 5.2: H 36, 29.09.2023, 09:45-10:00

Two dimensional LC-IRMS – The future of CSIA?

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Compound-specific stable isotope analysis (CSIA) has many applications, including the investigation of micropollutant sources and transformation processes. The coupling of liquid chromatography (LC) with an isotope ratio mass spectrometer (IRMS) allows the measurement of analytes in complex water samples. The use of organic eluents, buffers or modifiers in LC-IRMS can lead to false determination of the carbon isotope signatures of the analytes and must be avoided. This limits the use of established chromatographic separations based on the use of organic eluents, which account for over 90% of current LC-methods. One way to overcome this limitation is to combine two-dimensional LC (2D-LC) with LC-IRMS. Adaptation of the 2D system allows LC-methods taken from the literature to be used with organic additives in the first dimension without the need for method development. The analyte of interest is then transferred to the second dimension via heart-cut modulation, where the organic solvents are separated from the analyte prior to oxidation. In this study, we aim to investigate the potential of 2D-LC-IRMS to make CSIA more accessible to a wider range of applications. The initial development and optimisation of a 2D-LC-IRMS system is presented. Further development will include testing different forms of heart-cut modulations, e.g. sample loop, trap column or multiple heart-cut modulators. The long term aim is to apply this instrumentation to mechanistic investigations and the measurement of complex real life samples.

O.5 Methods, Models, Standards

O 5.3: H 36, 29.09.2023, 10:00-10:15

Accurate and comparable site-specific stable carbon isotope ratio measurement of vanillin methoxy group by IRMS and ^{13}C-qNMR

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Site specific isotope ratio measurements are an emerging field of study which could provide a new dimensionality to conventional bulk stable isotope ratio measurements used in food provenance, forensics and a number of other applications. Most often, this site specific stable isotope ratio analysis is done by NMR, which is also possible for each individual carbon atom in a molecule (13C-qNMR). However, for site-specific carbon isotopes, there is little data to confirm the accuracy of NMR measurements using other independent analytical methods.

Here we present a study of d^{13}C values of the methoxy group of vanillin standards using ^{13}C-qNMR and GC-IRMS. For the IRMS analysis site-specific carbon isotope analysis is accessible by converting the methoxy group into gaseous iodomethane using hydroiodic acid.

Values obtained by these different measurement principles demonstrated remarkable agreement. In the five studied vanillin material bulk carbon isotope delta values ranged from -31.30 to -25.85 ‰ whilst the methoxy (C_8) carbon delta values ranged from -62.47 to -30.59 ‰. The difference observed between the two analytical approaches were between 0.14 to 0.71 ‰ well within the analytical uncertainty. Overall, the GC-IRMS approach offers 3-5-fold better uncertainties and requires 100-fold less sample material compared to qNMR. Conversely the ^{13}C-qNMR approach was able to assign values to all carbons in the molecule not just the cleavable methoxy group.

O 5.4: H 36, 29.09.2023, 10:15-10:30

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 favored 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.

O.5 Methods, Models, Standards

O 5.5: H 36, 29.09.2023, 11:15-11:30

Laser ablation IRMS – the minimally destructive alternative for in-situ δ^{13}C analyses of solid or liquid matrices

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LA IRMS (laser ablation isotope ratio mass spectrometer) is a thrilling alternative to EA IRMS and opens a world of possibilities! We evaluated LA IRMS various organic materials (pollen, wood, collagen, bone, tooth, keratin, bee products, airborne particulate matter, blood, etc.). For some we also present EA data for method equivalency. We use two instrumental set-ups; sample introduction via 1. LSX 213 G2+ 213 nm wavelength laser ablation system or 2. Fusions CO2 laser (both Teledyne Photon Machines) and an HS2022 IRMS via a CryoFlex sample preparation module (all Sercon). The sample chamber is an isoScell Δ100 (Terra Analitic) specifically designed for LA IRMS. The EA IRMS used for inter-instrument comparison is also Sercon. This setup allows for blank levels as low as 6E-10 (ca. 2% of sample-peak size). Establishing the optimal laser parameters is a two-step process; the first one is fine tuning the laser energy to ensure the sample is ablated efficiently. The next step requires finding the optimal spot size and ablation time necessary for producing sufficient aerosol to be converted into CO2 in the combustion furnace. When spatial resolution is crucial samples (e.g., wood, hair, fingernail, tooth) can be ablated at intervals of down to 20 µm. As each ablation removes a minute amount of sample, replicate analysis will not be an issue for homogenous matrices.We show that with LA matrix-matching the reference material to the unknown sample might be unnecessary.

O.5 Methods, Models, Standards

O 5.6: H 36, 29.09.2023, 11:30-11:45

A new oxygen-free HTC pyrolysis reactor – first insights and results

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Numerous compound-specific isotope analyses (CSIA) methods have been developed and applied in various scientific fields during the last decades. Many of them focus on the carbon and hydrogen isotopic composition of lipid biomarkers. By contrast, albeit commercially available for about 20 years (e.g. Hener et al., 1998), compound-specific $\delta^{18}O$ analyses are hitherto hardly applied and thereby almost exclusively focus on sugar biomarkers (Bittner et al., 2022; Zech & Glaser, 2009). This can be explained with analytical challenges associated also with the commercially available $\delta^{18}O$ HTC pyrolysis reactor (Hitzfeld et al., 2017). Still, the oxygen isotopic composition of e.g. oxygenated lipids has large potential to improve our scientific knowledge in various fields (palaeo-environmental science, forensics, biogeochemical cycles). The current $\delta^{18}O$ HTC reactor is build up by an aluminium oxide ceramic tube containing a Pt tube fitted with several Ni wires. However, at high temperatures, oxygen diffuses through the Pt (Velho & Bartlett, 1972) and the oxygen-aluminium ceramic is a potential source of oxygen contamination. Additionally, neither the life-time nor the performance of these reactors is convincing and therefore alternatives are eagerly awaited. Here we present a new oxygen-free ceramic HTC pyrolysis reactor design without Pt tube, Ni wires, shielding gas, reactor conditioning or tricky balance of hydrogen and graphite. We present first results of the application of various compounds.

O 5.7: H 36, 29.09.2023, 11:45-12:00

Clumped isotope laser spectroscopy of non-CO_2 GHGs

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Abundances of doubly-substituted (i.e. clumped) isotopic species of non-CO_2 greenhouse gases (GHGs) are novel tracers, especially in cases where the average (or bulk) isotopic composition is ambiguous. Under equilibrium conditions, they represent intra-species thermometers to trace the molecular temperature history. For kinetically controlled formation and removal processes, clumped isotopic signatures are linked to molecular mechanisms, reflecting reversibility or combinatorics, and can thus be applied to refine biogeochemical cycles. On the planetary scale, model predictions indicate that atmospheric measurements of clumped isotopic species provide constraints on trends in global source and sink magnitudes beyond current knowledge.

We present our recent advances in mid-IR quantum-cascade laser spectroscopy for rapid and high-precision analysis of $^{13}CH_3D$ and $^{12}CH_2D_2$ in methane (CH_4) and $^{15}N^{14}N^{18}O$, $^{14}N^{15}N^{18}O$ and $^{15}N^{15}N^{16}O$ in nitrous oxide (N_2O). Analytical developments include selection of spectral regions with improved selectivity, customization of spectrometers with inlet systems for automated sample dilution and injections, and referencing of measurements to stochastic distributions. The two laser spectrometers offer a rapid and precise approach for investigating various aspects of CH_4 and N_2O cycles and origins. Currently, we target first applications in the thermal history of methane-rich sedimentary rocks and key microbial formation pathways of nitrous oxide.

