

Lehrstuhl für Hydrogeologie Fakultät Bau Geo Umwelt Technische Universität München



ASI 2018

Jahrestagung

der Arbeitsgemeinschaft Stabile Isotope e.V.

30.September – 3. Oktober 2018

Technische Universität München

Tagungszentrum Raitenhaslach

BOOK OF ABSTRACTS

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Willkommen, liebe Teilnehmer der ASI-Tagung 2018 im TUM-Akademiezentrum Raitenhaslach,

Wir freuen uns, Sie zu unserer Jahrestagung der Arbeitsgemeinschaft Stabile Isotope – ASI 2018 – begrüßen zu dürfen, die dieses Jahr im TUM Akademiezentrum Raitenhaslach stattfindet.

Das Akademiezentrum befindet sich im Südosten Bayerns, etwa 120 km von München. Das ehemalige Zisterzienserkloster wurde nach längeren Umbauarbeiten im Juni 2016 feierlich eröffnet. Auf rund 1.000 Quadratmetern bietet das Zentrum Wissenschaftlerinnen und Wissenschaftlern und den Mitarbeitenden und Studierenden der TUM unter anderem, Seminarräume, einen großen Gewölbesaal für die Ausrichtung von Tagungen und Studierzimmer. Deshalb freuen wir uns, dass das Akademiezentrum der TUM mit seinem historischen Charme uns die Möglichkeit bietet, die ASI-Tagung 2018 in diesen Räumen ausrichten und das Zentrum zum wissenschaftlichen Austausch nutzen zu können.

Ich wünsche uns und Ihnen eine interessante Veranstaltung, an deren Ende hoffentlich nicht nur Antworten, sondern auch neue wissenschaftliche Fragen stehen werden. Dadurch wird das Thema, insbesondere das der Isotopenhydrogeologie lebendig gehalten und verbessert die Chance u.a. auch unser Ökosystem "Grundwasser" besser zu verstehen.

Vielen Dank!

Florian Einsiedl

TUM München, Lehrstuhl für Hydrogeologie

Paul Königer, Michael Zech, Markus Greule

Vorstand der ASI

Leitung/ Wissenschaftliches Komitee

Tagungsleitung	Wissenschaftliches Komitee		
Prof. Dr. Florian Einsiedl, TU München	Prof. Dr. Karl Auerswald, TU München (Boden)		
Lakalaa Organiaatianakamitaa	Prof. Dr. Michael Böttcher, IOW (Klima)		
Lokales Organisationskomitee	Prof. Dr. Florian Einsiedl, TU München		
Christine Englmann	(Hydro)		
Fatemeh Shajari	Prof. Dr. Martin Elsner, TU München (Physiologie & Metabolismus)		
Florian Heine	Prof. Dr. Frank Keppler, Univ. Heidel- berg (Physiologie & Metabolismus)		
Sebastian Holzapfel			
Alejandra Peña	Dr. Paul Königer, BGR (Messtechnik)		
Lisa Wild	Dr. Christoph Mayr, FAU (Klima)		
Dr. Michael Zech	Prof. Dr. Bernhard Mayer, Univ. of Cal-		
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	Prof. Dr. Doerthe Tetzlaff, IGB (Hydro)		
	Dr. Arno Rein, TU München (Boden)		
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Thermo Fisher Scientific lädt am

Montag 19:30 im Hotel Glöcklhofer zu einem User Meeting ein

Programm

Uhrzeit	Sonntag 30.9.	Montag 1.10.	Dienstag 2.10.	Mittwoch 3.10.	Uhrzeit
09:00		Firmenpräsentationen		Klimaforschung und	09:00
09:30		/-vorträge/-tutorials	Hydrogeologie einschließlich Tiefengrundwässer	Stoffkreisläufe	09:30
10:00					10:00
10:30			Kaffeepause	Postersession mit Kaffee	10:30
11:00	1		Hydrologie und Hydrogeologie		11:00
11:30	1		einschließlich	Physiologie und Metabolismus	11:30
12:00	1	Eröffnung der Tagung	Liefendrundwasser		12:00
12:30	-	Analytik, Methoden,	Gemeinsames	Schlussworte/Preise	12:30
13:00	1	Techniken und Qualitätssicherung	Mittagessen		13:00
13:30		J. J			13:30
14:00	PhD Workshop	Postersession mit	Boden-Pflanzen-		14:00
14:30	Impulsreferate von	Kaffee	Atmosphäre		14:30
15:00	Dozenten (15-25 min) und Kurzvorträge der Teilnehmer/innen zu				15:00
15:30					15:30
16:00	laufenden und geplanten Projekten	Analytik, Methoden,			16:00
16:30	(ca. 10 min +	Techniken und Qualitätssicherung	ASI-Mitglieder-		16:30
17:00	Diskussion)		Versammlung		17:00
17:30		Lebensmittel, Forensik, Doping			17:30
18:00					18:00
18:30					18:30
19:00					19:00
19:30			Conference Dinner		19:30
20:00					20:00
20:30					20:30
21:00	1				21:00
21:30	1				21:30
22:00	1				22:00
22:30	1				22:30
23:00	1				23:00



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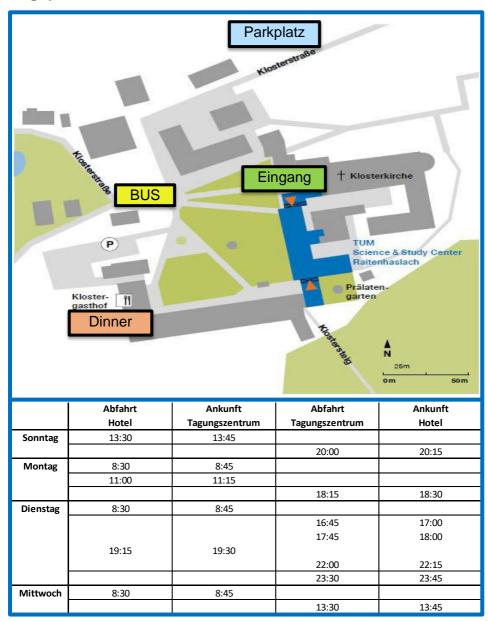
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Lageplan/Hotel-Bus-Shuttle



Wissenschaftliches Programm

Sonntag:

14:00-18:00 PhD Workshop

Impulsreferate von Dozenten (15-25 min) und Kurzvorträge der Teilnehmer/innen zu laufenden und geplanten Projekten (ca. 10 min + Diskussion)

Montag:

9:00-11:00 Firmenpräsentationen und Workshops

Raum A108:

9:00 Continuous stable isotope measurements with Cavity Ring-Down Spectroscopy. (Umwelt-Geräte-Technik GmbH)

9:20 Recent advances in bulk and compound specific IRMS measurements (Sercon Limited)

9:40 Calibration mixtures for improving accuracy of stable isotope measurement (Air Liquide)

10:00 Datenanalyse & Datenmanagement leicht gemacht - Standardisierung, grafische Darstellung, statistische Auswertung und arbeitsgruppenübergreifende Zusammenarbeit (Elementar Analysensysteme GmbH)

Raum A122:

10:00 Thermo Fisher Scientific Workshop

12:00 Begrüßung, Eröffnung der Tagung

12:30 Session 1: Analytik, Methoden, Techniken und Qualitätssicherung (1/2)

12:30 (#105) Clumped isotopes of nitrous oxide by mid-IR laser spectroscopy Kantnerová, Kristýna

12:50 (#139) Comparison of N2O isotope spectrometers for high-precision measurements in ambient air and incubation experiments

Mohn, Joachim

13:10 (#125) Development of international N2O reference materials for site preference measurements

Eggleston, Sarah

13:30 (#154) Measurement of challenging matrixes using the IsoFLOW headspace analyser

Volders, Filip

13:50 (#131) Utilizing Chromatographic Principles for High Sensitivity Isotope Ratio MS

Hilkert, Andreas

14:10 Postersession und Kaffee

16:00 Session 1: Analytik, Methoden, Techniken und Qualitätssicherung (2/2)

16:00 (#148) Methyl sulfates as methoxyl isotopic reference materials for $\delta 13C$ and $\delta 2H$ measurements

Greule, Markus

16:20 (#147) Improvements in sensitivity in IRMS measurements Atkinson, Helen

16:40 Session 2: Lebensmittel, Forensik, Doping

16:40 (#161) Stable hydrogen isotopes as a world forensic tool: Potential and pitfalls Voigt, Christian

17:00 (#104) Potential of multi-dimensional stable isotope fingerprinting for forensic identification of the organophosphorus pesticide chlorpyrifos

Kümmel, Steffen

17:20 (#130) Can mechanistic water isotope models predict the geographic origin of fruits?

Cueni, Florian

Dienstag:

9:00 Session 3: Hydrologie und Hydrogeologie inkl. Tiefengrundwässer (1/2)

9:00 (#101) Isotope im Niederschlag – Indikatoren für Herkunft und Prozesse Weise, Stephan M.

9:20 (#109) Integrated altitude isotope effects in rivers of high-relief terrains: A correction method to identify water recharge altitudes

Juhlke, T.R.

9:40 (#162) Integrative isotope techniques to evaluate the fate and transport of nitrogen in the Erlauf River catchment, Austria

Bujak, Izabela

10:00 (#149) Tomography of anthropogenic nitrate contribution along the Holtemme River, Germany

Müller, Christin

10:20 Kaffeepause

10:50 Session 3: Hydrologie und Hydrogeologie inkl. Tiefengrundwässer (2/2)

10:50 (#159) Beiträge zur Stickstoffdynamik im landwirtschaftlich und urban belasteten und als Trinkwasserressource genutzten Tai See, China - Einsichten aus geochemischen Analysen und Messungen stabiler Isotope

Wilhelms, Andre

11:10 (#126) Determining uncertainties of δ 15N-nitrate interpretation in groundwater with the use of Monte Carlo simulations

Wild, Lisa

11:30 (#136) A new approach of groundwater dating using dissolved organic radiocarbon (DOC) in a carbonate aquifer in the Bavarian Molasse Basin Heine, Florian

11:50 (#150) Isotopic approaches to assess potential impacts from shale gas development on shallow groundwater

Mayer, Bernhard

12:10 (#111) Isotope evidence for methane formation from cyanobacteria Klintzsch, Thomas

12:30 Gemeinsames Mittagessen

14:00 Session 4: Boden-Pflanzen-Atmosphäre

14:00 (#135) Foliar water uptake, the way to grow for Avicennia marina (Forsk.) Vierh.

Schreel, Jeroen

14:20 (#170) Measured and modeled xylem-sap isotopic composition in tree stems with a borehole-equilibration technique

Marshall, John

14:40 (#157) Variability in xylem water isotopic signature triggers incorrect assessment of root water uptake depth

De Deurwaerder, Hannes

15:00 (#158) Water use strategies of mature beeches – a comparison of pure and mixed stands

Magh, Ruth-Kristina

15:20 (#143) Nutrient addition changes water and carbon fluxes through biodiversity effects: partitioning evapotranspiration and net ecosystem exchange Kübert, Angelika

15:40 (#117) Is cheating on fungal partners among plants much more widespread? New insights for partial mycoheterotrophy in arbuscular mycorrhizae.

Giesemann, Philipp

16:00 (#116) Ecohydrological soil-plant feedbacks: a pool-weighted perspective on the two-water-worlds hypothesis

Dubbert, Maren

16:30 ASI Mitgliederversammlung

19:30 Konferenz-Abendessen

Mittwoch:

9:00 Session 5: Klimaforschung und Stoffkreisläufe

9:00 (#138) Intramolecular stable isotope variation: New ecophysiological signals, and consequences for isotope-based biogeochemistry

Schleucher, Jürgen

9:20 (#129) Interpretation of compound-specific δ 2H and δ 18O results from n-alkane and sugar biomarkers derived from Late Glacial to Early Holocene Lake Bergsee sediments

Hepp, Johannes

9:40 (#115) Simulating the isotopic composition of terrestrial N cycle components with the Stable Isotope MOdel for Nutrient cyclEs (SIMONE)

Denk, Tobias

10:00 (#132) Radiocarbon chronology and paleoclimate reconstruction based on coupled δ 2H/ δ 18O biomarker analyses of lacustrine sediments from Garba Guracha, Bale Mountains, Ethiopia

Bittner, Lucas

10:20 Postersession und Kaffee

11:20 Session 6: Physiologie und Metabolismus

11:20 (#112) The Effect of Parasite Infection on Stable Isotope Turnover Rates in Multiple Tissues of Eurasian Perch from Bodensee

Yohannes, Elizabeth

11:40 (#145) Compound-specific stable-isotope analysis for investigating bioavailability limitation of micro- pollutants in 2D flow-through tank experiments Sun, Fengchao

12:00 (#160) Heterotrophic 13CO2-Fixation – New insights to microbial DOC utilisation from stable isotope labelling?

Spona-Friedl, Marina

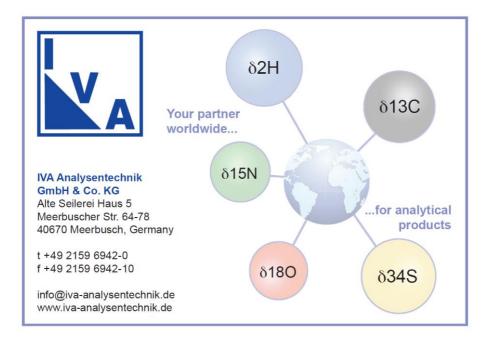
12:20 (#133) Bioavailability limitation influences the maintenance demand and physiology of Arthrobacter aurescens TC1 defining a limit of atrazine degradation at low concentrations

Kundu, Kankana

12:40 (#167) Measurement of albumin synthesis in endotoxemic pigs exposed to deoxynivalenol (DON) by using L-[2H5]-phenylalanine as tracer

t.b.a.

13:00 Abschlussworte, Preisverleihungen





Vorträge und Poster:

Session 1: Analytik, Methoden, Techniken und Qualitätssicherung

ID: 105 Vortrag Themen: Analytik, Methoden, Techniken und Qualitätssicherung

Clumped isotopes of nitrous oxide by mid-IR laser spectroscopy

<u>Kristýna Kantnerová</u>^{1,2}, Béla Tuzson¹, Lukas Emmenegger¹, Stefano M. Bernasconi², Joachim Mohn¹

¹Empa, Laboratory for Air Pollution / Environmental Technology, CH-8600 Dübendorf, Switzerland; ²ETH, Geological Institute, CH-8092 Zürich, Switzerland

For many years, nitrous oxide (N₂O) has been a major focus of greenhouse gas accounting agreements. Understanding the mechanisms of its formation and clarifying its sources and sinks is highly important for mitigating N₂O emissions. Measuring the doubly substituted "clumped" isotopocules of N₂O will add new and unique opportunities to fingerprint and constrain the biogeochemical cycle of this important greenhouse gas.^{1, 2}

Mid-IR spectroscopy is a highly attractive technique to analyze N₂O isotopocules based on their specific ro-vibrational absorption characteristics. We are developing an analytical technique for the selective and precise analysis of the most abundant clumped N₂O isotopic species $^{15}N^{14}N^{18}O$, $^{14}N^{18}O$, and $^{15}N^{16}O$. The measurement setup is based on a dual quantum cascade laser absorption spectrometer (QCLAS) with a multi-pass absorption cell. Under optimal measurement conditions, the instrument reaches precision levels of 0.1 ‰ for all isotope ratios.

As reference gases for clumped N₂O isotopes are not commercially available, we are currently elaborating strategies for a reference frame linking clumped N₂O measurements to stochastic distribution.³ Equilibration of the N–O bond has been achieved by heating N₂O over activated Al₂O₃ at different temperatures (100 – 200°C). We demonstrate that QCLAS technique using this reference frame is a very promising alternative to currently emerging high-resolution mass spectrometric approaches⁴ regarding ease-of-use, field deployability, sample throughput, precision, and its inherent selectivity for the clumped isotopomers ¹⁵N¹⁴N¹⁸O and ¹⁴N¹⁵N¹⁸O. In summary, this novel technique can offer a broad range of prospective applications from the biogeochemical N₂O cycle to stratospheric chemistry or industrial catalytic processes.

References

(1) J. A. Schmidt et al., Clumped isotope perturbation in tropospheric nitrous oxide from stratospheric photolysis, *Geophys. Res. Lett.* 42, 2015.

(2) J. Kaiser et al., Assessment of $^{15}N^{15}N^{16}O$ as a tracer of stratospheric processes, Geophys. Res. Lett. 30, 2003.

(3) Z. Wang et al., Equilibrium thermodynamics of multiply substituted isotopologues of molecular gases, *Geochim. Cosmochim. Acta* 68, 2004.

(4) P. M. Magyar et al.: Measurement of rare isotopologues of nitrous oxide by high-resolution multi-collector mass spectrometry, *Rapid Commun. Mass Spectrom.* 30, 2016.

ID: 139

Vortrag

Themen: Analytik, Methoden, Techniken und Qualitätssicherung

Comparison of N_2O isotope spectrometers for high-precision measurements in ambient air and incubation experiments

Stephen Harris^{1,2}, Jesper Liisberg³, Benjamin Wolf⁴, Longlong Xia⁴, Longfei Yu⁵, Jing Wei⁵, Bryce Kelly¹, Thomas Blunier³, <u>Joachim Mohn⁵</u>

¹UNSW Sydney, School of Biological, Earth and Environmental Sciences, Sydney, Australia; ²Australian Nuclear Science and Technology Organisation, Lucas Heights, Australia; ³University of Copenhagen, Centre for Ice and Climate, Niels Bohr Institute, Copenhagen, Denmark; ⁴Karlsruhe Institute of Technology, IMK-IFU, Garmisch-Partenkirchen, Germany; ⁵Empa, Laboratory for Air Pollution/Environmental Technology, Dübendorf, Switzerland

Over the last two decades, research involving N₂O site specific isotopic analysis has been stimulated by continuing analytical progress in isotope-ratio mass-spectrometry (IRMS) and more recently mid-infrared laser spectroscopy. This development has been triggered by the invention and availability of quantum cascade lasers (QCL), which offer high optical power in continuous wave operation at room temperature. QCL light sources have been combined with different detection schemes such as direct absorption (QCLAS), cavity ring down (CRDS) and off-axis integrated cavity output (OA-ICOS) to realize compact, field-deployable analyzers.

The availability of temporal resolved N₂O isotopic information in real-time will deepen our process-level understanding of the nitrogen cycle. It will also open up entirely new research areas that will attract an increasing number of application-oriented scientists. Provided that the novel laser spectrometers produce compatible and thus accurate results (i.e. traceable to the international isotope ratio scales, AIR-N₂ for ¹⁵N/¹⁴N and VSMOW for ¹⁸O/¹⁶O), the implementation of these instruments will lead to a further dissemination of N₂O isotopic research.

