HelmholtzZentrum münchen
Deutsches Forschungszentrum für Gesundheit und Umwelt

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Jahrestagung der Arbeitsgemeinschaft Stabile Isotope e. V.

15. – 17. Oktober 2014
München

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Vorträge

Session 1 – Analytik: Neue Methoden und Techniken

V 1
High Resolution Multi-Collector Gas Source Isotope Ratio MassSpectrometry High Resolution Multi-Collector Gas Source

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Gas isotope ratio mass spectrometry is based on the conversion of complex molecules into simple gases like H2, N2 and CO2 to allow high precision determination their isotope ratios. In most applications position-specific and clumped isotope information is lost. Hence the direct application of target molecules into the IRMS would be required with the consequence of more complex mass spectra and an increase of isobaric interferences on low abundant isotopologues being targeted in such applications. Medium or high mass resolution is the method of choice for accurate quantification of low abundant ion beams resolving them from isotopologues, contaminants and adducts with the same nominal mass.
The MAT 253 Ultra - a high resolution double-focusing isotope ratio mass spectrometer, which has been installed in the Caltech laboratories for stable isotope geochemistry in Dec. 2011. This instrument achieves mass resolving power of up to 26000 (M/ M, 5%, 95 % definition) and can analyze diverse gases and semi-volatile compounds by dual inlet and continuous flow sample introduction. It has a multicollector array with 7 detector positions. 6 of the collectors can be moved automatically to arrange for the simultaneous acquisition of the required masses in complex isotopologue systems. Ions can be registered through SEM or faraday collectors, spanning up to a 1013 range in signal strength. Abundance sensitivity is as good as 10-12, and precisions are commonly counting statistics limited down to levels of 0.01 ‰ (or better) for a wide range of species.

The MAT 253 Ultra enables many previously impossible isotopic analyses of gases and volatile organics and their fragment and adduct ions, such as: δ13C, δD and 13CH3D of methane; δ13C of propane and many of its fragments (enabling position-specific 13C determination); direct analysis of δ17O δ18O, δ15N and 15N-18O ‘clumping’ in N2O and its NO fragment and clumped isotope analysis of CO2 free of contaminant isobaric interferences.

We are presenting an update on our concepts and recent work on the MAT 253 Ultra high resolution double focusing IRMS. Recent applications performed on the MAT 253 Ultra prototype will be presented in cooperation with John Eiler et al., California Institute of Technology, Pasadena, CA.

V 2

Comparison of methods to determine triple oxygen isotope composition of N_2O by conversion to O_2: Introduction of foreign oxygen and sensitivity

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The $\Delta^{17}O$ (or ^{17}O anomaly), i.e. the deviation of the $^{18}O/^{16}O$ to $^{17}O/^{16}O$ ratio from "normal" mass dependent fractionation can be used as an oxygen tracer that is not affected by fractionation processes (as mass dependent fractionation will preserve the $\Delta^{17}O$ of the oxygen). However, in molecules like N_2O, the $\Delta^{17}O$ cannot be determined, as variations in the $^{15}N/^{14}N$ ratio will affect the ^{17}O signal. Therefore, N_2O must be converted to O_2 before $\Delta^{17}O$ may be measured.

There are different approaches published for the conversion of N_2O to O_2: thermal decomposition in a hot gold oven (Kaiser et al. 2007, Smirnoff et al. 2012) and microwave discharge (Mukotaka et al. 2013). Here we report results on the comparison of the approaches of Mukotaka et al. and Smirnoff et al. with regard to signal attenuation by introduction of foreign oxygen and sensitivity of the methods.

References

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V 3

N_2O isotopic fractionation method to quantify N_2O reduction to N_2 - a validation in He+O_2 atmosphere

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Quantifying denitrification in arable soils is crucial in predicting nitrogen fertiliser losses and N_2O emissions, but very challenging, because the final product, N_2, cannot be measured directly due to high atmospheric background. Stable isotopocule analyses of residual N_2O ($d^{15}N$, $d^{18}O$ and SP = ^{15}N site preference within the linear N_2O molecule) may be useful in determination of the N_2O reduction progress, but the knowledge on the associated isotopic fractionation mechanisms must be improved. Until now the isotopic fractionation factors (η) during N_2O reduction have been determined in anoxic experiments showing large range of values for $\eta^{18}O$ and $\eta^{15}N$ but quite robust vales for ηSP [1]. Hence, SP values of residual N_2O can serve as a potential tool to quantify N_2O reduction.

But are the fractionation factors from artificially regulated experiments transferable to natural field conditions? There is still a gap between the targeted laboratory incubations and field applications, namely, the experimental approaches are missing, where in conditions mostly similar to real soil conditions, fractionation factors are confirmed or refined. Here we present the first laboratory study for validation of isotopic fractionation factors associated with N_2O reduction under oxic atmosphere. We applied an enhanced experimental approach allowing for the simultaneous N_2O production and reduction within the same soil incubation vessel [1] and performed incubations in He or He/O_2 atmosphere where N_2 and N_2O fluxes were measured directly [2].

The results from arable silt loam soil incubation will be presented. The ηSP values determined by previous anoxic experiments have been confirmed for oxic atmosphere. But interestingly, the correlations between SP and $d^{15}N$ or $d^{18}O$ values are significantly different for oxic and anoxic atmosphere, whereas the correlations between $d^{15}N$ and $d^{18}O$ values are independent on oxygen abundance. This is probably the effect of N_2O diffusion from the soil matrix, which has an impact on $d^{15}N$ and $d^{18}O$ but not on SP values of N_2O. The denitrification product ratios ($N_2O/(N_2+N_2O)$) were calculated based on measured SP values and compared to the true product ratios measured directly. The results of these calculations are very sensitive to the accepted values for initial SP of produced N_2O and isotopic fractionation factor. If values determined in this experiment (oxic, dynamic) are used, the calculated product ratio is very consistent with the measured one (mean error 10%), but if values determined for this soil in previous experiments (anoxic, static) are used, large discrepancy is observed (mean error 40%). Hence, the exact determination of initial SP of produced N_2O and isotopic fractionation factor for particular conditions is crucial for proper application of this method.

References

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V 4

Novel tool for simultaneous carbon and nitrogen stable isotope analyses in aqueous samples

E. Federherr[1,2], F. Volders[1], C. Cerli[3], K. Kalbitz[3], T. Schmidt[2], H. J. Kupka[1], L. Lange[1], R. Dunsbach[1], R. Panetta[4]
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Investigation of transformation and transport processes of carbon and nitrogen in ecosystems plays an important role to understand and predict their dynamics and role in biogeochemistry. Consequently, suitable and accurate methods for concentration as well as stable isotopic composition analysis of carbon and nitrogen in waters and aqueous solutions play a significant role.

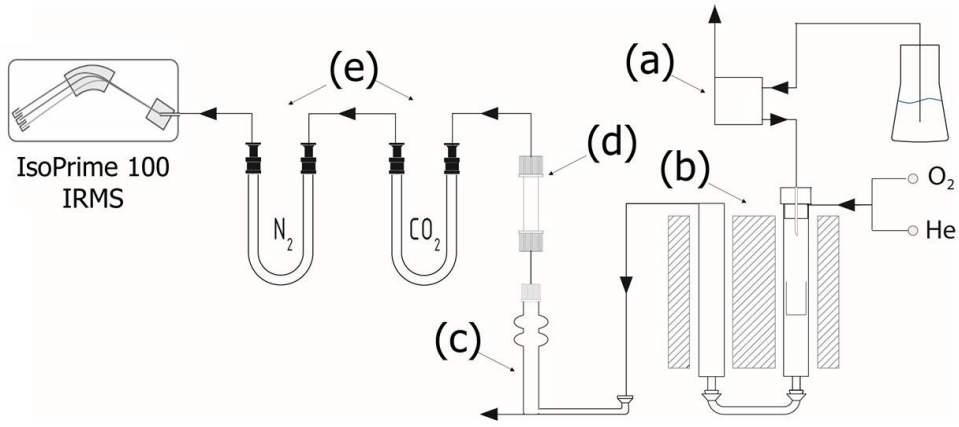
Traditionally dissolved carbon and nitrogen stable isotope analysis (SIA) is performed using either offline sample preparation followed by elemental analysis isotope ratio mass spectrometry (EA/IRMS) or modified wet chemical oxidation based device coupled to IRMS. Recently we presented a high temperature combustion system (HTC), which significantly improves upon these methods for dissolved organic carbon (DOC) SIA.

The analysis of $\delta^{15}N$ of dissolved nitrogen still has large limitations. Its low concentration makes EA/IRMS laborious, time and sample consuming. Systems based on wet chemical oxidation-IRMS bare the risk of sensitivity loss as well as of fractionation due to incomplete mineralization. In addition, the high solubility of molecular nitrogen in water remains a technical challenge, as it requires additional separation steps to distinguish between physically dissolved nitrogen and bound nitrogen.

Further development of our HTC system lead to the implementation of the $\delta^{15}N$ determination which now coupled, into a novel total organic carbon (TOC) analyzing system, especially designed for SIA of both, carbon and nitrogen. Integrated, innovative purge and trap technique (peak focusing) for nitrogen with aluminosilicate adsorber and peltier element based cooling system, in combination with high injection volume (up to 3 mL) as well as favorable carrier gas flow significantly improves sensitivity. Down to 1ppm and less total nitrogen can be measured with precision of ≤ 0.5‰. To lower the background caused by physically dissolved nitrogen new, membrane-vacuum based, degasser was designed for online separation of physically dissolved nitrogen.

This novel HTC system, “iso TOC cube”, provides an innovative tool with large potential in investigation of biogeochemical carbon and nitrogen cycles.

Anhang 1



(a) Degassing; (b) combustion/reduction; (c) condenser; (d) scrubber; (e) purge and trap

V 5

Selenium stable isotope variations as a process tracer in plants - chances and challenges

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[3]KIT, Botanical Institute, Karlsruhe, Deutschland

Selenium (Se) is an essential and toxic trace element with a narrow tolerance range for plants, animals and humans. The Se uptake and metabolism of plants is a key factor for Se accumulation in the environment and Se supply within the food chain. According to various studies (e.g. [1]) the determination of stable Se isotope fractionation is a powerful tool for the exploration of environmental processes with high fractionation at reduction and significant fractionation at enzymatic transformation reactions. Therefore it is promising also for the detection of plant related Se cycling. We are investigating in how far Se transport and transformation processes in plants induce stable Se isotope fractionation and if reconstruction of metabolic processes using isotope patterns is possible.

Based on previous studies (e.g. [2]) showing the variation of Se pathways with source Se species, we perform systematic plant cultivation experiments in a minimum parameter set up, separately exposing selenate (SeO_4^{2-}), selenite (SeO_3^{2-}) and selenomethionine (Se_{org}) in different concentrations. We observe uptake and translocation patterns strongly varying with Se species and concentration. This indicates the presence of rate limiting steps as well as the dependence of reaction and transport pathways based on Se related conditions. These are prerequisites for the reasonable use of Se isotope signatures to detect individual processes.

The accurate measurement of stable Se isotope ratios as well as the preparation and purification of plant material meeting the demands of the analytics is quite challenging. We use a multi-collector inductively coupled plasma mass spectrometer with on-line hydride generation and additional methane injection. Both measures increase the plasma temperature, stabilize the Se signal, and highly reduce isobaric interferences. For the correction of artificial fractionation due to sample preparation and instrumental mass bias we use the double spike technique ([3]), which requires the complete destruction of organic Se compounds during digestion. As the common plant microwave digestion method was proved to be insufficient for our purposes we set up an alternative one based on [4], which allows the use of lower acid amounts, reduces the blanks and memory effects and significantly increases the efficiency of organic destruction ([5]).

Precise and accurate Se isotope determinations require the removal of potential interferences in the sample matrix. For purification of samples with plant matrices we tested two methods based on flow through columns packed with different materials previously described for inorganic sediments [6] and bacterial samples [7]. We chose our preferential method with regard to Se yield, residual matrix elements and matrix effects during isotope measurements.

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Vorträge

Session 2 – Hydrologie und Hydrogeologie

V 6

Synthesis and Evaluation of Molecularly-Imprinted Polymers for Compound-Specific Isotope Analysis of Polar Organic Micropollutants

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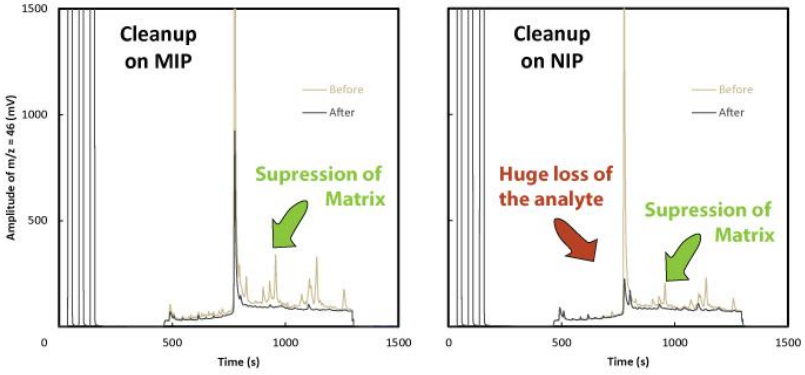
Polar organic micropollutants, such as pesticides, pharmaceuticals and consumer chemicals, are frequently detected in aquatic environments and hence are a major concern to the environment and human health. Compound-specific isotope analysis (CSIA) is a promising tool for assessing sources and transformation processes of polar organic micropollutants in aquatic environments. There are, however, two major challenges: (1) Polar organic micropollutants occur at very low levels and, as a consequence, large amounts of water are required to achieve analyte enrichment with factors exceeding 50'000, inevitably leading to large interferences from the matrix. (2) The polarity of these micropollutants impedes the use of typical non-polar sorbates for solid-phase enrichment without further cleanup steps. In view of these challenges, the use of molecularly imprinted polymers (MIP) is a promising approach to selectively retain polar organic micropollutants with reduced matrix interferences. In this work, we explore the use of MIP to selectively retain 1H-benzotriazole, a frequently found complexing agent used in dishwashing detergents and an important representative of polar aquatic micropollutants.

MIPs were synthesized in the presence of 1H-benzotriazole or similar analogous molecule as a template, which leaves cavities in the polymer matrix with a specific affinity to the template and closely related structures. After extraction of the template, specific recognition of substituted benzotriazoles and other compounds was tested in chromatographic columns packed with either the imprinted polymer (MIP) or the non-imprinted polymer (NIP). In addition, CSIA measurements of carbon and nitrogen were carried out for river water extracts before and after clean-up by the synthesized polymers.

Imprinting of benzotriazole molecule with factors larger than 1.0 was successfully achieved. No selectivity was observed for few other tested compounds with the exception of s-chloro-triazines (e.g. atrazine). Comparison of CSIA measurements before and after the selective cleanup indicates that no isotopic fractionation occurs on carbon during the process of loading the imprinted polymers with excess of 1H-benzotriazole. However, isotopic fractionation on nitrogen is induced if the recoveries are not complete. The ability of MIP to selectively suppress the matrix, in contrast to NIP, is demonstrated in the cleanup test of river water extracts.

This approach will enable us to enrich and clean large amounts of aqueous samples while minimizing interferences from organic matter and other organic micropollutants in the sample matrix and thus offer new perspectives for CSIA of polar organic micropollutants.

Anhang 1



V 7

Carbon Isotope signatures of DIC in temperate Tidal Areas of the southern North Sea trace Submarine Groundwater Discharge and Advective Pore water efflux

V. Winde[1], I. Schmiedinger[1], P. Escher[1], P. Böning[2], A. M. Al-Raei[3], B. Schneider[1], G. Liebezeit[4], M. E. Böttcher[1]
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We show a synthesis from different projects funded by BMBF, DFG, and IOW (BIOACID, 'BioGeoChemistry of theWaddenSea') dealing with tidal basins of theGermanWaddenSeain particular focusing here on the dissolved carbonate.

It was the aim of this study to investigate seasonal and tidal responses of the pelagic carbonate system in the basin without and under superimposition by *in-situ* transformation processes, like primary production and pelagic respiration. Both, the concentration and the stable carbon isotope composition of DIC are shown to be valuable tools to follow and analyze the tidal and spatial variations in the pelagic carbonate system of the tidal coastal waters.

The present study combines the sampling campaigns from seasonal, tidal and spatial resolutions that investigated the time and location response of the pelagic carbonate system under different magnitudes. In addition water samples from fresh water inlets, pore water, and coastal sediments were taken at different sites (e.g. Spiekeroog, Jade Bay). Salinity, temperature and pH were immediately measured. Water samples were filtered for stable isotope ($\delta^{13}C(DIC)$) and element (e.g. major and trace elements, nutrient, TA, DIC) composition. Finally, direct advective pore water efflux from permeable sediments during low tide was considered, too.

It has been shown that seasonal and tidal compositional variations occur in the investigation areas that indicate the mixing ofNorth Seawith fresh waters of different sources, superimposed by benthic-pelagic coupling. The combination of both, the concentration and the stable carbon isotope composition of DIC is shown to be valuable tools to follow and interpret the basic processes causing tidal and spatial variations in the pelagic carbonate system of the coastal waters.

An additional source for DIC and TA as well as nutrients and redox-sensitive elements is the benthic-pelagic coupling witch has been shown by outflow of nutrient enriched anoxic pore waters at intertidal sand plates in the back barrier tidal areas of the southern North Sea.

V 8

Artificial deuterium labeling for a quantification of groundwater recharge in semi-arid regions

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Proper estimations of groundwater recharge rates are essential for a sustainable management of water resources. Numerous methods are available (Scanlon et al., 2002); however, their applicability and reliability varies greatly depending on available data, spatiotemporal scales and climatic conditions within the studied area. The peak-displacement method (Saxena & Dressie, 1984) has been used extensively to estimate groundwater recharge rates in regions, where a distinctive seasonal variation of the stable isotopes oxygen-18 (^{18}O) and deuterium (^{2}H) in precipitation is present (Saxena, 1984; Adomako et al., 2010) . In semi-arid climates with only one rainy season this prerequisite is eventually not fulfilled; hence this simple and reliable method cannot be applied. In this study we present results of an artificial deuterium labeling experiment($^{2}H_2O$, 70%)in order to estimate groundwater recharge with the peak-shift method and characterize water movement during and after a synthetic rain event.

The study was carried out in the framework of the SASSCAL project in the Cuvelai-Etosha Basin in Northern Namibia. Experiments were carried out at two locations with different soil and vegetation types: A forest site ('Eenhana') with deep sandy soil and a shrub-/woodland site ('Okongo') characterized by dark loamy sand underlain by a thick layer of calcrete. At both locations, soils were first saturated to trigger typical rainy season conditions and avoid immediate evaporation of the deuterated water. Subsequently, 500 ml of $^{2}H_2O$ was applied homogenously over a 0.25 m^2 test plot at 25 cm depth. Finally, a 10 mm artificial rain event was applied onto the plot. Soil samples were collected every 10 cm to a maximum depth of 7.4 m with a hand auger after 1, 2 and 10 days as well as after the rainy season. From these, soil water was extracted in the laboratory and subsequently analyzed for $\delta^{2}H$ concentrations using a Picarro L2120-i cavity-ringdown (CRD) water vapor analyzer after vaporization and with a Los Gatos DL 100 directly in the field. Gravimetric water content and soil hydraulic properties were determined in the lab.

We found groundwater recharge rates of 9mm at Eenhana and 4mm at the Okongo site for the rainy season 2013/2014. The injected deuterium peaks travelled from 2.3 m to 5.5 m and from 0.5 to 0.9 m, respectively. Extremely high saturated conductivities were found at both sites. Potential for recharge, however, is markedly reduced at Okongo due to presence of the calcrete layer. The study shows that through the injection of $^{2}H_2O$, the peak-shift method can successfully be applied in semi-arid environments. Even with small amounts of $^{2}H_2O$, the tracer peak could be detected after one whole rainy season. The experiments demonstrate a valuable, hence cheap and reliable, technique to estimate groundwater recharge rates in semi-arid regions and areas with low data availability. Further validation of the method regarding spatial and temporal scales is needed.

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V 9

Hydro-chemical and isotope studies along the Caleque-Oshakati water carrier system: possible indicators of anthropogenic influence in the semiarid, densely populated area of Northern Namibia

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Since 1973 Kunene River water (currently between 47 and 63 Million m³ per year [1]) is carried from the Calueque Dam in Angola along a 150 km concrete canal to Oshakati in the central part of the Cuvelai-Etosha Basin which supplies drinking water to the most densely populated area of Namibia. Backup storage is held in the Olushandja Dam and in water towers at Ogongo, Oshakati and Ondangwa. About 4,000 km of pipeline radiates out from purification schemes and supplies most of the people and the livestock [2,3]. The canal is open along most of its course to Oshakati, allowing livestock and people living nearby to freely make use of the water. During the rainy season, flood water from the vast Oshana drainage system swashes into the canal bearing a potential health risk when consumed untreated.

Within the SASSCAL project (www.sasscal.org) water samples were collected during field campaigns in November 2013 right before the onset of the rainy season, and in June 2014 after the rainy season. Water samples were collected at 14 sites along the canal for hydro-chemical analyzes and stable water isotopes (deuterium and oxygen-18). Temperature, electric conductivity, pH-value, and oxygen content were measured in the field. A Picarro L2120-i water vapor analyzer was used for stable isotope analyzes with accuracies of 0.2‰ and 0.8‰ for $\delta^{18}O$ and $\delta^{2}H$, respectively. A discussion of isotope and hydro-chemical evolution of the canal water in comparison to local rain, Kunene source water and available groundwater will be presented in a context of water availability, vulnerability and water resources management.

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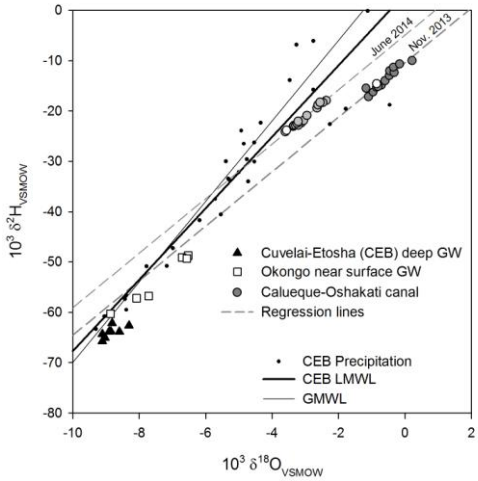
Fig. 1: Stable isotope values of precipitation (small black dots), groundwater (triangles and squares), Kunene River (white circles) and Calueque-Oshakati canal water (grey circles) in the Cuvelai-Etosha Basin (CEB), Northern Namibia.
Key words: Hydro-chemistry, stable isotopes, water supply, semiarid Northern Namibia

Anhang 1



V 10

Regional nitrogen dynamics in the Bode river system, Germany, as constained by stable isotope patterns

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Monitoring concept

We used nitrogen and oxygen isotopic signatures of riverine nitrate of main tributary streams from the Bode River in the Harz Mountains and Boerde region, Germany, to delineate nitrate sources and nitrogen transformation processes. Between March 2012 and December 2013 we collected monthly water samples from up to 133 tributary streams several times and determined hydrochemical parameters as well as $\delta^{15}N$ and $\delta^{18}O$ of nitrate. Precipitation and groundwater were sampled and considered as potential input factors. The catchment in the middle and lowlands is strongly influenced by agricultural land use that occupies an area of 2310 km², which is about 70 % of the overall size of the catchment.

Discussion of Results

Nitrate stemming from different sources such as ammonia (NH_4) fertilizer, soil-nitrogen, organic fertilizer or precipitation shows in part extremely significant $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ - differences, which can be used to characterize and quantify the different source contributions (Kendall and McDonnell, 1998). Generally, we observed a significant regional and partly temporal variation of nitrate isotopic signatures throughout the catchment. Stream section within the high mountains contain nitrate in low concentrations with low $\delta^{15}N_{NO3}$ values, whereas streams in the lowlands, affected by an increasing human impact, show a highly regional and seasonal variation in $\delta^{15}N_{NO3}$ ranging between 1 ‰ and 14 $‰_{AIR}$. A clear correlation seems to exist between the percentage of agricultural land use area in the sub-catchments and $\delta^{15}N_{NO3}$. Streams within catchments with a higher proportion of agricultural land use show high $\delta^{15}N_{NO3}$ signatures of about 8 ‰ to 11 $‰_{AIR}$ during all seasons. The correlation between land use area and $d^{15}N_{NO3}$ is superimposed by a season-depending impact of microbial denitrification. Denitrification, especially evident in the lowlands, predominantly takes place in the riverbeds. Beyond that, mixing processes of different nitrate sources and temperature-depending biological processes such as nitrification have to be taken into consideration.

Regional landscape information like land use, soil, geology, topology and recharge as well as quantitative discharge information is combined with the temporal and spatial isotope distribution patterns. The subsequent comprehensive geo-statistical analysis considering stream network topology by using the topological kriging method (Skøien et al., 2006) enables the recognition of dominant hydrological and microbiological processes and of hot spots of anthropogenic impacts. This information may be used for parameterization and validation of regional scale hydrological and matter flux models.

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V 11
Oberirdische Wasseraufnahme der Buche (Fagus sylvatica) in Abhängigkeit von Trockenstress

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Der Waldumbau von Fichtenreinbestanden (Picea abies [L.] Karst) in Mischwalder, v.a. durch die Einbringung der Buche (Fagus sylvatica), ist in Anbetracht des voranschreitenden Klimawandels und der prognostizierten Zunahme von Trockenheitsperioden während der Sommermonate in Deutschland in vollem Gange. Aus diesem Grund gewinnt vor allem die Erforschung des Wasserhaushaltes und der Trockenstresstoleranz von Waldbestanden und deren Baumarten an Bedeutung. Bei der Beurteilung der Trockenstresstoleranz verschiedener Baumarten, konnte deren Kapazitat zur Wasseraufnahme bei Regenereignissen über die oberirdischen Organe (Blatt und Spross) eine bisher unterschätzte Rolle spielen. Aus diesem Grund wurde anhand eines Klimakammerexperimentes mit Hilfe von Deuterium gelabeltem Wasser überprüft, ob junge Buchen zu einer oberirdischen Wasseraufnahme befähigt sind. Im Fokus standen die Fragen, inwieweit die aufgenommene Wassermenge von der Trockenstressdosis abhängig ist und über welche Pflanzenteile dieses Wasser aufgenommen wird. Hierzu wurden die jungen Buchen drei Trockenheitsstufen ("trocken• ", "halbtrocken• " und "feucht• ") ausgesetzt und der Trockenstress mittels pre-dawn Wasserpotential, der stomatären Leitfähigkeit und der Photosyntheserate quantifiziert. Alle drei Größen zeigten ein deutliches Absinken mit zunehmender Trockenheit des Bodens. Die Hälfte der Pflanzen einer Trockenstufe wurde als Kontrolle verwendet. Die oberirdische Biomasse der anderen Hälfte wurde zwei Mal im Abstand von 1,5 Stunden fur 5 Sekunden in mit Deuterium gelabeltes Wasser getaucht. Die Töpfe und die unteren Sprossabschnitte waren dabei sorgfaltig abgedichtet, so dass kein Wasser in den Boden gelangen konnte. Des Weiteren wurden die Kontroll- und Labelpflanzen zusatzlich in Plastiktuten gehüllt, um die Transpiration zu unterdrücken. Nach einer Zeitspanne von 3 Stunden wurde erneut das Wasserpotential gemessen und Xylemproben der befeuchteten und unbefeuchteten Pflanzenteile sowie Wurzelproben entnommen. Die Proben wurden anschliesend kryodestilliert und auf ihren Deuteriumgehalt untersucht. Die Ergebnisse zeigten einen Anstieg des Wasserpotentiales über den Wert des pre-dawn Wasserpotentiales für die Gruppen "feucht• " und "halbtrocken• " und einen signifikant höheren Deuteriumgehalt in allen gelabelten Pflanzen im Vergleich zu den Kontrollen. Ebenfalls zeigte sich ein deutlich erhöhter Deuteriumgehalt im Xylem bis in den unteren Spross und die Wurzeln. Somit konnte sowohl die Möglichkeit zur oberirdischen Aufnahme von Wasser als auch ein deszendenter Fluss bei der Buche nachgewiesen werden.

