

# ASI 2017

## Jahrestagung der Arbeitsgemeinschaft Stabile Isotope e. V.

9.–11. Oktober 2017

Leibniz Universität Hannover



**Book of Abstracts**

## Kontakt

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der Arbeitsgemeinschaft  
Stabile Isotope e. V.**

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## Herzlich Willkommen zur ASI-Tagung 2017

Wir freuen uns, Sie zu unserer Jahrestagung der Arbeitsgemeinschaft Stabile Isotope e. V., der ASI 2017, begrüßen zu dürfen. Erfahrungsgemäß bietet die Tagung Wissenschaftlerinnen und Wissenschaftlern der verschiedensten Fachgebiete eine ausgezeichnete Plattform neue Trends im Bereich der stabilen Isotope zu erfahren und mit den Kolleginnen und Kollegen auch anderer Fachgebiete in direkten Kontakt zu treten. Natürlich freuen wir uns Ihnen 60 Beiträge in Form von Postern und Vorträgen mit neuen Ideen und neuen Methoden, aber auch neueste Erkenntnisse aus den Fachgebieten bieten zu können und hoffen auf erkenntnisreiche Diskussionen. Dazu befinden sie sich im Leibnizhaus, dem Tagungszentrum der Leibniz Universität Hannover. 1831 von dem Gelehrten Karl Karmarsch gegründet, startete die „Höhere Gewerbeschule zu Hannover“ mit nur 64 Schülern. Heute lernen mehr als 25.000 Studierende in den Natur- und Ingenieurwissenschaften, den Geistes- und Sozialwissenschaften sowie den Rechts- und Wirtschaftswissenschaften an der Leibniz Universität Hannover.

Eine gute und erfolgreiche Zeit in Hannover wünscht das Organisationskomitee

## Komitees

### Organisationskomitee

Andrea Michels  
Georg Guggenberger  
Florian Stange

### Wissenschaftliches Komitee

Prof. Dr. Gerhard Gebauer  
Dr. Matthias Gehre  
Dr. Anette Giesemann  
Prof. Dr. Bruno Glaser  
Prof. Dr. Georg Guggenberger  
Prof. Dr. Frank Keppler  
Dr. Paul Königer  
Dr. Florian Stange  
Dr. Robert van Geldern  
Dr. Reinhard Well  
Prof. Dr. Christiane Werner  
Prof. Dr. Stefan Weyer  
Dr. Michael Zech

## Programmüberblick ASI-Tagung 2017

	Mo 09.10.2017	Di 10.10.2018	Mi 11.10.2019
09:00		Geologie, Hydrologie, Geohydrologie & geochemische Stoffkreisläufe	Ökosysteme und biogeochemische Prozesse II
10:00			Posterkaffee
		Kaffeepause	
11:00		Herkunftskontrolle- Lebensmittel, Forensik, Doping	Ökosysteme und biogeochemische Prozesse III
12:00	Eröffnung ASI2017	Mittagspause	Schlussworte/Preise
13:00	Analytik: Methoden, Techniken und Qualitätssicherung	Ökosysteme und biogeochemische Prozesse	
14:00		ISOTOPEN-Preis	Laborführung
15:00	Posterkaffee		
16:00		Posterkaffee	
	Analytik: Methoden, Techniken und Qualitätssicherung II		
17:00	Physiologie und Metabolismus	ASI-Mitglieder- versammlung	
18:00			
		ab 19:30 Konferenz- dinner im XII-Apostel	

## Programm

**MONTAG — 9.10.2017**

**12:30–13:00** Eröffnung der ASI-Tagung

### **SESSION 1:**

#### **Analytik: Methoden, Techniken und Qualitätssicherung**

Chair: Matthias Gehre

**13:00–13:20**

**ID: 108**

Development Of A Multidimensional Gas Chromatography/ Combustion/ Isotope Ratio Mass Spectrometry Method For The Investigation Of Carbon Isotope Ratios Of Urinary Steroids For Doping Control Purposes

Marlen Putz, Thomas Piper, Schänzer Wilhelm, Thevis Mario

**13:20–13:40**

**ID: 163**

SPIN-MIMS simplifying the SPIN-MAS instrumentation for online measurement of <sup>15</sup>N-abundances of ammonium, nitrite and nitrate in aqueous solutions

Wolfram. Eschenbach, Jens Dyckmans, Dominika Lewicka-Szczebak, Anette Giesemann, C. Florian Stange, Reinhard Well,

**13:40–14:00**

**ID: 110**

Universal chlorine isotope analysis of organic compounds using gas chromatography interfaced with multiple-collector inductively coupled plasma mass spectrometry (GC-MC-ICPMS)

Julian Renpenning, Axel Horst, Matthias Gehre

**14:00–14:20**

**ID: 134**

Chromatography-based EA-IRMS : Redesigning the combustion elemental analyzer around modern chromatographic principles

Andreas Hilkert, Christopher Brodie, Oliver Kracht

**14:20–14:40**

ID: 127

JRAS-06: Keeping up with changing internationally-distributed, light-element stable isotopic reference materials

Heiko Moossen, Tyler B. Coplen, Haiping Qi, Michael Rothe, Heike Geilmann, Jürgen Richter, Willi A. Brand

**14:40–16:30**

Posterkafee (Posterrundgang Analytik: Methoden, Techniken und Standardisierung und Physiologie und Metabolismus)

## **SESSION 2:**

### **Analytik: Methoden, Techniken und Qualitätssicherung II**

Chair: Reinhard Well

**16:30–16:50**

ID: 117

A Closer Look Into The Nitrogen Blank In Elemental Analyser/Isotope Ratio Mass Spectrometry measurements

Langel Reinhard, Jens Dyckmans

**16:50–17:10**

ID: 164

An LC-IRMS Interface for Flexible Compound-specific Stable Isotope Analysis

Filip Volders, Christian Schmidt, Sam Barker, Paul Wheeler, Lutz Lange, Hans-Peter Sieper

**17:10–17:30**

ID: 152

Validation of a  $\delta^{2}\text{Hn}$ -alkane- $\delta^{18}\text{O}$ hemicellulose-based paleohyrometer

Johannes Hepp, Imke Schäfer, Mario Tuthorn, Bruno Glaser, Dieter Juchelka, Kazimierz Rozanski, Roland Zech, Christoph Mayr, Michael Zech

**SESSION 3:**  
**Physiologie und Metabolismus**

Chair: Gerhard Gebauer

**17:30–17:50**

**ID: 109**

The Effect of Nitrate and Ammonium Nutrition on Carbon Stable Isotope Fractionation During Plant Respiration

Shiva Ghiasi, Roland Werner, Nina Buchmann, Rolf Siegwolf

**17:50–18:10**

**ID: 135**

Carbon allocation into biogenic volatile organic compounds (BVOCs) and respiratory carbon dioxide (CO<sub>2</sub>) traced by position-specific <sup>13</sup>C-pyruvate-labelling in *Halimium halimifolium* L.: A novel methodological approach for automated, simultaneous and real-time trace gas analysis

Lukas Fasbender, Ana Maria Yáñez-Serrano, Christiane Werner

**DIENSTAG — 10.10.2017**

**SESSION 4:**  
**Geologie, Hydrologie und Geohydrologie und geochemische Stoffkreisläufe**

Chair: Robert van Geldern

**9:00–9:30**

**ID: 157**

Using Mo and U isotope signatures of sediments as paleoredox proxy

Stefan Weyer, Annika Brüske, Nadja Neubert, Olaf Dellwig, Noah Planavki, Timothy Lyons, Ariel Anbar

**9:30–9:50**

**ID: 159**

Tracing complex igneous processes by in-situ analyses of Mg- and Fe isotope ratios in magmatic minerals

Martin Oeser, Max Collinet, Ralf Dohmen, Philipp Ruprecht, Lena K. Steinmann, Stefan Weyer

**9:50–10:10**

ID: 154

Acidic mine tailings and Fe / Cu isotope fractionation: modification and application of a sequential extraction method

Yvonne Roebbert, Katharina Rabe, Marina Lazarov, Axel Schippers, Bernhard Dold, Stefan Weyer

**10:10–10:30**

ID: 153

Iron Enrichment In Soils And Groundwater - The Fe Isotope Signature

Stephan Schuth, Tim Mansfeldt

**10:30–10:50**

ID: 112

Water flow and fate of pesticides in the unsaturated zone - Investigations based on stable water isotopes

Fatemeh Shajari, Florian Einsiedl, Arno Rein

**10:50-11:10** Kaffeepause

**SESSION 5:**

**Herkunfiskontrolle – Lebensmittel, Forensik, Doping**

Chair: Bruno Glaser

**11:10–11:30**

ID: 125

Complementary Use Of  $^1\text{H}$ -NMR And Multi-Element IRMS In Association With Chemometric Methods Enables Effective Origin Analysis Of High Quality Cocoa (Theobroma Cacao L.)

Stefan Bindereif, Jan-Marcel Schubert, Paul Rösch, Stephan Schwarzingler, Gerhard Gebauer

**11:30–11:50**

ID: 106

Same Same, but different! - Decoding the nutrition history of blow flies by EA-IRMS

Victoria Bernhardt, Nicole Scheid, Thomas Holdermann, Thomas Schäfer, Jens Amendt

**11:50–12:10**

ID: 107

Epiandrosterone Sulfate Prolongs The Detectability Of Testosterone, 4-Androstenedione And Dihydrotestosterone Misuse By Means Of Carbon Isotope Ratio Mass Spectrometry

Thomas Piper, Marlen Putz, Wilhelm Schänzer, Mario Thevis

**12:10–13:00** Mittagspause

**SESSION 6:**

**Ökosysteme und biogeochemische Prozesse I**

Chair: Anette Giesemann

**13:00–13:20**

ID: 158

Biotrasformation of Hexachlorocyclohexane during Anaerobic Digestion of Pesticide Contaminated Biomass Tracked by Compound Specific Stable Isotope Analysis

Shujuan Lian, Marcell Nikolausz, Ivonne Nijenhuis, Athaydes Leite, Hans Richnow

**13:20–13:40**

ID: 130

Drought-Induced Anomalies Of Soil Water Stable Isotopes Enable Identification Of Deep Root Water Uptake

Matthias Beyer, Paul Königer, Josefina T. Hamutoko, Thomas Himmelsbach

**13:40–14:00**

ID: 124

Picky Carnivorous Plants: Preferences For Preys' Trophic Levels

Saskia Klink, Gerhard Gebauer

**14:00–14:20**

ID: 128

Stable Isotopes As Flux Tracers: Assessing The Vegetation-Soil-Atmosphere Processes In Grasslands Under Drought Stress

Angelika Kübert, Youri Rothfuss, Maren Dubbert, Christiane Werner

**14:20–15:20** Verleihung des Isotopenpreis und Vortrag

**15:20–17:20** Posterkafee (Posterrundgang Geologie, Hydrologie und Geohydrologie und geochemische Stoffkreisläufe und Herkunftskontrolle)

**Ab 17:30** ASI-Mitgliederversammlung mit Vorstandswahlen

**Ab 19:30** Konferenzdinner im XII-Apostel

## **MITTWOCH — 11.10.2017**

### **SESSION 7:**

#### **Ökosysteme und biogeochemische Prozesse II**

Chair: Georg Guggenberger

#### **9:00–9:20**

ID: 140

Persistence of sugar-derived C in soil is controlled by the initial use of the C positions in the microbial metabolism

Ezekiel Bore, Yakov Kuzyakov, Michaela Dippold

#### **9:20–9:40**

ID: 142

Microbial Food Preference For Sorbed Versus Necromass C: Position-Specific Labeling Tells The Story

Jennifer Herschbach, Carolin Apostel, Sandra Spielvogel, Kuzyakov Yakov, Michaela Dippold

#### **9:40–10:00**

ID: 113

Solvent Stress Induced Changes Of Cell Membrane Fatty Acids Decrease Isotope Fractionation During Microbial Denitrification

Anja Wunderlich, Hermann Heipieper, Martin Elsner, Florian Einsiedl

**10:00–10:20**

ID: 116

Insights in N<sub>2</sub>O processes after grassland break-up by using N<sub>2</sub>O isotopocules

Caroline Buchen, Dominika Lewicka-Szczebak, Heinz Flessa, Reinhard Well

**10:20–11:40** Posterkafee (Posterrundgang Ökosysteme und biogeochemische Prozesse)

## **SESSION 8:**

### **Ökosysteme und biogeochemische Prozesse III**

Chair: Michael Zech

**11:40–12:00**

ID: 114

Two Dimensional Isotope Fingerprint Of Plant Methoxyl Groups – Application To Biogeochemical Research

Frank Keppler, Markus Greule, Tobias Anhäuser, Hanns-Ludwig Schmidt

**12:00–12:20**

ID: 131

The role of biological black carbon production for Chernozem genesis

Bruno Glaser

**12:20–12:40**

ID: 121

Assessment of Stable Isotope Fractionation during Diffusive Transport and Biogeochemical Transformations in the Subsurface

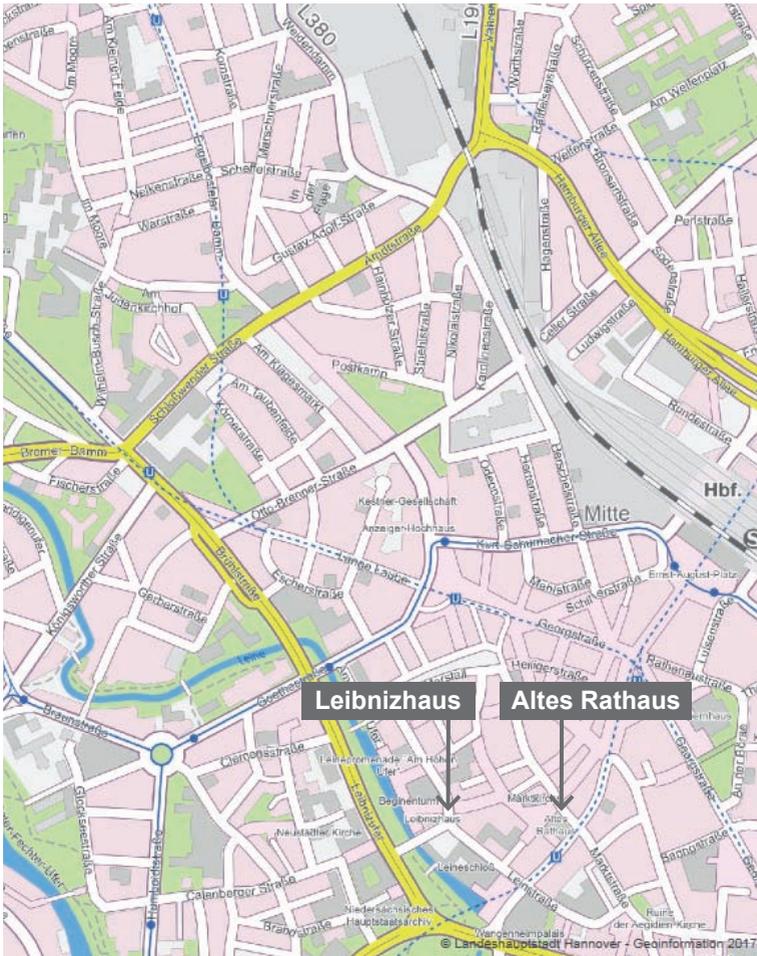
Martin Thullner, Ali M. Khan, Lukas Y. Wick, Susanne Stadler

**12:40–13:00** Schlussworte und ASI-Poster- und Vortrags-Preisverleihung

**Nachmittags:** Laborführung Uni Hannover und/oder BGR

## Tagungsort

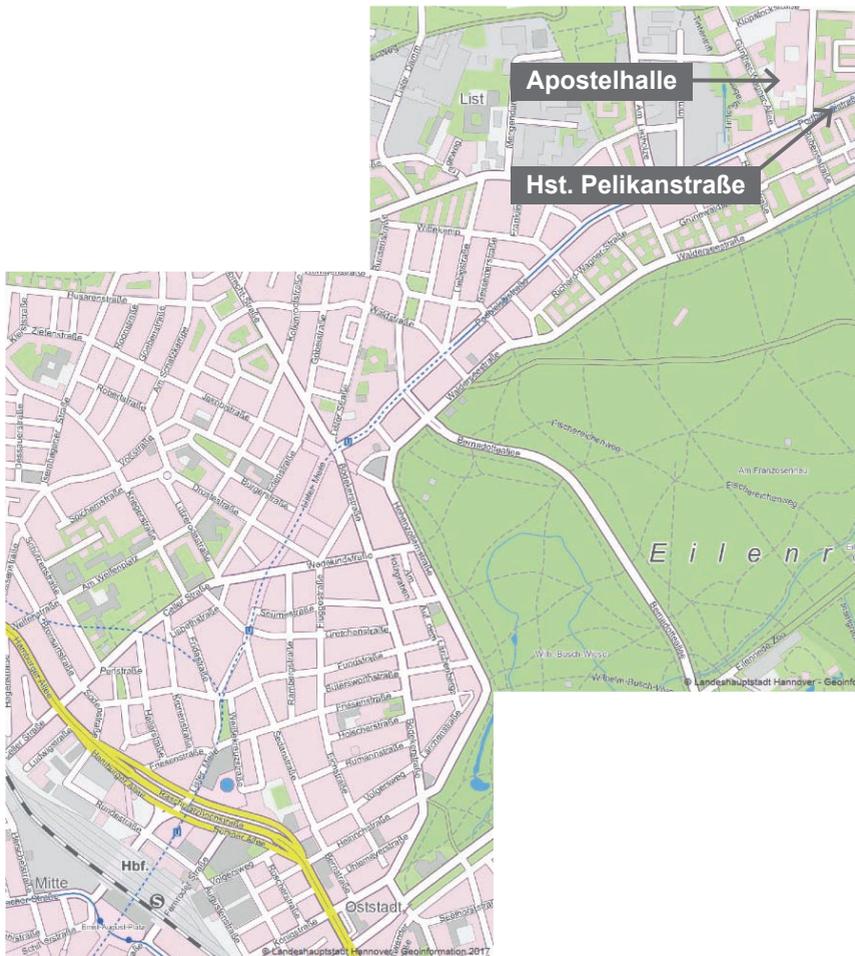
Leibnizhaus der Universität Hannover  
Holzmarkt 4–6  
30159 Hannover



## Konferenzdinner

im XII Apostel (Apostelhalle, Seiteneingang)  
am Di 10.10.2017  
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Erreichbar mit der U3, U7 und U9:  
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ID: 108

## Development Of A Multidimensional Gas Chromatography/ Combustion/ Isotope Ratio Mass Spectrometry Method For The Investigation Of Carbon Isotope Ratios Of Urinary Steroids For Doping Control Purposes

Marlen Putz, Thomas Piper, Schänzer Wilhelm, Thevis Mario

Zentrum für Präventive Dopingforschung – Institut für Biochemie, Deutsche Sporthochschule Köln, Deutschland

Testosterone is a steroid hormone with anabolic effects. It is misused for performance enhancement in sports and the administration of testosterone is prohibited by the World Anti-Doping Agency. [1] Testosterone is also produced endogenously in the human organism.

