

ASI 2021

Jahrestagung der Arbeitsgemeinschaft *Stabile Isotope e.V.*

Stabile Isotope in Geowissenschaft,
Öko- und Umweltforschung, Medizin und Forensik:

*Wasser • Sediment • Atmosphäre • Pflanze
Boden • Medizin • Forensik*

26.–29. September 2021

– Virtuelle Tagung –



TECHNISCHE
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Abstractband *Book of Abstracts*

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TAGUNGSLEITUNG & ORGANISATIONSKOMITEE

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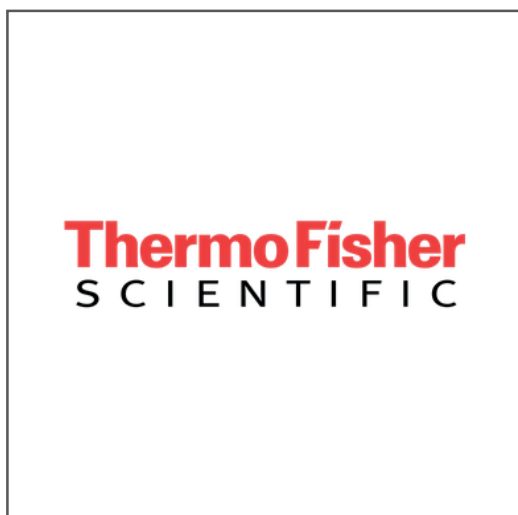
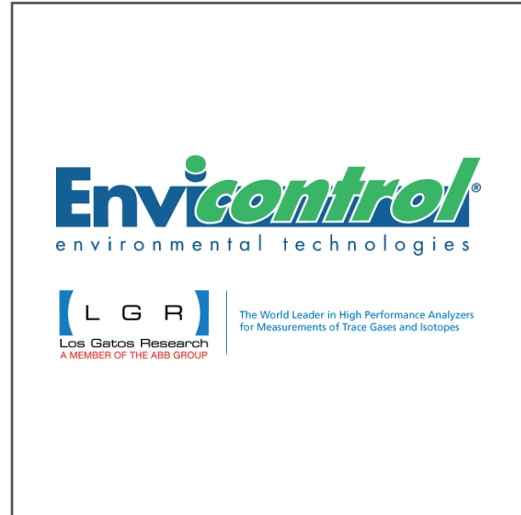
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Prof. Michael Zech

Paläoumweltforschung, Technische Universität Dresden

Ein herzliches Dankeschön den Firmen, die die ASI 2021 unterstützt haben!
A big thank you to the companies that supported the ASI 2021!



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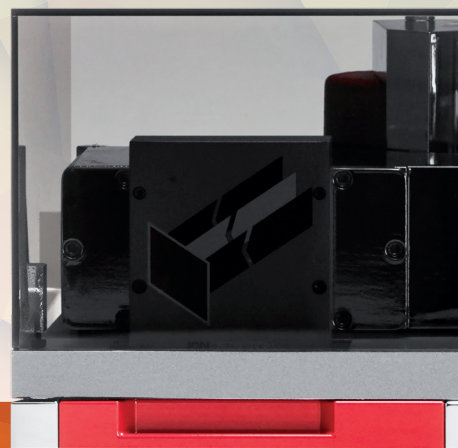
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Sonntag | Sunday, 26.09.2021

14:00 – 17:00 ASI-Juniors
Impulsvorträge Marshall / Barth / Van Geldern
PhD Workshop

Montag | Monday, 27.09.2021

10:00 – 12:30 Firmen – Geräte & Zubehör | Companies – Devices & Equipment

13:30 – 14:00 Eröffnung der Tagung | Conference Opening

14:00 – 15:30 **Block 1.1: Analytik, Methoden, Technik
und Qualitätssicherung stabiler Isotope**

Chairs: **Matthias Gehre**, UFZ, **Paul Königer**, BGR Bundesanstalt für Geowissenschaften und Rohstoffe

14:00 – 14:15

Compound Specific Stable Sulfur Isotope Analysis ($\delta^{34}\text{S}$ and $\delta^{33}\text{S}$) of Organic Compounds Using Gas Chromatography Hyphenated with Multiple Collector Inductively Coupled Plasma Mass Spectrometry (GC-MC-ICPMS)

Steffen Kümme¹, **Faina Gelman**², **Axel Horst**¹, **Harald Strauß**³, **Richnow Hans H.**¹, **Matthias Gehre**¹

1: Helmholtz-Zentrum für Umweltforschung GmbH – UFZ, Leipzig, Germany; 2: Geological Survey of Israel, Jerusalem, Israel; 3: Westfälische Wilhelms-Universität Münster, Institut für Geologie und Paläontologie, Münster, Germany

14:15 – 14:30

New Frontiers in Compound-Specific $\delta^2\text{H}$ Analysis

S. K. Lengger^{1,2,3}, **S. Kelly**⁴, **K. W. R. Taylor**⁵, **R. Berstan**⁵, **M. Seed**⁵, **I. D. Bull**¹, **J. Blewett**¹,
R. D. Pancost¹

1: University of Bristol, UK; 2: University of Plymouth, UK; 3: Silicon Austria Labs, Austria; 4: International Atomic Energy Agency, Austria; 5: Elementar UK Ltd, UK

14:30 – 14:45

A quick one-step sample preparation method with 2,2-Dimethoxypropane (DMP) for isotopic fingerprint analysis of vegetable oil – how does DMP influence the accuracy of the C- and H-CSIA by GC-C/Py-IRMS?"

Lili Xia, **Kaori Sakaguchi-Söder**, **Daniel Stanojkovski**, **Liselotte Schebek**

Stoffstrommanagement und Ressourcenwirtschaft, Institut IWAR, TU Darmstadt

14:45 – 15:00

Revisiting SPIN-MIRMS: N-isotopic composition of nitrate and ammonium from aqueous solutions by isotope ratio mass spectrometry

Jens Dyckmans¹, **Wolfram Eschenbach**¹, **Reinhard Langel**¹, **Lars Szewc**¹, **Reinhard Well**²

1: Universität Göttingen, Kompetenzzentrum Stabile Isotope, Deutschland; 2: Thuenen Institut für Agrarrelevante Klimaforschung, Braunschweig, Deutschland

15:00 – 15:15

$\delta^{13}\text{C}$ Analysis of DOC from Liquid Samples – Proof of Concept

Isabell von Rein, **Heike Geilmann**, **Heiko Moossen**

Max-Planck-Institut für Biogeochemie, Deutschland

15:30 – 16:00 Firmen | Companies' side-rooms

Pause | Break

16:00 – 17:00

Block 1.2: Analytik, Methoden, Technik und Qualitätssicherung stabiler Isotope

Chairs: **Matthias Gehre**, UFZ, **Paul Königer**, BGR Bundesanstalt für Geowissenschaften und Rohstoffe

16:00 – 16:15

Comprehensive Isotope Ratio MS of Oxyanions with an Electrospray-Orbitrap

Andreas Hilkert¹, **Cajetan Neubauer**²

1: Thermo Fisher Scientific, Deutschland; 2: University of Colorado, Boulder, USA

16:15 – 16:30

The next leap forward in gas IRMS

Mario Tuthorn, **Jenny Roberts**, **Oliver Kracht**, **Dieter Juchelka**, **Andreas Hilkert**

Thermo Fisher Scientific, Deutschland

16:30 – 16:45

Improved throughput for $\delta^{18}\text{O}$ and δD measurements of water with Cavity Ring-Down Spectroscopy

Magdalena Hofmann¹, **Jan Woźniak**¹, **Zhiwei Lin**², **Keren Drori**²

1: Picarro B.V., Niederlande; 2: Picarro Inc., USA

16:45 – 17:00

A new infiltration optimized tracer application method for ^{15}N and ^{18}O tracers in field soil experiments

Arne Tenspolde¹, **Jaqueline Berendt**¹, **Nicole Wrage-Mönnig**¹, **Tim J. Clough**²

1: Institut für Grünland und Futterbauwissenschaften, Agrar- und Umweltwissenschaftliche Fakultät, Universität Rostock, Germany; 2: Soil and Physical Sciences Department, Faculty of Agriculture and Life Sciences, Lincoln University, New Zealand

Dienstag | Tuesday, 28.09.2021

9:30 – 11:00

Block 2.1: Hydrogeologie, Hydrologie und Wasserisotope

Chairs: **Florian Einsiedl**, TUM, **Diana Burghardt**, TU Dresden, **Christoph Schüth**, TU Darmstadt

9:30 – 10:00

Session Keynote

Oxygen is all around...

Johannes A.C. Barth¹, **Robert van Geldern**²

1: GeoZentrum Nordbayern, Deutschland; 2: Friedrich-Alexander-Universität Erlangen-Nürnberg

10:00 – 10:15

Impact of the 2018-2020 drought in Central Germany on the nitrogen cycling in a meso-scale catchment: Insights from hydrochemical and stable isotope investigations

Christin Mueller, **Ronald Krieg**, **Ralf Merz**, **Kay Knoeller**

Helmholtz Centre for Environmental Research – UFZ, Deutschland

10:15 – 10:30

Spatiotemporal analysis of Central European young water fractions

Michael Stockinger, **Christine Stumpp**

Universität für Bodenkultur, Wien, Österreich

10:30 – 10:45

Stable water isotope analysis and improved lumped-parameter modeling for characterizing unsaturated subsurface flow

Anne Imig, Fatemeh Shajari, Florian Konrad, Florian Einsiedl, Arno Rein

Chair of Hydrogeology, Faculty of Civil, Geo and Environmental Engineering, Technical University of Munich, Germany

10:45 – 11:00

Identifizierung von Oberflächenwasser-Grundwasser-Interaktionen anhand von charakteristischen Isotopensignalen

Michael Engel^{1,2}, Simon Mischel¹, Sabrina Quanz¹, Dirk Radny¹, Francesco Comiti², Lars Düster¹, Axel Schmidt¹

1: Bundesanstalt für Gewässerkunde, Deutschland; 2: Freie Universität Bozen-Bolzano, Italien

11:00 – 11:15

Poster Kurzvorträge – Themenblock 2: Hydrogeologie, Hydrologie und Wasserisotope

Virtueller Veranstaltungsort: **Poster Kurzvorträge**

11:00 – 11:04

Stable water isotopes as natural tracers in a hydrogeological study of riverbank filtration in N'Djamena, Chad

Maïke Gröschke, Lilli Witt, Paul Königer, Sara Vassolo

Federal Institute for Geosciences and Natural Resources (BGR), Groundwater Resources – Quality and Dynamics

11:04 – 11:08

Isotopen-hydrobiogeochemische Untersuchungen an anoxischen Grundwässern off- und on-shore der norddeutschen Küste

Michael Ernst Böttcher^{1,2,3}, Anna-Kathrina Jenner^{1,3}, Cátia M.E. von Ahn^{1,2}, Iris Schmiedinger¹, Andreas Roskam⁴

1: Leibniz Institute of Baltic Sea Research (IOW), Deutschland; 2: University of Greifswald, Deutschland; 3: University of Rostock, Deutschland; 4: NLWKN Aurich, Deutschland

11:08 – 11:12

Measuring high-resolution geochemical depth-profiles in hyporheic stream sediments with focus on aerobic and anaerobic methane oxidation

Tamara Michaelis, Anja Wunderlich, Florian Einsiedl

Technische Universität München, Lehrstuhl Hydrogeologie, Deutschland

11:12 – 11:15

Karstic springs as strong emitters of CO₂

Kern Lee^{1,2}, Robert van Geldern¹, Johannes Barth¹

1: Friedrich-Alexander Universität Erlangen-Nürnberg (FAU), Deutschland; 2: Alberta Environment and Parks, Edmonton, Canada

11:15 – 11:30

Pause

11:30 – 12:15 **Block 2.2: Hydrogeologie, Hydrologie und Wasserisotope**
 Chairs: **Florian Einsiedl**, TUM, **Diana Burghardt**, TU Dresden, **Christoph Schüth**, TU Darmstadt

11:30 – 11:45

Neue Einblicke in die Infiltrationsbedingungen des Oberjura Thermalwassers in der südlichen Bayerischen Molasse mit Hilfe der $^{14}\text{C}_{\text{DOC}}$ Methode

Theis Winter, Florian Einsiedl

Technische Universität München, Deutschland

11:45 – 12:00

Supporting the interpretation of $\delta^{15}\text{N}$ values of dissolved NH_4^+ and NO_3^- in the water column of a seasonal stratified lake using Numerical modeling and PCR gene amplification

Gisela Alejandra Pena Sanchez¹, Florian Einsiedl¹, Clara Duffner^{2,4}, Stephanie Schulz^{2,4}, Bernhard Mayer³, Anja Wunderlich¹

1: Technical University of Munich; 2: TUM School of Life Sciences; 3: University of Calgary; 4: Helmholtz Centre Munich

12:00 – 12:15

Investigation of chloroform degradation mechanisms using multi-dimensional isotope fractionation analysis: Hydrodechlorination over Pd and Rh vs reductive dechlorination with Fe^0

Berhane Abbrha Asfaw^{1,2}, Kaori Sakaguchi-Söder², Christoph Schüth¹

1: Hydrogeology, Institute IAG, TU Darmstadt; 2: Material Flow Management and Resource Economics, Institute IWAR, TU Darmstadt

12:15 – 13:00 **Block 3: Paläoklima, Sedimentologie, Boden**
 Chairs: **Matthias Hinderer**, TU Darmstadt, **Michael Zech**, TU Dresden, **Christine Stumpp**, BOKU

12:15 – 12:30

Carbon isotope excursions in a Paleocene to early Eocene lignite bearing succession at the southern edge of the proto-North Sea (Schöningen, Germany)

Olaf K. Lenz^{1,2}, Mara Montag², Volker Wilde¹, Katharina Methner^{3,5}, Walter Riegel¹, Andreas Mulch^{3,4}

1: Senckenberg Forschungsinstitut und Naturmuseum Frankfurt, Deutschland; 2: Technische Universität Darmstadt, Institut Für Angewandte Geowissenschaften, Deutschland; 3: Senckenberg Biodiversity and Climate Research Centre (SBiK-F), Frankfurt am Main, Deutschland; 4: Goethe Universität Frankfurt, Institut für Geowissenschaften, Frankfurt am Main, Deutschland; 5: Stanford University, Department of Earth System Science, Department of Geological Sciences, USA

12:30 – 12:45

^{18}O analyses of bulk lipids as novel paleoclimate tool in loess research – a pilot study

Jakob Labahn¹, Philip Hirschmann¹, Lucas Bittner¹, Diana Burghardt², Bruno Glaser³, Slobodan Markovic⁴, **Michael Zech**¹

1: Physische Geographie mit SP Paläoumweltforschung, Technische Universität Dresden, Deutschland; 2: Institut für Grundwasserwirtschaft, Technische Universität Dresden; 3: Bodenbiogeochemie, Martin-Luther-Universität Halle-Wittenberg; 4: Universität Novi Sad, Serbien

12:45 – 13:00

Plant and fungal contributions to soil organic matter fractions assessed by ^{13}C and ^{15}N isotope natural abundances

Saskia Klink¹, Adrienne Keller², Andreas Wild¹, Vera Baumert⁴, Matthias Gube⁵, Eva Lehndorff³, Nele Meyer³, Carsten Mueller⁶, Richard Phillips², **Johanna Pausch**¹

1: Dept. Agroecology, Bayreuth Center of Ecology and Environmental Research (BayCEER), University of Bayreuth, Germany; 2: Dept. Biology, Indiana University Bloomington, IN, USA; 3: Dept. Soil Ecology, Bayreuth Center of Ecology and Env. Research (BayCEER), University of Bayreuth, Germany; 4: Chair of Soil Science, School of Life Sciences, TU Munich, Freising, Germany; 5: Soil Science of Temperate Ecosystems, Büsgen-Institute, Georg-August University Göttingen, Germany; 6: Dept. Geosciences and Natural Resource Management, University of Copenhagen, Denmark

13:00 – 14:00 **Mittagspause | Lunch break**

13:30–14:00 **Posterausstellung / Breakouträume**
 Poster side-rooms / all topics

14:00 – 14:45 **Vortrag Isotopenpreis**

14:45 – 15:30 **Block 4.1: Ökosysteme**
Chair: **Gerhard Gebauer**, Universität Bayreuth

14:45 – 15:00

Orchid *Cremastra appendiculata* on the path to self-supply with changing fungal companion

Franziska Zahn¹, Yung-I Lee², Gerhard Gebauer¹

1: BayCEER – Laboratory of Isotope Biogeochemistry, University of Bayreuth, Bayreuth, Germany; 2: Biology Department, National Museum of Natural Science, Taichung, Taiwan

15:00 – 15:15

Unravelling shoot:root drought responses in VOC emissions through ¹³C-pyruvate labelling

Erik Daber, Philipp Nolte, Jürgen Kreuzwieser, Mirjam Meischner, Christiane Werner

Chair of Ecosystem Physiology, Albert-Ludwigs-University of Freiburg, Germany

15:15 – 15:30

Field ¹⁵N pool dilution approach to determine gross nitrification rate

C. Florian Stange, Axel Lamparter, Julia Jaquemotte

BGR, Deutschland

15:30 – 15:45 **Poster Kurzvorträge | Short Communications –**
Themenblock 3: Paläoklima, Sedimentologie, Boden

15:30 – 15:33

Ein ~15 ka $\delta^2\text{H}_{n\text{-alkane}}$ -Record vom Bichlersee, Oberbayern

