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Topics: 1 Methodological Advances

Determining the carbon isotopic composition of inositol hexaphosphate (phytate) in soil: A novel approach to understanding organic phosphorus dynamics

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In soils, inositol hexaphosphate (phytate) is a recalcitrant form of organic phosphorus (OP). Hence, the ability to quantify phytate turnover in soils and to identify the factors that control it, is crucial for understanding phosphorus (P) cycling in terrestrial ecosystems. However, the lack of multiple stable P isotopes has hindered investigations of phytate dynamics under natural conditions over extended periods. To address this, we propose a novel technique for determining the carbon isotopic composition ($\delta^{13}C$) of inositol in phytate at a compound-specific level. For this purpose, phytate was extracted from soil, and purified via ion exchange chromatography, followed by dephosphorylation, derivatization, and analysis using GC-MS and GC-C-IRMS. Pure compounds were also analyzed to assess protocol efficiency, identify isotopic fractionations, and apply isotopic corrections due to derivatization. Phytate extracted from soil samples was identified using GC-MS chromatograms. Replicate analyses of the pure compounds showed that the protocol is highly reproducible. The proposed method was able to identify, quantify, and measure the $\delta^{13}C$ values of inositol in phytate separately from other sugar molecules such as glucose and fructose. The $\delta^{13}C$ values showed high reproducibility, with values varying by less than 0.5‰, and with no detectable isotopic fractionation during sample preparation. The $\delta^{13}C$ values of phytate in soil samples reflected the dominant vegetation type (C_3 or C_4) at the study site. This study introduces a novel approach to measuring the $\delta^{13}C$ values of inositol in phytate from environmental samples, offering new opportunities for investigating and quantifying OP dynamics using stable carbon isotopes.

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Topics: 1 Methodological Advances

Continuous-flow stable sulfur isotope analysis of organic and inorganic compounds using elemental analyzer coupled with multi-collector inductively coupled plasma mass spectrometry (EA-MC-ICPMS)

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Stable sulfur isotopes are crucial for studying geological, environmental, and biological processes, offering key insights into the sulfur cycle and related systems. This work presents a novel method for precise sulfur isotope ratio determination using an elemental analyzer coupled with multi-collector inductively coupled plasma mass spectrometry (EA-MC-ICPMS). The method enables accurate analysis of $^{34}S/^{32}S$ and $^{33}S/^{32}S$ ratios, providing a reliable tool for sulfur isotope research.

Validation with international reference materials, including Ag_2S and $BaSO_4$, demonstrated that $\delta^{34}S$ values agreed with reported values within ±0.3‰. The method also achieved a high analytical precision (σ), typically better than 0.3‰ for both $\delta^{33}S$ and $\delta^{34}S$, highlighting its robustness and reliability.

This versatile approach supports the analysis of bulk sulfur samples and addresses complex research questions. It is particularly suited for investigating mass-independent isotope effects in sulfur-containing organic compounds, which help uncover unique chemical pathways and reaction mechanisms. Additionally, it enables identification of sulfur sources and the tracking of biological and chemical transformations in environmental systems.

The EA-MC-ICPMS method delivers accurate and precise $\delta^{34}S$ and $\delta^{33}S$ data, making it a valuable tool for geochemical, environmental, and biogeochemical studies. Its capability to analyze isotopic variations in natural and anthropogenic systems ensures its relevance for advancing sulfur isotope research and addressing emerging scientific challenges.

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Topics: 1 Methodological Advances

Ni-wall coated microreactor to Increase Sensitivity and Selectivity and to Facilitate GCxGC for Compound-specific Isotope Analysis (CSIA)

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The online combustion of analytes between gas chromatography and isotope ratio mass spectrometry (GC-C-IRMS) has enabled compound-specific isotope analysis (CSIA) for various applications, such as assessment of environmental contaminants or doping in sports. However, CSIA is challenged by the need for complete peak separation and for best sensitivity. Comprehensive gas chromatography could deliver a breakthrough, but hinges on the development of robust miniaturized online combustion tubes that offer sufficient oxidation capacity and catalytic surface area to accomplish complete analyte conversion to CO_2, while being narrow enough to preserve narrow analyte peak shapes within the continuous flow carrier stream. The current step change when He carrier gas passes from GC capillary columns (inner diameter, i.d.: 0.22–0.32 mm) to commercial combustion tubes (i.d.: 0.5 mm) generates substantial peak broadening. Even smaller GC capillaries are needed, however, to support GCxGC applications and to improve sensitivity by reducing flows and, therefore, minimizing losses in an open split before IRMS. Since commercial reactor tubes are not compatible with fast GC-C-IRMS and GCxGC-C-IRMS, efforts have been directed at developing alternative miniaturized reactor tubes.

To pioneer the necessary dramatic reduction of reactor tube size, a Ni wall-coated catalytic microreactor is constructed by coating different capillaries (Alumina, Quartz and Fused silica) by electroless plating. An 18 cm long Ni layer is coated in the middle inner channel to fit the furnace hot zone. This approach has the benefit of simplicity, while allowing for the fabrication of narrow bore capillary reactors (inner diameter < 0.2 mm), which is not achievable with hand-loading of metal wires. The weight of the coating is determined by ICP-MS, while the layer thickness is measured by SEM and EDX. Precise and accurate data were obtained for Caffeine on quartz (o.d. 1.5 mm, i.d. 0.32 mm), with an overall mean $\Delta\delta^{13}C$ of -0.16‰ and a standard deviation of ±0.12‰.

