The 13th Austrian Stable Isotope User Group Meeting

21ST AND 22ND NOVEMBER 2014

BOOK OF ABSTRACTS

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Conference Schedule

	Friday, November 21
12:00	*Lunch*
13:30-13:40	Opening
13:40-14:15	Vasileois Gkinis (keynote): From magnets to light. A transition in isotope glaciology
14:15-14:35	Marc Luetscher, Harald Sodemann, Christoph Spötl: Orographic palaeo-rainout recorded in alpine speleothems
14:35-14:55	Juliane Meyer, Claudia Wrozyna, Albrecht Leis, Werner E. Piller: Stable oxygen and carbon isotopic composition of Peace River waters (Florida, USA) and its impact on shell chemistry of Cyprideis salebrosa (Ostracoda)
14:55-15:15	Flora Brocza, Micha Horacek, Leopold Krystyn: Marine C- and S-cycle perturbations at the Triassic-Jurassic boundary and in the Early Jurassic
15:15-15:20	Speed posters
15:20-15:50	*Coffee break*
15:50-16:25	Matthias Cuntz et al. (keynote): Separating the contributions of vegetation and soil to evapotranspiration using stable isotopes
16:25-16:45	F. Humer, Heike Brielmann, et al.: Identification of anthropogenic impacts on ground- and surface water combining nitrate stable isotopes and a new multi parameter test
16:45-17:05	Julieta Griboff, Magdalena V. Monferrán, Micha Horacek, Daniel A.Wunderlin: Use of carbon and nitrogen isotopes as chemical markers to distinguish regions with different degree and type of contamination in Argentinean lakes
17:05-17:25	Johannes Oehm, Andreas Zitek, Johanna Irrgeher, Anastassiya Tchaikovsky, Bettina Thalinger, Thomas Prohaska, Michael Traugott: Determining the feeding range of cormorants by elemental and isotopic provenancing of prey fish
17:25-18:30	Posters
18:30	*Conference dinner*

Saturday, November 22

9:00-9:35	Ansgar Kahmen (keynote): From paleohydrology to ecophysiology: New applications using hydrogen isotopes in plant derived organic compounds
9:35-9:55	Jasper Bloemen, Kathy Steppe: Tracing respired CO2 transport in the xylem at leaf, branch and tree level using carbon isotopes
9:55-10:15	Roland Hasibeder, Lucia Fuchslueger, Andreas Richter, Michael Bahn: Summer drought alters carbon allocation to roots and root respiration in mountain grassland
10:15-10:35	Harald Hertle, Andreas Hilkert, Dieter Juchelka: Next Generation of GC-IRMS Solutions
10:35-11:00	*Coffee break & group photo*
11:00-11:35	Tobias Kluge (keynote): Clumped isotopes and isotope geochemistry - new insights, significance and limitations
11:35-11:55	Filip Volders, E. Federherr, C. Cerli, K. Kalbitz, R. Panetta: Novel tool for simultaneous carbon and nitrogen stable isotope analyses in aqueous samples
11:55-12:15	Andrea Watzinger, P. Kinner, T.G. Reichenauer: Removal of diesel hydrocarbons by constructed wetlands – 13C labelling experiment to reveal degradation
12:15-12:35	Martin Dietzel, Albrecht Leis, et al.: Oxygen isotope anomaly of nitrate in palo waters indicates atmospheric origin and provides insights into paleo environmental conditions
12:35	*Closing, lunch, departure*

Posters:

Michael Bahn et al.: Responses of belowground carbon allocation dynamics to extended shading in mountain grassland

Kathrin Karer, Stefan Wyhlidal, Dieter Rank: A 50 years' isotope record of Lake Neusiedl and adjacent precipitation water - its relevance for hydrological, climatological and environmental research

Gabriella Koltai, Christoph Spötl, Hai Cheng: Late glacial to Holocene climate variations recorded by calcite-aragonite speleothems of the Vinschgau, Südtirol: first results of a multi-proxy approach

Sylvain Richoz, Leopold Krystyn: Late Triassic carbon cycle stability during biotic extinction and origination

Katrin Teufl, Bernd Degen, Micha Horacek: Control of declared origin of tropical timber: Application of stable isotopes

Yuri Dublyansky, Christoph Spötl: Isotopes in Holocene precipitation across Eurasia: The speleothem record

Abstracts

(alphabetic order)

Responses of belowground carbon allocation dynamics to extended shading in mountain grassland

Michael Bahn (1), Fernando A. Lattanzi (2), Roland Hasibeder (1), Birgit Wild (3), Marianne Koranda (3), Valentina Danese (1), Nicolas Brüggemann (4), Michael Schmitt (1), Rolf Siegwolf (5), Andreas Richter (3)

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Carbon (C) allocation strongly influences plant and soil processes. Short-term C allocation dynamics in ecosystems and their responses to environmental changes are still poorly understood. Using in situ $^{13}CO_2$ pulse labeling, we studied the effects of one week of shading on the transfer of recent photoassimilates between sugars and starch of above-and belowground plant organs and to soil microbial communities of a mountain meadow. C allocation to roots and microbial communities was rapid. Shading strongly reduced sucrose and starch concentrations in shoots, but not roots, and affected tracer dynamics in sucrose and starch of shoots, but not roots: recent C was slowly incorporated into root starch irrespective of the shading treatment. Shading reduced leaf respiration more strongly than root respiration. It caused no reduction in the amount of ^{13}C incorporated into fungi and gram-negative bacteria, but increased its residence time. These findings suggest that, under interrupted C supply, belowground C allocation (as reflected by the amount of tracer allocated to root starch, soil microbial communities and belowground respiration) was maintained at the expense of aboveground C status, and that C source strength may affect the turnover of recent plant-derived C in soil microbial communities.