Maximilian Prochnow¹, Marcel Bliedtner¹, Paul Strobel¹, Michael Zech², Roland Zech¹

1: Physical Geography, Institute of Geography, Friedrich Schiller University Jena, Jena, Germany; 2: Heisenberg Chair of Physical Geography, Institute of Geography, Technische Universität Dresden, Dresden, Germany

15:33 – 15:36

Last millennium hydroclimate variability from Lake Höglwörth, Bavaria, Germany

Sudip Acharya¹, Marcel Bliedtner¹, Paul Strobel¹, Josefin Sperling¹, Thomas Kasper¹,

Michael Zech², Roland Zech¹

1: Physical Geography, Institute of Geography, Friedrich Schiller University, Jena, Germany; 2: Heisenberg Chair of Physical Geography, Institute of Geography, Technische Universität Dresden, Dresden, Germany

15:36 – 15:39

Ca isotope partitioning upon experimental precipitation of carbonated hydroxy-apatite (CHAP)

Nikolaus Gussone¹, Michael Ernst Böttcher², Anika C. Conrad², Iris Schmiedinger², Jens Fiebig³, Markus Peltz⁴, Georg Grathoff⁴, Burkhard C. Schmidt⁵

1: Institut für Mineralogie, Westfälische Wilhelms Universität Münster; 2: Leibniz Institute of Baltic Sea Research and University of Greifswald, Deutschland; 3: Institute of Geosciences, Goethe-University of Frankfurt, Germany, and Senckenberg Biodiversity and Climate Research Center, Frankfurt (Main), Germany; 4: Economic Geology, University of Greifswald, Germany; 5: Department of Experimental and Applied Mineralogy, Georg-August-University of Göttingen, Germany

15:39 – 15:42

Stable isotopic and trace elemental fingerprints in carbonate precipitated by modern hard-water creeks of the temperate climate zone

Michael Ernst Böttcher^{1,2}, Vera Winde^{1,3}, Jens Bünning¹, Olaf Dellwig¹, Katrin Müller¹, Ulrich Struck⁴, Maria-Theresia Schafmeister⁵, Peter Escher^{1,6}

1: Leibniz Institute of Baltic Sea Research, FRG; 2: Marine Geochem., University of Greifswald, FRG; 3: Present address: Hydroisotop, Schweitenkirchen, FRG; 4: Naturhistorisches Museum, Berlin, FRG; 5: Applied Geology, University of Greifswald, FRG; 6: Ecoandmore, Freiburg, FRG

15:42 – 15:45

Identification of paleosols of a Namibian sediment core (WW203303) using pedogenic features, trace fossils and stable isotope compositions

Feiyu Wang¹, Paul Koeniger², Matthias Hinderer¹

1: TU Darmstadt, Deutschland; 2: Federal Institute for Geosciences and Natural Resources, Geozentrum Hannover

15:45 – 16:00

Pause

16:00 – 17:30

Block 4.2: Ökosysteme

Chair: **Gerhard Gebauer**, Universität Bayreuth

16:00 – 16:30 *Session Keynote*

Carbon isotope ratio as a measure of photosynthetic water-use efficiency: reconciling a biophysical discrepancy

John Marshall, SLU, Swedish University of Agricultural Sciences

16:30 – 16:45

Impact of nutrient and water availability on grassland functioning – achieving a process based understanding across scales

Maren Dubbert¹, Angelika Kübert², Youri Rothfuss³, Christiane Werner²

1: Zalf, Deutschland; 2: Uni Freiburg, Deutschland; 3: FZ Jülich, Deutschland

16:45 – 17:00

Application of 2-dimensional stable isotope measurements of methane to constrain sources and sinks in a seasonally stratified freshwater lake

Teresa Einzmann¹, Moritz Schroll¹, Jan F. Kleint^{1,2}, Thomas Klintzsch^{1,3}, Frank Keppler^{1,4}, Markus Greule¹

1: Institute of Earth Sciences, Heidelberg University, Germany; 2: MARUM – Center for Marine Environmental Sciences and Department of Geosciences, University of Bremen, Germany; 3: Institute for Plant Nutrition, Justus Liebig University, Giessen, Germany; 4: Heidelberg Center for the Environment (HCE), Heidelberg University, Germany

17:00 – 17:15

Belowground C allocation of tropical rainforests in response to drought: an ecosystem ¹³CO₂ labeling approach

Lingling Shi¹, Pratiksha Acharya¹, Xujuan Bai¹, Niklas Schmuecker¹, Nemiah Ladd², Christiane Werner², Laura.K Meredith^{3,4}, Michaela Dippold¹

1: Biogeochemistry of Agroecosystems, Department of Crop Science, Faculty of Agriculture, Georg August University of Göttingen; 2: Ecosystem Physiology, University of Freiburg, Freiburg, Germany; 3: School of Natural Resources and the Environment, University of Arizona, Tucson, United States of America; 4: Biosphere 2, University of Arizona, Tucson, United States of America

17:30 – 18:30

ASI Mitgliederversammlung

17:30–19:00

Posterausstellung / Breakouträume

poster side-rooms **Ausstellung aller Themenblöcke**

Mittwoch | Wednesday, 29.09.2021

9:00 – 9:30 Posterfrühstück | Poster Breakfast

9:30 – 10:30 **Block 6: Physiologie, Metabolismus, Medizin, Doping, Forensik, Lebensmittel**

Chair: **Frank Keppler**, Universität Heidelberg

9:30 – 9:45

Stable isotopes for planetary health: Synthetic methionine

Cajetan Neubauer

University of Colorado Boulder, USA

9:45 – 10:00

Carbon isotope ratios of endogenous steroids found in human serum – method development, validation, and reference population-derived thresholds

Thomas Piper, Hans Geyer, Mario Thevis

Deutsche Sporthochschule Köln, Deutschland

10:00 – 10:15

Making plant methane formation visible – the effect of light exposure and light intensity on plant methane formation by application of ¹³C-labelled dimethyl sulfoxide

Moritz Schroll¹, Katharina Lenhart^{2,3}, Steffen Greiner³, Frank Keppler^{1,4}

1: Heidelberg University, Heidelberg, Germany; 2: Bingen University of Applied Sciences, Bingen, Germany; 3: Center for Organismal Studies, Heidelberg, Germany; 4: Heidelberg Center for the Environment, Heidelberg University, Germany

10:15 – 10:30

Geographical provenance determination of wood through combination of isotope ratios

Jana C. Köhne¹, Bernd Degen¹, Anette Goeske²

1: Thünen-Institut für Forstgenetik, Deutschland; 2: Thünen-Institut für Agrarklimaschutz, Deutschland

10:30 – 10:50 Poster Kurzvorträge (Short Communications) – zu Themenblock 4; 1; 5

10:30 – 10:33

Using in-situ and destructive measurements of stable water isotopes to quantify ecohydrological feedback processes of different forest stands

Judith Mach, Laura Kinzinger, Stefan Seeger, Fabian Fritz, Paula Hilgert, Markus Weiler, Maren Dubbert, Christiane Werner, Natalie Orlowski

Albert-Ludwigs-Universität Freiburg, Professur für Hydrologie, Deutschland

10:33 – 10:36

Antibiotics increase methane production rates in freshwater sediments: Evidence from an anaerobic incubation

Eric Bollinger^{1,2}, Jochen P Zubrod^{1,2}, Sabine Filker³, Andreas Lorke¹, Mirco Bundschuh^{1,2,4}

1: IES Landau, Institute for Environmental Sciences, University of Koblenz-Landau; 2: Eusserthal Ecosystem Research Station, University of Koblenz-Landau; 3: Department of Molecular Ecology, University of Technology Kaiserslautern; 4: Department of Aquatic Sciences and Assessment, Swedish University of Agricultural Sciences

10:36 – 10:39

Exploring fundamentals of quantitative ¹³CO₂/¹²CO₂ tracer studies of CO₂ exchange and biomass in plants: assessment of system performance and determination of isotopic end-members for mixing model

Jianjun Zhu, Juan C. Baca Cabrera, Regina T. Hirl, Hans Schnyder, Rudi Schüftele

Technical University of Munich, Deutschland

10:39 – 10:42

Unravelling the diet of extinct cave bears in Romania using $\delta^{15}\text{N}$ isotopic analysis of amino acids

Peter Tung^{1,2}, Herve Bocherens^{1,2}, Dorothee Drucker^{1,2}, Yuichi Naito^{1,3}

1: Senckenberg Gesellschaft für Naturforschung, Deutschland; 2: Universität Tübingen, Deutschland; 3: Nagoya University Museum, Japan

10:42 – 10:45

Development of an open-split-based dual-inlet system for mass spectrometers

Stephan Räss^{1,2}, Markus Leuenberger^{1,2}

1: Universität Bern, Schweiz; 2: Oeschger Centre for Climate Change Research

10:45 – 10:48

Tracing nitrogen transformations induced by ^{15}N labelled cattle slurry applied with different techniques in winter wheat

Caroline Buchen-Tschiskale, Heinz Flessa, Reinhard Well

Thünen-Institut für Agrarklimaschutz, Deutschland

10:48 – 10:50

Applying the ^{15}N gas flux method in a lab incubation as an alternative to laborious field studies

Björn Kemmann¹, Reinhard Well¹, Stefan Burkart¹, Thorsten Ruf², Christoph Emmerling²

1: Thünen Institut für Agrarklimaschutz, Deutschland; 2: Universität Trier, Raum- und Umweltwissenschaften, Bodenkunde, Deutschland

10:50 – 11:00 **Pause**

11:00 – 12:30 **Block 7: Deutsches Isotopennetz GIN**

Chairs: **Robert van Geldern**, Universität Erlangen-Nürnberg, **Nils Michelsen**, TU Darmstadt,

11:00 – 11:15

Die Tritiumverteilung in Niederschlag und Oberflächenwasser in Deutschland – ein Beitrag zum deutschen Isotopennetzwerk

Axel Schmidt, Michael Engel, Rike Völpel, Lars Duester

Bundesanstalt für Gewässerkunde, Deutschland

11:15 – 11:30

Tritium in der südlichen Nordsee: ein Tracer für lokal gebildeten Wasserdampf

Jürgen Sültenfuß

Universität Bremen, Deutschland

11:30 – 11:45

Distribution of young groundwater in the North German Basin

Annika Desens, Georg Houben

BGR, Deutschland

11:45 – 12:00

Stable isotope patterns of German rivers with aspects of scales and continuity

Paul Königer¹, Christine Stumpp^{2,3}, Axel Schmidt⁴

1: Groundwater Resources Quality and Dynamics, Federal Institute for Geosciences and Natural Resources (BGR), Hannover, Germany; 2: Institute for Soil Physics and Rural Water Management, University of Natural Resources and Life Sciences (BOKU), Vienna, Austria; 3: Institute of Groundwater Ecology, Helmholtz Zentrum München, Neuherberg (HMGU), Germany; 4: Environmental Radioactivity and Monitoring, Federal Institute of Hydrology (BfG), Koblenz, Germany

12:00 – 12:15

Very high resolution Automated Rain Water Sampler for stable water isotope monitoring

Christoff Andermann, Torsten Queißer, Markus Reich, Oliver Rach, Niels Hovius, Dirk Sachse

GFZ Potsdam, Deutschland

12:15 – 12:30

GIN and beyond: Cumulative rain collectors for isotope studies in challenging climates

Nils Michelsen¹, Zeneb Najmi¹, Paul Königer^{1,2}, Christoph Schüth¹

1: Institute of Applied Geosciences, Technical University of Darmstadt, Germany; 2: BGR Bundesanstalt für Geowissenschaften und Rohstoffe, Hannover, Germany

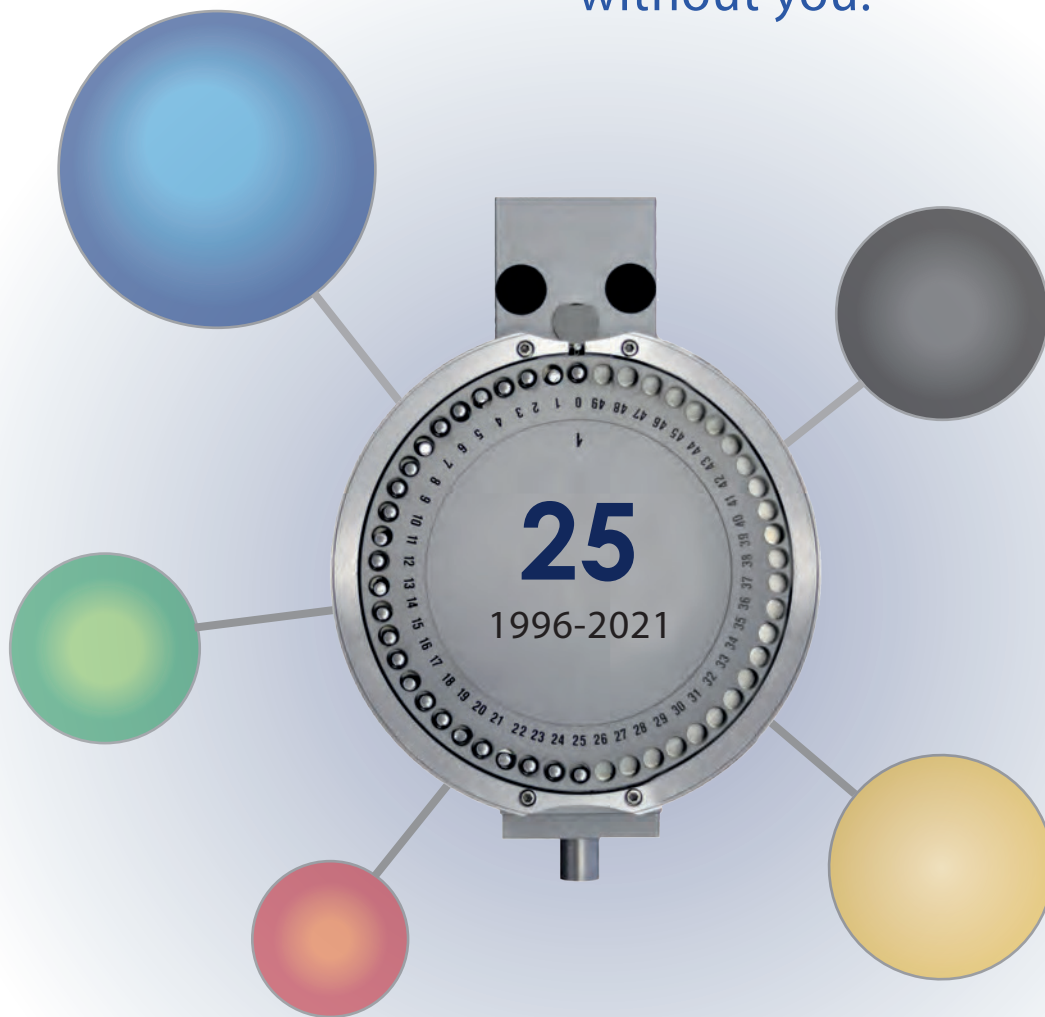
12:30 – 13:30

Poster/Vortragspreis: ASI-Preise und Abschluss

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1.1 Analytik, Methoden, Technik und Qualitätssicherung stabiler Isotope

Chairs: Matthias Gehre, UFZ, Paul Königer, BGR Bundesanstalt für Geowissenschaften und Rohstoffe, Deutschland

Compound Specific Stable Sulfur Isotope Analysis ($\delta^{34}\text{S}$ and $\delta^{33}\text{S}$) of Organic Compounds Using Gas Chromatography Hyphenated with Multiple Collector Inductively Coupled Plasma Mass Spectrometry (GC-MC-ICPMS)

Steffen Kümme¹, Faina Gelman², Axel Horst¹, Harald Strauß³, Richnow Hans H.¹, Matthias Gehre¹

¹Helmholtz-Zentrum für Umweltforschung GmbH – UFZ, Leipzig, Germany; ²Geological Survey of Israel, Jerusalem, Israel; ³Westfälische Wilhelms-Universität Münster, Institut für Geologie und Paläontologie, Münster, Germany

Stable sulfur isotope analysis is applicable in various fields in forensics and environmental analytics to investigate the sources and degradation of organic compounds, many of them being priority pollutants in groundwater and the atmosphere. A broader use of sulfur isotopes of organic compounds in environmental studies is still hampered by the availability of precise and easy-to-use techniques. Here we present a method for the determination of stable sulfur isotope ratios using gas chromatography coupled with multiple-collector inductively coupled plasma mass spectrometry (GC-MC-ICPMS) which can be used for both $\delta^{34}\text{S}$ and $\delta^{33}\text{S}$ analysis. The method was evaluated using the reference materials IAEA-S-1, IAEA-S-2 and IAEA-S-3 which were converted offline to SF₆ prior to analysis. Standardization was carried out by a two-point calibration approach. The $\delta^{34}\text{S}$ obtained by our method are in good agreement (within analytical uncertainty) with the results obtained by the conventional dual inlet method. Additionally, the impact of the used mass resolution (low and medium), the influence of auto-protonation of sulfur isotopes and the effect of isobaric interferences of O₂⁺ on the obtained isotopic ratios were investigated. Overall analytical uncertainty including normalization and reproducibility for $\delta^{34}\text{S}$ and $\delta^{33}\text{S}$ was usually better than ± 0.2 mUr (1 σ) for analytes containing at least 100 pmol of S. Thus, the presented compound-specific online method should be sufficiently precise to address a wide variety of research questions involving mass independent isotope effects of sulfur-containing organic compounds to discriminate sources or biological and chemical reactions in the environment.