Endogenous and exogenous testosterone and their metabolites can be unambiguously distinguished by their carbon isotope ratio if compared to endogenous reference compounds. The carbon isotope ratios of exogenous steroids are significantly depleted compared to endogenous steroids.

Isotope ratio mass spectrometry is well established for analyzing urinary steroids for doping control purposes. To achieve the required purity of all analytes, conventional procedures include up to two time-consuming HPLC clean up steps for sample preparation. [2] In order to accelerate the sample preparation, multidimensional gas chromatography was applied, which is known to be a suitable technique for the separation of complex matrices. [4] Multidimensional gas chromatography consists of two gas chromatographs connected by a pressure-controlled heart-cutting device. In the first dimension, a column was installed for peak purification. In the second dimension, separation was obtained employing a column of medium polarity. Retention time stability and cutting windows were monitored by a flame ionization detector. Detection was performed simultaneously by isotope ratio mass spectrometry and a single quadrupole mass spectrometer for structural confirmation and assessment of peak purity.

The developed sample preparation is based on solid-phase extraction, liquid-liquid extraction, enzymatic hydrolysis, and derivatization of the target analytes to their corresponding acetates. These steroid acetates are divided into two fractions by polarity. [2,3]

The method was validated in accordance to the guidelines of the World Anti-Doping Agency by means of linear mixing models for isotope ratio determinations of testosterone and its metabolites 5 $\alpha$ - androstenediol, 5 $\beta$ -androstenediol, etiocholanolone, and androsterone as target compounds

and pregnanediol, 11-ketoetiocholanolone and 16-androstenol as endogenous reference compounds. The results indicated that the method is fit for purpose.

## References

- [1] World Anti-Doping Agency. The 2017 Prohibited List. Available at: [https://www.wada-ama.org/sites/default/files/resources/files/2016-09-29\\_-\\_wada\\_prohibited\\_list\\_2017\\_eng\\_final.pdf](https://www.wada-ama.org/sites/default/files/resources/files/2016-09-29_-_wada_prohibited_list_2017_eng_final.pdf) [16 July 2017].
- [2] T. Piper, C. Emery, M. Saugy, Recent developments in the use of isotope ratio mass spectrometry in sports drug testing, *Anal Bioanal Chem* (2011) 401:433-47.
- [3] C. Saudan, C. Emery, F. Marclay, E. Strahm, P. Mangin, M. Saugy, Validation and performance comparison of two carbon isotope ratio methods to control the misuse of androgens in humans, *J Chromatogr B* (2009) 877:2321-2329.
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ID: 163

## SPIN-MIMS eine Vereinfachung der SPIN-MAS Technik für die Onlinemessung von $^{15}\text{N}$ -Gehalten von Ammonium, Nitrit und Nitrat in wässriger Lösung

Wolfram Eschenbach<sup>1,2</sup>, Jens Dyckmans<sup>1</sup>, D. Lewicka-Szczebak<sup>2</sup>, Anette Giesemann<sup>2</sup>, Florian Stange<sup>3</sup>, Reinhard Well<sup>2</sup>

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<sup>2</sup> Thünen Institut, Institut für Agrarklimaschutz, Braunschweig;

<sup>3</sup> Bundesanstalt für Geowissenschaften und Rohstoffe, Hannover

Übliche Methoden zur selektiven Messung der  $^{15}\text{N}$ -Häufigkeiten in  $\text{NH}_4^+$ ,  $\text{NO}_2^-$  und  $\text{NO}_3^-$  in Proben mit mehreren dieser N-Spezies sind arbeitsaufwändig.

Die SPIN-MAS-Technik (Stange et al. 2007) bietet eine automatisierte, schnelle und selektive Bestimmung von  $^{15}\text{N}$ -Häufigkeiten in  $\text{NH}_4^+$ ,  $\text{NO}_2^-$  und  $\text{NO}_3^-$  in wässrigen Proben. Bei einer **SPIN-MAS**-Messung wird eine von drei verschiedenen Reaktionslösungen mit der wässrigen Probe in einer **Sample Preparation unit for Inorganic N-species (SPIN)** vermischt. Die Reaktionslösung wird in Abhängigkeit der interessierenden N-Spezies gewählt. Die gasförmigen Reaktionsprodukte ( $\text{N}_2$  oder  $\text{NO}$ ) werden dann im Heliumstrom zu einem Quadrupol-Massenspektrometer (**MAS**) geleitet.

Wir haben diese Instrumentierung durch den Einsatz eines Membraneinlass-Massenspektrometers (MIMS) deutlich vereinfacht. Der hier vorgestellte **SPIN-MIMS**-Ansatz beruht auf der Verwendung einer Reaktionskapillare, bei der die Probe, die die N-Spezies von Interesse enthält, mit der entsprechenden Reaktionslösung gemischt wird. Die Mischung aus Reaktionslösung und Probe wird von der Reaktionskapillare direkt zum Membraneinlass des Massenspektrometers gepumpt. Die bei der Umsetzung von  $\text{NH}_4^+$ ,  $\text{NO}_2^-$  und  $\text{NO}_3^-$  gebildeten Reaktionsprodukte ( $\text{N}_2$  oder  $\text{NO}$ ) werden durch die gasdurchlässige Membran des Einlasses direkt in die Ionenquelle des Massenspektrometers geleitet.

$^{15}\text{N}$ -Standards mit unterschiedlichen atom%  $^{15}\text{N}$  ( $\text{NH}_4^+$ ,  $\text{NO}_2^-$  und  $\text{NO}_3^-$  jeweils in dist. Wasser) wurden verwendet, um die Leistungsfähigkeit des Systems zu testen. Insgesamt zeigten die SPIN-MIMS-Messungen eine gute Übereinstimmung zwischen gemessenen und erwarteten  $^{15}\text{N}$ -Abundanzen (Bereich 0,5 - 10 atom%  $^{15}\text{N}$  Abweichungen: < +/- 0,5 atom%  $^{15}\text{N}$  für  $\text{NH}_4^+$ , < +/- 0,25 atom% für  $\text{NO}_2^-$  und für  $\text{NO}_3^-$ -Standards, im Bereich 10 bis 75 atom% Abweichung < +/- 0,6 atom% für alle drei N-Spezies). Weiterhin wurden Bodenextrakte mit  $^{15}\text{N}$  markiertem  $\text{NH}_4^+$  und  $\text{NO}_3^-$  parallel mit der SPIN-MIMS

Methode und der Denitrifizierermethode gemessen. Der Vergleich zeigte eine gute Übereinstimmung beider Methoden.

Um das vorgestellte Messsystem weiterzuentwickeln wurden Versuche zur Messung von  $^{15}\text{N}$  Standards mit natürlicher  $^{15}\text{N}$  Abundanz für Ammonium und Nitrat durchgeführt. Dafür wurde im Fall des Nitrats  $\text{N}_2\text{O}$  als Messgas verwendet anstatt des bisher benutzten  $\text{NO}$ .

### Referenz

Eschenbach, W., Lewicka-Szczebak, D., Stange, C.F., Dyckmans, J. and Well, R.: Measuring  $^{15}\text{N}$  Abundance and Concentration of Aqueous Nitrate, Nitrite, and Ammonium by Membrane Inlet Quadrupole Mass Spectrometry, *Anal. Chem.*, doi:10.1021/acs.analchem.7b00724, 2017.

ID: 110

## Universal chlorine isotope analysis of organic compounds using gas chromatography interfaced with multiple-collector inductively coupled plasma mass spectrometry (GC-MC-ICPMS)

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Chlorinated hydrocarbons are priority pollutants in groundwater and soil, as well as in the atmosphere. Isotope analysis of organic compounds has considerably developed within the last decade due to increased interest in multi-dimensional approaches. Application of chlorine isotopes, however, was thus far limited by the availability of suitable analytical techniques. So far, existing methods suffer from large sample size (thermal ionisation mass spectrometry), low precision (gas chromatography quadrupole mass spectrometry) or limitation to a few compounds only (isotope ratio mass spectrometry). Here we present a universal method for chlorine isotope analysis of volatile and semi-volatile organics (i.e. chlorinated methanes, ethanes, benzenes, phenols and hexachlorocyclohexanes) that overcomes the limitations of previous techniques combining low detection limits and excellent precision. Using multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS) for chlorine isotopes has been considered challenging due to isobaric interference of the  $\text{ArH}^+$  dimer with  $^{37}\text{Cl}$ . We demonstrate that this interference is negligible under super dry plasma conditions. As a consequence, detection limits of about 2 nmol Cl could be achieved. The corresponding precision is usually below  $1\sigma \pm 0.25$  mUr. Measured  $\delta^{37}\text{Cl}$  consistently agree with previously published offline characterized values if a two point calibration is applied. This universal method considerably simplifies  $\delta^{37}\text{Cl}$  determination of mixtures of halogenated organic compounds and may be easily adapted to other GC-MC-ICP-MS systems.

## Chromatography-based EA-IRMS : Redesigning the combustion elemental analyzer around modern chromatographic principles

Andreas Hilkert, Christopher Brodie, Oliver Kracht

Thermo Fisher Scientific (Bremen GmbH), Deutschland

The elemental analyzer (EA) was invented by Justus Liebig in 1830 and is deeply rooted in analytical chemistry, but the steps to make it an analytical tool for biology and geochemistry came in 1968, when Carlo Erba replaced trapping of the gases from combustion with isothermal gas chromatography using a packed GC column. In 1980, when Professor Tom Preston put a Carlo Erba EA onto an IRMS, inventing „continuous flow-IRMS“. The technique was rapidly adopted and the work flow was extended from N to C and then S as well as to dual element (CN) and triple element (CNS) analyses.

In 2016, Thermo Fisher Scientific introduced the EA IsoLink, an evolutionary change to the combustion elemental analyzer, based on the common „injector-chromatography-detector“ philosophy. Every component of the elemental analyzer has been examined and either optimized or redesigned, from the autosampler to the TCD. The Dumas combustion products are now resolved on a GC column using variable He flow rates and GC temperature ramping, and for the first time, chromatographic terms like baseline and resolution are rigorously defined. The result is improved performance in every figure of merit, improved precision for every measurement (C, N, S, CN, CS, CNS) and sample size, at the same time as improving throughput and greatly reducing He consumption.

The presentation will focus on the principles of gas chromatography with respect to elemental analyzers showing examples of applications highlighting the essentials of the new EA-IRMS technology.

ID: 127

## JRAS-06: Keeping up with changing internationally-distributed, light-element stable isotopic reference materials

Heiko Moossen<sup>1</sup>, Tyler B. Coplen<sup>2</sup>, Haiping Qi<sup>2</sup>, Michael Rothe<sup>1</sup>, Heike Geilmann<sup>1</sup>, Jürgen Richter<sup>1</sup>, Willi A. Brand<sup>1</sup>

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One of the most critical aspects of measuring carbon isotopic signatures of atmospheric CO<sub>2</sub> is the stringent standardisation procedure which is required. Without it, inter-laboratory  $\delta^{13}\text{C}$  comparisons of atmospheric CO<sub>2</sub> are difficult at best, and impossible at worst. Following the “principle of identical treatment” (IT principle; Werner and Brand, 2001), isotopic reference materials for atmospheric CO<sub>2</sub> analysis should be chemically identical to analysed samples. For the last 10 years, the stable isotope laboratory at the Max-Planck-Institute for Biogeochemistry (BGC-IsoLab) has offered the Jena Reference Air Set (JRAS-06) to the scientific community. CO<sub>2</sub> for this set of reference materials is evolved from carbonates, including NBS 19 calcite ( $\delta^{13}\text{C} = +1.95$  mUr and  $\delta^{18}\text{O} = -2.2$  mUr) that anchors one end of the VPDB-LSVEC carbon-isotope scale and LSVEC lithium carbonate ( $\delta^{13}\text{C} = -46.6$  mUr), and it is diluted into CO<sub>2</sub>-free matrix air. Thus, an air-CO<sub>2</sub> scale has been produced that is linked directly to the VPDB-CO<sub>2(gas)</sub> scale. Use of JRAS-06 enables laboratories to follow the identical treatment principle and report their findings on the VPDB-CO<sub>2(gas)</sub> scale.

The year 2016 was a turbulent year for the VPDB oxygen-isotope scale and the VPDB-LSVEC carbon-isotope scale. The distribution of NBS 19 was discontinued because its supply was nearly exhausted. A new calcite, IAEA-603 (Carrara marble; [https://nucleus.iaea.org/rpst/referenceproducts/referencematerials/Stable\\_Isotopes/13C18and7Li/IAEA-603/index.htm](https://nucleus.iaea.org/rpst/referenceproducts/referencematerials/Stable_Isotopes/13C18and7Li/IAEA-603/index.htm);  $\delta^{13}\text{C} = +2.46 \pm 0.01$  mUr and  $\delta^{18}\text{O} = -2.37 \pm 0.04$  mUr) was introduced by the International Atomic Energy Agency as an internationally-distributed, secondary isotopic reference material to anchor measurement results to the carbon- and oxygen-isotope scales. Furthermore, LSVEC was deemed inappropriate as a second scale anchor because it can react with atmospheric CO<sub>2</sub>, thereby affecting its carbon isotopic signature. BGC-IsoLab is currently involved in a collaborative effort to quantify the  $\delta^{13}\text{C}$  value of a high purity calcium carbonate with a  $\delta^{13}\text{C}$  value of  $\sim -42$  mUr that is intended to serve as an internationally-distributed, secondary isotopic reference material to anchor measurement results to the VPDB-LSVEC carbon-isotope scale. This new material can also be used to anchor the JRAS-06 scale. Here, we

present preliminary results on this new high purity calcium carbonate whose  $\delta^{13}\text{C}$  value does not change with exposure to atmospheric  $\text{CO}_2$ . Additionally, we discuss some considerations that need to be made when determining isotope-delta values of secondary isotopic reference materials.

ID: 117

## A Closer Look Into The Nitrogen Blank In Elemental Analyser/ Isotope Ratio Mass Spectrometry measurements

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One important limitation for the precise measurement of minute amounts of N in solid samples by elemental analyser/isotope ratio mass spectrometry (EA/IRMS) is the accurate determination of the analyser blank value. This study was performed to identify different sources, amounts and isotopic composition of N blanks in EA/IRMS to identify measures for minimizing the effect of the N blank on N isotopic data quality. Sources of the blank is atmospheric N<sub>2</sub> leaking into the elemental analyser, trapped in the sample tin capsules or contained in the oxygen added for combustion. Another source of blank are the reaction tubes.. Also, cross contamination of previous samples may contribute up to 3.3 nmol N. As the sources of the blank differ, the isotopic composition of the blank is very variable.

For precise measurements of minute amounts of N in solid samples reduction of the N blank is the most promising strategy. Correcting for the remaining N blank is only meaningful if sample isotopic composition is very different from the N blank, because the precise determination of the isotopic composition of the N blank is not possible.

## An LC-IRMS Interface for Flexible Compound-specific Stable Isotope Analysis

ID: 164

Filip Volders, Christian Schmidt, Sam Barker, Paul Wheeler, Lutz Lange, Hans-Peter Sieper

Elementar Analysensysteme GmbH, Deutschland

In aqueous samples compound-specific stable isotope analysis (CSIA) plays an important role. Environmental and forensic sciences are prominent examples of such applications, utilizing naturally occurring fractionation processes during transport and transformation processes to, e.g., allocate contaminants or drugs sources. The broad range of involved application areas includes e.g. the food industry (food fraud) and sport (doping).

A novel high-temperature combustion interface was developed to hyphenate high-performance liquid chromatography with isotope ratio mass spectrometry in a more flexible way. In continuous operation virtually for all peaks in a chromatogram the stable isotope ratio can be analyzed.

Experimental data of different examples proof the performance and flexibility of such a system. Compounds were determined typically with a precision and trueness of  $\leq 0.5\%$  for different stable isotopes.

The development of a novel LC-IRMS interface resulted in the first high temperature combustion system reported.

ID: 152

## Validation of a $\delta^2\text{H}$ -alkane- $\delta^{18}\text{O}$ -hemicellulose-based paleohygrometer

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Leaf wax-derived biomarkers, e.g. long-chain *n*-alkanes and fatty acids, and their hydrogen isotope composition have become a valuable tool in paleoclimate research and in (paleo)hydrology. However, a variable degree of leaf water enrichment challenges their use as proxy of paleoprecipitation isotope composition. The coupling of  $\delta^2\text{H}$  of leaf wax-derived biomarkers with  $\delta^{18}\text{O}$  of hemicellulose-derived sugars has the potential to overcome this limitation and additionally allows reconstructing relative air humidity (Zech et al., 2013). This approach was recently validated by Tuthorn et al. (2015) by applying it to topsoil samples along a climate transect in Argentina. Accordingly, the biomarker-derived relative humidity significantly correlates with modern actual relative humidity from the respective study sites, showing the potential of the established 'paleohygrometer' approach. However, an experimental validation is still missing to answer open questions regarding this approach, e.g. about the robustness of biosynthetic fractionation factors.