Reference: Bahn et al. 2013. New Phytologist 198: 116–126

Tracing respired CO_2 transport in the xylem at leaf, branch and tree level using carbon isotopes

Jasper Bloemen (*), Kathy Steppe

Laboratory of Plant Ecology, Department of Applied Ecology and Environmental Biology, Faculty of Bioscience Engineering, Ghent University, Ghent, Belgium
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Stable-isotope-labeling techniques have successfully been applied in the context of tree carbon cycling in order to trace the flow of photosynthates from leaves to sinks via the phloem. For instance, pulse- labeling of the tree canopy and analyzing soil CO_2 efflux have revealed the fast coupling between leaf-level and belowground processes. However, important knowledge gaps still exist on carbon cycling in trees regarding the upward transfer of CO_2 with the transpiration stream. In trees, respired CO_2 can dissolve in xylem water and diffuse to the atmosphere or be assimilated within tissues remote from the site of respiration. This internal carbon flux compels us to rethink long-standing assumptions regarding tree physiology in which the use of stable isotopes might lead the way.

In this study, we summarize the findings from our recent studies at leaf, branch and tree level to illustrate the use of dissolved $^{13}CO_2$ and $^{11}CO_2$ as a tracer for xylem-transported CO_2 within trees. An isotope label was dissolved in water and either infused in the stem base of poplar trees (*Populus deltoides* Bartr. Ex. Marsh) in the field or supplied at detached poplar branches and leaves under controlled conditions, allowing manipulation of the transpiration rate by altering the vapor pressure deficit (VPD). The experiment on the field-grown trees showed that the label was transported from the base of the stem throughout the tree and assimilated in the different woody and leaf tissues. The largest fraction of the label (up to 94%) diffused to the atmosphere during upward transport. In the branch and the leaf experiments, higher tissue enrichment was observed under high VPD compared to low VPD, illustrating the importance of transpiration rate on assimilation of xylem-transported CO_2. The amount of xylem-transported CO_2 assimilated in the different tissues was low compared to atmospheric fixation (up to 1.9%), however this “recycling” of respired CO_2 might gain importance at higher VPD levels when atmospheric CO_2 assimilation might be limited and transpiration rate maximizes to a plateau level. Our findings indicate that labeling the transpiration stream with carbon isotopes can provide novel insights on the impact of xylem-transported CO_2 on tree assimilation and respiration.

Identification of anthropogenic impacts on ground- and surface water combining nitrate stable isotopes and a new multi parameter test

Humer F. (1), Brielmann, H. (1), H. Kralik M. (1), Grath J. (1), Clara M. (1), Weiß S. (1), Kulcsar S. (1), Scharf S. (1), Voerkelius S. (2)

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Diffuse agricultural emissions, leakage from sewer lines, septic tanks or wastewater treatment plants are potential sources of elevated nitrogen concentrations in ground- and surface water. Appropriate measures to safeguard ground- and drinking water resources require the identification of the source and magnitude of pollution.

While nitrogen and oxygen isotopes in nitrate are widely applied to differentiate potential sources of nitrate in groundwater such as precipitation, chemical fertilisers and manure or sewage water, without any additional tracers the source distinction of nitrate from manure or sewage water is still difficult. Even the application of boron isotopes can in some cases not avoid ambiguous interpretation. Therefore the Environment Agency Austria developed a new multi parametrical indicator test to allow the identification and quantification of pollution by domestic sewage water. The test analyses 8 substances well known to occur in sewage water: acesulfame and sucralose (two artificial, calorie-free sweeteners), benzotriazole and tolyltriazole (two industrial chemicals/corrosion inhibitors), metoprolol, sotalol, carbamazepine and the metabolite 10,11-Dihydro-10,11-dihydroxycarbamazepine (pharmaceuticals) [Humer et al., 2013]. These substances are polar and degradation in the aquatic system by microbiological processes is not documented. These 8 substances do not occur naturally which make them ideal tracers. The test is able to unveil about 0.1 % of wastewater in the analysed water sample.

In two areas characterized by intensive agricultural activities (Marchfeld and Wulkatal) ground- and surface waters with a different range of nitrate concentrations have been analysed for nitrogen and oxygen isotopes in nitrate to identify the nitrate source. To further differentiate between manure and sewage water the newly developed multi parametrical indicator test was successfully applied. In the Marchfeld region, some of the selected groundwater wells show a sewage influence of up to 1-3 %. In the Wulkatal area, the Wulka River itself is strongly impacted by sewage (about 25 %), while the investigated groundwater show negligible impacts of municipal sewage. In summary, the results allow a reasonable quantification of nitrate sources from different types of fertilizers as well as sewage water contributions close to villages and in wells recharged by bank filtration.

Reference: Humer et al. EGU2013-5332

Marine C- and S-cycle perturbations at the Triassic-Jurassic boundary and in the Early Jurassic

Flora Brocza (1,2), Micha Horacek (1,3), Leopold Krystyn (4)

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(2) Josephinum Research, Rottenhauser Straße 1, 3250 Wieselburg; (3) HBLFA Francisco-Josephinum, BLT Wieselburg, Rottenhauser Straße 1, 3250 Wieselburg; (4) Institute of Paleontology, University of Vienna, Althanstraße 14, 1090 Vienna.

Marine sediments accumulate records of the isotopic composition of the ocean. Their carbonate $\delta^{13}C_{carb}$ and organic matter $\delta^{13}C_{org}$ can give information as about changes in the ocean circulation and bioproduction, while marine $\delta^{34}S$ is mainly influenced by ocean circulation and the marine sulfur concentration.