New Frontiers in Compound-Specific $\delta^2\text{H}$ Analysis

S. K. Lengger^{1,2,3}, S. Kelly⁴, K. W. R. Taylor⁵, R. Berstan⁵, M. Seed⁵, I. D. Bull¹, J. Blewett¹, R. D. Pancost¹

¹University of Bristol, UK; ²University of Plymouth, UK;

³Silicon Austria Labs, Austria; ⁴International Atomic Energy Agency, Austria; ⁵Elementar UK Ltd, UK

The hydrogen isotopic composition ($\delta^2\text{H}$) of lipid “biomarker” compounds (molecules synthesized by and traceable to living organisms) have long been of interest to biogeochemists, with applications ranging from the investigation of food authenticity, to the reconstruction of ancient climate and environment. The preferred method of stable isotope analysis of such lipids employs gas chromatography-isotope ratio mass spectrometry (GC-IRMS), which effectively limits applications to those which measure compounds of relatively low molecular weight and polarity (i.e. compounds which elute from a typical capillary GC column at c. 320–350°C). As such, only very few compounds of molecular weight > c. 500 g/mol have been successfully analyzed intact by GC-IRMS to determine $\delta^2\text{H}$. However, the hydrogen isotopic composition of larger and/or polar compounds can be of significant interest.

Here we present two pioneering new techniques for the analysis of larger and/or more polar organic molecules of biogeochemical interest which are traditionally considered unsuitable for GC-IRMS analysis. This includes a rapid one-step derivatization procedure for the isotope analysis of the non-exchangeable hydrogen in mono and disaccharides and subsequent conversion to H₂ by chromium reduction (Abraham et al, 2020), and the development of a high-temperature GC-IRMS (HTGC-IRMS) methodology employed for the analysis of a suite of compounds of interest (Lengger et al., 2021). In particular we present the successful HTGC-IRMS analysis of triacylglycerides (TAGs), whose derivative fatty acids are often employed in studies of archaeological diet and modern food authenticity analysis, tetraether lipids including glycerol dialkyl glycerol tetraethers (GDGTs) which have been widely employed as proxies for paleoclimate and environmental analysis based on their relative distributions, and longer chain n-alkanes, the lower molecular weight homologues of which have been widely employed for paleohydrological analysis. We will present initial results demonstrating the performance and validation of the techniques, and their potential application to organic biogeochemistry.

References

Lengger S.K., Weber Y., Taylor K.W. R., Kopf S. H., Berstan R., Bull I.D., Mayser J., Leavitt W. D., Blewett J. & Pearson A. (2021). Determination of the $\delta^2\text{H}$ values of high molecular weight lipids by high temperature GC coupled to isotope ratio mass spectrometry. *Rapid Communications in Mass Spectrometry* **35**:e8983. <https://doi.org/10.1002/rcm.898310>

Abraham, A., Cannavan, A., & Kelly, S. (2020). Stable isotope analysis of non-exchangeable hydrogen in carbohydrates derivatised with N-methyl-bis-trifluoroacetamide by gas chromatography–Chromium silver reduction/High temperature Conversion-isotope ratio mass spectrometry (GC–CrAg/HTC–IRMS). *Food Chemistry* **318** (126413)

<https://doi.org/10.1016/j.foodchem.2020.126413>

A quick one-step sample preparation method with 2,2-Dimethoxypropane (DMP) for isotopic fingerprint analysis of vegetable oil – how does DMP influence the accuracy of the C- and H-CSIA by GC-C/Py-IRMS?

Lili Xia, Kaori Sakaguchi-Söder, Daniel Stanojkovski, Liselotte Schebek

Stoffstrommanagement und Ressourcenwirtschaft, Institut IWAR, TU Darmstadt, Deutschland

Compound-specific stable isotope analysis (CSIA) of fatty acids (FAs) is an important tool for the investigation of authentication of vegetable oil. Stable isotope ratios of carbon ($\delta^{13}\text{C}$) and hydrogen ($\delta^2\text{H}$) of individual FAs are to be determined from the $\delta^{13}\text{C}$ and $\delta^2\text{H}$ of fatty acid methyl ester (FAMES), which are produced by reactions of FAs in oil and methyl group ($-\text{CH}_3$) of methanol in the presence of catalysts. This transmethylation process generally involves multiple steps thus often becomes a bottleneck process of the investigation with a large number of samples.

Garcés and Mancha (1993) developed a quick sample preparation method to generate FAMES directly from seeds in one step in a single reactor. They optimized transmethylation efficiency by adding 2,2-Dimethoxypropane (DMP). The applicability of this one-step method was verified to determine the lipid content and the FA profile of different oilseeds. However, the verification of this method in determining the isotope composition of individual FAs has not yet been reported.

In this study, we evaluated the feasibility of the one-step method for C- and H-CSIA of individual FAMES in rapeseed samples with the following two concerns:

(1) the influence of the aggregate states of samples on the reproducibility of C- and H-CSIA, (2) the influence of DMP on the accuracy of $\delta^{13}\text{C}$ and $\delta^2\text{H}$ values of FAMES, consequently FAs, by Gas Chromatography-Combustion / Pyrolysis-Isotope Ratio Mass Spectrometry (GC-C/Py-IRMS). DMP in the one-step method will contribute to producing extra methanol as a reaction-intermediate, which can be consumed to generate FAMES. We investigated the isotope composition of FAMES produced with and without DMP and evaluated the extent of the involvement of the reaction intermediate methanol in the production of FAMES in the one-step method.

Our results showed that the reproducibility of the one-step method in C- and H-CSIA for the solid rapeseeds and fluid oil was comparable. Further, we confirmed that no significant differences arose in the carbon and hydrogen isotope compositions of the selected main FAMES produced with and without DMP, except for the H-CSIA value of C18:3. The reproducibility of the one-step method for rapeseed was in the range of ± 0.1 mUr to ± 0.3 mUr for C-CSIA and ± 1 mUr to ± 3 mUr for H-CSIA of the main FAMES. The performance of the one-step method for rapeseed samples for the determination of $\delta^{13}\text{C}$ and $\delta^2\text{H}$ values of FAMES is satisfying.

Revisiting SPIN-MIRMS: N-isotopic composition of nitrate and ammonium from aqueous solutions by isotope ratio mass spectrometry

Jens Dyckmans¹, Wolfram Eschenbach¹, Reinhard Langel¹, Lars Schwec¹, Reinhard Well²

¹Universität Göttingen, Kompetenzzentrum Stabile Isotope, Deutschland; ²Thuenen Institut für Agrarrelevante Klimaforschung, Braunschweig, Deutschland

Analyses of N-isotopic composition of nitrate and ammonium from aqueous solutions are difficult – especially at natural abundance. The SPIN-MIRMS technique presented previously has the key advantage that no sample pretreatment is necessary and analysis is fast.

Here we present recent insights into the performance and substrate specificity of the approach.

$\delta^{13}\text{C}$ Analysis of DOC from Liquid Samples – Proof of Concept

Isabell von Rein, Heike Geilmann, Heiko Moossen
Max-Planck-Institut für Biogeochemie, Deutschland

Both, dissolved organic carbon (DOC) and its corresponding $\delta^{13}\text{C}$ signature are important parameters for the investigation of the carbon cycle. For example, DOC concentration analyses reveal the organic matter flow in aquatic systems, while $\delta^{13}\text{C}$ values of DOC can give insights on origin and transformation of organic matter. The combined analysis of DOC and $\delta^{13}\text{C}$ can require either time-consuming and laborious sample preparation or a wet chemical oxidation method which can underestimate DOC concentrations and lead to isotopic fractionation.

Here we investigate the feasibility of using an elemental analyzer – isotope ratio mass spectrometer (EA-IRMS) system. By attaching a liquid autosampler to the EA and

installing a Nafion water trap between the reactor and the GC-column we analyze DOC concentrations and $\delta^{13}\text{C}$ values of liquids analogous to the way solid samples are measured. With this minor adjustment to the instrument configuration, $\delta^{13}\text{C}$ measurements with a precision of $< 0.1 \text{ ‰}$ can be made on DOC samples with a concentration of 10 mg/ml.

Preliminary tests were designed to test different parameters including linearity, memory effect, and stability. We also investigated whether dissolved carbonates yield a similar measurement precision as dissolved organic compounds, and whether a mix of DOC and DIC affect the overall fidelity of the measurements. For the analytical tests and data evaluation several in-house and international standards including urea, caffeine (IAEA-600), glutamic acid (USGS-40 and 41), carbonates (as inorganic standard) and sugars were dissolved in ultra-pure water. In the future, the method will be optimized for natural samples with smaller DOC concentrations by changing the injection amount or implementing a concentrating step. The preliminary results show that our method is easy to apply in laboratories for quick routine $\delta^{13}\text{C}$ characterization of high concentration samples.

1.2: Analytik, Methoden, Technik und Qualitätssicherung stabiler Isotope

Chairs: Matthias Gehre, UFZ, Paul Königer, BGR Bundesanstalt für Geowissenschaften und Rohstoffe, Deutschland

Comprehensive Isotope Ratio MS of Oxyanions with an Electrospray-Orbitrap

Andreas Hilkert¹, Cajetan Neubauer²

¹Thermo Fisher Scientific, Deutschland; ²University of Colorado, Boulder, USA

A new, comprehensive approach for IRMS using an electrospray ionization (ESI) Orbitrap gives access to multi-dimensional isotope signatures of intact polar compounds in liquid samples.

Customized sample introduction and automation, applying IRMS specific rules, were developed by using nitrate as a model compound. In total, 7 isotopologs of nitrate can be quantified simultaneously opening multiple pathways for calculating $\delta^{15}\text{N}$, $\delta^{18}\text{O}$, $\delta^{17}\text{O}$ and $\Delta^{17}\text{O}$ values with sub- ‰ precision and accuracy. It also offers a unique way to measure nonrandom isotopic distributions ("clumping") in oxyanions.

The approach can be applied to other oxyanions like nitrite and sulfate. First results will also be shown.

This study bridges the gap between bioanalytical MS and IRMS providing methods to measure new isotopic signatures in intact organic and inorganic compounds.

The next leap forward in gas IRMS

*Mario Tuthorn, Jenny Roberts, Oliver Kracht, Dieter Juchelka, Andreas Hilkert
Thermo Fisher Scientific, Deutschland*

Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution (ISDS) Software is carefully optimized to revolutionize your gas IRMS analyses, delivering simplicity, efficiency and quality in your laboratory. Built to cater to the most diverse applications, Qtegra ISDS Software provides you with the level of control that you require, within a logical, easy-to-use framework, enabling you to dramatically improve your productivity. Join us for a software tour.

To compliment the arrival of Qtegra ISDS Software, we are launching the next generation of Thermo Scientific™ DELTA Series IRMS – the Thermo Scientific™ DELTA Q™ IRMS. DELTA Q IRMS is the world's first net zero mass spectrometer launched as a part of the IsoFootprint project, a new initiative by the Inorganic Mass Spectrometry team with the aim to set the pathway towards true net zero. All the CO_2 emitted to the atmosphere during the manufacture of the instrument (from extraction of the raw materials to transport and assembly) will be removed from the atmosphere through investment in carbon dioxide removal projects. Projects were selected with priority given to those that were permanent, additional, globally sustainable and supporting nascent technology that has the ability to scale.

Join us to learn more about sustainable isotope analysis driven by Qtegra ISDS Software. The journey has begun.

Improved throughput for $\delta^{18}\text{O}$ and δD measurements of water with Cavity Ring-Down Spectroscopy

*Magdalena Hofmann¹, Jan Woźniak¹, Zhiwei Lin², Keren Drori²
¹Picarro B.V., Niederlande; ²Picarro Inc., USA*

Oxygen ($^{18}\text{O}/^{16}\text{O}$) and deuterium (D/H) isotopes are a widespread tool to trace physical and chemical processes in hydrology and biogeosciences. Precision and throughput are key parameters for water isotope analysis. Here, we will present two new methodologies for the Picarro L2130-i Cavity Ring-Down Spectroscopy (CRDS) water isotope analyzer that allow the user to increase the throughput without compromising data quality.

The Picarro Express Method now distinguishes between a memory reduction stage and a sample analysis stage and allows the user to measure up to 50 samples per day while maintaining the excellent precision of CRDS (i.e., 0.01 ‰ for

$\delta^{18}\text{O}$ and 0.05‰ for δD). This corresponds to doubling the throughput compared to the standard Picarro methodology. The Picarro Survey Method makes use of ultrafast injections and sorts the samples by their measured isotopic values, enabling a powerful new strategy to reduce memory effects. We present these different measurement strategies that increase the throughput for routine water isotope analysis. The improved methodologies use software based modifications of the injection procedure, and do not require any hardware changes.

A new infiltration optimized tracer application method for ^{15}N and ^{18}O tracers in field soil experiments

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Nitrous Oxide is a long-lived greenhouse gas with the third most important contribution to radiative forcing the dominant anthropogenic ozone-depleting substance emitted. There are many important pathways from agricultural soils for N_2O production besides nitrification and denitrification that are challenging to distinguish. Isotopic tracer methods are applied to aid differentiating between microbial and chemical sources. Commonly used application schemes apply $^{15}\text{N}\text{-NH}_4\text{NO}_3$ (triple labeling method) or additionally $^{18}\text{O}\text{-H}_2\text{O}$ and $^{18}\text{O}\text{-NO}_3$ (dual isotope method). Both methods assume a homogenous distribution of the tracers within the examined soil volume. Field experiments can further improve our understanding as they incorporate undisturbed soils with intact soil aggregates and plant effects. Preferential flow represents the biggest obstacle for a homogeneous, fast and large area application of tracer. This effects application methods used for field experiments like by watering can or with sprinklers as they promote ponding. Better infiltration patterns visualized by blue dye solution were achieved by slowing down application speed and promoting infiltration by capillary forces. For a ^{15}N comparative study in grassland, drip irrigation was chosen as it is scalable and a noninvasive method. Application by drip irrigation resulted in a smaller standard deviation of the ^{15}N concentrations and a larger recovery rate compared to application by sprinkler. After successful pretest, application by drip irrigation was implemented for the central experiment in Gießen of the DASIM project (Denitrification in Agricultural Soils: Integrated control and Modelling at various scales) for an area of 13 m² grassland. For this purpose, 3200 cost effective dropper bottles were made and placed onto

acrylic sheets closely above ground to set the pattern and spacing of infiltration points. Each dropper bottle provides a reservoir for each infiltration point, resulting in an even distribution of the tracer solution over the soil surface. A reliable dripping speed (100 ml \pm 55 min \pm 5 min) is assured by individual cannulas (0.8 mm x 120 mm) at the tip of each dropper bottle. Dripping can be started fast by removing a rubber stopper at the bottom of the bottle. The areas were split into two sets for application with each finishing within 2 hours with an acceptable failure rate. Tracer application by dropper bottles therefore represents a new, noninvasive and infiltration optimized application method for large field experiments. To solve problems arising from different tracer retention i.e. nitrate (NO_3^-) and ammonium (NH_4^+) invasive methods would be needed.

2.1: Hydrogeologie, Hydrologie und Wasserisotope

Chairs: Florian Einsiedl, TUM, Diana Burghardt, TU Dresden, Christoph Schüth, TU Darmstadt

KEYNOTE

Oxygen is all around...

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Oxygen is the most abundant element within the earth system. At the earth's surface and in its molecular form as O_2 it is also one of the most important RedOx agents in both gaseous and dissolved forms. For such reactions, tracing of oxygen can identify fundamental processes including photosynthesis, respiration and exchange between the atmosphere and water. Moreover, as part of the water molecule oxygen can serve as a tracer of origin, mixing and movement of H_2O . However, water can also release O_2 via its splitting by for instance photosynthesis. Such processes also offer relationships to carbon cycling on various scales. While tracing of water with oxygen stable isotope ratios finds applications in a wide spectrum of fields including hydro(geo)logy, plant sciences and medicine, isotope tracing of gaseous and dissolved O_2 is much less common. Future challenges and opportunities lie in combinations of water and molecular oxygen cycles via their stable isotope ratios to outline and constrain sources and sinks of this important element.

Impact of the 2018–2020 drought in Central Germany on the nitrogen cycling in a meso-scale catchment: Insights from hydrochemical and stable isotope investigations

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Recent investigations of the nitrate pollution in ground-water and surface water bodies in Germany confirm the well-known fact that the threshold value for nitrate concentrations (50 mg L^{-1}) is exceeded in 18 % of all sampling sites belonging to the nitrate monitoring network (German Federal Environmental Agency). Besides the input of excess nitrogen into the aquatic system by human activities, climate change related hydrological variability (extreme precipitation events or longer summer droughts) may also have an effect on nitrate loads in ground- and surface water.