Vorträge

Session 3 – Metabolismus und Physiologie

V 12
Stable isotope profiling of metabolism under complex conditions

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A powerful method to analyze metabolism under complex and physiological conditions is based on incorporation experiments using ^{13}C-labeled substrates. ^{13}C-Enrichments and positional isotope distributions in multiple metabolic products are analyzed by GC/MS and /or NMR spectroscopy providing detailed quantitative information about substrate usage, metabolic pathways and fluxes as well as the impacts of environmental factors upon these processes. In the meantime, the experimental-driven and model-free approach has provided crucial data about relative metabolic fluxes and adaptation in many bacterial pathogens also under intracellular growth. Using this method, biosynthetic pathways of isoprenoids could also be unraveled in whole plants under physiological conditions. Some examples will be presented showing the power and the limits of the method.

Multiple carbon usage including glucose, glucose-phosphate, glycerol and amino acids has been shown for intracellular *Listeria monocytogenes* and *Legionella pneumophila* in response to the specific conditions of various host cells. This documents the metabolic strategies of intracellular pathogens for efficient survival and replication. Indeed, there is growing evidence that central metabolic pathways are linked to virulence in many bacterial pathogens.

Recently, $^{13}CO_2$-pulse-chase experiments have elucidated the biosynthetic origin of commercially and medicinally important food additives and drugs from plants. The knowledge about metabolism in plants under physiological conditions is crucial in the interpretation of positional isotope ratios also for the future assignment of plant product authenticity.

V 13

Compound-specific labelling traces metabolic carbon allocation into plant volatile organic compounds and CO2

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Plant metabolic processes exert a large influence on global climate and air quality through the emission of the greenhouse gas CO_2 and volatile organic compounds (VOCs). Despite the enormous importance, processes controlling plant carbon allocation into primary and secondary metabolism, such as respiratory CO_2 emission and VOC synthesis, remains unclear.

The vegetation exerts a large isotopic imprint on the atmosphere through both, photosynthetic carbon isotope discrimination and fractionation during respiratory CO_2 release ($\delta^{13}C_{res}$). While the former is well understood, many processes driving carbon isotope fractionation during respiration are unknown. There are striking differences in variations of $\delta^{13}C_{res}$ between plant functional groups, which have been proposed to be related to carbon partitioning in the metabolic branching points of the respiratory pathways and secondary metabolism, which are linked via a number of interfaces including the central metabolite pyruvate. Notably, it is a known substrate in a large array of secondary pathways leading to the biosynthesis of many volatile organic compounds (VOCs), such as volatile isoprenoids, oxygenated VOCs, aromatics, fatty acid oxidation products, which can be emitted by plants.

Here we investigate if carbon isotope fractionation in light and dark respired CO_2 is associated with VOC emissions in the atmosphere. Specifically, we hypothesize that a high carbon flux through the pyruvate into various VOC synthesis pathways is associated with a pronounced ^{13}C-enrichment of respired CO_2 above the putative substrate, as it involves the decarboxylation of the ^{13}C-enriched C-1 from pyruvate.

Based on simultaneous real-time measurements of stable carbon isotope composition of branch respired CO_2 (CRDS) and VOC fluxes (PTR-MS) we traced carbon flow into these pathways by pyruvate positional labeling.

We demonstrated that in a Mediterranean shrub the ^{13}C-enriched C-1 from pyruvate is released in substantial amounts as CO_2 in the light. Simultaneously, naturally ^{13}C depleted C-2 and C-3 carbon atoms of the acetyl-moiety are emitted as a variety of VOCs. Moreover, during light-dark transitions leaf emission bursts of the oxygenated metabolite acetaldehyde were observed as part of the PDH bypass pathway in the cytosol[2]. This may be a new piece of evidence for the origin of ^{13}C-enriched $\delta^{13}CO_2$ which is released during Light-Enhanced Dark Respiration (LEDR).

Our study provides the first evidence that the isotopic signature of respired CO_2 is closely linked to carbon partitioning between anabolic and catabolic pathways and plants strategies of carbon investment into secondary compound synthesis.

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V 14
What determines $\delta^{13}CO_2$ during light enhanced dark respiration (LEDR)?

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Transferring light-acclimated leaves into complete darkness causes an immediate enhancement of CO2 respiration rates, which is known as “light enhanced dark respiration” (LEDR). During this metabolic transition between photosynthesis and respiration, leaf dark-respired CO2 (δ13CLEDR) can be heavily enriched in 13C (up to 16‰ compared to potential respiratory substrates). It was suggested that δ13CLEDR is determined by the C-4 position of malate, which should be 13C enriched compared to other molecule position due to an anapleurotic flux via the phosphoenolpyruvate carboxylase reaction. The C-4 position itself can be released by the mitochondrial malic enzyme reaction (mtME), which in turn might determine δ13CLEDR. However, experimental evidence for that mechanism is still lacking. Hence, we fed leaves via the xylem stream with position-specific labelled malate (13C-1, 13C-4) and pyruvate (13C-1, 13C-2) to determine the influence of different substrates on δ13CLEDR. Respiratory fluxes of 13CO2 were measured during light-dark transition courses of about 20 min in the light and 20 min in the dark using laser spectroscopy in Arabidopsis thaliana species (wild type and mutant) and in species differing in δ13CLEDR (Halimium halimifolium, Oxalis triangularis). δ13CLEDR of Arabidopsis wild type and mutant (nadme1x2; fully lacking mtME) did not differ at natural abundances. Also light dark-transition courses of mean 13CO2 fluxes of 13C-4 malate treated Arabidopsis plants showed no difference in their peak form, suggesting a minor relevance of mtME imprinting on δ13CLEDR. Furthermore, light-dark transition courses of mean 13CO2 fluxes of 13C-1 malate and 13C-1 pyruvate treated H. halimifolium and O. triangularis plants showed clear peaks shortly upon darkening, which were similar or higher compared to 13C-4 malate treated plants. This demonstrates that δ13CLEDR is not solely determined by mtME and by the C-4 position of malate and that also other enzymatic reactions and substrates must have a crucial role during LEDR.

V 15
αStable Carbon Isotope Fractionation in human Steroid Metabolism

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Most metabolic pathways are characterized by multiple branch points. If at least one of the branches features an isotope effect, this eventually will effect isotope fractionation. Typically, depletion of the heavy isotopes occurs on the product side. Theoretically, the isotope ratios of both products will then be largely controlled by relative proportions of the metabolic fluxes. In steady-state, these effects occur in parallel, i. e. the difference between the isotope ratios of the products remains constant.

In human steroid metabolism, this phenomenon can be observed for the intra-individual variance present in the $^{13}C/^{12}C$ ratios of the two abundant androgen metabolites androsterone (A) and etiocholanolone (E). These originate from identical substrates and thus represent a branched pathway. In accordance with population based reference data, E is consistently depleted in ^{13}C vs. A. This suggests presence of a significant isotope effect during steroid 5β-reduction which yields E. By contrast, 5α-reduction yields A. Both reactions are crucial in that they represent initial and rate limiting steps in steroid metabolism.

The phenomenon can be observed best in individuals who excrete comparably large total amounts of A and E. Again, this is consistent with theory, because A and E then possibly reflect a large proportion of gross androgen metabolic flux. Moreover, lower concentrations of E and A are associated with lower $^{13}C/^{12}C$ ratios of both compounds. This will be consistent with mass balance if an isotope effect for the reduction of the Δ^4-bond is assumed, but suggests significant contributions of additional catabolic pathways.

In contrast to physiological variations of metabolic fluxes, the administration of drugs will typically cause massive disturbances of the steady-state. Usually, the substrate input temporarily surpasses the maximum metabolic turnover. If the rate limiting metabolic step features an isotope effect, this will result in increasing accumulation of heavy isotopes in the substrate. Because the substrate is continuously metabolized, the isotope ratios of both, substrate and metabolites, will then increase systematically.

Consistent with these considerations, the bolus administration of 19-norandrostenedione results in increasing $^{13}C/^{12}C$ ratios of its 5β-metabolite 19-noretiocholanolone. Corresponding effects can be observed after boldenone administration. An increase of the $^{13}C/^{12}C$ ratios of ca. 4 ‰ can be observed within 40 h. Boldenone itself as well as its 5β-metabolite can be affected.

These findings nicely reflect and illustrate the principles of isotope fractionation processes in metabolic networks. Practically, $^{13}C/^{12}C$ analysis of the mentioned steroids is heavily employed to detect androgen abuse in sports drug testing. Our findings can therefore significantly support the interpretation of corresponding data. More generally, reliable source assignment of drugs based on isotope analysis of urinary compounds may be significantly be impeded by these phenomena.

V 16

Abiotic methanogenesis from organosulfur compounds under ambient conditions and its potential implications for methane formation in eukaryotes

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The greenhouse gas methane (CH_4) is the most abundant reduced organic trace gas in the atmosphere and plays an important role in tropospheric and stratospheric chemistry. Various sources of CH_4 are known to exist in nature and, recently, the number of suggested biological sources has been increased (1-4). However, the mechanism of CH_4 formation in eukaryotes still needs to be elucidated and precursor compounds to be identified. In this presentation we introduce a chemical reaction that readily forms methane from organosulfur compounds under highly oxidative conditions at ambient atmospheric pressure and temperature (5). Methyl groups of organosulfur compounds were shown to be efficiently converted into CH_4 when using iron(II/III), hydrogen peroxide and ascorbic acid as reagents. In particular several S-methyl- substituted sulfides, sulfoxides and sulfonium salts such as L-methionine (MET), S-adenosylmethionine (SAM), dimethylsulfoniopropionate (DMSP) and dimethyl sulfoxide (DMSO) were studied. In a first step, methyl sulfides were oxidised to the corresponding sulfoxides. In the next step demethylation of the sulfoxide via homolytic bond cleavage led to methyl radical formation and finally to CH_4 particularly at low local oxygen concentration. Because sulfoxidation of methyl sulfides is ubiquitous in the environment, this novel chemical route might mimic CH_4 formation in living aerobic organisms such as plants, fungi, algae and mammals. Finally we studied tobacco plants (*Nicotiana tabacum*) that were grown under sterile conditions and supplemented them with positionally labelled MET, where only the methyl group (-S-CH_3) was enriched with ^{13}C atoms. These experiments provided first evidence that MET, via its thio-methyl group, is a parent compound of CH_4 in tobacco plants (5).

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V 17

Online methods for the position specific analysis of ^{13}C in some light organic compounds

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Position-specific isotopic analysis (PSIA) of organic compounds is expected to be used for plant metabolism studies, botanical source or the adulteration detection. For some organic compounds, such as ethanol, acetic acid and vanillin, PSIA has been available due to emergence of on-line pyrolysis-gas chromatography-combustion-isotope ratio mass spectrometry (GC-C-IRMS) [1] and quantitative isotopic ^{13}C NMR spectroscopy [2]. Here we present recent advances in PSIA of light organic compounds.

First, we picked up ethanol, which $\delta^{13}C$ value can be a useful indicator for authentication purpose. We developed the measurement method of the molecular and intramolecular $\delta^{13}C$ value of ethanol in aqueous solution using an on-line pyrolysis- GC-C-IRMS [3]. The ^{13}C values of the pyrolytic fragments (CO, CH_4) can be measured with high repeatable result (S.D.<0.4‰) using the system, allowing correcting factors to be applied in order to back-calculate the original $\delta^{13}C_{CH2OH}$ and $\delta^{13}C_{CH3}$ values of ethanol. The method allows the determination of the $\delta^{13}C$ value of ethanol at the intramolecular and molecular levels, within a single run and a short experimental time (30 min), and with an easy sample preparation.

Other example of the popular and important chemical compounds is vinegar which is mainly consisting of acetic acid. Lately, the adulterations of acetic acid with other dangerous compounds have been found spread wide over the world. In other words, the intramolecular $d^{13}C$ distribution of acetic acid can be very useful to avoid the poisonous agent, which can be mixed with the original materials. Acetic acid can be pyrolyzed and results in three main fragments (CO, CH_4, CO_2). CO_2 fragment is corresponded to carboxyl part (COOH) while we expect the CH_4 fragment should correspond to methyl part (CH_3). Using five acetic acid standards to make the calibration curve and then we make the single injection with head space-solid phase micro-extraction (HS-SPME) into GC-Py-GC-C-IRMS system. Comparing with the offline pyrolysis method [4], the $d^{13}C$ have the repeatable result about <0.3 ‰ and <0.9‰ for COOH and CH_3 part respectively with the easy sample preparation with short experimental time (30mins) [5]. This method will also be very useful for applications of acetic acid and many study which is related to.

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V 18

N_2O production pathways in a partial nitritation-anammox reactor: Isotopic evidence for N_2O production associated with anaerobic NH_4^+ oxidation?

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Nitrous oxide is a strong greenhouse gas and the most important stratospheric ozone-depleting substance released in the 21st century[1]. Microbial N_2O production during wastewater treatment is an important and growing source of N_2O. This study presents the first online isotopic measurements of offgas N_2O from a 400 L pilot scale, single-stage partial-nitritation anammox reactor. The N_2O production pathways in the reactor are inferred based on the measured N_2O isotopic composition - in particular the N_2O isotopic site preference (SP = $\delta^{15}N^{\alpha}$ - $\delta^{15}N^{\beta}$), which is characteristic for different N_2O production pathways[2-5].

N_2O emissions were investigated both under normal (optimal) operating conditions and during a number of experiments, designed to cover the range of conditions commonly encountered during operation (Figure 1). When N_2O emissions peaked due to high dissolved O_2 ('high aeration' in Figure 1), low SP showed that N_2O was produced primarily via nitrifier denitrification by ammonia oxidizing bacteria (AOBs). N_2O production by AOBs via NH_2OH oxidation, in contrast, did not appear to be important under any conditions.

Figure 1. N_2O site preference and N_2O emissions per NH_4^+ consumed (N_2O/NH_4^+; %) over a range of experiments conducted with a single-stage partial nitritation-anammox reactor. Expected ranges for N_2O production via NH_2OH oxidation (biotic and abiotic) or denitrification are shown in blue and green respectively[2-5]; the red range indicates the measured SP values that cannot be explained by currently known N_2O production pathways.

Over the majority of the one-month measurement period, the measured SP was much higher than expected, reaching 41‰ during normal operating conditions and achieving a maximum of 45‰ when nitrite was added under anoxic conditions (Figure 1). An unknown N_2O production pathway with SP >45‰ mediated by anammox bacteria was the explanation most consistent with the results, although the possibility of strong N_2O reduction by heterotrophic denitrifiers could not be entirely discounted [6].

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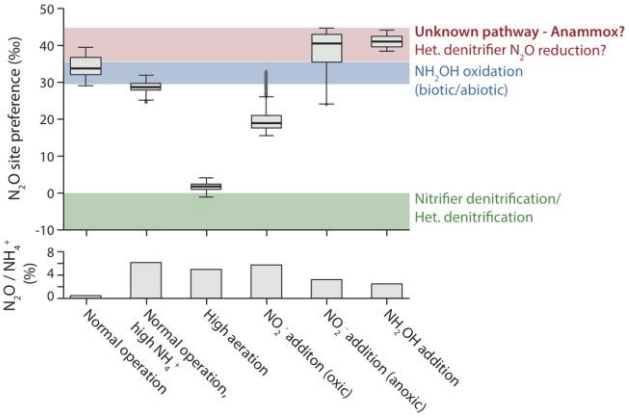
Anhang 1



V 19

Elementkonzentrations- und Isotopenverhältnisbestimmungen an menschlichen Haarsträhnen mittels induktiv gekoppeltes Plasma-Massenspektrometrie (ICP-MS) und Isotopenverhältnis-Massenspektrometrie (IRMS)

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Die Isotopenanalyse von Skelett- und Geweberesten für die Bestimmung der Herkunft, Lebensweise und Mobilität von vorzeitlichen Menschen und Tieren hat in den letzten Jahrzehnten in der Archäologie, Anthropologie und Paläontologie stark an Bedeutung gewonnen [1]. Auch auf dem Gebiet der Forensik wurden Isotopenverhältnisse leichter (C, N, H, O, S) und schwerer (Sr, Pb) Elemente zur Herkunftsbestimmung unbekannter Toter verwendet (vgl. z. B. [2]).
Um festzustellen, inwieweit aus element- und isotopenanalytischen Untersuchungen belastbare Erkenntnisse über Herkunft, Wohnort und/oder mögliche Ortswechsel von Personen gewonnen werden können, werden Analysen an humanbiologischen Materialien aus der Gegenwart (Haare und Fingernägel) durchgeführt.
Die Proben stammen von 3 unterschiedlichen Personengruppen: zu Gruppe 1 zählen Personen, die im Großraum Mainz/Wiesbaden leben und nur urlaubsbedingte Ortswechsel vornehmen (Referenzpopulation). In Gruppe 2 werden deutsche Staatsbürger zusammengefasst, die berufsbedingt für einige Monate bis hin zu einigen Jahren einen Aufenthalt im Ausland wahrnehmen. Zur 3. Gruppe zählen Personen, die aus dem Ausland stammen und sich für einige Monate beruflich in Deutschland aufhalten. Von Personen aus diesen 3 Gruppen werden vor und während eines Auslandsaufenthalts Haare und Fingernagelproben genommen. Diese Probennahme erfolgt auf freiwilliger Basis und alle personenbezogenen Daten werden anonymisiert.
Die elementanalytischen Untersuchungen der Proben werden mittels ICP-MS (Agilent 7700x, Santa Clara CA, USA) durchgeführt. Bei Verwendung des Desolvationssystem APEX Q (Firma ESI, Elemental Scientific Inc., Omaha, NE, USA) ist eine Probeneinwaage von 0,5 mg für die Analyse ausreichend.
Die Isotopenverhältnis-Bestimmungen der Proben werden mittels EA-IRMS (Flash EA 1112, ThermoFisher Scientific, Bremen; IRMS Typ Delta V plus, Thermo Scientific, Bremen) durchgeführt.
Im Vortrag/Poster werden die Elementkonzentrationsergebnisse der Haarproben mit den Ergebnissen aus den Isotopenverhältnisbestimmungen verglichen und diskutiert. Inwieweit diese Ergebnisse einen Hinweis auf einen getätigten Ortswechsel des Haarspenders liefern, soll ebenfalls erörtert werden.

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V 20

Global spatial distribution of natural stable carbon and nitrogen isotope ratios in modern humans

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Natural stable carbon ($\delta^{13}C$) and nitrogen isotope ratios ($\delta^{15}N$) of modern human tissue and (excreted) metabolised products are related to the individual's dietary habits and geographical origin. It is known that geographical differences in the isotope ratio of human diets are detectable by stable isotope analysis of e.g. fingernail and hair, as well as in urinary steroids. In forensic science the stable isotope analysis of human remains like bone, hair and fingernails is used for geographical allocation of the individual. Human $\delta^{13}C$ values are primarily correlated to the proportion of C3-, and C4-plants in the diet. Due to differences in the biosynthetic pathways C4-plants like maize, sugar cane, and sorghum show increased $\delta^{13}C$ values compared to C3-plants like wheat or potatoes. These differences can be detected by $\delta^{13}C$ analysis of e.g. human hair or urinary steroids. In general, human $\delta^{13}C$ values decrease with increasing latitude of the individual's residence. Thus, lowest $\delta^{13}C$ values are found for Scandinavian samples, whereas highest $\delta^{13}C$ values are found for subjects originating from Brazil. In contrast to carbon, the global spatial distribution of human $\delta^{15}N$ values is apparently not exclusively related to dietary but also to environmental factors.

In doping analysis individual $\delta^{13}C$ values of endogenous reference compounds (ERC) are used for the interpretation of a potential exogenous origin of target metabolites. Thus, geographical differences in the $\delta^{13}C$ values of ERCs may have an influence of the interpretation of such stable isotope analyses. The knowledge of the global spatial distribution of natural stable carbon isotope ratios of humans is one component in the interpretation of isotope ratio measurements of endogenous reference compounds in doping control as it is in forensic science. However, up to now no substantial global data sets on global human carbon (and nitrogen) isotope ratios are available, although for forensic investigations the amount of available data on human isotope ratios has increased within the last years. Hair is the preferred matrix in forensic stable isotope analysis due to the non-invasive sampling and comparatively easy analysis compared to the laborious and complex stable isotope analysis of urinary steroids. Information about global distribution of $\delta^{13}C$ values of human hair can be used for the interpretation of $\delta^{13}C$ values found for endogenous reference compounds in doping control as well as for educational purposes and general understanding of spatial patterns of natural stable carbon isotope ratios.

Vorträge

Session 4 – Geochemische Stoffkreisläufe und Schadstoffdynamik

V 21
Calibration of ($^{13}C/^{12}C$ and $^{2}H/^{1}H$)-isotope ratios in methane

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Methane is the second largest anthropogenic greenhouse gas present in the atmosphere. Methane concentrations in the atmosphere have more than doubled since the beginning of the industrial era. The more or less steady increase over time was interrupted from ~ 2000 to 2008, after which the increasing trend resumed. The cause of this change has been subject of a large debate among the scientists, but an agreement about the underlying mechanisms is still pending.

Several atmospheric models and scenarios have been proposed to explain this change. Quantitative results from such models can be verified with measurements of methane concentrations as well as its isotope ratios. Isotope measurements are used to partition the sources and sinks and verify model results. The required high-precision measurements are made in several specialized laboratories around the globe, analyzing samples from a large number of stations.

Comparisons of measurement results between different laboratories for samples from the same location have revealed scale offsets mainly for the stable isotope measurements; mole fraction measurements have turned out to be more consistent. Neglecting such offsets can lead to substantial modeling errors. A cross-network calibration is needed to take care of these effects. However, there are no internationally accepted reference materials for the stable isotopes of CH_4 in air available, yet. In this work, a start has been made in this direction, which should lead finally to an established independent scale for the CH_4 isotopes.

Eight methane cylinders have been calibrated against the international reference materials for $\delta^{13}C$ and $\delta^{2}H$. We calibrated one methane gas directly against the international standards for $\delta^{13}C$ and $\delta^{2}H$, LSVEC and NBS 19 (Mar-j1), and VSMOW respectively. This was done by converting the methane and carbonates directly to CO_2 in an elemental analyzer, and measuring the CO_2 in an isotope ratio mass spectrometer (IRMS). Methane and water were converted at a temperature of 1450 °C to H_2, which was measured in an IRMS. Seven other methane gases have been compared to the first methane gas by injecting them alternating into each system. An extended error analysis was done to account for the complete error budget. For $\delta^{13}C$ a range of −39 ‰ to −70 ‰ is covered; for $\delta^{2}H$ a range of − 320 ‰ to + 44 ‰ is covered. The new calibrated methane gases were mixed into methane free air for a comparison to the current scale. The comparison of this new scale to the current local scale shows an offset for carbon of +0.066 ± 0.0157 ‰; for hydrogen the offset is + 3.97 ± 1.056 ‰. Also, the local current scale is compared to the scale of the Institute for Marine and Atmospheric Research in Utrecht by measuring 10 air flasks from Lutjewad. The results show an offset of +3.82 ± 4.28 ‰ for $\delta^{2}H$, and an offset of −0.22 ± 0.33 ‰ for $\delta^{13}C$; The relatively large uncertainties are due to the low pressure in the flasks (below 1 bar) that affects the flow measurements in the IRMS and thus the isotopic measurements.

V 22

Kann die Sauerstoffisotopensignatur in N_2O zur Bestimmung des pilzlichen Anteils an der Denitrifikation genutzt werden?

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Welchen Anteil Pilze an der N_2O Bildung durch die Denitrifikation im Boden haben ist bisher weitgehend unerforscht. Bisher galt die ^{15}N Positionspräferenz im N_2O als eine aussichtsreiche Messgröße, um zwischen N_2O aus der Denitrifikation von Pilzen und Bakterien unterscheiden zu können.[1] Da Pilze und Bakterien während der Denitrifikation einen Sauerstoffaustausch (O Austausch) zwischen dem umgebenden Wasser und den Zwischenprodukten haben, wurde die ^{18}O Signatur im N_2O bisher zur Unterscheidung der Organismengruppen ausgeschlossen. Eigene Versuchsergebnisse deuten jedoch auf Unterschiede zwischen den ^{18}O Signaturen im N_2O beider Organismengruppen hin.

Pilzreinkulturen zeigten für N_2O aus der Denitrifikation $d^{18}O$ Werte von 33 bis 55‰.[2, 3] Der O Austausch im Zuge der Denitrifikation wurde unter Verwendung von ^{18}O angereichertem Wasser ermittelt und lag zwischen 11% und vollen Austausch. Die Inkubation von zwei Bodentypen ergab, dass die Bodenorganismen N_2O mit $d^{18}O$ Werten von 4 bis 16‰ bei einem O Austausch von 93 bis 97% produzierten. Die gemessene ^{15}N Positionspräferenz deutete auf eine Dominanz der Bakterien bei der Denitrifikation in diesen Böden hin. Aus diesen Ergebnissen kann vermutet werden, dass die ^{18}O Signatur in von Pilzen gebildetem N_2O weitaus höher ist als in N_2O bakteriellen Ursprungs.

In weitergehenden Versuchen mit Reinkulturen von Pilzen und Bakterien wird mit variierender ^{18}O Signatur des Wassers der O Austausch und die Isotopenfraktionierung bei der N_2O Produktion bestimmt, um Aufschluss darüber zu erhalten, inwiefern sich die natürliche ^{18}O Signatur des N_2O von Pilzen und Bakterien unterscheidet. Sollten die erwarteten Unterschiede bestätigt werden, könnte die ^{18}O Signatur des N_2O neben der ^{15}N Positionspräferenz dazu dienen zwischen N_2O pilzlichen bzw. bakteriellen Ursprungs zu unterscheiden.

Ein Fraktionierungsmodell[4, 5], das für die Denitrifikation von Bakterien entwickelt wurde, diente bei den oben genannten Pilzreinkulturversuchen zur Bestimmung der beteiligten Enzyme am O Austausch. Dieses Modell soll nun eingesetzt werden, um zu testen, ob sich die Enzyme, die hauptsächlich den O Austausch katalysieren zwischen Pilzen und Bakterien unterscheiden und dadurch die Unterschiede der ^{18}O Signaturen im N_2O entstehen. Erste Ergebnisse sollen vorgestellt werden.

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V 23

δD and $\delta^{13}C$ measurements of chloromethane from terrestrial and extraterrestrial matter and its implications for the search of organic matter on Mars

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Atmospheric chloromethane (CH_3Cl) is an ozone depleting gas contributing ~16% of tropospheric chlorine. Most atmospheric CH_3Cl is released from terrestrial vegetation with a significant fraction formed in dead and senescent leaf tissue, predominantly through an abiotic reaction between the methyl moiety of plant methoxyl groups (OCH_3) and chloride. Controversy continues as to whether CH_3Cl detected during pyrolysis of Martian soils by the Viking and Curiosity Mars landers is indicative of organic matter indigenous to Mars (1-4). In this study we investigate the potential CH_3Cl production from meteoritic matter. We present data obtained from the thermolysis (150 to 400°C) of samples of the Murchison meteorite (a well investigated carbonaceous chondrite of type CM2 that fell in Australia in 1969) both with and without chloride and perchlorate$^-$ supplementation. Our results clearly demonstrate formation of CH_3Cl from organic matter of extraterrestrial origin and confirm unequivocally by stable isotope analysis the extraterrestrial origin of the methyl group. These observations are consistent with the well-documented release of chloromethane in the terrestrial environment from the methoxyl pool of organic matter in the presence of chloride (5-7) and provide a rationale for the chloromethane emissions recorded by Mars landers experiments. Our work suggests that methoxyl groups of the intact organic matter reaching the Martian surface can be converted to chloromethane on pyrolysis with perchlorate or chloride in Martian soil. Thus chloromethane release reported by previous Mars landers is probably derived at least in part from organic matter from meteoritic debris although we do not discount an indigenous source. The stable carbon and hydrogen isotope signatures of chloromethane could potentially be utilized to determine the origin of chloromethane detected on Mars by distinguishing between terrestrial contamination, meteoritic infall and indigenous Martian sources. Indeed, for future planetary missions we suggest that chloromethane could be an important target compound for constraining the origin of any organics found.