We are currently investigating $\delta^{13}C$ and $\delta^{34}S$ isotopes of two sections spanning the late Triassic to Early Jurassic. This interval contains the Triassic-Jurassic boundary (TJB; 201,3 Ma), one of the five largest extinction events in Earth's history. Our study aims to complement the scarce sulfur isotope data on the TJB and Early Jurassic and to offer insight into observed carbon and sulfur cycle perturbations during this period.

The Arroyo Malo section is located in the Neuquén Basin (central-western Argentina), deposited on the Western margin of Pangea, belonging to the Panthalassa Ocean. The Canj section lies in the Montenegrin Budva Zone, deposited in the Tethys Ocean. While a concomitant negative $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ excursion at the TJB has been documented in multiple sections, the continuation of the curve into the early Jurassic has been investigated only by few research groups. They report positive $\delta^{13}C_{org}$ (but no systematic C_{carb}) excursions in the Hettangian stage of the Jurassic but a satisfying correlation has not been achieved globally, yet. As for sulfur, so far only Williford et al. 2009 report data from the latest Triassic to the Early Jurassic. They present concordant positive excursions of C- and S- isotopes, which they interpret as global anoxic conditions with a strongly reduced marine sulfur reservoir.

Our study of the Canj section will significantly extend the existing $\delta^{13}C$ record. The S-isotope investigation of the sections will add a new dataset to compare to the Williford data. Due to the different paleogeographic locations of this study's sections, the resulting $\delta^{34}S$ and $\delta^{13}C$ curves will give important clues on the global correlativity of Early Jurassic S-curves and on the primary or diagenetic origin of the signals.

We thus contribute two detailed datasets from different paleogeographic settings to improve the scarce sulfur data around the TJB and Early Jurassic and add new insight into the complex matter of reconstructing the paleo-ecological aftermath of the TJB in the long-run.

Separating the contributions of vegetation and soil to evapotranspiration using stable isotopes

Matthias Cuntz (1), Maren Dubbert (2), Arndt Piayda (1), Alexandra Correia (3), Filipe Costa e Silva (3), Olaf Kolle (4), Cristina Maguás (5), Alexander Mosena (2), João S Pereira (3), Corinna Rebmann (1), Christiane Werner (2)

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Semi-arid ecosystems contribute about 40% to global productivity, although water-availability limits carbon uptake. Evapotranspiration accounts there for up to 95% of water loss of the ecosystem. Thus functional understanding of evapotranspiration is key knowledge in forest management under future climate change.

Water isotopes trace water through the ecosystems. They are used to partition evapotranspiration *ET* into its components evaporation *E* and transpiration *T*. The method is, however, sensitive to the knowledge of the isotopic composition of water at the evaporating sites.

Here we present observations from a Portuguese bi-layered woodland with widely spaced cork-oak trees and a herbaceous understorey layer. Water fluxes and their isotopic compositions were measured on bare soil and vegetated plots with a transparent through-flow chamber and a water isotope laser. Soil moisture and temperature were measured in several depths and soil samples were taken for soil water isotope analysis. Based on these observations, we review current strategies of *ET* partitioning. We highlight pitfalls and show uncertainty analyses for the different approaches. We show that the isotopic composition of evaporation is very sensitive to sampling strategy but is described well by a steady-state formulation (Dubbert et al. 2013). The isotopic composition of transpiration, on the other hand, is not in steady state, most of the time (Dubbert et al. 2014a). We demonstrate the consequences for partitioning of ET by current simplifications.

Analysis of the water dynamics of the woodland (Piayda et al. 2014) showed that herbaceous understorey transpiration was always larger than soil evaporation *E*. Both fluxes stopped almost completely in summer, leaving transpiration *T* to contribute by more than 90% to *ET* (Dubbert et al. 2014b). The herbaceous understorey layer did, surprisingly, increase soil infiltration due to less runoff on vegetated ground (Dubbert et al. 2014c). The layer serves thus two purposes: 1. The legumes add nitrogen to the ecosystem that gets also used by the oak trees (Dubbert et al. 2014b). 2. The understorey layer helps infiltration of precipitation. It appears that the understorey layer in this cork-oak stand has an overall positive effect on the ecosystem, both in terms of nutrient and water availability.

Isotopes in Holocene precipitation across Eurasia: The speleothem record

Yuri Dublyansky, Christoph Spötl

Institute of Geology, Innsbruck University

Fluid inclusions are micron-sized vacuoles which form during the growth of speleothems (stalagmites) and trap the contemporaneous drip water. Stalagmites, therefore, represent natural “samplers” that collect and preserve samples of paleo-precipitation over millennia. Recent methodological breakthroughs allow analyzing these tiny samples of water and, given the superior dating possibilities of speleothems (using U-Th), both accurate and precise chronologies of paleo-precipitation can be obtained.

The aim of a recently launched project is to trace the evolution of stable isotopic composition of Holocene precipitation along a 8,500 km-long transect. The transect will extend, as a narrow band (45°-55°N), from the Atlantic coast of western Europe (9°W) to as far as eastern Siberia (105°E). It will follow the prevailing direction of moisture transport from the Atlantic source. The isotopic composition of precipitation along the transect is controlled primarily by continental rainout and recycling effects, as well as temperature. Our working hypotheses are that similar forcing mechanisms were operational during the Holocene, and that the changing parameters of the forcing, on the millennial time scale, can be expressed as changes in the stable isotope gradient along the transect. The questions to be addressed include: did the large-scale pattern of moisture transport across Eurasia change during the course of the Holocene? What were the forcing factors of this large-scale moisture transport? Was Holocene climate change synchronous across northern Eurasia?