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Topics: 1 Methodological Advances

Constraining uncertainty of in situ chamber-based estimates of the stable carbon isotope ratio of soil-respired CO2 via advances in automated sampling system technology. Keywords: flux partitioning, automated calibration, water transient, field measurement, soil gas flux chambers, carbon isotope ratio, soil respiration, carbon cycle

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Chamber-based measurements of soil CO_2 flux have long been a key tool in understanding the role of soil in ecosystem carbon cycling. However, bulk CO_2 flux measurements are limited in their ability to inform understanding of the processes contributing to observed fluxes. Estimation of the stable carbon isotope ratio ($\delta^{13}C$) of soil-respired CO_2 provides a more comprehensive measurement which can help disentangle the drivers of CO_2 fluxes, to gain a fuller picture of soil carbon dynamics.

Soil CO_2 flux has commonly been calculated using coupled chamber-infrared gas analyser (IRGA) systems. Enhanced cavity absorption analysers are increasingly used to measure CO_2 isotopologues and $\delta^{13}C$. However, combining this with chamber flux measurement to estimate soil-respired $\delta^{13}C$ has traditionally been challenging to perform *in situ*. When measuring low abundance gases, such as $^{13}CO_2$, one limitation is the magnitude of H_2O vapour transients during the measurement period. This is because the necessary H_2O corrections implemented in commercial gas analysers introduce potentially large levels of uncertainty. An additional source of uncertainty stems from the tendency in commercial analysers for the reported $\delta^{13}C$ value to exhibit a non-negligible CO_2 concentration dependency.

This work presents a detailed sensitivity analysis of the uncertainty in estimated soil $\delta^{13}C$ which can be introduced by both issues, revealing potential for a large magnitude of error in $\delta^{13}C$ estimates if H_2O and instrument effects are not minimized or properly accounted for. As well, a measurement system is presented which employs a novel, completely passive H_2O vapour equilibration system and simple, automated calibration apparatus which simultaneously reduces implementation complexity and improves the quality of field chamber-based estimates of the $\delta^{13}C$ of soil-respired CO_2.

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Topics: 1 Methodological Advances

Advancing CSIA: Overcoming LC-IRMS Limitations with 2D-LC Coupling

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Compound-specific stable isotope analysis (CSIA) is a powerful tool for investigating sources and transformation processes of micropollutants and verifying food authenticity. Using liquid chromatography coupled to an isotope ratio mass spectrometer (LC-IRMS), stable carbon isotope signatures in aqueous samples can be measured. However, the LC-IRMS interface requires wet chemical oxidation, where all oxidizable carbon is converted to carbon dioxide (CO_2). This necessitates avoiding organic eluents, buffers, or modifiers to prevent falsified isotope signatures. Consequently, chromatographic separations that rely on organic additives—widely used in conventional LC methods—are incompatible with this technique. This restricts method development to inorganic buffers and temperature adjustments, which can be labor-intensive, particularly for complex samples.

We present a novel approach integrating two-dimensional liquid chromatography (2D-LC) with LC-IRMS to address these challenges. This advanced coupling enables the use of established LC methods involving organic additives in the first dimension. Through heart-cut modulation, the analyte of interest is selectively transferred to the second dimension, where organic solvents are separated prior to oxidation.

Our results demonstrate how this innovative 2D-LC-IRMS system overcomes the limitations of traditional aqueous LC-IRMS methods. We will showcase its ability to handle complex sample matrices and resolve issues like analyte coelution, expanding the range of CSIA applications. This technique not only simplifies method development but also enhances the analytical potential of LC-IRMS in addressing critical environmental and authenticity challenges. Attendees will gain valuable insights into the system's development, implementation, and broader implications for the future of CSIA.

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Topics: 1 Methodological Advances

Life with a Clumped Isotope Mass Spectrometer in the South of France: Challenges and Lessons Learned

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The CEREGE, a research institute located in the southeast of France, acquired a Thermo Kiel IV & 253+ system in 2023, dedicated to the measurement of clumped isotopes. Notably, this was the first installation of such a system operating with Qtegra ISDS as its piloting software.

Following initial months of adjustments, interesting challenges, and fine-tuning, the system has begun to yield reliable data as of 2024. However, operating such highly sensitive equipment in a region subjected to acute temperature variations —with very hot summers and cold winter nights transitioning to warmer daytime temperatures— presents significant challenges that necessitate continuous adjustments and monitoring.

In our presentation, we will demonstrate how operating the system in Long Integration Dual Inlet “Bracketed” (LIDI 2) mode, compared to the standard LIDI and Change Over modes, can help mitigate the adverse effects of room temperature fluctuations. On the other hand, we will also shed light on the drawbacks and limitations of such mode and the reasons behind them.

We will also aim at sharing practical insights and strategies gathered from both existing literature and our hands-on laboratory experience through round-the-clock monitoring, aimed at minimizing fluctuations and improving data consistency.