We present coupled  $\delta^2\text{H}_{n\text{-alkane}}-\delta^{18}\text{O}_{\text{hemicellulose}}$  results obtained for leaf material from a climate chamber experiment, in which *Eucalyptus globulus*, *Vicia faba* and *Brassica oleracea* were grown under controlled conditions (Mayr, 2003). First, the  $^2\text{H}$  and  $^{18}\text{O}$  enrichments of leaf water strongly reflect actual relative humidity in the climate chambers. Second, the biomarker-based reconstructed relative humidity correlates well with the actual relative humidity

of the respective climate chamber, validating the proposed 'paleohygrometer' approach. Finally, the calculated fractionation factors of +27‰ for  $^{18}\text{O}$  in hemicellulose sugars (arabinose and xylose) and -155‰ for  $^2\text{H}$  in  $n$ -alkanes ( $n\text{-C}_{29}$  and  $n\text{-C}_{31}$ ) are identical/close to literature values. Nevertheless, minor dependencies of these biomarker fractionation factors from temperature and relative humidity of the climate chamber, as well as from the measured transpiration rate of the plants are evident from the data. As an outlook, the proposed coupled  $\delta^2\text{H}_{n\text{-alkane}} - \delta^{18}\text{O}_{\text{hemicellulose}}$  approach allows (i) more robust  $\delta^2\text{H}/\delta^{18}\text{O}_{\text{precipitation}}$  reconstructions and (ii) paleohygrography studies in future paleoclimate research.

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## The Effect of Nitrate and Ammonium Nutrition on Carbon Stable Isotope Fractionation During Plant Respiration

Shiva Ghiasi, Roland Werner, Nina Buchmann, Rolf Siegwolf

ETH Zurich, Schweiz

The assimilation of nitrate and ammonium in plants follows different biochemical pathways. Thus, different enzymatic reactions, energy requirements and carbon skeletons are needed to assimilate nitrogen from soil. For instance, uptake and assimilation of  $\text{NH}_4^+$  or  $\text{NO}_3^-$  influences the pH and charge balance in the cytosol. This is regulated by a mechanism involving phosphoenolpyruvate carboxylase (PEPC) and malic enzyme (ME) which fix and release  $\text{CO}_2$  depending on form and place of nitrogen assimilation with production or consumption of malate. Accordingly, we hypothesize that applying different nitrogen inorganic ions ( $\text{NO}_3^-$  or  $\text{NH}_4^+$ ) as the only source of nitrogen, will potentially influence respiration rate as well as the carbon isotopic composition of various biochemical intermediates and eventually of respired  $\text{CO}_2$  ( $d^{13}\text{C}_{\text{res}}$ ).

To address this hypothesis, we grew plants in a quartz sand medium along a nitrogen supply gradient ranging from 100%  $\text{NO}_3^-$  to 100%  $\text{NH}_4^+$  under controlled environmental conditions. After six weeks, plants were harvested and analyzed for  $d^{13}\text{C}$  of respired  $\text{CO}_2$ , and metabolic compounds in roots and leaves. Accounting for photosynthetic discrimination (by using  $d^{13}\text{C}_{\text{sugar}}$  as source of respiration) our results show that there is a stronger fractionation in leaves of  $\text{NO}_3^-$  treated plants than those of  $\text{NH}_4^+$  plants, which resulted in more enriched  $d^{13}\text{C}_{\text{res}}$  values in  $\text{NO}_3^-$  treated plants. In roots, on the other hand, such fractionation effect was more obvious in  $\text{NH}_4^+$  plants and not in  $\text{NO}_3^-$  fed ones. To further investigate the hypothesis, we analyzed organic acids compound specific and results show a decrease in concentration of malate and citrate in leaves and roots from  $\text{NO}_3^-$  towards  $\text{NH}_4^+$  plants. Moreover, PEPC activity in leaves and roots showed the same decreasing trend. The results bring us to the conclusion that  $\text{NO}_3^-$  fed plants produce more malate in leaves to support N assimilation and to regulate pH, therefore the respired  $\text{CO}_2$  is more enriched. The amount of malate being produced and replenish the TCA cycle in the roots of  $\text{NO}_3^-$  plants is less and the carbon source of this malate is more depleted; therefore, the respired  $\text{CO}_2$  in roots of  $\text{NO}_3^-$  plants is depleted. Under  $\text{NH}_4^+$  nutrition, the assimilation happens in the roots and as a result the malate produced in the leaves is transported to the roots to flow carbon skeleton into TCA cycle for N assimilation and to regulate pH. These together cause the respired  $\text{CO}_2$  in the roots of  $\text{NH}_4^+$  plants to be more enriched.

## Carbon allocation into biogenic volatile organic compounds (BVOCs) and respiratory carbon dioxide (CO<sub>2</sub>) traced by position-specific <sup>13</sup>C-pyruvate-labelling in *Halimium halimifolium* L.: A novel methodological approach for automated, simultaneous and real-time trace gas analysis

ID: 135

Lukas Fasbender, Ana Maria Yáñez-Serrano, Christiane Werner

University of Freiburg, Ecosystem Physiology, Germany

The greenhouse gas carbon dioxide (CO<sub>2</sub>) and biogenic volatile organic compounds (BVOCs) exert strong effects on global climate and air quality. However, processes controlling biogenic emissions of these trace gases remain poorly understood and account for some of the largest uncertainties in our understanding of the global carbon cycle. In particular, there is a lack of understanding of the carbon partitioning into anabolic and catabolic processes. Here we present a novel methodological approach combining  $\delta^{13}\text{C}\text{CO}_2$  laser spectroscopy with high sensitivity proton-transfer-reaction time-of-flight mass spectrometry (PTR-TOF-MS), connected to a multiple branch enclosure system, allowing synchronized, online detection of plant carbon partitioning into respiratory CO<sub>2</sub> and BVOC emissions and their natural fluxes under controlled environmental conditions. In a first application, this new measuring system was used to analyze trace gas emissions of *H. halimifolium* fed with <sup>13</sup>C-position specific labeled pyruvate solution in the light and during light-dark transitions. The results showed that the system is able to resolve rapid changes in gas fluxes, such as light enhanced dark respiration (LEDR) or post-illumination burst of some BVOCs, and to trace <sup>13</sup>C-label incorporation into CO<sub>2</sub> and BVOC-fluxes. In general, <sup>13</sup>C1-pyruvate labelling during illumination caused a markedly increased <sup>13</sup>CO<sub>2</sub>-flux, indicating that even in the light a significant CO<sub>2</sub>-flux derived from pyruvate C1-decarboxylation is emitted by the plants. In contrast, <sup>13</sup>C2-labelling did not change the <sup>13</sup>CO<sub>2</sub>-flux significantly. Some <sup>13</sup>C-BVOC-fluxes increased during <sup>13</sup>C2-labelling compared to <sup>13</sup>C1-label, indicating rapid incorporation of the <sup>13</sup>C2-label during *de novo* BVOC synthesis, whereas some other BVOC species did not. Thus, using position-specific labelling in combination with simultaneous measurements of  $\delta^{13}\text{C}\text{CO}_2$  and BVOC-fluxes is an innovative approach to trace the way of specific carbon atoms through plant biochemical cycles. Therefore, the expected link between biosynthesis of BVOCs and isotope dynamics during CO<sub>2</sub> decarboxylation in the light and dark can be further evaluated, as this connection may have important implications for assessment of plant respiration and secondary metabolism.

ID: 157

## Using Mo and U isotope signatures of sediments as paleo-redox proxy

**Stefan Weyer<sup>1</sup>, Annika Brüske<sup>1</sup>, Nadja Neubert<sup>1</sup>, Olaf Dellwig<sup>2</sup>, Noah Planavki<sup>3</sup>, Timothy Lyons<sup>4</sup>, Ariel Anbar<sup>5</sup>**

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Within the last two decades, analyses and application of so-called non-traditional isotopes have been developed, some of them being widely used meanwhile. Among them are a range of redox-sensitive transition metals that can be used to help unraveling the evolution of Earth oceans, atmosphere and life. Beside Fe, in particular Mo and U isotope signatures became powerful tools to estimate the expansion of seafloor anoxia of past oceans. Both elements behave conservative and have long residence time in modern oceans. However, in anoxic environments, they become reactive and are readily removed from the water column. Both elements also show distinct isotope fractionation between oxic and anoxic sedimentary sinks. However, in contrast to Mo, the fractionation of the long-lived U isotopes (<sup>238</sup>U and <sup>235</sup>U) is dominantly driven by a nuclear volume-dependent mechanism (nuclear field shift) that is opposite in direction to mass-dependent isotope fractionation. Accordingly, the combined use of Mo and U offers a variety of new opportunities. In our investigations, we show that Mo and U isotope signatures of sediments, deposited in anoxic environments, including the Black Sea, the Cariaco Basin, sediments from the Cretaceous oceanic anoxic event OAE2 and those from the early Jurassic T-OAE, are frequently negatively correlated. This negative correlation may enable to distinguish between isotope fractionation that occurred during the deposition of the sediments and that related to a shift of the Mo-U isotope signature of the global seawater reservoir. However, also the investigated modern basins define parallel and not identical trends. Potentially, a shift of the Mo-U isotope array may also be caused by different environment-dependent isotope fractionation mechanisms, for Mo, U or both elements. In particular, for U it has been shown that biotic and abiotic reduction may result in very different isotope fractionation. Accordingly, U isotopes may also bear a potential to trace biological pathways, which may be of interest not only in paleoceanography and early Earth studies, but also in environmental sciences.

## Tracing complex igneous processes by in-situ analyses of Mg- and Fe isotope ratios in magmatic minerals

ID: 159

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Several studies in recent years have demonstrated that the fractionation of metal stable isotopes at temperatures prevailing in volcanic systems is mainly driven by kinetic processes such as diffusion.<sup>1-3</sup> As light isotopes always diffuse slightly faster than their heavier counterparts, diffusive processes will generate large isotope variations.<sup>1</sup> Consequently, diffusion-generated chemical zoning of minerals in volcanic rocks should be coupled with pronounced isotopic zoning. In contrast, mineral growth in an evolving magma is regarded to be an equilibrium process and, thus, should be associated with limited isotope fractionation at high temperatures. Hence, *in situ* analyses of metal stable isotope ratios (such as <sup>56</sup>Fe/<sup>54</sup>Fe) in minerals, e.g. by laser ablation-MC-ICP-MS, represent a powerful means to distinguish between growth- and diffusion-generated chemical zoning of minerals.<sup>4,5</sup> This is important as such zoning is frequently used to estimate timescales of magmatic processes prior to volcanic eruptions by diffusion modeling.<sup>6-8</sup> However, in natural samples a combination of e.g. crystal growth and diffusion processes may significantly affect intra-mineral chemical and isotope variations, questioning the assumption that calculated diffusion timescales represent the timing of a specific magmatic process. In order to exploit the full potential of combining chemical and isotopic zoning in magmatic minerals, such as olivine ( [Mg,Fe]<sub>2</sub>SiO<sub>4</sub> ), we investigated the effects of Fe-Mg interdiffusion, crystal growth and crystal dissolution on chemical and isotopic zoning of olivine crystals theoretically. These model results were then applied to natural olivine crystals from various volcanic settings (mid-ocean ridges, intra-plate volcanoes, subduction zones, Mars) in order to simulate observed Fe-Mg isotopic (and chemical) variations which were determined by *in situ* Fe-Mg isotope analyses using femtosecond-laser ablation-MC-ICP-MS.<sup>9</sup> The results of our studies show that detailed chemical and isotopic profiles across magmatic olivines provide a more thorough picture of complex growth and diffusion histories of such crystals, leading to a better understanding of magmatic processes prior to volcanic eruptions.

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## Acidic mine tailings and Fe / Cu isotope fractionation: modification and application of a sequential extraction method

ID: 154

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Sulfidic mine tailings have a high potential for contamination of the environment by releasing acid mine drainage, hence it is crucial to understand metal mobilization processes and to develop monitoring tools. For Fe, a six steps sequential extraction method was applied, in order to separate potential Fe-bearing minerals (step 1-6: MQ-extractable, NH<sub>4</sub>-acetate-extractable, a dithionite-leach, NH<sub>4</sub>-oxalate-extractable, KClO<sub>3</sub>/HCl-extractable and residuals). For Cu, this method was modified to a four steps method (step 1, 2, 4 & 6 of above). Metal isotope fingerprinting as a potential monitoring tool for metal sulfide oxidation processes was in the focus of this study. Isotope fractionation during the extraction was investigated using minerals for which the mineral composition and the isotopic composition was known to verify accuracy and precision of the sequential extraction method for metal isotope analysis. The procedure led to a small loss in the elemental budget, but the isotope compositions were within uncertainties.

Sample investigation from the upper meter of two sites of a porphyry copper mine tailing in the Atacama Desert in Chile (Chañaral Bay) revealed homogeneous Fe contents and Fe isotope compositions with depth ( $\delta^{56}\text{Fe} \approx 0.2\text{-}0.3\text{‰}$ ). Only the deepest samples at ~60 cm exhibited lighter  $\delta^{56}\text{Fe}$  values (~0‰). The Cu isotope compositions of all bulk samples and individual fractions (except the Cu sulfides) of one site (Ch1) exhibited a decrease of the  $\delta^{65}\text{Cu}$  values from the depth towards the surface (the direction of water flow in the arid climate). These data in combination with the pH indicate preferential adsorption of the <sup>65</sup>Cu on Fe(oxy)hydroxides at site Ch1, which is associated with Cu isotope fractionation. Another site (Ch12), where pH at depths was likely not high enough for the formation of such Fe-minerals, only showed minor Cu isotope fractionation.

The results show that sequential extractions in combination with stable isotope analyses can provide important information on the distribution of Fe and Cu between different mineral phases like sulfates, oxides and sulfides, and thus improves our understanding of processes occurring in mine tailings.

## Iron Enrichment In Soils And Groundwater – The Fe Isotope Signature

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Bog iron ores (or *Raseneisenerz*) have been locally used as a source of iron (Fe) since the Iron Age. Formation of bog iron ore in soils is restricted to conditions that require a constant supply of dissolved Fe and its immobilization as Fe oxides. The mobility of dissolved Fe<sup>2+</sup> within soils is strongly affected by redox conditions, which also significantly influence the Fe input into groundwater and rivers. It is well known that the reaction of Fe<sup>2+</sup> with atmospheric oxygen results in precipitation of Fe<sup>3+</sup> oxides like goethite and ferrihydrite, consequently removing Fe from groundwater. Dissolution of Fe oxides due to biotic activity or absence of oxygen may mobilize Fe again.

However, the stability of bog iron ores at Fe reducing conditions and their formation processes are so far poorly constrained by field investigations. In this context, stable Fe isotope signatures given as  $\delta^{56}\text{Fe}$  provide a powerful tool for a detailed investigation of Fe translocation processes within, into and out of soils, and may shed more light on the formation of bog iron ores.

As a representative example, an iron-rich Gleysol from NW Germany was investigated to assess Fe mobility in response to steep changes of redox conditions. The studied soil is extremely enriched in Fe by up to ~40 wt.-% to depths of ~80 cm. Here, Fe is mostly present as goethite or ferrihydrite. At greater depths, the study area is marked by a largely Fe oxide-free sandy horizon.

Solid soil and groundwater were sampled at different depths. The dissolved Fe concentration and stable Fe isotope ratios varied significantly with abundance of solid Fe oxides. The lowest  $\delta^{56}\text{Fe}$  values (-1.7 ‰) and minimum Fe concentrations (~0.2 mg/L) were recorded in groundwater from the Fe-rich horizons despite persistent Fe reducing conditions. Consequently, the Fe oxide mineralogy is resistant to Fe mobilization. In contrast, the groundwater in the Fe-poor sandy horizon had significantly higher  $\delta^{56}\text{Fe}$  values (-0.4 ‰) and Fe concentrations of up to ~60 mg/L. The coupled low  $\delta^{56}\text{Fe}$  values and Fe concentrations are attributed to adsorption and exchange reactions between dissolved Fe and Fe oxides. In conclusion, the bog iron in the study area is not a source for dissolved Fe, but instead an Fe sink because of the high adsorption capacity of Fe oxides. Due to a constant supply of dissolved Fe from groundwater, formation of bog iron in the area is an ongoing process.

## Water flow and fate of pesticides in the unsaturated zone – Investigations based on stable water isotopes

ID: 112

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The increasing application of pesticides on crops, intended to increase agricultural productivity, may pose potential human health impacts and may also lead to negative effects on soil and groundwater ecosystems. Characterizing the water flow in the unsaturated zone is a first step for gaining knowledge on the fate of pesticides in aquatic habitats.

To characterize the water flow, we measured stable water isotope ratios ( $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ ) in precipitation and leaching water from two different lysimeters. Lysimeter 1 is filled with a sandy-gravel soil, while a second lysimeter is filled with a sandy-silt soil. Maize has been planted in the area of the both lysimeters and different pesticides (metolachlor, terbuthylazine, nicosulfuron, prosulfuron) were applied once a year to the lysimeters. We used a lumped-parameter model approach (LPM) considering transport through the soil matrix (advection and dispersion) and along preferential flow paths (piston flow), in order to obtain estimates for mean transit time of water (MTT) and the dispersion parameter ( $P_D$ ) for the different soils. When applying the LPM, uncertainties are in particular associated to the estimation of isotope contents in the recharging water (input function for the model). We have used four different methods to define the input function: (1) considering water isotopes measured in precipitation as input (no modification), (2) applying different weighting periods for leaching while neglecting evapotranspiration (ET) and water storage changes, (3) using the Haude approach as a simplified method and (4) the Penman-Monteith approach as a more complex method for estimating ET, implemented into the input function.

As preliminary results for water flow characterization, for Lysimeter 1, we found a MTT between 145 and 155 days, and  $P_D$ -values ranging from 0.06 to 0.09. In the second lysimeter, best fits were achieved with a MTT of 250 days, and a  $P_D$  of 0.10 to 0.20. When comparing the amount of sprayed pesticides (input) with pesticides and their metabolites leaching from the lysimeters, less than 12% of the applied pesticide mass was found in the outflow water of Lysimeter 1, while in the second lysimeter it was less than 1%. The remaining portions of pesticides were probably adsorbed to soil or taken up by plants. To obtain hints on biodegradation, compound-specific isotope analyses will be carried out on raw material (pesticides sprayed) and on water samples taken from the lysimeters.