6 Life Science, Forensics and Medicine

O 6.1: H 36, 29.09.2023, 12:00-12:15

Isotopologue ratio analysis in organic compounds using ESI-FTMS: origin of caffeine in foods

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Novel approaches using electrospray ionization (ESI) and Fourier transform mass spectrometry (FTMS) enable for the first time routine, simultaneous analysis of multiple isotope ratios on intact complex molecules. In this study Thermo Scientific™ Orbitrap™ MS was used for high precision and accuracy analysis of several caffeine isotopologue ratios. Alignment of this novel ESI-Orbitrap IRMS approach with the results of classical techniques for isotope ratio analysis will be shown for well characterized caffeine reference materials.

The presence of matrix contaminants can decrease the precision and accuracy of ESI-Orbitrap isotope ratio analysis. Therefore, isotope ratio analysis of caffeine in complex sample matrices requires prior purification. Different ways for the online coupling of reversed phase liquid chromatography were developed and evaluated with respect to high precision isotope ratio analysis of caffeine from complex sample matrices. These developments will be demonstrated for analysis of caffeine reference materials and caffeine in different drinks to obtain information about its natural or synthetic origin.

The online coupling of liquid chromatography with ESI-FTMS expands the application areas for compound specific isotope ratio analysis on polar compounds. This can enable the tracing of metabolites in complex systems with multiple reaction pathways without the need for heavy isotope labelling.

O.6 Life Science, Forensics, and Medicine

O 6.2: H 36, 29.09.2023, 12:15-12:30

IRMS of urinary norandrosterone in doping control analysis

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More than 20 year ago IRMS has been established in routine doping control analysis to identify a potential exogenous origin of 19-norandrosterone (NorA) in urine samples. In the past the analysis of the carbon isotope ratio of urinary steroids offered the opportunity to distinguish between an endogenous or exogenous origin of the urinary steroids of interest with concentrations down to 2 ng/ml. Concerning NorA, urinary traces might not be only an indicator of an exogenous application, but may also originate from endogenous origin or from the consumption of wild boar offal and meat. Additionally, in some cases NorA can be formed in urine by in-situ microbial degradation of androsterone.

Since 2003 the Cologne laboratory analyzed approximately 300 doping control samples with NorA concentrations below 15 ng/ml by IRMS. Negative samples show similar $\delta^{13}C$ values for NorA and the corresponding endogenous reference compounds, whereas NorA originating from pharmaceutical preparations usually showed ^{13}C depleted values. However, within the last years the identification of an exogenous origin of urinary NorA became more and more challenging, as pharmaceutical preparations of NorA precursors exhibited more and more enriched $\delta^{13}C$ values. Thus, an identification of such 'pseudo-endogenous' carbon isotope signatures by comparison with $\delta^{13}C$ values of endogenous reference compounds is impeded. Due to this additional testing and follow-up investigation strategies had to be developed and implemented in doping control.

O.6 Life Science, Forensics, and Medicine

O 6.3: H 36, 29.09.2023, 12:30-12:45

Assessment of energy expenditure using doubly labelled water during an altitude training camp in elite alpine skiers

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The doubly labelled water (DLW) method is considered as the gold standard for assessment of energy expenditure. Without interfering with everyday life or training schedules, it may also serve as an accurate field technique in elite sport settings. Alpine Skiing is characterized by a complex movement profile and phases of demanding on-snow glacier training in extreme environments, where maintaining energy balance and body composition is crucial for performance and may aid injury prevention. The present study investigated the impact of a short-term training camp at altitude on energy balance in world-class alpine skiers, using DLW as a reference method.

In a prospective observational study, active male (n=9, 27±2.9 yrs) and female (n=10, 25±3.0 yrs) international skiers completed a 7 to 15-day training camp at altitude (base: 1800m, glacier: 3500m). All athletes received a single oral dose of 0.5 g/kg $H_2{}^{18}O$ (10% enriched) and 0.3 g/kg D_2O (99,8% enriched). After calculating initial isotope enrichment from urine samples obtained prior to and following total body water equilibrium, athletes provided daily urine samples for a minimum of 6 days to determine elimination rates of both isotopes via the multipoint method. Body composition was assessed directly before and after the camp and body mass was monitored continuously. Food intake in altitude was assessed via observation by trained staff, and capillary blood was used for markers of energy balance, namely leptin and triiodothyronine.

O.6 Life Science, Forensics, and Medicine

O 6.4: H 36, 29.09.2023, 12:45-13:00

Radical-driven methane formation in humans evidenced by stable isotope studies

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Methane (CH_4), which is produced endogenously in animals and plants, was recently suggested to play a role in cellular physiology, potentially influencing the signaling pathways and regulatory mechanisms involved in nitrosative and oxidative stress responses. In addition, it was proposed that the supplementation of CH_4 to organisms may be beneficial for the treatment of several diseases, including ischemia, reperfusion injury, and inflammation. However, it is still unclear whether and how CH_4 is produced in mammalian cells without the help of microorganisms, and how CH_4 might be involved in physiological processes in humans. In this study, we provide first evidence of the principle that CH_4 is formed non-microbially in the human body by applying isotopically labeled methylated sulfur compounds, such as dimethyl sulfoxide (DMSO) and methionine, as carbon precursors to confirm cellular CH_4 formation. A volunteer applied isotopically labeled (^2H and ^{13}C) DMSO on the skin, orally, and to blood samples. The monitoring of stable isotope values of CH_4 convincingly showed the conversion of the methyl groups, as isotopically labeled CH_4 was formed during all experiments. Based on these results, we propose several hypotheses about endogenously formed CH_4 in humans, including physiological aspects and stress responses involving reactive oxygen species (ROS). Of particular importance is the potential to monitor CH_4 as an oxidative stress biomarker.

Poster

1 Trophic Interactions, Organic Matter, and Nutrient Cycling

P 1.1

Diet-consumer interactions under variable stressor conditions as revealed by stable isotope studies of individual amino acids

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This research aims to gain deeper insights into riverine food web dynamics under varying stressor conditions through stable isotope studies of individual amino acids (AAs), focusing on glutamic Acid (Glu) and phenylalanine (Phe). We employ Gas Chromatography-Isotope Ratio Mass Spectrometry (GC-IRMS) to analyse carbon and nitrogen isotopes in AAs. By studying the Carbon isotope signatures of essential amino acids (EAA) from primary producers and using Nitrogen isotope signatures of Glu and Phe for trophic position estimation, we assess food web structures based on amino group metabolic pathways. Our research reveals species' niches and trophic links under multiple stressors, providing insights into ecosystem structures and functions during degradation and recovery. We expect to observe changes in $\delta^{15}N$ and $\delta^{13}C$ values of AAs, indicating food web simplification under stress conditions. The study takes place in the Emscher/Boye catchment, reflecting a recovery gradient from pollution and hydromorphological degradation. Understanding diet-consumer interactions and food web dynamics amid stressors is vital for effective riverine ecosystem conservation and management. Our findings contribute to comprehending the spatial-temporal dynamics, crucial for preserving river ecosystem health and functionality in the face of environmental challenges.

