

Abstracts

36. Jahrestagung

der Arbeitsgemeinschaft Stabile Isotope (ASI) e. V.

30. September bis 02. Oktober 2013



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Wissenschaftliches Programm – Montag, 30.09.2013

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14:30 V1.4	Enhancing the performance of GC-IRMS for small samples <i>A. Hilkert (Bremen)</i>
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15:50 V1.6	Improved determination of $\delta^{13}\text{C}$ of soil-derived amino sugars by Ion Chromatography - Oxidation - Isotope Ratio Mass Spectrometry <i>S. Boesel (Halle, Saale)</i>
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Wissenschaftliches Programm – Dienstag, 1.10.2013

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09:00
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T. Piper (Köln)

09:20
V1.9 Future International Organic Stable Isotope Reference Materials
A. Schimmelmann (Bloomington, Indiana/US)

09:40
V1.10 Stable carbon isotope analysis of dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) in natural waters – Results from a worldwide proficiency test
R. van Geldern (Erlangen)

10:00–10:50 **Sektion 2 – Ökologie und Physiologie**

10:00
V2.1 Amino acids as precursors of methane in living plants
F. Keppler (Mainz)

10:20
V2.2 Metadatenätze von Isotopenhäufigkeiten als Werkzeug zur Aufklärung der vielschichtigen Ernährungsweisen bei mykoheterotrophen Pflanzen
G. Gebauer (Bayreuth)

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11:10–12:30 **Sektion 3 – Stoffkreisläufe in Ökosystemen**

11:10
V3.1 Relevance of Ca-isotope fractionation in pore waters in marine and terrestrial environments
C. Ockert (Jülich)

11:30
V3.2 Stabilisierung von pflanzlichen und mikrobiellen Kohlenhydraten in Böden mit C3-C4 Vegetationswechsel
A. Basler (Göttingen)

11:50
V3.3 C partitioning in soil microbial communities assessed by position-specific labeling and compound-specific isotope analysis of PLFA and amino sugars
M. Dippold (Göttingen)

12:10
V3.4 Real-time measurement of N₂O isotopomers and the ¹⁸O-N₂O isotopologue by laser spectroscopy above intensively managed grassland in Central Switzerland
B. Wolf (Dübendorf/CH)

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15:00 V4.1	Insights about natural atrazine degradation by the analysis of C and N isotope trends within the parent and its daughter compounds desethyl- and desisopropylatrazine <i>A. Meyer (Neuherberg)</i>
15:20 V4.2	Effect of phosphorus limitation on the $\delta^{18}\text{O}\text{-PO}_4$ of plant and soil phosphorus pools from a long term field experiment in Switzerland <i>V. Pfahler (Lindau/CH)</i>
15:40 V4.3	Multielement-Stabilisotopenanalyse offenbart partielle Mykoheterotrophie von Orchideen auf Almwiesen der Alpen <i>J. Schiebold (Bayreuth)</i>
16:00 V4.4	^{15}N tracer studies to evaluate nitrogen dynamics of food webs in two subtropical small scale aquaculture ponds under different management <i>J. Pucher (Stuttgart)</i>
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20:00	Conference Dinner

Wissenschaftliches Programm – Mittwoch, 2.10.2013

08:30–10:10	Sektion 5 – Klimaänderungen und -Rekonstruktionen
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08:50 V5.2	Combining ^{18}O and ^2H isotope biomarker analyses in paleoclimate research – a conceptual model, a calibration study and a first application <i>M. Zech (Bayreuth)</i>
09:10 V5.3	$\delta^{13}\text{C}$ from methoxyl groups a new climate proxy from high alpine larch trees <i>D.F. Riechermann (Mainz)</i>
09:30 V5.4	Influence of microsite conditions on oxygen isotope time series of <i>Pinus sylvestris</i> <i>M. Stantscheva (Mainz)</i>
09:50 V5.5	Compound-specific δD -analysis from Eifel maar deposits – a new palaeotemperature proxy derived from methoxyl groups? <i>T. Anhäuser (Mainz)</i>
10:10	Kaffeepause
10:50–11:50	Sektion 6 – Geologie und Hydrologie
10:50 V6.1	Effekte von Wasser-, Ton und Karbonatgehalten auf die ^2H - und ^{18}O -Isotopie des extrahierten Bodenwassers in Untersuchungen zur Wasseraufnahme von Bäumen <i>J. Dyckmans (Göttingen)</i>
11:10 V6.2	Zum Einfluss unterschiedlicher Windsysteme auf den Wasserhaushalt in einem Einzugsgebiet im westlichen Pamir Zentralasiens <i>C. Meier (Halle, Saale)</i>
11:30 V6.3	Stable isotope geochemistry of Franconian rivers – insights into hydrogeological processes and carbon turnover <i>R. van Geldern (Erlangen)</i>
12:30–13:00	Preisverleihung & Schlussworte
13:00–15:00	Laborführungen

From Inner Earth

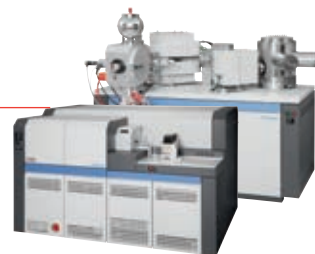
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ELEMENT 2, ELEMENT XR
and iCAP Q



Thermal Ionization MS
TRITON *Plus*
Multicollector ICP-MS
NEPTUNE *Plus*



Gas Isotope Ratio MS
MAT 253 and DELTA V



Noble Gas MS
ARGUS VI, HELIX MC *Plus* and
HELIX SFT



Vorträge – Sektion 1

Analytik: Neue Methoden und Techniken

V1.1

Optical Isotope Ratio Spectroscopy: Potential Impact from the European Metrology Programme

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¹Physikalisch-Technische Bundesanstalt, Braunschweig

Recent progress in optical spectrometry has led to an increased impact of the optical isotope ratio spectrometry (OIRS) to stable isotope measurements on gaseous molecular species containing C, N, O, H, or S atoms, both in environmental and geophysical as well as in agricultural research, respectively. OIRS measures molecular species as intact isotopologues, such being non-invasive and non-destructive. Several commercial OIRS instruments are on the market and often applied in real-world's applications. These commercial instruments, however, typically do not provide statements on traceability. Most instruments are laser-based OIRS methods. They can complement standard methods for isotope analysis such as isotope ratio mass spectrometry (IRMS). Laser OIRS techniques provide additional advantages to isotope ratio measurements due to their comparably small size and capabilities of resolving some issues of species interference known for conventional IRMS. In addition laser spectroscopic techniques are capable to perform in situ measurements onsite. At present, research projects are proposed within the European Metrology Research Programme (EMRP) [1] which shall address metrological aspects in OIRS applications such as traceability and measurement uncertainty assessments.

This presentation will summarize some of these metrological aspects and views on OIRS currently been introduced and promoted by the EMRP. The talk will focus on PTB's activities based on projects regarding water isotope analysis and conceptual OIRS strategies. The latter item is addressing the fact that there is some potential in OIRS to measure absolute isotope ratios rather than relative ones and the respective need for absolute spectral line data on isotope transitions in the infrared spectrum of the analyte. Questions concerning the traceability of commercial isotope analyzers will be discussed. Our isotope ratio measurement approach is relying on tunable diode laser absorption spectroscopy (TDLAS), cavity ring-down spectroscopy (CRDS), and Fourier-transform infrared (FTIR) spectroscopy, respectively.

[1] European Metrology Research Programme, <http://www.emrponline.eu>

V1.2

The use of a quantum cascade laser spectrometer to trace the C and O isotopic variation during CO₂ and H₂O gas exchange

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The use of stable isotopes in environmental research has experienced an impressive development in the past two decades. Even small variations in the ratio between heavy and light isotopes can reveal significant changes in plant ecophysiological processes, which are highly process specific. In studies of plant metabolic processes, C and O isotope ratios have been analyzed mostly on samples harvested in field experiments, using bulk organic material, which represents an integration of plant production over the vegetation period. During photosynthesis and growth several meteorological parameters affect plant metabolic processes simultaneously and with it isotope fractionation. For example, high light intensity usually co-occurs with high temperature. Warm and sunny weather conditions also tend to be dry (high vapor pressure deficit, VPD). Although it is difficult and often impossible to define, which of these three parameters is most responsible for certain fractionation events at the leaf, whole plant or even ecosystem level, important insights were still be gained on plant carbon water relations.

Yet, we have reached a level, where more detailed information is needed; e.g. how do specific environmental parameters (variations in irradiance, [CO₂], temperature and humidity) impact C and O isotope fractionation during plant metabolic processes. In this presentation we show the first data of CO₂ and H₂O gas exchange measurements, while the isotopic variability is simultaneously measured with a high resolution isotope laser spectrometer, coupled to a gas exchange system. In this study all the potential driving variables such as light (I), temperature (T), [CO₂] and VPD were kept constant while only one of these parameters was varied. Thus, we can assign the impact of each of these parameters on the magnitude of the fractionation processes. This will contribute to our understanding of isotopic variability, whether it is mostly controlled by the chain of diffusional conductance values, in particular stomatal or mesophyll conductance, or simply by changes in photosynthetic processes or changes in substrate use. To assess the changes in substrate use we will analyze individual compounds of leaf extracts from the same plants (by HPLC-IRMS for $\delta^{13}\text{C}$ and GC-pyrolysis for $\delta^{18}\text{O}$) with the goal to determine how the impact of the external factors is modified through biochemical fractionations.

The derived response patterns will be instrumental for the improvement of current isotope fractionation models, which are driven by the above mentioned variables. The potential for this new technique to study various plant stress factors such as drought, heat, chilling etc. will be discussed.

V1.3

A field-deployable CH₄ preconcentration unit for high-precision isotopic analysis by laser spectroscopy

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Methane (CH₄) is the most important non-CO₂ greenhouse gas (GHG) contributing 18% to total radiative forcing. Anthropogenic sources (e.g. ruminants, landfills) contribute 60% to total emissions and led to an increase in its atmospheric mixing ratio from 700 ppb in pre-industrial times to 1813 ± 2 ppb in 2011 [1]. Analysis of the most abundant methane isotopologues ¹²CH₄, ¹³CH₄ and ¹²CH₃D can be used to disentangle the various source/sink processes [2] and to develop target oriented reduction strategies. High precision isotopic analysis of CH₄ can be accomplished by isotope-ratio mass-spectrometry (IRMS) [2] and more recently by mid-infrared laser-based spectroscopic techniques. For high precision measurements in ambient air, however, both techniques rely on preconcentration of the target gas [3, 4].

In an on-going project, we developed a fully-automated, field-deployable CH₄ preconcentration unit that can be coupled to a quantum cascade laser absorption spectrometer (QCLAS) for real-time analysis of CH₄ isotopologues. The core part of the rack-mounted (19 inch) device is a highly-efficient adsorbent trap attached to a motorized linear drive system and enclosed in a vacuum chamber. Thereby, the adsorbent trap can be either coupled to the cold end of a Stirling cooler during CH₄ adsorption or de-coupled while heating the trap during desorption. This feature enables an effective thermal coupling between adsorbent trap and cooler which is vital in view of the low CH₄ boiling point of -162°C. A further key element in the design and development of the preconcentration device is the adsorption trap. Therefore, a wide variety of adsorbents was investigated, including: HayeSep D, molecular sieves (5Å and 13X) as well as the novel metal-organic frameworks (MOF) and carbon nanotubes (CNT). These materials were characterized regarding their surface area, isosteric enthalpy of adsorption and selectivity of methane over nitrogen. Based on these results, the most promising candidates were tested on the preconcentration device.

Our experiments show that quantitative adsorption/desorption and CH₄-preconcentration by a factor of >100 is feasible with the current instrumentation. Furthermore analytical interferants (e.g. N₂O, CO₂) can be separated by step-wise desorption of trace gases. Thus, our pre-concentration unit is a major step forward regarding field-applicability of trace gas preconcentration for subsequent high-precision analysis of isotopic composition or mixing ratios.

References:

- [1] WMO, *Greenhouse Gas Bulletin No. 8*, **2012**, WMO GAW, pp. 4.
- [2] H. Fischer, M. Behrens, M. Bock, U. Richter, J. Schmitt, L. Loulergue, J. Chappellaz, R. Spahni, T. Blunier, M. Leuenberger and T. F. Stocker, *Nature* **2008**, 452, 864-867.
- [3] J. Mohn, C. Guggenheim, B. Tuzson, M. K. Vollmer, S. Toyoda, N. Yoshida, and L. Emmenegger, *Atmos. Meas. Tech.*, **2010**, 3, 609-618.
- [4] J. Mohn, B. Tuzson, A. Manninen, N. Yoshida, S. Toyoda, W. A. Brand and L. Emmenegger, *Atmos. Meas. Tech.*, **2012**, 5, 1601-1609.

V1.4

Enhancing the performance of GC-IRMS for small samples

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The combination of Gas Chromatography with Isotope Ratio Mass Spectrometry (GC-IRMS) was introduced in 1988, opening the wide field of compound specific isotope analysis (CSIA). It combines the high purification efficiency of GC with the utmost precision of isotope ratio mass spectrometry.

Today compound specific isotope analysis of the main bioelements and their major isotopes ¹³C, ¹⁵N, ¹⁸O and ²H is a standard tool in many laboratories and is used in a wide range of applications. Consequently, this analytical tool is extending into new areas of research, in which smallest sample size at high precision is a must.

The development of more sensitive IRMS systems with optimized GC combustion and high temperature conversion interfaces is also related with modern sample introduction techniques, choice of GC columns, advanced GC technology, conversion technology and interfacing to the IRMS as well as data handling. New challenges in sample size and separation concern the improvement of sensitivity and GC resolution combined with full automation for higher sample throughput.

We will discuss in this presentation the neuralgic points in the GC-IRMS system with application examples on biomarkers and other important biomolecules linked to improvements in sample introduction techniques, GC- and reactor technology.

V1.5

New techniques to measure and reference the isotopic composition of CH₄ in air with high precision

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We developed an analytical setup to measure $\delta^2\text{H-CH}_4$ and $\delta^{13}\text{C-CH}_4$ simultaneously in one atmospheric sample. The setup is fully automated and measures up to 12 samples and 6 reference gases per day. We discuss relevant technical details and the system performance based on the first year of measurements.

Measurement accuracy offsets between laboratories and scale contraction artefacts are technical pitfalls in the isotopic analysis of atmospheric CH₄ that could be eliminated if a suite of isotope reference gases was available to all laboratories. Unfortunately, unique atmospheric reference gases for CH₄ in air do not exist. We are developing a method to quantitatively incorporate the hydrogen of VSMOW isotope scale material into CH₄, so the CH₄ is then itself representing the VSMOW reference scales for $\delta^2\text{H-CH}_4$. The produced $\delta^2\text{H-CH}_4$ isotope scale is then diluted with CH₄-free air so it can be used as an atmospheric isotope reference gas. We present our technical approach and show first results.