We will present results of an inter-comparison study on the three most common commercial N₂O isotope analyzers, including Aerodyne Research (dual QCLAS, with/without TREX), Picarro (G5131-i) and Los Gatos Research (Model 914-0027). Most importantly, gas matrix effects were investigated by determining the dependence of N₂O isotope deltas on the analysis in an "ambient" N₂/O₂/Ar/CO₂/CH₄/CO versus a simplified N₂/O₂/Ar or N₂/O₂ matrix. In addition, spectral interferences of enhanced trace gas concentrations (CO₂, CH₄, CO, H₂O) were characterized and strategies for removal tested. Short-term and long-term repeatability, drift and dependence of isotope deltas on N₂O concentrations were also quantified and compared among instruments. Based on these results a calibration strategy was established and the accuracy of individual analyzers assessed combining the studied uncertainty contributions.

Our study will guide the selection of instruments for specific applications (e.g. ambient air versus incubation studies), and foster the development of N_2O isotope reference gases optimized for laser spectrometers currently ongoing within the EMPIR project "Metrology for Stable Isotope Reference Standards (SIRS)".

ID: 125

Vortrag

Themen: Analytik, Methoden, Techniken und Qualitätssicherung

Development of international N_2O reference materials for site preference measurements

Sarah Eggleston¹, Sakae Toyoda², Heiko Moossen³, Christina Biasi⁴, Longfei Yu¹, Naohiro Yoshida^{2,5}, Paul Brewer⁶, Joachim Mohn¹

¹Empa, Laboratory for Air Pollution / Environmental Technology, 8600 Dübendorf, Switzerland; ²Department of Chemical Science and Engineering, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, 226-8502, Japan; ³Max-Planck-Institute for Biogeochemistry (MPI-BGC), Stable Isotope Laboratory (IsoLab), 07745 Jena, Germany; ⁴University of Eastern Finland, Biogeochemistry Research Group, 70211 Kuopio, Finland; ⁵Earth-Life Science Institute, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo, 152-8550, Japan; ⁶National Physical Laboratory, Gas and Particle Metrology, Teddington, TW11 0LW, UK

Nitrous oxide (N₂O) is one of the most important greenhouse gases in the Earth's atmosphere today, as well as a strong stratospheric ozone-depleting gas. The concentration of N₂O has been rising since the Industrial Revolution due to changes in many of its sources, both natural and anthropogenic. Measurements of the four most abundant stable isotopologues of N₂O ($^{14}N^{14}N^{16}O$, $^{15}N^{14}N^{16}O$, $^{14}N^{15}O$, and $^{14}N^{14}N^{18}O$) can provide a valuable constraint on source attribution of atmospheric N₂O.

Recent advancements in Optical Isotope Ratio Spectroscopy (OIRS) allow for specific and high precision analysis of ^{15}N substitution in the central (a) and terminal (b) nitrogen positions and thus ^{15}N site preference (SP= $\delta^{15}N^{\alpha}$ - $\delta^{15}N^{\beta}$) in N_2O. Commercial OIRS analyzers are becoming increasingly available, complementing well-established Isotope Ratio Mass Spectrometry (IRMS); however, to date, no international standards with stated uncertainty exist that link $\delta^{15}N^{\alpha}$ and $\delta^{15}N^{\beta}$ to the AIR-N_2 isotopic scale. In addition, calibration of OIRS analyzers requires N_2O isotope standards in whole air at ambient amount fractions, to account for gas matrix effects and spectral interferences.

Within the framework of the EMPIR project "Metrology for Stable Isotope Reference Standards (SIRS)," we aim to develop such standards to be made available to the global community. These will be gaseous standards available as pure N₂O or N₂O diluted in whole air. To tie the $\delta^{15}N^{\alpha}$ and $\delta^{15}N^{\beta}$ values to the AIR-N₂ scale, we are synthesizing NH₄NO₃ salts with a range of $\delta^{15}N$ -NO₃ and $\delta^{15}N$ -NH₄ values, each of which will be determined precisely by an international group of laboratories. Each salt will then be thermally decomposed to achieve a quantitative conversion of NH₄NO₃ to N₂O, thus providing several tie-points directly to the internationally accepted AIR-N₂ isotope scale.

Here, we present the details of this aspect of the EMPIR project and specifically the methods described above.

ID: 154 Vortrag Themen: Analytik, Methoden, Techniken und Qualitätssicherung

Measurement of challenging matrixes using the IsoFLOW headspace analyser <u>Filip Volders¹</u>, Lutz Lange¹, Sam Barker², Mike Seed²

¹Elementar, Germany; ²Elementar, UK

The measurement of stable isotopes of challenging samples is made easy using the clean-up and sample processing capacity of the new isoFLOW sample preparation unit. The capability of the system to deal with any type of interference such as ethanol vapours of wines and spirits, as well as VOC's from fruit juices will be demonstrated. The analysis of headspace samples of nonpure carbonates poses a serious challenge and high precision analysis are really only achieved using dual inlet preparation of the samples. The isoFlow demonstrates a unique capacity to deliver near dual inlet performance using the automatic acidify and purification capabilities of the isoFLOW.

ID: 131 Vortrag Themen: Analytik, Methoden, Techniken und Qualitätssicherung

Utilizing Chromatographic Principles for High Sensitivity Isotope Ratio MS

Andreas Hilkert, Oliver Kracht, Christopher Brodie, Dieter Juchelka, Mario Tuthorn

Thermo Fisher Scientific (Bremen) GmbH, Germany

Gas chromatography is a widely-used analytical technique with a great perspective of dramatically reducing both analysis time and the amount of material required for isotope analysis. Applying GC to IRMS mainly relies on column temperature and column flow rate, specifically the optimization of these parameters. The high efficiency of analytical improvements which were recently conducted on the Thermo Scientific™ EA IsoLink™ and Thermo Scientific™ GC IsoLink II™ IRMS Systems demonstrates how chromatography based innovative features push research boundaries at new levels, broadening the available analytical window for biomarker analysis.

This presentation will focus on how continuous flow IRMS utilizes chromatographic principles to routinely increase the sensitivity. For EA-IRMS, we will focus on the analysis of small concentrations of carbon, nitrogen and sulphur and illustrate with data, how the EA-IRMS utilises chromatographic principles to routinely increase the sensitivity on NCS measurements. Especially, the data illustrates the analysis of nitrogen, carbon and sulfur concentrations of less than 5 μ g and on very high C/N and C/S ratio samples whilst delivering automated routine analysis. Examples of the gains in sulfur sensitivity from measurements of bone collagen and wood demonstrate that data precision is significantly better than 0.3‰.

Optimizing the chromatographic parameters within GC-IRMS has enabled high-precision isotopic analysis of picomoles of carbon in organic biomarkers (Baczynski et al., 2017). The narrowbore capillary GC column improves the resolving power whilst low volumetric flow rates increase the efficiency of sample transfer to the ion source, ultimately resulting in reduced sample size requirements for compound-specific carbon isotopic analysis by about two orders of magnitude.

References

Baczynski, A.A., Polissar P.J., Juchelka D., Johannes Schwieters J., Hilkert A., Summons R.E., Freeman K.H., 2018. Pico-CSIA: Picomolar Scale Compound-Specific Isotope Analyses. Rapid Communications in Mass Spectrometry 32, 730-738.

ID: 148

Vortrag

Themen: Analytik, Methoden, Techniken und Qualitätssicherung

Methyl sulfates as methoxyl isotopic reference materials for $\delta^{13}C$ and δ^2H measurements

Markus Greule¹, Heiko Moossen², Heike Geilmann², Willi Brand², Frank Keppler¹

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Markus Greule¹, Heiko Moossen², Heike Geilmann², Willi Brand², Frank Keppler^{1,3}

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³ Heidelberg Center for the Environment (HCE), Heidelberg University, D-69120 Heidelberg, Germany

Abstract

Stable hydrogen and carbon isotope values of methoxyl groups (OCH₃)of plant organic matter have large potential for applications in biogeochemical, atmospheric and food research. So far, most of the analyses of plant methoxyl groups by isotope ratio mass spectrometry were generated by using liquid iodomethane, a substance difficult to handle (carcinogen, high volatility, decomposition in presence of air), as the reference material to normalize stable isotope measurements of plant methoxyl groups to isotope– δ scales. However, comparison of measurements of stable hydrogen and carbon isotopes of plant methoxyl groups are hampered by the lack of proper reference materials. We have investigated two methyl sulfate salts (HUBG1 and HUBG2) which exclusively contain carbon and hydrogen from one methoxyl group for their suitability to be applied as methoxyl reference materials. Firstly, the stable hydrogen and carbon isotope values of the bulk compounds were calibrated/determined against international reference substances by elemental analyser isotope ratio mass spectrometry (EA-IRMS, MPI-BGC, Jena) and in a second step compared with measurements using gas chromatography isotope ratio mass spectrometry (GC-IRMS, Heidelberg University) where prior to analysis the methoxyl groups are transformed to gaseous iodomethane.

The results obtained by EA-IRMS (δ^2 H and δ^{13} C values: -144.4 ± 1.8 mUr and -50.19 ± 0.16 mUr (HUGB1); -104.3 ± 0.8 mUr and +1.55 ± 0.05 mUr (HUGB2)) were in good agreement with results measured by GC-IRMS (δ^2 H and δ^{13} C values: -143.2 ± 1.5 mUr and -47.73 ± 0.21 mUr (HUGB1); -102.5 ± 1.0 mUr and +4.42 ± 0.40 mUr (HUBG2)).

We suggest that both methyl sulfates can be applied as reference materials for normalization of isotope measurements of hydrogen and carbon of plant methoxyl groups to isotope– δ scales and for inter-laboratory calibration.

ID: 147

Vortrag Themen: Analytik, Methoden, Techniken und Qualitätssicherung

Improvements in sensitivity in IRMS measurements

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An increase in the sensitivity of isotope ratio mass spectrometers is required to meet the demands of researchers for smaller sample sizes, higher resolution sampling, and increased precision. C: N ratios, archaeological collagen samples, which have very small amounts of sulfur, trace gases of very low concentrations, tree ring samples, where the temporal resolution is limited by sample size, or compound specific measurements.

Following an analysis of the ion optics of the seron Nier-type electron impact ion source, we have made it clear that the area of ionization is matched with the area of beam extraction. We have thus improved the overall efficiency of the source and the improvements in sensitivity are significant. Isotope community across different scientific disciplines

Poster # 1 Poster Themen: Analytik, Methoden, Techniken und Qualitätssicherung

Praxiserfahrungen und Modifikationen bei der Niederschlagssammlung mit isotopentreuen Totalisatoren

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Am Institut für Grundwasserwirtschaft der TU Dresden besteht eine langjährige Erfahrung hinsichtlich der isotopentreuen Niederschlagssammlung zu Forschungszwecken (Burghardt et al., 2014). Hierbei wurde bis vor kurzem ausschließlich auf die von der IAEA beschriebene Methode eines Totalisators mit verdunstungshindernder Paraffin- bzw. Silikonölschicht in einer gläsernen Sammelflasche (IAEA, 2002) zurückgegriffen [Silikonöl-Sammler]. Neuerdings wurden weitere Regensammler als Nachbau des von Gröning et al. (2012) beschriebenen, öl-freien Sammlerprinzips [Wickelschlauch-Sammler] ausgeführt und an mehreren Standorten in Sachsen aufgestellt und betrieben; unter anderem auf dem hydrogeologischen Testfeld der TU Dresden in Pirna und im Botanischen Garten der TU Dresden.

An ersterem Standort wurde im Januar 2016 eine langfristig angelegte Messreihe begonnen; zunächst mit einem Silikonöl-Sammler, seit Oktober 2016 dann mit einem parallel betriebenen Wickelschlauch-Sammler. Der Vergleich beider Reihen, wie auch ein Vergleich der Sammlerkonzepte unter kontrollierten Bedingungen in einer Versuchshalle lassen auf Vorteile des Wickelschlauch-Sammlers hinsichtlich Signalstabilität und Handhabung schließen und bestätigen die Erkenntnisse von Gröning et al. (2012).

Eine weitere Messreihe wurde zu Beginn des Jahres 2017 im Botanischen Garten der TU Dresden mit einem Wickelschlauch-Sammler begonnen. Der Vergleich der gesammelten Niederschlagsmengen mit Daten der städtischen Wetterstation am selben Standort ließ allerdings auf frostbedingte Probenbeeinflussung schließen.

Das Unterbringen des Sammelbehälters in einer festen, beheizbaren Umhausung, wie von Stadler (2002) vorgeschlagen, wiederspricht jedoch der Einfachheit des Sammlerkonzepts. Daher wurde der Wickelschlauch-Sammler mittels Heizmatte, Thermostat und mobiler Stromquelle zu einer temporär beheizten Sammlereinheit [Heiz-Sammler] modifiziert und – leider erst gegen Ende des Winters 17/18 – auf dem Testfeld Pirna getestet. Erste Ergebnisse zeigen Abweichungen der Stabilisotopen-Signaturen bei Sammelperioden mit Frosteinfluss. Mit fortlaufenden Parallelmessungen im kommenden Winter soll die Leistungsfähigkeit des Sammlerprinzips daher weiter validiert werden.

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Poster # 2 Poster Themen: Analytik, Methoden, Techniken und Qualitätssicherung

Graphene-modified polymer monoliths for high throughput extraction of micropollutants for compound-specific isotope analysis

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Compound-specific isotope analysis (CSIA) has been demonstrated to be highly suitable for the evaluation of sources and transformation processes of micropollutants, such as pesticides and pharmaceuticals, in laboratory experiments during the last decade. However, analytical challenges associated with low micropollutant concentrations (sub-µg/L range) in environmental water samples still limit applicability of CSIA approach to field studies due to large volumes of water necessary for extraction. Although traditional solid-phase extraction techniques are available for enrichment of micropollutants, they fail in processing large volumes in feasible timescales due to limited flow rates (i.e. few mL/min). Therefore, a high throughput concept for extraction is needed. To this end, monolith affinity filters (MAF) offer a promising solution to process large volumes of water in reasonable time (i.e. up to 1000 mL/min). MAFs are epoxybased polymers prepared by self-polymerization of polyglycerol-3-glycidyl ether in organic solvent as porogens. A highly cross-linked structure with high porosity (79%) and large pores (i.e. from 15 to 25 µm) enables high throughput of liquid samples. In recent years, application of MAFs has been demonstrated for capturing bacteria. Nevertheless, a successful extension of the concept to organic micropollutants has not been realized. In this work, we explore the use of graphene-oxide to modify the MAFs surface chemistry in order to enable pi-pi electron donoracceptor interactions with the micropollutants.

Tailored-made MAFs were successfully synthesized using toluene and *tert*-butyl methyl ether as porogen with volume ratio of 3:2. Amine groups were immobilized onto the pore surface via the reaction of epoxide groups with the polyetheramine Jeffamine. Subsequently, graphene oxide (GO) was covalently attached by coupling the amine groups using dicyclohexylcarbodiimide as a coupling agent. Polymer monoliths functionalized with reduced graphene oxide (rGO) were then obtained via chemical reduction by ascorbic acid. Sorption performance of selected pesticides and metabolites, namely isoproturon, terbuthylazine, s-metolachlor, and 2,6dichlorobenzamide, has been assessed on GO-functionalized and rGO-functionalized polymers, as well as on bulk GO and rGO in batch experiments. Results reveal that rGO exhibits higher sorption capacity towards isoproturon, terbuthylazine, s-metolachlor by factors of 15, 8, 13, respectively. 2,6-dichlorobenzamide equally sorbed on GO and rGO. First results exhibit the suitability of rGO for modification of MAFs surface chemistry. Recovery efficiency of the sorbed analytes is being investigated for different eluent solvents. Optimization of operation parameters, including sample pH, volume, and flow rate as well as desorption volume and flow rate, will be evaluated on the base of analyte recoveries.

Poster # 3 Poster Themen: Analytik, Methoden, Techniken und Qualitätssicherung

Methodenvergleich zur Lagerung von Sekundärstandards für die Wasserisotopenanalytik

Diana Burghardt, Doreen Degenhardt

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Isotopenhydrologische Fragestellungen bilden einen wichtigen Forschungsschwerpunkt des Institutes für Grundwasserwirtschaft (IGW) der TU Dresden. Seit 2011 können die Stabilisotopenverhältnisse von Wasserproben im eigenen Labor des Institutes analysiert werden. Um die Bandbreite der in Europa vorkommenden Wässer analytisch abdecken zu können, wurden 2012 vier natürliche Wässer (drei Mineralwässer und ein Schnee-Schmelzwasser) als sekundäre Standards (Laborstandards) eingemessen. Seitdem werden sie für die Nutzung im Routinebetrieb in gasdichten Beuteln gelagert. 2017 wurde eine gezielte Versuchsreihe zur Prüfung der Stabilität der Stabilisotopenverhältnisse bei Lagerung in gasdichten Spritzen, Tropfflaschen und GC-Vials ergänzt.

Gegenstand dieses Tagungsbeitrages soll eine Aus- und Bewertung der verschiedenen Lagerungsmethoden für die Sekundärstandards sein, welche am IGW zur Kalibrierung der Stabilisotopenanalysen von Wasserproben Verwendung finden.

Poster # 4 Poster Themen: Analytik, Methoden, Techniken und Qualitätssicherung

Water-compatible molecularly-imprinted polymers enable C isotope analysis of glyphosate and AMPA in aquatic environments

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Glyphosate-based herbicides, known commercially as Roundup®, is the most widely applied herbicide in the world. Due to its increasing use as a non-selective broad-spectrum weed killer, its ubiquitous occurrence has been soaring in the environment including surface-, and ground-water. Hence, determination of their source and fate in contaminated environmental compartments is invaluable. Compound-specific isotope analysis (CSIA) of glyphosate and AMPA offers a powerful approach to track sources and transformation processes of the herbicide. While numerous studies report on sensitive but laborious analyses of glyphosate and AMPA, none of them are in fact suited for CSIA for environmental samples owing to (i) the zwitterionic nature of glyphosate and AMPA that renders its extraction from water not efficient on conventional solid phases, and consequently (ii) chemical modification of the analytes is often employed to enable extraction from water. Owing to introduction of additional carbon in the analytes structure, derivatized analytes remains an inevitable requirement for CSIA of glyphosate and AMPA at environmental concentrations of microgram per liter.