P.1 Trophic Interactions, Organic Matter, and Nutrient Cycling

P 1.2

Pilot study: Determining the geographic origin of European Eel with stabile isotopes (SI)

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The European Eel (Anguilla anguilla) is an endangered species with a complex life cycle including long migrations in the ocean. Its continental range extends from North Africa in the south to northern Norway in the north and includes large parts of Europe. A sustainable stock management requires efficient techniques to trace the origin of the eels. This pilot study investigates the application of the SI ratios of carbon ($d^{13}C$), hydrogen ($d^{2}H$), nitrogen ($d^{15}N$) and oxygen ($d^{18}O$) to trace back the origin of individual eels. Therefore, eels from two fresh water habitats (River Ems and Mirower See) and one saltwater habitat in Germany (Buger Bodden, Baltic Sea) were analysed. Furthermore, eels of different sizes were compared in order to assess if body size has an influence on SI composition in eels. Muscle and liver tissue were analysed from each collected animal. The SI in the samples span ranges as $d^{13}C$ from – 37.7 to – 18.6 ‰, as $d^{2}H$ from – 204.6 to – 92.2 ‰, as $d^{15}N$ from 10.4 to 18.9 ‰ and as $d^{18}O$ from 14.0 to 24.6 ‰. There was no significant difference of $d^{13}C$ and $d^{15}N$ between the two tissue types but between the three habitats. Additionally, we observed a significant difference of $d^{15}N$ between big and small eel at the same location and interpreted this as an effect of age depending food differences. For liver tissue there is a significant difference in $d^{2}H$ and $d^{18}O$ between Ems and Buger Boden as well as between Ems and Mirower See.

P.1 Trophic Interactions, Organic Matter, and Nutrient Cycling

P 1.3

Novel insights into orchid mycorrhiza functioning from stable isotope signatures of fungal pelotons

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Stable isotope signatures of fungal sporocarps have been instrumental in identifying C gains of chlorophyllous orchids from a fungal source. Yet, not all mycorrhizal fungi produce sporocarps and frequently fungi of different taxa occur in parallel in orchid roots.

To overcome this obstacle, we investigated stable isotope signatures of fungal pelotons extracted from orchid roots and compared these data to the respective orchid and reference plant tissues. Anoectochilus sandvicensis and Epipactis palustris represented specialized or unspecialized rhizoctonia-associated orchids. Epipactis atrorubens and Epipactis leptochila are orchids considered ectomycorrhiza-associated with different preferences for Basidio- and Ascomycota.

^{13}C enrichment of rhizoctonia pelotons was minor compared to plant tissues and significantly lower than enrichments of pelotons from ectomycorrhizal Epipactis species. ^{15}N values of pelotons from E. leptochila and E. atrorubens showed similar patterns as known for respective sporocarps of ectomycorrhizal Asco- and Basidiomycota, yet, with an offset towards lower ^{15}N enrichments and N concentrations.

Our results suggest an explicit fungal nutrition source of orchids associated with ectomycorrhizal fungi, whereas the low ^{13}C enrichment in rhizoctonia-associated orchids and fungal pelotons hamper the detection of C gains from fungal partners. ^{15}N isotopic pattern of orchids further suggests a selective transfer of ^{15}N-enriched protein-nitrogen into orchids.

2 Climate Change and Physiology

P 2.1

Fate of recently assimilated carbon in the soil-plant system of a boreal Podzol under Vaccinium vitis-idaea and its response to warming

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Boreal dwarf shrubs like Vaccinium vitis-idaea L. constitute a significant component of forests in high latitude ecosystems, playing a crucial role in net carbon (C) assimilation and sequestration. Detailed understanding on C allocation patterns in these plant-soil systems and the response to warming is still lacking. Therefore, we conducted a translocation experiment combined with $^{13}CO_2$ pulse labelling to quantify (I) the allocation of ^{13}C in the plant-soils system, (II) the ^{13}C distribution in root tips and cells colonized by mycorrhizal fungi, and (III) the impact of warming on C allocation belowground. We translocated cores with soil and V. vitis-idaea from North- to South-Finland (+ 4 °C MAT). After 2.5 years, plants were pulse-labelled with $^{13}CO_2$. We traced ^{13}C in plant and soil compartments and measured its distribution in fine roots. After 7 days, the highest share of assimilated C remained in the leaves, followed by the shoot, and only a small amount was transferred belowground. The ^{13}C distribution in tips and cells with mycorrhizal fungi did not show a higher ^{13}C-enrichment than other parts of the fine roots. Additionally, warming did not alter the distribution of C in the system, except for a higher uptake of ^{13}C by microbes in the mineral soil. Our results indicate that dwarf shrubs in boreal forests allocate only a small share of recently assimilated C to roots and soil, and a short-term exposure to warming did not affect this allocation pattern.

P.2 Climate Change and Physiology

P 2.2

Root-derived carbon explains the pattern of soil carbon dynamics in well-watered and drought-stressed maize.

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The projected global warming risks due to high greenhouse gas emissions, increase the need for an agricultural practice with high carbon (C) sink capacity and low water requirements without compromising on crop productivity. On the one hand, it's well accepted that soil moisture directly affects microbial activity, whereas, on the other hand, drought stress was recently postulated to increase root exudates, which in turn will accelerate soil organic matter mineralization via priming effects. Thus, this study aimed to investigate the interplay between soil moisture (well-watered and drought-stressed) and maize (Zea mays L.) C allocation on soil C dynamics. The experiment consisted of three treatments: well-watered, drought-stressed maize plus an unplanted control. Soil CO_2 efflux and its ^{13}C were measured over three years in conjunction with soil temperature and moisture content. Under well-watered conditions, the annual average of CO_2 efflux was 0.12 g CO_2-C m^{-2} hr^{-1}, which was 24.5 and 20% significantly higher than under drought-stressed and the control, respectively. Moreover, well-watered maize had significantly greater primed carbon than drought-stressed maize. Overall, these results suggested that the root exudates decreased under drought conditions, thus explaining the lower soil respiration under drought-stressed than well-watered maize.

P.2 Climate Change and Physiology

P 2.3

Stable isotope composition of precipitation in Germany in context to current climate patterns and recent activities of the German Isotope Network (GIN)

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The stable isotope composition of precipitation (^{2}H, ^{18}O) in Germany is mainly affected by temperature and humidity conditions at the moisture source and dominating precipitation processes (e.g. altitude, continental, seasonal effects). Continuous observations of precipitation stable isotope patterns in high spatial and temporal resolution allow a reconstruction of source areas and an interpretation of dominating processes. In Germany, precipitation monitoring organized by the Federal Institute of Hydrology (BfG) started in the mid-1970s. Today, a monitoring network for monthly analysis of water isotopes (GIN) is active with more than 30 stations. Currently, the Federal Institute for Geosciences and Natural Resources (BGR) is analyzing stable isotope composition from 27 stations; for 19 of those stations time series of more than 10 years are available.

For Germany, most dominating stable isotope effects in precipitation are a seasonal and altitude effect, but also a continental effect is visible from delta^{18}O vs. delta^{2}H plots. Comparing precipitation of different sites and altitudes in Germany reveal topographical patterns. Interestingly, time series from the recent years indicate influence of extending dry and hot summers. Further, it is obvious that the maintenance of such a monitoring network requires lots of effort, also in reducing measurement uncertainties and establishing inter-laboratory comparisons within the GIN network community.

