

# TAGUNGSBAND

## 36. Jahrestagung der Arbeitsgemeinschaft Stabile Isotope e. V.

28. – 30. September 2015  
Heidelberg



INSTITUT FÜR  
GEOWISSENSCHAFTEN



UNIVERSITÄT  
HEIDELBERG  
ZUKUNFT  
SEIT 1386



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## Grußwort

Wir begrüßen Sie herzlich zur Jahrestagung der Arbeitsgemeinschaft Stabile Isotope e. V. an der Universität Heidelberg!

Die 1386 gegründete Ruperto Carola ist die älteste Universität Deutschlands und eine der forschungstärksten in Europa. Pfalzgraf und Kurfürst Ruprecht I. eröffnete die Universität Heidelberg mit päpstlicher Genehmigung 1386 in seiner Residenzstadt.

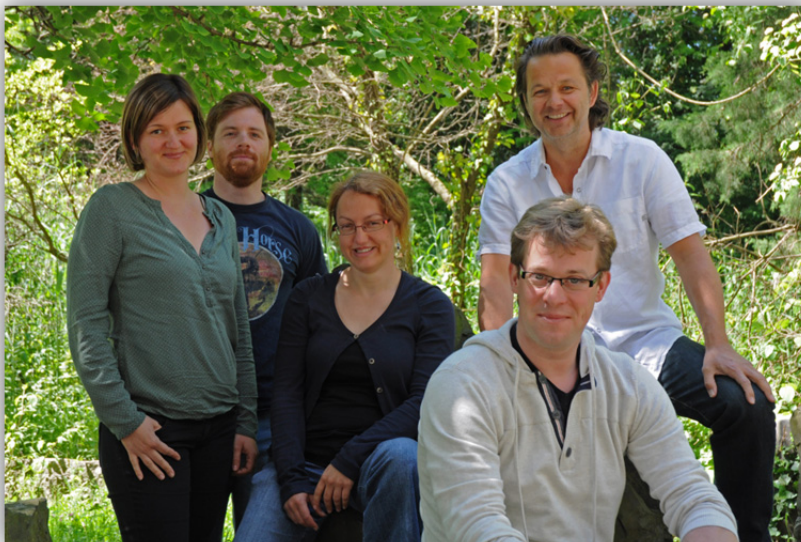
Die diesjährige Tagung findet im Museum des Instituts für Geowissenschaften der Universität Heidelberg statt. Die Sammlung des Instituts für Geowissenschaften beherbergt einen der wichtigsten Funde der Menschheit: den Unterkiefer des Homo heidelbergensis.

Geologisch-paläontologische Forschung und Lehre haben in Heidelberg eine über 200-jährige Tradition: die erste Vorlesung für Geologie wurde 1805 durch Johann Christian Zimmermann gehalten. In den letzten Jahrzehnten hat sich die Analyse von stabilen Isotopen in den Geowissenschaften zu einem der zentralen Werkzeuge entwickelt. Der Aufruf für Beiträge zur diesjährigen Jahrestagung der Arbeitsgruppe Stabile Isotope e.V. galt daher besonders den **geowissenschaftlichen Forschungsgebieten**.

Darüber hinaus gibt es weitere Schwerpunkte aus allen Forschungsgebieten, in denen stabile Isotope im Fokus der Arbeiten stehen. Die einzelnen Themengebiete sind: **Atmosphärische Prozesse, Geochemische Stoffkreisläufe und Hydrologie, (Paläo-) Klimaforschung, Lebensmittelherkunft und Forensik, Metabolismus und Physiologie und Ökosysteme**. Und natürlich – wie jedes Jahr – **Methodenentwicklung zur Analyse stabiler Isotope!**

Wir freuen uns, mit Ihnen gemeinsam neueste Forschungserkenntnisse auf dem Gebiet der stabilen Isotope zu diskutieren.

Ihr Organisationsteam



Frank Keppler, Markus Greule, Daniela Polag,  
Tobias Anhäuser und Nicole Jaeger





## Wissenschaftliches Programm • Montag, 28. September 2015

13:00 Begrüßung

### 13:15–15:30 Session 1 – Atmosphärische Prozesse

Chair F. Keppler (Heidelberg/DE)

13:15 Keynote–Presentation: The use of isotope measurements in atmospheric research.

**V1** T. Röckmann (Utrecht/NL)

13:50 Mapping methane plumes and the delta C-13 composition of anthropogenic sources around Heidelberg

**V2** M. Schmidt (Heidelberg/DE)

14:10 D/H Isotope Ratio Measurements of Atmospheric Volatile Organic Compounds

**V3** T. Meisehen (Wuppertal/DE)

14:30 Temperature dependence of the carbon kinetic isotope effect for the oxidation reaction of ethane by OH radicals under atmospherically relevant conditions: experimental and theoretical studies

**V4** T. Piansawan (Jülich/DE)

14:50 Modelling the isotopic composition of long lived trace gases with the AGAGE 12 Box model

**V5** E. Bahlmann (Hamburg/DE)

15:10 Tracking aerosol chemical age with stable carbon isotopes

**V6** J. Gensch (Jülich/DE)

### 15:30–16:30 Postersession und Kaffeepause

### 16:30–18:10 Session 2 – Analytik: Methoden, Techniken und Standardisierung I

Chair W. Brand (Jena/DE)

16:30 Real-time analysis of  $\delta^{13}\text{C}$ - and  $\delta\text{D}$ -CH<sub>4</sub> in ambient air with laser spectroscopy: Method development and intercomparison

**V7** J. Mohn (Dübendorf/CH)

16:50 Head space analysis of CO<sub>2</sub> isotopologues with an Isotope Ratio Infrared Spectrometer

**V8** H. J. Jost (Reinach/CH)

17:10 Automatic Data Calibration Strategies with IONOS

**V9** F. Volders (Hanau/DE)

17:30 Extending the boundaries of 10 kV isotope ratio MS

**V10** A. Hilkert (Bremen/DE)

17:50 A comparison of methods for triple isotopocule N<sub>2</sub> analysis

**V11** J. Dyckmans (Göttingen/DE)

**20:00 User Meeting Thermo Fisher Scientific GmbH**

## Wissenschaftliches Programm • Dienstag, 29. September 2015

<b>8:30–09:50</b> Chair	<b>Session 3 – Analytik: Methoden, Techniken und Standardisierung II</b> W. Brand (Jena/DE)
<b>8:30</b> <b>V12</b>	Compound-specific hydrogen isotope analysis of heteroatom-bearing compounds via gas chromatography – chromium/HTC – isotope ratio mass spectrometry (GC-Cr/HTC-IRMS) J. Renpenning (Leipzig/DE)
<b>8:50</b> <b>V13</b>	Comparison of carbon and oxygen isotope values from different wood preparation procedures in dendrochronology D. F. C. Riechelmann (Mainz/DE)
<b>9:10</b> <b>V14</b>	Limits and potentials determining stable water isotopes using in-situ measurements and soil water extractions M. Gaj (Hannover/DE)
<b>9:30</b> <b>V15</b>	Oxygen isotope analyses of individual carbohydrates with GC-Pyrolysis-IRMS – a new and precise method M. M. Lehmann (Villigen/CH)
<b>09:50–10:50</b>	<b>Postersession und Kaffeepause</b>
<b>10:50</b>	<b>Verleihung des Isotopenpreises</b>
<b>11:50–13:10</b>	<b>Mittagspause</b>
<b>13:10–14:50</b> Chair	<b>Session 4 – Geochemische Stoffkreisläufe und Hydrologie</b> M. Böttcher (Warnemünde/DE)
<b>13:10</b> <b>V16</b>	Investigation of sulfur-cycling processes in a BTEX contaminated porous aquifer by using a high-resolution sampling strategy F. Einsiedl (München/DE)
<b>13:30</b> <b>V17</b>	Isotope fractionation of dissolved O <sub>2</sub> reveals the rate-limiting step during enzymatic dioxygenation of (nitro)aromatic contaminants S. Pati (Dübendorf/CH)
<b>13:50</b> <b>V18</b>	What does $\delta^7\text{Li}$ in water tell us about flow paths in an alpine catchment? C. Meier (Halle a. d. Saale/DE)
<b>14:10</b> <b>V19</b>	Deuterium ( <sup>2</sup> H) as applied tracer in the vadose zone: experiences from semiarid Namibia M. Beyer (Hannover/DE)
<b>14:30</b> <b>V20</b>	Calcium isotopes as proxy for early diagenetic processes in marine porewaters N. Gussone (Münster/DE)
<b>14:50–15:10</b>	<b>Kaffeepause</b>

**Wissenschaftliches Programm • Dienstag, 29. September 2015**

**15:10–16:50     Session 5 – Klimaforschung**

Chair M. Zech (Halle a. d. Saale/DE)

15:10 V21	Novel Insights from Multi-Millennial Tree Ring Isotope Records of the Early and Mid-Holocene M. M. Ziehm (Bern/CH)
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15:30 **V22** Reconstructed isotopic composition of leaf water and precipitation provides new insight into hydrological changes in East Equatorial Africa during the Last Glacial J. Hepp (Bayreuth, Halle a. d. Saale/DE)

15:50 Compound-specific leaf wax  $\delta D$  and  $\delta^{13}C$  analyses from the Late Quaternary loess  
**V23** paleosol sequence El Paraiso, Central Spain  
 I. Schäfer (Bern/CH)

16:10 Late Glacial climate reconstruction based on stable isotopes in biomarkers from the  
**V24** Gemündener Maar, Germany  
 L. Wüthrich (Bern/CH)

16:30  
**V25** Glacial-interglacial productivity changes in the eastern equatorial Pacific upwelling system: a threshold response to Plio-Pleistocene ice-sheet dynamics? Implications from foraminiferal stable carbon and oxygen isotopes  
K. A. Jakob (Heidelberg/DE)

**16:50–18:00 ASI-Mitgliedertreffen**

**ab 19:00** Konferenz-Abendessen: Neckarfahrt mit dem Solarschiff „Neckarsonne“  
(pünktliches Ablegen um 19:00!)

## Wissenschaftliches Programm • Mittwoch, 30. September 2015

<b>8:50–10:10</b> Chair	<b>Session 6 – Lebensmittel, Forensik und Doping / Metabolismus und Physiologie</b> G. Gebauer (Bayreuth/DE)
8:50 <b>V26</b>	The EU funded project ‘SPICE-profiling’ (2015-2017): First results of the analytical characterization of Spice products containing the amino alkyl indole 5F-PB-22 by using stable isotope ratio mass spectrometry (IRMS) N. Scheid (Wiesbaden/DE)
9:10 <b>V27</b>	Stable Isotope Analysis as tool for the identification of authenticity and origin of fruits and fruit-products O. Nehlich (Neutal/AT)
9:30 <b>V28</b>	High intraspecific ability to adjust both carbon uptake and allocation under light and nutrient reduction in <i>Halimium halimifolium</i> L F. Wegener (Freiburg/DE)
9:50 <b>V29</b>	Direct incorporation of precursor fatty acids into microbial lipids in soils: Position-specific labeling tells the story M. Dippold (Göttingen/DE)
<b>10:10–11:10</b>	<b>Postersession und Kaffeepause</b>
<b>11:10 –12:30</b> Chair	<b>Session 7 – Ökosysteme</b> A. Giesemann (Braunschweig/DE)
11:10 <b>V30</b>	Can foliar $\delta^{15}\text{N}$ be retrieved from fresh leaf reflectance spectra? Evidence from an experimental labeling approach C. Hellmann (Bielefeld, Freiburg/DE)
11:30 <b>V31</b>	The importance of associations with saprotrophic non-Rhizoctonia fungi among fully mycoheterotrophic orchids is currently under-estimated: novel evidence from sub-tropical Asia G. Gebauer (Bayreuth/DE)
11:50 <b>V32</b>	Does “you are what you eat (plus a few permil)” also hold true for orchids? J. M.–I. Schiebold (Bayreuth/DE)
12:10 <b>V34</b>	Elucidation of microbial metabolic pathway activities in soil at low temperature using position-specific $^{13}\text{C}$ labeled glucose E. Bore (Göttingen/DE)
<b>12:30–13:15</b>	<b>Preisverleihungen und Schlussworte</b>



## Organisation

### Tagungsleitung

Prof. Dr. Frank Keppler	Ruprecht-Karls-Universität Heidelberg (Heidelberg/DE)
Dr. Daniela Polag	Ruprecht-Karls-Universität Heidelberg (Heidelberg/DE)
Dr. Markus Greule	Ruprecht-Karls-Universität Heidelberg (Heidelberg/DE)

### Wissenschaftliches Komitee

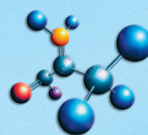
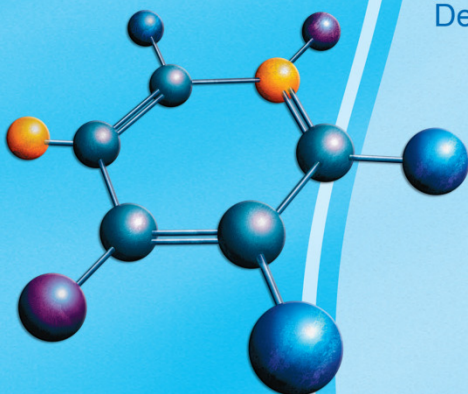
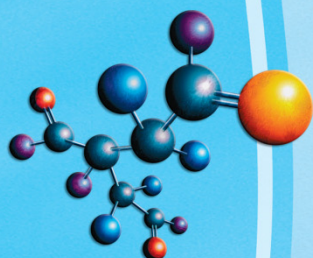
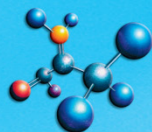
Wir danken dem wissenschaftlichen Komitee recht herzlich für eine hervorragende Zusammenarbeit im Rahmen der Jahrestagung!

Dr. Willi Brand	Max-Planck-Institut für Biogeochemie Jena (Jena/DE)
Dr. Martin Elsner	Helmholtz Zentrum München (München/DE)
Prof. Dr. Norbert Frank	Ruprecht-Karls-Universität Heidelberg (Heidelberg/DE)
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Prof. Dr. Frank Keppler	Ruprecht-Karls-Universität Heidelberg (Heidelberg/DE)
Dr. Daniela Polag	Ruprecht-Karls-Universität Heidelberg (Heidelberg/DE)
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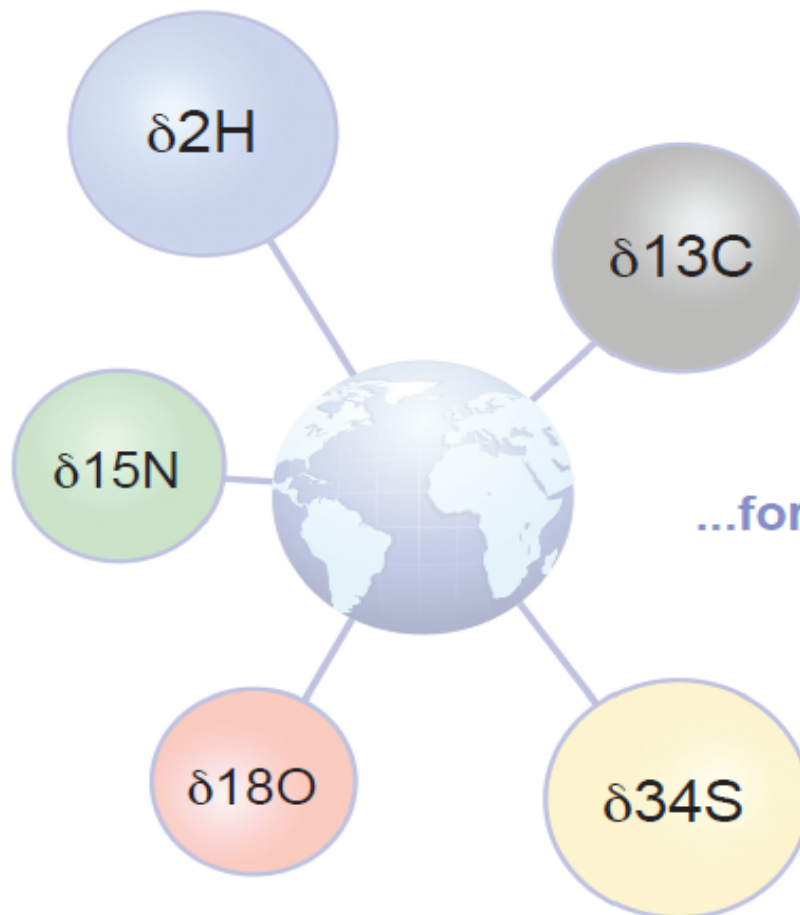
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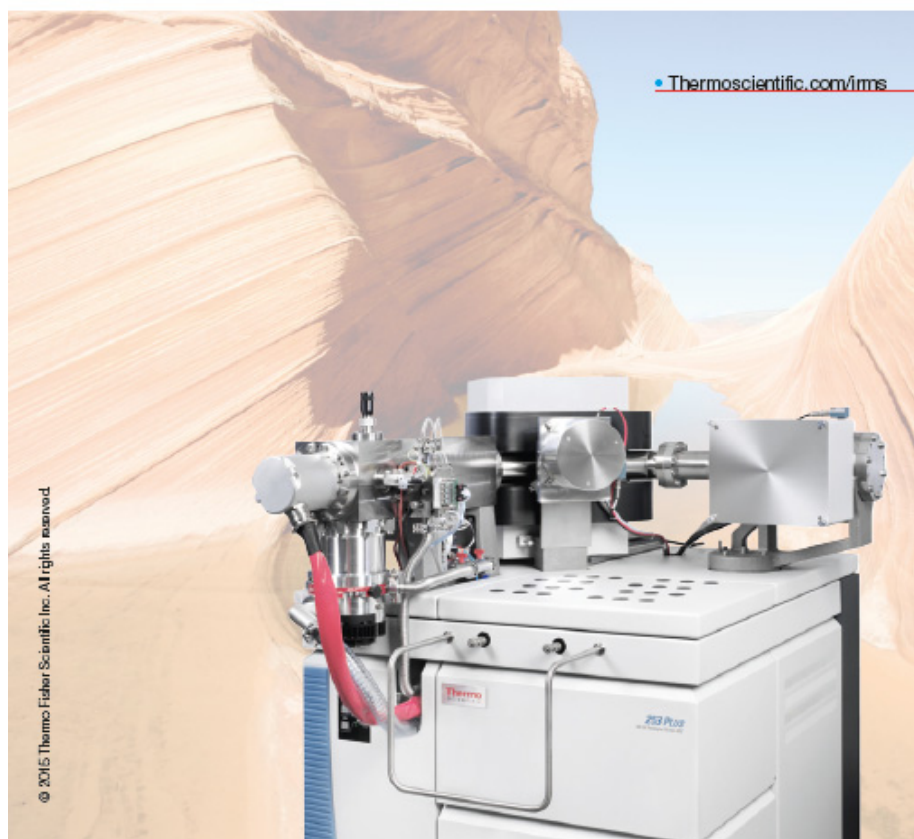


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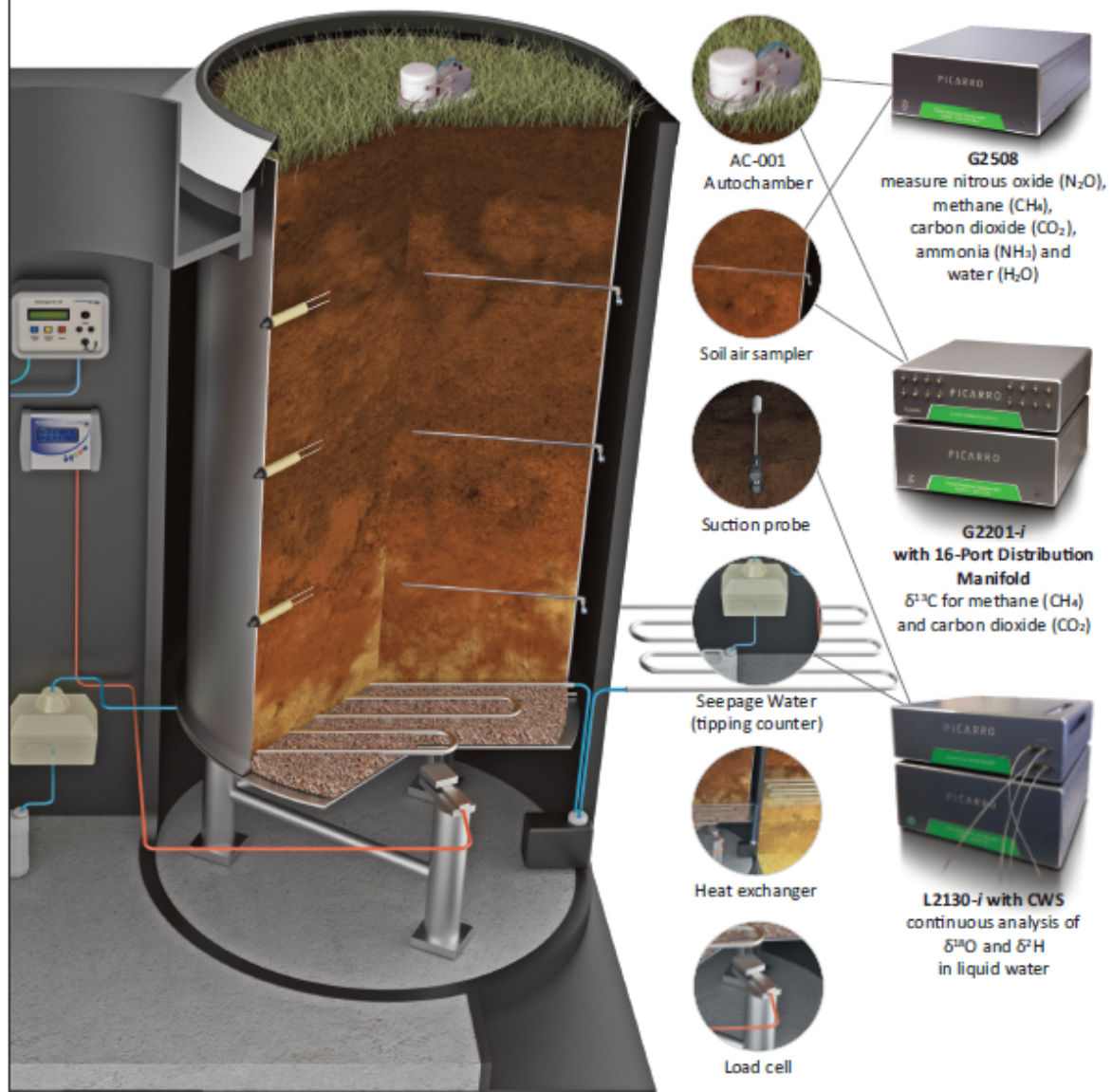
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UGT auf der

