ASI 2024

43rd Meeting of the German Association for Stable Isotope Research

Stable isotopes in geoscience, ecology, environmental science, medicine, and forensics

30 September – 2 October 2024

TECHNISCHE
UNIVERSITÄT
DARMSTADT

Book of Abstracts

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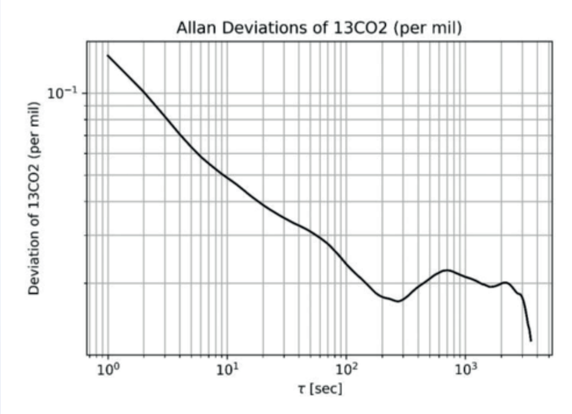
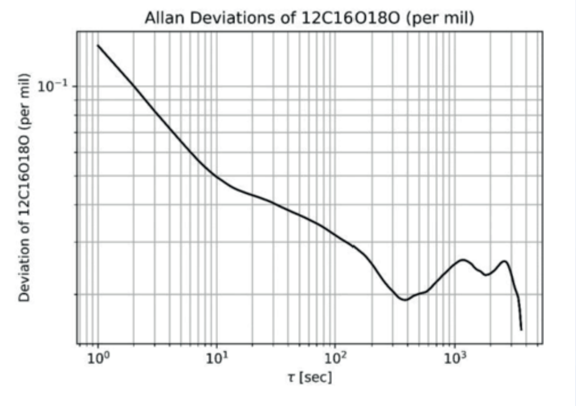
Aeris Technologies offers budgetary, robust, lightweight, fast 1-10Hz, very sensitive with typical <1ppb/s and stable (<1ppb/24h) trace gas analyzers in MIR.

Our newest addition is the CO_2 Isotope ratiometer for $\delta^{13}C$, $\delta^{18}O$ and $\delta^{17}O$:





Aeris' founders bring over 25 years of innovation and successful commercialization in laser-based gas analysis. Prior to founding Aeris, they launched two companies that were later acquired by Thermo Fisher and ABB. Aeris Technology is widely regarded as a true disruptor, driving a paradigm shift in the laser-based gas analysis industry with unmatched size, weight, power efficiency, performance, and price. By leveraging mid-infrared wavelengths between 2.8 µm and 5 µm, Aeris utilizes interband cascade lasers (ICLs), which provide significantly higher absorptivity in the mid-infrared spectrum compared to near-infrared systems. With a remarkably short 13-meter path length, the system achieves parts-per-trillion (ppt) measurement precision for most gases—making it the most efficient in its class.

CO_2 Isotopes/CH_4/C_2H_6/N_2O/CO/CO_2/OCS/CH_2O/EtO/C_3H_8/C_2H_2/C_6H_6

WELCOME ADDRESS

Dear isotope enthusiasts,

Welcome to Darmstadt – the city of science! This title ("Wissenschaftsstadt") was awarded to Darmstadt in 1997 by the State of Hesse, reflecting the city's scientific landscape with a diverse spectrum of research institutions and companies (GSI, ESA, Merck, etc.).

The most obvious member of this list is the Technical University of Darmstadt, which was founded in 1877 as "Technische Hochschule zu Darmstadt". With its 13 departments, 5,000 employees, and 24,000 students, the university's cutting-edge research focusses on three broad fields: Information and Intelligence (I&I), Matter and Materials (M&M), as well as Energy and Environment (E&E).

A part of the latter research is conducted at the Institute of Applied Geoscience, the host of this year's Meeting of the German Association for Stable Isotope Research (GASIR) – the 43rd meeting of our association. We are convinced to have compiled an interesting program for you, with 29 regular oral presentations, organized around four main topics, and four keynote lectures. The latter are given by valued colleagues that had received an Isotope Award (funded by the Dr.-Karleugen-Habfast-Stiftung) in the past and we are looking forward to learn how their journeys developed since then. These talks are complemented by 20 exciting posters.

We are happy to welcome you in our institute, look forward to an inspiring conference with interesting talks and posters as well as fruitful interdisciplinary discussions, and wish you a pleasant stay in the city of science Darmstadt.

With warm regards,

The Local Organization Committee

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Dr. Nils Michelsen

Dr. Kai Nitzsche

Dr. Kaori Sakaguchi-Söder

Prof. Dr. Moritz Bigalke

Prof. Dr. Matthias Hinderer

Prof. Dr. Christoph Schüth

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A big thank you to the companies that supported the ASI 2024!

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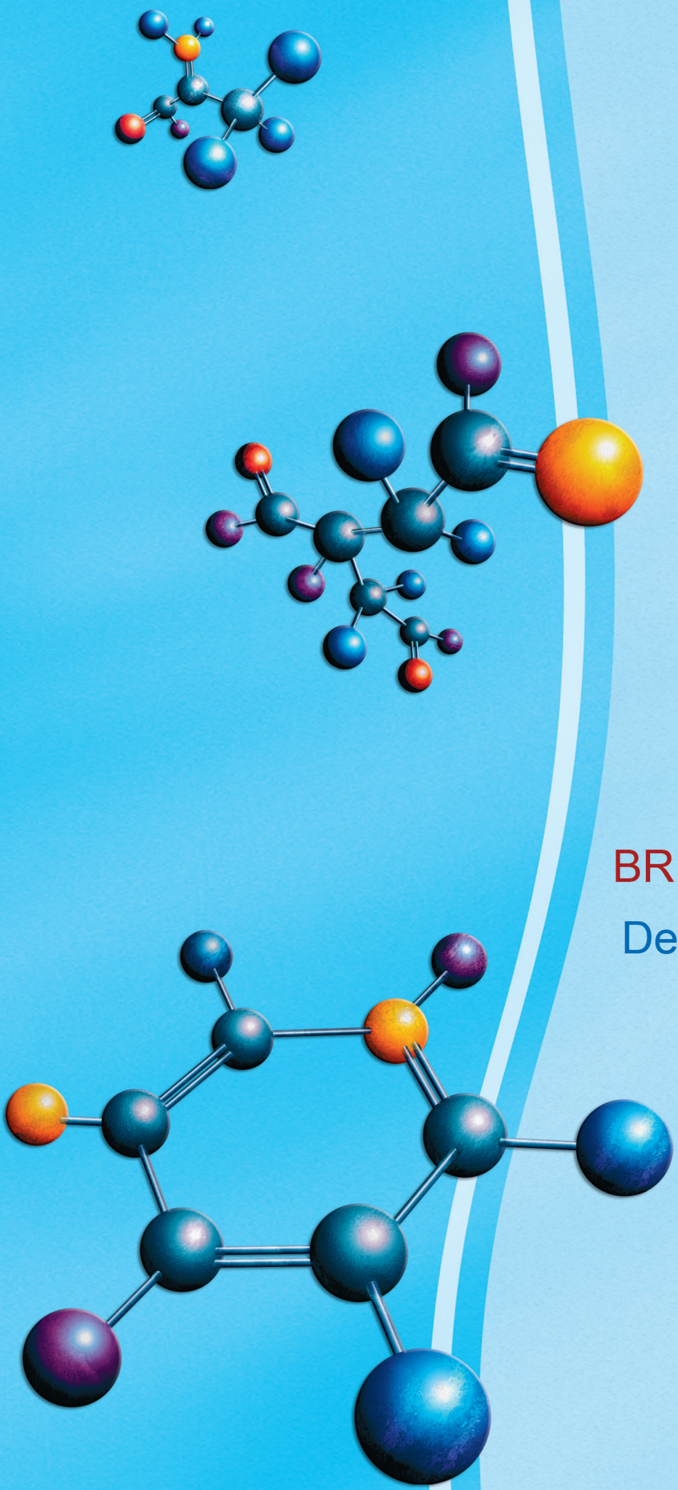

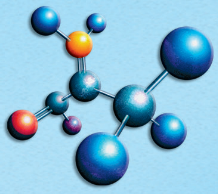

SUNDAY, 29.09.2024

14:00 – 17:00 **Workshop ASI Juniors**

MONDAY, 30.09.2024

10:00 – 12:00 **Company morning**

12:00 – 13:00 **Registration & coffee**

13:00 – 13:15 **Conference Opening**

13:15 – 14:45 **1.1: Analytics, Methods, Quality Assurance**

13:15 – 13:45

Session Keynote

A decade of in-situ stable water isotope observations: progress and challenges with a focus on isotope enabled gas-exchange

Maren Dubbert

ZALF, Deutschland

13:45 – 14:00

Coping with spectral interferences when measuring water stable isotopes of vegetables

Barbara Herbstritt[1], Lena Wengeler[1], Natalie Orlowski[2]

[1]Universität Freiburg, Hydrologie, 79098 Freiburg, Deutschland; [2]TU Dresden, Institute of Soil Science and Site Ecology, 01737 Tharandt, Deutschland

14:00 – 14:15

Comparison of gas matrix effects on three generations of cavity ring-down water stable isotope analyzers

Benjamin Gralher[1,2], Barbara Herbstritt[2], Markus Weiler[2]

[1]Institute of Groundwater Management, Dresden University of Technology, 01069 Dresden, Germany; [2]Chair of Hydrology, University of Freiburg, 79098 Freiburg, Germany

14:15 – 14:30

Laser spectroscopic analysis of N_2O isotopes: How to get trustworthy data?

Joachim Mohn[1], Julius Havsteen[1], Hannes Keck[1], Noémy Chénier[1], Paul Magyar[1], Simone Brunamonti[1], Andrea Pogany[2], Mehr Fatima[3], Thomas Hausmaninger[3], Benjamin Wolf[4], Klaus-Holger Knorr[5], Reinhard Well[6]

[1]Laboratory for Air Pollution / Environmental Technology, Empa, Dübendorf, Switzerland; [2]Department Analytical Chemistry of the Gas Phase, PTB, Braunschweig, Germany; [3]VTT Technical Research Center of Finland Ltd, National Institute of Metrology VTT MIKES, Espoo, Finland; [4]Terrestrial Bio-Geo-Chemistry, KIT/IMK-IFU, Garmisch-Partenkirchen, Germany; [5]Institute of Landscape Ecology, University of Münster, Münster, Germany; [6]Institute of Climate-Smart Agriculture, Johann Heinrich von Thünen-Institut, Braunschweig, Germany

14:30 – 14:45

Continuous-flow stable sulfur isotope analysis of organic and inorganic compounds using elemental analyzer coupled with multi-collector inductively coupled plasma mass spectrometry (EA-MC-ICPMS)

Steffen Kümmel[1], Axel Horst[1,2], Marcus Fahle[2], Matthias Gehre[1]

[1]Department of Technical Biogeochemistry, Helmholtz-Centre for Environmental Research GmbH - UFZ, Deutschland; [2]Research and Development Centre for Post Mining Areas, Federal Institute for Geosciences and Natural Resources - BGR

14:45 – 15:15 **Coffee break**

15:15 – 16:15 1.2: Analytics, Methods, Quality Assurance

15:15 – 15:30

What's going on with the $\delta^{13}C$ scale(s)?

Heiko Moossen[1], Pharahilda M. Steur[2], Federica Camin[3], Anett Enke[1], Heike Geilmann[1], Markus Lange[1], Harro A. J. Meijer[2]
[1]Max Planck Institute for Biogeochemistry, Germany; [2]University of Groningen, Netherlands; [3]International Atomic Energy Agency, Austria

15:30 – 15:45

Orbitrap Isotope Ratio MS – Improved Strategy for Sample and Reference Introduction

Nils Kuhlbusch[1], Andreas Hilkert[1], Issaku Kohl[2], Brett Davidheiser[1], Dieter Juchelka[1]
[1]Thermo Fisher Scientific, Deutschland; [2]University of Utah, USA

15:45 – 16:00

Advancing Greenhouse Gas Isotopic Measurements: Evaluating the Compatibility and Efficiency of Picarro Gas Autosampler with Picarro Isotopic Analyzers

Magdalena Hofmann[1], Jan Woźniak[1], Joyeeta Bhattachary[2], Jinshu Yan[2], Tina Hemenway[2], Keren Drori[2]
[1]Picarro B.V., The Netherlands; [2]Picarro Inc., USA

16:00 – 16:15

High precision stable isotope analysis of carbonate and water samples for paleoclimate applications using the Elementar iso DUAL INLET

Calum Preece[1], Mike Seed[1], Sam Barker[1], Will Price[1], Rob Berstan[1], Kathrin Rosenthal[2]
[1]Elementar UK Ltd, Stockport, SK8 6PT, Great Britain; [2]Elementar Analysensysteme GmbH, Elementar-Straße 1, 63505 Langenselbold, Germany

16:15 – 17:15 Postersession

18:45 Conference Dinner

TUESDAY, 01.10.2024

09:00 – 10:30 2.1: Hydro(geo)logy & German Isotope Network

09:00 – 09:30

Session Keynote

There and not back again: Isotope hydrobiogeochemistry of gradient systems

Michael Ernst Böttcher
Leibniz IOW und Universität Greifswald, Deutschland

09:30 – 09:45

Stable isotope composition of the Salalah monsoon, southern Oman

Thomas Müller[1], Robert van Geldern[2], Jan Friesen[3], Mark Schmidt[1], Ali Bakhit Ali Bait Said[4], Kay Knöller[3], Nils Michelsen[5]
[1]GEOMAR, Deutschland; [2]Friedrich-Alexander-Universität Erlangen-Nürnberg; [3]Helmholtz Centre for Environmental Research – UFZ; [4]Ministry of Regional Municipalities and Water Resources, Oman; [5]Technical University of Darmstadt

09:45 – 10:00

Isotopic distillation pattern during a major regional storm event

Ana-Voica Bojar[1,2], Christophe Lécuyer[3,4], Hans-Peter Bojar[2], François Fourel[5], Stanislaw Chmiel[6]

[1]Department of Geology, Salzburg University, Salzburg, Austria; [2]Department of Mineralogy, Universalmuseum Joanneum, Graz, Austria; [3]Laboratoire de Géologie de Lyon, Université Claude Bernard Lyon, France; [4]Institut Universitaire de France, Paris, France; [5]Laboratoire d'Ecologie des Hydrosystèmes Naturels et Anthropisés, Université Claude Bernard Lyon, France; [6]Faculty of Earth Sciences and Spatial Management, Maria Curie-Skłodowska University, Lublin, Poland

10:00 – 10:15

Partitioning denitrification pathways at an agricultural site using numerical modeling and stable isotopes of nitrate and sulfate

Juan Carlos Richard-Cerda[1], Matthias Bockstiegel[1], Edinsson Muñoz-Vega[1], Kay Knöller[1,2], Christoph Schüth[1,3], Stephan Schulz[1]

[1]Institute of Applied Geosciences, Technische Universität Darmstadt, Schnittspahnstraße 9, 64287 Darmstadt, Germany; [2]Helmholtz Centre for Environmental Research, Theodor-Lieser-Str. 4, 06120 Halle, Germany; [3]IWW Water Centre, Moritzstraße 26, 45476 Mülheim an der Ruhr, Germany

10:15 – 10:30

Balancing weathering and organic carbon input to a tropical river in Sri Lanka: a stable isotope approach

Sachintha Senarathne[1], Robert van Geldern[1], Rohana Chandrajith[1,2], Johannes A. C. Barth[1]

[1]Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Department Geographie und Geowissenschaften, 91054, Erlangen, GeoZentrum Nordbayern, Schlossgarten 5, Germany; [2]Department of Geology, Faculty of Science, University of Peradeniya, Peradeniya, Sri Lanka

10:30 – 11:00 **Coffee break**

11:00 – 12:00 2.2: Hydro(geo)logy & German Isotope Network

11:00 – 11:15

A depth-oriented investigation of hyporheic zone processes by isotopic and chemical analysis

Amani Mahindawansha, Matthias Gassmann

University of Kassel, Germany

11:15 – 11:30

Challenges of estimating groundwater recharge in forests through deuterium oxide labelling – How to trace soil water movement below the root zone?