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Poster

Topics: 1 Methodological Advances

Understanding catalytic mechanisms with stable isotopes: SSITKA-DRIFTS and other techniques

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The efficient catalytic transformation of greenhouse C_1 molecules (e.g., CO_2 and CH_4) into valuable chemical building blocks is critical for the sustainable energy transition. Advancing catalytic materials and processes requires a fundamental understanding of reaction mechanisms, and stable isotope techniques are powerful tools that provide molecular-level insights into catalytic reactions.

In this contribution, I will highlight isotope-based methodologies for probing the molecular details of CO_2 hydrogenation and CH_4 aromatization. I will describe the application of steady-state isotope transient kinetic analysis (SSITKA) and pulsed isotope transient techniques to investigate the reactivity of surface species and their interactions with gas-phase molecules. Furthermore, I will discuss how these isotope labeling methods can be combined with isotope-sensitive spectroscopic techniques, including infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy, to gain deeper mechanistic insights.

First, I will focus on how a combination of operando diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and $^{12}C/^{13}C$ SSITKA provided a mechanistic understanding of the unusual particle size effects in Co- and Ni-based catalysts for CO_2 hydrogenation to hydrocarbons [1,2]. Second, I will discuss our studies on CH_4 aromatization, where pulsed $^{12}C/^{13}C$ isotope transient techniques and $^{13}C/^{1}H$ NMR spectroscopy revealed an unexpected hydrocarbon pool mechanism. In this process, benzene forms through secondary reactions between confined polyaromatic carbon species and the primary products of methane activation. [3,4,5].

References

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Poster

Topics: 1 Methodological Advances

GC-IRMS: optimization of injection techniques for analysis of saturated hydrocarbons, VOCs and PAHs

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Rapidly expanding biogeochemical applications based on compound specific isotope ratios require instrumentation versatility to meet different analytical challenges. Here we present features and benefits of using the following GC injection techniques: on-column injection, Large Volume Injection (LVI) Programmed Temperature Vaporization (PTV) technique, Static Headspace Sampling (SHS) injection and conventional Split/Splitless injection. We will demonstrate capability of Thermo Scientific™ GC IsoLink™ II IRMS System to support these injection techniques to properly transfer a representative portion of the sample to the analytical column while avoiding discrimination and isotopic effects.

On-column injection is applied for analysis of thermally labile or unstable compounds, as well as for samples with large analyte-boiling-point differences. It can be advantageous in a wide area of applications, i.e. for investigations of alkenones and alkanes from soils and sediments. We will present an optimized GC-IRMS analytical setup for stable carbon isotope ratios analysis of saturated hydrocarbons.

The LVI PTV is an injection technique which allows the introduction of larger volumes of samples in the GC injector which can be particularly useful for analysis of organic pollutants present in very small quantities. Here we present an optimized methodology for analysis of very small amounts of saturated hydrocarbons.

The SHS injection via split/splitless injector eliminates the need for direct liquid sample injection, reducing column contamination and improving analyte separation and reproducibility of isotope data. Here we demonstrate excellent precision and accuracy for GC-C-IRMS analysis of VOCs by using an optimized method for SHS, including improved sensitivity and lower detection limits.

Finally, we also present an optimized workflow for the analysis of PAHs by GC-IRMS with conventional Splitless injection, including characterization of PAHs standards and data evaluation.

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Topics: 1 Methodological Advances

Optimized N, C and S isotopic analyses of collagen using EA-IRMS

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Carbon, nitrogen, and sulfur isotope signatures of bone collagen and dentine have been used as powerful tools to interpret diet and population mobility in archeological studies [1]. However, owing to extremely low S concentration (typically <0.3 wt%) and limited sample size of archeological samples, precise $\delta^{34}S$ measurements can be difficult, and simultaneous $\delta^{15}N$, $\delta^{13}C$ and $\delta^{34}S$ analyses are even more challenging.

Thermo Scientific™ EA IsoLink™ IRMS system provides a solution to this challenge with enhanced hardware components and an optimized analytical method that improve S sensitivity by 3 times and suppress S memory effect, thus achieving high precision S isotope data with only 3-5 µg S per analysis.

Here we present sequential $\delta^{15}N$, $\delta^{13}C$ and $\delta^{34}S$ measurements of well-certified collagen reference materials USGS88 and USGS89, and in-house standards Bovine Gelatine, Porcine Gelatine and Fish Gelatine using this optimized setup to assess SO_2 memory effect and the performance of NCS isotope measurements.

Replicates of these collagen standards with distinct $\delta^{34}S$ (~1.5mg, equivalent to 4-7 µg S) were run in sequences with one or two empty runs added in between as a cleaning procedure. Data showed great reproducibility with an uncertainty (1SD) of ≤ 0.3 ‰ on $\delta^{34}S$ and minimal SO_2 carry-over.

The quality control standard bovine gelatine was separately measured with USGS88 and USGS89 to check the sequential NCS isotope measurements. Bovine gelatine analyses (~1.5 mg, equivalent to 248 µg N, 669 µg C, 4 µg S) in two sequences gave averages values of $\delta^{15}N_{AIR} = 7.3 \pm 0.2$ ‰, $\delta^{13}C_{VPDB} = -17.1 \pm 0.1$ ‰ and $\delta^{34}S_{VCDT} = 6.8 \pm 0.1$ ‰ (n=27), after scale correction using USGS88 and USGS89. The measurement precision and accuracy on $\delta^{15}N$, $\delta^{13}C$ and $\delta^{34}S$ of bovine gelatine are well within the expected values [1].