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V 24

Carbon, Nitrogen, and Hydrogen Isotope Analysis of *N*-Nitrosodimethylamine (NDMA) Formed During Chloramination of Ranitidine-Containing Waters

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Mitigation of *N*-nitrosodimethylamine (NDMA) and other hazardous water disinfection by-products (DBP) is currently hampered by a limited understanding of DBP formation mechanisms. We explored compound-specific stable isotope analysis (CSIA) to identify precursors and to delineate formation pathways of NDMA based on changes of its $^{13}C/^{12}C$, $^{15}N/^{14}N$, and $^{2}H/^{1}H$ ratios. Solid-phase extraction coupled to gas chromatography and isotope ratio mass spectrometry (SPE-GC/IRMS) enabled the accurate quantification of C, N, and H isotope ratios of NDMA and four additional *N*-nitrosamines in aqueous samples at concentrations of 0.6 µM (45 µg NDMA L^{-1}). In laboratory experiments, chloramination of 3 µM of the pharmaceutical ranitidine resulted in NDMA formation with a yield of 97±4%. $\delta^{2}H$ and $\delta^{13}C$ values of NDMA remained stable during its formation. The $\delta^{2}H$ value of NDMA corresponded well to the $\delta^{2}H$ value of the *N*-$(CH^{3})_{2}$-group of ranitidine, which we measured using quantitative deuterium nuclear magnetic resonance spectroscopy. This observation implies that the *N*-$(CH^{3})_{2}$-moiety of ranitidine is transferred to NDMA without being chemically altered. $\delta^{15}N$ of NDMA, in contrast, increased owing to a normal ^{15}N-kinetic isotope effect associated with the cleavage of a bond to N in the rate-limiting step of NDMA formation. Our study illustrates how CSIA can contribute to the identification of NDMA precursors and formation pathways and thus support the design of effective mitigation measures.

V 25

Application of Compound-Specific Stable Isotope Analysis for Source Identification of Chlorinated Organic Pollutants

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Compound-specific isotope analysis (CSIA) is demonstrated to be an efficient tool to track sources and sinks of pollutants in the environment. In this study we have developed a concept for source identification of chlorinated pesticides and their metabolites in soil. Organochlorine pesticides Hexachlorocyclohexane (HCH, 4 stereoisomers) and DDT were selected as model compounds for method development. In addition, potential metabolites of HCH (chlorinated benzenes) and most abundant metabolites of DDT (DDE and DDD) were included in the study.

Pure phase samples of HCHs and DDT were collected from different producers worldwide. Carbon stable isotope compositions ($\delta^{13}C$) were measured by Elemental Analysis in tandem with Isotope Ratio Mass Spectrometry (EA-IRMS). In addition, isotopic fingerprints of target insecticides were measured in solutions of agricultural and pharmaceutical formulations by Gas Chromatography coupled to IRMS via combustion unit (GC-C-IRMS). Obtained collection showed significant variability in stable carbon isotope ratios, exploring high potential for developed concept.

Preliminary analysis of chlorine stable isotope composition ($\delta^{37}Cl$) of selected HCH samples showed a potential to distinguish between sources with similar $\delta^{13}C$ values. The analytical method for the determination of $\delta^{37}Cl$ by Dual-Inlet Isotope Ratio Mass Spectrometry (DI-IRMS)[1,2] was optimized to improve its accuracy, using pure phase γ-HCH sample. The accuracy of the optimized method was tested by analysing CH_3Cl sample with known $\delta^{37}Cl$ value reported vs. the SMOC scale (Standard Mean Ocean Chloride) before and after the whole procedure. The difference between product and initial CH_3Cl was 0.11 ± 0.04 ‰.

We tested well-known and novel techniques for extraction of semi-volatile compounds from soil samples[3]. All techniques were slightly modified from original procedures to be compatible with CSIA. For method development we used a soil matrix, spiked with a mixture of target compounds with known isotopic composition. Pre-concentration of the extract and different purification methods were also tested and optimized for compatibility with CSIA.

Most of the applied methods fulfilled the required accuracy for carbon isotope analysis of HCHs and chlorinated benzenes (isotopic composition was not significantly changed during extraction or purification procedures) and provided high extraction efficiencies for these compounds. Lower extraction efficiencies with related isotope effects were observed for DDT and its metabolites, when the water content in the soil was increased. Accuracy and efficiency of the best combination of extraction and preconcentration methods were validated on well-characterized soil samples, spiked with a mixture of target compounds.

Results obtained in this study provide a concept for source identification of chlorinated pesticides in the environment. Moreover, the evaluation of different sample preparation techniques for carbon and chlorine isotope analysis will help to extend the possibilities of CSIA to a wider range of environmental applications.

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V 26
Forensische Nutzung der IRMS: Profiling von „Crystal Meth“

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Mittels Isotopenverhältnismassenspektrometrie (IRMS) können zusätzliche Materialinformationen unterschiedlichster forensisch relevanter Materialarten (Drogen, Klebebänder, Massenprodukte allgemein, etc.) gewonnen werden, die häufig zur Erhöhung des Beweiswertes von Kriminaltechnik-Gutachten führen. Da jedes Material durch seinen Entstehungsprozess spezifische Änderungen der Isotopenverhältnisse erfährt, kann die IRMS sehr vielseitig eingesetzt werden.

Beispielsweise kann die IRMS im Bereich der Sicherstellung von Betäubungsmitteln (BtM) einen wertvollen Beitrag zum Materialvergleich leisten und auch bereits im Ermittlungsprozess als Mittel der „Forensic Intelligence“ eingesetzt werden. In Deutschland werden jedes Jahr einige illegale Laboratorien zur Herstellung synthetischer Drogen, wie z.B. Amphetamin und Methamphetamin (Crystal Meth), aufgedeckt und darin befindliche Chemikalien sichergestellt. Für die Ermittlerseite ist es oft von Interesse zu wissen, ob an unterschiedlichen Orten sichergestellte Chemikalien und Endprodukte mit Ausgangschemikalien oder mit bestimmten Herstellungslabors in Verbindung gebracht werden können.
Eine Übereinstimmung der Isotopenverhältnisse einer Tatprobe mit denen des Vergleichsmaterials ist z.B. ein Indiz für einen gemeinsamen Ursprung im Sinne eines Herstellungsprozesses. Je mehr Isotope (z.B. Kohlenstoff, Stickstoff und Wasserstoff) dabei überprüft wurden, desto besser kann eine Zuordnung durchgeführt werden.

Diese Präsentation stellt, anhand des Beispiels „Crystal Meth“, die IRMS als eine leistungsfähige Methode für Materialvergleiche in der Kriminaltechnik dar.

Vorträge

Session 5 – Klimaänderungen und -rekonstruktionen

V 27

Which climate factor does best explain carbon isotope variations in tree-rings: Temperature, precipitation or sunshine duration?

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Stable carbon isotope ratios in tree-rings have been successfully used for climate reconstruction for more than three decades now. Various climate parameters have been the target variable for reconstruction, ranging from temperature to precipitation or drought, and to sunshine duration, radiation or cloud cover. Yet, there is no clear pattern emerging where and why a certain climate variable is most important and often several factors seem to be co-dominant. Different species might also have different climate sensitivity. Based on the accepted isotope-fractionation model, all climate factors affecting stomatal conductance or photosynthesis are potentially important. Sunshine duration in high latitudes (photosynthesis not limited by water) has recently been suggested to dominate, while drought/precipitation is known to be reflected in carbon isotope variations in arid regions like the Southwestern United States. However, this obvious pattern is not always working. Generally, a negative relationship between precipitation and $\delta^{13}C$ is prevailing throughout Europe, much more stable than for ring-width, which shows clearly varying controls from South to North. A very strong regional drought-signal has been found for an Alpine larch site (*Larix decidua*), which seems counter-intuitive (Kress et al., 2014). Vegetation-model investigations could help to establish clearer patterns of different climate sensitivity of the carbon isotope ratios for different regions.

Reference

Kress A, Hangartner S, Bugmann H, Büntgen U, Frank DC, Leuenberger M, Siegwolf R, Saurer M. (2014). Swiss tree-rings reveal warm and wet summers during medieval times. Geophysical Research Letters, 10.1002/2013GL059081

V 28
Die Mischung macht's!? Facilitation zwischen adulten Buchen und Fichten im Trockenstress

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Die Resilienz- und Resistenz gegenüber Trockenstress von adulten Buchen und Fichten wurden entlang eines Niederschlagsgradienten analysiert. Besonderes Augenmerk lag dabei auf dem Vergleich zwischen in Monokultur gewachsenen Buchen und Fichten mit Mischungen dieser beiden Arten am gleichen Standort. Der Stress-Gradienten-Hypothese folgend werden positive Interaktionen, d.h. Facilitationsinteraktionen, besonders unter limitierenden Wachstumsbedingungen erwartet. Die hier präsentierten Ergebnisse sind Teil eines größeren Projekts zu Facilitations- und Konkurrenz-Interaktionen von adulten Buchen und Fichten unter Trockenstress (kroof.wzw.tum.de).

Analysiert wurden Stammbohrkerne von Buchen und Fichten an 5 Standorte mit unterschiedlichen Niederschlagssummen während der Vegetationsperiode (zwischen 300 und 830 mm). Der Fokus lag auf dem Trockenjahr 2003 mit der vergleichenden Analyse der Resilienz und Resistenz von Buchen oder Fichten aus der Monokultur mit der gleichen Art aus der Mischkultur. Vor allem für die Buche entsprach das Wachstumsverhalten den Erwartung der Stress-Gradienten-Hypothese: Im Trockenjahr 2003 war der Jahrringzuwachs in der Mischung weniger stark reduziert als in den Monokulturen, d.h. die Resistenz gegenüber dem Trockenstress im Jahr 2003 war in der Mischung erhöht. Gleichfalls zeigten die in der Mischung gewachsenen Buchen eine verbesserte Resilienz als Buchen, die in der Monokultur gewachsen sind. Für Buchen waren diese Effekte vor allem auf den trockenen Standorten ausgeprägt, während Fichten die Verbesserung der Resilienz und Resistenz gegenüber dem Trockenstress vor allem auf den feuchten Standorten zeigten. Diese Daten bestätigen den „Over-Yielding"-Effekt von Mischungen zwischen Buchen und Fichten, der vor allem auf armen Standorten ausgeprägt ist (Pretzsch et al. 2013).

Die gewonnenen Kohlenstoff-Isotopenverhältnisse aus den Jahrringen der Buchen und Fichten ergaben allerdings ein anderes Bild: Beide Arten zeigten den für ein Trockenjahr typischen Anstieg des $\delta^{13}C$ im Jahrring auf allen Standorten. Allerdings waren für beiden Arten sowohl die Resilienz als auch die Resistenz der Diskriminierung gegenüber $^{13}CO_2$ ($\Delta^{13}C$) in der Mischung reduziert - vor allem für die Buchen auf den trockenen Standorten. Das heißt in der Mischung zeigte sich im $\Delta^{13}C$ eine erhöhte Empfindlichkeit gegenüber dem Trockenstress und eine schwächere Erholung im Vergleich zur Monokultur. Gründe und Hypothesen für diesen gegenläufigen Trend zwischen Zuwachs und Kohlenstoffisotopendaten werden diskutiert.

Pretzsch H, Schütze G, Uhl E (2013) Resistance of European tree species to drought stress in mixed versus pure forests: evidence of stress release by inter-specific facilitation. Plant Biology 15: 483-495.

V 29
Revisiting Mt. Kilimanjaro - reinterpreting δ^2H results of *n*-alkane biomarkers

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During the last decade compound-specific deuterium (^2H) analysis of plant leaf wax-derived *n*-alkanes has become a promising and popular tool in paleoclimate research. This is based on the widely accepted assumption that *n*-alkanes in soils and sediments generally reflect δ^2H of precipitation (δ^2H_{prec}). Recently, several authors suggested that d^2H of *n*-alkanes ($\delta^2H_{n\text{-alkanes}}$) can also be used as proxy in paleoaltimetry studies.

Here we present results from a δ^2H transect study (~1500 to 4000 m a.s.l.) carried out on precipitation and soil samples taken from the humid southern slopes of Mt. Kilimanjaro.

Figure 1

Contrary to earlier suggestions, a distinct altitude effect in δ^2H_{prec} is present above ~2000 m a.s.l., i.e. δ^2H_{prec} values become more negative with increasing altitude (Fig. 1). The compound-specific δ^2H values of nC_{27} and nC_{29} do not confirm this altitudinal trend, but rather become more positive both in the O-layers (organic layers) and the A_h-horizons (mineral topsoils). Although our $\delta^2H_{n\text{-alkane}}$ results are in agreement with previously published results from the southern slopes of Mt. Kilimanjaro (Peterse et al., 2009), a major reinterpretation is required given that the $\delta^2H_{n\text{-alkane}}$ results do not reflect the δ^2H_{prec} results. The theoretical framework for this reinterpretation is based on the evaporative isotopic enrichment of leaf water associated with transpiration process. Modelling results show that relative humidity, decreasing considerably along the southern slopes of Mt. Kilimanjaro (from 78% in ~2000 m a.s.l. to 51% in 4000 m a.s.l.), strongly controls $\delta^2H_{leaf\ water}$. The modelled ^2H leaf water enrichment along the altitudinal transect matches well the measured ^2H leaf water enrichment as assessed by using the δ^2H_{prec} and $\delta^2H_{n\text{-alkane}}$ results and biosynthetic fractionation during *n*-alkane biosynthesis in leaves (Zech et al., 2014) (Fig. 1).

Given that our results clearly demonstrate that *n*-alkanes in soils do not simply reflect δ^2H_{prec} but rather $\delta^2H_{leaf\ water}$, we conclude that care has to be taken not to over-interpret $\delta^2H_{n\text{-alkane}}$ records from soils and sediments when reconstructing δ^2H of paleoprecipitation. Both in paleoaltimetry and in paleoclimate studies changes in relative humidity and consequently in $\delta^2H_{n\text{-alkane}}$ values can completely mask altitudinally or climatically-controlled changes in δ^2H_{prec}.

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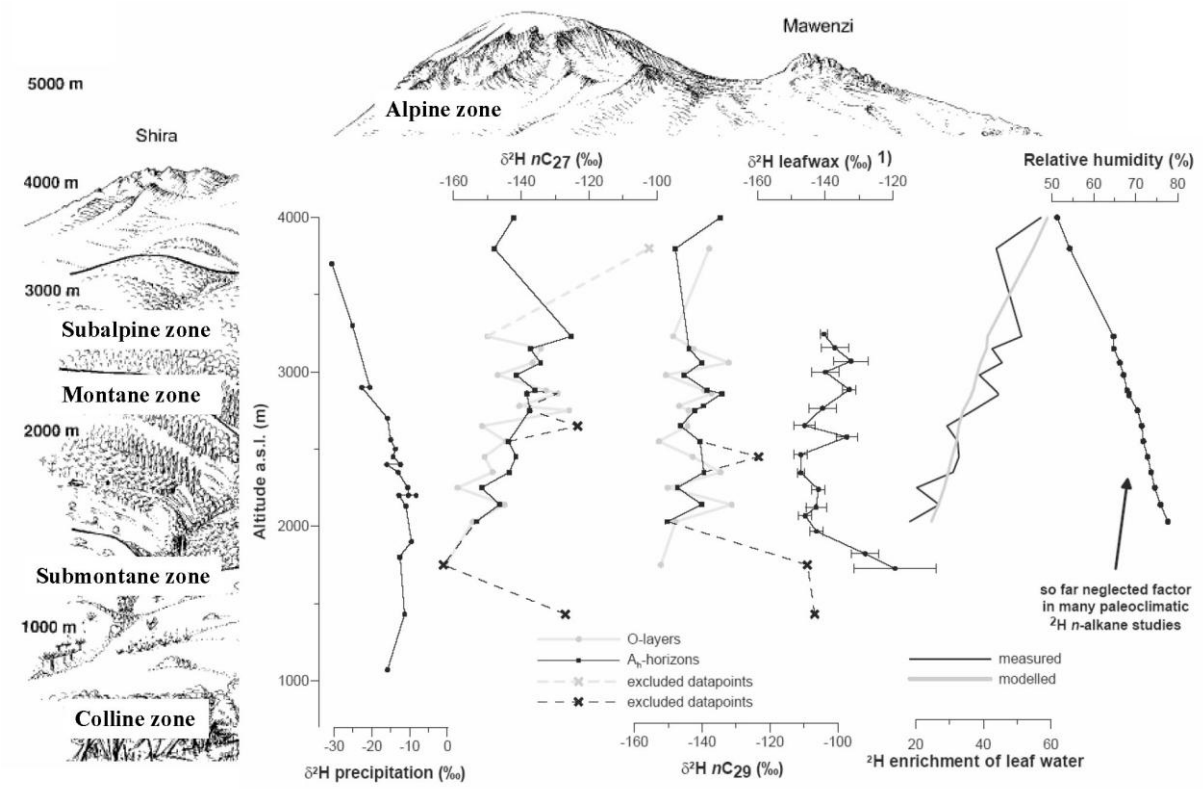
Zech, M., Zech, R., Rozanski, K., Hemp, A., Gleixner, G. and Zech, W.: Revisiting Mt. Kilimanjaro: Do n-alkane biomarkers in soils reflect the δ^2H isotopic composition of precipitation?, Biogeosciences Discussions, 11, 7823-7852, doi:10.5194/bgd-11-7823-2014.

Figure 1: Altitudinal change of $\delta^2H_{precipitation}$, $\delta^2H_{alkanes}$, and ^2H enrichment of leaf water (depending primarily on relative humidity). [1)] From Peterse et al., 2009

Anhang 1


Mawenzi
5000 m
Alpine zone
Shira
4000 m
3000 m
Subalpine zone
Montane zone
2000 m
Submontane zone
1000 m
Colline zone
Altitude a.s.l. (m)
δ²H nC27 (‰)
δ²H leafwax (‰) 1)
Relative humidity (%)
δ²H precipitation (‰)
δ²H nC29 (‰)
²H enrichment of leaf water
so far neglected factor in many paleoclimatic ²H n-alkane studies
O-layers
Ah-horizons
excluded datapoints
excluded datapoints
measured
modelled

V 30

Reconstructing lake evaporation history and the isotopic composition of precipitation by a coupled $\delta^{18}O$-$\delta^{2}H$ biomarker approach

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Over the past decades, $\delta^{18}O$ and $\delta^{2}H$ analyses of lacustrine sediments became an invaluable tool in paleohydrology and paleolimnology for reconstructing the isotopic composition of past lake water and precipitation. However, based on $\delta^{18}O$ or $\delta^{2}H$ records alone, it can be challenging to distinguish between changes of the precipitation signal and changes caused by evaporation. Here we propose a coupled $\delta^{18}O$-$\delta^{2}H$ biomarker approach that provides the possibility to disentangle between these two factors (Fig. 1).

Figure 1

The isotopic composition of long chain *n*-alkanes (*n*-C_{25}, *n*-C_{27}, *n*-C_{29}, *n*-C_{31}) were analysed in order to establish a 16 ka Late Glacial and Holocene $\delta^{2}H$ record for the sediment archive of Lake Panch Pokhari in High Himalaya, Nepal. The $\delta^{2}H_{n\text{-alkane}}$ record generally corroborates a previously established $\delta^{18}O_{sugar}$ record reporting on high values characterising the deglaciation and the Older and the Younger Dryas, and low values characterising the Bølling and the Allerød periods (Zech et al., 2014). Since the investigated *n*-alkane and sugar biomarkers are considered to be primarily of aquatic origin, they were used to reconstruct the isotopic composition of lake water (Fig. 1). The reconstructed deuterium excess of lake water ranges from +57‰ to -85‰ and is shown to serve as proxy for the evaporation history of Lake Panch Pokhari. Lake desiccation during the Deglaciation, the Older Dryas and the Younger Dryas is affirmed by a multi-proxy approach using the Hydrogen Index (HI) and the carbon to nitrogen ratio (C/N) as additional proxies for lake sediment organic matter mineralization (Hepp et al., 2014) (Figure 2).

Figure 2

Furthermore, the coupled $\delta^{18}O$ and $\delta^{2}H$ approach allows disentangling the lake water isotopic enrichment from variations of the isotopic composition of precipitation. The reconstructed 16 ka $\delta^{18}O_{precipitation}$ record of Lake Panch Pokhari is well in agreement with the $\delta^{18}O$ records of Chinese speleothems and presumably reflects the Indian Summer Monsoon variability.

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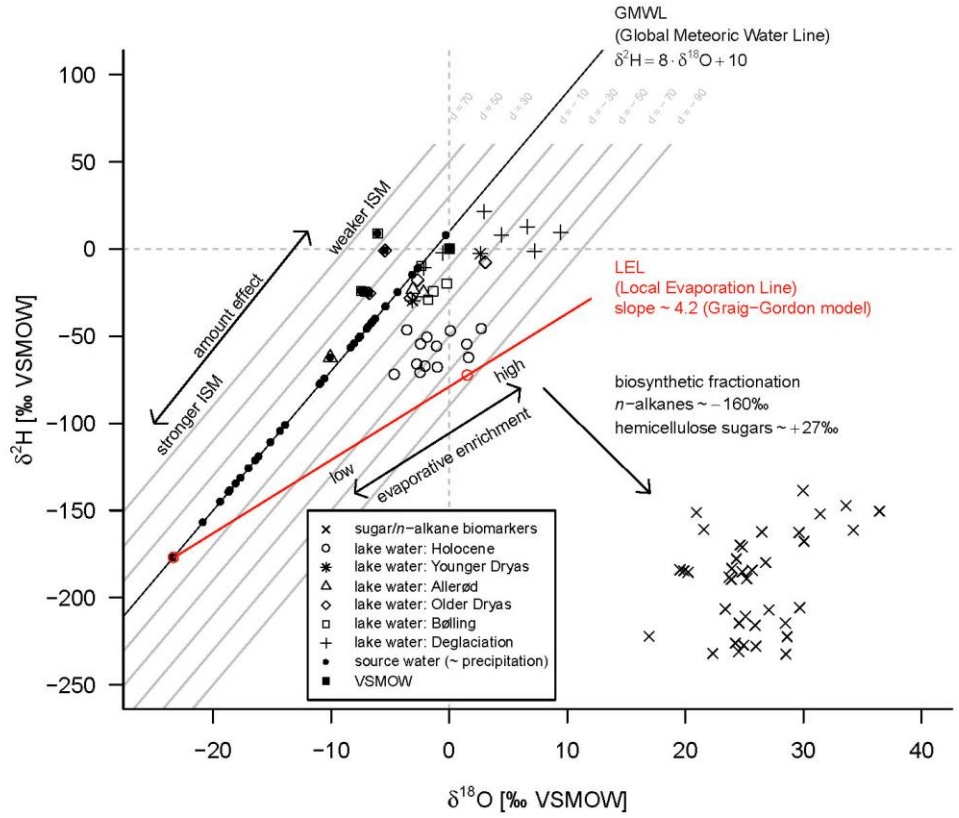
Zech, M., Tuthorn, M., Zech, R., Schluetz, F., Zech, W., Glaser, B., 2014. A 16-ka $\delta^{18}O$ record of lacustrine sugar biomarkers from the High Himalaya reflects Indian Summer Monsoon variability. Journal of Paleolimnology 51, 241-251.

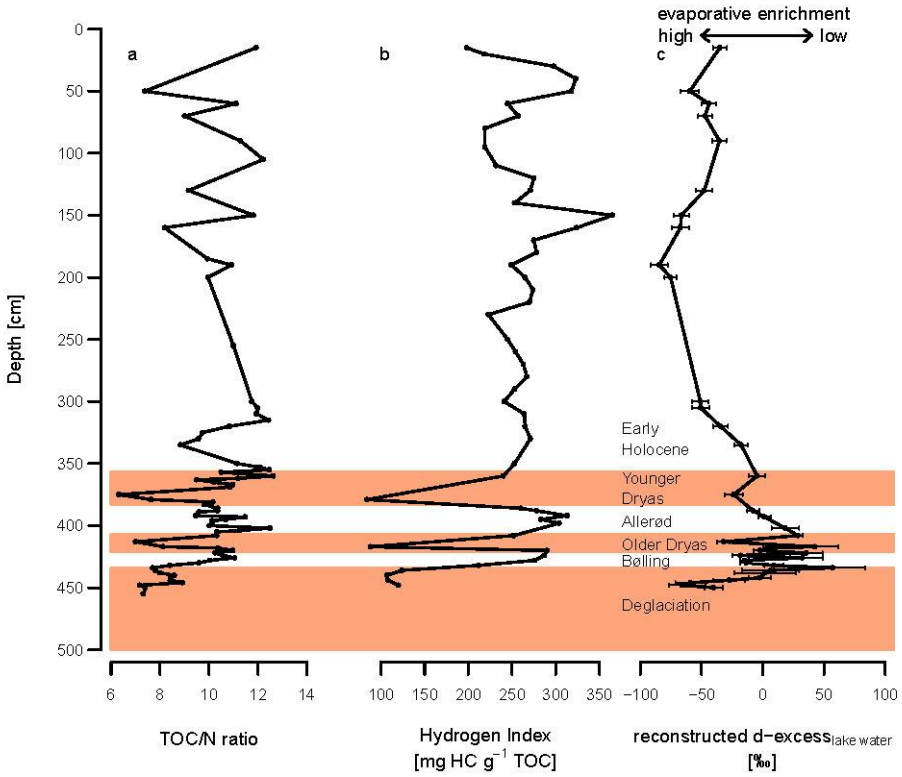
Figure 1: $\delta^{18}O$-$\delta^{2}H$ diagram illustrating the isotopic deviation of lake water (defined as deuterium-(d) excess) from the Global Meteoric Water Line (GMWL). $\delta^{18}O$ values of hemicellulose-derived sugars (mean of arabinose, fucose and xylose; from Zech *et al*., 2014b) and $\delta^{2}H$ values of *n*-alkanes (mean of *n*-C25, *n*-C27, *n*-C29, and *n*-C31) are used for reconstruction of the isotopic composition of Panch Pokhari lake water. $\delta^{2}H$ and $\delta^{18}O$ values of precipitation are calculated as intersections of the individual local evaporation lines (LEL) with the GMWL using a slope value of 4.2.

Figure 2: Comparison of (a) carbon to nitrogen (C/N) ratio, (b) Hydrogen Index (HI), and (c) deuterium-excess of lake water as proxies for evaporation history of Lake Panch Pokhari.

Anhang 1



Anhang 2



V 31
Isotopenpreisvortrag

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Vorträge

Session 6 – Ökosysteme

V 32
Geographical patterns in the isotopic ecology of wool, past and present

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In medieval Europe, sheep wool was one of the most important industrial commodities involved in long-distance exchange. It was produced all over the continent in various grades, some of which were valued highly and traded widely. These trade flows were clearly already considerable by the 12th century, when substantial documentation begins. Archaeologists are interested in being able to trace the earlier beginnings of these economic processes, by identifying non-local textiles among the wool finds from waterlogged archaeological deposits.

A multi-isotopic sheep wool isoscape ($\delta^{13}C$, $\delta^{15}N$, unexchangeable $\delta^{2}H$ and $\delta^{18}O$) for northern Europe is being developed, by analogy to food authenticity studies. This is based on data from modern wool (sampling sites n= 14, from Iceland to Finland), against which archaeological wool data (sampling sites n=5, sample n=102) is interpreted. Modern wool collection focused on fibre produced with relatively traditional grazing practices (no concentrate feeds, no artificial fertilizer on pasture), and mostly from heritage breeds. This presentation will demonstrate the construction of the isoscape, and discuss the ways in which modern sheep farming, and hence the modern sheep wool isoscape, differs systematically from that of the medieval past. Potential methods of resolving these differences, including the use of data from archaeological sheep bone and modern vegetation, will be discussed.

V 33

It's Complex: Using 13C/15N plant and soil isoscapes to capture environmental gradients, land-management effects and land-use patterns across a NE German agricultural landscape

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Agricultural landscapes are complex mosaics of landscape structures, vegetation, and land-use and management. Agricultural practices have the potential to mitigate or exacerbate climate change effects, highlighting the need to understand their impact on ecosystem biogeochemical cycles. There are limited tools available to gain a landscape perspective of biogeochemical cycling and usually studies are carried out at the field or plot scale. To gain a wider perspective we produced isoscapes (*iso*topic land*scapes*) based on plant, soil and sediment organic matter in order to characterize the carbon, water and nitrogen relations of the landscape. We use the isotopic footprint to understand the effects of environmental gradients, land-management, and land-use at a scale that directly addresses the complexity of agricultural landscapes. Our research area is part of the Quillow catchment in the moraine landscape of NE Germany, which is heavily utilized for agriculture and consists of numerous landscape features with different C/N dynamics. Typical landscape elements are small water bodies called "Sölle" (kettle holes), which are generally less than 1 ha in size, and which are interspersed across the landscape and predicted to undergo severe alterations in hydrology and biogeochemistry as the global climate changes. We collected plant and top-soil (2-15 cm) samples from a 38.2 km^2 rectangular area of the catchment, sampling a 250 m grid in the main 2013 growing season. Moreover, we sampled sediment cores and plants from 50 kettle holes that represent the geomorphological and hydrological variability within the study area. We constructed isoscapes ($\delta^{13}C$, $\Delta\delta^{15}N$, iWUE, P) using geostatistical interpolation and related them to multiple ecological processes both biotic and abiotic. On the basis of the intrinsic water use efficiency (iWUE) from crops, we are able to capture a small scale precipitation gradient. Generally, land-use types vary in their C/N dynamics and plants and soils are strongly linked and reflect land-management effects (e.g. fertilization, cultivation of maize) as well as the distance to urban areas. We can also show that the surrounding land-use type plays an important role on the biogeochemical processes in kettle holes. We conclude that isoscapes represent promising tools when dealing with complex landscapes at regional scales and that there are given many possible applications in terms of future biogeochemical and climate research.