Kolja Bosch[1], Paul Königer[1], Stefan Fleck[2], Bernd Ahrends[2], Erkki Hemmens[1], Susanne Stadler[1], Christoph Neukum[1]

[1]Bundesanstalt für Geowissenschaften und Rohstoffe, Deutschland; [2]Nordwestdeutsche Forstliche Versuchsanstalt, Deutschland

11:30 – 11:45

Climate indicators and stable isotope patterns in a region strongly impacted by lignite-mining (Lusatia, Germany)

Maike Gröschke, Anne Gädeke, Paul Koeniger

Federal Institute for Geosciences and Natural Resources (BGR)

11:45 – 12:00

Comparison of long-term precipitation stable isotopes monitoring at three selected stations of weekly resolution within the German Isotope Network (GIN)

Paul Koeniger[1], Anne Gädeke[1], Maike Gröschke[1], Axel Schmidt[2]

[1]BGR Bundesanstalt für Geowissenschaften und Rohstoffe, Hannover, Deutschland; [2]BfG Bundesanstalt für Gewässerkunde, Koblenz, Deutschland

12:00 – 13:30 **Lunch break**

13:30 – 14:30 **Isotope Award**

14:30 – 15:45 **3.1: Ecosystems and Biogeochemistry**

14:30 – 15:00

Session Keynote

N_2O isotopocules and mineral N isotopes in tracing N cycling in soils

Dominika Lewicka-Szczebak

University of Wrocław, Poland

15:00 – 15:15

Effect of nitrogen fertilization by red clover mulch in organic farming: An isotope analysis study

Diana Burghardt[1], Felix Seyfert[1], Finn Hendrik Hoefgen[1], Finn Mählig[1], Jette Stieber[2], Karsten Kalbitz[1]

[1]TU Dresden, Deutschland; [2]Sächsisches Landesamt für Umwelt, Landwirtschaft und Geologie, Referat Pflanzenbau

15:15 – 15:30

Water vapour diffusion from the atmosphere into the leaf is mostly ignored but relevant as shown by ^{18}O isotopes

Rolf TW Siegwolf[1], Christina E Reynolds[2], Haoyu Diao[1], Marco Lehmann[1], Matthias Saurer[1]

[1]Swiss Federal Institute for Forest, Snow and Landscape Research, WSL, Switzerland; [2]Paul Scherrer Institut, Lab of atmospheric chemistry

15:30 – 15:45

Multi-element stable isotope natural abundance in orchids from the Mediterranean region of Europe and SW-Australia

Gerhard Gebauer[1], Andreas C. Gebauer[1], Kingsley W. Dixon[2]

[1]Universität Bayreuth, Deutschland; [2]Curtin University, Perth, Australia

15:45 – 16:45 **Postersession**

16:45 – 18:15 **ASI general meeting**

19:00 **Thermo Fisher User Meeting**

WEDNESDAY, 02.10.2024

09:15 – 11:00 **3.2: Ecosystems and Biogeochemistry**

09:15 – 09:45

Session Keynote

The isotopic fingerprint of plant methoxy groups and its application in biogeochemical research

Frank Keppler

Institut für Geowissenschaften, Universität Heidelberg, Deutschland

09:45 – 10:00

^{18}O labeling experiments reveal new abiotic pathway of methanol and formaldehyde formation in soil

Jonas Hädeler[1], Gunasekaran Velmurugan[2], Rebekka Lauer[1], Peter Comba[2], Frank Keppler[1]

[1]Institut für Geowissenschaften, INF 234-236, Universität Heidelberg, D-69120 Heidelberg, Germany; [2]Anorganisch-Chemisches Institut INF 270 and Interdisciplinary Center for Scientific Computing, INF 205, Universität Heidelberg, D-69120 Heidelberg, Germany

10:00 – 10:15

Stable isotope insights into subglacial methane emissions from the Western Margin of the Greenland Ice Sheet

Moritz Schroll[1], Jesper Riis Christiansen[2], Christian Juncher Jørgensen[3], Getachew Agmuas Adnew[2,4], Sarah Elise Sapper[2], Thomas Röckmann[4], Carina van der Veen[4], Frank Keppler[1]

[1]Institute of Earth Science, Heidelberg University, Im Neuenheimer Feld 236, 69120, Heidelberg, Germany; [2]Forest, Nature and Biomass, Department of Geoscience and Nature Management, Copenhagen University, Rolighedsvej 23,1958, Frederiksberg C, Copenhagen, Denmark; [3]Arctic Environment, Department of Ecoscience, Aarhus University, Frederiksborgvej 399, 4000, Roskilde, Denmark; [4]Institute for Marine and Atmospheric research Utrecht, Utrecht University, Princetonplein 5, 3584 CC, Utrecht, the Netherlands

10:15 – 10:30

Experimental drought in a mature beech/spruce forest - using stable isotopes to study drought resistance and tree recovery

Thorsten Grams

Technical University of Munich, Germany

10:30 – 10:45

Using Cu stable isotope ratios to understand the cycling of Cu in Swiss grassland soils

Kai Nils Nitzsche[1], Martin Imseng[2], Matthias Wiggenhauser[3], Michael Müller[4], Emmanuel Frossard[3], Wolfgang Wilcke[5], Moritz Bigalke[1]

[1]Technische Universität Darmstadt, Deutschland; [2]Universität Bern, Schweiz; [3]ETH Zürich, Schweiz; [4]Nationale Bodenbeobachtung, Agroscope, Schweiz; [5]Karlsruher Institut für Technologie, Deutschland

10:45 – 11:00

Investigating Polyethylene Degradation in Soil Using a ^{13}C-labelling Approach

Hannah Forsyth[1], Filippo Vaccari[2], Andre Velescu[3], Edoardo Puglisi[2], Wolfgang Wilcke[3], Moritz Bigalke[1]

[1]Department of Soil Mineralogy and Soil Chemistry, Institute for Applied Geosciences, Technical University of Darmstadt, Schnittspahnstraße 9, 64287 Darmstadt, Germany; [2]Department for Sustainable Food Process, Università Cattolica del Sacro Cuore, Via Emilia Parmense 84, 29122 Piacenza, Italy; [3]Karlsruher Institut für Technologie (KIT), Institut für Geographie und Geoökologie, Reinhard-Baumeister-Platz 1, 76131 Karlsruhe, Germany

11:00 – 11:30 Coffee break

11:30 – 12:45 4: Physiology, Metabolism, Forensics, Food (+ further topics)

11:30 – 11:45

Evaluation of the potential of stable hydrogen isotopic composition of fatty acids for geographical traceability of vegetable oils

Lili Xia[1], Kaori Sakaguchi-Söder[1,2], Dorota Iwaszczuk[3], Liselotte Schebek[1]

[1]Material Flow Management and Resource Economy, Institute IWAR, TU Darmstadt; [2]Institute of Applied Geosciences, TU Darmstadt; [3]Remote Sensing and Image Analysis, Institute of Geodesy, TU Darmstadt

11:45 – 12:00

C-N-S-H-stable isotope data in human hair from the 1950s and more recent periods

Christine Lehn[1], Matthias Graw[1], Andreas Roßmann[2]
[1]LMU München, Deutschland; [2]isolab GmbH, Schweitenkirchen, Deutschland

12:00 – 12:15

Isotope Ratio Mass Spectrometry based profiling of *Ricinus communis* - A forensic approach

Lisa Scharrenbroch[1,2], Thomas Holdermann[1], Nicole Scheid[1], Thomas Schäfer[1], Björn Ahrens[1], Frederik Lermyte[2]
[1]Federal Criminal Police Office, Germany; [2]Technical University of Darmstadt, Germany

12:15 – 12:30

Geophysical Monitoring of simulated Graves and AI based Data Analysis – Subproject: Isotopic profiling of grass samples from the graves and nearby

Nicole Scheid[1], Jens Kirsten[2], Thomas Holdermann[1], Thomas Schäfer[1]
[1]Forensic Science Institute/Bundeskriminalamt, Central Analytics II; [2]Operational Technology/Bundeskriminalamt, UAS, cUAS and Remote Sensing

12:30 – 12:45

Carbon isotopes as reaction tracking tool in cement mineralogy

Marie Singer[1], Robert van Geldern[2], Johannes A.C. Barth[3], Daniel Jansen[4]
[1]GeoZentrum Nordbayern, FAU Erlangen-Nürnberg, Deutschland; [2]GeoZentrum Nordbayern, FAU Erlangen-Nürnberg, Deutschland; [3]GeoZentrum Nordbayern, FAU Erlangen-Nürnberg, Deutschland; [4]GeoZentrum Nordbayern, FAU Erlangen-Nürnberg, Deutschland

12:45 – 13:15 Awards, announcements, closing remarks

14:00 Excursions

14:00 – 15:30 – Botanical Garden

14:00 – 17:00 – GSI Helmholtzzentrum

1.1: Analytics, Methods, Quality Assurance

KEYNOTE

A decade of in-situ stable water isotope observations: progress and challenges with a focus on isotope enabled gas-exchange

Maren Dubbert
ZALF, Germany

Stable isotopes of water are widely used to trace ecohydrological processes and dynamics in ecosystems. In the last decade, the advent of laser spectrometers and the ability to measure stable water isotopes in the gas-phase has facilitated the development of multiple in-situ stable water isotope approaches, such as the coupling with semi permeable membranes recording soil and xylem isotopic signatures, in-situ analysis of atmospheric, precipitation and groundwater stable isotopic signatures and even the coupling of laser spectroscopy with eddy covariance. Almost 10 years ago, we have presented an overview on the coupling of gas-exchange chambers with laser spectroscopy enabling in-situ measurements of the isotopic signatures of transpiration or evapotranspiration.

Since then, there has been a tremendous developmental spurt of in-situ stable isotope techniques and this talk will give an overview of progress and challenges in using in-situ stable isotope techniques and particular isotope enable gas-exchange over the past decade.

Coping with spectral interferences when measuring water stable isotopes of vegetables

Barbara Herbstritt[1]*, Lena Wengeler1, Natalie Orlowski*[2]
[1]University of Freiburg, Hydrology, Germany; [2]TU Dresden, Institute of Soil Science and Site Ecology, Germany

RATIONALE Laser based analyzers are widely used in ecohydrology to analyze plant water isotopic compositions ($\delta^{18}O$ and $\delta^{2}H$). The suitability of three different water extraction and isotope equilibration techniques was compared. We examined whether co-extracted organic contaminants (VOCs) affect laser-based isotope measurements and used the instrument's spectral parameters to post-correct for interfering VOCs.

METHODS Cryogenic vacuum extraction, vapor headspace-equilibration in bags and vapor equilibration in-situ probes were used to extract liquid water or water vapor for laser-based isotope analysis (CRDS). Isotope data were calibrated by standards for each method separately. Spectral parameters of the instrument, appropriate to identify spectral interferences with MeOH and CH_4 were identified and used for post-correction. Differences between the three methods and between the origins of the vegetables were identified by statistical tests.

RESULTS VOCs were found in various amounts for the three different methods. They were co-extracted or co-equilibrated during the different extraction/equilibration methods. Correlation coefficients of isotope data and 'CH_4' (spectral parameter) were 0.99 or better, however slopes for $\delta^{18}O$ were similar on different instrument types but different for $\delta^{2}H$. Our correction approach improved results and inter-comparability of the methods considerably without knowing the chemical composition of the plant sap.

CONCLUSIONS All three methods were sensitive enough to distinguish and resolve differences in natural abundance. Data quality was improved by the 'CH_4-correction' approach but could probably be optimized by a plant species-specific correction. Standardized tools for contaminant removal or post-correction applications from manufacturers, in particular for vapor-mode analysis are still needed.

Comparison of gas matrix effects on three generations of cavity ring-down water stable isotope analyzers

Benjamin Gralher[1,2]*, Barbara Herbstritt*[2]*, Markus Weiler*[2]
[1]Institute of Groundwater Management, Dresden University of Technology, Germany; [2]Chair of Hydrology, University of Freiburg, Germany

Laser-based water stable isotope analyzers have become increasingly popular in the last one and a half decades. Their direct and continuous measurement capabilities make them perfectly suitable for, e.g. in situ isotope assays in environmental settings. However, field-deployed analyzers may be subjected to inconsistent background gas matrices between individual samples and compared to co-measured calibration standards. Therefore, we tested the gas matrix effects by varying the carrier gas proportions of nitrogen (N_2), oxygen (O_2) and carbon dioxide (CO_2) in naturally occurring ranges on three different generations of analyzers employing cavity ring-down spectrometry (CRDS, Picarro L21xx series). The observed magnitudes of gas matrix effects exceeded commonly accepted measurement uncertainties by two orders of magnitude on all analyzers tested but resulted in very contrasting patterns on the different generations. For example, oxygen isotope readings increased on all instruments as the carrier gas was transitioned from air to a mixture of 80 % N_2 and 20 % CO_2, which may be encountered on poorly aerated, organic-rich or contaminated sites. For the same transition, hydrogen isotope readings decreased on the L2120-i while they increased on all other instruments tested. Besides, we also checked for potential drift over the course of eight years on the oldest generation tested (L2120-i). Finally, we determined the consistency of the gas matrix effect on three different analyzers of the same generation (L2130-i). We present a post-measurement routine that reliably corrects for these effects and show how isotope data will be misinterpreted in dual isotope space if the suggested correction is omitted.

Laser spectroscopic analysis of N_2O isotopes: How to get trustworthy data?

