



Joint European Stable Isotope User Meeting 2022

UNIVERSITY OF
EASTERN FINLAND
Kuopio, Finland

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—*Abstracts*—

“The important thing is to never stop questioning” (Albert Einstein)

Topic groups: 03. Plant Ecophysiology,

Presentation types: Oral presentation

Title: Tracing carbon, water and VOC fluxes through soil-plant-atmosphere by ecosystem ^{13}C and ^2H Pulse-Labeling during drought and recovery

Lead author: Christiane Werner, University Freiburg

Author: S. Nemiah Ladd, Uni Basel; Laura Meredith, Uni Arizona; B2WALD Team, Universities

Keywords: ^{13}C labelling, deep water labelling, tropical forest, biosphere 2, carbon allocation, plant functional groups, drought, recovery

Content:

Severe droughts are increasing worldwide, however, how physiological plant responses drive ecosystem water, carbon and biogenic volatile organic compound (VOC) fluxes during drought and recovery remains poorly understood. To disentangle complex ecosystem dynamics we imposed a 9.5-week drought on the Biosphere 2 (B2) tropical rainforest in the Water, Atmosphere, and Life Dynamics (B2WALD) experiment [1]. We continuously measured isofluxes of ecosystem exchange, soil and leaf H_2O , CO_2 and BVOCs, over five months. To trace changes in soil-plant-atmosphere interactions we labelled the ecosystem with a ^{13}C -pulse during pre-drought and drought. Subsequently, we introduced ^2H -labelled deep-water label during severe drought, providing a unique opportunity to evaluate transit times and legacy effects during the recovery phase. Ecosystem ^{13}C -pulse-labeling showed that drought enhanced the mean residence times of freshly assimilated carbon, indicating down-regulation of carbon cycling velocity and delayed transport from leaves to trunk and roots. Despite reduced ecosystem carbon uptake and total VOC emissions, plants continued to allocate a similar proportion of fresh carbon to de novo VOC synthesis, as incorporation of ^{13}C into both isoprene and monoterpenes remained high. Maintaining carbon allocation into VOC synthesis demonstrates the fundamental role of these compounds in protecting plants from heat stress and photooxidative damage. VOC uptake increased immediately upon rain rewetting. Interestingly, all deep-rooted canopy trees tapped into deep-water reserves, but spared deep water reserves until severe drought and exhibited long transit times until ^2H -labelled water was transpired. These data highlight the importance of quantifying drought impacts on forest functioning beyond the intensity of (meteorological) drought, but also taking dynamics response of hydraulic regulation of different vegetation compounds and soil microbial activity of the forest into account. [1] Werner, C et al. 2021, Ecosystem fluxes during drought and recovery in an experimental forest. *Science* 374, 1514 (2021), DOI: 10.1126/science.abj6789

Topic groups: 09. Isoscape, Spatial Variability of Stable Isotopes (Migration, Food Webs),

Presentation types: Oral presentation

Title: Long- and short-term dietary shifts in a generalist predator, the wolverine (*Gulo gulo*) over a century of change.

Lead author: Clément Massé, University of Oulu

Author: Tamara Hiltunen, University of Oulu; Gerhardus Lansink, University of Oulu; Jeffrey Welker, University of Alaska Anchorage, University of Oulu, Uarctic; Katja Holmala, Natural Resources Institute Finland; Marja Isomursu, The Finnish Food Authority

Keywords: Diet shift, wolverine, carnivores, museum, long-term, short-term

Content:

Anthropogenic impact on the environment induces changes in species communities affecting the diets of animals, such as the wolverine (*Gulo gulo*), a generalist predator. While traditional dietary research methods are spatially and temporally limited by logistics and the elusiveness of this species, stable isotope analysis (SIA) can provide new insights into wolverine foraging ecology. Applied to samples from museum collections and ongoing non-invasive monitoring programs, SIA can help to identify isotopic niches and reconstruct past and present diets. Stable carbon ($\delta^{13}\text{C}$) and nitrogen ($\delta^{15}\text{N}$) isotopes were measured in hair samples from wolverines ($N = 68$) in Finland for the period 1906-2019, and on multiple tissues of a single individual from 2020. Additionally, we obtained isotope values of a large range of potential wolverine dietary sources. Long- and short-term dietary shifts were quantified by combining niche metrics and mixing models, and considered sex, individual, and seasonal variation in five regions. We provide evidence of a diet shift in the Finnish wolverine population between the 1900s and present day, with a mean depletion in $\delta^{13}\text{C}$ by 1.2 ‰ and enrichment in $\delta^{15}\text{N}$ by 0.4 ‰. Correspondingly, the isotopic niches before and after the year 2000 shifted, with the niche overlap being only 31 % throughout Finland, whereas 19 % regionally. Though no difference was found in dietary niches between previously identified genetic subpopulations, a difference was found between males and females, suggesting regional inter-sexual resource partitioning. While individual and seasonal diets showed high variability in prey contributions, our mixing model highlights the prime role of the rodent cycle on inter-annual changes in wolverine foraging strategies. The plasticity in the wolverine's diet throughout times of population fluctuation, translocation, range expansion, and through seasons, suggests a high resilience to food-web changes. Conclusively, the combination of well-established SIA methodologies applied on wolverines' tissues collected non-invasively, offers a cost-efficient tool to unravel both their complex feeding strategies and the temporal changes in the dynamics of their ecological communities.

Topic groups: 10. Geochemistry and Hydrology,

Presentation types: Oral presentation

Title: Using machine learning to generate historic European monthly precipitation isotope time series from the 20th century to present day

Lead author: Daniel Nelson, University of Basel

Author: David Basler, University of Basel; Ansgar Kahmen, University of Basel

Keywords: oxygen isotopes, hydrogen isotopes, precipitation, machine learning

Content:

Hydrogen and oxygen isotope values of precipitation are critically important quantities for applications in Earth, environmental, and biological sciences. However, direct measurements are not available at every location and time, and existing precipitation isotope models are often not sufficiently accurate for examining features such as long-term trends or interannual variability. This can limit applications that seek to use these values to identify the source history of water or to understand the hydrological or meteorological processes that determine these values. We developed a framework using gradient boosted regression tree-based machine learning, which we used to implement a procedure for calculating isotope time series at monthly resolution using available climate and location data at any coordinate location within the model spatial domain. Here we present two applications of our modelling framework, Piso.AI, one of which uses a diverse suite of climate and geographic data as predictor inputs to generate highly accurate monthly time series records beginning in 1950, and the second of which uses a restricted set of predictors to allow time series to be generated that begin in 1901 with slightly reduced accuracy compared to the 1950 model. Both products can be applied over most of Europe, and were trained on the historic archive of precipitation isotope data available from the Global Network of Isotopes in Precipitation. These model products facilitate simple, user-friendly predictions of precipitation isotope time series that can be generated on demand and are accurate enough to be used for exploration of interannual and long-term variability in both hydrogen and oxygen isotopic systems. These predictions provide important isotope input variables for ecological and hydrological applications, as well as powerful targets for paleoclimate proxy calibration, and they can serve as resources for probing historic patterns in the isotopic composition of precipitation with a high level of meteorological accuracy. Predictions from our modelling framework can be accessed at <https://isotope.bot.unibas.ch/PisoAI/>.

Topic groups: 06. Food Authenticity, Nutrition, Forensic,

Presentation types: Oral presentation

Title: Characterisation of beef coming from different European countries through stable isotope (H, C, N, S and Sr) ratio analysis

Lead author: Luana Bontempo, Fondazione Edmund Mach (TN, Italy); Federica Camin, International Atomic Energy Agency, Vienna International Centre, Vienna, Austria

Author: Silvia Pianezze, Fondazione Edmund Mach (TN, Italy); University of Udine (UD, Italy); Micha Horacek, BLT Wieselburg - HBLFA Francisco Josephinum, Wieselburg, Austria; Andreas Roßmann, Isolab GmbH, Woelkestr. 9/1, 85301 Schweitenkirchen, Germany; Simon Kelly, International Atomic Energy Agency, Vienna International Centre, Vienna, Austria; Freddy Thomas, Eurofins Analytics France, 44323 Nantes Cedex 3, France; Katharina Heinrich, Fera Science Ltd, Sand Hutton, YORK, YO41 1LZ, UK; MATTEO PERINI, Fondazione Edmund Mach (TN, Italy); Claus Schlicht, LGL Bayerisches Landesamt für Gesundheit und Lebensmittelsicherheit, Germany; Antje Schellenberg, LGL Bayerisches Landesamt für Gesundheit und Lebensmittelsicherheit, Germany; Jurian Hoogewerff, National Centre for Forensic Studies, University of Canberra, Australia; Stefan Hölzl, Staatliche Naturwissenschaftliche Sammlungen Bayerns, Nördlingen, Germany; Gerhard Heiss, AIT Austrian Institute of Technology GmbH, Giefinggasse 4, 1210 Vienna, Austria; Bernhard Wimmer, AIT Austrian Institute of Technology GmbH, Giefinggasse 4, 1210 Vienna, Austria

Keywords: beef, stable isotope, traceability, Thermal Ionization Mass Spectrometry, Isotope Ratio Mass Spectrometry

Content:

In the last few decades, the geographical authentication of food has become a topic of considerable interest from an industrial and commercial point of view. The analysis of the stable isotopes in food products can assist with this, as the isotopic composition of food often has a relation with local or regional climate, soil conditions and/or agricultural practices. During the EU-project "TRACE", 227 defatted beef samples from 13 regions within 8 European countries (Austria, France, Germany, Greece, Ireland, Italy, Spain and United Kingdom) were analysed by using Elemental Analysis coupled to Isotope Ratio Mass Spectrometry (EA-IRMS, TC/EA-IRMS) and Thermal Ionization Mass Spectrometry (TIMS). The combined data allowed distinguishing (i) regions close to the sea from the landlocked ones, (ii) northern and Alpine regions from the southern or lowland ones (close to the sea), (iii) regions having different geology and (iv) cattle farming practices (intense indoor rearing from extensive outdoor grazing). The results showed the potential of stable isotope ratio analysis to assign the origin of beef according to specific environmental conditions in the rearing areas. Statistical differences among countries based on ANOVA results are supported by applying multivariate statistical techniques, making it also possible to discriminate, in some cases, regions within the same country.

Topic groups: 03. Plant Ecophysiology,

Presentation types: Oral presentation

Title: Impact of varying $\text{NH}_4^+:\text{NO}_3^-$ on C-isotope composition of leaf- and root-respired CO_2 and putative respiratory substrates in *Phaseolus vulgaris* L.

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Keywords: inorganic N form, leaf gas exchange, ^{13}C , respiratory metabolism, anaplerotic pathway, PEPc activity, malate, citrate

Content:

C-isotope composition ($\delta^{13}\text{C}$) of plant organic material (OM) is mainly determined by the balance between photosynthetic capacity and conductances for CO_2 diffusion. It also varies with the relative activities of Rubisco and other carboxylases, mainly PEPc. Variable PEPc activity is related to nitrogen assimilation, which takes place in leaves or in roots depending on the N-type supplied (NO_3^- or NH_4^+). It is hypothesised that N-type nutrition should impact the $\delta^{13}\text{C}$ of OM and metabolites in leaves and roots and consequently that of respired CO_2 . Therefore, we investigated the $\delta^{13}\text{C}$ of OM, water-soluble OM (WSOM), sugars, organic acids (OA) and respired CO_2 of leaves and roots in bean plants grown across a N-form gradient, ranging from 100% NO_3^- to 100% NH_4^+ . It is expected that OA are less ^{13}C -depleted than sugars. The isotopic gap between the two substance classes as well as between malate and citrate should vary with day-time versus night-time and leaf versus root assimilation by PEPc. Photosynthesis, biomass production and respiration rates varied little across the N-form gradient. The $\delta^{13}\text{C}$ of OM was not correlated with the N-form gradient. As expected, the isotopic gap between OA and sugars was higher in leaves than in roots. The $\delta^{13}\text{C}$ of sugars and OA did not significantly change across the N-gradient, with the exception of root glucose and citrate. As opposed to this, WSOM and respired CO_2 of leaves became progressively more ^{13}C -depleted with increasing $\text{NH}_4^+\%$ and were positively correlated between each other. Leaf malate and citrate concentrations strongly decreased with increasing $\text{NH}_4^+:\text{NO}_3^-$ as did leaf PEPc and nitrate reductase (NR) activities. Thus, under NO_3^- , leaf-respired CO_2 was ^{13}C -enriched due to a higher fraction of substrates anaplerotically fixed by PEPc and putatively accumulated in the vacuole. Both root sugar concentrations, and PEPc and NR activities significantly increased with increasing $\text{NH}_4^+:\text{NO}_3^-$. Higher root PEPc activity at high $\text{NH}_4^+:\text{NO}_3^-$ was associated with higher ^{13}C content in root glucose and citrate. $\delta^{13}\text{C}$ of root WSOM and respired CO_2 was not correlated with the N-form gradient, probably due to the low isotopic gap between OA and sugars. The isotopic gap between malate and citrate was smaller than expected if simultaneous synthesis during day-time in leaves or preferential synthesis of citrate during night-time would prevail. These results are consistent with coupling of the malate and citrate branches in the open mode of the TCA-cycle in leaves during day-time.

Topic groups: 02. Terrestrial and Aquatic Biogeochemistry,

Presentation types: Oral presentation

Title: Stable Hydrogen and Oxygen Isotope Ratios of Dissolved Organic Matter in Inland Waters

Lead author: Travis Meador, Biology Centre CAS & Univ. South Bohemia, Czechia

Author: Matthias Pilecky, WasserCluster Lunz & Donau-Universität Krems, Austria; Samuel-Karl Kämmer, WasserCluster Lunz; Katharina Winter, WasserCluster Lunz; Petr Porcal, Biology Centre CAS, Czechia; Marek Kopaček, Biology Centre CAS, Czechia; Len Wassenaar, WasserCluster Lunz; Donau-Universität Krems, Austria; Univ. Saskatchewan, Canada; Martin Kainz, WasserCluster Lunz & Donau-Universität Krems, Austria

Keywords: DOM, peat, C-org transport, isotope hydrology

Content:

The sum of all living organisms in aquatic systems is dwarfed by a much larger pool of dissolved organic carbon (DOC). As such, mechanisms that control the transport of C between soil, aquatic, and atmospheric reservoirs are necessarily intertwined with an immense array of non-living yet functional organic compounds (i.e., dissolved organic matter; DOM). While molecular complexity obscures estimation of DOM contributions to C respiration, storage, and transport fluxes, stable C isotope ratios have been useful for estimating aquatic versus terrestrial inputs, for example. However, the scope of $\delta^{13}\text{C}$ -DOC as an indicator of DOM turnover is limited by the small relative differences in $^{13}\text{C}/^{12}\text{C}$ composition of DOC sources and the large magnitude of the DOC pool. We hypothesized that the incorporation of meteorological isotopic signals into DOM may better constrain its production and transformation history, such that the non-exchangeable stable H and O composition of DOM ($\delta^2\text{H}$ - and $\delta^{18}\text{O}$ -DOM) will help to resolve DOM reactivity. This study determined $\delta^2\text{H}$ and $\delta^{18}\text{O}$ composition of DOM isolated from limnic and peat-influenced waters, spanning a broad range of hydrological and climate settings, and thus a gradient of DOM production and transformation regimes. Initial results suggest that these proxies track regional, seasonal, and rapid changes in DOM, revealing a window of DOM reactivity that could not be seen through the lens of stable C isotope signals. Furthermore, the ratio of $^{18}\text{O}/^{16}\text{O}$ in DOM isolated in the limnic surface waters corresponded to the apparent complexation of minerals by DOM, such that DOM comprising elements other than CNOH exhibited higher $\delta^{18}\text{O}$ values. In accordance with the European Commission's 2030 Agenda goals, further deconvolution of $^2\text{H}/^1\text{H}$ and $^{18}\text{O}/^{16}\text{O}$ signals in DOM and implementation of this approach will help constrain C-org transformation and export fluxes in aquatic habitats.

Topic groups: 04. Paleoclimatology & Archaeology,

Presentation types: Oral presentation

Title: Historic reindeer mobility in northern Sweden – a study of diet, mobility, and climatic changes by multiple stable isotope analysis

Lead author: Markus Fjellström, History, Culture and Communications, Oulu University

Author: Anna-Kaisa Salmi, History, Culture and Communications, Oulu University; Kerstin Lidén, Archaeological Research Laboratory, Stockholm University; Aikaterini Glykou, Archaeological Research Laboratory, Stockholm University

Keywords: reindeer diet, mobility, climate, stable isotopes, stálla foundations, market places, hearths, Saami archaeology

Content:

Reindeer, wild or domesticated, has played an important role within the Saami community for centuries and has been used for different purposes. However, the reindeer diet is rather complex as it depends on seasonal availability of plants, the mobility of the animals, which can move over large areas, and on how much the reindeer is intertwined with the human society resulting in grazing freely or being fed. In this study we focus on a small number of unburnt reindeer skeletal remains from a series of archaeological features within the Piteå and Skellefteå River Valleys in northern Sweden, from the inland to the Bothnian coast. The reindeer samples were selected from stálla foundations, single hearths, marketplaces, and a probable cooking pit that has been dated to the Late Iron Age- 19th century. To create a baseline for the bioavailable strontium throughout specific areas in the Pite River Valley system in order to study mobility, we also collected a large number of reference samples (n= 96, plants, soil, and water) from different strategic reindeer grazing areas in different reindeer herding districts. By radiocarbon dating and multiple stable isotope analysis ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$, $\delta^{34}\text{S}$, $\delta^{18}\text{O}$ and $^{86}\text{Sr}/^{87}\text{Sr}$) we aim to study reindeer diet and mobility over time, in connection to different climatic conditions, and to understand mobility of the Saami population living in the area.

Topic groups: 11. Molecular & Intra-Molecular Biology,

Presentation types: Oral presentation

Title: Methanotrophy by putative monooxygenase in boreal spruce phyllosphere

Lead author: Henri Siljanen, University of Eastern Finland, Kuopio, Finland

Author: Antti Laihonen, University of Jyväskylä, Jyväskylä, Finland; Sanni Aalto, University of Jyväskylä, Jyväskylä, Finland; Inga Paasisalo, University of Eastern Finland, Kuopio, Finland; Richard Lamrecht, University of Eastern Finland, Kuopio, Finland; Christina Biasi, University of Eastern Finland, Kuopio, Finland; Marja Tirola, University of Jyväskylä, Jyväskylä, Finland

Keywords: methane, methanotrophy, monooxygenase, forest, boreal, phyllosphere

Content:

Current knowledge on methane (CH₄) sinks is limited to chemical processes in the atmosphere, and to methanotrophy in forest soils and peatlands. However, recent discoveries have indicated that also tree stems and branches, i.e. phyllosphere, may consume atmospheric CH₄, thus functioning as a novel CH₄ sink, but the mechanism is not yet resolved. Here, we show that leaves and needles of boreal trees had the potential to consume CH₄ in field and laboratory experiments. Inhibitor and sterilization treatments indicated that the phenomenon was a biological process. With molecular and stable isotope analyses, we confirmed that the activation of non-canonical proteobacterial methanotrophs carrying putative butane monooxygenase gene increased under CH₄ and acetate enrichment in spruce branches. Based on our results, microbial-mediated CH₄ consumption in tree canopies can be moderate, but yet globally significant, CH₄ sink. This novel symbiotic connection between microbes and plant cells can compensate the observed CH₄ emissions from boreal trees. Our results indicate that CH₄ consumption by butane monooxygenase plays an important role in the CH₄ uptake in boreal trees and ecosystem-scale carbon cycle.

Topic groups: 07. Atmospheric Sciences (Pollution, Climate Change, Cosmogeochimie),

Presentation types: Oral presentation

Title: Diurnal variations in N and O isotopes of atmospheric nitrogen dioxide and nitrate.

Lead author: Sarah Albertin, LATMOS/IPSL, Sorbonne Université, UVSQ, CNRS, 75005 Paris, France

Author: Joël Savarino, IGE, Univ. Grenoble Alpes, CNRS, IRD, Grenoble INP, 38000 Grenoble, France ; Slimane Bekki, LATMOS/IPSL, Sorbonne Université, UVSQ, CNRS, 75005 Paris, France; Roberto Grilli, IGE, Univ. Grenoble Alpes, CNRS, IRD, Grenoble INP, 38000 Grenoble, France ; Quentin Fournier, LIPhy, Univ. Grenoble Alpes, CNRS, 38000 Grenoble, France; Irène Ventrillard, LIPhy, Univ. Grenoble Alpes, CNRS, 38000 Grenoble, France; Nicolas Caillon, IGE, Univ. Grenoble Alpes, CNRS, IRD, Grenoble INP, 38000 Grenoble, France ; Kathy Law, LATMOS/IPSL, Sorbonne Université, UVSQ, CNRS, 75005 Paris, France

Keywords: Stable isotopes, atmospheric nitrate, nitrogen oxides, atmospheric chemistry, NOx sources, N fractionation

Content:

The use of stable isotopes over the past decades has demonstrated its ability to provide information relevant for tracing emission sources, individual chemical processes and budgets of atmospheric trace gases. Atmospheric nitrate (NO_3^-) is the end product of nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$) oxidation and an emblematic compound of this isotopic approach. Of particular interest is the propagation of the ozone distinctive oxygen-17 anomaly ($\Delta^{17}\text{O}$) into the reactive nitrogen cycle which has led to a better understanding of nitrate formation pathways in various environments. A very powerful approach is to combine isotopic measurements of different atoms in linked molecules, for instance O and N in NO_2 and nitrate. Here we report for the first time on measurements and analysis of $\Delta^{17}\text{O}$ and $\delta^{15}\text{N}$ in NO_2 and NO_3^- collected simultaneously in Chamonix, France, at high temporal resolution during two days in order to interpret more quantitatively the fate of reactive nitrogen. The $\delta^{15}\text{N}$ values of NO_2 and NO_3^- show strong variability (-10.6 to 19.7 ‰ and -4.2 to 14.9 ‰, respectively), suggesting important N fractionation during NO_x to nitrate conversion. We find a large diurnal variation in $\Delta^{17}\text{O}$ for both NO_2 and NO_3^- , with maximum values during the day (40.8 ‰ and 28.1 ‰, respectively) and minimum values at night (19.6 ‰ and 18.3 ‰, respectively). There is also a substantial variability in $\Delta^{17}\text{O}(\text{NO}_2)$ and $\Delta^{17}\text{O}(\text{NO}_3^-)$ during the day itself, certainly driven by changes in the O_3 to peroxy radical ratio. By collating atmospheric observations (NO , NO_2 , O_3 and PM concentrations) and $\Delta^{17}\text{O}/\delta^{15}\text{N}$ data, we investigate nitrate formation pathways, N fractionation effects, and the relative contribution of NO_x emission sources influencing our measurement site. The results demonstrate that the combined study of the NO_2 and NO_3^- multi-isotopic composition allow to better interpret NO_3^- isotopic composition records and provide more stringent and quantitative constraints on the atmospheric reactive nitrogen cycle.

Topic groups: 03. Plant Ecophysiology,

Presentation types: Oral presentation

Title: Accounting for the metabolic component in the hydrogen isotopic composition of plant carbohydrates

Lead author: Meisha-Marika Holloway-Phillips, University of Basel, Switzerland

Author: Marco M. Lehmann, Swiss Federal Institute for Forest, Snow and Landscape Research WSL; Jochem Baan, University of Basel, Switzerland; David Basler, University of Basel, Switzerland; Lucas Cernusak, James Cook University, Australia; Marc-Andre Cormier, University of Oxford, UK; Haoyu Diao, Swiss Federal Institute for Forest, Snow and Landscape Research WSL; Claudia Guidi, Swiss Federal Institute for Forest, Snow and Landscape Research WSL; Selina Hugger, University of Basel, Switzerland; Nemiah Ladd, University of Basel, Switzerland; Daniel Nelson, University of Basel, Switzerland; Richard Peters, University of Basel, Switzerland; Matthias Saurer, Swiss Federal Institute for Forest, Snow and Landscape Research WSL; Philipp Schuler, Swiss Federal Institute for Forest, Snow and Landscape Research WSL; Rolf Siegwolf, Swiss Federal Institute for Forest, Snow and Landscape Research WSL; Valentina Vitali, Swiss Federal Institute for Forest, Snow and Landscape Research WSL; Anina Wacker, University of Basel, Switzerland; Roland A. Werner, ETH Zurich, Switzerland; Ansgar Kahmen, University of Basel, Switzerland

Keywords: hydrogen isotopes, plant metabolism, hydrologic isotope signals, isotope models, structural and non-structural plant carbohydrates, compound specific isotope analysis

Content:

Hydrogen isotopes in plant organic material are derived solely from plant water. Since the water taken up by plants and the extent of ^2H -enrichment of leaf water during transpiration carries information about climatic conditions (e.g. air temperature and humidity), it has been widely assumed that the $\delta^2\text{H}$ values in plant organic material can be used as a proxy for these conditions. However, it is also well known that biochemical reactions that make and break bonds between carbon and hydrogen fractionate hydrogen isotopes. The net hydrogen isotope effect should be dependent on the partitioning of carbon through various metabolic pathways. In addition, hydrogen atoms are an intrinsic part of energy and redox metabolism of plants, with the latter involved in metabolic regulation. This may explain why the strength of climatic correlations has been mixed and generally weaker than what has been observed for oxygen isotopes in plant cellulose. As enzymes target particular carbon-hydrogen positions of metabolites, the associated kinetic hydrogen isotope effects leave a trace that can be observed as relative changes in the intramolecular abundance of ^2H , which can be measured by nuclear magnetic resonance (NMR) spectroscopy. However, due to the restrictive method requirements of NMR, there is a need to bridge the gap between theory and the current assumption of constant metabolic isotope effects. Recently, methods to measure $\delta^2\text{H}$ values of non-structural carbohydrates have been developed that provide the opportunity to explore how the H isotope signal is transferred and modified along the path from leaf water, sugars and starch, to cellulose. In this talk, I summarise the progress and challenges in interpreting variation in plant cellulose $\delta^2\text{H}$ values in the context of hydroclimatic changes in the environment and metabolic changes in plants, and outline how compound-specific sugar and starch $\delta^2\text{H}$ measurements allow the possibility to partition isotopic variation associated with autotrophic source leaf and heterotrophic sink cell metabolism. These ideas emerged from a local meeting in Switzerland among hydrogen isotope researchers where it became evident that there was a need to progress from observational studies testing the link between $\delta^2\text{H}$ variation and carbon metabolism to quantification of the metabolic isotope components through isotope models. We propose new experimental approaches to parameterise isotope models, generating a greater utility for interpreting $\delta^2\text{H}$ variation and advancing the idea that hydrogen isotopes of plant carbohydrates can be used as a metabolic proxy.

Topic groups: 06. Food Authenticity, Nutrition, Forensic,

Presentation types: Oral presentation

Title: Stable isotope analysis for the authenticity and traceability of food products, supplements and drugs

Lead author: Matteo Perini, Centro Trasferimento Tecnologico

Keywords: Stable isotope ratio analyzes, SIRA

Content:

Stable isotope ratio analyzes (SIRA) are nowadays increasingly used for the traceability and authenticity not only of food products (e.g. milk, cheese or vegetable oils), but also of drugs (such as curcumin) and food supplements with pharmacological properties (such as monakolin K, produced by the fermentation red yeast rice). The numerous official methods are flanked by various scientific works demonstrating the power of this technique and its applicability in official and non-official controls. Thanks to the coupling of isotope ratio mass spectrometry (IRMS) with separative techniques, such as liquid chromatography and gas chromatography, it is now possible to identify frauds ranging from the replacement of natural molecules with their synthetic form, to the identification of added adulterants, even in low concentration

Topic groups: 10. Geochemistry and Hydrology,

Presentation types: Oral presentation

Title: Delineating irrigation return flows and seawater intrusion in coastal karstic aquifers by solutes and stable isotopes

Lead author: Rohana Chandrajith, University of Peradeniya, Sri Lanka

Author: Saranga Diyabalanage, University of Sri Jayewardenepura, Sri Lanka; Robert van Geldern, Friedrich-Alexander University Erlangen-Nürnberg, Erlangen, Germany; Johannes A.C. Barth, Friedrich-Alexander University Erlangen-Nürnberg, Erlangen, Germany

Keywords: coastal aquifers; seawater intrusions; water isotopes; Sri Lanka

Content:

Coastal aquifers are highly productive, but also vulnerable due to seawater intrusion and anthropogenic pollution. Therefore, investigating geochemical processes and factors that control the composition of groundwater in coastal terrains are important for sustainable groundwater management. Sri Lanka is an island in the Indian ocean with a comparatively high coastline to land ratio. In addition, nearly 25 % of the country's total population lives close to the coast (i.e. about 5.6 million people), with additional water stress caused by irrigation and tourism. Two near-shore aquifers systems, namely Jaffna and Kalpitiya where groundwater resources are already under pressure, were investigated with nitrate (NO_3^-) and chloride (Cl^-) concentrations and stable isotope ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) compositions. In both regions, agricultural and domestic water supplies entirely depend on groundwater extracted from sandy aquifer systems. Elevated Cl^- contents served as the first indicators of seawater intrusions. This could however also have been enriched by agricultural irrigation returns and associated evaporation. This was confirmed by the stable isotope composition of groundwater that deviated from the local meteoric water lines (LMWL). In the Jaffna and Kalpitiya regions, groundwater samples plotted on typical evaporation lines denoted by $\delta^2\text{H} = 5.8 \times \delta^{18}\text{O} - 2.9$ ($r^2 = 0.98$) and $\delta^2\text{H} = 5.34 \times \delta^{18}\text{O} - 3.75$ ($r^2 = 0.930$), that were both lower than the LMWL. This is not only a sign of inefficient irrigation practices but also indicates substantial water losses during open irrigation. However, with combined stable isotope mass balances first rates of seawater intrusions were also observed with up to 12 %. Elevated NO_3^- concentrations derived from fertilizer applications and in the Kalpitiya region reached peak values of 1000 mg/L while in the Jaffna region they were always below 6 mg/L. It is possible that saltwater intrusions were mitigated by monsoon rainfalls that would move the seawater-freshwater interface towards the sea. While the aspect of natural mitigation by monsoon rains deserves further investigation, we indicate that integrated water management should critically monitor water resources in study regions to avoid overexploitation and further seawater intrusions.

Topic groups: 05. Health and Medical Sciences,

Presentation types: Oral presentation

Title: First Use of Triply Labelled Water analysis for energy expenditure measurements in mice

Lead author: Harro A.J. Meijer, Centre for Isotope Research (CIO), University of Groningen

Author: Xing Wang, Centre for Isotope Research (CIO), University of Groningen; Dehuang Kong, Behavioral Neuroscience, University of Groningen; Gertjan van Dijk, Behavioral Neuroscience, University of Groningen

Keywords: Doubly Labelled Water Triply Labelled Water Optical spectroscopy Energy Expenditure

Content:

The Doubly Labelled Water (DLW) method is widely used to determine energy expenditure of (free roaming) animals, and of humans. In this work, we demonstrate the addition of the third stable isotope, ^{17}O , to turn it into Triply Labelled Water (TLW), exploiting the modern three isotopes measurement capabilities of optical spectrometry. We performed TLW measurements for the analysis of the CO_2 production ($r\text{CO}_2$) of mice on different diets. Triply highly enriched water (with abundances of 30%, 55% and 8% for ^2H , ^{18}O and ^{17}O , respectively) was injected into mice, and the isotope enrichments of the distilled blood samples taken after 2, 24 and 48 hours, respectively, were measured by an Optical Spectroscopy instrument (LGR LWIA 912-0050). Analysis of the measurements was done using a bespoke data analysis program (written in R), which includes a sophisticated memory correction algorithm [1]. For these enriched samples such an algorithm is indispensable. For calibration of the measurements, we extended the range of available DLW reference waters [2] by preparing ^{17}O enriched reference waters on a gravimetric basis. We found that the values of the $r\text{CO}_2$ (which are proportional to the energy expenditure), calculated based on ^{18}O - ^2H , and on ^{17}O - ^2H , agreed very well, increasing the reliability and redundancy of the measurements and lowering the uncertainty in the calculated $r\text{CO}_2$ to $\pm 3\%$. However, like in a previous study using DLW [3], the TLW method overestimated the $r\text{CO}_2$ compared to the indirect calorimetry measurements that we also performed. Thanks to the addition of ^{17}O , we could now unambiguously identify ^2H isotope effects as the culprit. We hypothesize an extra loss or exchange mechanism with a high fractionation for ^2H to explain this difference. [1] S. Guidotti et al. (2013) Doubly Labelled Water analysis: Preparation, memory correction, calibration and quality assurance for delta H-2 and delta O-18 measurements over four orders of magnitudes, *Rapid Communications in Mass Spectrometry*. 27 1055–1066. <https://doi.org/10.1002/rcm.6540>. [2] V. Faghihi et al. (2015) A new high-quality set of singly (^2H) and doubly (^2H and ^{18}O) stable isotope labeled reference waters for biomedical and other isotope-labeled research, *Rapid Communications in Mass Spectrometry*. 29 311–321. <https://doi.org/10.1002/rcm.7108>. [3] S. Guidotti, H.A.J. Meijer, G. van Dijk (2013) Validity of the doubly labeled water method for estimating CO_2 production in mice under different nutritional conditions, *American Journal of Physiology - Endocrinology and Metabolism*. 305 E317–E324. <https://doi.org/10.1152/ajpendo.00192.2013>.

Topic groups: 02. Terrestrial and Aquatic Biogeochemistry,

Presentation types: Oral presentation

Title: Belowground C allocation of tropical rainforests in response to drought: an ecosystem $^{13}\text{CO}_2$ labeling experiment

Lead author: Michaela Dippold, Universität Tübingen; Christiane Werner, University of Freiburg

Author: Lingling Shi, University of Tuebingen; Pratiksha Acharya, University of Geottingen; Xuejuan Bai, University of Goettingen; Niklas Schmuecker, University of Goettingen; Nemiah Ladd, University of Basel; Laura Meredith, University of Arizona

Keywords: ecosystem pulse labeling, tropical rainforest, carbon allocation, belowground drought response strategies

Content:

Pulse labeling experiments remain an invaluable tool for tracing element allocation dynamics following disturbance events or environmental changes. They are largely used on single organisms, micro- to mesocosm or maximally plot scale and upscaling of their outcomes is frequently challenging because of a lack of spatial representativeness and the potential for interactions to be missed due to excluded ecosystem components. Therefore, we conducted a complete ecosystem pulse labeling drought stress experiment to explore the impact of extreme droughts on tropical rainforests using the “ecosystem in a box model” of Biosphere 2 in Arizona. The atmosphere of the tropical forest was exposed to a $^{13}\text{CO}_2$ pulse for several hours under ambient and drought conditions. Besides continuous monitoring (leaf, stem and soil $^{13}\text{CO}_2$ respiration), we performed regular post-pulse soil sampling campaigns to trace ecosystem belowground C allocations and monitor C partitioning at the soil–microbe–root interface. We aimed to identify key drought-adaptation strategies such as i) increased C allocation into subsoil layers which were expected to have higher moisture than dried-out topsoils and ii) increased relative C investment into rhizodeposits and mycorrhizal fungi fostering plant nutrition even from dry soil. We observed a high allocation of assimilated ^{13}C tracer into topsoil roots, but this C allocation did not contribute to a higher root biomass. This suggests that tropical plants might modify their root composition by forming osmolytes or increasing lignin content to resist the high topsoil drought stress. The rhizodeposition (allocation of assimilated C into rhizospheres soil) increased mainly in the subsoil, suggesting that trees aim to keep rhizo-microbial activity high in subsoils, where moisture was still available throughout the drought period. Especially under drought conditions, we observed high ^{13}C allocation into the 18:2 ω 6,9 biomarker representative for saprotroph and ectomycorrhizal fungi. This suggests trees invest C into their mycorrhizal partners most likely hoping for improved nutrient uptake via the small, drought-resistant fungi able to exploit small, still-moist microhabitats in soils. Generally, we found pronounced plot- and thus plant-specific differences in belowground C allocation, especially between plots with only understory versus those with tall trees, suggesting species- or functional plant type specific drought response strategies belowground. In summary, quantification of ecosystem C belowground allocation patterns at the plant-microbe-soil interface enables us to disentangle distinct belowground drought response strategies of tropical rainforests. This is essential to support those ecosystem traits that increase tropical rainforests’ resistance and resilience to climate change.

Topic groups: 03. Plant Ecophysiology,

Presentation types: Oral presentation

Title: Interpretation of intra-annual tree-ring $\delta^{13}\text{C}$ profiles of control, droughted and re-watered Scots pines

Lead author: Katja Rinne-Garmston, Luke

Author: Yu Tang; Elina Sahlstedt, Natural Resources Institute Finland (LUKE), Helsinki, Finland; Bartosz Adamczyk; Matthias Saurer, Forest Dynamics, WSL Birmensdorf, Switzerland; Yann Salmon; Maria Dominguez; Teemu Hölttä; Marco Lehmann; Tuula Jyske; Lan Mo; Giles Young, Natural Resources Institute Finland (LUKE), Helsinki, Finland

Keywords: carbon isotope, laser ablation, compound-specific, sugar, tree ring, drought, Scots pine

Content:

Intra-annual tree-ring $\delta^{13}\text{C}$ record has the potential to provide deep insights into past plant performance and environmental conditions. With concomitant high temporal resolution $\delta^{13}\text{C}$ analysis of non-structural carbohydrates, the processes behind observed low- and high-frequency $\delta^{13}\text{C}$ changes in tree-ring record could be interpreted more reliably. This is essential for predicting forest response to impacts of climate change, such as more frequent and severe drought episodes. To better understand post-photosynthetic carbon isotope fractionation processes and drought associated changes in tree function, we conducted a drought experiment with Scots pine saplings in a greenhouse during a growing season. Scots pine clones were exposed to two treatments: control trees, and trees exposed to drought and subsequent re-watering. We analysed $\delta^{13}\text{C}$ of individual sugars (compound-specific isotope analysis) and starch in leaves, phloem and roots at weekly resolution, to study how environmental changes were recorded in leaf assimilates and modified in down-stem transport. Tree physiological response was monitored to support interpretation. High resolution $\delta^{13}\text{C}$ profiles of tree-rings were obtained using laser ablation isotope ratio mass spectrometry, which enabled us to identify how the $\delta^{13}\text{C}$ signal of assimilates was finally recorded in stem xylem, and to determine which processes distorted this signal. The results shed new insight into the widely reported ^{13}C -enrichment of sink organs relative to leaves and demonstrate the potential of using high-resolution tree-ring $\delta^{13}\text{C}$ -profiling to understand drought associated processes in xylem formation.

Topic groups: 01. Methodological Advances,

Presentation types: Oral presentation

Title: Where do IRMS's go wrong? $\delta^{18}\text{O}$ SLAP determined at -56.3‰

Lead author: Anita Aerts-Bijma, University of Groningen

Author: Dipayan Paul, university of Groningen; Albert Van Buuren, university of Groningen; Harro Meijer, university of Groningen

Keywords: $\delta^{18}\text{O}$ of SLAP, VSMOW, ^{18}O enriched water, Quadrupole MS, LGR

Content:

The stable isotope scale of water has been successfully established and maintained by the two primary reference waters VSMOW and SLAP. In principle, only one reference material per isotope and per medium would be needed to define the isotopic scale, but two-point calibration leads to a dramatic improvement in inter-laboratory comparisons, due to various and variable scale contraction processes occurring in each measurement process. For deuterium, it is possible to (re) produce the primary reference waters based on gravimetric mixtures of isotopically pure waters. In this way, the absolute deuterium abundances of VSMOW and SLAP has been precisely determined. A similar experiment for oxygen is much harder, as pure ^{18}O and ^{16}O waters are not available. However, the 'absolute' determination of the $\delta^{18}\text{O}$ of SLAP versus VSMOW is feasible. In this study, we quantify the difference in $\delta^{18}\text{O}$ between VSMOW and SLAP by gravimetric mixing of a SLAP-like water with highly ^{18}O enriched water to mimic VSMOW and compared this with real VSMOW. The ^{18}O concentration of the highly enriched water, is precisely measured using an Extorr XT100 quadrupole mass spectrometer (Extorr Inc., USA). The isotope measurements were performed with an optical spectroscopy instrument (LGR LWIA 912-0050). The calculations of the isotopic abundances were done using a spreadsheet. To our surprise this study resulted in a $\delta^{18}\text{O}$ of SLAP value of $-56.33 \pm 0.02\text{‰}$ (average of 6 independent experiments). This is a much more negative value than the established value by consensus (-55.5‰) and also more negative than we and some colleague laboratories measure nowadays, when taking scale contraction effects into account (around -55.8‰). Although this finding as such does not influence the use of the VSMOW-SLAP scale, it raises the intriguing question, what we actually measure with our instruments, and why even a well-corrected measurement can be so far off. It might have consequences for issues like the transfer of $\delta^{18}\text{O}$ from and to the VPDB scale, various fractionation factors, and the $\Delta^{17}\text{O}$ and other more sophisticated isotope measurements, such as clumped isotopes. The cause of this discrepancy needs to be found.

Topic groups: 10. Geochemistry and Hydrology,

Presentation types: Oral presentation

Title: Stable isotope studies (d2H, d18O) of soil water movement in spruce and beech ecosystems at Solling, Germany

Lead author: Paul Koeniger, Federal Institute for Geosciences and Natural Resources (BGR)

Author: Henning Meeseburg, Northwest German Forest Research Institute (NW-FVA); Bernd Ahrends, Northwest German Forest Research Institute (NW-FVA); Susanne Stadler, Federal Institute for Geosciences and Natural Resources (BGR); Ursula Noell, Federal Institute for Geosciences and Natural Resources (BGR); Christoph Neukum, Federal Institute for Geosciences and Natural Resources (BGR)

Keywords: soil water movement, spruce, beech

Content:

Three-year time series of stable isotopes (d18O and d2H) in precipitation and soil water were collected at European beech and Norway spruce ecosystems at Solling in Northwest Germany. The aim of the isotope study is a better understanding of soil water movement and groundwater recharge at the long-term ecosystem monitoring sites [1]. Precipitation samples from collectors at the beech and spruce forest sites were taken as bi-weekly totals. Soil water samples were collected in bi-weekly totals from suction lysimeters installed at four different depths at beech and spruce sites, whenever soil water was available. All samples were analyzed for stable isotope composition at the Federal Institute for Geosciences and Natural Resources (BGR) in Hannover, Germany, using a Picarro L2120-i water vapor analyzer with long-term accuracies for quality check samples better than 0.2‰ and 0.8‰ for d18O and d2H, respectively. Visible variability of precipitation and soil water patterns (more than 1,000 samples) indicate soil water transport mechanisms. Beside general patterns (seasonality and trends) we focus on differences between forest type, as well as on the importance of amount weighing procedures, corrections for minor amounts and aspects of sample storage.

Topic groups: 12. Sponsor session,

Presentation types: Oral presentation

Title: The analysis of clumped isotopes in various gas species and fresh insights into petroleum and atmospheric research

Lead author: Nina Albrecht, Thermo Fisher Scientific

Keywords: Clumped Isotopes; Methane; Carbonate

Content:

Non-stochastic 'clumping' of heavy isotopes in methane (CH₄), nitrogen (N₂), hydrogen (H₂), and carbon dioxide (CO₂) have evolved to become powerful tools to better understand the origin and temperature history of natural gas or rock samples. Combined with classical stable gas isotopes (δD , $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, $\delta^{15}\text{N}$), clumped isotopes ($\Delta^{13}\text{CH}_3\text{D}$, $\Delta^{12}\text{CH}_2\text{D}_2$, $\Delta^{15}\text{N}^{15}\text{N}$, ΔD_2 , Δ_{47} , Δ_{48}) offer additional dimensions to forensic source discrimination and the characterization of formation processes. And while the geothermometric usability of classical stable gas isotopes is limited, clumped isotope equilibrium distributions are solely dependent on formation temperature [1] and it has been widely demonstrated that equilibrium clumping can be used to determine highly precise carbonate and methane formation temperatures [2, 3]. This presentation introduces the analytical methodologies to analyze clumped isotopes with (High Resolution-) Isotope Ratio Mass Spectrometry and showcases application examples to illustrate the scientific added value of these measurements. The focus is on clumped methane and clumped carbonate measurements, subordinately also clumped hydrogen and clumped nitrogen, and their usability in various scientific fields such as paleoclimate research, source apportionment of natural gases, maturity of oil and gas reservoirs, burial history reconstruction, carbon capture and storage, the identification of formation mechanisms, advanced geothermometry, and the resolution of kinetic biases in cases where the clumped isotopic composition of a sample deviates from the thermodynamic equilibrium. [1] Eiler, JM (2007) "Clumped-isotope" geochemistry—The study of naturally-occurring, multiply-substituted isotopologues. *Earth Planet Sci Lett* 262, 309-327. [2] Eldridge, DL, Korol, R, Lloyd, MK, Turner, AC, Webb, MA, Miller III, TF, Stolper, DA (2019) Comparison of Experimental vs Theoretical Abundances of ¹³CH₃D and ¹²CH₂D₂ for Isotopically Equilibrated Systems from 1 to 500°C. *ACS Earth Space Chem* 3(12), 2747–2764. [3] Fiebig, J, Daëron, M, Bernecker, M, Guo, W, Schneider, G, Boch, R, Bernasconi, SM, Jautzy, J, Dietzel, M (2021) Calibration of the dual clumped isotope thermometer for carbonates. *Geochim Cosmochim Acta* 312, 253-256.

Topic groups: 04. Paleoclimatology & Archaeology,

Presentation types: Oral presentation

Title: Bayesian uncertainty estimates for Atomic C:N Ratios in Archaeological Collagen

Lead author: Carlo Coccozza, LMU Munich; MPI-SHH Jena; Università di Caserta

Author: Noemi Mantile, Università di Caserta; Simona Altieri, Università di Caserta; Maria Rosa di Cicco, Università di Caserta; Sofia Panella, Università di Roma "La Sapienza"; Carmine Lubritto, Università di Caserta; Ricardo Fernandes, MPI-SHH Jena; University of Oxford; Masaryk University

Keywords: Atomic C:N Ratio; Stable Isotopes; Collagen; Diagenesis; Bayesian Modelling

Content:

In our contribution, we present a reassessment of the atomic C:N ratio criterion for bone collagen preservation status. Our aim was to define an error range in calculated atomic C:N ratios that takes into consideration analytical uncertainties. Such assessment may redefine the application of the criterion to archaeological research. A common concern in bioarchaeology is the assessment of the preservation status of collagen extracted from osteological materials. Contaminations from exogenous fatty acids and humic acids may result in an alteration of in vivo isotopic signals. To identify potential diagenetic alterations, a series of criteria (i.e. collagen yield, carbon and nitrogen concentrations, and atomic C:N ratio) were first established in the 1980's. However, the atomic C:N ratio became the most relevant criterion in deciding whether to exclude an isotopic measurement from data analysis and interpretation. For this ratio a standard range (2.9-3.6) is usually taken as reference for good quality collagen. However, comparisons with measured samples have not until now, to the best of our knowledge, taken into account the propagated error deriving from analytical uncertainties in %C and %N measurements. We investigated the accuracy and precision of elemental measurements. The %C and %N concentrations for amino acid replicates (Aspartic Acid, Tyrosine, Glycine, and Valine) were measured 12 times. A similar, experimental setup was also used for (12) archaeological collagen samples presenting a higher variability in %C and %N concentrations when compared to single amino-acids. Bayesian regression models were used to calibrate elemental measurements and to simulate the uncertainty to be reported for C:N ratios. We will discuss the implications that our results have for assessments of bone collagen preservation using the C:N atomic ratio criterion.