V1.6

Improved determination of $\delta^{13}\text{C}$ of soil-derived amino sugars by Ion Chromatography - Oxidation - Isotope Ratio Mass Spectrometry

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Amino sugars are the main constituent of microbial cell wall and are discussed to be the most relevant compound class of microbial-derived soil organic matter. To assess their dynamic $\delta^{13}\text{C}$ determination of this compound class became more and more demanded within the last decade and currently first LC-O-IRMS measurements arose. However, amino sugar determination sets several challenges to LC-O-IRMS measurements, due to high concentration difference within this compound class, high matrix content of hydrolysis extract, NaOH as eluent with CO_2 -binding activity and strongly different chromatographic behavior of basic and acidic amino sugars. Using further purification steps and an ion chromatograph instead HPLC we wanted to strongly facilitate $\delta^{13}\text{C}$ determination of amino sugars by liquid chromatography.

After acid hydrolysis we purified the extracts by iron precipitation, salt precipitation and a cation exchange resin to remove all components weakening chromatographic resolution. Measurement was performed by coupling an ion chromatograph (IC) to an isotope ratio mass spectrometer (IRMS). Performance of quantification as well as $\delta^{13}\text{C}$ determination was assessed by the standard addition approach.

The combination of iron and salt removal from gas chromatography protocols with purification via cation exchange resins adapted from liquid chromatography methods showed up to be an optimal sample preparation for performance and stability of chromatography as well as longevity of system components. In addition using an ion chromatograph sets clear advantages over HPLCs as metal and carbonate exclusion from the system avoids column contamination as well as disturbance of $\delta^{13}\text{C}$ determination by a carbonate background.

These improvements to previous methods enabled a parallel quantification and $\delta^{13}\text{C}$ determination of high-concentrated basic amino sugars and low-concentrated muramic acid. Recoveries ranged from 57-66% and internal standards (methylglucamine and fructose) can be used for correcting the losses during purification and enable quantification with a relative standard error <6%. The high differences in peak area of basic and acidic amino sugars require an amount dependent correction of $\delta^{13}\text{C}$ -values based on external standards. If done, accuracy of IC-O-IRMS was <1‰ for basic amino sugars and <1.5‰ for muramic acid compared to the PDB calibrated EA-IRMS values and a precision of <0.5‰ was gained. Isotopic LoQ of muramic acid enables its detection together with basic amino sugars in one measurement.

This method enables a parallel quantification and $\delta^{13}\text{C}$ determination of basic and acidic amino sugars in one chromatogram. Quality of quantification and $\delta^{13}\text{C}$ determination as well as sample throughput of this method met the demands for a spreading of this method in soil science. This can mainly be attributed to advantages of ion chromatography compared to classical HPLC for coupling with an isotope ratio mass spectrometer. Advantages of IC-O-IRMS compared to HPLC couplings are evident and might also bring advantages for other liquid chromatographic methods, whose broad use is frequently limited due to expensive and time consuming issues derived from carbonates or metals.

V1.7

Advancement in IRMS

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²Isoprime Ltd, Cheadle Hulme, Vereinigtes Königreich

Up until the present moment, the operation of an IRMS required the skilled presence of a trained technician to get good data out of the system. The setup and monitoring of the system required a high level of knowledge of the workings of such a system. The operation of a complete system requires a massive investment in time and money to get a new laboratory up and running. Together with our range of inlet products we present a solution that takes user error out of the equation and lets you concentrate on the important part, generating excellent data.

V1.8

Hydrogen Isotope Ratio Mass Spectrometry and High Resolution/High Accuracy Mass Spectrometry in Metabolite Identification Studies: Detecting Target Compounds for Sports Drug Testing

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²ThermoFisher Scientific, Bremen

Rationale: In sports drug testing, comprehensive studies on the metabolism of therapeutic agents with misuse potential are necessary to identify metabolites that provide utmost retrospectivity and specificity. By means of commonly employed approaches minor and/or long-term metabolites in urine might remain undetected. Hence, an alternative strategy to unambiguously identify the majority of urinary metabolites including low abundant representatives is desirable.

Methods: Urine samples were collected for 20 days during an elimination study with an oral dose of 5 mg of 17 α -C²H₃-metandienone. The specimens were processed according to established sample preparation procedures (including fractionation and deconjugation) and subjected to gas chromatography-hydrogen isotope ratio mass spectrometry (GC-TC-IRMS) analysis. Due to the deuteration of the administered drug, urinary metabolites bearing the deuterium label yield abundant and specific signals on the GC-TC-IRMS instrument resulting from the substantially affected ²H/¹H ratio. The sample aliquots were measured on a gas chromatography-time of flight mass spectrometer (GC-Q/TOF) using identical GC conditions as on the IRMS system allowing to assign high resolution/high accuracy mass data on all urinary metabolites previously identified by IRMS.

Results: Within the IRMS chromatograms, labeled metabolites were identified up to 20 days after administration at urinary concentration down to 0.25 ng/mL. Overall, more than 50 metabolites were observed with the earlier described long-term metabolite of metandienone, 18-nor-17 β -hydroxymethyl,17 α -methyl-androst-1,4,13-trien-3-one, being the most prominent glucuronidated metabolite in the studied time window. Moreover, in the fraction of sulfoconjugated steroids, a yet unknown metabolite was observed at m/z 283.1997 comprising the experimentally determined elemental composition of C₂₀H₂₁²H₃O.

Conclusion: The concept of combining IRMS with high resolution mass spectrometry considerably facilitates and accelerates metabolite identification of deuterium-labeled compounds in urine. Being of particular relevance in doping controls, the principle is applicable also to other arenas of drug research allowing to omit the preparation and administration of e.g. radioactively labeled substances.

V1.9

Future International Organic Stable Isotope Reference Materials

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The need for international organic H, C, N stable isotope reference materials

Currently there are few hydrogen, carbon, and nitrogen organic international stable isotope reference materials (RMs) available from the *International Atomic Energy Agency* (IAEA), the *U.S. Geological Survey* (USGS) or the *U.S. National Institute of Standards and Technology* (NIST). In the absence of suitable pairs of organic reference materials for proper 2-point calibrations along isotopic VSMOW, VPDB and AIR scales, many laboratories have to resort to questionable practices, for example by using 'reference gas pulses' for isotopic calibrations that violate the principle of identical treatment of sample and standard (see review by Elsner et al., 2012, and refs. therein). In 2011, the *U.S. National Science Foundation* (NSF) funded an initiative of 10 laboratories from 7 countries to jointly develop much needed new organic RMs for future distribution by international outlets such as the IAEA and the USGS.

Targeted organic compounds

The selection of targeted RMs attempts to cover various common compound classes of broad technical and scientific interest. We had to find compromises to approach the ideal of high chemical stability, lack of toxicity, availability, and price of raw materials. Hazardous gases and liquids were avoided in order to facilitate international shipping of future RMs. With the exception of polyethylene and vacuum pump oil, all organic RMs are individual chemically pure substances which can be used for compound-specific measurements in conjunction with liquid and gas chromatographic interfaces. The following listed preliminary or targeted δ -values are subject to accurate calibration by a group effort of participating laboratories.

→ Three hexadecanes (i.e. C₁₆ *n*-alkanes) with low, medium and high δ -values: $\delta^2\text{H}$ ca. -160, -15, +400‰; $\delta^{13}\text{C}$ ca. -35, -10, 0‰.

→ Three glycines with low, medium and high δ -values: $\delta^2\text{H}$ values express ca. 200‰ incremental increases; $\delta^2\text{H}$ to be determined; $\delta^{13}\text{C}$ ca. -41, -10, 0‰; $\delta^{15}\text{N}$ ca. 2, +20, +40‰.

→ Three L-valines (#1 to #3) with low, medium and high δ -values: $\delta^2\text{H}$ values express ca. 200‰ incremental increases; $\delta^2\text{H}$ values to be determined; $\delta^{13}\text{C}$ ca. -24, -9, 0‰; $\delta^{15}\text{N}$ ca. -5, +30, +60‰. Site-specific ²H- and ¹³C-enrichments at different molecular sites 1, 2 and 3 are currently not measurable with high precision, but were incorporated in prospective RMs for future use in site-specific carbon and hydrogen isotopic characterization.

→ methyl heptadecanoate (i.e. methyl ester of C₁₇ *n*-alkanoic fatty acid) with $\delta^2\text{H}$ ca. -200‰ and $\delta^{13}\text{C}$ ca. -31‰.

→ Three methyl icosanoates (i.e. methyl esters of C₂₀ *n*-alkanoic fatty acid) with low, medium and high δ -values: $\delta^2\text{H}$ ca. -175, 0, +400‰; $\delta^{13}\text{C}$ ca. -31, -10, 0‰.

Caffeines:

→ Three caffeines with low, medium and high δ -values: $\delta^2\text{H}$ ca. -170, +40, +200‰; $\delta^{13}\text{C}$ ca. -35, -15, 0‰; $\delta^{15}\text{N}$ ca. -3, +20, +40‰.

→ Two high-quality vacuum pump oils with and without a perdeuterated *n*-alkane spike, to serve as replacements of NBS 22 machine oil for 2-point hydrogen isotopic calibrations (targeted $\delta^2\text{H}$ ca. -120, +200‰; $\delta^{13}\text{C}$ to be determined).

→ Two polyethylene powders/foils with and without a perdeuterated *n*-alkane spike, for 2-point hydrogen isotopic calibrations; targeted $\delta^2\text{H}$ values ca. -74 and +400‰; $\delta^{13}\text{C}$ to be determined.

Reference

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V1.10

Stable carbon isotope analysis of dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) in natural waters - Results from a worldwide proficiency test

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Stable carbon isotope ratios of dissolved inorganic (DIC) and organic carbon (DOC) are of particular interest in aquatic geochemistry. The precision for this kind of analysis is typically reported in the range of 0.1‰ to 0.5‰. So far, no published attempt compares $\delta^{13}\text{C}$ measurements of DIC and DOC among different laboratories for natural water samples.

Five natural water samples (lake water, seawater, two geothermal waters, and petroleum well water) were analyzed for $\delta^{13}\text{C}_{\text{DIC}}$ and $\delta^{13}\text{C}_{\text{DOC}}$ by 5 laboratories with isotope ratio mass spectrometry (IRMS) in an international proficiency test.

Reported $\delta^{13}\text{C}_{\text{DIC}}$ values for lake water and seawater showed fairly good agreement within a range of about 1‰ whereas geothermal and petroleum waters were characterized by much larger differences (up to 6.6‰ between laboratories). $\delta^{13}\text{C}_{\text{DOC}}$ values were only comparable for seawater and showed differences of 10 to 21‰ for other samples.

This study [1] indicates that scatter in $\delta^{13}\text{C}_{\text{DIC}}$ isotope data can be in the range of several per mil for samples from extreme environments (geothermal waters) and may not yield reliable information with respect to dissolved carbon (petroleum wells). The analyses of lake water and seawater also revealed a larger than expected difference and researchers from various disciplines should be aware of this. Evaluation of analytical procedures of the participating laboratories indicated that the differences cannot be explained by analytical errors or different data normalization procedures and must be related to specific sample characteristics or secondary effects during sample storage and handling. Our results reveal the need for further research on sources of error and on method standardization.

[1] van Geldern R, Verma MP, Carvalho MC, Grassa F, Huertas AD, Barth JAC. Stable carbon isotope analysis of dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) in natural waters - Results from a worldwide proficiency test. *Rapid Communications in Mass Spectrometry* (in press).

Vorträge – Sektion 2 Ökologie und Physiologie

V2.1

Amino acids as precursors of methane in living plants

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The finding that terrestrial plants produce the greenhouse gas methane (Keppler et al. 2006) has led to much discussion and debate (Kirschbaum et al. 2007), not only about its contribution to the global methane budget, but also as regards the authenticity of the actual observation. Although the phenomenon has recently been accepted for both living and dead plants (Bruhn et al. 2012), the mechanism of formation in living plants still needs to be elucidated and its precursor compounds identified.

We made use of stable isotope techniques to verify in vivo formation of methane and to identify the carbon precursor by employing ¹³C-positionally labeled organic compounds. We demonstrate that the amino acid L-methionine acts as a methane precursor in living plants. Employing ¹³C-labelled methionine clearly identified the sulphur bound methyl group of methionine to be the carbon precursor for methane released from lavender and tobacco plants grown. Furthermore, when lavender plants were stressed physically, methane release rates and stable carbon isotope values greatly increased. Our results provide strong additional support that plants possess a biochemical mechanism for methanogenesis and suggest that methionine might play an important role in the aerobic formation of methane in living plants particularly when under stress conditions.

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V2.2

Metadatenätze von Isotopenhäufigkeiten als Werkzeug zur Aufklärung der vielschichtigen Ernährungsweisen bei mykoheterotrophen Pflanzen

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Eine enge Vergesellschaftung mit Pilzen ist ein weit verbreitetes Phänomen im Pflanzenreich. Über 80% aller Pflanzenarten gehen mit Pilzen in ihrem Wurzelraum eine Mykorrhiza ein. In den weitaus meisten Fällen profitieren sowohl der Pilz- als auch der Pflanzenpartner von dieser Interaktion. Der Pilzpartner wird mit Kohlenhydraten aus der pflanzlichen Photosynthese versorgt. Im Gegenzug wird die Versorgung des Pflanzenpartners mit mineralischen Nährstoffen durch das weitverzweigte Pilzmyzel verbessert.

Die Funktion der Mykorrhiza als mutualistische Symbiose wird allerdings von einer Reihe von Pflanzenarten in vielfältiger Weise unterlaufen. Pflanzen mit endospermlosen, staubfeinen Samen lassen sich z.B. in der Keimlingsphase vollständig vom Pilzpartner versorgen ohne Gegenleistungen zu liefern. Im adulten Stadium wird die Mehrheit dieser Pflanzen dann autotroph. Dementsprechend wird diese Ernährungsweise als anfängliche Mykoheterotrophie bezeichnet. Sämtliche Vertreter der artenreichen Familie der Orchideengewächse sind anfänglich mykoheterotroph. Darüber hinaus gibt es aber auch Pflanzenarten aus ganz unterschiedlichen taxonomischen Gruppen, die zeitlebens keine autotrophen Leistungen vollbringen und sich ausschließlich vom Pilzpartner versorgen lassen. Die Ernährungsweise dieser Pflanzen ist als vollständige Mykoheterotrophie bekannt. Aus eigenen Untersuchungen kennen wir aber auch bei einer Reihe von Pflanzenarten eine Ernährung durch autotrophe Leistungen und eine simultane Versorgung durch Pilzpartner. Diese Mischernährung wird partielle Mykoheterotrophie genannt. Noch komplexer wird die Pilz-/Pflanzen-Interaktion durch die Tatsache, dass bei der Mykoheterotrophie Pilzpartner aus unterschiedlichen funktionellen Gruppen involviert sind. Partner mykoheterotropher Pflanzen können sowohl ubiquitär saprotroph lebende Pilze als auch aggressive Holzersetzer sein oder gleichzeitig eine Ektomykorrhiza oder arbuskuläre Mykorrhiza mit Bäumen eingehen.