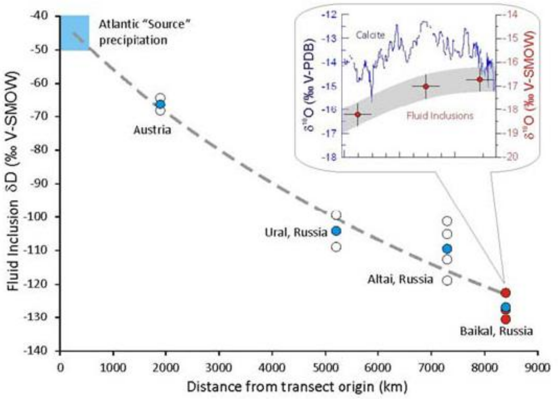

Fig. 1. The δD values of water trapped in Holocene stalagmites at four cave sites along the transect. Note a strong longitudinal gradient, similar to that observed in modern-day precipitation. Insert shows δD values compared with δ^{18}O record of the host calcite.

First data obtained for this project indicate that (1) Holocene δD and δ^{18}O values show a first-order continent-scale longitudinal trend (Fig. 1), and (2) the isotopes of fluid inclusion water appear to show some systematic variations within the Holocene (Fig. 1 insert).

This project is funded by Austrian Science Fund (FWF project P257160).

From magnets to light. A transition in isotope glaciology

Vasileios Gkinis

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The ratios of the stable isotopologues of polar precipitation have been for decades one of the most fundamental tools in paleoclimatology. Precise and accurate measurements were traditionally carried out using mass spectrometric techniques that required conversion of the water sample to some other compound as for example CO_2, CO or H_2. Sampling was carried out in a discrete fashion, resulting in a trade-off between the achievable resolution and the analytical throughput.

In this talk I will describe how in the recent years the field of ice core science has seen a vast transition in the way ice core isotopic analysis is performed. The adoption of commercially available IR spectrometers coupled to custom made continuous melting systems has helped in fully exploiting the true resolution of polar ice cores while in the same time improving the achievable sample throughput. Analytical systems of high precision and accuracy can now be deployed in the field while the achievable resolution of the measured time series allows for the development of new proxies based on the spectral analysis of the isotopic signal. The limits to what is possible are expanded even further with the addition of $H_2{}^{17}O$ and O^{17}excess that previously required a very challenging analytical method based on water fluorination and dual inlet mass spectrometry. I will discuss the technical aspects of the O^{17}excess measurement with the new 2140 Picarro analyzer and hopefully initiate a discussion on the SMOW-SLAP calibration issues involved in the measurement of $H_2{}^{17}O$ and O^{17}excess.

Use of carbon and nitrogen isotopes as chemical markers to distinguish regions with different degree and type of contamination in Argentinean lakes

Julieta Griboff (1), Magdalena V. Monferrán (1), Micha Horacek (2), Daniel A. Wunderlin (1)

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Stable isotopes have been used effectively in ecological studies to trace the impact of different components, like potential pollutants, on ecosystems, as well as to trace food webs. Coastal environments are often exposed to different anthropogenic contaminants that can cause evident differences in coastal ecosystems. For this reason the use of various organisms as an indicator offers an important ecological study (Rozic et al., 2014).

In this study, we measure $\delta^{13}C$ and $\delta^{15}N$ values in various organisms (from primary producers to upper consumers) to understand the influence of the different anthropogenic activities on the environment and the possibility to distinguish regions with different degree and type of contamination, as well as areas of greater or lesser risk to food production.

Study site samplings were carried out during wet season (April 2014) after a massive rain event in three lakes in Córdoba, Argentina: San Roque, Los Molinos and Río Tercero lakes. San Roque Lake supplies drinking water to Córdoba, and is also intended for recreational uses. It is surrounded by cities and settlements which are not fully connected to public sewage system. Los Molinos Lake provides water to the Southeast of the city of Córdoba and is used for recreational activities and irrigation. In the surrounding agriculture dominantly corn and sorghum is produced. Río Tercero lake is the largest artificial reservoir in the province of Córdoba and used for water supply and industrial activities, as providing cooling water for a nuclear power plant.

We collected water, sediment, plankton, shrimp (*Palaemonetes argentinus*) and fish (*Odontesthes bonariensis*) from each lake. Stable isotope analysis was performed an Isotope Ratio Mass Spectrometer, connected with an elemental analyzer (both Thermo Fisher Scientific). Results showed distinct differences in $\delta^{13}C$ and $\delta^{15}N$ between the investigated lakes that also identify lakes exposed to anthropogenic sewage. San Roque lake showed the highest $\delta^{15}N$ values, for all the samples, indicating the most prominent influence of sewage on the lake ecology. However, not all results can be unequivocally interpreted to date and repetition of sampling and measurements has to be performed to identify any possible influence of the rain event.

Summer drought alters carbon allocation to roots and root respiration in mountain grassland

Roland Hasibeder (1), Lucia Fuchslueger (2), Andreas Richter (2), Michael Bahn (1)

(1) Institute of Ecology, University of Innsbruck, Innsbruck, Austria; (2) Division of Terrestrial Ecosystem Research, Department of Chemical Ecology and Ecosystem Research, University of Vienna, Vienna, Austria

Meteorological extreme events like summer droughts are expected to occur more frequently in a future climate and exert a major impact on the carbon (C) balance of terrestrial ecosystems. Drought impairs the activity of C source (photosynthesis) and sinks (growth, respiration, storage) as well as C partitioning between aboveground and belowground plant organs. To date, little is known about effects of drought on the allocation dynamics of recently assimilated C in intact ecosystems. Combining experimental rain exclusion with $^{13}CO_2$ pulse labelling in a mountain meadow in the Austrian Central Alps, we investigated how summer drought impacts the translocation of fresh photosynthates to roots and the partitioning of this C input among different root carbohydrate pools and root respiration. Severe soil drying decreased the ecosystem C uptake and the amounts and velocity of C allocated to the root system. However, the proportion of C translocated belowground (relative to C uptake) remained unaffected by drought. Reduced root respiration, reflecting reduced C demand under drought, was increasingly sustained by C reserves, whilst recent assimilates were preferentially allocated to root storage and an enlarged pool of osmotically active carbohydrates. Overall, these results indicate that under drought conditions the usage of recent assimilated C is shifted from metabolic activity to osmotic adjustment and storage compounds.