V 34
Light limitation stimulates partial mycoheterothrophy in rhizoctonia-associated orchids

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Partial mycoheterotrophy (PMH) is the ability of a plant to obtain carbon (C) and other nutrients from mycorrhizal fungi simultaneously to autotrophy [1]. PMH is a continuous nutritional mode in members of the Orchidaceae plant family associated with ectomycorrhizal fungi (ECM). For this group of orchids a clear interaction between light availability and the degree of PMH was shown. An increase in fungal C gain with decreasing local light availability is mirrored in natural ^{13}C isotope signatures [2].

In this study we tested whether orchids with a mycorrhizal association with polyphyletic rhizoctonias show a similar light dependency of partial mycoheterotrophy under natural light climate gradients analyzing $d^{13}C$, $d^{15}N$ and $d^{2}H$ isotope abundances. The two orchid species *Ophrys insectifera* L. and *Neottia ovata* (L.) Bluff & Fingerh. growing in habitats ranging from mixed deciduous and coniferous forests strongly limited in light availability to open grasslands with rather high irradiation were sampled at two locations in the Nördliche Frankenalb (NE Bavaria). Leaf material of 12 orchid individuals per species and site and accompanying autotrophic non-orchid plants as references for site conditions [3] were resampled three times in the period of growth in 2012. Local light climate was continuously measured next to the sampled orchid individuals over the growing season. Stable isotope natural abundance analyses were conducted to test whether carbon (^{13}C) and nitrogen (^{15}N) are gained through autotrophic means or *via* mycorrhizal fungi. In 2013 five orchid individuals per species and site and autotrophic references were sampled additionally to further analyze hydrogen (^{2}H) natural stable isotope abundances.

O. insectifera and *N. ovata* individuals were significantly enriched in ^{13}C towards their autotrophic references at the forest site but not at the open grassland location. Contrasting the two species showed a significant enrichment in ^{15}N at both sites except for *N. ovata* at the forest site where the orchid cannot be distinguished from its reference species. Enrichment in ^{15}N in *O. insectifera* was significantly higher at the forest location. No temporal dynamics in ^{13}C and ^{15}N isotope abundances over the growing season were detected. N concentration was significantly higher towards autotrophic reference species at the forest site for both *O. insectifera* and *N. ovata*. Both species were significantly enriched in ^{2}H towards autotrophic references at the two sites. Our results demonstrate that local light availability also drives PMH in orchids associated with rhizoctonias as orchids at the light-limited forest site show a significant but proportionally smaller enrichment in ^{13}C towards orchids mycorrhizal with ECM. Nevertheless, significant enrichment in ^{2}H elucidates both rhizoctonia-associated orchids to be partially mycoheterotrophic regardless of microscale light availability.

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V 35

Intramolecular isotope distributions detect CO_2-driven increases in photosynthesis over centuries

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The century time scale is most important for climate models, for prediction of crop productivity, and for adaptation to climate change. That plants respond on century time scales is demonstrated by observed changes in stomatal index, but beyond this, very little is known. We argue that this is because of a glaring gap of methods that can bridge between ecophysiological experiments and paleo science. We present new stable isotope methods that fill this gap, by providing information on metabolic fluxes on time scales of centuries.

Isotope measurements usually determine isotope ratios (e.g. $\delta^{13}C$, δD) of whole molecules. However, it is well established that stable isotope abundance varies among intramolecular groups of metabolites, in other words each *isotopomer* has a distinct abundance. We have previously shown that this isotopomer variation reports on regulation of carbon metabolism.

Here, we apply deuterium (D) isotopomers to study the metabolic response of C_3 plants to increasing atmospheric [CO_2]. Greenhouse experiments show that D isotopomers of photosynthetic glucose depend on [CO_2] during growth. This dependence constitutes an isotopomer signal of the metabolic flux ratio oxygenation : carboxylation at Rubisco, which is a central determinant of net primary production. The isotopomer ratio has significant advantages: First, the signal is based on an intramolecular isotope ratio, and is therefore independent of the isotope ratio of source water. Second, because it is based on metabolic fluxes at Rubisco, it integrates all parameters that affect the flux ratio oxygenation : carboxylation.

We traced this isotopomer signal in historic material of two crop species and two species from the natural vegetation over the past 100 years and compared results with the greenhouse experiments. This allows estimating how much photorespiration has been reduced by the anthropogenic CO_2 increase during the 20^{th} century, and shows that plants have not acclimated to increasing [CO_2] during more than 100 growing seasons.

This first demonstration of isotopomer signals of long-term metabolic changes shows that isotopomers carry physiological signals, which can be retrieved from archives of plant material. Because D is fractionated both in the climate system and in biochemical reactions, D isotopomers of long-term archives of plant material may allow derivation of parallel physiological and climate signals, which may reveal plant-climate interactions. The principles governing isotopomer abundances are general for all metabolites and isotopes (D, ^{13}C), therefore isotopomers multiply the information content of paleo archives. In particular, they allow extraction of metabolic information on long time scales, thereby connecting plant physiology with paleo research.

V 36
Investigations of (soil) respiration in a long-term Free Air CO_2 Enrichment (FACE) experiment

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[2]Institut für Pflanzenökologie, Experimentelle Pflanzenökologie, Gießen, Deutschland

The increased C supply with increasing atmospheric CO_2 conditions enhances photosynthesis but also increases respiratory C losses from ecosystems with a yet unknown net effect for the net soil C stock. FACE experiments are an established tool in ecological research studies to investigate the behavior of ecosystems to increased atmospheric CO_2 concentrations under natural conditions in the field with only minor artificial effects.

Here we present ^{13}C signature values of several ecosystem compartments and from soil and ecosystem respiration of a permanent grassland ecosystem. After six years, the $\delta^{13}C$ value of the enrichment-CO_2 was switched from -25 to -48‰, to trace ecosystem C-fluxes without concomitant priming effects of the initial CO_2 step increase. To obtain a general picture on the C fluxes soil and plant samples were taken to measure carbon (C) pools and stable carbon isotope values. Gas samples were collected from soil air and ecosystem respiration (R_{eco}) to measure CO_2 concentration and $\delta^{13}C$ value of CO_2 ($\delta^{13}CO_2$).

We observed an annual trend of the $\delta^{13}CO_2$ value on R_{eco} and soil air CO_2. The $\delta^{13}CO_2$ of R_{eco} and soil air CO_2 showed lowest values during the growth period, indicating a higher contribution of plant-derived CO_2 at that time. Based on the $\delta^{13}C$ values of plants and soil C we calculated the contribution of plants and soil on respiration via two-component mixing model. Under elevated CO_2 +20%, the estimated contribution of root-derived soil respiration was 55% in the top 15 cm of the soil. The mean contribution of root, leaf and soil respiration on R_{eco} was 29 ±18%, 32 ±23% and 38 ±20%, respectively. A significant decrease in soil air $\delta^{13}CO_2$ with soil depth indicated a relatively higher contribution of root-derived CO_2 in the deeper soil layers. The $\delta^{13}CO_2$ gradient showed a clear annual dynamics with a significant impact of soil temperature. The steepest $\delta^{13}CO_2$ gradients occurred during winter but became less distinctive during summer.

During the observation period the CO_2 enrichment enhanced R_{eco} by 13% above ambient but did not result in increased soil C sequestration after 9 years of elevated CO_2. No CO_2-induced differences in the temporal dynamics of R_{eco}, soil air [CO_2] and the $\delta^{13}C$ values were observed. The seasonal variability recorded in the long-term monitoring may explain partly-contrasting findings of other studies where no long-term sampling was performed.

V 37

Using stable oxygen isotopes to assess vegetation impact on ecosystem water cycle and productivity in a Mediterranean oak woodland

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Water is one of the key factors driving ecosystem productivity, especially in water-limited ecosystems. Thus a separation of the component fluxes is needed to gain a functional understanding on the development of net ecosystem water and carbon fluxes. Oxygen isotope signatures are valuable tracers for such water movements within the ecosystem because of the distinct isotopic compositions of water in the soil and vegetation. In the past, determination of isotopic signatures of evaporative or transpirational fluxes has been challenging since measurements of water vapor isotopes were difficult to obtain using cold-trap methods. Recent developments in laser spectroscopy now enable direct high frequency measurements of the isotopic composition of atmospheric water vapor (δ_v), evapotranspiration (δ_{ET}), and its components and allow validations of common modeling approaches for estimating δ_E and δ_T based on Craig and Gordon (1965).

Here, a novel approach was used, combining a custom build flow-through gas-exchange branch chamber with a Cavity Ring-Down Spectrometer in a Mediterranean cork-oak woodland where two vegetation layers respond differently to drought: oak-trees (*Quercus suber L*.) avoid drought due to their access to ground water while herbaceous plants survive the summer as seeds. We used this approach to quantify the impact of the understory herbaceous vegetation on ecosystem carbon and water fluxes throughout the year and disentangle how *ET* components of the ecosystem relate to carbon dioxide exchange.

We present one year data set comparing modeled and measured stable oxygen isotope signatures ($\delta^{18}O$) of soil evaporation, confirming that the Craig and Gordon equation leads to good agreement with measured $\delta^{18}O$ of evaporation (Dubbert et al., 2013). Moreover, we found continuously strong deviations from isotopic steady-state in plant transpiration (Dubbert et al., 2014). This implies that assuming plant transpiration to be in the steady-state can have a huge impact for studies that distinguish relatively short time intervals (hours, e.g. partitioning studies). Finally. partitioning ecosystem *ET* and *NEE* into its three sources revealed that understory vegetation contributed markedly to ecosystem *ET* and gross primary production (*GPP;* max. 43 and 51%, respectively). It reached similar water-use efficiencies (*WUE*) as cork-oak trees and significantly contributed to the ecosystem sink-strength in spring and fall. The understory vegetation layer further strongly inhibited soil evaporation (*E*) and, although *E* was large during wet periods, it did not diminish ecosystem *WUE* during water-limited times.

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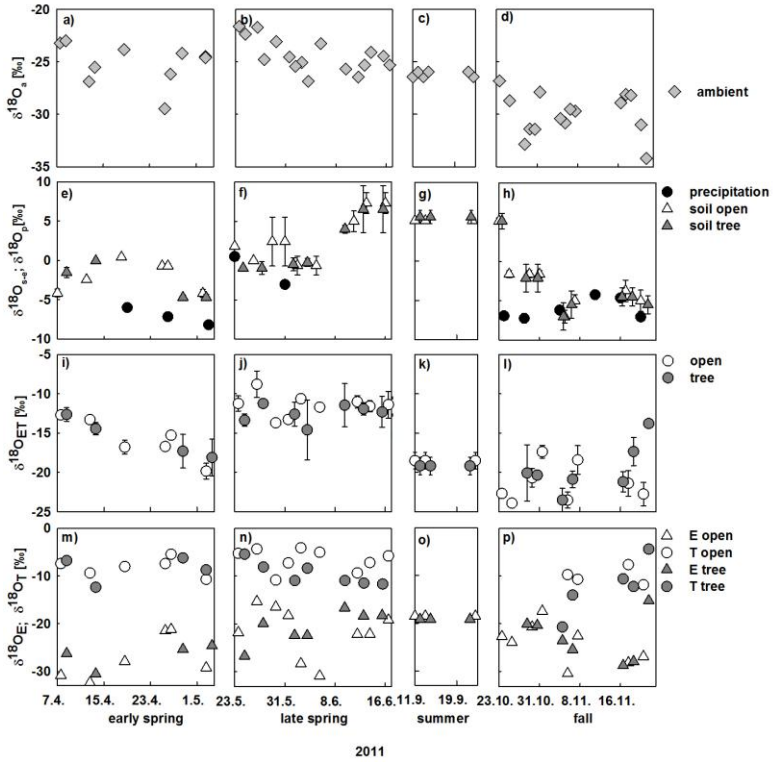
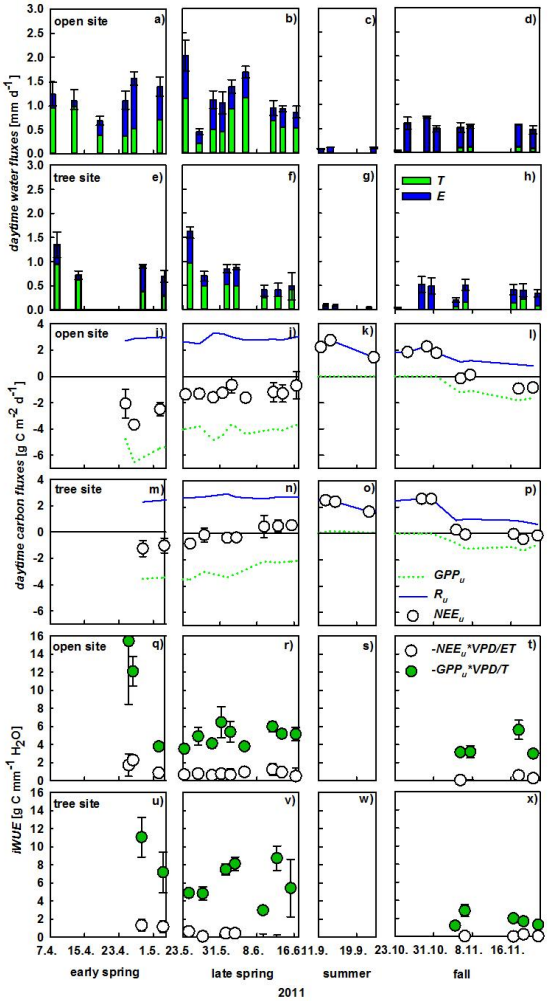
Dubbert M, Piayda A, Cuntz M, Werner C, 2014. Oxygen isotope signatures of transpired water vapor - the role of non-steady-state transpiration under natural conditions. New Phyt.

Anhang 1



Anhang 2



Poster

Session 1 – Analytik: Neue Methoden und Techniken

P 1
SPINMIMS eine Vereinfachung der SPINMAS Messtechnik zur online Messung der ^{15}N-Häufigkeiten in Ammonium, Nitrit und Nitrat

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Gängige Methoden zur Messung der ^{15}N Häufigkeit in einzelnen N-Spezies wie NH_4^+, NO_2^- und NO_3^- in Proben mit mehreren N-Spezies (z.B. die Diffusionsmethode) sind arbeitsintensiv und zeitaufwändig. Eine automatisierte, schnelle und selektive Bestimmung von ^{15}N Häufigkeiten in NH_4^+, NO_2^- und NO_3^- in wässrigen Proben ist durch die SPINMAS-Technik (Stange et al. 2007) möglich. Aufbauend auf Arbeiten von Russow et al. (1996) und Russow (1999) wird je nach N-Spezies eine bestimmte Reaktionslösung in einer Probenpräparationseinheit für anorganische N-Spezies (SPIN) mit der Probe vermischt. Die gasförmigen Reaktionsprodukte werden dann im He-Strom zu einem Quadrupolmassenspektrometer (MAS) geleitet.

Durch die Verwendung eines Membraneinlass-Massenspektrometers (MIMS) kann der für die SPINMASS Technik benötigte instrumentelle Aufbau deutlich vereinfacht werden. Der hier vorgestellte SPINMIMS Ansatz beruht auf der Verwendung einer Reaktionskapillare, in der die Probe mit den zu analysierenden N-Spezies und der entsprechenden Reaktionslösung gemischt werden. Von dort wird die Analysenlösung direkt zum Membraneinlass gepumpt, von wo die bei der Umsetzung von NH_4^+, NO_2^- und NO_3^- gebildeten Reaktionsprodukte (N_2 und NO) durch eine semipermeable Membran direkt in die Ionenquelle des Massenspektrometers geleitet werden.

^{15}N Standards (NH_4^+ und NO_3^- jeweils in dest. Wasser) mit verschiedenen at% ^{15}N wurden selbst erstellt und per IRMS Messungen die erwarteten ^{15}N Gehalte überprüft. Insgesamt zeigen die SPINMIMS-Messungen eine gute Übereinstimmung gemessener und erwarteter ^{15}N Häufigkeiten (Abweichung < 0,8 at% ^{15}N im Bereich von 1 - 99 at% ^{15}N für NH_4^+- und < 0,15 at% ^{15}N im Bereich von 0,6 - 10 at% ^{15}N für NO_3^--Standards). Bei hoch mit ^{15}N angereicherten NO_3^- Proben zeigt sich eine zunehmende Abweichung zwischen Ergebnissen der SPINMIMS-Messungen und den Erwartungswerten. Modellierend konnte gezeigt werden, dass dies durch in der Ionenquelle gebildete $^{30}N_2$ Fragmente, von bei der NO_3^- Umsetzung vermutlich gebildetem N_2O, erklärt werden könnte.

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P 2

Compound-specific isotope analysis of glyphosate and its metabolite AMPA during degradation

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Glyphosate (N-(phosphomethyl)-glycine) is a widely used herbicide in agricultural and landscape management. Glyphosate strongly adsorbs in soil and may be biodegraded by soil microorganisms giving AMPA (amino-methyl phosphoric acid) as main transformation product [1, 2]. Major research efforts have focused on assessing the environmental fate of glyphosate and its main metabolite AMPA which are frequently detected in surface and groundwater. To this end, concentration measurements alone are often not conclusive [3]. To advance an alternative approach, we (i) developed nitrogen stable isotope analysis ($^{15}N/^{14}N$) of glyphosate and AMPA by derivatization-gas chromatography/ isotope ratio mass spectrometry (GC/IRMS), Accurate $\delta^{15}N$ values were obtained (deviation from elemental analyzer-IRMS): 0.23‰ ± 0.88‰ for glyphosate and 0.37‰ ± 0.70‰ for AMPA [4]. We (ii) subsequently used the method to investigate nitrogen isotope fractionation during transformation of glyphosate at Manganese dioxide (MnO_2) surfaces [5], where we observed enrichment factors as high as ε_N = -17‰ ±0.5‰. Finally, we (iii) isolated glyphosate-degrading bacteria from soil to investigate carbon isotope fractionation (measured with liquid chromatography-IRMS) during glyphosate biodegradation. We successfully isolated bacteria from soils collected at a glyphosate applied vineyard from northern France that showed the ability to degrade glyphosate as Phosphorous source similar to other studies [6, 7]. Only small carbon isotope fractionation was observed during biodegradation of glyphosate ε_C = -6 ‰ indicating that intrinsic fractionation may be masked. There is promising potential to use CSIA (compound-specific isotope analysis) to study the degradation of glyphosate and its metabolite AMPA

Key words: glyphosate, AMPA, GC-IRMS, LC-IRMS, CSIA

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P 3

Optimization of an isotope ratio mass spectrometer and a cryogenic CO_2 extraction system for $\delta^{13}C(CO_2)$ and $\delta^{18}O(CO_2)$ analysis on air samples within the ICOS Infrastructure

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An Isotope ratio mass spectrometer (IRMS, ThermoFischer MAT 253) for $\delta^{13}C(CO_2)$ and $\delta^{18}O(CO_2)$ analysis of small air samples (2 litre at 1.2bar) is currently under installation at the MPI-BGC Jena.

With our IRMS, the numbers of CO_2 molecules with m/zs 44, 45 and 46 are measured simultaneously to calculate $^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratios. CO_2 measurements of dilute air samples become available utilizing a CO_2 cryo-trap technique, that was first developed at MPI-BGC in 2001[1]. In order to achieve the WMO target compatibility criteria[2] ($\Delta\delta^{13}C$ = 0.010‰, $\Delta\delta^{18}O$ = 0.050‰) extensive instrument tests were made and subsequent setup improvements were implemented.

We present results and conclusions from measurements taken during the optimization of the δ-measurement method, including:

- optimization of the signal stability at the Faraday cups

- characterization of the mass ratio stability including differences between reference and sample side

- observation of time delays after change over switching (η-effect)

- and optimization of the cryo-trap towards efficiency, long- time stability and general signal stability.

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P 4

Einsatz eines CO_2- Isotopenlasers im kontinuierlichen Betrieb an einer Mikrokosmenanlage zur Untersuchung von bodenökologischen Prozessen

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Zum Studium der Prozesse bei der Emission von Treibhausgasen aus Böden spielen Mikrokosmenanlagen eine große Rolle. Dazu werden Bodensäulen in Plexiglasbehältern (Mikrokosmen) unter klimatisierten Bedingungen mit synthetischer Luft kontrolliert. Aus der Abluft wird automatisch deren Gehalt an CO_2, N_2O und CH_4 mittels Gaschromatographen bestimmt. Die Durchflussrate der Luft durch die Säulen wird sequentiell an den einzelnen Säulen nacheinander gemessen und anhand einer Rückrechnung die Produktion dieser Gase in den Säulen bestimmt.

Über reine Konzentrationsmessungen hinaus werden im Rahmen der Untersuchung bodenökologischer Prozesse isotopisch markierte Substanzen eingesetzt. So werden z.B. den Böden ^{13}C angereicherte Substrate zugefügt um Umsetzungen, Verlagerung oder Sequestration des Kohlenstoffs zu untersuchen.

Eine Analyse der C -Isotopensignatur in den Abluftproben aus einem Mikrokosmenversuch, bei dem eine Vielzahl von Bodensäulen zum Einsatz kommen, ist mit klassischen Isotopenhäufigkeitsmassenspektrometern sehr arbeitsaufwendig und zeitintensiv. Außerdem sind durch einzelne Probenahmen zu fixen Terminen immer nur diskontinuierlich punktuelle Momentaufnahmen möglich.

Mit einem Laser-Isotopenanalysator (Picarro G1101-*i*) kann direkt online in der Abluft aus den einzelnen Bodensäulen die C-Isotopensignatur im CO_2 gemessen werden. Hierfür werden - wie bei den Konzentrationsbestimmungen auch - nacheinander die $d^{13}C$ Werte in der Säulenabluft gemessen.

Während die Flussraten durch die Säulen variieren können und meist bei 10 mL min^{-1} liegen, beträgt sie beim Picarro G1101-i jedoch 22 mL min^{-1}. Zur Lösung des Problems dieser Diskrepanz bieten sich verschiedene Möglichkeiten an.
Wenn die Flussrate durch die Säule geringer als die durch den Picarro ist, kann man den Picarro über ein T-Stück und ein Nadelventil zur Flussverringerung hinter den Flussmesser anschließen. Dies wird zwangsläufig zu einer deutlichen Verlängerung der Ansprechzeit führen.
Bei ausreichend hoher CO_2-Konzentration kann man die Abluft mit einem Make-Up-Gas verdünnen, um ein Nadelventil zu vermeiden.
Eine kürzere Ansprechzeit kann aber auch durch Integration des Picarro in einen Loop erreicht werden. Die Vakuumpumpe des Gerätes weist jedoch eine bauartbedingte Undichtigkeit auf.

Die Koppelung des Picarro an die im Thünen-Institut für Agrarklimaschutz vorhandene Mikrokosmenanlage wurde erstmals für einen Versuch mit Moorböden eingesetzt, bei dem der Verbleib des Kohlenstoffs aus ^{13}C markiertem Schafskot und -urin untersucht wurde. Wir haben die oben erwähnten Anschlussoptionen mit dem Moorbodenexperiment, aber auch mit Gasmischungen mit verschiedenen $d^{13}C$ Werten getestet im Hinblick auf ein optimales Umschaltintervall zwischen den Säulen bei guter Genauigkeit der gewonnenen Daten und stellen die Ergebnisse hier vor.

P 5

A preliminary refinement of the clumped isotope paleothermometer for biogenic apatite and an experimental approach for abiotic apatite

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Clumped isotope analysis of carbonates provides a new paleothermometer (Ghosh et al., 2006). The temperature dependence of the extent of ^{13}C-^{18}O clumping (expressed as Δ47) inside carbonateshas been investigated in several studies(e.g., Ghosh et al., 2006; Dennis and Schrag, 2010; Wacker et al. 2014), but little attentionwas paid to carbonate-bearing minerals, such asbiogenic and abiotic phosphates. First investigations by Eagle et al. (2010) implied that bio-apatites may follow aT-dependencesimilar to thatproposed for calcite by Ghosh et al. (2006). However, it has remainedin doubtif the calibration of Ghosh et al. (2006) is accurate (e.g., Wacker et al. 2013, 2014).

The aim of this work is to create a refined calibrationfor biogenic and abiotic (authigenic) carbonate-bearing apatites. So far, teeth of a Greenland shark (*Somniosus microcephalus*, growth T ~2°C) and of an African elephant (*Loxodonta africana*, T ~ 37°C) have been analyzed for their clumped isotope compositions using phosphoric acid digestion temperatures of 90°C and 110 °C. These investigations imply that the evolved CO_2 does not equilibrate inside the acidic environment. Enamel Δ47 seems to exhibit a T dependence that is very much different from results of Eagle et al. (2010), but much more similar to those of Wacker et al. (2014). Dentine, on the other hand, does not follow the T dependence of enamel. Reasons for the observed discrepancy between enamel and dentine will be discussed. Moreover, the clumped isotopic composition of enamel from a fossil tooth of *C. megalodon* has been analyzed to test the potential of the bioapatite clumped isotope thermometer for recording temperatures of the paleoocean and body temperatures of extinct vertebrates. Next, data from natural samples will be refined by measurements on abiotic samples prepared by different methods at T between 10°C and 60°C.

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P 6
Progress in compound-specific oxygen isotope analysis of sugars

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Determination of the oxygen isotope ratio (δ18O) of plant material has been widely used under controlled and field conditions to investigate biochemical and physiological isotope effects. As a result, detailed models describing fractionation processes in leaves have been developed. This enabled the use of δ18O analysis of tree-ring cellulose as a biomarker for plant physiological and climatic studies. Nowadays, methods for bulk analysis of δ18O of total soluble carbohydrates and stem cellulose are well established, while applicable methods are still missing for δ18O analysis of sugars as main precursor of cellulose. This is crucial due to the fact that δ18O of individual sugars hold potential information about detailed biochemical processes, which cannot be disentangled with bulk analysis, for instance, about the importance of mixing of different compounds, the exchange of carbonyl groups with water, and the impact of δ18O of sucrose on stem cellulose. Therefore, current methods for compound-specific oxygen isotope analysis (CSIA) of sugars should be improved or new methods established. CSIA measurements with GC-IRMS pyrolysis are still a great challenge and only very few data exist so far. Recently, we have developed a method using tri-methylsilylation derivatization to analyze δ18O of sugars with GC-IRMS, with good results for sucrose (Zech *et al.*, 2013). In a next step, we applied a novel method by using methylation derivatization, which led to more accurate results for sucrose than with tri-methylsilylation, but also to acceptable results for fructose and glucose, which could not be measured before. This new method promises to be a big step forward in analyzing δ18O of sugars.In future we want (1) to improve the precision of the method to analyze δ18O of sugars at natural abundance; (2) to make the method applicable also for other important sugars (galactose, raffinose) and sugar-alcohols (pinitol and myo-inositol); and (3) to apply this method to samples of field campaigns and of experiments performed under controlled conditions. Finally, we aim to provide a novel and easy to use method for δ18O analysis of sugars for wide-spread applications in diverse research fields.

Zech M, Saurer M, Tuthorn M, Rinne KT, Werner RA, Siegwolf RTW, Glaser B, Juchelka D. 2013. A novel methodological approach for δ18O analysis of sugars using gas chromatography-pyrolysis-isotope ratio mass spectrometry. *Isotopes in Environmental and Health Studies* **49**: 492-502.