Topic groups: 11. Molecular & Intra-Molecular Biology,

Presentation types: Oral presentation

Title: Position-Specific Isotope Analysis in Hopanoid Lipids

Lead author: Anca Amariei, University of Glasgow

Author: Mara Knapp, University of Strathclyde ; Mark Stillings, University of Strathclyde ; Jaime Toney, University of Glasgow ; Caroline Gauchotte-Lindsay , University of Glasgow

Keywords: position-specific isotope analysis, pyrolysis, methanotrophs, hopanoids, diploptene

Content:

Methanotrophs are bacteria able to consume methane (CH₄) as a source of carbon and energy, incorporating the CH₄ isotopic signature into the intramolecular structure of the membrane-located hopanoid lipids. However, due to source dilution and the fact that methanotrophs can use other sources of carbon, the hopanoid methanotroph isotopic signature can be muted in natural microbial communities. In pure laboratory cultures of type I and II methanotrophs, isotopic signatures of diploptene, a hopanoid lipid, ranged between -82.58‰ to -63.34‰ when fed on a -42.8‰ CH₄, showing a significant depletion. We present here theoretical and analytical methodologies using gaseous pyrolysis for position-specific isotope analysis (PSIA) that will enable the detection of methanotrophy at the intramolecular level. Theoretical mechanisms of diploptene pyrolysis were initially studied using Reaction Mechanism Generator (RMG, Gao et al., 2016). Above 600°C, the main fragment produced is isoprene, from squalene which occurs as an unstable intermediate. The hopanoid backbone is therefore unfolded, undoing the action of the squalene-hopene cyclase enzyme, and broken down. At higher temperatures, RMG predicted that isoprene could be further pyrolyzed to reach single carbon level. Thus, experimental PSIA of diploptene provides the following challenges: 1) low concentrations, 2) it is a high molecular weight compound and 3) presents a step-wise break down for accessing the CH₄ isotopic signature. We used an in-house preparational GC-FID (prep-GC), coupled with a pyrolyzer, a valve system and an oven-integrated cold trap that allowed us to trap, augment and pyrolyze compounds of interest. A heated transfer line permitted fragment identification on a second GC-FID and GC-MS. Diploptene pyrolysis in the prep-GC system has not yet been possible as the settings of the trap needed to be adapted to its high molecular weight. Nonetheless, gaseous phase pyrolysis of squalene matched RMG results. Isoprene was the main fragment formed above 500°C, confirming the second part of the theoretical pyrolysis model: diploptene-(squalene)-isoprene. For isoprene, however, theoretical and experimental results diverged. Polymerization and multiple secondary products were formed above 600°C, compromising the success of PSIA. Other gaseous phase reactions are being investigated to further break down diploptene-derived isoprene which, if successful, would allow us to access for the first time key intramolecular information in diploptene, and trace CH₄ incorporation into this molecule. Gao, C.W., Allen, J.W., Green, W.H. and West, R.H., 2016. Reaction Mechanism Generator: Automatic construction of chemical kinetic mechanisms. *Computer Physics Communications*, 203, pp.212-225.

Topic groups: 01. Methodological Advances,

Presentation types: Oral presentation

Title: GC-based concentration, pyrolysis and trapping prep-system for position specific stable isotope analysis

Lead author: Caroline Gauchotte-Lindsay , University of Glasgow

Author: Anca Amariei, University of Glasgow

Keywords: PSIA, gaseous pyrolysis, intramolecular, IRMS, hyphenated techniques

Content:

Position specific stable isotope analysis (PSIA) is the study of the isotopic signature of a particular atom or moiety inside a molecule. Molar distribution of isotopomers is not stochastic and is related to the origin of the molecule: biosynthetic pathway, mechanism, temperature and pressure of formation. PSIA has been acknowledged by many as the next frontier in stable isotope analysis (Eiler et al., 2013). In 1997, Prof Thomas Brenna's group at Cornell University first reported their design of a hyphenated system for on-line PSIA. Compounds of interest were isolated from a mixture by GC and then pyrolysed on-line in a gas furnace into smaller fragments before that the fragments were injected in the GC-IRMS for compound specific stable isotope analysis (CSIA); the isotopic signatures of the fragments reflecting the signature of an atom or a moiety in the parent molecule. Since then, however, on-line PSIA has remained a niche technology and only a handful of research groups have built similar systems. Challenges in PSIA with IRMS include a non-trivial relationship between the isotopic signatures of the pyrolysis fragments and that of their parent moieties and high limits of detection not directly compatible with "real life" samples. We have aimed to break the barriers to PSIA to the community by designing a prep system based on the modification of a GC-FID. The prep-GC system was designed with switching valves for heart-cutting the compound of interest from complex samples, an oven-integrated customizable cold-trap for enrichment through multiple injection and/or trapping the pyrolysis products prior to further analysis, and an online gas pyrolyser using a looped capillary in a furnace. A flexible heated transfer line can link the prep-GC system to a different GC for annotations of pyrolysis products (GC-MS) or their stable isotope measurements (GC-c-IRMS). We used methyl-tert-butyl ether, a molecule well studied for intramolecular stable isotope signatures, to calibrate the system against previous experimental work (Gauchotte et al., 2009) and theoretical mechanistic data from the reaction mechanism generator (RMG, Gao et al, 2016). The prep-GC system delivered MTBE pyrolysis that was reproducible and conformed to RMG prediction. We then carried out the on-line gaseous-phase pyrolysis of a series of compounds with various functional groups and molecular weight, MTBE, n-heptane, dimethyl naphthalenes, squalene, isoprene, in both pure standards and in mixtures.

Topic groups: 09. Isoscape, Spatial Variability of Stable Isotopes (Migration, Food Webs),

Presentation types: Oral presentation

Title: Stable isotopes provide a window into the diets of Eurasian reindeer at different temporal and spatial scales.

Lead author: Tamara Ann Hiltunen, University of Oulu

Author: Audun Stien, The Arctic University of Norway; Maria Väisänen, University of Oulu; Jouko Kumpula, Natural Resource Institute Finland (LUKE); Erik Ropstad, Norwegian University of Life Sciences; Jouni Aspi, University of Oulu; Jeffery Welker, University of Anchorage Alaska, University of Oulu, UArctic

Keywords: Reindeer, Svalbard, Finland, stable isotope, diet, trophic niche, climate change

Content:

Reindeer/ caribou (*Rangifer tarandus*) have a circumpolar distribution where they play important roles, in the cultures of indigenous people and in the environment as a keystone ecosystem engineer. In recent decades, these animals have experienced poorly understood population trends, with some populations collapsing and others increasing. The availability of forage is thought to be one of the main drivers behind these variable population dynamics. Thus populations with positive trends (Svalbard reindeer; *R. t. platyrhynchus*) or are intensively managed (semi-domesticated reindeer in Finland; *R. t. tarandus*) provide ideal study systems to investigate the dietary responses to changes in the foraging environment at different temporal and spatial scales. While the analysis of stable isotopes $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ provides an established method to reconstruct the dietary trends. In the first study system, we used Svalbard reindeer serum $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ to reconstruct the late winter diets over a 17-year period (1995–2012). Changes in the isotopic values were associated with increases in growing season temperatures, increases in the frequency of rain-on-snow events and increases in the population density. The reconstructed diets indicated a temporal increase in the consumption of graminoids and reduced use of mosses as modelled. Furthermore, the variance in isotopic niche positions, breadths and overlaps supports the temporal shift in the foraging niche and additionally demonstrates a deviation in the dietary response to extreme rain-on-snow events. This long-term study highlights how Svalbard reindeer modify their late winter diets in response to climate change-induced variations in forage availability and accessibility. In the second study system, we are investigating spatial and temporal variations in the foraging behaviour of semi-domesticated reindeer in northern Finland using GPS locations combined with stable isotope values. A comprehensive isotopic library of different reindeer tissues and plausible forage functional groups from areas frequented by collared reindeer has been developed. Location data from GPS-collared reindeer (2019 to 2022) will increase the understanding of how reindeer utilise and select pastures at different spatial and temporal scales. While the diets of the reindeer will be reconstructed using stable isotope mixing models, the reindeer and forage $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values. These studies will add to the current body of knowledge on reindeer foraging ecology in the 21st century. In addition, they highlight the versatility of bulk stable isotopes in studying the foraging ecology of a generalist herbivore in long-term studies or in combination with other methodologies, such as movement data, in short-term studies.

Topic groups: 07. Atmospheric Sciences (Pollution, Climate Change, Cosmogeochimistry),

Presentation types: Oral presentation

Title: Verification of method used to determine $\delta^{13}\text{CH}_4$ during mobile vehicle-based methane measurements

Lead author: Sara M Defratyka, University of Edinburgh (UoE); National Physical Laboratory (NPL)

Author: James L France, Royal Holloway, University of London; Environmental Defense Fund; Rebecca E Fisher, Royal Holloway, University of London; Dave Lowry, Royal Holloway, University of London; Julianne M Fernandez, Royal Holloway, University of London; Semra Bakkaloglu, Royal Holloway, University of London; Camille Yver-Kwok, Laboratoire des Sciences du Climat et de l'Environnement (LSCE-IPSL); Jean-Daniel Paris, Laboratoire des Sciences du Climat et de l'Environnement (LSCE-IPSL); Philippe Bousquet, Laboratoire des Sciences du Climat et de l'Environnement (LSCE-IPSL); Tim Arnold, University of Edinburgh (UoE); National Physical Laboratory (NPL); Chris Rennick, National Physical Laboratory (NPL); Jon Helmore, National Physical Laboratory (NPL); Euan G Nisbet, Royal Holloway, University of London

Keywords: methane, CH₄, controlled release, verification

Content:

Methane (CH₄) isotopic composition varies depending upon on a range of different factors, such as temperature of formation, oxidation or biological processes. Thus, studying the isotopic signature of atmospheric methane may improve the knowledge about origin of CH₄ released to the atmosphere and subsequently knowing CH₄ isotopic signatures can improve source attribution in top-down emission studies and help to verify CH₄ emission inventories. CH₄ isotopic signatures can be measured directly from the methane source or in near-source conditions and can be used to determine the likely source of an observed CH₄ plume. For the near-source studies, isotopic signature can be measured from ambient air by taking bag/canister samples and measured afterward in the laboratory or by in-situ measurements, for example with CRDS instrument with an AirCore (air storage) tool. To determine the isotopic signature of an observed CH₄ source, Keeling plots or Miller-Tans plots can be used. These methods are based on the principle of mass balance conservation. Due to that, observed enhancement of CH₄ mixing ratio is a combination of CH₄ atmospheric background and methane source mixing ratio. Both methods use a linear regression to determine isotopic signature of observed CH₄ source. Thus, the choice of calculation method to estimate the best linear fitting can have an impact for determine isotopic signature. The presented study is focused on using both Keeling and Miller-Tans methods to determine methane isotopic signature from mobile, vehicle-based methane measurements. We conducted a controlled release experiment during 5 days in September 2019, while methane was emitted in periods of 45 minutes, with invariable and unknown $\delta^{13}\text{CH}_4$. According to our knowledge, it is the first controlled release experiment focused on verification of methods used to determine CH₄ isotopic signature. Here, we are focused on verification of accuracy and detection limit of $\delta^{13}\text{CH}_4$ using both Keeling and Miller-Tans plot and have insight into an impact of chosen calculation methods for determined isotopic signature. Moreover, we compare results obtained using two different measurement techniques – IRMS and CRDS.

Topic groups: 07. Atmospheric Sciences (Pollution, Climate Change, Cosmogeochimistry),

Presentation types: Oral presentation

Title: Measuring and modelling four isotopologue ratios of methane in the atmosphere

Lead author: Tim Arnold, NPL and University of Edinburgh

Author: Ed Chung, NPL; Chris Rennick, NPL; Emmal Safi, NPL; Alice Drinkwater, University of Edinburgh; Caroline Dylag, NPL; Sara Defratyka, University of Edinburgh and NPL

Keywords: methane, hydroxyl, emissions verification, climate change

Content:

We present work on monitoring isotopologue ratios of methane (CH_4) to advance our understanding of fluxes at both the global and regional scales. Trends in global atmospheric CH_4 – both mixing ratios and isotope ratios – are explained by various flux scenarios, from tropical wetland emission increases through to reductions in global hydroxyl (OH). In regional scale studies the challenge for scientists is in making and interpreting higher frequency measurements for the spatial and sectoral breakdown of emissions to aid in the verification of greenhouse gas (GHG) inventories. We have modelled the potential of the doubly-substituted isotopologues ($\Delta^{13}\text{CH}_3\text{D}$ and $\Delta^{12}\text{CH}_2\text{D}_2$) to understand the longer-term global atmospheric CH_4 cycle (based on existing knowledge of sources and sinks for both $\Delta^{13}\text{CH}_3\text{D}$ and $\Delta^{12}\text{CH}_2\text{D}_2$). Measurements of $\Delta^{12}\text{CH}_2\text{D}_2$ in particular (alongside a global network of $\delta^{13}\text{C}$ and $\delta^2\text{H}$ measurements) could provide constraints for understanding trends in the global total source and sink magnitudes. Changes in OH concentration of 10% developed across three decades result in a difference of up to 2‰ in $\Delta^{12}\text{CH}_2\text{D}_2$, which would be observable given current measurement uncertainty limits. At regional scales the difficulty in making routine, high-quality and near-continuous measurements of the singly-substituted isotopologue ratios hampers their use in inverse modelling frameworks. We will present an instrument, 'Boreas', and data analysis and calibration procedures for making long term simultaneous measurements of $\delta^{13}\text{C}$ and $\delta^2\text{H}$ in ambient air. Excluding isotope ratio scale uncertainty, standard measurement uncertainty for an ambient air sample can reach 0.07‰ for $\delta^{13}\text{C}$ and 0.9‰ for $\delta^2\text{H}$. Following deployment to a tall tower GHG monitoring site in the UK we will present measurements to demonstrate the utility of continuous isotope ratio measurements for country-scale emissions verification. Finally, we will discuss the technical challenges faced in advancing this area of stable isotopic analysis for atmospheric CH_4 and the work that is planned in the following years.

Topic groups: 12. Sponsor session,

Presentation types: Oral presentation

Title: Analysis of dissolved nitrate stable isotopes using the one-step Ti (III) reduction method and iso FLOW GHG headspace analyzer

Lead author: Calum Preece, Elementar UK Ltd

Author: Sam Barker, Elementar UK Ltd; Davide Gastaldello, Elementar UK Ltd; Rob Berstan, Elementar UK Ltd; Mike Seed, Elementar UK Ltd

Keywords: Nitrate, nitrite, iso FLOW GHG, isoprime precisION, Ti (III) reduction, nitrogen, IRMS, N₂O

Content:

Identifying and quantifying sources and cycling of nitrogen is important for understanding not only aquatic ecosystems but also planning water resource management, mitigating urban and agricultural pollution, and optimizing government policy. Stable isotopes of dissolved nitrate and nitrite ($\delta^{15}\text{N}$, $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$) have been useful in distinguishing between the diverse nitrogen sources and sinks and help understand large scale global ocean processes as well as revealing major changes in agricultural land use and urbanization. Despite the strength of dissolved nitrate and nitrate stable isotope analysis, the strong barrier for uptake using the favored contemporary methods (bacterial denitrifier and Cd-azide reaction) due to the laborious multi-step methods, maintenance of anaerobic bacterial cultures and use of highly toxic chemicals has limited the analysis to highly specialized laboratories. We evaluate the performance of the iso FLOW GHG headspace analyzer and isoprime precisION using the new Ti (III) reduction method (Altabet et al., 2019) for one step conversion of nitrate into N₂O for IRMS analysis. Taking advantage of the inherent benefits of the isoprime precisION, the iso FLOW GHG has been developed for high performance analysis of CO₂, N₂O and CH₄ and has the capacity to be rapidly customized for specific needs with options for N₂ and N₂O, hydrogen isotopes in CH₄ and dissolved nitrate analysis.

Topic groups: 08. Soil Carbon and Nitrogen Cycling, with Focus on Agricultural Soils,

Presentation types: Oral presentation

Title: Increased C and N turnover after litter addition alters contribution of nitrification and denitrification to NO and N₂O formation

Lead author: Pauline Sophie Rummel, Plant Nutrition and Crop Physiology, University of Göttingen, Germany

Author: Paulina Englert, Plant Nutrition and Crop Physiology, University of Göttingen, Germany; Reinhard Well, Thünen Institute of Climate-Smart Agriculture, Braunschweig, Germany; Lukas Beule, Julius Kühn Institute for Ecological Chemistry, Berlin, Germany; Johanna Pausch, Agroecology, University of Bayreuth, Germany; Klaus Dittert, Plant Nutrition and Crop Physiology, University of Göttingen, Germany

Keywords: Nitrification, Denitrification, N and C cycling, arable grassland soil

Content:

Returning of crop residues is a common agricultural management strategy to prevent nutrient losses and to increase soil fertility. However, acceleration of N and C cycling processes often lead to increased losses of climate-relevant gases. When litter and soil organic matter (SOM) turnover are increased after litter addition, microbial O₂ demand increases with increasing microbial respiration. This may lead to formation of local hotspots with anoxic or microoxic conditions providing favorable conditions for denitrifying soil microorganisms. To investigate the effect of SOM content, soil moisture, and litter quality on CO₂, NO, N₂O, and N₂ emissions, we conducted laboratory incubation studies in controlled atmosphere with two soils (arable and grassland), different soil moisture (50-70 % WFPS), and different types of maize litter (*Zea mays* L., fresh leaves, roots, straw). We partitioned the CO₂ efflux into litter and SOM derived CO₂ based on the natural ¹³C isotope abundances and applied the N₂O isotopocule mapping approach to distinguish between N₂O emitting processes. Soil water extractable organic C, and inorganic N were measured in parallel samples. At the end of the experiment, abundance of bacteria, fungi, and functional N cycling genes were assessed. Maize litter increased total and SOM derived CO₂ emissions leading to positive priming effects. Litter addition significantly increased N₂O losses from both soils under all soil moistures. CO₂ and N₂O fluxes were strongly positively correlated confirming that easily degradable C promoted denitrification. NO fluxes differed between arable and grassland soil and were affected by soil moisture and litter addition. The NO/N₂O ratio indicated contribution of both nitrification and denitrification in the grassland soil. Isotopocule mapping confirmed contribution of different processes depending on soil type, moisture, and litter addition. In the grassland soil, fungal denitrification contributed to N₂O formation after litter addition, while nitrification contributed to N₂O formation without litter addition. In the arable soil, bacterial denitrification was the dominant process.

Topic groups: 03. Plant Ecophysiology,

Presentation types: Oral presentation

Title: Monitoring passage of a point-based label of ^2HHO through the soils and stems of a boreal pine forest

Lead author: John Marshall, Swedish University of Agricultural Sciences (SLU)

Author: Noelia Saavedra, Swedish University of Agricultural Sciences (SLU); Maren Dubbert, Leibniz-Zentrum für Agrarlandschaftsforschung (ZALF); Kathrin Kuehnhammer, IGOE, Environmental Geochemistry, Braunschweig, Germany; David Dubbert, Leibniz Institute of Freshwater Ecology and Inland Fisheries; Matthias Beyer, IGOE, Environmental Geochemistry, Braunschweig, Germany

Keywords: Xylem, transpiration, horizontal, root uptake, labeling

Content:

The isotopic composition of transpiration has been difficult to quantify due to the laboriousness of the traditional cryogenic extraction and to possible artifacts in the process. New methods provide continuous, in-situ measurements, relying on isotopic equilibration of sampled water vapor with the water flowing in the sapwood of the tree stem. The isotopic composition of the tree sap represents the daily integral of transpiration. Here we used the borehole equilibration method to detect the passage of a tracer through the system and to map the "rootspan" of surrounding trees. The ^2HHO tracer was applied to the soil surface within a 1-m² area and monitored as it passed through the stems of the surrounding trees. We observed a strong response in one of the trees nearest the labelled area. We also detected the label in several other trees in the vicinity, as far as 5 m from the labelled plot. Methodologically, this shows that the borehole method is able to detect the labelling and monitor temporal dynamics of the tracer uptake for several weeks at least. Ecologically, it describes a tree's functional rootspan in terms of its ability to collect water laterally from the soil.

Topic groups: 08. Soil Carbon and Nitrogen Cycling, with Focus on Agricultural Soils,

Presentation types: Oral presentation

Title: Stable isotope approaches to identify HONO production mechanisms from soil

Lead author: Hem Raj Bhattarai, University of Eastern Finland; Natural Resources Institute Finland

Author: Wolfgang Wanek, University of Vienna; Henri M.P. Siljanen, University of Eastern Finland; Jussi Ronkainen, University of Eastern Finland; Maarit Liimatainen, University of Eastern Finland; University of Oulu; Natural Resources Institute Finland; Yuntao Hu, University of Vienna; Lawrence Berkeley National Laboratory (LBNL); Hannu Nykänen, University of Eastern Finland; Christina Biasi, University of Eastern Finland; Marja Maljanen, University of Eastern Finland

Content:

Photolysis of nitrous acid (HONO) produces a significant amount of hydroxyl radicals (OH), key oxidants in the atmosphere. Soils are recognized as important HONO emitters, yet the role of soils as a HONO source has remained enigmatic as HONO production pathways and their relative contribution in most ecosystems are currently unknown. Here, by applying ^{15}N tracer and pool dilution techniques ($^{15}\text{NO}_3^-$, $^{15}\text{NH}_4^+$, and $^{15}\text{NO}_2^-$), we show that microbial processes are more important than abiotic processes for HONO emissions in boreal agricultural ecosystems. We show that microbial nitrate (NO_3^-) reduction (denitrification) considerably exceeded ammonium (NH_4^+) oxidation (nitrification) as a source of nitrite (NO_2^-), which is the central nitrogen pool connected with HONO emissions. With our method we show that of the total HONO produced, denitrification contributed 97% in a low organic matter (LOM) soil and 62% in a high organic matter (HOM) soil. Microbial NH_4^+ oxidation only produced HONO in the HOM soil (10%). Our findings indicate that microbial NO_3^- reduction is a vital HONO production pathway in aerobic soils. Our study suggests that soil processes contributing to HONO production can be partitioned and better understood by the combination of ^{15}N tracer and pool dilution techniques.

Topic groups: 08. Soil Carbon and Nitrogen Cycling, with Focus on Agricultural Soils,

Presentation types: Oral presentation

Title: Real-time mapping of subsurface nitrous oxide isotopes and other trace gases from diffusive gas probes under a cattle grazing pasture

Lead author: Rob Roscioli, Aerodyne Research, Inc.

Author: Joanne Shorter, Aerodyne Research, Inc.; Elizabeth Lunny, Aerodyne Research, Inc.; Scott Herndon, Aerodyne Research, Inc.; Nuria Casanova-Gomez, University of Illinois at Urbana-Champaign; Evan DeLucia, University of Illinois at Urbana-Champaign; Elena Blanc-Betes, University of Illinois at Urbana-Champaign; Peter Byck, Arizona State University

Keywords: agricultural, nitrous oxide, isotopes, cattle grazing, greenhouse gases

Content:

Cattle grazing of rangeland has the potential to be either a large source or sink of greenhouse gases, depending upon the land and grazing management practices. Understanding the subsurface processes that drive aboveground gas emissions, and the environmental conditions that alter them, is important to developing grazing strategies with low or negative carbon footprints. In combination with other indicators, isotopic signatures of trace gases can serve as messengers of their production pathways in soil. Here we present subsurface and aboveground trace gas measurements at an Adaptive Multi-Paddock grazing pasture in Alabama during wet and dry seasons. Real-time maps of subsurface carbon dioxide (CO₂), oxygen (O₂) and isotopically-resolved nitrous oxide (N₂O) were produced using an array of 24 novel diffusive soil probes connected to a central laser-based analyzer. Simultaneous eddy covariance measurements of N₂O, CO₂, and methane fluxes were obtained, allowing for a direct comparison of soil gases and their atmospheric impact. Here we focus on N₂O isotopic signatures and concentrations in the subsurface to aid in identifying the nitrogen-processing pathways that give rise to surface N₂O fluxes. We also explore spatial heterogeneity and the impact of subsurface “hot moments” and “hot spots” on surface emissions, with a specific focus on aboveground forcings (grazing, rain, and drought).

Topic groups: 09. Isoscape, Spatial Variability of Stable Isotopes (Migration, Food Webs),

Presentation types: Oral presentation

Title: Seasonal and spatial variability of pelagic-benthic coupling strength in the Northern Barents Sea: A benthic food web approach

Lead author: Amanda Ziegler, University of Tromsø

Author: Thaise Ricardo de Freitas, University of Oslo; Bodil Bluhm, University of Tromsø; Lis Jørgensen, Institute of Marine Research; Paul Renaud, Akvaplan-niva

Keywords: Barents Sea; food web; benthic; bulk stable isotope analysis

Content:

Phytoplankton and sea-ice algal detritus constitute the main food sources for benthic invertebrates in the Northern Barents Sea. The high spatial and seasonal variability in production and export of these food sources likely influence patterns of benthic food web structure and the strength of pelagic-benthic coupling. To assess benthic food web structure and pelagic-benthic coupling, benthic epifauna, infauna, and demersal fish were collected at 7 stations spanning 76-81°N in the Northern Barents Sea during 2018, 2019 and 2021, and analyzed for stable isotopes of carbon and nitrogen ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$). We find that the highest trophic level is typically occupied by surface and subsurface deposit feeding echinoderms (e.g. *Molpadia borealis*), predatory molluscs (e.g. *Buccinum hydrophanum*, *Rossia* sp.), shrimp (e.g. *Sabinea septemcarinata*, *Sclerocrangon ferox*) and demersal fish (e.g. *Leptagonus decagonus*). Lower trophic levels are a mix of suspension- and deposit-feeders (e.g. Annelids) that have wide isotopic niches in terms of both $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ suggesting these taxa are generalist feeders taking advantage of many food sources of varying quality. Some taxa (e.g. *Ophiacantha bidentata*, *Sabinea septemcarinata*) show a spatial, northward enrichment in $\delta^{13}\text{C}$ suggesting an increasing contribution of sympagic carbon and tight pelagic-benthic coupling in the northern portion of the Barents Sea compared to the south, however, additional baseline sampling is needed. The overall structure of the benthic food web remains similar across seasons, and the distance between benthic functional groups and the algal baseline are surprisingly similar throughout the year suggesting that the strength of pelagic-benthic coupling remains relatively constant in time. Continued assessment of pelagic-benthic coupling within the Barents Sea from a food web perspective will improve our understanding of seasonality within the benthic realm and provide insights into the future functioning of the benthic ecosystem.

Topic groups: 09. Isoscape, Spatial Variability of Stable Isotopes (Migration, Food Webs),

Presentation types: Oral presentation

Title: Towards fouling fauna fingerprinting: what is their contribution to the marine organic matter pool of an offshore wind farms?

Lead author: Esther Cepeda Gamella, Royal Belgian Institute of Natural Sciences

Author: Pascal Boeckx, Isotope Bioscience Laboratory, Ghent University ; Samuel Bode, Isotope Bioscience Laboratory, Ghent University ; Ulrike Braeckman, Marine Biology Research Group, Ghent University ; Carl Van Colen, Marine Biology Research Group, Ghent University ; Steven Degraer, Royal Belgian Institute of Natural Sciences ; Tom Moens, Marine Biology Research Group, Ghent University ; Jan Vanaverbeke, Royal Belgian Institute of Natural Sciences

Keywords: Fouling Fauna; Faecal Pellets; Organic Matter dynamics; Isotope Analysis; Amino Acids; *Mytilus edulis*; *Jassa herdmani*; *Metridium senile*; trophic position, food web, Offshore Wind Farm.

Content:

The North Sea is a world-leading region for capacity and expertise in Offshore Wind Farms (OWFs), acknowledging the European Union's effort to reduce the emission of Greenhouse Gases. By 2030, at least 32% of the energy production must be from renewable sources. Offshore wind farms are important contributors to reach this goal. However, the presence of wind turbines in the marine environment affects the local ecosystem structure and functioning. They provide new artificial hard substrates, which are perfect habitats for rapid colonization by epifaunal organisms. This fauna mainly consists of suspension-feeding communities dominated by blue mussel (*Mytilus edulis*), tube-building amphipods (*Jassa herdmani*), and plumose anemones (*Metridium senile*). They feed on suspended organic particles, phyto- and zooplankton present in the water column and can filter ca. 7.5 olympic swimming pools per day per turbine. Part of this feed is returned to the water column as faecal pellets (FP). These FP are thought to play a crucial role in the local organic matter (OM) dynamics and possibly contribute to carbon sequestration in the sediment surrounding the turbines. Therefore, to assess their importance within the pelagic and benthic OM pools of OWFs ecosystems, it is essential to develop tracers for the FP of the dominant species (*M. edulis*, *J. herdmani*, and *M. senile*) and the other components (phyto-, zooplankton, and bacteria-degraded OM). We apply Compound-Specific Stable Isotope Analysis of amino acids (CSSIA - AA) to develop isotopic tracers. The amino acid (AA) $\delta^{15}\text{N}$ signal of a FP species depends on its diet, the AA pathways from primary producers to consumers, and the possible alteration through the metazoan gut passage. Some AAs change little their $\delta^{15}\text{N}$ signal ("source" amino acids) while others undergo significant metabolic alterations ("trophic" amino acids). We have incubated the three species of interest in controlled lab conditions to harvest species-specific FP. We then analyzed the $\delta^{15}\text{N}$ signal of the AA in these FP, and the other components of the marine OM pool. Using different AAs $\delta^{15}\text{N}$ values as input for multivariate techniques, the AAs with the strongest discriminating power are identified. This multivariate set of tracers will subsequently be used in Bayesian Mixing Model, to finally estimate the proportional contribution of FP to the OM pool. The latter will be the first step to determine the fate of FP in the sediment, estimate the carbon sequestration potential of altered OWF sediments, and model the potential spatial dimensions of sediment enrichment.

Topic groups: 04. Paleoclimatology & Archaeology,

Presentation types: Oral presentation

Title: Unravelling dietary aspects of Late Mesolithic to Early/Middle Neolithic cultures in the Scheldt river valley, Belgium, by compound-specific ^{13}C analysis

Lead author: Marieke Vannoorenberghe, Ghent University, Dep. of Chemistry, Atomic and Mass Spectrometry – A&MS

Author: Samuel Bodé, Ghent University, Dep. of Green Chemistry and Technology, ISOFYS; Dimitri Teetaert, Ghent University, Dep. of Archaeology, Prehistory of Europe research group; Frank Vanhaecke, Ghent University, Dep. of Chemistry, Atomic and Mass Spectrometry – A&MS; Philippe Crombé, Ghent University, Dep. of Archaeology, Prehistory of Europe research group; Pascal Boeckx, Ghent University, Dep. of Green Chemistry and Technology, ISOFYS

Keywords: compound-specific stable isotope analysis, Fatty acid, Paleodiet reconstruction, Swifterbant culture

Content:

Determining dietary practices of cultures in history is important for archaeology. The analysis of organic residues found in pottery fragments discovered during archeologic excavations, helps to answer questions on the use of pottery as cooking and storage devices. Since the 1970's, the ability to separate complex mixtures of organic molecules and identify the compounds present by GC-MS led to a major increase in organic residue analyses. Next to the presence of biomarkers to identify the presence of certain food residues in the artefacts, more recently, compound-specific stable isotope analysis (CSSI) of certain molecules has further refined our capacity to determine the usage of ceramic ware. More specifically, $\delta^{13}\text{C}$ in individual fatty acids, such as, stearic (C18:0) and palmitic (C16:0) acids, determined using GC-c-IRMS is often relied on to determine the origin of the organic residues. This approach is widely accepted to discriminate between lipid residues of different animal classes (e.g. freshwater fish vs marine fish, ruminant meat vs. porcine meat) and even indications for the processing of milk products can be found in the isotopic values. The latter offers direct proof of animal husbandry in societies and is therefore an important tool in the study of past societies transitioning from a hunter-gatherer (Mesolithic) lifestyle towards an agricultural (Neolithic) lifestyle. In this work, 100 pottery sherds from nine Late Mesolithic and Early to Middle Neolithic archaeological sites in the Scheldt river valley in Belgium were selected for CSSI of ^{13}C in C16:0 and C18:0 fatty acids. The absorbed organic residues in the pores of the ceramics were extracted and methylated by a protocol based on the use of acidified methanol and the fatty acid methyl esters thus obtained were purified before ^{13}C analysis. This research is the first to analyse absorbed organic residues to shed light on the subsistence strategies of Mesolithic-Neolithic transitional cultures in Belgium. The results indicate that the ceramics of the Late Mesolithic to Early Neolithic Swifterbant culture in the lower Scheldt area were mainly, but not exclusively, used for the processing of freshwater fish. On the other hand, the ceramics of Early to Middle Neolithic cultures in both the upper and lower Scheldt areas indicate the processing of a broad range of foods including freshwater fish and ruminants meat. In addition, some of the Neolithic ceramics possess an isotopic signature indicating the processing of ruminant milk products.

Topic groups: 03. Plant Ecophysiology,

Presentation types: Oral presentation

Title: Interpreting tree ring carbon and oxygen isotopes as a response to selection harvest in a drained peatland forest

Lead author: Olli-Pekka Tikkasalo, Natural Resources Institute Finland (LUKE), Helsinki, Finland

Author: Kersti Leppä, Natural Resources Institute Finland (LUKE), Helsinki, Finland; Samuli Launiainen, Natural Resources Institute Finland (LUKE), Helsinki, Finland; Mikko Peltoniemi, Natural Resources Institute Finland (LUKE), Helsinki, Finland; Raisa Mäkipää, Natural Resources Institute Finland (LUKE), Helsinki, Finland; Katja Rinne-Garmston, Natural Resources Institute Finland (LUKE), Helsinki, Finland; Elina Sahlstedt, Natural Resources Institute Finland (LUKE), Helsinki, Finland; Giles Young, Natural Resources Institute Finland (LUKE), Helsinki, Finland; Aleksandra Bokareva, Natural Resources Institute Finland (LUKE), Helsinki, Finland; Annalea Lohila, Finnish Meteorological Institute, Helsinki, Finland; Mika Korhonen, Finnish Meteorological Institute, Helsinki, Finland; Pauliina Schiestl-Aalto, Institute for Atmospheric and Earth System Research (INAR), Helsinki, Finland; Alekski Lehtonen, Natural Resources Institute Finland (LUKE), Helsinki, Finland

Keywords: continuous-cover forestry, ^{13}C -discrimination, photosynthesis, ecosystem modelling

Content:

Even-aged management of peatland forests is the prevailing management method in Finland, but continuous-cover forestry has recently gained increasing interest (Nieminen et al., 2018). However, there are significant knowledge gaps on the ecophysiological response of previously suppressed trees to selection harvest. Tree ring stable isotope composition of carbon and oxygen ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, respectively) record changes in photosynthesis and water use and enable the quantification of changes in growth environment of trees. When the measured isotopic signals are compared to modelled isotope discrimination the underlying processes can be revealed. We studied the response of suppressed Norway spruce (*Picea abies*) trees to selection harvesting in a fertile drained peatland forest Lettosuo in southern Finland. Part of the studied site was harvested in March 2016 and part of the site was left intact as a control. From tree rings collected from both sites, we measured intra-annual $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ variation covering the period from 2010 to 2020 at the Stable Isotope Laboratory of Luke (SILL). The isotope measurements were complemented with simulations of tree response to changed microclimate using a vertically resolved ecosystem model (Launiainen et al., 2015). Our isotope data showed that, after the selection harvest, discrimination against ^{13}C decreased by ca. 2.5‰ while the $\delta^{18}\text{O}$ stayed relatively stable. These findings suggest a significant and immediate increase in needle-level photosynthesis after the selection harvest. The modelled harvest response agreed with the measured $\delta^{18}\text{O}$ values whereas the simulated response to ^{13}C -discrimination deviated from the measurements. We tested different ^{13}C -discrimination models to study how including different discrimination processes changes the deviation between modelled and measured discrimination. Detailed ecosystem modelling allowed us to further analyze what environmental and microclimate parameters are responsible for the changes in ^{13}C -discrimination. The results showed that, after the selection harvest, the decrease in ^{13}C -discrimination was mainly caused by increased availability of photosynthetically active radiation as well as decreased relative humidity adjacent to the remaining spruce needles. Furthermore, we assessed how changing photosynthesis and water use traits in the model would affect the ^{13}C -discrimination. References Nieminen et al., *Forest Ecology and Management*, 424, 78-84, 2018 Launiainen et al., *Ecological Modelling*, 312, 385-405, 2015

Topic groups: 02. Terrestrial and Aquatic Biogeochemistry,

Presentation types: Oral presentation

Title: Tracing N₂O formation in full-scale wastewater treatment with natural abundance isotopes

Lead author: Wenzel Gruber, Eawag, Department Process Engineering, Dübendorf, CH

Author: Joachim Mohn, Empa, Air Pollution / Environmental Technology, Dübendorf, CH; Paul Magyar, University of Basel, Aquatic and Isotope Biogeochemistry, Basel, CH; Kerstin Zeyer, Empa, Air Pollution / Environmental Technology, Dübendorf, CH; Luzia von Känel, ETH, Department of Civil, Environmental and Geomatic Engineering, Zürich, CH; Eberhard Morgenroth, Eawag, Department Process Engineering, Dübendorf, CH; Moritz F. Lehmann, University of Basel, Aquatic and Isotope Biogeochemistry, Basel, CH; Daniel Braun, ETH, Department of Civil, Environmental and Geomatic Engineering, Zürich, CH; Adriano Joss, Eawag, Department Process Engineering, Dübendorf, CH

Keywords: Nitrous oxide, isotopomer, wastewater, WWTP, denitrification

Content:

Nitrous oxide (N₂O) dominates greenhouse gas emissions in wastewater treatment plants (WWTPs). Formation of N₂O occurs during biological nitrogen removal, involves multiple microbial pathways, and is typically very dynamic. Consequently, N₂O mitigation strategies require an improved understanding of nitrogen transformation pathways and their modulating controls. Analyses of the nitrogen (N) and oxygen (O) isotopic composition of N₂O and its substrates at natural abundance have been shown to provide valuable information on formation and reduction pathways in laboratory settings, but have never been applied to full-scale WWTPs. Here we show that N-species isotope ratio measurements at natural abundance level, combined with long-term N₂O monitoring, allow identification of the N₂O production pathways in a full-scale plug-flow WWTP (Hofen, Switzerland). The proposed approach can also be applied to other activated sludge systems. Heterotrophic denitrification appears as the main N₂O production pathway under all tested process conditions, while nitrifier denitrification was less important, and more variable. N₂O production by hydroxylamine oxidation was not observed. Fractional N₂O elimination by reduction to dinitrogen (N₂) during anoxic conditions was clearly indicated by a concomitant increase in SP, $\delta^{18}\text{O}(\text{N}_2\text{O})$ and $\delta^{15}\text{N}(\text{N}_2\text{O})$. The extent of N₂O reduction correlated with the availability of dissolved inorganic N and organic substrates, which explains the link between diurnal N₂O emission dynamics and organic substrate fluctuations. Consequently, dosing ammonium-rich reject water under low-organic-substrate conditions is unfavourable, as it is very likely to cause high net N₂O emissions. Our results demonstrate that monitoring of the N₂O isotopic composition holds a high potential to disentangle N₂O formation mechanisms in engineered systems, such as full-scale WWTP. Our study serves as a starting point for advanced campaigns in the future combining isotopic technologies in WWTP with complementary approaches, such as mathematical modelling of N₂O formation or microbial assays to develop efficient N₂O mitigation strategies.

Topic groups: 03. Plant Ecophysiology,

Presentation types: Oral presentation

Title: Carbon transport and allocation of mature Norway spruce during recovery from five years of repeated summer drought

Lead author: Kyohsuke Hikino, Technical University of Munich ; Jasmin Danzberger, Helmholtz Zentrum München

Author: Vincent P. Riedel, University of Würzburg; Benjamin D. Hesse, Technical University of Munich ; Timo Gebhardt, Technical University of Munich ; Benjamin D. Hafner, Cornell University; Romy Rehschuh, Technical university of dresden; Nadine K. Ruehr, Karlsruhe Institute of Technology; Melanie Brunn, University Koblenz-Landau; Taryn L. Bauerle, Cornell University; Simon M. Landhäusser, University of Alberta; Marco M. Lehmann, Swiss Federal Institute for Forest, Snow and Landscape Research (WSL) ; Thomas Rötzer, Technical University of Munich; Hans Pretzsch, Technical University of Munich; Franz Buegger, Helmholtz Zentrum München; Fabian Weikl, Technical University of Munich; Karin Pritsch, Helmholtz Zentrum München; Thorsten E. E. Grams, Technical University of Munich

Keywords: ^{13}C labeling, Belowground carbon allocation, Carbon partitioning, Climate change, Forest ecosystems, Drought recovery, *Picea abies*, Watering

Content:

This contribution presents results from a ^{13}C labeling experiment on c. 70-year-old Norway spruce (*Picea abies* [L.] Karst.) trees in parallel with a controlled watering after five years of summer drought. In the Kranzberg forest roof (KROOF) experiment, mature spruce trees were exposed to a repeated drought during five entire growing seasons from 2014 to 2018. During that time significant drought effects were observed such as reduced total leaf area, stem growth, and fine root biomass. To assess their recovery processes, the drought stressed trees were watered in early summer 2019. In parallel with this watering, we performed a whole-tree and continuous ^{13}C labeling experiment and traced the newly assimilated carbon (C) in various above- and belowground sinks, to elucidate the resilience of C transport and the role of C allocation during post-drought recovery. Few days after watering, C transport speed from crown to soil CO_2 efflux was by 50% lower in previously drought-stressed trees compared to controls. However, two weeks after watering, the C transport speed fully recovered to the control level, thus showed high resilience to the long-term repeated drought. Furthermore, previously drought-stressed trees showed 10 times greater fine root growth during four weeks after drought release, which was supplied with a preferential allocation of newly assimilated C. Despite this preferential allocation belowground, more than half of the C used for the fine root growth was met by stored C. Thus, in addition to newly assimilated C, stored C plays an essential role for tree survival during the critical time of drought recovery. Under frequent and prolonged drought predicted in the future, the high resilience of C transport and the allocation of available C to stimulated belowground sinks are both crucial for Norway spruce trees to regenerate their water-absorbing root system and tree productivity after drought release.

Topic groups: 08. Soil Carbon and Nitrogen Cycling, with Focus on Agricultural Soils,

Presentation types: Oral presentation

Title: Tracing nitrogen transformations induced by ^{15}N labelled cattle slurry applied with different techniques in winter wheat

Lead author: Caroline Buchen-Tschiskale, Thünen Institute of Climate-Smart Agriculture

Author: Reinhard Well, Thünen Institute of Climate-Smart Agriculture; Heinz Flessa, Thünen Institute of Climate-Smart Agriculture

Keywords: N_2O emission, N_2 emission, nitrification, denitrification, ^{15}N recovery

Content:

The effects of slurry application techniques on ammonia (NH_3) volatilisation and nitrous oxide (N_2O) fluxes are well documented. However, application techniques may also impact dinitrogen (N_2) fluxes, as they can influence denitrification activity by changing slurry and soil aeration, NO_3^- formation and the pH value. Up to now, measuring N_2 fluxes and following pathways of slurry nitrogen (N) transformation under field conditions is still challenging. Thus, we applied a combined ^{15}N labelling approach including slurry NH_4^+-N and soil $\text{NO}_3^- -\text{N}$ in undisturbed soil cores with winter wheat, set up as small lysimeters. Slurry treatments include the common application techniques: trailing hose with and without acidification, slot injection with and without nitrification inhibitor. In a first step, soil NO_3^- was ^{15}N labelled by homogeneous injection of a $\text{K}^{15}\text{NO}_3^-$ solution at a low N application rate, while one week later, 68 kg N ha^{-1} ^{15}N -labelled cattle slurry was applied. N_2O and N_2 fluxes were measured using the modified ^{15}N gas flux method with N_2 -depleted atmosphere and NH_3 fluxes by Draeger tube method. To close the N balance and follow the different N transformation pathways, ^{15}N losses by leaching, ^{15}N uptake by plant and residual ^{15}N in belowground biomass, microbial biomass and soil were analysed by IRMS. The major gaseous loss pathway was NH_3 with up to 8 kg N ha^{-1} in the trailing hose treatment, while slot injection significantly reduced NH_3-N losses. Regardless the application technique, N_2O emissions were low (up to $0.1 \text{ kg N}_2\text{O}-\text{N ha}^{-1}$), while N_2 emissions reached up to 3 kg N ha^{-1} . The $\text{N}_2\text{O}/(\text{N}_2\text{O}+\text{N}_2)$ ratio of denitrification was always <0.1 . An effect of the different application techniques on N-leaching was not found. Plant uptake of ^{15}N labelled N was greater in slot injection than trailing hose treatments. Impacts of the application techniques on individual N pools, such as soil mineral nitrogen, total nitrogen and soil microbial biomass nitrogen were small, however, the ^{15}N recovery offered a chance to map the short-term effects. Indications for high N immobilisation in the slurry treatments could be derived from the applied N balance approach. In the present case, slot injection would score as the best application technology based on the highest NH_3 reduction, while N_2 and N_2O emissions were not enhanced.

Topic groups: 07. Atmospheric Sciences (Pollution, Climate Change, Cosmogeochimie),

Presentation types: Oral presentation

Title: A potential proxy for tracing ozone layer depletion events - sulfur isotope anomalies ($\Delta^{33}\text{S}$) in polar ice cores

Lead author: Sanjeev Dasari, Institut des Géosciences de L'Environnement (IGE), University Grenoble Alpes, C

Author: Guillaume Paris, Université de Lorraine, CNRS, CRPG 54000 Nancy, France; Julien Charreau, Université de Lorraine, CNRS, CRPG 54000 Nancy, France; Joel Savarino, Institut des Géosciences de L'Environnement (IGE), University Grenoble Alpes, C

Keywords: Cosmic-ray background, UV Radiation, Sulfur Mass-Independent Fractionation (S-MIF), $\Delta^{33}\text{S}$

Content:

The ozone layer, in the upper troposphere - lower stratosphere region, absorbs ultraviolet (UV) radiation, thereby, limiting the penetration of the harmful UV rays into the Earth's atmosphere. In the event of destruction or thinning of the ozone layer, this harmful UV radiation could penetrate deeper into the troposphere causing detrimental effects on humans. One of the possibilities for such an occurrence is through chemical reactions initiated due to changes in the cosmic-ray background of the Earth. However, observational evidence is still lacking. In a pilot study, we have tested our hypothesis that a depletion/thinning of the ozone layer could be geochemically traced by mass-independent fractionation (MIF) bearing sulfur isotope signals ($\Delta^{33}\text{S} \neq 0$). In the modern atmosphere, these anomalies occur only in the stratosphere through photochemical reactions involving abundant UV radiation. Such signals are then found in polar ice cores upon deposition of MIF-bearing sulfate e.g., after a volcanic eruption. These are thus absent from tropospheric (background) ice core sulfate records displaying $\Delta^{33}\text{S} = 0$. However, in the event of a depletion/thinning of the ozone layer, the UV rays could enter deeper towards the Earth's surface potentially creating a 'UV window', as such anomalous sulfur could then be produced in the troposphere and traced from ice core sulfate records for the corresponding periods. Our preliminary findings during two well-known events: the Boomerang Supernova (≈ 10 kBP) and the Laschamp Geomagnetic Excursion (≈ 41 kBP) reveal the existence of such tropospheric photochemical imprints on ice core sulfate thereby, observationally confirming the hypothesis. Together, this shows a potential new application for ice-core- $\Delta^{33}\text{S}$ records.