In meiner Arbeitsgruppe wurden in den letzten Jahren sämtliche aus der Literatur verfügbaren Kohlenstoff- und Stickstoff-Isotopenhäufigkeitsdaten von mykoheterotrophen Pflanzen zu einer Metadatei zusammengeführt. Die Analyse dieser Metadaten erlaubt eine detaillierte Differenzierung der unterschiedlichen Ausprägungen mykoheterotropher Ernährung anhand ihrer Kohlenstoff- und Stickstoff-Isotopenhäufigkeitsmuster (Hynson *et al.*, 2013). Bei einigen Pflanzenarten, die unter dem Verdacht partiell mykoheterotropher Ernährung stehen, reichen alleinige Kohlenstoff- und Stickstoff-Isotopenhäufigkeitsmuster zur zweifelsfreien Erhärtung der Ernährungsweise nicht mehr aus. In diesen Fällen hilft eine zusätzliche Wasserstoff-Isotopenhäufigkeitsanalyse weiter.

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Vorträge – Sektion 3

Stoffkreisläufe in Ökosystemen

V3.1

Relevance of Ca-isotope fractionation in pore waters in marine and terrestrial environments

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The marine sedimentary environment is characterized by multiple diagenetic processes which are coupled to the degradation of organic material. The increase in alkalinity in the pore water, which results from bacterial sulfate reduction, induces precipitation and dissolution of authigenic/biogenic Ca carbonate. These processes have been identified to alter Ca concentration and isotope ratios of marine pore waters (Teichert et al., 2009; Fantle and DePaolo, 2007). Another process which is linked to changing element concentrations due to organic matter decomposition, is sediment-fluid interaction. However, ion exchange processes have not been considered while interpreting Ca-isotope pore water profiles, even though there are indications that they occur (Teichert et al., 2009). Moreover, recent experimental investigations of Ockert et al. (2013) reveal that the exchange of Ca with clay minerals in the marine environment can be accompanied by isotopic fractionation which can shift pore water Ca isotope values by up to -2.5 ‰.

Determinations of Ca-isotope ratios from pore water of three sites in the North Atlantic (IODP Expedition 303) with different dominating lithologies were carried out to further explore this process in the natural environment. The $\delta^{44/40}\text{Ca}$ data show different trends with sediment depth for each site, mirroring the dominant processes at the specific sites. Indications for ion exchange reactions induced by ammonium or Ca concentration changes are visible at all sites but often masked by the more dominant Ca carbonate precipitation. The isotopic variations in the depth above the Ca carbonate precipitation region could be explained by either static reactions involving ammonium-Ca exchange or by kinetic fractionation during diffusion through the sediment column. These findings indicate that not only precipitation and dissolution of Ca carbonate but also fluid-sediment processes have an important effect on the pore water isotopy and must be considered when interpreting Ca-isotope pore water profiles.

Interestingly, in the terrestrial environment fluid-soil/sediment interactions may also be of importance as Ca is not only part of the soil and its structural components, but also an important nutrient (actively) taken up for plant growth. Investigating the impact of fluid based exchanges and transfers in terrestrial soils and sediments may help quantify effects on plant/soil/sediment Ca isotope values.

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V3.2

Stabilisierung von pflanzlichen und mikrobiellen Kohlenhydraten in Böden mit C3-C4 Vegetationswechsel

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Die Bodenorganische Substanz (SOM) stellt ein komplexes Gemisch aus unterschiedlichen Substanzklassen dar. Diese wiederum unterliegen bedingt durch ihre spezifische Struktur unterschiedlich stark den verschiedenen Abbau- und Stabilisierungsprozessen im Boden. Eine dieser Substanzklassen sind die Kohlenhydrate, deren Beitrag zum SOM bei bis zu 25% liegen kann. Bisherige Studien zeigten, dass der Kohlenhydratpool im Boden durch ähnlich lange Verweilzeiten charakterisiert ist wie der Gesamtkohlenstoff, obwohl die Kohlenhydratbausteine leicht abbaubar sind. Ziel dieser Studie ist es den Einfluss der Stabilisierung auf den Umsatz von Kohlenhydratbausteinen im Boden näher zu charakterisieren. Die Untersuchungen werden an einer Parabraunerde (A_p und A_L-Horizont) mit über 20 Jahre zurückliegenden Vegetationswechsel von C3 zu C4 Pflanzen durchgeführt

Kohlenhydrate können eine vorwiegend pflanzlich (Arabinose, Xylose) oder mikrobielle (Mannose, Galactose) Herkunft haben. Um den Beitrag der Stabilisierung auf die Umsatzzeiten des Kohlenhydratpools abzuschätzen werden die Zucker aus pflanzlicher sowie mikrobieller Herkunft miteinander verglichen. Die Umsatzzeiten der mikrobiellen Zucker können sowohl durch Stabilisierung als auch durch das Recyceln von "älteren" Kohlenstoffverbindungen beeinflusst werden, während die Dynamic der pflanzlichen Zucker ausschließlich durch Stabilisierungsmechanismen bestimmt wird. Die Analyse der Zuckermonomere und der Isotopie erfolgt nach TFA-Extraktion mit der HPLC -IRMS. Die neu entwickelte Methode ermöglicht es die Zuckermonomere reproduzierbarer und genauer substanzspezifisch auf ihre Isotopensignatur zu untersuchen, da eine Derivatisierung wie bei der üblich eingesetzten Trennung mit Gaschromatographie nicht erforderlich ist.

V3.3

C partitioning in soil microbial communities assessed by position-specific labeling and compound-specific isotope analysis of PLFA and amino sugars

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Low molecular weight organic substances (LMWOS) are the preferred substrate for microorganisms. These substrates are used by microorganisms either for energy production or for synthesis of the cell compounds. Various cell components have different turnover times in soil and consequently a different potential for stabilization in soil organic matter (SOM). Whereas incorporation of LMWOS-C in microbial biomass is already well investigated, knowledge about the distribution within individual cell components is rare. The objective of our study was to estimate the portion of glucose C partitioned into cytosolic C, phospholipid fatty acids (PLFA) and amino sugars. As PLFA and amino sugars function as microbial biomarkers the contribution of distinct microbial groups to the utilization of LMWOS-C was assessed. In addition, position-specific labeling enabled a reconstruction of the metabolic pathways used for synthesis of these individual cellular compounds.

We determined transformations of glucose in 3, 10 and 40 days by adding uniformly and position-specifically ¹³C labeled glucose into soil in a field experiment. We quantified the decomposition of the entire molecule as well as of individual C positions by bulk soil measurements. Microbial utilization was assessed by ¹³C-analysis of different microbial pools: 1) microbial biomass by chloroform-fumigation-extraction, 2) microbial membranes by ¹³C PLFA analysis via GC-C-IRMS and 3) microbial cell walls by IC-O-IRMS analysis of amino sugars. The microbial biomarkers also allowed a more specific look on the glucose metabolization pathways of individual members of the soil microbial community.

Three days after the labeling nearly half of the glucose ¹³C was respired. The rate of glucose degradation strongly declined during the following incubation period. However, partitioning of glucose ¹³C within the cellular compartments strongly changed during the incubation time: Whereas uptake in microbial cell membranes strongly decreased from day 3 to day 40 and slowly decreased in the cytoplasm, the incorporation into cell wall polymers increased for the entire incubation period. Total ¹³C incorporation into cell walls was ~10 times lower than into cytoplasm and ~3 times lower than into PLFA. Replacement of these microbial pools by the added ¹³C reflected that the soil amino sugar pool consists mainly of cell wall necromass with a slow turnover, whereas cytosolic biomass and PLFA are actively cycling microbial pools in soils.

Amino sugar ¹³C incorporation revealed that bacteria are more active in glucose utilization in agricultural soils than fungi. By ¹³C-PLFA analysis the gram-negatives could be identified as most active bacterial group. Turnover of cell wall and membrane compounds as well as pathways used for glucose incorporation into amino sugars revealed that fungi have a less active metabolism with a lower turnover of many cellular compounds than bacteria.

Thus, for the first time an analytical approach compared microbial biomass extraction with analysis of two compound-specifically measured pools of microbial metabolites. This enables to trace C partitioning within the microbial cells and microbial community in soils. Position-specific labeling reflects the underlying pathways causing the observed C partitioning. The combination of these techniques will improve our understanding of soil carbon fluxes.

V3.4

Real-time measurement of N₂O isotopomers and the ¹⁸O-N₂O isotopologue by laser spectroscopy above intensively managed grassland in Central Switzerland

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Estimations of N₂O budgets calculated using process oriented biogeochemical models are usually calibrated and validated based on measured total N₂O emission. However, this approach does not consider the partitioning of total soil-atmosphere N₂O exchange into the source processes nitrification and denitrification as in-situ measurements capable of source partitioning are not available. Therefore, it is unclear if the relative source strengths of nitrification and denitrification are represented adequately in process oriented models.

For the dominant bacterial production processes, characteristic isotopic signatures have been identified, so that the analysis of the four main isotopic N₂O species (¹⁴N¹⁵N¹⁶O / ¹⁵N¹⁴N¹⁶O / ¹⁴N¹⁴N¹⁸O / ¹⁴N¹⁴N¹⁶O) represents a tool for the allocation of emission sources (Wunderlin et al. 2013). This approach has been applied to identify relevant sources at different scales (Toyoda et al. 2013). However, current studies suffer from limited spatial and temporal resolution due to the combination of discrete flask sampling with laboratory-based mass spectrometric analysis.

Recent advances in quantum cascade laser based spectrometry allow the simultaneous measurement of the main isotopic N₂O species (Waechter et al. 2008) and this alternative measurement technique has been shown to be even more precise than IRMS measurements (Köster et al. 2013). In combination with preconcentration this approach has been shown to yield high precision even at ambient N₂O mixing ratios (Mohn et al. 2012).

Here we present the latest results from a measurement campaign on an intensively managed grassland site in Central Switzerland. N₂O isotopic analysis was accomplished using a state-of-the-art laser spectrometer employing a recently available cw-QCL laser source and a sensitive detection scheme. Repetitive preconcentration cycles resulted in a temporal resolution of less than one hour. A sophisticated calibration strategy was applied to ensure excellent accuracy and traceability of our measurements, yielding a long term precision for repetitive compressed air samples of 0.20, 0.16 and 0.10‰ for δ¹⁵N^α, δ¹⁵N^β and δ¹⁸O. N₂O emissions from the grassland and their isotopic composition responded to management practices such as mowing and fertilization and meteorological conditions. The potential of the derived N₂O isotopic signatures for partitioning of microbial source processes will be discussed in relation to available literature data.

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Vorträge – Sektion 4

Stabile Isotope in der Agrarforschung

V4.1

Insights about natural atrazine degradation by the analysis of C and N isotope trends within the parent and its daughter compounds desethyl- and desisopropylatrazine

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Compound specific isotope analyses (CSIA) have become a promising tool to detect degradation processes of contaminants in groundwater. Since (bio)chemical reactions are associated with kinetic isotope effects, often an enrichment of the heavier isotope in the remaining parent compound and a depletion of the heavier isotope in the product can be observed. Information on degradation can therefore be obtained from observable isotope fractionation in the parent as well as the daughter compound. In our work we analysed the $^{13}\text{C}/^{12}\text{C}$ and $^{15}\text{N}/^{14}\text{N}$ ratios of the herbicide atrazine (Atz) and its metabolites desethylatrazine (DEA) and desisopropylatrazine (DIA), which are still herbicidal and frequently detected in the aquatic environment. Interpretation of atrazine degradation in the environment is often difficult with current methods, which are mainly measuring concentrations, because their decrease is not only due to degradation, but also due to sorption and dilution and thus it is often not possible to close mass balances.

The scope of our study was to investigate isotope trends in parent and daughter compounds associated with different degradation scenarios of atrazine likely to occur in the environment. Therefore, in lab experiments, atrazine was dealkylated with (i) the bacterium *Rhodococcus* sp. NI86/21 and with (ii) permanganate as an abiotic reference system forming selective DEA. In both transformations, $^{13}\text{C}/^{12}\text{C}$ ratios of atrazine increased strongly ($\epsilon_{\text{carbon/permanganate}} = -4.6 \pm 0.6 \text{ ‰}$ and $\epsilon_{\text{carbon/Rhodococcus}} = -3.8 \pm 0.2 \text{ ‰}$) whereas nitrogen isotope fractionation was small. $^{13}\text{C}/^{12}\text{C}$ ratios of DEA showed the following trends. (i) When DEA was formed as only product (Atz + permanganate) $^{13}\text{C}/^{12}\text{C}$ remained constant, close to the initial value of Atz. (ii) When DEA was formed together with DIA (biodegradation of Atz) $^{13}\text{C}/^{12}\text{C}$ increased, but only within 2‰. (iii) Ongoing biodegradation of DEA and DIA lead to increasing $^{13}\text{C}/^{12}\text{C}$ ratios for both metabolites up to 9‰. Thus strong enrichment of $^{13}\text{C}/^{12}\text{C}$ in the metabolites in comparison to Atz can give strong proof for further metabolite's breakdown.

V4.2

Effect of phosphorus limitation on the $\delta^{18}\text{O-PO}_4$ of plant and soil phosphorus pools from a long term field experiment in Switzerland

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The isotopic composition of oxygen associated to phosphorus ($\delta^{18}\text{O-PO}_4$) has shown the potential for characterizing the P cycling in the soil/plant system. It is based on the fact that in nature, P is mostly associated to oxygen (O) and that biological processes favour the oxygen exchange between phosphate and ambient water. It is known that the inorganic pyrophosphatase (PPase) leads to a temperature-dependent equilibrium between oxygen in phosphate and oxygen in water. Also uptake by organisms can lead to a fractionation. In this study we focus on the effect of P limitation on the $\delta^{18}\text{O-PO}_4$ of plant and soil P pools. We analysed the $\delta^{18}\text{O-PO}_4$ of different P pools in plant and soil samples taken from a field trial in Rümlang, Switzerland. This field trial was established in 1989 and investigates the effect of different application rates of mineral P fertiliser on the yield of different crops. For soil tillage plow and harrow were used to a maximum depth of 20 cm. For our study we chose two different fertilisation rates: P supplied 5/3 of the need of the cultivated plant (control) or no P applied (limited).