Especially in the last years (2018–2020), a severe drought was observed in central Germany. In order to find out the potential impact of that drought on the catchment scale nitrogen cycling, we investigated the ground- and surface water compartments of the Holtemme watershed, a meso-scale river catchment in the Harz Mountains, Central Germany. The analysis of nitrate concentrations and corresponding isotopic signatures for groundwater and surface water samples were conducted during the entire dry period and were continued until discharge conditions went back to the long term mean in early 2021. The survey revealed decreasing nitrate concentrations for both compartments during drought conditions and a significant increase in the post-drought phase. Isotopic investigations allowed us to differentiate between distinct nitrate sources and microbial turnover processes. The time series analysis of $\delta^{15}\text{N-NO}_3$ showed regular oscillations within the year, which illustrates a periodic fertilizer application. Corresponding $\delta^{18}\text{O-NO}_3$ signatures show higher, seasonal-independent variations that can be explained by the normal isotopic variability of the ambient water that provides two thirds of the oxygen that is incorporated into the nitrate molecule during nitrification. However, flow paths for nitrate mobilization into the surface water seem to be unaffected by the drought because contributions of each nitrate source decreased equally during dry conditions. Nitrate concentrations increased after the dry period independently of recent nitrate supply. This implies that the soil system acts as a storage compartment, from which nitrate is easily released after the drought.

Our study confirms that hydrological variability is a highly important driver for nitrate mobilization at the catchment scale. Therefore, we suggest that the impact of changing hydrological conditions needs to be taken into consideration for management practices and policy actions.

Spatiotemporal analysis of Central European young water fractions

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The travel time of precipitation entering a catchment and leaving it as streamflow varies according to the flow paths precipitation takes. Fast precipitation travel times through catchments are especially interesting as they pose a high risk to river water quality. However, investigating influences on travel times is challenging due to complex water flow through heterogeneous landscapes. In this study, we investigated the fraction of streamflow younger than three months (Fyw) of nine major catchments in Central Europe and compared it to catchment characteristics and a teleconnection pattern that influences European large-scale weather: the North Atlantic Oscillation index (NAO). Adjacent catchments had similar long-term average and time-variable Fyw. These patterns were explained using catchment characteristics in a multiple regression analysis with prior collinearity removal, with grassland and 20–40 % tree cover density explaining 84 % of Fyw variability. Besides this spatial analysis, the annual changes in Fyw resembled each other in most catchments, leading to the hypothesis that a common, annually changing influence controls it. While total water storage in the catchments had no relationship to the time-variable Fyw, the NAO of the previous year was negatively correlated with this year's Fyw ($R^2 = 0.68$). Three hypotheses are discussed as to how this inter-annual correlation could have happened, but no distinct explanation could be found. We recommend additional studies into this relationship as well as multiple regression with prior collinearity removal for future studies of the complex interplay of spatiotemporal variables on Fyw.

Stable water isotope analysis and improved lumped-parameter modeling for characterizing unsaturated subsurface flow

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The characterization of water flow in the unsaturated zone is an important task, e.g., for evaluating water resources and stresses imposed by climate change and for protecting groundwater resources. In a 3-year field study, we have measured stable water isotopes ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) in precipitation and the outflow of two vegetated lysimeters situated in Wielenbach, Germany. The lysimeters contained soil cores of different textures, i.e. sandy gravel (Ly1) and clayey sandy silt (Ly2). Maize has been cultivated on top of the lysimeters,

and four different herbicides have been applied to the maize plantation.

Lumped-parameter modeling was applied for interpreting stable water isotope observations in lysimeter outflow and for determining the mean transit time of water in the subsurface and the dispersion coefficient. Usually, lumped-parameter model (LPM) approaches consider steady-state flow, which is due to their model structure that implements analytical solutions (with constant coefficients) for simulating stable water isotope transport. In this work, we have extended this approach by subdividing the simulation time into hydrologically relevant sub-periods. Flow and transport parameters vary between these sub-periods, so that temporally varying flow is mimicked (keeping constant coefficients in each sub-period). Furthermore, preferential flow paths were considered and implemented in the model. For validation, numerical modeling of unsaturated flow and stable water isotope transport was carried out using HYDRUS-1D.

Application of the extended LPM approach could significantly improve the simulation of stable water isotopes observed in lysimeter outflow, by considering seasonal changes of flow and transport parameters. In general, LPM results corresponded well to numerical modeling results. Observations were more difficult to describe for Ly2, where the seasonal fluctuation of stable water isotopes seems not fully met by numerical modeling. The consideration of a constant $\delta^{18}\text{O}$ upshift could improve simulations, i.e. representing, in a simplified assumption, the influence of immobile (isotopically enriched) water as an additional component that contributes to the isotopic signature of lysimeter outflow water. Both the LPM and numerical approach are hence considered to be well suited for decision support. As an advantage of the LPM approach, less input data and fitting parameters (with associated uncertainties) are required, making it a powerful tool for groundwater management methodologies.

Identifizierung von Oberflächenwasser-Grundwasser-Interaktionen anhand von charakteristischen Isotopensignalen

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Die Verwendung stabiler Wasserisotope kann entscheidend zum Prozessverständnis von Oberflächenwasser-Grundwasser-Interaktionen an Flüssen beitragen. Flusswasser weist im Gegensatz zu Grundwasser eine höhere Variabilität in der Isotopenzusammensetzung auf, die durch Abflus-

sereignisse wie Schneeschmelze oder Hochwasser nach Starkregenereignissen gesteuert wird. Die kontrastierende Isotopenzusammensetzung von Flusswasser und Grundwasser kann verwendet werden, um ein Mischungsmodell aus den Eingangsgrößen Flusswasser und Grundwasser vor sowie während des Ereignisses aufzustellen. Hierzu liefert der folgende Beitrag zwei Beispiele mit sehr unterschiedlich großen Einzugsgebieten aus der wissenschaftlichen Praxis.

An der Ahr, einem 53 km langen Gebirgsfluss mit einem Einzugsgebiet von 629 km² (in Südtirol, Italien) wurden monatliche Wasserproben von Flusswasser und Grundwasser von 2016 bis 2018 genommen und auf stabile Wasserisotope ($\delta^{18}\text{O}$ und $\delta^2\text{H}$) analysiert. Die durch Schneeschmelzereignisse ausgelöste, isotopisch leichtere Flusswassersignatur (z.B. $\delta^2\text{H}$: -88,2 bis -101 ‰) konnte als ein charakteristisches Isotopensignal verwendet werden, um ein Mischungsmodell von Flusswasser und Grundwasser aufzustellen. Die Analyse zeigt, dass das Ereigniswasser ca. 41 Tage \pm 10 bis zum Brunnen benötigt. Dies entspricht einer Fließgeschwindigkeit von ungefähr 0,2 bis 0,3 m d⁻¹. Der maximale Anteil an Flusswasser im Grundwasser konnte auf ca. 4 % \pm 1, 15 % \pm 2, 19 % \pm 4 and 51 % \pm 4 für die Ereignisse im Juni 2016, Mai 2017 sowie Mai und Juli 2018 geschätzt werden.

Im deutschen Teil der Mosel, einem 232 km langen Abschnitt des zweitlängsten Nebenflusses des Rheins, werden am Schleusenstandort Lehmen seit Sommer 2020 monatliche Wasserproben von der Mosel im Ober- und Unterpegel der Stauhaltung sowie Grundwasser von 4 Grundwassermessstellen genommen. Die Analyse auf stabile Wasserisotope zeigt, dass hier das Oberflächenwasser isotopisch etwas leichter ist ($\delta^2\text{H}$: -62,3 ‰) als das Grundwasser ($\delta^2\text{H}$: -51,3 ‰). Erste Ergebnisse deuten einen monatlichen Versatz der Flusswasser-Isotopensignatur im Grundwasser an. Eine Schleusenwartung im September 2020 führte zu einer Absenkung des Flusswasserspiegels um 1,5 m und damit zu einem veränderten hydraulischen Gradienten zwischen Fluss- und Grundwasser. Es konnten während dieser Zeit nur geringfügige Veränderungen in der Isotopenzusammensetzung des Grundwassers nachgewiesen werden.

Beide Beispiele bestätigen den Nutzen stabiler Wasserisotope bei grundlagenorientierten, wie auch angewandten hydrologischen Fragestellungen, um komplexe Vorgänge bei der Oberflächenwasser-Grundwasser-Interaktion zu verstehen.

**Poster-Kurzvorträge (Poster Short Communications) –
2: Hydrogeologie, Hydrologie und Wasserisotope**

*Chairs: Florian Einsiedl, TUM, & Diana Burghardt, TU Dresden,
Christoph Schüth, TU Darmstadt*

**Stable water isotopes as natural tracers in a
hydrogeological study of riverbank
filtration in N'Djamena, Chad**

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To assess the potential of riverbank filtration along the Chari River in the Lake Chad basin, a hydrogeological test site at a large water supply well located in close proximity to the river was established in N'Djamena, Chad. At the site, the aquifer is composed of Quaternary sediments with a total thickness of about 50–55 m and consist of alternating layers of sand and clay or silt. There are two high permeable layers at depths between ~ 23–27 m and ~ 45–50 m separated by a fine sand/silt layer. To date, the site consists of five deep and five shallow observation wells located around the supply well, and a shallow and a deep observation well on the opposite riverbank in Cameroon. Since 2019, samples from the Chari River, the supply well, and the observations wells on the Chadian side were collected every two weeks for hydrochemistry and water stable isotopes – with some interruptions – whereas groundwater levels were recorded with automatic data loggers.

The water level data shows that aquifer discharge conditions prevail throughout the year and that the hydraulic head in the shallow aquifer is always higher than in the deeper one. The largely fluctuating stable isotope compositions from the river can be traced in the shallow aquifer, which allow for an estimation of groundwater flow velocities (~ 0.9 m/d), while the isotopic compositions in the deep observations wells remain constant throughout the year. The isotopic composition of the water supply well lies between that of the shallow and the deep observation wells without any seasonal variations. It is still unclear whether different flow paths and travel times towards the well in the shallow aquifer dampen the isotopic signal, or if a significant groundwater flow component in the fine sand/silt separating the medium sand layers contributes to the water budget of the supply well.

**Isotopen-hydrobiogeochemische
Untersuchungen an anoxischen Grundwässern
off- und on-shore der norddeutschen Küste**

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Die Leybucht liegt im Einzugsgebiet der Osterems und wird durch die vorgelagerten ostfriesischen Inseln vor der offenen Nordsee geschützt. Seit dem Mittelalter steht die Leybucht unter dem Einfluss von Verlandungserscheinungen (NLÖ, 2001). Im Jahre 2017 wurde im Küstenvorfeld in größtenteils fein- und mittelsandigen Sedimenten eine Bohrung (R144) abgeteuft, die für die Grundwasserbeobachtung in 57 bis 61 m unter Geländekante verfiltert wurde. In der vorliegenden Studie wurden das Grundwasser dieser Bohrung sowie zwei on-shore Grundwässer (Leybuchtziel 1 und 2) in den Jahre 2019 und 2020 beprobt und hydrochemisch auf Haupt- und Spurenelemente analysiert. Diese Messungen wurden ergänzt um die Vermessung der stabilen Wasserisotope (²H, ¹⁸O), der C-Isotopenzusammensetzung des DIC sowie der S- und O-Isotopenzusammensetzung des gelösten SO₄. Die Daten wurden darüber hinaus einer physikochemischen Analyse mit PHREEQ-C unterzogen.

Die Untersuchungsergebnisse zeigen, dass alle Wässer anoxisch sind und sich durch hohe gelöste Eisengehalte auszeichnen. Die drei Grundwässer unterscheiden sich hinsichtlich ihrer Wasserisotopen-Signatur, liegen aber auf der für Cuxhaven etablierten lokalen meteorischen Wasserlinie und ähneln Süßwasser-beeinflussten Porenwässern, die in tiefen Sanden im Rückseitenwatt der Insel Spiekeroog gefunden wurden (Böttcher et al., 2014). Die Bohrungen R144 und Leybuchtziel 1 verzeichnen den Einfluss von Nordseewasser. Die Isotopenzusammensetzung des DIC und Sulfats verweist auf die Mineralisierung von gelöstem organischen Kohlenstoff hin unter Verwendung der Elektronenakzeptoren z.B. Sauerstoff, Nitrat und Sulfat, z.T. hat bereits Methanogenese stattgefunden. Die gelösten Eisengehalte können der dissimilatorisch-mikrobiellen Reduktion von Eisenoxiden und/oder der mikrobiell-katalysierten Zersetzung von Eisensulfiden stammen (z.B. Zhang et al., 2012). Ein Austritt dieser Wässer in der Nordsee hätte eine Erhöhung des Entgasungspotenzials für CO₂ zur Folge.

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Measuring high-resolution geochemical depth-profiles in hyporheic stream sediments with focus on aerobic and anaerobic methane oxidation

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A large part of carbon and nutrient cycling in rivers and streams takes place in the hyporheic zone, a hotspot of biogeochemical activity in the river bed where surface- and groundwater meet. Typically, redox zones with different dominant electron acceptors form sequentially, sorted by the energy yield of the respective redox reactions. This zonation is subject to the influence of multiple parameters such as sediment composition, river temperature, surface- and groundwater interaction, water and sediment chemical composition and others. In anaerobic sediments, methane production takes place as last step in this so-called redox ladder making many rivers net carbon emitters. Understanding sources and sinks of methane, the second most important greenhouse gas in the world, is crucial in times of climate change, but due to high spatial and temporal heterogeneity of redox processes in hyporheic sediments the relationship between methanogenesis and microbial methane oxidation is not yet fully understood.

To help filling this knowledge gap, our research group is measuring high-resolution depth-depending geochemical profiles at different locations across a stream bed. A sediment peeper is used to obtain pore water samples with a 1 cm depth-resolution. Concentration gradients of dissolved oxygen, nitrate, nitrite, sulfate, ammonia and methane show depth and width of the different redox zones. To explain the dominant methane production pathway and to interpret concentration gradients, stable carbon isotopes in methane ($\delta^{13}\text{C}-\text{CH}_4$) are measured. The $\delta^{13}\text{C}-\text{CH}_4$ in the methanogenic zone can be used to distinguish between acetoclastic and hydrogenotrophic methanogenesis. An isotopic enrichment in $\delta^{13}\text{C}$ values of methane towards the sediment surface may indicate microbial degradation while measurements of dissolved oxygen can be used to separate aerobic from anaerobic methane oxidation. In the absence of oxygen,

other electron acceptors may become relevant for microbial methane oxidation, for example nitrate, nitrite or sulfate. In addition, the performance of a simple 1D diffusion model will be compared with the results of a 1D diffusion-reaction model in their ability to capture the measured methane concentration gradients. This will be used as a supporting evidence of the findings from concentration and isotope measurements.

In a poster, we want to present geochemical profiles in combination with modeled concentration gradients and carbon stable isotope measurements in methane for different locations across the stream. The different sampling sites are compared in terms of sediment composition and location in the stream bed.

Karstic springs as strong emitters of CO_2

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Inland aquatic systems play an important role in the global carbon cycle. They not only transport terrestrial carbon to the oceans but also emit carbon in the form of carbon dioxide to the atmosphere. Among inland water types rivers are significant sources of CO_2 to the atmosphere, and karstic watersheds are particularly important in this respect due to their large availability of inorganic carbon.

In this context, few studies have quantified CO_2 fluxes from temperate source springs and headwaters in karstic basins yet. Our study addressed this information gap by investigating CO_2 outgassing from streams and groundwater-fed springs in a karstic terrain in central Germany, known as the Franconian Alb. We used DIC concentration and stable isotope ($\delta^{13}\text{C}_{\text{DIC}}$) data to separate biological and geological factors that might be responsible for temporal and spatial variations and gradients in CO_2 losses. This study examined characteristics of dissolved inorganic carbon (DIC) and excess partial pressures of CO_2 (epCO_2) in the source springs and headwaters of four watersheds in a Central European karstic region, via dissolved inorganic carbon concentration and stable carbon isotope measurements.

Our results showed the most ^{13}C -depleted $\delta^{13}\text{C}_{\text{DIC}}$ values at the source springs, which become rapidly enriched downstream due to CO_2 degassing. Concurrently, epCO_2 values, while consistently in excess of atmospheric concentrations at the spring sources, show decreases of up to 92 % within only 50 m downstream. In conjunction with the large observed flux estimates of up to $88 \text{ g C m}^{-2} \text{ day}^{-1}$, these findings suggest that karstic springs can act as focussed major CO_2 sources to the atmosphere. Because headwater

streams constitute the bulk of the surface area of most watersheds, they may provide a disproportionately large contribution to CO₂ effluxes in carbonate-dominated basins, in which source springs play a particularly important role.

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2.2: Hydrogeologie, Hydrologie und Wasserisotope

Chairs: Florian Einsiedl, TUM, Diana Burghardt, TU Dresden, Christoph Schüth, TU Darmstadt

Neue Einblicke in die Infiltrationsbedingungen des Oberjura-Thermalwassers in der südlichen Bayerischen Molasse mit Hilfe der ¹⁴C_{DOC}-Methode

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Der Oberjura-Thermalwasser-Aquifer im Süddeutschen Molassebecken ist der Hauptexplorationshorizont für die geothermische Energiegewinnung in Bayern. Der karbonatische Oberjura-Aquifer zeigt sowohl klein- als auch großräumig starke Heterogenitäten hinsichtlich seines strukturellen Aufbaus auf. So sind im Oberjura-Aquifer Karsterscheinungen und tiefreichende Störungssysteme zu finden. Die neuesten Literaturarbeiten unterscheiden, anhand von statistischen Clusteranalysen, zwischen drei unterschiedliche Wassertypen hinsichtlich der hydrochemischen und isotopengeochemischen Beschaffenheit im zentralen Teil des Süddeutschen Molassebeckens in Bayern und lassen ein alpennahes Infiltrationsgebiet im Süden des Süddeutschen Molassebeckens vermuten.