In this work, the selective enrichment of underivatized glyphosate and AMPA from environmental waters was developed using stoichiometric molecularly-imprinted polymers (MIP) based on ionic interactions of oxyanions with substituted urea monomers. Extraction was followed by concentration analysis on IC-ESI-MS/MS, as well as CSIA using liquid chromatography / isotope-ratio mass spectrometry (LC/IRMS) and flow injection analysis / isotope-ratio mass spectrometry (FIA/IRMS). Extraction efficiencies of the analytes from river-, creek-, and groundwater amounted to 94 ± 7, 97 ± 15, and 26 ± 5% for glyphosate, and to 92 ± 8, 105 ± 26, and 63 ± 7% for AMPA, respectively. Moreover, matrix effects associated with the use of MIP were investigated and found to be marginal on IC-ESI-MS/MS which ranged from -12 ± 2 to +7 ± 2% for glyphosate, and from +3 ± 0 to +6 ± 1% for AMPA. Measurements of δ^{13} C of glyphosate and AMPA over the developed analytical method demonstrate no significant deviations in δ^{13} C ($\Delta\delta^{13}$ C ≤ 1‰). These findings provide a simple analytical method suitable for both quantification and carbon isotope analysis. This work with the already existing lab-scale CSIA methods, enables investigation of source and fate of glyphosate and its metabolite AMPA on the field-scale.

Session 2: Lebensmittel, Forensik, Doping

ID: 161 Vortrag Themen: Analytik, Methoden, Techniken und Qualitätssicherung

Stable hydrogen isotopes as a world forensic tool: Potential and pitfalls Christian Voigt

Leibniz Institute for Zoo and Wildlife Research, Germany

Decades of research have used stable hydrogen isotopes to predict the geographic origin of products or animals, in particular for unravelling migration routes of birds and mammals. This approach is based on continent-wide patterns of stable hydrogen isotope ratios in precipitation water, so-called isoscapes; patterns that are mostly related to local precipitation intensity and ambient temperature. Here, I will summarize some of the recent advances and some pitfalls in using isoscapes for predicting the spatial origin of animals based on stable hydrogen isotope ratios in body products such as fur and feather keratin. A recently launched R-package, called IsoriX has facilitated the development of geographic assignment models, yet the guality of such models depends on various assumptions that quite often await a thorough validation. For example, reference points for precipitation stable hydrogen isotope ratios vary largely across continents, reflecting the spatial variation in international efforts to provide georeferenced values. Most importantly, reference points are coarsely distributed particularly at northern latitudes, where stable hydrogen isotopes in precipitation water are known to vary largely. Additionally, some continents such as Africa or Asia are still data deficient for stable hydrogen isotope ratios in precipitation water, which hamper a borader application of geographic assignments based on feather material from birds with an African or Asian wintering range. The quality of isoscape origin models depends largely on the accuracy and precision of so-called transfer functions. These transfer functions relate the stable hydrogen isotope ratios in keratin of animals of known location to those of local precipitation water. Larger efforts have to be undertaken to establish, guild-specific or even species-specific transfer functions for a larger variety of taxon. Despite these uncertainties, recent comparisons of the geographical origin of birds based on two independent measures, namely stable isotopes and geolocators, support an overall high quality of isoscape origin models. The recent launch of international standards for keratin stable hydrogen isotope ratios and the methodological breakthrough in measuring stable hydrogen isotope ratios independent of the adverse effects of ambient humidity will certainly promote a wider application of isoscape origin models beyond birds and mammals.

ID: 104 Vortrag Themen: Lebensmittel, Forensik, Doping

Potential of multi-dimensional stable isotope fingerprinting for forensic identification of the organophosphorus pesticide chlorpyrifos

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Organophosphorus pesticides (OPs) are a diverse family of pesticides that have been used since the 1940s. In contrast to organochlorine pesticides, OPs are less persistent and therefore applied worldwide. However, OPs such as the model compound chlorpyrifos are highly toxic, resulting in the inhibition of the neurotransmission in insects, animals and also humans. The high toxicity and presence of OPs in the environment is of great concern, as they have repeatedly been detected in soils, sediments, waterbodies, as well as within food and drinking water. Thus, tools are needed to understand sources, reactive transport pathways and sinks of OPs in the environment.

Stable isotope analysis has been proved as a valuable method for the detection of the origin of chemicals, as the isotopic profile reflects the isotopic composition of raw materials, synthetic pathways and purification processes. The aim of this study is to provide a database for the source identification of chlorpyrifos. For this reason, pure batches and commercial formulations of chlorpyrifos from more than 30 manufactures from India, China and Germany were collected and isotopically characterized using Elemental Analyzer – Isotope Ratio Mass Spectrometry (EA-IRMS) for analyzing the δ^{13} C, δ^2 H, δ^{18} O and δ^{15} N isotopic composition and Gas Chromatography – Multiple Collector – Inductively Coupled Plasma Mass Spectrometry (GC-MC-ICPMS) for determining the δ^{37} Cl isotopic signature.

The isotopic composition of analyzed chlorpyrifos samples varied from -31.9 \pm 0.1 ‰ to -24.1 \pm 0.1 ‰ for $\delta^{13}C$, -271.0 \pm 0.9 ‰ to -156.5 \pm 0.8 ‰ for $\delta^{2}H$, -0.9 \pm 0.1 ‰ to 24.6 \pm 0.1 ‰ for $\delta^{18}O$, -3.42 \pm 0.02 ‰ to -0.04 \pm 0.03 ‰ for $\delta^{15}N$ and -1.29 \pm 0.15 ‰ to 3.08 \pm 0.21 ‰ for $\delta^{37}C$ I. Taking the typical uncertainties of 0.5 ‰ for $\delta^{13}C$, 50 ‰ for $\delta^{2}H$, 0.5 ‰ for $\delta^{18}O$, 0.3 ‰ for $\delta^{15}N$ and 0.3 ‰ for $\delta^{37}C$ I into account the combination of different isotopic signatures give a unique fingerprint to track sources in the environment. Thus, this study highlights the potential of multi-dimensional stable isotope fingerprinting for identifying sources, and provides a database of the isotopic composition of chlorpyrifos that might improve the tracing of origin, transport pathways and the environmental fate of chlorpyrifos.

ID: 130 Vortrag Themen: Lebensmittel, Forensik, Doping

Can mechanistic water isotope models predict the geographic origin of fruits? <u>Florian Cueni¹</u>, Daniel Nelson¹, Markus Boner², Ansgar Kahmen¹

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Consumers are paying increasing attention to the geographic origin of agricultural products. Analytical tools that allow independent verification of the geographical origin of a product are thus in high demand for food quality control. Several descriptive tools using stable isotopes for origin analysis are used today, but these typically rely on time consuming and expensive collection of reference data sets, which also lack the capacity to account for interannual climate variability at a given location. In contrast, applications using mechanistic plant physiological water isotope (oxygen and/or hydrogen) models can potentially provide a faster, cheaper, and more adaptive way to predict the origin of agricultural products. Still, the implementation is complicated because such models require detailed knowledge of fractionation processes and water fluxes through a given agricultural crop. We are working to address these questions. Here we present results from experiments with raspberries and strawberries where we test if the Péclet-modified Craig Gordon model, that was originally developed for d2H and d18O values in leaf water can also predict the d2H and d18O values of water and carbohydrates in berries.

Sixty strawberry and sixty raspberry plants were grown in climate-controlled growth chambers at 30%, 50%, and 70% relative humidity, and plants were irrigated with water with a fixed isotope composition. These experimental conditions permit the direct comparison of fractionation steps for oxygen and hydrogen isotopes in leaf and berry water, oxygen isotopes in leaf and berry bulk material and cellulose, and hydrogen isotopes in leaf and berry lipids. Our results reveal that leaf and berry water has similar isotopic compositions. Thus, the Péclet-modified Craig-Gordon model that works well to predict the isotopic composition of leaf water, can also be used for berry water – but the Péclet effect needs to be adjusted. First results also suggest constant fractionation from leaf water to leaf bulk material independent of the humidity, with a slight difference between species (+20‰, SD \pm 1‰ raspberries; +18‰, SD \pm 0.7‰ strawberries). This suggests, that if the difference between leaves and berries can be quantified, modeled berry water isotope values and calibrated compound and species-specific fractionation factors may be capable of producing precise prediction models for samples of unknown origin.

Poster # 5 Poster Themen: Lebensmittel, Forensik, Doping

Determining the geographical origin of beer and its ingredients on regional scale

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The geographical origin of beers is becoming more and more important for consumers in Germany. Additionally, customers are willing to pay higher prices for products which they perceive to be produced from exclusively regional ingredients. However, with an increase in price, the chance of coming across a counterfeit or mislabelled product, wrongfully appearing to be of local origin rises. Therefore, it is crucial to establish methods that could distinguish whether foods are produced from regional ingredients or not. Carter *et al.* (2015) have already shown, that tracing the origin is possible on a global scale using, among other things, the oxygen and hydrogen isotopic composition of 162 beer samples. However, there is an urgent need for similar techniques on regional scale, especially in southern Germany where small scale breweries advertise with beers exclusively produced from local raw materials.

In my Master thesis, I am using a combined methodic approach to analyze around 125 beers and their ingredients, provided by breweries from all around Germany but mostly from the southern part of the country. Similar to Carter *et al.* (2015), we are using Isotopic Ratio Mass Spectrometry (IRMS) to determine the δ^{13} C, δ^{15} N, δ^{18} O, δ^{2} H ratios and Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) to determine the trace element composition of different beers and its ingredients. On the one hand the dry residue of the beers will be analyzed to investigate the sugar composition, crop mixture and consequently the type of beer and the origin of the crop. On the other hand, we will analyze the whole beer by ICP-OES to produce a trace-element fingerprint and detect if salts where added during brewing (Alcázar *et al.* 2012). The isotopic composition of the brewing water as well as the whole beer, will provide valuable information regarding the origin. Further, the δ^{13} C of CO₂ from carbonic acid will be measured to determine whether additional carbonic acid was added, which is against the german "Reinheitsgebot", a series of regulations limiting the ingredients in beer.

We are convinced, that this combination of methods will enable us to differentiate beers on a local scale, offering a powerful tool in the fight against mislabeled food stuffs.

Poster # 6 Poster Themen: Lebensmittel, Forensik, Doping

Stable isotope relationships between $\delta^2 H$ in collagen, $\delta^{18}O$ in apatite phosphate, and $\delta^{18}O$ in structural carbonate of modern human dentine

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Stable isotope analyses on different human tissues are used for provenancing of unknown individuals in forensics. Information about their location during childhood and youth can be obtained from teeth samples. The dentine of permanent teeth develops from the 4th to the 25th year of one's life. For determination of the whereabouts, C-N-S-H stable isotope signatures of dental collagen are assigned to geographical regions by using reference data from hair samples collected worldwide.

Additionally, the ¹⁸O content in tooth apatite can be used as a source of geographical information. Basically, hydrogen and oxygen isotope values in body tissues are linked to the δ^{18} O or δ^{2} H values of body water, which is connected to drinking water and food and predominantly contains information about the climate in the region of origin. δ^{18} O analyses can be performed on the apatite phosphate (δ^{18} O_p) or on the structural carbonate (δ^{18} O_c).

The relation of $\delta^{18}O$ values between apatite in enamel and drinking water for humans is well established, and for $\delta^{18}O_c$ and $\delta^{18}O_p$ in enamel of archaeological individuals a strong correlation could be documented. It can be reasonably considered that there a similar correlation for $\delta^{18}O_c$ and $\delta^{18}O_p$ in dentine exists.

29 tooth samples from modern humans were analysed for collagen $\delta^2 H$, $\delta^{18}O_p$, and $\delta^{18}O_c$ in dentine. The isotope results show a highly significant correlation between collagen $\delta^2 H$ and $\delta^{18}O_p$ as well as $\delta^{18}O_c$.values. Consequently, similar to the apatite $\delta^{18}O$ values, dental collagen $\delta^2 H$ values can be used as an indicator for the climatic condition at the individuals' whereabouts.

Poster # 7 Poster Themen: Lebensmittel, Forensik, Doping

Authenticity testing of cereals and related foodstuffs using IRMS and various spectral fingerprints – a work in progress

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Nowadays, a customer's purchase decision is drastically influenced by the authenticity of given food product. Parameters like traditional, organic and fair production as well as protected origin and high-quality varieties significantly gained in importance. At the same time, several food fraud scandals like the 2013 European horse meat scandal, have not only caused massive economical damage, they also led to a loss of consumer trust in the industry. As a reaction, the European parliament implemented an action plan and released a protocol (2013/2091 [INI]), naming cereals and related products at number five of the top ten foodstuffs that are most at risk of food fraud.

In present work, we want to present the AgrOr project, which was brought to life in 2017 in order to tackle the aforementioned issue. It aims to develop and combine scientific methods that enable the detection of varietal purity, cultivation method (e.g. organic or conventional), product quality and geographical origin of various cereals along the entire value chain including processed goods. To accomplish this task, we perform Raman spectroscopy, NIR, NMR and IRMS measurements of up to 1000 cereal samples per year and combine the data using multivariate statistics.

Preliminary results look very promising as we were able to correctly classify samples according to harvest year and cereal species (wheat, rye, spelt and barley). Consequently, we could successfully identify falsification of spelt flour with small amounts of cheaper wheat flour. Furthermore, we found good correlations between flour quality parameters from time consuming well-established traditional approaches and our data from modern techniques, which in future could act as an efficient replacement. Using IRMS, a first trend towards the differentiation between conventionally and organically produced samples could be observed, the latter often being enriched in ¹⁵N. Finally, we performed baking experiments, finding no significant fractionation in δ^{13} C, δ^{15} N or δ^{18} O between flour and respective baked product, potentially enabling traceability of raw materials. In general, classification in terms of geographical origin was already possible, however, the number of samples analysed up until now is too low for the creation of solid statistical models and valuable measurements of δ^2 H are pending.

In conclusion, we are convinced that with more samples, the addition of hydrogen isotope data and the effective linking of data, our multi-method approach provides the large number of parameters required to create an effective tool for authenticity testing of cereals and related foodstuffs. Poster # 8 Poster Themen: Lebensmittel, Forensik, Doping

The MK model – a user-friendly tool for predicting oxygen isotope composition in livestock

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Oxygen isotope composition (δ^{18} O) of body water or protein shows potential for tracing production systems even in animal products like milk. However, parameters influencing this value are difficult to investigate by controlled experiments due to fluctuating ambient conditions and due to the slow body water turnover that requires large amounts of isotopically constant diet (e.g. drinking water and feed moisture) to achieve equilibrium conditions. A mechanistic model (MK model) was developed as a promising assistant to predict environmental, physiological and animal management related influences on $\delta^{18}O$ of body water. A user-friendly spreadsheet calculator (MK calculator) allows running this model. Measured data of milk and hair were used for validation and showed a root mean squared error of 1.3 ‰ (n = 796) and a Nash-Sutcliffe modeling efficiency of 95%. Examples of application are divers like (1) evaluating the interaction of ambient conditions with feeding strategies: (2) investigating the influence of moisture contents in grass, grass silage, hay and concentrates; (3) predicting the influence of drinking water on body water depending on the feeding strategy; (4) assessing the half-life of body water depending on physiological state and ambient conditions. The MK calculator may be applied for a wide range of guestions related to δ^{18} O of body water like influences of animal behavior, of diseases, or of transhumance. The MK calculator is also easy to adapt to other animals than cows.

Session 3: Hydrologie und Hydrogeologie inkl. Tiefengrundwässer

ID: 101 Vortrag Themen: Hydrologie und Hydrogeologie einschließlich Tiefengrundwässer

Isotope im Niederschlag – Indikatoren für Herkunft und Prozesse Tobias Hartmann^{1,2}, Ronald Krieg¹, Jürgen Döring², <u>Stephan M. Weise¹</u>

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Das vom Harz ausgehende Einzugsgebiet der Bode überstreicht mit seinen ca. 3200 km² einen Höhenbereich von 1100 bis hinunter zu 55 m NHN. Seit Ende 2012 aufbauend wurden im Rahmen des TERENO-Forschungsprogramms monatliche Niederschlagsproben von 26 speziell konstruierten, verdunstungsarmen Sammlern entnommen und auf ihre Isotopenzusammensetzung (δ^2 H, δ^{18} O, in geringerem Umfang auch ³H) hin analysiert. Mit dem Code HYSPLIT wurde versucht, statistisch auffällige Messwerte mit besonderen Großwetterlagen zu korrelieren, was nur mit ³H-Werten gelang. Die aus den δ^2 H- und δ^{18} O-Werten erwartete Information über den Ursprung der Luftmassen scheint dagegen zu stark durch die lokalen Gegebenheiten wie Höhengradient und Luftfeuchte überprägt zu sein.

ID: 109

Vortrag

Themen: Hydrologie und Hydrogeologie einschließlich Tiefengrundwässer

Integrated altitude isotope effects in rivers of high-relief terrains: A correction method to identify water recharge altitudes

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Quantification of the isotope altitude effect from precipitation allows for identifying and outlining recharge areas in high-relief areas. This is primary importance for the future protection of spring water and groundwater resources. However, lacking isotope precipitation data, demanding logistics, and difficult maintenance of rain collectors in steep catchments frequently limit the possibility of this precipitation-based approach. Perennial rivers often provide easier, year-round access for water sampling and thus offer an easier straightforward option. A problem associated with the latter approach is that rivers in high-relief regions may not adequately represent regional precipitation isotope pattern because they integrate isotope signals from various subcatchments with variable height distributions along their course. This often results in local isotopic offsets between river water and precipitation and thus prevents the calculation of an altitudinal isotope gradient from river water samples. We present a study from the Tavignanu River catchment (Corsica, France) that shows how a river-based sampling approach served to estimate the altitude effect of precipitation after elevation-integrated area corrections were performed with geographic information system (GIS) tools. At first investigations river water samples unexpectedly showed increasing isotope values with increasing altitude in the upper reaches of the catchment. We refer to this inverse relationship as the apparent inverse altitude effect. When replacing the original sample site altitude by the mean upstream catchment elevation calculated from a digital elevation model allowed to establish a plausible altitude isotope effect from stream water. The results of this approach showed an average isotope altitude gradient of (-0.19 ± 0.02)‰ per 100 m elevation difference for δ^{18} O, which is in close agreement with published values for the region. We therefore propose that this correction method is able to overcome the problem of height integrated isotope signals in rivers in steep terrains. This approach can potentially be transferred to high relief terrains worldwide where precipitation sampling is difficult to realize.

ID: 162 Vortrag Themen: Hydrologie und Hydrogeologie einschließlich Tiefengrundwässer

Integrative isotope techniques to evaluate the fate and transport of nitrogen in the Erlauf River catchment, Austria

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In the last decades, the N-balance has been altered due to the extensive agricultural and urban development that resulted in raising N fluxes into surface and groundwater, deteriorating water quality, and eutrophication. A deep understanding of the interactions between sources, microbiological transformations processes and hydrological transport is crucial in predicting the effects of anthropogenic changes in the N-cycle on aquatic ecosystems. Former studies involving isotope techniques in catchment scale predominantly deduced information about the N sources and the N transformation processes by the analysis of nitrate concentrations and corresponding isotopic signatures (δ^{15} N, δ^{18} O), nevertheless, the origin and fate of N in a large and mesoscale river catchments characterized by mixed land use remains unclear. The appropriate nitrogen assessment and management is still challenging for water resource managers and policymakers.