# Jahrestagung der Arbeitsgemeinschaft Stabile Isotope e.V.

2015 in Heidelberg



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- Methan Isotopenanalysator  $\delta^{13}\text{C}$  und  $\text{CH}_4$
- Kohlendioxid Isotopenanalysator  $\delta^{13}\text{C}$  und  $\delta^{18}\text{O}$  in  $\text{CO}_2$
- Distickstoffoxid Isotopenanalysator  $\delta^{15}\text{N } \alpha$ ,  $\delta^{15}\text{N } \beta$  und  $\delta^{18}\text{O}$  in  $\text{N}_2\text{O}$
- Labor- und On-Line Geräte
- Einfache Bedienung, benutzerfreundliche Software



### Gas Konzentration Analysatoren

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- Kohlenmonoxid Analysator  $\text{CO}$
- Stickstoffdioxid Analysator  $\text{N}_2\text{O}$
- Ammoniak Analysator  $\text{NH}_3$
- Fluorwasserstoff Analysator  $\text{HF}$
- Distickstoffoxid, Kohlenmonoxid Analysator  $\text{N}_2\text{O}$ ,  $\text{CO}$
- Labor und On- Line Geräte
- Automatische Messstellenumschaltung für 8 oder 16 Kanäle



**V1****The use of isotope measurements in atmospheric research**T. Röckmann<sup>1</sup><sup>1</sup>Utrecht University, Utrecht, Niederlande

In the atmosphere, trace gases are generally formed from different sources and are destroyed by various removal processes. Understanding the global cycles of trace gases means that the contributions of each source and sink have to be well constrained, which is often difficult to achieve by measurements of the concentration alone. Isotope measurements help to distinguish different source and sink types when they have a different isotopic fingerprint and therefore contribute to a refined understanding of the atmospheric cycles of many trace gases. Important applications aim at the identification of observed elevations of a trace gas above a certain background level, and in recent years new mobile instruments have been developed to apply this technique at smaller spatial and temporal scales. On the global scale, isotope modules for global chemistry and transport models and even earth system models have been developed to use the isotopic information as hard constraint for trace gas budgets. For faster atmospheric reactions involving ozone ( $O_3$ ) in the atmosphere, the investigation of the mass-independent  $^{17}O$  anomaly ( $\Delta^{17}O$ ) has proven very useful, because this signature is created in very few reactions only and cannot be removed easily, so that it serves as a tracer for oxygen atom transfer reactions in the atmosphere. As a consequence, several applications from fast photochemistry to climate reconstructions from ice cores have been developed. A very new field is the use of multiple substituted isotopocules (clumped isotopes) in atmospheric research, which should provide new independent isotopic dimensions to constrain trace gas budgets. Whereas this is an exciting development, such measurements presently require far larger sample sizes than measurements of single-substituted isotopocules, and applications in the atmosphere are still limited to trace gases with relatively high concentrations.

**V2****Mapping methane plumes and the delta C-13 composition of anthropogenic sources around Heidelberg**

C. Yeman<sup>1</sup>, F. Dinger<sup>1</sup>, M. Schmidt<sup>1</sup>

<sup>1</sup>Institut für Umweltphysik, Universität Heidelberg, Heidelberg, Deutschland

A mobile analyser based on Cavity-Ring-Down Spectroscopy (Picarro G2301) was installed on a vehicle, together with a GPS receiver. This allows us to measure atmospheric methane and carbon dioxide mole fractions and the C-13 isotopes of both gases while driving. Methane mole fraction measurements show a good repeatability even for high frequency measurements whereas the  $^{13}\text{CH}_4$  measurements need a longer averaging time of 1 minute for 1 ‰ repeatability and 15 minutes for 0.23 ‰ repeatability. Driving through an emission plume, the signal is typically only 60 seconds long. To overcome the precision problem for the isotope measurements we filled a 25 m tubing when driving through the plume, which was then flushed back through our analyser during 30 minutes. With this setup, we visited a land fill site, a biogas plant, a dairy cow farm and a natural gas storage and measured an averaged isotopic methane signature(C-13 ) of  $-61 \pm 6 \text{ ‰}$ ,  $-61 \pm 1 \text{ ‰}$ ,  $-61 \pm 0.6 \text{ ‰}$ ,  $-37 \pm 11 \text{ ‰}$ , respectively.

**V3****D/H Isotope Ratio Measurements of Atmospheric Volatile Organic Compounds**

T. Meisehen<sup>1</sup>, F. Bühler<sup>1</sup>, R. Koppmann<sup>1</sup>, M. Krebsbach<sup>1</sup>

<sup>1</sup>Bergische Universität Wuppertal, Atmosphärenphysik, Wuppertal, Deutschland

Analysis of isotope ratios in atmospheric volatile organic compounds (VOC) is a reliable method to allocate their sources, to estimate atmospheric residence times and investigate physical and chemical processes on various temporal and spatial scales. Most investigations yet focus on carbon isotope ratios. Certainly more detailed information can be gained by the ratio of deuterium (D) to hydrogen (H) in VOC, especially due to the high mass ratio. Combining measurements of carbon and hydrogen isotopes could lead to considerable improvement in our understanding of atmospheric processes.

For this purpose we set up and thoroughly characterised a gas chromatograph pyrolysis isotope ratio mass spectrometer to measure the D/H ratio in atmospheric VOC. From a custom-made gas standard mixture VOC were adsorbed on Tenax®TA which has the advantage that CO<sub>2</sub> is not preconcentrated when measuring ambient air samples. Our results show that the pyrolysis method has significant impact on the D/H ratios. A pyrolysis temperature of at least 1723 K and conditioning of the ceramic tube on a regular basis is essential to obtain reproducible D/H isotope ratios. For an independent comparison D/H ratios of the pure VOC used in the gas standard were determined using elemental analysis by Agroisolab (Jülich, Germany). Comparisons of 10 VOC show perfect agreement within the standard deviations of our measurements and the errors given by Agroisolab, e.g. for n-pentane, toluene, 4-methyl-2-pentanone and n-octane. A slight mean difference of 5.1 ‰ was obtained for n-heptane while significant mean differences of 15.5 ‰ and 20.3‰ arose for 1,2,4-trimethylbenzene and isoprene, respectively.

We further demonstrate the stability of our system and show that the sample preparation does not affect the isotope ratios. Moreover the applicability of our system to ambient air samples is demonstrated.

**V4****Temperature dependence of the carbon kinetic isotope effect for the oxidation reaction of ethane by OH radicals under atmospherically relevant conditions: experimental and theoretical studies**

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Modelling of the global distribution of atmospheric ethane sources and sinks by using the  $^{13}\text{C}$  isotopic composition requires accurate knowledge of the carbon kinetic isotope effect (KIE) of atmospheric oxidation reactions. This implies the necessity to elucidate the quantum mechanically predicted KIE temperature dependence within an atmospherically relevant temperature range. In this study, the KIE temperature dependence of ethane oxidation by OH radicals was investigated experimentally at ambient pressure in a temperature range of 303 K down to 243 K. Chemical reactions were carried out in a 12 L FEP reaction chamber, suspended in a thermally controlled oven and isotope ratios of the gas phase components during the course of the reactions were measured by Thermal Desorption - Gas Chromatography - Isotopic Ratio Mass Spectrometry (TD-GC-IRMS). KIE of ethane with the OH radical was derived from the temporal evolution of the ethane  $\delta^{13}\text{C}$  and concentration using a method adapted from the relative reaction rate concept, at each temperature. At  $303 \pm 0.1$  and  $288.0 \pm 0.3$  K, the KIE of the ethane reaction with OH was found to be  $7.03 \pm 0.59$  and  $7.45 \pm 0.48$  ‰, respectively, showing a good agreement with the previously reported value of  $8.57 \pm 1.95$  ‰, at  $296 \pm 4$  K [Anderson et al. 2004], within the error range. At lower temperatures, the KIE slightly increases by  $0.3 \pm 0.1$  ‰ per 10 K. Quantum mechanical calculations together with semi-classical transition state theory were employed to theoretically investigate the temperature dependence of ethane oxidation KIE. The computed KIE values are overestimated compared to the experimental results. However, the calculated KIE shows the same trend like the observations in the experimentally investigated temperature range and steeply increases at temperatures lower than 243K.

Reference: Rebecca S. Anderson, Lin Huang, Richard Iannone, Alexandra E. Thompson, and Jochen Rudolph (2004), Carbon Kinetic Isotope Effects in the Gas Phase Reactions of Light Alkanes and Ethene with the OH Radical at  $296 \pm 4$  K, *J. Phys. Chem. A*, **108**, 11537-11544



**V5****Modelling the isotopic composition of long lived trace gases with the AGAGE 12 Box model**E. Bahlmann<sup>1</sup><sup>1</sup>Universität Hamburg, Department für Geowissenschaften, Hamburg, Deutschland

Simple 1 and 2 box models have frequently been used to model the isotopic composition of atmospheric trace gases such as CH<sub>4</sub>, N<sub>2</sub>O and CH<sub>3</sub>Cl. The AGAGE 12 box model has long been used to model the emissions and lifetimes of long lived trace gases such as CFCs, N<sub>2</sub>O and CH<sub>4</sub>. Here, we describe an extended version of the AGAGE model capable of modeling the distribution of the isotopologues of various long lived trace gases in the atmosphere and present results for CFC-12. Briefly, the model divides the atmosphere into four equal mass latitudinal sections with boundaries at 30N, 0N and 30S. Each section is divided into three vertical layers at 500hPa and 200hPa, with the stratosphere being represented by the four boxes above 200hPa. The tropospheric transport between the boxes is parameterized in terms of bulk advection and eddy diffusion having no direct effect on the isotopic composition of trace gases. For emissions entering the lower four tropospheric boxes the emission function for heavier isotopologues are specified from the respective isotope ratios. In AGAGE loss rates are specified as time scales. The timescales for the heavier isotopologues are derived from the respective apparent kinetic isotope effects.

Over the last decade tropospheric CFC-12 showed enrichment by  $0.44 \pm 0.05\text{‰ yr}^{-1}$ . In case of CFC-12 photolytic loss in the stratosphere is the only fractionating sink. With a constant isotopic source signature and an apparent KIE of  $-33\text{‰}$  (Zuiderweg et al. 2012) the model provides an average enrichment by  $0.24\text{‰ yr}^{-1}$ . In order to resemble the observed trend an apparent KIE of  $-59 \pm 5\text{‰}$  is required to induce a long term shift of in the isotopic composition of tropospheric CFC-12. Temporal variations of the isotopic source signature have a small effect on  $\Delta\delta^{13}\text{C}$  for the period after 2000, because the emissions are small compared to the atmospheric burden.

**V6****Tracking aerosol chemical age with stable carbon isotopes**

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Assessments of air quality impact from biomass burning emissions need a reliable source apportionment method. Therefore, receptor model studies are often employed. Based on measured concentrations of an inert tracer at the source and receptor, source contributions to the receptor site can be quantified. For reactive species, measured concentrations cannot be directly linked to the source strength. Levoglucosan has long been considered chemically stable in the atmosphere, fulfilling the requirements as a specific tracer for particulate matter emissions from biomass burning. Yet, recent laboratory studies have shown that levoglucosan reacts with hydroxyl radicals (OH), resulting in an atmospheric lifetime of a few days<sup>1, 2</sup>. Due to the kinetic isotope effect (KIE), the oxidative aging of levoglucosan in aerosol particles can be quantified, since chemical processing translates in changes of the relative abundance of heavy to light isotopes in the reactant. Moreover, due to the potential to fingerprint emissions as well as chemical and physical processes in the atmosphere, stable isotopes are considered as a promising tool to improve our understanding of sources and atmospheric fate of organic aerosol.

In this study, we show that for aerosol samples collected in the Guangdong province, China, levoglucosan  $\delta^{13}\text{C}$  increases with increasing atmospheric transport time. Combining laboratory KIE studies<sup>3</sup>, observed  $\delta^{13}\text{C}$  in source<sup>4</sup> and field samples, as well as back trajectory analyses, we show that a 30-hour residence time in the free troposphere leads to a chemical loss of levoglucosan of up to 70%. Thus,  $\delta^{13}\text{C}$  of levoglucosan promises to be an ideal tracer for aerosol aging.

<sup>1</sup> M. Mochida et al., Seasonal variation of levoglucosan in aerosols over the western North Pacific and its assessment as a biomass-burning tracer, *Atmos. Environ.*, 2010, 44, 3511-18

<sup>2</sup> C. J. Hennigan et al., Levoglucosan stability in biomass burning particles exposed to hydroxyl radicals, *Geophys. Res. Lett.*, 2010, 37, L09806,

<sup>3</sup> X.-F. Sang et al., Laboratory characterization of the kinetic isotope effect in photochemical loss of levoglucosan, in preparation

<sup>4</sup> X.-F. Sang et al., Stable carbon isotope ratio analysis of anhydrosugars in biomass burning aerosol particles from source samples, *Environ. Sci. Technol.*, 2012, 46, 3312-3318.

**V7****Real-time analysis of  $\delta^{13}\text{C}$ - and  $\delta\text{D-CH}_4$  in ambient air with laser spectroscopy: Method development and intercomparison**

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In situ and simultaneous measurement of the three most abundant isotopologues of methane using mid-infrared laser absorption spectroscopy is demonstrated. A field-deployable, autonomous platform is realized by coupling a compact quantum cascade laser absorption spectrometer (QCLAS) to a preconcentration unit, called TRace gas EXtractor (TREX). This unit enhances  $\text{CH}_4$  mole fractions by a factor of up to 500 above ambient levels and quantitatively separates interfering trace gases such as  $\text{N}_2\text{O}$  and  $\text{CO}_2$ . The analytical precision of the QCLAS isotope measurement on the preconcentrated (750 ppm, parts-per-million, mmole/mole) methane is 0.1‰ and 0.5 ‰ for  $\delta^{13}\text{C}$ - and  $\delta\text{D-CH}_4$  at 10 min averaging time.

Based on replicate measurements of compressed air during a two-week intercomparison campaign, the repeatability of the TREX-QCLAS was determined to be 0.19 ‰ and 1.9 ‰ for  $\delta^{13}\text{C}$  and  $\delta\text{D-CH}_4$ , respectively. In this intercomparison campaign the new in situ technique is compared to isotope-ratio mass-spectrometry (IRMS) based on glass flask and bag sampling and real time  $\text{CH}_4$  isotope analysis by two commercially available laser spectrometers. Both laser-based analyzers were limited to methane mole fraction and  $\delta^{13}\text{C-CH}_4$  analysis, and only one of them, a cavity ring down spectrometer, was capable to deliver meaningful data for the isotopic composition. After correcting for scale offsets, the average difference between TREX-QCLAS data and bag/flask sampling-IRMS values are within the extended WMO compatibility goals of 0.2 and 5 ‰ for  $\delta^{13}\text{C}$ - and  $\delta\text{D-CH}_4$ , respectively. Thus, the intercomparison also reveals the need for reference air samples with accurately determined isotopic composition of  $\text{CH}_4$  to further improve the interlaboratory compatibility.

**V8****Head space analysis of CO<sub>2</sub> isotopologues with an Isotope Ratio Infrared Spectrometer**

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We are presenting a middle-infrared Laser-based Isotope Ratio Infrared Spectrometer (Thermo Scientific Delta Ray™ IRIS) that is capable of simultaneously determining both  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  isotope ratios of carbon dioxide to precision as low as 0.05‰. Until now we have been mostly performing continuous, *in-situ* monitoring at ambient concentrations. We will present results from applying IRIS to head space analysis of select solid and liquid samples. The instrument can be deployed in the field such as on a research vessel.

Isotopic composition of DIC from pore water of a sediment core collected at the floor of Eckernförde Bay, Baltic sea, was analyzed using our instrument and we present a depth profile demonstrating different microbiological horizons in the sea bed. Up to 100 samples per day can be analyzed directly on board right after collecting the core eliminating the mandatory poisoning of the samples in the field.

It is also possible to perform isotopic carbonate analysis reliably with IRIS with sample amounts as low as 200 µg. Measurements of three reference materials (NBS 18, NBS 19 and LSVEC) were performed, and NBS 18 treated as an unknown. Five samples of NBS 18 were acidified using a few droplets of 100% H<sub>3</sub>PO<sub>4</sub> and left for equilibration overnight at 25°C. NBS 19 and LSVEC samples were treated identically and used for linearity calibration and scale contraction of the measured  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values. The obtained values for  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  were -5.0(1)‰ and -23.3(1)‰, respectively, in agreement with the values certified by IAEA of -5.01(4)‰ and -23.2(1)‰ within the analytical uncertainty.

Excellent linearity up to 25% <sup>13</sup>CO<sub>2</sub>/75% <sup>12</sup>CO<sub>2</sub> can also be achieved. CO<sub>2</sub> gas mixtures with different <sup>13</sup>CO<sub>2</sub>/<sup>12</sup>CO<sub>2</sub> ratios were prepared from two gas standards. Using a one point calibration at a ratio of 9.9%, we achieved a linearity of  $y = 0.982x + 0.003$  with an  $R^2 = 0.9998$  between a <sup>13</sup>CO<sub>2</sub>/<sup>12</sup>CO<sub>2</sub> ratio of 1.9% and 25%.

For each analysis, the required sample amounts is 80 µg or 40 µl of CO<sub>2</sub>. We will discuss other requirements to achieve best performance and accuracy whether you are in the field or in the lab.

**V9****Automatic Data Calibration Strategies with IONOS**

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<sup>2</sup>Isoprime Ltd., Cheadle Hulme, Großbritannien

The data processing in the stable isotope ratio software has always been characterised by the off-line nature of this process. The commercially available software has so far not contained any option to go from the so-called raw data to the final useable data point. Isoprime Ltd, has in conjunction with their new IRMS system, the visION, also released a completely new software for data processing, **IONOS**.

The new software from Isoprime, allows the import from all types of data, directly into the software, so that all users can take advantage of the software to provide the final data for their research. The software is characterised by a multitude of automated calibration and correction set-ups for both bulk and compounds specific data analysis. With fully configurable reporting and lookup of the data one can always retrace the data correction scheme that has been used. The **IONOS** software will allow users to easily standardise their data analysis protocols.

**V10****Extending the boundaries of 10 kV isotope ratio MS**A. Hilkert<sup>1</sup>, J. Radke<sup>1</sup><sup>1</sup>Thermo Fisher Scientific, Bremen, Deutschland

Because of its high acceleration voltage the 10 kV mass analyzer technology allows for highest sensitivity, best peakshape, best peakstability, best abundance sensitivity and most recently also for high mass resolution. As such the 10 kV analyzer technology is regarded to be the research platform in isotope ratio analysis to explore new fields of applications in particular where very small isotope signatures related with small isotope abundances and extended dynamic ranges need to be investigated. This is for instance required for the analysis of isotopomers and isotopologues containing clumped isotopes. Essential prerequisites for high precision isotope ratio analysis of small signals are the excellent stability and signal to noise behavior of the 10 kV systems such as the MAT 253. Furthermore, the quality of ion beams at such low abundances can be endangered by interfering isotopologues, isobaric ions of contaminants and adducts with the same nominal mass. Resolving such interferences by medium or high mass resolution is the method of choice for accurate quantification of low abundant ion beams. This requirement has been addressed by the 253 Ultra, a high resolution double focusing isotope ratio MS. Technical details and further improvements of the 10 kV technology in low and high resolution IRMS will be presented.

**V11****A comparison of methods for triple isotopocule N<sub>2</sub> analysis**

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For the determination of N<sub>2</sub> isotopic composition, usually only masses m/z 28 and 29 are used, because m/z 30 determination is impeded by NO, which is formed in the mass spectrometer source during the measurements. The calculation of <sup>15</sup>N/<sup>14</sup>N isotope ratios from these data is possible as long as the measured N<sub>2</sub> is in isotopic equilibrium (i.e. the isotopes are distributed statistically among all molecule masses m/z 28, 29 and 30).

When measuring a mix of N<sub>2</sub> from two different sources with different isotopic abundances [g1], this simple approach is no longer possible because the isotopes are not distributed statistically among the molecules in the mixture.

Two different approaches have been used to determine the triple isotopocule distribution of N<sub>2</sub>:

1) Measuring all three masses m/z 28, 29 and 30 while taking great care to reduce contribution of NO formation on m/z 30 (Lewicka-Szczebak et al. 2013)

2) Measuring the masses m/z 28 and 29 before and after establishing statistical distribution of the isotopes among all molecules (Well et al. 1998). The statistical distribution is accomplished by disintegrating N<sub>2</sub> molecules and subsequent instantaneous reformation of N<sub>2</sub>. Isotopes then are statistically distributed among the molecules. A set-up was developed, where measurements with and without equilibration are performed from the same sample in one run.

Here we present a comparison of the two methods with regard to handling and accuracy of results.

R. Well, K.-W. Becker, R. Langel, B. Meyer, A. Reineking. Continuous flow equilibration for mass spectrometric analysis of dinitrogen emissions. Soil Sci. Soc. Am. J. 1998, 62, 906.

D. Lewicka-Szczebak, R. Well, A. Gieseemann, L. Rohe, U. Wolf. An enhanced technique for automated determination of <sup>15</sup>N signatures of N<sub>2</sub>, (N<sub>2</sub>+N<sub>2</sub>O) and N<sub>2</sub>O in gas samples. Rapid Commun. Mass Spectrom. 2013, 27, 1548-1558.