Anhand hydrochemischer und isotopengeochemischer Parameter untersuchen wir die Infiltrationsbedingungen des Oberjura-Thermalwassers und grenzen den zeitlichen Rahmen der Infiltration mithilfe Piston Flow-Grundwasseralter ein.

Prinzipiell ist das Oberjura-Thermalwasser in diesem Gebiet vom Na-HCO₃-Cl Grundwassertyp, zeigt aber an den südlichen Standorten Ca²⁺ und Mg²⁺ Gehalte unter den zu erwartenden Gehalten. Die Werte der stabilen Wasserisotope liegen zwischen -10,6 und -11,7 ‰ für δ¹⁸O und -85,0 bis -86,0 ‰ für δ²H und deuten auf eine Infiltration insbesondere während kaltzeitlicher Bedingungen hin.

Die Kombination aus den Ergebnissen der Hydrochemie, stabilen Wasserisotopen und den Piston Flow-Grundwasseralter aus den ¹⁴C_{DOC} und ¹⁴C_{DIC} Altersbestimmungen in Verbindungen mit ⁸¹Kr-Altern aus der Literatur bestätigen die Ergebnisse der stabilen Wasserisotope und geben nun Hinweise darauf, dass sich das Thermalwasser des Oberjura im Süden aus mindestens zwei Grundwasserkomponenten zusammensetzt. Auf Grund der ermittelten Piston Flow-Alter der untersuchten Grundwässer ist eine Infiltration nur über „Bypass“-Strukturen, die in der überlagernden Molasse zu finden sind, zu erklären.

Supporting the interpretation of δ¹⁵N values of dissolved NH₄⁺ and NO₃⁻ in the water column of a seasonal stratified lake using Numerical modeling and PCR gene amplification

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Occurring simultaneously with denitrification in anaerobic environments, other pathways like anaerobic oxidation of ammonium (anammox) and dissimilatory nitrate reduction to ammonium (DNRA) may play an important role for the removal of fixed nitrogen (N) to gaseous N₂ from freshwater ecosystems. Recent studies that were conducted in freshwater ecosystems showed that the relevance of anammox, denitrification and DNRA, significantly changes depending on site conditions, and thus significance of anammox in freshwater is still largely unknown.

Here we investigate the pathways and relevance of nitrogen losses at the seasonal stratified lake Fohnsee during the development of the vertical redox stratification. Our approach combines concentration profiles and corresponding stable isotope compositions of NO₃⁻ and NH₄⁺, with qPCR of the hydrazine synthase gene (*hzsB*), nitrite reductase (*nirK* and *nirS*) genes, and numerical modeling of δ¹⁵N-NH₄⁺ values during the stratification period.

Increasing stable isotope values of nitrate (δ¹⁵N and δ¹⁸O) together with the identification of two specific marker genes for denitrification (*nirK* and *nirS*) indicate that denitrification is occurring in the anoxic water column of Fohnsee. However, stable isotope values of δ¹⁵N of ammonium and water chemistry results were ambiguous about the occurrence of anaerobic ammonium oxidation within the water column. Modeling results and qPCR analysis using *hzsB*

marker gene for anammox showed that the observed stable isotope shift in $\delta^{15}\text{N}$ of ammonium may be the result of mixing processes between ammonium remaining from nitrification in the oxic water column with strongly enriched $\delta^{15}\text{N}$ values of 25 ‰, and ammonium that is formed by degradation of organic carbon during methanogenesis in the lake sediments with $\delta^{15}\text{N}$ values of around 11 ‰.

We concluded that in a highly dynamic ecosystem such as seasonal stratified lakes, anammox bacteria only overcome limiting conditions occasionally, and may be active at most at low rates and on a temporal scale, thus, denitrification is suggested to be the principal path of nitrogen loss at the seasonal stratified lake Fohnsee. Finally, this study highlights the importance of solid understanding of the various transformations and isotope effects within a natural ecosystem for the successful interpretation of isotopic data.

Investigation of chloroform degradation mechanisms using multi-dimensional isotope fractionation analysis: Hydrodechlorination over Pd and Rh vs reductive dechlorination with Fe^0

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Multi-dimensional isotope fractionation analysis is a useful tool to investigate degradation mechanisms of organic substances. In this study, we investigated the chlorine, carbon and hydrogen isotope fractionation patterns of chloroform during catalytic hydrodechlorination using two commercial catalysts palladium-on-alumina ($\text{Pd}/\text{Al}_2\text{O}_3$) and rhodium-on-alumina ($\text{Rh}/\text{Al}_2\text{O}_3$). The fractionation patterns of catalytic reaction were further compared to the pattern of reductive dechlorination of chloroform with zero valent iron (Fe^0).

100 ml of deionized water in a reactor was saturated with hydrogen, which serves as an electron donor. The initial concentrations of chloroform and catalysts were designed to be 100 mg/l and 0.04 g/l, respectively. At specified time intervals, 1 ml of the water phase was taken from the reactor and placed in a 2 ml vial. Chlorine isotope analysis was implemented by GC-qMS (Agilent Technologies) coupled to a purge and trap sampler (PTA 3000, IMT GmbH) using the water phase from each 2 ml vial. For the carbon and hydrogen isotope analyses, a certain volume of the headspace in the 2 ml vial was injected into GC-C/Py-IRMS (Thermo Fisher Scientific).

The dual isotope slopes ($\Lambda_{\text{C-Cl}} = \Delta\delta^{13}\text{C}/\Delta\delta^{37}\text{Cl}$) during the catalytic dechlorination of chloroform over Pd and Rh were determined to be 2.3 ± 0.12 and 2.1 ± 0.14 , respectively. These values are significantly lower than the reported $\Lambda_{\text{C-Cl}}$ value of 8 ± 2 (Torrentó et al., 2017) and 8 ± 1 (Rodríguez-Fernández et al., 2018) for the reductive dechlorination of chloroform with ZVI. Our results indicate that the degradation mechanism of chloroform over Pd and Rh differs from the mechanisms with ZVI.

We further investigated the apparent kinetic isotope effects (AKIE) of carbon and chlorine isotopes. Whereas no significant difference was observed in AKIE_{C} between degradation with catalysts and ZVI, AKIE_{Cl} with Pd and Rh (1.037 and 1.032, respectively) are much higher than the theoretical limit for C-Cl bond cleavage ($\text{KIE}_{\text{Cl}} = 1.013$) by Elsner et al., 2005. The large AKIE_{Cl} with Pd and Rh suggest non-concerted, step-wise reaction, i.e. no intramolecular competition among the three chlorine atoms exists during the degradation process of chloroform, unlike concerted reaction that is known to take place during reductive dechlorination of chloroform with ZVI.

In summary, our study showed that 1) dual isotope slope and AKIE are useful tools to investigate degradation mechanisms and 2) chloroform degradation mechanism over Pd and Rh is assumed to be non-concerted, step-wise reaction based on the AKIE of Cl.

3: Paläoklima, Sedimentologie, Boden

Chairs: Matthias Hinderer, TU Darmstadt, Michael Zech, TU Dresden & Christine Stumpp, BOKU

Carbon isotope excursions in a Paleocene to early Eocene lignite bearing succession at the southern edge of the proto-North Sea (Schöningen, Germany)

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Long-term effects of present global warming on ecosystems on timescales beyond those covered by the human record of the last few centuries are still a matter of speculation. Since

long-term greenhouse periods and short-term warming events occurred repeatedly in the history of the earth, they may be the subject for detailed studies on the reaction of ecosystems to global warming on different timescales. The Early Eocene Climatic Optimum (EECO) and its superposed short-term warming events such as the Paleocene-Eocene Thermal Maximum (PETM) represent the last greenhouse period before today which is especially suited for comparisons to the presently developing greenhouse since fauna and flora had reached an evolutionary state already similar to today.

The sedimentary succession of the former Helmstedt Lignite Mining District in northern Germany covers the entire Paleogene greenhouse phase and its gentle demise between the upper Paleocene and the early middle Eocene almost continuously in an estuarine situation at the southern edge of the proto-North Sea. Due to the interaction between changes in sea level, salt withdrawal in the subsurface and climate-related changes in runoff from the hinterland the area was subject to frequent changes between marginal marine and terrestrial conditions, repeatedly leading to peat formation. This offers the rare opportunity to study Paleocene–Eocene near-coastal ecosystems and to trace the effects of long- and short-term climate perturbations on the diversity and composition of the plant communities across 10 million years during the Paleogene greenhouse.

Here, we present high-resolution carbon isotope data of bulk organic matter ($\delta^{13}\text{C}_{\text{TOC}}$) from a 98 m thick sequence from the lower part of the succession (Schöningen Formation). We observed six negative carbon isotope excursions (CIEs) reflecting massive short-term carbon cycle perturbations, which can be related to the PETM, probably to the Eocene Thermal Maximum 2 and to the EECO. Palynological analysis proved that shifts in $\delta^{13}\text{C}_{\text{TOC}}$ values are correlated with changes in the peat forming wetland vegetation. Furthermore, the PETM-related CIE shows a distinct rebound to higher $\delta^{13}\text{C}_{\text{TOC}}$ values shortly after the onset of the CIE, which is here recognized as a common feature of terrestrial and marginal marine PETM-records worldwide and may be related to changes in the vegetation.

^{18}O analyses of bulk lipids as novel paleoclimate tool in loess research – a pilot study

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The analysis of the stable oxygen isotopes ^{18}O and ^{16}O has revolutionized paleoclimate research since the middle of the last century. Particularly, ^{18}O of ice cores from Greenland and Antarctica is used as paleotemperature proxy and ^{18}O of deep-sea sediments is used as proxy for global ice volume. Important terrestrial archives to which ^{18}O as paleoclimate proxy is successfully applied are for instance speleothems, lake sediments or tree rings. By contrast, ^{18}O applications to loess-paleosol sequences (LPSs) are scarce, despite for instance a compound-specific ^{18}O analytical tool for sugar biomarkers was developed and presented already years ago (Zech et al., 2014. *Geochimica et Cosmochimica Acta* 126, 614–623).

Here we present a first continuous ^{18}O record ($n = 50$) for the LPS Crvenka in Serbia, SE Europe, spanning the last glacial-interglacial cycle. From a methodological point of view, we took advantage of a recently proposed paleoclimate/hydrological tool/proxy based on bulk ^{18}O analyses of plant-derived lipids. The $^{18}\text{O}_{\text{lipid}}$ values range between -10.2‰ and $+23.0\text{‰}$ and are systematically more positive in the interglacial and interstadial (paleo-)soils compared to the loess layers. In our conference contribution, we compare our $^{18}\text{O}_{\text{lipid}}$ record from the LPS Crvenka with the marine oxygen-isotope stages as well as with the Greenland $^{18}\text{O}_{\text{ice}}$ core records revealing the famous Dansgaard-Oeschger events (stadials and interstadials). Concerning the interpretation of our LPS $^{18}\text{O}_{\text{lipid}}$ record, we will discuss several influencing factors, such as temperature-control on ^{18}O , relative humidity-dependent evaporative leaf water enrichment, post-sedimentary effects and pool-effects.

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Plant and fungal contributions to soil organic matter fractions assessed by ^{13}C and ^{15}N isotope natural abundances

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Soil organic matter (SOM) consists of a multitude of organic compounds forming a continuum of decay, from fresh detritus to highly processed organic matter stabilized on mineral surfaces. To date, we still lack crucial knowledge about the contribution of plant and microbial residues to SOM fractions and we know almost nothing about the contribution of distinct fungal functional guilds such as arbuscular (AM), ectomycorrhizal (ECM), and saprotrophic (SAP) fungi to SOM fractions.

Aiming to address this knowledge gap, we investigated sources of particulate and mineral associated organic matter (POM and MAOM) around trees with distinct mycorrhizal types, *Liriodendron tulipifera* (AM association) and *Quercus alba* (ECM association), in a temperate deciduous forest in Indiana, USA. In ECM-associated systems, we expect ECM fungi to be the main contributors to SOM, while in AM-associated systems, SAP fungi will mainly contribute to SOM due to the facilitation by AM fungi.

To assess various sources of SOM fractions, we combined stable isotope natural abundance analyses with measurements of microbial residues using amino sugars. Specifically, the ^{13}C and ^{15}N signatures of large-, medium- and small-sized POM and MAOM fractions were analyzed and compared to that of leaves and roots of the two dominant tree species as well as to tissues of mycorrhizal and saprotrophic fungi. The sources of C and N to SOM fractions were calculated by a Bayesian inference isotope mixing model.

Our data revealed a shift from relatively ^{13}C - and ^{15}N -depleted POM, which is close to the isotopic composition of plant material, to ^{13}C - and ^{15}N -enriched MAOM. Mixing model calculations suggests a higher contribution of plant (~ 76 %) than fungal inputs to POM for both tree systems, with a higher contribution of saprotrophic (SAP) fungi than ectomycorrhizal (ECM) fungi (~ 17 % and ~ 5 %, respec-

tively). In contrast, the model for MAOM fractions suggests a dominance of fungal residues relative to plant C, with SAP fungi contributing more than ECM fungi in most SOM fractions, even under the ECM tree. As expected, AM fungal residues contribute only little to SOM fractions. Microbial necromass – measured as amino sugars – confirmed the important role of ECM and SAP fungal residues for SOC storage in both, POM and MAOM fractions.

Overall, our results highlight the importance of distinct fungal functional guilds for soil C storage and call for future studies on the role of mycorrhizal types for soil C storage in a changing world.

4.1: Ökosysteme

Chair: Gerhard Gebauer, Universität Bayreuth

Orchid *Cremastra appendiculata* on the path to self-supply with changing fungal companion

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Covering one achlorophyllous, leafless and three chlorophyllous, leafy species the orchid genus *Cremastra* from East Asia allows inference on the evolutionary development from autotrophy to mycoheterotrophy of plant lineages mycorrhizal with saprotrophic fungi (Ogura-Tsujita et al. 2021). Particularly, the chlorophyllous, terrestrial orchid *Cremastra appendiculata* is unique with respect to its fungal mycorrhiza partners. Rather specialized wood/litter-decaying saprotrophic fungi are known to induce seed germination in the initially mycoheterotrophic protocorm stage (Yagame et al. 2013), while adult individuals either exploit wood-decaying Psathyrellaceae being partially mycoheterotrophic (Suetsugu et al. 2021) or form mycorrhiza with fungi of the ubiquitous saprotrophic rhizoctonia group.

We examined how a change in fungal community and subterranean morphology accompanies a nutrition mode alteration during the life cycle of *Cremastra appendiculata*.

Trophic strategies were revealed by comparing different development stages of *Cremastra appendiculata* to surrounding autotrophic reference plants based on multi-element natural abundance stable isotope analyses ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$, $\delta^2\text{H}$, $\delta^{18}\text{O}$) and total N concentrations. Here we present the first stable isotope patterns of tiny protocorms related to non-rhizoctonia saprotrophic fungal partners and ^{18}O

and ^2H natural abundance isotopic signatures of fully myco-heterotrophic terrestrial orchid specimens associated with saprotrophic fungi. Mycorrhizal fungi in *Cremastra appendiculata* protocorms, rhizomes and roots of seedling, and roots of adult were determined using next generation DNA sequencing.

We identified saprotrophic non-rhizoctonia Psathyrellaceae as dominant mycorrhizal fungi in protocorm and seedling rhizomes, while roots of seedlings and mature *Cremastra appendiculata* were mainly colonized with rhizoctonia fungi. Mature *Cremastra appendiculata* did not differ in isotopic signature from autotrophic reference plants suggesting a fully autotrophic nutrition mode. Characteristic of orchid specimens entirely relying on fungal nutrition, *Cremastra appendiculata* protocorms were enriched in ^{15}N , ^{13}C and ^2H compared to reference plants. Seedlings with very early green leaves showed a dispersive, intermediate isotopic signature, underpinning their transitional nutrition mode and the differences in fungal community depending on their subterranean morphology.

In conclusion, chlorophyllous terrestrial orchid *Cremastra appendiculata* is a key species being able to feature both extremes on the continuous transition from autotrophy to mycoheterotrophy with changing fungal companion during its ontogenetic development. Our results on *Cremastra appendiculata* together with knowledge from recent literature (e.g. Suetsugu and Matsubayashi (2021)) suggest a high within-species variability in nutrition and fungal association depending on development stage and subterranean morphology of *Cremastra appendiculata*.

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Unravelling shoot:root drought responses in VOC emissions through ^{13}C -pyruvate labelling

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Plant shoots and roots reveal highly diverse and specialized metabolic adaptations to ensure plant survival above- and belowground while being faced by a multitude of external stressors. Plants hereby produce a plethora of biogenic volatile organic compounds (BVOCs) to communicate with their environment, e.g. to attract pollinators, repel herbivores or directly reduce effects of external stressors such as drought. Root and leaf metabolism are intertwined, with roots delivering minerals, nutrients and water, as well as carbohydrates to the leaves while receiving a multitude of metabolites from the leaves, including precursors for BVOC biosynthesis. Especially under drought stress, balanced resource allocation between leaves and roots is compromised. Even though many studies have focused on the complex dynamics of organ specific metabolome adaptations and changes in resource allocation under drought, little is known about metabolomic adjustments of BVOC biosynthesis of leaves relative to roots.