P 7
Pitfalls in nitrate isotope analysis and how to avoid them

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Nitrogen ($\delta^{15}N$) and oxygen ($\delta^{18}O$) isotope ratios of nitrate (NO_3^-) are often used to trace dominant NO_3^- pollution sources in water. Three methods are currently employed: (i) the silver nitrate ($AgNO_3$) method, (ii) the bacterial denitrification method and (iii) the cadmium reduction method. The $AgNO_3$ method is not applicable to saline samples and requires comparatively high concentrations of NO_3^- (100-200 mmol), because it relies on NO_3^- purification by anion-exchange and subsequent precipitation as $AgNO_3$, for analysis by elemental analyser-isotope ratio mass spectrometry (EA-IRMS). The existence of large blanks from dissolved organic matter can also be an issue in the application of this method. The bacterial denitrification method uses bacteria to convert NO_3^- into N_2O [1] and the cadmium method produces N_2O by chemical reduction of NO_3^- to NO_2^- with a subsequent reaction with azide [2]. Since the formation of N_2O eliminates any interferences and is amenable to gas chromatography-IRMS, the two "N_2O methods" have a detection limit below 1 µmol and can also be used for seawater samples. Despite these advantages, the N_2O methods are not yet universally adapted and a reliable method comparison is still missing.

Here we present a first systematic comparison of all three methods: the most typical pitfalls for each of these methods, starting from sample collection and preservation into method's application for isotope analysis. In the near future, we plan to compare these methods using river-, ground- and contaminated water samples having a wide range of $\delta^{15}N$- and $\delta^{18}O$-NO_3^-values and NO_3^- concentrations.

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P 8

Inter-laboratory assessment of nitrous oxide isotopomer analysis by isotope ratio mass spectrometry and laser spectroscopy: current status and perspectives

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In recent years, research and applications of the N_2O site-specific nitrogen isotope composition have advanced [*Toyoda et al.*, 2013], reflecting awareness of the contribution of N_2O to the anthropogenic greenhouse effect, and leading to significant progress in instrument development [*Wächter et al.*, 2008, *Mohn et al.*, 2012]. Further dissemination of N_2O isotopomer analysis, however, is hampered by a lack of internationally agreed gaseous N_2O reference materials and an uncertain compatibility of different laboratories and analytical techniques [*Köster at al.*, 2013, *Park et al.*, 2012].

In a first comparison approach, eleven laboratories were each provided with N_2O at tropospheric mole fractions (target gas T) and two reference gases (S1 and S2). The laboratories analyzed all gases, applying their specific analytical routines. Compatibility of laboratories was assessed based on N_2O isotopocule data for T, S1 and S2. Results for the T were then standardized using S1 and S2 to evaluate the potential of N_2O reference materials for improving compatibility between laboratories.

Compatibility between laboratories depended on the analytical technique: isotope ratio mass spectrometry (IRMS) results showed better compatibility for $d^{15}N$ while the performance of laser spectroscopy was superior with respect to N_2O site preference. This comparison, however, is restricted by the small number of participating laboratories applying laser spectroscopy. Offset and two-point calibration correction of the N_2O isotopomer data significantly improved the consistency of position-dependent nitrogen isotope data while the effect on $d^{15}N$ was only minor.

The study reveals that for future research on N_2O isotopocules, standardization against N_2O reference material is essential to improve interlaboratory compatibility. For atmospheric monitoring activities, we suggest N_2O in whole air as a unifying scale anchor.

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P 9

Real-time measurements of nitrous oxide isotopomers at a tall tower: Identifying sources and hot spots in Switzerland

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Atmospheric N_2O mixing ratios have been rising at a rate of 0.2-0.3% per year over the past decades due to enhanced microbial production in fertilized agricultural soils. N_2O sources are linked to different microbial processes occurring in soils, therefore sources are disperse and highly variable, complicating the development of effective mitigation strategies. Isotopic measurements have great potential to unravel spatial and temporal variations in sources and processes of N_2O. Recent developments in quantum cascade laser spectroscopy coupled to automated N_2O preconcentration (Mohn et al. 2012; Harris et al. 2014; Wolf et al. 2014) allow both the intermolecular distribution of ^{15}N substitutions ('site preference'; $^{15}N^{14}N^{16}O$ versus $^{14}N^{15}N^{16}O$) and the oxygen isotopic composition ($\delta^{18}O$) of N_2O to be measured with a precision of-1.

In this study, the performance of the laser-based measurement technique is further improved with respect to temporal resolution, accuracy and long-term precision for operation under field conditions. A special focus will be placed on the temperature stabilization of the spectrometer, removal of trace gas interferences, and anchoring of the measurement results (delta values and mixing ratios) to international standard scales. The foreseen real-time measurements of N_2O mixing ratios and site-specific isotopic composition at a tall tower in Central Switzerland (Beromünster), in combination with backward Lagrangian particle dispersion modelling and an inversion system, will then be applied to determine source strengths and their isotopic composition in Northern Switzerland.

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P 10
Investigation of the isotopic fractionation during direct photolysis of Sulfamethoxazol

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Sulfonamides and their antimicrobial properties are already known since 1908 [1]. In contrast to herbicides andveterinarydrugs the environmental aspects were not important for theaccreditationtill 2003 [2]. In the meantime, numerous studies of the effects of drug residuals in water samples were performed, including sulfamethoxazole, one of the most usedantibiotics[3-5]. Although photolysis is the dominant transformation pathway of sulfamethoxazole in surface waters its degradation mechanism was not investigated by using stable isotope analysis.

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

The aim of this work was to develop a method to determine compound-specific carbon isotope analysis of sulfamethoxazole and its photolytic degradation products by High Temperature Liquid Chromatography Isotope Ratio Mass Spectrometry (HT-LC-IRMS), which allows monitoring of environmental degradation processes in surface waters. This method was applied to study the direct photolysis of sulfamethoxazole. The monitoring of the degradation by HT-LC-IRMS has been carried out by the use of an X-Bridge C_{18} (Waters, 3.5 µm particle size, 100 × 2.1 mm) chromatographic column and an eluent of pure water (50%) mixed with a phosphate buffer (50%, 10 mM, pH 3). The calculated carbon isotopic enrichment factor for the direct photolysis of sulfamethoxazole was very low with a value of 0.7 ± 0.1 ‰. Since no carbon bonds are broken only secondary isotopic effects cause a fractionation.

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P 11

Validierung und Optimierung von Probenpräparationsmethoden für die $d^{15}N\text{-}NH_4$-Analytik an Wasser- und Bodenproben

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Gegenstand einer ersten Studienarbeit zur d15N-NH4-Isotopenanalytik am Institut für Grundwasserwirtschaft (Baumann, 2014) war die vergleichende Prüfung und Optimierung von Diffusionsmethoden, die bisher publiziert wurden.

Für die Aufbereitung von Wasserproben konnten dabei gute Ergebnisse mit einer Modifikation der Methode von (Sebilio et al., 2004) erzielt werden. Es konnten wertvolle Erkenntnisse zu den wichtigsten Voraussetzungen für eine vollständige und fraktionierungsfreien d15N-NH4- Analytik gewonnen werden, die die Basis weiterer Untersuchungen bilden werden.

Die modifizierte d15N-NH4-Probenvorbereitungsmethode konnte zudem erfolgreich an Grundwasserproben aus dem Berliner Urstromtal validiert werden, die im An- und Abstrom einer in-situ- Grundwassersanierungsmaßnahme zur Stimulation der Nitrifikation eines NH_4-Schadens entnommen wurden.

Weiterhin wurden erste Tests von in der Literatur beschriebenen Methoden durchgeführt, die sich der Präparation von NH4 zur d15N-Analytik widmen, welches in Bodenproben in kationenaustauschbar oder organisch gebundener Form vorliegt (z.B. Sorensen und Jensen, 1991, Carter und Gregorich, 2007). Hier konnten jedoch bisher keine zufriedenstellenden Ergebnisse erzielt werden.

P 12

Optimization of sample preparation procedure for Cl DI-IRMS measurement of organochlorines.

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The study aimed to optimize the analytical method to determine chlorine stable isotope composition ($\delta^{37}Cl$) of γ-Hexachlorocyclohexane (γ-HCH) by Dual-Inlet Isotope Ratio Mass Spectrometry (DI-IRMS). Sample preparation method, reported by Jendrzejewski et al.[1] and Holmstrand et al.[2], included sealed-tube combustion of organochlorine, followed by precipitation and subsequent conversion of formed inorganic chlorides to methyl chloride (CH_3Cl). We identified the most critical step - dissolution of inorganic copper chlorides, formed by combustion of g-HCH. We found that significant amount of chlorine was trapped in undissolved $CuCl_n$, leading to changes in $\delta^{37}Cl$ (with preferential trapping of heavy isotopes into $Cu^{35}Cl_n$). We have optimized the dissolution step to minimize losses of ^{35}Cl. We have tested the accuracy of the optimized method by analyzing CH_3Cl sample with known $\delta^{37}Cl$ value reported vs. the SMOC scale (Standard Mean Ocean Chloride) before and after the whole procedure. The difference between product and initial CH_3Cl was 0.11 ± 0.04 ‰. Moreover, our optimized method is suitable for the broad range of chlorinated organic compounds, as the most critical step is not related to the chemical structure of the starting material.

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P 13

Recharge estimation in a semi-arid environment using stable isotope methods: A discussion on in-situ field and laboratory techniques.

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Stable Isotopes of water are useful proxies for the description of water fluxes such as infiltration, evapotranspiration and plant water uptake in natural water resource systems. Especially the measurement of soil pore water provides information of soil hydraulic properties and interactions within the soil-plant-atmosphere-interface. To obtain such information advanced techniques are required to either extract soil pore water or to equilibrate the soil sample with dry gas at fixed temperature. It is not yet fully understood to what extent different methods affect the isotope composition and how results of these compare to each other.

The present study compares direct in situ measurements using a hydrophobic poly-propylene membrane installed at various depths in the soil. The isotopic composition of the soil water vapor was measured with a Los Gatos research DLT-100 spectroanalyser directly in the field. Additional soil physical parameters such as temperature, soil moisture and suction tension were also measured in field and additionally grain sizes in the lab.

It could be observed that suction tension was strongly related to the diurnal temperature cycle for a sandy soil. The upper 10cm show a development of filaments which have hydrophobic properties. Results of the in situ measurement indicate differences compared to the values derived from cryogenic vacuum extraction. For the upper soil layer results of the two diverge unexpectedly providing heavier values for the in situ measurements. Deuterium excess for the upper 20 cm plots parallel to the GMWL . The lower part of the soil plot with a slope between 3 and 4 in a 18O-2H diagram. Advances and pitfalls of field and laboratory techniques are discussed.

P 14

Performance of a laser based CO_2 Isotope Ratio Infrared Spectrometer to study biosphere-atmosphere exchange

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We are presenting results from a mid-infrared laser-based Isotope Ratio Infrared Spectrometers (IRIS) that is capable of simultaneously determining both $\delta^{18}O$ and $\delta^{13}C$ isotope ratios of carbon dioxide utilizing a simple, direct absorption approach with a robust multi pass cell and a cryogen free setup.

A simulation of ambient measurement conditions with a 75 ppm/hour change in CO_2 concentration from 350-650 ppm showed a precision of <0.05‰ for both $\delta^{18}O$ and $\delta^{13}C$ over 24 hours with 30 min averaging time. Comparison with Isotope Ratio Mass Spectrometer (IRMS) showed differences of 0.046 ‰ and 0.047 ‰, for $\delta^{13}C$ and $\delta^{18}O$, respectively.

In a plant chamber simulation, the concentration ramp speed was increased up to 40 ppm/min. For 1 minute averaged samples, the precision was $\delta^{13}C$ = 0.097 ‰ and $\delta^{18}O$ = 0.121 ‰. The comparison with IRMS gave a difference of 0.032 ‰ for $\delta^{13}C$ and 0.008 ‰ for $\delta^{18}O$.

An example of ambient air monitoring over 2 weeks shows periods of advected urban pollution with increasing CO_2 concentration as well as local photosynthetic activity that results in a draw down of the CO_2 concentration and corresponding more positive $\delta^{13}C$.

The IRIS analyzer was also integrated into a large plant chamber experiment involving multiple instruments to study CO_2 fluxes using $\delta^{18}O$-CO_2. Plant chamber in and out was alternatingly monitored for 5 minutes. A comparison of $\delta^{18}O$ with a TGA-200 gave a mean difference $\Delta\delta^{18}O$ = -0.49 ‰ +- 0.37 ‰.

Poster

Session 2 – Hydrologie und Hydrogeologie

P 15
The oxygen and hydrogen isotope composition of precipitation and surface waters in North Germany

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The hydrological cycle is reflected by specific water isotope signatures found in precipitation, surface, and ground waters (Dansgaard, 1964; Craig & Gordon, 1965; Gat, 1996). Since fresh waters of different generation and ages may enter the coastal areas it is expected that they carry characteristic stable isotope signatures. Informations about the specific composition of different fresh water sources allows for a use in mixing models for the origin of coastal waters. Traditionally, investigations focused on the fractionation of the isotopes H-1, H-2, O-16, and O-18. With the development of new analytical methods, also the O-17 isotope came into the focus of interest (Angert et al., 2004; Luz & Barkan, 2010).

We investigated the multi-isotope composition of different sources for fresh waters at sites with relevance for the southern coastal North and Baltic Sea areas (precipitation, river waters, coastal wells, coastal beach springs, fresh waters emerging from coastal marine sediments (SGD)). The composition of precipitation (rain, snow) at different locations in Northern Germany (Lüneburg, Oldenburg, Warnemünde) and the Netherlands (Texel Island) was analyzed to derive local meteoric water lines. Stable isotope measurements were conducted by means of a new Picarro CRDS system (L2140-i) giving results in the usual delta-notation versus V-SMOW, and informations about H-2 and O-17 excess. Results are compared to continuous measurements at the GNIP station in Cuxhaven (NW-Germany) and the GMWL. As an example, measurements in the towns Lüneburg and Oldenburg for the time period between December 2013 and June 2014 are represented by the respective non-amount-weighted correlation equations (updating an earlier report based on a shorter observation period; Böttcher et al., 2014):

$\delta^2H = 8.20_{*}\delta^{18}O + 10.75$ ($n = 75$; $r^2 = 0.99$),

and

$\delta^2H = 7.62_{*}\delta^{18}O + 5.87$ ($n = 82$; $r^2 = 0.95$).

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P 16

Ground waters emerging at the southern Baltic Sea coast: A multi-isotope hydrobiogeochemical study

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Iron-rich groundwater springs emerging at the shore zone of the southern Baltic Sea (close to Kühlungsborn) were examined on a seasonal base for a period of about three years. Water samples were analyzed for major and trace elements, stable isotopes of water (^{2}H, ^{18}O), tritium (^{3}H) and noble gases (^{3}He, ^{4}He, Ne), DIC, ^{13}C, and $^{34}SO_4$. Sediment from the stream beds was characterized via SEM-EDX and extracted for the geochemistry of authigenic precipitates.

The springs emerge from small pits yielding discharges close to 10 L/min. 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 their shape varied due to wind- and wave-driven forces. The ^{2}H and ^{18}O contents of the spring waters indicate the ground water to originate from relatively young mixed meteoric waters. Dating using the tritium-helium method yields ages of the emerging waters of 25 to 32 years, with different mixing proportions of tritium-free waters. The hydrochemistry of the springs showed some variability in between, which indicates that the genetic processes might differ slightly. The springs are characterized by dissolved Ca, Mg, Na, DIC, and SO_4 mainly reflecting the interaction with bedrocks in the recharge area that is dominated by marly till. The oxygen-free ground water is rich in dissolved Fe, P, and DIC. Fe and SO_4 originate from the oxidation of pyrite, as shown by the ^{34}S content in SO_4. The isotope signature of DIC indicates the dissolution of biogenic CO_2 in the soil zone followed by the dissolution of carbonate minerals. The above ground draining streams degas carbon dioxide and take up oxygen in contact with the atmosphere. Upon CO_2-degassing, ^{12}C is preferentially desorbed from the aqueous solution.

The water then passes to underground drainage into a subterranean mixing zone with brackish Baltic Sea waters. Iron(oxyhydr)oxide precipitates in the stream beds acting as a sink for dissolved PO_4 and minor Ca. Residues of iron oxidizing bacteria were found in the stream bed rust indicating an involvement of microbes to catalyse the dissolved iron removal. The investigation reveals that the surface precipitation on the beach leads to the formation of submarine groundwater discharge essentially free of dissolved Fe and PO_4. The formation of Fe-phases in the subterranean estuary is supposed at depth influencing the release of nutrients and metals into the coastal ecosystem.

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P 17
Determination of flow velocities by stable isotope geochemical methods

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Drinking water is often extracted from wells close to rivers and streams. Such bank filtrates may eventually be impacted by the infiltration of wastewater-derived micro-pollutants from surface waters. It therefore essential to know the flow velocity, i.e. the effective fluid velocity a conservative tracer would experience during its flow from the river towards the well group. Hydrogen and oxygen stable isotope of water proved to be excellent tracers to determine the pathway of the water molecule in numerous studies.

In the context of the research program RISK-IDENT that focus on the identification, and fate and behavior of micro pollutants in the environment we determined the fluid velocity by stable isotopes without the need of adding artificial tracers. The results of the stable isotope geochemical approach indicate a velocity of 2.9 m per day, which results in an average time of 50 days that is needed by a water molecule from the river to the drinking water well.

P 18
Tracing nitrate sources in pre-alpine groundwater catchments using environmental tracers

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Groundwater is one of the main resources for drinking water. Its quality is still threatened by the ubiquitous contaminant nitrate (NO_3^-). In order to manage groundwater resources in a sustainable manner, we need to find options of lowering nitrate input. Thus, a comprehensive knowledge of nitrate sources and time scales of transport are required. The objectives of the present study were to i) identify major sources of nitrate in groundwater and ii) investigate seasonal dynamics of nitrogen-compounds in oligotrophic aquifers. To achieve the objectives, we applied environmental tracer approaches in four pre-alpine groundwater catchments. Stable isotopes of water and tritium were used to study the hydrogeology and transit times. Furthermore, nitrate isotopes were applied to trace nitrogen from its sources to groundwater. The results of the nitrate isotope analysis showed that groundwater nitrate derived from ammonium nitrification from a variety of sources such as atmospheric deposition, mineral and organic fertilizers and soil organic matter. A direct influence of mineral fertilizer, atmospheric deposition and sewage were excluded. Since seasonal variations in stable isotopes of nitrate were detected only in surface water and locally at one groundwater monitoring well, aquifers appeared to be well mixed and influenced by a continuous nitrate input mainly from soil derived nitrogen. Hydrogeological analysis supported that the investigated aquifers were less vulnerable to rapid impacts due to long average transit times, ranging from five to 21 years. Our study revealed the importance of combining environmental tracer approaches and a comprehensive sampling campaign (local sources of nitrate, soil water, river water, and groundwater) to identify the nitrate sources in groundwater and its vulnerability. In the future, the achieved results will help develop targeted strategies for a sustainable groundwater management focusing more on soil nitrogen storage.

P 19

Isotope signatures to trace the origin and fate of nitrate in the Soyang Lake Watershed, South Korea

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The Monsoon season in South Korea has a great influence on the biogeochemical and hydrological processes in the entire country, but is specifically of concern in the Soyang Lake Watershed, the main drinking water reservoir for the 20 million metropolis Seoul. The Soyang Lake Watershed is composed of sub-catchments dominated by intensive agricultural management, and by pristine (semi-) natural broadleaf and coniferous forests. Therefore nitrate leaching into surface waters may have different origins.
Stable isotopes are a useful tool to quantify and determinate the origin of nitrate inputs into the Soyang Lake. The δ15N values of nitrate from different sources often show overlapping ranges but the additional measurement of the δ18O values allows a more precise classification (Durka et al., 1993; Mayer et al., 2002; Deutsch et al. 2006). The δ18O values of NO3- are especially useful for differentiating between NO3- deposited from the atmosphere and NO3- formed by microbial nitrification. The formation of NO3- in the atmosphere involves exchange of oxygen atoms with ozone which has a high δ18O value (Curtis et al 2011). In contrast NO3- formed by microbial nitrification derives most of its oxygen from water which has a lower δ18O value. (Curtis et al 2011). According with this principle the nitrate derive from sewage or manure or fertilizes is isotopically distinct between each other and from the other sources.
Within a sampling along the rivers and in the land around them, with a frequency ranging from one time after each rain event to every two hours, the sampling design was made to determinate the influence of the precipitation regime and the land use in the nitrate discharge into the Soyang Lake Watershed. River water samples, soil water samples and rain samples were taken before and during the monsoon season to analyse the nitrate concentration and 15N abundance in each phase of the nitrogen cycle. Data from amount of rain and river discharge were taken to quantify the total export of nitrate from these sub-catchments in this period. This data base within the climate information shows us already how the monsoon season behaves in the Haean Valley and in the forest around it.
Preliminary results suggested the heavy nitrogen fertilization in the agriculture-dominated Haean basin is the major contributor to the nitrate output into the ground water systems and into the Mandae River and therefore, nitrate input into the Soyang Lake. Nitrate from atmospheric nitrogen deposition or from a surplus of microbial nitrification in the forest-dominated sub-catchments also contributes in smaller amount to nitrate output to the rivers and also suggest differences in nitrate assimilation capacities between the broadleaf and coniferous forest.

Keywords: Sub-catchments, fertilizer, nitrate, isotopes signature, atmospheric nitrogen deposition, microbial nitrification, monsoon

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P 20

Tracing stable water isotopes from meteoric to groundwater in the small low-mountainous Schwingbach catchment, Germany

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Spatio-temporal sources of stream water in low angle catchments are still poorly understood. This is partly caused by damped stream water isotopic signatures excluding traditional hydrograph separations [1]. Unlike the distinct watershed components found in steeper headwater counterparts (hillslope, hollow), lowland areas often exhibit a complex groundwater-surface water interaction [1]. Conducting a dual stable water isotope (δ^2H and $\delta^{18}O$) study in the Schwingbach catchment helped to unravel dynamics and interactions between precipitation, stream, soil, and groundwater throughout a 2-year observation period.

Precipitation isotopic signatures - ranging from -167.6 to -8.3‰ for δ^2H - showed no significant spatial variance in the study area. However, seasonal variations based on temperature effects were observed. Summer precipitation signals differed significantly from stream and groundwater isotopic composition showing ~20‰ heavier δ^2H values. Damped seasonality of stream water isotopes and almost uniform δ-values were measured in groundwater, as complex bidirectional interactions between surface and groundwater occurred. Apparently, snowmelt played a fundamental role for groundwater recharge explaining the observed differences to precipitation δ-values.

Comparing the Local Meteoric Water Line (LMWL) of the Schwingbach catchment with the Global MWL showed that the slope is slightly lower due to stronger local evaporation conditions. Moreover, the LMWL of the study area assorts well with the LMWL of the closest GNIP (Global Network of Isotopes in Precipitation) station Koblenz.

For the soil compartment, enriched δ-values were measured at the soil surface due to evaporation during summer, while the range of isotopic composition decreased with depth. Contrary observations were made in the winter: Depleted isotopic signatures near the soil surface due to snowmelt influence. Evaluating the impact of small-scale factors (topographic wetness index, vegetation cover, distance to stream, and soil physical properties) on soil water isotopic signals revealed that only land use had a significant effect. It appeared that precipitation mixed with existing soil water to some degree and also pushed soil water downwards via piston flow. Thus, the land use influence decreased with depth and soil water approached nearly constant values similar to groundwater isotopic composition.

Tracing stable water isotopes through the water cycle showed that stream water isotopic signatures were in good agreement with groundwater isotopic composition, indicating bidirectional water exchange. However, the annual isotopic cycle of both streams and groundwater seemed to be decoupled from the isotopic cycle of precipitation. Thus, groundwater, which was mainly recharged by snowmelt, was the major water contributor to streamflow. Moreover, soil water isotopes were much less variable than that of precipitation and the observed land use impact decreased with depth and approached groundwater δ-values.

Tracing stable water isotopes through the water cycle helped to identify interactions between different water cycle components in a region with little change in individual isotope time series.

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P 21
Comparison of soil water isotope analysis techniques

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Environmental tracers like stable isotopes of water ($\delta^{18}O$, $\delta^{2}H$) have proven to be valuable tools to study water flow and transport processes in soils. Recently, a new technique for soil water isotope analysis has been developed that employs a vapor phase being in isothermal equilibrium with the liquid phase of interest. This has increased the potential application of water stable isotopes in unsaturated zone studies as it supersedes laborious extraction of soil water. However, uncertainties of analysis and influencing factors need to be considered. Therefore, the objective of this study was to evaluate different methodologies of analysing stable isotopes in soil water in order to identify possible pitfalls and assess resulting measurement uncertainty. The methodologies included different preparation procedures of natural soil cores for equilibration of vapor and soil water as well as soil water extractions and additional headspace GC analysis. Two different inflatable sample containers (freezer bags, bags containing a metal layer) and equilibration atmospheres (N_2, dry air) were tested. The results showed that uncertainties for $\delta^{18}O$ were higher compared to $\delta^{2}H$ that cannot be attributed to any specific detail of the processing routine. Particularly, soil samples with high contents of organic matter showed an apparent isotope enrichment which is indicative for fractionation due to evaporation. However, comparison of water samples obtained from cryogenic extraction or suction cups with the local meteoric water line indicated negligible fractionation processes in the investigated soils. We conclude that at least in our case apparent enrichment is an artefact owed to the modality of analysis and show possible correction approaches. We further conclude that the evaluated method is advantageous over traditional methods regarding simplicity, resource requirements and sample throughput but careful consideration needs to be made regarding sample handling and data processing.

P 22

Effects of soil properties on the apparent water-vapor isotope equilibrium fractionation: Implications for the headspace equilibration method

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Stable isotopes of the water molecule ($\delta^{18}O$, $\delta^{2}H$) have proven to be powerful tools in hydrology with a long record of applications in precipitation, surface water and groundwater studies. However, there are still significant restrictions when it comes to investigations of the unsaturated zone especially concerning soil water extraction for subsequent analysis. The recent invention of laser-based isotope analyzers facilitated a workaround and hence a new method for rapid determination of soil water stable isotope signatures. This method is based on analyzing the headspace vapor of a sample being in isothermal equilibrium with the soil water of interest. However, the employed analyzers are not only sensitive to the desired isotopic composition of a given vapor sample but also regarding any gaseous molecule with spectral features similar to those of the water molecule. We suspect that this has a significant and previously ignored impact on the observed water vapor isotope signature depending on isotope-independent soil characteristics and resulting headspace compositions. We therefore present the results of laboratory experiments which have been performed with five different natural soils and three additional technical substrates. All soils were dried and rewetted with water of known amount and isotopic signature. We also give an estimate of the uncertainty that must be attributed to the headspace equilibration method. Our findings indicate that elevated contents of clay or organic carbon have a systematic impact on apparent isotopic compositions. We propose that future calibration and correction procedures have to take into account these soil characteristics. Especially the co-measured standards used for calibration should be re-evaluated regarding similarity to the samples of interest.

P 23

Investigating surface water - groundwater interaction upstream of Hidan well field (Jordan) using stable isotopes

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INTRODUCTION: Stable Isotopes of water are an important tool in hydrogeological investigations and can be used to e.g. determine groundwater recharge zones or flow paths. In this study, we used stable isotopes in order to investigate the influence of surface water on groundwater contamination in a semi-arid catchment in central Jordan.

STUDY AREA: The study area is located 18 km southwest of the city of Madaba. Public water supply of Madaba is provided to 100 % by the Hidan well field, which is located at the western (downstream) end of the study area (Figure 1). By this well field, which is located inside the ephemeral wadi Wala, groundwater from a shallow limestone aquifer is extracted. Regular occurring bacterial contamination highly correlates with high surface discharge (flood events) and therefore indicates an exchange between surface water and groundwater. Declining groundwater tables have been stabilized by a recharge dam, which has been built around 7 km upstream of the well field. Along the wadi course, dry sections alternate with sections of perennial water flow due to several springs and seepage points.

FIGURE 1: a) Map of the study area, b) detailed view of the Hidan well field and c) regional map

OBJECTIVE: In the framework of the Technical Cooperation project “Water Aspects in Land Use Planning”, groundwater protection zones were delineated (Gassen et al., 2014). In this context, the hydrogeological conditions especially in respect to the origin of groundwater contamination were investigated. The objective of the here presented study was to use stable isotope data (deuterium, ^{2}H and oxygen-18, ^{18}O) for tracing infiltration water along the wadi, which originates from the reservoir of wadi Wala dam and is therefore enriched in ^{2}H and ^{18}O.

METHODS: Water samples were taken at 21 sites from both ground- and surface waters along wadi Wala over one year and analyzed for $d^{2}H$ and $d^{18}O$. At the same time, rainwater samples were collected in the vicinity of the infiltration dam.

RESULTS: Analyses indicate that the isotopic signature of both surface and groundwater becomes heavier along the wadi course. For the surface water, this effect can be explained by evaporation leading to fractionation. Continued infiltration of surface water along the wadi may also explain the similar evolution of groundwater along the course.