Sampling took place at three time points in 2011 (February, April, and May) and in 2012 (June, July, and September). The sampling points correspond to the development stages (after BBCH scale) 18, 62, and 79 of *Brassica nigra*, grown in 2011 and 15, 58, and 88 of *Glycine max*, grown in 2012. Soil samples were taken from the 0 - 10 cm layer and three different P pools were extracted sequentially. First plant available P was extracted with anion exchange membranes (resin P), in the second step the soil was extracted with NaOH-EDTA to obtain the organic P and P bound to e.g. iron oxides. In the last step the soil was extracted with 1 M HCl targeting mainly P bound to Ca and Mg minerals (HCl P). Due to difficulties with the extraction of the leaves of the *Brassica nigra* in 2011, only the plant samples from 2012 were analysed for their $\delta^{18}\text{O-PO}_4$ signature. Fully developed trifoliate leaves from *Glycine max* were sampled and P was extracted in a two-step sequential extraction. First P was extracted with 0.3 M trichloroacetic acid (TCA P) and then with 10 M HNO_3 (structural P). Resin P, HCl P, TCA P, and structural P were analysed for their $\delta^{18}\text{O-PO}_4$. Additionally we analysed the $\delta^{18}\text{O}$ of the soil and leaf water.

Phosphorus limitation seems to affect mainly the $\delta^{18}\text{O-PO}_4$ signature of TCA P in the leaves of *Glycine max* and of resin P in the soil. The $\delta^{18}\text{O-PO}_4$ of TCA P is less enriched in ^{18}O in the case of the P limited plants compared to the control plants. In both cases the $\delta^{18}\text{O-PO}_4$ of TCA P is not at equilibrium with the leaf water. The $\delta^{18}\text{O-PO}_4$ of resin P in the control plots is within the equilibrium range, whereas the $\delta^{18}\text{O-PO}_4$ of resin P in the limited plots is only within the equilibrium in February 2011, but is heavier for April and May in 2011 and lighter than the equilibrium in June, July, and September 2012. Deviations from the equilibrium in both cases could possibly be explained by the strategies of plants to deal with P limitation, for example increased activity of hydrolysing enzymes. The $\delta^{18}\text{O-PO}_4$ signature of more stable P pools does not seem to be affected by P limitation.

V4.3

Multielement-Stabilisotopenanalyse offenbart partielle Mykoheterotrophie von Orchideen auf Almwiesen der Alpen*

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Bergregionen beherbergen aufgrund ihrer großen Vielfalt an Lebensräumen auf kleinem Raum eine überdurchschnittlich hohe Biodiversität. Dabei sind Almwiesen besonders artenreiche Sekundärbiotope, die durch jahrhundertelange Bewirtschaftung durch den Menschen entstanden. Im Gegensatz zu Nutzungsaufgabe oder gar Intensivierung der Almwirtschaft, schützt die traditionelle extensive Nutzung den Artenreichtum der Almwiesen und somit auch wertvolle Arten wie Orchideen. Untersuchungen zu trophischen Strategien (z.B. Autotrophie, partielle oder vollständige Mykoheterotrophie) von Orchideen-Arten im Alpenraum fehlen nahezu komplett, obwohl die Artenvielfalt in der Familie der Orchidaceae dort besonders hoch ist. Im Rahmen eines interdisziplinären Geländepraktikums in den Nördlichen Kalkalpen (Marultal, Vorarlberg, Österreich) wurden sieben der dort vorkommenden grünblättrigen Orchideen-Arten aus den Unterfamilien der Orchidoideae und Epidendroideae und die chlorophylllose Orchidee *Neottia nidus-avis* bezüglich ihres Ernährungsverhaltens und ihrer Pilzpartner untersucht. Dazu wurden Blattproben der adulten Orchideen aus Nadelmischwäldern und landwirtschaftlich genutzten Almwiesen und jeweils fünf Arten autotropher Referenzpflanzen gesammelt. Häufigkeitsanalysen der stabilen Kohlenstoff-, Stickstoff- und Wasserstoffisotope in den Blattproben wurden mittels EA-IRMS- und TC-IRMS-Kopplung durchgeführt. δ -Werte wurden normalisiert und in Anreicherungsfaktoren ϵ umgerechnet, um Orchideen-Arten unterschiedlicher Standorte vergleichen und den Grad ihrer Mykoheterotrophie abschätzen zu können. Zudem wurden die Wurzeln der Orchideen beprobt, um die mit den Orchideen assoziierten Pilzpartner mittels DNA-Analysen zu identifizieren. Die Ergebnisse bestätigen, dass ausschließlich die Art *Neottia nidus-avis* aus der Unterfamilie der Epidendroideae, die in lichtlimitierten Wäldern vorkommt und mit Ektomykorrhiza (ECM)-Pilzen assoziiert ist, voll mykoheterotroph ist, sich also vollständig auf Kosten des Pilzpartners ernährt. *Epipactis helleborine* liegt in ihrer Anreicherung an ^{15}N und ^{13}C zwischen der voll mykoheterotrophen *Neottia nidus-avis* und den autotrophen Referenzpflanzen, kann folglich als partiell mykoheterotroph bezeichnet werden. Hingegen zeigten die meisten Wiesen-Orchideen eine leichte, jedoch von ihren autotrophen Referenzpflanzen signifikant unterschiedene Anreicherung an ^{15}N und nur geringfügige Unterschiede im ^{13}C . Dadurch wird angedeutet, dass die Orchideen geringe Mengen N aber scheinbar kein C von ihrem Pilzpartner beziehen. δD ermöglichte weitere Einsichten über die vermeintlich autotrophen Wiesen-Orchideen: Multielement-Isotopenanalysen unter Zuhilfenahme von ^2H deckten auf, dass die Arten *Nigritella nigra*, *Pseudorchis albida*, *Coeloglossum viride* und *Gymnadenia odoratissima* nun signifikante Unterschiede ($p \leq 0,001$) bezüglich ihrer voll autotrophen Referenzarten aufweisen. Lediglich für die Orchidaceae *Traunsteinera globosa* und *Gymnadenia conopsea* war die Anreicherung an Deuterium statistisch nicht mehr signifikant. Die Anwendung des stabilen Wasserstoffisotops Deuterium offenbart, dass partielle Mykoheterotrophie auch unter den grünen Wiesen-Orchideen als Ernährungsweise zu finden ist. Die Identifizierung der Pilzpartner grünblättriger Orchideen-Arten wird weitere Einsichten über den Grad ihrer Mykoheterotrophie liefern.

*Daten wurden während eines interdisziplinären Feldpraktikums in Marul/Österreich im Jahre 2012 von den Master-Studenten A. Aures, M. Christé, A. Endreß, L. Heuss, A. Makiola, N. Sängler, J. Schiebold und M. Thieme aufgenommen.

V4.4

¹⁵N tracer studies to evaluate nitrogen dynamics of food webs in two subtropical small scale aquaculture ponds under different management

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While nutrient dynamics of natural food webs in streams and intensive aquaculture facilities were frequently studied by stable isotope tracer experiments over the past decade, little is known about nutrient flows within food webs of semi-intensively managed ponds of small scale aquaculture activities which fish production and economic performance is significantly depending on the productivity of natural food resources. These aquaculture systems contribute significantly to food security and household income of small scale farmers around the world.

A tracer experiment was performed for 7 days in two ponds (~600 m² each, ~1 m depth) of small scale farmers in Son La province, northern Vietnam. The trial ponds were managed differently:

- One pond was managed traditionally as flow-through with grass carp as main species and silver carp, bighead carp, mrigal, common carp and tilapia as secondary species. Feeds and fertilizer consisted of plant material and ruminant manure.

- The second pond was managed as static pond with common carp as main species and grass carp, silver carp, bighead carp and tilapia as secondary species. Feeds and fertilizer consisted of supplemental pellet feeds, plant material, ruminant manure and chemical fertilizer.

¹⁵N was applied at once at a rate of 48 mg m⁻² by means of ammonium, corresponding to 1.07 % and 0.39 % of the total nitrogen (dissolved compounds, plankton, zoobenthos and fish) in the flow-through and static ponds. The tracer was dissolved in pond water and spread over the entire pond surface at 10 am.

Samples of plankton and zoobenthos were taken one hour before tracer application and at 10 am of day 1, 2, 3, 4, 5 and 7. For plankton sampling, duplicates of five x 10 L of pond water were taken at different sites of ponds and pooled. The 2 x 50 L was filled through a cascade of meshes of the sizes 200, 60 and 15 µm. The fractions were transferred into vials. The fraction < 15 µm was filtered through GF/C filters. Zoobenthos (> 0.5 mm) was segregated daily from ten bottom cores of each pond. Sedimentation rates were measured by installing five vials 3 cm above the pond bottom. On day 0, 3, 4, 5 and 7, all vials were sampled and replaced. Samples of plankton, zoobenthos and sedimented particles were stored at -18° C and freeze dried for analysis and biomass determination. C and N content as well as ¹⁵N-content of samples were determined by Elemental Analyzer (Euro Vector) and a Thermo Finnigan Delta Plus IR-MS (ThermoFinnigan).

The static pond showed significantly higher biomass in the plankton fractions 1-15 and 15-60 µm and sedimentation rate than compared to the flow-through pond. All other natural food resources were similar. The main fraction (24 % and 34 %) of tracer was found in 1-15 µm plankton at day one in the flow-through and day two in the static pond, respectively. Each other food resource fraction assimilated less than 1 % of applied tracer at any time. At the days 1 and 2, daily 50 % and 60 % of the tracer was found in the sedimented particles in the flow-through and static pond, respectively, suggesting a high re-suspension of sedimented nutrients into the pelagic food web. Generally, the tracer was removed from the pond more quickly in flow-through pond compared to the static water. These results clearly show the dominance of small sized plankton in semi-intensive aquaculture pond systems and high turnover rates of this fraction, suggesting that a steady nutrient supply could increase production.

Vorträge – Sektion 5

Klimaänderungen und -Rekonstruktionen

V5.1

A stable isotope based assessment of the MWP-LIA transition in Northern Scandinavia

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A global reorganization of climate has been recorded in precipitation and temperature sensitive climate proxies during the 13th and 14th centuries, also known as the Medieval Warm Period to the Little Ice Age Transition (MWP-LIA Transition) (Seager et al. 2007). This climate reorganization has been recorded in climate archives (e.g. ice cores and tree rings) and documentary data. This climate sensitive period exhibits a number of major volcanic events in the years 1206, 1211, 1222, 1279, 1337, 1349 that are also known from documentary data as famine years and Black Death periods.

The objective of our research was to assess the climate reorganization during the MWP-LIA Transition, using stable isotopes from tree rings and compare these with major cultural changes and price development data of crop harvest in Europe. We measured the traditional carbon stable isotopes from whole wood and compared it with a novel stable isotope method (carbon isotopes from lignin methoxyl groups analyzed according to Keppler et al. 2007 and Greule et al. 2009). The chronologies are annually resolved 200-year long timeseries derived from sub-fossil pine trees (*Pinus sylvestris*) preserved in boreal lakes of Northern Scandinavia. The data analysis is still in progress and first results will be shown and discussed in the presentation.

Greule, M., Mosandl, A., Hamilton, J.T.G., Keppler, F., (2009). A simple rapid method to precisely determine $^{13}\text{C}/^{12}\text{C}$ ratios of plant methoxyl groups. *Rapid Communications in Mass Spectrometry*, 23, 1710-1714.

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V5.2

Combining ^{18}O and ^2H isotope biomarker analyses in paleoclimate research - a conceptual model, a calibration study and a first application

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While compound-specific $\delta^2\text{H}$ analyses of biomarkers, especially of leaf wax-derived *n*-alkanes, have become a popular tool in paleohydrology and -climate research during the last ~15 years, a method for compound-specific $\delta^{18}\text{O}$ analyses of hemicellulose sugar biomarkers from soils and sediments was proposed only recently (Zech and Glaser, 2009; Zech et al., 2012). A major challenge when interpreting terrestrial $\delta^2\text{H}$ or $\delta^{18}\text{O}$ biomarker records is to differentiate between climatically controlled variations of plant source water ($\sim\delta^2\text{H}_{\text{precipitation}}$ and $\sim\delta^{18}\text{O}_{\text{precipitation}}$) and climatically controlled variations of evaporative ^2H and ^{18}O enrichment of leaf water during transpiration.

Here we propose a conceptual model which allows overcoming this limitation in a combined ^{18}O and ^2H biomarker approach (using a $\delta^2\text{H}$ versus $\delta^{18}\text{O}$ diagram). Accordingly, the isotopic composition of leaf water can be reconstructed from $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of sedimentary hemicellulose and leaf-wax biomarkers (pentoses and *n*-alkanes, respectively) by applying biosynthetic fractionation factors. The deuterium excess of reconstructed leaf water may then serve as proxy for evaporative enrichment and allows calculating relative air humidity using a Craig-Gordon model. Using the Craig-Gordon model for calculating the slope of a leaf water evaporation line, also $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of the plant source water ($\sim\text{precipitation}$) can be reconstructed.

We test this model using topsoil samples from a climate transect in Argentina. Accordingly, neither $\delta^{18}\text{O}$ of the sugar biomarkers nor $\delta^2\text{H}$ of the *n*-alkane biomarkers simply reflects the isotopic composition of precipitation. Rather, the combined $\delta^{18}\text{O}$ and $\delta^2\text{H}$ biomarker approach suggests that evaporative $\delta^{18}\text{O}$ and $\delta^2\text{H}$ enrichment of leaf water is the dominating factor along our climate transect. As it can be expected from our model, the deuterium excess of leaf water is well reflected by the isotopic composition of the investigated biomarkers and depends primarily on relative air humidity.

The application of the above suggested model to a 220 ka Siberian permafrost paleosol sequence allows reconstructing an aridisation trend for NE-Siberia, which is in agreement with progressively smaller ice sheet extensions in this study area. Furthermore, the model allows reconstructing a 220 ka $\delta^{18}\text{O}_{\text{precipitation}}$ record. The latter is well in agreement with the $\delta^{18}\text{O}_{\text{diatom}}$ record from close-by Crater Lake El'gygytyn in NE-Siberia (Chapligin et al., 2012) and enables a regional paleoclimate reconstruction and interpretation.

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V5.3

$\delta^{13}\text{C}$ from methoxyl groups a new climate proxy from high alpine larch trees

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At a high alpine site (2150 m above sea level) in the Simplon region (Switzerland) 37 *larix decidua* trees were sampled in September 2010. Every tree is sampled with two cores, which were taken with an increment corer in breast height. All cores were measured for their tree ring width. Five of these trees, with sufficiently thick growth rings, were selected for $\delta^{13}\text{C}$ analysis of the lignin methoxyl groups. A method which has been recently developed (Greule et al., 2009). The years 1971 to 2009 were measured with an annual resolution. All tree rings before 1971 were cut in five-year blocks (pentads) and then analysed for the carbon isotope signature of the methoxyl groups. The resulting five series with annual resolution and the five series of pentads were averaged to one chronology, respectively. For the pentad chronology, the years 1971 to 2009 were averaged to pentads. All $\delta^{13}\text{C}$ values were corrected for the anthropogenic atmospheric carbon input using three different correction functions. Also the tree ring width time series were averaged to one chronology and detrended with negative exponential function using the programme ARSTAN (Cook, 1985).