The present study examines the Erlauf River catchment with an area of 525 km²in Alpine foothills in Austria. The catchment is characterized by a strong anthropogenic gradient from forest conservation areas in the mountain region to agricultural areas in the lowlands. The seasonal surface water monitoring programme was conducted from 2012 to 2017. The approach based on the combination of multi-isotope techniques ($\delta^{15}N_{NO3-}$, $\delta^{21}N_{OA3-}$, $\delta^{21}N_{O20-}$, $\delta^{34}S_{SO42-}$, $\delta^{18}O_{SO42-}$ and $\delta^{13}C_{DIC}$) with data on water chemistry, hydrological modelling, and Bayesian isotope mixing model (MixSIAR) was used to quantify the contribution of different N sources in stream water during contrasting hydrological conditions (base flow and high flow), and to address subsequent biogeochemical processes.

The results indicate that the combination of multi-isotope approach with hydrological modeling and probabilistic methods allow better quantification of large-scale N fluxes and estimation of the influence of different hydrological conditions on the N-cycling.

ID: 149

Vortrag

Themen: Hydrologie und Hydrogeologie einschließlich Tiefengrundwässer

Tomography of anthropogenic nitrate contribution along the Holtemme River, Germany

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Spatially and temporally variable and often superimposing processes like mobilization and turnover of N-species strongly affect nitrate fluxes at catchment outlets. It remains thus challenging to determine dominant nitrate sources to derive an effective river management. Here, we combine data sets from two spatially highly resolved key-date monitoring campaigns of nitrate fluxes along a mesoscale catchment in Germany with four years of monitoring data from two representative sites within the catchment. The study area is characterized by a strong land use gradient from pristine headwaters to lowland sub-catchments with intense agricultural land use and wastewater sources. Flow conditions were assessed by a hydrograph separation showing the clear dominance of base flow during both investigations. However, the absolute amounts of discharge differed significantly from each other (outlet: 1.42 m³ s⁻¹ versus 0.43 m³ s ¹). Nitrate concentration and flux in the headwater was found to be low. In contrast, nitrate loads further downstream originate from anthropogenic sources such as effluents from wastewater treatment plants (WWTP) and agricultural land use. The agricultural contribution did not vary in terms of nitrate concentration and isotopic signature between the years but in terms of flux. The contrasting amounts of discharge between the years led to a strongly increased relative wastewater contribution with decreasing discharge. This was mainly manifested in elevated δ^{18} O-NO₃ values downstream from the wastewater discharge. The four-year monitoring at two sides clearly indicates the chemostatic character of the agricultural N-source and its distinct, yet stable isotopic fingerprint. Denitrification was found to play no dominant role only for controlling nitrate loads in the river. The spatially highly resolved monitoring approach helped to accurately define hot spots of nitrate inputs into the stream while the long-term information allowed a classification of the results with respect to the seasonal N-dynamics in the catchment.

ID: 159 Vortrag

Themen: Hydrologie und Hydrogeologie einschließlich Tiefengrundwässer

Beiträge zur Stickstoffdynamik im landwirtschaftlich und urban belasteten und als Trinkwasserressource genutzten Tai See, China - Einsichten aus geochemischen Analysen und Messungen stabiler Isotope

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Der Taihu, der drittgrößte Süßwassersee Chinas, ist ein Flachwassersee mit einer relativ hohen Umsatzrate. Er liegt etwa 120 km westlich von Shanghai und versorgt mehr als 10 Millionen Menschen mit Trinkwasser. Die Folge des starken Bevölkerungswachstums in dieser Region ist ein hoher Nährstoffeintrag in den See, welcher wiederum zu einer starken Eutrophierung und Algenbildung führt. Dadurch ist die Wasserqualität sowie die Versorgung mit Trinkwasser erheblich gefährdet. An dieser Stelle setzt das seit April 2015 vom Bundesministerium für Bildung und Forschung (BMBF) im Rahmen des deutsch-chinesischen Forschungs- und Innovationsprogramms Clean Water geförderte Projekt SIGN-DYNAQUA "Von der Quelle bis zum Wassershahn" an. SIGN-DYNAQUA hat dabei das Ziel, die Wasserqualität des Sees und die Trinkwassersersorgung der Region sicherzustellen.

Ein Hauptziel der Arbeiten dieses Projekts ist die Identifikation von Quellen der Nährstoffeinträge (vor allem N und P) sowie deren Mobilisierungs- und Demobilisierungsprozesse unter Berücksichtigung der Nährstoffkreisläufe zu bewerten. Hierfür erfolgten mehrere Probenahmekampagnen zu unterschiedlichen Jahreszeiten und mit einer möglichst guten räumlichen Verteilung. Neben der Entnahme von ausgewählten Wasser- und Sedimentkernproben für detaillierte chemische Analysen in den Laboren des Karlsruher Instituts für Technologie (KIT), wurden zusätzlich Messungen der stabilen Isotope von Wasser (¹⁶O, ²H), gelöstem Nitrat (¹⁵N, ¹⁸O) und den Sedimentproben (¹³C, ¹⁵N) in Kooperation mit der Firma Hydroisotop durchgeführt.

Die anorganischen Stickstoffkonzentrationen (Summe Nitrat-N und Ammonium-N) sind mit um die 1-5 mg N_{anorg}. für ein Oberflächengewässer als hoch einzustufen. Anreicherungen der N-Gehalte durch Verdunstungsprozesse konnten über die Bestimmung der Isotopengehalte des Wasser ausgeschlossen werden. Die Nitratisotopengehaltsbestimmungen zeigten, dass wesentliche Anteile des Nitratabbaus im See nicht statt finden. Die im Jahresverlauf schwankenden Stickstoffkomponenten gehen den analysierten Isotopengehalten zufolge hauptsächlich auf Verdünnungprozesse und auf zeitlich unterschiedlich hohe Stickstoffeinträge zurück. Als die wichtigsten Quellen für Nitrat konnten Abwässer aus Kläranlagen und Landwirtschaft identifiziert werden. In Flachwasserseen ist als eine weitere N-Eintragsquelle resupendiertes Sediment zu berücksichtigen, insbesondere nach starkem Wellengang. Die Isotopenanalyse an den Sedimenten zeigt bei manchen Proben einen Wechsel der N-Isotopengehalte mit der Tiefe, wodurch auf eine sich über die Jahre ändernde N-Quelle geschlossen werden kann.

ID: 126

Vortrag

Themen: Hydrologie und Hydrogeologie einschließlich Tiefengrundwässer

Determining uncertainties of δ 15N-nitrate interpretation in groundwater with the use of Monte Carlo simulations

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Many studies have shown the benefit of stable isotope analysis in groundwater systems. Anyhow, the isotope signature of nitrate may be altered by various processes such as isotope exchange reactions between water oxygen and nitrogenous oxides (NO_2^- in particular) that are formed during the (de)nitrification pathway, mixing of different nitrate sources and consequent hydrodynamic processes along the flow paths (advection, dispersion). Using Monte Carlo simulations, we want to explore the outcome of these different, potentially masking processes to better interpret the nitrate isotope signature in groundwater systems.

A heterogeneous porous aquifer in lower Bavaria, Germany, was analysed for $\delta^{15}N$ and $\delta^{18}O$ of nitrate along with various other parameters such as ${}^{3}H/{}^{3}He$, ${}^{14}C$ and the stable isotopes of water ($\delta^{2}H$ & $\delta^{18}O$) to model the mean transit times (MTT) (Wild et al., 2018). Using the data of the study area and the observed distribution patterns of $\delta^{15}N_{nitrate}$ in precipitation, manure and mineral fertilizers from Kendall et al. (1998), we ran Monte Carlo simulations with different mixing (I), transport (II) and denitrification (III) scenarios to determine the best fit for $\delta^{15}N_{nitrate}$ distributions measured in the groundwater of the study area.

Results indicate a source driven isotopic shift to heavier ¹⁵N values in nitrate and a trend to an increased manure fraction from the main aquifer to the perched aquifer (younger groundwater). This can be best explained by the mixing of different nitrate sources and the influence of transport processes, where a range of different assumptions including land use, mean transit time of groundwater, flow path length and dispersion parameter yielded good fits. A preliminary best fit was found assuming 80% agricultural use implying 90% manure for the perched aquifer and 50% manure for the main aquifer. Assuming different enrichment factors ($\varepsilon_{nitrate}$ -25 to - 15‰) of $\delta^{15}N_{nitrate}$, denitrification may not be a dominant process in the aquifer.

ID: 136

Vortrag

Themen: Hydrologie und Hydrogeologie einschließlich Tiefengrundwässer

A new approach of groundwater dating using dissolved organic radiocarbon (DOC) in a carbonate aquifer in the Bavarian Molasse Basin

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The challenges of radiocarbon (¹⁴C) dating in carbonate aquifers using dissolved inorganic carbon (DIC) are well attested (Purdy et al. 1992; Burr et al. 2001; Hershey et al. 2016). The effect of methanogenesis, bacterial sulfate reduction or dilution of inorganic carbon can significantly alter and mask groundwater radiocarbon ages in anoxic carbonate aquifers with matrix porosity. Therefore, Murphy et al. (1989) demonstrated the feasibility of using radiocarbon dating methods with dissolved organic carbon (DOC) in carbonate aquifers.

In this study, we investigated groundwater dating with ${}^{14}C_{DOC}$ in the karstic Upper Jurassic aquifer in the northern Bavarian Molasse Basin, where complex geochemical reactions under reducing conditions have characterised the chemical evolution of the groundwater (Frisch & Werner 1991; Frisch & Huber 2000). This groundwater system may also be affected by incongruent dissolution of different facies types, ion exchange, and to some extent by bacterial sulfate reduction (Einsiedl et al. 2008). In order to evaluate radiocarbon dating of groundwater in this aquifer, we compared measured ${}^{14}C$ values from DIC and DOC, and calculated model ages. Following this, we linked the apparent groundwater ages with the signatures of stable water isotopes and noble gas infiltration temperatures (NGT) derived from Frisch & Werner (1991).

Our approach was to isolate the DOC, which is partially composed of hydrophobic fulvic acids, by solid phase extraction with 1 g SPE-PPL cartridges after Dittmar et al. (2008). The extraction method is highly efficient and applicable for groundwater with low DOC content (Li et al. 2016). Our samples with low DOC concentrations of between 0.1 and 0.5 mg/l showed extraction efficiencies for 10 l samples from 70 to 100 %.

We calculated ¹⁴C_{DOC} groundwater ages between 5,000 and 23,000 years with ¹⁴C_{DOC} content from 5.7 to 51.1 pmC. In contrast, corrected radiocarbon ages that were obtained from ¹⁴C_{DIC} showed a range between 7,600 and 12,300 years with 11.0 to 21.3 pmC. According to the temperature distribution of climate models over the last 25,000 years (Shakun et al. 2012), the calculated ¹⁴C_{DOC} groundwater ages show a good correlation with measured $\delta^{18}O$ (-12.5 to -9.8 %) and the implicated infiltration conditions from the same wells as well as NGT (1.4 to 8.5 °C) (Frisch & Werner 1991). While the geochemical age correction models used for the carbonate aquifer were a good fit for the calcium-magnesium-hydrocarbonate water, they did not accurately model the radiocarbon age of ion exchange water (Na-HCO3-Cl type).

ID: 150 Vortrag

Themen: Hydrologie und Hydrogeologie einschließlich Tiefengrundwässer

Isotopic approaches to assess potential impacts from shale gas development on shallow groundwater

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With the advent of petroleum development from low permeability reservoirs facilitated by hydraulic fracturing it has become increasingly important to develop tracer tools to scientifically determine potential impacts of anthropogenically induced stray gas migration from depth on shallow aquifers. The presentation will outline a comprehensive approach based on the chemical and isotopic characterization of gases from the production zone, the intermediate zone, and the shallow groundwater zone that has high potential of detecting fugitive gas migration into shallow aquifers independent of the migration pathway at least for resource plays in Western Canada. The obtained results revealed marked and systematic differences among carbon isotope ratios of methane and heavier hydrocarbons and in the dryness parameters of gases among the shale gas production, intermediate, and groundwater zones of Western Canada. These results demonstrate that a chemical and isotopic tracer approach appears to be highly suitable for identifying potential contamination of shallow aquifers with fugitive gases from the intermediate or production zones induced by unconventional energy resource developments, provided that sufficient baseline data exist. This study was conducted within the G-Baseline project co-funded by NSERC in Canada and ANR in France.

ID: 111

Vortrag

Themen: Hydrologie und Hydrogeologie einschließlich Tiefengrundwässer

Isotope evidence for methane formation from cyanobacteria

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For a long time, biological methane (CH₄) production was considered to occur exclusively under strictly anaerobic conditions by methanogenic *Archaea*. During the past decade, evidence has been accumulating that also Eukaryotes such as plants (Keppler *et al.*, 2006), fungi (Lenhart *et al.*, 2012) and animals (Tuboly *et al.*, 2013) produce CH₄ independent of methanogenic *Archaea* via pathways that are not fully understood yet. Recently it was suggested that cyanobacteria produce CH₄ at substantial rates under light and dark oxic conditions (Bižić-Ionescu *et al.*, 2018).

To test the hypothesis that *Cyanobacteria* directly produce CH₄, nine different filamentous and unicellular cyanobacterial cultures were incubated with ¹³C labelled sodium hydrogen carbonate (NaH¹³CO₃) as a carbon source. All investigated cyanobacterial cultures showed substantial CH₄ formation with increasing δ^{13} C-CH₄ values. δ^{13} C-CH₄ ratios depended on the amount of released CH₄. These results unambiguously show that cyanobacteria produce CH₄*per se* and that CH₄ formation is most likely linked to the general cell metabolism such as photoautotrophic carbon fixation. With these findings we present cyanobacteria as a considerable source of CH₄ in lakes, oceans and terrestrial areas even in their oxygenated environments.

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Poster # 9 Poster

Themen: Hydrologie und Hydrogeologie einschließlich Tiefengrundwässer

Soil water balance in the Lake Chad Basin using soil water isotopes and chloride profiles

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Knowledge of soil evaporation rate and groundwater recharge is important for effective management of water resources especially in water scarce regions. Only few studies have been carried out to estimate the amount of groundwater recharge and soil evaporation in the Lake Chad Basin. This study aims to quantify the soil water balance components in four different locations scattered throughout the basin with varying degree of aridity (Salamat, Waza Logone, Bahr el Ghazal and West Chad). Soil water stable isotopes and chloride concentrations were analyzed in twelve vertical profiles to estimate soil evaporation and groundwater recharge, respectively. Soil water was extracted using a modified cryogenic vacuum extraction method after Koeniger et al. (2011) and analyzed for stable water isotopes (²H, ¹⁸O). Chloride concentrations were measured by ion chromatography.

First results of average soil evaporation rates in Salamat show variations in a range of 11 to 23 mm year⁻¹, whereas in Waza Logone they vary from 10 to 12 mm year⁻¹. Results show that from the two soil evaporation estimation methods applied, the decay length method is more applicable, if there are sufficient data points to produce a good linear fit, while the depth of evaporative front method performs better when narrow sampling interval and availability of water are ensured in the vapor zone (Barnes & Allison, 1983).

The average groundwater recharge rate estimated by means of the chloride mass balance, varies in the range of 2 to 73 mm year⁻¹ in Salamat and 20 to 85 mm year⁻¹ in Waza Logone. These relatively high recharge rates indicate that areas close to the profiles Gos Djarat (ST01) and Ouroumbale in Salamat as well as those close to all the Waza Logone profiles should be protected to avoid pollution of groundwater from the surface.

The recharge rate at the profiles of Bahr el Ghazal is less than 1mm year⁻¹, whereas at Sabrekouta and Kousserie in the West of Chad it is 1 and 2 mm year⁻¹, respectively.

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Poster # 10 Poster

Themen: Hydrologie und Hydrogeologie einschließlich Tiefengrundwässer

Pollutant source tracking in tributary backwaters of Three Gorges Reservoir by stable O and H isotopes of water

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There are more than 40000 dams in the catchment of Yangtze River over the last half century. Since the largest dam of China, Three Gorge Dam (TGD) and Reservoir (TGR) was built in the Yangtze River, the following environmental changes and problems in Yangtze River and surrounding regions attracted much attention from international environmental researchers and Chinese government. The fact is many water problems and potential problems have been predicted and later detected in the regions of TGR backwater (Holbach et al., 2014). One significant change of water quality was outbreaks of algal blooms and eutrophication in the impounded tributary backwaters became a hot issue after the huge outbreak of algae and boom in XXR in the summer of 2008.

In this study, the water stable isotopes of O and H were investigated in combination with concentrations of P, NO₃, Fe and other heavy metal compounds. Homogeneous water isotope distribution was found in the backwater of the Yangtze River main stream of Three Gorges Reservoir. The spatial distribution of water isotopic values in two of its tributary backwaters revealed that the water cycle in these areas was very slow and water is retained in the impounded tributary valleys (April, 2014). Following the water flow from main catchment to XXR and SNX, the highest concentration of different ions and heavy metals were found in the middle of tributaries, which was caused by the long residence of water during the storage period. Along the increasing of the temperature from winter to spring season, those existed nutrients could lead serious water bloom and water pollution in 2014. Poster # 11 Poster Themen: Hydrologie und Hydrogeologie einschließlich Tiefengrundwässer

Stable water isotope analysis and modeling for the characterization of water flow in two different soils planted with maize Fatemeh Shajari¹, Florian Einsiedl¹, Arno Rein¹

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A first step in gaining knowledge on pesticide fate in the subsurface is characterizing water flow processes. This can be done by using stable water isotopes (2H/1H, 18O/16O) as natural tracers in combination with modeling. In this study, two lysimeters installed in Wielenbach, Germany, were investigated: Lysimeter 1 is filled with sandy gravels, and Lysimeter 2 is filled with clayey-sandy silts. Maize has been cultivated at the site and different pesticides (metolachlor, terbuthylazine, nicosulfuron, prosulfuron) were applied once a year. In order to determine mean transit times of water (MTT), dispersion parameters (PD) and the contribution of preferential flow for the different soils, we have measured δ 18O and δ 2H in precipitation (input) and in the lysimeter outflow water (output) for 3 years. We used different lumped-parameter model approaches (LPM) considering transport through the soil matrix (advection and dispersion) and along preferential flow paths (piston flow). We considered different assumptions for the input function concerning evapotranspiration by implementing (a) water balance considerations, (b) the Haude and (c) the Penman-Monteith approach.