Joachim Mohn[1], Julius Havsteen[1], Hannes Keck[1], Noémy Chénier[1], Paul Magyar[1], Simone Brunamonti[1], Andrea Pogany[2], Mehr Fatima[3], Thomas Hausmaninger[3], Benjamin Wolf[4], Klaus-Holger Knorr[5], Reinhard Well[6]

[1]Laboratory for Air Pollution / Environmental Technology, Empa, Dübendorf, Switzerland; [2]Department Analytical Chemistry of the Gas Phase, PTB, Braunschweig, Germany; [3]VTT Technical Research Center of Finland Ltd, National Institute of Metrology VTT MIKES, Espoo, Finland; [4]Terrestrial Bio-Geo-Chemistry, KIT/IMK-IFU, Garmisch-Partenkirchen, Germany; [5]Institute of Landscape Ecology, University of Münster, Münster, Germany; [6]Institute of Climate-Smart Agriculture, Johann Heinrich von Thünen-Institut, Braunschweig, Germany

In recent years, various mid-IR laser spectrometers for N_2O isotope analysis have become commercially available, applying different detection schemes, such as direct absorption spectroscopy (DAS, Aerodyne Research Inc., MIRO Analytical AG), cavity ring-down spectroscopy (CRDS, Picarro Inc.) and off-axis integrated cavity output spectroscopy (OA-ICOS, LGR-ABB). While optical techniques offer advantages in terms of high temporal resolution, site-selectivity for ^{15}N substitution (^{15}NNO vs. N^{15}NO) and no or minimal sample treatment, variability in gas composition also poses significant challenges for data quality (Harris et al., 2020, doi.org/10.5194/amt-13-2797-2020).

We will showcase several application examples, ranging from pure microbial cultures, wastewater treatment, and agricultural soils to atmospheric monitoring, where we applied DAS, CRDS, and OA-ICOS analyzers to resolve temporal trends in N_2O isotopes. We notice that N_2O isotope laser spectrometer performance is governed by an interplay between instrumental precision, drift (e.g. temperature driven), and spectral artifacts, caused by changes in gas matrix (N_2, O_2, argon), spectral interferences and non-linearity.

We suggest two strategies to preserve trustworthy, i.e. accurate, data: 1) to minimize differences in composition between sample and reference gases by proving appropriate reference gases or by removing variable inference gases from the sample; where this is not feasible or wanted, 2) to post-correct deviations between sample and reference using predefined, analyser-specific correction functions. We developed and validated a mathematical framework along with a Matlab code that outlines the necessary corrections and suggests their logical order. Finally, we demonstrate potential of exemplary N_2O isotope data to interpret production / destruction processes.

Our suggested approach for data processing is well-aligned with a recently published guideline targeting CH_4 isotope analysis by CRDS (Sperlich et al., 2024, https://doi.org/10.61092/iaea.logm-wiux), so is broadly applicable for different isotopic species and laser spectroscopic detection schemes.

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Continuous-flow stable sulfur isotope analysis of organic and inorganic compounds using elemental analyzer coupled with multi-collector inductively coupled plasma mass spectrometry (EA-MC-ICPMS)

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Stable sulfur isotopes play a crucial role in understanding various geological, environmental, and biological processes. Here we present a novel method for the determination of stable sulfur isotope ratios using elemental analyzer coupled with multi-collector inductively coupled plasma mass spectrometry (EA-MC-ICPMS) which can be used for both ^{34}S/^{32}S as well as ^{33}S/^{32}S isotope ratio analysis. The method was evaluated using international Ag_2S and $BaSO_4$ reference materials. Measured δ^{34}S values of international reference materials agreed within ±0.3 ‰ with officially reported values. Overall analytical precision (σ) for both δ^{33}S and δ^{34}S was usually better than 0.3 ‰. Thus, the presented online bulk method should be sufficiently precise to address a wide variety of research questions, also including mass independent isotope effects of sulfur-containing organic compounds, to discriminate sources or biological and chemical reactions in the environment.

1.2: Analytics, Methods, Quality Assurance

What's going on with the δ^{13}C scale(s)?

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Carbon isotope measurements are now commonplace in nearly all scientific fields, from palaeoclimate-, medical-, forensic-, through to atmospheric research. In some fields like food adulteration studies, carbon isotope analyses may be applicable to legal proceedings. In others, like atmospheric sciences, very small natural variations need to be detected and inter-laboratory measurement compatibility goals are high (δ^{13}C-CO$_2$(atm): 0.01 ‰). Stringent standardization of carbon isotope measurements is especially important in these instances.

Unlike temperature (Kelvin), weight (Kilogram) and amount of substance (mole) scales that are now linked to nature constants, stable isotope scales are still linked to standard materials and as such dependent on their availability and stability over time. In case of carbon isotope measurements, the primary standard is a calcium carbonate called NBS19, which defines the Vienna-PeeDee Belemnite scale (VPDB). Since 2006 LSVEC, a lithium carbonate has been used as a second anchor point creating the VPDB-LSVEC scale which has been accepted by the IAEA and the IUPAC Comission on Isotope Abundances and Atomic Weights (CIAAW).

Unfortunately, LSVEC is isotopically unstable and NBS19 is no longer available to the wider scientific community. IAEA-603 has replaced NBS19, and two separate studies have been made that propose replacement materials for LSVEC. One was led by IAEA producing IAEA-610, -611 and -612 calcium carbonates, and the other by USGS proposing USGS44 calcium carbonate as a LSVEC alternative. Here we marry the proposed LSVEC replacements produced through separate attempts, IAEA-610, -611, -612 and USGS44, and produce best estimates of these values.

In January 2024 the IAEA experts meeting decided to keep both, the VPDB and VPDB-LSVEC scales in use. Here we discuss this decision, conversion equations between the scales and possible impacts on users.

Orbitrap Isotope Ratio MS – Improved Strategy for Sample and Reference Introduction

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Orbitrap-based Isotope Ratio MS (IRMS) is becoming increasingly visible in the community. It provides a unique and complimentary tool to classical IRMS techniques for measuring relative abundances of isotopologues. The soft Electrospray Ionization (ESI) of the Orbitrap IRMS produces intact molecular ions at high sensitivity giving unique insight into the molecular anatomy of polar compounds.

Orbitrap IRMS requires sample-standard bracketing for high precision and accuracy. This allows to correct for drift in isotope ratios, which is associated with ESI ionization. Two approaches are currently state of the art. The dual syringe inlet approach uses a diverter valve switching between two syringes filled with sample and standard solutions, enabling time efficient analysis. This method requires as little as 20 seconds idle time between sample and standard. The major drawback of this approach is the necessity for the operator to be present to load the syringes. The second approach automizes the alternating injection of sample and standard using an HPLC autosampler. This enables fully automated analyses while lacking the close temporal proximity of sample and standard due to cleaning and refilling of the autosampler loop, which causes a major gap of unused time between injections.

In this talk we will showcase a new workflow for isotope ratio standardization combining the best from dual syringe inlet and autosampler injections. This approach utilizes two flows of liquid controlled by a switching valve: one flow from the HPLC autosampler for sample and standard introduction, and a second flow for reference material. This setup allows the injection of reference material during the washout period of the HPLC autosampler loop. This reduces wasted time while simultaneously improving the quality of the measurements. The improved sample introduction technique enables efficient and fully automated sample analysis. Precision and accuracy are verified by drift correction and 1- or 2-point calibration.

The novel strategy for sample and reference introduction will be demonstrated on latest applications for inorganic (e.g. sulfate) and organic (e.g. vanillin) samples.

Advancing Greenhouse Gas Isotopic Measurements: Evaluating the Compatibility and Efficiency of Picarro Gas Autosampler with Picarro Isotopic Analyzers

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The greenhouse gas research community faces a growing demand for automated solutions tailored to isotopic measurements of greenhouse gases (e.g., isotopic CO_2/CH_4). Traditional solutions often entail significant initial and maintenance costs, intricate deployment and maintenance processes, and limited fieldwork adaptability. Anticipating this challenge, the Picarro Gas Autosampler is poised to attract growing interest for its anticipated compatibility with Picarro G2201-i analyzers featuring low flow rates (<50 scc/m), promising efficient isotopic measurements. This report delves into the compatibility, efficiency, and advantages of the Picarro Gas Autosampler when paired with the Picarro G2201-i analyzer. Our experiments showcase remarkable precision and accuracy in isotopic measurements of greenhouse gases. Additionally, we explore factors such as linearity in dilution factors and characterize carry over effects and variability across different gas species (e.g., comparing CO_2 vs CH_4). Moreover, the report offers practical recommendations on methods and best practices for conducting isotopic measurements of greenhouse gases. In summary, the Picarro Gas Autosampler, when combined with the Picarro G2201-i analyzer, emerges as a compelling, cost-effective, and user-friendly solution for isotopic measurements of greenhouse gases, offering a distinct advantage over traditional alternatives.

High precision stable isotope analysis of carbonate and water samples for paleoclimate applications using the Elementar iso DUAL INLET

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Paleoclimate research is important for understanding past, current and future climate, providing the data needed to model and predict current and future climate change scenarios. Stable isotope analysis provides an essential tool for gathering past climate information from natural archives such as waters including ice-cores, ground waters, and biological waters; and carbonate materials such as foraminifera and other fossilized carbonates. Due to the often limited and small sample sizes available for stable isotope analysis it is vital that highly precise and accurate analysis can be carried out on the smallest of sample sizes.

Dual inlet technology remains the most precise, accurate and sensitive technique for pure gas, carbonate and water analysis. The Elementar iso DUAL INLET is a valuable tool for paleoclimate applications, enabling the analysis of pure gas samples within an incredibly compact footprint via our powerful lyticOS software suite. The 14-ultra low dead volume valves with bodies machined from a single block of high purity stainless steel and dedicated turbomolecular pump for the changeover valve guarantees zero residual memory effects between reference and sample gas.

The iso DUAL INLET can be optionally enhanced for the automated analysis of carbonate and water samples. With the iso AQUA PREP enhancement, up to 180 water samples can be analysed achieving $\delta^{18}O$ precision better than 0.05‰ (1σ, n=10) and δD precision better than 1‰ (1σ, n = 10), for any environmental water sample. The iso CARB PREP enhancement enables automated analysis of up to 180 micro-fossil samples for ^{13}C and ^{18}O down to 20 µg sample size. For the highest productivity, both carbonate and water analysis can be performed with the iso MULTI PREP enhancement with switching between modes needing simply a change of needle. The IRMS collector configuration can also be upgraded for "clumped isotope analysis" of carbonate materials.

We will highlight the performance of the iso DUAL INLET with carbonate and water functionality across a range of sample types for paleoclimate applications, supporting researchers building a detailed understanding of the past to better inform policy makers for the future.

POSTERS – Analytics, Methods, Quality Assurance

Reference Materials for Position-Specific Isotope Analysis of Sulfamethoxazole by ESI-Orbitrap

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Isotope patterns at natural abundance within organic compounds offer valuable insights into their origin and environmental degradation. However, position-specific isotope analysis remains largely unexplored due to instrumental limitations. Currently, NMR is used for this purpose, but requires large amount of pure analyte, making it unsuitable for environmental samples. Compound-specific isotope analysis is a well-established technique that provides the isotopic signature of the entire compound. However, it faces challenges when analyzing compounds with numerous atoms of the isotope of interest, as the measured isotope effects become diluted and do not represent the isotope effect at specific positions. Moreover, positions not involved in transformation reactions may retain their original isotopic signature and, therefore, can still provide information about the original source. High-resolution mass spectrometry with an Orbitrap has shown great promise in assessing position-specific isotope analysis. In this method, the analyte is fragmented in the ion source and can undergo additional fragmentation in a collision cell. The resulting fragment ions retain structural information and may represent different combinations of atoms from the original molecule. Consequently, it is possible to access fragment- or even position-specific isotopic variations within a molecule by precisely measuring the isotope ratios of these complementary fragment ions. In our study, we investigated sulfamethoxazole (SMX), an antibiotic that is used in factory farming and found in elevated concentrations in the environment. It belongs to the class of sulfonamide antimicrobials and consists of an aniline moiety coupled over a sulfonamide bond to an isoxazole ring. We describe the initial steps of developing an ESI-Orbitrap method, beginning with (i) discovering respective positions and fragments that are accessible and (ii) developing a referencing strategy, including the preparation of reference materials. (i) First, the accessible positions of SMX are investigated by testing different energies for the in-source and collision cell fragmentation. For this, the mass fragments of m/z of 64 (SO_2), 92 (aniline moiety), and 99 (isoxazole ring) were identified to be of interest for isotope analysis. (ii) Secondly, referencing standards with a known isotopic signature at each specific position or within one accessible fragment are required and prepared for calibration of the method. We approached this by homogenizing SMX at natural abundance with a spike of SMX containing 99.9 atom% ^{13}C or ^{15}N at one position to change the isotope value at a specific position by 50 ‰. These standards are further characterized against EA-IRMS analysis and used for future method calibration.

Isotope Analysis of Nitrogenous Model Substances – Investigation of Wet Persulfate Oxidation in the Interface of the LC-IRMS

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LC-IRMS (liquid chromatography-isotope ratio mass spectrometry) is used for a wide range of applications, such as investigating the origin and degradation of pesticides. For reproducible and true results, complete oxidation of analytes and constant $\delta^{13}C$-values are of utmost importance.

During measurements, it was found that the $\delta^{13}C$-values of the insecticide imidacloprid (IMI) and related compounds depend on the carbon concentration. It is known that substances containing guanidine (GUA) and nitroguanidine (NGUA) moieties, as well as N-heterocycles and aromatic N-rings, are incompletely oxidized by acidic persulfate oxidation in the interface of the LC-IRMS. Discrimination of these structures during oxidation can result in inconsistent $\delta^{13}C$-values. Therefore, the oxidation of GUA and NGUA as well as of IMI and related compounds was investigated. Recoveries and $\delta^{13}C$-values of all compounds were measured and normalized with sodium bicarbonate under identical instrumental conditions. To determine the trueness of the measured $\delta^{13}C$-values, all compounds were analyzed with the EA (Elemental Analyzer)-IRMS, which generates true $\delta^{13}C$-values by normalization with international standard materials.

For the LC-IRMS, the influence on the oxidation efficiency and the $\delta^{13}C$-values of total flow, persulfate concentration, concentration of ortho-phosphoric acid, reactor temperature and addition of silver nitrate as a catalyst were investigated. The individual parameters were changed stepwise. Additionally, the linearity of the detector signal and the stability of the $\delta^{13}C$-values were tested.

GUA and NGUA do not appear to be suitable for analysis in LC-IRMS, as their $\delta^{13}C$-values and recoveries vary greatly depending on the amount of carbon injected and the measurement conditions. The $\delta^{13}C$-value of NGUA deviated by -99.10‰ ± 0.44‰ from its true value when silver nitrate and an elevated oxidant concentration were used. The lowest over-all recovery was 18.5% ± 0.2% for GUA at the highest silver nitrate concentration.

All other compounds could be analyzed more reliably. However, for many compounds full oxidation was hardly achieved, and the optimal condition depends on the individual compound. For IMI, a recovery of up to 93.9% ± 0.7% could be reached with silver nitrate. However, with -7.99‰ ± 0.28 ‰, the $\delta^{13}C$-value was less true than under other conditions.

Overall, every condition had an individual weakness such as less true $\delta^{13}C$-values for many compounds when silver nitrate was added and a high oxygen background at higher reactor temperatures. To further improve oxidation in the interface and counteract weaknesses, the combination of different parameters or a new reactor design should be investigated.