The resulting chronologies were tested for their climate sensitivity. Climate data from the nearby weather station Grächen (1866-2009) were used (meteoswiss). The correlations of the different corrected $\delta^{13}\text{C}$ chronologies and the tree ring width chronologies with the monthly mean temperatures are positive and highly significant. The highest correlations of these annually resolved chronologies are visible in summer season (June, July, August). For the pentad chronologies these correlations are even higher, especially in the summer season, which equals the growing season at such high altitudinal sites.

Furthermore, all chronologies were tested for their sensitivity to precipitation. Two annually resolved, corrected $\delta^{13}\text{C}$ chronologies show a significant negative correlation to July/August precipitation, which is likely related to the local climate of the Simplon region where warm and dry summers are typical. Two corrected $\delta^{13}\text{C}$ and the tree ring width pentad chronologies show highly significant positive correlations with April/May precipitation.

These results show that $\delta^{13}\text{C}$ analyses from tree-ring methoxyl groups are suitable as a summer temperature proxy. In further studies this new method can be used to reconstruct past temperatures from tree rings at high alpine sites.

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V5.4

Influence of microsite conditions on oxygen isotope time series of *Pinus sylvestris*

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Oxygen isotopes in tree rings have frequently been utilized to reconstruct temperature and precipitation variations (Battipaglia et al. 2008). However, the $\delta^{18}\text{O}$ variability among trees with respect to changing microsite conditions has rarely been investigated. The range of $\delta^{18}\text{O}$ values among trees at a single sampling site can be as large as 1 to 4‰ for oxygen stable isotopes (Leavitt et al. 2010). In this project, we investigated the influence of microsite conditions and water access on oxygen isotope time series from *Pinus sylvestris* at boreal lakes in northern and central Sweden. At each of these study sites, we selected one microsite directly at the lakeshore with water access to the lake water and the other microsite near the lake without direct water access for the trees. The presented chronologies are annually resolved and cover the time interval 1900-2010. We assume that oxygen isotopes are linked to the soil water or precipitation, relative humidity and temperature. The variability of these climatic factors also account for the variability among trees of different microsites.

Inter-tree variability of isotope records and tree-ring width were examined for differences between the microsites. We investigated the influence of a number of climatic parameters (precipitation, potential evapotranspiration, hydrological balance, global radiation, cloud cover, minimum, maximum and average temperature) on the oxygen isotope records of the microsites.

We expect differences in the correlations between climate and $\delta^{18}\text{O}$ values of both microsites and between the northern and southern site. We also conclude differences in the stomatal conductance and photosynthetic activity between micro-sites.

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V5.5

Compound-specific δD -analysis from Eifel maar deposits - a new palaeotemperature proxy derived from methoxyl groups?

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Stable hydrogen isotope ratio measurements (expressed as δD values) of specific organic compounds are useful tools for determining geographical origin, identity or authenticity from a variety of sources, such as sediments and plants. Increasing effort is focused on using compound-specific analysis to adapt or broaden applications on palaeoclimate and palaeohydrology investigations. In this context, δD values of methoxyl groups seem very promising based on a strong linear correlation with δD of their source water ($R^2 = 0.95$ [1] and $R^2 = 0.91$ [2], respectively). This agrees with current knowledge that assumes a constant isotope fractionation between source water and organic matter [3]. Moreover, a simple and rapid extraction method exists, allowing analysis using gas chromatography/thermo conversion/ isotope ratio mass spectrometer (GC/TC/IRMS) [4].

Here, the method's adaptability is specifically tested on methoxyl groups from sediment archives dating back into Late Glacial times. Samples are received from two Eifel maar sediment cores containing methoxyl groups derived from different sample types, such as wood samples, bulk sediment and oospores.

With respect to the internal precision of the GC/TC/IRMS of $\pm 2\text{‰}$, a principle adaptability can be shown, since precise δD values derived from methoxyl groups were measured for all sample types (mean standard deviations within the range of 1.3‰ and 3.3‰, 1σ). First evaluations regarding palaeoclimatic implications are made. Considering a North-South transect across Europe, δD fluctuations within precipitation and lake water are strikingly linearly correlated with the local mean annual air temperature ($R^2 = 0.99$ and $R^2 = 0.93$, respectively [5]), leading also to a tight gradient of 4-6‰ per 1°C . Applying the range of gradients on the assumed constant fractionation between δD of source water and methoxyl groups suggests a potential palaeotemperature proxy. Bulk sediment's organic and oospores reveal promising results, as they approach realistic temperature differences for the covered time. Especially oospores exhibit enormous potential based on their clearly distinguishable and uniform origin.

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Vorträge – Sektion 6 Geologie und Hydrologie

V6.1

Effekte von Wasser-, Ton und Karbonatgehalten auf die ^2H - und ^{18}O -Isotopie des extrahierten Bodenwassers in Untersuchungen zur Wasseraufnahme von Bäumen

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Die stabilen Isotopen ^2H und ^{18}O werden häufig verwendet, um die Wasseraufnahmetiefen von Bäumen zu bestimmen. In der vorliegenden Studie haben wir untersucht, in welchem Ausmaß die Bodenfeuchte, der Ton- und der Karbonatgehalt von Böden die isotopische Zusammensetzung des extrahierten Bodenwassers beeinflusst. Dazu wurde getrockneten Bodenproben eine geringe Menge isotopisch bestimmten Wassers zugegeben.

Unsere Ergebnisse zeigen, dass sowohl $\delta^{18}\text{O}$ als auch $\delta^2\text{H}$ des extrahierten Wassers mit zunehmendem Tongehalt und abnehmender Wasserzugabe abnehmen. In kalkhaltigen Böden war der $\delta^{18}\text{O}$ -Wert der Proben beeinträchtigt, nicht aber der $\delta^2\text{H}$.

V6.2

Zum Einfluss unterschiedlicher Windsysteme auf den Wasserhaushalt in einem Einzugsgebiet im westlichen Pamir Zentralasiens

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Wasserknappheit ist ein weit verbreitetes Problem in großen Teilen der Welt. Auch die zentralasiatischen Ebenen, die stark landwirtschaftlich genutzt werden, sind davon betroffen. Die Wasserversorgung wird über die großen Flusssysteme des Amudarja und Syrdarja sichergestellt, welche hauptsächlich durch Schnee- und Gletscherschmelzen im Pamir und Tien Shan gespeist werden. Im Zuge des Klimawandels könnte es daher zu einer Verschärfung der Wasserknappheit in dieser Region kommen.

Um die verschiedenen Abflusskomponenten identifizieren und quantifizieren zu können, haben wir im Amudarja-Quellgebiet ein für den Pamir charakteristisches Einzugsgebiet - das Gunteinzugsgebiet mit einer Fläche von circa 14000 km² - ausgewählt. Dieses Gebiet wird sowohl von den Westwinden als auch vom Indischen Monsun beeinflusst und weist eine Gletscherbedeckung von etwa 5% auf. Ziemlich in der Mitte des Einzugsgebiets befindet sich ein See (Yashilkul) mit einer Fläche von rund 40 km², der durch einen Bergsturz entstanden ist.

Im monatlichen Rhythmus werden Oberflächenwasser- und Niederschlagsproben gesammelt und hydrochemisch und isopenhydrologisch untersucht. Damit werden neben den Abflusskomponenten auch die Niederschlagsherkünfte und -einflüsse erfasst, um letztendlich ein hydrologisches Modell für diese Region kalibrieren zu können.

Die mit einem Höhenintervall von 2000 bis 6700 m extreme Lage und die alpine Morphologie des Untersuchungsgebietes führen zu sehr kontrastreichen Isotopenwerten. Deuterium-Exzess-Werte (d) von deutlich über 10 ‰ deuten für die Niederschläge auf Luftfeuchte aus Re-Evaporation und damit auf einen Ursprung vom Kaspischen Meer und/oder dem Mittelmeer hin. Für die Oberflächenwässer sind die hohen Exzesswerte wesentlich auf ihren Ursprung aus Schnee und Gletscherwasser zu interpretieren.

Unterschiede werden auch durch die jeweilige Öffnung der Seitentäler innerhalb des untersuchten Gebietes ausgelöst. Verschieden hohe d-Werte charakterisieren dort verschieden starke Einflüsse bevorzugt nördlicher bzw. südlicher Luftmassen-Ursprünge.

V6.3

Stable isotope geochemistry of Franconian rivers - insights into hydrogeological processes and carbon turnover

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The Franconian Alp and its surrounding areas in Northern Bavaria are drained by several small to medium size streams such as the Wiesent, Schwabach, Pegnitz, Regnitz and Aisch. All rivers are tributaries to the Main River. These rivers were investigated by major ion analysis and standard hydrological field parameters (Alkalinity, EC, pH, Eh, T, O₂) together with water stable isotope analysis ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) to obtain insights into changes and influences on river water chemistry. Such changes can be induced by natural process as changes in the geology or the weathering regime but can also be related to agricultural land use or urban influences in the more densely populated area around Nuremberg.

Another key question is the carbon turnover and carbon flux of such river systems. For this purpose, the relevant carbon species have been investigated by means of stable isotope geochemistry. We analyzed $\delta^{13}\text{C}$ of dissolved inorganic carbon (DIC), dissolved organic carbon (DOC) and for some rivers also the particulate organic matter (POM). The combination of water isotopes with carbon isotopes of dissolved and particulate organic matter reveals seasonally variable in-river production of biomass in these sensitive aquatic ecosystems. This river network data set also enables insights into the response of the hydrologic cycle to environmental and anthropogenic changes.

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Poster – Sektion 1

Analytik: Neue Methoden und Techniken

P1.1

Nitrogen isotope analysis of glyphosate and AMPA by derivatization - gas chromatography - isotope ratio mass spectrometer (GC-IRMS).

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Glyphosate (*N*-(phosphonomethyl) glycine) is a widely used herbicide effective against weeds control in agricultural and domestic applications. Microbial activity (biotic) is the main degradation process of glyphosate leading to formation of the metabolite AMPA (aminomethylphosphonic acid). The increased detection of glyphosate and AMPA in surface and groundwater has motivated much research on their environmental fate. Current approaches on concentration measurement and source identification can often not adequately assess degradation of glyphosate and its metabolite AMPA because of the difficulty of establishing mass balances - to this end, an expensive sampling network would be needed. We bring forward compound-specific isotope analysis (CSIA) of glyphosate and AMPA analysis as an alternative approach to detect glyphosate and AMPA degradation. To this end, in this work we present a method to measure nitrogen isotope ratios of glyphosate and AMPA by derivatization and gas chromatography coupled to isotope ratio mass spectrometry (GC-IRMS). We demonstrate a two-step derivatization of glyphosate and AMPA by (1) isopropyl chloroformate (iso-PCF) and (2) trimethylsilyldiazomethane (TMSD). Further, we show that pH 10 is the optimum pH required during the derivatization by (iso-PCF) and that ratios (iso-PCF: analyte) of (10-24) are sufficient to produce accurate nitrogen isotope ratios. The limit for accurate nitrogen isotope analysis of glyphosate and AMPA was determined. The dual- isotope plot (d¹³C&d¹⁵N) of the different commercial products shows discrimination of some products. The d¹⁵N of the commercial samples ranged from +3.33‰ to -1.9‰ while d¹³C varied between -24.59‰ and -33.69‰. Thus, combined analyses of carbon and nitrogen isotopes bear potential to trace sources of glyphosate and AMPA metabolite.

P1.2

Stable selenium isotope signatures as a tool to examine the selenium transformation processes leading to accumulation and depletion in plants

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The trace element selenium (Se) is of high environmental significance, because it is an essential nutrient and a toxin with a narrow tolerance range. Selenium is dominantly transported to the organisms via the food chain. That is why a deep understanding of processes dominating the Se cycle in the “critical zone” (soil-plant-groundwater) is crucial. Based on that, the natural biogeochemical conditions as well as the applied cultivation methods in problematic areas can be monitored and adapted with the aim of an appropriate Se supply.

Examining Se isotope fractionation patterns is a promising tool to explore plant related processes, as several studies ([1]; [2]; [3]; [4]; [5]; [6]) found a characteristic relation between isotopic signatures and (a)biotic processes in the critical zone, e.g. redox reactions, sorption and volatilization. However, most processes within plants and interfaces between plant, soil and groundwater have not been examined concerning their isotope fractionation.

Under controlled conditions we will investigate the isotope fractionation in different plant parts induced by the processes mentioned above. The experiments will vary in Se species added, culture medium (see [7]), cultivation time and plant species. We will analyze different plant parts (root, stem, leaf, grain) and the surrounding environment (water, soil) with regard to their isotopic composition. Our goal is to clarify the characteristic isotope patterns and therefore allow the reconstruction of underlying processes from in situ plant material by their isotope signatures.

MC-ICP-MS enables highly accurate measurements of the stable Se isotopic composition of environmental samples (e.g. [8]). Isotope fractionation during sample preparation and instrumental mass bias is corrected by a ⁷⁴Se/⁷⁷Se double spike ([8]). An on-line hydride generator is connected to exclusively carry the hydride generating elements (e.g. Se, As, Ge) into the spectrometer. This step amplifies the Se signal and separates the main matrix elements from the target element Se.

The basic prerequisite is that the Se analyte is highly purified from the sample matrix in order to minimize isobaric interferences. Two different Se separation methods are prominently described in literature ([5] (1); [9] (2)). Both of them are based on anion exchange techniques in flow-through columns packed with different materials (BioRad AG1-X8 resin (1), thiol activated cellulose powder (2)). We tested and optimized these methods for different matrices with regard to purity and Se yield as well as time and cost efforts. Each method has its strengths and weaknesses, depending on matrix and element concentrations.

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P1.3

Investigation of possible isotopic fractionation by coupling ITEX to GC/IRMS

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Stable isotope analysis is a useful tool in many scientific disciplines, as it allows to distinguish between the origin of analytes (C3- or C4-plant, natural or synthetic) or gives an insight into the degradation of substances as well as reaction mechanisms. This is achieved by monitoring the change of isotopic ratio of the heavier and the lighter isotope (¹³C/¹²C) of the analytes, caused by thermodynamic or kinetic isotope effects.

For precise isotope ratio mass spectrometry (IRMS) of volatile organic compounds in aqueous samples a sufficient amount of carbon on column is required. Common headspace analysis in combination with purge and trap enrichment needs a complex analytical setup. Hence, the recently introduced in-tube extraction (ITEX) is an appropriate alternative. The basic element of this system is a syringe with a packed needle, through which an aliquot of the sample headspace is aspirated and dispensed in several cycles. The needle is surrounded by a heating unit in the area of the packing material for efficient desorption. The sorbent is exchangeable with the needle, reducing the potential of contamination. Additionally, combinations of different sorbents are possible. Furthermore, the heating unit of ITEX makes the desorption step independent from the injector.