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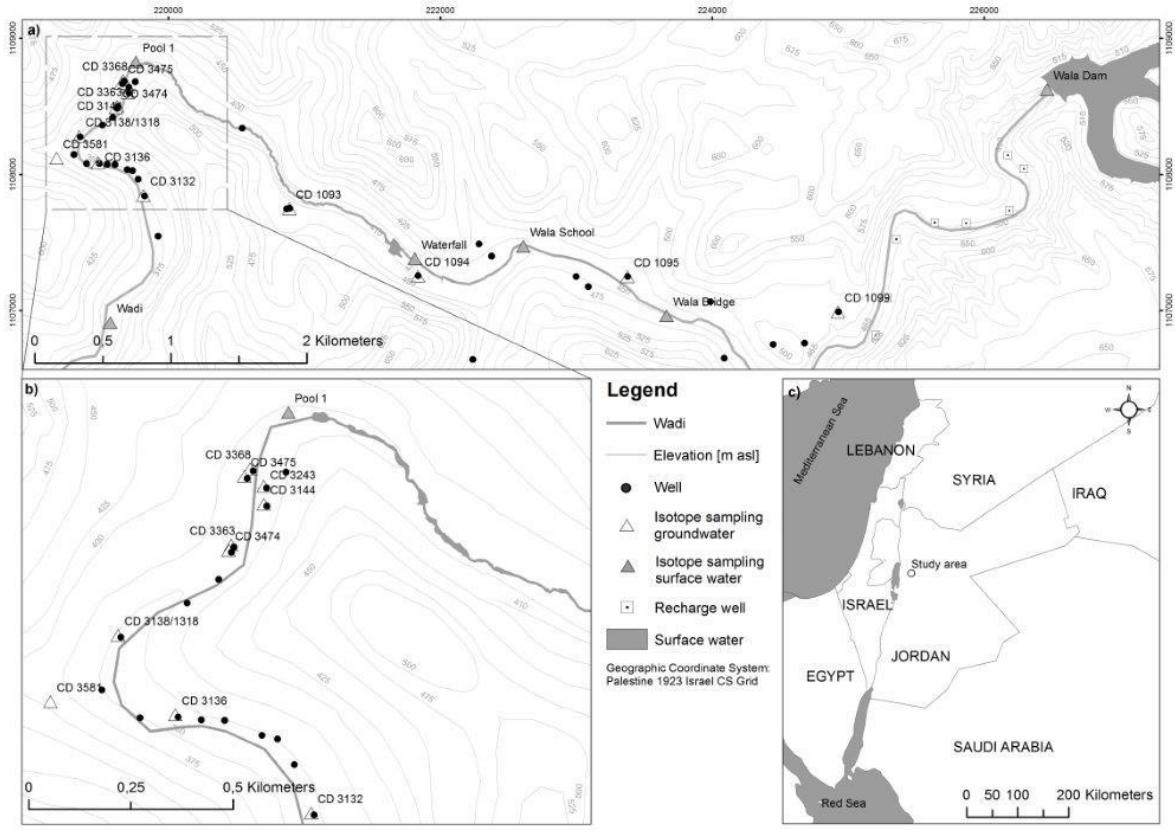
Anhang 1


a)
Pool 1
CD 3368
CD 3475
CD 3474
CD 3581
CD 3136
CD 3132
CD 1093
Waterfall
CD 1094
Wala School
CD 1095
Wala Bridge
CD 1099
Wala Dam
Wadi
0 0,5 1 2 Kilometers
b)
Pool 1
CD 3368
CD 3475
CD 3243
CD 3144
CD 3363
CD 3474
CD 3138/1318
CD 3581
CD 3136
CD 3132
0 0,25 0,5 Kilometers
Legend
Wadi
Elevation [m asl]
Well
Isotope sampling groundwater
Isotope sampling surface water
Recharge well
Surface water
Geographic Coordinate System: Palestine 1923 Israel CS Grid
c)
Mediterranean Sea
LEBANON
SYRIA
IRAQ
Study area
ISRAEL
JORDAN
EGYPT
SAUDI ARABIA
Red Sea
0 50 100 200 Kilometers

P 24

Erforschung von Abflusskomponenten im Tadschikischen Pamir mittels δ^7Li und ^{87}Sr/^{86}Sr

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Der Aralsee wird von zwei großen Zuflüssen, dem Amudarja und dem Syrdarja, gespeist, die ihre Ursprünge im Pamir und Tienshan haben. Im Amudarjaquellgebiet liegt das Einzugsgebiet des Flusses Gunt, welches eine Fläche von ca. 14000 km² umfasst und Höhen zwischen 2000m und 6700m ü. NN aufweist. Die meisten Niederschläge erhält das kalt-aride Gebiet im Winter und Frühling als Regen und Schnee. Dies führt dazu, dass der Abfluss von Schnee- und Gletscherschmelzwasser dominiert wird. Eine große Unbekannte ist der Beitrag von Grundwasser zum Abflussgeschehen.

Um die einzelnen Abflusskomponenten voneinander abtrennen zu können, wurde eine Multi-Isotopenstudie durchgeführt. Dazu wurden entlang des Flusslaufes insgesamt ca. 50 Wasserproben des Hauptstroms, seiner Zuflüsse und an einzelnen Stellen auch Proben von Gletscherschmelz- und Thermalwasser genommen. An den Proben wurden neben den Isotopen des Wassers (D, ^{18}O und ^{3}H) und den Ionenkonzentrationen auch die stabilen Umweltisotope ^{7}Li und ^{87}Sr untersucht.

Sowohl die Li- als auch die Sr-Isotopensignaturen weisen große Unterschiede in ihrer räumlichen Verteilung im Untersuchungsgebiet auf. Die gemessenen Lithium-Isotopenverhältnisse liegen im Bereich der in der Literatur genannten Werte für Flusswasserproben und besitzen eine große Spannbreite zwischen 8‰ und 28‰. Der höchste δ^7Li-Wert wurde an einer Gletscherwasserprobe, der niedrigste Wert an einer Thermalwasserprobe gemessen. Die Li-Isotopenverhältnisse des Gunt bleiben entlang seiner Fließstrecke von ca. 100km annähernd konstant (δ^7Li=10‰±3‰), wogegen die Zuflüsse untereinander große Variationen ($\delta^7Li_{Zuflüsse}$≥10‰; $\Delta\delta^7$Li ≈ 12‰) aufweisen. Ebenso divers wie die δ^7Li-Daten sind die Ergebnisse der ^{87}Sr/^{86}Sr-Analysen. Hier reichen die Messwerte der ^{87}Sr/^{86}Sr-Verhältnisse von 0,7107 zu 0,7185. Dabei ist mit zunehmender Fließlänge des Flusses Gunt eine Erhöhung der ^{87}Sr/^{86}Sr-Verhältnisse zu beobachten; auch die Zuflüsse variieren in ihren Sr-Isotopenverhältnissen (Δ^{87}Sr/^{86}Sr ≈ 0,007). In den in dieser Studie untersuchten ^{87}Sr- und ^{7}Li-Isotopenverhältnissen spiegeln sich die unterschiedlichen Quellen und Fließstrecken der Flüsse wider.

P 25
Towards a Local Meteoric Water Line for Riyadh, Saudi Arabia

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For arid countries like Saudi Arabia a thorough groundwater resources assessment is crucial and the isotopes ^{18}O and D provide a powerful tool to study the provenance of groundwaters and the (paleo)climatic conditions during their recharge. Yet, in order to evaluate the isotopic signature of the groundwater, the one of current precipitation has to be known as well. Although a few rain water analyses are available for Central Saudi Arabia in the literature - mostly in unpublished consultant reports - a Local Meteoric Water Line has never been established.

In order to complement the available data, 28 rain events occurring in Riyadh between 2009 and 2013 were studied for their stable isotope composition. Samples were collected as integral samples, i.e., they represent the entire precipitation event. Moreover, one event was sampled several times, aiming at an evaluation of intra-storm variability. During selected storms a grab sample was taken for ^{3}H analysis.

The event samples showed $\delta^{18}O$ and δD values scattering between -6.5 and +9.5 and between -30 and +50 ‰ V-SMOW, respectively. In the course of the event that was sampled several times, an isotopic depletion was observed with respect to both isotopes. The relatively large ranges of δ values for ^{18}O and D of approximately 7 and 31 ‰ V-SMOW highlight the general need for integral sampling. The obtained grab samples are characterized by moderate ^{3}H concentrations of a few Tritium Units.

Further results will be presented and discussed in view of associated weather data (e.g. rain amount and temperature) and the probable moisture sources derived from back-trajectories, which were calculated using HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory Model; Draxler & Rolph, 2003).

References

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Poster

Session 3 – Metabolismus und Physiologie

P 26
Determination of $^{13}C/^{12}C$ Ratios of Endogenous Urinary AICAR

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Rationale: AICAR (5-Aminoimidazole-4-carboxamide 1β-D-ribofuranoside) is prohibited in sport according to rules established by the World Anti-Doping Agency. Doping control laboratories identify samples suspicious of AICAR abuse by measuring its urinary concentration and comparing the observed level to naturally occurring concentrations. As the inter-individual variance of urinary AICAR concentrations is large, this approach requires a complementary method to unambiguously prove the exogenous origin of AICAR. Therefore a method for the determination of carbon isotope ratios (CIR) of urinary AICAR has been developed and validated.

Methods:Concentrated urine samples were fractionated by means of liquid chromatography for analyte clean up. Derivatization of AICAR yielding the trimethylsilylated analog was necessary to enable CIR determinations by gas chromatography-combustion-isotope ratio mass spectrometry. The method was tested for its repeatability and stability over time and a linear mixing model was applied to test for possible isotopic discrimination. A reference population of n = 63 males and females was investigated to calculate appropriate reference limits to differentiate endogenous from exogenous urinary AICAR. These limits were tested by an AICAR elimination study.

Results:The developed method fulfills all requirements for adequate sports drug testing and was found to be fit for purpose. The investigated reference population showed a larger variability in CIR of AICAR as for endogenous steroids. Nevertheless, the calculated thresholds for differences between AICAR and endogenous steroids can be applied straightforward to evaluate suspicious doping control samples with the same statistical confidence as established e.g. for testosterone misuse. These thresholds enabled the detection of a single oral AICAR administration for more than 40 h.

Conclusion:Determination of CIR is the method of choice to distinguish between an endogenous or exogenous source of urinary AICAR. The developed method will enable investigations into doping control samples with elevated urinary concentrations of AICAR and clearly differentiate between naturally produced/elevated and illicitly administered AICAR.

P 27
Nitrogen Isotope Ratios of Endogenous Urinary AICAR

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AICAR (5-Aminoimidazole-4-carboxamide 1β-D-ribofuranoside) is prohibited in sport according to rules established by the World Anti-Doping Agency. Doping control laboratories identify samples suspicious of AICAR abuse by measuring its urinary concentration and comparing the observed level to naturally occurring concentrations. As the inter-individual variance of urinary AICAR concentrations is large, this approach requires a complementary method to unambiguously prove the exogenous origin of AICAR. In parallel to carbon isotope ratios the $^{15}N/^{14}N$ ratio of AICAR should allow for allocation of urinary AICAR regarding its endogenous or exogenous source.

The nitrogen atoms in AICAR (being part of the purine biosynthesis pathway) derive from glutamine, glycine and aspartatic acid. In parallel to amino acids investigated in hair, plasma or bone tissue it is expected that endogenous nitrogen isotope ratios show enriched values of up to +15 ‰ ($\delta^{15}N_{AIR}$).

Sample preparation was done accordingly to the method employed for carbon isotope ratios. As expected, limits of detection were found approx. 5 times higher than for carbon measurements resulting in a minimum required urinary concentration of 1000 ng/mL AICAR for a 3 mL aliquot. Within this preliminary investigation 4 blank urines containing only endogenous AICAR (as ensured by $^{13}C/^{12}C$ measurements), 1 post administration sample collected after oral ingestion of 10 g of AICAR and a reference standard were determined. The standard was also investigated by means of elemental analyzer/isotope ratio mass spectrometry to test for bias introduced by gas chromatographic separation and online conversion of samples prior to isotope ratio measurements. Reference material IAEA 600 was used to calibrate nitrogen tank gas.

Within these first measurements no significant difference was found between the nitrogen isotope ratios of endogenous AICAR, the post-administration value and the standard material. Further AICAR standards and seized black market products should be analyzed to verify a similar homogenous isotopic signature for nitrogen as was found for carbon isotope ratios so far.

P 28

The metabolic effect of pre- and probiotics on the renal and faecal nitrogen and ammonia excretion in humans as measured by lactose-[$^{15}N_2$]ureide degradation

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Introduction: It can be considered as certain that both pre- and probiotics in the form of resistant starch (RS) and yoghurt, respectively, have a significant impact on the colonic ammonia metabolism in humans. It is assumed that the metabolic interplay of RS and yoghurt when supplemented simultaneously contributes to an increased saccharolytic activity and to a corresponding decreased proteolytic activity of the colonic microbiota which is beneficial for the host. This may cause an enhanced detoxification effect by discharging ammonia via the faeces resulting in a corresponding reduced excretion in urine, particularly in urinary ammonia. The evaluation of ammonia detoxification by pre- and probiotics, respectively, by means of bacterial lactose-[$^{15}N_2$]ureide (^{15}N-LU) degradation to $^{15}NH_3$ and its excretion is still of great interest, scientifically in terms of nutrition physiology, and commercially. In the present study, RS and *Lactobacillus acidophilus* yoghurt (LC1) were supplemented simultaneously to evaluate the effect on the urinary and faecal nitrogen and ammonia excretion by means of ^{15}N-LU degradation.

Material and Methods: A total of 19 healthy adults (14 female, 5 male) aged 20-32 years received a regular daily diet either without (no treatment, NT) or with supplementation of a RS-LC1-mixture (MIX) composed of 15 g fibre of potatoes (RS type 1), 15 g wrinkle pea starch (RS type 2, Emsland Group, Emlichheim, Germany), and 190 g LC1 (Nestlé AG, Frankfurt/Main, Germany) over a 20-day period in randomized order. Thereafter, 5.7 mg/kg body weight ^{15}N-LU was administered together with breakfast. Urine and faeces were collected over a period of 48 and 72 h, respectively. Urinary ammonia was separated in micro-diffusion vessels followed by alkalization and trapped in boric acid. The ^{15}N-abundances were measured by isotope ratio mass spectrometry (TracerMass 20-20, SerCon, Crewe, UK).

Results: The mean renal ^{15}N-excretion differed significantly (t-test) between the supplementation of the MIX and NT (34.9 vs. 43.8%, p=0.015). The mean faecal ^{15}N-excretion amounted to 43.6% (MIX) and 34.1% (NT). In comparison with NT (0.1%) the urinary $^{15}NH_3$-excretion was significantly decreased after the MIX supplementation (0.05%, p=0.001).

Conclusions: The urinary ^{15}N-excretion between 0-6 h mainly reflects the glucose-[$^{15}N_2$]ureide absorption deriving from the enzymatic degradation of ^{15}N-LU by β-galactosidase in the small bowel. The intake of a pre- and probiotic mixture composed of RS1+RS2+LC1 significantly lowered the colonic generation and the renal excretion of toxic $^{15}NH_3$ and functioned as an ammonia shift from urinary to faecal ^{15}N-excretion when using ^{15}N-LU as a xenobiotic marker. When summarising our findings, we are convinced that ^{15}N-LU is a valid tool for investigating nitrogen and ammonia metabolism in the colon. The measurement the urinary $^{15}NH_3$-excretion using ^{15}N-LU is a novelty.

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P 29

Surprising effect of experimental bacterial infection of grass carp on $\delta^{13}C$ in fish in spite of only minimal intense clinical symptoms

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The macro-herbivorous grass carp is one of the most produced fish species worldwide. In Asia, there are regional mass mortalities of grass carp which occur seasonally. The mass mortalities might be caused by a multi-factorial disease triggered by environmental factors, malnutrition, pesticides and bacterial infection with *Aeromonas hydrophila* (Pucher *et al*. 2013). Asian farmers use banana leaves to prevent disease outbreaks without any scientific proof yet. In this study, banana leaves were used as feed for grass carp to investigate its phyto-prophylactic effect to prevent clinical signs through the infection with *Aeromonas hydrophila*. Further, the effect of the bacterial infection and feeding on the isotopic signature in grass carp was tested.

In a 42 weeks feeding and infection trial, 6 groups of 10 grass carp (15-20 cm body length) were fed by one of three different feeds managements. All fish were fed by full pellet feed (Garant-Tiernahrung GmbH) at 7 g $kg^{-0.8}$. Six groups were additionally fed fresh banana leaves and six other by fresh maize leaves (Table 1). After 10 month, three groups of each feeding treatment were challenged by *Aeromonas hydrophila*. Growth performance and clinical signs were observed. After 10 days, fish were analysed for chemical composition. In extracted lipid and lipid-free fish and feeds, isotopic signatures of carbon were determined by Elemental Analyzer (Euro Vector) and a Thermo Finnigan Delta Plus IR-MS.

Fish growth was similar regardless feeds and infection. Intramuscular infection of fish resulted in skin irritations; 14 fish died. Any phyto-prophylactic effects were identified. Fish fed only pellet feed had a significant higher lipid content.

TABLE 1

The different leaves as feed changed significantly the carbon isotopic signature in the lipid and lipid-free fraction. Infection significantly changed carbon isotopic signature in lipids regardless the feeds.

As a conclusion, no phyto-prophylactic effect of banana leave as feed for grass carp was detected. Carbon isotopic signature of the lipid fraction might be worth to look at as a potential indicator for bacterial infections.

Reference

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Table 1: Isotopic composition of the lipid and lipid-free fraction of feeds and of fish under the three feeding managements and infection.

Anhang 1

		$\delta^{13}C$	
Feeds		**Lipid**	**Lipid-free**
Pellets		-26.0	-24.7
Banana leaves (C_3)		-30.7	-26.7
Maize leaves (C_4)		-20.6	-12.4
Fish	**Infection**		
Pellets	yes	-27.3±0.0	-22.8±0.0
	no	-27.4±0.1	-22.8±0.0
Pellets +	yes	-27.5±0.1	-23.0±0.0
Banana leaves	no	-27.6±0.0	-23.0±0.1
Pellets +	yes	-26.7±0.1	-21.8±0.2
Maize leaves	no	-26.8±0.1	-21.6±0.2
Effect	Feed	**	**
	Infection	*	-
	Interaction	-	-

* statistically significant at $p < 0.05$
** statistically significant at $p < 0.01$

P 30

„Hydraulic redistribution“ über Wurzeln von Buche, Eiche und Fichte - Ergebnisse eines „Split-root“-Experiments

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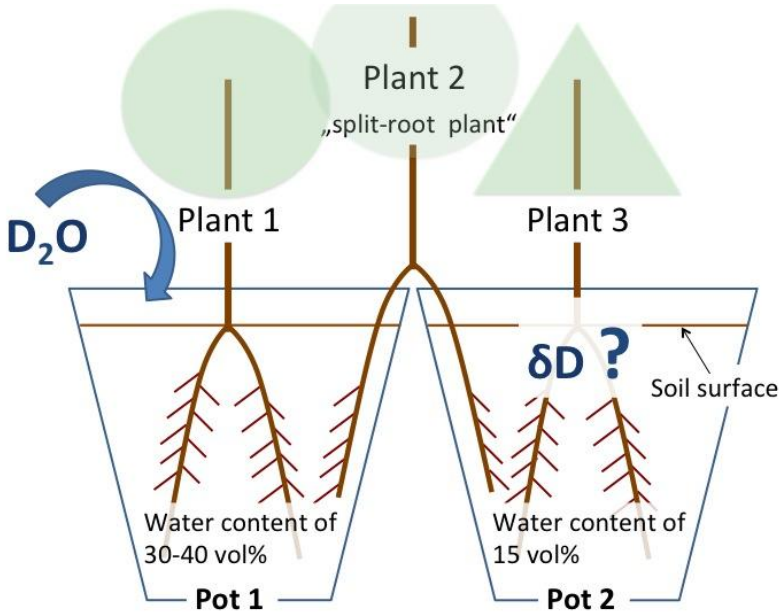
„Hydraulic Redistribution“ bezeichnet die Umverteilung von Wasser im Boden durch die Wurzeln einer Pflanze. Diese Umverteilung richtet sich entlang eines Wasserpotenzialgradienten. Sie kann sowohl vertikal als auch horizontal erfolgen. In dem hier vorgestellten „Split-root“-Experiment wird das Potential zur hydraulischen Umverteilung verschiedener Baumarten untersucht.

Junge Buchen, Eichen und Fichten (2 Jahre alt, 30-60 cm groß) wurden in „Split-root“-Töpfe gepflanzt, d.h. je drei Bäume wurden auf je zwei Pflanztöpfe so aufgeteilt, dass sich pro Topf eine Pflanze befand und die dritte so gepflanzt wurde, dass ihre Wurzeln in beiden Töpfen wachsen konnten (Abb. 1). Ein Kontakt zwischen den beiden Töpfen bestand anschließend ausschließlich durch die Wurzeln der mittleren Pflanze („split-root plant“). Gepflanzt wurden jeweils 3 Buchen, Fichten oder Eichen und verschiedene Kombinationen dieser 3 Arten. Je Kombination wurden 7 Wiederholungen angelegt. Nachdem die Pflanzen 4 Monate anwachsen konnten, wurde ein Feuchtigkeitsgradient zwischen den Töpfen eingestellt. Die Pflanze in Topf 2 wurde trockengestresst wofür der Wassergehalt auf ca. 15 vol.% reduziert wurde, während die Pflanze in Topf 1 weiterhin gut bewässert wurde (Wassergehalt 30-40 vol.%). Nachdem der Gradient über mehrere Tage stabil war (regelmäßige Überprüfung mit einer TDR Sonde), wurde die gut bewässerte Pflanze (Topf 1) mit 300 mL Deuterium-gelabeltem Wasser gegossen (δD: ca. 6.000 ‰). Nach 1 und 3 Tagen wurden Proben von Boden, Xylem und Wurzel aus dem gelabelten und ungelabelten Topf sowie der „split-root“-Pflanze genommen, um eine mögliche horizontale Umverteilung des Wassers über die „split-root“-Pflanze nachzuweisen. Sollte gelabeltes Wasser im Boden, der Wurzel oder dem Xylem der ungelabelten Seite vorhanden sein, wäre „Hydraulic Redistribution“ nachgewiesen. Hierfür wurde per Cryo-Destillation das Wasser aus den Proben extrahiert und dieses schließlich mit einem Isotopenverhältnis-Massenspektrometer (IRMS, Isotope-Ratio-Mass-Spectrometry) auf den Deuteriumgehalt analysiert.

Die Hypothesen lauten, dass (1) alle drei Baumarten (Buchen, Eichen und Fichten) in der Lage sind, entlang einem Feuchtigkeitsgradienten Wasser umzuverteilen, (2) dass dieses Wasser anderen Pflanzen zur Verfügung steht und (3) die Menge des umverteilten Wassers proportional zu dem bestehenden Feuchtigkeitsgradienten ist.

Anhang 1



P 31
$^{13}C/^{12}C$ ratios of 5α-androst-1-ene-3,17-dione in human urine

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5α-Androst-1-ene-3,17-dione (1-AD) is an anabolic-androgenic steroid listed on the *World Anti-Doping Agency's* prohibited list under section S1.a (exogenous anabolic androgenic steroids). Within the years 2004 to 2014 several routine doping control samples were tested positive for this steroid.

In the last two years several urine specimens, obtained during routine doping control showed evidence of bacterial activity combined with trace amounts of 1-AD in the range of 7-40ng/mL.

If in only low concentrations, several studies showed that 17β-hydroxyandrosta-1,4-dien-3-one (Boldenone, Bo) of potentially endogenous origin can be detected in human urine. A probable reason for the formation of Bo in humans can be found in bacterial enzymes with Δ^1-dehydrogenase activity. Corresponding bacteria (e.g. *Clostridium paraputrificum, Escherichia coli*) are known to exist in human intestine or in urine.

The existence of an analogues pathway to 1-AD appears reasonable

Although, samples with bacterial activity are reported as invalid to the doping control authorities the investigation of the origin of 1-AD in this urines appears reasonable. Fundamentally, GC-C-IRMS analysis is the method of choice to discriminate between endogenous or synthetic origin of these compounds.

In order to investigate the source of 1-AD a method for $^{13}C/^{12}C$ analysis of urinary 1-AD has been developed. This includes several (HPLC) purification steps. $^{13}C/^{12}C$ ratios of 1-AD and other selected endogenous steroids were determined.

Additionally $^{13}C/^{12}C$ data from an excretion study with 1-AD were analyzed to demonstrate the general possibility to distinguish between an endogenous or synthetic origin of 1-AD. These data fundamentally demonstrate the synthetic origin of 1-AD. After application a strong enrichment in ^{13}C of 1-AD over the time of sample collection was observed.

By contrast, the analysis of the routine doping control samples with bacterial activity yielded in inconsistent results.

P 32

Distribution of recently assimilated carbohydrates from $^{13}CO_2$ between different species of ectomycorrhizal fungi under water stress conditions

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To better predict reactions of vegetation on future climate changes our knowledge on water stress has to be improved considerably (Xu *et al.*, 2013). It has been shown that mycorrhizal plants have an improved water status compared to non mycorrhizal controls (Lehto & Zwiazek, 2011). Different mycorrhizal fungi are ecologically beneficial to the plant in very varying ways (Agerer, 2001; Pritsch *et al.*, 2004). To gain more insight into the regulation (i.e. carbon supply) of the mycorrhiza by the plant (Kiers *et al.*, 2011) under water stress conditions we want to analyse the distribution of recently assimilated carbohydrates from $^{13}CO_2$ between different species of ectomycorrhizal fungi. With analyses of $\delta^{13}C$ of the root tips in a time course we are able to follow the temporal distribution of the assimilates within the plant (Högberg *et al.*, 2008). By using two complementary methods (RNA-SIP and NanoSIMS) we want to identify the most active fungal partners of the plant before and after rewatering and in addition study the spatial distribution of labelled carbohydrates within the mycorrhizal root tip. First preliminary results from the experiment “BuKlim” at the WSL in Switzerland will be presented.

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P 33

Transamination governs the heterogeneity in nitrogen isotope composition of amino acids in the muscle

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The nitrogen isotope composition (δ15N) of different amino acids carries different dietary information. We hypothesized that differences in their biochemical pathways create three groups that largely explain their dietary information. The groups divide into (i) transaminating, (ii) non-transaminating and essential and (iii) non-transaminating and non-essential amino acids.

To this end, rats were fed with 15N-labeled amino acids, where each amino acid had an individual nitrogen isotope composition that varied by ~1000‰ among amino acids. The redistribution of the dietary 15N labels among the amino acids in the muscle of the rat was analyzed. Subsequently, the labeling was changed and the nitrogen isotope turnover was analyzed.

The amino acids had a common nitrogen half-life of ∼20 d, but differed in δ15N. Nontransaminating and essential amino acids largely conserved the δ15N of the diet and, hence, trace the origin in heterogeneous diets. Nonessential and nontransaminating amino acids showed a nitrogen isotope composition between their dietary composition and that of their de novo synthesis pool, likely indicating their fraction of de novo synthesis. The bulk of amino acids, which are transaminating, derived their N from a common N pool and hence their δ15N in the muscle was similar, although it varied by two orders of magnitude in the diet.

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P 34

Carbon allocation to new leaves increases carbon isotope differences between plant organs

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Plant organs of C3 plants differ in their carbon (C) isotopic signature ($\delta^{13}C$). In general, leaves are ^{13}C-depleted relative to other organs. To investigate the development of spatial $\delta^{13}C$-patterns, we induced different C-allocation strategies by reducing light and nutrient availability for twelve months in the Mediterranean shrub *Halimium halimifolium* L. We measured morphological and physiological traits and the spatial $\delta^{13}C$-variation between up to seven tissue classes during the experiment. A reduction of light (*Low L* treatment) increased aboveground C-allocation, plant height and specific leaf area (SLA). Reduced nutrient availability (*Low N* treatment) enhanced C-allocation into fine roots and reduced the spatial $\delta^{13}C$-variation. In contrast, *control* and *Low L* plants with high C allocation in new leaves showed a high $\delta^{13}C$-variation within the plant (up to 2.5‰). The spatial $\delta^{13}C$-variation was significantly correlated to the percentage of the second generation leaves from the whole plant biomass (R^2=0.46). According to our results fractionation in dark respiration may influence C-isotope composition of the plant tissues but it cannot explain the spatial pattern. Our study indicates that the main reason for the observed spatial $\delta^{13}C$-pattern in *H. halimifolium* is a foliar depletion in ^{13}C during leaf development combined with export of relatively ^{13}C enriched C by mature source leaves.