## V12

**Compound-specific hydrogen isotope analysis of heteroatom-bearing compounds via gas chromatography - chromium/HTC - isotope ratio mass spectrometry (GC-Cr/HTC-IRMS)**

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The traditional high-temperature conversion (HTC) approach toward compound-specific stable isotope analysis (CSIA) of hydrogen for heteroatom-bearing (i.e. N, Cl, S) compounds has been afflicted by fractionation bias due to formation of byproducts HCN, HCl, and H<sub>2</sub>S. This study presents a novel chromium-based high-temperature conversion (Cr/HTC) approach for organic compounds containing nitrogen, chlorine and sulfur.

Following peak separation along a gas chromatographic (GC) column, the use of thermally stable ceramic Cr/HTC reactors at 1100 to 1500 °C and chemical sequestration of N, Cl, and S by chromium result in quantitative conversion of compound-specific organic hydrogen to H<sub>2</sub> analyte gas. The overall hydrogen isotope analysis via GC-Cr/HTC-isotope ratio mass spectrometry (IRMS) achieved a precision of better than  $\pm 5$  mUr along the VSMOW-SLAP scale. The accuracy of GC-Cr/HTC-IRMS was validated with organic reference materials (RM) in comparison with online EA-Cr/HTC-IRMS and offline dual-inlet IRMS. The utility and reliability of the GC-Cr/HTC-IRMS system were documented during the routine measurement of > 500 heteroatom bearing organic samples spanning a  $\delta^2\text{H}$  range of -181 to 629 mUr.

The novel chromium-based GC-Cr/HTC-IRMS system is a versatile and promising extension of the arsenal for compound-specific hydrogen isotope analysis. The method especially targets a broad range of heteroatom-bearing compounds for which accurate on-line determinations of  $\delta^2\text{H}$  values was not possible by the conventional HTC approach. The introduction of tubular ceramic reactors filled with elemental chromium powder allows HTC operating temperatures above 1100 °C. This extension of Cr/HTC significantly (1) improves the conversion of organic hydrogen to H<sub>2</sub> from heteroelement-bearing compounds and (2) reduces the formation of hydrogen-containing byproducts that limit H<sub>2</sub> yields and lead to isotope fractionation. Construction of a GC-Cr/HTC reactor takes advantage of commercially available standard equipment for routine GC-HTC-IRMS, inexpensive chromium powder, and standard ceramic tubes.

Abb. 1

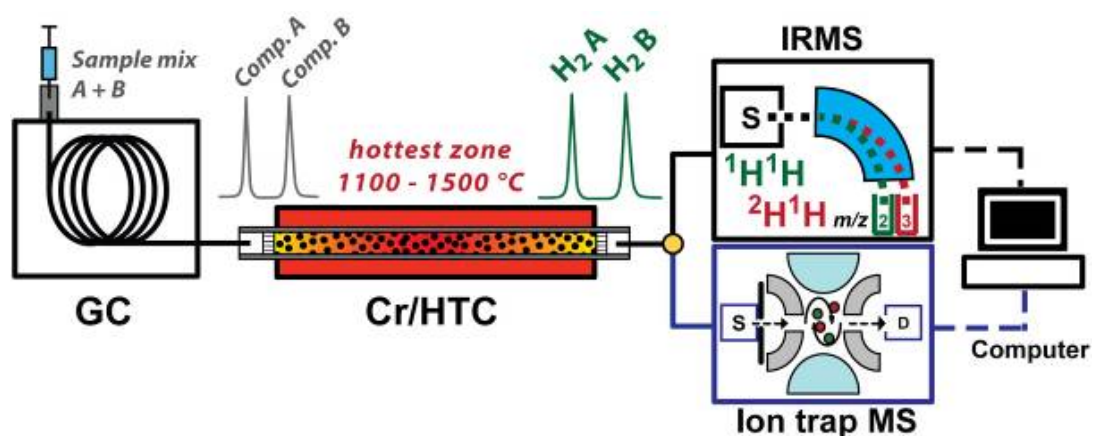
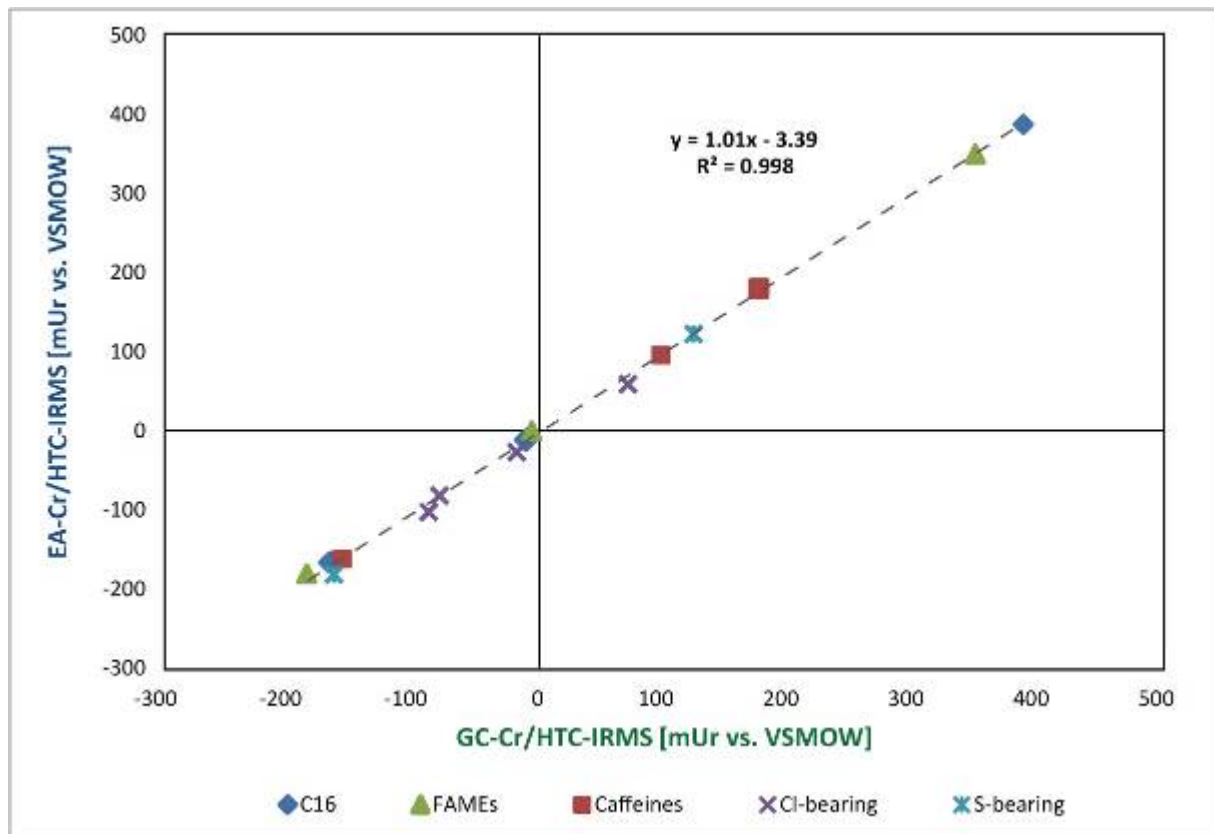




Abb. 2



**V13****Comparison of carbon and oxygen isotope values from different wood preparation procedures in dendrochronology**

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This study evaluated the effects of different preparation methods of tree-ring whole wood samples on  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values. We used sub-samples of a 5 cm<sup>3</sup> wood piece of a single tree-ring from a lowland white fir and milled them (i) with different numbers of stainless-steel balls (two and three), (ii) for different amounts of time (3, 5 and 8 minutes), and (iii) applied discontinuous and continuous milling. Our results show that varying milling procedures do not alter the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values in comparison to non-milled blank samples. For short milling times, an increased variance of  $\delta^{18}\text{O}$  values is recorded, likely caused by isotopic gradients between earlywood and latewood portions of the tree-ring and thereby biasing the insufficiently homogenised samples. No overheating effects on  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values were detected (Riechelmann et al., 2014).

$\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values from sapwood of a single *Pinus uncinata* were then determined to evaluate differences between whole wood and resin-free whole wood samples. Results were also compared with published isotope values from  $\alpha$ -cellulose samples from the same tree (Konter et al., 2014). The differences in  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  between whole wood and resin-free whole wood vary within the analytical uncertainty of 0.3‰ and 0.5‰, respectively, indicating that resin extraction is not necessary for *Pinus uncinata*. Mean differences between cellulose and whole wood are 0.9‰ ( $\delta^{13}\text{C}$ ) and 5.0‰ ( $\delta^{18}\text{O}$ ), respectively. The residual time series show increasing ( $\delta^{13}\text{C}$ ) and decreasing ( $\delta^{18}\text{O}$ ) trends over 40 years, however. Further tests from different species and other sites are recommended to evaluate if the findings reported here are generally valid (Riechelmann et al., in review).

Konter, O., Holzkämper, S., Helle, G., Büntgen, U., Saurer, M. & Esper, J. (2014): Climate sensitivity and parameter coherency in annually resolved  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  from *Pinus uncinata* tree-ring data in the Spanish Pyrenees.- *Chemical Geology*, 377: 12-19.

Riechelmann, D. F. C., Maus, M., Dindorf, W., Konter, O., Schöne, B. R. & Esper, J. (in review): Comparison of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  from cellulose, whole wood and resin-free whole wood from a high elevation *Pinus uncinata* in the Spanish central Pyrenees.- *Isotopes in Environmental and Health Studies*.

Riechelmann, D. F. C., Maus, M., Dindorf, W., Schöne, B. R., Scholz, D. & Esper, J. (2014): Sensitivity of whole wood stable carbon and oxygen isotope values to milling procedures.- *Rapid Communications in Mass Spectrometry*, 28: 1371-1375.

**V14****Limits and potentials determining stable water isotopes using in-situ measurements and soil water extractions.**

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Dual isotope approaches can be used to study soil water root uptake, transit time and evaporation patterns. However, the comparability of unsaturated zone studies and isotope ratios derived from different soil types might be debatable considering interactions of oxygen with cations on clay minerals (Oerter et al., 2014) and different behaviour of deuterium (Steward 1967). In addition to interactions and fractionation that can occur between water and substrate the compareability of different methods needs further investigation. Even the application of one method can lead to very different results depending on soil type and applied sequence.

Therefore, the present study presents results from spike test and will discuss limits and potentials regarding the recovery of water from different soil types using the cryogenic vacuum extraction method. Soils within a catchment in the Cuvelai-Etосha-Basin (CEB), Namibia are different in terms of cation exchange capacity and mineral composition. Soil water extractions using temperatures up to 200°C halved the analytical error for sandy soils. The bias between spike water and extracted water can be reduced for clay rich soils. Further, a relationship between clay content and the offset between spiked and recovered water could be found. However, full recovery could not be achieved for fine textured soils and values of the extracted water fall on a evaporation line. It is strongly recommended that studies using the cryogenic vacuum extraction method for soil water studies conduct spike tests with their particular soils and their specific technical setup prior to sample treatment. In addition in-situ measurements at different locations in the CEB are compared to isotope depth profiles destructively sampled and subsequently extracted. It can be shown that soil type specific calibration needs consideration.

**V15****Oxygen isotope analyses of individual carbohydrates with GC-Pyrolysis-IRMS - a new and precise method**

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The oxygen isotopic composition ( $\delta^{18}\text{O}$ ) of carbohydrates derived from plants, animals, soils, and sediments contains important information about biochemical and physiological processes, past environmental conditions, and geographical origin, which are otherwise not available. Nowadays,  $\delta^{18}\text{O}$  analyses are often performed on carbohydrate bulk material, while  $\delta^{18}\text{O}$  analyses of individual carbohydrates remain challenging due to a lack of methods for compound-specific isotope analysis. Here we developed a new methylation derivatization method for the determination of  $\delta^{18}\text{O}$  in individual carbohydrates with GC-Pyr-IRMS. Carbohydrates were fully methylated within 24 h in an easy-to-handle one-pot reaction in acetonitrile, using silver oxide to abstract the alcoholic protons, methyl iodide as a methyl group carrier, and dimethyl sulfide as a catalyst. The  $\delta^{18}\text{O}$  precision of the method ranged between 0.23 and 1.08‰ for various individual carbohydrates of different classes (mono- and disaccharides, alditols), which is unrivalled so far. The oxygen isotope ratio of monosaccharides such as glucose and fructose could be precisely analyzed for the first time. Repetition of the methylation protocol on the same compounds caused relatively high variation in peak areas. However, this did not affect  $\delta^{18}\text{O}$  values. We tested the method on standard mixes, honey samples, and leaf carbohydrates, showing that the method is also applicable on complex carbohydrate mixtures. This new methylation method promises to be a big step forward in determining  $\delta^{18}\text{O}$  of individual carbohydrates with GC-Pyr-IRMS and could find a wide spread application.

**V16****Investigation of sulfur-cycling processes in a BTEX contaminated porous aquifer by using a high-resolution sampling strategy**

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Dissimilatory sulphate reduction represents one of the most important process in the anaerobic degradation of organic contaminants in groundwater ecosystems. Here we demonstrate that a BTEX plume which interacts with the water table leads to a zone of variable redox conditions, in which redox cycling complicates the interpretation of concentration measurements to the point that reactive transport models have previously failed to reproduce observed trends.

This geochemical complexity is studied by measurements of sulfur intermediates such as  $S^0$ ,  $SO_3^{2-}$ , and  $S_2O_3^{2-}$  in conjunction with high-resolution sampling of the aquifer and by measurements of stable isotopes in dissolved sulphate, hydrogen sulfide and elemental sulfur.

The isotopic enriched  $\delta^{34}S$  values of dissolved sulphate linked to decreasing toluene concentrations near the water table are indicative that BTEX were oxidized at the upper plume fringe under sulphate reducing conditions. The  $\delta^{18}O$  values of oxygen in dissolved sulphate from the same depth suggest a re-oxidation of up to 70% reduced sulphur to dissolved sulphate. Concentrations of measured sulfur intermediates at the upper and lower plume fringes were twice as high that of other sampling depth and support the interpretation of intensive redox cycling processes near the water table. In addition these results also show that the plume fringes represent the hot-spots where biodegradation occurs. An isotopic shift in  $\delta^{34}S$  of  $S^0$  of a few per mil compared to the  $\delta^{34}S$  values of  $H_2S$  from the same in the same depth may be indicative of oxidation of  $S^0$  to sulphate in this zone.

**V17****Isotope fractionation of dissolved O<sub>2</sub> reveals the rate-limiting step during enzymatic dioxygenation of (nitro)aromatic contaminants**

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In contaminated environments, microorganisms have evolved several strategies to utilize aromatic pollutants as an energy source by initiating their degradation with enzymes such as oxidases and oxygenases. These enzymes utilize activated forms of molecular O<sub>2</sub> to facilitate the oxidation of recalcitrant compounds, such as aromatic contaminants, to products that can be further metabolized by bacteria. Biodegradation of alkyl-, nitro-, and chloro-aromatic pollutants can typically be assessed with compound-specific isotope analysis (CSIA), where C and H isotope fractionation are used as proxies for quantifying the extent of degradation. However, C and H isotope effects reported for the dioxygenation of aromatic contaminants are very substrate-dependent. The cause of this variability is currently unclear. It is also unknown whether this variability can compromise the application of CSIA for assessing contaminant degradation in the environment. In this work, we explored the role of enzymatic O<sub>2</sub>-activation as the potentially rate-limiting step of aromatic contaminant dioxygenation. To this end, we (i) developed a method for quantifying oxygen isotope fractionation of dissolved O<sub>2</sub> in lab-scale experiments and (ii) determined <sup>18</sup>O-kinetic isotope effects (KIEs) for the dioxygenation of nitroaromatic compounds.

Our method enables the measurement of oxygen isotope signatures ( $\delta^{18}\text{O}$ ) in aqueous samples with dissolved O<sub>2</sub> concentration of 20-270  $\mu\text{M}$  using automated split-injection in a standard GC setup. Samples were prepared in 10-mL headspace vials with butyl stoppers and crimp seals by filling the vials completely with aqueous solution. Dissolved O<sub>2</sub> was stripped from solution either before or after partial consumption of O<sub>2</sub> by creating a headspace of N<sub>2</sub> gas and partitioning of O<sub>2</sub> to the gas phase. Headspace samples were injected automatically and a 30-m molecular sieve column was used to separate O<sub>2</sub> from N<sub>2</sub> before ionization in the IRMS. Blank samples obtained by purging with N<sub>2</sub> gas, were treated identically to apply a blank-correction to all measured  $\delta^{18}\text{O}$  values.

Incorporation of O<sub>2</sub> into three widely found nitroaromatic contaminants (i.e., nitrobenzene, 3-nitrotoluene, and 2,6-dinitrotoluene) by nitrobenzene dioxygenase (NBDO) occurred with varying efficiencies resulting in dioxygenation product yields between 37% and 71%. The remainder of the consumed O<sub>2</sub> was released as hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) in a so-called uncoupling reaction. However, regardless of the ratio between substrate dioxygenation and O<sub>2</sub> uncoupling, isotope fractionation determined in dissolved O<sub>2</sub> was identical for all nitroaromatic contaminants with <sup>18</sup>O-KIEs of 1.014 to 1.016. The magnitude of <sup>18</sup>O-KIEs suggests the formation of an iron-bound peroxide species as the rate-limiting step of O<sub>2</sub> consumption for both nitroarene dioxygenation and O<sub>2</sub> uncoupling. This observation implies that the differences in substrate C and H isotope fractionation arise from variations in activation energies of reaction steps that occur after the O<sub>2</sub> activation step. Our data indicate that enzymatic activation of molecular O<sub>2</sub> is not only the energetic bottle-neck during biodegradation of (nitro)aromatic contaminants but may also be responsible for variations in observed contaminant isotope fractionation.

**V18****What does  $\delta^7\text{Li}$  in water tell us about flow paths in an alpine catchment?**

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**Objective**

In contrast to other geochemical and isotopic signatures (e.g.,  $^{87}\text{Sr}/^{86}\text{Sr}$ ), the lithium isotopic composition ( $\delta^7\text{Li}$ ) of surface- and groundwaters within river catchments is not primarily controlled by the lithology. The lithium concentrations and  $\delta^7\text{Li}$  values are a result of chemical weathering intensity and particularly the formation of secondary minerals that include strong lithium isotope fractionation. As we know from literature, the occurrence and magnitude of this fractionation during the precipitation of secondary minerals was confirmed in several lab experiments. On catchment scale, however, the hydrological conditions and flow processes controlling the enriched lithium isotope signatures, which had been observed in many catchments, are still poorly understood.

In this study we are aiming to gain a better understanding of lithium isotope systematics on a bigger scale, assessing the governing processes of lithium isotope fractionation in river catchments, and linking them with water flow paths and travel times.

**Methods**

During several field trips in 2011, 2013, and 2014, more than 50 samples of river water, subsurface water, glacier melt, and thermal water were collected in an alpine, glacier dominated catchment in the Pamir Mountains. Additionally, a variety of rock material was taken to represent the regional geology. Lithium isotope ratios were determined by a Multi-Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS; Neptune, ThermoElectron). Isotopic compositions of the samples will be given in delta notation related to the NIST L-SVEC standard solution having an overall precision of  $2\sigma = 1\text{‰}$ .

**Results**

We detected a wide range of  $\delta^7\text{Li}$  values in water ( $\delta^7\text{Li}$  from +4.5‰ to +28.1‰), whereas the highest values were found in glacial melt water ( $\delta^7\text{Li} = +28.2\text{‰}$ ) collected at the glacier snout and from two small tributary streams ( $\delta^7\text{Li}$  of +35‰). The lowest values were found in the samples of thermal water and springs in solid rock ( $\delta^7\text{Li}$  between +4.5‰ and +8.4‰). The samples of river water were placed in between. In contrast to the water samples, the analysis of  $\delta^7\text{Li}$  of samples from the granitic environment of the catchment (n=15) revealed negative values (median of -5.3‰). The riverine samples (main river stream and several tributaries) showed an obvious pattern in their  $\delta^7\text{Li}$  values with a significant difference between north (highly enriched values) and south exposed subcatchments.

**Conclusions**

We assume that water samples having low  $\delta^7\text{Li}$  values must have attained a chemical and isotopic steady state according to the local geochemical conditions on their flow paths as a result of long residence times and ongoing water-rock-interactions within the subsurface.

Enriched  $\delta^7\text{Li}$  signatures were presumably caused by flow paths with relatively short residence times connecting segments of high with segments of low ratios of weathering (of primary minerals) to precipitation (of secondary minerals) rates, which resulted in a progressive (Rayleigh-type) isotope fractionation and a decrease in Li concentrations.



The differences in  $\delta^7\text{Li}$  values between the subcatchments can be attributed to variations in catchment sizes and therefore different subsurface residence times as well as different weathering characteristics. Subcatchments on the northern boundary showing higher  $\delta^7\text{Li}$  values have smaller catchment areas and shorter flow paths accompanied by shorter transit times. Southern sub basins showed opposite characteristics.

**V19****Deuterium ( $^2\text{H}$ ) as applied tracer in the vadose zone: experiences from semiarid Namibia**

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Since the 1960's, the stable isotope deuterium ( $^2\text{H}$ ) has successfully been used as applied tracer for investigating (eco-)hydrological processes at the soil-vegetation-atmosphere interface (Zimmermann et al., 1966). After a recession of its application due to the extensive use of tritium ( $^3\text{H}$ ), the tracer is becoming increasingly popular at present. In contrast to  $^3\text{H}_2\text{O}$  (tritiated water), little experimental evidence exists on the fate of artificially introduced  $^2\text{H}_2\text{O}$  (deuterated water) in the unsaturated zone of dry climates, and the necessary input concentrations and methods of application are poorly understood (Becker and Coplen, 2001).

We present different field applications of labeling studies using  $^2\text{H}$  that were carried out in the framework of the project SASSCAL (Southern African Science Service Centre for Climate Change and Adaptive Land Management) in the semiarid Cuvelai-Etoshia Basin, Namibia, and discuss potential and limitations of using artificial deuterium. Examples include i) The quantification of groundwater recharge; ii) the determination of maximum rooting depths and iii) the investigation of water vapor transport.