Topic groups: 09. Isoscape, Spatial Variability of Stable Isotopes (Migration, Food Webs),

Presentation types: Oral presentation

Title: Body size and depth drive trophic functioning: a case study of the English Channel-Celtic Sea continuum

Lead author: Andrea Walters, University of Tasmania; IFREMER, Science and Halieutic Technology Research Unit

Author: Dorothee Kopp, IFREMER, Science and Halieutic Technology Research Unit; Pierre Cresson, IFREMER, Channel and North Sea Fisheries Research Unit; Marianne Robert, IFREMER, Science and Halieutic Technology Research Unit

Keywords: resource use; body size; depth; stable isotopes; trophic functioning; cross-ecosystem; trophic level

Content:

Understanding how energy is transferred across trophic levels within and across ecosystems is of prime importance, in order to better understand drivers and future consequences of shifts in energy pathways and to inform ecosystem-based management. Yet major research gaps still need to be addressed to quantify the linkages between production and trophic functioning at large spatial and functional scales in marine ecosystems. Here, we used stable isotope ratios of fish collected across the English Channel-Celtic Sea continuum to assess cross-ecosystem differences in trophic functioning. Resource use (benthic and pelagic trophic resources) and trophic level variability were quantified in four fish functional groups (informed by diet and life stage data): benthivore, zoobenthivore, piscivore and generalist planktivore fishes. We examined the influence of body size and depth, considered influential in explaining the trophic functioning of the system, on resource use and trophic level variability at different levels of biological organization (community and functional). Individuals in the fish community spanned three trophic levels with functional groups spread across benthic and pelagic trophic pathways. Despite the hypothesis of size-based predation, the relationship between trophic level and body size varied among functional groups. A significant positive relationship between trophic level and body size was found for zoobenthivore and piscivore fishes, whereas benthivore fishes tended to have negative relationships. For piscivore fishes, there was a gradual increase in the coupling of benthic and pelagic trophic pathways at larger size and higher trophic levels, highlighting the importance of larger consumers coupling energy across different food web compartments. No significant change in average trophic level with increasing body size was found for generalist planktivore fish. In all cases, a decreasing trend of trophic level with increasing depth was found. The amplitude of the change in average trophic level with depth was equivalent to more than one trophic level for generalist planktivore and piscivore fishes. Results indicate that the role of body size and depth in determining trophic interactions may vary across food web compartments and could have important consequences for energy pathways and ecosystem functioning.

Topic groups: 02. Terrestrial and Aquatic Biogeochemistry,

Presentation types: Oral presentation

Title: Nitrogen isotopes reveal a particulate-matter driven biogeochemical reactor in a temperate estuary

Lead author: Kirstin Dähnke, Helmholtz-Zentrum Hereon, Institute for Carbon Cycles, Geesthacht, Germany

Author: Tina Sanders, Helmholtz-Zentrum Hereon, Institute for Carbon Cycles, Geesthacht, Germany; Yoana Voynova, Helmholtz-Zentrum Hereon, Institute for Carbon Cycles, Geesthacht, Germany; Scott D. Wankel, Woods Hole Oceanographic Institution, MA 02543, USA

Keywords: Elbe Estuary, nitrogen stable isotopes, box-model, particulate matter

Content:

Estuaries and rivers are important biogeochemical reactors that act to modify nutrient loads and composition in the intensively used coastal zone. In a case study during July 2013, we sampled an 80km transect along the Elbe estuary under unusually low-oxygen conditions. To better elucidate specific mechanisms of estuarine nitrogen processing, we tracked the evolution of the stable isotopic composition of nitrate, nitrite, particulate matter, and ammonium through the water column. We used this exceptional summer situation to constrain the in-situ isotope effects of ammonium and nitrite oxidation and of remineralization at the reach scale. The isotope effects of nitrite oxidation and ammonium oxidation are consistent with pure culture assessments. We found that estuarine biogeochemistry is governed by settling, resuspension, and remineralization of particulate matter. We used the stable isotope data to further quantify sources and sinks of nitrogen in the Elbe estuary. An isotope mass balance box-model was developed to reproduce internal N-cycling and associated isotope dynamics. The model underscores the role of the delivery and reactivity of particulate matter, but also allowed us to pinpoint additional sinks of reactive nitrogen, such as the denitrification of water column nitrate in the intensively dredged and deep Hamburg harbour basin, and assimilation of ammonium by phytoplankton in the middle section of the estuary.

Topic groups: 01. Methodological Advances,

Presentation types: Oral presentation

Title: Tunable infra-red laser differential absorption spectroscopy (TILDAS) measurement of multiple clumped isotope ratios in carbonates: progress and new horizons

Lead author: David Dettman, University of Arizona

Author: Scott Herndon, Aerodyne Research, Inc.; Nitzan Yanay, University of Arizona; Zhennan Wang, University of Arizona; Jay Quade, University of Arizona; David Nelson, Aerodyne Research, Inc.

Keywords: Clumped isotopes, $\delta^{17}\text{O}$, laser absorption, thermometry

Content:

Clumped isotope ratios in carbonates are a powerful indicator of crystallization temperature in many environmental contexts, but the analysis tends to be time consuming and expensive when measured with traditional isotope ratio mass spectrometry (IRMS). By turning to laser absorption spectroscopic techniques, the high precision analysis of isotope ratios of many different isotopologues of carbon dioxide can be performed quickly and without the problem of common mass interferences that are seen in IRMS measurements. We here present descriptions of two instruments. First, a fully automated TILDAS instrument that extracts CO_2 from carbonate samples, cryogenically removes water and non-condensables, and then measures the four isotope species of CO_2 that are required for a clumped isotope measurement ($^{16}\text{O}^{12}\text{C}^{16}\text{O}$, $^{16}\text{O}^{13}\text{C}^{16}\text{O}$, $^{16}\text{O}^{12}\text{C}^{18}\text{O}$, and $^{16}\text{O}^{13}\text{C}^{18}\text{O}$). This system achieves precision equivalent to high quality IRMS data (0.01‰, 1 S.E.), and it surpasses typical IRMS measurements in several features: rapid measurement (50 minutes per carbonate sample); small sample size (<20 μmol of CO_2 , or <2 mg equivalent calcite); and no need for an assumed ^{17}O abundance in the sample to correct for common-mass interference. An empirical calibration, using synthetic calcites grown or equilibrated across a temperature range of 6°C to 1100°C is consistent with other published calibrations. The second instrument is a prototype in development by Aerodyne Research Inc. This TILDAS instrument is designed to simultaneously measure the three most common clumped isotopologues and the $^{17}\text{O}/^{16}\text{O}$ ratio of a CO_2 sample. Using the HITRAN isotope notation (designated by the second digit of the atomic mass, i.e. ^{16}O is "6"), this instrument measures 626, 636, 627, 628, 637, 638, and 828 abundances, which can be ratioed to produce D638, D637, D828, and $\delta^{17}\text{O}$. The $\delta^{17}\text{O}$ ratio is very difficult to measure with IRMS, and we are not aware of any prior measurements of D637. The instrument uses a carefully selected spectral range, operates at low sample pressure, and employs automated laser frequency hopping. Although the results are very preliminary and the precision is yet not adequate for geochemical studies, this instrument is very promising. For example, it can measure D637 in CO_2 with a standard deviation of 0.1‰ in 5 minutes, and it is very stable over a period of days, indicating that longer measurement times, combined with comparison to a reference gas, will significantly improve the precision of this measurement. This approach holds tremendous promise for rapid high precision isotope analysis.

Topic groups: 12. Sponsor session,

Presentation types: Oral presentation

Title: Improved throughput for $\delta^{18}\text{O}$ and δD measurements of water with Cavity Ring-Down Spectroscopy

Lead author: Magdalena E. G. Hofmann, Picarro B.V.

Author: Jan Woźniak, Picarro B.V.; Erik Heeren, Picarro B.V.; Keren Drori, Picarro Inc.

Keywords: stable isotopes of water, hydrology

Content:

Oxygen ($^{18}\text{O}/^{16}\text{O}$) and deuterium (D/H) isotopes are a widespread tool to trace physical and chemical processes in hydrology and biogeosciences. Precision and throughput are key parameters for water isotope analysis. Here, we will present two new methodologies for the Picarro L2130-i Cavity Ring-Down Spectroscopy (CRDS) water isotope analyzer that allow the user to increase the throughput without compromising data quality. The Picarro Express Method now distinguishes between a memory reduction stage and a sample analysis stage and allows the user to measure up to 50 samples per day while maintaining the excellent precision of CRDS (i.e., 0.01‰ for $\delta^{18}\text{O}$ and 0.05‰ for δD). This corresponds to doubling the throughput compared to the standard Picarro methodology. The Picarro Survey Method makes use of ultrafast injections and sorts the samples by their measured isotopic values, enabling a powerful new strategy to reduce memory effects. We present these different measurement strategies that increase the throughput for routine water isotope analysis. The improved methodologies use software based modifications of the injection procedure, and do not require any hardware changes. If you are interested in Picarro's off-the-shelf solution for existing and future installations, please visit us at the Picarro booth.

Topic groups: 07. Atmospheric Sciences (Pollution, Climate Change, Cosmogeochimistry),

Presentation types: Oral presentation

Title: Isotopic ratios of aerosols for air pollution observation and its assessment as source indicators

Lead author: Vidmantas Remeikis, FTMC; Andrius Garbaras, FTMC; Ulrike Dusek, CIO

Author: Agne Masalaite, FTMC

Keywords: carbonaceous aerosol, source apportionment, stable carbon isotope, aerosol aging

Content:

Atmospheric aerosol particles play an important role in many environmental processes, influencing climate change processes and human health. The stable carbon isotope ^{13}C has the potential to give insights into the sources and processing of organic aerosol. However, the use for source apportionment has been somewhat limited, because the ^{13}C source signatures vary and show some overlap. We demonstrate with an extensive source study that in Lithuania and likely other Eastern European regions, the main anthropogenic primary sources for organic carbon (OC) have distinct isotopic signatures. Stable carbon isotope ratios of total carbon (TC) and OC were measured in fine carbonaceous aerosol fractions sampled at urban, coastal, and forest sites in Lithuania. $\delta^{13}\text{C}$ values of TC for all three sites over the whole measurement period varied from -29.3 to -26.6 ‰, which is in the range of particles emitted by fossil fuel combustion in Eastern Europe. The isotopic composition at the forest and coastal sites showed a similar variation during two contrasting pollution periods. $\delta^{13}\text{C}$ values in the clean period were more variable, whereas the polluted period was characterized by a gradual enrichment in $\delta^{13}\text{C}$ compared to the clean period. Oxidative processing during long-range transport or the different source signatures (e.g., enriched ^{13}C signature of gasoline used in Western Europe vs. Eastern Europe) could cause less negative $\delta^{13}\text{C}_{\text{OC}}$ values during the polluted episode. $\delta^{13}\text{C}$ for OC desorbed from the filter samples was separately measured during three different temperature steps (200 °C, 350 °C, and 650 °C). OC desorbed at 200 °C had the most depleted ^{13}C signature of around -29 ‰ at all three sites. A comparison with previously published data measured during the winter at the same sites showed that both TC and OC had less negative $\delta^{13}\text{C}$ values in winter than in summer, which can be explained by the contribution of biomass/coal burning sources in winter. At the urban site $\delta^{13}\text{C}$ of OC did not change much with increasing desorption temperature in winter, which is typical for primary sources, but in the summer $\delta^{13}\text{C}$ of OC was depleted for lower desorption temperatures, possibly due to the influence of secondary organic aerosol formation. A higher fraction of more refractory OC in summer compared to winter-time suggests active photochemical processing of the primary organic aerosol as an important process at all three sites.

Topic groups: 10. Geochemistry and Hydrology,

Presentation types: Oral presentation

Title: New insights into the paleoclimate and recharge history of the Upper Jurassic aquifer using noble gas infiltration temperatures and $^{14}\text{CDOC}$.

Lead author: Theis Winter, Technical University of Munich

Author: Florian Einsiedl, Technical University of Munich

Keywords: Noble gas temperatures, $^{14}\text{CDOC}$, groundwater dating, paleoclimate

Content:

The Upper Jurassic aquifer (UJA) within the South German Molasse Basin (SGMB) is the most important exploration horizon for geothermal energy supply in Bavaria. This aquifer shows a heterogeneous geology which is composed of karstic features and fault-zones and a deep understanding of the recharge area and infiltrations conditions is needed. Several studies from different sedimentary basins worldwide have found a substantial cooling in the world climate during the Last Glacial Maximum (LGM) of up to 10°C . There was also the discovery of the so called LGM recharge gap which is a gap in continuous groundwater recharge due to the cover of the basins with glaciers and permafrost during the LGM. Our study focuses on the determination of infiltration temperatures from noble gas records linked with apparent groundwater ages. However, in contrast to many other former studies in this field we used $^{14}\text{CDOC}$ to determine the apparent groundwater ages of the aquifer to reconstruct the paleoclimate during the Pleistocene and Holocene. Advantages of the newly developed $^{14}\text{CDOC}$ methods compared to the commonly used $^{14}\text{CDIC}$ methods are discussed in respect to the interpretation of calculated noble gas temperatures within the UJA. We show that estimated noble gas infiltrations temperatures for the SGMB range between 2 and 4°C resulting in a maximum cooling of up to 8°C . Our results are in good agreement with earlier observations from other European sedimentary basins such as the Ledo-Paniselian aquifer in Belgium. The groundwater infiltration under a cold climate is furthermore backed up by stable water isotope values ranging between -10.66 to -11.76 ‰ for $\delta^{18}\text{O}$ and -85 to -86.06 ‰ for $\delta^2\text{H}$ and may also indicate a meteoric origin. However, contrary to the observation of the LGM recharge gap within other basins the $^{14}\text{CDOC}$ apparent groundwater ages of the SGMB may indicate that there was no interruption in groundwater recharge during the LGM.

Topic groups: 09. Isoscape, Spatial Variability of Stable Isotopes (Migration, Food Webs),

Presentation types: Oral presentation

Title: The variable food webs in cold-water lakes

Lead author: Antti Eloranta, University of Jyväskylä

Author:

Keywords: Food web, littoral-pelagic coupling, salmonid fish, subarctic lakes, $d^{13}C$, $d^{15}N$

Content:

Cold-water lakes in high-latitude and alpine regions are subject to rapid environmental changes due to various local (e.g. land use activities, hydropower operations and invasive species) and large-scale (e.g. climate change and acidification) human impacts. The altered abiotic and biotic conditions in cold-water lakes can induce marked changes in the structure and function of food webs, which are reflected to the trophic ecology and population dynamics of top predator salmonid fishes. In this talk, I will summarize some of our findings to illustrate how the natural characteristics (e.g. lake size and community composition) and various human impacts (e.g. invasive species and hydropower-induced water level fluctuations) can influence littoral benthic and pelagic planktonic food-web compartments in Fennoscandian cold-water lakes. I will also introduce our recently started Academy Research Fellow project "COLDWEBS", where we compile stable isotope data from >100 Fennoscandian lakes to investigate lake food-web dynamics along large biogeographical gradients. Our large-scale research of highly-valued, vulnerable salmonid fish populations and food webs aims to provide new knowledge that supports future development of sustainable management and mitigation actions in subarctic and alpine Fennoscandian lakes.

Topic groups: 04. Paleoclimatology & Archaeology,

Presentation types: Oral presentation

Title: Stable isotopes tell the dietary history of the last two millennia Lithuanian inhabitants

Lead author: Raminta Skipitytė, Center for Physical Sciences and Technology

Author: Kerstin Lidén, Stockholm University; Gunilla Eriksson, Stockholm University; Rimantas Jankauskas, Vilnius University

Keywords: Diet, Lithuania, stable isotopes

Content:

The bioarcheological material of humans collected in Lithuania made it possible to get deeper into their lifestyles in the past. Therefore, this study was carried out in bone collagen and bioapatite samples using stable isotope ratios of carbon ($\delta^{13}\text{C}$) and nitrogen ($\delta^{15}\text{N}$) as a valuable tool for paleodietary reconstruction. The consumption of nutritional resources in the historical period undoubtedly had to change. The main factors that led to this change and different access to food sources may have been residence, age, gender, social status, etc. This study summarizes stable isotope results from the past two millennia. Based on the archaeological human bone collagen analysis, the influence of biological factors (men-women); the importance of diachronic factors (I – II millennia); the influence of technological (agricultural development) factors; as well as the significance of social/cultural factors (dietary characteristics of rural, urban people, social elites) on the distribution of their stable isotope values was determined. The material of the early period before the established state (Grand Duchy of Lithuania, from the 13th century) represents small farmer communities and greater reliance on agriculture, significant differences were found between males and females, while the latter period reflects regional influence on people's diet due to the socioeconomic stratification. Isotopic dietary differences were found between the urban, rural, coastal and social elite' data, but not between males and females.

Topic groups: 04. Paleoclimatology & Archaeology,

Presentation types: Oral presentation

Title: Environmental and Anthropogenic Effects on Plant Amino Acid Nitrogen Isotope Values

Lead author: Sean Hixon, Max Planck Institute for the Science of Human History

Author: Ricardo Fernandes, Max Planck Institute for the Science of Human History; Philip Riekenberg, Royal Netherlands Institute for Sea Research

Keywords: crop, manuring, aridity, diet, food web

Content:

Differences among the stable nitrogen isotope ($\delta^{15}\text{N}$) values of plant amino acids (AAs) vary according to N cycling during uptake and assimilation. Components of past and present food webs can be inferred when primary producer AA $\delta^{15}\text{N}$ patterns are conserved or predictably modified in consumer protein. However, the specificity of this inference is limited by multiple environmental and anthropogenic effects on N cycling that drive overlapping variation in plant AA $\delta^{15}\text{N}$ patterns according to season, structure, and plant part. We present $\delta^{15}\text{N}$ values from AAs in the seeds of common crops (e.g., wheat, barley, and millet) that were grown under controlled conditions with different soil nutrients. We compare our results with previously published AA $\delta^{15}\text{N}$ data from plant tissue collected from both controlled and uncontrolled settings. Given the observed species-specific differences and inherent variation among plants, we discuss general implications for the use of consumer AA $\delta^{15}\text{N}$ data to infer aspects of diet quality. This includes commonly applied AA-based trophic level estimates and approximations of N derived from human-modified soils.

Topic groups: 05. Health and Medical Sciences,

Presentation types: Oral presentation

Title: Tracking nutrient metabolic pathways and detecting protein malnutrition using isotopic tracers

Lead author: Ricardo Fernandes, Max Planck Institute for the Science of Human History

Author:

Keywords: isotopes; nutrition; feeding experiments; multi-proxy;

Content:

Knowledge of metabolic routing mechanisms is essential to understand how food nutrients are incorporated into consumer tissues. Pertinent information can be obtained using controlled feeding experiments and appropriate tracers. In this respect, stable isotope studies have been a valuable source of information although some aspects remain unexplored. For instance, precise quantification of the relative contribution from different macronutrients toward consumer tissues is lacking. Nor is it precisely known how malnutrition can impact consumer isotopic values. To clarify such aspects, it becomes advantageous to explore the use of multi-proxy approaches that combine bulk and compound-specific analysis using a variety of isotopic tracers. This includes traditional stable isotope analysis plus radiocarbon (^{14}C). For the latter, isotopic concentrations are corrected for isotopic fractionation. A series of feeding experiments were carried out on omnivorous mammals. Isotopic measurements (stable C, N, S, O, Sr and ^{14}C) were carried out on bulk tissues (e.g., bone collagen, hair keratin, bioapatite) and on single amino acids from food, water, and consumer tissues. Experimental setups consisted of a wide variety of food and macronutrient types with contrasting isotopic values. In addition, foods with various protein contents were employed to assess isotopic detection of protein malnutrition. Obtained results allowed for the quantification of the elemental contributions from food macronutrients (proteins, carbohydrates, lipids) and water toward consumer tissues and specific compounds. The implications that obtained results have for the study of nutrition physiology, the use of isotopic methods for dietary and spatial mobility reconstruction, and for dietary radiocarbon reservoir effect corrections will be discussed.

Topic groups: 12. Sponsor session,

Presentation types: Oral presentation

Title: Workflow advancements in high precision $\delta^{18}\text{O}$ analysis of water by means of low-T $\text{CO}_2\text{-H}_2\text{O}$ equilibration

Lead author: Meike Fischer, Thermo Fisher Scientific (Bremen) GmbH

Author: Sukanya Sengupta, Thermo Fisher Scientific (Bremen) GmbH; Jens Radke, Thermo Fisher Scientific (Bremen) GmbH

Keywords: oxygen isotopes, $\text{CO}_2\text{-H}_2\text{O}$ equilibration, GasBench Plus IRMS

Content:

One of the most important applications of isotope ratio mass spectrometry is the measurement of $^{18}\text{O}/^{16}\text{O}$ ratios in a variety of sample types like water, wine, sediments, air etc. Seawater and ice-core samples are an important sample type where oxygen isotope ratios, expressed commonly as $\delta^{18}\text{O}$, are investigated for better understanding of the modern water cycle and for reconstructing past climate. Such applications have assumed prime importance today, particularly paleoclimate studies which have important implications for modern climate change. These applications benefit greatly from high precision/high accuracy/high throughput $^{18}\text{O}/^{16}\text{O}$ analysis on small sample volumes. Recent advancements of the Thermo Scientific™ GasBench Plus Isotope Ratio Mass Spectrometry (IRMS) System allow for higher productivity through extended tray capacity and dedicated Thermo Scientific™ Qtegra™ ISDS Software workflows that simplify analysis setup. We will demonstrate how high precision $\delta^{18}\text{O}$ data can be achieved by maintaining a low equilibration temperature around room temperature or lower ($\sim 16^\circ\text{C}$) and discuss how the GasBench Plus System with the advanced Thermo Scientific™ TriPlus™ RSH SMART Autosampler supports the equilibration workflow, yielding high precision $\delta^{18}\text{O}$ analysis in the range of $<0.06\text{‰}$ (room temperature)/ $<0.04\text{‰}$ ($\sim 16^\circ\text{C}$) that is comparable to conventional dual-inlet techniques.

Topic groups: 13. Keynote,

Presentation types: Oral presentation

Title: Absolute Isotope Ratios

Lead author: Lukas Flierl, Physikalisch-Technische Bundesanstalt

Keywords: Metrology, SI-traceability, absolute isotope ratios

Content:

Mass spectrometry is in many cases the method of choice for isotope analysis. Therefore, there is a vast variation of different inlet systems, ion sources, analyzers, and detection systems. These can be almost arbitrarily combined, depending on the purpose and research focus. No matter which combination is used, all mass spectrometers have one issue in common: Absolute isotope ratios – traceable to the SI unit mole – are not directly available. This is due to many effects: Ions with different masses exhibit different efficiencies of detection or ion transmission. All these effects are commonly summarized by the term “mass bias” or “instrumental isotopic fractionation” and cannot be avoided. Since mass bias is an intrinsic feature of mass spectrometry, certified isotope reference materials are used. With the knowledge of the isotopic composition of the reference material, the measured isotope ratios of the unknown samples can be corrected for mass bias, provided both have been measured under the same conditions. Additionally, reference and sample have to be as similar as possible with respect to their chemical and physical properties. Since the knowledge of the isotopic composition of the reference material is crucial and on the other hand absolute isotope ratios are not directly available by mass spectrometry, an urgent question arises: “How do we obtain the absolute isotope ratios of reference materials in the first place?” In this talk, the primary method of gravimetric isotope mixtures is presented as the solution to the above dilemma. This method allows the determination of absolute isotope ratios without any prior knowledge. The talk will comprehensively explain the theoretical background and potential pitfalls. Real-life examples will be given. Additionally, it will be shown how this approach, which has been developed for atomic systems, can be modified to cover also molecular systems like carbon dioxide.

Topic groups: 12. Sponsor session,

Presentation types: Oral presentation

Title: Integration of Laser Spectrometers with Diffusive In Situ Probes for Real Time Monitoring of Isotopes and Isotopologues of Soil Gases

Lead author: Joanne Shorter, Aerodyne Research, Inc.

Author: Joseph R. Roscioli, Aerodyne Research, Inc.; Elizabeth Lunny, Aerodyne Research, Inc.; Laura Meredith, University of Arizona; Juliana Gil-Loaiza, University of Arizona

Keywords: soil, nitrous oxide, isotopologues, in situ probes

Content:

The direct measurement of soil gases provides insight into the biogeochemical processes responsible for micro- and macro-nutrient cycling, respiration, signaling, and environmental responses in soils. The concentrations and isotopic signatures of soil gases are effective markers of pathways active in the soil. Fast, spatially resolved measurements of these soil gas concentrations and isotopic signatures afford unique insights into characteristic responses of these systems to changes in environmental conditions, such as recovery from drought. To advance in situ subsurface monitoring of isotopic signatures, we have developed a fast monitoring system consisting of diffusive soil probes coupled with a Tunable Infrared Laser Direct Absorption Spectrometer (TILDAS) modified for analysis of small gas volumes. The probes are coupled to the TILDAS via a multi-sample selector (MSS) for automated, autonomous sampling of soil gases from an array of buried probes, enabling real-time subsurface mapping of trace gases and their isotopic signatures. Here we present laboratory studies of subsurface biogeochemical processes during controlled rewetting and fertilization events. Soil probes at 3 depths in triplicate soil columns were coupled with two TILDAS instruments to monitor isotopologues of nitrous oxide (N₂O) including ¹⁴N¹⁵NO, ¹⁵N¹⁴NO, and N₂¹⁸O, methane (¹³CH₄ and ¹²CH₄), as well NO, NO₂, and CO₂. Development of additional sampling schemes for application of the soil probes and TILDAS system to monitor other soil gases and their isotopic signatures will also be discussed.

Topic groups: 06. Food Authenticity, Nutrition, Forensic,

Presentation types: Oral presentation

Title: Stable isotope investigations to control of declared geographic origin of Austrian and Slovak apricots, and apricots from other countries

Lead author: Kurt Krammer, HBLFA Francisco-Josephinum BLT Wieselburg

Author: Micha Horacek, HBLA & BA Klosterneuburg; Lenka Klcova, National Agricultural and Food Centre Research Institute of Plant Production; Martina Hudcovicova, National Agricultural and Food Centre Research Institute of Plant Production; Katarina Ondreickova, National Agricultural and Food Centre Research Institute of Plant Production; Jozef Gubis, National Agricultural and Food Centre Research Institute of Plant Production; Elisabeth Riegler, HBLFA Francisco-Josephinum BLT Wieselburg; Stefan Hölzl, Rieskrater Museum Nördlingen

Keywords: provenance, authenticity, fruit, Wachau, environmental conditions, weather

Content:

Food products of certain geographic origin are more valued by consumers than the same commodities from other regions. Thus, the control of declared geographic origin is necessary to ensure correct labelling and to identify fraud, as there is the risk and fear that incorrect labelling and declaration of geographic origin can occur to increase profit, and numerous cases already have been reported. For this purpose, in an EU-project, apricot samples of the recent vintages (2019, 2020 and 2021) we investigated to differentiate samples from different apricot-producing regions in Austria, Slovakia and other countries. The isotope composition of the elements hydrogen (H), carbon (C), nitrogen (N) and oxygen (O) of fruit pulp (H, C, N, O), fruit stone (H, C, O), fruit juice (O) and the $87/86\text{Sr}$ ratio was analysed to find appropriate parameters for the differentiation of geographic origin. The investigation of different sample tissues (pulp, stone, juice) supports a better differentiation of geographic origin due to different seasonal intervals influencing the respective commodities. The results demonstrate differing isotope patterns between individual vintages, documenting the influence of weather varying between the years. These weather variations also result in differing success of differentiation between different regions of apricot production, by generally high success-rates. The differentiation of geographic origin by $87/86\text{Sr}$ -ratio, a geogenic parameter documents the potential of this method, however by also showing its drawbacks, as some regions possess a very heterogeneous geology resulting in a large range of isotope values. Combination of methods results in highest differentiation.

Topic groups: 02. Terrestrial and Aquatic Biogeochemistry,

Presentation types: Oral presentation

Title: Characterizing the transformation of hexachlorocyclohexane in soil-plant systems from lab to field scale using multi-element compound specific isotope analysis

Lead author: Hans Hermann Richnow, Helmholtz Centre for Environmental Research

Author: Xiao Liu, Helmholtz Centre for Environmental Research ; Steffen Kümmel, Helmholtz Centre for Environmental Research

Keywords: hexachlorocyclohexane isomers, multi element compound specific isotope analysis, transformation, phytoremediation

Content:

The transport and accumulation of persistent organic pollutants (POP) such as hexachlorocyclohexane (HCH) isomers in food webs is getting more attention due to the possible threats for human beings. Plant uptake of HCH from soil or water is one of the first steps to enter food webs. In order to understand the translocation and transformation processes of HCH in the rhizosphere and during the plant uptake multi element compound specific isotope analysis (ME-CSIA) and enantiomer fractionation (EF) were employed in order to characterize possible bond cleavage processes governing transformation pathways. Thereby, a central element of the study to explore and evaluate the usage of ME-CSIA for analysing transformation pathways of HCH across scales from various soil-plant experiments in the lab to application at the field scale. The transformation of α -HCH by both soil bacteria and plant derived enzymes or endophytes was revealed, which promotes the current concept of phytoremediation of HCH. Meanwhile the limitation of transforming β -HCH by wheat enzymes or endophytic bacteria was also examined. The selective transformation of HCH isomers should be taken into consideration for future phytoremediation concepts at HCH contaminated field sites. Furthermore, the transformation of β -HCH by plant endophytes was evaluated and those endophytes originated from soil bacteria when historically contaminated soil was used, indicating that the transformation of β -HCH by plant endophytes requires a soil microbial community with the ability to transform β -HCH. In a case study, ME-CSIA was applied to track the changes of concentration and isotopic composition of HCH in different species of trees in a contaminated field site over a growth cycle to explore the dynamics of uptake and degradation processes. We will discuss the opportunities to make use of ME-CSIA for tracking the fate of HCH in plants in the field also for developing the phytoremediation approaches using with trees and grass land.

Topic groups: 03. Plant Ecophysiology,

Presentation types: Oral presentation

Title: Geometrid moth outbreaks alter understory plant nutrient and carbon dynamics in northern Finland's mountain birch forest.

Lead author: Mirella Karppinen, University of Oulu

Author: Tamara Hiltunen, University of Oulu; Maria Väisänen, University of Oulu, University of Lapland; Jeffrey Welker, University of Alaska Anchorage

Keywords: Plant-herbivory interaction, *Epirrita autumnata*, *Operophtera brumata*, Subarctic birch forest, Stable isotope analysis

Content:

In northern Fennoscandia, increased insect pest outbreaks are one of the most severe impacts of global climate change. Outbreaks of two canopy feeding geometrid moth species, *Epirrita autumnata* and *Operophtera brumata*, occur infrequently in subarctic mountain birch (*Betula pubescens* ssp. *czerepanovii*) forests. The intensive defoliation associated with these outbreaks leads to short and long-term effects on the understory nutrient and carbon dynamics. In addition, sharp vegetation state transitions have been observed in the short term (dwarf shrub-dominated understory vegetation becomes grass-dominated) and in the long term, mountain birch forests shift to open secondary heaths. We conducted a study in the Kaldoaivi wilderness area in northern Finland, a region that has experienced extreme outbreaks in the 1960s and 2000s resulting in over 1 000km² of these novel secondary open heaths. Foliar stable isotopes ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$) in addition to the quality (C:N) and quantity (biomass) of different vegetation functional groups (evergreen dwarf shrubs, deciduous dwarf shrubs, grasses, deciduous shrubs, and mountain birch) were analysed. In order to address the following research questions about the understory nutrient and carbon dynamics: firstly do secondary treeless heaths behave differently or similarly to an undamaged forest or a natural treeless heath and secondly, does outbreak and recovery history have an influence. Preliminary results suggest that the carbon and nutrient dynamics of the different functional groups in secondary heaths, natural forests and natural heaths are different. Some of the groups in the secondary heaths are functioning like the natural forest, others are like the natural heaths while other groups do not function like either. These groups suggest that secondary open heaths have unique nutrient and carbon dynamics. Differences in the nutrient cycling, between natural forests and secondary open heaths have the potential to affect the carbon sequestration ability of the region, ultimately affecting the climate and climate change target achievement. Overall, we hope our findings will promote an understanding of how these severe defoliation events impact the nutrient and carbon cycling of these vulnerable northern boreal ecosystems.

Topic groups: 07. Atmospheric Sciences (Pollution, Climate Change, Cosmogeochimistry),

Presentation types: Oral presentation

Title: Stable chlorine isotopic composition of CH₃Cl and CFC-12 in tropospheric air samples

Lead author: Axel Horst, Helmholtz Centre for Environmental Research - UFZ

Author: Steffen Kümmel, Helmholtz Centre for Environmental Research - UFZ

Keywords: stable chlorine isotopes, CFC, chloromethane, ozone depletion, air sampling

Content:

CFC-12 (Dichlorodifluoromethane) and CH₃Cl (chloromethane) belong to the most abundant chlorinated compounds in the atmosphere. Together with other halogenated compounds and nitrogen species (N₂O) they are responsible for destruction of the stratospheric ozone layer. CH₃Cl is an unregulated compound that originates mainly from natural sources but also possesses some anthropogenic sources. The sources and sinks of CH₃Cl are not well quantified and the atmospheric budget of this substance has remained unbalanced with the sinks outweighing the sources by about 20%. Stable isotope analysis has often been suggested to improve budget estimates and to find potentially unconsidered sources of CH₃Cl but the use of stable carbon isotope analysis alone was not sufficient to further improve budget estimates. CFC-12 is entirely of anthropogenic origin but production was banned due to the regulations of the Montreal Protocol and its amendments. Hence, CFC-12 has no significant sources anymore and atmospheric mixing ratios are slowly declining due to loss to the stratosphere. In the current study we took air samples at an urban site in Germany (city of Leipzig) in order to evaluate whether there is enough variability in the stable chlorine isotopic composition of atmospheric CH₃Cl. This variability is a prerequisite for future efforts aiming at identifying and better quantifying sources and sinks of CH₃Cl by using the isotopes of one or several elements in that compound. First samples were collected by a cryogenic sampling method and ³⁷Cl/³⁵Cl isotopic ratios were measured via GC-MC-ICPMS (Gaschromatography - Multiple Collector-Inductively Coupled Plasma Mass Spectrometry). The δ³⁷Cl of CH₃Cl in samples collected between end of January and beginning of April ranged from – 0.9 ‰ to +2.2 ‰ SMOC which may reflect the influence of different sources or sink processes. For CFC-12 the variation of δ³⁷Cl was, as hypothesized, considerably smaller (+1.4 to +1.8 ‰ SMOC). The atmospheric mixing ratios of CFC-12 change extremely slowly due to long atmospheric lifetime and with no apparent sources the δ³⁷Cl may be considered constant over months or even years. Consequently, this variability of the δ³⁷Cl of CFC-12 should reflect the overall uncertainty induced by air sampling and the analytical method. Since the sampling campaign is ongoing, more data will be presented at the conference. Apart from further ³⁷Cl/³⁵Cl measurements of CH₃Cl and CFC-12, stable chlorine isotopic values of HCFC-22, CFC-11, CFC-113 and CCl₄ will be measured and presented.

Topic groups: 08. Soil Carbon and Nitrogen Cycling, with Focus on Agricultural Soils,

Presentation types: Oral presentation

Title: Continental-scale effects on the natural ^{15}N abundance of plants and soils and isotope fractionation

Lead author: Shasha Zhang

Author: Wolfgang Wanek, University of Vienna; Yuntao Hu; Qing Zheng; Lisa Noll

Keywords: Natural ^{15}N abundance, isotope fractionation, modeling, soils, continental transect

Content:

Natural ^{15}N abundance approaches have been used to study nitrogen (N) dynamics at multiple scales in natural and managed ecosystems, as it provides integral information of N inputs, N losses and internal N transformations that cause ^{15}N isotope fractionation between different N pools and result in characteristic isotopic fingerprints. In this study, we determined the $\delta^{15}\text{N}$ values of plants (foliar litter and roots) and soil N pools at the continental scale and made an attempt to explore the main drivers controlling the spatial variability in $\delta^{15}\text{N}$ values of plant and soil N pools across Europe. Considering the difference of soil physicochemical properties caused by differences in geology, climate and human disturbance, we sampled mineral and organic soils from croplands, managed grasslands and forest ecosystems along a latitudinal transect spanning from the Mediterranean to Northern Scandinavia, allowing us to estimate the relative importance of land-use versus climate effects on ecosystem $\delta^{15}\text{N}$ values. Moreover, we used iterative isotope modeling according to Rayleigh isotope fractionation to derive the fractions of substrates consumed and to evaluate the isotope fractionation of the processes depolymerization, microbial organic N uptake, mineralization, nitrification, and N losses through nitrate leaching and denitrification using the Excel Solver macro. In contrast to global trends, we found that both plant and soil $\delta^{15}\text{N}$ values in managed and natural ecosystems were generally invariant with latitude/climate in Europe, while forest soil $\delta^{15}\text{N}$ and grassland root $\delta^{15}\text{N}$ even increased with latitude, indicating a decrease in ecosystem N limitation towards higher latitudes. Across the European transect ecosystem $\delta^{15}\text{N}$ values were strongly influenced by land use, linked to the "openness" of ecosystem N cycles. Both plant and soil $\delta^{15}\text{N}$ values were markedly higher in managed ecosystems (croplands and grasslands) than in natural ecosystems (forests), suggesting that human management (N fertilization, crop harvest, mowing and grazing) caused a pronounced nitrogen isotope imprint on plants and soils. Isotope modelling allowed further unprecedented insights into changes in soil N processes with climate, geology and agricultural management across this transect.

Topic groups: 02. Terrestrial and Aquatic Biogeochemistry,

Presentation types: Oral presentation

Title: Mosses as biofilters for ditch methane emissions from forestry drained peatlands

Lead author: Tuula Larmola, Natural Resources Institute Finland

Author: Antti J. Rissanen, Natural Resources Institute Finland; Paavo Ojanen, Natural Resources Institute Finland; Leena Stenberg, Natural Resources Institute Finland; Raisa Mäkipää, Natural Resources Institute Finland

Keywords: aquatic, drainage, forest, methane oxidation, peat, Sphagnum

Content:

In forestry drained peatlands, drainage ditches cover ca. 3% of the area, but contribute to up to 100% of methane (CH₄) emission. Peat soil can be a CH₄ sink especially under efficient drainage. Therefore, emissions from ditches will impact whether drained peatland is a net CH₄ sink or source. The net CH₄ flux is likely to be impacted by the conditions in the ditches such as the extent and type of plant cover and the time since drainage. In order to provide more accurate ditch CH₄ emission factors for national greenhouse gas (GHG) inventory, we examined the fluxes and the underlying CH₄ cycling processes in a nutrient rich peatland forest in Ränskälänkorpi, Southern Finland during May-October 2021. We compared the ecosystem-atmosphere CH₄ fluxes and their $\delta^{13}\text{C}$ values from moss dominated and open water ditches. We determined CH₄ and CO₂ mixing ratios and their $\delta^{13}\text{C}$ values in water and in sediment using gas chromatography and Picarro isotope and gas analyzer. We also assessed the role of CH₄ as a carbon source for Sphagnum mosses growing in ditches, by analyzing $\delta^{13}\text{C}$ values in submerged and partly submerged Sphagnum using Isotope-ratio mass spectrometer. We found that mean seasonal CH₄ emissions from moss dominated ditches were 90% lower than from open water surfaces. In this dry summer, moss-dominated ditches were occasionally net sinks of atmospheric CH₄. These results can be explained by CH₄ consuming microbes inhabiting surface water and moss layer and using CH₄ as a source of carbon and energy. Isotopic mass balance calculations accounting for the measured $\delta^{13}\text{C}$ values of Sphagnum moss, dissolved CO₂ and CH₄ as well as fractionation against ¹³C during (mass-transfer-limited) CO₂ fixation of moss, indicated that 10-28% of carbon in ditch Sphagnum mosses potentially originated from oxidized CH₄. Ditch network maintenance, including removing mosses, is likely to decrease along with changing peatland forest management, e.g., continuous cover forestry. Our results suggest that ditches overgrown by mosses have potential to reduce CH₄ emissions from drained peatland forests and could serve as an additional GHG mitigation measure to management practices that maintain a continuous forest cover, attenuate the changes in soil water level and thus reduce CH₄ emissions from peat soils.

Topic groups: 10. Geochemistry and Hydrology,

Presentation types: Oral presentation

Title: Exploring the influence of lake and watershed properties on lake water balances with water isotopes in the Canadian Arctic

Lead author: Evan James Wilcox, Wilfrid Laurier University

Author:

Keywords: lakes, water isotopes, arctic, permafrost, hydrology, water balance

Content:

Thermokarst lakes are widespread features in permafrost environments and increases in air temperature and permafrost thaw are altering lake water balances. Lakes have responded to these changes non-uniformly because lake-specific properties influence a lake's water balance. By understanding which lake and watershed properties have the greatest influence on lake water balance, we can predict how lakes may respond to future climate change based on their lake and watershed properties. Stable water isotopes (^{18}O , ^2H) measured from a variety of different lake waters offers a relatively fast and cheap approach to capturing hydrological information about a large set of lakes with varying lake and watershed properties, especially in remote areas like the Arctic. We used water isotope samples collected from 25 thermokarst lakes along the Inuvik-Tuktoyaktuk Highway, Northwest Territories, Canada from May-September 2018 to estimate 1) the contribution of different water sources to freshet runoff, 2) the amount of lake water replaced by freshet runoff, 3) spatial and temporal drivers of the isotope composition of input waters (δI), and 4) spatial and temporal drivers of ratio of evaporation to inflow (E/I). The amount of lake water replaced by freshet runoff ranged widely from 5 – 50% and was dependent on lake depth, with deeper lakes retaining less freshet runoff. Additionally, the sources of freshet runoff remaining in lakes was a combination of soil-sourced and snow-sourced water. After the freshet, E/I ratios increased until the end of July, when air temperatures cooled, and rainfall increased to lower E/I ratios by September. The δI of most lakes remained rainfall-like throughout the study period, indicating the presence of snowmelt bypass during the freshet period and the strong mixing of soil water in the soil column. Average E/I for the 25 lakes ranged from 0.00 to 0.43 and was well explained by the relative size of a lake's watershed (watershed area/lake area, WA/LA). Lakes with smaller WA/LA experienced increased E/I ratios ($r^2 = 0.74$). The strong relationship between E/I and WA/LA provides a basis for identifying lakes that may be more vulnerable to increasing evaporation as a consequence of longer ice-free periods and rising air temperatures.

Topic groups: 08. Soil Carbon and Nitrogen Cycling, with Focus on Agricultural Soils,

Presentation types: Oral presentation

Title: Direct effects of temperature on the balance between priming and entombing effects under controlled conditions

Lead author: ANGELA KATHERINE MARTIN VIVANCO, helsinki university

Author:

Keywords: Soil organic carbon, Priming effect, Soil respiration, Microbial residues

Content:

In recent years the importance of microbial metabolism for soil carbon and nutrient cycling and their feedbacks to climate warming have received increasing attention . It is estimated that per year, soil microbial respiration releases about 60 petagrams of C as CO₂ and the predicted warming is expected to accelerate carbon release into the atmosphere especially from old native SOM , due to its higher temperature sensitivity. With warming, the accumulation of litter and root exudate C inputs could further accelerate decomposition of older SOM via priming effects, which may be even higher than the direct temperature effects on SOM decomposition. On the other hand, microorganisms can grow and turn over rapidly producing a more stable microbial-derived C pool in soils. Since entombing could even exceed C losses due to priming, the balance between the two is important to determine. Warming could increase microbial turnover without change in microbial growth efficiency, thus warming could in some cases also promote carbon accumulation in soil . We are interested in the balance between priming and entombing effect; furthermore, we want to investigate the effect of temperature and C availability on this balance. For this research we obtained intact soil cores from the Kosñipata gradient (1500 to 3050 m a.s.l.) from the Peruvian Amazon. In this gradient, we expect to observe differences in soil nutrient availability (C:N) and microbial community, both of which might influence the magnitude and direction of the priming. We designed a long-term incubation priming experiment with ¹³C labelled glucose at two temperatures. We aimed to answer the question of whether the C loss via priming depend on the incubation temperature, how the formation of more stable microbial C depend on the temperature, and what was the balance between these two. We did this by tracing the fate of the ¹³C added at the beginning of the incubation, as respired ¹³CO₂ throughout the 7-month incubation. And at the end of the incubation, we measured the ¹³C incorporated in the microbial biomass and amino sugars, the C stabilised in soil microbial residues. We studied how the fate of the added C depended on the soil properties, in situ soil temperatures of the sites, and incubation temperatures.

Topic groups: 10. Geochemistry and Hydrology,

Presentation types: Oral presentation

Title: High frequency isotope monitoring for assessing hydrological extremes in the mesoscale Bode river catchment, Germany

Lead author: Christin Müller, Helmholtz-Centre for Environmental Research, UFZ

Author: Christina Radtke, Helmholtz-Centre for Environmental Research, UFZ; Hong Wei, Helmholtz-Centre for Environmental Research, UFZ; Ralf Merz, Helmholtz-Centre for Environmental Research, UFZ; Kay Knöller, Helmholtz-Centre for Environmental Research, UFZ

Keywords: isotopes, monitoring, autosampler, hydrological extremes

Content:

More frequent and intense hydrological extreme events are consequences of a changing climate. European regions that historically did not suffer from heavy rainfall, floods, droughts or heat waves, are becoming increasingly affected by such weather extremes. This development calls for an adopted monitoring scheme involving high frequency isotope-monitoring in order to address the following research questions: I) How do hydrological (extreme) events impact flow paths and thereby alter transient time distributions (TTD)? II) What is the relationship between (extreme) hydrological events and retention, mobilization and turnover of nutrients. In order to tackle this challenge, we conceptualized, developed and put into operation an isotope monitoring network using low-cost autosamplers that are capable of collecting groundwater, surface water and precipitation samples for subsequent off-site isotope analysis. The autosampler design is modular consisting of a programable pumping module with a 12V-battery, a rotor to fill 18 HDPE-bottles (250mL) and a control unit to program the rotation interval. Sample bottles are closed right upon sampling. Nevertheless, a diffusion barrier tubing is installed to avoid any evaporation during the actual sampling procedure. The sampling intervals can be varied freely with hourly steps between 1 and 72 hours so the total unattended operation time of the devices is between 18 hours and 54 days. The pilot stage monitoring network was tested in the mesoscale Bode river catchment in the Harz Mountains, Germany. We selected eight surface water locations along streams at different scales for automated water sample collection. Besides, we installed one sampler for the collection of groundwater samples and five precipitation collectors. Our monitoring network was complemented by daily manual samples from one surface water location and three precipitation collecting locations taken by local residents (citizen scientists). Preliminary results revealed that our monitoring network is capable of producing high quality data sets. The design of the network balances the scientific need driven by the research questions on the one hand and personnel and laboratory resources on the other hand. The implementation of daily nitrate and water isotope data from precipitation and surface water into transient time models provided a conclusive picture of the water travel time dynamics with a high model efficiency. Besides, nitrate isotopes gave information on nitrate ages and showed that median nitrate transient times are 40 days shorter than median water transient times at the catchment scale of a selected sub-catchment.