P.2 Climate Change and Physiology

P 2.4

Stable Isotope and AI supported model development for high frequency, cross scale water partitioning (ISO SCALE)

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Changing climate conditions and accelerating human demands on agricultural systems and ecosystem services increase the importance and urgency of understanding water movement in the soil-plant-atmosphere continuum (SPAC) and developing sustainable water management strategies for croplands. Non-linear dependencies among SPAC processes require dynamic and high-resolution monitoring to identify the spatio-temporal variability of water movement along SPAC interfaces. Recent technological advances have made water isotopes more affordable and widely applicable tracers. They are commonly used in natural systems for monitoring water movement and integrating process knowledge but are rarely applied to cropland. High-resolution data are needed to successfully predict the long-term effects of climate change-related disturbances and associated legacy effects on ecosystem resilience and crop water use strategies. Thus, in the ISO-SCALE project, we aim to achieve a novel integrated, cross-compartmental and cross-scale understanding of water partitioning and its spatio-temporal dynamics through high temporal resolution data. We will use in situ isotopic monitoring techniques to characterize the spatio-temporal patterns of water movement along the SPAC interfaces in a cropland. Particularly, we will investigate the temporal and spatial variability of ecosystem evapotranspiration, soil evaporation, plant transpiration, and soil water partitioning.

P.2 Climate Change and Physiology

P 2.5

Advances in the use of stable hydrogen isotopes of wood lignin methoxy groups as a proxy to determine plant source water and for climate variability

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Stable hydrogen isotope values of tree-lignin methoxy groups (δ^2H_{LM}) are increasingly used to reconstruct the stable hydrogen isotope composition of precipitation (δ^2H_{precip}) and mean annual temperatures in mid-latitude regions. The climate reconstructions are typically derived considering an isotope fractionation of -200 mUr to -216 mUr between lignin methoxy groups and tree source water (Keppler et al. 2007, Anhäuser et al. 2017, Greule et al., 2021, Porter et al. 2022, Wieland et al. 2022). This empirical relationship was derived from different tree species collected along a European north-south transect at altitudes below 1000 m above sea level. However, the influence of various environmental and tree physiological factors on biochemical hydrogen isotope fractionation between lignin methoxy group and precipitation is still unknown.

In order to discuss the improvements and limitations of δ^2H_{LM} values as a climate proxy at different spatial and temporal scales, we present several recent studies that show how environmental and tree physiological factors might influence δ^2H_{LM} values. Our research involves various investigations, including the phylogenetic range by comparing 70 different tree species grown under similar climatic conditions, the influence of salinity by analysing different mangrove species from Australia, and finally the influence of altitude on δ^2H_{LM} values with respect to variations in growing season and source water availability.

3 Earth System Science and Reconstruction

P 3.1

Isotope hydrobiogeochemical composition of a managed river entering the southern Baltic Sea: A seasonal perspective

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The composition of a river, the Warnow River (WR), flowing into the Baltic Sea off Warnemünde (Germany), was investigated. A spatial study was carried out to follow the variations from the origin to the estuary. A temporal study was conducted at one site just before WR meets the estuary. Surface water was sampled to analyze nutrients, major and trace elements, stable (H, C, O ,S), and Ra isotopes. The composition was controlled by its tributaries, in situ processes, exchange with the atmosphere, and diffuse groundwater. The WR is like a lake system, leading to high evaporation and interaction with sediments/soils. The WR was a source of dissolved inorganic carbon to the estuary, which may further impact the Baltic coastal waters. The calculated CO_2 partial pressure was higher than the modern atmospheric value, indicating that WR is a source of CO_2 to the atmosphere. Due to CO_2 degassing and photosynthetic activity, calcium carbonate may be formed, which causes a decrease in dissolved Ca. In spring, pelagic primary production strongly impacts pH and redox-sensitive elements. In summer and autumn, influences occurred by benthic microbial activity, diffusive release from soils/sediments and tributaries. The results highlight the need to investigate surface water systems discharging into coastal areas to better understand the coastal carbon cycle.

The study was supported by BALTIC TRANSCOAST (DFG),
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P.3 Earth System Science and Reconstruction

P 3.2

Isotope biogeochemical in a temperate coastal peatland after flooding by brackish water

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The biogeochemical impact of brackish water rewetting was investigated using stable isotopes, DIC, major ions and nutrient concentration of a coastal peatland in southern Germany (Drammendorf).Soils and pore water samples were collected before and after brackish water intrusion from a lagoon (Kubitzer Bodden).Pore waters were extracted before soil and pore water analyses.Pore water samples were measured for water and dissolved inorganic carbon (DIC) stable isotopes, physical parameters, major ions and nutrients concentrations.Soil samples were analyzed for acid-extractable metals and nutrients, CNS contents, acid-volatile sulfides and chromium-reducible sulfides concentrations.Results showed the vertical signatures of recent brackish water intrusion and previous freshwater rewetting using water stable isotopes, Mg and Na concentrations.The intrusion influenced organic and inorganic compounds, DIC releases and authigenic minerals formation and dissolution.The soil TOC decrease indicates the persistence of organic matter decomposition and diagenesis.δ^{13}C-DIC indicated DIC from organic matter/methane oxidation, carbonate dissolution and seawater-derived DIC. P and Ca increases indicate nutrient release and mineral dissolution. Additional sulfate concentrations influenced diagenesis and led to the formation of authigenic minerals.AVS/CRS ratio indicates pyrite formation below and upper soil surface volatile sulfides enrichment.The study shows the influence of peatland rewetting with possible future sea level rise perspective.

P.3 Earth System Science and Reconstruction

P 3.3

An isotope view on water and carbon transfer in a tidal basin under impact of submarine groundwater discharge

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The role that of fresh surface and ground water sources play on the coastal water and element balances, and the associated biogeochemical processes is still a matter of debate. Fresh and saline water mixing in coastal areas is allowed by stable water isotopes and further hydrochemical tracers. Here, we report on investigations of surface, pore and ground waters from Königshafen Bay (Sylt) and potential mixing endmembers. Besides dissolved major and minor elements, the stable water isotope composition is used to characterize the temporal and spatial distribution of different water sources to the bay and the seasonal dynamics in the water column. Porewater gradients indicate different degrees of freshening, locally already in the top 50 cmbsf 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 SGD impact, that differ in composition from surface water sources 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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P 3.4

Groundwater around Lake Sevan, Armenia: Insights from stable isotopes of water and nitrate

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Lake Sevan (at 1900 m a.s.l., approx. 1280 km^2) is of paramount importance for Armenia, for economic and ecologic reasons (water supply, fishing, recreation, tourism, biodiversity, etc.). Due to a number of environmental problems, incl. eutrophication, the lake received quite some attention over the last years, but this does not apply to the surrounding groundwater. Thus, aspects such as groundwater quality, prevailing residence times, recharge mechanisms, and eventually the role of groundwater in the lake's water budget are not well understood.

In a recent survey, we found isotopically depleted groundwaters, with $\delta^{18}O$ values mostly ranging between -14 and -9 ‰ V-SMOW. These values are lower than the amount-weighted mean precipitation signal of a monitoring station at the lakeshore, which reflects a seasonal recharge bias (snowmelt season) and an elevation effect. ^3H concentrations range from below detection limit to several TU, indicating a modern recharge component. Partly even artesian wells show ^3H, which suggests a certain groundwater vulnerability. The latter is supported by elevated nitrate concentrations (up to 130 and 44 mg/l in non-artesian and artesian wells, respectively). $\delta^{15}N$ and $\delta^{18}O$ of groundwater nitrate show limited scatter (4.9 to 9.7 ‰ AIR and 0.1 to 4.6 ‰ V-SMOW, respectively) and hence point towards a uniform but hitherto unidentified source.