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Topics: 1 Methodological Advances

Coping with spectral interferences when measuring water stable isotopes of vegetables

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Laser based analyzers are widely used in ecohydrology to analyze plant water isotopic compositions ($\delta^{18}O$ and $\delta^{2}H$). The suitability of three different water extraction and isotope equilibration techniques was compared. We examined whether co-extracted organic contaminants (VOCs) affect laser-based isotope measurements and used the instrument's spectral parameters to post-correct for interfering VOCs.

Cryogenic vacuum extraction, vapor headspace-equilibration in bags and vapor equilibration in-situ probes were used to extract liquid water or water vapor for laser-based isotope analysis (CRDS). Isotope data were calibrated by standards for each method separately. Spectral parameters of the instrument, appropriate to identify spectral interferences with MeOH and CH_4 were identified and used for post-correction. Differences between the three methods and between the origins of the vegetables were identified by statistical tests.

VOCs were found in various amounts for the three different methods. They were co-extracted or co-equilibrated during the different extraction/equilibration methods. Correlation coefficients of isotope data and 'CH4' (spectral parameter) were 0.99 or better, however slopes for $\delta^{18}O$ were similar on different instrument types but different for $\delta^{2}H$. Our correction approach improved results and inter-comparability of the methods considerably without knowing the chemical composition of the plant sap.

All three methods were sensitive enough to distinguish and resolve differences in natural abundance. Data quality was improved by the 'CH4-correction' approach but could probably be optimized by a plant species-specific correction. Standardized tools for contaminant removal or post-correction applications from manufacturers, in particular for vapor-mode analysis are still needed.

Keywords

water extraction, volatile organic compound, plant water stable isotopes, laser-based isotope analysis (CRDS), spectral interference, organics correction

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Topics: 1 Methodological Advances

SIRMS Lab – a multidisciplinary research facility at the University of Southampton

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The Stable Isotope Mass Spectrometry Laboratory (SIRMS Lab) at the University of Southampton is a state-of-the-art research, teaching and analytical facility dedicated to high-precision light stable isotope analysis across a diverse range of scientific disciplines. Located within the Ocean and Earth Science department of the University of Southampton at the National Oceanography Centre Southampton, Waterfront Campus, the lab supports academic research, external collaboration and commercial sample analysis, whilst offering expert guidance on sample preparation, analysis, and data interpretation.

Equipped with several advanced gas source isotope ratio mass spectrometers (IRMS) and peripheral devices operating in both dual inlet and continuous flow modes, the SIRMS lab specializes in analysing light stable isotopes such as δ^2H, $\delta^{13}C$, $\delta^{15}N$, $\delta^{18}O$, and $\delta^{34}S$ across a wide array of organic and inorganic materials. This analytical capability supports research in environmental sciences, oceanography, geology, archaeology, biology, and climate science. Researchers benefit from tailored support by dedicated personnel for sample preparation, instrument maintenance, method development, quality assurance and sample analysis, ensuring high-quality data and robust interpretations. The lab staff is actively involved in training and mentoring students and postdoctoral researchers, fostering the next generation of scientists in stable isotope techniques. Here we present an overview of the lab and its capabilities, introduce our new instrumentation with examples of recent research applications, demonstrating its role in advancing scientific understanding across multiple fields.

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Topics: 1 Methodological Advances

An Enhanced Analyzer for High-Precision Nitrous Oxide Isotope Measurements

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Nitrous oxide (N_2O) is a potent greenhouse gas that contributes to global warming and ozone depletion. Precise measurements of its stable isotopes are essential for understanding nitrogen cycling across soil, ocean, atmospheric, and wastewater systems. In response to the growing demand for high-precision N_2O isotope analysis, Picarro introduces the PI5131-i isotopic and gas concentration analyzer. This instrument enables simultaneous measurements of site-specific isotopic signatures ($\delta^{15}N_\alpha$, $\delta^{15}N_\beta$) along with bulk $\delta^{15}N$ and $\delta^{18}O$. It is based on the renowned mid-infrared, laser-based cavity ring-down spectrometry (CRDS) technology, but with significant software and hardware enhancements, ensuring a robust and stable measurement platform. Here, we present the analyzer's capabilities and performance metrics for continuous N_2O isotope measurements, including precision and long-term stability.