Topic groups: 13. Keynote,

Presentation types: Oral presentation

Title: Using stable isotope approaches to distinguish carbon sources in marine food webs

Lead author: Doreen Kohlbach, Norwegian Polar Institute, Norway

Keywords: marine food webs, carbon sources, compound-specific stable isotope analysis (CSIA), bulk stable isotope analysis (BSIA), multi-trophic marker approach

Content:

Stable isotope approaches can be used to study predator-prey relationships of marine organisms and trace the carbon (energy) flow within marine food webs. To determine the trophic position of a consumer, nitrogen stable isotope ratios ($\delta^{15}\text{N}$: $^{15}\text{N}/^{14}\text{N}$), assessed via bulk stable isotope analysis (BSIA), can serve as an indicator of heterotrophic (re)cycling. In Arctic and Antarctic food webs, carbon sources can be distinguished and quantified based on the carbon isotopic composition ($\delta^{13}\text{C}$: $^{13}\text{C}/^{12}\text{C}$) of primary producers (i.e. ice algae and phytoplankton) and consumers via BSIA or compound-specific stable isotope analysis (CSIA) of specific fatty acids (FAs). Marine algae biosynthesize certain FAs that are transferred along the food chain without significant changes (trophic marker FAs), i.e. they can be traced in the consumers across multiple trophic levels. The isotopic signatures of these trophic marker FAs often differ between ice algae and phytoplankton. This isotopic separation allows for the discrimination of the consumer's carbon sources, i.e. ice algae-derived or phytoplankton-derived, since this difference in $\delta^{13}\text{C}$ is also transferred from the algae to the consumers. Applications, advantages and possible drawbacks of isotopic approaches for the exploration of food-web structures and interactions in polar environments as well as the combination with other biochemical tools (multi-trophic marker approach) are discussed.

Topic groups: 02. Terrestrial and Aquatic Biogeochemistry,

Presentation types: Oral presentation

Title: Combining isotope mixing and fractionation with a new modelling tool applying the Monte Carlo approach

Lead author: Dominika Lewicka-Szczebak, Laboratory of Isotope Geology and Geoecology, Institute of Geological Sciences

Author: Maciej Lewicki; Greg Skrzypek

Keywords: isotope mixing model

Content:

The available stable isotope mixing models allow advanced quantification of mixing proportions but usually do not account for the stable isotope fractionation of the product. Here we present the newly developed model using Markov Chain Monte Carlo approach: isotope FRactionation And Mixing Evaluation (FRAME), with a user-friendly graphical interface that can simultaneously determine mixing proportions and progress of the fractionating process. The isotope fractionation may be defined by the user for specific requirements of the particular isotope system, e.g., open or closed system fractionation. The model can integrate up to three stable isotope signatures of each compound. This modelling approach has been designed and already validated for identifying N₂O production pathways and quantifying N₂O reduction progress in soil incubation experiments (Lewicka-Szczebak et al., 2020). However, it can be applied to other isotope systems where both isotope mixing and fractionation may coexist. In this presentation, we show the model performance based on two different case studies: (i) the soil-derived N₂O isotope studies and (ii) the river nitrate isotope budget. For (i) the model includes three isotope parameters ($\delta^{18}\text{O}$, $\delta^{15}\text{N}$, and SP – site preference – the difference in $\delta^{15}\text{N}$ value between central and peripheral position of the linear N₂O molecule) to determine the contribution of four N₂O production pathways and the progress of N₂O reduction to N₂. For (ii) the model includes two isotope parameters ($\delta^{18}\text{O}$, $\delta^{15}\text{N}$) to determine fractions of three nitrate sources and the progress of nitrate fractionation associated with denitrification. The model is potentially applicable across various study fields that employ isotope analysis. The open mathematical design allows for the implementation of additional processes that alternate the characteristics of the final mixture and can be applied to a broad range of mixing and fractionation models.

Topic groups: 01. Methodological Advances, Datatype not found, 02 or 07,

Presentation types: Oral presentation

Title: Belowground Methane Turnover at a Boreal Peatland: Quantifying the Processes with in-situ Stable Isotope Methods

Lead author: Xuefei Li, University of Helsinki

Author:

Keywords: boreal peatland, methane, pulse labelling, isotope natural abundance

Content:

Boreal peatlands emit substantial amount of CH₄, a potent greenhouse gas, to the atmosphere. Despite decades of effort made on studying CH₄ efflux to the atmosphere, quantifying the processes underlying CH₄ emission such as the different pathways of production and oxidation remains a challenge in peatland CH₄ modeling. To this end, we conducted a first systematic study with carbon stable isotopes quantifying in-situ major CH₄ turnover processes along a peat profile with high temporal resolution in a typical boreal peatland (Siikaneva fen) in Southern Finland. A cavity ring-down spectrometer is utilized to capture the dynamics of belowground dissolved CH₄ and CO₂ concentrations and their δ¹³C natural abundance signatures at 10, 30 and 50cm belowground. This novel approach continuously monitors the real-time CH₄ turnover processes of the steady-state conditions along a vertical profile. Additionally, comprehensive ¹³C pulse labelling experiments targeting acetoclastic methanogenesis, hydrogenotrophic methanogenesis and methanotrophy were for the first time performed in-situ to trace all these processes which cannot be separated by the isotope natural abundance approach alone. We also analyzed the background microbial communities in the field as well as in the lab. Preliminary results indicated a successful implementation of these novel methods. Unprecedented dataset for the optimization and validation of mechanistic CH₄ models have been produced and that our project has potential to profoundly renew our knowledge on belowground CH₄ dynamics especially in the less-studied winter and shoulder seasons.

Topic groups: 01. Methodological Advances,

Presentation types: Oral presentation

Title: Raman spectroscopy as a tool to quantify the (relative) abundances of isotopologues of CO₂

Lead author: Christian Ostertag-Henning, Federal Institute for Geosciences and Natural Resources

Keywords: Raman spectroscopy, CO₂, isotopologues

Content:

The application of stable isotope ratios as tool in a diverse set of topics in geoscience from climate reconstruction to subsurface process understanding is well established – usually with a focus on the most abundant stable isotopes and only recently corroborated by analyzing the relative abundances of isotopologues for some molecules. One reason for the focus on the ratios of isotopes in molecules – and not the abundance of individual isotopologues – was the long-term dominance of gas phase isotope mass spectrometry, which for conventional isotope mass spectrometers can not resolve most isotopologues of carbon dioxide (only ¹⁶O¹²C¹⁶O and ¹⁸O¹³C¹⁸O have no interfering masses on these instruments [1]). New developments in high resolution mass spectrometry [2] now allow the differentiation of a few additional isotopologues as ¹⁶O¹²C¹⁷O and ¹⁶O¹³C¹⁶O. But the ability of spectroscopic analyses to resolve all the isotopologues has paved the way from mass spectrometry towards using IR and Raman spectroscopy as analytical tools in this field of research [e.g. 3]. This contribution documents the first Raman spectroscopic measurements resolving the 24 Fermi diad bands of all twelve isotopologues of CO₂. Therefore different mixtures of ¹²CO₂ and ¹³CO₂ with ¹⁶O-, ¹⁷O- or ¹⁸O-labelled H₂O were prepared in sealed quartz glass tubes. After equilibration the analyses were performed in the gas phase on different Raman spectrometer systems with high spectral resolution and 0.03 to 0.3 MPa partial pressures of the isotopologues. The contribution describes in detail the steps for calibration and quality assurance and compares the data to the few published values of experiments by other groups for some isotopologues and the available results from calculations based on IR data for all CO₂ isotopologues. In ongoing experiments the Raman scattering cross-sections for the individual bands of the isotopologues are determined relative to N₂ in mixtures of the isotopologues with N₂. This will enable the quantitative determination of individual isotopologue abundances – in natural samples, in samples from experiments using an isotope label and in gas samples for method development of quantitative analyses of isotopes and isotopologues [4].

References [1] Santrock et al. (1985) Anal. Chem. 57: 1444-1448. [2] Eiler et al. (2013) Int. J. Mass Spectr. 335: 45-56.

[3] Castrillo et al. (2007) Optics letters 32: 3047-3049. [4] Flierl et al. (2020) J. Anal. At. Spectr. 35: 2545-2564.

Topic groups: 05. Health and Medical Sciences,

Presentation types: Oral presentation

Title: Development of mass spectrometry-based methods for the detection of 11-ketotestosterone, a novel doping agent

Lead author: Thomas Piper, Institute of Biochemistry - German Sport University Cologne

Author: Mario Thevis, Institute of Biochemistry - German Sport University Cologne

Keywords: Doping Control Analysis, Anabolic Agents, Human Metabolism, Isotope Ratio Mass Spectrometry, High Resolution/High Accuracy Mass Spectrometry

Content:

In recent years, several publications showed up dealing with the topic of the anabolic properties of 11-hydroxyandrostenedione (11OHA4) and its physiologically active metabolites 11-ketotestosterone (11KT) and 11-ketodihydrotestosterone (11KDHT). Especially 11KT became easily available via internet-based providers and its usefulness in the context of body-building is thoroughly discussed. No doping control methods for the detection of 11KT or 11KDHT exist, neither on the initial testing procedure level nor as confirmation method. The prohormone of 11OHA4 – adrenosterone (androst-4-ene-3,11,17-trione, A4TR) has already been addressed several years ago and the suggested urinary marker for its misuse was mainly the concentration of 11-hydroxyandrosterone (11OHA) to be greater than 10,000 ng/mL and for confirmation purposes the carbon isotope ratios (CIR) were taken into consideration. Due to the relatively high urinary concentrations of 11OHA being a major metabolite of adrenal gland steroid production, the detection windows were rather short and most probably not sensitive enough to detect the potential misuse of 11KT. Therefore, we investigated the human metabolism of 11KT focusing on all urinary metabolites in order to enable the detection of 11KT and its prohormone A4TR. Two volunteers (one female and one male) orally administered 20 mg of 11KT each and urine samples were collected for 5 days. In a first step, urinary concentrations of 11KT and its potential metabolites were investigated to enable implementation of reasonable metabolites into current screening procedures. A reference population encompassing 100 males and 100 females was investigated regarding baseline urinary concentrations of relevant metabolites in order to elucidate preliminary thresholds for identification of suspicious samples. As confirmation procedure, an isotope ratio mass spectrometry-based method was developed and validated in order to determine the carbon isotope ratios (CIR) of 11KT and all relevant metabolites. After oral application of 20 mg of 11KT significantly elevated urinary concentrations were found for not more than 8 hours, depleted CIR were detected until 24 hours after administration pointing towards a fast metabolism of 11KT. Several new metabolites of 11KT have been detected, but they could not significantly prolong the detection times, neither during the screening procedure, nor considering their CIR.

Topic groups: 01. Methodological Advances,

Presentation types: Oral presentation

Title: Calibration of a preconcentrator and laser spectrometer for $\delta^{13}\text{C}(\text{CH}_4)$ and $\delta\text{D}(\text{CH}_4)$ measurement in ambient air

Lead author: Chris Rennick, National Physical Laboratory

Author:

Keywords: methane; atmospheric; laser; OIRS

Content:

Methane (CH_4) has the second strongest anthropogenic contribution to radiative forcing, following carbon dioxide (CO_2). It is emitted by distinct sources such as agriculture, landfill, and fossil fuel use, and has a short atmospheric lifetime so is an attractive target for emission mitigation strategies. While the atmospheric amount fraction of methane is routinely measured by atmospheric monitoring stations for emissions estimates using regional-scale inversion modelling, it is not currently possible to disaggregate the relative proportion of each emission category. The different sources emit methane with distinct isotopic ratios, so continuous isotopic measurements will provide an important extra observable. We present a new instrument for automated measurement of carbon and deuterium isotope ratios in methane, capable of long-term continuous deployment to atmospheric monitoring stations. Boreas is an automated preconcentrator sample preparation system coupled to an infrared laser spectrometer, capable of making hourly measurements of $\delta^{13}\text{C}(\text{CH}_4)$ and $\delta\text{D}(\text{CH}_4)$ of ambient air samples. The typical standard measurement uncertainty is 0.07 ‰ for $\delta^{13}\text{C}(\text{CH}_4)$ and 0.9 ‰ for $\delta\text{D}(\text{CH}_4)$, which is the lowest reported for a laser spectrometry-based system and comparable to laboratory-based isotope ratio mass spectrometry. Such optical instruments are currently limited in the availability of reference materials traceable to international isotopic standards, and interference from matrix gases. We will present our implementation of a calibration strategy based on synthetic gas reference materials prepared gravimetrically from a pure methane source with a single isotopic composition. This approach is validated using different methane gas mixtures, and we quantify the contributions to the measurement uncertainty. We will also quantify the sensitivity to potentially interferences – oxygen, argon and krypton – and verify that the preconcentrator is separating these gases from the air sample. These reference materials were produced under the EMPIR project “Stable isotope metrology to enable climate action and regulation”.

Topic groups: 05. Health and Medical Sciences,

Presentation types: Oral presentation

Title: Changes in the Nitrogen Isotope Composition of Serum Amino Acids in a Longterm Feeding Trial

Lead author: Noreen Tuross, Harvard University

Author: Linda Reynard, Boise State University

Keywords: human, compound specific amino acids, diet,

Content:

The impact of changes in diet on the natural abundance of isotopes in humans has been difficult to assess and few longitudinal studies are found in the literature. We utilized biobanked serum samples from a well know clinical trial (Ebbeling et al, BMJ 2018;363:k4583) to determine whether a change in the nitrogen isotopic composition in serum was observed in whole serum and in the individual amino acids derived from serum protein during the 32-week trial in which all food was supplied to the participants. We document a narrow range in the nitrogen isotopic composition of the whole serum both in the prediet population and at the end of controlled dietary input. In contrast, robust differences were seen in several individual amino acids between the baseline and end of trial data. Significant declines in the $\delta^{15}\text{N}$ of Leucine, Tyrosine, and Threonine were observed in nearly all participants between the beginning and end of the trial. These results confirm and extend the utility of compound-specific amino acid measurements for documenting the incorporation of nutrients that are invisible in bulk tissue. In addition, the use of the natural isotopic composition in foods could be developed as markers of dietary adherence.

Topic groups: 09. Isoscape, Spatial Variability of Stable Isotopes (Migration, Food Webs),

Presentation types: Oral presentation

Title: Reconstructing the diet, trophic level and migration pattern of mysticete whales based on baleen isotopic composition

Lead author: Philip Riekenberg, NIOZ

Keywords: Fasting, compound specific, temporal, migration

Content:

Baleen from mysticete whales is a well-preserved proteinaceous material that can be used to identify migrations and feeding habits for species whose migration pathways are unknown. Bulk analyses of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values from baleen have been used to infer migration patterns for individuals. However, this approach has largely fallen short of identifying migrations between regions as it is difficult to identify isotopic shifts occurring in the environment without concurrent temporal sampling of prey items. Here, we apply analysis of $\delta^{15}\text{N}$ values of amino acids to five baleen plates belonging to three species, revealing novel insights on trophic position, metabolic state and migration between regions. Humpback and minke whales had higher reconstructed trophic levels than fin whales (3.7–3.8 versus 3–3.2, respectively) as expected due to different feeding specializations between krill and fish. Isotopic niche areas between baleen minima and maxima were well separated, indicating regional resource use for individuals during migration that aligned with isotopic gradients in Atlantic Ocean particulate organic matter. Phenylalanine $\delta^{15}\text{N}$ values confirmed regional separation between the niche areas for two fin whales as migrations occurred and elevated glycine and threonine $\delta^{15}\text{N}$ values suggested physiological changes due to fasting. Simultaneous resolution of trophic level and physiological changes will allow for clearer identification of regional migrations in mysticetes.

Topic groups: 08. Soil Carbon and Nitrogen Cycling, with Focus on Agricultural Soils,

Presentation types: Oral presentation

Title: Nitrogen but not phosphorus addition affects symbiotic N₂ fixation by legumes in natural and semi-natural grasslands located on four continents

Lead author: Marie Spohn, Swedish Agricultural University

Author: Eduardo Vazquez Garcia, Swedish Agricultural University

Keywords: N₂ fixation, ¹⁵N natural abundance method, legumes, grasslands, nitrogen addition, phosphorus addition

Content:

The amount of nitrogen (N) derived from symbiotic N₂ fixation by legumes in grasslands might be affected by anthropogenic N and phosphorus (P) inputs, but the underlying mechanisms are not known. We evaluated symbiotic N₂ fixation in 17 natural and semi-natural grasslands on four continents that are subjected to the same full-factorial N and P addition experiment, using the ¹⁵N natural abundance method. N as well as combined N and P (NP) addition reduced aboveground legume biomass by 65% and 45%, respectively, compared to the control, whereas P addition had no significant impact. Addition of N and/or P had no significant effect on the symbiotic N₂ fixation per unit legume biomass. In consequence, the amount of N fixed annually per grassland area was less than half in the N addition treatments compared to control and P addition, irrespective of whether the dominant legumes were annuals or perennials. Our results reveal that N addition mainly impacts symbiotic N₂ fixation via reduced biomass of legumes rather than changes in N₂ fixation per unit legume biomass. This study shows that soil N enrichment by anthropogenic activities significantly reduces N₂ fixation in grasslands, and these effects cannot be reversed by additional P amendment. Further, the unique global design of this study allowed us to derive an equation to correct for the effect of elevation on the isotope signature of N in grasses and non-fixing forbs which will be useful in future studies.

Topic groups: 09. Isoscape, Spatial Variability of Stable Isotopes (Migration, Food Webs),

Presentation types: Oral presentation

Title: Exploiting biogeochemical and physiological isotope systematics to address ecological questions

Lead author: Clive Trueman, Ocean and Earth Science, National Oceanography Centre

Content:

Light stable isotopes have wide applicability as tracers because the elements we exploit are fundamental building blocks of essential nutrients and metabolites for all life on earth, as well as being involved in hydrological cycles. Fractionation of isotopes through these physical, biochemical and biogeochemical processes creates the isotopic signals we use to infer process - but the same complexity clouds our interpretation of stable isotope compositions. Stable isotope ecology is therefore a compromise between understanding the fundamental biogeochemical and physiological mechanisms underpinning fractionation and isotopic discrimination at multiple scales, and simplifying that complexity to a manageable level. In this talk I will illustrate the trade-off between understanding and application using three common applications of isotopes in ecology: Animal migration, diet tracing and reconstructing metabolic rates. I will try to highlight areas of promising emerging work, including the use of simulation modelling and prediction to test how well our conceptual understanding of isotopic process explains the isotopic variability observed in nature.

Topic groups: 07. Atmospheric Sciences (Pollution, Climate Change, Cosmogeochimistry),

Presentation types: Oral presentation

Title: Evaluating the Atmospheric Dynamics of Nitrate in New England in Response to Emission Regulations Utilizing Novel Isotope Observations

Lead author: Wendell Walters, Brown University

Content:

Atmospheric deposition of nitrogen is a major terrestrial stressor, which has important implications for land and water quality and important interacting effects with climate. However, there are key uncertainties in linking precursor reductions to atmospheric deposition changes due to complicated production mechanisms of atmospheric nitrate driven by non-linear chemical feedback associated with oxidant availability, cloud water chemistry, heterogeneous chemistry, and gas/particle partitioning. This has led to disagreements between model predictions of atmospheric nitrogen deposition and observations, indicating that a thorough understanding of the processes associated with atmospheric deposition is needed to improve the existing Clean Air Act Secondary Standards. The stable oxygen and nitrogen isotope composition are powerful tools that can further our understanding of the atmospheric dynamics of atmospheric nitrate. The oxygen isotope composition ($\Delta^{17}\text{O}$) has been shown to provide quantitative observational constraints on atmospheric nitrate and sulfate production mechanisms. At the same time, nitrogen ($\delta^{15}\text{N}$) can aid in our understanding of connecting emission source contributions to atmospheric deposition. Here I will present recent results of a unique combination of concentration and isotope observations from several CASTNET locations located within New England from 2016-2018 to investigate spatial patterns in atmospheric nitrate (nitric acid (HNO_3) + particulate nitrate (pNO_3^-)) dynamics. These new observational constraints will enable a process-level understanding of the connection between emission regulations and oxidation chemistry with important implications for predicting air quality and climate responses. Our results indicate significant spatial differences in HNO_3 and pNO_3^- production within New England that tend to be consistently dominated by fuelcombustion emissions of NO_x across this region. These novel observational constraints on oxidation chemistry and emission source spatiotemporal changes will be compared with atmospheric chemistry simulations to evaluate model representations of nitrate chemistry and precursor source contributions in New England in response to emission regulations.

Topic groups: 03. Plant Ecophysiology,

Presentation types: Poster

Title: Tracing plant water source dynamics by continuous in-situ isotope measurements of transpiration

Lead author: Angelika Kübert, INAR, Univ. of Helsinki, Finland; Ecosystem Physiology, Univ. of Freiburg, Germany

Author: Maren Dubbert, Landscape Functioning, ZALF, Müncheberg; Ines Bamberger, Atmospheric Chemistry, University of Bayreuth, Germany; Kathrin Kühnhammer, Institute for Geoecology, Technical University of Braunschweig, Germany; Matthias Beyer, Institute for Geoecology, Technical University of Braunschweig, Germany; Joost van Haren, Biosphere 2 and Honors College, University of Arizona, United States of America; Kinzie Bailey, School of Natural Resources and the Environment, University of Arizona, USA; Jia Hu, School of Natural Resources and the Environment, University of Arizona, USA; Laura K. Meredith, School of Natural Resources and the Environment, University of Arizona, USA; S. Nemiah Ladd, Ecosystem Physiology, University of Freiburg, Germany; Christiane Werner, Ecosystem Physiology, University of Freiburg, Germany

Keywords: xylem, water stable isotopes, CRDS, laser spectroscopy, method comparison, plant water use, herbaceous, non-woody, woody, species,

Content:

The isotopic composition of xylem water (δX) is of great interest for plant water source studies. A common approach to derive δX values is based on destructive sampling and subsequent cryogenic vacuum extraction (CVE) of the samples' water content in the laboratory. However, CVE has many practical constraints and its potential analytical biases have placed the method under increased scrutiny. New in-situ methods to derive δX values have been proposed in recent years. Yet, they are still in the development- and test phase, and their application intrusive. Gas exchange chamber techniques, on the other hand, have been well established for decades and allow the isotopic composition of transpiration (δT) to be monitored in-situ and at high temporal resolution. As δT values approach δX values when transpiration is at isotopic steady state, measurements of δT values may provide a good proxy for δX values. We tested this approach by using flow-through leaf chambers connected to a water isotope analyzer to monitor 2-hourly δT dynamics in two tropical plant species, one canopy tree and one understory herbaceous species. Parallel to continuous measurements of δT values, branch samples were collected at 5 time points throughout the experiment to determine δX values from CVE. We observed δT dynamics in response to increasing drought and subsequent recovery during a large-scale drought experiment of more than 60 days in a model rainforest ecosystem (Biosphere 2 WALD campaign). At the end of a severe drought a deep-water pulse strongly enriched in 2H was applied before starting the regular rain. We found that δT values provided a good proxy for δX values when using the daily averages of δT values, weighted by the transpiration flux. This was the case for both species under well-watered and drought conditions. Transpiration-derived $\delta^{18}O_X$ matched those of CVE. In contrast, transpiration-derived δ^2H_X values were depleted in 2H in comparison to CVE-derived values, which is probably linked to the isotopic effects of CVE on δ^2H , recently observed in several studies. Moreover, adding a 2H deep water pulse, δT values allowed us to distinguish between deep and shallow soil water use and derive uptake velocities of newly added water. In-situ monitoring of transpiration and its isotopic composition provides a good proxy for δX values in order to address research questions concerning plant water sources and usage and at the same time gives additional information on the plant water status.

Topic groups: 10. Geochemistry and Hydrology,

Presentation types: Poster

Title: Development of physical-biological filters for groundwater remediation of tetrachloroethene and naphthalene

Lead author: Simon Leitner, University of Natural Resources and Life Sciences, Vienna

Author: Theresa Ugochukwu Ukwamedua , University of Natural Resources and Life Sciences, Vienna; Gerhard Soja, AIT Austrian Institute of Technology; Katharina Keiblinger, University of Natural Resources and Life Sciences, Vienna; Christine Stumpp, University of Natural Resources and Life Sciences, Vienna; Andrea Watzinger, University of Natural Resources and Life Sciences, Vienna

Keywords: Biochar, Biofilter, Groundwater Remediation, Biofilm,

Content:

Hydrophobic organic solvents such as tetrachloroethylene (PCE) and naphthalene account for a large number of soil and groundwater contaminated sites in Europe. Most ex-situ remediation strategies follow a two-step procedure, sorbing the volatiles on activated carbon and exchanging the sorbent when its capacity is exhausted. Hence, the overall goal of this study is the development of a physical-biological ex-situ filter without the need of such frequent sorbent exchanges. A combined approach of physical adsorption to charcoal and on-site degradation by microbial consortia was designed for that. Charcoal versions comprised internally produced biochars and activated carbon. Microbial consortia were made available by in-house consortia and cultures from an industrial partner. Lab work comprised hydraulic and chemical characterization of charcoals, adsorption isotherms and kinetics, batch and column experiments, monitoring sorption and dehalorespiration of chlorinated ethenes. Latter were measured by gas chromatography coupled to mass spectrometry, and isotope-ratio mass spectrometry (GC/MS-C/IRMS). While naphthalene was analysed for the stable isotope ratio of carbon and hydrogen chlorinated ethenes were analysed for carbon only. Results so far revealed that sorption of PCE to charcoals most significantly increased with their production temperature. Ultimately, however, the biochars had to be selected on the basis of their mechanical strength in order to avoid filter clogging. In addition, high adsorption capacity can compromise bioavailability, affecting the overall goal of the project, compound degradation. Microcosm experiments showed various degradation patterns of PCE facilitating the selection of most vital consortia (one in-house culture and the consortia KB-1[®] from SiREM) which all showed complete dehalorespiration of PCE to ethene. Isotope enrichment in the carbon of PCE was observed for both, adsorption and dehalorespiration but with major differences ranging from $\delta^{13}\text{C}$ shifts of +0.5 ‰ for adsorption and up to +25 ‰ for dehalorespiration. The effect of biochars on dehalorespiration of PCE revealed two major conclusions so far. First, PCE-dehalorespiration was enhanced at the presence of biochars as compared to media-only microcosms. Second, the bioavailable fraction of PCE is mostly limited to the non-adsorbed fraction, which appears to be more pronounced in charcoals with higher adsorption capacity. Experiments are currently being converted from batch scale to column experiments. Upcoming tasks also include repeating the work carried out with the second main compound, naphthalene. We will present up-to-date results of the underlying project CHARBAK, funded by Kommunalkredit Public Consulting (KPC) at the conference meeting.

Topic groups: 10. Geochemistry and Hydrology,

Presentation types: Poster

Title: Analysis of radiocarbon distribution in the eutrophic lake fish assemblage using stable C, N, S isotopes

Lead author: Vytautas Rakauskas, State Research Institute Nature Research Centre, Lithuania; Žilvinas Ežerinskis, State Research Institute Center for Physical Sciences and Technology, Lithuania; Justina Šapolaitė, State research institute Center for Physical Sciences and Technology, Lithuania

Author: Rūta Barisevičiūtė, State Research Institute Center for Physical Sciences and Technology, Lithuania

Keywords: lakes, fishes, radiocarbon, sulfur, nitrogen

Content:

The present study focuses on the $^{14}\text{C}/^{12}\text{C}$ ratio variation within the fish assemblage of the shallow lake Tapeliai. Lake Tapeliai (54°46'28"N, 25°26'45"E) is located 17 km northeast of the city Vilnius, Lithuania. During spring flood periods or after heavy rains, this lake is fed by an inflow of coloured water from the surrounding watershed mires. Repetitive inflows of such water highly enriched in organic compounds not only affects photosynthetic activity but also causes short-term changes in content and composition of organic and inorganic matter which may impact radiocarbon distribution in lake ecosystem. Thus, it was decided not to perform any stable isotope ratio or radiocarbon dating measurements in dissolved inorganic, dissolved organic carbon, particulate organic carbon, water column sulphates. The aim of this study was to investigate the radiocarbon distribution within fish species of different diet and trophic levels, and possibility to relate radiocarbon distribution in fishes of this constantly changing ecosystem with their stable C, N, and especially S isotope ratio values. The radiocarbon age within the fishes in this lake varied from 119 to 693 yr. No relationship of carbon isotope ratio values with sulphur or nitrogen isotope ratios were observed in studied ecosystem. However, $^{14}\text{C}/^{12}\text{C}$ measurements correlated significantly with $\delta^{13}\text{C}$ values in fish tissues. values ($r=0.85$ $p<0.001$). This is not typical for water ecosystems of the temperate zone, where C3 plants predominate. Carbon stable isotope values of modern (fresh plants), "old" (terrestrial soil, peat) terrestrial organic matter as well as plants of the fresh water ecosystem overlap. Thus, the $^{13}\text{C}/^{12}\text{C}$ and $^{14}\text{C}/^{12}\text{C}$ ratio values in organic and inorganic matter of aquatic ecosystems usually do not correlate. Analyzing carbon dynamics in freshwater lakes, ^{14}C analysis is essential to distinguish modern terrestrial carbon fraction. However, in reconstructing the diet of fish such as carp, adapted to penetrate deep (up to one meter) into sediments, it is necessary to examine sediments themselves; how have they been affected by ^{14}C from bomb peak. It was our previous sediment studies that showed that deeper sediment layers were not enriched in ^{14}C due to the bomb peak (in our cases it was the opposite - they were depleted in ^{14}C) and helped determine that carp were supplementary fed by an allochthonous food sources provided by anglers.

Topic groups: 03. Plant Ecophysiology,

Presentation types: Poster

Title: Fast recovery of suppressed Norway spruce trees after selection harvest on a drained peatland forest site

Lead author: Aleksi Lehtonen, Natural Resources Institute Finland

Author: Kersti Leppä, Natural Resources Institute Finland; Katja T. Rinne-Garmston, Natural Resources Institute Finland; Elina Sahlstedt, Natural Resources Institute Finland; Pauliina Schiestl-Aalto, University of Helsinki; Juha Heikkinen, Natural Resources Institute Finland; Giles H.F. Young, Natural Resources Institute Finland; Mika Korhonen, Finnish Meteorological Institute; Mikko Peltoniemi, Natural Resources Institute Finland; Sakari Sarkkola, Natural Resources Institute Finland; Annalea Lohila, Finnish Meteorological Institute; Raisa Mäkipää, Natural Resources Institute Finland

Keywords: carbon isotope, water use efficiency, selection harvest

Content:

Continuous cover forestry (CCF) has been promoted as an environmentally sustainable option for drained boreal peatlands. The CCF management has also been challenged due to potentially lower tree growth compared to traditional even-aged management, especially with suppressed trees that are released during a selection harvest under CCF management. Our objective was to quantify the time lag of stem diameter growth (at breast height, 1.3 m) response of suppressed Norway spruce trees (*Picea abies* Karst.) after a selection harvest of the stand. We also tested if the carbon assimilation of the trees increases immediately after selection harvest. We used tree radial increment cores from suppressed Norway spruce trees to estimate the impact of selection harvest on the diameter growth and photosynthetic rate. The study was conducted in the Lettosuo experimental site in southern Finland, where a part of the stand, ca. 70 % of the initial stand volume ($278 \text{ m}^3\text{ha}^{-1}$) and area (18.5 ha) was harvested according to CCF principles, and rest of the area was divided to intact control and to clear-cut area. We measured carbon isotope composition ($\delta^{13}\text{C}$) at intra- and inter-annual resolution, to quantify how the reduced competition between trees altered the ratio of photosynthetic rate (A) and stomatal conductance (g) of sampled trees. The response of the sample trees from the harvested area were then compared to those from the control area. Our results show that there was an average delay of 2 years with only a slight response of the diameter growth of the suppressed trees to selection harvest, whereas the most significant growth-enhancing effect occurred with a delay of 3-4 years after selection harvest. In contrast to the delay in the increment, photosynthetic rates relative to stomatal conductance increased immediately after selection harvest, as shown by the instant 2.5‰ change in $\delta^{13}\text{C}$ during the following summer. Our results show that carbon uptake increased immediately for suppressed Norway spruce trees after selection harvest, but it did not induce stem diameter growth during the first years since harvesting.

Topic groups: 06. Food Authenticity, Nutrition, Forensic,

Presentation types: Poster

Title: Italian garlic (*Allium sativum* L.) characterization through gas chromatography-isotope ratio mass spectrometry and headspace gas chromatography-mass spectrometry volatile profile

Lead author: Silvia Pianezze, Fondazione Edmund Mach (TN, Italy); University of Udine (UD, Italy); Matteo Perini, Fondazione Edmund Mach, San Michele all'Adige (TN), Italy; Angelo Antonio D'Archivio, University of L'Aquila (AQ, Italy)

Author: Mauro Paolini, Fondazione Edmund Mach, San Michele all'Adige (TN), Italy

Keywords: garlic, stable isotopes, traceability, mass spectrometry, volatile compounds

Content:

Italian garlic (*Allium sativum* L.) is worldwide appreciated for its unique flavour and taste. Excellence varieties such as Aglio di Voghiera and Aglio Bianco di Polesano have been officially recognised by the European Commission through the attribution of the Protected Designation of Origin (PDO) certification mark [1]. On this basis, an effective tool to preserve the reputation and the commercial value of this appreciated product, by assessing its geographical identity, is therefore required. For the first time, solid phase microextraction (SPME) followed by gas chromatography-isotope ratio mass spectrometry (GC-IRMS) was used to characterize 49 red garlic (*Allium sativum* L.) samples coming from 3 different Italian regions (Abruzzo, Lazio and Sicily). The developed method made it possible to measure the carbon isotopic ratio of 3 major volatile components of garlic (namely, allyl alcohol, diallyl sulphide and triallyl disulphide). Moreover, the quantification of the just mentioned compounds was carried out through gas chromatography-mass spectrometry (GC-MS). The compound specific analysis aimed to attempt the discrimination of Italian garlic samples depending on their geographical origin and to eventually give additional information with respect to those provided by the bulk garlic isotopic analysis. [1] Quality products registers. (2018, August 14). Retrieved 18 January 2019, from https://ec.europa.eu/info/food-farming-fisheries/food-safety-and-quality/certification/quality/labels/quality-products-registers_en

Topic groups: 08. Soil Carbon and Nitrogen Cycling, with Focus on Agricultural Soils,

Presentation types: Poster

Title: Cover crop C inputs; isotope insights from a long-term field trial.

Lead author: Rebecca Hood-Nowotny, Institute of Soil Research, Department of Forest- and Soil Sciences, University

Author: Anna Wawra, Department for Soil Health and Plant Nutrition, AGES Austrian Agency for Health ; Katharina Schott, Institute of Soil Research, Department of Forest- and Soil Sciences, University ; Maria Heiling , Soil and Water Management & Crop Nutrition Laboratory of the Joint FAO/IAEA Cent; Gerd Dercon, Soil and Water Management & Crop Nutrition Laboratory of the Joint FAO/IAEA Cent

Keywords: soil fractionation, POM, MOAM, microbial biomass

Content:

Use of cover crops, mulches and other soil management practices have been widely promoted within the EU, as measures to draw down carbon dioxide and increase soil organic carbon in the fight against climate change. These approaches are being investigated in a number of programs and projects EU-wide, for example the EJP-SOIL program. We used a long-term fully replicated maize based field trial with different crop and soil management practices, namely residue incorporation and/or inclusion of a cover crop, to explore carbon sequestration potential. We used natural abundance stable isotope approaches to follow the fate and residence time of mulched residues and to determine the most stable organic matter pools in these systems. We measured isotope signatures in particulate organic matter (POM), mineral associated organic matter (MOAM), stable aggregate bound organic matter (SABOM) and soil microbial biomass (Mi-BIO) to characterize the impact of the soil fraction, on the fate and stability of the carbon pool and to test a number of emerging paradigms in soil science. We hypothesized that the residence time of the POM fraction and MOAM fractions would be lower under higher nitrogen inputs and that it would be possible to detect these shifts using a stable isotope approach. Preliminary results show that even at low mulch rates (<3 t plant material ha⁻¹) mulching significantly increased soil carbon storage in the long term, albeit at lower rates than predicted. This increase was due to increases in SOM in the top-soil. As hypothesized mulch with lower C:N ratios contributed less to overall soil carbon storage, but whether this was due to differences in carbon accumulation in the short-term POM pool or long-term MOAM pool remains to be revealed by on-going isotope analysis. The high replication and detailed investigation of this long term field trial should allow us to tease out a number of processes in the carbon and nitrogen cycle and allow us recommend suitable management practices for increasing soil organic carbon stocks.

Topic groups: 08. Soil Carbon and Nitrogen Cycling, with Focus on Agricultural Soils,

Presentation types: Poster

Title: EJP Soil Project MaxRoot-C Optimizing roots for sustainable crop production in Europe—pure cultures and cover crops.

Lead author: Rebecca Hood-Nowotny, Institute of Soil Research, University of Natural Resources and Life Sciences Vi

Author: Anna Wawra , Ages, Vienna, Austria ; MaxRoot-C Consortium, EJP-SOIL

Keywords: roots, labelling,

Content:

To build climate-smart sustainable management practices of agricultural soils, agricultural carbon sequestration is an indispensable addition to European wide climate change mitigation efforts and needs to be found equivalent profitable for crop producers. One option that is most viable yet neglected to increase C sequestration without yield loss is through increased and deeper roots of main and cover crops. MaxRoot-C will pioneer assessment methods closing this knowledge gap by providing robust hard data on the root C inputs of main crop varieties and different cover crops across Europe. MaxRoot-C will examine a combination of root traits, such as: root biomass, root stoichiometry, root architecture, and rhizodeposition, in conjunction with environmental factors, like soil type, strength and fertility, to predict the effect of root systems on SOC stocks. Additionally, soil-crop management practices that optimise carbon sequestration will be selected. Using a combination of state of the art experimental and modelling approaches, we will quantify the belowground C allocation for the most prevalent cropping systems. Using a stable isotope labelling approach, we can estimate root carbon inputs and sequestration potential of different management practices, crop varieties and cover crop mixtures, in farmer's fields over significantly shorter times scales than traditional long-term experimental approaches, that usually require ten years of repeated measurements to detect significant impacts on soil carbon build-up. With isotopes we can determine net annual C inputs and their retention, moreover follow their biological fate and turnover, allowing us to maximise root derived carbon storage and persistence in relation to specific root traits and functions. This approach will be applied in 12 European countries to follow fate of root carbon in a robust replicated manner. The project will evaluate the potential impact of promising C sequestering management interventions, such as: cover cropping, targeted-breeding, and soil management in these foremost cropping systems aiming at widespread adoption of more sustainable carbon sequestering and soil restorative practices. We poster will present concepts, approaches and preliminary results from the up-coming season's experiments.

Topic groups: 03. Plant Ecophysiology,

Presentation types: Poster

Title: Linking climate change induced drought stress and bark beetle susceptibility in Austrian forests with stable isotope methods (^{13}C , ^{18}O)

Lead author: Katharina Schott, University of Natural Resources and Life Sciences

Author: Barbara Kitzler, Federal Research and Training Centre for Forests, Natural Hazards and Landscape ; Gernot Hoch, Federal Research and Training Centre for Forests, Natural Hazards and Landscape ; Andrea Watzinger, University of Natural Resources and Life Sciences Vienna; Elisabeth Ziss, University of Natural Resources and Life Sciences Vienna; Michael Grabner, University of Natural Resources and Life Sciences Vienna; Christoph Bauerhansl, Federal Research and Training Centre for Forests, Natural Hazards and Landscape; Rebecca Hood-Nowotny, University of Natural Resources and Life Sciences Vienna

Keywords: Norway spruce, tree rings, climate change, $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, drought stress, *Ips typographus*

Content:

Norway spruce is the most economically important and abundant species in Austrian forestry systems. It is high yielding, easily managed and has a number of economic advantages compared to broadleaved tree production. As a result, in the last century, blanket planting was encouraged across Austria, often leading to planting in regions where the production risk for Norway spruce was, and remains high. This planting policy legacy means that stands are often still grown on sites where the site characteristics are close to the limit of suitability. Climate change clearly has major effects on plant growth, plant performance, spatial distribution and species composition. Aside from the direct effects, climate change will have proximate effects, specifically on plant pathogenic pest communities. These pests will possibly have bigger impacts than the direct effects on plant growth and forestry production. Effects will clearly be context and region specific. In regions where productivity is restricted by low temperatures such as at high altitudes, the productivity is predicted to increase with climbing temperatures, whilst in regions where water availability is limited, productivity is expected to decrease due to more frequent and longer droughts or changes in precipitation patterns. Norway spruce is particularly prone to drought, as it has shallow roots and less access to deeper soil moisture. It can be assumed that trees which suffer under changing site conditions will be more susceptible to disease and insect attack than trees which don't have this additional site pressures. In an effort to identify sites prone to past and future drought stress which are prone to possible proximate pest impacts, a tree ring stable isotope prediction tool methodology was developed. Specifically, we will test whether we can predict bark beetle attack susceptibility by identifying past drought susceptibility based the legacy isotope signatures in the tree rings Tree ring stable isotope (^{13}C , ^{18}O) data provides an accurate archive of information on past climate variability and physiological responses to environmental and geomorphological conditions, specifically soil water availability and usage. It offers historic insight into individual tree water status, temperature and source water use, that can be retrospectively correlated with detailed archived weather data and available and easily measured parameters such as tree canopy temperature or spectral data. We will present our approach, and the initial data, based on samples collected from the Austrian Forest Inventory and augmented with data from additional beetle attack sites.

Topic groups: 11. Molecular & Intra-Molecular Biology,

Presentation types: Poster

Title: NitroBiome -project: Microbial mechanisms regulating N₂O metabolism in above-ground vegetation - significant northern N₂O sink?

Lead author: Henri Siljanen, University of Eastern Finland, Kuopio, Finland

Author: Johanna Kerttula, University of Eastern Finland, Kuopio, Finland; Khrisnapryia Thiyagarasaiyar, University of Eastern Finland, Kuopio, Finland; Dhiraj Paul, University of Eastern Finland, Kuopio, Finland

Keywords: climate change, nitrogen management, coniferous forest, peatland, microbiome, denitrification, nitrous oxide, genetic regulation, metaomics, metagenome, metatranscriptomics, metabolomics

Content:

Nitrous oxide (N₂O), strong greenhouse gas (GHG), sink strength of boreal and arctic peatlands and forests in warming climate is a key question for climate change mitigation and climate policy. There are indications, and our own findings, that above ground vegetation and cryptogams can increase N₂O sink strength in northern areas. Current vegetation, climate change assessment and GHG flux models, are lacking information on microbiological mechanisms consuming atmospheric N₂O within above-ground vegetation. To improve management of N₂O sink and climate policy, this proposal brings new knowledge about the role of above ground vegetation of peatlands and forests, and their microbiomes as a part of N₂O dynamics of northern ecosystems. We utilize existing infrastructure for manual and automated GHG flux measurements, collect samples across transect from temperate to Arctic region and study functioning of N₂O consuming microbes with novel methods in molecular microbiology and isotope-labelled-metabolomics. The main aim of this project is to identify N₂O uptake in above ground vegetation in Boreal coniferous forests, and peatlands and forests in different climatic zones to make comparison, and via that, to understand the importance of plant-microbe interactions and their contribution on N₂O metabolism. More specifically, we will characterize (1) N₂O consuming microbiome of different above ground vegetation;(2) the microbial functions metabolizing N₂O in vegetation; and (3) their dynamics associated with spatially and seasonally variable environmental conditions. Diversities and community structures of N₂O consuming microbes will be analyzed by through searches of public gene-bank databases, using functional gene targeted PCR and novel targeted metagenomics for microbial nitrogen (N) cycling genes from plant and soil samples collected from the study sites across the transect from temperate to arctic region and along the growing seasons. The N₂O fluxes, microbial activity and diversity data of vegetation will be compared with the soil chemical, metabolic functions and plant community composition and coverage data, to make regional estimations of N₂O consumption in vegetation and it's impact on overall N₂O budget of the ecosystem. The project generates novel ideas and methodologies for sustainable peatland and forestry management, and promote spin-off of innovations and products activating microbial and plant N₂O sequestration management strategies and technological applications.

Topic groups: 08. Soil Carbon and Nitrogen Cycling, with Focus on Agricultural Soils,

Presentation types: Poster

Title: Budgeting $\delta^{15}\text{N}$ translocation and distribution under biochar-vermicompost amendments in sub-tropical alluvial soil: A field experiment

Lead author: Linee Goswami, Örebro University; Alf Ekblad, Örebro University; Satya Sundar Bhattacharya, Tezpur University

Author: Sarmistha Paul, Tezpur University; Ratul Pegu, Tezpur University; Gurvindra Singh, Tezpur University

Keywords: Soil fertility, Field Study, Inceptisol, Stable isotope, Nutrient cycling

Content:

Soil works as limiting factor for maintaining life on this Earth. Over exploitation and rigorous agricultural practices jeopardize the soil environment. In many parts of World, major concern is declining soil fertility with depleted N content and soil organic matter (SOM), and increased soil acidification. Also, the reduced cation exchange and base saturation capabilities of soils; coupled with the reduction in the water holding capacity and aggregate stability. Biochar, is a stable source of soil organic C vis-à-vis SOM and alkaline in nature. As a result, biochar is considered as an efficient soil amendment. Vermicompost, on the other hand, is nutrient rich manure laden with beneficial microorganism, primarily contributed by the earthworm gut-flora. However, amalgamation of biochar and vermicompost may not always result in enhanced crop yields. Reasons behind such fluctuations are not clear. But one could hypothesize that the possibility of applied N be microbially immobilized in the biochar causing reduced N availability for the crops. Such presumptions cannot be drawn for vermicompost because it is more friable in nature and nutrients, like N, are mostly in bioavailable form. In fact, the poor performance of vermicompost regarding crop yield could be due to slow and untimely release of N in the rhizosphere. In such case, released N can also be lost through leaching. However, the knowledge base in this context is poor. Therefore, we carried out a regional experiment to study the impact of biochar, vermicompost amendments on subtropical alluvial soils, tagged with stable isotopes of N ($\delta^{15}\text{N}$) and investigate their distribution patterns and mechanisms involved. The soil of the experimental area was an inceptisol, class-typic endoaquepts. We followed standard agronomic practices to grow Maize (*Zea mays*). The cultivation pattern was Maize-Fallow-Maize-Fallow-Maize. Biochar was produced using C-3 plant biomass, while vermicompost was prepared using *Eisenia fetida* on substrates composed of textile sludge and cow dung. To study the impact, partitioning of both above and below ground biomass, physicochemical analyses in terms of pH, water retention capacity, microbial biomass, nutrient (NPK) bioavailability, and SOC were recorded. They showed interesting pattern and correlation among the governing factors. In this project, we aim towards studying the impact of biochar on N-partitioning in soil-plant system. In addition, we are interested to learn whether the negative impacts of biochar can be conditioned by using vermicompost and chemical fertilizers and complementary inputs.