As preliminary results for water flow characterization, estimated MTT was higher for silt (362 d) than for gravel (129 d). The PD was estimated 0.7 for silt, while it was considered as 0.12 for gravel. The higher MTT and PD may be explained by small pores dominating in the silt, which may lead to slower water movement (higher transit time) and a higher tortuosity (increased dispersion) as compared to the gravel soil. Consideration of preferential flow together with matrix flow (13% contribution of preferential flow for gravel, 10% contribution of preferential flow for silt) could describe the flow processes in both lysimeters more adequately.

The LPM as a simplified approach implementing analytical solutions has the advantage of a comparatively low data need (measured water isotope input and output as a function of time), and it requires only two fitting parameters for matrix flow (MTT and PD). For the next step, we will simulate water flow using a discrete tipping buckets water balance model (TBM) and a numerical flow model (Hydrus 1D) in order to verify the LPM results and to obtain further insights into water flow dynamics and the distribution of water content in the subsurface of the studied lysimeters.

Poster # 12 Poster Themen: Hydrologie und Hydrogeologie einschließlich Tiefengrundwässer

Deutsches Isotopenmessnetz (GIN) Status und Möglichkeiten zur Entwicklung eines Isotopenmessnetzes für Deutschland - Current status and goals in developing a German Isotope Network (GIN)

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In der WISER Datenbank der IAEA/WMO werden derzeit 39 deutsche Stationen für Niederschlag (GNIP) und 52 Stationen für Oberflächenwasser (GNIR) geführt. Die längsten Messreihen reichen bis in die 1960er Jahre zurück und beinhalten mehr als 600 Monatswerte (z.B., Stuttgart, Langwedel-Weser). Bisher wurden für deutsche Stationen die stabilen Isotope (δ^2 H, δ^{18} O) größten Teils am Helmholtz Institut für Grundwasserökologie (IGOE) des Helmholtz Zentrums München (früher GSF) und Tritium (³H) an BfG und IGOE gemessen und durch weitere Stationsniederschläge von Forschungseinrichtungen und Universitäten ergänzt [1, 2, 3]. Während ³H-Beobachtungen in Deutschland zum überwiegenden Teil auf Grund gesetzlicher Vorlagen und Richtlinien (StrISchG / AVV-IMIS) zum radiologischen Überwachungsmessnetz gehören und eine staatliche Überwachungsaufgabe ist, wurden die stabilen Sauerstoff- und Wasserstoff Isotope im Niederschlag bisher vorwiegend aus Forschungsinteresse gemessen.

Für Deutschland bemühen sich derzeit BGR, BfG und DWD als staatliche Behörden gemeinsam, die bisherigen Stationen auch für die Bestimmung stabiler Isotope im Niederschlag dauerhaft zu nutzen, um damit die bisherigen Datenreihen langfristig fortzusetzen. Die bisherige Messnetzdichte soll möglichst ausgebaut werden und auch weitere Labors mit einbeziehen. Daten aus Forschungsprojekten mit höherer zeitlicher Auflösung aus Niederschlag, Oberflächenabfluss, Grundwasser und Ökosystemen sollen integriert und allen Fachkreisen zugänglich gemacht werden. Wie in anderen nationalen Netzwerken soll GIN Isotopendaten deutschlandweit sammeln, und diese nach Erstpublikation durch die Labors oder gemeinsam im Autorenkollektiv, regelmäßig über eine Website zugänglich machen und dann an die internationale Datenbank der IAEA/WMO überführen.

Dieser Beitrag will versuchen, interdisziplinäre und internationale Möglichkeiten eines starken deutschen Isotopennetzes zu diskutieren, dabei weitere Partner, Isotopenlabors und Interessenten anzusprechen und durch Ringversuche und regelmäßige Treffen zu verbinden; vor allem aber längerfristig die Datengrundlagen zu sichern und die Isotopengemeinschaft in Deutschland zu stärken.

Literatur:

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Poster # 13 Poster Themen: Hydrologie und Hydrogeologie einschließlich Tiefengrundwässer

Spatial and temporal isotopic characterization (2H/1H and 18O/16O) of modern day precipitation in the Bale Mountains, Ethiopia

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Abstract

The Bale Mountains are an eastern afromontane biodiversity hotspot area encompassing high rate of endemic fauna and flora. Nevertheless, this internationally recognized habitat is increasingly under threat by climate change and anthropogenic impacts. The main objective of the present study is the spatial and temporal isotopic characterization (²H/¹H and ¹⁸O/¹⁶O) of modern day precipitation towards improving understanding of the modern day atmospheric circulation patterns of the area. A total of 164 precipitation samples were collected from February 2017 to February 2018. Samples were collected twice a month in fifteen days intervals from ten weather stations located in altitudinal ranges of 4375 to 1304m a.s.l. The isotopic composition of δ^{18} O and δ^2 H varied from +10.5% to -8.7% and +38.1% to -38.2%, respectively. The local meteoric water line (LMWL) is characterized by more positive d-excess values compared to the global meteoric water line (GMWL) and a slope that is smaller than 8. Both the altitude and the amount of precipitation clearly influence the isotopic signal. In all stations, $\delta^{18}O$ and $\delta^{2}H$ of precipitation show a seasonal pattern reflecting rainy versus dry season. During the pronounced dry season in winter (November to February) as well as during the dry season in June/July precipitation is more positive. By contrast, high precipitation amounts recorded in May coincide with the most negative isotope values. Ongoing work focusses on interpreting this finding by coupling the isotope results with trajectory studies revealing the main source areas of precipitation in the course of the drv and rainv seasons.

Key Words: East Africa, local meteoric water line, $\delta^2 H$, $\delta^{18}O$, amount effect, altitude effect

Poster # 14 Poster Themen: Hydrologie und Hydrogeologie einschließlich Tiefengrundwässer

Isotopen-Hydrobiogeochemische Untersuchungen der saisonalen Dynamik von Oberflächengewässern in der Land-Ostsee-Übergangszone

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Diese Studie berichtet über Ergebnisse einer Isotopen-hydrobiogeochemischen Untersuchung an einem Fliessgewässer sowie einem Küstenmoor am südlichen Rand der Ostsee.

Den ersten Untersuchungsgegenstand stellt der Unterlauf der Warnow da. Im Rahmen einer Zeitreihenstudie wurde an vier Stellen entlang des Fließweges eine wöchentliche Beprobung des Oberflächenwassers durchgeführt. Auch hierbei wurden neben physikalischen Parametern, die Gehalte an Haupt-, Spurenelementen und Nährstoffen gemessen, sowie die isotopische Zusammensetzung von Wasser (H-2, O-18), DIC (C-13), und Sulfat (S-34, O-18) ermittelt.

Das Hütelmoor ist ein wieder-vernässtes Küstenmoorgebiet östlich des Flusses Warnow, das an die südliche Ostsee angrenzt. Es zeichnet sich durch einen hohen Organik-Gehalt in den Böden und ein Grabensystem aus, welches ehemals der Entwässerung und landwirtschaftlichen Nutzung des Gebietes diente, und sich heute in einer Phase der Renaturalisierung befindet. Die Nähe zur Ostsee führte und führt zu Ereignis-artigen Brackwassereinträgen in das Gebiet. Diese führen zu räumlichen und zeitlich heterogenen Erhöhungen der Salinität, mit besonderen Konsequenzen für die biogeochemischen Prozesse im C-S-Kreislauf. In der Studie sollte der Einfluss von Umsatzprozessen auf die hydrogeochemische und isotopengeochemische Zusammensetzung der Oberflächenwässer räumlich und im Frühjahr-Sommer Vergleich charakterisiert werden. Neben den stabilen Wasserisotopen, ermöglicht die isotopische Charakterisierung von gelösten Spezies Elementquellen und -senken sowie mikrobiell-induzierter und abiotische Transformationen.

Die Ergebnisse zeigen eine räumliche und zeitliche Dynamik in beiden Systemen. In der Warnow sind saisonale Variationen zu beobachten die in der Unter-Warnow temporär zusätzlich durch Mischungsprozesse mit dem brackischen Wasser der Ostsee überlagert werden. In den Oberflächenwässern des Hütelmoores zeugen die Isotopensysteme von einem Einfluß der Oberflächenwässer durch ehemals anoxische Bodenlösungen, eine intensive Zyklierung des aus der Ostsee stammende Sulfats und damit verbundene Mineralsierung von organischem Material. Mit seinen teilweise überflücten Gräben, ist im Moor eine hohe räumliche Variabilität, bzgl. des Ausmaßes dieser Wechselwirkungen festzustellen.

Poster # 15 Poster

Themen: Hydrologie und Hydrogeologie einschließlich Tiefengrundwässer

Groundwater evolution in North-eastern Germany as deduced from the hydrogeochemical and stable isotope composition

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The evolution of ground waters in Mecklenburg-Western Pomerania (North-Eastern Germany), one of the catchment areas of the southern Baltic Sea, is impacted by different natural and anthropogenic factors. The composition of ground water is mostly controlled by the composition of evaporated rain, followed influenced by processes in the soil zone and aqueifer rock-ground water interactions. Furthermore, due to anthropogenic activity, ground water may be loaded with enhanced amounts of DOC and/or nutrients. This is affecting the mass balance in elemental cycles like the sulphur and carbon cycles not only in ground and surface waters, but also, via submarine ground water discharge, coastal ecosystems.

In the present study the isotope (H, C, O, S) hydrobiogeochemical composition of shallow and deep ground waters was investigated.

The combined sulfur and oxygen isotope composition of dissolved sulfate indicates different sulfate sources, including the oxidation of pyrite, using different electron acceptor at a number of settings. Furthermore, dissimilatory bacterial sulfate reduction is indicated as several sites. The ground water system of dissolved inorganic carbon is found to be controlled by the dissolution of biogenic carbon dioxide, the dissolution of (marine) carbonates and oxidation of anthropogenically introduced DOC and at a few sites biogenic methane.

A combined isotope mass-balance approach is combined with physico-chemical modeling to define the different processes taking place during the ground water development.

Poster # 33

Poster

Themen: Hydrologie und Hydrogeologie einschließlich Tiefengrundwässer

First Water – Isotope – Map (δ^{18} O, δ^{2} H, ³H) of Austria: Applications, Extremes and Trends

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The isotopic ratios of oxygen and hydrogen in water (2 H/ 1 H and 18 O/ 16 O) are important tools to characterise waters cycles. Tritium formed by natural cosmic radiation in the upper atmosphere and in the last century by tests of thermonuclear bombs, is an ideal age-marker during the last 60 years.

To determine the origin and mean age of waters in many scientific projects and in those concerning water supply and engineering in the last 45 years on more than 1,350 sites more than 40,000 isotope measurements were performed in Austria.

The median value of oxygen-18 of all sites is δ^{18} O -10.7 ‰ and for hydrogen-2 δ^{2} H -75 ‰. As the fractionation is mainly temperature dependent the lowest negative values are observed in winter precipitation (oxygen-18 as low as δ^{18} O -23 ‰) and in springs in the mountain regions (δ^{18} O -15.1 ‰). In contrast the highest values were observed in summer precipitation (up to δ^{18} O -0.5 %). In contrast the lowest here constructed in summer precipitation (up to δ^{18} O -0.5 %).

-0.5 ‰) and in shallow lakes in the Seewinkel close to the Hungarian border (up to δ^{18} O + 5 ‰).

The median of all deuterium-excess values is d-excess = $9.4 \$. The lowest negative value of - 7.4 $\$ was measured in the surface water sample of a gravel pit in the Leibnitzer Feld (Southern Styria). The highest d-excess value of 15.7 $\$ is documented from a mountain spring at the southern border of Austria.

The median value of all 1,120 sampling sites of decay corrected (2015) tritium measurements is 6.2 tritium units (TU). This is somewhat smaller than the median value of all precipitation stations with 7.2 TU. The tritium concentration increases in the summer up to 10 - 11 TU and decreases in winter down to 3 - 4 TU. A mean tritium concentration in aquifers smaller than approximately 3.5 TU indicates that a large amount of this water is older than 60 years. Waters with approximately more than 12 TU contains still tritium from the 1960s and 1970s originating from thermonuclear bomb experiments in the atmosphere. In Austria the highest tritium values can be observed in the rivers Danube and March which show periodic or permanent tritum contamination up to 70 TU coming from nuclear power plants in the neighbouring countries.

Session 4: Boden-Pflanzen-Atmosphäre

ID: 135 Vortrag Themen: Boden-Pflanzen-Atmosphäre

Foliar water uptake, the way to grow for Avicennia marina (Forsk.) Vierh.

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Mangrove forest are a diverse group of evergreen trees, shrubs and ferns functioning as stabilizers for riverbanks and coastlines, food and wood providers both for animals and people and protectors of more inland areas against storm surges. Due to their exceptional location, these forests are known to have an abundance of water at the root-level. However, due to the high salinity, this water is not readily available for these forests and even induces physiological drought. This partly explains why the latitudinal distribution of mangroves coincides with the geographical limits of arid regions, suggesting that the distribution of mangroves is more limited by precipitation and aridity rather than air temperature. This hypothesis has been confirmed by recent research that indicated the direct uptake of canopy rainwater (foliar water uptake; FWU) which caused turgor-driven growth spurts in full grown Avicennia marina trees, a widely distributed mangrove species. It was clear that diameter growth of this species in the absence of rainfall events was negligible, thus illustrating the importance of precipitation events for this species. FWU has been intensively studied for full grown trees of different species from the tropics, however, the importance of this plant trait on saplings has been widely neglected. As such, FWU was investigated for A. marina saplings by using both dendrometers and sap flow sensors as well as deuterium tracing. It was found that the effect of FWU on the turgor-driven growth was even larger for saplings compared to full grown trees. Even more, by performing a deuterium tracing experiment it was clear that top leaves absorbed more water compared to the lower leaves and that the water taken up by FWU was redistributed to the stem and directly correlated with the observed turgor-driven growth. These results indicate that FWU is an essential trait for the growth of A. marina saplings and possibly even their establishment, thus indicating that the distribution of mangrove species might be more affected by the upcoming climate change driven changes in precipitation patterns than previously thought.

ID: 170 Vortrag Themen: Boden-Pflanzen-Atmosphäre

Measured and modeled xylem-sap isotopic composition in tree stems with a borehole-equilibration technique

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The isotopic composition of xylem sap is a key parameter in models of the isotopic composition of water fluxes in forests. The data can identify water sources, describe canopy fluxes, and interpret tree-ring measurements. Traditionally, water is extracted by cryogenic distillation, which is technically challenging, slow, expensive, and discontinuous. A recent paper has proposed a headspace equilibration technique, which could be simpler and continuous, but it remains somewhat complicated. Here we propose a method that is simpler yet, requiring only the pumping of ambient air through a borehole traversing the tree stem. We present experimental tests of the method as well as a theoretical model. The experimental tests rely on borehole measurements through severed Scots pine (Pinus sylvestris L.) stems placed in a bucket of water with known isotopic composition. Because Scots pine produces considerable pitch in the borehole, it provides a particularly rigorous test of the method. The model describes laminar flow through the borehole and the approach to steady state along the flowpath, including water vapor fluxes to and from the borehole atmosphere. Both the empirical data and the theoretical model support the notion that the water vapor leaving the borehole is in isotopic equilibrium with the source water in the xylem, leading us to propose that this method will provide simple, continuous measurements of the isotopic composition of xvlem sap.

ID: 157 Vortrag Themen: Boden-Pflanzen-Atmosphäre

Variability in xylem water isotopic signature triggers incorrect assessment of root water uptake depth

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Assessing root water uptake (RWU) from plant xylem water isotopic signature is an increasingly popular technique within the ecohydrological community. This technique relies on the assumption of a uniform xylem isotopic signature along the length of the lignified plant. This crucial assumption is, however, poorly corroborated by scientific studies and maybe suspect. Here, we hypothesize that major alterations in the xylem water isotopic signatures along the length of a lignified plant is in fact rather likely since RWU depths and sapflow speed experience diurnal fluctuations as a result of changing water potential gradients (Goldstein *et al.*, 1998; Huang *et al.*, 2017).

To explore how spatiotemporal variation in RWU and sapflow speed affect the xylem water isotopic signature, we developed a very simple individual plant hydraulic model and coupled this to a soil water isotopic depth profile. Our model predicts that significant variation in isotopic xylem water signatures both rapidly develop with diurnal spatiotemporal RWU fluctuations and persist along the length of an individual plant. Additionally, we predict significant differences in xylem water isotopic signature between individuals with equal RWU depths but different sapflow speeds. Our model results were corroborated by field data of intra-individual xylem water isotopic signatures ($\delta^2 H$ and δ^{18} O) along the height of six tropical canopy trees and six tropical liana species sampled in Laussat, French Guiana. The measured intra-individual variability ranged up to 20% in $\delta^2 H$ and 4% in δ^{18} O, vastly exceeding acceptable error ranges. Our model and field data show that strong variation in xylem water isotopic signatures exist, and arise quickly in even simple plant hydrological models which muddies RWU depths assessment using the classical approaches.

We conclude that the fundamental assumption is easily and rapidly falsified and should be rejected. Our work also raises the possibility that interpretation and calculation errors may exist in literature, and illustrates the importance of including sapflow measurements in future RWU assessments. Finally, we build on our model, and present a new theoretical approach enabling spatiotemporal RWU assessment of an individual plant by simultaneous monitoring of sapflow, xylem water and soil water isotopic signatures and soil water potentials.

ID: 158 Vortrag Themen: Boden-Pflanzen-Atmosphäre

Water use strategies of mature beeches – a comparison of pure and mixed stands

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Extreme events as prolonged drought and heat with subsequent heavy precipitation events are prognosticated to happen frequently with ongoing climate change (Vilhar and Simončič, 2012; IPCC, 2013). This can have negative impacts on ecosystem functioning regarding e.g. carbon sequestration, water relations or nutrient cycling. Thus, the future performance of the socio-economically important native forest in Germany is frequently discussed (Bundesministerium für Ernährung und Landwirtschaft, 2017). Common beech (*Fagus sylvatica* L.) is a key species in the German forest, and due to its drought sensibility likely to be most affected by climate change.

We investigated mixed stands of beech and silver-fir (*Abies alba* MILL.), compared to pure beech stands, regarding their water relations at a field site in the black forest area. We induced an artificial drought over three months and examined the resulting water uptake patterns of individual beech and silver-fir trees towards a subsequent artificial heavy-precipitation event using deuterated water as tracer (δD of ca. 1600‰). Branches were cut every two hours over the whole day, and xylem was extracted using a scholander pressure chamber.