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Topics: 1 Methodological Advances

Comparison of gas matrix effects on three generations of cavity ring-down water stable isotope analyzers

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Laser-based water stable isotope analyzers have become increasingly popular in the last one and a half decades. Their direct and continuous measurement capabilities make them perfectly suitable for, e.g., in situ isotope assays in environmental settings. However, field-deployed analyzers may be subjected to inconsistent background gas matrices between individual samples and compared to co-measured calibration standards. Therefore, we tested the gas matrix effects by varying the carrier gas proportions of nitrogen (N_2), oxygen (O_2) and carbon dioxide (CO_2) in naturally occurring ranges on three different generations of analyzers employing cavity ring-down spectrometry (Picarro L21xx series). The observed magnitudes of gas matrix effects exceeded commonly accepted measurement uncertainty by two orders of magnitude on all analyzers tested but with very contrasting patterns being displayed by the different generations. For example, oxygen isotope readings increased on all instruments as the carrier gas was transitioned from air to a mixture of 80% N_2 and 20% CO_2, which may be encountered on poorly aerated, organic-rich or contaminated sites. For the same transition, hydrogen isotope readings decreased on the L2120-i while they increased on all other instruments tested. Besides, we also checked for potential drift over the course of eight years on the oldest generation tested (L2120-i). Finally, we determined the consistency of the gas matrix effect on three different analyzers of the same generation (L2130-i). We present a post-measurement routine how the effects can be reliably corrected for and how isotope data would be misinterpreted in dual isotope space when the suggested correction is omitted.

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Topics: 1 Methodological Advances

Guidance for uncertainty estimation for isotopic reference materials characterised by interlaboratory study

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Reference materials (RMs) are essential to allow traceable measurements of isotope delta values to be made in laboratories around the world. Often, new isotope delta RMs have been characterized by inter-laboratory studies. These involve several laboratories each making measurements on the candidate RM using their own measurement protocol and data processing procedures. This provides additional confidence in the assigned isotope delta values but makes the estimation of the single assigned value and associated uncertainty more challenging. Some published approaches have been criticized for providing uncertainties that are too small with a potential cause being inadequate separation of random (e.g. precision of measurement results) and systematic (e.g. assigned values of existing RMs used for calibration) sources of uncertainty [1].

In this work, we use a dataset from the interlaboratory characterization of various nitrous oxide candidate RMs [2] to attempt to address these shortcomings. Each participating laboratory was completely free to apply the measurement methods they normally would and to process the data following their usual procedures. These included both elemental analyzer (EA) and dual-inlet (DI) isotope ratio mass spectrometry (IRMS) as well as optical isotope ratio spectroscopy (OIRS).

Participating laboratories provided uncalibrated data, so the final step of calibrating measured isotope delta values to the international reporting scale could be done centrally while also propagating uncertainties. This approach allowed complete separation of random from systematic sources of uncertainty through each calculation stage. It also allowed correlations among laboratories arising from the use of the same RMs for calibration to be accounted for. Several fundamental features of single- and two-point calibration of isotope delta by DI- and EA-IRMS and resulting measurement uncertainty for both individual laboratories and for combinations of inter-laboratory data will be presented.

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[2] https://doi.org/10.1002/rcm.9296

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Topics: 1 Methodological Advances

Harmonisation of Methane Isotope Measurements

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Establishing compatibility among laboratories measuring high-precision stable isotopes of atmospheric methane (CH_4) is challenging because the reference materials differ from the measured samples. Significant offsets are common as each laboratory has a different tie to the VPDB or SMO-SLAP scales. Likewise, for clumped isotopes, since the measurements are not done against a standard, but against the isotopologues' respective stochastic distribution to calculate the anomaly of the clumping, laboratories have to periodically compare cylinders, measurement procedures, and extraction protocols. Inter-laboratory comparison of CH_4 isotope measurements, both stable and clumped, is essential so that the data from different laboratories can be compared and consolidated for scientific interpretation. This process is referred to as harmonisation of isotopic measurements.

To achieve this, we adopt methods to quantify and adjust inter-laboratory scales. For stable isotopes, we compare routine atmospheric measurements conducted by these laboratories at high-latitude stations in the Northern and Southern Hemispheres, where we assume that the air masses are sufficiently homogenized for direct comparison. The long-term mean offsets are verified against various inter-laboratory round-robin exercises and align well with the findings of Umezawa et al. (2018). For clumped isotopes, we compare the measurement procedures and results for both mass spectrometry and laser spectroscopy methods by circulating pure CH_4 samples among participating laboratories. Although the clumping anomaly data cannot be verified against a standard scale, they do agree well among the laboratories and with the theoretical thermal equilibration scale of CH_4 isotopologues. We present the results from both exercises and report noteworthy agreement among laboratories, especially given the substantial effort, complexity, and logistical challenges involved in conducting CH_4 isotope measurements. Continuous intercomparison and harmonisation efforts are crucial for maintaining high precision and consistency in isotopic measurements, ultimately improving our understanding of methane's role in the global carbon cycle and its impact on climate change.

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Topics: 1 Methodological Advances

Fully automated technique for NH2OH concentration and stable isotope measurements in the aquatic environments

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Hydroxylamine (NH_2OH) is a short-lived compound of the marine N cycle (Ward, 2008) and is formed as an intermediate during the nitrification (Yoshida and Alexander, 1964). Greenhouse gas N_2O is produced from hydroxylamine in a side reaction during ammonium oxidation in the water. The detection of dissolved hydroxylamine and its stable isotopes in oceanic waters is a key to additional insights in the mechanisms of the marine N cycle and especially the production mechanisms of N_2O since it could serve as a tracer for the occurrence of bacterial nitrification in the water column. In 2011, Casciotti *et al* suggested that the measurement of $\delta^{18}O$ in NH_2OH is necessary to understand the isotope effect for O incorporation by certain bacteria.