Topic groups: 07. Atmospheric Sciences (Pollution, Climate Change, Cosmogeochimistry),

Presentation types: Poster

Title: Diel and seasonal variation in the carbon isotope composition of atmospheric CO₂ in Vienna

Lead author: Kathiravan Meeran, Institute of Soil Research, Universität für Bodenkultur Wien

Author: Bradley Matthews, Institute of Forest Ecology, Universität für Bodenkultur Wien; Simon Leitner, Institute of Soil Research, Universität für Bodenkultur Wien; Hans Sanden, Institute of Forest Ecology, Universität für Bodenkultur Wien; Jia Chen, Technical University of Munich; Andrea Watzinger, Institute of Soil Research, Universität für Bodenkultur Wien

Keywords: Urban CO₂, stable isotopes, Atmospheric CO₂, Anthropogenic emissions

Content:

Cities sustain the majority of the human population and contribute to up to 75 % of global anthropogenic carbon dioxide (CO₂) emissions. Understanding urban CO₂ emissions is therefore essential to designing, implementing and monitoring climate change mitigation measures. In Vienna, and in many other cities, local emissions are mostly assessed based on greenhouse gas inventory estimates provided by federal and/or municipal institutions. However, these estimates can be highly uncertain and are often available only at coarse temporal and spatial resolutions e.g. annual and aggregate city scales. Measurement methods are therefore emerging that can help verify inventory estimates and provide valuable temporal and spatial information on local CO₂ fluxes. Measurements of atmospheric CO₂ mixing ratios and stable carbon isotopic composition ($\delta^{13}\text{C}$) can provide constraints in differentiating sources of CO₂, including ecosystem respiration and combustion of fossil fuels, such as petroleum and natural gas. Moreover, advancements in infrared isotope spectroscopy facilitates in situ measurements of $\delta^{13}\text{C}$ in atmospheric CO₂ with high frequency and precision. As part of Vienna Urban Carbon Laboratory, we are measuring CO₂ mixing ratios and $\delta^{13}\text{C}$ using an online laser spectrometer (Picarro G2201i) placed on a tall tower at 144 m to represent a large city area. We aim to 1) identify the local emitting sources 2) assess the diel dynamics of $\delta^{13}\text{C}$ of atmospheric CO₂ and 3) identify the relative contribution of sources over time. Our contribution to the session 'Atmospheric Sciences' will present results from the initial measurement campaign happening from spring to summer of 2022. During this campaign, we expect decrease in CO₂ concentration and an increase in $\delta^{13}\text{C}$ given that seasonal decline in space heating emissions, the fluxes will likely be dominated by fossil fuel combustions next to vegetation C fluxes. In addition to results on CO₂ emission and contributing sources, our presentation will discuss the uncertainties in laser isotopic measurements as well as associated calibration procedures applying isotope ratio mass spectrometry.

Topic groups: 03. Plant Ecophysiology,

Presentation types: Poster

Title: Using carbon and oxygen isotopes in herbarium specimen to infer long-term physiological response of plants to global environmental change

Lead author: Ansgar Kahmen, University of Basel

Author: David Basler, University of Basel, Switzerland; Daniel Nelson, University of Basel; Jurriaan de Vos, University of Basel; Cristina Moreno Guterrez, University of Basel

Keywords: global change, stomatal conductance, herbarium, net photosynthesis

Content:

The isotope analysis of archived plant material offers the exciting opportunity to reconstruct the physiological responses of plants to environmental change. In this regard, the carbon isotope composition of plants is a good proxy of leaf-level intrinsic water use efficiency (which is the ratio of net photosynthesis over stomatal conductance), and the oxygen isotope composition can provide time-integrated information on leaf stomatal conductance. In combination, the stable isotope analysis of carbon and oxygen thus allows to explicitly determine integrated values for net photosynthesis and stomatal conductance. The analysis and interpretation of the carbon isotope composition of plant materials is well established and is today widely applied to infer the effects of global environmental change on the intrinsic water use efficiency of plants. In contrast, the use of oxygen isotope analysis of plant materials is more complex and has been used by only very few studies. Largely this is, because not only stomatal conductance but also atmospheric humidity, the environmental sensitivity of plant-internal fractionation factors as well as the oxygen isotope composition of the plants' source water determine the oxygen isotope composition of plant material. This makes it often difficult to disentangle physiological from biochemical and environmental signals recorded in the oxygen isotope composition of plant materials. In my presentation, I will show how carbon and oxygen isotope data of 3000 herbarium specimen, that have been collected across Switzerland over the past century, can be used to infer long-term physiological responses of plants to global environmental change for more than 70 different plant species that grew in a large range of different habitats. For our study we overcame the multi-signal problem of oxygen isotope signal by applying a multi-model approach allowing to disentangle environmental and biochemical from physiological effects on the oxygen isotope signals in plants. The analysis shows that plants from all taxa and irrespective of their growing conditions improved their water use efficiency over the past century. However, the contribution of net photosynthesis or stomatal conductance to changes in intrinsic water use efficiency dramatically different among different plant functional groups (i.e. herbs, legumes, grasses and sedges). Our study demonstrates that the carbon and water relations of plants respond to long-term changes in the environment but that the physiological nature of these responses differ among plant functional groups.

Topic groups: 10. Geochemistry and Hydrology,

Presentation types: Poster

Title: Using stable isotopes of dissolved sulphates and nitrates to determine contamination sources in two characteristics water systems of southern Spain

Lead author: José Manuel Muñoz-Redondo, Andalusian Institute of Agricultural and Fisheries Research and Training (IFAPA)

Author: Iñaki Vadillo-Pérez, Group of Hydrogeology, Department of Geology, University of Malaga; Pablo Jiménez-Gavilán, Group of Hydrogeology, Department of Geology, University of Malaga; Dídac Navarro-Ciurana, Departament de Mineralogia, Petrologia i Geologia Aplicada, Universitat de Barcelona; Albert Soler, Departament de Mineralogia, Petrologia i Geologia Aplicada, Universitat de Barcelona; Clara Torrentó, Geologia Aplicada, Universitat de Barcelona; Mónica Sánchez-Parra, Andalusian Institute of Agricultural and Fisheries Research and Training (IFAPA); Jose Manuel Moreno-Rojas, Andalusian Institute of Agricultural and Fisheries Research and Training (IFAPA)

Keywords: Diffuse-source pollution, European water Directive, Natural background levels

Content:

Diffuse-source pollution of surface and groundwater is a widespread problem of European countries, being considered a central problem in the environmental and agricultural policies of the European Union. Thus, the Directive 91/676/EEC focuses on the protection of waters against pollution caused by nitrates from agricultural sources, and the Directives 2000/60/EC and, mainly 2006/118/EC, establish a framework for Community action in water policy, ensuring the protection of water bodies. More recently, European strategies such as "from farm to fork" were proposed in this regard, being included in the European Green Deal, which contributes to challenge this problem. The levels of nitrate in water bodies may have a natural origin (dissolution of minerals or bacterial oxidation of organic matter) or a human origin. Therefore, to correctly determine their nitrate pollution status, the natural background levels (NBLs) have to be determined. Different techniques have been used for this purpose, including the methodology defined in the BRIDGE project from the European Commission or statistical methods. However, these methods are subjective or have levels of uncertainty, respectively. More recently, stable isotopes ratios of NO_3^- and SO_4^{2-} have been successfully used to trace the main origin of pollution in different contexts, solving the main disadvantages of the previous methods. We collected 20 water samples from two characteristics systems located in southern Spain: the largest intensive horticultural crop zone in Europe (Almeria), and the higher Andalusian olive cultivation sited in the river of Guadalquivir (Cordoba), during the 2021 campaign. A high correlation between NO_3^- and SO_4^{2-} was observed, indicating an agricultural origin of both compounds in the samples with medium and high concentrations. The stable isotopes of nitrates ($\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$) and sulfates ($\delta^{34}\text{S-SO}_4$ and $\delta^{18}\text{O-SO}_4$) were determined. The wide variation range values of $\delta^{15}\text{N-NO}_3$ (from +0.5 to +85.4 ‰) revealed anthropogenic sources signals due to the use of fertilizers in several sampling points. These values were highly correlated with the $\delta^{18}\text{O-NO}_3$ ones (from +2.1 to +54.2 ‰). The isotopic data of sulfates allowed to identify natural sources from evaporitic rocks ($\delta^{34}\text{S} > 12$ ‰), and anthropic sources by fertilization with sulfates ($\delta^{34}\text{S} < 12$ ‰). Since other sulfate sources could be ruled out, a binary mixing system was established to estimate the percentages of anthropogenic sulfate contribution to groundwater. Finally, the NBLs of natural sulfate were established. The results of this study demonstrated the potential of stable isotopes to determine contamination sources in water bodies.

Topic groups: 02. Terrestrial and Aquatic Biogeochemistry,

Presentation types: Poster

Title: How does wildfire and post-fire management affect the nitrogen soil cycle in a Swedish boreal forest?

Lead author: LOUISE ANDRESEN, GÖTEBORGS UNIVERSITET

Author: Theresa S. Ibáñez, Dep. Wildlife, Fish Env. studies, Swedish University of Agricultural Sciences; Stefan Doerr, Department of Geography, Swansea University, United Kingdom; Cristina Santin, Research Institute of Biodiversity, Spanish National Research Council, Spain; Julia Kelly, Centre for Environmental and Climate Science (CEC), Lund University; Johannes Rousk, Department of Biology, Lund University; Margarida Soares, Centre for Environmental and Climate Science (CEC), Lund University; Johan Ekroos, Department of Agricultural Sciences, University of Helsinki; Florian Stange, Federal Institute for Geosciences and Natural Resources, Germany; Natascha Kljun, Centre for Environmental and Climate Science (CEC), Lund University

Keywords: ¹⁵N pool dilution, gross mineralization- nitrification- and immobilization rates

Content:

In year 2018, Sweden faced one of the most extreme wildfire seasons in modern history, highly impacting parts of the boreal forest ecosystem. It is uncertain how the nitrogen (N) cycle is affected by wildfire and post-fire management in these forests. The knowledge gap is important to address because a warmer climate may result in more frequent and intense wildfires, and there is a need to identify sustainable post-fire management strategies. We address this by investigating Sweden's largest wildfire of 2018, to capture the effects of (i) fire severity (i.e., high, low and unburnt), (ii) forest management (i.e., salvage logging vs. non-salvage logging), and (iii) stand age (i.e., 10 vs. ~100 years old) on: gross N mineralization, consumption and nitrification rates, three years after the wildfire. We hypothesized that high fire severity would impact the N soil cycle due to the consumption of a substantial fraction of the soil organic layer and high tree mortality. In the Summer of 2021, we measured gross N mineralization and nitrification rate using the ¹⁵N-pool dilution technique by injecting ¹⁵N labels in the soil in situ. In addition, the plant N demand to meet the tree biomass growth was estimated and we traced the plant uptake of ammonium and nitrate by ¹⁵N labelling the soil around individual tree seedlings. Three years after the fire, the soil and ground vegetation had not fully recovered, but the microbial life had recolonized in the high fire severity soils, exhibiting more saprotrophic fungal biomass than the non-burnt control. The gross nitrification rate was lower in the high fire severity soils compared to unburnt, but the gross N mineralization rate did not differ now. The impact of salvage logging after a severe fire resulted in higher gross nitrification and nitrate consumption rates, compared to leaving the trees standing after the fire. Furthermore, rates of microbial growth and respiration were still inhibited three years after the high severity fire without salvage logging operation; we found relatively low rates of bacterial growth and large declines in soil respiration. Overall, the total soil N pools were much smaller in the burnt compared to the unburnt stand. In conclusion, our study shows that both high fire severity and salvage logging affect the soil nutrient cycling and microbial community, and this could further have a detrimental impact in the long term for boreal forest regeneration.

Topic groups: 01. Methodological Advances,

Presentation types: Poster

Title: Improved metrologically compatible calibration approaches for CO₂ stable isotope ratio measurements using optical isotope ratio spectroscopy (OIRS)

Lead author: Anas Emad, PTB

Author: Javis Nwaboh, PTB; Christina Biasi, UEF; Michela Segal, INRIM; Francesca Durbiano, INRIM; Matej Znamenko; Farilde Steur, University of Groningen; Stefano Pavarelli, INRIM; Volker Ebert, PTB

Keywords: OIRS, CO₂, spectroscopy, calibration, GUM

Content:

Continuous measurements of CO₂ stable isotopes provide key insights into the source attribution of atmospheric emissions of CO₂. The isotopic signature allows to distinguish and monitor the dynamics and controls of anthropogenic and natural emissions. For atmospheric CO₂ isotope ratio measurements, optical isotope ratio spectroscopy (OIRS) instruments have been demonstrated to be able to provide continuous isotope ratio measurements for CO₂ ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$) in the field, with faster response times and precisions near to those of well-established isotope ratio mass spectrometry (IRMS) instruments. For accurate CO₂ isotope ratio measurements, accurate calibration approaches need to be implemented to provide a link between amount fractions of isotopologues (analysed by OIRS) and the international isotope ratio scales (VPDB, VSMOW/SLAP). In addition, GUM (Guide to the expression of uncertainty in measurement) compliant uncertainty calculations have to be compiled in an uncertainty budget and the compatibility of OIRS techniques assessed towards WMO-GAW compatibility goals (extended compatibility goals - 0.02 ‰ for $\delta^{13}\text{C}$ -CO₂, 0.05 ‰ for $\delta^{18}\text{O}$ -CO₂). Here, we report on the development and validation of improved metrologically compatible calibration approaches for CO₂ isotope ratio measurements, touch on correction approaches to account for spectral interferences of other trace gases, and present a rigorous GUM compliant uncertainty estimation procedure. The results reported are within the scope of the European metrology research project 19ENV05 STELLAR (Stable isotope metrology to enable climate action and regulation) and are supported by the pilot study CCQM-P204.

Topic groups: 02. Terrestrial and Aquatic Biogeochemistry,

Presentation types: Poster

Title: Transport and turnover of reactive nitrogen in the Lena River Delta

Lead author: Tina Sanders, Helmholtz-Zentrum Hereon, Institute for Carbon Cycles, Geesthacht, Germany

Author: Claudia Fiencke, Universität Hamburg, Institute of Soil Science, Hamburg, Germany; Bennet Juhls, Alfred Wegener Institute, Helmholtz Centre for Polar and Marine Research; Olga Ogneva, Alfred Wegener Institute, Helmholtz Centre for Polar and Marine Research; Jens Strauss, Alfred Wegener Institute, Helmholtz Centre for Polar and Marine Research; Tuerena Robyn E., Scottish Association for Marine Science, Dunstaffnage, Oban PA37 1QA, UK; Kirstin Dähnke, Helmholtz-Zentrum Hereon, Institute for Carbon Cycles, Geesthacht, Germany

Keywords: Lena River, nitrogen isotopes, Arctic Ocean

Content:

Permafrost-affected soils around the Arctic Ocean contain a large reservoir of organic matter and nitrogen, which can reach the river after thawing, degradation and erosion of permafrost. After mobilization, reactive remineralised nitrogen is either used for primary production, microbial processing or is transported to coastal waters. Analyzing the natural abundance stable isotopes of different form of nitrogen components, we aim to unravel the balance of transport and biological nitrogen turnover processes and in consequence the fate of transported nitrogen. We analyzed soil, suspended matter and dissolved inorganic and organic nitrogen for their contents and nitrogen stable isotope composition to create a baseline for a nitrogen inventory of the Lena River Delta in 2019/2020. We used samples from two transect cruises in March and August 2019, a monitoring program at Samoylov Island in the central delta (2019/2020), and different soil type samples from Samoylov and Kurunghak Island. Our aim was to determine nitrogen sources, sinks and transformation processes during transport in river and delta. Our data show that in winter the nitrogen transported from the delta to the Laptev Sea were dominated by dissolved organic nitrogen and nitrate, which occur in similar amounts of approx. 10 $\mu\text{mol/L}$. The load of nitrate during the transect cruise, increased slightly in the delta, while we observed no changes to the isotope values of DON and nitrate indicating a lack of biological activity in the winter season and the lateral transport from soils was the likely source. In summer, nitrogen was mainly transported as DON and as particulate nitrogen, and nitrate was mainly below 1 $\mu\text{mol/L}$. The nitrogen stable isotope values of the different nitrogen components were 0.5 to 4.5‰, and were subsequently enriched from the soils via suspended particulate matter (SPM)/sediment and DON to nitrate. These light values indicate soil nitrogen mainly originates from atmospheric nitrogen fixation. During transport and remineralization, biogeochemical recycling via nitrification and assimilation by phytoplankton led to an isotopic enrichment in summer. In the coastal waters of the Laptev Sea, the river water is mixed with marine nitrate-containing waters from the Arctic Ocean, and a part of the riverine organic nitrogen is buried in the sediments. Our data provide a baseline for isoscape analyses and can be used as an endmember for modeling approaches

Topic groups: 07. Atmospheric Sciences (Pollution, Climate Change, Cosmogeochimistry),

Presentation types: Poster

Title: Boreas: A new instrument for in-situ measurements of $\delta^{13}\text{C}(\text{CH}_4)$ and $\delta^2\text{H}(\text{CH}_4)$

Lead author: Tim Arnold, National Physical Laboratory and Edinburgh University

Author: Emmal Safi, National Physical Laboratory; Chris Rennick, National Physical Laboratory; Alice Drinkwater, National Physical Laboratory and Edinburgh University

Keywords: methane, isotope ratios, laser spectroscopy, preconcentrator, isotopic signatures

Content:

Methane (CH_4) is the second most abundant anthropogenic greenhouse gas (GHG) in the atmosphere after carbon dioxide (CO_2) and has a high global warming potential. Due to this, current emissions rates must be reduced to meet reduction targets. Individual countries and governments are stepping up their efforts to reduce regional CH_4 emissions. To estimate these CH_4 emissions, for verification of inventories, isotope ratio measurements are becoming a useful tool. To allow for a sectoral breakdown of emissions estimates, measurements at high enough frequencies are required. Laser spectrometers can make high-frequency measurements of $\delta^{13}\text{C}(\text{CH}_4)$ and $\delta^2\text{H}(\text{CH}_4)$ with low enough maintenance requirements that would provide data needed for regional scale inversion modelling. However, commercial instruments are unable to make measurements at high enough precision due to the low abundance of CH_4 in ambient air ($<2 \mu\text{mol mol}^{-1}$), hence resulting in poor signal-to-noise ratios. One method to improve the signal-to-noise ratio is to concentrate CH_4 out of ambient air, however this comes with its own set of challenges in terms of the large volumes of air needed and the purity of the CH_4 extracted needs to be high for analysis. To this end, we have developed "Boreas" a field deployable preconcentrator capable of coupling to a laser spectrometer. Boreas is able to make high precision, hourly measurements of $\delta^{13}\text{C}(\text{CH}_4)$ and $\delta^2\text{H}(\text{CH}_4)$ isotope ratios in ambient air. It was developed at the National Physical Laboratory (NPL) and deployed to our tall-tower atmospheric monitoring site located South of London in May 2021. We will present data obtained from measurements since deployment and show isotopic signatures consistent with pollution events from around the region.

Topic groups: 01. Methodological Advances, SCIENTIFIC PROGRAMME, poster next to each other (60, 119 and 165),

Presentation types: Poster

Title: Discontinuity in the realization of the VPDB carbon isotope ratio scale

Lead author: Jean-Francois Helie, Geotop-UQAM

Author: Agnieszka Adamowicz-Walczak, Geotop-UQAM; Paul Middlestead, University of Ottawa; Michelle M.G. Chartrand, National Research Council Canada; Zoltan Mester, National Research Council Canada; Juris Meija, National Research Council Canada

Keywords: Carbon, stable isotopes, scale, VPDB

Content:

By convention, carbon isotope ratios are expressed relative to VPDB defined by the calcite standard NBS19 in the 1980s. To improve the realization of the VPDB scale, a second fixed point (lithium carbonate, LSVEC) was introduced in 2006 which is now known to be isotopically unstable. With high-quality reference materials made available in 2020, it is now possible to realize the VPDB scale with high confidence. Here we report the analysis of 25 reference materials using isotope ratio combustion mass spectrometry, show the discontinuity between the values measured against the new IAEA reference materials and the values currently assigned to these reference materials on the VPDB2006, and provide a link bringing these materials onto the new VPDB2020.

Topic groups: 08. Soil Carbon and Nitrogen Cycling, with Focus on Agricultural Soils,

Presentation types: Poster

Title: Impact of EDTA soil washing on microbial life and ecosystem functions - a stable isotope labelling approach

Lead author: Corinna Eichinger, Institute of Soil Research, Department of Forest- and Soil Sciences, University

Author: Christoph Noller; Wolfgang Friesl-Han; Rebecca Hood-Nowotny ; Andrea Watzinger

Keywords: EDTA soil washing, soil nutrient cycling

Content:

Soils contaminated with potential toxic metals (PTMs) are a threat to human health, since PTMs are non-degradable and can accumulate along the food webs and in crops meant for human consumption. Soil washing and removal of PTMs with ethylenediamine tetraacetate (EDTA) is viewed as a soil preserving remediation option. However, EDTA is a non-selective chelator and has an impact on soil microbial life and ecosystem functions which could limit the use of this technology. Hence amelioration by compost and biochar amendment is proposed after remediation. Using ^{13}C and ^{15}N labelled plant residues of *Spinacia oleracea* as a tracer this case study aimed to better understand the impact of EDTA and amendments on the mineralisation of organic matter and nutrient cycling. We assessed nitrogen mineralisation and transformation by targeting available inorganic ^{15}N via microdiffusion extraction and ^{15}N analysis of plant tissues (*Raphanus sativus* var. *Sativus*). Carbon mineralisation was monitored through ^{13}C - CO_2 emissions and ^{13}C -phospholipid fatty-acid (PLFAs) analysis of the soil microbial communities. The experiment was conducted over a timeline of 164 days and samples were taken in scheduled intervals. In respect to the nutrient cycling, our results showed that N mineralization of plant residues was seemingly stalled due to soil remediation leading to decreased concentrations of NH_4 of the washed treatments by approx. 60%. Nevertheless, after mineralisation, nitrification was instantly and quantitatively converting NH_4 into NO_3 leading to a higher nitrogen availability for plant uptake and increased N levels in leave tissues by 18% and 29% in the washed and amended soil respectively. The mineralisation rate of labelled plant C after double exponential additive curve-fitting was significantly higher in EDTA washed soil in comparison to the control soil. Amendments did not increase mineralisation rates. A PERMANOVA analysis revealed significant changes in the soil microbial community structure after remediation. Actinobacteria turned out to be the most impacted group, their amount declined by almost 50% and was not able to recover with the addition of amendments over the timeline. ^{13}C incorporation was significantly higher after soil washing and amendments further increased uptake by 5-10%. There was no significant difference in the temporal pattern of ^{13}C incorporation with peak levels after 4 weeks. To summarize, EDTA washing changed the microbial community structure and increased C and N cycling, amendments did have an additional positive impact on plant residue mineralisation.

Topic groups: 02. Terrestrial and Aquatic Biogeochemistry,

Presentation types: Poster

Title: Primary production determined by ^{13}C -labelling is a viable alternative to radiocarbon

Lead author: Alexander H. Frank, Leibniz Institute for Freshwater Ecology and Inland Fisheries; University of Bayreuth

Author: Tobias Goldhammer, Leibniz Institute for Freshwater Ecology and Inland Fisheries; Christine Kiel, Leibniz Institute for Freshwater Ecology and Inland Fisheries; Stella A. Berger, Leibniz Institute for Freshwater Ecology and Inland Fisheries; Robert van Geldern, Friedrich-Alexander-Universität Erlangen-Nürnberg; Johannes A.C. Barth, Friedrich-Alexander-Universität Erlangen-Nürnberg; Mark O. Gessner, Leibniz Institute for Freshwater Ecology and Inland Fisheries; Berlin Institute of Technology

Keywords: Pelagic primary production, aquatic ecosystems, non-radioactive ^{13}C

Content:

Pelagic primary production is one of the most central processes in aquatic ecosystems. For more than 6 decades now, the method of choice to monitor aquatic productivity has been paired dark and light bottle incubations with ^{14}C -labelled bicarbonate. However, with growing environmental awareness, increasingly restrictive regulations, and associated high costs, these monitoring programs have become increasingly challenging and prohibitively expensive. Here we take advantage of advances in stable-isotope technology to evaluate whether incubations with non-radioactive ^{13}C can replace the ^{14}C method to ensure the continuation of monitoring efforts without disrupting long-term time series. While the natural ^{14}C abundance is in the range of 1 part per trillion (ppt, 10-12), the natural ^{13}C abundance is approximately 1%. Therefore, ^{13}C label concentrations must be considerably higher than those of ^{14}C labels. Moreover, as ^{13}C of particular organic carbon (POC) is measured by mass spectrometry, incubations must be stopped and samples need to be preserved without introducing additional carbon. A series of methodological experiments and comparisons with standard ^{14}C incubations over one year showed that the novel approach of ^{13}C incubation serves as an excellent alternative to measuring primary production in lakes. The approach is cost-efficient and environmentally friendly. Production rates determined along complete depth profiles over a full annual cycle show that ^{13}C - and ^{14}C -methods are interchangeable so that the comparison of results does not even require the establishment of empirical conversion factors.

Topic groups: 10. Geochemistry and Hydrology,

Presentation types: Poster

Title: Combined isotopic (C-Cl) and molecular approach for the assessment of EVO biostimulation treatment of an aquifer polluted with chlorinated ethenes

Lead author: Sergio Gil-Villalba, Grup MAiMA, Facultat de Ciències de la Terra, Universitat de Barcelona (UB)

Author: Mònica Rosell, Grup MAiMA, Facultat de Ciències de la Terra, Universitat de Barcelona (UB); Jesica M. Soder-Walz, Dept. of Chemical, Biological and Env. Eng., Universitat Autònoma de Barcelona; Jordi Corregidor, Environmental Resources Management; Miguel A. Vallecillo, Environmental Resources Management; Andrea Tirado, Environmental Resources Management; Orfan Shouakar-Stash, Department of Earth and Environmental Sciences, University of Waterloo; Marc Viñas, IRTA, GIRO Joint Research Unit IRTA-UPC; Jordi Palau, Grup MAiMA, Facultat de Ciències de la Terra, Universitat de Barcelona (UB)

Keywords: Groundwater; Remediation; Bioremediation; Carbon; Chlorine; Stable isotopes; Microcosms; Chloroethenes;

Content:

Bioremediation is a sustainable technology that has recently emerged as a cost-effective alternative to cleaning up aquifers polluted by chlorinated solvents compared to conventional physicochemical techniques. This biological approach uses the metabolism of bacteria to transform the contaminants and detoxify groundwater. In the last years, research has focused on understanding the physiology and biochemistry of such degrading mechanisms, however, its successful implementation in the field is still limited. This research aims to assess and expand the knowledge of in-situ anaerobic biodegradation processes of chlorinated solvents. A biostimulation remediation treatment, using a commercial emulsified vegetable oil (EVO-EOSpro®), B12 vitamin, and lactate was applied to a sedimentary unconfined aquifer polluted with chloroethenes. A combined approach was used to identify the effectiveness of the treatment and the processes that occur in the field by dual C-Cl isotope analysis, hydrochemical data, and molecular analysis (Dehalococcoides 16S rRNA and functional genes) of the bacterial community. First, microcosm experiments were carried out using the aquifer bacterial community. Sampled groundwater was initially purged to remove the original volatile compounds. Three parallel experiments were prepared in an anoxic chamber where PCE, TCE, and cisDCE were spiked separately and lactate was added to reproduce the biostimulation processes as they will occur at the site, characterize the corresponding C-Cl isotopic fractionation pattern, and assess bacterial growth. Secondly, abiotic experiments were carried out to evaluate a possible isotopic fractionation during the oil-water phase distribution of the chloroethenes. A water solution with PCE, TCE, and cisDCE of known concentration and carbon isotopic composition was in contact, through a dialysis membrane, with EVO and sampled at 12 and 48 hours to assess possible changes. Finally, the biostimulation treatment was applied at the contaminated site and monitored in eleven piezometers by one pre-injection sampling and five post-injection samplings. Concentration and C-Cl isotopic composition were measured for the parental PCE and the degradation products TCE, cisDCE, and VC. Preliminary results show a rapid decrease in PCE and TCE concentrations in the field. Isotopic data confirms that degradation to ethene is taking place after some months, as $\delta^{13}\text{C}$ enrichments over +30‰ were calculated from the isotopic balance, corresponding to a degradation efficiency over 95% in some piezometers. Dual C-Cl isotope slope (Λ) and molecular results will allow comparing in situ degradation process with the laboratory experiments and previously reported values, to understand the processes occurring in the field application.

Topic groups: 08. Soil Carbon and Nitrogen Cycling, with Focus on Agricultural Soils,

Presentation types: Poster

Title: Trans-European decomposition index study in arable soils with different crop species diversity using ¹³C-labelled litter

Lead author: Ansa Palojarvi, Natural Resources Institute Finland (LUKE)

Author: Jim Rasmussen, Aarhus University, Department of Agroecology ; Monika Toleikiene, Lithuanian Research Centre for Agriculture and Forestry; Jose Antonio Navarro, INIA-CSIC; Frederique Louault, INRAE; Josef Haki, Czech University of Life Sciences; Ievina Sturite, NIBIO; Abad Chabbi, INRAE; José A. González-Pérez, IRNAS-CSIC; Abdulkadir Bal, TAGEM; Katharina H. E. Meurer, SLU; Pirjo Yli-Hemminki, LUKE; Isabelle Bertrand, INRAE; Anna Wawra, AGES; Rebecca Hood-Nowotny, BOKU

Keywords: Mixed cropping, Diversity, ¹³C labelled, Maize litter, Monoculture, Carbon

Content:

Mixed species systems are currently increasing in area in Europe providing opportunities for sustainable intensification of agriculture. The agroforestry systems cover about 9% of the utilized agricultural area and integrated crop livestock systems occupy a major part in the European agricultural area including perennial forage grasses and grasslands sown with varying degrees of duration. Intercropping and other mixed cash crop systems are currently less developed in the EU. The aim of the EU EJP-SOIL funded MIXROOT-C project (2021-2024) is to gain a management-oriented understanding of the effect of mixed-species root systems on carbon flow and organic matter accumulation in European agricultural soils. As part of the project, we will conduct a pan-European in-situ experiment across pedo-climatic conditions, field experiments and treatments ((i) monoculture (1 species), (ii) low diversity (2-4 different plant species in the mix culture) and (iii) high diversity (≥ 5 different plant species in the mix culture)). The main interest lies in studying the impact of increased plant diversity on the organic matter breakdown in the topsoil (0-15 cm) and the development of a trans-European decomposition index. To do so, we will monitor the decomposition of ¹³C-labelled maize litter in mixed agroecosystems and in the main crop monocultures across Europe. The ¹³C-labelled maize material is mixed with the local soil from the treatment plots, packed in mesh bags, buried in the treatment plots at the top 15 cm depth. After the vegetative period (ca. 6 months), the bags will be excavated for analysis. This experiment, which includes sites in 10 countries on different climates and cropping systems, will provide information on the rate of litter decomposition, C immobilization in microbial biomass and the inclusion of litter C in different soil OM pools depending on the climatic condition, soil type and management. Furthermore, the experiment will provide information on litter turnover and link this process to soil C storage. We will measure the effect of increased crop species diversity on the rate of decomposition of litter, assuming that microbial biomass will be more abundant and decomposition rates faster in diversified agroecosystems. This approach will show to what extent plant species or trait diversity affect residue turnover and to what extent indigenous soil condition affect this turnover. We will produce the trans-European decomposition index in parallel with the EJP-SOIL MAXROOT C-project. Data will be used to model belowground C inputs in single and mixed species systems.

Topic groups: 10. Geochemistry and Hydrology,

Presentation types: Poster

Title: Event-based stable isotope data of precipitation from the high-altitude Sonnblick Observatory (Hohe Tauern, Austria)

Lead author: Julia Wenske, Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU)

Author: Robert van Geldern, Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU); Johannes A.C. Barth, Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU); Giorgio Höfer-Öllinger, GEOCONSULT ZT GmbH, Wals/Salzburg; Elke Ludewig, Sonnblick Observatorium, Zentralanstalt für Meteorologie und Geodynamik (ZAMG)

Keywords: precipitation, deuterium excess, backward trajectory, Sonnblick Observatory

Content:

Event-based precipitation samples were collected at the Sonnblick Observatory (SBO) in Austria in July/August 2021 providing precise insights into temporal highly resolved precipitation events. In contrast to common monthly samples, as for instance in the GNIP, this study focuses on single rainfall events instead of four-week integrated samples. The isotopic composition of oxygen and hydrogen ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) as well as the calculation of the deuterium excess (d) aims to achieve a clearer understanding of the origin of air masses and moisture, respectively. Due to the exceptional location of the research station in the Alps with an elevation of 3106 m a.s.l. and the available meteorological infrastructure, investigations of interactions between atmospheric parameters and isotopic fractionation is particularly feasible. Overall, the isotopic ratios show a high variability and cover a wider range compared to daily or monthly taken samples. As a consequence of appearing rain, fog, hail and snow, the values of $\delta^{18}\text{O}$ vary between -3.3 and -21.7 ‰ and those of $\delta^2\text{H}$ between -18 to -181 ‰. A temperature dependence has been observed but also other meteorological parameters like wind speed might have impact and play a potential role during isotopic fractionation in the atmosphere. The application of the backward trajectory model HYSPLIT was used for tracing the air masses in order to ascertain possible moisture sources. Within the first week of observation, higher values of the deuterium excess confirm an origin in the Southern Mediterranean while lower d-values refer to a significant influence of Atlantic air masses in the second week.

Topic groups: 06. Food Authenticity, Nutrition, Forensic,

Presentation types: Poster

Title: Combining optical spectroscopy and IRMS for the measurement of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of water and ethanol directly in wine

Lead author: Harro A.J. Meijer, Centre for Isotope Research (CIO), University of Groningen

Author: Xing Wang, Centre for Isotope Research (CIO), University of Groningen; Henk G. Jansen, Centre for Isotope Research (CIO), University of Groningen

Keywords: Wine, stable isotopes, ^2H , ^{18}O , Optical Spectroscopy, ^2H -NMR, IRMS

Content:

Officially certified methods for stable isotope analysis for wine authentication are limited to $\delta^{18}\text{O}$ measurements of the wine water, and to (site-specific) $\delta^2\text{H}$ of the wine ethanol using NMR. Nowadays, optical spectroscopy has become an easier alternative to quantify both $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of wine water straight in the wine. We utilized an optical analyser (OA-ICOS, LGR) with Spectral Contaminant Identifier to measure the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of water in 27 wine samples without any pre-treatment. These results reveal a wealth of information about the authenticity and growth conditions of the wines, and we recommend to extend the official $\delta^{18}\text{O}$ wine water method by $\delta^2\text{H}$. We also performed high-temperature pyrolysis and chromium reduction combined with IRMS measurements to obtain the "whole wine" isotope ratios. The $\delta^{18}\text{O}$ results of OA-ICOS and IRMS show non-significant differences, but the $\delta^2\text{H}$ results of both methods differ much more. This is expected, and the $\delta^2\text{H}$ difference between these two methods is mainly caused by the ethanol. Therefore, we investigated the possibility to deduce the $\delta^2\text{H}$ of wine ethanol from this difference. However, the results contain large uncertainties, and also deviate from the ^2H -NMR results following the official method. The, rather constant, deviation is caused by the other constituents in the wine, that can be corrected for, but the uncertainty is due to the limited precision of the SCI-based correction. We recommend to improve the spectral fit of the optical method, and thereby the SCI, so one can obtain the $\delta^2\text{H}$ values of ethanol as alternative for the ^2H -NMR method. Whereas the site specificity of NMR can of course not be obtained this way, the average $\delta^2\text{H}$ value can serve as an indicator for possible fraudulent processes. As a side result, the SCI produces a quite accurate number for the ethanol concentration of the wine.

Topic groups: 09. Isoscape, Spatial Variability of Stable Isotopes (Migration, Food Webs),

Presentation types: Poster

Title: The effect of increased DOC concentration on food sources and life history of *Daphnia* – insights from compound-specific stable isotopes

Lead author: Minna Hiltunen, University of Jyväskylä

Author: Alidu Abdul-Hafiz, University of Jyväskylä; Marco Calderini, University of Jyväskylä; Jussi Vesamäki, University of Jyväskylä; Sami Taipale, University of Jyväskylä

Keywords: zooplankton, fatty acids, browning,

Content:

Many lakes in the northern hemisphere are experiencing browning due to increased loading of dissolved organic carbon (DOC) from the catchment. The coloured DOC alters the light climate experienced by phytoplankton and can provide an additional food source for zooplankton via the microbial loop. Compound-specific stable isotope analysis has been used to elucidate food web interactions and consumer food sources, and could provide insights in zooplankton resource use with increasing DOC. We performed a laboratory experiment to study the effects of increasing concentrations of DOC on zooplankton survival, reproduction, and fatty acid composition. We also analyzed stable isotopes of carbon ($\delta^{13}\text{C}$) in fatty acids to estimate resource use of the zooplankton. The model zooplankton species *Daphnia magna* was grown in DOC concentrations of 0, 10, 30, and 90 mg/L and fed high nutritional quality phytoplankton (*Cryptomonas* sp.). The phytoplankton were grown in corresponding DOC concentrations, and the media was labelled with ^{13}C bicarbonate ($\text{NaH}^{13}\text{CO}_3$) to facilitate the separation of the food sources (DOC and phytoplankton) in subsequent stable isotope analysis. The experiment lasted for 14 days. The preliminary results indicate that DOC had a positive effect on *D. magna* reproduction, suggesting that *D. magna* can utilize this additional resource. This was supported by increasing amounts of bacterial fatty acids (odd-number and iso- and anteiso branched fatty acids) in *D. magna*, which shows that they were feeding more on bacteria in high DOC treatments. Stable isotopes of carbon will be analyzed from the fatty acids to estimate changes in the contribution of the different food sources for *D. magna* with increasing DOC concentration.

Topic groups: 01. Methodological Advances,

Presentation types: Poster

Title: Qtegra ISDS Software – Driving Isotope Analysis

Lead author: Nina Albrecht, Thermo Fisher Scientific

Author: Mario Tuthorn, Thermo Fisher Scientific; Qiong Li, Thermo Fisher Scientific

Keywords: Software; Isotopes; Clumped; Carbonate

Content:

Driven by recent technical advancements, stable gas isotope applications in Earth science are continuously evolving. We developed Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software for our gas IRMS instruments with all the flexibility to accommodate the most demanding stable isotope applications, aiming to turn analytical challenges into routine and to bring easy-to-obtain high quality data into the reach of every lab. Qtegra ISDS Software has an intelligent workflow that drives you from sample to result, presented in a layered approach that simplifies visualization of statistics across multiple samples. Here we demonstrate software features of the new Qtegra ISDS Software for gas IRMS, using the examples of classical clumped carbonate analyses with Thermo Scientific™ 253 Plus™ 10 kV IRMS and advanced clumped methane isotope analyses with Thermo Scientific™ Ultra™ HR-IRMS. We highlight how Qtegra ISDS Software eases the handling of instrument control, data acquisition, and data evaluation, and increases efficiency and data quality.

Topic groups: 03. Plant Ecophysiology,

Presentation types: Poster

Title: Ecological implications of leaf water deuterium enrichment

Lead author: Charlotte Angove, Natural Resources Institute Finland

Author: Marco Lehmann; Matthias Saurer, Forest Dynamics, WSL Birmensdorf, Switzerland; Kersti Leppä, Natural Resources Institute Finland; Yu Tang; Ansgar Kahmen, University of Basel, Switzerland; Katja Rinne-Garmston, Luke

Keywords: Deuterium, eddy covariance, evapotranspiration, leaf water, water isotopes

Content:

Leaf water isotopic enrichment is the original source of climatic information stored in tree-ring $\delta^{18}\text{O}$ and δD . Tree-ring $\delta^{18}\text{O}$ temporal variability has been correlated to environmental variables such as temperature, precipitation, relative humidity, and phenomena such as tropical cyclones and drought. Meanwhile, more development is needed to use tree-ring δD temporal variability as a paleoclimatic bioindicator. An increased understanding of the climatic signal of leaf water D enrichment ($\Delta\text{D}[\text{LW}]$) could help to better interpret the temporal variability of tree-ring δD . Compared to $\Delta\text{D}[\text{LW}]$, leaf-water ^{18}O enrichment ($\Delta^{18}\text{O}[\text{LW}]$) exhibits stronger relationships to environmental variables such as relative humidity, and stronger relationships to physiological rates such as transpiration rate. Whereas $\Delta\text{D}[\text{LW}]$ has been correlated to the disequilibrium between atmospheric water vapor δD ($\delta\text{D}[\text{WV}]$) and plant stem water δD . Such a disequilibrium can be caused by variation in plant stem water δD and/or variation in $\delta\text{D}[\text{WV}]$. Since $\delta\text{D}[\text{WV}]$ varies more frequently than plant stem water δD in forests, $\delta\text{D}[\text{WV}]$ might be more responsible for short-term changes in the water vapor-stem water δD disequilibrium that is reflected by leaf water deuterium enrichment. If this is true, then $\Delta\text{D}[\text{LW}]$ may be correlated to diurnal drivers of $\delta\text{D}[\text{WV}]$ such as ecosystem-level evapotranspiration. Resultantly, there may be previously unidentified relationships between $\Delta\text{D}[\text{LW}]$ and ecosystem-level processes. In this study, we aimed to explore the potential of $\Delta\text{D}[\text{LW}]$ as a bioindicator of ecosystem-scale processes such as evapotranspiration and gross primary productivity. We used a temporal survey of water vapor and *P. sylvestris* leaf water isotopic variability, and eddy covariance data, during 2019 at Hyytiälä, central Finland. This poster shows our findings after comparing $\Delta\text{D}[\text{LW}]$ and $\Delta^{18}\text{O}[\text{LW}]$ to climatic variables and ecosystem processes to gain new insights about $\Delta\text{D}[\text{LW}]$ as a bioindicator of ecosystem processes.

Topic groups: 03. Plant Ecophysiology,

Presentation types: Poster

Title: Continuous observations and gap filling strategies of evapotranspiration and its isotopic signature using a gantry crane

Lead author: Dubbert Maren, ZALF

Author: Adrian Dahlmann, Zalf; Mathias Hoffmann, ZALF; Michael Sommer, ZALF; Jürgen Augustin, ZALF

Keywords: Evapotranspiration; Transpiration, Evaporation, Stable Water Isotopes

Content:

In light of ongoing global climate change and related increases in extreme hydrological events, it is becoming increasingly important to have a comprehensive knowledge of the ecosystem water cycle to assess ecosystem stability and in agricultural systems to ensure sustainable management and food security. Evapotranspiration (ET) plays a crucial role returning up to 90 % of incoming precipitation back to the atmosphere. In agriculture, further knowledge about plant transpiration (T) and evaporation (E) of different soils could lead to more efficient water use in the future, which will become necessary for agricultural practice in many regions due to climate change related increase in drought events. Here, we wanted to explore impacts of soil types (representing a full soil erosion gradient) on ecosystem water budgets (ET) and agronomic water use efficiencies (WUE_{agro}). We conducted a plot experiment with winter rye (September 17, 2020 to June 30, 2021) at the "CarboZALF-D" experimental field which is located in the hilly and dry ground moraine landscape of the Uckermark region in NE Germany. Along an experimental plot (110 m x 16 m) a modern automated gantry crane was built and used for the first time to continuously determine evapotranspiration alongside its isotopic signature with two automated chambers. A major advantage of this system is the opportunity to assess management and soil type effects (compared to eddy covariance setups), without corroborating measurement frequency (compared to manual chamber setups). Three soil types representing the full soil erosion gradient of the hummocky ground moraine landscape (extremely eroded: Calcaric Regosol, strongly eroded: Nudiargic Luvisol, non-eroded: Calcic Luvisol) within each soil type were investigated (randomized block design, 3 replicates per treatment). In addition, we used five different gap-filling methods and compared them in light of their potential to acquire precise water budgets over the entire growth period as well as reproduce short water flux and isotopic dynamics realistically. The best performance was achieved with methods based on mean-diurnal-variation (MDV) and support vector machine (SVM), including a validation step SVM yielded best predictions of measured ET. Subsequently, we simulated half-hourly ET fluxes and calculated balances of evapotranspiration for the cropping period.

Topic groups: 06. Food Authenticity, Nutrition, Forensic,

Presentation types: Poster

Title: Verifying the Origin of Slovenian Fruit and Vegetables Based on Isotopic and Elemental Profiles Using a One-Class Chemometric Model

Lead author: Bor Krajnc, Jozef Stefan Institute

Author: Lidija Strojnik, Jožef Stefan Institute; Jožef Stefan International Postgraduate School; Doris Potočnik, Jožef Stefan Institute; Marta Jagodic Hudobivnik, Jožef Stefan Institute; Darja Mazej, Jožef Stefan Institute; Katja Babič, Jožef Stefan Institute; Jožef Stefan International Postgraduate School; Boštjan Japel, Novartis d.d, Ljubljana; Andrija Čirič, University of Kragujevac; Nadja Škrk, Ministry of Agriculture, Forestry and Food of the Republic of Slovenia; Suzana Marolt, Ministry of Agriculture, Forestry and Food of the Republic of Slovenia; David Heath, Jožef Stefan Institute; Nives Ogrinc, Jožef Stefan Institute; Jožef Stefan International Postgraduate School

Keywords: agricultural products; geographical origin; authenticity; stable isotope; element composition; DD-SIMCA

Content:

This study demonstrates how stable isotopes of light elements and elemental profiles combined with a one-class chemometric model Data-Driven Soft Independent Modelling of Class analogy (DD-SIMCA) can be used to verify the declared origin of selected vegetables (garlic, asparagus) and fruits (cherry, apple, kaki) on the market. Samples were obtained from different geographical production areas in Slovenia between 2018 to 2020 for garlic and strawberries, 2019 to 2020 for cherry and asparagus, while apples and kaki were collected in 2020. A database of 222 authentic Slovenian samples was used to develop the verification models, while 128 imported samples were used to assess their reliability. The models were then used to check the validity of 91 test samples from the market with declared Slovenian origin. The method proved highly sensitive and specific, ranging from 94.1% to 97.6% and 66.7 to 100%, respectively. Class models for strawberries generated by DD-SIMCA had high sensitivity (96% to 97%) and good specificity (81% to 91%) on a yearly basis, while a more generalised model combining total yearly data gave a lower specificity (63%). The main important discriminating variables were $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, $\delta^{34}\text{S}$, Na, S, Fe, Ni, Sr, Mo, Cd, Cs and Ba. Of the commercial samples with declared Slovenian origin, approximately 35% were classified as non-Slovenian. Overall, the presented methodology provides a firm basis on which an appropriate traceability system could be established.