We conclude that deuterium is a suitable tracer extending possibilities for process-oriented research at the soil-vegetation-atmosphere interface. Field studies can support the parameterization of SVAT (soil-vegetation-atmosphere transfer) models. Experimental design and application have to be planned carefully and attention has to be paid towards high concentrations of  $^2\text{H}$ . Limitations include long-term studies (> 1 year) and the use as tracer in groundwater. The potential to obtain quantitative (not purely qualitative) results and low application amounts in combination with recently developed insitu measurement techniques create excellent prerequisites for further applications of  $^2\text{H}_2\text{O}$ .

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**V20****Calcium isotopes as proxy for early diagenetic processes in marine porewaters**

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Diagenetic reactions are of great significance as they alter the physical and chemical properties of marine sediments, with effects on slope stability, porosity and permeability and geochemical signatures of paleo-environmental proxies. Calcium is of special interest as it plays an important role for the formation of cements and as main constituent of archives. In carbonate sediments, dissolution and recrystallization are the dominating processes that can be identified through the Ca isotopic composition of porewater and bulk carbonate enabling even the determination of rates (Fantle and DePaolo, 2007; Turchyn and DePaolo, 2011). In clastic dominated settings, the dominating processes are less well understood and seem to be more complicated due to different superimposed processes (Teichert et al., 2009). The decrease of Ca concentration in the porewater within the upper 100 meters is a general observation and has been agreed on to be the result of authigenic carbonate formation within the sediments. However, the corresponding heavy Ca isotope signal, the predicted result of carbonate formation, has in most locations not been observed. The release of adsorbed light Ca isotopes from clay minerals has been proposed to overprint this signal (Teichert et al., 2009). Results from experiments with clay minerals (Ockert et al., in 2013) enable us to monitor this process of cation exchange as a function of clay mineralogy and abundance. It also reveals a significant additional pool of Ca to the porewater which is released if the equilibrium between dissolved and adsorbed Ca is affected by authigenic calcium carbonate formation or ammonium production during organic matter remineralization. The new results offer the unique possibility to observe and characterize the two most dominating processes influencing Ca geochemistry in the upper 100 meters of different clastic dominated sediment sequences - the release of light Ca isotopes from clay minerals and authigenic calcium carbonate precipitation - and their interplay.

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**V21****Novel Insights from Multi-Millennial Tree Ring Isotope Records of the Early and Mid-Holocene**

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The reconstruction of Holocene climate, its evolution and variability in the Alps is mainly based on low frequency archives such as glacier and tree line fluctuations. Investigated low-frequency records expose an evolution of Holocene climate from a generally warm Early and Mid to a relatively cool Late Holocene. High resolution records are rare and often do not indicate a general long-term trend; causes and mechanism behind this disagreement are not fully understood yet.

However; recent finds of wood remains of long-lived trees in Alpine glacier forefields changed the concept of Holocene glacier variability as well as the present understanding of Holocene climate dynamics. They prove that glaciers in the Alps were relatively small and short in their extension during the Early and Mid-Holocene (Joerin et al., 2008; Nicolussi and Schlüchter, 2012). Therefore, these wood remains prove that the natural variability of postglacial climate is still not sufficiently known. However; such knowledge is essential for climate model input and the ability to disentangle natural from anthropogenic influences on the Earth's climate.

Therefore, the study aims at establishing highly resolved isotope records from the mentioned, calendar-dated wood remains covering the past 9000 years. Samples are collected in glacier forefields in the Alps covering a broad SW- NE transect. Wood samples are separated into 5-year tree ring blocks from which cellulose is extracted and crushed by ultrasonic homogenization (Boettger et al., 2007; Laumer et al., 2009). Stable isotopes of carbon, oxygen and hydrogen are simultaneously measured using a recently developed method by Loader et al. (2015). Stable isotope records, containing of a sample replication of four samples per 5-year tree ring block, allow to establish stable isotope chronologies over the Holocene.

During the Early and Mid-Holocene, the investigated multi-millennial tree ring isotope records (9000 to 6000 yr b2k) display novel insights into the high frequency archive of tree rings from glacial wood remains. The carbon, oxygen and hydrogen records reveal interesting low frequency variability as well as expected offsets between the measurements of individual trees which are also investigated separately by sampling site, tree species as well as age structure and growth trend. The measured Deuterium records reveal a species- specific isotope signature for the investigated species *Larix decidua* and *Pinus cembra*, which is not resembled in the oxygen and hydrogen records. Further, first comparisons with reconstructions of solar and orbital parameters show a correlation between the long-term variability displayed by the carbon isotope records and the reconstructed solar irradiance during the Early and Mid-Holocene (Steinhilber et al., 2009). This is - though to a lesser degree - resembled by the species-dependent hydrogen isotope variations.

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## V22

**Reconstructed isotopic composition of leaf water and precipitation provides new insight into hydrological changes in East Equatorial Africa during the Last Glacial**

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The reconstruction of isotopic composition of precipitation is one of the major objectives in paleoclimate and -hydrological research. However, by using single isotope ( $d^2H/d^{18}O$ ) records it is often challenging to distinguish between the precipitation and the evapotranspirative enrichment signal incorporated in biomarkers. In order to get new insight into East Equatorial African climate history we couple compound-specific  $d^2H$  results of leaf wax-derived  $n$ -alkanes with compound-specific  $d^{18}O$  results of hemicellulose-derived sugars extracted from the 6.5 m thick loess-paleosol-sequence Maundi (3°10'27.5"S, 37°31'05.8"E), located on the south-eastern slopes of Mt. Kilimanjaro (2780 m asl.). According to  $^{14}C$  results and extrapolation of the age depth profile, the sedimentation history began during the early Late Pleistocene approximately 100 ka BP. The coupled biomarker approach ( $d^{18}O_{sugar}-d^2H_{n-alkane}$ ) was recently suggested by Zech et al. (2013) and has been shown to be a promising tool for reconstructing day-time relative humidity during the vegetation period as well as the isotopic composition of precipitation more robustly compared to single isotope studies (Tuthorn et al., 2015).

The Maundi  $d^2H_{n-alkane}$  record shows in comparison to existing  $d^2H_{leaf\ wax}$  records from Lake Challa, Lake Tanganyika and Lake Malawi a clear altitude effect. Also the above mentioned challenging distinction between amount effect and variations caused by evaporative enrichment became obvious. However, by coupling the Maundi  $d^2H_{n-alkane}$  with  $d^{18}O_{sugar}$  results the deuterium-excess of leaf water can be calculated and converted into day-time relative humidity during the vegetation period. Now a more robust comparison to other "humidity" records can be conducted. In brief, the observable "Holocene Climate Optimum", "Younger Dryas", "African Humid Period", "Last Glacial Maximum", and a mega drought period are well in agreement with the literature. Moreover, the reconstructed isotopic composition of precipitation (Maundi  $d^{18}O_{prec}$  and  $d^2H_{prec}$ ) gives hints on controls of paleoprecipitation in East Equatorial Africa. The amount effect seems to be inappropriate for the Maundi paleoprecipitation record. One reason for overprinting the amount effect could be strong local and/or regional evapotranspirative buffering effects of the vegetation (Rozanski et al., 1982; Zech et al., 2015). A second cause could be the Indian Ocean Dipole (IOD), a recently described ocean-atmosphere circulation system, leading to a distinct precipitation amount pattern between East Africa and Indonesia. If the IOD has a significant influence on East African precipitation supply on longer time scales, then the Maundi  $d^{18}O_{prec}$  record reflects primarily the IOD strength, which can be described as distance between evaporation source and the study area and/or as wind velocity. Moreover, the negative correlation between Maundi  $d^{18}O_{prec}$  and Borneo  $d^{18}O_{stalagmite}$  record (Carolin et al., 2013) suggests a long term ENSO-IOD co-evolution.

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**V23****Compound-specific leaf wax  $\delta D$  and  $\delta^{13}C$  analyses from the Late Quaternary loess paleosol sequence El Paraiso, Central Spain**

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Long-chain *n*-alkanes are important constituents of the leaf wax layer of higher plants. The chain length pattern, as well as the stable carbon and deuterium isotope composition of the leaf waxes depend on the type of vegetation and climate. Leaf waxes are therefore used for paleoenvironmental and -climate reconstructions. Here we present leaf wax and compound-specific stable isotope records from the 8 m high Late Pleistocene Loess Paleosol Sequence El Paraíso, Central Spain. Alkane patterns show a decrease in chain length at ~2 m depth, which might indicate an increase in deciduous tree-derived leaf waxes and less arid conditions than assumed so far for the Last Glacial Maximum. The carbon isotope composition becomes more negative since ~35 ka and interpreting this in terms of less water stress supports the above hypothesis. The leaf wax deuterium record shows a general trend to more enriched values, most likely due to evapotranspirative enrichment and/or changes in the source signal.

**V24****Late Glacial climate reconstruction based on stable isotopes in biomarkers from the Gemündener Maar, Germany**

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Lake sediments are valuable archives for the reconstruction of past changes in climate and vegetation. In the present study, we analyse samples from the Gemündener Maar, a lake situated in the western Eifel, Germany, for their isotopic composition of *n*-alkanes (<sup>2</sup>H) and sugars (<sup>18</sup>O). Both isotopes can be used to reconstruct the isotopic composition of precipitation. But this approach is hampered by evaporative enrichment of leaf water. The solution for this problem might be the combination of both isotopes, which allows calculating not only the isotopic composition of paleo-precipitation but also relative humidity (rh) based on reconstructed d-excess of leaf water. Preliminary results suggest that the rh was lower during the Younger Dryas compared to the very humid Alleröd. The onset of the Holocene was even drier than the Younger Dryas, except for one very humid spell. Only with the transition Preboreal/Boreal, rh increased again. Apart from the analysis of isotopic composition, different chain lengths of *n*-alkanes are used to reconstruct paleovegetation.

## V25

**Glacial-interglacial productivity changes in the eastern equatorial Pacific upwelling system: a threshold response to Plio-Pleistocene ice-sheet dynamics? Implications from foraminiferal stable carbon and oxygen isotopes**

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Oceanic upwelling regions play a key role in controlling the Earth's climate change. Removal of CO<sub>2</sub> from surface waters and thus from the atmosphere during phytoplankton photosynthesis and the formation of organic matter within these upwelling zones has a significant influence on both the global carbon and nutrient cycles<sup>[1]</sup>. An ideal natural laboratory for studying dynamics in an upwelling system is the eastern equatorial Pacific (EEP), which harbors >10% of the present-day global ocean primary production<sup>[2]</sup>, making it an important factor in the Earth's atmospheric and marine carbon budget. However, the reasons for EEP primary productivity changes during the Plio-Pleistocene transition have yet remained poorly understood. Traditionally, it has been argued, that EEP productivity changes are dominated by upwelling strength since the intensification of Northern Hemisphere Glaciation (iNHG), which is in turn controlled by trade-wind strength<sup>[3]</sup>. An alternative hypothesis claims that productivity in (sub)tropical upwelling regions was primarily controlled by the nutrient availability of upwelled waters deriving from high latitudes<sup>[4]</sup>. Here we present new late Pliocene/early Pleistocene high-resolution data from Ocean Drilling Program Site 849 (0°11'N, 110°31'W), located in the heart of the EEP upwelling system. We use benthic and planktonic foraminiferal carbon isotope and sand fraction data to investigate the dynamics and origin of glacial-interglacial (G-IG) productivity changes covering the time interval from 2.65 to 2.4 Ma. This interval includes the first three major glacials during iNHG<sup>[5]</sup>, which should have influenced the behavior of the upwelling system via altered oceanic/atmospheric circulation. Our results indicate that productivity was enhanced during glacials from marine isotope stage (MIS) 100 onwards and that upwelled waters in the EEP mainly derived from the Southern Ocean. Glacial-Interglacial productivity changes in this higher-latitude source area strongly controlled EEP late Pliocene/early Pleistocene production. Additionally, upwelling intensification favored EEP productivity during MIS 96. This may represent the first analog during iNHG for mechanisms nearly identical to late Pleistocene ice-sheet dynamics, where a specific ice-volume threshold is crossed and resulting feedback mechanisms developed.

**Figure 1:**

(top) LR04 stack<sup>[5]</sup> for the last 3.5 Ma. (bottom) High-resolution proxy records from ODP Site 849 for MIS 104-96 tuned to the LR04 stack<sup>[5]</sup>. (a) LR04 stack<sup>[5]</sup>. (b)  $\delta^{18}\text{O}_b$  from Site 849, containing a combination of own measurements and data from [6]. Red line (a-b) shows tie points for tuning. (c) Percentage of >63  $\mu\text{m}$  fraction from Site 849. (d) C<sub>37</sub> alkenone abundances from Sites 846<sup>[4]</sup> and (e) 1239<sup>[7]</sup>, plotted with their original age-models. Yellow bars (c-e) combine peaks, which are assumed to occur synchronously. The offsets between the individual proxy records most likely result from the use of individual age-models. (f)  $\delta^{13}\text{C}_b$  and (g)  $\delta^{13}\text{C}_p$  from Site 849.

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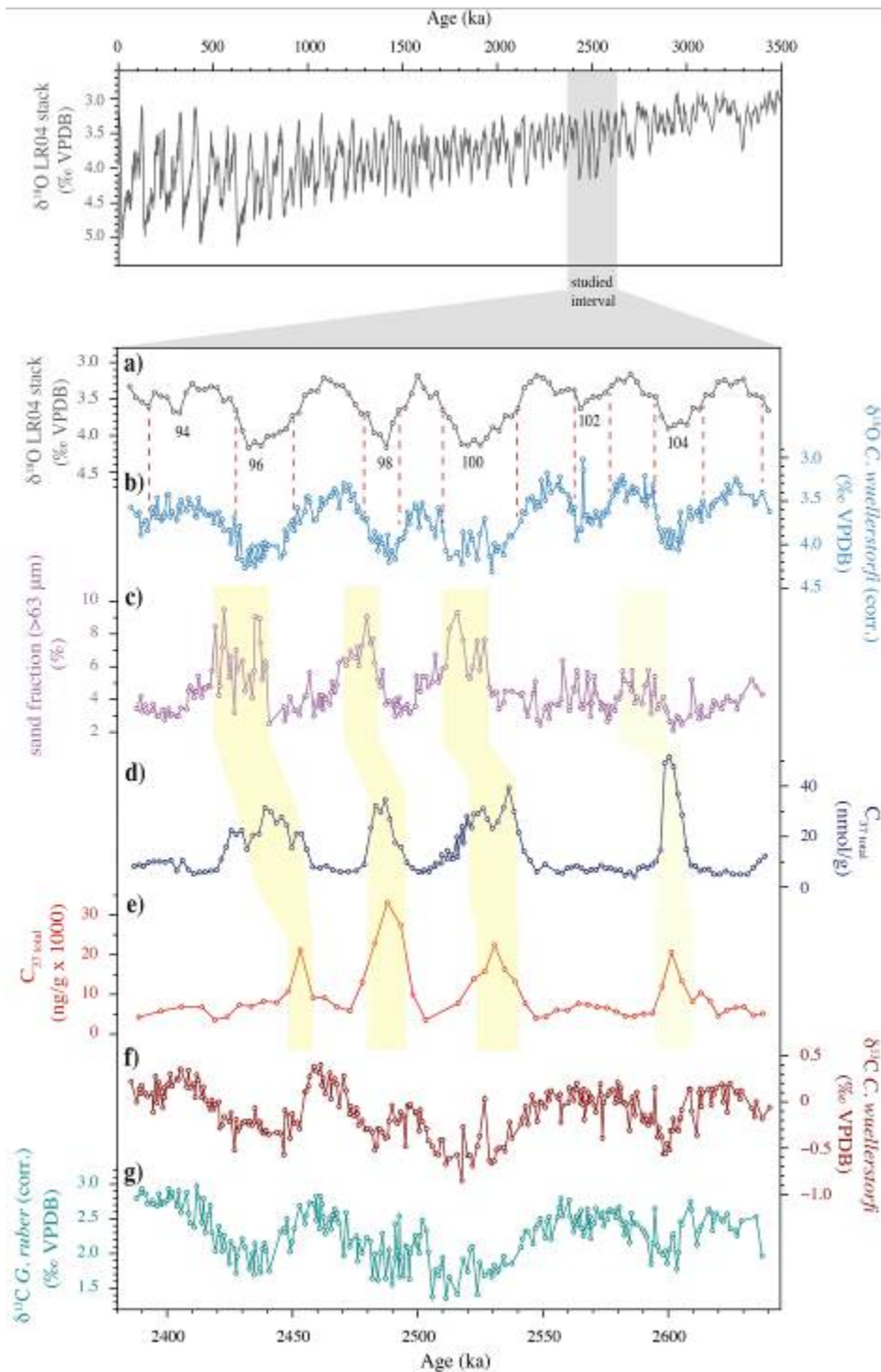
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**Abb. 1**



**V26****The EU funded project 'SPICE-profiling' (2015-2017): First results of the analytical characterization of Spice products containing the amino alkyl indole 5F-PB-22 by using stable isotope ratio mass spectrometry (IRMS)**

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The project SPICE-profiling, funded within the EU's ISEC 2013 programme (JUST/2013/ISEC/DRUGS/AG/ISEC/4000006421), will develop integrated and innovative approaches tackling the phenomenon of new psychoactive substances (NPS). Since 2008, the numbers of these substances are increasing dramatically on the European drug market and are mainly represented by synthetic cannabinoids and bath salts [1]. Many of the NPS are highly potent and produce unpredictable effects on consumers; therefore the NPS phenomenon is one of the most urgent drug-related problems in the European Union. The NPS samples will be collected from test purchases in internet shops, controlled laboratory syntheses and from seizures by custom and police. By analyzing these substances, information about the manufacturing procedures, the required key chemicals, the origin of adulterants and plant matrices and the chemical relations between different products should be obtained. For the chemical impurity profiling, gas chromatography- and ultra high performance liquid chromatography-mass spectrometry (GC-MS/UHPLC-MS) will be used. The stable isotope ratios of carbon, nitrogen and hydrogen will be analyzed by using EA- and GC-IRMS. One goal of the isotopic profiling is to evaluate the impact of IRMS techniques for linking different seizures and linking seizures to clandestine producers. The first results of a preliminary study on the synthetic cannabinoid 5F-PB-22 (1-Pentylfluoro-1H-indole-3-carboxylic acid-8-quinolinyl ester) will be presented. This amino alkyl indole based NPS was extracted from 14 different Spice product brands (herbal material) including 11 product samples from a big police seizure in one internet shop. Additionally, two pure 5F-PB-22 samples from different police seizures were available for analysis. The determined isotope ratios of the extracted samples will be compared to each other and the differences and similarities will be discussed.

[1] European Monitoring Centre for Drugs and Drug Addiction (EMCDDA) 2014, Perspectives on drugs - Controlling new psychoactive substances [<http://www.emcdda.europa.eu/topics/pods/controlling-new-psychoactive-substances>]

**V27****Stable Isotope Analysis as tool for the identification of authenticity and origin of fruits and fruit-products**

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The access to fresh produce from all around the world in our globalized economy is easy and cheap. However, there is a trend of rising awareness for locally produced food, especially fresh fruits, vegetables and other food products. The increasing demand of such regional products stimulates criminals for mislabelling and food fraud. Therefore, the analysis of the origin of produce is a critical and challenging task, because these food products have certain fragile qualities, which makes handling and analysing more difficult. The loss of water, over-ripening and mould are only few parameters complicating the identification of the origin in the laboratory. The aim of this study is to establish a database for the proof of identity of the origin of fresh fruits and other produces.

Stable isotope analysis of food and agricultural products can be used to assess the origin and authenticity. The isotopic signatures of carbon, nitrogen, hydrogen, oxygen, and sulphur reflect local environmental, climatic and industrial conditions during growth and processing and therefore, can be used for the identification of locality and identity. However, alterations of the isotopic signatures are highly likely and therefore, we have undertaken research to establish robust proxies for the reconstruction of the food origin. The analysis of certain fruit components and multi-isotopic patterns increase the obtained information and discriminatory power of the results. This technique allows for direct extraction of independent information from the products itself and was applied on a large series of strawberries and other fruits from Central Europe, Eastern Europe and worldwide.

In this study we want to demonstrate the development of robust measures for the analyses of fresh fruits. As examples we will demonstrate, how the origin of strawberries and other fruits can be detected trustfully. This research has been part of the larger research project 'Foodprint Analytics' (funded by the Austrian Science Foundation FFG) and was done with industrial support. Our research focuses on the analysis of specific component of the fruits (or fruit products) for database building, statistical data evaluation and simulation and exploring of discriminatory factors. The database provides a general level of resolution to distinguish the origin of different countries and a second more detailed level to separate national and regional localities. Therefore, stable isotope analysis provides a powerful tool for authenticity control and testing of fruits and food products.

**V28****High intraspecific ability to adjust both carbon uptake and allocation under light and nutrient reduction in *Halimium halimifolium* L.**

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The allocation of recently assimilated carbon (C) by plants depends on developmental stage and on environmental factors, but the underlying mechanisms are still a matter of debate. In the present study we investigated the regulation of C uptake and allocation and their adjustments during plant growth. We induced different allocation strategies in the Mediterranean shrub *Halimium halimifolium* L. by a reduction of light (*Low L* treatment) and nutrient availability (*Low N* treatment) and analyzed allocation parameters as well as morphological and physiological traits for 15 months. Finally, we conducted a <sup>13</sup>CO<sub>2</sub> pulse-labeling and followed the way of recently assimilated carbon to eight different tissue classes and respiration for 13 days. The plant responses were remarkably distinct in our study, with mainly morphological/physiological adaptations in case of light reduction and adjustment of C allocation in case of nutrient reduction. The transport of recently assimilated C to the root system was enhanced in amount (c. 200%) and velocity under nutrient limited conditions compared to control plants. Despite the 57% light reduction the total biomass production was not affected in the *Low L* treatment. The plants probably compensated light reduction by an improvement of their ability to fix C. Thus, our results support the concept that photosynthesis is, at least in a medium term perspective, influenced by the C demand of the plant and not exclusively by environmental factors. Finally, our results indicate that growing heterotrophic tissues strongly reduce the C reflux from storage and structural C pools and therefore enhance the fraction of recent assimilates allocated to respiration. We propose that this interruption of the C reflux from storage and structural C pools could be a regulation mechanism for C translocation in plants.