Next Generation of GC-IRMS Solutions

Harald Hertle (1), Andreas Hilkert (2), Dieter Juchelka (2)

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

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

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

More complex chromatograms require on-line verification of the molecular structure of the individual compounds analyzed by GC-IRMS. The new GC IsoLink II solution integrates the hyphenation with a quadrupole MS as a standard option for GC/MS/IRMS applications.

We will discuss in this presentation modern GC-IRMS systems with application examples on biomarkers and other examples linked to improvements in sample introduction techniques, GC- and reactor technology.

From paleohydrology to ecophysiology: New applications using hydrogen isotopes in plant derived organic compounds

Ansgar Kahmen

Department of Environmental Sciences – Botany, University of Basel, Switzerland

In contrast to the stable C, N and O isotope composition of plant materials, the hydrogen isotope composition of plants has not yet been established as tool in modern ecological or biogeochemical research. With the development of new analytical instruments that allow the hydrogen isotope analysis of selected plant compounds, there has however been growing interest to explore the power of hydrogen isotopes as tools for ecological and biogeochemical research. In my talk I will highlight recent work from my lab that addresses the key environmental and physiological drivers that influence the hydrogen isotope composition in terrestrial plants. I will further show examples how the hydrogen isotope signals of defined plant compounds can be applied as new and powerful tool in ecological, biogeochemical and paleohydrological research.

A 50 years' isotope record of Lake Neusiedl and adjacent precipitation water - its relevance for hydrological, climatological and environmental research

Kathrin Karer (1), Stefan Wyhlidal (1), Dieter Rank (2)

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Lake Neusiedl, the largest lake in Austria, is especially sensitive to short-term climatic variations due to its extreme shallowness. Hence the lake is a representative for a shallow steppe-lake. The lake is of great importance for the microclimatic environment for agricultural use (e.g. winegrowing, market gardening) and for nature conservation areas (e.g. the Austrian–Hungarian national park–Nationalpark Neusiedler See Seewinkel).

The isotope ratios of hydrogen and oxygen in Lake Neusiedl water have been measured since 1967 (^{3}H, stable isotopes ^{2}H and ^{18}O since 1976). This is probably one of the worldwide longest isotope records of a lake. Precipitation contributes about 80 % to the recharge of the lake, surface water inflow about 20 %, groundwater inflow is negligible (below 2 %). From the ^{2}H-^{18}O relation ("d-excess") can be concluded that the isotopic composition in the Lake Neusiedl water clearly reflects evaporation effects with a much smaller slope compared to the local meteoric water line of the precipitation water from Podersdorf (Fig. 1).

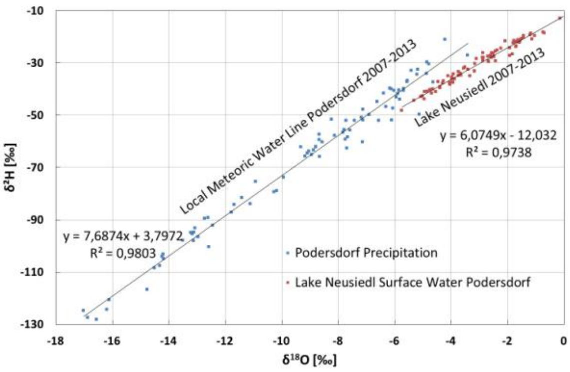

Fig. 1: Local meteoric water line of Podersdorf (LMW-P) and Lake Neusiedl water line (LNWL)

The isotope time series of the precipitation station Podersdorf (1965-2014) show a significant long-term trend. The 10-year running mean of Podersdorf indicates a pronounced increase in δ^{18}O of about 1 ‰. The increasing δ^{18}O values during the observation period (1973-2014) can mainly be attributed to an increase in mean air temperature and can be used as an additional indicator of climate change.

Since 1952, the ^{3}H content of precipitation and consequently also in the Lake Neusiedl water has been dominated by the ^{3}H releases of nuclear weapon tests. As a consequence the ^{3}H concentration of precipitation- and lake water increased by about a factor 1000 in 1963 (maximum) followed by a continuous decrease. During the last two decades ^{3}H values have approached "pre-bomb" levels again. The main outcome of the isotopic investigations at Lake Neusiedl is that groundwater inflow to the lake is negligible and that the mean residence time of lake water is about one year.

Clumped isotopes and isotope geochemistry - new insights, significance and limitations

Tobias Kluge

Institute of Environmental Physics, Heidelberg University, Im Neuenheimer Feld 229, 69120 Heidelberg, Germany, tobias.kluge@iup.uni-heidelberg.de

The study of multiply-substituted isotopologues is a relatively young branch of isotope geochemistry and only emerged a decade ago. First applications focused on the analysis of atmospheric CO_2 (e.g., Affek and Eiler, 2006), but encompasses today a wide range of carbonates (Eiler et al., 2011) and already expands into the field of alkanes (methane, ethane; Clog et al., 2013; Stolper et al., 2014).

Multiply-substituted isotopologues contain two or more rare isotopes and are therefore colloquially termed 'clumped isotopes'. The best investigated example for multiply-substituted isotopologues is $^{13}C^{18}O^{16}O$ in CO_2 gas (either in gaseous samples or from phosphoric acid digestion of carbonates). The abundance of multiply-substituted isotopologues is governed by thermodynamic principles and, in general, increases with decreasing temperature (Wang et al., 2004).