Topic groups: 06. Food Authenticity, Nutrition, Forensic,

Presentation types: Poster

Title: Traceability of protein hydrolysed fertilizers authorised in organic production

Lead author: José Manuel Muñoz-Redondo, Andalusian Institute of Agricultural and Fisheries Research and Training (IFAPA)

Author: José Carlos Montenegro, Andalusian Institute of Agricultural and Fisheries Research and Training (IFAPA); Rafael Baeza, Andalusian Institute of Agricultural and Fisheries Research and Training (IFAPA); José Manuel Moreno Rojas, Andalusian Institute of Agricultural and Fisheries Research and Training (IFAPA)

Keywords: Stable isotopes, IRMS, Metabolomics, Organic production regulation

Content:

In recent years, protein hydrolysed fertilizers (PHFs) have gained great attention among organic producers due to its valuable nutrients for plants, being related with increases in soil fertility, and its alignment with the green, circular and bioeconomy strategies in compliance with the EU regulations. This has boosted a strong development of these agricultural inputs in organic management, displaying a wide diversity of origins and methods of synthesis that can led to a large chemical diversity. In this sense, hydrolysed protein fertilizers are mainly produced by the denaturing and hydrolysis of various protein sources, such as plants, animals or microorganism derivatives. PHFs of animal origin were recognized by the organic European legislation as fertilizers and soil conditioners in the paragraph 'products or by-products of animal origin' of Annex I 889/2008, modified by the 354/2014 of European Commission. However, PHFs of vegetal origin were included in this regulation as pesticides, making their usage controversial. More recently, the European Regulation 2021/1165 authorised the use of these agricultural inputs as fertilizers and soil conditioners, gaining the same status than the animal-derived counterparts. This nuance in legislative definition is partly explained by the wide chemical diversity of PHFs, being still an analytical research issue that needs to be addressed along with traceability methodologies to ensure their origin. The aim of this study was to characterize the chemical profile of 70 PHFs from different origins and methods of synthesis, and to demonstrate the potential of two analytical techniques to differentiate these agricultural inputs. Isotope ratio mass spectrometry (IRMS) was used to determine the $\delta^{15}\text{N}$ values of the PHFs due to its known for discrimination of products from animal and vegetal origin as well as the organic products. Meanwhile, a metabolomic approach based on liquid chromatography mass spectrometry (LC-MS) combined with statistical techniques was used for the chemical characterization and authentication of PHFs. The results of this study showed a high potential of both techniques to identify fertilizers based on their animal or vegetable origin. Meanwhile, differentiation of PHFs based on their method of synthesis was only achieved by the metabolomic approach. This could be explained by the chemical processes linked to the type of hydrolysis that conduct the modulation of the metabolite profile of PHFs. The results of this study contribute to clarify the origin of PHFs for their adaptation in the organic production regulations.

Topic groups: 01. Methodological Advances,

Presentation types: Poster

Title: A new high-resolution sampling methodology for monitoring hyporheic zone geochemistry

Lead author: Tamara Michaelis, Chair of Hydrogeology, School of Engineering and Design, TU Munich

Author: Anja Wunderlich, Hydrogeology, School of Engineering and Design, TU Munich; Thomas Baumann, Hydrogeology, School of Engineering and Design, TU Munich; Florian Einsiedl, Hydrogeology, School of Engineering and Design, TU Munich

Keywords: hyporheic zone, anaerobic oxidation of methane, denitrification

Content:

Large amounts of the potent greenhouse gas (GHG) methane (CH₄) are produced in the hyporheic zone (HZ), the volume in a stream bed penetrated by river water. In aerobic and anaerobic methane oxidation, CH₄ is transformed to water-soluble CO₂, which reduces the global warming potential of GHG emissions from streams. At the same time, human activities have pushed the global nitrogen cycle out of balance, making eutrophication a severe problem for aquatic ecosystems. Rivers possess a great denitrification potential, most of which is happening in the HZ. We are focusing our research on the anaerobic oxidation of methane (AOM) coupled to denitrification, a process with the potential to reduce GHG emissions to the atmosphere and nitrate (NO₃⁻) loading in streams. Designing measurement strategies for HZ geochemistry is extremely challenging due to large spatial and temporal heterogeneities. For capturing temporal dynamics, we installed a monitoring station in a stream in southern Germany. The catchment lies in the Munich Gravel Plain and is dominated by carbonates. The monitoring station allows depth-distributed continuous temperature monitoring, repeated pore-water sampling and high-resolution dissolved oxygen profiling. With this, we want to gain a combined understanding of river bed hydraulics and geochemistry. Temperature will be used as a tracer for vertical hyporheic exchange which determines uptake rates of oxygen and nutrients from surface water. Repeated pore-water extraction with a vertical resolution of 3 cm is realized through micro-filters permanently installed in the sediment. Concentrations of relevant anions and cations as well as CH₄ in the pore-water samples will be used to delineate redox zones. Pore-water samples will also be used for stable isotope measurements. Carbon stable isotopes in methane ($\delta^{13}\text{C-CH}_4$) shall help to find zones of methane oxidation while isotopic analyses of NO₃⁻ ($\delta^{15}\text{N-NO}_3^-$) will be used to detect denitrification. In addition, with high-resolution oxygen profiles, measured with an optical-sensing technique, we want to precisely locate the oxic-anoxic interface and separate oxic from anoxic biogeochemical processes. In a poster, we want to present the monitoring station and selected field results. Here we will focus on methane oxidation coupled to denitrification through the stable isotope measurements. If these two processes occur below the oxic-anoxic interface, this could be a first in-situ evidence for AOM coupled to denitrification.

Topic groups: 03. Plant Ecophysiology,

Presentation types: Poster

Title: Carbon allocation to banana suckers under optimal and drought conditions – evidence from a $^{13}\text{CO}_2$ pulse-labeling experiment

Lead author: Mathilde Vantghem, IAEA, KU Leuven, BOKU

Author: Eline Beelen, KU Leuven; Rebecca Hood-Nowotny, BOKU; Roel Merckx, KU Leuven; Gerd Dercon, IAEA

Keywords: Musa, source-sink relationships, isotope labeling, drought stress

Content:

Drought stress is the most important abiotic limitation to banana production worldwide. Research on drought-resilient varieties and agronomic practices is ongoing, but progress is hindered by a lack of field-applicable drought evaluation methods. $\delta^{13}\text{C}$ values have strong potential as proxies for drought stress, but their interpretation in banana plants is complicated. Banana typically reproduces vegetatively through the formation of suckers or so-called daughter plants. Mother and daughter plants are both photosynthetically active, but their connection allows the exchange of photo-assimilates. Daughter plants were found to have more negative $\delta^{13}\text{C}$ values than mother plants. As some of the carbon in a daughter plant might originate from the mother plant, we cannot unambiguously link this difference to a difference in drought stress. Moreover, the difference in $\delta^{13}\text{C}$ between mother and daughter plants increased when drought stress occurred. This could indicate that the carbon allocation in banana is directly influenced by stress. In order to understand the effect of drought on the banana mat as a whole and to be able to correctly interpret $\delta^{13}\text{C}$ values of daughter plants, we attempted to quantify the carbon flux from mother to daughter plant. We pulse-labeled 24 Grand Nain banana mother plants with enriched $^{13}\text{CO}_2$ in a growth chamber, while attached daughter plants were air-sealed. Half the plants were subjected to a drought treatment (50% field capacity) and half to an optimal treatment (100% field capacity). Of half the plants, the daughter plants were removed just before labeling. Completely sealed control plants were included as well, to assess potential ^{13}C contamination. After labeling, leaf, phloem sap and corm samples were collected at designated times, from both mother and daughter plant. Destructive sampling took place after one and two weeks, whereby also roots and petioles were collected. The $\delta^{13}\text{C}$ value was determined for all bulk plant samples, as well as for the cellulose, sugar and starch fraction of a number of samples through Isotope Ratio Mass Spectrometry. Results from the experiment, which confirm the existence of a carbon flux from mother to daughter plant, will be presented.

Topic groups: 02. Terrestrial and Aquatic Biogeochemistry,

Presentation types: Poster

Title: Molecular tracers for characterization and distribution of organic matter in a freshwater lake system from lesser Himalaya

Lead author: Diptimayee Behera, IISER Mohali

Keywords: Aquatic systems; Indian Himalaya; Lipid biomarkers; n-alkane indices

Content:

The understanding of distribution and sources of organic matter (OM) is important to understand biogeochemical cycling of carbon in aquatic environments. In this study, we intend to evaluate quantitative contributions of OM sources and their distribution in Renuka Lake in lesser Himalayas using bulk geochemical parameters (TOC and $\delta^{13}\text{C}_{\text{bulk}}$), n-alkane indexes and source specific biomarkers (7-methylheptadecane). The principal sources of OM in the sediments were algae with secondary input from aquatic and terrestrial plants, which varied from littoral to central part of the lake. The cyanobacteria blooms in Renuka lake were established using branched alkanes (7-methylheptadecane), whereas pristane/phytane (Pr/Ph) depicts depositional conditions of the lake system. The strong runoff around the eastern and western margins of Renuka Lake created a substantial concentration of terrigenous OM. The nutrient content and sedimentological features of surface sediments have a significant impact on the occurrence of OM from aquatic and microbiological sources. Bathymetry and grain size analysis were used to investigate the multiple reasons and processes that govern the spatial heterogeneity of the distribution of sedimentary organic matter. Understanding the OM source and its regional variability in a lake system is critical for understanding constraining the ecological status and evaluating appropriate conservation methods. In addition, determining the n-alkane distribution and the environmental factors that govern it, as well as the uncertainties that come with it, is critical for paleoclimatic and paleoenvironmental reconstructions.

Topic groups: 06. Food Authenticity, Nutrition, Forensic,

Presentation types: Poster

Title: Strontium isotopes in identification of food forgeries in Finland

Lead author: Jenniina Siira, Finnish Food Authority/University of Helsinki, Department of Geosciences; Maria Lahtinen, Finnish Food Authority/University of Helsinki, Laboratory of Chronology

Author: Christoph Beier, University of Helsinki, Department of Geography and Geosciences; Simo Jokinen, Finnish Food Authority; Saira Karhu, National Resources Institute Finland; Marja Rantanen, National Resources Institute Finland; Annikki Welling, Finnish Food Authority

Keywords: food authenticity, strontium isotope ratios, agricultural soils

Content:

Food forgeries are a world-wide problem that have been emergingly observed within the European Union. They encompass both the forging of origin and consistency of food. Protection of local food production by identifying food forgeries is extremely important in order to maintain food safety and security of supply, and to preserve competitive advantage in global food market. One example of counterfeited food in Finland would be fresh berries, such as strawberries (*Fragaria x ananassa*): it is relatively effortless to forge the provenance of the berries only by changing the packaging labels. The focus of this research is the forging of origin of food, and the aim is to develop a reliable method based on strontium isotopes ($^{87}\text{Sr}/^{86}\text{Sr}$) for identifying the food provenance forgeries in Finland. The strontium isotope ratios of natural materials depict the origins of bioavailable strontium during the time when the substance has formed. Strontium behaves like calcium, and small amounts of strontium is transported from soil, ground- and surface water, and precipitation to plants. Since strontium is an element with a relatively great mass, its isotopic fractionation is scarce when it is transported from soil to the plant or to the animal eating the plant. Therefore, the strontium isotopes act as geochemical fingerprints that can be used to identify the geological provenance of the material. This is the first study where the strontium isotopes are widely applied on provenance analysis of foodstuff or organic materials in Finland. This study covers a large part of Finland and can also consider possible interference of later glacial sedimentary formations such as tills to the strontium isotope ratio baselines. In addition, there are barely any previous studies on the effects of liming of agricultural soils and the acidity of soil to the solubility of bioavailable strontium. The bedrock and soil formations of Finland are well mapped and would allow a good interpolation of the data, and therefore provide an excellent study area. This study aims to define $^{87}\text{Sr}/^{86}\text{Sr}$ baselines for Finland and create an isoscape, a map of bioavailable strontium, that would cover the majority of Finland. These isoscapes can be used as baselines in different studies and applications, such as identifying the potential source of plant-based materials, and human and animal individuals.

Topic groups: 02. Terrestrial and Aquatic Biogeochemistry,

Presentation types: Poster

Title: Winter nitrogen cycling in sediments of boreal lakes affected by browning and mining

Lead author: Anssi Vainikka, University of Eastern Finland

Author: Carlos Palacin-Lizarbe, University of Eastern Finland; Stefan Bertilsson, Swedish University of Agricultural Sciences; Henri Siljanen, University of Eastern Finland; Hannu Nykänen, University of Eastern Finland; Christina Biasi, University of Eastern Finland; Mikko Kiljunen, University of Jyväskylä; Jukka Pumpanen, University of Eastern Finland

Keywords: Nitrogen cycle, denitrification, DNRA, N₂O, winter limnology, sediment microbiome

Content:

Ice-covered period of boreal lakes last almost half a year. This period has contrasting environmental conditions respect to the ice-free period, with cold temperatures, absence of light, and no gas exchange between water and atmosphere, overall favouring the growth of prokaryotes respect to eukaryotes. Focusing on the nitrogen (N) cycle, winter seems a suitable period for N-transforming prokaryotes with a high availability of ammonia and nitrate due to a lower competence as there is minor assimilation by the light-dependent primary producers. However, there is limited data about winter N cycling rates and the microbes involved on, perhaps due to the wrong idea that N cycle is slowed down due to the dark and cold conditions. Also, there is limited knowledge about the role of organic matter quality on N cycling processes. We studied two oligotrophic big boreal lakes in North Karelia, Finland, Lake Viinijärvi and Lake Höytiäinen, each lake with clear-water and brown-water sides. Viinijärvi has an additional side affected by mining activities in the catchment showing higher nitrate and sulphate levels in the hypolimnion. During winter of 2021 we sampled two times these five sites, at the beginning (January-February) and at the end (March-April) of the ice-covered period. Using the Isotope Pairing Technique we incubated sediment cores with ¹⁵NO₃⁻ quantifying the products of 1) complete denitrification (N₂), 2) truncated denitrification (N₂O), and 3) dissimilatory nitrate reduction to ammonium (DNRA, NH₄⁺) to infer the process rates. In addition, to see the role of organic matter, we perform anoxic slurry incubations of the top sediment layer with ¹⁵NO₃⁻ and 1) lake water, 2) miliQ water, 3) algal dissolved organic matter (DOM) extract as a source of labile and autochthonous C, and 4) peatland DOM extract as a source of recalcitrant and allochthonous C. We characterised the DOM using FT-ICR MS. We also explore the genetic potential (DNA) of the sediment microbiome by using several sequencing techniques: 1) amplicon (16S rRNA), 2) captured, capturing the main N and CH₄ functional genes, and 3) shotgun. Results show changing nitrate consuming activities and N genetic potentials between the clear-water, the brown-water, and the mining affected sites.

Topic groups: 06. Food Authenticity, Nutrition, Forensic,

Presentation types: Poster

Title: Authentication of Spanish avocado (*Persea americana* Mill) through multi-element and stable isotopes: a data fusion approach

Lead author: José Manuel Muñoz-Redondo, Andalusian Institute of Agricultural and Fisheries Research and Training (IFAPA)

Author: Daniela Bertoldi, Technology Transfer Centre, Fondazione Edmund Mach; Agostino Tonon, Research and Innovation Centre, Fondazione Edmund Mach; Luca Ziller, Research and Innovation Centre, Fondazione Edmund Mach; Mónica Sánchez-Parra, Andalusian Institute of Agricultural and Fisheries Research and Training (IFAPA); Federica Camin, International Atomic Energy Agency; Jose Manuel Moreno-Rojas, Andalusian Institute of Agricultural and Fisheries Research and Training (IFAPA)

Keywords: Traceability, food authenticity, protected geographical indication, data fusion

Content:

Avocado (*Persea americana* Mill) is a fruit consumed worldwide due to its valuable organoleptic and health-promoting properties such as preventing cardiovascular diseases and diabetes, and reducing cholesterol. In the last decade, the worldwide production of avocado has increased at a faster rate than all other tropical fruits, with an annual average rate of 6%, reaching 6.3 million tonnes and the export volume of 2.1 million tonnes in 2018. The main export destinations of avocados are the United States of America (around 50% of global exports) and the European Union (around 28%). Spain is the only European country that produces and exports avocados, with most of the cultivars distributed along the southern coastal strip of Andalusia (Malaga and Granada). This enables a rapid distribution of this high-quality product to the European market at an optimum ripeness degree. Recently, the Spanish tropical fruit producers formed an association, seeking to obtain a protected geographical indication (PGI) for the avocados produced on the coastal strip of Andalusia (Malaga and Granada provinces). This recognition emphasises the link between a product and a particular geographical area in at least some of the production, processing or preparation stages (Regulation (EU) No 1151/2012). Thus, PGI may enable consumers to trust and recognize avocados produced in Andalusia and to protect local producers. In this sense, traceability is of essential importance to ensure the geographical origin, quality and safety of this product. Several studies addressed this matter by determining different quality traits such as fatty acids, sugars, flavonoids, soluble proteins and lipid fingerprint combined with chemometrics. However, the authentication results were not satisfactory or unfocused (not covering the main production areas of Malaga and Granada). In this study, we determined the stable isotopes of five light bio-elements (C, N, S, H, O) in the lipid and protein fraction, and the mineral content of avocados from eight producing regions (Spain, Mexico, Colombia, Peru, Brazil, Chile, Kenya and South Africa). The results were combined with chemometrics to create binary models able to determine whether an avocado was produced in Spain or not. The results of the discriminant models enabled to select six stable isotopes ($\delta^{18}\text{O}_{\text{lipid}}$, $\delta^{18}\text{O}_{\text{protein}}$, $\delta^2\text{H}_{\text{lipid}}$, $\delta^{13}\text{C}_{\text{protein}}$, $\delta^2\text{H}_{\text{protein}}$, $\delta^{15}\text{N}_{\text{protein}}$) and eight elements (Fe, Ca, Mn, Sr, Rb, Eu, Ba and Mg) as markers used to achieve a high classification rate of 98 %. The results of this study could contribute towards the establishment of a PGI.

Topic groups: 06. Food Authenticity, Nutrition, Forensic,

Presentation types: Poster

Title: Traceability of commercial Spanish mango (*Mangifera indica* L.) using stable isotopes, mineral content and chemometrics

Lead author: José Manuel Muñoz-Redondo, Andalusian Institute of Agricultural and Fisheries Research and Training (IFAPA)

Author: Daniela Bertoldi, Technology Transfer Centre, Fondazione Edmund Mach; Luca Ziller, Research and Innovation Centre, Fondazione Edmund Mach; Agostino Tonon, Research and Innovation Centre, Fondazione Edmund Mach; Mónica Sánchez-Parra, Andalusian Institute of Agricultural and Fisheries Research and Training (IFAPA); Federica Camin, International Atomic Energy Agency; Jose Manuel Moreno-Rojas, Andalusian Institute of Agricultural and Fisheries Research and Training (IFAPA)

Keywords: Traceability, tropical fruit, biostatistics, food authenticity, protected geographical indication

Content:

Mango (*Mangifera indica* L.) is a predominantly tropical fruit that reached a worldwide production of 39 million tonnes in 2018, meaning more than 50% of the global production of major tropical fruits. In recent years, Spain has joined the production of mango as the only European country, taking advantage of its logistical strategic position due to its geographical proximity to this market. However, the current market globalization may leave Spanish mango producers in vulnerable situations. For this reason, Mango producers from the southern coastal strip of Spain (Granada and Malaga) have recently initiated a claim to register a protected geographical indication (PGI) to make their product more competitive and attractive, and reinforce their position as the only European producer. A PGI origin-label generally impacts in greater economic rewards for the product and improves social perception, making them attractive for competitors to imitate and fraudulently sell them as authentic. This may damage its reputation and economic income, so that traceability of these product has become a major concern. Several studies have addressed the traceability of mangoes using different analytical techniques, including the impact of geographic location on the volatile composition and quality parameters, the authentication of specific mango varieties through the analysis of their volatile profile and near-infrared spectroscopy (NIR), or even the differentiation of organic and conventional mangoes by means of their mineral content. However, no studies have been performed to establish an analytical methodology able to identify the mangoes produced in a specific location. Thus, new tools for simple and accurate geographical traceability of mangoes could be of great interest to support the Spanish PGI of this fruit. The aim of this study was to assess the effectiveness of the stable isotopes of five light bio-elements (C, N, S, H, O) and mineral fingerprinting to identify the commercial mangoes produced in Spain. The results for both analytical platforms were combined with chemometrics to select the most discriminative variables, and were assessed independent and jointly to improve the classification yielding. We observed high classification rates in all the cases, although the best performance was achieved for the combined model (99% of classification rate and 100 % of sensitivity). These results showed the viability of establish a PGI of Spanish mangoes, although the models need to be supported by a sampling extended and maintained over the time.

Topic groups: 03. Plant Ecophysiology,

Presentation types: Poster

Title: Unique drought and deep water labelling experiment at Biosphere 2 reveals differences in tree water uptake, transport and storage

Lead author: Kathrin Kuehnhammer, IGOE, Environmental Geochemistry, TU Braunschweig, Germany

Author: Joost van Haren, Biosphere 2 and Honors college, University of Arizona, USA; Angelika Kuebert, Ecosystem Physiology, University of Freiburg, Germany; Maren Dubbert, Isotope Biogeochemistry and Gasfluxes, ZALF, Germany; Nemiah Ladd, Department of Environmental Sciences, University of Basel, Switzerland; Laura K. Meredith, Biosphere 2 and School of Nat. Res. & the Envir., University of Arizona, USA; Christiane Werner, Ecosystem Physiology, University of Freiburg, Germany; Matthias Beyer, IGOE, Environmental Geochemistry, TU Braunschweig, Germany

Keywords: water stable isotopes; in situ methods; deep roots; root water uptake; water use strategies; isotopic labelling; tropical trees

Content:

Due to climate and land use change, ecosystem water availability is altered across the globe. Humid tropical forests, which evolved under conditions of abundant water, might be particularly vulnerable to water stress. One important factor in a tree's resilience to a less reliable water supply from precipitation is a root system that reaches deep into the ground. However, accessing deep soil regions as well as observing active deep root water uptake is challenging. Consequently, the occurrence, functioning and importance of deep roots are not well understood. The Biosphere 2 Tropical Rainforest in Arizona, USA offers a unique possibility to investigate deep water uptake because climatic and hydrological conditions can be fully controlled. Within the B2 WALD (Water, Atmosphere, and Life Dynamics) project, we imposed a two-month drought on the enclosed ecosystem. To identify deep water uptake, we utilised the fact that soil can be accessed from below and homogeneously supplied water labelled with 2H isotopes through a drainage system in 2-3 m soil depth at the peak of the drought. We used novel in situ methods to follow the response of isotope values of tree and soil water to labelling in high temporal resolution. We also monitored atmospheric conditions, soil water content as well as tree sap flow and stem water content to obtain a comprehensive picture of dynamic tree water use reactions following our manipulations in water supply. Combining all measurements in 10 tree individuals of 5 different species, we found contrasting reactions to the water added from below. All canopy trees had access to deep water, suggesting that deep roots could be a common feature among tropical tree species. However, trees did not use deep water in the same way. We observed differences in the speed and timing of the reaction as well as in within-tree water dynamics. While some individuals first refilled their stem water storage, others used the deep water source to preserve their sap flow and transpiration stream. This not only impacted the time course of tree water isotopes but knowledge of those different behaviors is pivotal for better understanding and predicting tree performance, survival and ecosystem water cycling. In summary, our data illustrate the need for an extensive network combining different measurements to correctly interpret tree water isotope dynamics, tree water use strategies and to further uncover the functioning of deep roots and assess their importance for ecosystem resilience in a changing climate.

Topic groups: 08. Soil Carbon and Nitrogen Cycling, with Focus on Agricultural Soils,

Presentation types: Poster

Title: Studying the decomposition and priming effect of two forestry-drained peatland soils with different nutrient status

Lead author: Maiju Linkosalmi, Finnish Meteorological Institute

Author: Annalea Lohila, Finnish Meteorological Institute; Christina Biasi, University of Eastern Finland

Keywords: Peat soil, Priming effect, ^{13}C , Nutrient availability

Content:

Among other land-use changes, also forestry-drainage alters the characteristics of organic peatland soil, for example by decreasing the water table and increasing the vegetation biomass. These changes further affect the carbon (C) balance of the ecosystem. The respiration fluxes and priming effect (PE) of forestry-drained peat soils with different nutrient status were studied in a two-week laboratory experiment. The nutrient status of a forestry-drained peatland is highly dependent on the original peatland type and most likely the nutrient availability in soil further affects the processes impacting the ecosystem C balance. Batches of surface peat soil samples were collected from two forestry-drained boreal peatlands, nutrient-rich and nutrient-poor sites, and the carbon dioxide (CO_2) fluxes were monitored from these samples during the experiment. To study the PE, i.e. the effect of fresh C addition on the decomposition of old soil organic matter (SOM), half of the peat samples were labelled with ^{13}C -glucose. The soil- and sugar-derived respirations and the extent of the PE were determined with the isotopic method and mixing model. The nutrient-rich peat soil showed generally higher basal respiration rates than the nutrient-poor peat, and these results were in accordance with the CO_2 flux measurements observed in-situ. The respiration rates also imply that there are differences in the quality of the peat and thus decomposition between the sites. A negative PE was observed in both peat soils; the addition of fresh C in form of ^{13}C -glucose decreased the SOM decomposition in comparison to control peat samples. These results suggest that in these peat soils the microbes prefer to utilize fresh C instead of old soil C. In addition, the nutrient-poor peat soil showed significantly stronger negative PE than the nutrient-rich peat soil, thus the higher nutrient availability seemed to suppress the negative PE. According to these results our data implies that at forestry-drained peatlands the presence of fresh C inputs from vegetation could suppress the peat decomposition, the effect being even more pronounced in peat soil with lower nutrient availability.

Topic groups: 09. Isoscape, Spatial Variability of Stable Isotopes (Migration, Food Webs),

Presentation types: Poster

Title: Isotopic turnover in Polar cod (*Boreogadus saida*) muscle determined through a controlled feeding experiment

Lead author: Amanda Ziegler, University of Tromsø

Author: Bodil Bluhm, University of Tromsø; Paul Renaud, Akvaplan-niva; Lis Jørgensen, Institute of Marine Research

Keywords: Isotopic turnover; trophic discrimination; experiment; Arctic

Content:

Polar cod (*Boreogadus saida*) are an important trophic link within in Arctic marine food webs and are likely to experience diet shifts in response to climate change. Stable isotope analysis has improved the ability to monitor the diet of this species in time and space, however, key parameters necessary for determining trophic position, modeling diet composition, and interpreting the temporal context of stable isotope composition data are lacking. This study provides the first experimental derivation of isotopic turnover rates (half-life) and Trophic Discrimination Factors (TDF) of both $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ for adult polar cod muscle. We found isotopic turnover rates of approximately 31-60 days and TDFs of 2.51 and 3.95 for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$, respectively. Metabolism accounted for more than 95% of the isotopic turnover we observed and the half-life values we present are applicable to adult polar cod (>2 years) experiencing little to no somatic growth. We conclude that the applying the commonly used TDF of $\sim 1\text{‰}$ for $\delta^{13}\text{C}$ is an underestimate for adult polar cod, while the use of 3.4 ‰ or 3.8 ‰ for $\delta^{15}\text{N}$ is appropriate. Based on our findings, we recommend that studies investigating seasonal shifts in the diet of adult polar cod sample at temporal intervals of at least 60 days to account for isotopic turnover in polar cod muscle, and applications requiring TDFs for polar cod should utilize values of approximately 2.5 ‰ and 4 ‰ for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$, respectively.

Topic groups: 08. Soil Carbon and Nitrogen Cycling, with Focus on Agricultural Soils,

Presentation types: Poster

Title: Rhizosphere priming: Phenology controls through exudate quality and quantity

Lead author: Ezekiel Bore, University of Helsinki

Author: Lukas Kohl, University of Helsinki; Markku Koskinen, University of Helsinki; Jussi Heinonsalo, University of Helsinki; Kristiina Karhu, University of Helsinki; Mari Pihlatie, University of Helsinki

Keywords: Rhizosphere, priming, exudates, ¹³C labeling

Content:

Atmospheric CO₂ captured by plants through photosynthesis is utilized for biomass synthesis. Partly, the C captured is exudated to meet other requirements such as nutrient mobilization either directly through complexation of metal ions or indirectly through activation of microbes. However, plant phenology control of rhizosphere priming remains unclear. In this study, rhizosphere priming effects of spring barley (*Hordeum vulgare* L.) were investigated at three phenological stages in a greenhouse experiment using ¹³C tracer. Plant phenology significantly influenced the rhizosphere priming effect. The priming effect reached 200% above the non-planted control at vegetative stage and declined afterwards. This effect complimented microbial biomass carbon, suggesting an apparent priming mechanism. These results point towards the role of exudate quality and quantity as a driver of rhizosphere priming. Therefore, management strategies to minimize C losses and increase carbon sequestration in barley fields should focus on vegetative stage.

Topic groups: 09. Isoscape, Spatial Variability of Stable Isotopes (Migration, Food Webs),

Presentation types: Poster

Title: Food web structure and trophic interactions at the recently discovered deep-sea La Scala hydrothermal vent field (SW Pacific)

Lead author: Loic N. Michel, Ifremer Brittany, France

Author: Simon Gourdon, Ifremer Brittany, France; Alize Bouriat, Ifremer Brittany, France; Eve-Julie Pernet, Ifremer Brittany, France; Eric Thiebaut, Roscoff Biological Station, France; Didier Jollivet, Roscoff Biological Station, France; Gilles Lepoint, University of Liege, Belgium

Keywords: carbon, nitrogen, sulphur, trophic ecology, benthic invertebrates, marine ecology, chemosynthesis

Content:

Hydrothermal vents are features of the seafloor where fluids (acidic, geothermally heated water enriched in chemical compounds such as hydrogen sulphide) discharge in the water column. These fluid emissions sustain unusual chemosynthesis-based ecosystems where abundant micro-organisms and animal communities can thrive under extreme conditions. In May 2019, the La Scala vent field was discovered in Woodlark Basin (Papua New Guinea, SW Pacific). Several active "black smokers" harbouring dense fauna were found at depths ranging from 3300 to 3400 m. The main engineer species were symbiont-bearing gastropods *Ifremeria nautilei* and *Alviniconcha* spp. in more active diffuse areas, and stalked barnacles *Vulcanolepas* sp. nov. in mildly active areas. At least 44 taxa were observed in these habitats. Here, we used trophic markers (stable isotope ratios of C, N and S) to identify energy fluxes supporting those communities, and understand how their feeding habits could influence interspecific interactions. Most sampled animals primarily depended (either directly or indirectly) on endogenous chemosynthetic vent production for their nutrition. This dependence spanned all sampled taxonomic and functional groups. It extended to organisms considered as peripheral fauna, or not strictly found at vents, such as *Vulcanolepas* sp. nov., anemones, or scavenging gastropods. Moreover, other peripheral fauna fed on a mix of both chemosynthesis- and photosynthesis-derived items. This emphasizes the importance of exported vent production for the surrounding deep-sea fauna. Animal communities showed considerable trophic diversity, and depended on several bacterial production mechanisms. Many taxa co-relied on two or more carbon sources, and inter- and intra-taxon differences in feeding habits could lead to a more even segregation of available food resources. While many questions about environmental and biological drivers of food web structure at La Scala vent field remain open, our results constitute a first glimpse at processes shaping those freshly discovered communities.

Topic groups: 08. Soil Carbon and Nitrogen Cycling, with Focus on Agricultural Soils,

Presentation types: Poster

Title: ^{13}C PLFA/FA fingerprinting to assess taxonomic and functional development of the soil microbial community and mesofauna after heavy metal remediation

Lead author: Christoph Noller, University of Natural Resources and Life Sciences, Vienna, Austria

Author: Janet Wissuwa, University of Natural Resources and Life Sciences, Vienna, Austria; Wolfgang Friesl-Hanl, University of Natural Resources and Life Sciences, Vienna, Austria; Rebecca Hood-Nowotny, University of Natural Resources and Life Sciences, Vienna, Austria; Alexander Bruckner, University of Natural Resources and Life Sciences, Vienna, Austria; Andrea Watzinger, University of Natural Resources and Life Sciences, Vienna, Austria

Keywords: PLFA, mesofauna, heavy metals, remediation

Content:

Remediation of heavy metal contaminated soils is an important tool to rehabilitate agricultural land in time of continuing soil loss due to sealing and land degradation. Soil washing with the chelating agent EDTA is a technique to remove heavy metals while maintaining the soil physicochemical functionality. The recovery of the soil biota following EDTA washing and associated impact on the soil carbon cycle were clarified as part of the remediation technology assessment. A pot trial under greenhouse conditions was conducted using the original contaminated soil (bioavailable: Pb 8.27, Cd 1.03, Zn 45.8 mg kg⁻¹) and two EDTA washed variants (bioavailable: Pb 0.87, Cd 0.27, Zn 0.28 mg kg⁻¹), one amended with 2.6 %wt vermicompost and 2.4 %wt biochar. The pots were inoculated with mesofauna and kept under controlled greenhouse conditions for seven months. Labeled maize straw ($\delta^{13}\text{C} = 400\text{‰}$) was applied as a carbon source one month before the extraction of soil microbes and fauna. Stable isotopes were measured in the fatty acids of single mesofauna groups (Collembola, Gamasida, Oribatida, Astigmata) and the microbial phospholipid fatty acids. Abundance of total mesofauna and specifically of Collembola and Oribatida significantly increased by 100 and 160 % respectively after remediation, while soil microbial biomass was significantly decreased by 18 % after soil washing. The organic amendment increased the microbial biomass back to the original level. Incorporation of ^{13}C into fatty acids showed an increasing trend for all mesofauna groups after soil washing but was only significant for Gamasida (+ 115 %) and the microbial incorporation (+ 109 %), indicating improved growth conditions after remediation. Both, soil washing and organic amendment resulted in a significant difference in the fatty acid distribution in the microbial community, while a significant change in the mesofauna groups were only observed in the amended treatment. These differences indicate changes in the feed and possibly species composition. To conclude, soil washing as a heavy metal remediation technique improved the environmental conditions for mesofauna. The different functional and nutritional roles of the mesofauna groups was confirmed as Collembola and Oribatida abundance profited more from remediation while ^{13}C incorporation was higher in Astigmata and Gamasida.

Topic groups: 07. Atmospheric Sciences (Pollution, Climate Change, Cosmogeochimistry),

Presentation types: Poster

Title: Research Gate Discussion Group: Isotopic tools to study N₂O in soil and aquatic systems

Lead author: Caroline Buchen-Tschiskale, Climate-Smart Agriculture, Thünen Institute, Braunschweig, Germany

Author: Amanda Matson, Climate-Smart Agriculture, Thünen Institute, Braunschweig, Germany; Eliza Harris, Swiss Data Science Centre, ETH Zürich, Switzerland; Dominika Lewicka-Szczebak, Laboratory of Isotope Geology and Geoecology, University of Wrocław, Poland; Lena Rohe, Climate-Smart Agriculture, Thünen Institute, Braunschweig, Germany; Reinhard Well, Climate-Smart Agriculture, Thünen Institute, Braunschweig, Germany

Keywords:

Content:

Isotopic methods using natural abundance or labelling techniques are indispensable to identify and quantify N₂O production and consumption pathways. However, all methods are subject to limitations and possible biases, as well as underlying assumptions, which are not always fulfilled and are often difficult to verify. Moreover, stable isotope analysis of N₂O, N₂, and precursor compounds is challenging, particularly regarding calibration, instrumentation, and intercomparability between laboratories. Finally, methods that elucidate process dynamics by combining measurements from different compartments – such as soil air, soil solutes, and surface flux data – offer new possibilities, but limitations and assumptions are currently not well understood. Despite these challenges, interest in the use of stable isotope methods to understand N₂O production and consumption pathways is growing, and the number of publications per year is rising steadily. Communication channels for the discussion of methodologies – such as conferences, workshops, reviews and publications – are limited in access and continuity, and allow only for slow progress. This motivated us to start an open discussion group to enable rapid exchange on this topic. We want to offer a forum to address four general areas: · Experimental Methods: Discuss technical issues and present ideas for new methods · Analytical Methods: Share data on performance and comparison of methods · Data analysis: Discuss advantages, disadvantages, limitations, possible biases, and solutions relating to existing data analysis methods · Modelling: Discuss modelling approaches to evaluate experimental data We invite participation from interested researchers via: i) following the discussion group to stay up to date, ii) adding comments and ideas to ongoing discussions in the Project Log, and iii) contacting us with suggestions for new discussion topics. We hope to see you soon!
[https://www.researchgate.net/project/Discussion-on-isotopic-tools-to-study-soil-N₂O](https://www.researchgate.net/project/Discussion-on-isotopic-tools-to-study-soil-N2O)

Topic groups: 07. Atmospheric Sciences (Pollution, Climate Change, Cosmogeochimistry),

Presentation types: Poster

Title: Characterization of urban aerosol pollution sources by sulfur and carbon isotope analysis

Lead author: Laurynas Bučinskas, Center for Physical sciences and Technology

Author: Inga Garbarienė, Center for Physical sciences and Technology; Justina Šapolaitė, Center for Physical sciences and Technology; Žilvinas Ežerinskis, Center for Physical sciences and Technology; Andrius Garbaras, Center for Physical sciences and Technology

Keywords: Aerosol, pm1, sulfur, carbon, radiocarbon, air quality, stable isotope, apportionment

Content:

Atmospheric sulfur and carbon aerosols are formed during various natural and anthropogenic activities, which in turn can have a negative impact on human health and play a key role in atmospheric chemistry and climate change [1], [2]. Sources of urban aerosol include power plants, vehicle traffic, home heating, biomass combustion and other industrial emissions. Sources of carbon and sulfur aerosol pollution can be differentiated in great detail by applying a combination of stable isotope and radiocarbon analysis methods. Such an approach was employed in the present study to characterize local and remote sources of aerosol pollution. Aerosol PM₁ samples were taken in Vilnius, Lithuania in a period of 5 months. Measurements of stable isotopes values $\delta^{34}\text{S}$ and $\delta^{13}\text{C}$ were performed with a stable isotope mass spectrometer, and ^{14}C measurements were performed using a single-stage accelerator mass spectrometer. Mixing equations were applied to determine the inputs of biomass, coal and traffic-related emissions of carbonaceous aerosol. Apportionment of sulfur sources revealed that the main polluters were coal emissions and biomass burning. Then, the previous results along with total carbon and sulfate concentrations were related to HYSPLIT air mass backward trajectory plots. This method allows a detailed description of the sources of sulfur and carbon aerosol pollution and provides important information on local air quality. [1] C. A. Pope and D. W. Dockery, "Health effects of fine particulate air pollution: Lines that connect", *J. Air Waste Manag. Assoc.*, t. 56, nr. 6, 2006. [2] C. Tomasi, C. Lanconelli, M. Mazzola, and A. Lupi, "Aerosol and Climate Change: Direct and Indirect Aerosol Effects on Climate", *Atmospheric Aerosols*, 2016.

Topic groups: 09. Isoscape, Spatial Variability of Stable Isotopes (Migration, Food Webs),

Presentation types: Poster

Title: Unraveling the land-to-reef continuum: Stable isotope signatures of benthic reef communities along the coast of Curaçao

Lead author: Nienke C.J. van de Loosdrecht, University of Amsterdam

Author: Petra M. Visser, University of Amsterdam; Mark J.A. Vermeij, University of Amsterdam, Caribbean Research and Management of Biodiversity Foundation; Jasper M. de Goeij, University of Amsterdam, Caribbean Research and Management of Biodiversity Foundation

Keywords: coral reef ecology; nutrient input; nutrient fluxes; trophodynamics; food web

Content:

In coastal waters, water quality is affected by nutrients and other substances of oceanic, terrestrial, and even aerial origin. Tropical coral reefs are residing in oligotrophic (i.e., nutrient-poor) waters, often fringing coasts of islands and therefore directly influenced by relatively small changes in nutrient input from both sea- and land-based sources. However, surprisingly little is known on the actual fluxes of terrestrial versus oceanic inputs and its effect on coral reef benthic communities. As part of the larger "SEALINK" project, consisting of nine, interdisciplinary PhD projects from several universities and research institutes in the Netherlands and Curaçao, we aim to link the terrestrial processes to the coral reef health in the Dutch Caribbean islands. Therefore, as first step, the spatial distribution of ^{13}C - and ^{15}N -stable-isotope signatures of different benthic reef communities (i.e., sediment, sponges, macroalgae) were assessed at 18 reef sites along a depth gradient on the fringing reefs of Curaçao. The ^{13}C - and ^{15}N -isotopic signatures will provide insights in the sources and proportion/distribution of nutrients along the coast. The seasonal effect of run-off will be integrated by analyzing differences in isotopic signatures during the wet and dry season. In addition, based on the spatial distribution of these signatures, a dual-isotope mixing model will be applied to construct food web frameworks at sites with least and most terrestrial inputs, in order to understand how terrestrial sources influence local reef nutrient fluxes and trophodynamics of benthic communities.

Topic groups: 07. Atmospheric Sciences (Pollution, Climate Change, Cosmogeochimistry),

Presentation types: Poster

Title: Ammonium stable isotopes in Ice Core: volatile versus thermic emissions in Europe

Lead author: Alexis LAMOTHE, Univ. Grenoble Alpes, CNRS, IRD, INP-G, IGE (UMR 5001), Grenoble, France

Author: Joël SAVARINO, Univ. Grenoble Alpes, CNRS, IRD, INP-G, IGE (UMR 5001), Grenoble, France; Patrick GINOT, Univ. Grenoble Alpes, CNRS, IRD, INP-G, IGE (UMR 5001), Grenoble, France; Sophie DARFEUIL, Univ. Grenoble Alpes, CNRS, IRD, INP-G, IGE (UMR 5001), Grenoble, France; Nicolas CAILLON, Univ. Grenoble Alpes, CNRS, IRD, INP-G, IGE (UMR 5001), Grenoble, France

Keywords: ice core, ammonium stable isotopes, Alps, pollution

Content:

Ammonium is a proxy of ammonia. As the latter is fundamental in controlling the formation and production of inorganic aerosols through acid-base reactions, it plays a role in soil acidification and health hazards. Yet, through the last century, emissions have tripled and are thought to double by 2050 with the rapid emergence of Haber-Bosch fertilizers and manure application. To better constrain natural and anthropogenic sources of ammonia at the European scale, an ice core from the Col du Dôme glacier (4,250 m above sea level, Mont-Blanc massif), drilled in 2016 in the framework of the Ice Memory programme, is used to reconstruct the past variability of ammonium. With this in mind, we have developed a method to measure nitrogen stable isotope in ammonium. Here we present the very first data of 120 m of $\delta^{15}\text{N}(\text{NH}_4^+)$ in an ice core revealing seasonal cycling and multi-decadal trends. Our data both show the minor impact transport has on isotopic composition and the change of ammonia emissions from a two-emission source system at the beginning of the 20th century - natural background and thermic emissions -, to a three-emission source system in which volatile and thermic emissions outweigh natural background.

Topic groups: 01. Methodological Advances, Datatype not found, poster next to each other (60, 119 and 165),

Presentation types: Poster

Title: Isotope delta scales

Lead author: Federica Camin, IAEA

Author: Manfred Gröning, IAEA

Keywords: delta scales, reference materials

Content:

Isotope delta scales are established by international agreements. Scales are generally defined by the isotope ratio of one selected material. The realization of isotope delta scales is done by measurements of one or two primary reference materials. The scale realization can also be ensured by using secondary reference materials, having been carefully calibrated versus the primary reference materials. This allows to match the matrix of the considered samples, in agreement with the 'principle of identical treatment'. This presentation will focus on the available primary and secondary reference materials for scale definition and realization of the stable isotope ratios of H, C, N, O and S, with particular emphasis on the recent multi-point realization scheme of the $\delta(^{13}\text{C})\text{VPDB}$ scale.

Topic groups: 03. Plant Ecophysiology,

Presentation types: Poster

Title: Late-season biosynthesis of leaf fatty acids and n-alkanes of a mature beech tree traced via $^{13}\text{CO}_2$ pulse-chase labelling

Lead author: Tatjana Carina Speckert, Department of Geography, University of Zurich

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Keywords: Cuticular leaf waxes, Fatty acids, n-Alkanes, *Fagus sylvatica*, $^{13}\text{CO}_2$ labelling, compound-specific isotope analysis (CSIA)

Content:

The predicted warming of 2-4 °C in Central Europe will affect forest composition and dynamics (2081-2100, RCP4.5; Bussotti et al., 2015). European beech (*F. sylvatica*), one of the economically most important tree species in European forests, is known to be sensitive to warming-induced drought events, which can limit its growth and competitiveness (Walthert et al., 2021). Among physiological and defence mechanisms, leaf waxes play an important role in limiting water loss and preventing external aggressions (e.g., insect attacks). Variation in leaf wax abundance and composition is thus a promising proxy to better understand the tree fitness and response to its environment. However, little is known on the leaf wax renewal during the growing season. In this study, the aim was to determine the wax dynamics of sun-exposed and shaded leaves of a ~200-year-old beech tree (*F. sylvatica*) sampled in Switzerland from August to October 2018 that followed the heatwave and drought from April to July 2018. A $^{13}\text{CO}_2$ pulse-chase labelling experiment was conducted to determine the de-novo synthesis of leaf waxes by characterizing the abundance and composition of n-alkanes and fatty acids (FAs). A maximum in the ^{13}C -excess of FAs was observed one week after labelling (shade: $3.63 \pm 0.49\%$, sun: $2.65 \pm 1.27\%$), while the weighted ^{13}C -excess of n-alkanes showed a low ^{13}C -enrichment in all leaves compared to the natural $\delta^{13}\text{C}$ abundance ($< 0.03 \pm 0.01\%$). The ^{13}C -excess trends were coherent with the changes in concentration and composition of alkanes and FA. Our experiment suggested ongoing de-novo biosynthesis of leaf waxes, especially of FAs, even during the late growing season. We show variation in leaf wax abundance and composition of a mature beech tree, especially between sun-exposed and shaded leaves. FAs appeared as a more sensitive trait to environmental conditions and ontogeny than n-alkanes.

References Bussotti, F., Pollastrini, M., Holland, V., and Brueggemann, W. (2015). Functional traits and adaptive capacity of European forests to climate change. *Environmental and Experimental Botany*, 111, 91-113. Walthert, L., Ganthaler, A., Mayr, S., Saurer, M., Waldner, P., Walser, M., Zweifel, R., and von Arx, G. (2021). From the comfort zone to crown dieback: Sequence of physiological stress thresholds in mature European beech trees across progressive drought. *Science of The Total Environment*, 753, 141792.