We repeatedly observed high variations in xylem water δD over the day from the same tree. Apart from that, we were able to trace the water uptake of mature trees, looking at pure and mixed stands separately. The time lag between the precipitation event and water uptake varied between eight to twelve days, depending on species and association. In addition, we extracted soil water using a cryogenic extraction line comparing obtained water signatures to water sampled with suction cups onsite. We did not observe significant differences between those two approaches, indicating that suction cups might be a suitable and non-destructive alternative of sampling soil water at least for tracer experiments. We modelled changes in root water uptake distribution for beeches in response to the irrigation event and found a shift from shallow to deeper soil layers in the mixed stands and a reversed pattern in the pure stands.

Our results indicate different responses to extended drought and subsequent heavy precipitation in forested ecosystems, with changes in root water uptake patterns related to species and association.

ID: 143 Vortrag Themen: Boden-Pflanzen-Atmosphäre

Nutrient addition changes water and carbon fluxes through biodiversity effects: partitioning evapotranspiration and net ecosystem exchange

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With currently storing about 343 gigaton of carbon, grassland ecosystems largely contribute to carbon sequestration worldwide (Suttie et al., 2005, FAO, 2010). However, the increase of extreme drought events and nutrient addition, due to pollution and agricultural fertilizing, pose major threats to grassland ecosystems. These threats may cause changes in species abundance and diversity and thus influence water and carbon fluxes of grassland ecosystems. Therefore, understanding the impact of drought stress and nutrient addition on these fluxes is imperative. Stable isotopes such as ¹⁸O and ²H are powerful tools to partition evapotranspiration and to trace water movements across scales. Using stable isotope techniques, we analysed the close link between water and carbon fluxes and the effects of (limited) water and nutrient availability on a grassland community.

Measurements took place in a temperate grassland, located in Freiburg im Breisgau, Germany, from April to September covering the vegetation period of the grassland ecosystem. A one in a 100-year drought was simulated and was additionally combined with a nitrogen fertilization treatment. Fluxes and isotopic signature of evapotranspiration were measured by coupling a cavity ring-down spectrometer and infrared gas analyser to open gas exchange chambers. Additionally, leaf and soil samples were taken, cryogenically extracted and their isotopic signature determined. This allowed us to model soil evaporation and transpiration in order to partition ecosystem evapotranspiration.

Both treatments (precipitation exclusion, nitrogen addition) had a clear effect on the grassland community. Nitrogen fertilized plots were strongly dominated by grass species and showed higher or similar productivity in spring peak compared to control plots. However, productivity strongly declined during the summer drought and they became carbon sources due to a dieback of the above-ground biomass. Control plots, though, maintained productivity during summer drought, which might be related to the higher species diversity and the distinct species strategies against drought stress. Since assimilation and transpiration are closely linked, this die-back of nitrogen treated plots also led to a clear drop in evapotranspiration during the summer drought, which was less pronounced for control plots. Water and carbon fluxes of drought treated plots were, generally, lower throughout the vegetation period. Water use efficiency (assimilation/transpiration) of the grassland community increased during the summer drought, however, did not differ significantly between treatments.

Our results show clear responses of the studied grassland community to water limitation and nutrient addition, however, with changes in carbon and water fluxes strongly related to changes in species composition.

ID: 117 Vortrag Themen: Boden-Pflanzen-Atmosphäre

Is cheating on fungal partners among plants much more widespread? New insights for partial mycoheterotrophy in arbuscular mycorrhizae

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Introduction/Aim:

Plant-fungus-interactions known as mycorrhizas are probably the most ancient and widespread symbioses. Fungal root endophytes are known to either be mutualistic, represented by a bidirectional nutrient exchange between the plant and the fungus ('mycorrhizas'), or antagonistic ('mycoheterotrophy') were the plant exploits the fungus for carbon-nutrients. Obviously, achlorophyllous plants, unable to perform photosynthesis, must exploit their endomycorrhizal partners for receiving carbon-nutrients. Interestingly, stable isotope approaches established themselves as useful tool to unmask achlorophyllous but even photosynthetic-active plants to rob carbon-nutrients from their fungal partners.

For the globally distributed arbuscular mycorrhizae (AM, ~200.000 species) we can distinguish at least two subtypes; (i) *Arum*-subtype (after *Arum maculatum*) forming hyphae along cortical intercellular airspace, (ii) *Paris*-subtype (after *Paris quadrifolia*) forming intracellular hyphal coils. So far, every achlorophyllous mycoheterotrophic AM plant species reveals hyphal coils of the *Paris*-subtype which are like intracellular 'pelotons' in orchid and 'hyphal pegs' in monotropoid and pyroloid mycorrhizas also known for mycoheterotrophy.

We aim to compare green plant species of the *Arum*-type and *Paris*-type with the expectation that *Paris*-type species are enriched in ¹³C and ²H as in analogy to hyphal coil forming mycoheterotrophs.

Materials and Methods:

Arum maculatum (*n* = 10), *Paris quadrifolia* (*n* = 10) and co-occurring plants as references (*n* = 30) were sampled in two separated forest sites (LK-Garmisch-Partenkirchen, LK-Forchheim; Germany). Additionally, we reviewed the literature to relate AM-subtypes to stable isotope data and found suitable plots from Germany (Betzenstein forest, *n* = 35) [1], Austria (Alp meadow, *n* = 94) [2] and Italy (grassland, *n* = 318) [3-5]. Plant material were measured for ¹³C, ¹⁵N (EA-IRMS) and exemplary subsamples for ²H and ¹⁸O (TC-IRMS).

Results:

The comparison of *Arum maculatum* to *Paris quadrifolia* showed equal results as the reviewed *Arum*-type and *Paris*-type plants. *Paris quadrifolia* and further *Paris*-type plants were significantly enriched in ¹³C and ²H while in very most cases no differences were found for ¹⁸O and ¹⁵N.

Discussion:

For the first time, we could show that the arbuscular mycorrhizal subtypes reveal differences in their natural stable ¹³C and ²H isotope abundances. This result could indicate that not only green orchids (~30.000 species) and pyroloids (~40) digest their fungal partners for nutrient-gain but also half of the green arbuscular mycorrhizal plants are potentially weak partial mycoheterotrophs (~100.000). Therefore, we may have to change our current view that 'most mycorrhizas are beneficial for both partners' but definitively more research is needed on this investigation!

ID: 116 Vortrag Themen: Boden-Pflanzen-Atmosphäre

Ecohydrological soil-plant feedbacks: a pool-weighted perspective on the twowater-worlds hypothesis

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One of the central questions in ecohydrology is to understand the mechanisms controlling the partitioning between precipitation into groundwater recharge and stream flow and water vapor returning to the atmosphere via evaporation and plant transpiration (Asbjornsen et al., 2011). Soils and in particular the unsaturated zone play a critical role in these processes, as their properties control infiltration, percolation and storage capacity and influence soil evaporation and plant transpiration (see Sprenger et al. (2016) for an overview). Stable water isotopes are an excellent tracer of water transfer in soils, through plants and at the soil-vegetationatmosphere interface (Yakir & Sternberg, 2000; Werner & Dubbert, 2016). Within the last decade, dual isotope approaches have been increasingly employed in ecohydrological studies (Brooks et al., 2010; Goldsmith et al., 2012; Brooks, 2015; Evaristo et al., 2015; Evaristo & McDonnell, 2017). Brooks et al. (2010) found significant differences between groundwater. stream flow and precipitation on the one hand and shallow soil layers and plant water on the other hand. Based on these observations, Brooks et al. (2010) postulated ecohydrological separation between soil/plant water and stream flow later on termed the "Two-Water-Worlds" (TWW) hypothesis (McDonnell, 2014). Off-sets between meteoric water lines and evaporation lines, i.e. quantified as deuterium-excess or line-conditioned-excess (LC-excess), are then used to quantify the degree ecohydrological separation between waters of different origin (Evaristo et al., 2016).

We tested the pool-weighted impact of isotopically distinct water pools for hydrological cycling, the influence of species-specific water use and the degree of ecohydrological separation. We combined stable isotope analysis of ecosystem water pools of precipitation, groundwater, soil water, plant xylem water of two distinct species (*Quercus suber, Cistus ladanifer*) with observations of soil water contents and plant sap flow.

Shallow soil water was evaporatively enriched during dry-down periods, but enrichment faded strongly with depth and upon precipitation events. Despite clearly distinct water sources and water-use strategies, both species displayed a highly opportunistic root-water-uptake pattern.

Our results do not support the two critical assumptions of the "two-water-worlds" hypothesis: Neither did we find evidence for low/lacking connectivity between bound and mobile water nor preferential root-water-uptake of bound water. Pool weighting the contribution of evaporatively enriched soil water reveals only minor annual impacts of these sources to ecosystem water cycling (~11% of bulk soil water and ~ 15% of transpired water).

Poster # 17 Poster Themen: Boden-Pflanzen-Atmosphäre

Apple replant disease causes carbon bleeding by a shift in the fungal community

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Apple replant disease (ARD) is a global problem and threatens nurseries and orchards. ARD reduces fruit yield for up to 50 % in a tree's lifetime and also plants growth is reduced. So far it is not known what is the main cause of this disease, but both biotic (especially fungal pathogens) and abjotic factors were associated with ARD, pointing towards a multi-causal triggering. For deciphering the plants response on the carbon investment into the rhizosphere, we planted Malus domestica "M26" apple seedlings in three soil variants from two locations (Meckenheim and Klei): ARD soil, gamma-irradiated ARD soil (Gamma) and non-ARD soil (Grass). After a ¹³CO₂ pulse labeling for 2 hours, carbon flux rates were determined by stable isotope tracing in shoot, root, bulk soil, microbial biomass (chloroform fumigation extraction, CFE) 0, 6, 24, 71, 168 hours after label application, and of CO₂ trapped from soil respiration (sampled twice a day for the duration of the ¹³C incubation). Additionally, we determined the ¹³C-signature of phosphorous- and neutral lipid fatty acids (PLFA/NLFA) in order to relate photoassimilate consumption to broader microbial functional groups. Furthermore, an ITS amplicon sequencing, using illumina miseq, was executed to break down the fungal community composition. We found that plants exposed to ARD invested a higher share of their photoassimilates belowground. In addition, a high accumulation of ¹³C in the arbuscular mycorrhiza fungi (AMF) NLFA biomarker suggests that the plant increases its interactions with AMF to (probably) overcome ARD. Additionally. ARD induced a shift in the fungal community composition.

Poster # 18 Poster Themen: Boden-Pflanzen-Atmosphäre

A continuous, dual-labeling pulse chase to describe vertical and lateral water uptake by trees in a boreal forest in Sweden

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Boreal forests, mainly sustained by snowmelt water in spring and summer, are the largest natural reservoir of freshwater on Earth. However, predicted changes in climate can affect the availability of these water sources. Water stable isotopes are a valuable tool to improve our understanding of ecohydrological processes belowground to identify tree water sources and root spatial distribution. In this study, we developed and applied an *in-situ* method for monitoring the isotope ratios of 15 trees and 8 soil depths in real time. We combined this with a dual injection of 0.8 % deuteurium at the mineral-soil surface and 2 L of 350 % H₂¹⁸O at 70 cm depth to one m² of soil.

Therefore, our study aims to 1) analyze tree water use compared to the pools available during the summer; 2) to investigate the lateral root spread by detecting the signal of the tracer on trees at different locations, 3) to quantify the transit time of the tracer through the soil until it is detected in the stem and 4) to study the possible relation between the strength of the signal detected in the tree and the distance from the location where the tracer has been applied. The holistic approach enables the study of ecohydrological feedbacks at a resolution that could not be achieved previously, opening up opportunities for source water partitioning studies both vertically and horizontally.

We established a labeling experiment in a Scots pine forest at the Rosinedal experimental site, Sweden. We monitored the xylem water passing through boreholes that were drilled through the stems of 15 trees. The air was directed to a Picarro L2130-i isotopic water analyzer. For calibration, we used a Standards Delivery Module. We also measured the soil water isotopic composition at eight soil depths (0.05, 0.10, 0.15, 0.2, 0.3, 0.5, 0.7 and 1 m) continuously and in "realtime" on a second Picarro L2130-i. The soil measurements were calibrated using standard bags where temperature, water vapor concentration and isotopic ratios were measured after each cycle. In addition, soil volumetric water content and temperature as well as matric potential was recorded at five different depths (0.1, 0.3, 0.5, 0.7 and 1 m). Twice per week, stem cores, water from porous-cup lysimeters, branches, and soil samples were collected on a transect away from the labeled plot for validation and to study the spatial dynamics of the tracer transport. Poster # 19 Poster Themen: Boden-Pflanzen-Atmosphäre

Late Glacial and Holocene landscape evolution of the Sanetti Plateau, Bale Mountains (Ethiopia), as deduced from biogeochemical properties of lacustrine sediments

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The Bale Mountains were one of the three extensively glaciated higher elevation areas in Ethiopia during last glacial maximum. After deglaciation, several small depressions on the Sanetti Plateau turned into shallow lakes. Today, some of these lakes dry out seasonally due to the alternation between monsoonal precipitation in summer and dry north-easterlies in winter. Drastically decreasing of Erica vegetation at higher altitude was recorded on the study area. But the driving factors of this vegetation change remain still unclear. Therefore, we aim at contributing to the reconstruction of the Late Glacial and Holocene vegetation history of the Sanetti Plateau, by studying depression sediments based on the hypothesis that any process initiated by climate fluctuations or human impact should be documented in the physical, chemical and biological properties of depression sediments. Carbon and nitrogen stable isotopes were used as key parameters to infer environmental dynamics, especially vegetation changes in combination with radiocarbon dating, analysis of TOC, TOC/N, black carbon, pollen, alkanes and grain size distribution. We investigated partly laminated lake sediments at high-resolution from a depression located at 4115 m asl on the Sanetti Plateau. According to the results thick sediments were deposited during the last 18 cal ka BP. d¹³C values between -20 to -14‰ likely reflecting expansion of C4 grasses, methanogenesis and long lasting ice covers, $\delta^{15}N$ values increase from -2‰ in 2.55 m at the base of the sediments to 19‰ in 45 cm depth (ca. 8.5 cal ka BP) indicating despite pronounced fluctuations an opening of the N cycle likely correlating with a general improvement of the environmental conditions. Total organic carbon (TOC) concentrations reach almost 8% during the time between 18 and 16 cal. Ka but are very low (~1%) in the sediments deposited with the beginning of the Younger Dryas at 12.7 cal. ka BP. Low odd-over-even predominances (OEP) of n-alkane lipid biomarkers as well as low TOC/N ratios corroborate the interpretation of highly degraded organic material building up the upper 70 cm of the sediments under study. High accumulation of the fire proxy black carbon characterizes the sediments accumulated at about 17 and between 16 - 13 cal, ka BP.

Poster # 20 Poster Themen: Boden-Pflanzen-Atmosphäre

Switching the organic layer off - A ¹³C labeling approach to trace carbon dynamics in the subsoil

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Carbon in subsoils contributes substantially to the overall global carbon storage in soils. Translocation of dissolved organic matter (DOM) from carbon-rich topsoils is considered an important source of organic matter (OM) within subsoils. But the quantitative contribution of the cascade of sorptive retention, remobilization, and degradation of OM during downward translocation is still uncertain. We hypothesize the contribution of fresh litter-derived OM decreased strongly with soil depth as result of sorptive interactions with reactive mineral surfaces. Further, we expect a higher proportion of soluble litter-derived OM in the subsoil compared to the topsoil. We conducted a ¹³C labeling experiment on a sandy Dystric Cambisol under beech near Hanover, Germany, where on three plots the natural litter layer was replaced by an equal amount of ¹³C-enriched beech litter (1240 δ‰). After two years under field conditions, it was again replaced by natural litter to stop the input of the ¹³C signal. Soil samples were collected at the time of natural litter replacement and 18 months later by taking soil cores down to 2 m depth. The contribution of litter-derived OM in soil depths of 0-50 cm and 100-140 cm was determined by EA-IRMS in bulk samples, density fractions (i.e. mineral organic associations; MOAs), and the solutions after fractionation. Our results show that ¹³C enrichment was < 1.5 ‰ below 10 cm soil depth in all density fractions. The density solution (1.6 g/cm³ sodium-polytungstate, SPT), however, had enrichments of 2-11 ‰ in the upper 50 cm of the soil, implying that a considerable amount of ¹³C was present in a mobilizable form, likely representing weakly mineral-bound OM. Carbon in the deeper subsoil (< 100 cm) showed ¹³C enrichment of < 1 ‰ also for the SPT solution. A considerable enrichment of ca. 2 ‰ was found in the washing water of the heavy mineral fraction of the deeper subsoil, maybe as a result of a pronounced soil dispersion and OM desorption during washing with ultra-pure water, suggesting a change in OM composition towards compounds being less sorptive to minerals.. We calculated that OM input and transport from a recent litter layer contributes to about 4-14 % to the carbon storage in a depth of 0-50 cm, while it was only 0.04-0.4 % in a depth of 100-140 cm.

Poster 21 Poster Themen: Boden-Pflanzen-Atmosphäre

A new in-situ setup for monitoring plant water uptake of herbaceous species in the laboratory using water stable isotopes

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Plant water uptake plays a crucial role in the water cycle, as it is the largest flux on land surfaces returning water to the atmosphere. Its complex dynamics are however still not well understood. Especially on short time scales, high uncertainty exists in the plasticity of water uptake and its associated driving forces. In view of an increase in hydrological extremes and a changing climate, a more mechanistic understanding is however crucial.

For five decades, water stable isotopes substantially improved our knowledge about plant water uptake. However, monitoring short-term variations was restricted, due to the necessity for destructive sampling and laborious sample analysis. Recent methodological advances offer possibilities to overcome these constraints and triggered the development of approaches, which enable an in-situ monitoring of water stable isotopes in soil water and water taken up by plants. First combined in-situ measurements were already conducted in trees, but have not yet been applied to the examination of root water uptake in herbaceous species.

We tested a new method that allows for in-situ sampling of water stable isotopes across a soil column and in plant transpiration under controlled conditions in the laboratory, using Cavity Ring-Down Spectroscopy. For this purpose, an existing soil column setup was expanded by a plant component. Dual isotope data in daily and sub-daily temporal resolution was collected across soil profiles and transpiration of *Centaurea jacea*, respectively.

Measured transpiration values reflected a mixture of soil water differing in its isotopic composition across the profile throughout a period of six weeks, despite pronounced dynamic changes in both systems. Derived measurement precision was comparable to that of established and newly developed in-situ methods. The setup proved to be an adequate tool for capturing shortterm variations in root water uptake in response to differences of water availability. To visualize water uptake profiles, data sets of the isotopic composition in plant transpiration and soil profiles were combined in a statistical multi-source mixing model.