A significant advantage of multiply-substituted isotopologues compared to traditional geothermometers such as carbonate $\delta^{18}O$ is that the Δ value (difference to the stochastic distribution; $\Delta47$ for CO_2) is independent of the solution $\delta^{18}O$ and $\delta^{13}C$ value. Benefitting from this property the solution $\delta^{18}O$ value can be reconstructed from the carbonate $\delta^{18}O$ value using the temperature information provided by $\Delta47$ measurements in CO_2 produced from carbonates.

Carbonate clumped isotopes (dealing with the abundance of $Ca^{13}C^{18}O^{16}O$; Schauble et al., 2006) are now widely applied to many geosciences questions, most prominently for thermometry (e.g., Came et al., 2007; Finnegan et al., 2011) and the investigation of the fluid source that was involved in the formation of specific carbonate phases (e.g., Bristow et al., 2011; Budd et al., 2013; Dale et al., 2014). Thermometry applications include paleoclimate studies, paleoaltimetry and the investigation of the thermal history of certain geological units. Beyond thermometry, carbonate clumped isotope measurements can be used to assess if dissolved inorganic carbon (DIC) was at isotopic equilibrium prior to mineral formation (Kluge et al., 2014). Case examples are stalagmites which exhibit measurable non-equilibrium $\Delta47$ values (e.g., Affek et al., 2008; Dareon et al., 2011; Kluge and Affek, 2012).

The broader application of clumped isotopes is affected by several limiting effects. The $\Delta47$ value of sub-surface precipitates that involved solutions with pH values differing from the typical range of laboratory calibrations ($7<pH<9$) may be influenced by DIC speciation during rapid mineral formation (Hill et al., 2014). Measurements of vent travertine samples from various slightly acidic hydrothermal springs confirmed a small positive offset (with a maximum of +0.04‰ relative to the laboratory calibration). Salinity may further affect Δ47 values of marine samples or precipitates from subsurface brines via changes in the DIC speciation (Hill et al., 2014) or by an ionic effect that leads to isotope partitioning between 'free' water molecules and 'bound' water in the hydration sphere of cations. Laboratory experiments show that the ionic effect is negligible for Na, Cl and Mg ions, but could have a limited influence if the solution contains higher Ca concentrations (on the order of +0.03‰ per mol Ca/litre). Ancient fossils (ages on the order of 100 Ma) may have been altered by diagenesis and require intensive investigation prior to meaningful (clumped) isotope studies. Bond re-ordering could additionally play a role if minerals were subject to elevated temperatures exceeding 150°C during burial (e.g., Dennis and Schrag, 2010; Passey and Henkes, 2012).

Further complicating are difficulties in unifying existing experimental and empirical Δ47 calibration curves of different laboratories and in assessing the causes for observed deviations. The acid digestion temperature is thought to have a significant influence as the phosphoric acid reaction at 25°C and 90°C yields two significantly different calibration lines (Fernandez et al., 2014). Importantly, the calibration lines are generally consistent amongst the laboratories that use the same acid reaction temperature. Inter-calibration studies are currently performed to determine potential factors causing the divergence of the calibration lines.

In summary, complicating effects seem to be limited and restricted to a few specific systems. Apart from mentioned methodological constraints, carbonate clumped isotopes are able to provide new and unique insights into many environmental and geosciences questions, in particular with regard to thermometry and fluid $\delta^{18}O$ reconstruction.

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late glacial to Holocene climate variations recorded by calcite-aragonite speleothems of the Vinschgau, Südtirol: First results of a multi-proxy approach

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The Vinschgau is an inneralpine valley in the Southern Alps (Ötztal Alps). The area is characterised by anomalously low precipitation, but local climate archives (e.g. debris-flow fans, speleothems) suggest that the Holocene and the Late Glacial were characterised by periods of a distinctly more humid climate.

The region is built up by metamorphic rocks characterised by a high degree of tectonic deformation. Speleothems occur along the South-facing slope of this valley, although carbonate rocks are very rare and karst features are not known in this area. The speleothems in these crystalline rocks formed as a result of a water-rock interaction combined with evaporation (Spötl et al., 2002).

Inactive calcite-aragonite flowstones were analysed by various petrographic methods in order to identify characteristic fabrics and evidence of mineralogical alteration (e.g. replacement of aragonite by calcite). In addition to stable carbon and oxygen isotope measurements, high-resolution U-series dating was performed.

The stable isotope analyses of most samples show covariation between $\delta^{13}C$ and $\delta^{18}O$, implying kinetic isotope fractionation during carbonate precipitation. Aragonite layers are characterised by elevated $\delta^{13}C$ and $\delta^{18}O$ values. The presence of aragonite is regarded as an indicator of reduced recharge of the fractured aquifer, i.e. a dry climate. $\delta^{18}O$ of both polymorphs show significant (e.g. 2 ‰) variability, suggesting changing hydrological conditions over time. Although such conditions may reflect variations in climate, local factors, such as strong evaporation, can amplify these primary climate signals. Flowstone deposition occurred intermittently between ca. 14.1±0.1 ka and 0.4±0.01 ka BP. By using a multi-proxy approach, the study of these speleothems can open the door to reconstruct changes in the hydrological balance and precipitation for this inneralpine area for the last 14 ka.