Topic groups: 01. Methodological Advances,

Presentation types: Poster

Title: A dilution method for obtaining dry ambient 'air' samples from pure CO₂ for stable isotope analysis using laser absorption spectroscopy

Lead author: Pharahilda Steur, University of Groningen

Author: Hubertus Scheeren, University of Groningen; Kaushal Chaniyara, University of Groningen; Harro Meijer, University of Groningen; Wouter Peters, University of Groningen/Wageningen University and Research Centre

Keywords: "CO₂" "dilution" "reference" "IRMS" "Laser absorption spectroscopy"

Content:

We present a reliable and stable dilution method for pure CO₂ samples allowing for the analysis on laser absorption spectrometer systems for measurement of stable isotopes of CO₂. We use a novel dual-laser infrared absorption spectrometer (Aerodyne Inc.) developed for the simultaneous measurement of $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, and $\delta^{17}\text{O}$ of CO₂ in dry ambient air referred to as the SICAS (Stable Isotope of CO₂ Absorption Spectrometer) (Steur et al., 2021). The dilution method allows for scale intercomparisons between the SICAS and our Isotope Ratio Mass Spectrometry (IRMS) systems using pure CO₂ isotopic reference materials. In addition, it offers an alternative measurement method to IRMS for isotopic analysis of pure CO₂ samples extracted from ambient air. In brief, the dilution method has the following steps: 1) The CO₂ sample from the storage container (e.g flame sealed tube) is released and let through a water trap (dry ice/ethanol) into a calibrated volume using LN₂; 2) The pressure reading in the calibrated volume at room temperature then determines how much dilutor gas will be required to make the final concentration in the flask of 400 ± 25 ppm; 3) The sample is transferred into a freeze finger using LN₂ attached to an evacuated 0.85 L sample flask; 4) Finally, the sample is combined with the dilutor gas, consisting of dry ambient air that has been scrubbed of CO₂ (using Ascarite) and H₂O traces (using Magnesium Perchlorate) and left undisturbed for at least 12 hours to allow for a homogeneous mixture. As such, the system is able to measure amounts of CO₂ from 0.45 mg and up corresponding to >375 ppm of CO₂ in 0.85 L of ambient air. The dilution method is currently applied to handle a large amount of flame sealed tubes containing CO₂ extracted from ambient air samples collected during an extensive sampling program called ASICA (Airborne Stable Isotopes of Carbon from the Amazon) that took place over the Brazilian Amazon from early 2016 until end of 2018. Here we present the set-up and test results of our dilution system using reference materials in comparison to our IRMS, as well as first measurement results of a number of ASICA samples on the SICAS.

Topic groups: 04. Paleoclimatology & Archaeology,

Presentation types: Poster

Title: A Bayesian high-resolution osteo-biography of an unknown individual from Early Medieval Sorrento

Lead author: Carlo Coccozza, LMU Munich; MPI-SHH Jena; Università di Caserta

Author: Christoph Klose, FSU Jena; Mary Lucas, MPI-SHH Jena; Christian Hamann, CAU Kiel; Ricardo Rodríguez-Varela, Stockholm University; Anders Götherström, Stockholm University; Fallen Teoh, MPI-SHH Jena; Carmine Lubritto, Università di Caserta; Patrick Roberts, MPI-SHH Jena; University of Queensland; Wolf-Rüdiger Teegen, LMU Munich; Ricardo Fernandes, MPI-SHH Jena; University of Oxford; Masaryk University

Keywords: Stable Isotopes; Bayesian Modelling; aDNA; Proteomics; Radiocarbon; Osteo-biography; Multi-Proxy

Content:

In our contribution, we present a Bayesian high-resolution osteo-biography of an individual from Sorrento (Italy) dating to the Byzantine period. A multi-proxy approach was adopted that combined different biomolecular and osteological techniques. This included isotopic measurements (C, N, O), aDNA, proteomics, and radiocarbon dating together with physical anthropology analysis and information from written sources. In 2019, during the excavation of a Roman villa in Sorrento (Italy), a small cemetery area was identified. This was associated with the remains of a medieval rural chapel built in the abandoned villa. The only explored grave (grave archaeological ID as CDS1), contained bone and teeth fragments from an adult individual and no grave goods. Ribs were sampled for bulk collagen and bioapatite stable isotope analysis and radiocarbon dating while teeth were sampled for proteomics, aDNA, and incremental dentine and enamel stable isotope analysis. Bayesian modelling of isotopic data was employed to trace temporal changes in diet and mobility. Radiocarbon results showed that this individual likely lived during the 8th century, when Sorrento was part of the Byzantine duchy of Naples. The anthropological analysis could not assess the biological sex of the individual, but reported an age at death of c. 25-35 years and pathological evidence for hard physical work. Bayesian isotopic modelling showed a similarity between the start and onset of weaning (6 months - 2 years) and known Roman and Byzantine medical recommendations. The diet was mainly based on C3 plants and this individual likely moved during his/her childhood. The burial context, reconstructed diet, and osteological stress pathologies suggest a low social status for this individual. Thus, the high level of childhood mobility, which is unexpected in low status medieval individuals, could suggest that was enslaved and travelled with household members. This is something attested in Byzantine sources. Our contribution shows the potential of multi-proxy approaches paired with Bayesian modelling to reconstruct past osteo-biographies.

Topic groups: 09. Isoscape, Spatial Variability of Stable Isotopes (Migration, Food Webs),

Presentation types: Poster

Title: How variable are Sr isotope ratios in soil associations? – implications for extrapolating isoscapes

Lead author: Carol-Ann Craig, The James Hutton Institute, Aberdeen, UK

Author: Allan Lilly, The James Hutton Institute, Aberdeen, UK; Andrew J. Midwood, Terramera, Vancouver, BC, Canada; Barry Thornton, The James Hutton Institute, Aberdeen, UK; Gillian Green, The James Hutton Institute, Aberdeen, UK

Keywords: Strontium, $^{87}\text{Sr}/^{86}\text{Sr}$, Scotland, isoscape, soil

Content:

Strontium (Sr) isotope ratios ($^{87}\text{Sr}/^{86}\text{Sr}$) vary geographically and are a useful for food provenance, archaeological and forensic investigations, but all these applications require reference isoscape databases to correlate any measurements with possible locations. Existing isoscapes of bioavailable Sr isotopes for Scotland have been extrapolated based on underlying geology from a limited number of unevenly spread sampling points (Evans et al., 2018). However, the complex and highly variable nature of Scottish geology and soils may render this approach limited. This study examined bioavailable $^{87}\text{Sr}/^{86}\text{Sr}$ in soils for several transects across Scotland to assess if there was correlation with soil association, whether soil association was useful as an extrapolation tool and the influence of depth on soil Sr isotopes. Ninety-seven soil samples from the Scottish National Soil Archive held at the James Hutton Institute were analysed. The soils were from four discrete soil associations each which have similar parent materials or have developed within a particular landform. Bioavailable Sr was extracted using a method based on BS ISO19730:2009 (NH_4NO_3) and analysed for $^{87}\text{Sr}/^{86}\text{Sr}$ by Thermal Ionisation Mass Spectrometry. Soils from the same soil associations have variable $^{87}\text{Sr}/^{86}\text{Sr}$ values over a wide geographic area. Local influences on the parent ratio may be from the variability in radiogenic parent materials, marine aerosols, mixed drift material, and/or soil treatments. For the four depth profiles both soil depth, and soil treatments appear to affect Sr isotope ratios. Generally, soils from deeper in the profiles had $^{87}\text{Sr}/^{86}\text{Sr}$ aligned with the expected bedrock Sr ratio but in the upper soil profile the $^{87}\text{Sr}/^{86}\text{Sr}$ values were closer to the meteoric values. Shallower samples from the managed land also showed $^{87}\text{Sr}/^{86}\text{Sr}$ values slightly lower than meteoric water/expected ratios suggesting an additional influence, possibly soil treatment. This has implications for extrapolation of Sr isotope data over managed and non-managed land but also for the Sr isotope signature of plants differing in rooting depths at a single site. Ongoing work involves determination of the bioavailable Sr isotope ratios of additional agricultural soils across Scotland plus the harvested material of associated crop plants. REFERENCES Evans, Jane A., Mee, K., Chenery, C.A., Cartwright, C.E., Lee, K.A., Marchant, A.P., (2018). User guide for the Biosphere Isotope Domains GB (Version 1) dataset and web portal. In: British Geological Survey Open Report, OR/18/005, 21pp. International Organisation for Standardisation. (2009). Soil quality. Extraction of trace elements from soil using ammonium nitrate solution (ISO Standard No. 17930)

Topic groups: 03. Plant Ecophysiology,

Presentation types: Poster

Title: Characteristics of water isotopes translocation and fractionation in soil-plant system

Lead author: COSTINEL Diana, National R&D Institute for Cryogenics and Isotopic Technologies ICSI Valcea

Author: IONETE Roxana Elena, National R&D Institute for Cryogenics and Isotopic Technologies ICSI Valcea; BOTORAN Oana Romina, National R&D Institute for Cryogenics and Isotopic Technologies ICSI Valcea

Keywords: deuterium, oxygen 18, soil, deuterium depleted water, deuterated water

Content:

Eco-hydrological research using measurements of water-stable isotopes has evolved with technological and methodological advances (e.g. marker perspective to develop models of root water uptake). In this context, our work aims to assess aspects regarding the transport of waters with varying content in heavy stable isotope (^2H and ^{18}O), from soil to plants (two varieties of salad: Lettuce lollo bionda and *Lactuca sativa*), by following the isotopic profile of water transferred from soil to plants. Three distinct isotopic water types have been considered for incorporation in the soil-plant system: (i) tap water (TW), with stable isotope composition of $-9.6 \pm 0.3\text{‰}$ for $\delta^{18}\text{O}$, and $-67 \pm 1\text{‰}$ for $\delta^2\text{H}$ (~ 145 ppm of Deuterium, calculated after Hagemann (Hagemann, R. et al., 1970)); (ii) deuterium depleted water (DDW), with a stable isotope fingerprint of $-139.0 \pm 0.5\text{‰}$ for $\delta^{18}\text{O}$ and $-840 \pm 2\text{‰}$ for $\delta^2\text{H}$ (~ 25 ppm Deuterium content, calculated using water dilution techniques); and (iii) deuterated water (DW), having $+22.3 \pm 0.3\text{‰}$ for $\delta^{18}\text{O}$ and $+155 \pm 1\text{‰}$ for $\delta^2\text{H}$ (180 ppm of Deuterium). Using narrow and deeper grow bags, we attempted to decrease as much as possible the isotopic exchange between the soil and the environment. The "zero point" representing the water extracted from soil (universal soil), before watering, had the isotopic fingerprint of $-95 \pm 1\text{‰}$ for $\delta^2\text{H}$ (~ 141 ppm content in Deuterium) and $-12.0 \pm 0.3\text{‰}$ for $\delta^{18}\text{O}$; soil humidity was 54%. The isotopic content of irrigation waters, the isotopic exchange at the air-soil interface, and the phase of plant growth all had a role in the observed enrichment or depletion of heavy stable isotopes of hydrogen and oxygen in water extracted from plants and soils. In the first 6 days of observation, a decrease in deuterium content was observed for soils watered with DDW, followed by an approximately constant mean value of 73 ± 3 ppm deuterium content between sampling. Similar behaviors were observed for soil samples watered with TW: was calculate an average value of around 146 ± 1 ppm; for soil samples watered with DW, an average value of approximately 167 ± 2 ppm between sampling. In addition, deuterium-depleted water was shown to have a positive impact on plant evolution (e.g. the earlier formation of roots and stems) when compared to DW water. Heavy isotopes were concentrated when the plants entered in the vegetation. This in situ approach represent a novel and important solution to address the disentangle isotope effects challenges at soil-plant-atmosphere interactions based on water stable isotopes.

Topic groups: 02. Terrestrial and Aquatic Biogeochemistry,

Presentation types: Poster

Title: Stable isotopes quantify organic matter turnover into dissolved inorganic carbon in a drinking water reservoir

Lead author: Marlene Dordoni, Friedrich-Alexander Universität Erlangen-Nürnberg

Author:

Keywords: Carbon stable isotopes, Dissolved inorganic carbon, Dissolved organic carbon, Particulate organic carbon, Sedimentary matter, Organic matter, Drinking water reservoir, Metalimnetic Oxygen Minimum

Content:

Turnover of organic matter (OM) is essential in inland water bodies to outline their ecological status, potential of DOC removal for water quality and emissions of CO₂. Various sources (DOC, POC, and sedimentary matter) were investigated in the metalimnion and in the hypolimnion as the zones of most obvious respiration in a temperate water body (Rappbode Reservoir, Germany). Investigated parameters were inorganic carbon contents and stable carbon isotope ratios of DOC, POC, and sedimentary matter. Our work used data collected below a depth of 12 meters over an observation period of nine months with fortnightly sampling events between two stratification turnovers in March and December. DIC concentrations ranged between 0.30 and 0.53 mmolL⁻¹ and its stable carbon isotope ratios ($\delta^{13}\text{C}(\text{DIC})$) were between -15.1 and -7.2 ‰ vs VPDB. Our calculations applied DIC concentrations and $\delta^{13}\text{C}(\text{DIC})$ values together with isotope data of dissolved organic carbon ($\delta^{13}\text{C}(\text{DOC})$) and of in situ produced particulate organic carbon ($\delta^{13}\text{C}(\text{POC})$) as input parameters for mass balances. These ranged between -28.8 and -27.6 ‰ for $\delta^{13}\text{C}(\text{DOC})$ and between -35.2 and -26.8 ‰ for $\delta^{13}\text{C}(\text{POC})$. The isotope composition of sedimentary material ($\delta^{13}\text{C}(\text{SED})$) and external POC ($\delta^{13}\text{C}(\text{ExtPOC})$) were inferred from bibliographic records and corresponded to -30.7 ‰ and -31.8 ‰, respectively. Comparison of DIC concentration gains and stable isotope mass balances outlined that in situ produced POC (i.e. of aquatic origin) was the main contributor to DIC increases while contributions of DOC, ExtPOC and SED were minor. Within the metalimnion, samples from the Metalimnetic Oxygen Minimum (MOM) described a clear trend that further emphasized strong relationships between POC of aquatic origin and DIC. Our work shows the importance of in situ POC production as a major carbon source for turnover. It also shows that DOC removal by hypolimnetic and metalimnetic respiration is of minor importance.

Topic groups: 02. Terrestrial and Aquatic Biogeochemistry,

Presentation types: Poster

Title: A decade of measuring nitrate stable isotopes along the Elbe estuary

Lead author: Gesa Schulz, Helmholtz Center Hereon

Author: Tina Sanders, Helmholtz Center Hereon; Kirstin Dähnke, Helmholtz Center Hereon

Keywords: Eutrophication, nitrate stable isotopes, nitrogen turnover, estuary

Content:

The Elbe estuary (Germany) is the largest source of nitrogen to the German Bight/Southern North Sea, which is heavily affected by eutrophication. Estuaries can act as filters for coastal waters and as nitrate sources or sinks. The Elbe estuary – especially the port of Hamburg – produces nitrate that almost doubles the estuary's nitrate concentration in summer and thus fuels the pressing problem of eutrophication in the North Sea. In our study, we aimed to identify seasonal variation and long-term trends of riverine nitrogen input and turnover processes. We also aim to scale the nitrate load and turnover to agriculture using nitrate stable isotope analysis. Our dataset encompasses seasonal isotope and nutrient data from a total of 24 cruises along the estuary from 2011 to 2021. We evaluate stable isotope signatures and link them with dissolved inorganic nitrogen concentrations, oxygen saturation and turbidity to unravel nitrate sources and nitrate processing. Additional biweekly samples from the river input to the estuary are included in the evaluation. Using an isotope mixing model, we find that that on average 63 % of riverine nitrate input in winter is due to agriculture while 34 % come from forested regions. Temperature-dependent nitrogen turnover processes cause fractionation in the summer months. In the river section, fractionation is caused by denitrification leading to low nitrate concentrations entering the estuary. In contrast, two spots of nitrate production are evident in the estuary: the Hamburg port region and the estuarine maximum turbidity zone. The Hamburg port region in particular produces high amounts of nitrate that are conservatively transported downstream towards the maximum turbidity. In the maximum turbidity zone, isotope and concentration data suggest that marine fresh organic matter again fuels nitrification. Overall, the isotope data clearly confirm the dominance of agricultural nitrogen sources to the Elbe River. In summer months, additional nitrate production occurred at varying rates along the estuary, with clear effects on nitrate loads and nitrate isotopic composition. Though tentative, our data seem to suggest that reactivity in the estuarine turbidity zone increased, but this speculative result awaits confirmation in future campaigns and measurements. Overall, it is unclear how changing discharge and temperature patterns will affect nitrate production and transport in the future.

Topic groups: 02. Terrestrial and Aquatic Biogeochemistry,

Presentation types: Poster

Title: Nitrification rates and their driving microbial communities along the Elbe estuary

Lead author: Vanessa Russnak, Helmholtz-Zentrum hereon; Kirstin Dähnke, Helmholtz-Zentrum hereon

Author: Gesa Schulz, Helmholtz-Zentrum hereon; Tina Sanders, Helmholtz-Zentrum hereon

Keywords: Nitrification, microbial community, estuary

Content:

The Elbe estuary is one of the largest rivers in Germany, and is subject to intense maintenance dredging and shipping. Due to ongoing dredging and sediment input by tidal pumping, the water column in the estuary between the Hamburg harbor and the North Sea is in constant change. Organic matter concentrations in the estuary area have increased, which can enhance remineralization/nitrification in oxic waters. Global change can further affect turnover via external influences such as temperature and discharge. In our study, we evaluated nitrification potential, its changes and control mechanisms in the Elbe River and its estuary from the freshwater section to the North Sea. In particular, we aimed to assess variables that control nitrate generation in the water column and the influence of the port region on nitrification. Our dataset consist of seasonal isotope and nutrient data from a total of 6 stations along the estuary from 2021 and 2022. We used the isotope dilution method and nutrient uptake rates of ammonium & nitrate to determine the seasonal difference in nitrification. To map the multidimensionality of the Elbe estuary, we will use meta-genomics to map the abundance of the bacterial and archaeal community in the Elbe. We will assess the impact of community changes on natural abundance of stable isotope variations and isotope effects of nitrification in the water column. First results support that nitrification rates are highest in the harbor and the maximum turbidity zone of the Elbe River, and that they vary seasonally depending on the season, with highest rates found in spring and summer months when organic matter is abundant. The first mega-genomic analyses indicate clear differences in the microbial community between the sampling locations and seasons of the Elbe. However, it remains uncertain how further changing of discharge, sea level rise and temperature patterns will affect nitrate production and transport in the future.

Topic groups: 02. Terrestrial and Aquatic Biogeochemistry,

Presentation types: Poster

Title: Stable isotopes as indicators for the remaining gas generation potential at the Brånåsdalen decommissioned municipal waste landfill

Lead author: Christian Schöpke, Institute for Energy Technology

Author: Peter Dörsch, Norwegian University of Life Sciences; Ingar Johansen, Institute for Energy Technology; Stephane Polteau, Institute for Energy Technology; Pål Tore Mørkved, University of Bergen

Keywords: Landfills, methane oxidation, flux, anaerobic methanogenesis

Content:

Stable isotope measurements have been used as a tool for understanding landfill processes for over two decades. The stable isotope natural abundance signatures of CH₄ and CO₂ give insight into the extent and duration of processes forming and consuming landfill gas, based on known kinetic fractionation factors for carbon turnover, carbon decomposition, methanogenesis and methane oxidation. Variations in isotopic ratios of carbon in CH₄ isotopocules have been documented for many landfills and can be interpreted in terms of methanogenesis, gaseous transport (both diffusive and by mass-flow) and oxidation. The aim of this contribution is to test that $\delta^{13}\text{C}$ signatures of CO₂/CH₄ from different locations within a landfill, as well as the $\delta^2\text{H}$ signature of CH₄, reflect the remaining gas production potential of waste at different regions within a decommissioned municipal waste landfill based on principles of Rayleigh fractionation. Measured isotope ratios of gas from within the landfill will be compared to isotope ratios of diffuse emissions through the cover layer and at other release points. The results will be integrated into a landfill isotopic model used to estimate the remaining CH₄ emission potential at different locations within the landfill site as well as regional variations in oxidation efficiency of the cover layer. The results from this study are relevant for landfill owners and operators as a tool to estimate the spatial distribution, duration, and volume of gas emissions at a particular site and to define the landfill management strategy appropriately. In this presentation, we present preliminary results from the first phase of this project indicating a spatial heterogeneity of gas generation rates and isotopic composition throughout the landfill. We also present work on flux measurements from the landfill surface and ongoing integration of field isotope instrumentation with the aim of measuring the isotopic composition of surface emissions in situ.

Topic groups: 03. Plant Ecophysiology,

Presentation types: Poster

Title: Information hidden in tiny root fungi: Assessing stable isotope signatures of fungal pelotons of three *Epipactis* orchid species

Lead author: Franziska E. Zahn, BayCEER – Laboratory of Isotope Biogeochemistry, University of Bayreuth, Germany

Author: Erik Söll, BayCEER – Laboratory of Isotope Biogeochemistry, University of Bayreuth, Germany; Gerhard Gebauer, BayCEER – Laboratory of Isotope Biogeochemistry, University of Bayreuth, Germany

Keywords: orchid, peloton, mycorrhiza, stable isotopes, ^{15}N , ^{13}C , ^2H , *Epipactis*, mycoheterotrophy

Content:

Green orchids are known to depend on carbon supply from mycorrhizal fungi in their roots to a different extent. Stable isotope natural abundance analysis has become a common tool to identify trophical strategies since mycoheterotrophic plants depending on fungal carbon mirror the isotope signatures of their associating fungi. For many fungi, it has been straightforward to analyse their fruit bodies to aid in the assessment of mycoheterotrophy in plants. However, this proves difficult for the fungal partners of most orchid species, so-called Rhizoctonia as many of these ubiquitous saprotrophic fungi do not produce fruit bodies. Intracellular coils of hyphal loops called pelotons are the typical morphological feature of mycorrhizal fungi in orchid roots. Here we used a new approach examining the isotopic signature of pelotons mechanically extracted from three *Epipactis* species growing in different habitats in Bavaria (Germany). We determined total N concentration and $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of extracted pelotons as well as leaves and other fractions of the orchids and reference plants. Leaf isotopic signature and high leaf-N-concentrations of the three species were similar to previous findings and are likely due to their different fungal partners (Schiebold et al., 2017). ^{13}C enrichment of pelotons was highest compared to all orchid compounds, however, ^{13}C enrichment of pelotons extracted from *E. palustris*, a rhizoctonia-associated orchid, was relatively small. Further considering, that *E. palustris* pelotons differed neither in ^{15}N isotopic signature nor N concentration from leaves of reference plants, the small enrichment of ^{13}C of Rhizoctonia cannot be used as an indicator for the nutrition of rhizoctonia-associated orchids. Interestingly, all pelotons showed only a small or no enrichment in ^{15}N and similar N-concentrations as orchid leaves probably being the result of lysis of the fungi in the orchid roots. We suggest a selective fungus-to-plant compound transfer of rather ^{15}N -enriched protein-N while ^{15}N -depleted chitin-N of the fungal cell walls remains in the extracted pelotons. Our findings provide first hints towards a hitherto mostly unsolved mechanistic understanding of the fungus-to-plant matter exchange in orchids. References Schiebold, J M-I, Bidartondo, M I, Karasch, P, Gravendeel, B, Gebauer G. 2017. You are what you get from your fungi: nitrogen stable isotope patterns in *Epipactis* species. *Annals of Botany* 119(7): 1085-1095.

Topic groups: 04. Paleoclimatology & Archaeology,

Presentation types: Poster

Title: Terrestrial and Aquatic Snails from the Sultanate of Oman: Combined, an Excellent Climate Archive of the Early Bronze Age?

Lead author: Katharina E. Schmitt, Johannes Gutenberg-Universität Mainz

Author: Bernd R. Schöne, Johannes Gutenberg-Universität Mainz; Conrad Schmidt, Eberhard Karls Universität Tübingen

Keywords: Early Bronze Age, preservation state, climate reconstruction, Sultanate of Oman, bivalve sclerochronology

Content:

Al-Khashbah, today a small village in the Sultanate of Oman, is considered an important archaeological site because it is here where some of the first copper production sites, dating back to the Hafit period (Early Bronze Age), in Eastern Arabia, were found. It is still debated how an entire community could have supplied itself with water under the hot and dry climatic conditions similar to those of the present, because the irrigation system used until today, the falaj, was established in this area much later, in the Iron Age. One theory put forward by archaeologists is that so-called ditches, which surround many of the Early Bronze Age buildings called "towers", were filled with water and used for irrigation. This theory is supported by the aquatic snails (*Melanoides tuberculata*) found on the bottom of the ditches. These shells, dated to the Early Bronze Age, were examined for their state of preservation and the results obtained were compared with recent shells to determine possible diagenesis. Classical methods such as X-ray diffraction (XRD), Raman spectroscopy, inductively coupled plasma optical emission spectrometry (ICP-OES), cathodoluminescence (CL) and scanning electron microscope (SEM) were used. Additionally, immersion in Feigl solution was applied. If the shell was classified as well preserved, high-resolution sampling (micromilling) for stable isotope composition via GC-IRMS was applied. The stable oxygen isotope series from the aquatic shells were used to reconstruct water temperatures. However, since aquatic snails are not suitable for vegetation reconstruction and the determination of the origin of palaeo-precipitation regimes, representatives of a terrestrial snail species (*Zooteucus insularis*) were used for this purpose. Like the aquatic snails, they were radiocarbon dated, examined for diagenesis and then isotopically (stable carbon isotope values) analysed. Therefore, a combination of the two species made it possible to draw a fairly accurate picture of the climate during the Early Bronze Age.

Topic groups: 04. Paleoclimatology & Archaeology, 09. Isoscape, Spatial Variability of Stable Isotopes (Migration, Food Webs)

Presentation types: Poster

Title: Tracking the global human dietary history under the IsoMemo initiative

Lead author: Ricardo Fernandes, Max Planck Institute for the Science of Human History

Author:

Keywords: IsoMemo; global diet history; isotopes

Content:

The exploitation of food resources by humans shaped the Earth's history. A main historical division is usually made between hunter-gatherer and agriculturist modes of subsistence with many parts of the world showing a transition from the former to the latter. Within both of these, there were various degrees of environmental impacts and humans from across the globe consumed a wide variety of wild and domesticated animal and plant species. Tracking human diets has been one of the main applications of isotopic methods in archaeological research. Large volumes of isotopic data obtained from the analysis of human remains are now available allowing for broad-scale dietary studies. Under the IsoMemo initiative, a collaborative network was established among independent databases collecting isotopic data from different historical periods and regions across the world. This allowed for a near-global coverage of spatially and chronologically referenced archaeological human isotopic data. In this contribution, a global diachronic human isoscape will be presented. This will be used to discuss the various dietary histories across the globe, what the data can tell us about the impact that humans had on the landscape, and how such an isoscape can be used to identify data gaps and suggest future research targets.

Topic groups: 08. Soil Carbon and Nitrogen Cycling, with Focus on Agricultural Soils,

Presentation types: Poster

Title: New technique reveals low gross nitrification rates and high variability in field applications

Lead author: C. Florian Stange, BGR

Author: Susanne Stadler, BGR

Keywords: Nitrification, Heterogeneity, Soil, Nitrogen cycle

Content:

Nitrification is one major part of the terrestrial nitrogen cycle and is responsible for the nitrogen supply for microbes and plants in agriculture. A growing interest in quantifying actual gross rates of nitrification results from an increasing contribution to the pollution of ground- and surface water and climate change. Laboratory experiments and measurements of nitrification in soil cores of the last decades suggest very high gross nitrification rates – much higher than net nitrification rates. Yet, there are only few studies that investigate gross rates directly in the field without separating the investigated soil part from the rest of the soil. The poster presents the newly developed and the results and discusses potential explanations for the observations of the low gross nitrification rates on agricultural soils. In total, nitrification rates were determined on 11 plots of 2 x 2 m² each on a cultivated sandy soil in the Fuhrberger Feld, Germany, transferring the 15N-pool dilution method to the field, showing gross nitrification rates between 3.9 and 17.9 μmol kg⁻¹ soil d⁻¹. The rates of the 11 individual plots show a correlation with the mean soil temperature during field incubation. The temperature-normalized nitrification rates (20°C) show a negative linear correlation with the C/N ratio of the plots ($r^2=0.78$). This supports the hypothesis that nitrification in the field strongly depends on the amount of the substrates ammonium or ammonia, respectively, or on its supply by N-mineralization. Our study provides the base for further in-field investigations of gross nitrification to ensure the transferability of extensive existing knowledge from laboratory experiments to the field.

Topic groups: 06. Food Authenticity, Nutrition, Forensic,

Presentation types: Poster

Title: Wild or captive bred? Stable isotope analysis of shed skins of green tree pythons as forensic evidence for prohibited trade

Lead author: Jitka Kufnerova, ?Institute for Environmental Studies, Charles University

Author: Kateřina Jandová, ?Institute for Environmental Studies, Charles University; Jaroslav Kukla, ?Institute for Environmental Studies, Charles University; Jakub Trubač, Institute of Geochemistry, Mineralogy and Mineral Resources, Charles University; Jaroslava Frouzová, ?Institute for Environmental Studies, Charles University; Eliška Rajmonová, ?Institute for Environmental Studies, Charles University

Keywords: multielement stable isotope analysis, provenance analysis, wildlife forensics, CITES

Content:

Green tree pythons (*Morelia viridis*) are highly sought-after Indonesian/Papuan NG/Australian snakes that are extensively internationally traded as a pet. The trade with wild animals is prohibited because they are subject to the Convention on International Trade in Endangered Species of Flora and Fauna, CITES. However, there are doubts about the true origin of animals supposedly bred in captivity, because the wild caught animals might be channelled through breeding farms. Now there are very few possibilities of distinguishing wild from captive bred animals. Thus, we are proposing to develop a new non-invasive method as a tool applicable in wildlife forensics based on multielement stable isotope and trace element analysis combined with a multivariate discriminant analysis on shed skins to distinguish wild from captive bred animals. So far, multielement stable isotope analysis was performed on shed skins of 22 individuals traded from their country of origin, Indonesia, to Czech Republic. Differences in stable isotope composition of H, C, N, O, S in skins shed immediately after being traded from Indonesia and skins shed after staying in the Czech Republic are expected. In addition, the effect of position on a snake body that is sampled (neck ventral, neck dorsal, mid body ventral, mid body dorsal, tail) as well as the effect of washing the skins with chloroform-methanol mixture before analysis are also tested.

Topic groups: 06. Food Authenticity, Nutrition, Forensic,

Presentation types: Poster

Title: Legal or illegal pet tortoises? Stable isotope analysis can provide an answer

Lead author: Jitka Kufnerova, Institute for Environmental Studies, Faculty of Science, Charles University, Ben

Author: Jaroslav Kukla, Institute for Environmental Studies, Faculty of Science, Charles University, Ben; Kateřina Jandová, Institute for Environmental Studies, Faculty of Science, Charles University, Ben; Jakub Trubač, Institute of Geochemistry, Mineralogy and Mineral Resources, Faculty of Science; Jaroslava Frouzová, Institute for Environmental Studies, Faculty of Science, Charles University, Ben; Eliška Rajmonová, Institute for Environmental Studies, Faculty of Science, Charles University, Ben

Keywords: multielement stable isotope analysis, wildlife forensics, CITES, tortoises,

Content:

European species of tortoises of the genus *Testudo* (*T.hermanni*, *T.graeca*, *T.marginata*) are very popular pets. Therefore, they have also become the object of illegal trade, where even current statistics of seized live specimens list hundreds of individuals who are illegally trafficked each year. Legal trade is allowed in the EU with proven captive-bred specimens. Declaring smuggled turtles as bred in captivity is one of the most often used misdeclarations that proves poorly to the accused. One of the promising method to distinguish wild caught from captive bred specimen is stable isotope analysis. With its help, it is possible to better estimate the geographical origin of animals. Carapace protein keratin is an ideal material for stable isotope analysis. Sampling from the edge of the carapace is not considered to be an invasive method, so it can be easily applied to live specimens without any harm. In our study, we analyze the basic set of stable isotopes (H, C, N, O, S) within the collection of dozens of shells of European tortoises. Our material comes from the CITES rescue center, where the specimens were placed after their seizure.

Topic groups: 06. Food Authenticity, Nutrition, Forensic,

Presentation types: Poster

Title: Applications of the stable isotope ratio method to identify the raw materials for explosives

Lead author: Andrius Garbaras, General Jonas Zemaitis Lithuanian Military Academy

Author:

Keywords: Explosives origin identification

Content:

Explosives can be identified using current analytical methods, but it is often not possible to distinguish the sources of the material from which the explosives are made. The stable isotope ratio ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$, $\delta^{18}\text{O}$, $\delta^{34}\text{S}$, δD) method is used to facilitate the identification of raw materials. For example the results of 30 different PETN, TNT and ANFO samples show that the different families of explosives are clearly distinguished both by their specific isotope ratios and by their combination with the respective element concentrations. Linking two or more isotopes results in an even more precise separation according to the origin of the explosives and / or the manufacturing process. Information on isotope ratios of the following explosives can be found in the literature: TNT, ANFO, PETN, RDX, HMX, nitroglycerin, gunpowder, ammonium nitrate, Semtex, perchlorates, TATB, LX. Countries where explosives were manufactured: France, former Yugoslavia, USA, Australia, Philippines, Lithuania (manufacturer not provided), Indonesia, China. Delta values (of carbon, nitrogen, sulphur) of the following substances are presented in the work: sulphur, magnesium sulfate, ammonium sulfate, potassium fertilizers, activated carbon. Materials purchased in stores from different suppliers in Lithuania for agricultural use. Measurements were made with EA-IRMS system (FlashEA 1112 – Delta V Advantage, Thermo) in Isotopic Research Laboratory, FTMC, Vilnius, Lithuania.

Topic groups: 03. Plant Ecophysiology,

Presentation types: Poster

Title: The underappreciated value of hydrogen isotopes in elucidating heterotrophic carbon gains by plants

Lead author: Gerhard Gebauer, BayCEER - Laboratory of Isotope Biogeochemistry, University of Bayreuth

Keywords: Carbon isotopes, hydrogen isotopes, nitrogen isotopes, mycorrhiza, mycoheterotrophy, photosynthesis

Content:

Green plants are conventionally considered as photoautotrophic organisms, i.e. as primary producers covering their entire carbon demand through photosynthesis. Only very few exceptions from this dogma, e.g. carnivorous plants capable of capturing insects, have been accepted as curiosities for long times by plant sciences. With the discovery of simultaneous carbon gains from photosynthesis and from a fungal source by green orchids thriving in the deepest shade of forest grounds based on stable isotope abundance analysis (Gebauer & Meyer, 2003) this simplistic view on plant carbon nutrition was for the first time seriously called into question. This finding of a mixotrophic carbon nutrition initiated a whole bunch of investigations confirming partially mycoheterotrophic carbon gains as taxonomically and geographically widely distributed among plants collected in a wide set of habitats worldwide and occurring across different types of mycorrhiza and taxonomic groups of fungi. Vastly developing molecular ecological approaches became important tools to identify the players involved in belowground plant-fungal networks of steadily increasing complexity. Despite all these developments, stable isotope natural abundance analysis remained a core tool to separate heterotrophic fungus-to-plant carbon fluxes from carbon gains through photosynthesis. In the beginning, natural ^{13}C and ^{15}N enrichment in tissues of fungi simultaneously forming ectomycorrhizas with temperate forest trees was used to elucidate fungus-to-plant organic matter fluxes. Later on it turned out that not all fungal groups are necessarily enriched in ^{13}C . Based on ^{15}N enrichments without simultaneous ^{13}C enrichment found for green orchids mycorrhizal with fungi of the saprotrophic rhizoctonia group a "cryptic mycoheterotrophy" was postulated for this important group among the Orchidaceae (Hynson et al. 2013). This puzzle of cryptic carbon gain from a fungal source was solved by adding hydrogen isotope abundance to carbon and nitrogen (Gebauer et al. 2016). Here I present for the first time a comparison of carbon and hydrogen isotope natural abundances in order to test their suitability as a tool to quantify mycoheterotrophic carbon gains based on linear two-source mixing models. Both variables turned out as closely correlated ($R^2 = 0.845$) and hydrogen isotope abundance was even better suited for quantification purposes of heterotrophic carbon gains due to smaller within-species standard deviations. References Gebauer G., Meyer M. (2003) *New Phytologist* 160: 209-223. Gebauer G. et al. (2016) *New Phytologist* 211: 11-15. Hynson N.A., ... Gebauer G. (2013) The Physiological Ecology of Mycoheterotrophy. In: V.S.F.T. Merckx (ed.) *Mycoheterotrophy: The Biology of Plants Living on Fungi*, pp 297-342.

Topic groups: 03. Plant Ecophysiology,

Presentation types: Poster

Title: Drought effect on tree-ring $\delta^{13}\text{C}$ of sessile oak from Thayatal national park

Lead author: Kathiravan Meeran, Institute of Soil Research, Universität für Bodenkultur Wien

Author: Michael Grabner, Institute of Wood Technology and Renewable Materials, Universität für Bodenkultur; Katharina Schott, Institute of Soil Research, Universität für Bodenkultur Wien; Marcela Van Loo, Austrian Research Centre for Forests; Roman Ufimov, Austrian Research Centre for Forests; Andrea Watzinger, Institute of Soil Research, Universität für Bodenkultur Wien

Keywords: Drought, stable isotopes, tree-rings, sessile oak

Content:

Sessile oak (*Quercus petraea*) is an ecologically and economically important species in middle Europe. Its high tolerance to a wide range of environmental and climatic conditions such as drought makes it an ideal candidate for studying climate change adaptation strategies in forestry. However, less is known about the vulnerability of individuals within the species which is crucial to understand why some trees survive while others succumb to drought. The difference in the vulnerability of trees within a species can be related to several factors such as long-term climatic stressors, water-use strategies, genetic traits and inter- and intraspecific competition. Moreover, we expect that autochthonous oak stands in the national park might pose an important genetic resource, especially with respect to drought tolerance. As a part of the TERZ (Thayataler Eichen - genetische Ressource für die Zukunft) project, we sampled tree-rings from 404 Sessile oak trees spatially distributed across the Thayatal reserve forest. We measured tree-ring width to investigate the tree radial growth rate. Using an elemental analyzer (Flash 2000) coupled to an isotope ratio mass spectrometer (Delta V advantage), we measured the $\delta^{13}\text{C}$ and C content in tree-rings of a wet year (1987) and a drought year (1994) to infer the change in tree water-use strategies. Our preliminary results suggest that $\delta^{13}\text{C}$ and carbon content in tree rings was higher during the drought year than during the wet year indicating that photosynthetic capacity and/or stomatal conductance were altered under drought. Our presentation at the meeting will further discuss the linkage of drought response of $\delta^{13}\text{C}$ and carbon content in tree-rings to the genetic traits, tree growth rate as well as long-term climatic and environmental stressors.

Topic groups: 01. Methodological Advances,

Presentation types: Poster

Title: Mobile, discrete vapor sampling for in-situ measurements of matrix-bound water stable isotopes

Lead author: Barbara Herbstritt, Chair of Hydrology, Albert Ludwigs University, Freiburg, Germany

Author: Benjamin Gralher, Department of Hydrosociences, Technical University of Dresden, Germany; Stefan Seeger, Chair of Hydrology, Albert Ludwigs University, Freiburg, Germany; Michael Rinderer, geo7, Bern, Switzerland; Markus Weiler, Chair of Hydrology, Albert Ludwigs University, Freiburg, Germany

Keywords: water stable isotopes, laser-based isotope analysis, CRDS, mobile water vapor sampling, sample storage

Content:

Measurement of water stable isotopes ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) allows tracking water movement along ecohydrological pathways and has proven to be a powerful tool in ecohydrology. With traditional methods, soils and plants are sampled destructively followed by water extraction and isotope analysis of the gained water samples. The invention of laser-based analyzers with their continuous measurement capabilities allowed for the development of non-destructive and minimal-invasive approaches. Moreover, due to their potential field-deployability in-situ applications became feasible. However, isotope analyzers are expensive and sensitive devices, which are heavy and rely on electrical power. In-situ isotope analyses in rough and spacious terrain are thus almost impossible. To overcome these limitations, we aimed at collecting discrete vapor samples in the field for later analysis in the lab. Commercially available gas sampling bags tend to be either oversized (> 2.5 L) or not suitable for long-term storage (> 3 to 7 days). Hence, a custom-made solution was needed. We tested different bag materials, combined with different types of valves and closures for diffusion-tightness and inertness during storage as well as for practical handling during filling and analysis. To re-use sampling bags, flushing protocols with dry gas vs vapor of different moistures were systematically tested. For validation, repeated gasbag measurements were compared to direct measurements through the in-situ probes from which the bags were filled. Calibration with co-measured standards sufficing the principle of identical treatment yielded accuracies of 0.41% for $\delta^{18}\text{O}$ and 1.93% for $\delta^2\text{H}$ after one day of storage. Our technique is inexpensive and particularly suitable in combination with minimal invasive water vapor sampling probes that are routinely used in soils and tree xylem in the field (Volkman et al., 2014, Volkman et al., 2016a). It is an important step towards monitoring stable isotope distributions in soils and trees without bringing heavy and expensive equipment to the field and therefore a promising tool for many applications in ecohydrology.

Topic groups: 01. Methodological Advances,

Presentation types: Poster

Title: Practical measurements of water stable isotopes in tree stems and soils using conservative water vapor storage

Lead author: Ruth-Kristina Magh, Swedish University of Agricultural Sciences, Forest Ecology Management, Sweden

Author: Benjamin Gralher, Hydrology, University of Freiburg, Germany; Barbara Herbstritt, Hydrology, University of Freiburg, Germany; Angelika Kübert, Ecosystem Physiology, University of Freiburg, Germany; Hyungwoo Lim, Swedish University of Agricultural Sciences, Forest Ecology Management, Sweden; Tomas Lundmark, Swedish University of Agricultural Sciences, Forest Ecology Management, Sweden; John Marshall, Swedish University of Agricultural Sciences, Forest Ecology Management, Sweden

Keywords: water stable isotopes, laser-based isotope analysis, CRDS, mobile water vapor sampling, sample storage

Content:

The interest of inferring plant water uptake depths/patterns and water movements through the soil matrix grew tremendously in recent years and, studies have shown the use of in-situ measurement systems based on laser absorption spectroscopy making e.g. plant or soil water stable isotope datasets available on-site and in real-time. However useful, in-situ systems are limited to sites with power supply and require constant care. We tested, first in the lab and then in the field, a method for equilibrating, collecting, storing, and finally analysing water vapour for its isotopic composition. We used a vapour storage vial system (VSVS) that relies on in-situ sampling, using a pump and a flow meter powered through a small battery into crimp neck vials with a double coated lid, and measuring the samples in a laboratory. We tested the utility of the sampling method and the reliability of the VSVS to faithfully store the isotopic composition of its content by sampling a range of water vapour of known isotopic compositions (from -95 to 1700‰ for $\delta^2\text{H}$) and measuring the isotopic signature after the storage period. Samples for the field trial were taken in a tracer pulse chase experiment in a boreal forest in Northern Sweden. We were able to prove the utility of the sampling method within defined uncertainties (0.6 to 4.4‰ for $\delta^2\text{H}$ and 0.6 to 0.8‰ for $\delta^{18}\text{O}$) for natural abundance. For in ^2H -enriched samples the range was adapted to higher uncertainty. We detected a small change in the isotopic composition of the sample after a longer storage period, which was consistently greater for oxygen but correctable by linear models. Our method has the potential to combine the best of two worlds: sampling in-situ in high spatial or temporal resolution while measuring in the laboratory, could solve problems with location biases and give the community a tool that is not only cost-efficient but also easy to use while all components are commercially available.

Topic groups: 08. Soil Carbon and Nitrogen Cycling, with Focus on Agricultural Soils,

Presentation types: Poster

Title: Impact of plant diversity on microbial community and carbon use efficiency in boreal agricultural soil

Lead author: Rashmi Shrestha, University of Helsinki

Author: Jussi Heinonsalo, University of Helsinki

Keywords: Plant diversity, cover crops, carbon use efficiency, carbon sequestration

Content:

Soil biodiversity loss caused by conventional agricultural practices has been identified as a major threat to SOC storage, which is crucial for both soil health and climate regulation. So, improved agricultural management is needed to enhance soil biodiversity and SOC storage and mitigate climate change. Using diverse cover crops avoiding winter bare fields may be one of the climate friendly practices. However, the effectiveness of cover cropping relies on microbial activities. Soil microbes use most plant-derived carbon and either they produce CO₂ or incorporate carbon into their biomass and after death microbial necromass may contribute to stable carbon. Soil microbial carbon use efficiency (CUE), amount of carbon used for microbial growth relative to total carbon uptake, is an important physiological feature in determining the fate of carbon during decomposition in soils. CUE can be influenced by several factors such as soil properties, microbial community structure and composition. In addition, impacts of plant diversity including plant species richness, functional group richness and presence and abundance of specific plant functional groups, on microbial community structure and CUE and SOC storage can be highly peculiar to agroecosystems. Therefore, studying effect of diverse cover cropping on soil microbial community composition and CUE at regional scale is essential to understand the soil carbon cycling and assess its viability as a climate friendly practice. Here we used the field experiment established in May 2019 in Viikki research farm at University of Helsinki, Finland to study plant diversity (species richness and functional diversity) impacts on microbial community structure and CUE and SOC storage. Barley was grown as main crop with 1,2,4 and 8 undersown cover crop species to obtain four diversity levels. Barley alone with and without herbicide and bare plots were used as controls. The grouping was designed based on the functional traits of cover crops (shallow vs deep-rooted, N₂-fixation vs no fixation). We collected soil samples in August 2020 and performed CUE analysis by incubating soil with ¹⁸O labelled water. We measured the enrichment level of ¹⁸O-molecules using Isotope-ratio mass spectrometry and sequenced bacterial and fungal community from the same soil using Miseq approach. We will present the results and discuss effects of plant diversity on microbial growth, respiration, CUE and microbial biomass turnover in relation to microbial community composition. Obtained results will provide answers if diverse cover cropping is suitable climate smart agricultural practice in boreal region.

Topic groups: 01. Methodological Advances,

Presentation types: Poster

Title: Coping with spectral interferences when measuring vegetables' water (vapor) isotopic composition

Lead author: Natalie Orlowski, University of Freiburg, Chair of Hydrology

Author: Lena Wengeler, University of Freiburg, Chair of Hydrology; Barbara Herbstritt, University of Freiburg, Chair of Hydrology

Keywords: water isotopes, spectral interferences, water extraction, VOC

Content:

Ecohydrological, biogeochemical and atmospheric research rely on accurate and precise measurements of ^{18}O and ^2H isotope ratios for tracing water movement through the critical zone. Many studies apply different water extraction or water vapor equilibration techniques to obtain $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values from soil and plant water. However, volatile organic compounds can be co-extracted (or equilibrated with the water vapor) together with the soil or plant water (vapor), which can lead to isotopic discrepancies through spectral interferences in isotope ratio infrared spectroscopic (IRIS) analysis. While some software solutions exist for spectral interference detection during liquid water IRIS analysis, limited tools exist for the post-correction of direct vapor-mode IRIS data e.g., from in situ water vapor measurements or the direct water vapor equilibration laser spectrometry method (DVE-LS). Our study investigates how different water stable isotope extraction/equilibration techniques i.e., direct in situ vapor measurements, DVE-LS and cryogenic vacuum extraction compare to each other for measurements of different types of vegetables via cavity ring-down spectrometry (CRDS). We further examine how co-extracted organic contaminants (i.e., methanol and ethanol) affect the isotopic ratios of these measured vegetables (liquid vs. vapor CRDS measurements). We explore different options of post-correcting isotopic discrepancies in order to maximize the accuracy and precision of CRDS measurements from vegetables. Our study highlights the importance and necessity of plant water (vapor) data post-correction from laser based isotope measurements.