In our controlled climate chamber experiment, we aimed to unravel these dynamics by measuring compound-specific ^{13}C -incorporation in BVOCs after position-specific ($[1-^{13}\text{C}]$ / $[2-^{13}\text{C}]$ -pyruvate) labelling of leaves and roots of potted, two-year old *Fagus sylvatica* and *Picea abies* saplings before and during drought stress, using flow-through chambers. BVOC emissions were measured online by PTR-TOF-MS in combination with GC-C-IRMS for further compound validation and ^{13}C incorporation into specific monoterpenes. To quantify $[1-^{13}\text{C}]$ - and $[2-^{13}\text{C}]$ -pyruvate allocation into decarboxylation processes during primary and secondary metabolism, we used $^{13}\text{C}\text{CO}_2$ laser spectroscopy. Drought stress was determined by controlling soil moisture and measuring of plant physiological traits, such as leaf transpiration, assimilation rate and leaf water potential.

With this approach, we aim to identify active metabolic pathways responsible for BVOC biosynthesis in leaves and roots and how regulatory patterns changed due to drought. Considering our preliminary results, net CO_2 assimilation, transpiration and respiration declined under drought. Overall BVOC composition and drought response, however, varied between organs in both species. Leaf emissions showed higher BVOC diversity even under drought. Monoterpene composition in leaves and roots of *Fagus sylvatica* differed and overall emissions were higher in roots. Contribution of de-novo synthesis of BVOCs in leaves was elevated due to storage depletion under drought in both species. Our

results indicate major changes in BVOC emission pattern in leaves and roots under drought stress, providing first insights to elucidate drought-induced trade-offs in resource allocation into BVOCs above- and belowground.

Field ^{15}N pool dilution approach to determine gross nitrification rate

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Nitrification is the microbial oxidation of ammonium (NH_4^+) to nitrate (NO_3^-) and is one of the most important processes of the terrestrial nitrogen cycle. Nitrification is known to promote nitrogen leaching from soils as the less mobile cation ammonium (NH_4^+) is oxidized by nitrifiers to the mobile anion nitrate (NO_3^-). Additionally, nitrification promotes NO and N_2O formation, directly as a by-product of nitrate formation and indirectly as a source of substrate for denitrification.

In numerous studies gross nitrification rates are determined using ^{15}N pool dilution technique in laboratories, but only few field experiments with undisturbed soil structure were done. An appropriate in situ sprinkler method with a low irrigation rate and very even ^{15}N -nitrate application was developed 2018 for sandy soils. The first test with a tracer solution confirmed that high amounts of the soil water can be replaced from the top soil by applying a low irrigation rate by a special sprinkling device, and therefore all assumptions of the ^{15}N -pool dilution technique can be fulfilled in the field by this method. Subsequently, the method was used to measure the small scale field heterogeneity (dm to m) and variability between field of gross nitrification at eight $3\text{ m} \times 3\text{ m}$ plots at sites with sandy soils (Fuhrberger Feld, northern Germany) in spring 2021. The results of the first application of the new method and der measurements in the Fuhrberger Feld will be shown. Different approaches to calculate the nitrification rates between two sampling dates t_0 and t_1 will be presented, and the heterogeneity of the nitrification rate will be discussed.

Poster-Kurzvorträge (Poster Short Communications) 3: Paläoklima, Sedimentologie, Boden

Ein ~15 ka $\delta^2\text{Hn}$ -alkane-Record vom Bichlersee, Oberbayern

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Die Alpen sind eine Schlüsselregion, um vergangene Veränderungen des Klimas und der atmosphärischen Zirkulation in Europa zu rekonstruieren. Biomarker- und komponentenspezifische Stabilisotopenanalysen in Seesedimenten bieten dabei großes Potenzial, sind aber bisher im Alpenraum kaum angewendet worden. Wir präsentieren neueste Ergebnisse vom Bichlersee, Oberbayern, die vor allem das Spätglazial hochaufgelöst (50 Proben) abdecken. Die Blattwachsmuster (n-Alkane) zeigen durchweg einen dominanten Eintrag langkettiger Homologe (C^{27} bis C^{33}), also ein terrestrisches Signal (im Vergleich zu kürzerkettigen, aquatischen Homologen von Algen und Makrophyten). Die markante Abnahme der mittleren Kettenlänge von > 30 auf < 30 am Ende der Jüngerer Dryas hängt vermutlich mit der Wiederbewaldung zu Beginn des Holozäns zusammen. Die ^2H -Isotopie der dominanten C^{29} - und C^{31} -Kettenlängen ändert sich sehr konsistent und nahezu stetig im Verlauf des Spätglazials von -180 auf -210 ‰, um dann im Holozän wieder auf positivere Werte anzusteigen. Auch wenn wir dies im Moment insbesondere auf eine Änderung der Niederschlagsisotopie zurückführen, können wir den Einfluss sich verändernder Vegetation – z. B. durch mehr Gräser während des Spätglazials – und evapotranspirativer Anreicherung nicht quantifizieren. Dazu sind für die folgenden Arbeiten komponentenspezifische ^{18}O -Analysen an Zuckern geplant.

Last millennium hydroclimate variability from Lake Höglwörth, Bavaria, Germany

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During the past decades, unusual rapid warming and significant changes in the precipitation seasonality and pattern have been recorded in almost the entire European Alps. To put these recent changes and climate projections into an adequate context, reconstructions of paleoenvironmental and –climate dynamics on a regional and local scale are

prerequisite. Moreover, paleoenvironmental studies help to identify drivers and forcings of past (hydro)climate variability. In this study we present a high resolution continuous environmental and hydroclimatic record from a small forealpine lake "Lake Höglwörth" (Bavaria, Germany), covering the past millennium based on n-alkanes and their compound-specific isotopic composition ($\delta^2\text{H}$). The relatively high abundance of C^{27} to C^{33} indicates input from higher terrestrial plants, but also abundance of C^{23} and C^{25} document the presence of aquatic plants, particularly from AD 1100 to 1300, between AD 1550 and 1750, as well as since 1850. C^{29} and C^{31} reveal very similar isotopic ($\delta^2\text{H}$) signal and down-core trends. They are relatively enriched (~ -202.1 ‰ for C^{31}) between AD 1100 and 1450 with maximum enrichment (~ -180 ‰ for C^{31}) between AD 1200 and 1300. Rather depleted values (~ -210 ‰ for C^{31}) are found from AD 1450 to 1650, however, an enrichment is obvious after 1650. Due to the primarily origin of the C^{29} and C^{31} in terrestrial vegetation, we assume that $\delta^2\text{H}$ of these n-alkanes mainly reflects past changes in the isotopic composition of precipitation. However, effects related to changing vegetation and evapotranspirative enrichment cannot be ruled out. However, C^{23} is variably enriched compared to C^{29} and C^{31} , and we suggest that this reflects the evaporative enrichment of the lake water and might thus enable to calculate relative humidity. We are now aiming to (i) increase the temporal resolution (continuous \sim decadal), (ii) compare our results to other regional records, and (iii) establish high-resolution d^{18}O records from sugar biomarkers in order to more robustly disentangle the various factors influencing the isotopic composition of the leaf waxes.

Ca isotope partitioning upon experimental precipitation of carbonated hydroxy-apatite (CHAP)

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Carbonated hydroxy-apatite (CHAP) was experimentally synthesized in batch-type set-ups by mixing of calcium (Ca)- and phosphate-bearing aqueous solutions and the transformation of calcite powder in aqueous solution between 11° and 65°C (Gussone et al., 2020). Compositional changes of the experimental solution and solid phase products were followed by elemental analysis, Raman spectroscopy, scanning-electron microscopy, and powder XRD.

In the mixing experiments, crystallization of CHAP took place following the precipitation of metastable brushite as precursor that was then transformed into CHAP. In the transformation experiments using synthetic calcite as a precursor phase it was found that the reaction at pH values between 7.5 and 7.9 occurs via the direct replacement of calcium carbonate by CHAP.

Calcium isotope fractionation led to an enrichment of the light isotope in the solid CHAP compared to the aqueous solution by about -0.5 to -1.1 ‰, independent from the experimental approach, and the magnitude was essentially independent of temperature. The metastable brushite formed prior to transformation to CHAP showed a reduced fractionation compared to the CHAP. The observed Ca isotope fractionation into the CHAP lattice resembles that of natural phosphorites and lies within the range of the view existing theoretical and experimental studies.

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Stable isotopic and trace elemental fingerprints in carbonate precipitated by modern hard-water creeks of the temperate climate zone

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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.

Two examples of recent sinter formation from streams in the temperate climate zone were investigated: Site R is positioned in a cliff zone of Rügen Island, southern Baltic Sea and Site W near Westerhof in the south-western Harz foreland. Two phases of surface water development can be differentiated: An induction period starting at the spring, where only degassing of carbon dioxide takes place, and a second stage where calcite formation from the highly supersaturated solution is continuously driven by further degassing. The liberation of CO₂ is associated with an enrichment of the heavy carbon isotope in the remaining dissolved inorganic carbon. By following the isotope and trace element composition of aqueous solutions and recent calcite precipitates along the flow path, distribution coefficient (Li, Na, Mg, Sr, Ba, SO₄, ¹³C, ¹⁸O) are derived. The empirical quantitative observations at Site W can be compared with observations dating back to the late 60 s of the last century. Those at Site R are compared to results from laboratory experiments using the natural water as starting solution. Furthermore, the distribution coefficients are compared to calibrated experimental studies to estimate calcite precipitation rates. Trace-element based rate estimates for Site W are higher than published direct measurements, which is likely due to hydrodynamic boundary conditions impacting the in-situ growth experiments. Idiomorphic BaSO₄ was observed in recent carbonate sinter at Site W for the first time, which is in agreement with slight supersaturations modeled for the stream water.

At the bottom of the cliff (Site R), the carbonate stream water is finally entering the Baltic Sea where mixing with brackish surface waters occur. The excess in dissolved CO₂ compared to the atmosphere is enhancing the degassing capacity in the mixed coastal waters.

Identification of paleosols of a Namibian sediment core (WW203303) using pedogenic features, trace fossils and stable isotope compositions

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Stable carbon and oxygen isotopes of carbonates from paleosols can be used as proxies to reconstruct paleoclimate and paleoenvironment conditions (Cerling & Quade,

1993). Paleosols are identified from the Namibian sediment core WW203302 (Houben et al., 2020) using stable isotopes, pedogenic features and a conceptual model generated by Hasiotis et al. (2012). Pedogenic features such as nodules, mottling and peds are clear indexes for paleosol in sediment. However, these features appear only sporadically in this 400 m long sediment core, trace fossils are used as index to distinguish paleosols from sediment.

Bioturbation patterns generally created by trace fossils occur nearly in the entire sediment core. Density, abundance, and depth of bioturbation follow the degree of soil development (Hasiotis et al. 2012). Pedogenesis, bioturbation and sedimentology are criteria to classify paleosols in sediment sections, from which nodules were selected, into compound, composite, and cumulative fractions (Kraus, 1999). Stable carbon and oxygen isotopes of bulk samples from different types of paleosols are compared to that of nodules to examine whether bulk samples from this sediment core can be used for paleoclimate interpretations.

The δ¹³C values of all types of bulk samples show basically the same trend as nodule samples (r² = 0.88), bulk samples from well-developed paleosols, compound and composite paleosols show a better correlation to corresponding nodule samples than cumulative paleosols and phreatic layers for δ¹⁸O values (r² = 0.64). Covering sands of nodule samples are more negative than corresponding nodules for δ¹⁸O, but either more negative or positive than nodules for δ¹³C, regardless of soil types. Furthermore, dolomites as a component of nodule samples, are generally more enriched in δ¹⁸O and mostly depleted in δ¹³C, regardless of soil type.

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4.2: Ökosysteme

Chair: Gerhard Gebauer, University of Bayreuth

KEYNOTE

Carbon isotope ratio as a measure of photosynthetic water-use efficiency: Reconciling a biophysical discrepancy

John Marshall

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In most plants, $d^{13}C$ of their tissues provides an estimate of the carbon:water exchange, or water-use efficiency, of photosynthesis. This is important because photosynthesis and transpiration represent an important evolutionary trade-off for plants, but also because they link two major parts of the ecosystem carbon and water cycles. The discovery that this trade-off could be quantified with $d^{13}C$ led to a burst of research in fields as diverse as plant breeding, ecosystem ecology, and global climate change. However, there was always some concern that the predicted isotopic composition did not exactly match biophysical theory, which was essentially a Rayleigh distillation model with a strong enzymatic fractionation. The discrepancy favoured overestimates and was approximately as large as the isotope effects under study, leading to some scepticism about the isotopic technique. I will review proposed explanations for the discrepancy, ending with the recent convergence on mesophyll conductance. Mesophyll conductance can now be measured with high precision in the field, offering a mechanistic adjustment leading to water-use efficiency estimates with high precision and accuracy. Eliminating this discrepancy returns $d^{13}C$ to a position of credibility as a measure of the linkage between carbon and water fluxes of plant leaves and canopies.

Impact of nutrient and water availability on grassland functioning – achieving a process based understanding across scales

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Two important threats to the sustainable functioning of seminatural grasslands in temperate zones are (1) nutrient loading due to agricultural fertilization and pollution, and (2) the increase of extreme drought events due to climate change. These threats may cause substantial shifts in species diversity and abundance and considerably affect the carbon and water balance of ecosystems. The synergistic effects

between those two threats, however, can be complex and are poorly understood. Here, we experimentally investigated the effects of nitrogen addition and extreme drought (separately and in combination) on a seminatural temperate grassland, located in Freiburg (South Germany). To study the grassland response, we combined eddy-covariance techniques, open gas exchange systems from the leaf to the plot scale with biomass and biodiversity assessments. Open gas exchange chambers were connected to an infrared gas analyzer and water isotope spectrometer, which allowed the partitioning of net ecosystem exchange and evapotranspiration. Vegetation parameters were described by species richness, species abundance, and leaf area index. Our results suggest that grassland communities, strongly weakened in their stress response by nitrogen loading, can substantially lose their carbon sink function during drought. While nitrogen addition caused a significant loss in forb species (–25 %), precipitation reduction promoted a strong dominance of grass species at season start. Consequently, the grass-dominated and species-poor community suffered from a strong above-ground dieback during the dry summer months, likely caused by lower water use efficiency and weaker drought adaptations of the species community. Over the growing season (April–September), the carbon sequestration of the studied grassland was reduced by more than 60 % as a consequence of nitrogen addition. Nitrogen addition in combination with precipitation reduction decreased carbon sequestration by 73 %. Eutrophication can severely threaten the resilient functioning of grasslands, in particular when drought periods will increase as predicted by future climate scenarios. Our findings emphasize the importance of preserving high diversity of grasslands to strengthen their resistance against extreme events such as droughts.

Application of 2-dimensional stable isotope measurements of methane to constrain sources and sinks in a seasonally stratified freshwater lake

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Supersaturation of methane (CH_4) in the oxic surface water layer of lakes has been suggested to play an important role in releasing CH_4 to the atmosphere and emissions are predicted to increase with future climate change. Microbial

CH₄ oxidation in limnic systems as a counteracting sink has the potential to efficiently diminish CH₄ effluxes. In this study, sources and sinks of CH₄ were investigated in a seasonally stratified, eutrophic lake in southwestern Germany during summer using carbon and hydrogen stable isotope measurements.

In the lake water body, aerobic CH₄ oxidation at the oxic-anoxic interface increased in intensity with rising CH₄ concentrations over summer. This was accompanied by a strong increase in stable carbon and hydrogen isotope values of the CH₄ pool. Incubation experiments with ¹³C-labeled CH₄ revealed CH₄ oxidation rates varying between 49–106 nM/d. In the lake sediment, anaerobically produced CH₄ was reduced in its concentration through microbial anaerobic CH₄ oxidation in sulfate-methane transition zones possible due to high sulfate concentrations in the lake (~2 mmol/l). The decrease in upward migrating sedimentary CH₄ was partly accompanied by increasing stable carbon and hydrogen isotope values.

Sources of CH₄ were characterized using a novel isotope indicator Δ(2,13) recently introduced by Tsunogai et al. (2020), which is based on dual isotope characterization of CH₄ and corrects for isotopic fractionation effects caused by CH₄ oxidation. Surface water CH₄ showed different Δ(2,13) values if compared with CH₄ from the hypolimnion and sediment and was furthermore distinguishable from littoral Δ(2,13) values. In order to investigate the occurrence of oxic CH₄ production in the surface water layer, an incubation experiment was performed with ¹³C-labeled methylphosphonate, a known precursor substrate for aerobic CH₄ formation, which showed a strong increase in the stable carbon isotopic composition of CH₄ over time. In conclusion, our results strongly indicate internal oxic CH₄ production by aerobic organisms as a possible source of excess CH₄ in the surface water layer of the lake.

Reference

Tsunogai, U. et al. 2020. Dual stable isotope characterization of excess methane in oxic waters of a mesotrophic lake. *Limnol. Oceanogr.* 65: 2937–2952.