Comparison of three milling methods for wood homogenisation for stable isotope and element analyses

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Though, with the EUTR coming into force already 2013, still more and enhanced methods are needed to help the traders to fulfill their due diligence to declare undoubtedly the species and origin of traded timber. Elemental and isotopic composition of wood are important methods to identify the origin of traded timber. While establishing the use of isotopic composition to determine wood origin (for poplar and birch), we encountered difficulties and wanted to test the effectiveness of elemental composition to improve our results. In the laboratory for elemental analyses regularly a vibration disc mill with a tungsten carbide cup is used to homogenise samples. Our wood samples were already milled with a ball mill in stainless steel containers and were therefore expected to cause higher concentrations for certain elements e.g., Fe and Mn, as stated by the lab. To get an idea of the scale of this difference, we started a comparison between the two mills and an additional homogenisation method often used in our lab, thereby restarting preliminary tests from 2019. The first results from 2019 indicated a difference in isotopic composition for samples milled with a ball mill or with a vibration disc mill. For this current study, aliquots of three freshly cut poplar and birch samples as well as two Carapa guianesis and two Dipteryx ferrea samples from storage were dried at 103°C in a drying cabinet and milled with the three different methods: (i) with a ball mill in stainless steel containers with a stainless steel ball, (ii) with a beat raptor in plastique containers with ceramic beats, and (iii) with a vibration disc mill in a tungsten carbide container. 19 elements and four isotopes ($\delta^{13}C$, $\delta^{2}H$, $\delta^{15}N$ & $\delta^{18}O$) were analysed and the results for the different mills compared. These first results will be presented.

Position-Specific Isotope Analysis of Serine Using ESI-Orbitrap

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Serine is a proteinogenic amino acid and an essential nutrient for the bacterium Legionella pneumophila, which relies on serine as its primary carbon and energy source. Consequently, variations in the metabolism of L. pneumophila are expected to be reflected in the carbon isotope ratios of serine within its proteins.

Traditional methods for serine isotope ratio analysis have relied on bulk isotope analysis of pure serine using EA-IRMS, with position-specific analysis of the carboxy carbon achieved through ninhydrin reaction and subsequent CO_2 measurement. Comprehensive position-specific isotope analysis of serine has previously required extensive derivatization for GC-Orbitrap analysis.

We have explored a novel method for position-specific isotope analysis of serine using ESI-Orbitrap, eliminating the need for derivatization. This method combines whole-molecule isotope ratio measurements with those obtained from various fragments generated in a collision cell, in both positive and negative ESI modes.

To support this method, we have prepared homogeneous position-specific carbon isotope standards for all carbon atoms in serine, resulting in eight distinct standards with varying $^{13}C/^{12}C$ isotope ratios. These standards enable precise calibration and referencing of serine isotope measurements on the Orbitrap and facilitate inter-laboratory comparisons of measured isotope ratios.

In the future we want to conduct metabolic studies of L. pneumophila by monitoring the change of serin carbon isotope ratios without the need of expensive ^{13}C-labeled serin in the growth medium. This might also allow metabolic studies of L. pneumophila samples directly from the environment.

2.1: Hydro(geo)logy & German Isotope Network

KEYNOTE

There and not back again: Isotope hydro-biogeochemistry of gradient systems

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The isotope biogeochemistry of the coupled low temperature carbon (C)-sulfur (S)-water cycles was a main driver from the early beginning on. After a start on the impact of anthropogenic sulfur on modern karst environments (1), the introduction of an introduction dual (S, O) isotope approach on microbial sulfate reduction allowed from now on for an estimate of cellular microbial sulfate reduction rates from pore water profiles or authigenic sulfate minerals (2). Then, 2001 followed (3). The link of the oxidative S cycle to the element barium (Ba), introduced in collaboration with Bern University, showed substantial Ba isotope fractionation in the low-T geochemical cycle (4), that builds the base for a still rising application in (paleo)oceanographic and biogeochemical studies (5). Molybdenum (Mo) isotope fractionation, another element linked to S, was introduced as another tracer for understating anomalies in aquatic ecosystems (6).

In recent times, the studies focus more on multi isotope (H, O, C, Ra) partitioning in studies on marine C cycling (7) and submarine groundwater discharge (8). The exciting journey continues, together with students, colleagues, friends, …

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Stable isotope composition of the Salalah monsoon, southern Oman

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Many studies argue that the fossil groundwater resources of the Arabian Peninsula are linked to paleomonsoon rainfall in the geological past (Fleitmann et al., 2004). While the region's climate is arid today, a modern equivalent of this monsoon still prevails in the Salalah area of Southern Oman. Here, the annual Indian Summer Monsoon (ISM) offers the unique possibility to gain important insights into isotopic relationships between water compartments and paleoclimate archives such as speleothems. Yet, despite the practical importance (e.g. water supply) and scientific relevance of the ISM in this key region, data on the weather phenomenon, especially isotope hydrology data, are still limited (Clark 1987).

Hence, we comprehensively sampled an entire monsoon season (Jun-Sep 2018) from the Salalah coastal plain into the Dhofar Mountains, to study the stable isotope composition ($\delta^{2}H$, $\delta^{18}O$) of precipitation along an altitudinal gradient from sea level to 700 m above sea level. Samples were gathered as weekly integral samples with an automatic collector (Michelsen et al., 2019). To examine how today's climate conditions control the isotopic composition of water vapor and rainfall, we applied a 3-step model, incorporating (1) seawater evaporation in the moisture source region with subsequent vapor transport, (2) cloud condensation in the Dhofar Mountains, and (3) sub-cloud evaporation from precipitation droplets.

The identified isotope signatures indicate that rain samples from the coastal plain are isotopically heavier than those collected at higher elevations. While such a pattern can, in principle, be caused by 1) the classical elevation effect and/or by 2) sub-cloud evaporation, the modelling exercise clearly points towards the latter explanation. The obtained data and insights may have implications for the interpretation of isotope-based paleoclimate archives in the region and beyond.

Isotopic distillation pattern during a major regional storm event

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During the last years, summer heat waves are associated with subsequent storms, covering large sectors of the European continent and causing considerable damages. In the present study we detailed sampled such a regional developed storm event, which stroked the sector between the South Carpathians and the Danube in July 2019, lasting over 8 hours. In order to develop isotopic time series on rain samples we continuously monitored temperature, rain intensity and collected water sample using a special designed apparatus. The acquired data were modeled and linked to available meteorological information, proposing a mechanism for storm development. The records provide quantitative insights into the event and evaluate the impact of a severe storm in a region with temperature variations of over 25 °C between winter and summer, and a high continentality index. The main conclusions of these study have several implications: a) deuterium excess data indicate changing moisture sources, starting with recycled continental water and followed by moisture from a marine domain; b) the storm tracks indicate that, for the investigated region this event transported moisture from the Mediterranean basin; c) stable isotope values of precipitation along with rain intensity data support the income of distinct rain bands; d) successive rain bands are supported by the stable isotope data plotted on a Rayleigh condensation trend; e) the Rayleigh model output indicates that about 40 % of the moisture was lost as condensate.

Reference

Ana-Voica Bojar, Christophe Lécuyer, Hans-Peter Bojar, François Fourel & Stanislaw Chmiel, 2024. Monitoring of stable isotope composition of precipitation reveals thunderstorm dynamics, Isotopes in Environmental and Health Studies, DOI: 10.1080/10256016.2024.2380059

Partitioning denitrification pathways at an agricultural site using numerical modeling and stable isotopes of nitrate and sulfate

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Despite regulatory efforts, nitrogen contamination in groundwater continues to pose a significant environmental and health risk worldwide. Germany, alongside Malta, is one of the EU countries with the highest proportion of nitrate-affected groundwater monitoring sites. The Hessian Ried is a particularly notable hotspot due to its intensive agricultural practices, which have led to its designation as a nitrate-vulnerable zone.

Denitrifying bacteria are crucial for mitigating nitrogen pollution, reducing nitrogen loads through two main pathways: heterotrophic and autolithotrophic denitrification. Heterotrophic denitrification relies on readily available organic carbon as an electron donor, producing bicarbonate as a byproduct. In contrast, autolithotrophic denitrification uses iron sulfides, generating sulfate as a byproduct. Nevertheless, iron sulfides are usually present in only trace amounts and are irreversibly consumed during denitrification. As a result, the denitrification potential of the system is expected to decline over time.

Stable isotope data for nitrate and sulfate provide valuable insights into hydrogeochemical processes in soils and aquifers. Nitrate isotopes help elucidate transport pathways and transformation processes such as nitrification and denitrification. Sulfate isotopes, on the other hand, reveal sulfur sources and reaction pathways, including the consumption of sulfides during autolithotrophic denitrification and the production of sulfate from the oxidation of iron sulfides by dissolved oxygen.

In this study, we conducted high-resolution hydrogeochemical monitoring of an agricultural site over a 40-month period. We developed a solute transport model based on first-order decay rates derived from continuous redox potential measurements, which in conjunction to the stable isotope data allowed us to partition denitrification processes through electron balances.

Our findings indicate that the dominant denitrification pathway shifts above and below the 200 mV isoline, with the autolithotrophic component contributing ≤27% above this threshold and about 60% below it. Overall, approximately 45% of denitrification results from the oxidation of iron sulfides. The limited and non-replenished supply of these compounds leads to a downward shift in the redoxcline, significantly diminishing the denitrification potential of the soil-aquifer system.

Balancing weathering and organic carbon input to a tropical river in Sri Lanka: a stable isotope approach

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To date, the understanding of global carbon dynamics hardly includes small-scale tropical catchments. To address these uncertainties, this study investigated the carbon cycle in the silicate-dominated Deduru Oya River (DOR) in Sri Lanka. For this purpose, 31 surface water and 12 groundwater locations were investigated in five campaigns during and in between monsoon events of 2022–2023. The study included pH, temperature, major ions and concentrations of dissolved and particulate carbon phases (DIC, DOC and POC) together with their stable carbon isotopes (expressed as $\delta^{13}C$ in ‰). Dissolved inorganic carbon (DIC) concentrations and $\delta^{13}C_{DIC}$ composition of surface water varied from 0.15 to 12.3 mmol L-1 and -1.1 to -16.5 ‰, respectively. Furthermore, the DIC contribution to the total carbon pool varied between 67 and 89 %. The lithological properties and molar ratios between Ca^{2+}, Mg^{2+} and HCO_3^- indicated rock weathering mostly governed by CO_2 and carbonic acid. The fraction of silicate weathering was determined via ratios of Ca^{2+}, Mg^{2+}, Na^+, K^+ and Cl^- and served as the best proxy for groundwater input. This fraction served as input for ta new isotope mass balance with $\delta^{13}C$ values for groundwater input (-15.9 ‰), carbonate weathering (-12.7 ‰) and organic matter (~-28 ‰). This isotope mass balance only yielded plausible results after correcting for effects of degassing and photosynthesis that both altered $\delta^{13}C_{DIC}$ values in the river. Our study demonstrated that in this environment carbonate weathering and organic matter turnover are essential components of the river carbon cycle even in a silicate dominated catchment. They can represent up to 60 % of the DIC pool. Our study is one of the few that examines all three carbon sinks, i.e. DIC, DOC and POC, together with their $\delta^{13}C$ values.

Reference

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2.2: Hydro(geo)logy & German Isotope Network

A depth-oriented investigation of hyporheic zone processes by isotopic and chemical analysis

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The hyporheic zone is a crucial transitional area where active exchange occurs between subsurface and surface waters. This exchange is influenced by physical properties and variations in hydraulic pressure, resulting in a zone that exhibits characteristics of both stream and groundwater ecosystems without a distinct boundary between them. To obtain a detailed understanding of the differences in hyporheic zone functions at different depths, isotopic analyses (^{18}O and ^{2}H) together with chemical and physical parameters, were conducted in two streams, Ahna and Losse, located in North Hesse, Germany. Multi-level interstitial probes were installed in the streambed to collect subsurface pore water samples from depths of up to 0.5 m.

We distinguished three different hyporheic zones: in the Ahna upstream, Ahna downstream, and Losse stream. The Ahna upstream hyporheic zone acted as a less permeable barrier with low water fluxes but high reactivity, whereas the downstream zone was more permeable with higher vertical fluxes and lower reactivity. The Losse hyporheic zone, while non-reactive, exhibited good hydraulic circulation due to rapid downward flow. Groundwater was the main water source for both streams and their hyporheic zones, with rainwater potentially serving as a secondary source. Isotopic analysis highlighted notable differences between upstream and downstream of Ahna, showing increased evaporation, complex mixing with other water sources, and fast subsurface flows in downstream compared to the upstream zone. Hydrochemical dynamics revealed higher ion concentrations downstream, influenced by anthropogenic activities along the stream. Upstream, denitrification prevailed due to low oxygen conditions resulting from slow infiltration and limited mixing. This study underscores the spatial variability of hyporheic zone processes and emphasizes the importance of examining these conditions at a local scale.

Challenges of estimating groundwater recharge in forests through deuterium oxide labelling – How to trace soil water movement below the root zone?

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Forests in Germany severely suffer from climate change induced biotic and abiotic risks of damage. A forest management strategy to minimize risks is the conversion of pure spruce and pine forests to mixed stands with alternative tree species like Douglas fir. However, information on the impact of this tree species on groundwater recharge is scarce. To better understand groundwater recharge driving processes in Scots Pine and Douglas fir forests, deuterium oxide (D_2O) labelling methods were used within an interdisciplinary research project ("Effects of climate-adapted tree species selection on groundwater recharge – KLIBW-GW"). The joint research project of the Federal Institute for Geosciences and Natural Resources (BGR) and the Northwest German Forest Research Institute (NW-FVA) is funded by the Forest Climate Fund (WKF). The movement of a tracer peak through the unsaturated zone has widely been used to estimate groundwater recharge for various land uses [1, 2]. The application of this peak-shift method requires vertical piston flow soil water movement and relies on the assumption that the depth displacement of the tracer peak concentration in the soil water and the respective displacement time reflect the infiltration rate. However, in a forest soil these assumptions are challenged because of preferential flow paths along root channels and because of tracer consumption by root water uptake. We present results of two D_2O-labelling experiments in a Douglas fir stand and a nearby Scots Pine stand in Northern Germany from January 2023 to April 2024, reaching below the root zone of a sandy soil. The experiments reveal that root water uptake takes place up to a depth of 1.9 m in the Douglas fir stand and up to 2.2 m in the Scots pine stand. The results emphasize that the depth displacement of the tracer peak concentration is not only controlled by vertical soil water movement, but also by tracer consumption in the root zone and dilution during soil rewetting periods. To address these issues, we will present an improved experimental setup that aims at tracing the soil water movement below the root zone.