Butler and Gordon (1986) developed a FAS conversion method which is based on the oxidation of NH_2OH to N_2O using iron (III) as oxidation agent and subsequent quantitative analysis of the resulting N_2O. It is the only available method for this measurement at nanomolar level. Based on this we have developed a new fully automated method by using McIlvin and Casciotti (2010) approach. We have successfully measured the concentration and stable isotope signatures of NH_2OH for both marine and freshwater samples collected from the Otago Harbor and Leith river respectively. We have attained the best conversion ratio of NH_2OH for the natural waters withing 4-10 hours. The recovery rate was 32- 44% between standards of 5-50 nM. This is the first attempt to measure the $\delta^{18}O$ and $\delta^{15}N$ signature of NH_2OH and these results will give more insights in to the nitrification pathways in the oceanic waters during N_2O formation.

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Poster

Topics: 1 Methodological Advances

Improving the detection of N2 and N2O fluxes from 15N-labelled N pools by mass spectrometry

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Quantification of N_2 and N_2O fluxes from agricultural ecosystems is needed to investigate gaseous fertilizer losses and greenhouse gas fluxes. The non-random distribution of N_2 and N_2O isotopologues evolved from ^{15}N-labelled N pools is used to quantify the ^{15}N enrichment of the N pool producing N_2 and N_2O (ap values) and the pool-derived fluxes (fp values). Accuracy and precision for ap and fp depends on the flux strength and the limit of detection (LOD) of the IRMS approach, i.e. LOD for ^{29}R and ^{30}R for N_2 and ^{45}R and ^{46}R for N_2O. For robust evaluation of accuracy, standard gases are needed containing defined contents of single and double-substituted N_2 and N_2O.

Sensitivity for N_2 fluxes has been improved by establishing N_2-depleted atmospheres in the lab and in the field. Combining ^{15}N tracing and natural abundance approaches can be used to distinguish heterotrophic denitrification and nitrifier denitrification, but this requires precise determination of fp, which can be subject to bias by inaccurate instrumental calibration.

We developed and analyzed multiple isotopic standard gases containing defined concentrations of single and double substituted N_2 and N_2O. N_2 background concentrations were either atmospheric or similar to the N_2 -depleted atmospheres (0.5 or 2% N_2) of respective experiments. Stock mixtures were designed as part of the DASIM project where premixtures were produced by Thünen and stock mixtures manufactured by Westfalen AG, Hörstel, Germany. Moreover, stock mixtures for N_2O were further diluted with Helium and unlabeled N_2O to obtain defined mixtures close to the LOD of the IRMS. To optimize drift correction of the IRMS, we extended the system to enable alternating sample and standard gas injections.

We will explain the production of the manufactured standard gases and show first results of analysis in comparison with ideal values.

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Topics: 2 Progress in Reference Material

Testing unified working standards for water stable isotope analyses: Results of laboratory comparison tests of the German Isotope Network (GIN)

Paul Koeniger[1], Michael Ernst Böttcher[2], Stefan Terzer-Wassmuth[3], Kay Knöller[4], Florian Eichinger[5], Diana Burghardt[6], Axel Schmidt[7], Jessica Landgraf[7], Barbara Herbstritt[8], Andrej Voropaev[5], Franziska Schmid[9], Dörthe Tetzlaff[9], Stoyanka Schumann[4], Sebastian Friebe[1], Iris Schmiedinger[2], Falk Bratfisch[10], Heinrich Eisenmann[10], Robert van Geldern[11], Claudia Cosma[12], Nils Michelsen[12], David Dubbert[13], Maren Dubbert[13], Julian Zinke[14], Ursula Telgmann[14], Amir Sahraei[15], Lutz Breuer[15], David Windhorst[15], Heiko Moossen[16], Peter Swinkels[17], Jan Woźniak[17], Magdalena Hofmann[17]

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Within the German Isotope Network (GIN) five laboratory inter-comparison tests were conducted between 2018 and 2024 with between 8 and 17 participating laboratories. For the most recent comparison GIN5 in 2024, three objectives were to be met: First, participants measured ten unknown water samples using their established procedures and working standards akin to earlier comparisons. The second task was to measure the same ten unknown water samples but using unified laboratory working standards that were distributed to all laboratories together with the unknown samples. Third, all laboratories were asked to measure a unified control standard as often as possible during their daily measurements to compare laboratory accuracies for long-term measurements of a quality check sample.

Thirteen out of seventeen laboratories returned results in time for the GIN5 comparison. The results clearly indicate a better overall accuracy for each of the ten unknown water samples measured during the test when all laboratories use the same working standards. For all five inter-comparison tests, we discuss the accuracy and comparability of lab results when independently calibrated working standards were used. In addition to well established international inter-comparison tests (e.g., WICO by IAEA), we highlight and discuss potentials and challenges for inter-comparison tests that are organized and conducted on a national level.

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Topics: 2 Progress in Reference Material

Facilitating the development of a global measurement infrastructure for the measurement of stable isotope ratios for greenhouse gases source apportionment

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Recent progress in the field of laser spectroscopy has transformed the measurement of atmospheric greenhouse gases, enabling *in-situ* field measurements of carbon dioxide (CO_2) and methane (CH_4) stable isotope ratios. These new measurement capabilities have generated an urgent demand for commutable isotopic gas reference materials for CO_2 and CH_4 at ambient amount fractions. However, achieving the level of uncertainty required for such reference materials remains challenging. Additionally, reliance on individual calibration procedures by end-users has resulted in inconsistent data, hindering comparability across datasets.