Observed trends can logically be interpreted with existing knowledge on water uptake plasticity, while highlighting knowledge gaps in the mechanistic understanding of underlying processes. Prospectively, the implementation of data sets, obtained with the tested method, in mechanistic state-of-the-art models could help to further disentangle complex interactions between soils and root systems. On the other hand modeling approaches across scales that now more commonly include water stable isotopes, will potentially benefit from recorded time series.

Poster # 22 Poster Themen: Boden-Pflanzen-Atmosphäre

Stable isotope natural abundance of isolated fungal hyphae will shed light into the role of arbuscular mycorrhizal fungi in carbon and nutrient cycling

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Background

Despite forming symbiotic associations with 71% of all land plants [1], our knowledge on the role of arbuscular mycorrhizal (AM) fungi in ecosystem carbon and nutrient cycling is still limited. Stable isotope approaches have proven to be important tools for decoding the dynamics of carbon and nutrients within plant-fungus-associations [2]. They are, however, limited by difficulties with sampling and identification of mycorrhiza hyphae in the field [2]. Fruiting bodies of fungi were assumed to mirror the isotopic signatures of belowground hyphae of saprotrophic and of ectomycorrhizal fungi (ECM) [2, 3], but the analyses of isotopic signatures of AM fungi, creating their hyphal structures mainly within the roots, remains a challenge. The aim of this study was to 1) test various extraction methods for AM hyphae from roots and soil, 2) compare the carbon and nutrient economy of AM and ECM trees.

Method

Internal hyphae from roots and external hyphae from soil were collected around an AM (Tulip poplar) and an ECM (White oak) tree at Moore's Creek forest, Indiana in May 2018. Hyphae within roots were isolated by applying (i) a mechanical approach with an ultrasonic bath and a blender, and (ii) an enzymatic extraction modified after Saito (1995). The extraction of hyphae from soil was performed by density separation (Brundrett, 1994). Extracted hyphae were analysed for their ¹³C and ¹⁵N isotopic signatures using EA-IRMS. In addition, root colonization rates, hyphal length and extraction efficiencies of the methods were determined.

Expected outcome

Using both, the mechanical and the enzymatic approach, internal hyphae were successfully isolated from plants and purified from plant debris. We will present preliminary data of carbon and nitrogen isotope signatures of AM hyphae. Overcoming the methodological obstacle of using fruiting bodies as supposedly adequate surrogate for fungal hyphae, the combination of hyphal isolation and determination of isotopic patterns will largely enhance our understanding of mechanisms of carbon and nutrient transfer between the plant and the soil via mycorrhizal fungi. In a broader context, our method will help answering continuative questions related to mycorrhiza-associated nutrient economies of either ECM-associated (organic nutrient economy) or mineral-nutrient driven AM-associated trees (mineral nutrient economy) [4].

- [1] Brundrett & Tedersoo (2018), New Phytologist
- [2] Hobbie et al. (1999), Oecologia
- [3] Handley et al. (1996), Rapid Communication Mass Spectrometry
- [4] Phillips et al. (2013), New Phytologist

Poster # 23 Poster Themen: Boden-Pflanzen-Atmosphäre

Stable hydrogen isotope ratios in soil organic matter

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Stable H isotope ratios are a promising indicator of OM transformation processes (Schimmelmann et al., 2006). δ2H values of bulk organic matter and of specific organic compounds can be used as ecological tracer and forensic tool if the proportion of H that readily exchanges with ambient moisture is accounted for (Wassenaar & Hobson, 1998). There are a few reports about the H isotope ratios in plant-soil systems illustrating that there is little knowledge of the controls of the isotopic composition of the non-exchangeable H fraction of bulk OM (Schimmelmann et al., 2006: Ruppenthal et al., 2015). The increasingly closer relationship between δ 2H values of rainfall and of non-exchangeable H in OM (δ 2Hn) in the order, plant – plant litter (above- and belowground) - soil along a climatic gradient (Ruppenthal et al., 2015) suggests that decomposition influences δ 2Hn values in OM in a systematic way. However, there is a lack of knowledge concerning the fractionation factors and the extent of incorporation of ambient water-H into the nonexchangeable fraction of H in OM during decomposition. Our research will focus on the mechanisms responsible for the strong correlation between $\delta 2H$ values in rainfall and $\delta 2Hn$ values of SOM. Therefore, our study aims to investigate (1) the incorporation of ambient water-H into the nonexchangeable H fraction in OM during decomposition by heterotrophic bacteria as model organisms and quantify apparent fractionation factors. (2) the extent of incorporation of ambient water into the nonexchangeable H fraction of OM by the soil microbial community under laboratory conditions, and (3) the extent to which H is incorporated into nonexchangeable OM pool from ambient water during decomposition of aboveground litter under field conditions. We will work with microcosms using two bacteria species and determine decomposition rates of litter. Steam equilibration (Ruppenthal et al., 2015) and TC/EA-IRMS are used as analytical tools. We expect that different decomposition rates because of differences in litter quality will be reflected by the extent of H incorporation from ambient water into the nonexchangeable H fraction of the products. Additionally, different litter types enriched in 2H will be buried in soil of forest stands. We hypothesize that the incorporation of 2H-depleted ambient water into 2Henriched nonexchangeable H fraction of OM will depend on litter type, soil moisture/ temperature, and the heterotrophic activity during the experiment.

Poster # 24 Poster Themen: Boden-Pflanzen-Atmosphäre

Mineral N uptake efficiency and internal distribution in 'Conference' pear trees <u>Ben Colpaert</u>^{1,3}, Kathy Steppe¹, Serge Remy², Ann Gomand², Bart Vanhoutte², Pascal Boeckx³

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The objective of this project is, by means of fertilization schedules conducted with ¹⁵N labelled calcium nitrate, to achieve an optimized fertilization schedule for pear trees, which results in maximum N utilization efficiency, fruit yield and quality, a balanced growth of the trees and minimum environmental impact. Specific objectives are: 1) determining the temporal evolution of the N fraction originating from calcium nitrate fertilization in organs of newly produced biomass (sampled organs include twigs, leaves, flower buds, fruit, bark, fine roots), 2) determining the N use efficiency of calcium nitrate fertilization schedules during one complete growing season, and 3) determining the temporal dynamics of the N fraction from calcium nitrate fertilization schedules during one complete growin in the xylem sap flow. In order to accomplish this, eight year-old pear trees are grown in pallet boxes (built as zero tension piezometers) and subjected to different fertilizer application regimes whereof at least one fraction of calcium nitrate is labelled with ¹⁵N (excluding the control group which receives no calcium nitrate). Additionally, this project aims at determining the ecophysiological response of pear trees exposed to the different fertilization schedules by using both continuous measurements (i.e. radial stem growth and sap flow) as well as discrete measurements (i.e. photosynthesis, transpiration and N distribution via spectral data).

Session 5: Klimaforschung und Stoffkreisläufe

ID: 138 Vortrag Themen: Klimaforschung und Stoffkreisläufe

Intramolecular stable isotope variation: New ecophysiological signals, and consequences for isotope-based biogeochemistry

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Stable isotopes have long been used in ecophysiology and for reconstruction of environmental variables. For decades it has also been known that stable isotopes are distributed unevenly **IN** biological metabolites. Consequently, conventional δ values are whole-molecule averages over varying intramolecular values (i.e. isotopomer abundances). However, this biochemical knowledge has not been applied in plant ecophysiology or biogeochemistry, because the first measurements of intramolecular isotope distributions required cumbersome breakdown of metabolites into small molecules for IRMS measurements. Recently, NMR methodology has advanced so that intramolecular isotope distributions can routinely be measured (Chaintreau et al., Anal. Chim. Acta 2013), although large samples are needed. Here we demonstrate the potential of intramolecular isotope distributions with several examples.

1. We show that ¹³C is distributed unevenly in the glucose units of tree-ring cellulose, with important consequences (Wieloch et al., Sci. Rep 2018): When wood enters soil organic matter and is broken down, the δ^{13} C of respired CO₂ will only follow δ^{13} C of cellulose if the glucose units are fully respired. If part of the glucose molecules enters other pathways, such as the oxidative pentose phosphate pathway, δ^{13} C of liberated CO₂ can deviate markedly from the whole-molecule value. This may have consequences for using ^{δ^{11}}C of CO₂ to unravel ecosystem C exchange fluxes.

2. Intramolecular isotope distributions are created by enzyme isotope effects, hence they constitute fingerprints of biosynthetic pathways and can report on regulation of metabolism on time scales up to millennia. As particular advantage, this information can be encoded in *isotopomer ratios*, and can be extracted independent of the source isotope source (Augusti et al., Chem. Geol. 2008; Ehlers et al., PNAS 2015).

3. We demonstrate that intramolecular ¹³C distributions of the glucose units of tree-ring cellulose vary over time. This implies that ¹³C fractionations mechanisms beyond the well-known stoma-ta-Rubisco mechanism exist. The time-dependent intramolecular variation constitutes new ecophysiological information.

4. When δ^{13} C or δ D are used as proxies for ecophysiological parameters, correlation coefficients between both quantities are restricted to low values, limiting the power of isotope-based reconstructions. We show that this limitation is at least partly caused by intramolecular isotope variation. Conversely, higher correlation coefficients can be observed between intramolecular isotope parameters and ecophysiological parameters. Thus, intramolecular isotope data allow for more powerful reconstructions of physiological and environmental parameters (Wieloch et al., Sci. Rep 2018).

ID: 129 Vortrag

Themen: Klimaforschung und Stoffkreisläufe

Interpretation of compound-specific $\delta^2 H$ and $\delta^{18}O$ results from n-alkane and sugar biomarkers derived from Late Glacial to Early Holocene Lake Bergsee sediments

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Lacustrine sedimentary aquatic-derived biomarkers, e.g. short and mid-chain n-alkanes, and their hydrogen isotopic composition (aquatic $\delta^2 H_{\text{particular}}$) are proved to be of a value in paleohydrology research. In most cases those $\delta^2 H$ values reflects the isotope composition of lake water, and therefore often precipitation. Due to evaporation, however, the lake water signal can be altered to an unknown degree. Alternatively, leaf wax-derived biomarkers, e.g. long chain nalkanes, are extraced from lacustrine sediments and measured compound-specifically in order to obtain terrestrial $\delta^2 H_{n-alkane}$ values. Those values in turn reflect the isotope composition of leaf water from higher terrestrial plants grown in the catchment, which can be related to precipitation modified by leaf water ²H enrichment, caused by evapo(transpi)ration. Therefore, the interpreation of single $\delta^2 H_{\rho-alkane}$ -based climate proxies often remains challenging and not quantitive. During the last decade, compound-specific δ^{18} O analysis was developed to measure individual sugar biomarkers, yielding $\overline{\delta}^{18}O_{sugar}$ values. The interpretation of $\overline{\delta}^{18}O_{sugar}$ values is comparable to the $\delta^2 H_{ralkane}$ ones. When the sugars originate from aquatic sources, they reflect lake water and can thus be thus interpreted either in terms of reflecting δ^{18} O of paleoprecipitation or as precipitation/evaporation ratio due to lake water evaporative ¹⁸O enrichment. When sugars originate primarily from terrestrial sources, more specifically from the leaf biomass of higher terrestrial plants grown in the lake catchment, then they reflect precipitation modified by evapo(transpi)rative enrichment of leaf water.

More recently the coupling of *n*-alkane-derived $\delta^2 H$ results with $\delta^{18}O$ results from sugars has been shown to have the potential to overcome this limitation. Either lake water evaporation history or past relative humidity values can be reconstructed, depending on the aquatic or terrestrial origin of the biomarkers. This points to the fact, that the fundamental question about the origin of the sedimentary biomarkers, whether they are of autochthonous (aquatic) or allochthonous (terrestrial) origin, have to be reviewed carefully before the $\delta^2 H_{n-alkane}$ and $\delta^{18}O_{sugar}$ records can interpreted and coupled, respectively.

We present $\delta^2 H_{\text{n-alkane}}$ and $\delta^{18}O_{\text{sugar}}$ results of lacustrine sediment samples from Lake Bergsee, South Germany, located in the Black Forest region. The investigated core section covers the time between 16.0 ka and 10.8 ka BP, including the well-known Younger Dryas period, the largest cold spell occurring in the Northern Hemisphere during the Late Glacial. In our presentation, we will present the coupling of the $\delta^2 H_{\text{n-alkane}}$ and $\delta^{18}O_{\text{sugar}}$ results and discuss the origin of the investigated biomarkers.

ID: 115 Vortrag Themen: Klimaforschung und Stoffkreisläufe

Simulating the isotopic composition of terrestrial N cycle components with the Stable Isotope MOdel for Nutrient cyclEs (SIMONE)

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The excessive use of Nitrogen (N) fertilizers on the one hand has boosted global population growth, but on the other hand had detrimental effects on the environment. For instance, the surplus of reactive N, i.e. inorganic and organic N forms, in terrestrial ecosystems has led to increased soil emissions of nitrous oxide (N₂O), which depletes stratospheric ozone and increases radiative forcing. Process-based biogeochemical models are increasingly used to track N compounds and soil N₂O emission sources and to develop targeted strategies to mitigate soil N₂O emissions as well as nitrate leaching from agricultural systems. Although such models consider all relevant N cycling processes, they are usually calibrated and validated with individual, measurable quantities at ecosystem scale e.g. exchange rates of N compounds or N in harvested plant products. However, the improvement and validation of biogeochemical models requires information on processes underlying soil N₂O emissions. The isotopic composition of large N pools, e.g. the soil N pool, reflect the dominant N cycle processes in a specific environment and, thus, may be used as additional integrative validation quantity.

With SIMONE we present a module that allows tracking changes in the isotopic composition of the various N compounds due to physico-chemical and biological N cycling in ecosystems. This isotope model builds upon the biogeochemical model LandscapeDNDC and uses isotopic fractionation factors for isotope calculations. Here we present a review of available data on N isotope effects and assess the sensitivity of the simulated isotopic composition of different N compounds in view of the uncertainty of isotope effects, process rates and meteorological conditions. The performance of SIMONE will be discussed based on a comparison of simulated and measured d¹⁵N in soil emitted N₂O using datasets obtained during field campaigns conducted at the grassland sites Chamau and Beromünster, central Switzerland. During these campaigns, also the isotopic quantity "site preference" was determined, i.e. the difference of d¹⁵N of N₂O substituted with ¹⁵N at the central and terminal position, respectively, which is considered a powerful tool for partitioning soil N₂O emissions to the contributions of nitrification and denitrification. The dynamics of measured and simulated site preference will be discussed in view of management action and meteorological conditions.

ID: 132 Vortrag Themen: Klimaforschung und Stoffkreisläufe

Radiocarbon chronology and paleoclimate reconstruction based on coupled δ^2 H/ δ^{18} O biomarker analyses of lacustrine sediments from Garba Guracha, Bale Mountains, Ethiopia

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East Africa is a region of extreme climate variability in the past. These climate changes are one of the key factors for human dispersal and migration and therefore highly discussed. To contribute to this discussion, we investigate the sediment archive of Garba Guracha in the Bale Mountains, Ethiopia. Garba. It was investigated previously by Umer et al. (2007, QSR 26) and Tiercelin et al. (2008, QSR 27), focusing on pollen and geochemical analyses respectively. Our work aims at (i) establishing a robust chronology based on radiocarbon dating of bulk sedimentary organic matter, bulk n-alkanes and charcoal, as well as on tephrochronology; (ii) paleoclimate reconstruction based on biomarker and stable isotope analyses. All four dating techniques yield ages that are in good agreement. We find no evidence for preaging of lipids. These results indicate that we can establish a robust Late Glacial and Holocene chronology for the sediments of Garba Guracha.

Compound-specific δ^{18} O analyses of plant-derived sugars (c.f. Zech et al., 2014, JOPL 51) yield more negative values for early Holocene core sections than for the rest of the sedimentary archive. We tentatively interpret this finding in terms of higher rainfall amount associated with the African Humid Period. Ongoing work focuses on compound-specific δ^2 H analyses of plant-derived n-alkane biomarkers. We present the first results for Garba Guracha from a coupled δ^2 H- δ^{18} O biomarker approach (c.f. Hepp et al., 2015, HYDROL 529). The coupled approach enables us (i) to reconstruct the lake evaporation history and/or relative humidity and (ii) reconstruct more robustly the isotopic composition of precipitation than hitherto possible based on δ^2 H or δ^{18} O results alone.

This study is part of the Research Group DFG FOR 2358.

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Umer, M., Lamb, H. F., Bonnefille, R., Lézine, A. M., Tiercelin, J. J., Gibert, E., Watrin, J. (2007): Late Pleistocene and Holocene vegetation history of the Bale Mountains, Ethiopia.

Zech, M., Tuthorn, M., Zech, R., Schlütz, F., Zech, W. & Glaser, B. (2014): A 16-ka δ^{18} O record of lacustrine sugar biomarkers from the High Himalaya reflects Indian Summer Monsoon variability.

Poster # 25 Poster Themen: Klimaforschung und Stoffkreisläufe

Sources and diagenesis of amino acids in Swiss lakes

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Lakes cover only an area about 35 times smaller than the oceans but it is expected that the carbon burial in lakes is around the same order of magnitude or even higher than the oceans carbon burial. Therefore, the understanding of the processes responsible for organic carbon burial in lacustrine systems is essential. Work in marine environment on amino acid composition and stable isotope composition of amino acids have led to useful amino acid based proxies which should also be valid in lakes. Those proxies were used for this study to examine three different lakes systems which differ in trophic state and also in the amount of terrestrial contribution to the sedimentary organic matter. Additionally, carbon isotope fingerprinting of amino acids was used to characterise the source and fate of the amino acids. It could be shown that the amino acids are mostly of autochthonous origin. Furthermore, it was shown that amino acids only contribute for about 30-50 % of the carbon found in the liquid fraction (AS fraction) after the hydrolysis of a lipid-free sample. Therefore, another major fraction must be present in the AS fraction which was shown to be from terrestrial origin. Furthermore, it could be shown that methanotrophic bacteria leads to increased values for the proxy for bacterial reworking (SV) and extraordinarily low d¹³C values (-30 to -60 ‰) for the amino acids. Additionally, extracellular protein hydrolysis was suggested to be responsible for very high nitrogen isotope composition in the water column of Lake Biel. However, this extracellular protein hydrolysis cannot be detected with the common proxies for bacterial reworking or trophic level.