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Climate indicators and stable isotope patterns in a region strongly impacted by lignite-mining (Lusatia, Germany)

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Northeastern Germany, including the lignite-mining region of Lusatian (Spree, Schwarze Elster, Lusatian Neiße watersheds) and the capital Berlin, has experienced dry and hot springs and summers in recent years, with adverse consequences for water resources, ecosystems and society. Here, we quantified long-term changes in i) extreme climate and drought indicators (1948–2022) and ii) the isotopic composition ($\delta^{18}O$, $\delta^{2}H$, d-excess) of precipitation (1978–2022). Our results show increases in the number of extreme temperature related indices ((very) hot days, warm nights) and in the number of dry days (> 6.5% in Berlin 1991–2020 versus 1961–1990). Concurrently, the number of frost and snow days decreased, especially in recent years. The frequency of severe and extreme droughts, represented by the climatic water balance deficit (SPEI), has increased. Between 2018 and 2022, Berlin experienced the longest period of precipitation and climatic water balance deficit since 1948. The observed climatic changes coincides with a significant positive trend in the 45-year record of isotopic composition ($\delta^{18}O$, $\delta^{2}H$) of precipitation, which is statistically significant ($p > 0.05$) on the annual ($\delta^{18}O$: 0.3 ‰ decade^{-1}) basis as well as during spring (March–May) and summer (June-August). We show that the positive trend in isotope composition ($\delta^{18}O$) is weakly correlated with air temperature. For the Lusatian mining region, the results suggest that multiple water-related challenges are overlapping and that climate change needs to be urgently considered in regional water management.

Comparison of long-term precipitation stable isotopes monitoring at three selected stations of weekly resolution within the German Isotope Network (GIN)

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In Germany stable isotopes of precipitation (^{2}H, ^{18}O) are 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 isotopes in high spatial and temporal resolution allow a reconstruction of source areas and potentially climate effects. A monitoring network (GIN) for monthly analysis of water isotopes including tritium (^{3}H) is active with more than 30 stations mainly based on precipitation monitoring organized by the Federal Institute of Hydrology (BfG). Currently, BGR is analyzing the stable isotope composition of 27 stations; for 19 of those stations time series of more than 10 years are available. For three selected stations in Northern Germany that are situated on a west east traverse, weekly monitoring was conducted (Hannover since 2008, Berlin-Spandau since 2021, Cottbus since 2023).

We compare weekly precipitation patterns of selected stations with monthly patterns for most dominating stable isotope effects. 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 reveals a typical topographical pattern. Interestingly, time series from the recent years indicate influence of extending dry and hot summers. Further, we highlight on efforts, pros and cons of maintaining and organizing a precipitation-monitoring network for Germany.

POSTERS – Hydro(geo)logy & German Isotope Network

Isotopic evidence ($\delta^{13}C$, $\delta^{37}Cl$, $\delta^{2}H$) for distinct transformation mechanisms of chloroform: Catalyzed H_2-water system vs. zero-valent iron (ZVI)

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Chloroform (CF), from various sources, is a commonly detected volatile organic compound in groundwater. An efficient technology for degrading organochlorinated compounds, such as CF in the environment into harmless products, is catalytic hydrodechlorination. Compound-specific stable isotope analysis (CSIA) of multiple elements is widely used for the investigation of degradation mechanisms. Yet, its application in the study of catalytic hydrodechlorination is still limited. We have applied CSIA to derive chlorine, carbon, and hydrogen isotope enrichment factors (ε) during the degradation of CF over Pd/Al_2O_3 and over Rh/Al_2O_3 commercial catalysts. Moreover, the enrichment factors for the same isotopes were determined for the reaction of CF with zero-valent iron (ZVI) for comparison. The results revealed εC values (-21.9 ± 0.25 ‰ and -23.4 ± 2.30 ‰) and εCl values (-12.1 ± 1.7 ‰ and -10.3 ± 0.6 ‰) for the reactions of CF over Pd / Al_2O_3 and over Rh/Al_2O_3, respectively. The corresponding εC and εCl values, for the dechlorination of CF with ZVI, were -22.2 ± 2.80 ‰ and -4.7 ± 0.45 ‰, respectively. The hydrogen isotope enrichment factors (εH) were not calculated for the catalyzed reactions since there was no clear trend according to the Rayleigh model. However, an inverse secondary hydrogen isotope effect, with εH value of 28.7 ± 2.5 ‰, was observed for the reaction of CF with ZVI. Based on the enrichment factors determined in this study, the apparent kinetic isotope effects (AKIE) were evaluated. The AKIEs of Cl suggest that the transformation mechanism in the catalyzed hydrogen-water system is a non-concerted reaction, unlike the known reductive dechlorination of CF with ZVI. In addition, the dual-isotope slopes ($\Lambda C/Cl$) for both catalyzed reactions ($\Lambda Pd=1.8 \pm 0.13$ and $\Lambda Rh= 2.1 \pm 0.14$) are significantly different than for the ZVI ($\Lambda ZVI=5.8 \pm 0.41$) obtained in this study. For the former two cases, there are no published values for comparison. Whereas the value for the ZVI reaction, is comparable to data reported in the literature. The slopes reflect that the reactions proceed in different mechanisms. The findings in this work will support field investigations in which catalyzed hydrodechlorination is the method of choice in remediating CF-contaminated sites.

Langzeit-Isotopenuntersuchung im Niederschlag und Lysimetersickerwasser für das Prozessverständnis klimatischer Effekte auf die Grundwasserneubildung

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Lysimeter eignen sich, um Wassermassenflüsse (+ und -) in der ungesättigten Zone zu untersuchen. Sie stellen damit ein wichtiges Bindeglied zwischen Niederschlag und Grundwasserneubildung dar. Im Rahmen von BMBF-Lurch IsoGW werden u.a. an verschiedenen Pilotstandorten Isotopenuntersuchungen (Monatssammelproben ^{3}H, $^{18}O/^{2}H$) an den Lysimetersickerwässern im Vergleich zu lokalen Niederschlägen über den Zeitraum von deutlich mehr als 24 Monaten untersucht. Hierdurch kann die Übertragung der Niederschlagssignale in die Grundwasserneubildung näher untersucht und quantifiziert werden. Neben der Prüfung der Fließheterogenität im Lysimeter sollen wichtige klimatische Effekte, lokal und überregional, für das Prozessverständnis abgeleitet werden, die für die Generierung von Inputfunktionen (wichtige Basis der Auswertung von Isotopendaten aus Grundwasseranalysen) relevant sind und mit klassischen Ansätzen für die Einbeziehung der potentiellen Evapotranspiration (Daten aus lokalen Wetterstationen) verglichen werden können.

Methodisch gleichgeartete Untersuchungen stehen für den Zeitraum 1993 bis 2006 an Niederschlags- und Lysimetersickerwässern der Station Steisslingen (Baden-Württemberg) zur Verfügung. Sie dienen im Lurch IsoGW-Teilprojekt für auswertende Vergleiche und der Diskretisierung von klimabedingten Veränderungen mit erkennbarer Wirkung auf die Isotopensignaturen der aktuellen Grundwasserneubildung. Die angestrebten Auswertungen der Ergebnisse aus den Lysimeteruntersuchungen sollen insbesondere die gängige Praxis der Inputgenerierung aus Isotopendaten des regionalen Niederschlags überprüfen und im Sinne von „Best-Practice" weiter optimieren.

Wir stellen die „Halbzeitbilanz" der Ergebnisse dieser Untersuchungen vor.

Hochauflösende Langzeit-Isotopenuntersuchung der Uferfiltration und ihre Nutzung für die nachhaltige Bewirtschaftung von Grundwasserressourcen in der Nähe von Flüssen

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Uferfiltration ist eine ökonomische Methode, flussnahe Grundwasserressourcen nachhaltig zu bewirtschaften. Gerade die Frage nach Trinkwasser aber auch Brauchwasser (Landwirtschaft, geothermische Nutzung) stellt eine stetig wachsende Herausforderung für die Wasserwirtschaft dar.
Im Rahmen von BMBF-Lurch IsoGW werden u.a. Best Practice Teilprojekte an verschiedenen Pilotstandorten für einen Best Practice Leitfaden (Anwendung von etablierten isotopenhydrologischen Methoden für Wasserversorger und beratende Büros) durchgeführt.
Um die Variabilität der hydrologischen Prozesse bei der Uferfiltration in hoher Auflösung näher zu untersuchen, wird am Standort Ofterschwang im Oberallgäu über einen Zeitraum von mehr als 2 Jahren der Beitrag der Iller an der Grundwasserneubildung in hoher zeitlicher Auflösung bestimmt. Für die Charakterisierung der Grundwasserneubildungskomponenten, Abstandsgeschwindigkeiten oder Mischungsbilanzen dienen die stabilen Wasserisotope in Verbindung mit hydraulischen und hydrochemischen Messdaten.
Wir stellen die „Halbzeitbilanz" der Ergebnisse dieser Untersuchungen vor.

Do-it-yourself rain collectors for stable isotope studies (δ^2H, $\delta^{18}O$) in hot and arid climates

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Many isotope studies relying on δ^2H and/or $\delta^{18}O$, require corresponding precipitation data for comparison. To gather such samples, we need cumulative precipitation collectors that effectively reduce post-sampling evaporation from the collection bottle and the associated isotope fractionation. Hot and arid climates are particularly challenging in this regard.
Although dedicated collectors are available on the market (Gröning et al., 2012; Palmex, http://www.rainsampler.com/) and have generally proven useful (Michelsen et al., 2018), we experimented with a number of do-it-yourself (DIY) designs. Pre-filled collectors were tested 1) in a modified laboratory oven (diurnal temp. change 22–50 °C, mean rel. humidity 11%) for four months and 2) on a rooftop in Riyadh (Saudi Arabia) for about seven months (Mar–Oct 2022). All low-cost DIY collectors performed well, despite the harsh conditions and long exposure times. Aluminum-lined bags showed negligible evaporative mass losses and isotope shifts, and hence represent particularly promising alternatives to established collectors.

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Monitoring stable isotope composition ($\delta^{18}O$, δD) at lake Tiefer See Klocksin (NE-Germany) – Seasonal evaporation from a deep lake

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Lake Tiefer See is a long-term study site within the TERENO-NE (Terrestrial Environmental Observatories-North East) initiative of the Helmholtz Association to understand the evaporation processes in lakes for assessing regional impacts of global climate change in a lake dominated landscape like NE Germany. The stable isotope composition of lake water ($\delta^{18}O$, δD) is a suitable tool to provide insights into lake water hydrology and especially evaporation processes (e.g. Steinmann et al., 2010). This study is accompanied by a comprehensively long-term monitoring of the influencing factors like precipitation and groundwater (https://www.gfz-potsdam.de/en/section/climate-dynamics-and-landscape-evolution/projects/tereno-northeast-lake-monitoring-tiefer-see).
The lake water is sampled monthly in different water depths on the deepest part of the lake (63 m) since 2012. Water temperatures are measured using temperature loggers installed in a dense spacing down to 55 m water depth. Meteorological data measured on site include temperature, relative humidity, solar radiation, rainfall and wind speed. Precipitation water is collected also in monthly increments since December 2016.
The stable isotope ratios ($\delta^{18}O$ and δD) are measured with a PICARRO L2130-i and L2120-i analyzer and the values of precipitation vary between -3.6‰ to -13.6 ‰ for $\delta^{18}O$ and -23‰ to -103‰ for dD. The relationship of $\delta^{18}O$ and δD results in a Local Meteoric Water Line (LMWL) of $y=7.3x+2.8$. The $\delta^{18}O$ values of the epilimnic lake waters vary seasonally between -2.6‰ and -4.7‰ with increasing values during summer

stratification and higher temperatures. The seasonal +2‰ enrichment of $\delta^{18}O$ indicates an evaporative loss of surface water of up to 12 % corresponding to the observed lake level drop of 50 cm in average after summertime. Furthermore, the $\delta^{18}O$ values of both, the mean epilimnic and deep water are generally more positive than the annual precipitation water mean ($\delta^{18}O$: -8‰). On the one hand, this proves an evaporative enrichment of the surface water as expressed also in the local evaporation line (LEL) y=4x-19. On the other hand, the enriched deep water $\delta^{18}O$ suggests a long water residence time in the lake due to the lack of major in and outflows and minor groundwater inflow.

Stable isotopes and hydro chemistry of precipitation and surface water in the Niger River Basin

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An observation network for stable isotopes of precipitation ($\delta^{18}O$, $\delta^{2}H$) was initiated within technical cooperation of BGR and nine countries located in the catchment of the Niger Basin. So far precipitation samples were collected from Niger (at Niamey from 05/2017 to 09/2023, n=128 event samples; Agadez 08/2022 to 09/2023, n= 13; Timia, 06/2023 to 10/2023, n=3), from Mali (at Bamako from 06/2022 to 10/2023, n=39), Burkina Faso (at Ouagadougou from 06/2022 to 09/2023, n= 30), Chad (at Gonouya from 08/2022 to 09/2023, n=59) and Ivory Coast (at Samatigula from 06/2023 to 08/2023, n=3). The rain collectors used (Palmex, RS2i) are designed to minimise evaporation and thus avoid fractionation of stable isotopes. The sampling intervals at the different sites range from daily samplings to mainly event-based sampling. In addition to precipitation, surface water samples were collected and analysed for stable isotopes and hydro chemical parameters from rivers in Mali, Niger and Nigeria, which will complement the results.

The results show that local meteoric water lines (LMWLs), which assign equal amount of precipitation to all data points, over-represent events with only small precipitation and overweigh fairly enriched stable isotope compositions. This was particularly observed when the distribution of precipitation was heterogeneous, as it is the case for several areas of the Sahel region. Precipitation data, evaporation influence and patterns of surface water samples from Mali and Niger will be discussed within this work.

3.1: Ecosystems and Biogeochemistry

KEYNOTE

N_2O isotopocules and mineral N isotopes in tracing N cycling in soils

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The complex nitrogen cycling in the environment associated with diverse microbial N transformations is crucial in the interplay of agriculture and environmental issues. Nitrogen, added to arable soils as fertilizer, is not only assimilated by plants, but also transformed by soil microorganisms and released to the atmosphere in gaseous forms or leached to groundwaters. These cause not only a significant loss of the added nitrogen but also severe environmental problems, i.e., groundwater pollution and greenhouse gas emissions. Mitigation of these problems is difficult since the understanding of the complex nitrogen transformation processes in soils is still limited, e.g., N_2 emission, not measurable due to high atmospheric background, is still a big unknown and precludes closure of the N balance.

The critical knowledge gaps in the nitrogen cycle can be possibly approached by isotopic studies of different N compounds. Isotope signatures can be used not only to detect particular N transformations but also to quantify unknown N fluxes.

Isotopocule analyses of N_2O, includes not only nitrogen and oxygen isotope values, but also the site specific N analysis, which differentiates the isotope enrichment on different N positions in the linear N_2O molecule. Hence, with isotope analysis of N_2O molecule, we obtain three isotope signatures, which are governed by the N_2O production pathways as well as by N_2O reduction. These results are rich in information, but also challenging in their interpretation. Our calculation software for isotope FRActionation and Mixing Evaluation (FRAME) [1] allows source partitioning of different N_2O production pathways as well as estimation of the N_2O fraction reduced to N_2, hence may help in quantification of the main missing compound in the N balance.

N_2O isotopocule analyses combined with isotope analyses of mineral nitrogen compounds, including ammonium, nitrate and nitrite, can provide a very detailed and complex insight into the ongoing processes. Nitrite isotope analyses in soils is a novel approach [2], which may open new interpretation perspectives, since it is an intermediate product of nearly all known N transformations. The linkage between mineral N transformations and gaseous emissions evaluated with advanced modeling approaches may help in unravelling important knowledge gaps.