ITEX workflow can be divided into four steps: 1. sample conditioning by steering and heating the sample, 2. adsorption by aspirating and dispensing the sample headspace along the trapping phase with a defined number of cycles, 3. desorption by heating of the trap up to 350 °C, and dispensing the sample into the injector and finally 4. the trap cleaning. But the ITEX system might cause a possible isotopic fractionation due to the several phase transition steps involved. Therefore the extent of fractionation is investigated in dependency of the ITEX parameters.

A GC/IRMS is used for δ -values measurement of twelve exemplary volatile environmental contaminants. The GC is equipped with an autosampler and the ITEX option. Further, a cryo focusing unit is used to realize the complete transfer from ITEX on to the column.

The ITEX-GC/IRMS δ -values are compared to δ -values obtained by liquid injection of the pure compounds to the GC/IRMS system. Based on method parameters which were already proposed for optimal yields the ITEX method was varied to study potential effects on the δ -values. The two main goals are maximal extraction yields and complete sample introduction into the GC system. The former is mainly affected by the extraction strokes and extraction flow, which were 15, 30, 60, 120, 240 and 25 μLs^{-1} , 50 μLs^{-1} , 100 μLs^{-1} , 200 μLs^{-1} respectively. To obtain the correct δ -values the extraction should be complete, otherwise the δ -values might be falsified.

As expected, more extraction strokes lead to higher extraction yields and the same applies for lower extraction flows. A dependency of extraction yield and δ -values and thus a trend can be seen for certain compounds. Compared to the δ -values obtained by liquid injection the ITEX measurements show an offset, especially for the halogenated. Never the less, the isotope ratio measurement shows stable results for constant ITEX conditions.

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P1.4

Analysis of Carbon Isotope Fractionation by Oxidative Degradative Reaction of the Herbicide Glyphosate by LC-IRMS

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

There are two ways of environmental degradation for glyphosate. Besides biodegradation, one possible way of abiotic degradation is oxidation catalyzed by manganese dioxide (K⁺-birnessite). For this reaction Cordeiro *et al.* proposed a free radical pathway for oxidative breakdown of phosphonates^[2] The products, sarcosine and glycine, are not specific, because they are also naturally present in the environment. Thus, a clear evidence of degradation in the environment solely by the identification of products or concentration losses is barely possible.

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

However, up to now compound-specific isotope analysis of glyphosate has not been reported in literature.

The aim of this work was to develop a method to determine compound-specific $\delta^{13}\text{C}$ of glyphosate by Liquid Chromatography Isotope Ratio Mass Spectrometry (LC-IRMS), which allows monitoring of the environmental degradation processes of glyphosate. This method was applied to study the abiotic degradation of glyphosate by manganese dioxide mentioned above. The monitoring of the degradation by LC-IRMS has been carried out by the use of a Hypercarb[®] chromatographic column and an eluent of pure water (75%) mixed with a phosphate buffer (25%, 10 mM, pH 1.9). The calculated carbon isotopic enrichment factor was for the degradation reactions by K⁺birnessite in a range from $-3.68\text{‰} \pm 0.55\text{‰}$. The influences of different parameters (e.g. temperature or different reagent concentration) on degradation were investigated and both have an influence on the degradation. The rate constant for second order reactions shows a temperature dependency.

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P1.5

Salt-induced shifts of stable isotope values in fluids - methodological comparison of isotope ratio infrared spectroscopy (IRIS) and isotope ratio mass spectrometry (IRMS)

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The presence of salts in fluids may influence measured stable isotope values, which has been shown to be the case for gas-water equilibration methods (e.g. Horita et al., 1993) by isotope ratio mass spectrometry (IRMS). The isotope shift is a function of the respective salt type and concentration (Martineau et al., 2012, Lécuyer et al, 2009). Direct conversion techniques like pyrolysis or the new laser stable isotope instruments allow the direct measurement of the water molecule from the sample and should therefore not suffer from salt effects, i.e. no shifts should occur. However, due to high salt concentrations technical problems with the analytical hardware (e.g. clogging of syringe) may occur which may require labor-intensive sample preparation such as vacuum distillation that also might introduce additional bias.

Our presented study evaluates instrument related effects of a laser-based IRIS (isotope ratio infrared spectroscopy) instrument for liquid water injection (Picarro L2120-i) without liner system. Synthetic salt solutions (NaCl, KCl, CaCl₂, MgCl₂, MgCl₂·6H₂O, MgSO₄·7H₂O) and natural brines collected from the Stassfurt Salt Anticline (Germany; Stadler et al., 2012) were measured and compared to the IRMS equilibration technique (Thermo Gasbench II coupled to Delta plus XP). First results show that equilibration (IRMS) and vaporization (IRIS) methods suffer from different effects: Chemical effects on ion activities require correction factors for IRMS, whereas physical-technical (i.e. instrument) effects hamper IRIS analyses. For example, the effect of salt accumulation in the vaporizer module and the influence of brine density on sampling volumes during injection can be problematic during the analysis of samples with high concentrations.

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Poster – Sektion 2 Ökologie und Physiologie

P2.1

Lichtabhängige Mykoheterotrophie bei Orchideen: Stabile Isotope liefern neue Einblicke

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Die vielfältigen und faszinierenden Lebensweisen innerhalb der Pflanzenfamilie der Orchideen sind Gegenstand aktueller Forschung. Angesichts ihrer winzigen und fast endospermlosen Samen, teilen alle der weltweit geschätzten über 20.000 Orchideenspezies das Merkmal einer anfangs vollständigen Mykoheterotrophie. Dies bedeutet eine absolute Abhängigkeit durch die vom Wirtspilz gelieferten Kohlenstoffverbindungen und mineralischen Nährstoffe in ihrer sehr frühen Keimungsphase. Später entwickelt die Mehrzahl an Orchideen grüne Blätter. Aufgrund dieser Tatsache wird für diese Arten häufig eine vollständig autotrophe Ernährung angenommen. Allerdings bleiben ca. 200 Orchideenspezies auch im adulten Stadium chlorophyllfrei und somit während ihres gesamten Lebenszyklus vollständig mykoheterotroph. Aktuelle Studien, gestützt auf stabile Kohlenstoff- und Stickstoffisotopenhäufigkeiten, enthüllten für einige grünblättrige adulte Waldorchideen der Epidendroideae eine parallele Nutzung von zwei unterschiedlichen Kohlenstoffquellen: Eigene Fotosynthese und gleichzeitiger Kohlenstoffgewinn aus einem assoziierten Wirtspilz, dessen Pilzhypen die Wurzeln von Waldbäumen infizieren. Diese Fähigkeit der sog. partiellen Mykoheterotrophie scheint äußerst sinnvoll in schattigen Wäldern, da das Anzapfen einer zusätzlichen Kohlenstoffquelle bei Lichtmangel einen kompetitiven Vorteil mit sich bringt. Das Weiße Waldvögelein *Cephalanthera damasonium* ist eine partiell mykoheterotrophe Waldorchideenart, bei der neben grünen selten auch Albinos und panaschierte Individuen auftreten. Mit Hilfe von stabilen C- und N-Isotopenhäufigkeiten konnte eine Abhängigkeit des Mykoheterotrophiegrades vom Chlorophyllgehalt in den Blättern und der Lichtverfügbarkeit am Orchideenstandort bereits nachgewiesen werden. Basierend auf dieser jüngsten Entdeckung ist es von größtem Interesse diesen zugrundeliegenden Mechanismus auch bei anderen Orchideenarten zu untersuchen. Sichtungen von scheinbaren Albinos und panaschierten Individuen des Großen Zweiblatts *Neottia ovata*, einer nahen Verwandten des bekanntermaßen vollständig mykoheterotrophen und Ektomykorrhiza bildenden Vogel-Nestwurz *Neottia nidus-avis*, legten den Verdacht nahe, dass auch diese Art partiell mykoheterotroph sein könnte. Unsere Arbeit zeigt aber, dass das Auftreten der gelben und chlorophyllfreien *Neottia ovata* Individuen nicht auf verschiedene Mykoheterotrophiegrade zurückzuführen ist, sondern sehr wahrscheinlich auf unterschiedliche Stadien der Seneszenz. Unsere Erkenntnisse stützen sich auf stabile Isotopenverhältnisse in den Orchideen verglichen mit umliegenden vollständig autotrophen Referenzpflanzen, Korrelationen zwischen Chlorophyllkonzentrationen, relativer Lichtverfügbarkeit an den Orchideenstandorten und N- sowie C-Konzentrationen in den Orchideenblättern. Für eine zusätzliche Bestätigung unserer Ergebnisse, wäre eine DNA Analyse der im Wurzelraum der Orchidee assoziierten Pilze äußerst vielversprechend. Trotz des Auftretens von panaschierten und komplett chlorophyllfreien *Neottia ovata* Individuen konnten wir mit Hilfe von stabilen Isotopen keine partielle Mykoheterotrophie für diese Spezies nachweisen. Stabile Isotope gewähren somit nicht nur unter natürlichen Bedingungen Einblicke in das Ernährungsverhalten von Orchideen, sondern tragen auch maßgeblich zum Verständnis ihrer Ökologie bei.

P2.2

Metabolic origin of carbon isotope composition of CO₂ respired by darkened light acclimated leaves in three different plant species

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Significant diel variations of leaf dark-respired CO₂ ($\delta^{13}\text{C}_{\text{Res}}$) were observed in many plant species with largest diel variations of up to 14.8‰ (for a review see Werner & Gessler 2011). $\delta^{13}\text{C}_{\text{Res}}$ values are increasing under illumination and decreasing during darkness. The degree of diel variability and ^{13}C enrichment of $\delta^{13}\text{C}_{\text{Res}}$ was shown to be species-dependent, with evergreens, shrubs and some herbaceous species showing the largest diel variations (Werner *et al.* 2009) in contrast to fast-growing herbs and grasses (Priault *et al.* 2009). These large variations in $\delta^{13}\text{C}_{\text{Res}}$ and the extent of ^{13}C enrichment in respired CO₂ cannot be explained by the carbon isotopic composition of putative respiratory substrates alone (Werner & Gessler 2011). The anaplerotic CO₂ fixing PEPc in leaves of C₃ plants could be responsible for the extent of ^{13}C enrichment of $\delta^{13}\text{C}_{\text{Res}}$. A connection between PEPc activity in leaves of C₃-plants and ^{13}C enrichment of $\delta^{13}\text{C}_{\text{Res}}$ (during LEDR) was already discussed by Gessler *et al.* (2009), Werner *et al.* (2009) and Werner *et al.* (2011). In this project, we aim to identify the origin of the sometimes exceptionally high diel variation of $\delta^{13}\text{C}_{\text{Res}}$ of *Halimium halimifolium* and *Arbutus unedo* in comparison to *Oxalis triangularis*, previously shown to have a more moderate diel cycle and diurnal ^{13}C enrichment of $\delta^{13}\text{C}_{\text{Res}}$. The $\delta^{13}\text{C}_{\text{Res}}$ values and the amount of respired CO₂ were measured by the in-tube-incubation technique (Werner *et al.* 2007). In parallel, we determined the $\delta^{13}\text{C}$ value and amount of malate with compound-specific LC-IRMS. *Halimium* showed the highest ^{13}C enrichment in respired CO₂ and the highest respiratory CO₂ flux. In contrast to recent findings, $\delta^{13}\text{C}_{\text{Res}}$ of *Oxalis triangularis* was similar to those of *Arbutus*; both species showed similar CO₂ production. *Halimium* showed the most negative $\delta^{13}\text{C}$ value of malate and the lowest malate concentration. *Oxalis* showed the most positive $\delta^{13}\text{C}$ values of malate (up to -11.2‰) and a concentration of malate at a medium level, whereas *Arbutus* had the highest concentration of malate and a $\delta^{13}\text{C}$ value at the medium level. To summarize: High amount of respired CO₂ with high ^{13}C enrichment seems to be connected to low concentration and negative $\delta^{13}\text{C}$ values of malate (*Halimium*). Light-activation of PEPc in C₃ plant leaves is known to replenish the Krebs cycle with carbon in case C is removed in form of CO₂ and/or carbon skeletons for biosynthesis (Bowsher *et al.* 2008). Surplus malate (and/or citrate) can temporarily be stored (Bowsher *et al.* 2008) and later on metabolized. The results will be discussed on basis of partitioning of malate (around the Krebs cycle) into storage, energy-gaining processes and biosynthesis of amino acids.

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Poster – Sektion 3

Stoffkreisläufe in Ökosystemen

P3.1

Carbon and nitrogen balance as well as $\delta^{15}\text{N}$ $\delta^{13}\text{C}$ depth gradient in soils with different lime treatment.

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1 to 2 cm thin soil layers from an experimental liming experiment in a spruce forest started in 1981 were investigated to make up a balance of carbon and nitrogen. Simultaneously the $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ ratios were determined.

In comparison of the balances and the isotope ratios from control plot and limed plots the effect of liming could be demonstrated. Highest effects were found in nitrogen balance and $\delta^{15}\text{N}$ ratios. The lighter nitrogen isotope ^{14}N is depleted from top soil layers. $\delta^{15}\text{N}$ is enriched in deeper horizons. The enrichment of ^{15}N may be an indicator for higher microorganism activity resulting in smaller N-stocks in these horizons.

Carbon was also depleted from the top soil, but ^{13}C isn't accumulated in the same intensity as ^{15}N .

The stable isotope changes in the limed profiles are more intense for nitrogen as for carbon, that means, that nitrogenous carbon compounds are metabolized more intensive than non nitrogenous carbon compounds.

P3.2

Carbon isotope fractionation during anaerobic digestion in biogas plants

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Currently, the planet earth exceeds the number of 7 billion of people, which leads to a raising demand for energy and waste treatment. Due to the excessive production of greenhouse gases during combustion of finite fossil resources, alternative renewable energy sources such as biogas from organic wastes and energy crops become essentially important. However, the complex microbial processes of biogas formation from the degradation of polymeric organic compounds to methane and CO₂ are not fully understood yet. There is still an insufficient understanding of the specific degradation steps and methanogenic pathways depending on the microbial composition which have an influence on the efficiency and stability of biogas plants. To draw conclusions about the present methanogenic pathways and the correspondent microbiota, we used a combination of microbiological methods and stable isotope techniques. In a first approach, we cultivated several species of methanogenic Archaea as pure and mixed cultures in growth media including specific carbon sources (i.e., carbon dioxide, acetate, methanol, formate) to study the carbon-isotope fractionation in the evolving methane and carbon dioxide. In this context, the isotopic signature depends on the specific methanogenic Archaeum, the available carbon sources and the culture conditions. In an additional approach, we used ¹³C-labelled compounds in pure and mixed cultures as well as in samples from anaerobic digestors to determine the specific metabolic pathways and typical carbon flows. In a final step, the data obtained from the culture experiments will be used together with an online isotopic spectrograph (d¹³C_{CH₄} and d¹³C_{CO₂}) applied to the headspace gas outlet of biogas plants, which allows a real-time process control.