ID: 125

## Complementary Use Of $^1\text{H}$ -NMR And Multi-Element IRMS In Association With Chemometric Methods Enables Effective Origin Analysis Of High Quality Cocoa (*Theobroma Cacao L.*)

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Within the market of fine cocoa (*Theobroma cacao L.*), quality and prices are mainly determined by geographical origin, making traceability indispensable. However, a solid scientific method for this purpose has not been developed yet. For this reason, various cocoa samples from 20 countries have been profiled using, for the first time for cocoa, a combination of multielement isotope-ratio mass spectrometry (IRMS) and nuclear magnetic resonance (NMR).

Dimensionality reduction of NMR data resulted in six sets of signals, which could be assigned to substances well-suited for discrimination purposes. Principal component analysis (PCA) as well as cross-validated partial least squares discriminant analysis (PLS-DA) of combined isotope data ( $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ ,  $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ , %C, %N, %O, %H) and  $^1\text{H}$ -NMR fingerprints achieved improved separation with increased classification rates compared to classification with data of the isolated methods. Loading plots revealed complementary properties of the two analytical techniques, as IRMS contributed primarily to discrimination between countries, while NMR significantly contributed to the separation of regions and varieties. Combination of datasets from different analytical methods each providing a larger number of parameters, is proposed as a general tool to enhance both, accuracy and precision, in testing of foodstuffs for authenticity.

## Same Same, but different! – Decoding the nutrition history of blow flies by EA-IRMS

ID: 106

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Only the feeding larval stages of forensically important flies can be assigned to a particular corpse with certainty. The association of empty puparia or adult flies and a decomposing human cadaver at a crime scene may be called into doubt, as such specimens could result from another food source and not from the corpse in question. This is especially valid for adult flies but also for their empty cases where they developed in. In light of the fact that recent techniques in forensic entomology target age estimation of adult flies and weathering of empty puparia as new tools for the analysis of the minimum time since death, there is need of a way to guarantee that specimens actually developed on the corpse in question.

We analysed stable carbon ( $d^{13}C$ ) and nitrogen ( $d^{15}N$ ) isotopes in human muscle tissues ( $n=10$ ) and in the muscle tissue of 13 different animal species ( $n=3-5$  each) by means of elemental analyzer-isotope ratio mass spectrometry. These isotopes were also investigated for adult specimens of the forensically important blow fly *Lucilia sericata* that had been reared on the above mentioned tissues and, additionally, for the empty puparial cases.

Adult flies grown on human tissue revealed an average  $d^{13}C$  value of  $-23.05\%$  ( $\pm 0.55\%$ ) and an average  $d^{15}N$  value of  $11.38\%$  ( $\pm 0.95\%$ ). This displays an average  $d^{13}C$  depletion of  $-0.39\%$  and an average  $d^{15}N$  enrichment of  $2.64\%$  in adult flies compared to the human tissue itself. In empty puparia, we observed an average  $d^{13}C$  value of  $-23.35\%$  ( $\pm 0.63\%$ ) and an average  $d^{15}N$  value of  $6.49\%$  ( $\pm 0.81\%$ ). Compared to human muscle tissue, we found an average  $d^{13}C$  depletion of  $-0.69\%$  and an average  $d^{15}N$  depletion of  $-2.25\%$  in empty puparia.

The  $d^{13}C$  and  $d^{15}N$  ratios of the human muscle tissues were in accordance with literature values for Germany. During metamorphosis, adult flies become enriched in  $^{15}N$ , as can be observed at each change of trophic level. Since chemical bonds including  $^{14}N$  break down more rapidly than chemical bonds including  $^{15}N$ , excretion products -such as the chitin in empty puparia- are  $^{15}N$ -depleted.

ID: 107

## Epiandrosterone Sulfate Prolongs The Detectability Of Testosterone, 4-Androstenedione And Dihydrotestosterone Misuse By Means Of Carbon Isotope Ratio Mass Spectrometry

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In the course of investigations into the metabolism of testosterone (T) by means of deuterated T and hydrogen isotope ratio mass spectrometry, a pronounced influence of the oral administration of T on sulfoconjugated steroid metabolites was observed. Especially in case of epiandrosterone sulfate (EPIA\_S), the contribution of exogenous T to the urinary metabolite was traceable up to 8 days after a single oral dose of 40 mg of T. These findings initiated follow-up studies on the capability of EPIA\_S to extend the detection of T and T analogue misuse by carbon isotope ratio (CIR) mass spectrometry in sports drug testing.

Excretion study urine samples obtained after transdermal application of T and after oral administration of 4-androstenedione, dihydrotestosterone, and EPIA were investigated regarding urinary concentrations and CIR. With each administered steroid, EPIA\_S was significantly depleted and prolonged the detectability when compared to routinely used steroidal target compounds by a factor of 2 to 5.

In order to simplify the sample preparation procedure for sulfoconjugated compounds, enzymatic cleavage by *Pseudomonas aeruginosa* arylsulfatase was tested and implemented into CIR measurements for the first time. Further simplification was achieved by employing multidimensional gas chromatography to ensure the required peak purity for CIR determinations, instead of sample purification strategies using liquid chromatographic fractionation.

Taking into account these results that demonstrate the unique and broad applicability of EPIA\_S for the detection of illicit administrations of T or T-related steroids, careful consideration of how this steroid can be implemented into routine doping control analysis appears warranted.



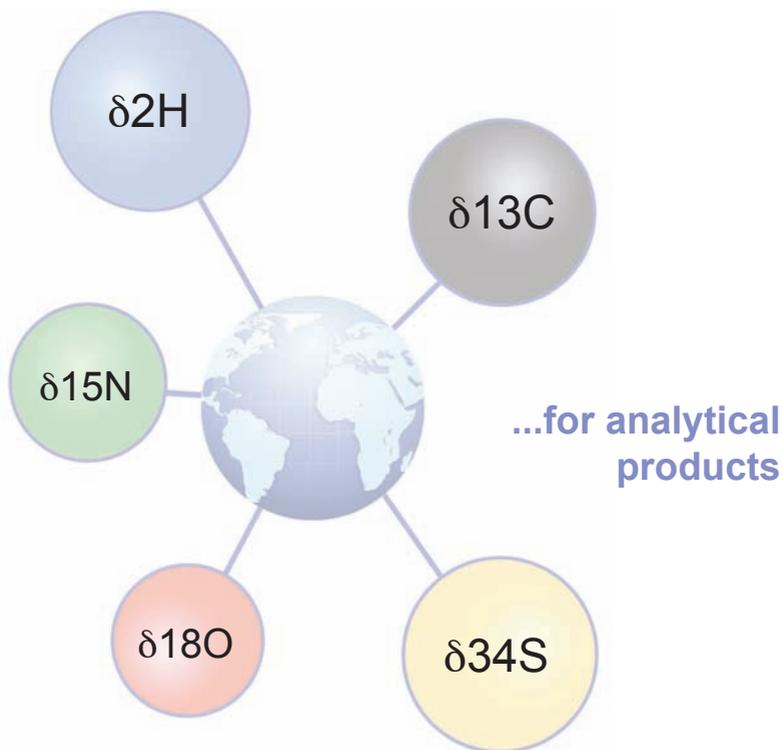
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ID: 158

## Biotransformation of Hexachlorocyclohexane during Anaerobic Digestion of Pesticide Contaminated Biomass Tracked by Compound Specific Stable Isotope Analysis

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The Stockholm Convention in 2009 classified hexachlorocyclohexanes (HCHs) as persistent organic pollutants due to its harmful and adverse effects on the environment. A huge amount of Lindane ( $\gamma$ -HCH) was used as pesticide worldwide and other HCH isomers are still found at high concentration in contaminated fields. Inappropriate treatments of HCH containing waste caused serious environmental issues. For clean-up of contaminated sites and biomass, anaerobic digestion (AD) of pesticide-contaminated materials to produce biogas could be a promising strategy. Lab-scale batch reactors were set up to measure methanogenic activity and metabolic pathway in AD system during HCH biotransformation.

AD system under different concentration levels of mixed  $\alpha$ - and  $\gamma$ -HCH (5 mg/L, 50 mg/L and 150 mg/L for each chemical) was set up to study the toxicity of HCHs. Inhibitory effect on biogas yield was observed only at high concentration HCH-set (150 mg/L). Carbon isotope composition of methane ( $\delta^{13}\text{C}_{\text{CH}_4}$ ) showed significant fluctuation after inhibition phase (from  $-57.3 \pm 0.2$  ‰ to  $-19.3 \pm 0.3$  ‰), indicating that the HCH toxicity influenced mainly activity of acetoclastic methanogens, deduced from apparent fractionation factor ( $\alpha_c$ ). Isotope fractionation of  $\gamma$ - and  $\alpha$ -HCH under aerobic or anaerobic conditions has been demonstrated<sup>1</sup>, implying the potential to track biotransformation in microbial systems. The carbon stable isotope fractionation in AD system gave similar carbon isotope enrichment factors ( $\epsilon_c$ ,  $-3.2 \pm 0.2$  ‰ for  $\gamma$ -HCH and  $-3.8 \pm 0.3$  ‰ for  $\alpha$ -HCH), compared with anaerobic transformation under sulfate reducing conditions. This suggests that reductive dehalogenation is a major transformation pathway in the AD reaction.

Our results suggest that the isotope fractionation of HCH allows tracking transformation pathways and the isotope composition of  $\text{CO}_2$  and  $\text{CH}_4$  allows monitoring performance of biogas formation<sup>2</sup>. In addition, AD appears to be an option for the treatment of HCH contaminated biomass.

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ID: 130

## Drought-Induced Anomalies Of Soil Water Stable Isotopes Enable Identification Of Deep Root Water Uptake

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The biophysical process of transpiration recently received increased attention by ecohydrologists as it was proven the largest water flux on earth (Evaristo et al., 2015). However, fundamental aspects related to the questions how and from which sources plants obtain water remain poorly understood (Pierret et al., 2016).

In this study, we leverage on drought-induced variations of the isotope depth profiles of soil water in order to investigate root water uptake depths during an extreme situation in semiarid Namibia. The Bayesian mixing model MixSIAR was used to identify source water contributions of the most abundant plant species on site (*A. erioloba*, *B. plurijuga*, *C. collinum*, *S. luebertii* and *T. sericea*). Subsequently, a technique based on depth-specific deuterium labeling ( $^2\text{H}_2\text{O}$ ) and monitoring of successive uptake by plants was applied for constraining water uptake depths and to derive a root distribution.

The results obtained from MixSIAR reveal that most of the studied trees utilize either shallow (median source contribution: 19%) or deep soil water (median source contribution: 55%). Remarkably, individuals of *A. erioloba* are capable of accessing groundwater from the aquifer located at approximately 25m depth (median source contribution of groundwater: 37%). Combining these findings with the labeling experiments, we find that the lateral root zone at this site ends in between 2m and 2.5m. However, deeper uptake through taproots occurs frequently.

We discuss deep root water uptake in the larger context of understanding vadose zone water transport and methods of investigation using the example of semiarid Namibia. There is a need to develop field techniques for studying deep root water uptake and ecohydrological separation as well as to incorporate these aspects into modeling approaches.

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ID: 124

## Picky Carnivorous Plants: Preferences For Preys' Trophic Levels

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### *Introduction.*

Carnivorous plants invest carbon and nutrients in extraordinary trap structures which fascinate humans all over the globe. Those traps are necessary to survive in nutrient-limited habitats by receiving extra benefits from trapped prey.

Many studies were performed about their costs-and-benefit balance utilizing stable isotope approaches in tropical and subtropical hotspots while there is an obvious knowledge gap for temperate specimens, for instance within the bladderwort family (Lentibulariaceae). Despite representing the largest carnivorous plant family with members occupying both aquatic and terrestrial habitats the nutrient-translocation from prey to plant was scarcely analysed. Here, we aimed to compare the nutrient-translocation of terrestrial and aquatic Lentibulariaceae to further carnivorous plants with a focus on their specific prey preferences.

### *Material & Methods.*

Costs in terms of physio-environmental stress ( $^{13}\text{C}$ ) and benefits in terms of prey-derived nutrient gain ( $^{15}\text{N}$ ) of the carnivorous life strategy of two species, each terrestrial butterworts and aquatic bladderworts, from Germany and Austria were analysed (EA-IRMS).

To calculate the nutrient-uptake efficiency non-carnivorous references (terrestrial autotrophic plants, aquatic phytoplankton) and prey animals (insects, spiders, aquatic zooplankton) were used as end-members for the linear mixing model. Prey animals were graded by trophic level to identify trophic-level-dependent influences of plants' enrichment.

### *Results.*

The natural stable isotope abundances were successfully used to calculate the contribution of prey-derived nitrogen to carnivorous plants' tissue (*Pinguicula alpina* 54 %, *Utricularia australis* 24 % and *U. minor* 21 %). Habitat conditions could lead to either an underestimation of nutrient-uptake-efficiency for *P. vulgaris* or the plants were not restricted to prey capture for nitrogen nutrient-

gain. *Pinguicula* species fed mostly on phytophagous prey, while apart from nitrogen the species utilized a proportion of carbon additionally. For aquatic *Utricularia* zooplankton contributed to a smaller proportion to the plants' nutrition, but phytoplankton seems to be utilized as additional source.

#### *Conclusion.*

The efficiency of terrestrial *Pinguicula* species in gaining prey-derived nutrients is similar to other sticky leaf plants (e.g. *Drosera*). The efficiency-calculation using the linear mixing model depends on suitable data, which can be influenced by habitat properties (e.g. N-deposition). A certain proportion of carbon is taken up from prey, but habitat properties seem to influence carnivores'  $^{13}\text{C}$  values additionally. Aquatic *Utricularia* turned out to be equally effective as other aquatic carnivorous plants. The utilization of plankton as end-members of the linear mixing model states itself as elegant method to circumvent issues with a lack of suitable aquatic reference plants.

ID: 128

## Stable Isotopes As Flux Tracers: Assessing The Vegetation-Soil-Atmosphere Processes In Grasslands Under Drought Stress

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The functional understanding of plant-soil-feedbacks within the water cycle and their coupling to productivity is of particular interest in shallow rooted ecosystems with no access to groundwater, like for instance grasslands. Stable isotopes are an excellent tool to trace and assess these plant-soil-feedbacks, they provide insights into water fluxes in the soil and at the soil-plant interface.

The aim of our project is to study the effects of extreme drought stress on the water and carbon cycling of a temperate grassland. For this purpose, a 1 in a 100-year drought is simulated by rain-out shelters in a temperate grassland area, located in Freiburg im Breisgau, Germany. In addition, we combined the drought stress treatment with a nitrogen fertilizer treatment. Our project focuses on the functional understanding of ecohydrological feedbacks between vegetation, soil and atmosphere and their link to nutrient availability and productivity.

Water stable isotopes are used as primary tool in our project. We combine laser spectroscopy with a) gas-exchange chamber systems (Dubbert et al., 2013) and b) gas-permeable polypropylene tubing in order to continuously measure ecosystem (water) fluxes and their isotopic signatures. The gas-permeable tubes are a novel method that allows the undisturbed, in-situ and high-frequency monitoring of water vapour equilibrated to the soil water (Rothfuss et al., 2013). In addition, stable isotope techniques are combined with soil data (volumetric water content, soil temperature), micrometeorological data (eddy covariance, climate data) and ecophysiological methods.

The combination of these methods will enable us to partition ecosystem evapotranspiration in its components soil evaporation and transpiration and to assess their key drivers. Partitioning evapotranspiration is pivotal to draw a complete picture of the ecosystem water cycling and quantify its components, in particular the ecosystem water loss for plant productivity. Moreover, we can monitor changes in plant water uptake profiles in response to drought and nitrogen addition as well as altered soil water distribution.

We expect that extreme drought stress will probably cause a shift in the species composition and abundance of the grassland and, thus, will change the vegetation cover of the ecosystem. A decreased productivity and reduced vegetation cover due to drought stress will likely increase soil evaporation, which again decreases soil water availability and enhances the drought stress on the vegetation. Changes in vegetation cover are likely controlled by species-specific ecohydrological responses to drought stress, in particular in the uptake/loss of water and the water use efficiency.

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## Persistence of sugar-derived C in soil is controlled by the initial use of the C positions in the microbial metabolism

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Transformation of organic substances by microorganisms is a key process influencing carbon (C) stabilization in soil. To reveal the mechanisms responsible for the persistence of labile compounds in soil, the fate of position-specific and uniformly  $^{13}\text{C}$  labeled glucose and ribose were studied under field conditions for 800 days.  $^{13}\text{C}$  was quantified in bulk soil, microbial biomass and dissolved organic carbon (DOC).

Incorporation of glucose C-4 and C-1 were lower than C-2 and C-6 in bulk soil (BS) and microbial biomass (MB) on day 3. Ribose utilization showed lower incorporation of C-1 than C-5 in BS and MB on day 3. Low incorporation of glucose C-4 and ribose C-1 reveal that glycolysis and the pentose phosphate pathway (PPP) were simultaneously involved in the transformation of sugars. However, the mean residence time (MRT) of uniformly labeled  $^{13}\text{C}$  ribose in BS and MB were 3 and 2 times higher than glucose, respectively. This suggests that ribose and glucose were incorporated into different cellular components. Continuous decrease of glucose  $^{13}\text{C}$  in BS and MB over time revealed that recycling dominated glucose transformation in soil. The differences in MRT of individual glucose C positions indicate intensive metabolization and incorporation of modified compounds. Unexpectedly, the MRT of glucose C-1 and C-4 was higher than C-2 and C-6 in BS and MB. This could reflect incorporation of C-1 and C-4 into cellular components with lower turnover such as amino sugars directly or by backflux via gluconeogenesis after mineralization. On contrary, ribose  $^{13}\text{C}$  in soil stabilized after 250 days, implying stabilization in non-living soil organic matter (SOM). As expected, the MRT of ribose C-1 was 2- and 3-fold lower in BS and MB than C-5, respectively, confirming that recycling of ribose occur to a minor extend. On direct utilization of ribose, is the formation of ribonucleotide backbone of nucleic acids. After cell death, the nucleic acid interacts strongly with mineral fractions in the soil, becoming unavailable for microbial reuse. This reflects the differences in biochemical utilization of ribose and glucose, and subsequent differences in stabilization mechanisms in soil.