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Effect of nitrogen fertilization by red clover mulch in organic farming: An isotope analysis study

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As mineral nitrogen fertilizers are prohibited in organic farming, the use of fine-seeded legumes with their high natural nitrogen content could be an alternative. To investigate the effectiveness of such organic nitrogen fertilization, an agricultural field trial is carried out by the Department of Plant Production of the Saxony State Office for the Environment, Agriculture and Geology (LfULG) in Nossen (near Leipzig) from 2022 to 2025. Hereby, the suitability of red clover mulch for fertilizing different crops (potato, winter oilseed rape, winter wheat and maize) is investigated. To quantify the nitrogen transfer from the red clover mulch to the plants and the soil, a part of each crop is fertilized with red clover previously labelled with δ^{15}N-urea. In addition, three different soil coverings with clover mulch-straw mixtures were investigated because the addition of straw could improve soil erosion control and influence nitrogen turnover by increasing the C:N ratio.

For the 2022 (potato) and 2023 (rapeseed) growing seasons, the δ^{15}N analyses of soil and plant samples at characteristic development stages have already been evaluated and the nitrogen transfer from the mulch to the crops has been determined. Fertilization with δ^{15}N-labelled red clover mulch (+127.8 ‰ for fertilization of the potato and +81.8‰ for fertilization of rapeseed) increased the nitrogen content of the soil by an average of 4%. The mean transfer of ^{15}N to the potato plants was 6% of the applied nitrogen and to the rapeseed plants 17%. Actually, the soil and plant samples from the 2024 growing season (winter wheat) are analysed, so that a comparison with the previous growing seasons is possible.

Water vapour diffusion from the atmosphere into the leaf is mostly ignored but relevant as shown by ^{18}O isotopes

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During H_2O gas exchange, water vapor molecules diffuse out of and into the leaves. The diffusion of ambient water vapor into the foliage leaves its fingerprint on the isotope ratio of the total leaf water (δ^{18}Olw), and subsequently, on the organic matter of plant tissue/tree ring cellulose δ^{18}Otrc. In most cases the isotopic values of the leaf and source water (δ^{18}Osw, xylem water) are distinctly different than that of the ambient water vapor (δ^{18}Oav). For retrospective analyses (paleoclimatology, tree physiology) tree ring δ^{18}Otrc is used to reconstruct temperature and/or ambient humidity. However, it is often difficult to assign δ^{18}Otrc to the relevant environmental drivers, i.e., temperature, vapor pressure deficit (VPD) or relative humidity (RH), and for the physiological aspect, stomatal conductance (gs). Since leaf water enrichment (δ^{18}Olw) is also determined by the stomatal conductance (via Peclet effect), which impacts the water vapor exchange, δ^{18}Otrc values can also be used to evaluate the role of gs on carbon water relations retrospectively during its biomass production. In this presentation the impact of gs on δ^{18}Olw and ultimately on organic matter is shown by means of experimental data and its potential implications for retrospective isotope analyses in tree rings

Multi-element stable isotope natural abundance in orchids from the Mediterranean region of Europe and SW-Australia

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Within the Orchidaceae the usually mutualistic mycorrhizal symbiosis has been modified in several directions. In nature, all orchids start into their life by completely relying on their mycorrhizal fungi as nutrient source. This unique initially mycoheterotrophic nutrition provides a predisposition to remain relying on fungal partners as nutrient supplier throughout the entire life cycle. In fact, more than 200 orchid species are known to survive achlorophyllous in a fully mycoheterotrophic nutrition mode. These orchids thrive in light-limited forest-ground habitats and use fungi simultaneously forming ectomycorrhizas with trees or wood or litter decomposing fungi as mycorrhizal hosts. Initially and fully mycoheterotrophic orchids bear the isotopic composition of their host fungi and thus, are isotopically distinguished from accompanying autotrophic plants. Due to an isotopic positioning between autotrophic and mycoheterotrophic plants, a steadily increasing number of adult chlorophyllous orchids is identified as gaining carbon simultaneously from two sources, own photosynthesis and fungal hosts. This mixotrophic mode of nutrition is known as partial mycoheterotrophy. Fungal partners of partially mycoheterotrophic orchids can be either ectomycorrhizal fungi or saprotrophic fungi of the ubiquitary rhizoctonia group or both of them. Specifically, hydrogen stable isotope abundance turned out as an elegant tool to identify partial mycoheterotrophy among rhizoctonia-mycorrhizal orchids.

This presentation reports on five investigations elucidating partial mycoheterotrophy among orchids in the European and Southwestern Australian Mediterranean region. From a total of 28 investigated species 24 turned out as exclusively Rhizoctonia-mycorrhizal. Among these 24 species 13 were partially mycoheterotrophic based on hydrogen isotope signatures, and 11 species were obviously fully autotrophic as adults. Interestingly, all of the six investigated orchid species from SW Australia belong to the group of apparently adult autotrophic orchids. Implications of this knowledge on orchid nutrition for conservation concepts are discussed.

3.2: Ecosystems and Biogeochemistry

KEYNOTE

The isotopic fingerprint of plant methoxy groups and its application in biogeochemical research

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The biospheric C1 methyl (CH_3) pool of plant origin, including mainly lignin and pectin methoxy groups (OCH_3) plays an important role in carbon cycling as they comprise up to 10% of the total amount of organic matter in plant biomass or soil. Some twenty years ago, at the GASIR conference organized by the MPI for Biogeochemistry in Jena, we presented our first results about the 'Carbon isotope anomaly in the major plant C1 pool'. We found that relative to the bulk biomass of plants, the carbon isotope fractionation exhibited by the plant methoxy pool covers large areas attaining an apparent fractionation of up to −50 mUr, the largest ever yet observed value in the plant kingdom. Two years later, at the GASIR conference in Bayreuth in 2007 we reported a striking ^2H depletion of wood methoxy groups relative to source water with a uniform apparent isotopic fractionation of around -200 mUr noted over a range of δ^2H values for meteoric water from −20 to −120 mUr.

Since then, the distinct pattern of stable hydrogen and carbon isotope values of plant methoxy groups have been applied for several research fields. In this presentation, I will show the recent advances of analytical measurements of stable carbon and hydrogen isotope values of plant methoxy groups (including development and application of reliable reference materials) and discuss/propose fundamental biochemical reasons for their distinct isotopic patterns. The second part of my talk will focus on practical applications in several research fields. Examples will be provided for the fields of food science, paleoclimate studies, plant and atmospheric sciences. Very recently the distinct 2-dimensional isotopic signature of methoxy groups between different plant tissues was also suggested to assist with historical apportionments of particulate organic matter and sediment sources.

^{18}O labeling experiments reveal new abiotic pathway of methanol and formaldehyde formation in soil

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Formation of methanol and formaldehyde in soil is usually ascribed to demethylation processes of organic matter by bacteria or fungi. We investigated a selection of soil samples and lignin-like monomeric units such as methoxyphenols for their potential of abiotic formation of methanol and formaldehyde. We found unexpected large amounts of methanol and formaldehyde formed both in wet soil and methoxyphenols in aqueous solution containing iron species and hydrogen peroxide. Typically, the formation of methanol and formaldehyde from lignin or lignin-like monomers is explained by demethylation processes and respective oxidization of the methyl group. However, using isotopically ^{18}O and ^2H labeled 2-Methoxyphenol we unambiguously demonstrate that the methoxy group (OCH_3) is cleaved off to form methanol, which subsequently is partially oxidized to formaldehyde. We further used different soils that were sterilized prior to experiments and added isotopically labeled (^2H,^{18}O) 2-methoxyphenol. The formation of ^{18}O labelled methanol confirmed our hypothesis that the composition of soil is capable to cleave off the methoxy group from 2-methoxyphenol. Additionally, when methoxy groups were removed from soil organic matter a drastically reduction of methanol and formaldehyde production was observed. Based on the isotopic results and computational modeling (density functional theory and ab initio quantum-chemical studies) we present a hitherto unknown mechanism of methanol formation that might be widespread in soil, potentially feeding a diverse pool of soil microorganisms and might effect the global carbon cycle.

Stable isotope insights into subglacial methane emissions from the Western Margin of the Greenland Ice Sheet

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Methane (CH_4) emissions from subglacial environments, such as the Greenland Ice Sheet (GrIS), have only recently been discovered. Their magnitude, similar to emissions from major world rivers, indicates a significant, but yet still not accounted, role in the global CH_4 budget. To estimate CH_4 emissions from GrIS meltwater and their relevance to the global carbon budget, it is essential to understand their sources and controlling mechanisms. We analysed the stable carbon and hydrogen isotopic composition of CH_4 and CO_2, as well as the Bernard ratio (methane / [ethane + propane]) of samples extracted from supraglacial and subglacial meltwater, and air samples collected from an ice cave at the edge of the GrIS. Our goal was to identify the sources of subglacial CH_4 and understand its controlling mechanisms.

In June 2022, we found that dissolved CH_4 concentrations in a subglacial stream at GrIS were at least 100 times higher and dissolved CO_2 concentrations were twice as high compared to the supraglacial meltwater. The stable isotope values of CH_4 and CO_2 ranged from -37 to -49 mUr for $\delta^{13}C\text{-}CH_4$, -160 to -240 mUr for $\delta^{2}H\text{-}CH_4$, and -14 to -19 mUr for $\delta^{13}C\text{-}CO_2$. These findings did not allow a clear source identification using classical stable isotope identification schemes. Additionally, the Bernard ratios ranged from 300 to 700, which is neither clearly indicative of a single CH_4 source with Bernard ratios of microbial CH_4 formation typically being typically above 1000 and below 100 for non-microbial CH_4 formation.

Our results indicate either a mixing of microbial and non-microbial CH_4 sources and/or that CH_4 oxidation, which is ubiquitous in this environment, affects the stable isotope values and Bernard ratios, strongly complicating CH_4 source identification. Hence, our findings reveal a complex interplay of CH_4 sources and sinks in the subglacial environment and also leave open the possibility of other recently reported abiotic CH_4 formation pathways and their contribution to the observed CH_4 at this site. Further investigation into the source signatures of CH_4 sources and the impact of CH_4 oxidation on the stable isotope composition of CH_4 in the subglacial environment is needed to better disentangle the sources and sinks of CH_4 and accurately estimate the contribution of different CH_4 sources.

Experimental drought in a mature beech/spruce forest using stable isotopes to study drought resistance and tree recovery

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This presentation will provide an overview of the responses of mature European beech and Norway spruce to five years of experimental drought and subsequent recovery. The focus is on the use of stable isotopes to study ecophysiological processes describing drought response and acclimation of trees. The data come from 10 years of research in the Kranzberg Forest Roof Project (KROOF), a throughfall exclusion experiment in a mature beech-spruce forest in southern Germany. We studied 70–80 year old trees, accessible by canopy crane, growing in either monospecific or mixed situations. The study includes about 100 trees in 12 plots of about 150 m^2 each. The trees were exposed to experimentally induced summer drought for five consecutive years by excluding precipitation throughfall during the growing season. In the following five years, the recovery of the trees under natural conditions was assessed.

During the first two dry summers, when both species were not yet acclimated to drought, the most severe negative effects were present. Both species showed strong reductions in physiological responses (e.g. photosynthesis, stomatal conductance, phloem sugar transport, xylem sap flow) and growth. From the third year of drought, successful acclimation led to alleviation of drought stress. After five consecutive years of throughfall exclusion, drought release was initiated in early summer 2019 in a large-scale H2 labelling experiment. In general, the physiological performance of the trees recovered much faster than the morphological parameters.

The presentation will mainly focus on how ecophysiological processes can be studied using stable C, H and O isotopes. I will present data from different ^{13}C-labelling approaches investigating C residence times in leaves and phloem transport of sugars along branches and stems. In addition, water isotopes (natural abundance and ^{2}H-labelling) have been used to infer root access to water and to study water transport in trees. Finally, I will give an example of the effects of mixing between tree species and whether during drought hydraulic redistribution of soil water occurs through the root system of beech trees.

Using Cu stable isotope ratios to understand the cycling of Cu in Swiss grassland soils

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Copper (Cu) is an essential micronutrient but can at elevated concentrations also become a contaminant in agricultural systems. We measured the Cu inputs (atmospheric deposition, manure, mineral weathering) and outputs (seepage water, biomass harvest) at three Swiss grassland sites during one hydrological year. In addition, we collected soil samples from the 0–10 cm, 10–20 cm, 20–50 cm, 50–75 cm, and > 75 cm layers and from the parent materials. Moreover, we determined stable Cu isotope ratios (δ^{65}Cu values) in all samples. Animal manure was the greatest Cu input (97-98 %; 225–527 g Cu ha^{-1} yr^{-1}) leading to net Cu accumulations (104–425 g Cu ha^{-1} yr^{-1}) at all three study sites. Animal manure was Cu-isotopically heavier than soils (Δ^{65}Cusoil(0–75 cm)-manure = -0.34 ± 0.21 ‰). An anthropogenic and atmospheric impact model was used to estimate the bulk soil Cu stocks and the δ^{65}Cu values in the year 1915, i.e. before the sites underwent intensive agricultural practices. Human activities have changed the Cu stocks in the topsoil (0–20 cm) by -3 %, +3 % and +30 %, and they have increased the δ65Cu values by 0.06 ‰, 0.07 ‰ and 0.32 ‰ between 1915 and 2015, at our three study sites, respectively. If the Cu inputs and outputs remain constant at today's level, the Cu stocks in the topsoil will increase by 14 %, 21 % and 70 %, and the δ^{65}Cu by 0.08 ‰, 0.12 ‰ and 0.23 ‰ in the year 2100, respectively. Furthermore, the Cu concentrations in the topsoil will surpass the Swiss threshold values for Cu of 40 mg kg^{-1} in the years 2160 and 2575, while for one study site, the threshold value was already exceeded in 2015, respectively. Therefore, the addition of Cu to feed should be adjusted for each site individually.

Investigating Polyethylene Degradation in Soil Using a ^{13}C-labelling Approach

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Plastic waste is pervasive in agricultural soil, with polyethylene (PE) being the major contributor. Polyethylene is often applied in the form of a mulch film for one growing period and then removed. However, removal is not always complete, and plastic remains in the soil. This polyethylene degrades into micro- and nano-plastics over time. These can affect soil properties and plant health, posing risks to ecosystem services. However, quantitative bacterial mineralization rates of polyethylene, as well as the fate of polymer-derived C in different soil compartments (incorporation into microorganisms, soil structure, etc) are not known. Traditional techniques, such as spectroscopic and imaging techniques, weight loss studies, and microbial respiration lack precision in quantifying PE degradation rates and confirming microbial involvement. Employing ^{13}C-labelled PE is a promising approach, offering precise quantification of mineralization rates and the ability to track polymer-derived carbon assimilation by microorganisms. This can be done by sequencing of the ^{13}C-containing DNA (identifying plastic degraders) and through analysis by nanoscale secondary ion mass spectrometry (NanoSIMS, tracking the polymer-derived C in soil).