Poster # 26 Poster Themen: Klimaforschung und Stoffkreisläufe

Interpreting hydro-isotope records from Patagonia by means of backward trajectories, surface water surveys and refined isotope proxies

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Very strong and persistent zonal atmospheric flow in the mid-latitudes of the Southern Hemisphere forms the westerly wind belt. This wind belt advects moist air masses from the Pacific Ocean towards the Andes and leads to precipitation on its upstream side due to orographic lifting but aridity on the downwind side due to a foehn effect. Knowledge is scarce about the exact regions of moisture uptakes and their respective movement patterns. Moisture origins have been evaluated by backward trajectories and compared with hydrogen and oxygen stable isotope composition of precipitation of stations from the Global Network for Isotopes in Precipitation. Stations downstream of the Andes show isotopic depletion caused by Rayleigh-type isotope fractionation compared to upstream stations, despite of similar moisture sources. Moisture recycling above the continent plays a major role for a station further east at the Atlantic leading to heavy-isotope-enriched rainfall there.

This information is of high significance for the interpretation of oxygen isotope records from Patagonian lake sediments, peats or tree-rings used to reconstruct past atmospheric and hydrological dynamics. Beside a few GNIP stations, the modern database needed for the calibration of isotope proxies from remote Patagonia areas is extremely poor. To overcome this lack of data, lentic and lotic waters from Chile and Argentina were sampled between 2013 and 2018. We show that the water balance has a strong influence on the isotopic composition of lentic waters. Bathymetry, exposition to wind, inflows, outflows, and climatic settings influence their water balances, and in turn have a strong influence on the isotopic composition of lakes. Thus, the choice of sites and of reliable proxies for the oxygen isotopic composition of the lake water is especially important. Methodologically refined proxies, such as oxygen isotope ratios of aquatic cellulose and chironomid head capsules, provided promising results in our calibration studies.

Poster # 27 Poster Themen: Klimaforschung und Stoffkreisläufe

Implementation of the ¹⁵N-pool dilution technique for the calculation of gross transformation rates of nitrate and its heterogeneity in the field

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Nitrification is one of the main processes in the terrestrial nitrogen cycle that plays an important role for the emission of greenhouse gases and the pollution of groundwater, especially on agricultural soils. For deeper understanding, gross nitrification rates are commonly determined by isotopic pool dilution technique (Kirkham & Bartholomew 1954). Our study aimed at transferring the ¹⁵N-pool dilution technique to the field, attempting to establish an appropriate method for determining gross nitrification rates in undisturbed soils. At the same time the spatial variability of transformation rates was investigated on the plot scale. This variability is based on the irregular spatial distribution of soil properties, like organic carbon content, C/N-ratio, pH-value and microbial activity. This has so far not been considered by most authors.

A field experiment was implemented on a cultivated sandy soil in March 2018 in north-western Lower Saxony, Germany. A large-scale irrigation system, developed at the Federal Institute for Geosciences and Natural Resources (BGR), Hannover, was used to isotopically enrich the soil with K¹⁵NO₃, D₂O and with LiBr and to obtain a homogeneous distribution of the tracer solution. To consider small-scale differences of nitrification rates, soil samples were taken from five depths (0-50 cm in 10 cm increments) at 18 points of a 4 m²-plot. Two soil samples were taken from each sampling point at different dates to enable the calculation of the transformation rates for every sampling point. ¹⁵N-abundances and NO₃⁻-concentrations were measured by the latest SPINMAS technique.

Preliminary results have shown that the calculation of gross nitrification rates in the field is complicated for different reasons. ¹⁵N-abundances and NO₃-concentrations showed an irregular distribution of the tracer solution, even among sample pairs. Furthermore, water flow in the soil was observed even during incubation time, so that two processes affect the ¹⁵NO₃-abundance: transport and microbial activity. Other challenges concern the measurement by the SPINMAS unit, established at the BGR. Hence, the calculation itself and the determination of variabilities of nitrification rates was complicated. By improving knowledge concerning the effects of spatial variabilities of soil properties and microbial activity on nitrification rates, the presented method appears to be appropriate for field application.

Poster # 28 Poster Themen: Klimaforschung und Stoffkreisläufe

Water isotope geochemistry of interstitial fluids from the eastern Mediterranean Sea (ODP Leg 160)

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Interstitial waters extracted from long sediment cores retrieved during Leg 160 of the Ocean Drilling Program (ODP) were analysed for the stable water isotope ($^{2}H/^{1}H$, $^{18}O/^{16}O$) composition to constrain hydrographic changes in the eastern Mediterranean Sea prior to modern time. Measurements cover samples from ODP Sites 963 to 973, covering the geographical range between the Strait of Sicily and the eastern end of the Libyan Sea. The measurements demonstrate substantial downcore variations in both water isotope ratios covering overall dynamics of more than 8 ‰ (d¹⁸O) and 35 ‰ (d²H).

The stable isotope results are compared to recent isotope measurements on modern Mediterranean surface waters from a transect between the Strait of Gibraltar and the Black Sea retrieved during RV Maria S. Merian cruise MSM 33. The Leg 160 pore waters from shallow sediment depths are close to a Mediterranean seawater evaporation trend as defined by salinitystable isotope and d^2H - $d^{18}O$ covariations found for the modern surface waters. Trends for sites impacted by deep-seated salty solutions indicate a substantial variation towards a lighter water isotope composition.

At mud volcano sites, a reversed trend towards heavier and lighter O and H isotope compositions, respectively, are observed. This is due to the dehydration of clay minerals at enhanced depth into fluids, later migrating upwards to mud volcano sites (Dählmann & de Lange, 2003).

Session 6: Physiologie und Metabolismus

ID: 112 Vortrag Themen: Physiologie und Metabolismus

The Effect of Parasite Infection on Stable Isotope Turnover Rates in Multiple Tissues of Eurasian Perch from Bodensee

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Accurate interpretation of stable isotope values requires knowledge of tissue-specific isotopic turnover that will help to describe differences in the isotopic composition of tissues and diet. We performed a diet-switch experiment using captive-reared parasite-free Eurasian perch (Perca fluviatilis) and wild caught specimens of the same species, infected with the pike tapeworm Triaenophorus nodulosus living in host liver tissue. We hypothesize that metabolic processes related to infection status play a major role in isotopic turnover and examined the influence of parasite infection on isotopic turn-over rate of carbon (δ^{13} C), nitrogen (δ^{15} N) and sulphur (δ^{34} S) in liver, blood and muscle. The δ^{15} N and δ^{13} C turnovers were fastest in liver tissues, followed by blood and muscle. In infected fish, liver and blood δ^{15} N and δ^{13} C turnover rates were similar. However, in infected fish, liver and blood δ^{13} C turnover was faster than that of δ^{15} N. Moreover, in infected subjects, liver $\delta^{15}N$ and $\delta^{13}C$ turnover rates were three to five times faster than in livers of uninfected subjects (isotopic half-life of ca.3-4 days compared to 16 and 10 days, respectively). Blood δ^{34} S turnover rate were about twice faster in non-infected individuals implying that parasite infection could retard the turnover rate of δ^{34} S and sulphur containing amino acids. Slower turnover rate of essential amino acid could probably decrease individual immune function. These indicate potential hidden costs of chronic and persistent infections that may have accumulated adverse effects and might eventually impair life-history fitness. For the first time, we were able to shift the isotope values of parasites encapsulated in the liver by changing the dietary source of the host. We also report variability in isotopic turnover rates between tissues. elements and between infected and parasite-free individuals. These results contribute to our understanding of data obtained from field and commercial hatcheries; and strongly improve the applicability of the stable isotope method in understanding life-history and trophic ecology of fish populations.

ID: 145 Vortrag Themen: Physiologie und Metabolismus

Compound-specific stable-isotope analysis for investigating bioavailability limitation of micro- pollutants in 2D flow-through tank experiments

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Biodegradation of organic micropollutants in groundwater appears to stop at low concentrations. Compound-specific isotope analysis (CSIA) has been developed as a promising approach to explore the onset of bioavailability limitations in biodegradation at low-level concentrations ^[1]. The role of membrane permeability as a barrier to atrazine biodegradation at low levels has been highlighted in a recent batch study. gram negative bacteria ^[2]. To further explore whether bioavailability limitation becomes prominent at low contaminant concentration in environmental systems, two-dimensional sediment tank experiments, where a high-to-low concentration of 2,6-dichlorobenzamide (BAM) at its natural isotopic abundance is produced by transverse dispersion. The experiments were conducted in both abiotic phase and biotic phase to study the influence of different hydrological dynamics on the observed isotopic fractionation. The isometric fractionation of BAM (13 C / 12 C and 15 N / 14 N) due to hydraulic dispersion was negligible. For the biotic tank experiment, Aminobacter sp. Strain MSH1 was inoculated into the tank. Bioavailability limitation during biodegradation of micropollutants and to explore the range of bioavailability limitations.

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ID: 160 Vortrag Themen: Physiologie und Metabolismus

Heterotrophic ¹³CO₂-Fixation – New insights to microbial DOC utilisation from stable isotope labelling?

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Virtually all heterotrophs incorporate CO_2 . So far no one made use of the fact that heterotrophic fixation of CO_2 depends on the organic substrate and thus this process has the potential to show which carbon source was utilised by the heterotroph.

Bacillus subtilis was grown in M9 minimal medium in the presence of $H^{13}CO_3^-$ and various organic substrates. The ^{13}C -incorporation into bacterial biomass was determined by EA-IRMS and the ^{13}C -distribution in protein-derived amino acids was measured by GCMS.

The enzyme pyruvate carboxylase (PC) catalyses the conversion of pyruvate to oxaloacetate via the addition of CO_2 , thus replenishing the TCA-cycle. PC occupies a vital position in a metabolic hub of the central carbon metabolism, being responsible for the regulation of the carbon flux in the cell. Depending on the carbon source, we expect different ¹³C enrichment patterns of metabolic products, with an indicative pattern for each carbon source.

We found that growth on substrates that are funnelled through glycolysis led to enrichment in ¹³C of up to 12% in the amino acids directly derived from TCA-cycle metabolites. In case of growth on substrates that enter the central carbon metabolism "between" glycolysis and the TCA-cycle, the amino acids directly derived from TCA-cycle metabolites were enriched in ¹³C as well as the amino acid glycine, which was derived from gluconeogenic metabolites. In both cases, the replenishment of the TCA-cycle through PC was crucial and we found the expected distribution of ¹³C in the amino acids. In contrast, during growth on TCA-cycle metabolites the replenishment of the TCA-cycle through PC is negligible. This clearly shows that the CO₂-fixation patterns are indicative for different carbon sources and can be used to differentiate amongst them.

ID: 133 Vortrag Themen: Physiologie und Metabolismus

Bioavailability limitation influences the maintenance demand and physiology of Arthrobacter aurescens TC1 defining a limit of atrazine degradation at low concentrations

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Exploring adaptive strategies by which microorganisms function and survive in low-energy natural environments remains a grand goal of microbiology, and may help address a prime challenge of the 21 st century: the removal of man-made chemicals at low Concentrations ("micropollutants") from the environment. Here we explore physiological adaptation and maintenance requirements of a pesticide (atrazine) -degrading microorganism (*Arthrobacter aurescens* TC1) while concomitantly observing bioavailability limits directly by compound-specific isotopic fractionation analysis. Chemostat-based growth triggered the onset of bioavailability limitations at residual concentrations of 30 µg L⁻¹ with a doubling time (t_d) induced by near-zero retentate-based growth (t_d = 265 days) at 12 ± 3 µg L⁻¹ residual atrazine. This resulted in (i) complete bioavailability limitation evidenced by the disappearance of isotopic fractionation ($\epsilon^{13}C = -0.45 \% \pm 0.36 \%$) and (ii) a two-fold decrease in maintenance energy requirement compared to chemostat cultivation. Proteomics revealed that retardostat and chemostat cultivation and bioavailability limitation exidenced slow-down of metabolism results in an active metabolizing microbial population that imposes a limit of atrazine degradation below 10 µg L⁻¹.

ID: 167 Vortrag Themen: Physiologie und Metabolismus

Measurement of albumin synthesis in endotoxemic pigs exposed to deoxynivalenol (DON) by using L-[${}^{2}H_{5}$]-phenylalanine as tracer

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Measurement of albumin synthesis in endotoxemic pigs exposed to deoxynivalenol (DON) by using L- $[{}^{2}H_{5}]$ -phenylalanine as tracer DON is a *Fusarium* mycotoxin which frequently contaminates feedstuffs for pigs and affects protein synthesis. Lipopolysaccharides (LPS) are constituents of the cell wall of Gram-negative bacteria and potent inducers of an acute phase response (APR) whereby they are acting as endotoxins. Albumin is a negative reactant of the APR and the major hepatic exported protein.

The aim of the present study was to examine the effects of DON on albumin synthesis in a porcine endotoxemic animal model. Briefly, a total of 44 barrows (German Landrace) with an initial mean body weight (BW) of 25.8 ± 3.7 kg were fed either a control diet (**CON**, 0.12 mg DON/kg diet) or a diet mainly contaminated with DON (**DON**, 4.59 mg DON/kg diet) for 4 weeks. At day 27 of experiment they were surgically equipped with permanent indwelling systemic (post-hepatic) and portal (pre-hepatic) blood vessel catheters. At day 29 of experiment pigs of the two feeding groups were randomly assigned to 3 infusion groups each and were infused for 60 min with LPS (**LPS**, 7.5µg/kg B, *Escherichia coli* O111:B4), either jugular or portal (**LPSju** or **LPSpo**, respectively), or with a NaCl solution (**CONju** and **CONpo**, respectively).

For isotope tracing in newly synthesized albumin the so-called large or flooding dose technique was applied. All pigs were injected with 5 mL/kg BW of a phenylalanine (phe) solution (150 mMol/L, 29 molar percent L-[$^{2}H_{5}$] phe excess, **MPE**, 125 mg total phe/kg BW) prepared from L-phe and L-[$^{2}H_{5}$]-phe at 105 min relative to the start of LPS/saline infusion into the internal jugular vein. Blood samples were collected at 30, 45, 60 and 90 min from the external jugular vein and prepared for HPLC-MS/MS analyses as described elsewhere (Kullik et al., 2013).

Fractional synthesis rate (FSR) of albumin was calculated as the ratio between the time-related linear increase in MPE of albumin and the corresponding area under the MPE–time curve of the precursor pool (plasma–free L-phe) multiplied by 100 (Ballmer et al., 1990).

The albumin FSR (%) amounted to: CON_CONju/CONpo, 38.0; CON_CONju/LPSpo, 22.5; CON_LPSju/CONpo, 23.4; DON_CONju/CONpo, 39.7; DON_CONju/LPSpo, 24.7; DON_LPSju/CONpo, 22.0.

In conclusion, albumin synthesis was significantly reduced in all LPS infused pigs irrespective of oral DON exposure and LPS entry site (jugular vs. portal).

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Poster # 29 Poster Themen: Physiologie und Metabolismus

Compound-specific isotope analysis (CSIA) for the investigation of bottlenecks for atrazine degradation with Arthrobacter aurescens TC1 under varying nutrient availabilities

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Degradation of organic contaminants including herbicides can become limited at low concentrations (ug/l range). The extent to which degradation-associated compound-specific isotopic fractionation was masked at low residual atrazine concentrations (< 50 µg/L) recently revealed that degradation by Arthrobacter aurescens TC1 became bioavailability-limited (in communication). The particular role of the cell wall as barrier transport through the cell membrane was highlighted by a complementary study with gram positive and gram negative bacteria [1]. Partial retentostat experiments with an additional source of carbon (acetate) showed that physiological changes also contributed to the decrease in atrazine biodegradation under oligotrophic conditions [2]. To further investigate the effect of nutrient availability on atrazine degradation by Arthrobacter aurescens TC1, we perform retentostat experiments comparing conditions of higher nitrogen availability (addition of nitrate), higher nitrogen and carbon availability (addition of nitrate and lactate), and low substrate availability (atrazine only). To shed light on bottlenecks for degradation under these varying conditions, a range of analytical tools will be used including CSIA, proteomic analyses, as well as metabolomic analyses. The results obtained will assist in understanding bottlenecks for contaminant degradation and help develop strategies to increase the effectiveness of bioremediation and biofiltration approaches.

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Stable Isotope Fractionation during Hydrogen Oxidation by D. vulgaris str. Miyazaki

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Hydrogen is a widespread substrate in the subsurface and used by several taxonomical and ecophysiological different microorganisms as electron donor or acceptor, catalyzed by the enzyme hydrogenase. Besides reducing protons or oxidizing molecular hydrogen, hydrogenases catalyze an equilibrium isotopic exchange between molecular hydrogen and protons of water. Both of these reactions can be catalysed quasi-simultaneously. Previous studies indicated that stable isotope effects associated with the exchange reaction can become dominant, thus complicating approaches to determine the stable hydrogen isotope fractionation of the hydrogen oxidation reaction. On the other hand, isotope effects of the exchange reaction may be applicable for environmental monitoring of hydrogen oxidation processes as the equilibrium isotope exchange without catalyst is considerably slower. In this study, we investigate stable isotope effects during hydrogen oxidation by the model organism Desulfovibrio vulgaris str. Miyazaki F (DSM 19637) containing a cytochrome c3 hydrogenase, monitored by analysis of δD of H2 via GC-IRMS. We aim to vary physio-chemical parameters (e.g., pH, temperature, shaking speed) as well as D/H isotope ratios of added hydrogen and water during autotrophic growth with hydrogen as electron donor for testing whether stable isotope effects are robust or not, thus elucidating changes in the reaction rates of the exchange and the oxidation reaction. Long-term goal is to develop an isotope monitoring tool for detection of hydrogen oxidation processes at hydrogen storage sites

Poster # 31 Poster Themen: Physiologie und Metabolismus

Reconstructing Lake ecosystem history using carbon isotopes in resting Daphnia eggs

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To reconstruct lake food webs in lake ecosystems, stable isotope analysis became a widely used method. While $\delta^{15}N$ tends to increase from food source to consumer and thereby give information about the trophic position, δ^{13} C signature reflects dietary sources. To see if and how environmental conditions during eutrophication influenced the food web of lakes, bulk stable isotope signatures of Daphnid fossil resting eggs (ephippia) in sediment cores were analysed. In Lake Constance, one of the largest lakes in Central Europe, eutrophication occurred from 1960-2000 with a peak in 1980. Therefore we investigated $\delta^{15}N$ and $\delta^{13}C$ signatures of resting eggs and their shells separately from 1960-2000 to see if there is a shift during eutrophication and the system response reversible when reoligotrophication occurs. Five years of sediment layers were pooled to one sample to get a sufficient number of eggs to analyse. Our data show an increase for δ^{13} C values until 1980/1985 for resting eggs and also for shells and a decrease after 1985. This might be explained by the increase of phosphor concentration during eutrophication, which caused an increase in primary production. The higher primary production has probably led to a corresponding rise in δ^{13} C values. For future research we aim to investigate compound specific amino acids of resting eggs and shells to get a deeper understanding of the influence of environmental conditions to the lake food web.

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