**V29****Direct incorporation of precursor fatty acids into microbial lipids in soils: Position-specific labeling tells the story**

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Fatty acids have been used as plant and microbial biomarkers to trace the pathways of C stabilization and soil organic matter (SOM) formation. Therefore, knowledge of the transformation pathways in soils is crucial for the interpretation of fatty acid fingerprints, especially because the formation and decomposition processes are ongoing simultaneously. Therefore, we analyzed the formation of microbial fatty acids from their precursor acetate and palmitate in soil by coupling position-specific <sup>13</sup>C labeling with compound-specific <sup>13</sup>C analysis.

Position-specifically and uniformly <sup>13</sup>C-labeled acetate and palmitate were applied in an agricultural Luvisol. Pathways of fatty acids were traced by analyzing microbial utilization of C from individual molecule positions of acetate and palmitate and their incorporation into phospholipid fatty acids (PLFA).

Fate of acetate <sup>13</sup>C in the soil was characterized by the main pathways of microbial metabolism: C-1 was preferentially oxidized to CO<sub>2</sub> in the citric acid cycle, whereas C-2 was preferentially incorporated into microbial biomass. Similarly, odd and even positions of palmitate reflected a preferential oxidation of odd and incorporation of even positions - a result of palmitate cleavage to acetyl-CoA and further use in the main pathways of C metabolism. However, we also observed a direct incorporation of more than 6% of the added palmitate <sup>13</sup>C into microbial cell membranes, indicating the important role of palmitate as direct precursor for microbial fatty acids. In this case, the C backbone of palmitate was not cleaved, but modified (e.g. desaturated, elongated or branched) according to the fatty acid demand of the soil microbial community. If acetate <sup>13</sup>C was used for PLFA formation, the construction of new C backbones of fatty acids was of minor importance. Instead, acetate <sup>13</sup>C was incorporated into microbial PLFA by elongation or branching of already existing fatty acids. Therefore, the previous assumption, that fatty acids are generally newly formed from substrates added has to be discarded. Future PLFA studies have to consider the reuse of existing plant and microbial-derived fatty acids.

Discrimination of acetate positions by PLFA formation was lowest in the microbial groups with the highest competitiveness for acetate uptake. Palmitate uptake and transformations were specific for the individual microbial groups in soil. For both substrates, it could be concluded that more direct, less complex metabolic pathways are characteristic of fast-growing microbial groups with high turnover.

This study proves the fast microbial turnover of the free fatty acids like palmitate in soils, as well as the high turnover and transformation of cellular PLFA. Knowledge about these microbial transformations of fatty acids in soils is crucial for the interpretations of microbial fatty acid fingerprints. Furthermore, tracing the formation and transformation of lipids in soils improves our understanding of C fluxes and the stabilization of microbial residues in soils.



**V30****Can foliar  $\delta^{15}\text{N}$  be retrieved from fresh leaf reflectance spectra? Evidence from an experimental labeling approach**

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Linking stable isotope ecology to remote sensing methodology can provide a promising approach to study ecological processes from small to large spatial scales. Previous studies suggest that  $\delta^{15}\text{N}$  of leaves and/or canopies can be modelled using spectroscopic measurements, indicating that the  $^{15}\text{N}$  isotope may affect the optical properties of plant foliage. However, with field samples, it is difficult to determine whether correlations between  $\delta^{15}\text{N}$  and spectral information are driven by direct influence of the heavy  $^{15}\text{N}$  atom on absorption properties of leaf biochemical compounds, or if the effect is based on covariation between foliar  $\delta^{15}\text{N}$  and total leaf nitrogen content or other leaf properties that potentially correlate with  $\delta^{15}\text{N}$ .

Using a  $^{15}\text{N}$ -labeling approach, we experimentally varied  $\delta^{15}\text{N}$  independently of any other leaf properties in three plant species. Fresh leaf reflectance spectra were recorded using an ASD FieldSpec 3 spectroradiometer and subsequently, foliar  $\delta^{15}\text{N}$  was measured with conventional isotope ratio mass spectrometry as a reference.  $\delta^{15}\text{N}$  could successfully be modeled from reflectance spectra by means of partial least squares (PLS) regressions. PLS models explained 53-73% of the variation in  $\delta^{15}\text{N}$  within species. Several wavelength regions important for predicting  $\delta^{15}\text{N}$  were consistent across species and could furthermore be related to known absorption features of N-containing molecular bonds.

Since covariation with other leaf properties was eliminated and thus cannot be the reason for the observed relationship of leaf reflectance with foliar  $\delta^{15}\text{N}$ , our results show that  $^{15}\text{N}$  has an inherent effect on reflectance spectra. Thus, our study confirms the use of spectroscopic measurements to retrieve isotopic signatures and encourages future development. Furthermore, these results open promising future perspectives based on the potential use of hyperspectral measurements for up-scaling isotope ecology to larger spatial scales.

**V31****The importance of associations with saprotrophic non-*Rhizoctonia* fungi among fully mycoheterotrophic orchids is currently under-estimated: novel evidence from sub-tropical Asia**

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**Background and Aims**

Most fully mycoheterotrophic orchids investigated to date are mycorrhizal with fungi that simultaneously form ectomycorrhizas with forest trees. Only a few mycoheterotrophic orchids are currently known to be mycorrhizal with saprotrophic, mostly wood-decomposing, fungi instead of ectomycorrhizal fungi. This study (Lee *et al.*, 2015) provides evidence that the importance of associations between mycoheterotrophic orchids and saprotrophic non-*Rhizoctonia* fungi is currently under-estimated.

**Methods**

Using microscopic techniques and molecular approaches, mycorrhizal fungi were localized and identified for seven mycoheterotrophic orchid species from four genera and two subfamilies, Vanilloideae and Epidendroideae, growing in four humid and warm sub-tropical forests in Taiwan. Carbon and nitrogen stable isotope natural abundances of mycoheterotrophic orchids and autotrophic reference plants were used in order to elucidate the nutritional resources utilized by the orchids.

**Key Results**

Six out of the seven mycoheterotrophic orchid species were mycorrhizal with either wood- or litter-decaying saprotrophic fungi. Only one orchid species was associated with ectomycorrhizal fungi. Stable isotope abundance patterns showed significant distinctions between orchids mycorrhizal with the three groups of fungal hosts. Thus, this is the first report on significantly different carbon and nitrogen stable isotope natural abundance patterns in mycoheterotrophic orchids mycorrhizal with wood- and litter-decomposing fungi.

**Conclusions**

Mycoheterotrophic orchids utilizing saprotrophic non-*Rhizoctonia* fungi as a carbon and nutrient source are clearly more frequent than hitherto assumed. On the basis of this kind of nutrition, orchids can thrive in deeply shaded, light-limiting forest understoreys even without support from ectomycorrhizal fungi. Sub-tropical East Asia appears to be a hotspot for orchids mycorrhizal with saprotrophic non-*Rhizoctonia* fungi.

**Reference**

Lee Y.-I., Yang C.-K. and Gebauer G. (2015) *Annals of Botany* doi: 10.1093/aob/mcv085

## V32

**Does “you are what you eat (plus a few pernil)” also hold true for orchids?**

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The orchid genus *Epipactis* contains 49 terrestrial species distributed throughout the Northern hemisphere which occur in diverse habitats ranging from closed forests to open wetlands. The roots of several *Epipactis* species form orchid mycorrhiza with rhizoctonias or ectomycorrhizal (ECM) fungi of forest trees (Bidartondo *et al.*, 2004). Nonetheless, until now information about fungal partners and trophic strategies such as autotrophy, partial or full mycoheterotrophy of only six *Epipactis* species is available.

In this study we sampled leaves and roots of another eight *Epipactis* species growing in forest habitats and accompanying autotrophic plant species as reference for site conditions at 11 locations in NE Bavaria and on the North Sea coastline of the Netherlands during the orchids' flowering season. Fruiting bodies of ECM fungi were sampled at the corresponding sites in autumn and winter.  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  stable isotope natural abundance analyses and determination of N concentrations of dried leaf and sporocarp material were conducted simultaneously using EA-IRMS coupling.  $\delta$  values were normalized and converted into enrichment factors  $\epsilon$  to estimate the orchids' degree of mycoheterotrophy and to enable site-independent comparisons between the species. Identity of mycorrhizal fungi present in the *Epipactis* roots and of the collected sporocarps were determined using ITS sequencing.

Stable isotope abundances showed that all *Epipactis* species in this survey were significantly enriched in  $^{13}\text{C}$  and  $^{15}\text{N}$  towards autotrophic references elucidating partial mycoheterotrophy as nutritional mode. Strikingly, *Epipactis* species lie on a gradient in  $^{15}\text{N}$  enrichment between 3 and 25 ‰. Analyses of fungal partners separate *Epipactis* species into three clusters: Species mostly associated with ECM ascomycetes (*Tuber*, *Wilcoxina*), ones that form mycorrhiza with obligate ECM basidiomycetes (*Entoloma*, *Hebeloma*, *Hygrophorus*, *Russula*, *Thanatephorus*, *Tomentella*) and rhizoctonial *E. gigantea* and *E. palustris*. Apparently, the type of fungal partner drives the degree of isotopic enrichment to distinctive clusters: The cluster of *Epipactis* species associated with ECM basidiomycetes showed an intermediate enrichment in both  $^{13}\text{C}$  and  $^{15}\text{N}$  between the clusters of species forming orchid mycorrhiza with ECM ascomycetes and rhizoctonias. *Epipactis* species mycorrhizal with ECM ascomycetes exhibited an especially high enrichment in  $^{15}\text{N}$  with on average 20 ‰.

The stable isotope profiles in  $^{15}\text{N}$  of sporocarps of ECM ascomycetes and ECM basidiomycetes corresponded to the  $^{15}\text{N}$  enrichment of the *Epipactis* clusters mycorrhizal with ECM ascomycetes and ECM basidiomycetes, respectively. This allows drawing conclusions to food-web interactions: ectomycorrhizal *Epipactis* species obviously obtain carbon simultaneously from photosynthesis and the mycorrhizal fungi while the complete nitrogen gain seems to be from the fungal source.

**V34****Elucidation of microbial metabolic pathway activities in soil at low temperature using position-specific  $^{13}\text{C}$  labeled glucose**

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Microbial transformation of organic substances in the soil is the most important process of the C cycle. Most of the current studies base their information about transformation of organic substances on incubation studies under laboratory conditions and thus, we have a profound knowledge on SOM transformations at ambient temperatures. However, metabolic pathway activities at low temperature are not well understood, despite the fact that the processes are relevant for many soils globally and seasonally.

To analyze soil metabolism at low temperature, isotopomers of position-specifically  $^{13}\text{C}$  labeled glucose were applied at +5°C with and without sodium azide and at -5°C. Sodium azide was used to inhibit electron transport chains in the soil before application of the tracer. Soils were incubated for 1, 3 and 10 days. Transformation of glucose was quantified by determining amount of  $^{13}\text{C}$  from individual molecule position in respired  $\text{CO}_2$ . Incorporation of  $^{13}\text{C}$  in bulk soil, extractable microbial biomass by chloroform fumigation extraction (CFE) and cell membranes of different microbial communities classified by  $^{13}\text{C}$  phospholipid fatty acid analysis (-PLFA) was carried out.  $^{13}\text{CO}_2$  data showed a dominance of C-1 respiration at +5°C for treatments with and without sodium azide, but total respiration for sodium azide inhibited treatments increased by 14%. In contrast, at -5°C metabolic behavior showed intermingling of preferential respiration of the glucose C-4 and C-1 positions.

Here we show that at +5°C, pentose phosphate pathway activity is a dominant metabolic pathway used by microorganisms to metabolize glucose. The respiration increase due to  $\text{NaN}_3$  inhibition was attributed to endoenzymes released from dead organisms that are stabilized and activated at the soil matrix and have access to suitable substrate and co-factors to permit their functions. Our PLFA analysis showed that incorporation of glucose  $^{13}\text{C}$  was higher in Gram negative bacteria than other microbial groups as they are most competitive for LMWOS. Only a limited amount of microbial groups maintained their glucose utilizing activity at -5°C and they strongly shifted towards a metabolization of glucose via both glycolysis and pentose phosphate pathways indicating both growth and cellular maintenance. This study revealed a remarkable microbial activity at low temperatures which differs significantly from our observations at ambient temperature, which could be unraveled based on position-specific labeling.

**P1****Messung von stabilen Isotopen in Luftproben für das ICOS Netzwerk**

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Das Integrated Carbon Observation System (ICOS) ist ein europäisches Messstationen-Netzwerk zur zeitlich und örtlich hochaufgelösten und hochpräzisen Langzeit-Konzentrationsbestimmung von Treibhausgasen (CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O...). Zusätzliche Informationen über Treibhausgasquellen können über die Isotopie der Treibhausgase gewonnen werden. Unter anderem zur Messung der Isotopie von an den ICOS Messstationen gesammelten Luftproben wurde ein zentrales Analysenlabor ICOS-CAL eingerichtet.

Wir berichten über im ICOS-CAL in Jena durchgeführte Messungen der stabilen Isotope von CO<sub>2</sub> in Luft ( $\delta^{13}\text{C}(\text{CO}_2)$  und  $\delta^{18}\text{O}(\text{CO}_2)$ ) sowie über das analytische System zur Messung der O<sub>2</sub>/N<sub>2</sub>, Ar/N<sub>2</sub> und CO<sub>2</sub>/N<sub>2</sub> Verhältnisse in Luftproben, das derzeit aufgebaut wird. Die Skala der stabilen CO<sub>2</sub> Isotope wird derzeit mit der Primärskala JRAS06 am IsoLab des MPI-BGC abgeglichen. Aktuelle Resultate werden präsentiert.

**P2****Challenges in using cryogenic water extraction to trace plant's source water**

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For more than twenty years, cryogenic water extraction has been the gold standard to extract soil and/or plant water for isotope analyses. However, recent studies showed that cryogenic extraction conditions (extraction time, temperature, vacuum threshold) and physicochemical soil properties considerably impacted the extracted soil water isotope results. These findings have broad implications for interpretations of extraction results, especially in the light of plant water uptake depths calculations, use of a soil water component for hydrograph separation, or mean transit time estimation. The ultimate question therefore is: Which soil water pool/s are we actually extracting cryogenically under certain extraction conditions and is this soil water pool the source of plant water uptake?

We conducted a greenhouse trial with five different plant species grown on two physicochemically different soils (sandy soil and clayey loam) to test the effects of varying cryogenic extraction conditions and physicochemical soil properties on extracted soil water isotope results. We further aimed to identify the unique soil water isotopic signature which mirrors plant's water source. We sampled root crowns and an aliquot of the first and second soil layer for cryogenic water extraction. To determine the plant water available soil water pool/s, we varied water extraction parameters for soil samples with extraction durations of 30, 60, 180, and 240 min; extraction temperatures of 80°, 120°, and 200°C; and an extraction vacuum of 0.001 Pa. For plant samples, we do not have reasons to believe that extraction temperature or vacuum impact the extracted isotope results. We therefore applied fixed extraction parameters to all root crown samples (90°C, 180 min, 0.001 Pa). Extracted water isotopic signatures were measured via off-axis cavity ring-down spectroscopy and checked for potential spectral interferences caused by organic compounds co-extracted from plant tissues.

Our results indicated that physicochemical soil properties (i.e. clay content, pore size) and extraction parameters lead to isotope fractionation of soil water. While extraction temperature and time significantly impacted isotope results of clayey loam samples, no effect could be observed for the sandy soil. However, longer extraction times and higher temperatures resulted in enriched isotopic signatures for water extracts of both soil types, although this influence was more pronounced for the clayey loam. For identifying plant's water sources, we selected two out of five plants, which donated the most suitable root crown tissues for cryogenic extraction: Common dandelion and Geranium. Determining ideal soil water extraction parameters to identify available soil water pools for Common dandelion and Geranium revealed that various parameter settings were suitable for both soils depending on which isotope (<sup>2</sup>H or <sup>18</sup>O) was considered, e.g. clayey loam samples extracted at 200°C for >30 min best reflected Geranium's  $\delta^{18}\text{O}$  signatures.

Our study indicated that extracted water isotope results appear to be a function of extraction conditions along with soil physicochemical properties. In view of the increasing number of laboratories, which nowadays apply cryogenic water extraction, especially in the context of ecohydrological (e.g. plant water uptake) studies, it seems timely to develop a standard extraction protocol for extraction settings in order to generate meaningful and comparable isotope results.

**P3****Clumped isotope thermometry of carbonate-bearing apatites: Digestion techniques and calibrations**

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$\Delta_{47}$  data published by Eagle et al. (2010) indicate that  $^{13}\text{C}$ - $^{18}\text{O}$  clumping in carbonate groups of bioapatites ( $\text{Ca}_5(\text{PO}_4, \text{CO}_3)_3(\text{OH}, \text{F})$ ) may follow the Ghosh et al. (2006) calibration of the clumped isotope thermometer established for synthetic calcite. Eagle et al. (2011) used this T- $\Delta_{47}$  relationship to reconstruct body temperatures of extinct vertebrates such as dinosaurs.

Here we refine a previous calibration for bioapatite and extend the studied temperature range to 2 to 37 °C. The conventional acid digestion technique that is commonly used for clumped isotope analysis of carbonates was modified and the reaction temperature was raised to 110 °C. Beside of this, we investigated the influence of the pre-treatment of sample material on  $\Delta_{47}$  data. Teeth of a greenland shark, ragged tooth sharks that lived under controlled conditions, crocodiles, an african elephant, and modern humans were analyzed for their clumped isotopic compositions. Distinct  $\Delta_{47}$  values were determined for dentine and enamel. Finally, the calibration based on enamel seems to exhibit a similar temperature sensitivity like the T- $\Delta_{47}$  relationship of Wacker et al. (2014).

For calibration under well defined abiotic conditions, carbonate-bearing hydroxyapatite was synthesized at different temperatures (10-60 °C) following two different experimental approaches: (1) Mixing experiments of two different solutions modified after Lécuyer et al. (2010), and (2) recrystallization of calcium carbonate powders in aqueous phosphate/bicarbonate bearing solutions containing different alkali salts. First results indicate that the  $\Delta_{47}$  values determined using material prepared after the (2) approach at 60°C support the calibration data obtained for the bioapatites, thereby extending to range of the calibration curve. We currently investigate whether A and B type substitution of the carbonate group has an influence on the  $\Delta_{47}$  values.

Eagle et al. (2010), PNAS 107 ; Ghosh et al. (2006), GCA 70 ; Eagle et al. (2011), Science 333; Wacker et al. (2014), GCA 141; Lécuyer et al. (2010), GCA 74.

**P4****An isotopic perspective on the levoglucosan chemical stability**

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Levoglucosan is employed in chemical mass balance receptor models as the specific inert tracer of particulate matter emissions from biomass burning. Yet, several laboratory studies showed that the levoglucosan concentration strongly decays in aerosol particles exposed to hydroxyl radicals (OH)<sup>1</sup>. Isotopic analyses, complementarily to concentration measurements, can provide additional evidence for chemical processing due to the kinetic isotope effect (KIE) which causes changes in the relative abundance of heavy to light isotopes.

In this study, we investigate the chemical stability of levoglucosan, by exploring its isotopic fractionation during oxidation in both, aqueous and particle phase by OH radicals. The samples, experiencing different extent of processing, were isotopically analyzed by Thermal Desorption /Liquid Extraction - Two Dimensional Gas Chromatography - Isotope Ratio Mass Spectrometry (TD/LE-2DGC-IRMS)<sup>2</sup>. In both cases, we show that the  $\delta^{13}\text{C}$  of levoglucosan increases with the extent of processing. From the dependence of levoglucosan  $\delta^{13}\text{C}$  and concentration on the reaction extent, we determined the KIE of levoglucosan oxidation by OH in aqueous solution and aerosol particles, being  $1.00187 \pm 0.00009$  and  $1.00228 \pm 0.00006$ , respectively. Both values show good agreement, being also within the range of predicted KIE for alkanes with the same number of carbon atoms<sup>3</sup>.

<sup>1</sup> C. J. Hennigan et al., Levoglucosan stability in biomass burning particles exposed to hydroxyl radicals *Geophys. Res. Lett.*, 2010, 37, L09806.

<sup>2</sup> X.-F. Sang et al., Stable carbon isotope ratio analysis of anhydrosugars in biomass burning aerosol particles from source samples, *Environ. Sci. Technol.*, 46(6), 3312-3318.

<sup>3</sup> Rudolph, J. (2007), Gas chromatography - isotope ratio mass spectrometry, in *Volatile organic compounds in the atmosphere*, edited by R. Koppmann, pp. 388-466, Wiley-Blackwell.