This study incubates ^{13}C-labelled PE, aged by UV for the equivalent of 1 growing period, in a soil microcosm for 2 years. CO_2 formed through microbial mineralisation is trapped in NaOH and quantified via total inorganic carbon concentrations and δ^{13}C values are determined via elemental analysis isotope ratio mass spectrometry (EA-IRMS) every 4 weeks. Soil samples are collected at 1, 6, 12, and 24 months to identify plastic-degrading microbes. Initial results show <0.12 mol% of C in PE degraded after 12 months, with a decreasing monthly degradation.

The ^{13}C-labelling approach allows for quantification of PE mineralization at very low rates and short timescales and can provide unequivocal proof of biodegradation by microorganisms. Additionally, it is possible to map incorporation of polymer – derived C into soil and microorganisms via NanoSIMS and DNA sequencing. Our study offers an important contribution to understanding the environmental fate of polyethylene, allowing risk assessment to be carried out and addressing pressing concerns related to soil health, crop productivity, and food security.

POSTERS – Ecosystems and Biogeochemistry

Investigating Chloromethane (CH_3Cl) Formation Processes in Ginkgo Trees (*Ginkgo biloba*) – Insights from In-Vivo Monitoring and ^{13}C-Labelling Experiments

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The global budget of atmospheric chloromethane (CH_3Cl) remains highly uncertain despite its significant role in catalyzing stratospheric ozone loss. Several plant species are known to emit CH_3Cl naturally via an enzymatically-mediated reaction of the universal methyl group donor S-adenosyl-L-methionine (SAM) with chloride ions. Additionally, CH_3Cl may be synthesized abiotically by chlorination of methoxyl groups in the plant structural components pectin and lignin, although this process is much more efficient under elevated temperatures, such as during biomass burning.

Similar to other plant-derived C1 volatile organic compounds (VOCs) such as methanol (CH3OH), stable isotope analyses of CH_3Cl emitted by various living plants revealed strongly depleted $\delta^{13}C$ and δ^2H values (e.g., Hartmann et al. 2023), indicating a common origin from the plant methyl pool. Recently, Kolby et al. (2024) employed stable isotope labelling to investigate biochemical formation mechanisms of methylated biopolymers and metabolites such as methylated pectin, associated with plant growth. They demonstrated that plant leaves exposed to $^{13}CO_2$ rapidly translate ^{13}C-labelling to leaf serine, methionine, pectin methyl esters and CH_3OH within minutes of light exposure, thereby providing evidence of a "photosynthetic C1 pathway" linking photosynthetic carbon assimilation directly to plant growth.

Building on these findings, we aim to explore biochemical CH_3Cl formation pathways using stable isotope analyses. Therefore, we conducted branch enclosure experiments on a Ginkgo tree (*Ginkgo biloba*) at Heidelberg University over the growing season (April to October) and analyzed in-vivo CH_3Cl emission rates as well as stable isotope values ($\delta^{13}C$ and δ^2H), confirming the depletion patterns previously described for other plant species. We observed substantial variations in CH_3Cl emission rates over the leaf growth and maturity periods, which we related to influencing factors such as temperature sensitivity and leaf chloride content. Additionally, consistent with Kolby et al.'s approach, we demonstrated the in-vivo formation of $^{13}CH_3Cl$ by leaves of *Ginkgo biloba* upon adding $^{13}CO_2$ into our plant chamber. These findings establish a direct link between foliar CH_3Cl emission and carbon assimilation during photosynthesis, suggesting that the anticipated effects of carbon fertilization and temperature increases under climate change may affect CH_3Cl emissions from plants.

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Isotopic investigation of plant part-specific nitrous oxide production in roots and shoots of chicory (C. intybus)

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Nitrous oxide (N_2O) is the third most important anthropogenic greenhouse gas and contributes substantially to ozone degradation in the stratosphere. However, global budget calculations of the sources and sinks of N_2O indicate that there may still be unknown or underestimated natural sources of N_2O. In this context, an increasing number of laboratory studies suggest that plants may also produce and release N_2O through their leaves. However, the processes and source strength are still unknown.

We performed experiments to clarify the role of vegetation as a source of N_2O where we incubated shoots and roots of chicory (C. intybus) separately in glass flasks under sterile conditions. Subsequently, their N_2O production rates and isotopic composition of the emitted N_2O were investigated via cavity ring-down spectroscopy. For the first time we could show that N_2O formation in chicory plants occurred in both root and shoot parts of the plant at similar rates when normalized to dry weight, suggesting that N_2O formation in plants is not plant-part specific. N_2O formation per dry weight was higher in shoot cultures compared to the root cultures when the shoots were incubated in the dark. When incubated in the light, N_2O formation in the shoots was significantly lower compared to dark conditions, indicating an influence of light and possibly photosynthesis on N_2O formation or degradation within chicory shoots.

By adding ^{15}N-labelled nitrate (NO^{3-}) and ^{15}N-labelled ammonium (NH^{4+}) to the incubated shoots and roots of C. intybus and analysing the $\delta^{15}N\text{-}N_2O$ values of the emitted N_2O, the further aim was to gain new insights into precursor compounds and reaction pathways of N_2O production in plants. The addition of ^{15}N-labelled NO^{3-} resulted in increasing $\delta^{15}N\text{-}N_2O$ values, unambiguously identifying this compound as a precursor of plant N_2O emissions. Contrary to this observation, the addition of ^{15}N-labelled NH^{4+} did not lead to increases in $^{15}N\text{-}N_2O$ but substantially increased N_2O formation rates in these plants compared to the controls or plants where NO^{3-} was supplemented. Our study highlights the need for a better understanding of plant N_2O emissions and demonstrates the potential of isotopic labelling of precursor compounds in investigating the underlying mechanisms.

DFG Research Unit Land-Atmosphere Feedback Observatory (LAFI): Using real-time isotopic in-situ measurements to partition evapotranspiration into soil evaporation and plant transpiration at two distinct cropland sites

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Agricultural crops play a vital role in the global water cycle. However, climate change may modify crop's physiology, agricultural ecosystems and interactions within the land-atmosphere (L-A) system. For predicting future hydroclimatic conditions and evaluating agricultural land use practices, particularly in light of the increased frequency of extreme events, it is critical to gain knowledge about crop transpiration (T) and soil evaporation (E) rates on a local scale, their temporal dynamics, and their connection to the L-A system.

Here, we present the recently started DFG Research Unit "LAFI" subproject: Using real-time isotopic in-situ measurements to partition evapotranspiration into soil evaporation and plant transpiration.

For the project, we will use coupled water and isotope flux measurements along the L-A system to investigate water-related processes at high temporal and spatial resolution, via canopy and leaf chambers for ET and T and membrane probes for soil vapor isotope measurements. Such novel isotope measurement platform will allow us to determine crop (wheat, maize) root water uptake (RWU) contributions and depths at the Land-Atmosphere Feedback Observatory (Uni Hohenheim) and assess water transit times and partition evapotranspiration. Analyses will be crop species-specific and test the influence of varying environmental conditions on RWU, transit times, ET and the partitioning of ET. Our results will help to assess crop species' vulnerability to future, climatically induced changes in precipitation and soil moisture.

4: Physiology, Metabolism, Forensics, Food (& further topics)

Evaluation of the potential of stable hydrogen isotopic composition of fatty acids for geographical traceability of vegetable oils

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The stable isotopic analysis of light elements, combined with chemometric techniques, has effectively determined the geographical origin of vegetable oils. However, the application of stable hydrogen isotopic composition (δ^2H) of fatty acids (FAs) for this purpose remains underexplored. This is partly because δ^2H of FAs is influenced by multiple factors, including climatic conditions and soil properties within the soil-plant-atmosphere continuum1,2,3,4. The relative impact of these factors on δ^2H of FAs is still unclear, leading to uncertainty regarding the efficacy of δ^2H of FAs in identifying the geographical origin of vegetable oils.

This study aimed to analyze the correlation between the δ^2H of major FAs in vegetable oil and climatic and soil factors of their growth locations, using rapeseed from Hesse, Germany, as a case study.

Between 2017 and 2020, Landesbetrieb Landwirtschaft Hessen (LLH) provided us with approx. 70 rapeseed and corresponding soil samples each year. From the stock, 121 samples were randomly selected for this study. These rapeseeds were prepared using a one-step sample preparation method5. The δ^2H values of major FAs (C18:1, C18:2, C18:3, C16:0) were determined using GC-Py-IRMS. Climate and soil data were obtained from publicly available databases or measured using standardized laboratory methods. Using a total of 89 climatic and soil factors, stepwise linear regression analysis was applied to identify and prioritize the factors affecting the δ^2H values of FAs.

The analysis revealed significant correlations between the δ^2H of FAs in rapeseed oil and specific environmental factors, such as air temperatures in February and May, precipitation amounts in April, and silt content at the sampling sites. Climatic conditions, in particular, were found to have a more pronounced influence on the δ^2H of FAs than the selected soil properties. These findings suggest that the δ^2H of FAs can serve as markers for discerning the geographical origin of vegetable oils, particularly when the origins exhibit distinct climates or soil factors. Further, the results suggest that climatic factors obtained through remote sensing can be a powerful dataset for the geographical traceability of vegetable oils.

C-N-S-H-stable isotope data in human hair from the 1950s and more recent periods

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The stable isotope signature in the body tissues of current people can only be compared with those of people from earlier periods to a limited extent. A shift in values is to be expected, particularly within the last few decades. Reasons such as the worldwide burning of fossil fuels, the globalisation of trade in goods and the changed production conditions in agriculture are likely to have had an effect on the stable isotope values in basic foodstuffs. Furthermore, the introduction of food products that were previously uncommon in Central European diet (e.g. algae, soya, chia, tropical fruits) and the year-round availability of almost all types of fruit and vegetables are also likely to have changed the eating habits of many consumers and thus the isotopic composition of their diet.

The legal medicine institute's archive contained hair samples from the 1950s, which we could analyse for their stable isotope composition. The C-N-S-H stable isotope values of around 50 hair samples each from Bavaria from 1956/57 and more recent periods were compared.

We found significant differences for the $\delta^{15}N$ and $\delta^{34}S$ values between the hair samples from the 1950s and 2005 resp. 2017, but no differences for the $\delta^{13}C$ and $\delta^{2}H$ values.

With the data obtained it is expected to make a more precise assessment of the geographical locations of unknown dead people in forensics, especially for persons who were already living in the 1950s. Taking into account the isotopic differences, the isotope signatures in the human body tissues that were formed decades ago can be statistically evaluated directly via the current reference hair isotope database. This means that the geographical origin of a person can be assigned to or differentiated from Bavaria/Germany with much greater certainty.

Isotope Ratio Mass Spectrometry based profiling of *Ricinus communis* – A forensic approach

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Recent incidents in France, Germany, and worldwide highlight the global threat posed by biotoxins. Particularly the plant toxin ricin, found in the seeds of the castor oil plant *Ricinus communis* (*R.c.*), is of special forensic interest due to its worldwide availability, high toxicity, and lack of medical countermeasures. Analytical methods for the detection of ricin have already been established, but supplementary molecular forensic analysis is crucial to link different pieces of evidence to a common source or toxin extraction process. The identification of light-element stable isotope ratios of crude *Ricinus communis* seeds and purified ricin containing materials can provide not yet available forensic information by potentially establishing correlations between crime scenes, preparation sites and suspects.

To raise the evidential value of forensic investigation in this field, $\delta^{13}C$ and $\delta^{15}N$ values of crude *Ricinus communis* seeds as well as purified ricin materials were determined as part of a proof-of-principle study. Samples were analyzed on a Flash Elemental Analyzer 1112 coupled via a Conflo IV Interface to a Delta V Plus isotope ratio mass spectrometer (all Thermo Scientific, Bremen, Germany). Based on total carbon and nitrogen isotope ratios determined by EA-IRMS, *Ricinus communis* seeds from known geographic origins but unknown cultivar as well as seeds from known cultivar but commercially purchased (unknown geographic origin) could be distinguished in pairwise comparison. In addition to crude *R.c.* seeds, carbon and nitrogen stable isotope ratios of purified acetone and n-hexane extracted ricin materials were determined and evaluated. Purified seed materials could be distinguished from respective crude *R.c.* seeds and regression analyses of the $\delta^{13}C$ and $\delta^{15}N$ values of purified ricin material against the $\delta^{13}C$ and $\delta^{15}N$ values of the original source seeds imply strong correlations for both extraction solvents (acetone or n-hexane) used. This indicates that $\delta^{13}C$ and $\delta^{15}N$ measurements can be used to correlate potential source seeds found at a preparation site to purified ricin material at a crime scene. In addition, carbon and nitrogen mass concentrations can be used to estimate the degree of toxin purification independent of the *R.c.* seed origin and cultivar.

In summary, carbon and nitrogen isotope ratio mass spectrometry based profiling of *Ricinus communis* can help to retrospectively categorize ricin-containing materials. This information can be implemented in profiling strategies and is of high value for forensic intelligence in terms of sample comparison.

Geophysical Monitoring of simulated Graves and AI based Data Analysis – Subproject: Isotopic profiling of grass samples from the graves and nearby

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The detection of human remains is an important task in police investigations. Especially in unpaved terrains the discovery of such clandestine burial sites remains challenging and there is a need for effective instrumental techniques. Therefore, a project was initiated at the Federal Criminal Police Office aiming at identifying and remotely sensing simulated graves.

At the beginning of the project, several graves were created with various contents such as bones, weapons, and ammunition. To study the environmental changes over time and identify the most effective methods to detect a grave – even after several years – the burial sites were monitored using geophysical methods and instruments (e.g., georadar, multispectral sensors, as well as drones for aerial surveillance).

In 2020, four pigs were buried in four simulated graves. These pigs were packed up in different materials before being placed in the graves: one pig was wrapped in a carpet, one in plastic foil and two pigs were naked. For these buried pigs, an interesting observation was made: One year after the burial, extremely tall and dark green grass was observed over the graves, distinctly different in color and shape from the surrounding meadow. To further investigate this finding, a second burial site was prepared at another meadow in 2022. The buried pigs were again wrapped in different materials (naked, blanket, plastic foil); additionally, an empty grave was also prepared as negative control. Isotope ratio mass spectrometry was then employed to study the stable carbon and nitrogen isotope ratios in the grass growing at the graves and collected at several time points after burial.

The isotope ratios of $\delta^{13}C$ and $\delta^{15}N$ were determined using an elemental analyzer (FlashEA) coupled to an isotope ratio mass spectrometer. The primary question is whether the grass is feeding on the decomposing pigs. First results showed very negative $\delta^{15}N$ values (up to -15 ‰) of the grass samples, especially over the graves containing the naked pigs.

Processes in the dissolved carbonate system of surface waters may contribute and are sensitive to variations of boundary conditions associated with climate change. Carbon dioxide super- and calcium carbonate -saturated ground waters that emerge from springs lose dissolved carbon dioxide to the atmosphere; this process leads to the development of $CaCO_3$ supersaturation of the aqueous solution. When exceeding a critical value, solid carbonates precipitate, thereby linking the past marine with the present terrestrial carbon cycles. The associated distribution of trace elements and stable isotopes leads to proxy formations. The magnitude of trace element and isotope fractionations is linked to non-equilibrium processes, impacted by the initial solution composition, hydrodynamics, and possible biological activity in the stream beds.