P3.3

Labeling study on the influence of sheep excreta on GHG emission from a histic Gleysol

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Sheep grazing is an important extensive management activity on peatlands, in particular on nature protection areas. It aims at removing nutrients, keeping areas open, and preventing succession of forest vegetation.

A microcosm experiment on the influence of sheep excreta on GHG emissions on a histic Gleysol was set up using the stable isotope tracer technique. Labeled sheep feces and urine were obtained by feeding enriched material. Subsequently, excreta were applied to peat columns in microcosms.

Sheep labeling was accomplished by feeding corn silage (¹³C label of C4 plant) and ¹⁵N-NH₄Cl. Enriched food was applied for 10 days. Sheep feces and urine were collected separately twice a day. After the labeling period, excreta were collected for another week recording declining tracer signals. Every 4-5 days hair samples were collected for studying transfer of label via the sheep's metabolism.

Undisturbed peat columns from the "Grosses Moor" (peatland near Gifhorn, northern Germany) were installed in an automated microcosm system and incubated at 15 °C. Suction plates were kept a constant pressure of -150 hPa. After 10 days pre-incubation labeled material was added.

Tracer addition was carried out by applying 40 mL urine and 33 g feces in different combinations to peat columns depending on the respective treatment. GHG fluxes were recorded on a daily (start) to weekly basis. N_{min} of each column was analysed as a collective solution sample from the suction flasks every four days. At the end of the experiment microbial biomass was extracted to show tracer incorporation into this pool.

The ¹⁵N signature of feces and urine during labeling showed a typical bell-shaped curve over the whole labeling period resulting in maximum enrichments of 13 and 9 atom % ¹⁵N, respectively. After 5 days the label was found in the sheep hair showing a delayed ¹⁵N signal in comparison to the excreta. The maximum signal (ca. 5 atom % ¹⁵N) in hair occurred 14 days after beginning of the labeling period.

First results from the incubation experiment show low positive N₂O-fluxes as well as low positive CO₂-fluxes. GHG fluxes of manured peat columns were low during the whole experiment. First ¹⁵N-N₂O results show high enrichments on the first labeling days.

P3.4

Site preference von N₂O zeigt Denitrifikationsregionen innerhalb eines Bodenprofils während eines Düngungsexperiments (Fichtelgebirge)

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Lachgas (N₂O) ist das drittwichtigste langlebige Treibhausgas nach CO₂ und CH₄ (WMO greenhouse gas bulletin, 2011). Der bisher oft verwendete $\delta^{15}\text{N}^{\text{bulk}}$ -Wert kann Informationen über die Stoffwechselweg geben, bei denen N₂O produziert oder konsumiert wird. Dieser Wert ist jedoch von der Isotopie des Substrats beeinflusst, welche oft nicht schnell und einfach ermittelbar ist. Die zusätzliche Messung der site preference (SP), der intramolekularen Verteilung des schweren Stickstoff-Isotops ¹⁵N im asymmetrisch linearen Lachgasmolekül N₂O, zeigt hier eine unkomplizierte Lösung, da sie unabhängig von der isotopischen Zusammensetzung des Substrats ist (Ostrom, 2011). Sie ist definiert als die Differenz des $\delta^{15}\text{N}$ -Werts zwischen dem zentralen (α) und dem terminalen (β) Stickstoff-Atom des N₂O-Moleküls ($\delta^{15}\text{N}^{\alpha}-\text{N}^{\beta}-\text{O}$). Derzeit liegen nur sehr wenige Informationen über die SP für Bodenluftproben aus Tiefenprofilen vor (Park et al. 2011). Es wird z.B. erwartet, dass die SP bei der Reduktion von N₂O zu N₂ (Park et al. 2011) ansteigt.

Ziel der hier vorgestellten Studie war es, SP-Werte für ein Bodenprofil (Haplic Podsol) eines Fichtenbestandes (*Picea abies* (L.) Karst.) im Fichtelgebirge zu gewinnen und Produktions- sowie Konsumptionszonen von N₂O basierend auf der SP zu ermitteln.

Die siebenwöchige Düngungsstudie beinhaltete fünf Probenahmen auf drei Düngungs- und drei Kontrollflächen mit jeweils drei Messstellen. Auf den Düngungsflächen wurden drei Liter KNO₃-Lösung pro Quadratmeter (105 kg N ha⁻¹) ausgebracht, um mit dem enthaltenen Nitrat (NO₃⁻) die mikrobielle Denitrifikation zu stimulieren. Die Kontrollflächen hingegen wurden mit der gleichen Menge destilliertem Wasser versehen. Bodenwasserproben aus drei verschiedenen Tiefenstufen wurden mittels Saugplatten (organische Schicht) und Saugkerzen (installiert in 20cm und 90cm Tiefe) wöchentlich gesammelt und bezüglich ihrer NO₃⁻-Konzentration und des $\delta^{15}\text{N}$ -Werts des NO₃⁻ mittels HPLC (High Pressure Liquid Chromatography) resp. EA-IRMS-Kopplung untersucht. Bodenluft wurde durch installierte Bodenluftsonden in sieben verschiedenen Tiefen (von 10cm bis 100cm) mit Hilfe evakuierter Gasmäuse (100mL) gesammelt und das darin enthaltene N₂O auf seine $\delta^{15}\text{N}^{\text{bulk}}$ -, $\delta^{18}\text{O}$ -, $\delta^{15}\text{N}^{\alpha}$ - und $\delta^{15}\text{N}^{\beta}$ -Werte sowie auf ihre N₂O-Konzentration mittels PreCon-GC-IRMS untersucht. Die SP wurde ermittelt indem der $\delta^{15}\text{N}^{\beta}$ - vom $\delta^{15}\text{N}^{\alpha}$ -Wert subtrahiert wurde.

Die höchsten SP-Werte wurden im N₂O der Bodenluft innerhalb 10 bis 30cm Tiefe der Düngungsplots gefunden, begleitet von einem $^{15}\text{N}^{\text{bulk}}$ -angereicherten N₂O-Wert und einer niedrigen N₂O-Konzentration. Dies indiziert eine dominierende Denitrifikation zum Endprodukt N₂ in dieser Bodentiefe.

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P3.5

N₂O isotopologues in a landfill of mechanical-biological treated waste

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In Germany, deposition of municipal solid waste on landfills is only allowed if it contains less than 18 % organic carbon. Consequently, waste has to be pre-treated prior to deposition. An alternative to waste incineration is mechanical-biological treatment (MBT). MBT consists of a separation of fine and coarse fraction and biological treatment (e.g., fermentation and/or rotting) of the fine fraction, which contains large concentrations of labile organic matter. After treatment the material is depleted in labile organic carbon, but enriched in ammonium.

Measurements of N₂O fluxes from and N₂O concentrations in an MBT landfill were conducted in November and December 2011. Extremely high fluxes (up to 430 mg N m⁻² h⁻¹) and concentrations (up to 2.4 %-vol.) were observed close to the working face of the landfill indicating highly active nitrogen transformations after aeration during tipping operations (Harborth et al., 2013). However, it is unknown so far which processes actually produce the N₂O.

We measured d¹⁵N_{bulk}, d¹⁸O and site preference (SP) in N₂O from landfill gas. Clear trends and correlations of these parameters were observed, which indicate a high potential to resolve processes in combination with labeling experiments.

Peter Harborth, Roland Fuß, Kai Münnich, Heinz Flessa, Klaus Fricke: Spatial variability of nitrous oxide and methane emissions from an MBT landfill in operation: Strong N₂O hotspots at the working face, Waste Management, Available online 28 February 2013, doi: 10.1016/j.wasman.2013.01.028

Poster – Sektion 4

Stabile Isotope in der Agrarforschung

P4.1

Compound-specific isotope analysis of chloridazon and desphenylchloridazon

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Contamination of groundwater with nitrate and pesticides can adversely affect aquatic ecosystem and human health. Micro-pollutants, such as pesticides, consumer care products or pharmaceuticals, are introduced into groundwater systems by anthropogenic activity and have a potential for toxic effects even at low concentrations. The isotopic composition of a chemical can be used as a fingerprint to determine its origin. Additionally, isotope values may be measured to detect, quantify, and even identify abiotic or biotic transformation reactions of organic compounds based on the kinetic isotope fractionation associated with their (bio)chemical degradation reactions.

In this project we aim to investigate the fate of **chloridazon**, **desphenylchloridazon** and other prominent contaminants in the groundwater environment. For this purpose we will first develop a method, which would allow us to analyse the isotopic composition of common organic micropollutants at field-relevant low concentration levels. In the next step we will use the multi-isotope approach (¹³C/¹²C, ¹⁵N/¹⁴N, ³⁷Cl/³⁵Cl) to gain unique insight into pathways of micropollutant degradation. Finally lysimeter and column experiments will be performed to identify and quantify transformation processes based on micropollutants' isotope ratios under field conditions.

The project is expected to bring the CSIA method a substantial step forward towards its field application as unique method to characterize the long-term micropollutant fate in aquatic systems, a pressing issue for society. This project is funded by Swiss National Science Foundation (SNF) in the frame of Sinergia Project with two main partners Switzerland: the University in Neuchâtel (UNINE) and the Swiss Federal Institute of Aquatic Science (Eawag).

P4.2

Phenotypic plasticity of carbon discrimination in barley genotypes

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For predicting and managing negative and positive effects of future climate change on crops, understanding of phenotypic plasticity and its underlying genomic causes of cultivars is of importance for the development of adequate breeding strategies. Under current atmospheric CO₂-concentrations photosynthesis and hence yield and biomass production of C3-plants are not maximised and inter- and intraspecific differences are known.

As variation in discrimination against ¹³C during CO₂ assimilation is due to both stomatal functioning and enzymatic processes during photosynthesis we use carbon isotope discrimination as integrative tool to screen a subset of a barley diversity set. Here we report on the genotypic variation of barley flag leaf carbon isotope discrimination under current ambient CO₂ levels and how this is correlated to crop growth and the maximum photosynthesis. The genotypes were grown in open-top chambers (OTC) under field conditions. All genotypes were fertilized according to agricultural practice and well watered (plant available soil water content > 65%) during the whole experiment. The fully developed flag leaves of 57 genotypes were harvested at BBCH39, dried at 105°C, and analysed for their isotope composition (δ¹³C).

Yield and biomass (dry weight) of each genotype were estimated after harvest. δ¹³C of the flag leaves of the 57 genotypes under evaluations differed significantly, with genotype no. 27 having the strongest and genotype no. 38 having the weakest ¹³C discrimination ranging from approx. -32 ‰ to -26 ‰. δ¹³C did not correlate with yield, yield parameters, or total aboveground biomass, but there was a correlation with the dry weight of stems (r= 0.36836, p=0.0108, n=47). A correlation, though not significant, was found between δ¹³C and the maximum photosynthesis.

To avoid hampered gas exchange between the atmosphere and the leaves and provide all flag leaves the same CO₂ composition and amount we optimized and unified the growing conditions to achieve maximal stomatal opening. Given that reduced stomatal conductance does not play a role and the conductance is equal for all genotypes the differences in ¹³C carbon discrimination were mainly caused during photosynthesis either by different amounts or different activity of RuBisCO. Assuming the highest possible stomatal conductance excludes the RuBisCO effectiveness as a reason for the δ¹³C. Since flag leaf photosynthesis is responsible for a major part of grain filling and hence yield, we expected high yielding genotypes with more negative δ¹³C values. However, neither yield nor total biomass correlated with δ¹³C. The significant correlation of δ¹³C and stem dry weight might be a hint that the leaves contain a very high amount of or very active RuBisCO and stems are the highest carbon sinks. Additionally, there seems to be a restricted translocation of carbon compounds to the generative plant organs. In a subsequent experiment we'll investigate carbon discrimination of genotypes grown under ambient air and elevated CO₂ in parallel to gain knowledge about the genotypic variation under future climate conditions. No systematic evaluation of a wide barley gene pool was undertaken so far.

P4.3

$\delta^{13}\text{C}$ in faba beans and its involvement in drought stress response

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Faba beans (*Vicia faba*) are well adapted to the cool climatic conditions of Northern Europe. They have a high yield potential, but yield stability is often low. One reason for this is their sensitivity to drought. Winter faba beans with a developmental advantage of about 2 - 4 weeks compared to spring types can use winter precipitation more effectively. However, little is known about the variability present in winter faba beans with regard to physiological differences concerning their response to drought stress. To get information on this, 200 winter faba bean inbred lines are phenotyped under highly controlled conditions in single leaf/leaf disc tests regarding physiological traits related to drought tolerance, e.g. leaf water content, content of free proline and soluble sugars, membrane stability and chlorophyll content. To relate these results to field conditions, rain out-shelter trials are carried out with a subset of 40 out of these 200 winter inbred lines for determining yield and yield parameters under control vs. stress conditions.

In these trials, ^{13}C discrimination is regarded as a trait related to water use efficiency (WUE) as several studies (theoretical as well as empirical) have shown a high correlation between C isotope discrimination and WUE.

The first rain out-shelter trial in 2012 revealed significant differences in yield between genotypes as well as between control and stress conditions (7.1 – 37.0 g/plant in control vs. 6.2 – 18.2 g/plant in stress treatment). The same was true for the $\delta^{13}\text{C}$ values (-27.94‰ – -30.54 ‰ in control vs. -25.86 ‰ – -27.78‰ in stress treatment), proving that ^{13}C discrimination is to a certain extent indicative of drought stress.

$\delta^{13}\text{C}$ was in tendency positively correlated to yield, number of grains and thousand kernel weight under stress conditions, but interestingly, this trend was negative under control conditions.

The shift in $\delta^{13}\text{C}$ to less negative values was significantly but not strongly correlated to yield stability, i.e. relative yield ($r = 0.38^*$) indicating that water saving and therefore discrimination against ^{13}C could be seen as an inherent character and possibly early indicator of yield stability under drought stress in faba beans. The rain out-shelter trial is currently repeated.

Amongst the physiological parameters determined under controlled conditions, the highest correlation of $\delta^{13}\text{C}$ was found with total content of soluble sugars under drought stress ($r = 0.44^*$), which is assumed to contribute to osmotic adaptation. Osmotic adaptation plays a major role in water saving under drought stress as water is retained within the cells.

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Poster – Sektion 5

Klimaänderungen und -Rekonstruktionen

P5.1

Climate data and $\delta^{13}\text{C}$ in tree rings - What sampling size is necessary to prove significant differences in $\delta^{13}\text{C}$ for small differences in temperature and precipitation in German Midrange Mountains?

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Climate change in Central Europe causes higher temperatures and drought periods in summer, stressing the dominant tree species which are adapted on temperate cool temperatures and rainfall without long lasting drought periods. With the aid of stable isotopes analysis (Farquhar et al. 1989, Saurer et al. 1995) in the cellulose of tree rings it is possible to document the ^{13}C discrimination and the intrinsic water use efficiency (A/E) during their creation time.