P 35

Nachweis präferenzieller Aufnahme von ^{15}N-, ^{18}O- und ^{2}H- Tracer in unterschiedlichen Pflanzenorganen von Weizen und Bohnen

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Stabilisotopenanalysen sind zu einem wertvollen Werkzeug in vielen unterschiedlichen wissenschaftlichen Bereichen geworden. Auch bei der Untersuchung von Stoffkreisläufen und pflanzenphysiologischen Fragestellungen können entsprechende Ergebnisse wertvolle Erkenntnisse liefern.

Im Rahmen der hier vorgestellten Studie wurden wenige Tage alte Weizen- und Bohnenpflanzen mit ^{15}N (KNO_3), ^{2}H- und ^{18}O (H_2O)-Tracer gelabelt um zu untersuchen ob der Einbau der Tracer in unterschiedlichen Pflanzenorganen präferenziell erfolgt. Zwei Tage nach Applikation der Tracer erfolgte die Beprobung. Bei den Bohnen wurden die Wurzeln, der Halm sowie der äussere- und innere Teil des ersten Blattes beprobt; beim Weizen wurden die Wurzeln, der untere und obere Teil des Keimblattes sowie der untere, mittlere und obere Teil des Sprosses beprobt.

Die Ergebnisse zeigen, dass bei den Bohnen die Traceraufnahme in unterschiedliche Pflanzenorgane abhängig vom verwendeten Tracer variieren kann. Beim Weizen zeigt sich dagegen eine stark präferenzielle Aufnahme aller Tracer im unteren Teil des Keimblattes wie auch dem unteren Teil des Sprosses. Erklären lässt sich dieses Ergebniss mit den interkalaren Wachstumsmeristemen von Gräsern und der dort stattfindenden hohen Biomasseproduktion.

Von Bedeutung ist dieser Befund u.a. für paläoklimatische Studien die $\delta^{2}H$ von Alkanbiomarkern oder $\delta^{18}O$ von Zuckerbiomarkern untersuchen. Die Ergebnisse verdeutlichen nämlich, dass diese Biomarker in Gräsern nicht primär an den Blattspitzen produziert werden wo starke Isotopenanreicherung durch Verdunstung stattgefunden hat, sondern primär im Bereich der interkalaren Wachstumsmeristeme wo noch keine signifikante Verdunstung stattgefunden hat.

P 36
Isotopic alterations during phloem translocation in two forest tree species

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The carbon and oxygen isotopic signatures of assimilated carbohydrates keep record of the ecophysiological conditions under which they were formed. Extracts of water-soluble organic matter from leaves have been shown to represent the fast turnover fraction and can be related to water-use efficiency, stomatal conductance and the rate of photosynthesis of the preceding hours or days. However, in the process of phloem loading and transport to the stem, the signals may be altered. Therefore, the quality of ecophysiological information that is retained during the travel to the stem phloem is under current debate. Knowledge of these relationships is also a prerequisite for the use of tree ring cellulose for ecological studies.

In our study, we followed the isotopic signals of water-soluble organic matter from the foliage of three different canopy heights across twig and branch phloem down to the stem phloem. The sampling was repeated seasonally in European beech and Douglas-fir growing in pure and mixed stands.

In the water-soluble organic matter, the oxygen isotope enrichment was strongly dampened from the leaf to the twig phloem. The dampening was most pronounced in the shaded crown layers of species. In the upper crown regions, phloem organic matter kept most of the leaf signal in mid and late summer. In comparison, the further alterations of the oxygen isotopic signatures on the way down to the stem phloem were inferior. However, while the depletion of ^{18}O with decreasing height was mostly continuous in Douglas-fir, the lowest $D^{18}O$ values (28.9 ± 1.5‰) in beech were found at the crown base rather than at breast height.

Our results give evidence, that, in the two investigated species, the oxygen isotopic signature of stem phloem organic matter is partly uncoupled from the leaf level.

Keywords: $d^{18}O$, $d^{13}C$, *Fagus sylvatica*, *Pseudotsuga menziesii*

Poster

Session 4 – Geochemische Stoffkreisläufe und Schadstoffdynamik

P 37
Methodenvergleich zur Bestimmung der Denitrifikation im Freiland - ^{15}N Tracertechnik vs. Isotopomere

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Denitrifikation, die Reduktion von Nitrat (NO_3^-) und Nitrit (NO_2^-) zu Stickoxiden (NO_x), Lachgas (N_2O) und molekularem Stickstoff (N_2) gilt als Senkenprozess für reaktiven Stickstoff in Ökosystemen. Sie stellt eine zentrale Bilanzgröße für die Verfügbarkeit von mineralischem Stickstoff für die Verminderung von NO_3^- Einträgen in Grund- und Oberflächengewässer, sowie Emissionen des klimarelevanten Treibhausgases N_2O in landwirtschaftlich genutzten Systemen dar.

Die Teilreaktionen der Denitrifikation sind jedoch nicht leicht zu bestimmen und eine große Unsicherheit ergibt sich bei der Abschätzung der N_2O Reduktion zu N_2, welche besonders im Freiland äußerst schwierig zu messen ist. Zur Quantifizierung dieser Prozesse werden in einem Freilandversuch zu Grünlanderneuerung und -umbruch erstmals zwei unterschiedliche Methoden (Isotopomer-Ansatz und die $^{15}N_2$-Methode) verglichen:

Im Isotopomer-Ansatz werden unter Anwendung eines Isotopenfraktionierungsmodells (Lewicka-Szczebak, Well et al. 2014) wöchentlich die $\delta^{18}O$, $\delta^{15}N$ und die ^{15}N Positionspräferenz (SP) von N_2O in Gasproben aus geschlossenen Kammern auf Parzellenebene bestimmt. Gleichzeitig erfolgt die Bestimmung von $\delta^{15}N$ und $\delta^{18}O$ im NO_3^- und $\delta^{18}O$ im Bodenwasser, als Vorläuferverbindung von N_2O aus der Denitrifikation.

Zur Anwendung der $^{15}N_2$-Methode erfolgte eine ^{15}N-Markierung des Nitratpools in Mikroplots. Über eine Versuchsdauer von 8 Wochen wurden NO_3^--Konzentration und ^{15}N-Anreicherung in der Bodenlösung sowie die N_2 und N_2O Emissionen in Gasproben aus geschlossenen Kammern und Bodensonden bestimmt.

Erste Ergebnisse des Isotopomer-Ansatzes weisen auf hohe Denitrifikationsraten sowie eine weitgehende N_2O-Reduktion zu N_2 hin, welches durch die großen N_2 Emissionen nach ^{15}N Markierung sowie ein geringes $N_2O/(N_2+N_2O)$-Verhältnis bestätigt werden kann. Weitere Ergebnisse des Methodenvergleichs werden folgen.

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P 38

Enzymatische Hydrolyse von Atrazin: $^{15}N/^{14}N$ Isotopeneffekte liefern Hinweise für *N*-Protonierung in Amidohydrolase TrzN und dessen Mutant TrzN-E241Q

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Fragestellung

Der biologische Abbau von Atrazin ist von großem Interesse, da es sich bei diesem Herbizid um einen potentiellen Grundwasserschadstoff handelt. Einen der wichtigsten Abbauwege stellt die mikrobiologische Umwandlung von Atrazin zu 2-Hydroxyatrazin dar, die durch das Enzym TrzN katalysiert wird. Die Kristallstruktur von TrzN wurde von Seffernick *et al.* (2010) aufgeklärt und lässt vermuten, dass sich Glutaminsäure E241 in unmittelbarer Nähe zu einem Stickstoffatom des Substratringes befindet und dort durch Protonierung den Katalysezyklus startet. Der Protonierung folgt dann eine nucleophile aromatische Substitution (S_NAr) der C-Cl Bindung. Experimente mit dem Bakterienstamm *Arthrobacter aurescens* TC1, der das Enzym TrzN exprimiert (Meyer *et al.*, 2009), zeigten eine inverse Stickstoffisotopenfraktionierung und stützen damit den von Seffernick *et al*. (2010), vorgeschlagenen Katalysezyklus (*N*-Protonierung, gefolgt von S_NAr). Ähnliche Experimente auf Enzymebene fehlten jedoch bisher. Im Mutanten TrzN-E241Q wurde im reaktiven Zentrum, durch eine zielgerichtete Mutagenese von TrzN, Glutaminsäure E241 durch Glutamin Q241 ersetzt. Dieser Mutant zeigte im Vergleich zum nativen Enzym TrzN einen langsameren Substratumsatz (Seffernick *et al.*, 2010). Dies wirft die Frage auf, ob die Fähigkeit zur Protonierung - und somit zum Abbau von Atrazin - im mutierten Enzym weiter besteht oder das Substrat auf andere Weise zu 2-Hydroxyatrazin umgewandelt wird. Zu diesem Zweck wurden in der vorliegenden Studie die substanzspezifischen Kohlenstoff- und Stickstoffisotopeneffekte bei der Reaktion von Atrazin mit TrzN und bei der Reaktion von Atrazin mit TrzN-E241Q bestimmt. Dabei werden inverse Stickstoffisotopeneffekte erwartet, wenn Stickstoffatome protoniert werden, andernfalls werden normale Isotopeneffekte erwartet. Für Kohlenstoff werden in beiden Fällen normale Isotopeneffekte erwartet.

Ergebnisse und Schlussfolgerungen

Die Messung der Isotopeneffekte mittels GC-IRMS (Gaschromatographie-Isotopenverhältnismassenspektrometrie) ergab für beide Reaktionen *normale Kohlenstoff*-isotopeneffekte. Der *Stickstoff*isotopeneffekt war überraschenderweise in beiden Fällen *invers*. Dies deutet darauf hin, dass das mutierte Enzym TrzN-E241Q trotz Verlustes der Säurefunktion weiterhin das Substrat protoniert. Eine mögliche Erklärung für diese Ergebnisse lieferte eine erneute Analyse der Kristallstrukturen von TrzN und TrzN-E241Q, bei der zwei Wassermoleküle eine wichtige Rolle spielen. Eines dieser Wassermoleküle überträgt sein Proton über Histidin H274 an E241. Das verbleibende Hydroxidion dient im weiteren Verlauf der Reaktion als Nucleophil. Das zweite Wassermolekül befindet sich mit einem Abstand von 2.83 Å in unmittelbarer Nähe des Substratringes und könnte im Falle des mutierten Enzyms TrzN-E241Q die Protonierung des Substrates übernehmen. Diese Überlegungen werden durch quantenmechanische Berechnungen gestützt.

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P 39

Tracking photochemical transformation of chloroanilines using compound-specific isotope analysis

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Due to their use as industrial chemicals, biocides, and pharmaceuticals, substituted anilines are frequently found in the environment. Identifying the transformation pathways of substituted anilines is challenging because these compounds can undergo both biological and abiotic oxidation as well as photochemical reactions with excited triplet states of natural organic matter and direct photolysis. To identify and distinguish these pathways without the need for finding reaction products, we explore the use of compound-specific isotope analysis. This approach is based on the combined interpretation of changing C and N isotope composition of substituted anilines due to kinetic and equilibrium isotope effects as indicators for transformation. While some information the isotope effects associated with microbial and abiotic oxidation already exists, none is available for *photochemical* reactions. In the present study, we explore the apparent ^{13}C- and ^{15}N-kinetik isotope effects (AKIEs) associated with the direct photolysis of chlorinated anilines. Our results have shown that chlorinated anilines exhibit a very variable isotope fractionation associated with different mechanisms of photochemical dechlorination reactions. The isotope effects are sensitive to substrate speciation in the pH-range 2.0 to 9.0 and the position of the aromatic Cl substituent. ^{13}C- and ^{15}N-AKIE-values for 4-Cl-aniline range from 1.005 to 1.017 and 1.001 to 1.008, respectively. Smaller ^{13}C- and ^{15}N-AKIEs that were almost identical in magnitude were observed for 3-Cl-aniline photolysis (0.997 at pH 2.0 to 1.002 at pH 7.0). Finally, ^{13}C-AKIEs for 2-Cl-aniline photolysis were inverse (0.990 at pH 4.0 and 0.992 at pH 7.0), while ^{15}N-AKIEs were normal (1.003 at pH 4.0 and 7.0). Using singlet quencher, we found that the pH-dependent isotope fractionation of 4-Cl-aniline is likely due to reactions from singlet vs. triplet excited states. Similar trends were also observed for 2-Cl- and 3-Cl-aniline. The large variation in both ^{13}C- and ^{15}N-AKIE-values suggests that direct photolysis is associated with mass-independent isotope fractionation, which is distinctly different from that found in biotic and abiotic oxidation reactions.

P 40
DDT's isotopic signature: Tracing pollutant turnover by NMR

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Persistent organic pollutants (POPs) have severe toxic effects on the environment and pose risks to all living organisms. They are transported in the environment, undergo transformations, biomagnify in food chains and are universally found in humans and animals. Understanding their fate in the environment and tracing them back to their sources is important, but difficult.

The insecticide DDT has effectively been used to combat malaria; however its extensive use in agriculture led to severe ecotoxicological problems like egg-shell thinning in Baltic birds. Because of these deleterious effects DDT is classified as POP and the global use of DDT has been drastically reduced in the last decades. But DDT is still ubiquitous in nature and still threatens people's health (Turosov et al., 2002). DDT is usually abundant in environmental samples in combination with structurally related compounds like DDD (Fig 1). DDD is a pollutant itself and can result as a by-product of the technical DDT synthesis or it can be formed by degradation of DDT in the environment.

We analyzed DDT and DDD samples to trace DDT dynamics in the environment and to demonstrate how stable heavy isotopes can be used as tracers of POP turnover.

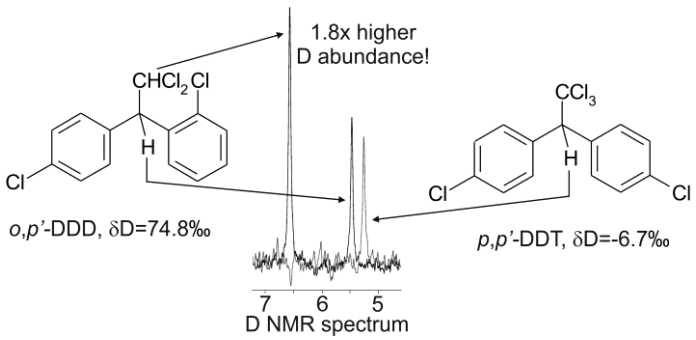
Stable heavy isotopes are ever-present tracers: their natural abundances get modulated by physical and chemical isotope effects and therefore reflect synthesis and transformation pathways. Stable isotope abundances are conventionally measured as whole-molecule δ values, however, chemical reactions modulate isotope abundances of individual intramolecular positions (isotopomer abundances). We apply NMR spectroscopy to determine individual deuterium (D) isotopomer abundances of DDT and related compounds and we link these isotopomer abundances to synthesis and transformation processes of DDT.

Reference samples of DDT and DDD differ in their δD by up to 80 ‰ (Vetter et al., 2006) which indicates different sources for these compounds. However, by measuring individual D isotopomer abundances of both compounds we observed that the difference in the whole-molecule δD value is caused by only one intramolecular position (Fig 1), while common molecular parts do not differ. This leads to the conclusion that both compounds can have the same source. We trace the strong D enrichment of this individual DDD isotopomer back to the technical DDT synthesis and show how the isotopomer pattern of DDD formed by anaerobic degradation of DDT differs greatly from synthetic DDD. The D isotopomer patterns allow a clear distinction between these sources.

Tracing pollutant turnover by isotopomer analysis has the power to understand transformation processes, identify sources and polluters, and evaluate the effectiveness of remediation approaches.

Figure 1: Overlay of expansions of D NMR spectra of reference samples of *o*,*p*'-DDD and *p*,*p*'-DDT. The NMR signal intensity is proportional to the isotopomer abundance.

Anhang 1



P 41

Isotope Effects of Enzymatic Dioxygenation of Nitrobenzene and 2-Nitrotoluene by Nitrobenzene Dioxygenase

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Oxygenation of aromatic rings is a frequent initial step in the biodegradation of persistent contaminants, and the accompanying isotope fractionation is increasingly used to assess the extent of transformation in the environment. Here, we systematically investigated the dioxygenation of two nitroaromatic compounds (nitrobenzene and 2-nitrotoluene) by nitrobenzene dioxygenase (NBDO) to obtain insights into the factors governing its C, H, and N isotope fractionation. Experiments were carried out at different levels of biological complexity from whole bacterial cells to pure enzyme. C, H, and N isotope enrichment factors and kinetic isotope effects (KIEs) were derived from the compound-specific isotope analysis of nitroarenes, whereas C isotope fractionation was also quantified in the oxygenated reaction products. Dioxygenation of nitrobenzene to catechol and 2-nitrotoluene to 3-methylcatechol showed large C isotope enrichment factors, ε_C, of −4.1 ± 0.2‰ and −2.5 ± 0.2‰, respectively, and was observed consistently in the substrates and dioxygenation products. ε_H- and ε_N-values were smaller, that is −5.7 ± 1.3‰ and −1.0 ± 0.3‰, respectively. C isotope fractionation was also identical in experiments with whole bacterial cells and pure enzymes. The corresponding ^{13}C-KIEs for the dioxygenation of nitrobenzene and 2-nitrotoluene were 1.025 ± 0.001 and 1.018 ± 0.001 and suggest a moderate substrate specificity. Our study illustrates that dioxygenation of nitroaromatic contaminants exhibits a large C isotope fractionation, which is not masked by substrate transport and uptake processes and larger than dioxygenation of other aromatic hydrocarbons.

P 42

Mechanistic insights into the anaerobic biodegradation of trichloroethene with dual element carbon and chlorine isotope analysis

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Tricloroethene (TCE) is a toxic industrial solvent commonly found in contaminated groundwater. Here, the primary biotransformation mechanism for TCE is reductive dechlorination under anaerobic conditions, which involves the sequential replacement of Cl atoms with H atoms. Compound specific isotope analysis (CSIA) is an analytical method that measures the ratio of naturally occurring stable isotopes in specific compounds. CSIA can be used to quantify the in situ biodegradation of toxic chlorinated ethenes, such as TCE, in groundwater. Despite the importance of reductive dechlorination for biological treatment of TCE-contaminated groundwater, the underlying reaction mechanisms remain unclear. For instance, the magnitude of observed kinetic isotope effects for carbon has varied widely for different bacteria and enrichment cultures [1]. This variability could indicate different initial transition states within the reaction mechanism or masking of the observed carbon kinetic isotope effect due to additional rate-limiting steps (e.g. substrate binding, mass transfer limitations) during the degradation of TCE. Isotopic-masking effects can be circumvented by simultaneously analyzing changes in isotope ratios for two elements in so-called dual plots, since the extent of such effects is generally similar for both elements and non-fractionating.

Here, we probe the details of the reductive dechlorination mechanism of TCE in anaerobic dechlorinating cultures grown in batch mode using dual element ($\Delta\delta^{13}C/\Delta\delta^{37}Cl$) isotope analysis.The slopes of dual element isotope plots remain largely constant even when masking suppresses observable kinetic isotope effects, so different slopes indicate a different initial transition state in the degradation mechanism [2]. Changes in carbon and chlorine stable isotope ratios were monitored during TCE biodegradation by a highly enriched Geobacter lovleyi strain KB-1 culture and two mixed cultures dominated by Dehalococcoides mccartyi and Dehalogenimonas sp., respectively. These cultures had been amended and enriched for months with other chorinated ethenes/ethanes prior to incubation with TCE as follows: G. lovleyi with tetrachlorothene (PCE), the D. mccartyi enrichment with 1,2-dichloroethane (1,2-DCA) and the Dehalogenimonas enrichment with trans-dichloroethene (trans-DCE). Molecular analysis of the reductive dehalogenase genes present in these cultures (rdh genes) indicate that the dominant organisms bear different reductive dehalogenases that are responsible for the reductive dechlorination process. Dual isotope ($\Delta\delta^{13}C/\Delta\delta^{37}Cl$) plots showed similar slopes for the G. lovleyi- (3.0 ± 0.1, $R2=1$) and the D. mccartyi- (4.5 ± 0.9, $R2=0.92$) dominated cultures and a different slope for the Dehalogenimonas-dominated culture (9.9 ± 3.5, $R2=0.82$). The slopes for G. lovleyi and D. mccartyi are similar to those previously reported for G. lovleyi strain GT and Desulfitobacterium hafniense Y51, which have been related to a single electron transfer mechanism [3]. Results for the Dehalogenimonas enrichment suggest a potential novel biodegradation mechanism for TCE. Dual element CSIA can be a powerful tool in elucidating biodegradation pathways.

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P 43

Substanz-spezifische Isotopenanalytik: neue Ansätze zur Beurteilung von Schadstoffen in der aquatischen Umwelt

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Verschiedene biogeochemische Prozesse (Sorption, Transport und Abbau) beeinflussen das Verhalten von Schadstoffen in der Umwelt. Für eine bessere Beurteilung der dominierenden Vorgänge benötigt es neuer analytischer Ansätze. Die substanz-spezifische Isotopenanalytik ist in den letzten Jahren vielversprechend zur Anwendungen gekommen, um den Abbau von Grundwasserkontaminanten (BTEX, LCKWs) zu charakterisieren (Schmidt et al. 2004). Unser Ziel ist es gewesen, erstmals die substanz-spezifische Isotopenanalytik für die Analyse von umweltrelevanten Herbiziden zu etablieren, um Veränderungen in deren natürlichen Isotopenverhältnissen ($^{13}C/^{12}C$; $^{15}N/^{14}N$) analysieren zu können. Diese Veränderungen ermöglichen es Abbauprozesse von Sorption- und Transportprozessen zu unterscheiden. Im Verlauf der letzten Jahre entwickelten wir sowohl neue analytische, als auch Anreicherungsmethoden für die gaschromatographischer Isotopenverhältnis-Massenspektrometrie (GC-IRMS) der Herbizide Atrazin (Meyer et al., 2008, Schreglmann et al. 2013), Isoproturon (Penning und Elsner, 2007), MCPA, Dichlobenil, Bentazon (Reinnicke et al., 2010) und Phenoxyessigsäuren (Maier et al., 2013). Mit Hilfe dieser Methoden ist es uns in *batch*-Experimenten gelungen abbaubedingte Veränderungen in den $^{13}C/^{12}C$ und $^{15}N/^{14}N$ Isotopenverhältnissen der Herbizide zu detektieren(Reinnicke et al. 2011; Penning et al., 2010). Darüber hinaus, konnten wir im Fall von Atrazin zeigen, dass verschiedene natürliche Abbauwege mit unterschiedlichen zweidimensionalen Isotopenplots ($d^{13}C/ d^{15}N$) assoziiert sind (Meyer und Elsner, 2013).

In einer aktuelle Studie kombinierten wir enantioselektive Gaschromatographie-Isotopenverhältnis-Massenspektrometrie mit enantioselektiven Analysen von Phenoxyessigsäuren (Qiu et al., 2014). Gegensätzliche Ergebnisse in der Kohlenstoffisotopenfraktionierung und in der Selektivität der Enantiomere ermöglichte die Identifikation von „Flaschenhälsen“ im biologischen Abbau. Solche Flaschenhälse können auftreten bei i) der Anlagerung und Freisetzung des Herbizides von Sorptionsplätzen und Massentransfer in Lösung, ii) bei der Aufnahme in die Zelle und iii) während der enzymatischen Reaktion. Im ersten Szenario erwartet man weder Isotopenfraktionierung noch Fraktionierung in den Enantiomeren der Phenoxyessigsäuren (Limitierung durch Massentransfer). Im zweiten Szenario wäre nur eine Selektivität in den Enantiomeren wahrscheinlich, da die Isotopenfraktionierung aufgrund des Membrantransportes (geschwindigkeitsbestimmender Schritt) „maskiert“ wäre. Im Fall der enzymatischen Reaktion (drittes Szenario) sollte aufgrund ihres selektiven Verhaltens sowohl Isotopen- , als auch Enantiomerfraktionierung auftreten.

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P 44

Einfluss von Umweltfaktoren auf die stabilen Isotope von Stickstoff und Sauerstoff in gelöstem Nitrat währen der Denitrifikation - Kohlenstoffquellen und Wasserisotopenaustausch

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Stabile Isotope von Stickstoff und Sauerstoff in gelöstem Nitrat werden häufig zur Quellenbestimmung erhöhter Nitratkonzentrationen im Grundwasser herangezogen. Durch mikrobielle Denitrifikation werden die leichteren Isotope (^{14}N, ^{16}O) aus dem Restnitrat entfernt und es reichern sich die schwereren Isotope (^{15}N, ^{18}O) im Restnitrat isotopenchemisch an. Bisherige Studien zu den Anreicherungsfaktoren (ε) und der relativen Anreichung von $\delta^{18}O$ im Verhältnis zu $\delta^{15}N$ ($\Delta\delta^{18}O/\Delta\delta^{15}N$) während des Nitratabbaus zeigen eine große Bandbreite an Ergebnissen. Dadurch wird eine Anwendung von Isotopenanalysen in gelöstem Nitrat für die Quantifizierung des Nitratabbaus mit Hilfe der Rayleigh Gleichung, sowie die Quellenbestimmung von teilweise mikrobiell abgebautem Nitrat erschwehrt.

In Mikrokosmenversuchen haben wir einige der möglichen Umwelteinflüsse auf die Isotopenfraktionierung bei der Denitrifikation untersucht. Unsere Ergebnisse zeigen eine Abhängigkeit der Anreicherungsfaktoren von der vorhandenen Kohlenstoffquelle. Im Besonderen sehen wir einen deutlichen Unterschied zwischen komplexen Kohlenwasserstoffringen (Toluol, Benzoat) und einfachen Kohlenwasserstoffen wie Acetat.

Wir haben Hypothesen zur Erklärung dieses Einflusses basierend auf einer Veränderung der relativen Prozesskinetiken des Nitrattransportes in die Zelle im Vergleich zur intrazellulären Nitratreduktion formuliert. Diese postulieren eine Minderung des potentiellen Nitrattransportrates in die Zelle als Erklärung für unsere Beobachtungen.

Weiterhin untersuchten wir einen möglichen Einfluss der Isotopenkomposition von Wasser auf Nitratisotope durch eine partielle Umkehr der Nitratreduktionsreaktion. Ein solcher Einbau von Sauerstoffatomen aus dem umgebenden Wasser würde die ^{18}O-Isotopenwerte des gelösten Restnitrats beeinflussen. Unsere Versuche ergaben, dass wenn nitrifizierende Bakterien mit dem NXR Enzym (Nitritoxidoreduktase) unter anaeroben Bedingungen Nitrat reduzieren ein solcher Isotopenaustausch stattfindet. In Reinkulturen von gewöhnlichen Denitrifizierern mit dem NaR Enzym (Nitratreduktase) findet jedoch kein Austausch statt. Der Einbau von Sauerstoffatomen aus Wasser in das verbleibende Nitrat kann durch die Reversibilität des NXR Enzyms erklärt werden und betrug in unseren zeitlich begrenzen Inkubationen von natürlichen Sedimenten bis zu 5% des Sauerstoffs im verbliebenen gelösten Nitrat (Fig. 2). Dadurch verschiebt sich das Verhältnis $\Delta\delta^{18}O/\Delta\delta^{15}N$ während der Denitrifikation und können die in der Umwelt beobachteten variierenden Steigungen nun erklären.