## P5

**Molecularly-imprinted polymers enable the C and N isotope analysis of polar organic micropollutants in the  $\mu\text{g/L}$  range**

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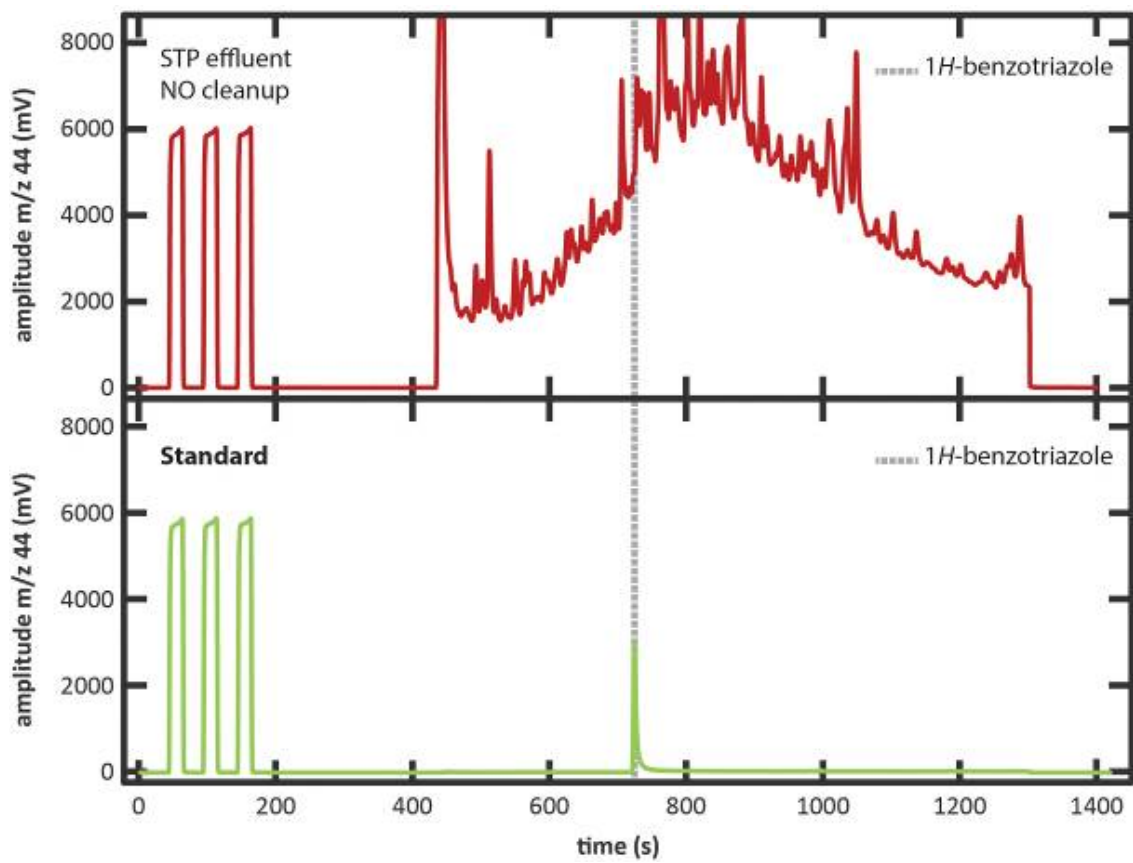
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Understanding the transport and transformation processes of organic micropollutants in soil and water is a key step in addressing their impact on both human health and the environment. Monitoring changes of the isotope ratios of these chemicals in the environment by compound-specific isotope analysis (CSIA) is invaluable with regard to the identity of degradation reactions as well as the extent of transformation. However, CSIA for polar organic micropollutants such as pesticides, pharmaceuticals, and consumer chemicals currently faces major challenges that impede its use. (1) Organic micropollutants occur in natural systems at low concentrations (i.e. ng/L -  $\mu\text{g/L}$ ), which are up to 50'000 times below the typical quantification limits of gas chromatographs coupled to isotope-ratio mass spectrometer (i.e. mg/L). (2) As a consequence, very large volumes of water (e.g.  $\geq 10$  L) must be enriched to obtain the necessary mass of analyte for precise and accurate isotope ratio measurements. These two facts inevitably lead to partial co-enrichment of interfering substances, which deteriorates the quality of the acquired isotopic data or even impedes reasonable measurements (see figure). The use of molecularly-imprinted polymers (MIPs) offers a new avenue to CSIA of micropollutants through the selective cleanup of target analytes and elimination of interfering organic matter matrices.

In this work, we explore the use of tailor-made MIPs for the isotopic analysis of two widely found anthropogenic micropollutants, namely 1*H*-benzotriazoles as well as chloro-s-triazines. Samples were taken from typical environments where 1*H*-benzotriazole and chloro-s-triazines occur at low concentrations, such as in waste water and in soil organic matter leachates, respectively. Our approach included commercially available MIPs as well as newly self-synthesized ones to check the applicability of MIP-CSIA in general. Both MIPs showed viability in eliminating the interfering matrices up to several volts during  $^{13}\text{C}/^{12}\text{C}$  analysis by GC-IRMS. Comparison of  $^{13}\text{C}/^{12}\text{C}$  and  $^{15}\text{N}/^{14}\text{N}$  ratio measurements before and after the MIP shows no consequences on the integrity of the isotopic ratios using the optimized methodologies. However, due to unfavorable analyte to matrix ratios and the typical limited retention capacities of MIP materials, large MIP amounts (i.e. 1-5 g) are necessary which could make the synthesis or availability of MIPs a challenge. Nevertheless, results from the studied systems demonstrate the applicability of the proposed approach which represents an important step towards assessing the transformation processes of many micropollutants in aquatic environments.

Abb. 1



## P6

**Development of non-covalent molecularly-imprinted polymers for stable carbon and nitrogen isotope analysis of 1H-benzotriazole; from synthesis to application**

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Molecular recognition plays a vital role in living systems, such as antibodies, nucleic acids and enzymes. Interactions in molecular recognition have been exploited for decades to produce synthetic materials that mimic nature in specificity. Molecular imprinted polymers (MIP), synthetic materials that are custom-made to produce selectivity, have increasingly become an interesting tool for selective retention in analytical applications. Compound-specific isotope analysis (CSIA) is a likely technique to benefit from the selective character of MIP for sample preparation of environmental samples. However, there are shortcomings associated with the application of MIP, which renders its implementation for CSIA a challenging task. (1) The most generic approach for molecular-imprinting (i.e. non-covalent) employs forces such as hydrogen bonding which are easily disrupted in presence of water. (2) Although MIP possesses high selectivity towards the imprinted template, its capacity is limited compared to conventional non-selective sorbates. The requirements of CSIA of micropollutants in environmental samples face these two shortcomings that we address in this work.

Synthesis of MIP in presence of 1H-benzotriazole was successfully achieved by using photopolymerization at 2°C. 1H-benzotriazole, 5-methyl-benzotriazole and benzimidazole were used as templates (T), methacrylic acid as a functional monomer (FM), and diethylene glycol dimethacrylate as a crosslinker (XL). A molecular ratio of 1:4:20 was used for T:FM:XL in an aprotic solvent such as dichloromethane. Non-imprinted polymers (NIP) were also produced in absence of any template. After extraction of the templates, the produced polymers were crushed, sieved, sedimented and packed either in cartridges or in high-performance liquid chromatography columns. Assessment of the produced MIPs showed that the highest selectivity (imprinting factor 1.7) was achieved when using 1H-benzotriazole as a template, whereas no selectivity (imprinting factor 1.0) was obtained towards molecules like naphthalene and benzothiazole. Additionally, enthalpies of sorption were measured for interaction of 1H-benzotriazole on the MIP ( $\Delta H = -13.8$ ) and on the NIP ( $\Delta H = -9.5$  kJ/mol). The more exothermic value obtained on the MIP indicates stronger interactions which further confirms its selectivity towards 1H-benzotriazole.

Assessment of performance for a real sample was tested by pre-enrichment of 10 L of Swiss river water (Bünz creek) spiked with 1H-benzotriazole using conventional solid-phase extraction to replace water with dichloromethane which is compatible with MIP. Subsequently, the 1H-benzotriazole-containing fraction in dichloromethane was loaded on MIP and eluted with methanol. Substantial removal of the matrix was observed on the imprinted polymers, whereas, the non-imprinted polymers led to loss of both the matrix and 1H-benzotriazole.

**P7****Application of laser absorption spectroscopy ( $^{13}\text{C}$ -CH<sub>4</sub> and  $^{13}\text{C}$ -CO<sub>2</sub>) for online monitoring in biogas plants**

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Energy production by biomass decomposition within biogas plants plays an important role in the renewable energy sector of Germany. In recent years, the number of biogas plants has greatly increased and this upward trend appears to continue. For example, in Germany during the last 10 years the number of biogas plants has grown from 1000 to 7500. Efficient operation and stability of biogas plants requires a continuous monitoring of the digester content. Traditional laboratory analysis of digester sludge is often complex and time-consuming and shows a delayed response to disruptions within the fermentation process. As a new approach, we apply laser absorption spectrometers (LGR, Los Gatos Research) for real-time monitoring of the stable carbon isotopes of methane and CO<sub>2</sub> ( $\text{d}^{13}\text{C}_{\text{CH}_4}$  and  $\text{d}^{13}\text{C}_{\text{CO}_2}$ ) in a pilot-scale biogas digester located at Deutsches Biomasseforschungszentrum in Leipzig, Germany. The general aim is use  $\text{d}^{13}\text{C}_{\text{CH}_4}$  and  $\text{d}^{13}\text{C}_{\text{CO}_2}$  as new process indicators to characterize the actual process state of the anaerobic digesters and to indicate possible process changes at an early stage. Therefore, we connected the laser absorption spectrometer to the gas outlet of a 190m<sup>3</sup> maize-digester and carried out high-resolution monitoring of the stable isotopes under variable organic loading rates (2-13 kg oTS/m<sup>3</sup>×d). We compared the isotopic values with different fermenter parameters such as gas production rate, gas composition, VFA composition, and pH. Further, fermenter sludge samples were taken and were analyzed for microbiological composition (quantitative qPCR-analysis). These samples were also used as starter cultures for batch experiments with various C-sources to deduce the specific isotopic signature depending on the actual methanogenic pathway.

The  $\text{d}^{13}\text{C}_{\text{CH}_4}$ -values reacted promptly to abrupt changes in the process state such as feeding events and also indicated a long-term variability depending on the environmental conditions. During a phase of high organic loading  $\text{d}^{13}\text{C}_{\text{CH}_4}$ -values showed a strong increase (enrichment) of about 10‰. The strong isotopic enrichment occurs 5-10 days prior to a significant change in the other parameter values.

Thus, for process control, it might be possible to estimate 'critical' isotopic values with respect to fermenter conditions. As a new parameter tool the stable isotopes even might be coupled to automatisisation routines (i.e., amount and intervals of digester feeding) in future time.

**P8****Photocatalyzed Glyphosate Degradation by Titanium Dioxide Characterized with LC-IRMS**

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As one of the most common total herbicides *N*-(phosphonomethyl) glycine (glyphosate) is used in the production of cotton, soybeans, crops and corn.<sup>1</sup>

Glyphosate can be transformed in the environment or technical processes such as photocatalytic degradation by titanium dioxide. Degradation leads to the products sarcosine and glycine, which are not specific, because they are present in the environment as well.

Thus, a clear evidence of degradation in the environment solely by the identification of transformation products or concentration losses is barely possible.

Since reactions can be associated with isotope effects, the analysis of stable isotope compositions ( $\delta^{13}\text{C}$ ) of the reactant offers a possibility to get information about the degradation process without the need for detecting specific degradation products.

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**P9****Measurement of delta O-18 and delta H-2 in atmospheric water vapour and precipitation in Heidelberg using two commercial laser-based spectrometers**M. Schmidt<sup>1</sup>, D. Leinfelder<sup>1</sup>, M. Sabasch<sup>1</sup>, E. Zepf<sup>1</sup><sup>1</sup>Institut für Umweltphysik, Universität Heidelberg, Heidelberg, Deutschland

In the past few years, stable water isotopes in water vapour and liquid water have become measurable at a high frequency using commercial laser spectroscopic techniques. At the Institut für Umweltphysik in Heidelberg, we run two commercial laser spectroscopic systems: In 2013 we installed an analyser based on cavity ring-down spectroscopy (Picarro) and in 2015 a second analyser based on off-axis integrated cavity output spectroscopy (Los Gatos Research). Both analysers are equipped with an autosampler and a vaporiser for liquid water samples and with an inlet for water vapour measurements of ambient air in Heidelberg. In this study we present our laboratory experiments carried out to characterize the performance of our two analysers measuring liquid water and water vapour isotopes. We discuss the instrument stability, the calibration strategy and the correction of the memory effect. In the second part, we present results from precipitation and water vapour measurements in Heidelberg.

**P10****Analysis of N<sub>2</sub>O isotopic composition at a tall tower in central Switzerland to identify emission sources and hot spots**

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The isotopic composition of nitrous oxide (N<sub>2</sub>O) provides important information on N<sub>2</sub>O sources, because microbial processes exhibit characteristic isotopic signatures [1]. Therefore, quasi-continuous measurements of ambient N<sub>2</sub>O concentration and isotopic composition in combination with atmospheric modelling can be used to identify local and regional emission hotspots and disentangle production pathways [2]. Quantum cascade laser absorption spectroscopy (QCLAS) in combination with preconcentration allows simultaneous and high-precision analysis of the four main stable N<sub>2</sub>O isotopologues (<sup>14</sup>N<sup>14</sup>N<sup>16</sup>O, <sup>14</sup>N<sup>15</sup>N<sup>16</sup>O, <sup>15</sup>N<sup>14</sup>N<sup>16</sup>O and <sup>14</sup>N<sup>14</sup>N<sup>18</sup>O) at ambient mixing ratios [3].

In the presented project, we will initiate quasi-continuous measurements of N<sub>2</sub>O isotopologues at the Beromünster tall tower in central Switzerland [4]. For the two inlet heights 12 and 212 m, maximum changes in the N<sub>2</sub>O mixing ratios of 50 and 10 ppb are anticipated, which would result in delta value changes in the order of 3 and 0.6 ‰, assuming a 20 ‰ depletion in delta values for the main source processes. To resolve differences in N<sub>2</sub>O isotopic composition at the highest inlet the repeatability of delta value measurements has to be improved to < 0.1 ‰. In an ongoing laboratory phase we significantly enhanced the long-term stability of the laser spectrometer by reducing the dependency of cell temperature on ambient temperature changes from 100 mK K<sup>-1</sup> to 10 mK K<sup>-1</sup>. Thereby, the required precision level is maintained for a 10 times longer period, which results in an accuracy of < 0.1‰ for the targeted isotope ratios. In addition, a novel preconcentration device [5] was set up and optimized with respect to temporal resolution. The results from the Beromünster tall tower will be combined with atmospheric transport simulations to determine the spatio-temporal variability of N<sub>2</sub>O emissions and its isotopic signatures in central Switzerland.

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**P37****Evaluating the contribution of water resources to crop growth of rice and maize by stable water isotopes**

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Rice is one of the most water-consuming crops in the world. Understanding water source utilization of rice will help us to improve water use efficiency (WUE) in paddy management (Shen, Zhang et al. 2015).

The objectives of our study are to evaluate the isotopic compositions of surface ponded water, soil water, groundwater, rain water and plant water. And based on stable water isotope signatures we will then evaluate the contributions of various water sources to plant growth (wet rice, aerobic rice and maize) during wet and dry seasons. We will further investigate the contribution of different soil horizons for rice and maize in different maturity periods during both seasons. Finally we will compare the water balances and crop yields in both crops during wet and dry seasons and calculate the water use efficiencies. This will help to identify the most efficient water management systems in rice based cropping ecosystems.

Soil samples are collected from different depths at 0, 5, 10, 15, 20, 20-30, 30-40, 40-50, 50-60 cm in vegetative, reproductive and matured periods of plant growth together with stem sampling. Soil and plant samples are extracted by cryogenic vacuum extraction (Orlowski, Frede et al. 2013). Root samples are collected up to 60 cm depth from 10 cm intercepts. Root length, density and dry weight are calculated using winRHIZO software. Groundwater, surface water, rain water and irrigation water are sampled weekly. All water samples are analysed for hydrogen and oxygen isotope ratios (d18O and dD) using Los Gatos Research DLT100. Rainfall records, ground water level, surface water level fluctuations and the amount of water irrigated in each paddy field will be measured by water meter during the sampling period. WUE will be defined here as the grain yield divided by the amount of irrigation water (Shi, Zeng et al. 2002).

The direct inference approach which is based on comparing isotopic compositions (dD and d18O) between plant stem water and soil water will be used to determine water sources taken up by plant (Asbjornsen, Mora et al. 2007, Liu, Liu et al. 2010). Iso-source mixing model (Phillips and Gregg 2003) will be used to evaluate the relative contribution of each water pool (ponded water and soil water) to rice stem water. This model facilitates the calculations of all feasible solutions of source contributions based on multisource mass balance.

Multiple-source mass balance assessment can provide the estimated range of potential contributions of water from each soil depth to root water uptake of a crop. (Shen, Zhang et al. 2015). These evaluations will be used to determine the proportion of water from upper soil horizons and deep horizons for rice and maize in different maturity periods during wet and dry seasons. Finally we will estimate the influence of groundwater and surface water during the both seasons by irrigation water and/or by precipitation can be determined. We will present a general layout of our sampling design and the underlying methodological background. First results of the sampling during the wet season 2015 will be shown.



**P11****Carbon diagenesis in sediments of the subtropical Beibu Gulf, South China Sea: A stable isotope and modeling study**

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Beibu Gulf is characteristic of highly complex depositional systems as a shallow shelf sea. Deposits are formed under specific combinations of hydrodynamics, physiography and sediment sources. We used a model approach to investigate the effects of sediment depositional environments on carbon isotope distributions of dissolved organic carbon (DIC) in the three sampling sites (SO-43, SO-45 and SO-50) of this Gulf. In the site SO-43, the rapid decrease of  $\delta^{13}\text{C}$ -DIC in the top 8 cm is mainly due to high organic matter (OM) degradation rate (around 0.0018mM/a), resulting from relatively higher input of Fe and Mn-hydroxides. Whereas in the sites SO-45 and SO-50, a non-steady state processes dominate the variation in the shallow sediment due to fresh and brackish water mixing. In both sites, seawater intrusion into fresh water sediment and a thickness of 600cm sediment was deposited over the last 10ka, with a sedimentation rate of about 0.5m/ka. The concentration profiles of  $\text{SO}_4^{2-}$ , DIC,  $\text{Cl}^-$  and  $\text{Ca}^{2+}$  and carbon isotopic composition of DIC demonstrated these two processes. The main difference between SO-45 and SO-50 is the resulting OM degradation rate. The latter is much higher.

**P12** **$\delta^{81}\text{Br}$  and  $\delta^{37}\text{Cl}$  - what do they tell us about the origin and fate of fluids in highly saline settings?  
Case study in the Zechstein formation of the Northern German Basin.**S. Stadler<sup>1</sup>, O. Shouakar-Stash<sup>2</sup><sup>1</sup>BGR, Hannover, Deutschland<sup>2</sup>University of Waterloo, Waterloo, Ontario, Canada

Chloride and bromine are important constituents of ocean water and interstitial brines derived from them. They have a low reactivity allowing them to display isotopic effects of physical processes relatively straightforwardly. Bromine has 31 isotopes, with a mass range between 67 and 97, only two of which are stable ( $^{79}\text{Br}$  and  $^{81}\text{Br}$ ). Only few studies of the behavior of bromine stable isotopes in the geosphere have been published so far (Eggenkamp and Coleman (2000), Shouakar-Stash et al. (2007) and Eggenkamp (2014). Other studies mainly focused on analytical techniques for measuring bromine isotopes, and described some isotope variations in natural samples (Eggenkamp and Coleman (2000), Shouakar-Stash et al. (2005), Sylva et al. (2007), Eggenkamp (2014). Chlorine stable isotope analysis can be used to determine the source of salinity, water-rock interaction, and mixing of water components. Physical processes such as salt precipitation, brine evaporation, ion filtration, ion exchange and diffusion result in stable chlorine isotopic fractionation.

In our study we investigated groundwater and rock samples from the former rock salt and potash mining town of Stassfurt, Germany. The site is characterized by ongoing land subsidence following salt mining activities and subsequent drowning and flooding of the mine. Causes and extents of associated subsidence processes and the role of groundwater are still under debate. We show data from the Zechstein formation and overlying aquifers and discuss the origin and fate of fluids with special focus on distinguishing water from flooding from residual brines, and on the interaction between the different aquifers.

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**P13****Discharge driven nitrogen dynamics in a large river catchment: an isotope study**

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**Question**

Nitrate contents in surface and groundwater have increased in the last decades due to landuse change and accompanying application of fertilizer in agriculture as well as industrial exhaust fumes in the atmospheric deposition. This rising concentrations of nitrogen, which is an essential nutrient for organisms, has a major impact on eutrophication of rivers and coastal ecosystems. Therefore, it is important to quantify potential nitrate sources and ongoing nitrate process dynamics with its drivers in a river system.

**Investigation area and methods**

The investigated Bode River catchment (total size of 3200 m<sup>2</sup>) in the Harz Mountains in Germany was intensively observed by a closed monitoring approach with 133 sampling points for a period of two years. The area is characterized by a strong anthropogenic gradient, with conservation areas in the high mountains, grassland, and intensively mixed farming in the lowlands. Consecutive discharge simulations using the mesoscale Hydrological Model (mHM) allow a quantitative analysis of nitrate for all observed tributaries. Combined nitrate isotopic signatures enable differentiating between different nitrate sources (NO<sub>3</sub><sup>-</sup> in precipitation and NO<sub>3</sub><sup>-</sup> from microbial nitrification) and identify potentially ongoing degradation processes like bacterial denitrification. The following interpretations were focused on the Selke river, a major tributary of the Bode river, and comparative on large regional scale on the entire Bode catchment.

**Results**

The Selke tributary with a measured mean annual discharge of 1.1 m<sup>3</sup>/s in 2012, evidences high  $\delta^{15}\text{N}_{\text{NO}_3}$  variations (range between 4.5 and 12.9 ‰<sub>AIR</sub>) compared to low nitrogen isotopic variations on the Bode outlet (range between 8.2 and 11.8 ‰<sub>AIR</sub> with a mean discharge of 8.3 m<sup>3</sup>/s in 2012). These variation differences are caused by stronger mixing processes with increasing discharge. On the Bode outlet, denitrification processes are not significant in the surface water, since nitrate isotopic signatures would increase with decreasing concentrations. In contrast, within the smaller Selke catchment it becomes apparent, that nitrate ( $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$ ) isotopic signatures increase downstream which might be generated by increased bacterial denitrification in the anoxic soil zone, in the groundwater that discharges into the river and in the hyporheic zone. A significant decrease of nitrate isotopic signatures during precipitation events results in the mobilization of isotopically lighter nitrate reservoirs, like nitrified soil nitrogen or artificial nitrogen from fertilizers. The isotopic signature of NO<sub>3</sub> in precipitation does not affect significantly the isotopic signature of the Selke tributary because of low nitrate concentrations compared to stream nitrate contents. It can be assumed that back calculations to determine relevant nitrate sources and microbial processes are limited on catchment size.