Persistence of glucose C in soil is dominated by recycling while stabilization in non-living SOM accounts for persistence of ribose. This information is not only useful in broadening the understanding of the persistence of labile compounds in soil, but also underscores the role microbial processes in SOM stabilization.

## Microbial Food Preference For Sorbed Versus Necromass C: Position-Specific Labeling Tells The Story

ID: 142

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Sorption to mineral surfaces is one of the most important processes contributing to soil organic matter (SOM) stabilization. While this stabilization is commonly attributed to inaccessibility of the sorbed SOM to microorganisms, recent findings have revealed increased metabolic efficiency from sorbed substrates. The application of position-specifically <sup>13</sup>C labeled sorbed tracer, combined with compound-specific <sup>13</sup>C analysis of phospholipid fatty acids (PLFA), enables determination of whether this higher efficiency is due to a metabolic shift in a) the whole microbial community or b) microbial specialists adapted to sorbed C sources.

To assess metabolic changes induced by sorption in individual microbial groups, we added uniformly and position-specifically <sup>13</sup>C labeled alanine to a loamy Luvisol and incubated the soil samples for 10 days. Two different amendments were compared: i) alanine sorbed to sterilized soil, and ii) free alanine in solution. Incorporation of C from individual alanine positions was evaluated in distinct microbial groups classified by <sup>13</sup>C-PLFA analysis.

Most of the microbial groups took up sorbed and free alanine equally. The metabolic pattern was also similar in most microbial groups: incorporation of C from carboxylic C-1 into PLFA was negligible, whereas C from the amino-bound C-2 and the methyl C-3 were preferentially incorporated into PLFA. This pattern reflects the basic microbial metabolism of C<sub>3</sub> molecules - fast mineralization of C-1 via pyruvate decarboxylation. Only fungi incorporated more C from sorbed than free alanine into their PLFA. Their metabolic pattern also revealed a more complex metabolization via gluconeogenesis, followed by pentose-phosphate pathway. While the incorporation into most microbial groups' PLFA remained stable or decreased over 10 days, the <sup>13</sup>C in Actinobacteria's PLFA increased up to 7 times from day 1 to day 10. This strong <sup>13</sup>C increase in Actinobacteria was explained by their uptake

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of secondary substrates derived from microbial necromass or secretion products.

This experiment showed that the more efficient metabolization of sorbed substrates is the work of microbial specialists: While uniform labeling revealed the higher incorporation of sorbed than free substrate into fungal PLFAs, position-specific labeling allowed the reconstruction of metabolic changes triggered by sorption of the substrate.

## Solvent Stress Induced Changes Of Cell Membrane Fatty Acids Decrease Isotope Fractionation During Microbial Denitrification

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Nitrogen loss in aquatic environments is mostly due to heterotrophic or autotrophic nitrate respiration to N<sub>2</sub>. Analysis of nitrogen stable isotope fractionation is a valuable tool for assessing denitrification processes. This process produces nitrogen isotope effects in the residual nitrate which are driven by so far largely unknown environmental and physiological factors. If the mechanistic understanding of fractionation during heterotrophic denitrification is understood, stable isotope analysis of nitrate could potentially be used to quantify denitrification in aquatic habitats.

We found an influence of solvent stress induced by organic contaminants on the nitrate reduction isotope enrichment factor and correlated it to a major indicator of solvent stress on the cell: the composition of the fatty acids in the lipid cell membrane. An increase in maximum membrane composition of two different organic solvents produces an increase in the degree of saturation of the fatty acids in the membrane and indicates cell stress. At the same time, the extent of stable isotope fractionation is lessened, causing less negative isotope enrichment factors measured in the residual nitrate during denitrification by a well-studied pure culture. We hypothesize that a reduction in nitrate transport across the cell's (cytoplasmic) membrane in relation to the nitrate reduction process within the cell is the explanation for the observed effects. The transport limitation, specifically the limitation of efflux of unreacted nitrate, would mask the isotope effects originally created within the cell during enzymatic nitrate reduction, since less nitrate is able to transfer this isotopic signature outside the cell. If this effect is not considered during application of isotope enrichment factors for the quantification of denitrification in stressful aquatic environments, an underestimation of the real nitrate reduction is likely.

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## Insights in N<sub>2</sub>O processes after grassland break-up by using N<sub>2</sub>O isotopocules

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Increased nitrogen mineralisation due to soil organic matter and old grass sward decomposition is a major consequence of grassland break-up. This can result in enhanced nitrous oxide (N<sub>2</sub>O) emissions, while N<sub>2</sub>O is one of the most important greenhouse gases contributing to climate change. To provide mitigation options, it is necessary to understand the processes involved in N<sub>2</sub>O production, as well as N<sub>2</sub>O consumption (i.e. N<sub>2</sub>O reduction to N<sub>2</sub>).

Stable isotope analyses of soil-emitted N<sub>2</sub>O ( $\delta^{18}\text{O}_{\text{N}_2\text{O}}$  and  $\delta^{15}\text{N}_{\text{N}_2\text{O}}^{\text{SP}}$ , i.e. the intramolecular distribution of <sup>15</sup>N within the linear N<sub>2</sub>O molecule) were used in an isotopocule mapping approach to simultaneously estimate the magnitude of N<sub>2</sub>O reduction to N<sub>2</sub> and the origin of the N<sub>2</sub>O, i.e. the fraction of N<sub>2</sub>O emitting from the bacterial denitrification pathway or fungal denitrification and/or nitrification. This approach is based on the comparison of measured isotopic signatures with mixing endmember areas of isotopic values for the N<sub>2</sub>O produced from different sources reported in the literature. Two main scenarios with different assumptions for N<sub>2</sub>O produced were calculated: N<sub>2</sub>O is reduced to N<sub>2</sub> before residual N<sub>2</sub>O is mixed with N<sub>2</sub>O of various sources and vice versa. Seven different scenario variations using a range of isotopic endmember values and assuming different fractionation factors of N<sub>2</sub>O reduction were applied to find the most reliable scenario. Investigations were carried out over one year following grassland renewal and grassland conversion to maize cropping on two different soil sites (Plaggic Anthrosol and Histic Gleysol) near Oldenburg, Lower Saxony Germany.

Results indicated heterotrophic bacterial denitrification and/or nitrifier denitrification as the main source of N<sub>2</sub>O production, with a significant contribution of N<sub>2</sub>O reduction to N<sub>2</sub> rather than nitrification and fungal denitrification throughout the entire study period. A tendency to a higher proportion of N<sub>2</sub>O reduction to N<sub>2</sub> was observed for the often water-saturated Histic Gleysol, while lower N<sub>2</sub>O reduction was found for the Plaggic Anthrosol.

## Two Dimensional Isotope Fingerprint Of Plant Methoxyl Groups – Application To Biogeochemical Research

ID: 114

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The biospheric C<sub>1</sub> methyl (CH<sub>3</sub>) pool of plant origin, including mainly lignin and pectin methoxyl groups (OCH<sub>3</sub>), comprises ca 2.5% of the total amount of carbon in plant biomass. We have discovered that plant methoxyl groups have both distinct stable hydrogen isotope ( $\delta^2\text{H}$ ) and carbon isotope ( $\delta^{13}\text{C}$ ) values (1-4). Relative to the bulk biomass of plants, the carbon isotope fractionation exhibited by the plant methoxyl pool covers large areas attaining a fractionation of up to -50‰, the largest ever yet observed value in the plant kingdom (1). On the other hand, a striking <sup>2</sup>H depletion of wood methoxyl groups relative to source water was observed with a uniform apparent isotopic fractionation (mean  $-213 \pm 17$  ‰) noted over a range of  $\delta^2\text{H}$  values for meteoric water from -20 to -120 ‰ (4) indicating that methoxyl groups reflect the isotope values of the woody plants meteoric source water. These particular  $\delta^2\text{H}$  and  $\delta^{13}\text{C}$  isotopic signatures have large potential for applications in biogeochemical research.

In this presentation we compile the recent advances of measurements of stable carbon and hydrogen isotope values of plant methoxyl groups, discuss/propose fundamental reasons of their origin and show several examples for their applications in the field of biogeochemical research. We provide examples for studies of paleoclimate (e.g. tree rings of the Holocene and Eocene), food science (e.g. authenticity of vanillin) and origin of volatile organic compounds (e.g. methanol and chloromethane) in the atmosphere.

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## The role of biological black carbon production for Chernozem genesis

ID: 131

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Chernozems are typical soils of native semiarid temperate grasslands and characterized by a deep and dark topsoil due to pronounced accumulation of soil organic matter. Chernozems preserve large amounts of stable polycondensed aromatic carbon (black carbon) covering about 10–45% of soil organic carbon being one key factor for their high soil organic matter stocks and also for their enhanced soil fertility. Chernozem genesis is still matter of speculation. Soil forming processes range from soil organic matter accumulation by high biomass production and limited degradation due to summer drought and winter coldness to accumulation of fire-derived pyrogenic organic matter (black carbon). Timing of formation covers several periods throughout the Holocene, especially the early Holocene. Vegetation cover ranges from grass to forest steppe. The aim of our study was to compare soil organic matter quantity and quality of a buried Chernozem in Central Germany developed until  $8,066 \pm 378$  cal. a BP with an adjacent typical Chernozem being exposed to soil formation and degradation during the whole Holocene. For this purpose, we analysed benzenepolycarboxylic acids as molecular markers for black carbon concentration and source in combination with microbial residues (bacterial muramic acid vs. fungal amino sugars).

Our results revealed an older and faster formation of Chernozems in Central Germany, at least for the buried Chernozem at the Salty Lake Amsleben. Soil organic matter and black carbon contents were lower compared to the reference Chernozem. Black carbon contribution to total organic carbon of the buried Chernozem was similar to other Chernozems. As demonstrated by benzenepolycarboxylic acid patterns, black carbon sources were similar in all Chernozems of the World. At least part of it (about 20%) were formed by biological black carbon production, e.g. black pigments of *Aspergillus niger* and other, yet unknown soil organisms producing polycondensed aromatic moieties similar to black carbon. Amino sugar analysis revealed a lower contribution of fungal residues in the buried Chernozem compared to the adjacent Chernozem. What still remains unclear are the significant correlations between black carbon contents and a) soil organic matter contents and b) wetter climatic conditions, which need further research attention.

## Assessment of Stable Isotope Fractionation during Diffusive Transport and Biogeochemical Transformations in the Subsurface

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Stable isotope signatures of reactive compounds and their changes during reactive transformations in the subsurface have become an important tool for the detection and understanding of biogeochemical processes. For the interpretation of observed stable isotope signatures it is however necessary to consider the potential impact of transport or other non-reactive processes on the available data. In particular, molecular diffusion may significantly affect the distribution of stable isotope signatures even in cases where the diffusion process is not leading to any additional stable isotope fractionation. This can lead to severe challenges in the quantitative and qualitative assessment of observed isotope data.

There is thus a need for conceptual approaches allowing for the consideration of biogeochemical transformation and diffusive transport for assessing biogeochemical transformations and stable isotope fractionation of reactive compounds during diffusive transport the subsurface. Beside mathematical analyses, numerical modeling approaches have a high potential to study the interaction of reactive and transport processes and their combined effect on stable isotope data. This allows for studying the relevance of diffusive transport for the interpretation of observed data and can also be used to explore the validity of theoretical assessment schemes used for the analysis of the data.

The present study uses a numerical reactive transport modeling approach to study the biogeochemical transformation and stable isotope fractionation of organic compounds in two typical porous media settings dominated by diffusive transport: aqueous diffusion of dissolved solutes in marine sediments and gas-phase diffusion of volatile compounds in water-unsaturated porous packings. In the marine sediment example the sequential transformation of organic compounds along a decay chain is studied considering the impact of their diffusion along the sediment column. Theoretical assessment concepts for such decay chain from the literature have been expanded and their validity has been tested. Results of the analysis show that these theoretical concepts are only applicable if diffusion would not be compound specific. In the

unsaturated porous packing biodegradation and stable isotope fractionation of a volatile organic compound have been investigated considering gas-phase diffusion as dominant transport process. Results show that available theoretical concepts can be adapted to obtain quantitative estimates of the observed stable isotope fractionation process.

In combination the obtained results show that the interpretation of stable isotope data systems with diffusion dominated transport is not straight forward. Reactive transport modeling can support the interpretation of such data and can determine the limits of theoretical assessment schemes.

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## Simplified Method To Determine Chlorine and Bromine Isotope Ratios Of Chloride and Bromide In Water By GC-qMS

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Compound-specific stable isotope analysis (CSIA) is a technique to determine stable isotope ratio of a certain element in an organic compound. The application of CSIA for chlorine (Cl-CSIA) or bromine (Br-CSIA) is highly relevant to study fate and transport of pollutants in the environment, since many of environmental pollutants are halogenated organic compounds. Yet, their application is limited due to mainly three difficulties: (1) the use of high-resolution mass spectrometer (IRMS), which is not readily available, (2) the requirement of an upstream, time-consuming chemical conversion of chlorine or chloride to methyl chloride (CH<sub>3</sub>Cl) for IRMS analysis and (3) an absence of standards that can be injected to gas chromatograph (GC). Available isotope standards for chlorine and bromine are in a form of chloride or bromide, not in a form of organic compounds. Here, we present a set of simple and innovative techniques for Cl- and Br-CSIA for chloride and bromide in the water phase. The techniques were developed through a collaboration between Hydroisotop GmbH (Schweitenkirchen) and TU Darmstadt.

Hydroisotop GmbH has successfully developed a quick and innovative method to convert chloride in the water phase to isopropyl chloride (IPCl) and bromide to isopropyl bromide (IPBr). Briefly, a water sample containing chloride and/or bromide in a vial is to be evaporated to dryness at 120 °C. Then, phosphoric acid and isopropanol are added to the vial. The vial is closed tightly and heated at 80 °C for 20 hours. After cooling, the headspace sample containing IPCl and/or IPBr is ready for Cl- as well as Br-CSIA.

TU Darmstadt has developed a simple and precise method for Cl-CSIA and Br-CSIA for IPCl and IPBr. The Cl- and Br-CSIA is carried out using a standard GC/quadrupole MS online connected to a Purge and Trap for sample enrichment. IPCl, IPBr and possible residue in a sample were separated in GC. Then, the peak signal intensities of the masses of 63, 65, 78 and 80 for IPCl also the masses of 122 and 124 for IPBr were determined in SIM mode in qMS. Using a set of unique mathematical equations developed in this study, the chlorine and bromine isotope ratios for these compounds are determined. The precision of  $\pm 0,5 \text{ ‰}$  or better was achieved for both Cl-CSIA and Br-CSIA under optimized conditions.

This is the first method that enables Cl-CSIA for IPCl as well as Br-CSIA for IPBr using GC/qMS.

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## Online-measurements of $^{15}\text{N}_2$ and $^{15}\text{N}_2\text{O}$ from soil incubation experiments coupled to an IRMS system – first results

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Determining the N Isotopic composition of gaseous (i.e.  $^{15}\text{N}_2$  and  $^{15}\text{N}_2\text{O}$ ) products from  $^{15}\text{N}$  enriched pools produced during soil incubation experiments is carried out to distinguish different  $\text{N}_2$  and  $\text{N}_2\text{O}$  forming processes.

So far, gas samples are collected from incubation experiments and measured offline. This is done using a modified commercially available automatic preparation system consisting of a modified gas-bench coupled to an IRMS as described in Lewicka-Szczebak et al. (2013).

Such offline results only give punctual insight into short time spans of the  $\text{N}_2$  and  $\text{N}_2\text{O}$  production processes during the conducted experiments. Especially information on longer incubation periods thus is lacking. To overcome this gap in information on the processes we connected the head space of a soil incubation mesocosm to the above mentioned modified IRMS system and aimed at measuring the stable isotope ratios  $^{29}\text{N}_2/^{28}\text{N}_2$  and  $^{30}\text{N}_2/^{28}\text{N}_2$  originating from  $\text{N}_2$  alone,  $\text{N}_2 + \text{N}_2\text{O}$  and  $\text{N}_2\text{O}$  alone online in a flow-through-mode. The soil in this mesocosm had been supplied with  $^{15}\text{N}$  labelled nitrate and glucose shortly before the measurements started. As expected, we continuously observed enrichment in  $^{15}\text{N}$  of both  $\text{N}_2\text{O}$  and  $\text{N}_2$  during the measurement.

Reference gas measurements were conducted replacing the mesocosm by a bottle which contained either  $\text{N}_2$  alone or  $(\text{N}_2 + \text{N}_2\text{O})$  reference gas. Results from repeated online measurements showed reasonable standard deviations of about 0.08‰. The first results of these online measurements will be presented.