Carbon isotopes as reaction tracking tool in cement mineralogy

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In this study, we used stable carbon isotopes to receive direct insights into cement mineralogy reactions during wet carbonation. Stable carbon isotope ratios in CO_2, dissolved inorganic carbon (DIC) and carbonate phases were measured. The aim of this study was to investigate carbon isotope ratio changes during the reaction of C_2S (Ca_2SiO_4) with CO_2 to calcium carbonate and silica gel. If a systematic fractionation of carbon isotopes occurs during the reaction, it can help to quantify the carbonation reaction. During the carbonation process over 48 h, we found carbon isotope distributions from the gaseous phase to the solution and ultimately to the solid phase. Calculations confirm the direct relation of isotope values to the carbonation progress. Additionally, the progress of carbonation was detected by more "classic" methods, such as quantitative X-ray diffraction and thermogravimetric analysis often applied in mineralogy. With this, stable isotope measurements offer a promising tool to monitor the reaction progress in-situ.

POSTERS – Physiology, Metabolism, Forensics, Food

Exploring Reaction Paths for Sulfonamide Hydrolysis: Insight from Experiments and Computations

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Over the past few decades, antibiotics, an emerging class of environmental micropollutants, have drawn increasing attention for their potential to give rise to the development of antibiotic resistance. In particular, sulfonamides (SAs) have been widely used as human and veterinary medicine. Furthermore, in many countries, they are applied intensively in livestock and aquaculture with the intention of preventing disease and/or promoting growth. As a result, large amounts of SAs are released in partially degraded and undegraded form into the environment, which may affect natural microbial communities and give rise to antibiotic-resistant bacteria. To safeguard global health, developing innovative efficient methods for targeted removal of SAs from water are therefore of great interest. In this context, limited information is available on the reaction mechanisms that would break SAs down via facilitated hydrolysis such as in an enzymatic environment. Here, our project aims to take a first step to accruing experimental and computational evidence on the fundamental hydrolysis mechanisms of SAs under different pH conditions.

Eight sulfonamide compounds, sulphamethoxazole, sulphisoxazole, sulphamethiazole, sulphathiazole, sulphapyridine, sulphadiazine, sulphadimidine and sulphadimethoxine were exposed to a range of pH conditions (2.0, 4.0, 6.0, 8.0, or 10.0) over three months. While all selected SAs were hydrolytically stable in buffer solutions at pH 4.0, 6.0, 8.0, and 10.0, 5 out of 8 SAs (sulphisoxazole, sulphapyridine, sulphadiazine, sulphadimidine, and sulphadimethoxine) were degraded effectively at pH 2.0. In addition, hydrolytic metabolites, such as sulphanilic acid, sulphanilamide, aniline and corresponding leaving groups were identified and quantified by HPLC-UV.

To explore this further, on the one hand, we aim to identify further SAs transformation products by analysis with Orbitrap high-resolution mass spectrometry (HRMS). On the other hand, isotope effects of target elements (e.g., $^{13}C/^{12}C$, ^{15}N/14N) in individual sulfonamide compounds during hydrolysis are obtained by measuring their isotope ratios on gas chromatography - isotope ratio mass spectrometry (GC-IRMS). Such compound-specific isotope analysis (CSIA) can inform about the elements involved in bond formation / cleavage. In conjunction with, quantum chemical calculations they further allow testing hypotheses about transition-state geometries and transient intermediates thereby revealing what until now has been "black box" when it came to understanding reaction pathways in SAs hydrolysis. We aim to use this mechanistic understanding as computational guidance for directed evolution to generate novel enzymes for curbing micropollutant contamination in drinking and waste water.

POSTERS – Paleoclimate, Sedimentology, Soils

A Late Glacial and Holocene ^{18}O and 2H isotope paleoclimate record from Africa's largest afro-alpine ecosystem: Central Lake in the Bale Mountains of Southeastern Ethiopia

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Understanding past climate variabilities is of paramount importance in successful prediction and mitigation of present and future climate challenges. Stable isotope analysis of organic matter extracted from sediment archives are now becoming mainstream in palaeoclimate studies. Afro-alpine ecosystems offer pristine climate archives mainly due to their remoteness from modern anthropogenic influences. The Bale Mountains of the Southeastern Ethiopian Highlands are the largest and most contagious afro-alpine ecosystem in Africa. It's also situated in close proximity to the East African Rift which is also home to most of early hominin sites. The juxtaposition of rift and alpine systems coupled with complex climate dynamics offer unique perspectives to understand pre-industrial climate–human interaction.

During a 2017 field campaign, a total of 4.8 meter core were retrieved form the shorelines of Central Lake in the Bale Mountains. 12 radiocarbon dates were used to reconstruct a 17 thousand year sedimentary history. Here we present preliminary results form a multi-proxy investigation on this archive. We extracted and analyzed $\delta^{18}O$ and $\delta^{2}H$ from hemicellulose sugar biomarkers and leaf wax n-alkanes respectively. The sugar biomarkers are aquatic in origin, hence the isotopic variability is linked with $\delta^{18}O$ of lake water driven by precipitation/evaporation. Conversely, the n-alkanes are interpreted to be primarily of terrestrial origin and their $\delta^{2}H$ variability thus represents changes in precipitation. Despite having different sources, both isotopic records show similar trends, suggesting common response to environmental changes and allow the comparison with other regional (e.g. Bittner et al., 2022; Mekonnen et al., 2023) over over-regional paleoclimate and –environmental records.

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A multi-isotope geochemical perspective on lacustrine carbon diagenesis in dolomite- and calcite-bearing sediments of Lake Constance

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Many marginal seas had a freshwater phase during the last glaciation. These sediments are often modified by later diagenesis by downward-diffusing ions. Understanding the original processes requires calibration by lacustrine analogues. Lake Constance is one of the largest lakes of Central Europe, and the hard water lake chemistry makes it an ideal laboratory to investigate carbon-diagenesis in detail. The (post-)glacial sediment deposits were investigated in up to 24 m long cores recovered from the northernmost deep portions of the lake. The benthic carbon cycle and mineral sources and (trans)formations, were investigated through porewaters and sedimentary solid phases analyses for stable isotope signatures (CHOS), and major- and trace element compositions.

The water isotope signatures display a trend towards lighter data with depth, reflecting the development in the lake water composition with time under impact by diffusion processes. The dissolved inorganic carbon (DIC) concentrations increased below the sediment-water interface and were generally higher in the postglacial sediments due to organic matter (OM) mineralization. The δ^{13}C-DIC showed the lightest values in the glacial sediments and displays an enrichment in Holocene sediments, together with pore water hydrochemistry, indicative of OM oxidation, carbonate dissolution, and potential methane cycling. Bulk carbonate isotope signatures show variations controlled by detrital carbonates, including dolomite. Vertical variations in the composition of porewaters, bulk, and extractable elements and SEM-EDX investigations, allow insights about the proxy capacity of mineral phases in the sedimentary record.

POSTERS – Climate and Atmosphere

Combining different methodological approaches for estimating N_2O processes and N_2O reduction in the field

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Nitrous oxide (N_2O) emissions are a significant contributor to greenhouse gas effects and are primarily produced through agricultural practices, particularly following the application of nitrogen-based fertilizers. Identifying the specific microbial processes responsible for N_2O emissions is crucial to better understand the underlying mechanisms and develop targeted climate change mitigation strategies. However, a key factor determining the extent of N_2O emissions under different soil conditions is the reduction of N_2O to N_2, which is challenging to measure due to its high background concentration.

During the last decades, the analysis of abundance of the four most abundant isotopocules of N_2O ($^{14}N^{14}N^{16}O$, $^{14}N^{15}N^{16}O$, $^{15}N^{14}N^{16}O$, $^{14}N^{14}N^{18}O$) presented a promising alternative for assessing N_2O production pathways (heterotrophic bacterial denitrification, nitrifier-denitrification, fungal denitrification, nitrification) and N_2O reduction. To obtain a best estimate for N_2O reduction, this approach can be combined with the ^{15}N gas flux method with N_2-depleted atmosphere (^{15}NGF+), which allows direct quantification of N_2 in the field. Nevertheless, the N_2O isotopocule approach cannot differentiate between heterotrophic bacterial denitrification and nitrifier denitrification. The ^{15}NGF+ method cannot differentiate between nitrifier-denitrification and nitrification, but between fungal denitrification/heterotrophic bacterial denitrification and nitrifier denitrification/nitrification. Thus, the combination of both approaches provides values for heterotrophic bacterial denitrification and nitrifier-denitrification, completing our understanding of the N_2O processes.

We will present a combined dataset of N_2O isotopocules and ^{15}NGF+ from the MinDen project, where different slurry application techniques were investigated during winter wheat cropping in spring 2024.

Real-time analysis of δ^{13}C- and δD-CH$_4$ in ambient air with a QCL based absorption spectrometer coupled to a trace gas extractor (TREX-III)

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Methane (CH$_4$) is the second most significant anthropogenic greenhouse gas after carbon dioxide (CO$_2$). Over the past 150 years, the concentration of methane in the atmosphere has increased from approximately 772 parts per billion (ppb) in pre-industrial times to 1931 ppb in 2024 (Lan et al., 2024). The most abundant methane isotopologues, ^{13}CH$_4$ and ^{12}CH$_3$D, have been proposed as potential proxies for distinguishing between natural sources, such as wetlands, termites and the ocean, and anthropogenic sources, including agriculture, fossil fuels and waste.

In the context of regionally focused studies, involving significant local fluxes, WMO/GAW (Word Meteorological Organization/Global Atmosphere Watch) have suggest extended compatibility goals between laboratories of ±5 ppb for CH$_4$ mole fractions as well as ±0.2 ‰, and ±5 ‰ for the isotope deltas δ^{13}C-CH$_4$ and δD-CH$_4$ (GAW-Report No 292, 2022). It is only possible to achieve these levels of compatibility with an analytical technique that demonstrates high precision, repeatability and analytical uncertainty.

In this study, we present an enhanced analytical system consisting of a new preconcentration device (TREX-III, Prokhorov et al., 2022) equipped with cryo-focusing trap and an upgraded dual-laser QCLAS (Aerodyne Research, Inc., USA). The QCLAS achieves an Allan precision of 0.04 ‰ and 0.2 ‰ for δ^{13}C- and δD-CH$_4$, at enhance CH$_4$ mole fractions, respectively. The repeatability of measurements (30 times) in compressed ambient air cylinder was found to be ± 0.1 ‰ and ± 0.5 ‰ for δ^{13}C- and δD-CH$_4$, respectively. To link measurements to international isotope ratio scales (VPDB, VSMOW), applied reference gases are currently analyzed by high-precision IRMS at MPI-BGC.

At present the instrument is deployed for monitoring of CH$_4$ sources at a suburban site close to Zürich (Empa campus) within the Horizon-CL5-2022-D1-02 project PARIS.

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POSTERS – Further topics

On-line analysis of isotopic composition in N$_2$O emitted during biological nitrogen removal in wastewater treatment

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The potent greenhouse gas nitrous oxide (N$_2$O) is a byproduct of biological nitrogen removal and dominates the climate impact of wastewater treatment. Switzerland aims to reduce the climate impact of its wastewater treatment sector, making a detailed understanding of N$_2$O production essential. While research often focuses on the seasonal dynamics of N$_2$O emissions, short-term dynamics, which are primarily influenced by influent composition and weather conditions, are frequently overlooked. Understanding the mechanisms behind the dynamics of biological N$_2$O production and reduction is essential for comprehending both short-term and long-term emission patterns. High temporal resolution analysis of the N$_2$O isotopologues ^{14}N^{15}N^{16}O, ^{15}N^{14}N^{16}O, and ^{14}N^{14}N^{18}O provides an opportunity for improving our process understanding at timescales relevant for plant operation. Within the Swiss Center of Excellence on Net Zero Emissions (SCENE), we currently conduct experiments at the Eawag pilot wastewater treatment plant in Dübendorf, Switzerland. In a first phase, potential short-term effects on N$_2$O reduction are investigated. The experiments include nitrite addition, with and without increased oxygen availability and sulfide addition. On-line and grab sample isotopic measurements are performed using off-axis integrated cavity output spectroscopy (OA-ICOS) and cavity ring-down spectroscopy (CRDS). Preliminary data suggest that denitrification is the dominant source of N$_2$O, while nitrification is of minor importance. Increased oxygen availability and sulfide addition both decrease the extent of N$_2$O reduction, as indicated by lower site preference (SP) and δ^{18}O values. By analyzing N$_2$O isotopologues, we can gain insights into the short-term effects of influent composition on the N$_2$O reduction dynamics in wastewater treatment. Furthermore, it supports the evaluation of management strategies to reduce N$_2$O emission and therefore minimize the climate impact of wastewater treatment.

Bioconversion of CO_2 to CH_4 during anaerobic digestion of Alfalfa inidcated by $^{13}CO_2$-Labeling

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In recent years, the demand for renewable energies and the reduction of greenhouse gases has become increasingly important as part of the energy transition. Energy production by anaerobic digestion makes an important contribution to the renewable energy portfolio of Germany. In addition to the production of energy-rich methane (CH_4), approximately the same amount of CO_2 is produced, and the digestate can have a considerable CH_4 potential. There is therefore potential for optimizing the biogas process by (i) reducing CO_2 emissions and (ii) transformation of CO_2 into energetically usable CH_4.
Recent studies investigating the anaerobic digestion of different input substrates (sewage sludge, maize, sugar beet, alfalfa) have shown that the injection of solely CO_2 led to (i) an increase in CH_4 yield and (ii) improved process stability. To study the underlying mechanisms, stable isotope techniques were applied. To monitor the dynamics of the bioconversion of CO_2 to CH_4, ^{13}C labeled CO_2 was injected into the biogas reactor via a bubble column. The reactor was fed daily with alfalfa. The liquid working volume was 35 L and temperature was set to 38°C. The initial $\delta^{13}CO_2$ value of the injected CO_2 was ~4000 mUr. During the $^{13}CO_2$-injection, $\delta^{13}C$-CO_2 gradually increased from -15 mUr to +200 mUr. After feeding the reactor with alfalfa, which stimulates substrate turnover, bioconversion of CO_2 to CH_4 takes place, as evidenced by a simultaneous decrease in $\delta^{13}CO_2$ value and an increase in $\delta^{13}CH_4$. Maximum $\delta^{13}CH_4$ values of ~0 mUr were observed 400 minutes after injection. The initial $\delta^{13}CH_4$ value isotope value was reached again after approximately one week. Thus, $^{13}CO_2$ labeling experiments unambiguously prove that the injected CO_2 is immediately converted into energetically usable CH_4, which reduces the residual CH_4 potential in the digestate. The isotope pattern also indicates that CO_2 injection, which currently takes place every two to three days, should be increased to at least every day in order to keep bioconversion at a constant level.
In a next step, the incorporation of ^{13}C-labeled CO_2 for acetate and bicarbonate in the fermentation substrate will be investigated to determine the contribution of potential precursor substrates to CH_4 production and to reveal the underlying mechanisms including metagenomic studies.

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