This climatological archive in each tree would give us information over the climatological growing conditions of the individuals. As therefor we have a tool to assess climatological stress periods in former times. That allows a comparison of the same tree species on different stands and a differentiation of stress in a species area. So it is possible to investigate whether the European Beech (*Fagus sylvatica*) will survive the climatic scenarios which are forecasted.

For this purpose we choose two beech stands of same site conditions (same age in equal altitude (500m a.s.l.), equal exposition (south) and slope, equal soil conditions) but differing in humidity (precipitation and vpd). In the area of Donnersberg (with a mean temperature of 8,3°C and a precipitation sum of 749 mm and on in the area of Idarwald (part of the Hunsrück mountains with a mean temperature of 8.1°C and a precipitation sum of 879 mm in each case measured from 1988-2004). The Idarwald site is a little bit more humid than the warmer Donnersberg stand, which is located closer to the Rhine valley. Mc Carroll and Loader (2004) and Treydte et al. (2004) argue that sample sizes from 4 to 6 trees are enough to differentiate different climate with stable isotope analysis. Our investigation shows that we find a typical trend but for significant results in discrimination of ^{13}C or WUE, we need more than 10 samples to show significant results on $\alpha=0.05$ level.

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Mc Carol

P5.2

A central facility for greenhouse gas analyses within the ICOS network (Integrated Carbon Observation System)

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The Integrated Carbon Observation System (ICOS) is a European-wide research infrastructure that aims at providing high quality observational data for the long-term monitoring of the European greenhouse gases balance. We are currently building up the Flask and Calibration Laboratory (FCL) in Jena (Germany), a central facility of the ICOS research infrastructure. It will be responsible for measurements of CO₂, CH₄, N₂O, CO, H₂, SF₆ and O₂/N₂ ratios as well as stable isotope analyses (CO₂ and CH₄) of flask air samples collected at atmospheric and oceanic observing platforms of the ICOS monitoring network. The samples will be taken regularly in 2L glass flasks with the help of an automated air sampling system, which is currently being developed at the Max-Planck Institute for Biogeochemistry. The second major task of the FCL is the provision of real air reference standards calibrated relative to the respective World Meteorological Organization (WMO) calibration scales for the calibration and quality control of continuous measurement systems at the monitoring stations.

A new team has started with the implementation of the tasks related to this job. This includes the set up of the following measurement systems:

- (i) a cavity ringdown spectrometer (Picarro G2301) for CO₂ and CH₄ measurements,
- (ii) a FTIR Spectrometer (Ecotech Spectronus FTIR) for CO₂, N₂O, CO, and CH₄,
- (iii) a multi-species gaschromatographic system (Agilent 7890A) for flask air analyses (detector types: FID, ECD, PDD, RGD) and
- (iv) a gas source isotope ratio mass spectrometer (IRMS, MAT 253, Thermo Fisher) and a cryogenic CO₂ extraction system for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ analyses on carbon dioxide[1].

All analytical systems are designed for automated performance and to ensure maximum capacity with advanced precision of measurement. In addition, we are also establishing a spiking system for the production of user-defined reference air mixtures and a relational database management system.

In our contribution we will show an overview of the laboratory setup and the first results from performance tests and measurements of the IRMS fed on the cryogenic extraction line.

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P5.3

Comparison of the carbon isotope fractionation by microbial methane oxidation between batch reactor and cell culture experiments

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Methane (CH₄) and carbon dioxide (CO₂) represent the major global greenhouse gases (GHG) produced from landfills. Since the emissions of the landfill gas are variable, and also decrease throughout the landfill's lifetime its use for energy production is uneconomical. When burning of the gas becomes very costly, biological treatment represents a powerful alternative for CH₄-removal. This is usually achieved by applying cover materials onto the waste. Methanotrophs within this layer are capable of metabolizing the C1 compound. They thrive at different conditions and are commonly divided into two types. Type I grows better at low CH₄-concentrations and uses the ribulose monophosphate pathway for formaldehyde assimilation. In contrast, type II tends to outgrow type I at high CH₄ levels and uses the serine pathway for assimilation. As a result of the difference in metabolism the carbon isotopic fractionation among substrate and products may vary, accordingly.

In order to estimate the fractionation of methane oxidation as a result of metabolic activity of methanotrophs experiments were performed at different conditions, favoring either methanotroph type I or II and at different temperatures. The samples with cell cultures in serum flasks with initial gas concentrations of 10% and 5% CH₄ were analysed by GC-IRMS. The obtained enrichment factors are compared together with enrichment factors from previous experiments with batch reactors. In both cases the factors are within the reported range of $\epsilon = 13\text{-}49\text{ ‰}$ for landfill cover materials from different sites¹.

¹ Chanton, J. P., Powelson, D. K., Abichou, T., Fields, D., Green, R., *Effect of Temperature and Oxidation Rate on Carbon-isotope Fractionation during Methane Oxidation by Landfill Cover Materials*, Environmental Science and Technology, 2008, **41**, 7818-7823

Poster – Sektion 6 Geologie und Hydrologie

P6.1

Räumlich hochaufgelöste Untersuchung von stabilen Isotopen im Grundwasser eines Lockergesteinsaquifers (Trinkwassereinzugsgebiet Fuhrberger Feld)

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Stabile Isotope ($\delta^2\text{H}$, $\delta^{18}\text{O}$) in Boden- und Grundwasser werden häufig zur Untersuchung von Schadstofftransport, Bodenwasserbewegung, Verdunstungseinfluss und Grundwasserneubildung herangezogen. Im Fuhrberger Feld, dem Haupttrinkwassereinzugsgebiet der Landeshauptstadt Hannover, werden bodenkundliche, hydrogeologische und hydrogeochemische Prozesse bereits seit langem untersucht und Wasserqualitätsparameter permanent überwacht.

Innerhalb weniger Wochen wurden im Sommer 2012 16 Multilevel-Messstellen im Untersuchungsgebiet Fuhrberger Feld beprobt und insgesamt 369 Wasserproben im Wasserlabor der BGR hydrochemisch und isopenhydrologisch untersucht. Die Ergebnisse zeigen auffällige Muster von Fraktionierung der stabilen Isotope die einerseits auf Verdunstungseinfluss und schnelle Infiltration von Niederschlag und andererseits auf Wintersignale und saisonale Schichtung interpretiert werden können. Erst in tieferen Bereichen zeigen sich einheitlich konstante Isotopenkonzentrationen wie für einen Lockergesteinsaquifer erwartet wird. Die gemessenen hydrochemischen Parameter ermöglichen eine zusätzliche bodenchemische Interpretationen und insbesondere die gemessenen TIC/TOC Gehalte der Wasserproben erlauben wertvolle Hinweise zur Überprüfung der für die stabilen Isotope verwendeten Laseranalytik (Picarro L2120-i CRD).

P6.2

Exploring catchment complexity by linking isotopic and hydrometric data in a small low-mountainous catchment

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Knowledge about water flow paths is essential for understanding biogeochemical fluxes in developed agricultural landscapes, i. e. the input of nutrients into surface waters, soil erosion, or pesticide fate. Several methods are available to study rainfall-runoff process and flux partitioning: hydrometric based approaches, chemical tracers, modeling, and stable isotope applications. In this study data from a hydrometric observation network were combined with stable water isotope analysis to gain insights into streamflow generating processes and small-catchment functioning at the Vollnkirchener Bach. While stable isotope data alone provide valuable integrative information about the overall catchment functioning, distributed hydrometric observations can help link these large scale observations to smaller scale processes and their spatial distribution along the studied stream reach.

The hydrometric measuring network at the Vollnkirchener Bach consists of a climate station, two RBC-flume discharge gauges and 20 piezometers distributed along a stream reach of the Vollnkirchener Bach. Most observation points are equipped with water level and temperature loggers for continuous measurements of stream water level/discharge and groundwater head. Isotopic samples were collected in several precipitation collectors, three stream water and twelve groundwater sampling points. Water samples were taken on a weekly to biweekly basis over a 2 years period. Additionally, high temporal resolution event-based sampling was conducted.

Preliminary results indicate that the catchment responds differently to precipitation input signals and that dominant processes contributing to runoff generation changed throughout the year (e.g. due to different saturation conditions, or rainfall intensities).

At low flow conditions bidirectional interactions between the groundwater body ($\delta^{18}\text{O}$ -8.16 ± 0.82) in the riparian zone and stream water ($\delta^{18}\text{O}$ -8.34 ± 0.50) could be observed, which led to similarities in isotopic composition of both. Furthermore, no spatial isotopic differences between the stream water sampling points were seen under baseflow. The same was true for different precipitation sampling points. However, precipitation isotopic signatures ($\delta^{18}\text{O}$ -6.19 ± 3.11) differed significantly from stream and groundwater signatures, which could not be explained by liquid precipitation input. Thus, snowmelt ($\delta^{18}\text{O}$ -17.19 ± 1.88) apparently played a fundamental role for groundwater recharge. The studied stream reach is net losing water to the groundwater during dryer periods of the year. This can be explained by the topography leading to groundwater outflow at the lower end of the reach.

However, the net water balance is changing in wet periods, which seemed to be related to ephemeral groundwater sources becoming active. During storm flow large contributions of fast runoff generation processes occurred, that could be related to temporarily active point sources (anthropogenic channels) and observed surface runoff from clay-sandstone dominated forested sites. More event-based isotopic data are currently analyzed.

The study revealed that the collection of hydrometric data combined with isotopic tracers, provided fundamental information on the processes dominating the runoff generation at small-catchment scale.

P6.3

The hydro- and multi-isotope geochemistry of iron-rich ground waters generating SGD at the southern Baltic Sea coast

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Iron-rich groundwater springs emerging at the shore zone of the southern Baltic Sea (BS; Site Meschendorf) were examined on a seasonal base for a period of about two years. Besides major, minor, and trace elements, stable isotopes of water (H-2, O-18), dissolved inorganic carbon (DIC; C-13), and sulfate (S-34) were analyzed. The stream bed sediment was extracted for the geochemistry of the newly formed precipitates and further characterized via SEM-EDAX. Subsequently, the hydrogeochemical results were subjected to a thermodynamic analysis via the PHREEQC speciation model.

The springs emerge from small pits (about 60 cm diameter; up to 15 cm depth). Surrounding sediments are sandy with gravels found at depth and corresponding high permeabilities. The positions of different springs on the shore zone were stable during the investigation period while the shape of the pits and the stream beds may vary due to wind- and wave-driven forces. Selected measurements of spring yield discharges close to 10 L/min. The H-2 and O-18 contents of the spring waters indicate the ground water to originate from relatively young mixed meteoric waters. The hydrochemistry of the springs was similar and showed some variability in between which indicates that the genetic processes for the ground water before reaching the surface may slightly differ. The springs are characterized by dissolved Ca, Mg, Na, DIC and sulfate, mainly reflecting the interaction with soils and bedrocks in the recharge area that is dominated by marly till. The oxygen-free ground water is rich in Fe, P, and DIC. Iron and dissolved sulfate originate from the oxidation of pyrite, as further confirmed by the 34-S signature of sulfate. The carbon isotope signature of DIC indicates a mixture of biogenic CO₂ from the soil zone with some water-rock interaction with carbonate minerals. The streams flow towards the BS and, in contact with the atmosphere, outgas carbon dioxide and takes up oxygen. Upon CO₂-degassing, C-12 is preferentially desorbed from the aqueous solution. The changes in the stream composition lead to the formation of iron(oxyhydr)oxide precipitates in the stream bed before the waters pass to underground drainage into a subterranean mixing zone with brackish BS waters. These ochrous precipitates act as a sink for dissolved phosphate and minor calcium. P:Fe ratios and Ca:Fe ratios are about 0.08 and 0.2, respectively, which are caused by P adsorption and a mixture with minor CaCO₃ and/or Ca-phosphate.

The investigation reveals that the surface precipitation on the beach leads to the formation of SGD essentially free of dissolved iron and strongly depleted in phosphate. Similar iron phases may also be an important part of the subterranean estuary supposed at that coast line, where retention of nutrients and heavy metals by iron(oxyhydr)oxides could influence the release of nutrients into the coastal ecosystem. Fe- and P-rich surface precipitates, however, are transported in suspension into the Baltic Sea during wind-driven flood events. Acknowledgements: This work was partly supported by the BONUS⁺project AMBER and the Leibniz IOW.

P6.4

Landscape structure and hydrology patterns influence mean transit times derived from stable water isotopes – results from a nested catchment approach in Paramo ecosystems of Ecuador

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Improved understanding of catchment functioning and rainfall-runoff generation in Andean paramo regions is essential, given the importance of these ecosystems for water resources. The remote location of the Andean paramo contributes to the lack of proper data to develop suitable hydrological, process-based modeling tools needed for water resources management.

Stable isotopes have been widely used in different studies to better understand catchment functioning. Mean transit times (MTT) of water can be estimated based on stable water analyses in precipitation, soil water, stream water and groundwater. We will investigate how landscape structures, land use, topography and hydrology patterns influence MTT in the Zhurucay basin, Ecuador.

A nested sampling approach consisting of 10 subcatchments was used for the collection of stream water samples, each close to an existing weir where discharge is continuously recorded. Soil water samples of the organic and mineral horizons were collected in five representative locations, three in wetlands and two in grasslands area. In each, suction cups were installed in different horizons. Rock water samples were collected in three places. Weekly to biweekly precipitation samples as well as water grab samples at all sites were taken from May 2011 to July 2013. Further, three field campaigns to collect samples in rainfall events were organized from May to June 2011, April to Jun 2012 and March to April 2013 respectively. Hydrometric and meteorological information is available for the same periods.

Preliminary results indicate wide variations in the isotopic concentration of ²H and ¹⁸O present among the different sources of contributing waters. This translates into significant variation of MTT in the different subcatchments, despite their seemingly homogeneity with regard to land use. We conclude that subsurface structures, soil properties and topographic indices such as distance to stream likely explain observed variation in MTT. This is currently being analyzed by stepwise multiple regressions.



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- Distickstoffoxid, Kohlenmonoxid Analysator N_2O , CO
- Labor und On- Line Geräte
- Automatische Messstellenumschaltung für 8 oder 16 Kanäle

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Notizen

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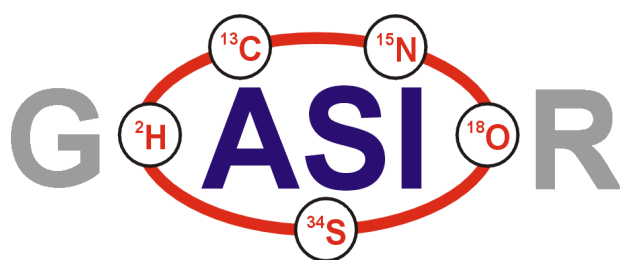
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