P 3.5

The unusual carbon cycle budget of the Gravona (Corsica) - A small stream in a mountain silicate terrain

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The current research of carbon cycling in inland waters lacks a sound knowledge of carbon outgassing from small streams. Consequently, the terrestrial water cycle compartments might still be seriously underrepresented in estimates of global carbon transfer budgets from land surfaces. This study investigated carbon sources and sinks of the high-relief silicate catchment of the Gravona river (Corsica, France) on the basis of field parameters, dissolved inorganic carbon (DIC) and its stable carbon isotopes ($\delta^{13}C_{DIC}$). The source region was characterised by low DIC and high $\delta^{13}C_{DIC}$. Higher respiration and weathering influences in the lower river sections induced increasing DIC concentrations and seasonality, while the $\delta^{13}C_{DIC}$ decreased. The aqueous partial pressure ($pCO_{2(aq)}$) was lowest at the source. Samples from the cold season even showed undersaturation that led to atmospheric CO_2 uptake. Downstream, the seasonality of $pCO_{2(aq)}$ increased with pronounced CO_2 degassing at the river mouth. Average DIC flux along the river was 0.129 Gg C yr^{-1} and was almost equal to CO_2 degassing from the river surface with 0.128 Gg C yr^{-1}. Our study showed that on an annual basis the river is an overall weak to medium source of CO_2 to the atmosphere even though headwater parts of the river seasonally act as CO_2 sinks.

P 3.6

Tracking the evaporation front with stable isotopes of water in a drying sand column

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We performed a long-term evaporation experiment to improve our ability to derive water flow and transport parameters from the isotopic information temporally archived in natural soils. Specifically, we treated the surface of an initially water-saturated sand column with a continuous dry gas stream. We monitored the column's weight loss and in situ the concentration and isotopic composition of water vapor at different depths as well as in the outgoing gas stream. After several days, stable isotope and vapor concentration readings stabilized. We identified this as the stage I evaporation phase, which is characterized by a stagnant evaporation front near the surface and a constant evaporation stream that is maintained by capillary rise of water from lower depths. Stage II evaporation, which is characterized by gradual downward movement of the evaporation front due to breakdown of the capillary rise, started after 120 days. We identified it by the gradual decrease of both vapor concentration in the exported gas stream and the column's weight loss rate. At the depth of the in situ probes, we identified the passing-through of the evaporation front at the different observation depths by respective increases of isotopic compositions before and a decrease of vapor concentration afterwards. Our setup was perfectly suitable to observe stage I and stage II evaporation from the combination of vapor concentration and isotope readings. The employed in situ probes proved to be critical for the success.

P.3 Earth System Science and Reconstruction

P 3.7

Project launch: The groundwater isotope map of Germany

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The overall objective of the new joint project with a total of nine partners from science, federal and state authorities and industry is to create for the first time a nation-wide interpolated isotope map (isoscape) of stable water isotopes and tritium concentrations in groundwater for Germany. The project start is scheduled for early 2023. The data will be made available to potential users in an interactive, long-term and expandable and adjustable manner. This is done from existing data of individual state offices, from literature, from companies as well as from new measurement campaigns within the project. The system will be expandable via historical data as well as future measurements after the end of the project. Signals of climate change, as they are already visible in the isotope ratios of precipitation, lysimeter seepage water and surface water, will be recorded for the first time with isotope data of the water of different compartments and can be systematically evaluated.

A first attempt to collect and measure groundwater isotopes values for a larger area was made 2015 during a groundwater sampling campaign in the state of Bavaria. A total of ~650 samples were analyzed for their $\delta^{18}O$ and $\delta^{2}H$ values. This data set gives the first state-wide overview of isotope values in groundwater for Bavaria. During the project the data set will be expanded to entire Germany. A joint European initiative on this tool for the sustainable use of water resources is a future vision of the project.

4 Environment and Pollution

P 4.1

Stable carbon isotopes as tracers for benthic sources of dissolved inorganic carbon in the Eastern North Sea: The Skagerrak area

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Marine sediments may act as a sink for carbon. Substrate and electron donor availabilities, sedimentology, as well as biological activity may influence the carbon cycling, impacting the release of TA and DIC. The North Sea is a highly dynamic system with shallow tidal areas and fresh water tributaries delivering nutrients and dissolved carbon. For the southern part, benthic DIC sources have been identified, with tidal areas being further hot spots, some being impacted by submarine fresh water discharge. The Skagerrak provides the unique opportunity of studying benthic DIC production under the impact of different dominant electron acceptors. Potential transformation of carbonates may impact release of TA and DIC. Here, we focused on the role of different electron acceptors in sediments from the North Sea, with a special focus on the Skagerrak. The pelagic and benthic system was investigated for the DIC source function and carbon storage capacity. The carbon (and oxygen) isotope composition of dissolved and solid phases was used to understand the specific biogeochemical processes dominating benthic mineralization and carbonate dissolution. Besides physical in-situ parameters, nutrients, and the stable isotope (H, C, O) composition were analyzed by ICP-OES, nutrient analyzer, gas irmMS, and CRDS techniques.

The present study was supported by the BMBF project COOLSTYLE as part of CARBOSTORE, and by Leibniz IOW.

P. 4 Environment and Pollution

P 4.2

Critical switch towards bicarbonate uptake during cyanobacteria blooms at much higher than expected pH values as shown by multiple carbon isotope investigations

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Cyanobacteria blooms can affect turnover of aqueous carbon, including dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), and particulate organic carbon (POC). We investigated them in a pond for 23 months. During these events POC isotope values (δ^{13}CPOC) increased up to −17.4 ‰, after aqueous CO_2 ($CO_{2(aq)}$) fell below an atmospheric equilibration value of 412 µatm. Additionally, carbon isotope enrichment between $CO_{2(aq)}$ and POC (e$CO_{2\text{-phyto}}$) ranged of between values of 2.0 and 21.5 ‰ with lowest fractionations observed at pH values above 8.9. The increase of δ^{13}CPOC and decrease of $\varepsilon CO_{2\text{-phyto}}$ values at low pCO_2 and high pH was plausibly caused by the activation of the carbon concentrating mechanism (CCM). This mechanism correlated with prevalent assimilation of ^{13}C-enriched HCO_3^- species. Surprisingly, $CO_{2(aq)}$ still contributed more than 50% to the POC pool down to pCO_2 values of around 150 µatm. Only after this threshold, the reduced $\varepsilon CO_{2\text{-phyto}}$ suggested incorporation of ^{13}C-enriched HCO_3^-. This work is based on a publication by (Piatka et al., 2022).