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Oxygen isotope anomaly of nitrate in paleo waters indicates atmospheric origin and provides insights into paleo environmental conditions

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Saharan paleo groundwater from Hasouna well field in Libya contains up to 1.8 mM of nitrate with a still disputed origin. In the present study we used an integrated hydrogeochemical and isotopic approach to trace the origin of NO_3 and to reconstruct the paleo environmental conditions during the recharge of Saharan groundwater. The composition of water isotopes accounts for recharge under rather cool and humid paleo climate conditions without significant evaporation. Additionally we applied the outstanding feature of $\delta^{17}O_{NO3}$ values to trace atmospheric NO_3 as the ^{17}O-excess of dissolved NO_3 is not being affected by terrestrial fractionation processes (MDF). The ^{17}O anomaly is caused by mass independent oxygen isotope fractionation via photochemical reactions and thus tracing atmospheric NO_3. $\delta^{17}O_{NO3}$ values clearly indicate up to 20 mol% of NO_3 originated from the Earth`s atmosphere besides microbial NO_3. Here we show that a ^{17}O anomaly in NO_3 ($\delta^{17}O_{NO3} = \delta^{17}O_{NO3} - 0.52\ \delta^{18}O_{NO3}$) is well preserved in this old Saharan groundwater reservoir. This verifies that the oxygen isotope anomaly of nitrate in paleo waters survived up to thousands of years and can still be used to estimate the $NO_{3,atm}$ proportion of total dissolved NO_3 during ancient recharge. Moreover the isotope signals of nitrate indicate flood events from periodic heavy precipitation with rather instantaneous infiltration, which is documented by high $NO_{3,atm}$ proportions at elevated NO_3 concentrations.

Orographic palaeo-rainout recorded in alpine speleothems

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Stable isotopes ($\delta^{18}O$, $\delta^{2}H$) in meteoric precipitation are increasingly used as natural tracers of atmospheric circulation. Whilst data from the Global Network of Isotopes in Precipitation (GNIP) provide valuable insights into spatial and temporal patterns during the last 40 years or so, reconstructions of long-term climate changes are primarily relying on natural archives, such as polar ice or, more recently, speleothems (i.e. secondary carbonate deposits in caves).

Here we use a speleothem record from the Last Glacial Maximum, to evaluate processes involved in the fractionation of ^{18}O some 30,000 years ago. In particular, we demonstrate that this climate archive not only recorded a regional air temperature signal but also responded sensitively to a change in the main moisture transport trajectories. We suggest that periods of lower $\delta^{18}O$ values were preferentially associated with enhanced orographic rainout due to a dominant meridional moisture transport (as opposed to today´s predominantly zonal transport). These results are consistent with independent geomorphologic evidence and argue for a non-uniform ice build-up in the Alps during the last ice age.

Stable oxygen and carbon isotopic composition of Peace River waters (Florida, USA) and its impact on shell chemistry of Cyprideis salebrosa (Ostracoda)

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Isotopic measurements have become a standard method in palaeontology to reconstruct palaeoenvironmental conditions from biogenic carbonates. This application depends on the knowledge of recent processes and controlling factors during the formation of the biomineral. Due to the fast calcification of their shell (hours to days), ostracods can provide a snapshot of the isotopic composition of their host water. However, calibration with modern water is often missing to apply the full potential of this method to palaeontology.

We used water samples from Peace River (Florida) and its surrounding area from November 2013 and August 2014 to analyse their isotopic composition. The total range of stable deuterium, oxygen and carbon isotopes covers -6.4 to 13.2 ‰, -1.86 to 2.37 ‰ and -14.55 to -3.63 ‰, respectively. Longer residence time is the major parameter leading to higher oxygen isotopic values and habitat type reflects the scatter of the carbon isotopes.

Surface sediment samples from a secondary branch of the Peace River taken in summer and winter provide modern ostracod material. Shells of the species *Cyprideis salebrosa* van den Bold were used to determine their oxygen and carbon isotopic composition. The stable isotopic values of *C. salebrosa* range from -3.89 to 0.47 ‰ for $\delta^{18}O_{Ostracod}$ and from -10.71 to -8.27 ‰ for $\delta^{13}C_{Ostracod}$, respectively. The $\delta^{13}C$ values have a higher range in winter and the $\delta^{18}O$ values in summer. *C. salebrosa* shows a positive vital offset in comparison to its host water of +1.14 ±0.99 ‰ in winter and +2.63 ‰ ±0.56 in summer for the oxygen isotopes. In general, there is a shift to more negative $\delta^{18}O$ values from the winter to summer data, showing the temperature dependence on the shell composition.

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Determining the feeding range of cormorants by elemental and isotopic provenancing of prey fish

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Great Cormorants (*Phalacrocorax carbo sinensis*) are fish-eating birds inhabiting freshwaters of the Alpine foreland. Their perennial predation pressure on fish stocks in European freshwaters is heavily disputed and therefore a sound knowledge of cormorant feeding ecology is needed to estimate their impact on fish populations. One aspect of the cormorant feeding ecology, which has not been studied yet, is from which water bodies these birds take their prey to determine their foraging range. In this study we aim to determine the birds’ foraging range using prey remains found in the cormorants’ pellets, which contain indigestible prey hardparts, in a colony at lake Chiemsee (Bavaria, Germany). We make use of water body-specific micro-chemical signatures incorporated in these fish hardparts (particularly fish ear-stones) to provenance the fish prey of cormorants. The differences in water chemistry between potential feeding grounds around lake Chiemsee and their reflection in the fish’ ear-stones were investigated by establishing a reference database for water and fish. Elemental patterns and $^{87}Sr/^{86}Sr$ isotope ratio were measured via inductively coupled plasma mass spectrometry (ICP-MS). This database allows allocating prey hard parts out of the birds’ pellets to their origin water bodies and, consequently, to determine the birds’ foraging range.