Addressing these challenges requires the development of new isotopic reference materials, improved validation protocols, and standardised calibration guidelines. This effort is essential to ensure traceability for field-deployable spectroscopic methods and traditional offline flask sampling techniques using mass spectrometry.

In response to the growing need for improved metrological support, a joint CCQM GAWG/IRWG Isotope Ratio Task Group was established in April 2023. This group coordinates efforts among National Metrology Institutes (NMIs), Designated Institutes (DIs), and intergovernmental organisations to develop a robust infrastructure for traceable isotopic reference materials and calibration guidelines, ensuring accurate measurement of stable isotope ratios for atmospheric greenhouse gases.

As part of its foundational work, the task group recently submitted a comprehensive paper outlining key recommendations for advancing the measurement of CH_4 stable isotope ratios. The paper also reviews Calibration and Measurement Capabilities (CMCs) to help NMIs and DIs develop their capabilities in support of the atmospheric measurement community.

This presentation will summarise the task group's objectives, progress, and key recommendations. Additionally, it will provide preliminary results from a global survey conducted in early 2025, mapping current capabilities for the measurement of the stable isotope ratio of CH_4.

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Poster

Topics: 7 Geosciences and Hydrology

Application of Water Isotopes at Riverbank Filtration Pilotsites in Germany

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The objective of the IsoGW-project funded by the German LURCH initiative is to create a nation-wide interpolated isotope map (i.e. isoscape) of stable water isotope ratios (δ^2H and δ^{18}O) and of tritium (^{3}H) concentrations in the upper unconfined aquifer in Germany. This groundwater dataset is completed with isotope data from precipitation and surface waters, allowing systematical and large-scale assessments of various compartments of the water cycle. δ^2H, δ^{18}O and 3H analyses can also be applied locally to quantify contributions of river water and groundwater where river bank filtration occurs.

Here, three pilotsites have been selected across Germany to investigate the surface water/groundwater interactions in regions where drinking water is gained from river bank filtration. These sites cover different conditions in terms of topography, urban influence, hydrogeology and groundwater extraction. Data was collected via bimonthly samplings over one year at each site. The analyses combine stable isotope measurements with main ions and urban settlement indicators such as gadolinium. Results show good applicability of these isotopes to quantify mixing processes between groundwater and freshly infiltrated river water. More diverging results are obtained when quantifying the travel velocity of the groundwater. Overall, the data obtained so far provided valuable insights in the mixing processes thus supporting that isotopes are good for such assessments, but ideally would necessitate longer time-series to improve accuracy.

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Poster

Topics: 7 Geosciences and Hydrology

Germany-wide Interpolations of Groundwater Isotopes with IsoGW

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Landuse and climate change alter hydrological processes and affect drinking water resources. Practical tools for understanding and quantifying these processes becomes increasingly important, for example to sustainably manage groundwater reservoirs. Analyses of the water isotopes deuterium ($\delta^{2}H$), oxygen ($\delta^{18}O$), and tritium (^{3}H) provide useful tools, which can be applied to determine groundwater ages, assess bank filtration quantities or to identify mixings of groundwater aquifers.

The objective of the IsoGW-project (2023-2026) is to create nation-wide interpolated isotope maps (i.e., isoscapes) of $\delta^{2}H$, $\delta^{18}O$ and of ^{3}H concentrations in German groundwaters. By establishing such a service for the first time, Germany is following its European partners, which have already published some preliminary work on the matter. Data has been collected from all 16 german federal states authorities, additional samplings, partner laboratories and literature. With more than 4 000 groundwater sampling points and additional surface water and precipitation stations, our work relies on a dataset with an exceptionally high density. Priorities of the data analysis and management include filtering the data to focus on the upper unconfined aquifer and the extension of the database with additional information. These are needed as covariables for the interpolation of the stable isotopes. At the same time, different methods accounting for the ^{3}H half-life of 12.3 years are compared. Overall, we are confident that this isoscapes and the data publication coming along with it will enable systematic large-scale assessments of the water cycle and provide an important work basis for local studies and sustainable groundwater management.

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Poster

Topics: 7 Geosciences and Hydrology

Multi-isotope (COSH) biogeochemical and mineral phase investigations in the high-energy subterranean estuary of a barrier island

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Subterranean estuaries (STE) connect the water and some element cycles on land with the marine coastal area and represent areas of steep biogeochemical gradients that affect, for example, the transport and transformation of carbon and sulfur species. The availability of dissolved sulphate is of particular importance for carbon mineralization. Interactions with the mineral solid phases in the aquifer and sediment contribute to the hydrochemical modulation of the solutions finally leaving the sediment, and minerals act as sources/sinks for elements upon biogeochemical cycling. DynaDeep deals with the processes in a STE characterised by permeable sands in the north of Spiekeroog Island. The beach system, in contact with the southern North Sea, represents a unique and highly dynamic system, previously unexplored in a regional and global context, which enables the interactions between fresh and salt water with a view to current and future system changes. Boreholes and multi-level wells allow seasonal observations of the composition in pore waters as well as sediment sampling. This study presents the results of multi-isotope (COSH) studies on water, dissolved C species and sulphate as well as iron sulphides, combined with the hydrochemical gradients and phase analysis of sedimentary minerals. The water isotope ratios characterise the mixing with fresh water. The C isotope signatures in the DIC identify the degradation of organic matter, but also the corrosion of marine carbonates as sources. The isotope signatures of dissolved sulphate and iron sulphides indicate the origin of reduced phases from microbial sulphate reduction, and potential sulphide oxidation near the surface or an addition of non-marine sulphate sources with decreasing salinities. Micro and phase analytical investigations indicate the presence of calcite, apatite, and barite in the sediments, all probably of in-situ and/or detrital origin. Dolomite, which may act as further alkalinity source is of detrital origin.