Reference:

Piatka, D. R., Frank, A. H., Köhler, I., Castiglione, K., van Geldern, R., & Barth, J. A. C. (2022). Balance of carbon species combined with stable isotope ratios show critical switch towards bicarbonate uptake during cyanobacteria blooms. Science of the Total Environment, 807. doi:10.1016/j.scitotenv.2021.151067

P. 4 Environment and Pollution

P 4.3

Application of dual carbon and sulfur isotopes as tracers of PM1 pollution sources

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The aim of this work was to apply a multiple isotope approach to the characterization and source apportionment of sulfate and carbonaceous particulate matter in an urban environment. Sulfur and total carbon (TC) concentrations and isotopic compositions were measured in PM$_1$ samples collected during a period from 11/11/2020 to 21/10/2021 in Vilnius, Lithuania. Dual carbon (^{14}C/^{12}C, ^{13}C/^{12}C) and sulfur isotope analyzes (^{34}S/^{32}S) were performed to quantify the contribution of fossil and non-fossil emissions to carbon- and sulfur-containing PM$_1$. Source apportionment revealed three main sources of TC emissions: biomass burning, coal burning and transportation. TC concentrations were in the same range before and during the COVID-19 lockdown but the pandemic lockdown affected the TC isotopic composition (δ^{13}C) and source distribution, additionally the transport emission fraction was on average 2.3 times lower. The dominant sources of sulfate were coal burning and biomass burning. However, biomass burning becomes the predominant local source of PM$_1$-related sulfate in Lithuania, associated with increased household heating activities in winter. In addition, the origin of the air masses were also considered to interpret changes in isotopic composition and the PM1 source contributions.

P. 4 Environment and Pollution

P 4.4

Isotope analyses to asses sediment cores from freshwater lakes in Jiangsu Region

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The lakes in the Jiangsu province of China provide water to 30 million residents. Pollution of the lakes has been ongoing for decades in spite of efforts to reduce pollution. In 1993 alone, one billion tons of wastewater, 450,000 tons of garbage, and 880,000 tons of animal waste were dumped into the shallow lake Taihu. So lake Taihu was taken over by a massive bloom in May 2007.

The sediment cores of two lakes (Taihu and Yangcheng) are predicted to record the interaction of the sediment with the water column. Isotope and organic matter (d^{13}C, ^{15}N, TIC, NDOC (non-dissolvable organic Carbon), NDON (non-dissolvable organic nitrogen), d ^{13}C-non-target-GC-CF-IRMS-MS), and element analyses were carried out to improve our understanding of the history and fate.

The inorganic parameters show differences between the possible precipitated Ca-species and the belonging anions. d^{13}C-TIC shows values starting from marine carbonate in the deepest layer to fresh water carbonate in the upper layers of lake Taihu. d^{13}C-TIC in lake Yangcheng shows an inverse trend.

The organic parameters show that each core has a different history and fate of the OM. These are preserved for the d^{13}C-NDOC, d^{15}N-NDON as well as the compound ^{13}C-non-target-GC-CF-IRMS-MS. The found OM had different time-dependent sources. The sources of organic matter also change by time with the sediment core depth.

This investigation provides an improved understanding of the interaction between sediment and lake water.

P. 4 Environment and Pollution

P 4.5

Carbon isotope fractionation of the neonicotinoid insecticide imidacloprid during photolytic degradation

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Compound specific isotope analysis (CSIA) can be used to improve our understanding of how degradation mechanisms of environmental pollutants change under varying photolysis conditions. The influence of factors like pH, light wavelength and dissolved oxygen content can be investigated in laboratory batch experiments. However, polar and thermally labile materials like imidacloprid present a particular challenge in CSIA. Using GC-IRMS is not straightforward for such compounds as they are not volatile and existing derivatization protocols are not suitable for this application. LC-IRMS offers a way to separate non-volatile substances like imidacloprid from its transformation products and convert them to CO_2 for carbon isotope analysis by wet chemical persulfate oxidation.

In this study a simple aqueos LC-IRMS method to separate imidacloprid from its transformation products is presented. This method can be used to study various types of abiotic imidacloprid degradation regarding their carbon isotope fractionation. Degradation by hydrolysis, photolysis or different radical species can be compared. Changes in degradation mechanisms dependend on factors like pH, oxygen content or lamp type are investigated. Photolysis as a major pathway has been tested by means of a filtered xenon-lamp as a sunlight simulator (λ>280nm). The results were contrasted with a UVC-lamp (λ=254nm). This data shall improve our knowledge about the degradation process.

P. 4 Environment and Pollution

P 4.6

N2O fluxes by fungal denitrification, quantification, control and foreseen modelling

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Denitrification is one of the main N_2O production processes in soils and can be carried out by bacteria and fungi. Since most fungi lack the enzyme N_2O reductase, N_2O is the major end product (Shoun et al. 1992). So far, reliable methods to quantify fungal contribution to N_2O fluxes from denitrification are lacking, although studies with growth inhibition indicated considerable N_2O production by fungi (Laughlin and Stevens, 2002) and N_2O isotopic signatures differ between bacterial and fungal denitrifiers in pure culture experiments (Rohe et al. 2017; Sutka et al. 2008). However, understanding of fungal denitrification is necessary to improve modelling of N_2O emissions and to develop mitigation strategies.

Thus, a set of isotope and inhibition approaches will be used to evaluate and improve methods to quantify the contribution of fungi to soil-derived N_2O fluxes and unravel their controls. Data will be evaluated using “isotope mapping” approaches (Lewicka-Szczebak et al. 2017) including the calculation tool FRAME (Lewicki et al. 2022). By identifying fungal key players and their regulation, our experimental results will help to develop conceptual approaches of how to integrate fungal denitrification into biogeochemical models.

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P 4.7

Annual and seasonal dynamics of anaerobic oxidation of ammonium and denitrification linked with methane in a dimictic lake

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In aquatic ecosystems, nitrogen (N) loading is mitigated in redox transition zones principally through the processes of denitrification and anaerobic oxidation of ammonium (anammox). Here we investigate the N cycling processes in the water column of a seasonal stratified lake in Southern Germany (Fohnsee) over several years. We looked closer to the development of the vertical redox stratification between April and September and stuied the concentration profiles and stable isotope compositions of CH_4, NO_3^- and NH_4^+ together with numerical modeling and quantification of the hydrazine synthase gene (hzsB) and nitrite reductase (nirK and nirS) genes to identify the predominant nitrogen transformation processes at lake Fohnsee throughout the spring and summer periods.

P. 4 Environment and Pollution

P 4.8

Assessing Organic Fertilizer Nitrogen Cycling and Translocation into adjacent Aquatic Systems using 15N Tracing at different Scales

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Nitrogen (N) fertilization is essential to increase agricultural productivity, but losses of excess N to the environment, especially from organic fertilization, are causing environmental and health issues. Thus, optimized cattle slurry management targeted to increase nitrogen use efficiency (NUE) can be fundamental for limiting fertilizer N losses from agricultural grasslands. This study aims to further investigate the nitrogen interactions between the pedosphere and hydrosphere at two different scales. At a 1 m^2 plot scale we assess the effect of different slurry application techniques on NUE and N losses. For this, ^{15}N enriched slurry was applied using traditional broadcast spreading as well as modern injection techniques. Fates of fertilizer N such as plant uptake, immobilization and leaching are being investigated by ^{15}N tracing and recovery approaches in order to create full fertilizer N balances. Second, a larger-scale ^{15}N experiment is conducted on a 200 m^2 strip of a grassland slope to assess spatiotemporal patterns and pathways of N translocation along the slope to the buffer strip and into the adjacent creek. Soil and plant biomass, sediment within the creek and soil water are being sampled with subsequent ^{15}N analysis. From the two ^{15}N tracing experiments, we expect an in-depth understanding of how modern slurry application techniques alter N allocation and loss in the grassland plant-soil system, as well as of the translocation of leached N on a landscape scale.