## Simultane Analyse atmosphärischer CO<sub>2</sub>- und CH<sub>4</sub>-Konzentrationen und δ<sup>13</sup>C-CH<sub>4</sub>-Werten in diskreten Gasproben aus einem Isotopenverdünnungsexperiment (CH<sub>4</sub>ScarabDetect) mit Hilfe von Cavity-Ring-Down-Spektroskopie

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<sup>3</sup> University College Dublin

Die Messung des Methanaustausches zwischen Böden und der Atmosphäre mit der manuellen Haubenmessmethode in Kombination mit einer Isotopenverdünnungstechnik ermöglicht die nicht-invasive Bestimmung von Netto- und Bruttomethanflüssen. Allerdings ist dieser Messansatz noch nicht weit verbreitet (u. a. wegen benötigter Probengasmenge, Verfügbarkeit und Kosten von Messsystemen zur Analyse stabiler Kohlenstoffisotope). Der Picarro Cavity-Ring-Down-Spektrometer (CRDS) G2201-i in Verbindung mit einem Small Sample Isotope Module (SSIM) bietet die Möglichkeit der Messung von δ<sup>13</sup>C-CH<sub>4</sub>-Werten in diskreten Gasproben (≤ 20 ml). Allerdings wurde der G2201-i zur Bestimmung natürlich vorkommender δ<sup>13</sup>C-CH<sub>4</sub>-Werte in der Atmosphäre entwickelt und das SSIM ist bei Probenmengen unter 40 ml nicht für Gaskonzentrationsmessungen geeignet. In der hier vorgestellten Studie testen wir derzeit, ob 1) das SSIM nicht doch für Konzentrationsmessungen verwendet werden und damit einen Gaschromatographen (GC) ersetzen kann, und 2) ob das Messsystem auch für die Messung von Proben mit hohen <sup>13</sup>C-CH<sub>4</sub>-Konzentrationen geeignet ist. Die Proben stammen aus einem Mesokosmen-Freilandexperiment (CH<sub>4</sub>ScarabDetect). Zu Beginn der Messungen wurde die <sup>13</sup>C-CH<sub>4</sub>-Konzentration in den Hauben auf 2 – 6 at. % erhöht. Anschließend wurden über eine Haubenschließzeit von 40 Minuten alle 10 Minuten zwei Luftproben gezogen und in Glasfläschchen injiziert – je eine Probe für einen SRI Instruments 8610C GC mit Autosampler (25 ml in 12 ml Exetainer) und eine für den CRDS (45 ml in 20 ml Headspace Vial). Für die CRDS-Messung mussten die Proben manuell in das SSIM injiziert werden, von dem sie dann in einen Trägergasstrom (Nullluft) geleitet wurden. Probenmengen unter 20 ml wurden im SSIM zuerst mit Nullluft auf 20 ml aufgefüllt. Erste Messungen (n=100) zeigten, dass es mit Hilfe des SSIM-internen Drucksensors möglich ist, Kalibrationskurven zur Berechnung der injizierten Probenmengen zu erstellen. Die aus den Headspace Vials extrahierbare Probenmenge lag bei durchschnittlich 15±3 ml. Die verdünnungskorrigierten CO<sub>2</sub>- und CH<sub>4</sub>-

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Konzentrationen wichen im Durchschnitt nur um 3,10 bzw. 0,01 ppm von den GC-Messwerten ab – allerdings mit sehr hohen Standardabweichungen (55,87 bzw. 0,09 ppm). Eine zweistufige Verdünnungskorrektur der CRDS-Konzentrationsmesswerte scheint notwendig, um eine verlässliche Qualität der Messergebnisse bei Probenmengen unter 20 ml zu erreichen. Bei  $\delta^{13}\text{C-CH}_4$ -Werten über 700 ‰ gab der G2201-i regelmäßig eine Warnmeldung ab, was den Messvorgang jedoch nicht beeinträchtigte und es wurden auch keine Probenverschleppungseffekte beobachtet. Die gemessenen  $\delta^{13}\text{C-CH}_4$ -Werte stimmten mit den theoretisch erwarteten Werten überein und werden in einem nächsten Schritt mit NIST-Standards verglichen.

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## Determination of $N_2O$ and $N_2$ production in soil via $15N$ labeling and incubation in $N_2$ depleted atmosphere in an automated soil mesocosm system

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Agricultural soils are a major source of atmospheric  $N_2O$ , a potent greenhouse gas and ozone depleting substance. Improving  $N_2O$  mitigation options requires better understanding of the involved microbial processes and their controlling factors.

To further investigate these controls, we deployed an automated soil mesocosm incubation system. In this system, up to 64 intact or repacked soil cores can be incubated at preselected temperature regimes. The soil moisture in these soil cores can be adjusted and manipulated throughout the incubation via an irrigation system in the lid and vacuum underneath a suction plate at the bottom of each mesocosm. The headspace of each soil core is flowed through by an incubation atmosphere at constant rate, and in the efflux gas the concentrations of  $CO_2$ ,  $N_2O$ ,  $CH_4$ ,  $O_2$ , and  $N_2$  are continuously monitored by online gas chromatography. In studies targeting  $N_2$  production via denitrification  $15N$  labeled nitrate is applied to the soil and gas samples are collected at the outlets of the soil cores headspaces for  $N_2O$  and  $N_2$  isotope analysis by IRMS according to Lewicka-Szczebak et al. (2013). Here, an  $N_2$  depleted incubation atmosphere containing 2%  $N_2$  in helium and oxygen significantly increases the analytical sensitivity for  $15N_2$ .

In the present study a sandy soil was amended with 60 at%  $15N$  labeled potassium nitrate and with or without ground ryegrass as organic carbon source and incubated under  $N_2$  depleted helium atmosphere with varying  $O_2$  levels (0 – 20%  $O_2$ ). Parallel treatments received unlabeled nitrate and were incubated in synthetic air to allow  $N_2O$  isotopomer analysis by IRMS as described before (e.g. Köster et al., 2013) to gain information about contributing  $N_2O$  source processes.

During the session we will present first results of this study.

Dominika Lewicka-Szczebak, Reinhard Well, Anette Giesemann, Lena Rohe, Ulrike Wolf: An enhanced technique for automated determination of  $15N$  signatures of  $N_2$ , ( $N_2+N_2O$ ) and  $N_2O$  in gas samples. RCM 2013, 27, 1548-1558

ID: 115

## Improving Accuracy of Environmental Measurements with Natural Air

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The increase in concentrations of green house gases (GHG) in the atmosphere, attributed in large part to human activities, has contributed to an increase in global temperatures. Many countries have entered into agreements to limit and / or decrease GHG emissions. This requires precise measurements by region to clearly evaluate GHG emissions, sinks and evolution as well as mitigation strategies. High precision measurements are a key requirement to study and evaluate the global carbon cycle and its effect on climate change.

Calibrating the analytical instruments used to make atmospheric measurements are often done using standards prepared in synthetic air. There are significant differences between synthetic air and natural air which can introduce bias into some measurements; therefore natural air is preferred. This presentation will examine the natural air and isotopic mixture preparation process and the role of precisely characterized materials, highlighting stability of isotopic mixtures in natural air. Emphasis will focus on adjustment of isotope ratios to more closely bracket sample types without the reliance on combusting naturally occurring materials, thereby improving analytical accuracy.

## Low ppm Sulphur Measurements Using Flash Organic Elemental Analyzer

ID: 111

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Brechbühler AG, Schweiz

The importance of sulfur determination has grown significantly in geology, agronomy, petrochemistry, environmental sciences, food authenticity and forensics. Today many of the classical methods are no longer suitable for routine analysis. However, analytical instruments improve the reliability of data and laboratory productivity, without the use of hazardous chemicals.

Using Organic Elemental analyzer coupled to a FPD we are able to quantitate down to 3ppm samples and achieve a LOD of estimated 0.5ppm for the sulfur determination in solids i.e soils.

ID: 156

## A new in situ method for Li isotope measurements with femtosecond-LA-MC-ICP-MS

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At magmatic temperatures metal isotope fractionation is mainly caused by diffusion, as shown by previous studies. These processes can be observed as isotopic zonation in magmatic olivines and pyroxenes where the fast-moving element Li is of special interest to give insights into the timescales of fast-paced volcanic processes. Modeling of chemical and isotopic diffusion profiles may provide valuable information on cooling or degassing processes shortly before a volcanic eruption. So far, in situ Li isotope analyses have been performed with SIMS, but these analyses seem to suffer from composition-dependent matrix effects. Furthermore, conventional LA-MC-ICP-MS techniques have been applied which generate relatively large (50-150  $\mu\text{m}$ ) and deep laser spots. However, a laser spot size of  $\sim 30 \mu\text{m}$  is required to analyze diffusion profiles of magmatic minerals ( $< 500 \mu\text{m}$ ) with sufficient spatial resolution. A femtosecond laser ablation system coupled to a Neptune Plus MC-ICP-MS allows for this spatial resolution as well as an ablation depth of only a few  $\mu\text{m}$ , and furthermore it enables largely matrix-independent metal isotope analyses and increased internal precision, repeatability and accuracy. Here, we analyzed various silicate reference glasses with low Li concentrations (3-20 ppm) by fs-LA-MC-ICP-MS in order to establish an analytical setup for Li isotope analyses of chemically and isotopically zoned olivine and clinopyroxene crystals with  $< 10 \text{ ppm Li}$ .

Due to the low concentration of the element of interest, signal intensities of only some mV can be obtained which raises the question of the ideal detector assembly. The lighter isotope  $^6\text{Li}$  is measured with an ion counter whereas the heavier isotope  $^7\text{Li}$  is measured on a faraday cup. In this case, internal precisions of individual analyses mainly depend on the amplifier which is used on the faraday cup. Materials with concentrations down to 3 ppm can be measured with a  $10^{11} \Omega$  resistor with acceptable precisions of  $< 1.2 \text{ ‰}$  (2 RSE). Lower Li concentrations, yielding signal intensities of only 5-10 mV for  $^7\text{Li}$ , can be measured with a  $10^{13} \Omega$  resistor with a precision of  $< 1.4 \text{ ‰}$  (2RSE). The time delay of the  $10^{13} \Omega$  resistor has to be corrected by a  $\tau$ -correction which improves the internal precision of a measurement by up to 30 % compared to blank corrected results. With the latter combination precise in situ  $\delta^7\text{Li}$  values can be determined for minerals and glasses with Li concentrations of  $\sim 1 \text{ ppm}$ . Two natural olivines have been analyzed successfully with this method so far.

## Performance of various glass fiber filter types for organic C content and stable isotope ratios of suspended particulate organic carbon (POC)

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To date, no consistent method for the determination of concentrations and stable isotope ratios of particulate organic matter (POC) in natural waters is established. However, these parameters have major importance for understanding the global carbon cycle and to classify natural waters in aquatic chemistry. The main purpose of this study was the comparison of common filtration methods for the gravimetric analyses of carbon concentrations (%-carbon) and the corresponding stable isotope ratios ( $\delta^{13}\text{C}$ ) of POC in natural aquatic systems. The efficiency and reproducibility of four different types of glass fiber filters have been examined systematically. In addition, the influence of different drying methods, storage conditions and storage time on total suspended matter, particulate organic carbon and  $\delta^{13}\text{C}$ POC values was investigated.

The results show that pore sizes larger than 0.5 mm are not appropriate for a proper determination of particular parameters in natural waters. The method of drying can significantly impact the record of POC concentrations. Freeze drying and oven drying with 60 °C are nearly identical with respect to suitability and efficiency. However, oven drying with a temperature of 105 °C showed systemically higher concentrations of suspended matter and POC. The exact reason is so far unclear but it is suspected that drying at high temperatures is vulnerable for cross-contamination inside the drying oven. In contrast to the carbon concentrations, the  $\delta^{13}\text{C}$  values showed almost identical values by various combinations of different filter types and drying methods. With respect to storage conditions, significant changes in all parameters occurred at all tested temperatures after ten days of storage.

ID: 123

## Shit happens – but under which climate: On the potential of stable isotope analyses in midden research

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In the western USA and northern Mexico the atmospheric circulation pattern since the late Pleistocene have been under constant debate. We aim to contribute to this discussion by applying a newly developed coupled isotope biomarker paleohygrometer approach that uses  $\delta^2\text{H}$  of plant leaf-wax *n*-alkanes and  $\delta^{18}\text{O}$  of sugars. Both can serve independently as proxies in (paleo)-environmental studies. By coupling these two proxies, they can be used to reconstruct paleoaridity (Zech et al. 2013). Here we present first results from faecal pellets of packrat midden from the Guadalupe Canyon, northern Mexico (Borrelli and Holmgren, 2016). The coupled biomarker analyses approach has not yet been applied to packrat midden. The specific aims of our study are (i) to test the feasibility of the coupled biomarker approach on faecal pellets, (ii) to address the question whether paleoclimate information can be inferred from the isotopic composition of the faecal pellets and (iii) to explore whether it is moreover also possible to draw conclusions on paleoatmospheric circulation pattern. Acknowledgements: We would like to cordially thank Marianne Benesch and Heike Maennicke from the Biogeochemistry Group at the MLU Halle-Wittenberg for support of the laboratory work.

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Borelli and Holmgren, 2016. Dietary modifications of packrats in response to changing plant communities: Evidence from fossil plant cuticles spanning 55,000 years in Sonoran Desert packrat middens. *Journal of Arid Environments* 135, 1-8. Zech, M., Tuthorn, M., Detsch, F., Rozanski, K., Zech, R., Zöller, L., Zech, W. and Glaser, B., 2013. A 220 ka terrestrial  $\delta^{18}\text{O}$  and deuterium excess biomarker record from an eolian permafrost paleosol sequence, NE-Siberia. *Chemical Geology* 360-361, 220-230.

## Development of a LC-IRMS method for the compound-specific carbon stable isotope analysis of halobenzoates

ID: 155

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Compound-specific stable isotope analysis (CSIA) has been developed and applied over the last decades for the investigation of in situ transformation as well as of reaction mechanisms of common environmental pollutants. Thus far, approaches are well established and available for common GC-amenable groundwater contaminants such as chlorinated ethenes or BTEX-substances, however, they are still challenging for more polar pollutants such as halogenated benzoic acids.

The occurrence of halogenated benzoic acids in the environment is related to their agricultural use, as for pure substances in herbicides or metabolites of other halogenated compounds as fungicides. Under anaerobic, denitrifying conditions halo-benzoates can be degraded by e.g. *Thauera chlorobenzoica* by using 3-chloro-, 3-bromo- as well as 2-fluoro- and 4-fluorobenzoic acids as their sole source of carbon and energy (Kuntze et al. 2011). The class I benzoyl-CoA-reductases (BCRs) were responsible for dehalogenation and the proposed mechanism for meta-substitution showed a primary dearomatization of the aromatic ring followed by a rearomatization under halogen-elimination.

To further investigate the mechanism involved, we aimed to characterize the reductive dehalogenation by *T. chlorobenzoica* 3CB-1T for degradation of various mono-halogenated benzoates using CSIA. Regarding carbon stable isotope analysis of polar compounds using liquid chromatography - isotope ratio mass spectrometry (LC-IRMS), the main challenges are the requirement for a carbon-free liquid carrier phase as well as the instability of commercially available LC-columns in pure aqueous systems. Therefore, a method was established to separate halogenated and non-halogenated benzoic acids using solely inorganic buffer conditions. All tested halogenated benzoic acids could be eluted by using a potassium hydrogenphosphate buffer as carrier phase. Subsequently, the method was employed to study the isotope fractionation occurring during the course of dehalogenation of halobenzoates by *T. chlorobenzoica* 3CB-1T.

### Reference:

Kuntze, K., Kiefer, P., Baumann, S., Seifert, J., von Bergen, M., Vorholt J. A., Boll, M.; „Enzymes involved in the anaerobic degradation of meta-substituted halobenzoates“, *Mol. Microbiol.* (2011) 82(3): 758-769.

ID: 137

## A First Technical Approach To Quantify System Efficiency With Stable Isotopes Of Dissolved Oxygen During Engineered Growth Of *Galdieria Sulphuraria*

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*Galdieria sulphuraria* is an eukaryotic microalgae that can tolerate high temperatures and low pH-values. Due to this flexibility regarding various environments it is used to exploit secondary metabolic products such as carotenoids, vitamins and phycobiliproteins. For this study it was grown in a first technical approach in a closed system experiment for 29 days. In this time period, 6 separate flasks were sampled for oxygen concentration and their stable isotope ratios ( $^{18}\text{O}/^{16}\text{O}$ ) in dissolved and headspace phases. The oxygen isotope composition of the water was also analyzed as an input for the transfer of its  $^{18}\text{O}/^{16}\text{O}$  ratio to molecular oxygen via production by algae. This photosynthetic transfer of the isotope composition of water was counterbalanced by oxygen consumption that enriched both phases in  $^{18}\text{O}$ . For this reason, neither dissolved oxygen nor oxygen in the headspace reached the  $^{18}\text{O}$ -depleted oxygen isotope ratio of  $\text{H}_2\text{O}$  despite excessive photosynthesis. Oxygen that was produced by photosynthesis accumulated with a yield of  $13.96 \text{ mmol L}^{-1}$  in the headspace and with  $0.5 \text{ mmol L}^{-1}$  in the fluid phase. This difference was due to rapid degassing of the solution. It was further amplified by preferential consumption of the dissolved  $\text{O}_2$  phase. In order to quantify oxygen production and its consumption we determined photosynthesis/respiration (P/R) ratios with a formula that combined  $\text{O}_2$  concentrations and its isotope ratios. It revealed P/R ratio of 7.7 after 11 days. After this it decreased again and moved towards dominance of respiration. With this our results introduce a new method to monitor the growth and efficiency of algae in controlled experiments.

## Sauna, Sweat and Science II: Do We Sweat What We Drink?

ID: 151

**Michael Zech<sup>1,2</sup>, Marianne Benesch<sup>1</sup>, Johannes Hepp<sup>1</sup>, Steven Polifka<sup>1</sup>, Bruno Glaser<sup>1</sup>**

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In a previous study, we used 2H- and 18O-labelled water in a sauna experiment in order to quantify the proportion of condensation water versus sweat on the skin of test persons (Zech et al., 2015). In this follow-up study we aim at addressing the question how fast and how efficient is drinking water secreted as sweat and urine by sauna visitors. The experimental setup comprised 6 test persons: one serving as control, four performing pulse labelling by drinking half a liter of labelled Cola-Weizen and one test person repeating the pulse labelling three more times in approximately 40 min intervals. The labelled Cola-Weizen was prepared by adding 2 ml D2H (99.8%) resulting in a  $\delta^2\text{H}$  value of approximately 25,600‰. Sweat was collected using autosampler vials for gas chromatography and  $\delta^2\text{H}$  was measured on a Thermo Conversion - IRMS coupling.