Poster

Session 5 – Klimaänderungen und -rekonstruktionen

P 45
Stable hydrogen and carbon isotope ratios of methoxyl groups during plant litter decomposition

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Stable hydrogen and carbon isotope ratios of methoxyl groups ($\delta D_{methoxyl}$ and $\delta^{13}C_{methoxyl}$ values, respectively) in plant material were discovered to have characteristic signatures. These isotopic signatures can be used for a variety of applications such as constraining the geographical origin and authenticity of biomaterials [1-3]. Recently it has also been suggested that $\delta D_{methoxyl}$ values of sedimentary organic matter of geological archives might serve as a palaeoclimate/-hydrology proxy [4]. However, organic matter in geological archives is usually subject to both biotic and abiotic degradation processes and an evaluation of its potential impact on the $\delta D_{methoxyl}$ and $\delta^{13}C_{methoxyl}$ values would allow more reliable interpretations of both isotopic signatures. Here we tested this potential influence exemplarily by measuring $\delta D_{methoxyl}$ and $\delta^{13}C_{methoxyl}$ values from foliar litter of five different tree species (Sycamore maple, Mountain ash, European beech, Norway spruce and Scots pine) which were exposed to natural degradation in a field experiment. The samples were collected over a 27 months period and further parameters including the total mass loss as well as the degradation of lignin and cellulose were determined [5,6]. The $\delta D_{methoxyl}$ values of all investigated litter species showed no significant temporal trend throughout the degradation experiment and fluctuations can be explained reasonably by considering the analytical and internal precision of the applied method. Whilst $\delta^{13}C_{methoxyl}$ values of two litter species (Sycamore maple and European beech) showed also no obvious temporal trends, three litter species (Mountain ash, Scots pine and Norway spruce) became ^{13}C enriched by about 4‰ on average already after 9 month of degradation. These findings allow us a first estimation of the potential impact of degradation processes on $\delta D_{methoxyl}$ and $\delta^{13}C_{methoxyl}$ values of organic matter. We propose that $\delta D_{methoxyl}$ values of organic matter might be unaffected by degradation processes and have the potential to be applied to a wide range of climate archives such as tree rings and sediments containing organic matter. On the other hand care may have to be taken if $\delta^{13}C_{methoxyl}$ values of degraded organic matter are used for paleoclimate/-environmental investigations.

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P 46

Neue Ergebnisse zur Klimageschichte Ostafrikas anhand eines gekoppelten ^{2}H-^{18}O Biomarker Ansatzes

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Die Stabilisotopie von Niederschlagswasser ($\delta^{2}H$ und $\delta^{18}O$) ist maßgeblich klimatisch gesteuert. Es verwundert daher nicht, dass entsprechende Stabilisotopenanalysen zu einem der wichtigsten Werkzeuge für die Rekonstruktion von Klimageschichte wurden. Um einen Beitrag zur Rekonstruktion der Klimageschichte Ostafrikas zu leisten, untersuchen wir eine 6.5 m mächtige Löß-Paläoboden-Sequenz im Maundi Krater (3°10‘27.5‘‘S, 37°31’05.8’’E) der an den Süd-Osthängen des Mt. Kilimandscharo auf 2780 m ü. NN gelegen ist. Die Maundi-Sedimente in 3.15 m Tiefe datieren gemäß den ^{14}C-Datierungsergebnissen auf ca. 41 cal ka BP. Die Sedimentationsgeschichte begann jedoch vermutlich schon im frühen Jungpleistozän (ca. 100 ka BP), abgeleitet aus der linearen Extrapolation der ^{14}C-Datierungsergebnissen.

Unsere methodische Herangehensweise umfasst insbesondere substanzspezifische $\delta^{2}H$-Analysen von Pflanzenwachs-bürtigen Alkanbiomarkern und substanzspezifische $\delta^{18}O$-Analysen von Hemizellulose-bürtigen Zuckerbiomarkern. Dieser kombinierte ^{2}H-^{18}O Biomarker Ansatz erlaubt es zwischen dem Niederschlagssignal und der Blattwasseranreicherung (deuterium-excess des Blattwassers als Proxy für relative Luftfeuchte) zu unterscheiden (Zech et al., 2013. Chemical Geology). Die Berechnung der Isotopensignatur der Paleoniederschläge erfolgt hierbei über die lokale Evaporationslinie und deren Schnittpunkt mit der lokalen meteorischen Wasserlinie des Kilimanjaro Südhangs.

(Abbildung 1)

Die hier vorgestellten ersten vorläufigen Ergebnisse bestätigen das Vorherrschen humider Klimabedingungen während der „African Humid Period“ (AHP) und trockenerer Klimabedingungen während der Jüngeren Dryas (YD) und dem „Last Glacial Maximum“ (LGM). (Abbildung 1). Der rekonstruierte deuterium-excess des Blattwassers deutet zudem auf ein „megadrought“ (MD) Ereignis zwischen ca. 68 - 61 ka BP hin. Diese deuterium-excess Ergebnisse stehen jedoch interessanterweise nicht im Einklang mit den entsprechenden rekonstruierten Isotopenwerten des Niederschlagswassers sofern diese im Sinne des „amount effects“ interpretiert werden (Abbildung 1). Durch den Vergleich unserer rekonstruierter Blattwasser- und Niederschlagswerte mit bestehenden Isotopen-Klimakurven des Challa Sees, Tanganyika Sees und des Malawi Sees hoffen wir in Zukunft die Klimageschichte Ostafrikas sowie die verantwortlichen klimatischen Steuerungsmechanismen besser verstehen zu können.

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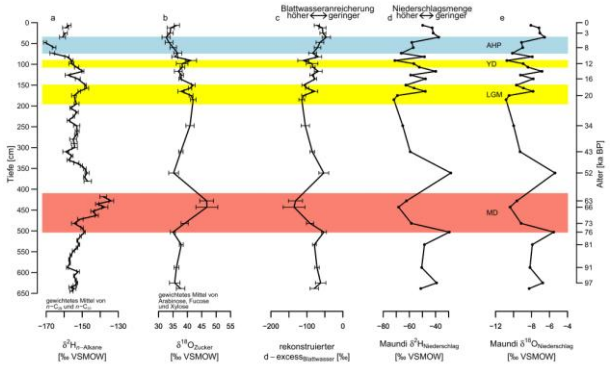
Abbildung 1: $\delta^{2}H$ *n*-Alkane, $\delta^{18}O$ Zucker, deuterium-excess, und rekonstruierte NS-Werte für das ca. 100 ka zurückreichende Klimaarchiv des Maundi-Kraters am Kilimandscharo. MD = „megadrought“, LGM = „Last Glacial Maximum“, YD = Jüngere Dryas, AHP = „African Humid Period“.

Anhang 1



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Erste ^{18}O Zuckerbiomarker-Ergebnisse von Spätglazialen und Frühholozänen Seesedimenten des Gemündener Maars in der Eifel

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Die Stabilisotopie von Niederschlagswasser und Seewasser (δ^2H und $\delta^{18}O$) ist maßgeblich klimatisch gesteuert. Für die Rekonstruktion von Paläoklima werden daher u.a. ^{18}O-Isotopenanalysen von Seesedimenten durchgeführt. Um einen Beitrag zur Rekonstruktion der Klimageschichte Mitteleuropas und zu einem verbesserten Verständnis der Klimasteuernden Mechanismen zu leisten untersuchen wir die Spätglazialen und Frühholozänen Seesedimente des Gemündener Maars in der Eifel (Sirocko et al., 2013). Im Fokus unserer hier vorgestellten Untersuchungen stehen insbesondere Zuckerbiomarker und deren ^{18}O-Isotopensignatur, die mittels einer Gaschromatographie-^{18}OPyrolyse-Isotopenmassenspektrometrie (GC-^{18}OPy-IRMS) ermittelt wurde (Zech and Glaser, 2009)

Aufgrund der relativen Häufigkeit von Fucose im Verhältnis zu Arabinose und Xylose (fuc/(ara+xyl) > 0,4) kann von einem hauptsächlich aquatischen Ursprung der Zuckerbiomarker im Gemündener Maar ausgegangen werden (Zech et al., 2014). Die Zuckerbiomarker spiegeln daher im Wesentlichen die ^{18}O-Isotopie des Seewassers des Gemündener Maars wider. Sowohl Arabinose, Fucose als auch Xylose weisen die gleichen ^{18}O-Trends auf und zeigen im Frühholozän deutlich positivere Werte (35 bis 40‰) als in der Jüngeren Dryas mit einem markanten Shift von über 5‰ während des Übergangs (Abbildung 1). Leicht positivere Werte (2-3‰) charakterisieren des Weiteren die Sedimente des Bölling/Alleröds.

Abbildung 1

Damit entspricht der Verlauf der hier anhand von Zuckerbiomarkern aufgestellten ^{18}O Klimakurve in etwa dem Verlauf der ^{18}O Klimakurven Grönländischer Eisbohrkerne. Dies spiegelt die dominante Steuerung des Mitteleuropäischen Klimas durch den Nordatlantik wider und lässt vermuten, dass die ^{18}O Klimakurve der Seesedimente des Gemündener Maars zumindest teilweise im Sinne von Temperaturschwankungen interpretiert werden kann. Ob darüber hinaus auch eine Anreicherung des Seewasssers durch Verdunstung die hier aufgestellt ^{18}O-Klimakurve beeinflusst hat, wird derzeit im Rahmen von δ^2H Analysen an Alkanen und einem gekoppelten ^2H-^{18}O Ansatz untersucht.

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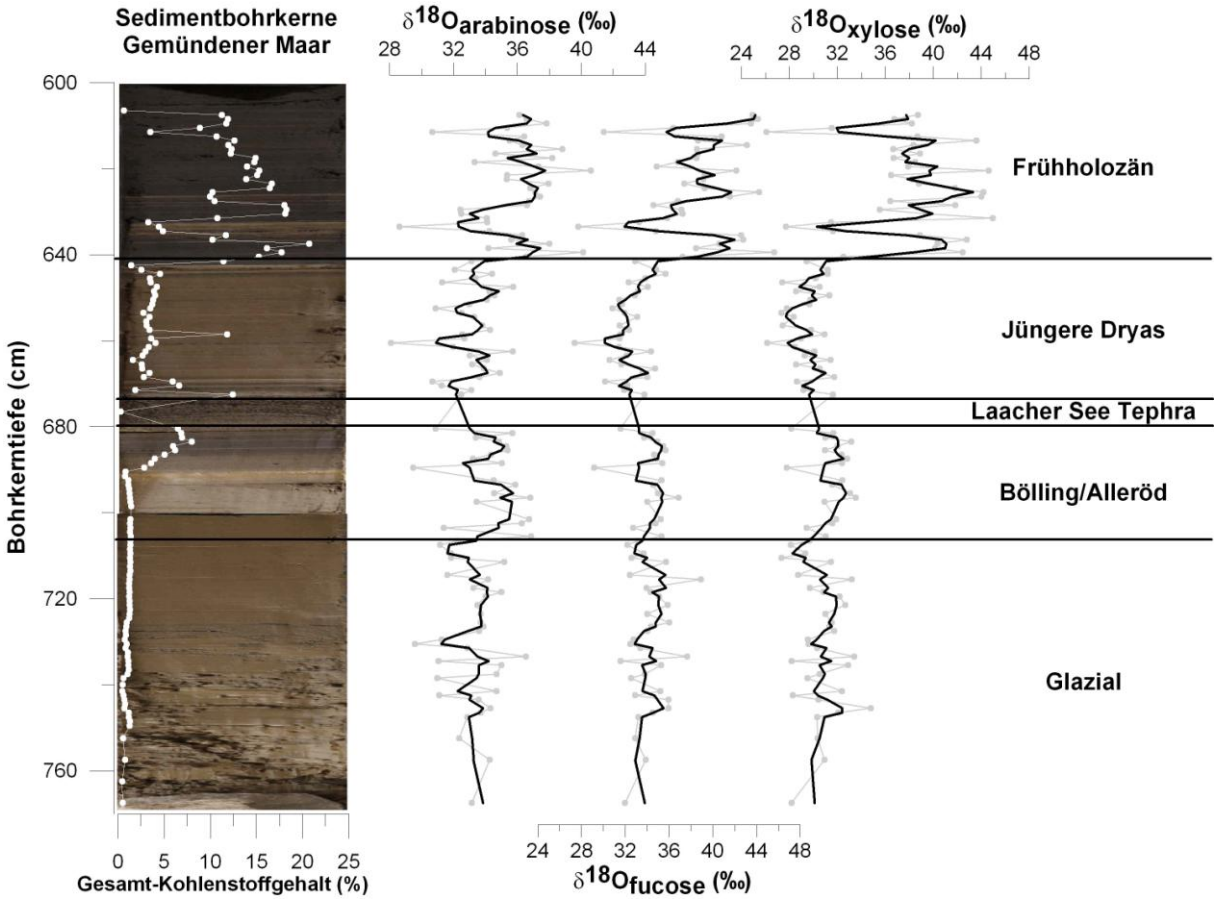
Abbildung 1: Gesamtkohlenstoffkurve der Gemündener Maar Seesedimente von 6 bis 7,7 m Bohrkerntiefe und $\delta^{18}O$ Klimakurven der Zuckerbiomarker Arabinose, Fucose und Xylose.

Anhang 1


Sedimentbohrkerne
Gemündener Maar
δ18Oarabinose (‰)
28 32 36 40 44
δ18Oxylose (‰)
24 28 32 36 40 44 48
600
640
680
720
760
Bohrkerntiefe (cm)
Frühholozän
Jüngere Dryas
Laacher See Tephra
Bölling/Alleröd
Glazial
0 5 10 15 20 25
Gesamt-Kohlenstoffgehalt (%)
24 28 32 36 40 44 48
δ18Ofucose (‰)

Poster

Session 6 – Ökosysteme

P 48

Improved calculation of N_2 and N_2O fluxes from ^{15}N-labelled NO_3^- in soil for combined ^{15}N analysis of N_2, N_2+N_2O and N_2O in gas samples

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Dinitrogen ($N_{2)}$ and nitrous oxide (N_2O) fluxes from denitrification in soil can be quantified using the ^{15}N tracer technique. This includes ^{15}N labelling of nitrate (NO_3^-) in soil and subsequent isotope analysis of gas samples from enclosures, i.e. mixtures of soil-derived and atmospheric N_2 and N_2O. Measuring pool-derived N_2 or N_2O has been shown to include two calculation problems, (i) arising from multiple pools (Mulvaney, 1988, Arah , 1992) and (ii) dealing with the non-random distribution of N_2 and N_2O mole masses (Hauck et al., 1958). Non-randomness can be solved in case of two distinct pools (i.e. soil and atmosphere) if m/z 28, 29 and 30 are correctly analysed and the ^{15}N enrichment of one pool is known (). In case of three pools, it can also be solved if the N enrichment of two pools is known (Spott & Stange, 2008). Moreover, NO_3^- pools generating N_2 and N_2O can be identical or different, e.g. if N_2O evolved from higher enriched NO_3^- in deeper soil was more reduced to N_2 compared to N_2O evolved from N_2O from shallow soil with lower enrichment, or vice versa.

Taking these effects into account and, using the additional information from the sequential measurement of ^{15}N isotope signatures of N_2 , N_2O and N_2+N_2O (Lewicka-Szczebak et al., 2013), we propose some improved routines for data analysis. Model calculations are conducted to illustrate potential errors and deviations between previous and improved calculations. Finally a laboratory data set is analysed to illustrate the potential progress in process identification when using improved calculations.

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P 49

The stable isotope and elemental response of *Fucus vesiculosus* on acidification, warming and eutrophication in mesocosm studies (Kiel, Sylt)

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In the frame of the German BIOACID II project the separate and combined effects of different stress factors (acidification, warming, eutrophication) on the elemental and stable isotope composition of *Fucus vesiculosus* are investigated by means of benthic mesocosm experiments in coastal waters of the Baltic and the North Sea. We aim for a calibration of the geochemical and stable isotope composition of Fucus in response to single and combined temperature, pCO_2 (pH), and nutrient changes.

Benthocosm experiments are carried out in the Kiel Fjord and at the waddenSeastation of the AWI in List (Sylt) with a fully crossed array of 2 stressors: an increase in temperature and an increase in atmospheric CO_2 partial pressure. The experiments run for almost 3 months per season. Additionally, in summer an experiment with a parallel combination of elevated CO_2 and temperature with and without elevated nutrients were carried out. On both a regular (weekly) and high resolution (24H-cycle) base, the aquatic chemistry (e.g. TA, pH, $\delta^{13}C$(DIC)) as well as the composition of the grown *Fucus vesiculosus* organic tissue (e.g. CNSP, C, N, and S stable isotope ratios) are followed. In the 24h-cycles the community response to diurnal light cycles was followed in high time resolution.

It was found, that seasonal variations in the composition of the input solutions (brackish water from the Kiel Fjord or North Sea) were reflected by changes in the experiments with short time delay. The changes in the aquatic chemistry of the mesocosms, however, were strongly superimposed for most parameters during daytime by biological activity (photosynthesis, respiration). The biological activity during the 24h-campaigns, alternating phases of net respiration and photosynthesis, was creating strong variations in the dissolved carbonate system and significant changes in the carbon isotope composition of DIC. The atmosphere of some experimental set-ups was enriched with isotopically light gaseous carbon dioxide. This caused fast corresponding changes in the isotopic composition of DIC, thereby acting as a tracer for newly formed organic tissue and carbonates. The chemical and isotopic parameters of the dissolved carbonate system showed differences between the set ups. The organic tissue of *Fucus vesiculosus* shows seasonal variability in the C, N, S contents and the isotopic composition.

P 50

Variations of stable isotope signatures and element stoichiometry of *Fucus vesiculosus* under anthropogenic impact in the Kiel Bight, Baltic Sea

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In the frame of the BMBF project BIOACID II we aim for an understanding of the natural distribution and variation of isotopic and element composition (e.g. CNSP) in *Fucus vesiculosus* growing around the coast line of the Kiel Fjord (part of the Baltic Sea). Also the environmental conditions (aquatic chemistry, temperature, salinity) are important for the Fucus composition. Some changes in aquatic chemistry are related to stress factors like human activity (e.g. waste input) and further factors leading to specific changes in the composition of *Fucus vesiculosus*.

On different Station at the west and east coast of the Kiel Fjord three size classes (small, medium, large) of Fucus vesiuculosus and there habitat (water sample) were sampled. For each sampling station the composition of the Fucus vesiculosus organic tissues (stoichiometry and stable isotope composition of carbon, nitrogen, sulphur) as well as the aquatic chemistry (TA, pH, salinity, $\delta^{13}C$(DIC), main and trace elements and nutrients) are analysed.

It is shown, that *Fucus vesiculosus* indicates clear differences in the N contents and stable isotopes between the west and the east site of the Kiel Fjord. Stable nitrogen isotope signatures in *Fucus vesiculosus*, are useful proxies to identify the influence factors in the Fucus habitat. From the data it is obtained that the influence of human activity (wastewater treatment plant, harbour), small streams and drainage channels, which flow from the near coastal area into the bight, leads to different *Fucus vesiculosus* compositions. In future work, it is intended to extend the investigation to trace element signatures to further estimate environmental impacts.

P 51
Tracing nutrient flows from offshore aquaculture - possible application for SIA?

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An increasing demand for seafood in a situation of declining fish landings made aquaculture the fastest growing food production sector in recent years. The resulting conflict of interests for space in coastal areas (e.g., traffic, tourism, nature conservation) forces future aquaculture operations to move further offshore. However, moving aquaculture endeavors into offshore waters is met by a number of new challenges that are currently the focus of intense research activities. For example, rough offshore conditions with high dilution potential and deeper water depths complicate the retraceability of any aquaculture impacts on the environment, most importantly nutrient emissions. However, since the EU Marine Strategy Framework Directive and other international agreements explicitly demand the study of potential effects, methods need to be developed to trace potential emissions from aquaculture operations.

Stable isotopes (i.e., $\delta^{13}C$ and $\delta^{15}N$) can be measured in small concentrations and therefore lend themselves to tracing nutrients associated with fish production through the food chain, even in rough, offshore environments. As part of the project “Offshore site selection for a sustainable and multifunctional use of marine areas in heavily utilized seas with the North Sea as an example” we will examine the potential of stable isotope patterns as tracers for fish production in offshore waters.

Since the nutritional impact from fish production is likely to predominantly affect benthic organisms, brittle stars (*Ophiura ophiura* and *O. albida*) were identified as potential indicator species for anthropogenic nutrient enrichment because they are opportunistic feeders and therefore likely to incorporate any available organic matter, are widely distributed in the area and can typically be sampled throughout the year in quantities sufficient for analysis.

To date, stable isotope analysis (SIA) has been conducted on brittle stars from a potential offshore aquaculture site in the German North Sea to define a baseline, i.e., the natural isotopic pattern. In addition, stable isotope patterns of potential fish feed ingredients were analyzed and tested during an 8-week feeding trial to determine the best SI signal from fish production. All samples have been defatted prior to EA-IRMS.

Figure 1

Plant protein sources in fish feed like soy and wheat gluten differ substancially from the marine background, thus indicating that these compounds will likely lend themselves to providing a stable isotope signal clearly different from the baseline of the benthic indicator species. But also the commercial feed shows a large distance from marine sources, indicating a heavy use of terrestrial proteins.

Thus, our data suggest that plant protein sources in fish feed may help to identify and trace nutrient emissions from aquaculture in offshore waters of the North Sea.

This study has been partly funded by Bundesanstalt für Landwirtschaft und Ernährung (BLE), upon a decision of Deutscher Bundestag.

Anhang 1

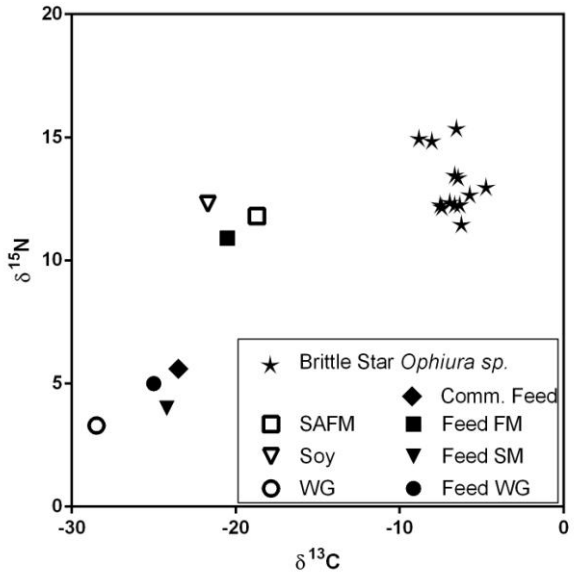

Figure 1: Isotopic data of benthic brittle star *Ophiura sp.*, feed ingredients South American fish meal (SAFM), soy, wheat gluten (WG) as well as feeds made thereof and a commercial feed

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Effect of light exclusion on $^{13}CO_2$ efflux from branches of European beech in late winter

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In woody trees, branch internal CO_2 is expected to be re-assimilate by bark photosynthetic whenever sufficient light for such activity is present (Cernusak et al. 2001). As the CO_2-fixing enzym Rubisco discriminates against $^{13}CO_2$ by about 29‰ (Raven & Farquhar, 1990), $^{13}CO_2$ should accumulate in the bark cortex, increasing the $\delta^{13}C$ of the CO_2 difusing out of the branches. This contribution tests this hypothesis in branches of adult European beech trees during the winter months before the leaf flush.

To this end, we measured the carbon isotopic composition of CO_2 respired by branch sections of six adult *F. sylvatica* individuals. On each tree, one transparent and one darkened branch chamber (covered with aluminum foil) was installed. After a period of 20 to 30 days, CO_2 was sampled after flushing the chambers with CO_2-free air (Damesin et al. 2005). Sampling was done during day and night in order to evaluate the diurnal pattern of $^{13}CO_2$ efflux from dark and sunlight exposed branches. In addition and to verify the influence of the darkened chamber, $^{13}CO_2$ efflux was assessed 4 and 24 hours as well as 8 and 20 days after the removal of the aluminum foil. CO_2 refixation by bark photosynthetic resulted in significantly different values between darkened and sunlight exposed beech branches ($t_{(8,4)}$ = 2,553; p = 0,033) with average values of the sampled CO_2 of -26,5 ± 1,9 ‰ and -22,9 ± 3,0 ‰, respectively. In contract to the darkened chambers, uncovered branches displayed a diurnal pattern ($F_{4, 62}$= 4, 9, p= 0,001). The highest $\delta^{13}C$ for uncovered branches were sampled during the afternoon and ranged between -22,0 and -23,1 ‰, while the lowest values was -29,83 ‰ measured at midnight. Four hours after the removal of the aluminum foil, the $\delta^{13}C$ of the CO_2 efflux from branches displayed and increase by 2,4 ‰. In the subsequent 20 days after the foil removal, this value did not change significnatly ($F_{(3,15)}$ = 2,151; p >0,29).

Our results give evidence for a strong influence of Rubisco discrimination on the $\delta^{13}C$ of CO_2 diffusing out of the branches by directly affecting the branch-internal CO2. Thus, the lowest observed $\delta^{13}C$ in darkened branches and during the night might be explained by the absence of Rubisco activity under these conditions. On the other hand, in sun-exposed branches, parts of branch-internal CO_2 may be refixed by Rubisco, increasing both the $^{13}\delta C$ of the branch-internal CO_2 and thus of the CO_2 defusing out of the branch.

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P 53

Soil microbial C and N turnover under *Cupressus lusitanica* and natural forests in southern Ethiopia assessed by decomposition of ^{13}C- and ^{15}N-labelled litter under field conditions

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In the Munessa forest south of Addis Ababa (Ethiopia), increased demand of wood leads to a widespread deforestation strongly reducing species-rich natural forests dominated by *Croton macrostachys*, *Podocarpus falcatus* and *Prunus africana*. Parts of the deforested land have been reforested with exotic tree species such as *Cupressus lusitanica*, but little is known about consequences of this land use change for soil C and N dynamics. Therefore, the question arises whether silvicultural management practices of differently aged *Cupressus* plantations influence soil microbial C and N turnover under the sub-humid site conditions of the Munessa forest.

The objectives of the study were: (i) quantification of microbial litter-derived C and N incorporation under field conditions, (ii) identification of forest management effects on microbial litter-derived C and N incorporation (**tree species effects**: natural forest vs. *Cupressus* plantation with no management, **thinning effects**: *Cupressus* plantation with no management vs. Intense Promotion vs. Conversion, **age class effects**: *Cupressus* age class I vs. age class III) and (iii) elucidation of **soil moisture effects** (dry soil conditions vs. wet soil conditions) on microbial litter-derived C and N utilization. To address these objectives, a labelling experiment with ^{13}C- and ^{15}N-enriched litter was installed and litter degradation was studied over 2 years. Chloroform fumigation extraction allowed the quantification of microbial C and N storage (C_{SMB} and N_{SMB}) and the analysis of litter-derived tracer ^{13}C and ^{15}N incorporation into SMB.

Most of the ^{13}C and ^{15}N Tracer remained in the litter or was incorporated into bulk soil, whereas soil microbial biomass (SMB) showed minor incorporation. Microbial incorporation of litter-derived N was not significantly affected by the investigated variables over the whole experimental period. However, microbial litter-derived ^{13}C utilization was higher under natural forest during dry soil conditions, whereas *Cupressus* litter was less utilized by SMB. Wet soil conditions improved microbial litter-derived C utilization under *Cupressus*. Within the plantation plots, thinning led to increased microbial litter-derived C incorporation during dry soil conditions but heavy rains during wet phases resulted in anoxic conditions, inhibiting SMB. The intensity of thinning (Intense Promotion vs. Conversion) did not show any significant effect on litter-derived microbial C incorporation. Furthermore, our experiment confirmed that in the Munessa ecosystem, soil humidity is the main influencing factor, resulting in significantly different nutrient turnover during dry and wet soil conditions. Our findings suggest that fast growing tree plantations established on Mollic Nitisols in the Munessa forest not necessarily contribute to a decline of soil sustainability with respect to short-term (microbial) C and N turnover.

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C and N stable isotopes as possible indicators of food-web changes related to river restoration

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Since “you are what you eat (plus a few ‰)” (DeNiro & Epstein 1976), many ecological studies nowadays use stabele isotopes of carbon and nitrogen to investigate the resource base, to establish feeding links between organisms and to construct food webs. In this study, carried out within the EU-funded project REFORM (Restoring rivers FOR effective catchment Management, http://reformrivers.eu/), we applied stable isotope analysis of C and N in context of river restoration to quantitatively characterize patterns in trophic structure. We sampled different components of food webs on paired restored and non-restored reaches of rivers in 20 different catchments throughout Europe. Amongst others, the sampling contained elements of the resource base (particulate organic matter, aquatic and riparian plant material, periphyton) and macroinvertebrates comprising the major taxa within different functional feeding groups. Based on $\delta^{13}C$ and $\delta^{15}N$-ratios we then (pairwise) compared (1) the total extent of the community members in $\delta^{13}C$ - $\delta^{15}N$ bi-plot-space representing the total extent of trophic diversity within a food web, (2) the C- range characterizing the diversity of sources and (3) the N-range identifying the trophic length. In most cases restoration increased the diversity of sources as indicated by higher ranges in macroinvertebrates $\delta^{13}C$. Here, methods and first results of this study are presented.

DeNiro, M.J. & Epstein, S. (1976) You are what you eta (plus a few ‰): the carbon isotope cycle in food chains. Geol. Soc. Am. Abs. Prog. 8, 834-835

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