P 4.9

Increasing methane productivity in anaerobic digesters by addition of CO2 – the use of stable isotope techniques to identify the mechanisms

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In recent years, the demand for renewable energy and the reduction of greenhouse gases such as CO_2 has become increasingly important within the framework of energy transition. Sato and Ochi showed in 1994 that CO_2 is converted into energetically usable methane (CH_4) without the addition of hydrogen (H_2). They observed increased CH_4 gas production in anaerobic sewage sludge digesters when maintaining high CO_2 gas concentration in the headspace. Although follow-up studies confirmed those findings, none of the few recently published studies were able to elucidate the basic effects leading to the bioconversion of CO_2 to CH_4. Our project (supported by the Fachagentur für Nachwachsende Rohstoffe) investigates bioconversion of CO_2 to CH_4 with the overall aim of reducing industrial CO_2 emissions and transformation of CO_2 into energetically usable CH_4. This is studied in a long-term anaerobic digestion experiment using different substrates (sewage sludge, maize silage, homogenized organic residuals) and applying stable isotope techniques to identify the underlying mechanisms leading to increased CH_4 formation observed within previous studies. For this purpose, two continuous 28 L anaerobic digestion systems were established (reactor with CO_2 injection and control) and $\delta^{13}C$-CH_4, $\delta^{13}C$-CO_2 and $\delta^{2}H$-CH_4 values in the headspace gas were measured to investigate the underlying CO_2 to CH_4 bioconversion pathways, targeting the mechanisms hypothesized so far.

5 Methods, Models, Standards

P 5.1

A large-volume air sampling system (LVASS) for isotope determination of atmospheric chloromethane

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The global budget of chloromethane (CH_3Cl) remains highly uncertain despite its significant role in catalyzing stratospheric ozone loss. Since conventional, concentration-based methods have limitations in improving current budget estimates including the balance of sources and sinks, stable isotopes offer an alternative approach to address these uncertainties. However, a crucial prerequisite for this concept is the determination of average tropospheric δ^2H_{CH3Cl}, $\delta^{13}C_{CH3Cl}$ and $\delta^{37}Cl_{CH3Cl}$ values, which poses a considerable analytical challenge due to the low abundance of atmospheric CH_3Cl of around ~550 parts per trillion by volume. Hence, we constructed a large-volume air sampling system (LVASS) capable of collecting sufficient amounts of CH_3Cl from 50 to 500 L of air at three distinct locations in Germany: Heidelberg University (urban), Hohenpeißenberg (boundary layer) and Schneefernerhaus (free troposphere).

We present preliminary results of δ^2H_{CH3Cl} and $\delta^{13}C_{CH3Cl}$ values from the first sampling campaigns applying the LVASS at these three locations. The δ^2H_{CH3Cl} and $\delta^{13}C_{CH3Cl}$ values were measured by stable isotope ratio mass spectrometry. We will particularly focus on the reliability of the atmospheric measurements and the evaluation of potential fractionation processes associated with the LVASS, purification system and analysis by IRMS.

P.5 Methods, Models, Standards

P 5.2

Miniature combustion reactors to increase sensitivity and selectivity, and to facilitate GCxGC for compound-specific isotope analysis (CSIA)

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The online combustion of analytes between gas chromatography and isotope ratio mass spectrometry (GC-C-IRMS) has enabled compound-specific isotope analysis (CSIA) for various applications, such as assessment of environmental contaminants or doping in sports. However, CSIA is challenged by the need for complete peak separation and the need for improved sensitivity. Comprehensive gas chromatography (GCxGC) could deliver a breakthrough, but hinges on developing robust miniaturized online combustion tubes. They must offer sufficient oxidation capacity and catalytic surface area to accomplish complete analyte conversion to CO_2, while being narrow enough to preserve narrow analyte peak shapes within the continuous flow carrier stream for subsequent IRMS analysis.

The current step change when He carrier gas passes from GC capillary columns (inner diameter, i.d.: 0.22–0.32 mm) to commercial combustion tubes (i.d.: 0.5 mm) generates substantial peak broadening. Even smaller GC capillaries are needed, however, to support GCxGC applications and to improve sensitivity by reducing flows and, therefore, minimizing losses in an open split before IRMS. We aim to explore the promise of two designs - a wall-coated capillary (WCC) reactor and a solid-electrolyte reactor (SER) - to pioneer robust solutions for miniaturized reactors that can facilitate routine GCxGC-C-IRMS.

P.5 Methods, Models, Standards

P 5.3

What is a typical GC-IRMS performance? Long-term records of backgrounds, linearity, sensitivity, precision, and trueness on different GC-IRMS instruments

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Gas chromatography - isotope ratio (monitoring) mass spectrometry instruments are installed with specifications on quality assurance parameters, and these parameters are regularly monitored in routine operation. Backgrounds in morning tests are recorded to inform about the leak-tightness of a system. The amplitude of monitoring gas pulses or air injections is an indicator of the sensitivity of the mass detector. Monitoring gas pulses are introduced at different amounts to test for linearity meaning that resultant isotope measurements should ideally be amount-independent. The standard deviation of isotope values informs about the precision of isotope analysis.

In addition, laboratories need to purchase external reference materials and establish a set of in-house standards to ensure the trueness of target compound analysis over days, months, years, and decades. Long-term performance data over these time scales, however, are rare. While the precision of GC-IRMS analysis is typically specified as ±0.2‰ to ±0.3‰, and total uncertainty including both precision and trueness is indicated as ±0.5‰, publications on systematic data on long-term performance are seldom.

Here we will share such quality assurance data over more than 10 years from three different GC-IRMS instruments in our laboratory. We would like to stimulate an exchange with other labs of experience and best practice.

P 5.4

^{15}N-isotope analysis of sulfamethoxazole by derivatization-gas chromatography-isotope ratio mass spectrometry

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Compound-specific isotope analysis is a powerful tool for characterizing degradation pathways through occurring isotopic effects. However, relying solely on isotopic information from a single element can present challenges in identifying transformation reactions in the field. Masking effects can lead to variations in isotope fractionation even if the same underlying degradation reaction prevails. In these cases, observed isotope enrichment factors may not accurately reflect the full isotope effects generated by the underlying reaction mechanism. Therefore, changes in isotope ratios of two elements relative to each other can allow for the distinction of different transformation pathways. The commonly employed technique for measuring polar and non-volatile compounds – LC-IRMS – is, however, restricted to carbon isotope measurements. To overcome this limitation and analyze nitrogen isotope values, we have spearheaded derivatization-GC-IRMS as an alternative. This work shows the development, optimization, and validation of a derivatization-GC-IRMS method for nitrogen isotope analysis of sulfamethoxazole, an antibiotic of environmental concern, as a basis for dual-element isotope analysis. Sulfamethoxazole was derivatized by methylation of the N^1-position using TMSD. Different reaction times, temperatures, and TMSD equivalents showed yields of up to 87%, highlighting the potential for compound-specific isotope analysis.

P.5 Methods, Models, Standards

P 5.5

Qtegra ISDS Software – driving analyses of the Thermo Scientific™ gas IRMS portfolio

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Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution (ISDS) Software is the new software platform for stable gas IRMS analysis. It has a logical, streamlined interface that intuitively provides the analyst with the appropriate tools at each point in the analytical workflow.

Here, we will demonstrate how Qtegra ISDS Software simplifies analysis setup and the data evaluation based on examples from the gas IRMS portfolio covering continuous flow as well as dual inlet system configurations including the Thermo Scientific™ DELTA™ Q IRMS or 253 Plus™ 10 kV IRMS.