During six rounds of sauna, the sweat  $\delta^2\text{H}$  value of the control person increased gradually from -29 to +23‰. This reflects that the water vapor in the sauna became progressively 2H-enriched and part of this vapor was condensing at the skin (Zech et al., 2015). The first sweat samples of the pulse-labelled test persons taken 10 to 15 min after labelling yielded  $\delta^2\text{H}$  values of  $73 \pm 40$ ‰. Two sauna rounds later, i.e. approximately after 90 min, the  $\delta^2\text{H}$  values reached  $195 \pm 37$ ‰ and did not further increase for the rest of the sauna experiment except for the test person that repeated the pulse labelling three more times and reached a final  $\delta^2\text{H}$  value in its sweat of 741‰. Urine of this later test person reached a maximum  $\delta^2\text{H}$  value of 870‰ approximately 20 hours after the labelling and then gradually decreased again. It can be concluded that at least in the short-term, we do not sweat what we drink (195 versus 25,600‰). Given that furthermore the  $\delta^2\text{H}$  values of sweat did not reach values that can be expected when the label would have completely mixed with body water (this would have resulted in approximately 250‰ according to a mass balance calculation), we pose the question: where did the rest of the label go?

ID: 151

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## **A stable isotope (H, C, N, O, S) hydrobiogeochemical characterization of ground waters in Northeastern Gemany**

ID: 139

**Anna-Kathrina Jenner<sup>1</sup>, Michael E. Böttcher<sup>1</sup>, Iris Schmiedinger<sup>1</sup>, Maren Voss<sup>1</sup>, Gerd Böttcher<sup>2</sup>, Beate Schwerdtfeger<sup>2</sup>**

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The evolution of ground waters in Mecklenburg-Vorpommern (MV; North-Eastern Germany) one of the catchment areas for the southern Baltic Sea, is controlled by different natural and anthropogenic factors. In the present study the hydrochemical and stable isotope (H, C, O, S) composition of shallow ground waters was investigated. A mass balance approach is combined with physico-chemical modeling to define the mineral dissolution/precipitation potential as well as the processes taking place during the ground water development.

The dissolved inorganic carbon system of the ground waters is found to be controlled by the dissolution of biogenic carbon dioxide, the dissolution of (marin) carbonates and oxidation of anthropogenically introduced DOC and at a few sites biogenic methane. The sulfur isotope composition of dissolved sulfate indicates the substantial impact from the oxidation of sedimentary pyrite using oxygen or nitrate as electron acceptor at a number of settings. The nitrogen and oxygen isotope composition of dissolved nitrate indicate its origin as well as further microbial superimposition. The combined results are the base for a quantitative reaction path analysis.

## Intercomparison of Cumulative Rain Collectors Used in Stable Isotope Studies

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Many isotope studies require a sound knowledge of the isotopic composition ( $\delta^2\text{H}$ ,  $\delta^{18}\text{O}$ ) of precipitation. To gather the corresponding samples, a range of cumulative rain collectors is available (IAEA 2014). Yet, to our surprise, we were unable to find a comprehensive intercomparison of these collectors and their ability to reduce evaporation in the published literature.

In this study, we rigorously tested a set of established (IAEA 2014) and unconventional collectors (floating ball-based, float-based). To this end, we partially filled them with water of known isotopic composition and placed them for 32 days in a modified laboratory oven. In this oven, we simulated a rather harsh climate with a relative humidity of approx. 5 % and a diurnal temperature regime (26–45°C). Evaporative mass losses were determined by weighing the collectors once a day. Every four days, we took water samples for isotopic analyses.

The classic paraffin oil-based collector showed the smallest mass losses and isotopic shifts. However, also the tube-dip-in-water collector with pressure equilibration tube (Gröning et al. 2012) performed well. Although it exhibited greater mass losses and isotopic shifts, the results were still acceptable. From a practical view point, it also has the advantage that it is easier to handle since it does not require the at times complicated oil separation step. Hence, we think it represents a good compromise.

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Gröning, M., Lutz, H.O., Roller-Lutz, Z., Kralik, M., Gourcy, L., Pölsenstein, L. (2012): A simple rain collector preventing water re-evaporation dedicated for  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  analysis of cumulative precipitation samples. *Journal of Hydrology*, 448-449, 195-200.

IAEA (2014): IAEA/GNIP precipitation sampling guide.

## Hydrogeologische Untersuchungen im Chongwe Einzugsgebiet in Sambia

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Within the Groundwater Resources Management Support Programme, a bilateral cooperation project between the German Federal Institute for Geosciences and Natural Resources and the Zambian Water Resources Management Authority, stable isotopes were sampled from the Chongwe catchment as part of the Middle Zambezi catchment in Zambia. It covers a total area of 5,150 km<sup>2</sup> with prevailing schist, quartzite and basement complex lithologies as well as one moderately yielding aquifer consisting of a carbonate lens. In two sampling campaigns for water quality in December 2014 and March/April 2015 stable isotopes were taken from over 40 groundwater sampling points. Stable isotopes were also sampled from rainfall in Chongwe town for one rainy season. Additional data from nearby Lusaka where rainfall had been sampled between 2012 and 2015 was used for a Local Meteoric Water Line.

There is a strong indication for direct groundwater recharge happening all over the Chongwe catchment. The samples occur between -40 ‰ and -50 ‰  $\delta^{2}\text{H}$  and -6 ‰ and -8 ‰  $\delta^{18}\text{O}$  with an arithmetic mean of -7 ‰  $\delta^{2}\text{H}$  and -45 ‰  $\delta^{18}\text{O}$ . In relation to the weighted mean values per month, the groundwater samples are relatively depleted. In fact they are lighter than the arithmetic mean of all rainfall samples from Lusaka and Chongwe. This can only be explained by mixing with a lighter end member (around -8 ‰  $\delta^{2}\text{H}$  and -55 ‰  $\delta^{18}\text{O}$ ) which hasn't been identified yet, or with an amount effect, which would imply that only rainfall events with relatively depleted values contribute to groundwater recharge. However, correlating the Lusaka and Chongwe rainfall  $\delta^{2}\text{H}$  values with the rainfall amount per event during two rainy seasons does not show a clear amount effect.

Findings from the stable isotope analysis suggest a groundwater recharge process that includes direct recharge without being ultimately clarified.

ID: 129

## Nutzung isotopehydrologischer Wasseranalysen für eine Beurteilung von Oberflächenwasser-Grundwasser-Wechselwirkungen

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Um den Schutz von Grundwasserressourcen gewährleisten zu können, müssen die Grundwasserneubildungsgebiete und Wechselwirkungen mit Oberflächenwässern bekannt sein. Da Oberflächen-, Grund- und Niederschlagswässer sich aufgrund von Verdunstungs- und Kondensationsprozessen im natürlichen Wasserkreislauf in ihren d18O- und d2H- Stabilisotopensignaturen unterscheiden und diese sich nach dem Eintritt in Grundwassersysteme nur noch durch Mischung ändern, können d18O und d2H als natürliche Tracer zur Identifikation der Herkunft und Zusammensetzung eines Wassers genutzt werden.

Im Rahmen des BMBF-Projektes StygoTracing-EZG (FKZ: 031B0245) wird, in Zusammenarbeit mit dem Institut für Grundwasserökologie IGÖ GmbH, die Wechselwirkung zwischen Grund- und Oberflächenwasser mittels d18O- und d2H-Daten analysiert. Im Vorfeld wurden durch die Universität Landau sieben Untersuchungsgebiete ausgewählt. Vier dieser Gebiete befinden sich in Bayern, und jeweils ein Gebiet in Sachsen, Baden-Württemberg und Rheinland-Pfalz. Die insgesamt 57 Beprobungen (Interstitial, Hydranten, Brunnen, Grundwassermessstellen und Quellen) erfolgten im Herbst 2016.

Der Oberflächenwasseranteil in einer Grundwasserprobe wurde durch eine Zweikomponentenmischungsrechnung ermittelt. Als Eingangssignale fungierten lokale, langjährig gewichtete und höhenkorrigierte Isotopensignaturen deutscher GNIP-Stationen sowie jeweils eine Probe aus dem Datenkollektiv eines Untersuchungsgebietes als unbeeinflusstes Grundwasser. Mittels der Mischungsrechnung konnten die Proben in Oberflächenwasser-beeinflusstes und geogen geprägtes Grundwasser (<50 % Oberflächenwasseranteil) unterteilt werden. Weiterführende Analysen basieren ausschließlich auf der Datenmenge der geogen geprägten Grundwässer. So wurden einerseits die beprobten Grundwässer auf die lokalen Effekte der Höhe und Kontinentalität, welche bei deutschen GNIP-Isotopensignaturen festgestellt werden konnten, durch Korrelation überprüft. Andererseits wurde die Höhenlage des Grundwasserneubildungsgebietes des jeweiligen Untersuchungsgebietes

auf Basis einer linearen Regression der langjährigen mittleren  $d^{18}O$ -/  $d^2H$ -Daten nahegelegener GNIP-Stationen abgeschätzt. Abschließend erfolgte die Durchführung einer Clusteranalyse nach dem Medianverfahren zur Identifikation isotopenhydrologischer Ähnlichkeiten.

Die Mischungsrechnung ergab für die geogen geprägten Grundwässer einen Oberflächenwasseranteil zwischen 13 % und 33 %. Die lokalen Effekte der Höhe bzw. Kontinentalität konnten mit einem Korrelationskoeffizienten von -0,92 bzw. -0,73 in den beprobten Grundwässern nachgewiesen werden. Die Schätzung der Höhenlage der Grundwasserneubildungsgebiete ergab in Rücksichtnahme auf topographische und hydrogeologische Gegebenheiten plausible Ergebnisse. Die Clusteranalyse zeigte, dass stabilisotopenhydrologische Ähnlichkeiten nicht nur durch lokale Nähe, sondern auch durch ähnliche Ausprägungen des Höheneffekts hervorgerufen werden. Große Ähnlichkeiten lassen auf gemeinsame bzw. nahegelegene Grundwasserneubildungsgebiete schließen.

**ID: 120**

## **Event sampling campaigns of stable isotopes indicating groundwater and anthropogenic influences in the large scale Weser River Basin**

**Kelly Stanley<sup>1</sup>, Paul Koeniger<sup>2</sup>**

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Hydro chemical and isotope hydrological investigations in large river basins are relatively rare most likely due to logistical reasons. Such comparative studies of high spatial and adequate temporal resolution provide multiple sources of information on river basin influences and characteristics, such as geogenic background, possible pollutants, processes (runoff characterisation, residence times of runoff components, e.g., direct flow and groundwater). At the Weser river basin (42,000 km<sup>2</sup>) several sampling campaigns have been conducted during 2008 (May), 2009 (January, August) (Koeniger et al. 2009) and 2017 (March, May, July), within which surface water samples were collected at about 40 sites within the river basin.

During the 2017 campaigns, additional hydro chemical parameters (major anion and cation concentrations, trace elements) and stable isotopes (above deuterium and oxygen-18 from water, also nitrogen-15 and oxygen-18 from nitrate) were investigated. In addition to seasonal and altitude patterns of the stable water isotopes, anthropogenic influences and potential pollution sources derived from the hydro chemistry and stable isotope characteristics will be discussed.

## Identification of freshwater flow paths in salt mine collapses at Soltvyno, Ukraine

ID: 148

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Recently, the two last operational salt mines in Soltvyno, Ukraine, were unexpectedly flooded. As a result, large craters with diameters of up to 250 m, collapse and subsidence with associated tensional fractures formed and continue to develop. An advisory mission by the European Commission was launched in fall 2016 to conduct a detailed risk assessment. The expert team with specializations in mining, geology, hydrogeology, risk assessment, and civil engineering conducted field investigations and collected data with the help of Ukrainian scientists in order to assess the level of risk.

In addition to field observations, and interferometric synthetic aperture radar (SAR) to study ground movements, hydrogeological measurements (water level, chemistry, and stable isotopes) were used to identify groundwater flow paths. Water samples were taken from different locations (mine craters, shafts, surface water and ground water) and sent to BGR laboratories in Hannover for analyses. The situation of the Tisza River that borders the former mining area is also evaluated with respect to the potential for pollution on an international scale. Stable isotopes especially served for identifying different water types and to better understand the overall flow dynamics in the former mining area of Soltvyno. This study shows the advantage of an interdisciplinary approach to conduct a risk assessment in the case of large mine collapses.

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## Understanding groundwater recharge mechanisms in the Lake Chad Basin using soil water isotopes and chloride profiles

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The Lake Chad Basin is a transboundary catchment with an enormous importance for the entire region. Because it is located in an arid area, groundwater is the main source of water supply. For an effective management of groundwater resources, potential recharge areas need to be identified and protected. However, at present, almost no field research exploring unsaturated zone water transport process have been conducted.

In this study, depth profiles of soil water stable isotopes and chloride from six sites in the Salamat (3) and Waza-Logone (3) regions of Chad are analyzed and interpreted in order to characterize water transport processes, identify recharge pathways, and estimate groundwater recharge through the unsaturated zone. The samples were collected at a vertical resolution of 0.1m in December 2016 and June 2017. Soil water was extracted using an optimized setup of the cryogenic vacuum extraction method after Koeniger et al. (2011) and analyzed for stable water isotopes (2H, 18O) using a Picarro L2120i. Chloride concentrations were measured by ion chromatography after aqueous extraction from the soil samples.

The isotope depth profiles of Gos Djarat (Salamat) and Katoa (Waza-Logone) show 'typical' isotopic profiles (Allison et al., 1983) and suggest the possibility of direct ground water recharge. In contrast, the profile of the periodically inundated site Kach Kacha (Salamat) is enriched in 2H and 18O at depth with multiple peaks indicating the presence of indirect groundwater recharge. The chloride profiles for this site corroborate this finding by revealing several peaks of chloride displacement over depth, which might conserve the infiltration history over decades. An analysis of flood events from satellite images in conjunction with historic climate data might allow for identifying particular recharge events and thus enable defining local groundwater vulnerability. First estimates of recharge using the chloride mass balance method yield average groundwater recharge rates between 2 and 10 mmy<sup>-1</sup>.

## Low Oxygen Reduction Rates in a Porous Aquifer Suggest Lack of Denitrification

ID: 118

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Nitrate concentrations in the porous groundwater system of Hohenthann, Lower Bavaria, are among the highest in Bavaria with up to 120 mg/L (measured in 2014), more than twice the allowed threshold value of 50 mg/L for drinking water. Microbially driven redox processes markedly control the fate of organic and inorganic contaminants. Denitrification is such a redox process that has the potential to lower nitrate concentrations in groundwater under favourable conditions. As oxygen respiration is the most energetically favourable redox process, oxygen has an inhibitory effect on denitrification. For a better understanding of the prevalent redox conditions at the study region, O<sub>2</sub> reduction rates were determined using modelled mean groundwater transit times (MTT). This was done by using environmental isotopes (δ<sup>2</sup>H & δ<sup>18</sup>O, 3H/3He, 14C) linked with a lumped parameter modelling approach. In addition, we also analysed stable isotope compositions of dissolved nitrate (δ<sup>15</sup>N & δ<sup>18</sup>O) to evaluate the effect of O<sub>2</sub> concentrations on potential denitrification in the aquifer.

Results indicate that the main source of nitrate contamination is excess manure application, mixed with reacted and unreacted mineral fertilisers, indicated by slightly elevated δ<sup>18</sup>O values of nitrate (Median of δ<sup>18</sup>O = 2.6‰) and δ<sup>15</sup>N values ranging from -0.61 to 19.7‰ with a median of 8.3‰. This may also indicate that denitrification is not a dominant process in this groundwater system. Groundwater MTT in the perched aquifer were determined to range between 2 and 5 years. Wells in the main groundwater body access a mix of very old water with up to a few thousands of years (14C) and relatively young water with 20 to 40 years (3H/3He and 3H time series). O<sub>2</sub> concentrations in the perched aquifer are generally high with a median of 275 μmol/L and decrease to 200 μmol/L in the main groundwater storey. In the very old groundwater storey of the limnic layers O<sub>2</sub> concentrations are low with a median of 56,3 μmol/L.

The O<sub>2</sub> reduction rate (zero-order) in the perched aquifer storey and the main GW storey was determined to ~1.9 μmol/(L \* year), which is fairly low in comparison to rates of up to 140 μmol/(L \* year) in DOC-rich shallow riparian zones. By extrapolating the O<sub>2</sub> reduction rates beyond the apparent MTT range of sampled groundwater, denitrification lag times of approximately 130 years were calculated. It is suggested that O<sub>2</sub> reduction processes are limited due to a lack of electron--donors.

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**Back-tracking the origin of alabaster from the ‚Ulrich Epitaph‘, Güstrow, Germany by means of stable S and O isotopes**

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Natural calcium sulphate minerals (like gypsum, in the variety of ‚alabaster‘) have been used for a long time for art and ornamental works despite it’s high solubility in aqueous solution due to its easy way of recovery and handling. To identify different European source provenances, geochemical and stable isotope forensic methods have been applied, thereby defining historical pathways of trade. A detailed geochemical characterization of both alabaster samples from the monument and potential sources is a pre-requisite for a backtracking material sources. Several tracers have been tested in the past identifying the coupled sulfur and oxygen isotope composition of the sulfate molecule in the evaporite minerals to be highly characteristic.

In the present study, we analyzed the stable sulfur and oxygen isotope composition of raw alabaster from the famous Ulrich Epitaph in Güstrow, Northeastern Germany, and compared the results with new measurements from one of the major European contributors of alabaster in the 16th century, the Cellaston quarry, Derbyshire (England) and literature data for further potential Spanish and French source quarries (Kloppmann et al., 2014; Archaeometry, 56).

We found that the stable sulfur and oxygen isotope signatures of alabaster from the Ulrich Epitaph indicate the origin from the Upper Triassic (Keuper) evaporites of the English Cellaston quarry and are not related to other potential alabaster sources. This further illustrates the alabaster trade way between England and Germany in the late 16th century.

## Influences Of Silvicultural Management Of *Cupressus Lusitana* On The Microbial Community In The Munessa Forest, Ethiopia: A Litter <sup>13</sup>C Labelling Study

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During the last decades, the demand for wood and agricultural areas in Ethiopia increased drastically. That is why intensive clear-cutting of natural forests was carried out e.g. in the Munessa region. To provide fast-growing wood, exotic tree species such as *Cupressus lusitana* were used in monocultural plantations to replace the bio diverse natural forests. Up to now, little is known on the effects of such intensive anthropogenic disturbance of pristine environments on soil properties, especially soil microbial ecology. Therefore, we studied if litter turnover by specific microbial groups and carbon sequestration into soil are affected by the transformation of natural forest into *Cupressus* plantation and by the silvicultural management (rotation age and thinning) of these plantation stands. To answer these questions, we replaced natural litter by <sup>13</sup>C- and <sup>15</sup>N-labelled litter in the Munessa forest and quantified microbial litter turnover over 2 years by <sup>13</sup>C incorporation into individual phospholipid fatty acids, which enabled us tracing of litter-derived C incorporation into distinct microbial groups.