Late Triassic carbon cycle stability during biotic extinction and origination

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A key climate-relevant question is how the uptake of increased atmospheric CO_2 into the ocean affects the ocean ecosystem. The dissolution of atmospheric CO_2 surplus in the ocean lowers pH and reduces the $CaCO_3$ saturation state. But the formation of calcite skeletons in the oceanic surface layer and their post-mortem sinking to depth modifies the alkalinity of the ocean, inducing that a change in calcification rate will directly affect air/sea CO_2 exchange and thus atmospheric CO_2 concentration. One particular point of interest is the effect of the emergence of the calcifying plankton on the marine ecosystem, which shifts the major carbonate production from the shallow seas to the open marine realm. Recent works have constrained this major evolution to the Upper Triassic, more exactly the Norian-Rhaetian boundary. This time slice sees the first occurrence of the coccolitophorids, an explosion of the other calcareous nannoplankton, a reefal bloom, but at the same time an important extinction among higher nektonic organisms. In order to better constrain the effect of these biotic changes on the seawater chemistry, we first established a new high-resolution carbon isotope record from the lower Norian to the late Rhaetian in the Northern Calcareous Alps. The new curve based on four sections has an excellent biostratigraphic control based on ammonoids and conodonts. The middle Norian to lower Rhaetian is composed of a sequence of different Hallstatt-type limestone. The terrigenous Rhaetian Zlambach Formation is overlying, with alternating marls, micritic limestone and episodic allodapic carbonate. The carbon isotope curve display a gentle decrease from the late early Norian (3.5 ‰) to the base of the Rhaetian (1.8 ‰) with two accelerated steps, one in the middle Norian and the other one just after the Norian-Rhaetian Boundary. This last 1 ‰ decrease corresponds however to the change in lithology between the Hallstatt facies and the alternation of marls and limestone. The values show then a small increase during the early Rhaetian, with a maximum in the middle Rhaetian (at 2.4 ‰). The general stability of the curve, through the Norian-Rhaetian boundary crisis event and despite the emergence of the calcareous nannoplankton describes a stable oceanic structure.

Control of declared origin of tropical timber: Application of stable isotopes

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Tropical timber is a highly esteemed raw material. It is estimated that globally 20-40% of all logging is illegal, with probably an even higher percentage in many tropical countries. Therefore, controlling the declared timber provenance is an important action to identify illegally logged wood. We are currently investigating wood from Western (Ivory Coast and Ghana) and Central Africa (Cameroon, Congo and Democratic Republic of Congo). The aim of this project is to establish a database that will host the measured parameters of authentic tropical timber. This shall serve as a reference for provenance control in the future. This project thus aims to help to reduce and combat illegal logging by identifying illegally logged timber. We investigate wood of the tree *Triplochiton scleroxylon*, also called Abachi or Ayous. *Triplochiton scleroxylon* used to be the major timber tree in Western and Central Africa but has been heavily overexploited, therefore it has become rare in the forests. This fact emphasises the need for control of Ayous wood provenance.

The samples were measured for their isotopic ratio of the elements hydrogen, oxygen, carbon, sulphur and nitrogen.

First results show a good discrimination between Ayous samples from Western and Central Africa. Furthermore it is also possible to separate the samples from the Democratic Republic of Congo from these of the other countries investigated. Sulphur, hydrogen and oxygen are the most relevant parameters for discrimination.

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

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Dissolved organic matter plays an important role in the determination of transport and transformation processes in the ecosystem. In order to achieve more information on these processes a precise and routine capable analysis of $\delta^{13}C$ and $\delta^{15}N$ is needed.

The development of a HTC system makes the determination of $\delta^{13}C$ in DOC for a wide range of concentrations (0.2-150.0 mg C/L) and $\delta^{15}N$ in dissolved nitrogen down to a concentration of 1 ppm possible.

Removal of diesel hydrocarbons by constructed wetlands: ^{13}C labelling experiment to reveal degradation

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Bioremediation of the saturated and unsaturated zone of a petroleum hydrocarbon contaminated site in Vienna is tested in a pilot plant. While the unsaturated zone is treated by bioventing in combination with nutrients addition, the groundwater of the unsaturated zone is pumped and treated in four different constructed wetlands; sand, sand+ (sand receiving high groundwater loads), liapor and sand & biochar. The removal of diesel hydrocarbons by constructed wetlands was excellent, higher than 95 %. However, concerns were raised whether removal resulted from biodegradation or adsorption processes. Following this, a lab experiment was conducted using ^{13}C labelled hexadecane, the major component of diesel. The mineralization of hexadecane was monitored by measuring CO_2 evolution and ^{13}C-CO_2 content. Uptake of hexadecane into microorganisms was investigated by ^{13}C-PLFA (phospholipid fatty acid) analyses. Remaining hexadecane and total hydrocarbon were determined. The mineralization of hexadecane in the sandy substrates (sand, sand+ and sand & biochar) was three times higher than in the liapor, 3 and 1 µg CO_2 g^{-1} d^{-1} respectively. The mineralization generally followed zero order kinetics. After 40 days of incubation around 80 % (sandy substrates) and 20 % (liapor) of the added ^{13}C hexadecane were mineralized. The microbial community composition of the constructed wetland microcosms was dominated by gram negative bacterial PLFAs and differed between different substrates. The total PLFA concentration was significantly higher in the substrates sand & biochar and sand. After 40 days of incubation all microbial PLFAs were ^{13}C labelled. The total PFLAs of liapor were labelled 2.5 times higher than those from the sandy substrates. Generally only about 2 % of the labelled hexadecane was preserved in the microbial biomass; most of it was mineralized as CO_2. In liapor, total petroleum hydrocarbon other than hexadecane increased during incubation and indicated abiotic reactions (7 % of the added hexadecane). Assuming a purification layer of 1 m we can expect around 8000 mg TPC m^{-2} d^{-1} being treated in the sandy wetlands and around 1000 mg TPC m^{-2} d^{-1} in the liapor wetland. This amount is much lower than the amount currently applied to the constructed wetlands.

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