Belowground C allocation of tropical rainforests in response to drought: an ecosystem ¹³C₂ labeling approach

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Drought affects carbon (C) sources and sinks in forest ecosystems, with potential consequences for belowground C allocation, a vital process of the terrestrial C cycle. However, the extreme drought impacts on the ecosystem are poorly understood, particularly in the tropical rainforests. Within the framework of our large-scale ecosystem manipulation experiment on “Rain Forest Water, Atmosphere, and Life Dynamics” (WALD) at the Biosphere 2 in Arizona, we conducted a whole ecosystem stable isotope labeling with atmospheric ¹³C₂ to gain in-depth insights into tree belowground C allocations and the C partitioning at the soil–microbe–root interface under ambient conditions and drought stress. In particular, we hypothesized that key drought-adaptation strategies would include i) increased C allocation into subsoil layers that drought down slower than topsoil and ii) increased C investment into rhizodeposits and mycorrhizal fungi. Our data on tree C allocation highlight that drought stress increased the proportion of recently assimilated C translocated into the roots in both the top- and sub-soil with no correlation of C allocation with soil water content or root biomass. In response to drought, the rhizodeposition, and thus allocation of assimilated C into rhizospheres soil, was reduced in topsoil but increased in subsoil. However, we found pronounced plot-specific differences in belowground C allocation, especially between plots with only understory plants vs those with tall trees, suggesting species-specific drought response strategies. However, generally our observations underline that trees attempt to invest assimilated C into the deeper soil layers’ roots and rhizosphere to access subsoil resources. The C investment into deeper soil layers and the absence of any correlation with root biomass suggest that drought adaptation strategies are based on rhizomicrobial mechanisms rather than on C investment into root growth. The upcoming results of ¹³C incorporation into phospholipid fatty acids will provide further insights into microbial C utilization in the rhizosphere and complete our picture of belowground drought adaptation strategies. In summary, quantification of tree C belowground allocation patterns at the plant-microbe-soil interface will enable us to disentangle belowground drought response strategies of tropical rainforests.

6: Physiologie, Metabolismus, Medizin, Doping, Forensik, Lebensmittel

Chair: Frank Keppler, University of Heidelberg

Stable isotopes for planetary health: Synthetic methionine

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Methionine is an amino acid that humans and farm animals must derive from food. This metabolite, a tightly regulated resource in ecosystems, has become a mass commodity in the global economy, with well over 1 million tons being produced annually from petroleum to fortify livestock feed. Methionine synthesis is an excellent exemplar of a planetary scale anthropogenic activity that manifests at the molecular scale of cellular metabolism, with potential systemic effects on human health and environments. Taking a planetary health perspective, I will explore in this talk the scale and historical trajectory of the methionine industry and provide a preliminary model for tracing this amino acid through the food supply into the human body.[1] We now want to test this model empirically using isotope analytics to quantify the synthetic proportion of methionine in foods and humans. The proposed approach is to use a mass spectrometry method developed in the last five years that is based on ESI-Orbitrap. It can reveal intramolecular stable isotope compositions of organic molecules at the natural abundance level.[2] I will also briefly discuss alternative isotope approaches for this project, as well as highlight topics where the new stable isotope technology might contribute insights in a biomedical context.

Related publications

1. Neubauer C, Landecker H (2021) A planetary health perspective on synthetic methionine: Implications of opening the tap on a historically limiting nutrient. *Lancet Planet Health*
2. Neubauer C, Sweredoski MJ, Moradian A, Newman DK, Robins RJ, Eiler JM (2018). Scanning the isotopic structure of molecules by tandem mass spectrometry. *Int J Mass Spec*

Carbon isotope ratios of endogenous steroids found in human serum – method development, validation, and reference population-derived thresholds

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In order to detect the misuse of testosterone (T) and testosterone prohormones, urinary steroids and steroid ratios are quantified and monitored in a longitudinal manner to enable the identification of atypical samples. These suspicious samples are then forwarded to isotope ratio mass spectrometry (IRMS)-based methods for confirmation. Especially concentration ratios like T over epitestosterone (E) or 5 α -androstane diol (5 α Adiol) over E proved to be valuable markers. Unfortunately, depending on the UGT2B17 genotype and/or the gender of the athlete, these markers may fail to provide evidence for T administrations when focusing exclusively urine samples.

In recent years, the potential of plasma steroids has been carefully investigated, which were found to be suitable to detect T administrations especially in female volunteers. [1–5] A current drawback of this approach is the missing possibility to confirm that elevated steroid concentrations found in plasma are solely derived from an administration of T or T-prohormones and cannot be attributed to possible confounding factors. Therefore, and in parallel to the procedure applied to urine samples, an IRMS method for plasma steroids has been developed and validated taking into account the limited sample volume for serum samples (usually not more than 1 mL). As endogenous reference compounds, unconjugated cholesterol and dehydroepiandrosterone-sulfate were found suitable while androsterone and epiandrosterone (both sulfoconjugated) were chosen as target analytes.

The method was based on multi-dimensional gas chromatography coupled to IRMS in order to increase recovery compared to liquid chromatography-based sample clean-up.[6] The method was validated employing linear mixing models, and finally a reference population encompassing n = 65 males and females was investigated to enable the calculation of population-based thresholds. As proof-of-concept, several serum samples from volunteers participating in T-replacement therapies were analyzed and found to be significantly depleted in their serum steroid target analytes.

References

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Making plant methane formation visible – the effect of light exposure and light intensity on plant methane formation by application of ¹³C-labelled dimethyl sulfoxide

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In recent years methane (CH₄) formation by vegetation in the presence of oxygen has been studied intensively, but its underlying formation process(es) are still poorly understood. Currently, reported CH₄ emission rates vary by orders of magnitude and thus make global estimates of CH₄ emissions by vegetation difficult. In addition, the process(es) of plant CH₄ formation are mostly unknown. In this presentation, we introduce a new approach for a making CH₄ formation by plants visible. By application of ¹³C-labelled dimethyl sulfoxide (DMSO) onto the leaves of tobacco plants (*Nicotiana tabacum*) and Chinese silver grass (*Miscanthus sinensis*), DMSO was identified as a precursor of CH₄ in plants and the effect of light on CH₄ formation was examined by measuring δ¹³C-CH₄ values during incubations via Cavity Ring-Down Spectroscopy.

Both plant species clearly showed an increase in δ¹³C-CH₄ values, and therefore CH₄ formation, during the incubations while exposed to light. Higher light intensities lead to higher CH₄ formation rates in *N. tabacum* and to lower CH₄ formation rates in *M. sinensis*. When examined in the dark no formation of CH₄ could be detected for *N. tabacum*, whilst *M. sinensis* still produced around 50 % of CH₄ in the dark when compared to light exposure. Our findings unambiguously confirm DMSO as a precursor of plant CH₄ and suggest that CH₄ formation in plants is highly dependent on light exposure, light intensity, and plant species. Furthermore, our work presents a new isotopic approach for investigating mechanisms of CH₄ formation in plants which has the potential to identify the underlying physiological processes, that without the use of stable isotopes could not be solely determined by CH₄ concentration measurements.

Geographical provenance determination of wood through combination of isotope ratios

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As illegal logging develops more and more into a global problem, analytical methods to proof timber origin are necessary. In two pilot studies wood samples were collected to examine the possibilities of provenance determination of wood with stable isotope analyses as an addition of the “Large Scale Project” to develop genetic reference data to identify timber origin. The project was led by the Thuenen-Institute of Forest Genetics. In the first pilot study, wood samples of the tree species *Carapa guianensis* and *Hymenaea courbaril* were collected on a country scale at five locations for both species and an additional location for *Hymenaea courbaril* in Brazil with multiple 100 km distances up to 3,000 km between the geographical groups (locations) (Large Scale). The second pilot study addressed the regional scale in three different countries (Small Scale). In a range of 100 km wood samples were gathered for *Hymenaea courbaril* and *H. jutai* in two forest concessions in Brazil and for *Dipteryx ferrea* in Peru and *Lophira alata* in Cameroon in three concessions each. Forest concession are areas where logging companies received the permission for timber harvest from the state.

In the Large Scale study most isotope ratios showed differences between the geographical groups with most differences being statistical significant. Furthermore, weak significant correlations with latitude and longitude for d18O were observed, for d¹³C and d²H only with longitude and d¹⁵N correlated weakly with latitude. In a statistical self-assignment, the success rate in total was 59 % for *Carapa guianensis* and 54 % for *Hymenaea sp.* Nevertheless, the locations in Brazil were not distinguishable from each other in a principal component analysis.

In the Small Scale study, the isotope ratios of C and N, measured so far, did not allow for a significant separation of forest concession nor did they show significant correlation with latitude or longitude.

In conclusion there seems to be a geographical signal in the isotope results of the different location for the four isotope ratios of C, N, O and H but it was not strong enough for a secure geographic assignment. As next steps we want to check the performance of a combined application of gene markers and stable isotopes for geographic assignment of timber. Sampling design and lab methods also offer space for optimisation.

Poster-Kurzvorträge (Poster Short Communications) zu

4: Ökosysteme

1: Analytik, Methoden, Technik und Qualitätssicherung stabiler Isotope

5: Klima und Atmosphäre

Using in-situ and destructive measurements of stable water isotopes to quantify ecohydrological feedback processes of different forest stands

Judith Mach, Laura Kinzinger, Stefan Seeger, Fabian Fritz, Paula Hilgert, Markus Weiler, Maren Dubbert, Christiane Werner, Natalie Orłowski
Albert-Ludwigs-Universität Freiburg, Professur für Hydrologie, Deutschland

Stable water isotopes are a promising tracer for studying water movement through ecosystems. Traditionally, destructive sampling techniques are applied to measure the isotopic signature in soils and plant xylem but these methods are limited in their temporal resolution and have proven to be fraught with uncertainty. Recent development of in-situ membrane-based probes for direct measurements of soil and tree xylem water isotopes (SWIP) allow continuous observations along soil profiles or within trees at different heights. Such new in-situ measurements provide an unprecedented combination of high temporal and spatial resolution data. Also, by using the same probes for the soil as well as the plant compartment, all measurements can be compared directly.

Here, we present preliminary results of our in-situ isotope measuring platform from different forest stands in the Black Forest (Germany). The measurement setup encompasses three experimental treatments: i) pure beech, ii) pure spruce and iii) mixed beech and spruce stands. By measuring soil water in different depths as well as xylem water at different heights, we will not only identify species-specific differences in their water uptake patterns but also the impact of interspecific competition for water. Additional destructive measurements of stable water isotopes from throughfall, stemflow, soil and tree xylem water will be used to gain further information but also to compare in-situ with destructive isotope measurement techniques.

Antibiotics increase methane production rates in freshwater sediments: Evidence from an anaerobic incubation

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Methane (CH₄) is after carbon dioxide (CO₂) the second most important greenhouse gas and is *inter alia* produced in natural freshwater ecosystems. In the face of increasing CH₄ emissions from natural sources, researchers have investigated environmental factors and climate change feedbacks to explain this increment. Despite being omnipresent in freshwaters, knowledge on the influence of chemical stressors of anthropogenic origin (e.g. antibiotics) on methanogenesis is not present to date. To address this knowledge gap, we incubated freshwater sediment for 42 days under anaerobic conditions in presence of a five-component antibiotic mixture at four levels (from 0 to 5000 µg/L). Weekly measurements of CH₄ and CO₂ in the headspace showed that the CH₄ production rate can be increased by up to 94 % at 5000 µg/L and up to 29 % at field-relevant concentrations (i.e., 50 µg/L). The compound-specific δ¹³C values of CH₄ and CO₂ indicate that the processing dynamics are changed while the successional stages are not. Despite the complications of transferring experimental CH₄ production rates to realistic field relevant CH₄ emissions, the study suggests that chemical stressors contribute to the emissions of greenhouse gases by affecting the methanogenesis in freshwaters.

Exploring fundamentals of quantitative ¹³CO₂/¹²CO₂ tracer studies of CO₂ exchange and biomass in plants: Assessment of system performance and determination of isotopic end-members for mixing model

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Labelling with carbon isotopes is the technique of choice to study carbon dynamics in plants, including CO₂ exchange, biomass and carbohydrates. Labelling experiments consist of two phases: An establishment phase, where plants are grown in the presence of CO₂ with constant isotopic composition, and a labeling phase, where the establishment CO₂ is replaced by a CO₂ with differing isotopic composition. However, labelling systems can be prone to technical

artifacts like contamination with extraneous CO₂, fluctuations of the isotopic composition of the establishment and labelling CO₂ etc. Also, the accurate determination of carbon tracer kinetics requires an accurate determination of the two end-members for isotopic mixing models. So far, systematic testing of labelling systems has been rare and incomplete. Here, we present details of a chamber labelling system for plant mesocosms and the analysis of its performance with respect to possible technical artifacts. This also includes the analysis of different approaches for the end-member determination. We performed labelling experiments with perennial ryegrass (*Lolium perenne* L.) combined with ¹³CO₂/¹²CO₂ gas exchange and carbohydrate measurements, in growth chambers under three CO₂ concentrations: 200, 400, and 800 mmol mol⁻¹. Each treatment was run in two growth chambers, with identical growth conditions but with two different CO₂ sources (¹³C-depleted: δ¹³C -43.5 ‰ or ¹³C-rich: δ¹³C -5.6 ‰). After the establishment phase, the CO₂ supplied to each chamber was switched from depleted to enriched or vice versa for a 7 days-long labelling phase. When gas exchange rates were approximately steady on a day-by-day basis, CO₂ concentrations and δ¹³C in the chambers were also virtually constant over time. The spread in δ¹³C of the CO₂ sources during the establishment phase matched the spread in δ¹³C of the two CO₂-sources at the chamber outlets at all CO₂ concentrations, showing that chamber CO₂ was not contaminated with extraneous CO₂. This was also confirmed by the close correspondence of C-isotope discrimination (Δ) during gas exchange in the light at every CO₂ concentration. However, due to inevitable opening of the chambers during maintenance and plant sampling operations, Δ determined on respiratory CO₂, shoot and root biomass as well as shoot carbohydrates was slightly (1.1 ‰), but consistently (P < 0.01) smaller in the ¹³C-depleted relative to the ¹³C-rich CO₂ chambers during the establishment phase. Thus, for precise analyses of tracer kinetics in respiratory CO₂, biomass or carbohydrates, the determination of the end-members of the mixing model had to be based on sample type-specific Δ measurements.

Unravelling the diet of extinct cave bears in Romania using δ¹⁵N isotopic analysis of amino acids

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Compound specific isotopic analysis of individual amino acids (CSIA-AA) was performed to unravel dietary information on Late Pleistocene cave bears (*Ursus spelaeus*). In contrast to other regions of Europe, *U. spelaeus* from Roma-

nia showed variable and exceptionally high δ¹⁵N values (5.2 to 9.8 ‰) that leads to speculation of meat consumption. The CSIA-AA approach used is unique in that it offsets the natural baseline δ¹⁵N variation (e.g. environmental, behavioural or physiological traits). It can thereby provide a more accurate estimate of trophic position (TP).

Amino acids from ancient bone collagen of *U. spelaeus* were derivatized, separated via gas chromatography, combusted/reduced, then measured for δ¹⁵N using stable isotope mass spectrometry (GC-C-IRMS). This method is based on the differential fractionation of two amino acid groups: trophic AAs (i.e., glutamic acid) that fractionate ¹⁵N greatly (~8.0 ‰) compared to source AAs (i.e., phenylalanine) that fractionate ¹⁵N very little (~0.4 ‰) per trophic step. The latter (δ¹⁵N_{phe}) thus reflects the nitrogen source baseline (i.e. the primary producers) of the ecosystem.

Results rule out (i) significant dietary aquatic resources; (ii) carnivory as the main feeding behaviour. Rather, TPs of 1.8–2.2 (N = 6) are indicative of a plant-dependent diet, including for those cave bears with high bulk δ¹⁵N values. Using CSIA-AA, TPs of 1.9–2.1 were determined for *U. spelaeus* confirming a pure herbivorous diet. Bulk collagen δ¹⁵N values of can be explained by (i) a δ¹⁵N shift of the baseline in the local ecosystem, and/or (ii) the consumption of some specific plants with high δ¹⁵N values. Our findings have interesting implications regarding the evolution of herbivory among carnivorans. Furthermore, understanding feeding behaviour of *U. spelaeus* may provide key insights into their extinction.

We used an Agilent 7890B GC coupled to an Elementar GC5 Interface module in line with a reduction furnace, cryogenic trap (LN₂) and an IsoPrime 100 IRMS.

Reference

Naito, Y.I., Meleg, I.N., Robu, M. et al. Heavy reliance on plants for Romanian cave bears evidenced by amino acid nitrogen isotope analysis. *Sci Rep* 10, 6612 (2020). <https://doi.org/10.1038/s41598-020-62990-0>

Development of an open-split-based dual-inlet system for mass spectrometers

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The inlet system integrated into the Elementar isoprime precisION is a changeover-valve-based dual-inlet system which is not ideally suitable for high-precision measurements of elemental and stable isotope ratios. In order to attain higher precisions an open-split-based dual-inlet

system was designed and built by the Climate and Environmental Physics Division of the University of Bern featuring almost no metallic surfaces and altering the pressure of the measured gases in the ionization chamber as little as possible. By means of these two measures the occurrence of fractionation processes during the transfer of gases from the gas containers to the mass spectrometer as well as in the ionization chamber is noticeably reduced by the in-house built dual-inlet system when compared to the dual-inlet system built by Elementar.

Since 2020, an in-house built dual-inlet system, which was named „NIS-II“, is installed at the high altitude research station Jungfrauoch, Switzerland, for measuring various delta values of atmospheric gas samples such as $\delta\text{O}_2/\text{N}_2$ and $\delta\text{Ar}/\text{N}_2$ and $\delta^{17}\text{O}$, $\delta^{18}\text{O}$ of O_2 and $\delta^{15}\text{N}_2$ of N_2 . Furthermore, an NIS-II was recently taken into operation in Bern in order to check whether it is possible to measure clumped isotopes of oxygen, nitrogen and carbon dioxide molecules on gaseous samples of different origins.