Most of the labelled litter-C remained in the litter pool (53% 2 months after the labelling and 10% after 2 years) or was incorporated into the bulk soil pool (8% over the whole experimental period), whereas litter-C turnover by the soil microbial biomass was minor (1 to 3%). However, the key factors regulating litter-C turnover by individual microbial groups were litter quality, soil organic carbon, total nitrogen and soil water content. Most of the labelled litter-C in the Munessa forest was turned over by gram-negative bacteria, followed by gram-positive bacteria. Thereby, litter turnover was negatively affected by the transformation of natural forests into *Cupressus* plantation. During maturation of *Cupressus* plantations, a significant reduction of litter turnover by gram-positive bacteria and actinobacteria could be observed,

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probably evoked by declining soil organic matter levels. Thinning of young *Cupressus* stands decreased litter turnover by actinobacteria, while the opposite was observed when thinning was carried out in mature *Cupressus* stands.

Our study clearly shows that silvicultural management in the Munessa forest mainly decreases litter turnover by gram-negative bacteria, gram-positive bacteria and actinobacteria, while other microbial groups were not affected (saprotrophic fungi, protozoa and arbuscular mycorrhiza). Thus, a short-term C-sequestration in the microbial pool (especially the main decomposers) is negatively affected by the silvicultural management, whereas C-sequestration in the bulk soil pool remained more or less stable over the experimental period.

## Carbon isotopes and trace metals as tracers for carbon cycling in tidal marshes along an estuarine salinity gradient of the Elbe river (Germany)

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The temporal dynamics of the dissolved carbon system in four tidal marshes under impact of the Elbe river (Germany) were studied along a salinity gradient (0.3 to 30.7) to assess their impact as source/sink areas for DIC, TA, and selected trace elements for the southeastern coastal North Sea. Besides pH, TA, major and trace metals (Sr, Ba, Mn), the concentrations and stable carbon isotope composition DIC were followed in the main creeks of each sampling station over complete tidal cycles at different seasons.

Substantial differences in salinity and tidal responses in concentrations of trace elements and the dissolved inorganic and organic carbon system were observed. Carbon isotope signatures of DIC down to -13.9 ‰ vs. VPDB were observed, with the isotopically most enriched DIC (up to -1.5 ‰ vs. VPDB) found to be associated with the highest salinities. The tidal dynamic in dissolved concentrations of DIC was high, showing an up to 3-fold difference between low and high tide waters. Whereas, Sr was impacted by mixing processes and carbonate dissolution, Ba showed a dependence from sulfate availability, and dissolved Mn was controlled by benthic microbial activity and fluxes across the sediment-water interface. The application of a binary mixing model based on the cationic and stable isotope composition reveal that both carbonate mineral dissolution at all sites and benthic microbial sulfate reduction at the brackish sites are important sources for producing alkalinity.

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## Sulfur isotope biogeochemistry of sediments and soils from a temperate coastal-wetland transition zone, southern Baltic Sea

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Land-ocean interactions in the coastal zone (LOICZ) are of particular interest regarding the exchange of elements, like nutrients, carbon and sulfur. We present here new results on the sulfur biogeochemistry of coastal sediments and an adjacent recently rewetted wetland (Hütelmoor, southern Baltic Sea) that are dynamically connected via water exchange (flooding events, SGD, surface water drainage). Several long stationary and mobile pore water lances were applied to follow the dynamics of the pore water composition in the coastal sediments with time. Beside of this, up to 10 meter long sediment cores from the Hütelmoor were investigated (isotope) geochemically. The sites are positioned at different distances to the Baltic Sea coastline. The soils were analyzed for the elemental composition (CNS), reactive iron and sedimentary sulfur contents, iron sulfide micro-textures, as well as the stable sulfur isotope composition of inorganic and organic sulfur fractions to understand signal development for the biogeochemical carbon-sulfur cycles in such a dynamic ecosystem.

Following a recent flooding event with brackish Baltic Sea water, the sulfur isotope composition of sulfate in surface waters draining the peatland indicate the impact of solutions that were modified by net microbial sulfate reduction. In the peat cores, we found evidence for the activity of dissimilatory sulfate-reducing microorganisms and the associated formation of pyrite with different textures (framboids, single euhedral crystals and clusters) and sulfurization of organic matter. Sedimentary sulfur fractions and their stable isotope signatures are controlled by the availability of dissolved organic matter or methane, reactive iron, and in particular dissolved sulfate and thereby from the relative position to the coast line and the given lithology. Sulfur isotope values in the pyrite fraction vary in a wide range between -21 and +15 per mil versus VCDT, in agreement with spatial and temporal dynamics in the extend of sulfate-limiting conditions during the oxidation of reduced carbon.

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## **A Multi-Element Stable Isotope Natural Abundance Approach Indicates Partial Mycoheterotrophy Already For Equisetum Species – Living Fossils Among The Vascular Plants**

ID: 126

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### *Introduction/Aim:*

The ability to fix atmospheric CO<sub>2</sub> and convert it into sugars through photosynthesis sets plants apart from other organisms and is the key to primary productivity on earth. However, not all plants are photoautotrophic. Carnivorous, parasitic and mycoheterotrophic plants turned the tables covering their carbon demand at least partially or timewise through heterotrophy. In the case of mycoheterotrophic plants fungi serve as exclusive or additional carbon source.

Orchidaceae and Ericaceae are currently the most intensively investigated plant families with mycoheterotrophic representatives. During the last decade in both of these families, green-leaved species were unmasked as partially mycoheterotrophic in addition to achlorophyllous fully or initially mycoheterotrophic species. Unfortunately, a lack of investigations on partial mycoheterotrophy exists for the most widespread type of plant-fungus-interaction, namely the arbuscular mycorrhiza (AM). While more than 500 achlorophyllous AM species from ten angiosperm families and in addition AM gametophytes of mosses, lycopods and ferns are known as fully mycoheterotrophic, evidence for partial mycoheterotrophy in AM plants are currently scarce (few Burmanniaceae and Gentianaceae).

A one-hundred years' controversy discussed the mycorrhizal status of the last recent ancestor of the horse tails Equisetum which is considered as at least showing habitat-dependent AM. The aim of this study was to evaluate the mycorrhizal and mycoheterotrophic status of one representative of the first vascular plant clades on earth.

### *Materials and Methods:*

Microphylls and spread leaves of six Equisetum species and fully autotrophic co-occurring reference plants (RP) were collected in NE-Bavaria, Germany. Carbon and nitrogen stable isotope natural abundances were analysed (EA-IRMS). Additionally, for E. palustre and E. sylvaticum and their RPs hydrogen and oxygen stable isotopes were measured (TC-IRMS).

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*Results:*

Fungal colonisation was found for Equisetum roots. Microphylls of Equisetum were enriched in  $^{13}\text{C}$  (except for *E. palustre*) and  $2\text{H}$  compared to RPs. They also were more enriched in  $^{15}\text{N}$  (except for *E. arvense*) and mostly had higher nitrogen concentrations than RPs.

*Discussion:*

The isotope abundance and nitrogen concentration patterns found for Equisetum are known from green orchids and pyroloids to indicate partially mycoheterotrophic carbon and nutrient gain. Thus, Equisetum should be considered as a new clade of partially mycoheterotrophic plants.

*Conclusion:*

During the era of the Carboniferous coal forests, 30 m tall scale bark trees overtopped 10 m tall Equisetum ancestors. The potential of mycoheterotrophy could explain their carbon gain under these light-limited conditions and their restricted photosynthetic active leaf area (microphylls).

## Quantifizierung des Kohlenstoffabbaus in gärtnerischen Substraten unter Kulturbedingungen, Methodenentwicklung mit Hilfe der $\delta^{13}\text{C}$ – Analytik

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Für die Herstellung von Kultursubstraten und Blumenerden werden in Deutschland jährlich ca. 8,5 Mio. m<sup>3</sup> Torf verwendet, ca. 77% davon kommen aus Niedersachsen. Mit dem Abbau des Rohstoffes Torf sind große ökologische Probleme verbunden: Erhöhte Treibhausgas-Emissionen, Landschaftswandel, Verlust der biologischen Vielfalt und Veränderung des Landschaftswasserhaushalts.

Durch den künftig vermehrten Einsatz torfreduzierter und torffreier Substrate soll dem entgegengewirkt werden – dies wird aber zu einer Änderung der Substrateigenschaften führen, die Erwerbsgartenbauer in Deutschland seit Jahrzehnten eingesetzt haben. Diese neuen Substrate müssen daher diverse Güte- und Qualitätsanforderungen erfüllen, die chemischen, biologischen und physikalischen Eigenschaften umfassen.

Die Qualität von Substraten und der darauf angebauten Kultur wird maßgeblich durch dessen physikalische und v.a. auch chemische Stabilität bestimmt, d.h. durch längerfristige bzw. über eine bestimmte Kulturdauer andauernde Resistenz gegenüber mikrobiellem Kohlenstoffabbau.

Entsprechende Methoden zur Qualitätssicherung von Kultursubstraten werden in der Regel durch den Verband deutscher landwirtschaftlicher Untersuchungs- und Forschungsanstalten (VDLUFA) entwickelt. In Kultursubstraten, die in Containern zur Produktion eingesetzt werden, wurden bisher in situ keine Untersuchungen zum Kohlenstoffumsatz durchgeführt, da Methoden zur Quantifizierung des Substratabbaus fehlen.

Ziel dieses Versuches war es mittels der  $\delta^{13}\text{C}$  Stabilisotopentechnik einen Methodenansatz zu entwickeln, um langfristig eine neue Prüfmethode zur Qualitätssicherung von Substraten zu liefern. Dabei sollen die Kohlenstoffabbauraten der Substrate in Containerkultur in situ untersucht werden. Über eine Versuchsdauer von sechs Monaten wurde *Miscanthus giganteus* (C4) im Freiland als Containerkultur in zwei verschiedene Substrate (C3) getopft. An zwei Ernteterminen wurde der Abbau des Substratkohlenstoffs

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in Abhängigkeit von der Rhizomanzahl mittels der natural abundance Technik bestimmt. Auf diese Weise konnte in den ersten drei Monaten nach Versuchsbeginn in den eingesetzten Substraten ein Kohlenstoffabbau von ca. 10% nachgewiesen werden. Bis zum Ende des Versuches nach sechs Monaten stieg der Kohlenstoffabbau nicht mehr signifikant an. Diese Ergebnisse deuten darauf hin, dass die Stabilisotopenmethode auch in situ unter Kulturbedingungen eingesetzt werden kann. Die Schwankungen des Kohlenstoffabbaus zwischen den einzelnen Wiederholungen einer Variante bieten noch Möglichkeiten zur Verbesserung des Versuchsdesigns, z. B. der Wurzelarchitektur eingesetzten C4-Pflanzen.

## Tracing the Isotopic Signature of Carbon Sources for Marine Dissolved Inorganic Carbon via Keeling Plot Analysis

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In marine environments, dissolved inorganic carbon (DIC) concentrations often increase with depth together with an isotopic carbon signature shift to lighter values due to organic matter (OM) mineralization. The Keeling plot method was commonly used to determine the isotopic signature of carbon sources for ecosystem respiration. Conventionally, the influence of respiratory depletion of  $^{13}\text{C}\text{O}_2$  on the isotopic composition of the atmosphere was studied in terrestrial and limnic biogeochemistry. For this purpose, changes in concentration and  $\delta^{13}\text{C}$  of DIC over time were analysed. The basis of the Keeling plot method is conservation of mass. The same approach can be applied on OM mineralization in sediments and the water column. Mixing of bottom water derived background DIC and DIC released into the environment during organic carbon decomposition is assumed. In a modification of previous approaches, where changes in concentration and  $\delta^{13}\text{C}$  of DIC were followed over time, we analyzed vertical profiles which represent time-dependent variations superimposed by transport processes.

We used  $\text{DI}^{13}\text{C}$  gradients in the water column of the Black Sea and pore water profiles in the Black Sea and the Baltic Sea to estimate the  $^{13}\text{C}$  signature of the mineralized organic carbon via Keeling plot analysis. The Black Sea water column reveals a  $\delta^{13}\text{C}$  signature of the OM source of  $-22 \pm 2.3 \text{ ‰}$  which is close to the signature of typical particulate organic matter (POM) in the ocean ( $-18$  to  $-22 \text{ ‰}$ ) and previously reported values for the Black Sea euphotic zone ( $-24$  to  $-21.5 \text{ ‰}$ ). In the pore waters of Black Sea sediments (from short and long sediment cores), Keeling plot analysis clearly demonstrates that the released DIC at depth can be derived from different sources. An isotopically very light carbon source ( $<-60 \text{ ‰}$ ) was associated with anaerobic oxidation of methane in the Black Sea. Marine OM is the principal source for DIC in the deeps of Baltic Sea basins, while in sediments of basin margins, sand flats or bays, the calculated carbon source isotopic signature is shifted to less negative, hence, heavier values compared to marine OM. Shifts towards heavier  $\delta^{13}\text{C}$  signatures are attributed to potential dissolution of sedimentary carbonates or organic inputs of terrestrial  $\text{C}_4$  vascular plants like maize and other agricultural plants. The carbon source isotopic composition calculated via Keeling plot analysis correlates well with directly measured  $\delta^{13}\text{C}$  signatures of surface sediments POM.

## Carbon Input by Roots into the Soil: Quantification of Rhizodeposition from Root to Ecosystem Scale

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Despite its fundamental role for carbon (C) and nutrient cycling, rhizodeposition remains the hidden half of the hidden half: it is highly dynamic and rhizodeposits are rapidly incorporated into microorganisms, soil organic matter, and decomposed to CO<sub>2</sub>. Therefore, rhizodeposition is rarely quantified and remains the most uncertain part of the soil C cycle and of C fluxes in terrestrial ecosystems.

The present review synthesizes and generalizes the literature on C inputs by rhizodeposition under crops and grasslands (281 data sets). The allocation dynamics of assimilated C (after <sup>13</sup>C-CO<sub>2</sub> or <sup>14</sup>C-CO<sub>2</sub> labeling of plants) were quantified within shoots, shoot respiration, roots, net rhizodeposition (i.e., C remaining in soil for longer periods), root-derived CO<sub>2</sub>, and microorganisms. Partitioning of C pools and fluxes were used to extrapolate belowground C inputs via rhizodeposition to ecosystem level.

Allocation from shoots to roots reaches a maximum within the first day after C assimilation. Annual crops retained more C (45% of assimilated <sup>13</sup>C or <sup>14</sup>C) in shoots than grasses (34%), mainly perennials, and allocated 1.5 times less C belowground. For crops, belowground C allocation was maximal during the first 1-2 months of growth and decreased very fast thereafter. For grasses, it peaked after 2-4 months and remained very high within the second year causing much longer allocation periods.

Despite higher belowground C allocation by grasses (33%) than crops (21%), its distribution between various belowground pools remain very similar. Hence, the total C allocated belowground depends on the plant species, but its further fate is species independent.

This literature survey demonstrates that C partitioning can be used in various approaches, e.g. root sampling, CO<sub>2</sub> flux measurements, to assess rhizodeposits' pools and fluxes at pot, plot, field and ecosystem scale and so, to close the most uncertain gap of the terrestrial C cycle.

## Increased CO<sub>2</sub> fluxes from a sandy Cambisol under agricultural use three years after biochar substrate application in the Wendland region, Northern Germany

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In recent years, biochar as fertilizer additive has been discussed as an opportunity for carbon sequestration in arable soils. Field experiments under realistic conditions investigating the CO<sub>2</sub> emission from soil after biochar fertilizer addition are scarce. Therefore, we investigated the CO<sub>2</sub> emission and its isotopic signature after the addition of compost, biogas digestate and mineral fertilizer with and without biochar (0, 3, 10, 40 Mg biochar ha<sup>-1</sup>) to a sandy Cambisol in Northern Germany. Green waste was pyrolyzed at ~650 °C to obtain biochar with C<sub>3</sub> signature (-27.6 mUr). All treatments were fertilized with different C<sub>4</sub>-derived fertilizers (ranging from -12.7 to -17.4 mUr). Three years after the application of the biochar substrates, gas samples were taken biweekly during one growing season of *Lupinus angustifolius* using static chambers. The CO<sub>2</sub> concentration and its δ<sup>13</sup>C isotopic signature were detected using a gas chromatograph coupled to an isotope ratio mass spectrometer (GC-IRMS). The origin of the emissions was determined by a two-source mixing model.

During the growing season, the isotopic signatures of all treatments shift from a fertilizer-derived C<sub>4</sub> signal to a more C<sub>3</sub> influenced signal (soil organic matter), which indicates a preferential fertilizer mineralization after the application. Furthermore, the addition of biochar (10 Mg biochar ha<sup>-1</sup>) to compost does not affect the isotopic composition of the carbon emission. When high biochar amounts (40 Mg biochar ha<sup>-1</sup>) were applied together with mineral fertilizer or biogas digestate, CO<sub>2</sub> emissions increased by 30-60%. On average 49% ± 8% of the CO<sub>2</sub> emissions of these treatments originate from a C<sub>3</sub> source. The corresponding controls (0 Mg biochar ha<sup>-1</sup>) show similar emission patterns (52 % ± 5%). As biochar addition do not significantly change the isotopic composition of the total emissions (ratio of C<sub>3</sub>-derived emission to C<sub>4</sub>-derived emission) it is likely that co-metabolic degradation of biochar does not directly boost the CO<sub>2</sub> emissions. However, due to the increased total CO<sub>2</sub> emission after biochar application it is rather conceivable that the microporous surface of biochar supplies a suitable habitat and protection against predators as well as additional soil physical benefits for soil microbial biomass. These favorable soil conditions lead to an enhanced microbial respiration.

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