**P14****Evidence for methane formation from algae in oxic seawater using a stable isotope approach**

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Methane (CH<sub>4</sub>) is an important greenhouse gas that affects radiation balance and consequently the earth's climate, while uncertainties of CH<sub>4</sub> sinks and sources still exist. The world's oceans are considered to be a source of CH<sub>4</sub> to the atmosphere, although the biogeochemical processes involved in CH<sub>4</sub> formation are not fully understood. This comprises for example the observation of a CH<sub>4</sub> oversaturating state within the surface mixed layer -called the "oceanic methane paradox".

Normally, since the ocean water column is oxygen saturated and methanotrophic bacteria will consume CH<sub>4</sub> solved in the water, a depletion of CH<sub>4</sub> in surface waters occurs compared to atmospheric CH<sub>4</sub> concentrations. However, sometimes regional and temporal oversaturation of surface waters occurs<sup>(1, 2, 3)</sup>, where its cause is still topic of debate<sup>(4)</sup>.

In the past decade, studies have confirmed direct CH<sub>4</sub> release from eukaryotes including plants<sup>(5)</sup>, animals<sup>(6)</sup>, fungi<sup>(7)</sup> and lichens<sup>(8)</sup>, even in the absence of microbes and in the presence of oxygen. These novel CH<sub>4</sub> production pathways have been termed 'aerobic CH<sub>4</sub> production' to distinguish them from the well-known anaerobic pathway, which involves catalytic activity by methanogenic enzymes. Additionally, methionine has been shown to be involved in CH<sub>4</sub> formation in saprotrophic fungi<sup>(7)</sup>, tobacco<sup>(9)</sup> and lavender plants<sup>(10)</sup>.

In this study we investigated marine algae as a possible source of CH<sub>4</sub>. Therefore, the coccolithophore *Emiliania huxleyi* was grown under controlled laboratory conditions and supplemented with two <sup>13</sup>C-labelled substrates, namely bicarbonate and a position-specific <sup>13</sup>C-labelled methionine (R-S-<sup>13</sup>CH<sub>3</sub>).

In all cases the algae cell number correlated with CH<sub>4</sub> formation. The production rate ranged from 23 to 28 × 10<sup>-18</sup> g CH<sub>4</sub> cell<sup>-1</sup> day<sup>-1</sup>. After supplementation of the cultures with the <sup>13</sup>C labelled substrates, in both cases the label could be traced in the headspace-CH<sub>4</sub> (Fig.1). Moreover, the presence of methanogenic Archaea during the incubation was excluded by real time PCR and cultivation approaches.

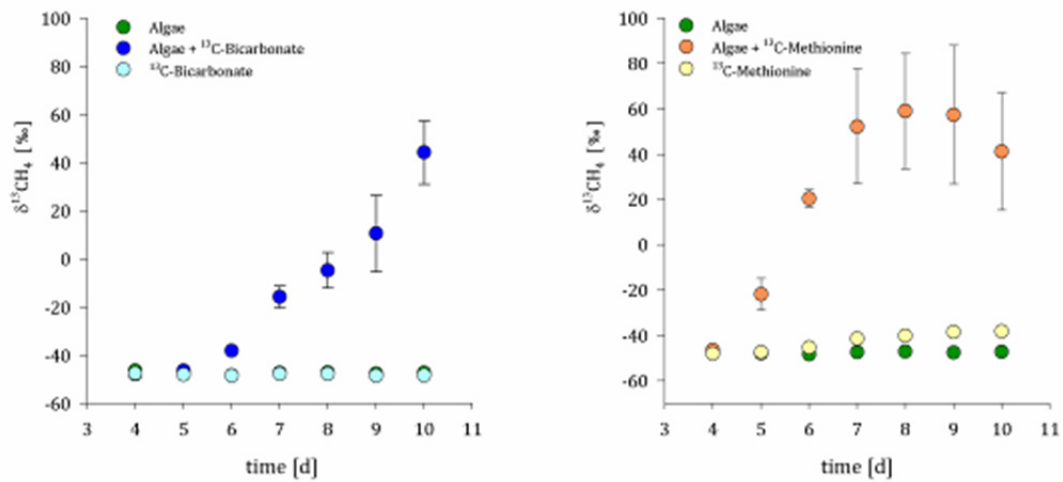
Our results show that algae are capable to produce CH<sub>4</sub> under oxic conditions by using the ubiquitous C source bicarbonate and the amino acid methionine. Thus, they might contribute to the observed spatial and temporal restricted CH<sub>4</sub> oversaturation in the ocean-mixed layer.

Figure1: δ<sup>13</sup>C values of headspace-CH<sub>4</sub>

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**Abb. 1**

**P15****Assessment of land subsidence mechanisms triggered by dolomitic marble dissolution from hydrogeochemistry and stable isotopes of spring waters**

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This study presents geochemical results of springs draining a small humid tropical watershed composed of geologically dolomitic marbles in Central Sri Lanka. Water samples were investigated for their major ion chemistry, water stable isotope composition ( $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ ) and isotope composition of dissolved inorganic carbon ( $\delta^{13}\text{C}_{\text{DIC}}$ ). From major ion chemistry  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  were the dominant cations and were balanced mostly by bicarbonate. All collected spring water samples scattered around the local meteoric water line with values from -31.9‰ to -46.8‰ for  $\delta^2\text{H}$  and from -5.5‰ to -7.4‰ for  $\delta^{18}\text{O}$  against VSMOW. This indicates local groundwater recharge pathways by regional precipitation rather than water from deeper aquifer systems. Concentrations of dissolved inorganic carbon (DIC) ranged from 0.91 to 9.38 mM/L and  $\delta^{13}\text{C}_{\text{DIC}}$  ranged from -22‰ to -14‰ against VPDB with an average of -16‰. Samples of spring water from carbonate rocks had increased DIC and  $\delta^{13}\text{C}_{\text{DIC}}$  together with elevated pH values. Combined  $\delta^{13}\text{C}_{\text{DIC}}$  and  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  contents suggest that groundwater evolution was dominated by dissolution of dolomitic marble. This unexpected weathering process was favored by intense rain and high ambient temperatures and excessive  $\text{CO}_2$  production in tropical soils. The intense weathering resulted in karst structures with high hydraulic conductivities that rendered the terrain tectonically less stable.

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**P16****Oxygen isotope fractionation in double carbonates**Y.- F. Zheng<sup>1</sup>, M. E. Böttcher<sup>2</sup><sup>1</sup>CAS Key Laboratory of Crust–Mantle Materials and Environments, School of Earth and Space Sciences, University of Science and Technology of China, Hefei, China<sup>2</sup>Leibniz IOW, Geochemie & Isotopenbiogeochemie, Warnemünde, Deutschland

Oxygen isotope fractionations in double carbonates of different crystal structures were calculated by the increment method (Zheng, 1999; Zheng & Böttcher, 2014). Synthesis experiments were performed at 60 °C and 100 °C to determine oxygen and carbon isotope fractionations involving  $\text{PbMg}[\text{CO}_3]_2$ . The calculations reveal that the double carbonates of calcite structure are systematically enriched in  $^{18}\text{O}$  relative to those of aragonite and mixture structures. Internally consistent oxygen isotope fractionation factors are obtained for these minerals with respect to quartz, calcite and water at a temperature range of 0 - 1200 °C. The calculated fractionation factors for double carbonate-water systems are generally consistent with the data available from laboratory experiments. The experimentally determined fractionation factors for  $\text{PbMg}[\text{CO}_3]_2$ ,  $\text{BaMg}[\text{CO}_3]_2$  and  $\text{CaMg}[\text{CO}_3]_2$  against water fall between fractionation factors involving pure carbonate end-members and are close to the calculated fractionation factors.

Experimentally determined carbon isotope fractionation factors between  $\text{PbMg}[\text{CO}_3]_2$  and carbon dioxide are, in contrast to the oxygen isotope system, much closer to theoretical predictions for the cerussite- $\text{CO}_2$  system than for the magnesite- $\text{CO}_2$  system, similar to the fractionation behavior for  $\text{BaMg}[\text{CO}_3]_2$  (Böttcher, 2000). Therefore, the combined theoretical and experimental results provide insights into the effects of crystal structure and chemical composition on oxygen isotope partitioning in double carbonates over a wide range of environmental conditions.

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**P17****The stable isotope hydrogeochemistry of ground waters in Mecklenburg-Western Pommerania**

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In 2014, ground waters of Mecklenburg-Western Pommerania were sampled within the LUNG observational net work and characterized for their hydrogeochemical and stable isotope compositions. The isotopic compositions of hydrogen and oxygen (water), and carbon (dissolved inorganic carbon, DIC) and the contents of major and trace elements were followed to derive water source characterization and quantitative estimates for element sources and sinks of relevance for subterranean water-rock interactions and potential anthropogenic impacts. In addition, the local meteoric water line for precipitation in Warnemünde (southern Baltic Sea coastline) is developed based on precipitation samples collected in the years 2013 to 2015. H and O isotope measurements were carried out using a Picarro L2140-I CRDS-system, and the carbon isotope composition of DIC by means of a Thermo Gas Bench II coupled to a Thermo Finnigan MAT 253 gas mass spectrometer via a Thermo ConFlo IV interface. Results are given in the usual  $\delta$ -notation against international standards. In addition, selected rain water samples were analyzed for the hydrochemical composition using ICP-OES/MS (Thermo iCAP 6300 Duo, Element II). The characterization of the dissolved carbon system allows for an identification of biogenic and geogenic DIC sources like soil carbon dioxide and carbonate rocks, as well as anthropogenic sources like decomposed DOC and even methane. At selected sites, the sulfur isotope composition of dissolved sulfate helped to clearly identify the impact of pyrite oxidation on the ground water composition. These latter measurements will be extended to the whole set of ground water samples in the near future.



**P18****Multi-isotope composition of fresh water sources for the North-German coast**

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The hydrological cycle is reflected by specific water isotope signatures found in precipitation, surface, and ground waters. Since fresh waters of different generation and ages may enter the coastal areas it is expected that they carry characteristic stable isotope signatures. Information about the specific composition of different fresh water sources allows for a use in mixing models for the origin of coastal waters and the deduction of benthic-pelagic coupling. Traditionally, investigations focused on the abundance of the isotopes H-1, H-2, O-16, and O-18. With the development of new analytical methods, also the O-17 isotope came into the focus of interest.

We investigate the multi-isotope composition of different sources for fresh waters at sites with relevance for the North German coastal areas (precipitation, rivers, fresh water inlets, coastal beach springs, fresh waters in and emerging from coastal marine sediments (SGD)). The composition of precipitation (rain, snow) at locations in Northern Germany (Warnemünde, Oldenburg (Oldb.), Lüneburg) and the Netherlands (Texel Island) is analyzed to derive local meteoric water lines in order to compare the measurements with the GNIP station in Cuxhaven (NW-Germany) and the GMWL. Selected precipitation events were resolved in enhanced time resolution. Isotope measurements were conducted by means of a Picarro CRDS system (L2140-i) giving results in the usual delta-notation versus V-SMOW, and informations about H-2 and O-17 excess. Results are compared to continuous measurements at the GNIP station in Cuxhaven (NW-Germany) and the GMWL. Stable isotope results are further complemented by selected hydrogeochemical analyses (major and trace elements, nutrients).

**P19****The stable water isotope composition of surface waters from European marginal seas (Baltic, Black, Mediterranean, North Seas)**

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The hydrological cycle in different climate zones is reflected by specific water isotope signatures. Traditionally, investigations focused on the fractionation of the isotopes H-1, H-2, O-16, and O-18. With the development of new analytical methods, also the consideration of the O-17 isotope went into the focus of interest. Stable isotope measurements were conducted by means of a Picarro cavity ring down spectrometer (CRDS) system (L2140-i) giving results in the usual delta-notation versus V-SMOW, and H-2 and O-17 excess values are derived. The impact of salt contents on stable isotope measurements was investigated for stable H and O isotopes.

The multi-isotope fractionation in sea surface waters of marginal seas from different climate zones of the European continent (Baltic Sea, Black Sea, Mediterranean Sea, North Sea) show the relationships between different climate-impacted modern hydrological cycles and the resulting isotope signatures. Results are compared to continuous measurements at relevant GNIP stations and the GMWL. It is found that the slopes between normalized O-17 and H-2 contents as well as H-2 and O-17 excess values differ for the investigated aquatic systems.

**P20****The application of  $\delta^{34}\text{S}$ ,  $\delta^{13}\text{C}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  to differentiate water resources in the western Dead Sea multi-aquifer system**

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The complex structural and geological inventory of the multi-aquifer system, building up the western Dead Sea flank, leads to hydraulic interactions between single aquifers and to highly uncertainties in respect to flow-directions, residence times and recharge areas. Reaching the Graben, the eastwards dipping Upper Cretaceous carbonatic aquifers are truncated by the main Jordan fault and discharge either directly through springs or recharge the massive Quaternary Graben filling: consisting of coarse sediments, arenites and calcareous silt; intercalated by layers of anhydrite/gypsum, chalk and sandstone. However, brines, hosted in the Graben filling, act as antagonistic fluid bodies.

By investigating their isotopic composition, we aim to outline the evolvement of the fresh groundwater resources, which are the vital backbone of the area and their interaction with brines and evaporitic minerals.

In the groundwater,  $\delta^{34}\text{S}$  composition and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios, which are the consequence of water/rock interactions within the hosting strata, allow the differentiation between both groundwaters of the Upper Cretaceous formations, but also indicate occurring influences of brines. Groundwaters from the Quaternary aquifer do show distinct different isotopic compositions in respect to sulphur, but less in respect to  $\delta^{13}\text{C}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$ .

The higher  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in the Upper Judea Group aquifer ( $>0.7081$ ) refer to a stronger influence of rainwater signatures, which may be preserved due to short residence times. Contrastingly, the lower Cretaceous aquifer contains significantly lower  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios ( $<0.7079$ ), tending to the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the aquifer matrix. Since characteristics of recharge areas are similar in respect to  $\delta^{13}\text{C}$  signatures, the variability of the latter in Upper Cretaceous groundwaters arise from variable dissolution rates (karstification) in the limestone aquifers. Fresh to brackish groundwaters emerging through springs along the Dead Sea shore refer to the Lower Judea Group aquifer as major contributor.

Wells, drilled into the Cretaceous rocks, close to the Graben show influences by Graben brines, probably due to overuse and subsequent depression cones in the water table.

**P21****Can changes in the natural isotopic composition of N-Nitrosodimethylamine provide new insights into its formation pathway?**

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Proposing mitigation strategies for disinfection by-products such as *N*-nitrosodimethylamine (NDMA) generated during chlor(am)ination or ozonation requires a detailed understanding of its formation mechanisms and the identification of precursor materials. We explored the use of compound-specific isotope analysis (CSIA) to identify reactive NDMA precursors and to delineate different formation pathways based on the natural abundance stable isotope ratios of NDMA. Changes of <sup>13</sup>C/<sup>12</sup>C, <sup>2</sup>H/<sup>1</sup>H, and <sup>15</sup>N/<sup>14</sup>N ratios of NDMA during its formation can (1) be characteristic for reactive moieties in the precursor materials and (2) convey information about the NDMA formation mechanism.

We investigated NDMA formation during chloramination of tertiary amines, namely ranitidine, 5-dimethylamino-methyl-furfuryl alcohol, and *N,N*-dimethylthiophene-2-methylamine, which are all known to produce NDMA with yields of 75 - 100%. Reactions of precursor materials were accompanied by N isotope fractionation that could originate from the addition of the disinfectant as well as H<sup>+</sup> exchange reactions. Changes in C isotope ratios were less pronounced and do not imply disinfectant attack at any of the C atoms.

Regardless of the precursor, C and H isotope ratios of NDMA remained constant during its formation, providing evidence that the N(CH<sub>3</sub>)<sub>2</sub>-moiety remains intact during its transfer from the precursor compound to NDMA. In contrast, NDMA was enriched with <sup>15</sup>N over the time course of the reaction - a trend that was similar for all precursors. N isotope fractionation suggests that NDMA formation from chloramination of the selected class of precursors occurs via the same reaction mechanism. The last irreversible step leading to NDMA exhibits a <sup>15</sup>N kinetic isotope effect of 1.02 to 1.03 and is either a N-O bond formation during dissolved oxygen incorporation or the cleavage of a bond to N during the elimination of NDMA from reactive intermediates.

Our study provides first evidence that changes in the natural isotopic composition of NDMA can be used as proxies for its formation pathways during water disinfection and warrants further isotopic analyses of NDMA formation with other disinfectants and precursors.

**P22****Tracking biotransformation of hexachlorocyclohexane isomers by compound-specific isotope analysis**

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Hexachlorocyclohexanes (HCHs) are frequently used in agriculture and medicine due to the pesticidal activity of the  $\gamma$ -isomer. The persistence of HCH led to their frequent detection as diffuse pollution in the environment and as point sources at abandoned production and dumpsites. To date, production and use of HCHs is prohibited in many countries and the  $\alpha$ -,  $\beta$ - and  $\gamma$ -isomers are listed as persistent organic pollutants in the Stockholm Convention. Remediation strategies rely on the biodegradation of HCH isomers under oxic conditions, which is initiated through a sequence of substitution and elimination reactions to chlorohydroquinones which are further metabolized via maleylacetate in the citric acid cycle. In this work, we explore the use of compound-specific isotope analysis (CSIA) for assessing the extent and pathway of HCH biodegradation. As has been shown in studies with nitroaromatic compounds and fuel constituents such as methyl tert-butyl ether (MTBE) CSIA can give insight on the different predominant reaction mechanisms. To quantify the C- and Cl-kinetic isotope effects of HCH biodegradation by substitution and elimination reactions, we use experimental systems with purified LinA and B enzymes, originating from *Sphingobium japonicum* UT26 and *Sphingobium indicum* B90A respectively. LinA and B are produced in our laboratory using arabinose and isopropyl  $\beta$ -D-1-thiogalactopyranoside inducible expression systems in *E. coli* BL21 and are then purified via fast protein liquid chromatography (FPLC). Concentration and isotope signatures of HCH and reaction products are measured in GC/MS and in GC/IRMS systems respectively.

First experiments with LinA2 and  $\gamma$ -HCH show that even at low turnover, C-isotope fractionation can be detected in substrate and product. Next steps include determining the fractionation at higher turnover rates. Current work focuses on adapting and improving the experimental setup for model systems, in order to quantify leaving group chloride leaving group isotope effects.

**P23****Controls of the pelagic dissolved carbon system in a temperate tidal basin: A long-term hydrochemical and stable carbon isotope study**

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Results are presented of a 5-years continuous study on the weekly dynamics in pelagic hydrochemistry and the dissolved inorganic carbon (DIC) system of a tidal basin in the German Wadden Sea, the Sylt-Rømø basin, North Sea.

It was the purpose of this study to investigate seasonal variations and long-term cycles of the pelagic dissolved carbon system under varying magnitudes of biological and physical impacts. The coupling of the concentration with the stable carbon isotope composition of DIC are shown to be a very effective tool to follow and analyze the sinks, sources and internal transformations responsible for temporal variations in the pelagic carbonate system of the coastal waters, that are under impact of mixing processes with fresh water, benthic-pelagic and pelagic-atmosphere coupling, and in-situ transformations. Due to climate-induced changes of the atmospheric carbon dioxide concentration and further changes in hydrological and biogeochemical land-ocean-interaction.

Besides continuous weekly measurements in the Sylt-Rømø Basin the temporal and spatial scale of high-resolution tide cycles and transects through the basin are reported. Salinity, temperature and pH were immediately measured during the field cruises. Furthermore, water samples were sampled for stable isotope ( $\delta^{13}\text{C}(\text{DIC})$ ) and elemental (e.g., major and trace elements, nutrients, alkalinity, DIC) composition.

The observations on the different scales clearly demonstrate the influence of biological and physical impacts on the mixing behaviour with fresh waters and processes of reduced-carbon formation and re-oxidation.

**P24****Two water worlds? The use of  $^{18}\text{O}$  and  $^2\text{H}$  to trace water sources through vegetation and stream flow and partition evapotranspiration fluxes**

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Recent isotopic evidence has shown that streams and vegetation appear to return different pools of water to the hydrosphere. Moreover, from a vegetation perspective separating water fluxes into transpirational fluxes driving biomass production and unproductive evaporative loss is a major concern in understanding response of agricultural and natural vegetation to future changes in water availability. We explore the potential to use  $^{18}\text{O}$  and  $^2\text{H}$ -isotopes to trace the water flow in ecosystems and partition evaporation from transpirational fluxes.

**P25****Element fluxes across the sediment-water interface and mixing processes in surface sediments of the Baltic Sea**

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Organic matter is mineralized in brackish marine sediments by microbial activity using different electron acceptors. Porewater profiles sensitively reflect the zones of dominant biogeochemical processes, net transformation rates and fluxes of dissolved species across the sediment-water interface. They are controlled by different factors like microbial activity, bottom water redox conditions, and availability of electron acceptors/donors. Microbial activity in the sediment leads to changes in redox conditions, formation of metabolites and may lead to the formation of authigenic minerals. For example, organic matter mineralization and reduction of FeOOH may lead to the release of phosphate into the bottom waters. Hypoxic bottom water conditions may enhance this process. We present the results of a detailed biogeochemical investigation of interstitial waters from modern surface sediments to study the biogeochemical processes and associated element fluxes at the sediment-water interface in different areas of the Baltic Sea. Porewater and sediment samples were retrieved from short sediment cores that were collected with multi-coring devices in key regions of the Baltic Sea. Porewaters were taken in sufficient depth resolution and analyzed for metals, nutrients and metabolites concentrations (e.g., Mn, SO<sub>4</sub>, HS, PO<sub>4</sub>,  $\delta^{13}\text{C}$ ) to allow a modeling of steady-state transformation volumetric transformation rates and element fluxes. Element fluxes across the sediment-water interface depend from bottom water redox conditions, sedimentology, organic contents, and formation conditions. Advective fluxes induced by sedimentation events, macro zoobenthos and waves can affect the top sections of the sediment, thereby modifying shallow concentration gradients. Carrying out (non)steady state modelling of pore waters we were able to identify the impact of mixing processes and sedimentation events. In particular, the carbon isotope composition of DIC is found to be a highly sensitive tool for model parameterization, including the estimation of effective diffusion coefficients.