Tracing nitrogen transformations induced by ^{15}N labelled cattle slurry applied with different techniques in winter wheat

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The effects of slurry application techniques on ammonia (NH_3) volatilisation and nitrous oxide (N_2O) fluxes are well documented. However, application techniques may also impact dinitrogen (N_2) fluxes, as they can influence denitrification activity by changing slurry and soil aeration (e.g. by injection techniques), nitrate formation (e.g. by adding nitrification inhibitors) and the pH value (e.g. by slurry acidification). Up to now, measuring N_2 fluxes and following pathways of slurry nitrogen (N) transformation under field conditions is still challenging.

Thus, we applied a combined ^{15}N labelling approach including slurry $\text{NH}_4^+\text{-N}$ and soil $\text{NO}_3^-\text{-N}$ in undisturbed soil cores, set up as lysimeters and with growing winter wheat for a study period of 60 days. Slurry treatments include the following application techniques: trailing hose with and without acidification (H_2SO_4), slot injection with and without nitrification inhibitor (DMPP). Soil cores without slurry application were used as control. In a first step, soil nitrate was ^{15}N labelled by homogeneous injection of a $\text{K}^{15}\text{NO}_3^-$ solution at a low N application rate (4 kg N ha^{-1}), while one week later, 68 kg N ha^{-1} ^{15}N -labelled cattle slurry was applied. The ^{15}N labelled cattle slurry consisted of fresh dairy cattle faeces (natural abundance), water and ^{15}N labelled synthetic urine. N_2O and N_2 emission were measured using the modified

^{15}N gas flux method with N_2 -depleted atmosphere. To close the N balance and follow the different N transformation pathways, ^{15}N losses by leaching, ^{15}N uptake by plant and residual ^{15}N in belowground biomass, microbial biomass and soil were analysed by IRMS.

The major gaseous loss pathway was NH_3 with up to 8 kg N ha^{-1} in the trailing hose treatment, while slot injection significantly reduced $\text{NH}_3\text{-N}$ losses. Regardless the application technique, N_2O fluxes were very low (up to $0.1 \text{ kg N}_2\text{O-N ha}^{-1}$), while N_2 reached up to 3 kg N ha^{-1} . The $\text{N}_2\text{O}/(\text{N}_2\text{O}+\text{N}_2)$ ratio of denitrification was always < 0.1 . The main pathways of the total N budget were gaseous N losses (NH_3 , N_2O , N_2) with 11–44 %, soil N pool with 32–48 % and plant uptake with 18–26 % of ^{15}N applied. N leaching and changes in the residual mineral nitrogen pool played only a minor role in the total N balance. Although there were no differences in the application techniques, it should be highlighted that the ^{15}N recovery was almost complete, indicating that the experiment was able to capture the relevant ^{15}N fates with the comprehensive setup that was applied.

Applying the ^{15}N gas flux method in a lab incubation as an alternative to laborious field studies

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Applying the ^{15}N gas flux method (^{15}NGF) in the field can be very challenging. The establishment of a reliable setup is time consuming, expensive, and requires a decent infrastructure at the field sites. Additionally, the atmospheric N_2 background reduces measurement precision for detecting low tracer-derived N_2 emissions. We incubated undisturbed soil cores (14.4 cm diameter and 35 cm height) from two remote field sites: an annual cropping system (*Zea mays*) and a perennial cropping system (*Silphium perfoliatum*). The incubation took place in a fully-automated facility, which provided us with an N-reduced atmosphere, options to control temperature, irrigation and drainage, and allowed better control over the homogeneity of ^{15}N -nitrate pool labelling, as compared to what is possible in the field. Using the ^{15}NGF method with undisturbed soil cores allowed us to quantify differences in source-specific N_2 and N_2O emissions while including the effect of soil structure under dynamic waterlogged conditions. Additional information about nitrogen transformation processes between the cropping systems were obtained in bulk soil by analysing soil mineral ^{15}N (NO_3^- and NH_4^+) via membrane-inlet mass spectrometry. The incubation experiment consisted of three different

phases with increasing soil water content: (1) entire core just below field capacity; (2) lower 10 cm waterlogged; and (3) lower 25 cm waterlogged. The soil from the *S. perfoliatum* field had a significantly lower product ratio of denitrification (N_2O/N_2+N_2O) with increasing waterlogging than the *Z. mays* soil. However, pool-derived N_2O emissions from the *S. perfoliatum* soil were not significantly lower than from *Z. mays* soil. Hence, we could show that the soil structure from the perennial cropping field resulted in higher N_2 emissions rather than lower N_2O emissions. Although perennial systems are generally expected to provide a greenhouse gas mitigation potential, we were able to replicate conditions that could not have been easily addressed in the field, and show that, in comparing soil from these fields, that was not the case.

7: Deutsches Isotopennetz GIN

Chairs: Robert van Geldern, Universität Erlangen-Nürnberg, Deutschland, Nils Michelsen, TU Darmstadt, Deutschland

Die Tritiumverteilung in Niederschlag und Oberflächenwasser in Deutschland – ein Beitrag zum deutschen Isotopennetzwerk

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An der Bundesanstalt für Gewässerkunde (BfG) werden seit den 1970er Jahren Oberflächenwasser- und Niederschlagsproben auf Tritium untersucht. Hierzu betreibt die BfG – mit Unterstützung der Wasserstraßen- und Schifffahrtsverwaltung (WSV), des Deutschen Wetterdienstes (DWD) und einiger Landesämter – ein bundesweites Netz aus insgesamt 69 Probenahmestationen mit dem Ziel, die Umweltradioaktivität großräumig zu überwachen. Dazu werden die Wasserproben aller Stationen als Monatsmischproben in den Laboren der BfG elektrolytisch angereichert und radiochemisch analysiert. Mittlerweile liegen alleine für Tritium mehr als 8.000 Einzeldatensätze für Niederschlag und 23.000 Einzeldatensätze für Oberflächenwasser frei zugänglich vor und können z.B. im Rahmen der Initiative „German Isotope Network – GIN“ verwendet werden.

Tritium ($H-3$) wird natürlicherweise durch Spallationsreaktionen in der Atmosphäre gebildet, anschließend zu überschwerem Wasser oxidiert und durch Niederschlag in die Oberflächengewässer eingetragen, wodurch es Bestandteil des hydrologischen Kreislaufes ist.

Die Tritiumkonzentrationen im Niederschlag sind im langjährigen Mittel (Untersuchungszeitraum 2010–2020) an der Station Cuxhaven (Nordsee) mit 10 TU am höchsten; landeinwärts verringern sich die Gehalte generell und liegen

beispielsweise bei 8,9 TU an der Station Garmisch (Alpen). Das „Spring Leak“-Phänomen führt im Frühsommer, im Vergleich zum restlichen Jahr, zu erhöhten Werten. Ebenso lagen die Tritiumkonzentrationen aufgrund geringer Niederschläge im Jahr 2018 an allen Stationen zwischen 15 % und 25 % über dem langjährigen Mittel.

Die Tritiumgehalte der Oberflächenwasserproben sind ebenfalls an der Nordseeküste mit etwa 33 TU (Station Helgoland) am höchsten; im Bereich der Ostsee liegen sie bei 7 TU (Station Travemünde) und sind damit mit den Konzentrationen im Landesinneren vergleichbar (z.B. 6,3 TU – Station Ulm). Überlagert werden diese natürlichen Werte durch z.T. stark erhöhte Tritiumkonzentrationen im Bereich von Kernkraftwerken, da diese im Rahmen ihres Routinebetriebes Tritium-haltiges Wasser diskontinuierlich über die Vorfluter in die Flüsse abgeben. So wird beispielsweise durch das französische Kernkraftwerk Cattenom regelmäßig Tritium in die Mosel eingeleitet, welches dann mit dem Fluss transportiert und durch Dispersionsprozesse verdünnt wird. So werden beispielsweise bis zu 500 TU im Oberflächenwasser an der Station Wincheringen (Fluss-km 222) und bis zu 200 TU an der Station Koblenz (Fluss-km 1,2) gemessen.

Diese Tritiumvariationen im Oberflächen- und Niederschlagswasser lassen sich für eine Vielzahl von wissenschaftlichen Fragestellungen verwenden. Im Rahmen dieser Präsentation sollen einige Anwendungen vorgestellt und anhand dessen die Möglichkeiten der Nutzung von Tritium als aquatischer Tracer auch heutzutage skizziert werden.

Tritium in der südlichen Nordsee: ein Tracer für lokal gebildeten Wasserdampf

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Weltweit wurden ab Beginn der Wasserstoffbombentests Tritium-Konzentrationen im Niederschlag aufgezeichnet.

Das Global Network of Isotopes in Precipitation (GNIP) wurde 1958 von der IAEA und der WMO gegründet und ging 1961 in Betrieb. Seit dieser Zeit nahm die Anzahl der durchgeführten Analysen kontinuierlich ab. In der südlichen Hemisphäre und auch in tropischen und subtropischen Regionen der Nordhemisphäre verringerten sich Tritiumkonzentrationen bis heute auf Werte, die der Grenze der technisch möglichen Auslösung mit Szintillationszählern entsprechen. Die Bedeutung der Messwerte aus diesen Regionen nahm daher stark ab und Messprogramme wurden eingestellt.

Das Bundesamt für Gewässerkunde (BfG) misst Tritium im Niederschlag als Monatsmittel aus fast zwei Dutzend Orten

in Deutschland. Diese Datenreihen und deren Besonderheiten werden mit Tritium im Niederschlag in der deutschen Küstenregion der Nordsee verglichen.

Merkmale, Besonderheiten:

1. Unterschiede zwischen Maximum Konzentration im Sommer und Minimum Konzentrationen im Winter geben Hinweise auf Zumischung von Wasserdampf mit geringen Tritiumkonzentrationen aus dem Ozean während eines Jahres.
2. Identifizierung der Variation der natürlichen atmosphärischen Tritium Produktionsrate aufgrund der Änderung des solaren Partikelstroms.
3. Beitrag von lokalen Wasserdampfquellen am Niederschlagswasser.
4. Abnahme des anthropogenen Tritiumbeitrags: sind historische Messungen des natürlichen Tritiums plausibel?
5. Wie verlässlich sind gemessene Tritiumkonzentrationen im Niederschlag für die Rekonstruktion des zurückliegenden Tritiumeintrags in das Grundwasser?

Es werden Tritiumkonzentrationen im Niederschlag der Stationen des BfG mit Tritiumkonzentrationen im Grundwasser nahe der Deutschen Bucht verglichen.

Messungen von Tritium im Oberflächenwasser der Nordsee zeigen einen starken Anstieg der Werte seit Mitte der 1990er Jahre. Zu dieser Zeit stiegen die Tritiumemissionen der Wiederaufbereitungsanlage in LaHague massiv.

Die Regensammler Station in Cuxhaven zeigt bis 1990 Tritiumwerte unterhalb anderer Stationen in Deutschland. Nach 2000 liegen die Werte aus Cuxhaven aber immer oberhalb der Werte anderer Stationen. Auch Grundwasserproben von den Ostfriesischen Inseln und nahe der Nordseeküste in Schleswig-Holsteins datiert auf Neubildungszeiten nach 2000 weisen deutlich höhere Tritiumkonzentrationen als der deutschlandweite Mittelwert der Niederschläge auf.

In der Nordsee zeigt sich die Ausbreitung von Tritium aus LaHague im östlich strömenden Küstenrandstrom und beschränkt damit räumlich die Region in der tritiumreicher Wasserdampf gebildet werden kann.

Distribution of young groundwater in the North German Basin

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The Federal Institute for Geosciences and Natural Resources (BGR) is currently collecting all available groundwater age

data on the territory of the Federal Republic of Germany. The background to this is that the German Site Selection Act for radioactive waste disposal sites defines groundwater age as an exclusion criterion. If young groundwater is detected in the vicinity of potential host formations, these sites must be excluded as a repository for high-level radioactive waste. In the by-laws, detectable concentrations of tritium (^3H) and carbon-14 (^{14}C) are specifically mentioned as indicators for young groundwater.

Groundwater ages also can be used for many other scientific questions, e.g. for studies on the transport of pollutants, such as nitrate and pesticides, for groundwater recharge estimations and for the calibration of regional groundwater models.

In addition to the collection of data, which will be archived in a publicly accessible database, the project will investigate the influence of various parameters on the determination of groundwater age, e.g. the screen length and the recharge rate and the distribution of young groundwater in the various hydrogeological units.

In the presentation, a short introduction to the database will be given and the first results on the spatial distribution will be shown. In addition, the first statistical evaluations on the depth-specific distribution of young groundwater in the North German Basin will be presented.

Stable isotope patterns of German rivers with aspects of scales and continuity

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The stable isotope composition of river water (^2H , ^{18}O) in large basins mainly reflect precipitation, snow-melt or ice-melt inputs and modifications due to surface storage, mixing and contributions of time delayed groundwater components. Continuous observations of river water stable isotope patterns in high-resolution of time and space serve as characteristic fingerprints for specific locations or whole river basins. In Germany, river monitoring for radioactive isotopes started in the mid 1970s organized by the Federal Institute of Hydrology (BfG). Today a monitoring network for stable isotopes at 50 stations in monthly resolution is available [1, 2, 3] as part of the monitoring program of the BfG. The time series for stable isotopes are longer than three

years and for some stations of up to 30 years. Additionally, daily river water samples were collected during the extraordinary dry autumn in October 2018 until January 2019 at six selected stations in the Rhine and five stations in the Elbe basin.

Most dominating stable isotope effects in river water are those of seasonality and altitudes, but also a continental effect is visible from $\delta^{18}\text{O}$ vs. $\delta^2\text{H}$ plots. Snow and ice-melt contribution in the Rhine and Danube during the summer months and a consecutive dilution of these signals by tributary rivers is visible. Close to the coasts in northern Germany, stable isotope patterns reflect influence of seawater and tides. Daily patterns during the dry season 2018/2019 do surprisingly not exhibit extreme changes but rather trends on enhanced groundwater contribution. Comparing German river basins of different sizes and mean catchment altitude reveal influences of scales. Long time series allows a discussion of the challenge to collect continuous data, but also uncertainties of measurements and the need for laboratory inter-comparisons.

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Very high resolution Automated Rain Water Sampler for stable water isotope monitoring

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With changing climate, increasing world population, the linked shortage of resources and pollution of the environment necessitates adequate tools and technics to monitor the Earth's system. Measuring isotope ratios and trace elements dissolved in rainwater are useful utensils to understand the system and trace sources and pathways as well as to examine the timescales of transport of rainwater. Yet, it is very difficult to track, trace and measure rainwater pathways over landscapes and oceans. In particular, sampling and sample preservation is notoriously difficult and, in many cases, very laborious in manpower and technical demanding. Comprehensive and automated monitoring of precipitation waters

in space and time can improve our process understanding to better predict the nature and magnitude of future hydrometeorological changes. Today, no commercial, and only a few research level, automated sampling devices for rainwater exist. However, no existing sampling technology fulfills the quality criteria for sophisticated hydro-chemical rainwater analysis in particular in remote areas over long time periods.

Facing this lack of high-quality technical solutions, we present a newly developed automatic and autonomous precipitation water sampler for stable water isotope analysis of rainwater. Our autosampler can take 165 discrete rainwater samples with a minimum time resolution of 5 min or volume wise 2 mm of rainfall. The device is designed to be highly autonomous and robust for long-term deployment in harsh and remote areas and fulfills the high demands on sampling and storage for isotope analysis (i.e. sealing of samples from atmospheric influences, no contamination and preservation of the sample material). The sampling device is portable, has low power consumption, is remotely accessible and thus has a real-time adaptable sampling protocol strategy, and can be maintained at distance without any need to visit the location.

The device was tested in several evaluation and benchmarking cycles. First lab tests with dyed waters and waters with strongly differing isotopic signature demonstrate that the device can obtain, store and conserve samples without cross contamination over long periods of time. The device has been tested so far under several conditions, e.g. heavy summer thunderstorms with more than 50 mm/24 h of rainfall, sustained winter rainfall and in cold conditions involving melting of snow. Furthermore, we run a benchmark test with several devices in parallel. Finally, in October 2020, we had installed six devices, in collaboration with Germany's National Meteorological Service (Deutscher Wetterdienst DWD), in a South-West to North-East transect across the Harz mountains in Germany.

This automated rainwater sampler provides a sophisticated technological solution for monitoring moisture pathways and water transfer processes with the analytical quality of laboratory standard measurements on a new level of temporal and spatial resolution.

GIN and beyond: Cumulative rain collectors for isotope studies in challenging climates

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Data on the isotopic composition of precipitation often represent a key component in isotope studies of the water cycle. For gathering the corresponding samples, various types of cumulative precipitation collectors are available. Among these samplers, the tube-dip-in-water collector with pressure equilibration tube (Gröning et al., 2012) is particularly popular, largely due to its simplicity and rather effective evaporation reduction (Michelsen et al., 2018).

In cool climates however, the use of this sampler can be challenging, because water may freeze inside the collection bottle and block the inlet tube (Gröning et al., 2012). Extended exposure to warm conditions can be problematic as well, particularly if the collected water volume is small compared to the size of the collection vessel (Michelsen et al., 2018).

Here, we outline a few simple designs, which can help to overcome the above-mentioned difficulties and may hence be useful in the German Isotope Network (GIN) and beyond.

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