Qtegra ISDS Software significantly improves data visualization allowing easier method development and optimization. This is additionally supported with templates, pre-settings, and a standards library to simplify the introduction to the new software. The software provides data evaluation features which allow in-software data evaluation and normalization, storing the crucial method information together with the results in one place, the LabBook, to support data transparency. Qtegra ISDS Software allows you to export all aspects of your data, from chromatograms to system control metadata and the isotope ratio results, providing you with complete ownership of your data.

Additionally, the new software platform ensures the utmost integrity and traceability for all data through a user management system, making sure that the system is configured to comply with GxP and 21 CFR Part 11 regulations.

P.5 Methods, Models, Standards

P 5.6

Water vapor sampling - a novel method for semi-*in situ* soil and plant water isotope analysis

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In the last decade, in situ soil and plant water isotope sampling has made substantial progress, enabling researchers to study water transport processes in the soil-plant-atmosphere continuum in great detail and improve process understanding. However, in situ soil and plant water isotope measurements have been criticized as methodologically challenging, laborious and expensive (due to the need for an isotope analyzer in the field). We present a novel way of collecting equilibrated soil and plant xylem water vapor for a subsequent isotope analysis in the laboratory. The method is based on directing dry air through the desired soil depth (via a gas permeable membrane) or tree xylem (via stem boreholes, Marshall et al., 2020), allowing for isotopic equilibration within the media to be measured, and collecting the sample in tighly sealed 250ml headspace vials. The proposed method allows for a control of flow rates and test for isotopic equilibrium. We present a comparison of liquid isotope standards, soil and xylem water isotope values with established methods and find good agreement. This novel way of sample collection and analysis will enable researchers to collect soil and plant water isotope data in a high temporal resolution without the need for extensive destructive sampling and be of great value for ecohydrological studies.

P.5 Methods, Models, Standards

P 5.7

Separation of organic and inorganic carbon – a method assessment.

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Different methods are described in the literature, detailing the separation of organic and inorganic carbon in soil and sediment samples, so as to get accurate organic carbon concentration (C_{org}) and isotope ($\delta^{13}C_{org}$) data. Most of these methods use either hydrochloric or sulphurous acid to oxidise carbonates to CO_2, leaving organic carbon behind for analyses. The literature consensus is that acidification methods can cause significant offsets in the C/N ratio, the $\delta^{13}C$ and $\delta^{15}N$ ratios of treated natural samples. In this study we present data from two acidification methods, and one thermogravimetric method, and assess their impact on isotopic measurements. Rather than using natural samples we produce synthetic samples made of carbonates, mixed with different organic compounds in a matrix of sea sand to better understand the impact of the pre-treatment methods on different types of organic materials. Among the organic compounds are those that can be found in soil samples, such as glucose, lignin, humic acid, but we also use in-house isotope standards such as caffeine. We show that the thermogravimetric method is not suitable for our synthetic samples as some of the organics seem to be charred, rather than oxidised to CO_2. Nitrogen bearing compounds show the largest isotope offset between acid treated and non-acid treated samples, and surprisingly the acidification treatments have the smallest effect on the carbon isotopic composition of large organic molecules such as lignin and humic acid.

P.5 Methods, Models, Standards

P 5.8

Production of standard gases for routine calibration of stable isotope ratios of N_2 and N_2O

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There is need to calibrate raw data of N_2 and N_2O isotopocules due to effects of non-linearity, instability, matrix effects and interference with trace gases. Our objective was thus to supply a variety of suitable standard gases for members of the DASIM research unit (www.DASIM.de) and their partners in sufficient amount for routine use to enable calibration for extended time. In total 23 different mixtures were produced to cover all isotopic approaches to study N_2 and N_2O production and cycling in soils with stable isotopes and suitable for IRMS and laser spectroscopy.

Standards for the ^{15}N gas flux method should mimic mixtures of N_2 and N_2O emitted from highly ^{15}N enriched nitrate in soil and atmospheric background. These must thus contain unlabelled, single-labelled as well as double-labelled N_2 and N_2O.

N_2O standards for natural abundance must cover a range of N_2O concentrations and isotopocule values typically found in field flux and laboratory incubation studies to correct for non-linearity and bias.

Premixtures were prepared by mixing isotopically enriched or depleted gases which were either commercially available or produced in the lab. Moreover, pure N_2O of natural abundance was supplied from a previous project (Mohn et al., 2022, https://doi.org/10.1002/rcm.9296). Premixtures were diluted in artificial atmospheres and compressed in commercial tanks.

We will explain the production of mixtures, give an overview of the manufactured mixtures and show first results of analysis in comparison with ideal values.

6 Life Science, Forensics, and Medicine

P 6.1

Stable isotopes for the differentiation of eggs from barn, free-range and organic farming in the German food retail market

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The National Reference Centre for Authentic Food (NRZ-Authent), which supports the official food control authorities in Germany in the fight against food fraud, is responsible for developing analytical authentication methods and providing databases with reference data sets. High profits can be made by labelling conventional eggs as organic, as consumer prices for organic eggs are 2-3 times higher in food retail. Previous studies on eggs using $\delta^{13}C$ and $\delta^{15}N$ values showed good approaches to differentiation, but no clear allocation of conventional and organic eggs. However, these studies did not consider potential variations in isotope values due to seasonal changes in feed composition. Fluctuations may be due to natural variations in vegetation and insect abundance, but also to the application of seasonal feeding practices. The present pilot study aimed to improve the identification of eggs from all three farming systems (barn, free-range, organic) considering seasonal variations as well as phases of compulsory stabling (during avian influenza) through high-resolution monthly sampling for the first time. A total of 180 egg samples from Schleswig-Holstein and Bavaria were analysed for their CNS isotopes, which showed a high variability over the studied 15-month period. The results will serve as a basis for an IRMS database supporting food German control authorities of the federal states and will be expanded in further studies with authentic samples from additional locations.

P.6 Life Sciences, Forensics, and Medicine

P 6.2

Laser Ablation IRMS analyses of $\delta^{13}C$ in both solid and liquid foodstuff

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Laser ablation (LA) offers speed, high sample throughput, minimal sample preparation and is economical when considering consumables and operating costs. For stable isotope analyses the elemental analyzer (EA) is the standard sample introduction method for solid samples. A few pioneer labs have adopted LA for IRMS analyses and we believe that LA IRMS should become the go-to method for stable isotope ratio measurements. We present a series of sugars/sweeteners made from a variety of plants and a set of vegetable oils extracted from various plans as well, analyzed via LA IRMS. The analytical setup is composed of a Teledyne Photon Machines LSX 213 G2+ 213 nm wavelength laser ablation system connected to a Sercon HS2022 IRMS via a CryoPrep sample preparation module. A specially designed sample chamber was used (isoScell Δ100, Terra Analitic). Split sugar samples were also analyzed via traditional EA IRMS (Sercon), for inter-instrument comparison. Cellulose (IAEA CH6) was used as reference in both instruments. LA IRMS offers accurate and precise determination of **δ**13C in most solid, organic matrices with the advantage of drastically reduced sample preparation and overall analytical costs. Given the minuscule amount of sample removed through ablation repeat analysis is always an option with LA. A single sugar crystal is enough for more than ten ablations and the standard deviation in our tests was 0.03‰. Liquid samples are just as easy to analyze!

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