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**P26****Stable Isotope Signatures of Groundwaters from the Biyadh Aquifer, Saudi Arabia**

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The Biyadh Sandstone (Early to Middle Cretaceous) represents an important aquifer in Central Saudi Arabia. In the present study, water samples from this aquifer were analyzed for their stable isotope signatures ( $^{18}\text{O}$  and  $^2\text{H}$ ), aiming at a characterization of the (paleo)climatic conditions during recharge. Moreover, isotope data from unpublished consulting reports were considered.

The obtained  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values range from about -8 to -2 ‰ V-SMOW and from about -62 to -3 ‰ V-SMOW, respectively. These depleted signatures do not match well with the isotopic composition of rain in Riyadh (Michelsen et al., in press), i.e., most groundwaters are isotopically lighter than current precipitation and plot below the Local Meteoric Water Line in the  $\delta^2\text{H}$  vs.  $\delta^{18}\text{O}$  scatter plot. Moreover, a clear spatial trend is noteworthy -  $\delta$  values decrease along the flow paths.

Based on these findings, it can be stated that the bulk of the Biyadh water was replenished under more humid conditions thousands or even tens of thousands of years ago. Yet, less depleted signatures of unconfined groundwaters in the outcrop areas suggest that limited recharge takes place even under the currently arid climatic conditions. This replenishment, however, seems to be restricted to recharge-favoring settings like wadis, in which surface runoff is accumulated.

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**P27****The fate of sulfur and implications for methane emissions in a rewetted brackish peatland**

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The natural abundance of stable isotopes in ecosystem studies indicates origin and fate of matters as well as the underlying biogeochemical processes. We use concentration patterns and stable isotope signatures of sulfate, dissolved carbonate, methane and water ( $\delta^{34}\text{S}$ ,  $\delta^2\text{H}$ ,  $\delta^{18}\text{O}$ ) to investigate the sulfur (S) and carbon (C) metabolic cycle in a degraded, rewetted peatland at the interface between terrestrial and marine. In this specific environment, intermittent brackish water intrusion from the nearby Baltic Sea is supposed to result in intense sulfate cycling and thus, to the suppression of methane emission, despite otherwise favourable conditions for microbial methane production (anaerobic conditions and high abundance of labile C sources). However, 7 years of greenhouse gas emission and groundwater monitoring revealed the peatland to act as a massive methane source (e. g. up to  $3.4 \text{ t CH}_4 \text{ ha}^{-1} \text{ a}^{-1}$  in 2010) despite of high sulfate concentrations (up to 37 mM). To resolve this seeming contradiction, we conducted a comprehensive biogeochemical survey that comprises 4 pore water and peat profiles within a transect of 300-1500 m distance to the Baltic Sea.

High pore water chloride concentrations (up to 93 mM) still reveal a distinct marine impact, indeed. Yet, sulfate derived from the Baltic Sea is almost completely depleted in most profiles and depths. The remaining sulfate pool is remarkably enriched in  $^{34}\text{S}$  (up to +86.4‰) in comparison to Baltic Sea sulfate (+21‰). Also  $\delta^{34}\text{S}$ -CRS (chromium reducible sulfur, i. e. S finally precipitated as pyrite,  $\text{FeS}_2$ ) was comparably high and decreased from the top (~+10‰) to the bottom (-2‰). High  $^{34}\text{S}$  fractionation indicates intense anaerobic S cycling, probably associated with thiosulfate disproportionation. Under the high abundance of ferrous iron, sulfides are finally stably bond as pyrite, the depth profile of which reflects former non-steady-state conditions. However, one pore water profile situated 1150 m from the Baltic Sea coast line exhibited a completely different pattern. Here, significant excess of sulfate relative to the Baltic Sea water (up to 32.8 mM) and a comparatively low  $\delta^{34}\text{S}$  value (+22.7‰) indicate local processes such as pyrite oxidation from former peatland drainage to supply additional sulfate of epigenetic origin.

After intense anaerobic S cycling under non-steady-state conditions most of the S derived from the Baltic Sea was stably precipitated as pyrite. Locally high sulfate concentrations were relics of former land use change rather than of marine origin. However, even such local sulfate hotspots were situated in > 30 cm depth and did not affect efficient methane production in the upper peat layers. Correspondingly, thermodynamically favorable conditions for methanogenesis were confirmed by  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$  values of methane (-68 to -57‰ and -133 to -157‰, respectively). Thus, due to a rapid depletion of the sulfate pool, degraded, coastal peatlands can act as strong sources for methane.

**P28****A  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  biomarker transect study from Central to Northern Europe**

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The isotopic composition of precipitation ( $\text{d}^2\text{H}_{\text{prec}}$  and  $\text{d}^{18}\text{O}_{\text{prec}}$ ) is mainly driven by climatic factors. Therefore compound specific isotope  $\text{d}^2\text{H}$  and  $\text{d}^{18}\text{O}$  analyses of biomarkers are a useful tool for establishing high informative climate records. However, by using an single isotope approach it is often challenging to distinguish between the precipitation and the evapo(transpi)rative enrichment signal incorporated in biomarkers. To overcome this limitation a coupled  $\text{d}^{18}\text{O}_{\text{sugar}}\text{-d}^2\text{H}_{n\text{-alkane}}$  model was suggested by Zech et al. (2013). This coupled biomarker approach has been shown to have the potential to reconstruct day-time relative humidity during the vegetation period as well as the isotopic composition of precipitation more robust compared to single isotope studies (Tuthorn et al., 2015). In order to validate the coupled biomarker approach for an application on European climate archives we analyse 29 topsoil samples from a climate transect spanning from Southern Sweden to Southern Germany. Mean annual temperature ranges from 5 to 11°C and mean annual precipitation ranges from ~ 500 to 1700 mm. At each of the 16 sampling locations we tried to get samples from three different main vegetation types, namely coniferous forests, deciduous forests and grasslands. The isotopic signature incorporated in the biomarkers shows, in contrast to *n*-alkane and *n*-alkanoic acids pattern (Lanny et al., submitted to Organic Geochemistry), a distinct climate-caused West-East trend. However, they do not solely reflect the isotopic composition of precipitation due to leaf water isotopic enrichment caused by evapotranspiration. Therefore we suggest that the coupled biomarker approach could provide new insights into relative humidity and temperature history of Central and North Europe.

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**P29****Compound-specific leaf-wax  $\delta D$  analyses in the loess-paleosol sequence Krems-Wachtberg, Austria**

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Loess-paleosol sequences (LPS) are prominent terrestrial paleoenvironmental archives, containing information about ecological and climatic changes throughout the Quaternary. The LPS Krems-Wachtberg is located at the climatic transition from oceanic influences to the west and increasingly continental climate in Eastern Europe (mean annual precipitation  $\sim 500$  mm, mean annual temperature =  $9.4^{\circ}\text{C}$ ). The sequence comprises  $\sim 8$  m thick Upper Pleistocene loess and documents paleoenvironmental and paleoclimatic fluctuations between 20 and 40 ka BP, i.e. the transition from marine isotope stage (MIS) 3 to MIS 2. We analysed 71 samples from Krems-Wachtberg to establish a detailed leaf-wax and compound-specific  $\delta D$  record. n-Alkanes are well preserved and show a dominance of C31, indicating that grass vegetation was likely a more important source than deciduous tree for the whole time. The compound-specific  $\delta D$  values (concentration-weighted mean of C29 and C31) range from  $-221.9$  to  $-148.0$  ‰ vs. V-SMOW.  $\delta D$  n-C29 ranges from  $-215.7$  to  $-156.5$  ‰ and  $\delta D$  n-C31 ranges from  $-225.8$  to  $-143.4$  ‰. Both  $\delta D$  n-C29 and  $\delta D$  n-C31 follow mostly the same pattern throughout the sequence ( $r^2 = 0.59$ ). However, we observed not negligible differences between  $\delta D$  n-C29 and  $\delta D$  n-C31 where in comparison  $\delta D$  n-C31, in the majority of cases, gives a rather depleted D-signal.

The observed long-term trend towards more enriched values resembles the NGRIP 18O data from Greenland and records changes in the isotopic composition of the precipitation (source and temperature effects). However, our record also shows a stepwise increase at  $\sim 32$  ka BP, which might document more evapotranspirative enrichment of leaf water and more arid conditions towards the Last Glacial Maximum. The high-frequency variability in our record might reflect the characteristic pattern of the Greenland Interstadials, but current uncertainties in age control prevent robust correlations.

Ongoing work focusses on compound-specific radiocarbon dating to establish a more robust age-depth model for Krems-Wachtberg.

**P30****Optimizing the sampling strategy for carbon and oxygen isotope analysis of an annually laminated stalagmite from Zoolithencave (Bavaria, Germany)**

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The speleothem Zoo-rez-1 from Zoolithencave (Bavaria, Germany) grew from 1800 to 1970 AD and shows visible, elemental and fluorescent laminae (Riechelmann et al., in prep.). These laminae have been shown to be annual, which provides the opportunity to reconstruct past climate variability at annual resolution. Such high-resolution records are of great importance for reconstructing Holocene climate variability and, in particular, short-term extreme events. The classical climate proxies obtained from speleothems are stable carbon and oxygen isotope values ( $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ ).

We have analysed the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of Zoo-rez-1 at annual resolution by CF-IRMS (MAT 253 ThermoFinnigan). To optimize the sampling strategy, two different approaches have been tested. Firstly, one stable isotope sample track has been micro-milled at a constant resolution of 50  $\mu\text{m}$ . For a second track, the sampling resolution has been adjusted to the thickness of the individual visible laminae. The results of the two approaches have then been compared to each other to determine the best sampling strategy.

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**P31*****Fucus vesiculosus* as proxy for climate change induced impacts on North Sea coastal waters**

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Benthic mesocosm experiments were conducted in coastal waters of the eastern North Sea to test *Fucus vesiculosus* under in-situ experimental conditions for its potential as biogeochemical mirror for environmental stress. The aim of the experiments was to calibrate the influence of separate and combined effects of different stress factors like acidification, warming, and eutrophication on the elemental and stable isotope composition of *Fucus vesiculosus*. Natural coastal waters were used that, after a presaturation in a tank, was used to feed the experiments. The experimental set-up allowed for a simulation of tidal changes in water height.

Benthocosm experiments established close to intertidal flats at the Wadden Sea station of the AWI in List (Sylt) with an individual duration of up to three months per season. During a spring experiment, stressors like a rise in atmospheric CO<sub>2</sub> or temperature was fully crossed. In the summer and autumn experiments a parallel combination of temperature and CO<sub>2</sub> was combined with and without elevated nutrient concentration. Basic parameters (salinity, temperature, pH, carbon dioxide partial pressure) were continuously monitored, and aqueous solutions were sampled for a complete hydrochemical and stable isotope analysis on a base. Additionally high-resolution daily cycles were carried out. The elemental (CNSP) and stable isotope (CNS) composition of newly grown organic tissue of *Fucus vesiculosus* was collected at the end of the experiments.

The seasonal changes in the aquatic chemistry of the mesocosms were strongly superimposed by biological activity (photosynthesis, respiration). This was in particular demonstrated by the impact of light during the 24h-campaigns, where the alternating phases of net respiration and photosynthesis were creating strong variations in the dissolved carbonate system and significant changes in the carbon isotope composition of DIC. That allow for a calibration of the fractionation factor for distinct system responses to the applied stress factors. The organic tissue of *Fucus vesiculosus* reflected seasonal changes in the C, N, S contents and the stable isotope composition.

## P32

**Annual temperatures of cold and temperate regions derived from stable hydrogen isotope values of wood lignin methoxyl groups**

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Stable hydrogen isotope ratios of plant methoxyl groups ( $\delta^2\text{H}_{\text{methoxyl}}$ ) have been shown to reflect the  $\delta^2\text{H}$  values of the plant's source water (1, 2). These isotopic signatures can be used for a variety of applications such as constraining the geographical origin and authenticity of biomaterials (3, 4). Furthermore, it is known that  $\delta^2\text{H}$  values of precipitation ( $\delta^2\text{H}_{\text{precipitation}}$ ) in temperate and cold regions are primarily controlled by climate parameters such as temperature. A recent tree-ring study measuring  $\delta^2\text{H}_{\text{methoxyl}}$  values of *Pinus sylvestris* showed high correlations with temperatures and was also correlated with ring width, indicating its potential as a temperature proxy (5).

Here, we evaluate  $\delta^2\text{H}_{\text{methoxyl}}$  values of tree rings from various species collected in cold and temperate regions and compare them with their mean annual  $\delta^2\text{H}$  values of precipitation. A high correlation was observed between the  $\delta^2\text{H}$  values of the methoxyl groups and the weighed mean annual  $\delta^2\text{H}_{\text{precipitation}}$  values with a relatively uniform fractionation. We also evaluated the relationship between  $\delta^2\text{H}_{\text{methoxyl}}$ ,  $\delta^2\text{H}_{\text{precipitation}}$  and mean annual temperature. Our investigations might allow us to calculate mean annual temperatures of trees that were grown in cold and temperate regions based on the  $\delta^2\text{H}$  values of their methoxyl groups. These results indicate that measurements of the stable hydrogen isotope composition of tree ring methoxyl groups have a huge potential to be applied as a temperature proxy on paleoclimate archives of the Holocene.

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**P33****Effects of reduced energy-intake on  $^{13}\text{C}/^{12}\text{C}$  ratios of urinary steroids - a case study**

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In sports drug testing analysis  $^{13}\text{C}/^{12}\text{C}$  ratio analysis is the method of choice to discriminate between an endogenous or possible synthetic origin of androgenic anabolic steroids. Several physiological factors are known which may take effect on  $^{13}\text{C}/^{12}\text{C}$  ratios of urinary steroids. E.g., the variation of diet, the intake of hormonal contraceptives and pregnancy. In spite of its potential relevance, there is little knowledge concerning the possible influence of energy restriction on  $^{13}\text{C}/^{12}\text{C}$  ratios of endogenous steroids.

It has been shown before, though that food deprivation results in a suppression of cholesterol biosynthesis. Cholesterol is the obligate precursor of steroid hormones in humans. At the same time the key reaction of cholesterol biosynthesis seems to cause fractionation of the carbon isotopes. Therefore effects of fasting on the  $^{13}\text{C}/^{12}\text{C}$  ratios of urinary steroids can be postulated.

In order to investigate the possible influence of energy restriction on the  $^{13}\text{C}/^{12}\text{C}$  ratios of urinary steroids, urine specimens supplied by a female volunteer during a seven day fasting period were analyzed.

$^{13}\text{C}/^{12}\text{C}$  analysis showed a depletion in  $^{13}\text{C}$  in some steroids. Also changes in  $\Delta\delta^{13}\text{C}$  values were observed. In addition, correlations between steroid  $^{13}\text{C}/^{12}\text{C}$  ratios and  $^{13}\text{C}/^{12}\text{C}$  ratios of total urinary carbon were observed.



**P34****Isotopic composition of polyhalomethanes from marine macrophytes -Systematic effects of the halogen substituents on the isotopic composition**

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Halocarbons are important vectors of reactive halogens to the atmosphere, where the latter participate in several chemical key processes. An improved understanding of the biogeochemical controls of the production - destruction equilibrium on halocarbons is of vital importance to address potential future changes in their fluxes to the atmosphere. Carbon stable isotope ratios of halocarbons could provide valuable additional information on their sources and fate that cannot be derived from mixing ratios alone. We have determined the  $\delta^{13}\text{C}$  values of 13 polyhalomethanes (PHMs) from three brown algae species (*Laminaria digitata*, *Fucus vesiculosus*, *Fucus serratus*) and one seagrass species (*Zostera noltii*). The  $\delta^{13}\text{C}$  values were determined in laboratory incubations under variable environmental conditions such as light, water levels (to simulate tidal events) and addition of hydrogenperoxide ( $\text{H}_2\text{O}_2$ ). The  $\delta^{13}\text{C}$  values of the PHMs ranged from  $-42.2 \pm 3.5\text{‰}$  for  $\text{CHCl}_3$  to  $6.9 \pm 4.5\text{‰}$  for  $\text{CHI}_2\text{Br}$ . Though variable, the isotopic composition of PHMs may provide useful additional information to discriminate marine PHM sources.

Our data revealed a systematic effect of the halogen substituents that could empirically be described in terms of linear free energy relationships (LFER) using Tafts parameter. We further observed enrichment in the  $\delta^{13}\text{C}$  of the PHMs with decreasing PHM yield. We attributed both trends to the PHM yields in relation to competing halogenated products such as halogenated ketones and suggest LFER as a powerful tool to investigate isotope effects in complex reactions.

**P35****Using position-specific  $^{13}\text{C}$  and  $^{14}\text{C}$  labeling and  $^{13}\text{C}$ -PLFA analysis to assess microbial transformations of free versus sorbed Alanine**

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Sorption of charged or partially charged low molecular weight organic substances (LMWOS) to soil mineral surfaces delays microbial uptake and therefore mineralization of LMWOS to  $\text{CO}_2$ , as well as all other biochemical transformations. We used position-specific labeling, a tool of isotope applications novel to soil sciences, to compare the transformation mechanisms of sorbed and non-sorbed Alanine in soil. Alanine as an amino acid links C- and N-cycles in soil and therefore is a model representative for the pool of LMWOS.

To assess transformations of sorbed Alanine, we combined position-specific and uniformly  $^{13}\text{C}$  and  $^{14}\text{C}$  labeled Alanine tracer to soil that had previously been sterilized by  $\gamma$ -radiation. All non-sorbed Alanine was removed by shaking with millipore water. The labeled soil was added to non-sterilized soil from the same site and incubated. Soil labeled with the same tracers without previous sorption was prepared and incubated as well. We captured the respired  $\text{CO}_2$  and determined its  $^{14}\text{C}$ -activity at increasing time steps. The incorporation of  $^{14}\text{C}$  into microbial biomass was determined by CFE, and utilization of individual C positions by distinct microbial groups was evaluated by  $^{13}\text{C}$ -PLFA analysis.

A dual peak in the respired  $\text{CO}_2$  revealed the influence of two sorption mechanisms. Microbial uptake and transformation of the sorbed Alanine was 3 times slower compared to non-sorbed Alanine. To compare the fate of individual C atoms independent of their concentration and pool size in soil, we introduced the divergence index (DI). The DI reveals the convergent or divergent behavior of C from individual molecule positions during microbial utilization. Alanines C-1 position was mainly oxidized to  $\text{CO}_2$ , while its C-2 and C-3 were preferentially incorporated in microbial biomass and PLFAs. This indicates that sorption by the COOH group does not protect this group from preferential oxidation. Microbial metabolism is determinative for the preferential oxidation of individual molecule positions. Uptake into the PLFA of gram negatives was highest for both the sorbed and non-sorbed treatment, showing that this group is not only highly competitive regarding the uptake of free LMWOS (like root exudates) but are also able to desorb and utilize sorbed LMWOS.

The use of position-specific labeling revealed mechanisms and kinetics of microbial utilization of sorbed and non-sorbed Alanine, as well as interactions between microbial groups, soils and LMWOS. None of these findings could have been achieved without the use of position-specific tracers, therefore this method will improve our understanding of stabilization processes and soil C fluxes.

## P36

**Direct photolysis of sulfamethoxazole at different irradiation conditions and the resulting carbon stable isotope fractionation**

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Worldwide, the number of organic micropollutants detected in aquatic environments increased in recent years.<sup>[1]</sup> In that regard one important representative is the sulfonamide antibiotic sulfamethoxazole (SMX). SMX is nowadays widely used in veterinary medicine as preventive measure. Common fields of application are poultry-farming or aquacultures<sup>[1]</sup>. As a result, SMX is frequently detected in related surface or ground waters<sup>[1]</sup>. Moreover, SMX is poorly eliminated in wastewater treatment plants<sup>[1]</sup>. In the aquatic environment microbial- and photo-degradation are main pathways of SMX degradation in the aquatic environment<sup>[1,2]</sup>.

Compound stable isotope analysis (CSIA) can be an important tool to differentiate between pathways of SMX degradation since degradation processes may reveal specific isotopic fractionation. Birkigt et al.<sup>[2]</sup> have shown that degradation of SMX samples by microbial degradation and direct photolysis in a sunlight simulator resulted in different carbon isotope enrichment factors, what allows distinguishing between these degradation pathways by CSIA. However, a detailed investigation of isotopic fractioning of direct SMX photolysis is still missing.

The aim of this study was to determine the carbon stable isotope fractionation of SMX during direct photolysis at different irradiation conditions. For this purpose two different UV-lamp types were chosen, i.e. a low-pressure (LP) lamp (emission of nearly monochromatic UV-radiation at 254 nm) and a medium-pressure (MP) lamp (emission of polychromatic radiation of UV-C, UV-B, UV-A and visible light; radiation below 310 nm was cut off by a filter solution). All samples were irradiated using a merry-go-round type photo-reactor. SMX samples were irradiated at two different pH values to investigate the photolysis of the neutral and the anionic species. The method of Kujawinski et al.<sup>[3]</sup> was applied for LC-IRMS measurements of SMX. No significant isotope fractionation could be observed for both species irradiated with the LP lamp. The calculated carbon isotope enrichment factor for the neutral species directly photolysed using the MP lamp were more pronounced with  $\epsilon = 4,7 \text{ ‰}$  enabling a differentiation between direct photolysis by UV-C which is used in technical systems (e.g., water disinfection) and a combination of UV-B, UV-A, which is predominant in natural sunlight (note that visible light >400 nm does not contribute to the direct photolysis of SMX).

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[2] Birkigt, J., Gilevska, T., Ricken, B., Richnow, H.-H., Vione, D., Corvini, P.F.-X., Nijenhuis, I., Cichocka, D. (2015): *Carbon stable isotope fractionation of sulfamethoxazole during biodegradation by microbacterium sp. strain BR1 and upon direct photolysis*. Environmental Science and Technology, 49 (10), pp. 6029-6036

[3] Kujawinski, D.M., Zhang, L., Schmidt, T.C., Jochmann, M.A. (2012): *When other separation techniques fail: Compound-specific carbon isotope ratio analysis of sulfonamide containing pharmaceuticals by high-temperature- liquid chromatography-isotope ratio mass spectrometry*. Analytical Chemistry, 84 (18), pp. 7656-7663

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