Topic groups: 09. Isoscape, Spatial Variability of Stable Isotopes (Migration, Food Webs), 01. Methodological Advances

Presentation types: Poster

Title: Lipid-normalization of hydrogen stable isotope ratios of tissues from aquatic organisms

Lead author: Mikko Kiljunen, University of Jyväskylä

Author: Roger Jones, University of Jyväskylä; Heikki Hämäläinen, University of Jyväskylä; Jos Schilder, University of Jyväskylä

Keywords: Deuterium, Fish, Lipid-extraction, Muscle tissue, Models, Whole fish

Content:

In addressing ecological problems, hydrogen stable isotopes ($\delta^2\text{H}$) have mainly been restricted to studies of animal migration. However, in recent years, applications using hydrogen stable isotopes have demonstrated their potential to provide novel insights in food web studies, especially of aquatic systems. As lipids are isotopically lighter than other tissues, routing of lipids directly from dietary items is expected to have a significant impact on bulk tissue-diet hydrogen isotope relations, as is well established for carbon. Correction of carbon isotope values to take account of the varying content of ^{13}C -depleted lipids is commonly undertaken using lipid-normalization models, but no such procedures for hydrogen currently exist. Here we aim to address two questions concerning lipid-normalization of hydrogen isotope ratios: 1) Is it necessary to account for the effects of variation in lipid content on hydrogen isotope ratios? 2) If so, can a simple procedure be developed to deal with this variation, comparable to that already used for carbon? To answer these questions, we extracted lipids from around 100 individual freshwater fish tissue samples (8 species) with varying lipid content. The original tissue, lipid-extracted tissue and extracted lipids were analysed for hydrogen stable isotope ratios, and for the amount of carbon and nitrogen. We also estimated the lipid content of the original tissue. The mean difference in $\delta^2\text{H}$ between lipid-extracted tissue and lipids was 118‰ (SD: 28, min-max: 73-194). The mean change in tissue $\delta^2\text{H}$ following lipid removal ($\Delta^2\text{H}$) was 29‰ (SD:18, min-max: 7-96). We found a strong inverse relationship between $\Delta^2\text{H}$ and the original C:N ratio of a sample, enabling development of a simple model for lipid-normalization of tissue hydrogen isotope values. Our results indicate that lipids may cause substantial variability in hydrogen stable isotope values of fish tissues, so it would appear prudent to remove such variability prior to using the data in diet and food web models. Our new lipid-normalization model is a cost-effective way to normalize the $\delta^2\text{H}$ values of large numbers of samples and should be applicable to a wide range of freshwater fish species (and potentially to other organisms) in studies applying $\delta^2\text{H}$ analyses to ecological problems.

Topic groups: 01. Methodological Advances,

Presentation types: Poster

Title: Modified GasBench and GC-Isolink peripherals to determine stable isotope ratios of nitrate and trace quantities of methane

Lead author: Ljubov Polakova, Biology Centre Czech Academy of Sciences

Author: Stanislav Jabinski, Biology Centre Czech Academy of Sciences & University of South Bohemia; Travis Meador, Biology Centre Czech Academy of Sciences & University of South Bohemia

Keywords: methane, nitrate, nitrous oxide, valco, GasBench, GC-Isolink

Content:

Methane (CH₄) and nitrous oxide (N₂O) represent substrates and products of redox reactions in soils and sediments and have important consequences for ecosystem energy balance and global climate. N₂O further serves as an analyte in the investigation of nitrate cycling and contamination in aquatic systems. Here we demonstrate a modified, continuous-flow instrument configuration to determine the stable C and H isotope ratios of CH₄ and stable N and O isotopes of nitrate. The GasBench double-needle, high-flow (25 mL min⁻¹) "Flush-Fill" interface was modified to support headspace sampling and subsequent purification, concentration, and separation of CH₄ and N₂O from atmospheric gases. For CH₄ analysis, flow from the GasBench interface is diverted to the combustion or high-temperature conversion reactors of a GC-Isolink interface via microchannel devices, then eventually to a Conflo interface and finally to the isotope ratio mass spectrometer (IRMS). Precision of δ¹³C- and δ²H-CH₄ measurements at the limit of detection (5 ppm and 400 ppm, respectively) were < 2‰ and < 4‰, respectively. For nitrate analyses, measurement uncertainty (± one standard deviation of the mean) for both δ¹⁵N and δ¹⁸O of nitrate was < 0.5‰ at 0.4 ppm (NO₃-N), and < 0.7‰ and 0.5‰, respectively, at 0.1 ppm (NO₃-N).

Topic groups: 06. Food Authenticity, Nutrition, Forensic,

Presentation types: Poster

Title: Stable isotope reference database of Finnish strawberries

Lead author: Annikki Welling, Finnish Food Authority

Author: Simo Jokinen, Finnish Food Authority

Keywords: reference database, stable light isotopes, strawberry, food fraud,

Content:

Welling Annikki¹, Jokinen Simo¹, Järvinen Janne¹, Karhu Saila², Rantanen Marja², Nieminen Janne¹ ¹Finnish Food Authority, ²Natural Resources Institute Finland (Luke) Food frauds are ever increasing problem in globalizing food market with increasing production chains. Mislabeling genetic or geographical origin or production method (conventional versus organic) or high value products can provide easy way to gain profit, mislead the consumers and disturb commercial competition. Several methods have been developed to verify the authenticity of the original product or to reveal fraud. The analyses of stable isotope ratios of chemical elements have proven very efficient in studies of geographic origin of various food products. These methods require a reference database that is statistical model of analytical results from the same food products that are subject for forgery. This type of reference databases has not been available in Finland for agricultural products. Finnish strawberries are highly valued and are known to be subject for counterfeit especially during the beginning and at the end of the season. To adopt a new method that could be used for studying geographical origin of Finnish strawberries, we collected berries from the strawberry fields covering the whole growing region of Finland during three consecutive years. Isotope ratios of oxygen (¹⁸O/¹⁶O) and hydrogen (D/H) from cellular water and oxygen (¹⁸O/¹⁶O), hydrogen (D/H), carbon (¹³C/¹²C), sulfur (³⁴S/³²S) and nitrogen (¹⁵N/¹⁴N) from solid material were analyzed. The following approaches was used: EA-IRMS (¹³C/¹²C, ³⁴S/³²S ja ¹⁵N/¹⁴N from solid matrix), pyrolyse-EA-IRMS (¹⁸O/¹⁶O ja D/H from sold matrix), EA-Chrom-IRMS (D/H from cellular water) and head space equilibrium-IRMS (¹⁸O/¹⁶O from cellular water). The resulting isotope ratios were used to create a statistical model. This model could be used to predict whether unknow strawberry samples are of Finnish origin or not based on their analyzed isotope ratios. We will discuss the various factors that should be considered when collecting samples for this type of reference database and how this database should be maintained. In addition, we discuss what are the chemical elements that are the most powerful in distinguishing the geographic origin in high latitudes such as in Finland. And finally, we discuss the practical approach of this type of methods, taking into consideration from where the import of fraudulent products is most likely to occur.

Topic groups: 01. Methodological Advances,

Presentation types: Poster

Title: The effects of freezing and thawing to a stable isotopic composition of different elements in an organic sample

Lead author: Simo Jokinen, Finnish Food Authority

Author: Maria Lahtinen, Finnish Food Authority; Annikki Welling, Finnish Food Authority

Keywords: $2\text{H}/1\text{H}$, $13\text{C}/12\text{C}$, $15\text{N}/14\text{N}$, $18\text{O}/16\text{O}$, sample storage, freeze-thaw

Content:

Freezing of a sample consisting of liquids or solid organic matter, is a common laboratory procedure for storage or transporting, before the actual sample analysis. A frozen sample can be thawed and re-frozen from few to numerous times due to a sub-sampling of it, if different laboratory analyses are intended to be made. Additionally, sample might be kept frozen for long periods of time before the actual laboratory analysis will be conducted. The possible effects of either repeated cycles of freezing and thawing of a sample, or a long freezing time of sample, are not well known to the stable isotopic composition of different elements such as hydrogen ($2\text{H}/1\text{H}$), carbon ($13\text{C}/12\text{C}$), nitrogen ($15\text{N}/14\text{N}$) or oxygen ($18\text{O}/16\text{O}$). We conducted two experiments to study i) the effect of repeated cycles of freezing and thawing on a sample, and ii) the effect of a long freezing time, to four different sample types. The following stable isotope ratios were planned to be analyzed: $2\text{H}/1\text{H}$, $13\text{C}/12\text{C}$, $15\text{N}/14\text{N}$ and $18\text{O}/16\text{O}$ from the solids as well as $2\text{H}/1\text{H}$ and $18\text{O}/16\text{O}$ from the liquids. Samples were chosen based on two different categories. First, samples needed to be growing in Finnish agricultural conditions, and be potentially vulnerable for food frauds such as mislabeling of the geographical origin. Second, the composition of the samples needed to be distinct from each other based on their contents of water, carbohydrates, dietary fiber or protein. The chosen samples were strawberry (*Fragaria ananassa*), potato (*Solanum tuberosum*), champignon (*Agaricus bisporus*) and pea (*Lathyrus oleraceus*). All samples except pea are known to be targets to the mislabeling of a geographical origin. The nutritional compositions are clearly distinct between the sample types. During the experiment i), a sample was first frozen for a certain time and thawed. After thawing, sub-samples were taken for different stable isotope analyses. The same sample was then re-frozen immediately to be equally sampled after a certain time. Altogether, the experiment consisted of six sampling times during the two months experiment for each sample type, and a starting point. During the experiment ii), samples were frozen for minimum 1 yr storage time before the thawing and analyses. Results from both experiments are compared to the starting point of the experiments, when all the above-listed analyses were also made to the unfrozen sample types. The initial results of the experiments will be presented and discussed.

Topic groups: 08. Soil Carbon and Nitrogen Cycling, with Focus on Agricultural Soils,

Presentation types: Poster

Title: Temperature sensitivity of mineral-associated soil organic carbon is not related to its age

Lead author: Kristiina Karhu, University of Helsinki

Author:

Keywords: Soil organic matter, temperature sensitivity, decomposition, climate change, ^{13}C natural abundance, Bayesian statistics

Content:

Most of the carbon (C) stored in temperate arable soils is present in the mineral-associated organic-matter (MOM) fraction. Better estimates on the temperature sensitivity of C residing in the MOM fraction are needed for reliable predictions of soil C turnover responses to global warming, and the long-term flux of carbon dioxide (CO_2) from soils to the atmosphere. The decomposition rate of particulate organic matter (POM) has been linked to its intrinsic chemical complexity, whereas the decomposition rate of stabilized OM relates to its incorporation into organo-mineral complexes and association with mineral surfaces. Our objectives were to quantify 1) the temperature sensitivity of POM and MOM fractions, and 2) the sensitivity of older and younger C within these size fractions. We hypothesized: 1) that the temperature sensitivity of POM increases with increasing age (and thus presumably with increasing chemical recalcitrance) following the Arrhenius equation, and 2) that the temperature sensitivity of C in MOM is less affected by age than C in POM. We also hypothesized, 3) that overall, the decomposition of MOM is less sensitive to temperature than POM, because the mineral-association limits the decomposition of MOM. We utilized a Danish long-term experiment, where C4-plant silage maize had replaced C3-crops 25 years ago, which allowed us to calculate the contribution of old, C3-C (> 25 years), and recent C4-C (<25 years) in soil C fractions and CO_2 produced from soil. The fractions were separated with physical size separation (POM>63 μm , MOM<63 μm). We incubated the size fractions (POM and MOM), and bulk soils (<2 mm) sequentially at 6, 18, 26 and 34 °C. From the evolution of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ at different temperatures we calculated the temperature sensitivity of old and recent C in the POM and MOM fractions. Overall, the temperature sensitivity was slightly higher or similar for POM than for MOM fractions. Within the POM fraction, it seemed that the temperature sensitivity followed the carbon quality-temperature hypothesis, and was higher for the older, presumably more recalcitrant C. For the MOM fraction, the temperature sensitivity was unrelated to the age of C. This suggests that stabilizing mechanisms rather than chemical quality of C determine the temperature sensitivity of C residing in the MOM fraction, and thus for the large part of soil C. Reference: Karhu, K. et al. (2019): Similar temperature sensitivity of soil mineral-associated organic carbon regardless of age. *Soil Biology & Biochemistry*, 136: p. 107527.

Topic groups: 08. Soil Carbon and Nitrogen Cycling, with Focus on Agricultural Soils,

Presentation types: Poster

Title: How passive warming changes mineral soil microbial communities and stabilization of microbial residues to soil?

Lead author: Outi-Maaria Sietiö, Department of Forest Sciences, University of Helsinki, Finland

Author: Tero Tuomivirta, Natural Resources Institute Finland; Aino Seppänen, Department of Forest Sciences, University of Helsinki, Finland; Kevin Mganga, Department of Forest Sciences, University of Helsinki, Finland; Päivi Merilä, Natural Resources Institute Finland; Nele Meyer, Department of Soil Ecology, University of Bayreuth, Germany; Kristiina Karhu, Department of Forest Sciences, University of Helsinki, Finland

Keywords: plant carbon flow, soil microbial community, experimental warming

Content:

Due to climate warming, growing seasons are estimated to prolong and the plant photosynthetic C and litter input to soil to increase. Especially the ecosystems in the northern hemisphere are expected to experience drastic effects of climate warming. Increase in mean annual temperature is estimated to prolong the growing seasons, which will increase the net photosynthetic C flow from plants to soil and soil inhabiting microbes. In addition of possibly changing the soil microbial community composition, the increased plant C-flow to soil may (1) increase the overall activity of soil microbes and lead to degradation of old and recalcitrant soil C pools, thus increasing soil respiration, or (2) accelerate the growth of microbes due to the plant-derived C, thus stabilizing part of the excess C to soil as microbial necromass. We studied in a field experiment the effects of increased mean annual temperatures and prolonged growing season on mineral soil microbial communities, microbial biomass, necromass and C stocks. For this, we established a field experiment where soils were passively warmed with +4 °C by transporting them from north to south of Finland. The experimental sites were pine dominated forests with *Vaccinium myrtillus* dominated ground vegetation. At October 2019, 20 cm soil profiles were translocated in PVC tubes (diameter 7.5 cm) from north, and planted on site in south within 3 days of collection. Control tubes were translocated on site in both north and south study sites. Each tube contained *V. myrtillus* plant, which was growing naturally at the experimental site. At the middle of 1st growing season (2020), ¹³C-glucose, or water, was injected to E-layer to subset of translocated soils, followed by serial sampling withing 1d, 3d, 10d, 1m, 3m, and 1y after labeling. To determine the effect of warming to E-layer inhabiting ¹³C-glucose utilizing microbial community, ¹³C-DNA-SIP and ¹³C-PLFA-SIP were performed to samples collected 10d after labeling. The effect of warming of microbial necromass stabilization to soil was determined with determining ¹³C from the total amino sugar pool. Additionally, soil total fungal and bacterial community structures were determined from samples collected during 1st and 2nd growing season after translocation (2020 and 2021, respectively). Soil total ¹³C was determined from samples collected at each timepoint. Preliminary results will be presented and discussed during the poster presentation.

Topic groups: 06. Food Authenticity, Nutrition, Forensic,

Presentation types: Poster

Title: Tracing geographical origin of Argan oil using carbon and oxygen isotope fingerprints

Lead author: Fouad Taous, Centre National de l'Énergie des Sciences et des Techniques Nucléaires

Author: Hamid Marah, Centre National de l'Énergie des Sciences et des Techniques Nucléaires; Oliver Kracht, Thermo Fisher Scientific; Simon Kelly, International Atomic Energy Agency; Mario Tuthorn, Thermo Fisher Scientific

Keywords: EA-IRMS, elemental analysis, isotopes, authenticity, argan oil

Content:

Argan oil is extracted from Argan tree fruit seeds in a labor-intensive hand-made process. Argan tree (*Argania spinosa*) is an endemic species from south-western Morocco. Because of this, Argan oil has received a protected geographical indication status (PGI-MA-906), which assures that both local producers and consumers are protected. Such high quality and highly consumed products are also the target of economically motivated fraud. Argan oil production has tremendous environmental, social and economic importance for Morocco, and it is necessary to verify authenticity and provenance of this valuable product to ensure its reputation protected and promoted. Argan oil has an inherent isotopic fingerprint, a unique chemical signature that allows its provenance to be confirmed. Analyzing oxygen and carbon isotope fingerprints of Argan oil by Elemental Analysis Isotope Ratio Mass Spectrometry (EA-IRMS) allows the differentiation of samples from different regions and creates a framework for using isotopes as a tool for verifying Argan oil origin. Here we report on 47 Argan oil samples analyzed for authenticity control in collaboration with CNESTEN.

Topic groups: 02. Terrestrial and Aquatic Biogeochemistry,

Presentation types: Poster

Title: Spatial and temporal variation of ^{13}C signature of methane emitted from a temperate mire

Lead author: Janne Rinne, Natural Resources Institute Finland / Lund University

Author: Patryk Łakomic, Lund University; Patrik Vestin, Lund University; Joel White, Lund University; Per Weslien, University of Gothenburg; Julia Kelly, Lund University; Natascha Kljun, Lund University; Lena Ström, Lund University; Leif Klemmedtsson, University of Gothenburg

Keywords: Methane, wetland, greenhouse gas, emission

Content:

The relative importance of processes leading to spatial and temporal variation of methane emission from mire ecosystems are not fully understood, as different mechanisms can lead to similar variations. However, stable isotope signatures of the emitted methane can offer cues to the causes of these variations. We measured the methane emission and ^{13}C -signature of emitted methane by automated chambers at a temperate mire in South-Western Sweden for two growing seasons. In addition, we measured ambient methane mixing ratios and $\delta^{13}\text{C}\text{-CH}_4$ above mire surface to calculate a mire-scale ^{13}C signature using a nocturnal boundary-layer accumulation approach. The chamber measurements showed large and systematic spatial variations in $\delta^{13}\text{C}\text{-CH}_4$ of up to 15 ‰ but smaller and less systematic temporal variation. The trophic status of methanogenesis was estimated to be the dominant factor explaining most of the spatial variation. The temporal variation of methane emission and $\delta^{13}\text{C}\text{-CH}_4$ over the growing seasons showed hysteresis-like behavior, indicative of time-lagged responses to temperature and trophic status. The up-scaled chamber measurements and nocturnal boundary-layer accumulation measurements showed similar average $\delta^{13}\text{C}\text{-CH}_4$ values. The results obtained can constrain our theories on the variability of methane emission from mire ecosystems and be useful in development of numerical models of mire biogeochemistry.

Topic groups: 02. Terrestrial and Aquatic Biogeochemistry,

Presentation types: Poster

Title: Effects of water table and glucose addition to dissolved organic carbon in drained boreal peatland

Lead author: Niko Kinnunen, University of Eastern Finland

Author:

Keywords: Peatland, Forestry, Water, DOC

Content:

Boreal peatlands are among the greatest terrestrial carbon sinks, due to their characteristic waterlogged, anoxic conditions slowing organic matter decomposition and promoting its accumulation as peat. However, they are also major sources of dissolved organic carbon (DOC) and nutrients (nitrogen (N) and phosphorous (P)) to surrounding water bodies. This can be amplified by climate change and various disruptive forms of land use, such as farming and forestry. Continuous cover forestry has been proposed to cause less adverse effects on the environment than conventional clear-cutting practices, but information regarding its benefits to the runoff water quality is still lacking. We conducted a pulse labeling study with ¹³C-labelled glucose and ¹⁵N-labelled glycine in a common garden experiment using peat cores, to study how forest management, groundwater table and availability of easily decomposable carbon and nitrogen affect the decomposability of DOC. The forest clear-cut and continuous cover forestry did not change the DOC and nutrient concentrations compared to an uncut control forest. However, the DOC and DON concentrations increased significantly during the first month of the experiment, but this increase was significantly less with glucose addition. These findings indicate that lowering of the ground-water table stimulates the biodegradation of soil organic matter in the peat resulting in a higher decomposability of DOC. They also reinforce the idea that the forest management effect is shown through various abiotic factors such as the temperature and water table.

Topic groups: 02. Terrestrial and Aquatic Biogeochemistry,

Presentation types: Poster

Title: Violation of Keeling plot assumptions in peatland static chamber $\delta^{13}\text{C-CH}_4$ measurements

Lead author: Lukas Kohl, University of Helsinki

Author: Markku Koskinen, University of Helsinki; Salla Tenhovirta, University of Helsinki; Mari Pihlatie, University of Helsinki; Annalea Lohila, Finnish Meteorological Institute

Keywords: Keeling plot, peatland, methane

Content:

The Keeling plot is the standard method to estimate the isotope value of a trace gas in chamber measurements and commonly use to e.g. estimate carbon isotope values of methane ($\delta^{13}\text{C-CH}_4$) emitted by peatlands. Such inference is necessary because $\delta^{13}\text{C-CH}_4$ is always measured in a mixture of methane by the peatland soil and atmospheric methane present at the beginning of the chamber closure. By plotting the $\delta^{13}\text{C-CH}_4$ values measured during a chamber closure against the inverse concentration, the $\delta^{13}\text{C-CH}_4$ of methane emissions is inferred as the intercept of a linear fit. One key assumption of this method is that the $\delta^{13}\text{C-CH}_4$ values of the emitted methane stays constant throughout the chamber closure. This assumption that is hard to verify based on the offline analysis of discrete gas samples but can now be evaluated with field-portable isotope analysers. Here, we present measurements conducted with a Picarro G2201i at a subarctic mire (Lompolojänkämä) in Northwestern Finland. The analyser was set up such that a constant air stream was pulled out of the measurement chamber and replaced by ambient air. The sample flow (0.5 L min^{-1}) was relatively small compared to the chamber volume, such that the chamber acted as a static chamber (increasing methane concentrations) during the onset of a measurement and as a dynamic chamber (with steady state conditions, i.e., constant methane concentration) during advanced stages of a chamber closure. With this setup, we show that initial methane emissions are relatively ^{13}C depleted compared to emissions during the steady state phase of the closure. Source $\delta^{13}\text{C-CH}_4$ values calculated by Keeling plots using the initial part of the closure were $>10\%$ more negative (e.g. -73%) compared to source $\delta^{13}\text{C-CH}_4$ values calculated based on mass balance during the steady state phase (e.g. -60%). One possible explanation for this behavior would be if closing the chamber increases the methane flux from the soil to the chamber volume compared to the flux from soil to atmosphere prior to closure. Such increased emissions rates can result from the chamber fan accelerating the 'wind' speed the chamber (Koskinen et al, 2014), which would lead to a preferential degassing of the lighter isotope until steady state conditions are established. References: Koskinen, Minkkinen, Ojanen, Kämäräinen, Laurila, and Lohila: Measurements of CO_2 exchange with an automated chamber system throughout the year: challenges in measuring night-time respiration on porous peat soil, *Biogeosciences*, 11, 347–363, <https://doi.org/10.5194/bg-11-347-2014>, 2014.

Topic groups: 01. Methodological Advances, Datatype not found, positioned next to each other 60, 119 and 165,

Presentation types: Poster

Title: Assessment of international standards on the carbon isotope VPDB scale

Lead author: Heiko Moossen, Max Planck Institute for Biogeochemistry

Author: Farilde Steur, University of Groningen; Isabell von Rein, Max Planck Institute for Biogeochemistry; Harro Meijer, University of Groningen

Keywords: carbon isotope, standardisation, standards, VPDB scale

Content:

Carbon isotope measurements are now commonplace in nearly all scientific fields, from palaeoclimate, medical, forensic, through to atmospheric research. In some fields, for example food authentication, carbon isotope analyses may be applicable to legal proceedings. In others, like atmospheric sciences, very small natural variations need to be detected and inter-laboratory measurement compatibility goals are high ($\delta^{13}\text{C-CO}_2(\text{atm})$: 0.01 ‰). Stringent standardisation of carbon isotope measurements is especially important in these instances. Unlike temperature, weight and amount of substance scales that are now linked to nature constants, stable isotope scales are still linked to standard materials and as such rely on substance availability and stability over time. In case of carbon isotope measurements the primary standard is a calcium carbonate called NBS19, which defines the Vienna-PeeDee Belemnite scale (VPDB). Since 2006 LSVEC, a lithium carbonate has been used as a second anchor point on the VPDB scale. Unfortunately LSVEC is isotopically unstable and NBS19 is no longer available to the wider scientific community. IAEA-603 has replaced NBS19, and two separate studies have been made that propose replacement materials for LSVEC. One was led by IAEA producing IAEA-610, 611 and 612 calcium carbonates, and the other by USGS proposing USGS44 calcium carbonate as a LSVEC alternative. Whether these new VPDB carbon isotope scale affecting standards will lead to a scale revision is under discussion in expert meetings. In the meantime, more data needs to be produced to provide a solid information base for any future decision that may be taken by for example IAEA experts, or the Commission on Isotopic Abundances and Atomic Weights (CIAAW). Here we assess major components that affect carbon isotope value assignment to calcium carbonate standards. We compare different approaches to the phosphoric acid reaction which is required to produce CO_2 from calcium carbonates. Furthermore we assess the impact of analyzing identical CO_2 samples in different laboratories. Finally, in the course of this study, we marry the proposed LSVEC replacements produced through separate attempts, IAEA-610, -611, -612 and USGS44, and discuss advantages and disadvantages of a possible future carbon isotope scale revision.

Topic groups: 01. Methodological Advances,

Presentation types: Poster

Title: Grip on drifting oxygen isotopes in glass sample flasks

Lead author: Pharahilda Steur, University of Groningen

Author: Hubertus Scheeren, University of Groningen; Heiko Moossen, Max-Planck-Institute for Biogeochemistry; Harro Meijer, University of Groningen

Keywords: "Oxygen isotopes" "Storage" "Stability" "Drift" "Glass flasks" "Viton" "PCTFE"

Content:

$\delta^{18}\text{O}$ of atmospheric CO_2 contains information on carbon fluxes and water isotope variability (Cuntz et al., 2003) and its measurement is therefore of great value for climate research. Variations of $\delta^{18}\text{O}$ of atmospheric CO_2 are low, and so the WMO/GAW inter-laboratory compatibility goals are set at 0.05‰. Besides highly precise, accurate and well-calibrated measurement techniques, thorough sampling and storage procedures are required to reach these goals. $\delta^{18}\text{O}$ - CO_2 values of air stored in glass flasks are prone to drifts of which the degree is highly dependent on the humidity of the air, as water can condensate and attach to the glass walls and CO_2 will equilibrate with it (Gemery, 1996). Therefore, it is now common practice at our lab to dry the air (air is cooled to -40°C) before filling sample flasks when oxygen isotopes are to be measured. When sample flasks are stored longer than 14 days, negative deviations in the $\delta^{18}\text{O}$ values are, however, still observed in flasks sealed with Viton O-rings. We conducted a series of experiments to find out the mechanism behind the observed drifts. For this purpose, flasks sealed with Viton O-rings and PCTFE-on-glass sealed flasks were compared, as well as different flask conditioning methods and storage conditions (for example in air moisturised with isotopically enriched water). We observe a stronger drift caused by permeation of water through the Viton O-rings than through the PCTFE-on-glass valves. For storage times below 2 months the PCTFE flasks show no drifts higher than the measurement error ($\sim 0.05\text{‰}$), while for the Viton flasks drifts up to -0.15‰ are observed. Viton flasks show lower variability between flasks and a lower mean drift when flasks were stripped from water attached to the walls by evacuating the flasks for 72 hours while heating them to 60°C . Our results indicate that drift is caused by a combination of water already present inside the flasks and water permeating through the Viton O-rings.

References: Cuntz, M., Ciais, P., Hoffmann, G., & Knorr, W. (2003). A comprehensive global three-dimensional model of $\delta^{18}\text{O}$ in atmospheric CO_2 : 1. Validation of surface processes. *Journal of Geophysical Research*, 108(D17), 4527.

<https://doi.org/10.1029/2002JD003153> Gemery, P. A. (1996). Oxygen isotope exchange between carbon dioxide and water following atmospheric sampling using glass flasks. *Journal of Geophysical Research Atmospheres*, 101(D9), 14415–14420.

<https://doi.org/10.1029/96JD00053>

Topic groups: 02. Terrestrial and Aquatic Biogeochemistry,

Presentation types: Poster

Title: Application of stable isotope dilution to identify novel proxies of sediment reactivity

Lead author: Fabrizio Minutolo, Helmholtz - Zentrum Hereon

Author:

Keywords: sedimentary nitrogen turnover, permeable sediment, isotope dilution

Content:

Sediment reactivity and sedimentary nitrogen turnover are crucial for nutrient management, - retention, and to determine productivity in ecosystems. However, especially the turnover of nitrogen as an important nutrient is not easily experimentally constrained in permeable sediment. Sediment reactivity is of special interest in coastal areas, since coastal areas often are exposed to anthropogenic disturbances such as riverine nutrient inputs or sediment disturbance by dredging, bottom trawling, etc. The parametrization of nutrient turnover in sediments will enable us to obtain specific reaction rates across various sediment types, thereby greatly reducing time and resources spent on sampling, incubations, and analyses. We incubated sandy German Bight sediments, using flow through reactors specifically designed to mimic advective processes in permeable sediment. Aerobic and anaerobic incubations were set up, in order to allow for differentiation between oxic and anoxic processes. By applying the sediment isotope dilution method and enriching flow through reactors with $^{15}\text{NH}_4^+$ and $^{15}\text{NO}_3^-$, gross ammonification and nitrification rates were assessed, respectively. This ^{15}N dilution approach is particularly well suited for short-term N-transformations. No specific proxy could be identified yet based on net turnover rates, but the gross ammonification rates derived from the isotope dilution approach markedly correlated with phaeophytin ($R^2=0,88$), a chlorophyll degradation product and thus a proxy for plankton biomass. This correlation can be used to parameterize sediment reactivity, in order to integrate N-turnover in process-driven biogeochemical models. Interestingly, gross nitrification rates did not correlate with pigment content. In the future, we will use this proxy to implement a benthic model to analyze the response of benthic N-transformations in various scenarios of bottom trawling fishing pressure.

Topic groups: 09. Isoscape, Spatial Variability of Stable Isotopes (Migration, Food Webs),

Presentation types: Poster

Title: Tracing carbon allocation and associated changes in $\delta^{13}\text{C}$ from leaf photosynthates to mycorrhizal fungi

Lead author: Lan Mo, Natural Resources Institute Finland

Author:

Keywords: Despite many studies on plant-fungi interaction, we know little about the seasonal carbon (C) transfer from trees to fungi sporocarps and how the natural carbon isotopic composition ($\delta^{13}\text{C}$) is shaped during that process. To gain insights into $\delta^{13}\text{C}$ patterns and underlying processes, along the C transfer pathway from pine trees (*Pinus sylvestris* L.) to different ectomycorrhizal fungi (ECM), we measured ($\delta^{13}\text{C}$) values in soluble sugars of needles and phloem of twig, stem and root, organic matter of hyphae material, and sugars of sporocarps. All samplings were conducted during the fungal growing season from July to October in Hyytiälä, Finland. Generally, we observed an increase in $\delta^{13}\text{C}$ values along the C transport pathway from the needles to the ECM sporocarps. Moreover, we found that the $\delta^{13}\text{C}$ values of ECM fungi sporocarps are tightly connected to those in needles over the course of the growing season. Correlation analyses showed a time lag between changes in $\delta^{13}\text{C}$ of carbohydrates in needles and ECM ranging from 12 (adjusted $R \sim 0.91$) in *Lactarius* and *Russula* to 20 days in *Cortinarius* (adjusted $R \sim 0.98$). The strong seasonal $\delta^{13}\text{C}$ connection in sugars highlights the ecological importance of ECM fungi for pine trees.

Content:

Despite many studies on plant-fungi interaction, we know little about the seasonal carbon (C) transfer from trees to fungi sporocarps and how the natural carbon isotopic composition ($\delta^{13}\text{C}$) is shaped during that process. To gain insights into $\delta^{13}\text{C}$ patterns and underlying processes, along the C transfer pathway from pine trees (*Pinus sylvestris* L.) to different ectomycorrhizal fungi (ECM), we measured ($\delta^{13}\text{C}$) values in soluble sugars of needles and phloem of twig, stem and root, organic matter of hyphae material, and sugars of sporocarps. All samplings were conducted during the fungal growing season from July to October in Hyytiälä, Finland. Generally, we observed an increase in $\delta^{13}\text{C}$ values along the C transport pathway from the needles to the ECM sporocarps. Moreover, we found that the $\delta^{13}\text{C}$ values of ECM fungi sporocarps are tightly connected to those in needles over the course of the growing season. Correlation analyses showed a time lag between changes in $\delta^{13}\text{C}$ of carbohydrates in needles and ECM ranging from 12 (adjusted $R \approx 0.91$) in *Lactarius* and *Russula* to 20 days in *Cortinarius* (adjusted $R \approx 0.98$). The strong seasonal $\delta^{13}\text{C}$ connection in sugars highlights the ecological importance of ECM fungi for pine trees.

Topic groups: 03. Plant Ecophysiology,

Presentation types: Poster

Title: Tracing carbon allocation and associated changes in $\delta^{13}\text{C}$ from leaf photosynthates to mycorrhizal fungi

Lead author: Lan Mo, Natural Resources Institute Finland (Luke)

Author:

Keywords: ECM fungi, seasonal $\delta^{13}\text{C}$ variation, soluble sugar transport, *Pinus sylvestris* L. plant-fungi interaction

Content:

Authors: Lan Mo, Marco M. Lehmann, Yann Salmon, Giles Young, Siiri Bienz, Yu Tang, Erik Hobbie, Pyry Veteli, Pauliina Schiestl-Aalto, Elina Sahlstedt, Taina Pennanen and Katja T. Rinne-Garmston

Despite many studies on plant-fungi interaction, significant knowledge gaps remain about the seasonal carbon transfer from trees to sporocarps of ectomycorrhizal fungi. The stable carbon isotopic composition ($\delta^{13}\text{C}$) of organic compounds transferred from trees to ECM fungi can shed light on the physiological processes underlying carbon transport. To gain such insight, we measured $\delta^{13}\text{C}$ values of soluble sugars in needles, phloem of twigs and stems, and roots of *Pinus sylvestris*, as well as $\delta^{13}\text{C}$ of hyphae and sugars of ectomycorrhizal sporocarps for one growing season. The seasonal sampling was from July to October and was conducted in Hyytiälä, Finland. Generally, a total increase of 2.8‰ in $\delta^{13}\text{C}$ values along the carbon transport pathway from the needles to the sporocarps. The seasonal changes in $\delta^{13}\text{C}$ values of sporocarps tracked the seasonal changes in $\delta^{13}\text{C}$ of needle sugars with lag times of several weeks. According to correlation analysis, the time lag for carbon transport was 20 days for *Cortinarius* (adjusted $R \approx 0.98$) and 12 days (adjusted $R \approx 0.91$) for *Lactarius* and *Russula*. The long lag time for *Cortinarius* sporocarp production presumably reflects the greater storage potential for fungal carbohydrates in the more extensive belowground mycelial networks of *Cortinarius* compared to *Lactarius* and *Russula*. The strong seasonal $\delta^{13}\text{C}$ connection between sugars in needles and sporocarps highlights the important ecological relationship between ectomycorrhizal fungi and their host pine trees.

Topic groups: 07. Atmospheric Sciences (Pollution, Climate Change, Cosmogeochimistry),

Presentation types: Poster

Title: Real-time analysis of $\delta^{13}\text{C}$ - and δD - CH_4 in ambient air with a QCL based absorption spectrometer: Method development

Lead author: Kerstin Zeyer, Empa

Author: Ivan Prokhorov, Empa; Béla Tuzson, Empa; Joachim Mohn, Empa

Keywords: Real-time analysis, $\delta^{13}\text{C}$ - and δD - CH_4 , quantum cascade laser absorption spectroscopy, trace gas extractor

Content:

Methane (CH_4) is the second most important anthropogenically emitted greenhouse gas after carbon dioxide (CO_2). Over the last 150 years the CH_4 concentrations in the atmosphere has increased from around 772 ppb (parts-per-billion, nmole mole⁻¹) in pre- industrial times to 1906 ppb in 2021 (Ed Dlugokencky, NOAA/GML (gml.noaa.gov/ccgg/trends_ch4/)). High-precision analyses of the most abundant methane isotopologues $^{13}\text{CH}_4$ and $^{12}\text{CH}_3\text{D}$ have been suggested as natural proxies to discriminate between different source categories. For regionally focused studies, with large local fluxes, WMO/GAW suggests extended compatibility targets between laboratories of ± 5 ppb, ± 0.2 ‰, and ± 5 ‰, for CH_4 mole fractions and isotope ratios, $\delta^{13}\text{C}$ - CH_4 , δD - CH_4 , respectively (Crotwell et al., 2020). This stringent compatibility levels can only be reached with an analytical technique demonstrating high precision and repeatability. Our previous research demonstrated that quantum cascade laser absorption spectroscopy (QCLAS) coupled to a trace gas extractor (TREX) can achieves these requirements (Eyer et al., 2016; Röckmann et al., 2016). Only the $\delta^{13}\text{C}$ - CH_4 data showed about 2 ‰ offset, which was attributed to enhanced O_2 levels after preconcentration. In this work, we present an upgraded analytical system consisting of a new preconcentration device (TREX-III) equipped with cryo-focusing trap and a new dual-laser QCLAS (Aerodyne Research, Inc., USA). Within 1 h cycle TREX-III can process up to 18 liters (STP) of ambient air and quantitatively separate CH_4 from bulk air constituents (N_2 , O_2 , Ar) and trace gases (CO_2 , N_2O). The QCLAS achieves precisions around 0.04 ‰ and 0.2 ‰ for $\delta^{13}\text{C}$ - and δD - CH_4 , respectively. Coupling to the TREX and laboratory validation experiments are ongoing. The instrument will be deployed for monitoring of CH_4 isotopes in the city of Zürich within the EURAMET funded metrology project (19ENV05 STELLAR).

Topic groups: 01. Methodological Advances,

Presentation types: Poster

Title: High precision CO₂- δ¹³C analysis of 1-mL air samples: from vial preparation and storage, to GasBench continuous flow IRMS analysis

Lead author: Joana Sauze, CNRS Ecotron

Author: Clément Piel, CNRS Ecotron

Keywords: carbone isotope, IRMS, vial storage, 1-mL air samples

Content:

The carbon isotope signature of atmospheric air (CO₂- δ¹³C), or soil gaseous spaces, can be used as a useful tool to investigate the global carbon cycle. In most cases a 'Keeling Plot' approach is applied. With this approach, the carbon isotopic ratio of CO₂ air is plotted against the inverse of the CO₂ mixing ratio, to estimate the carbon isotopic signature of ecosystem-respired CO₂. Since several years, advances in continuous-flow isotope ratio mass spectrometry have made possible automated, less expensive and more handy analysis of δ¹³C and CO₂ concentration in air from typically 12-mL vials. However, the classical GasBench approach was designed for gas samples with a volume of at least 3-mL and up to 12-mL, and several studies have demonstrated that vial storage time is a critical issue. In order to apply this approach to very small gas exchange system in climate-controlled experiments (i.e. typically growth chamber-based experiment involving few kilograms of ecosystem) we developed a new GasBench continuous flow method to analyse δ¹³C and CO₂ concentration with only 1-mL samples of atmospheric air. The sample stability issue, emphasised by the very small working volume, was tackled with a new preparation and storage vial method. Combining measurement with our improved Gasbench-IRMS and our sample preparation/storage methods, we achieved a repeatability of 0.1 permil, for δ¹³C of 1ml atmospheric samples stored during one week.

Topic groups: 01. Methodological Advances,

Presentation types: Poster

Title: High resolution spatial analysis of carbon isotope composition by laser ablation IRMS using an automated system

Lead author: Elina Sahlstedt, Natural Resources Institute Finland

Author: Katja Rinne-Garmston, Natural Resources Institute Finland

Keywords: laser ablation, LA-IRMS, $\delta^{13}\text{C}$

Content:

Laser ablation aided, on-line analysis of carbon isotope composition ($\delta^{13}\text{C}$) of organic matter was introduced in the late 1990's. Since then, this type of instrumentation has been used only in few laboratories over the world, with the focus on producing high resolution $\delta^{13}\text{C}$ data for organic materials, particularly tree rings. A fully automated system which enables high sample throughput was recently developed, incorporating a 213 nm Nd:YAG laser. In this work we describe this system, located at the Stable Isotope Laboratory of Luke (Natural Resources Institute Finland), and outline the performance of the instrument in providing high resolution data from organic materials. In short, the instrument is comprised of a laser ablation system (LSX-213 G+, Teledyne Photon Machines) coupled to an isotope ratio mass spectrometer (IRMS; 20-22, Sercon) via a peripheral containing gas trapping and purification systems (Cryoprep-2, Sercon). The laser cell (IsoSCell, Terra Analytic) is specifically designed for stable isotope applications. The laser ablation and the IRMS instruments are controlled by two separate PC's. The laser controlling software allows designing of the sampling protocol, i.e. selecting a sequence of laser targets and the order in which they will be run, and selection of ablation settings, such as laser spot size and laser energy. The software controlling the IRMS measurements determines the valve operation of the Cryoprep-2 and IRMS units and triggers the laser ablation software to start an ablation process. The instrument combination allows a high throughput, high resolution sampling from organic material, which in our laboratory has mostly been wood samples. Laser settings can be adjusted according to sample material, but the characteristics of the sample (e.g. C-content, size and shape) determines sampling resolution. For intra-annual analysis of tree rings we have achieved sampling resolution of 40 μm (40 μm laser spot size with a track length of 300-350 μm), translating to roughly 10 analysis per year, depending on the size of the ring. At very small sample sizes (measured signal ≤ 10 nAs), the measured $\delta^{13}\text{C}$ becomes unreliable, which in practice determines the lower limit of sampling resolution. Tests with reference materials with distinct $\delta^{13}\text{C}$ values have indicated that memory effects are negligible. Such instrumentation as described here will prove to be a valuable means of acquiring $\delta^{13}\text{C}$ data at a very high resolution in the future, as this data can be obtained with relative ease and lesser time commitment compared to conventional methods.

Topic groups: 05. Health and Medical Sciences,

Presentation types: Poster

Title: Stable isotope labeling, measurement accuracy, and challenges to unravel food web structure of slow sand filters in drinking water production

Lead author: Salima Sadeghi, Utrecht University, Department of Earth Sciences, Faculty of Geosciences

Author:

Keywords: Slow sand filter, stable isotope labeling, food web, carbon cycling

Content:

Slow Sand Filters (SSF) are the last cleaning steps in drinking water production. Microorganisms on top layer of the filters play a key role in filtering contaminants and removal efficiency of the slow sand filters. Food web structure and microbial diversity in this manipulated and dark-mixotrophic ecosystem has not been yet determined. In the current study, three different full-scale slow sand filters in the Netherlands were sampled from 2020 to 2022. To unravel the internal carbon cycling within the food web of slow sand filters, ^{13}C enriched glucose molecule was added as a tracer in a specific labeling set up designed for this experiment. For better understanding of the structure of food web in each SSFs, meiofaunal different taxa and specific bacterial lipid biomarkers were extracted and their natural and labeled isotopic signatures were measured with Elemental Analyzer-Isotope Ratio Mass Spectrometry (EA-IRMS) and Gas Chromatography Isotope Ratio Mass Spectrometry (GC-IRMS) systems. Low and high flow gas combustion were applied for accurate measurement with EA-IRMS. Further, DNA extracted from different layers and locations of sediment within the filters and amplicon 16S rRNA gene sequencing was performed to determine both the bacterial/archaeal diversity in the different samples. Stable isotope labeling showed high uptake of glucose in microbial lipids followed by label transfer to higher organisms. Accurate measurements of isotope ratios are required to elucidate the carbon fluxes among microbes and consumers (including predators). This approach will help to enhance the understanding of the food web in SSF with reduced downtime. Targeting biomarkers of bacteria and archaea will provide visions about the contribution of these two domains of prokaryotes to the degradation of organic matter and eventually maturation of bioactive layer in SSFs.

Topic groups: 04. Paleoclimatology & Archaeology,

Presentation types: Poster

Title: Terrestrial and Aquatic Snails from the Sultanate of Oman: Combined, an Excellent Climate Archive of the Early Bronze Age?

Lead author: Katharina Schmitt, Johannes Gutenberg-Universität Mainz

Author:

Keywords: Early Bronze Age, preservation state, climate reconstruction, Sultanate of Oman, bivalve sclerochronology

Content:

Al-Khashbah, today a small village in the Sultanate of Oman, is considered an important archaeological site because it is here where some of the first copper production sites, dating back to the Hafit period (Early Bronze Age), in Eastern Arabia, were found. It is still debated how an entire community could have supplied itself with water under the hot and dry climatic conditions similar to those of the present, because the irrigation system used until today, the falaj, was established in this area much later, in the Iron Age. One theory put forward by archaeologists is that so-called ditches, which surround many of the Early Bronze Age buildings called "towers", were filled with water and used for irrigation. This theory is supported by the aquatic snails (*Melanoides tuberculata*) found on the bottom of the ditches. These shells, dated to the Early Bronze Age, were examined for their state of preservation and the results obtained were compared with recent shells to determine possible diagenesis. Classical methods such as X-ray diffraction (XRD), Raman spectroscopy, inductively coupled plasma optical emission spectrometry (ICP-OES), cathodoluminescence (CL) and scanning electron microscope (SEM) were used. Additionally, immersion in Feigl solution was applied. If the shell was classified as well preserved, high-resolution sampling (micromilling) for stable isotope composition via GC-IRMS was applied. The stable oxygen isotope series from the aquatic shells were used to reconstruct water temperatures. However, since aquatic snails are not suitable for vegetation reconstruction and the determination of the origin of palaeo-precipitation regimes, representatives of a terrestrial snail species (*Zooteucus insularis*) were used for this purpose. Like the aquatic snails, they were radiocarbon dated, examined for diagenesis and then isotopically (stable carbon isotope values) analysed. Therefore, a combination of the two species made it possible to draw a fairly accurate picture of the climate during the Early Bronze Age.

Topic groups: 12. Sponsor session,

Presentation types: Session

Title: Comprehensive Isotope Ratio MS with Electrospray-Orbitrap

Lead author: Dieter Juchelka, Thermo Fisher Scientific (Bremen) GmbH, Bremen, Germany

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Keywords: clumping, position specific isotope analysis, Orbitrap, ESI

Content:

A new, comprehensive approach to Isotope Ratio MS using an electrospray ionization (ESI) Orbitrap gives access to a wide range of isotopic information from wide variety of intact polar compounds in liquid samples. It delivers isotope ratios of singly substituted isotopologs, mass independent fractionation, clumped isotopes and, for organic molecules, position specific isotope analysis. We have developed two sample introduction methods and automation, applying IRMS specific rules by using nitrate as a model compound. In total, 7 isotopologs of nitrate can be quantified simultaneously opening multiple pathways for calculating $\delta^{15}\text{N}$, $\delta^{18}\text{O}$, $\delta^{17}\text{O}$ and $\Delta^{17}\text{O}$ values with sub-‰ precision and accuracy [1]. It also opens a unique way to measure non-random isotopic distributions (“clumping”) in oxyanions. The general validity of this new development was proven by a full characterization of two recently published sulfates with mass independent sulfur isotope ratios, with in total 13 isotope ratios and triple isotope results. Based on these advances we will present the latest results and milestones for the development of the Orbitrap Exploris Iso, a variant of the Orbitrap Exploris series that is optimized for the purpose of routinely enabling isotope analysis by soft-ionization MS techniques.