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Poster

Topics: 7 Geosciences and Hydrology

Impact of soil hydraulic factors on the assessment of isotope-derived recharge rates

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A quantitative assessment of water fluxes and dynamics is crucial for a sustainable use of groundwater ressources. Aside from other key features of the soil water budget the determination of seepage water is of high relevance. Isotope-based methods can be used for this purpose, yet these approaches often apply simplified assumptions regarding water movement in the soil. To which extent, or under which conditions this yields imprecise results requires further reseach, especially in the context of changing system properties and/or changing environmental conditions. Our contribution addresses the impact of soil physical parameters on observed isotope signatures in seepage water and the resulting estimates of groundwater recharge.

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Poster

Topics: 7 Geosciences and Hydrology

Isotopic and hydrochemical diagnostic of an agro-based semi-arid carbonate aquifer, Zimbabwe

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Rapid expansion of subsistence agricultural activities and commercial farming in semi-arid regions could be attributed to the need to enhance food security in the face of unpredictable rainfall regimes. Substantial water availability as a result of the unique inherent features in karst systems provides for a predominant source for groundwater-based irrigation in Sub-Saharan Africa. This potentially poses a significant threat to sustainable use, quality and management of karst resources in this region. It is therefore not clear how preferential groundwater pathways influence the mobilisation of contaminants in agricultural-based karst systems in this region. Biogeochemical processes affecting solute transformation in these dynamic groundwater systems are also not properly understood. We coupled multi-isotopes ($\delta^{15}N$-NO_3, $\delta^{18}O$-NO_3, $\delta^{2}H$-H_2O, $\delta^{18}O$-H_2O) with geochemical tracers and non-target screening of organic compounds from 50 (groundwater, surface water, spring) sampling sites within the Lomagundi Dolomite aquifer in Zimbabwe. Rock–water interactions were the dominant processes influencing groundwater evolution as characterised by predominately Mg-Ca-HCO_3 facies. Water stable isotopic ($\delta^{2}H$-H_2O, $\delta^{18}O$-H_2O) composition of groundwater mainly clustered near the Local Meteoric Water Line (LMWL) indicative of rapid recharge and larger offsets from the LMWL towards enriched signatures were attributed to possible irrigation return flow. Elevated NO_3^- concentrations (up to 78 mg/L) were observed in sites under intensive irrigation and overall isotopic signatures of $\delta^{15}N$-NO_3 and $\delta^{18}O$-NO_3 showed overlapping sources of NO_3^- concentrations in all samples. Denitrification was only distinct in surface water samples as depicted by enriched $\delta^{15}N$-NO_3 and $\delta^{18}O$-NO_3 signatures alongside decreased NO_3^- concentrations. Preliminary conclusions indicate the aquifer's vulnerability to surface-borne contaminants as depicted by co-occurrence of agro-based compounds with other organic compounds. These findings could potentially be useful to better inform management of groundwater resources in Zimbabwe.

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Poster

Topics: 9 Ecology - marine, aquatic and terrestrial

Just Hitching a Ride: Stable Isotopes Reveal Non-Feeding Behaviour of Anisakis simplex Within Its Host Fish

Amandine Sabadel[1,2], Melanie Gay[3], Henry Lane[2], Odile Bourgau[3], Sarah Bury[2], Josette Delgado[2], Maureen Duflot[3,4]

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Anisakis simplex larvae, commonly found in marine fish, cause anisakiasis in humans, resulting in gastric to gastro-allergic symptoms. Despite known health risks, the impact of Anisakidae larvae on fish hosts is less understood. This study aimed to investigate this interaction by assessing the feeding strategy of *A. simplex*. Anisakis larvae were isolated from North Sea *Merluccius merluccius* tissues (stomach, body cavity, liver and muscle) and were analysed for carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) isotope values. Significant differences in $\delta^{13}C$ values were found among host tissues, with the liver differing from muscle and stomach tissues. In contrast, no differences were noted for the associated parasites. Additionally, $\delta^{15}N$ values indicated that the host occupied a significantly higher relative trophic position than its parasite. This suggests a lack of direct nutrient transfer from host to parasite, as the parasite would typically exhibit higher stable isotope values than the tissue they feed on. Therefore, *A. simplex*'s stable isotope values might reflect those of its previous host (crustacean and/or small fish), providing insights into diet and movement of the paratenic *M. merluccius* host. Further research is needed to confirm these findings across different fish species and to explore *A. simplex* as a proxy for trophic ecology.

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Poster

Topics: 9 Ecology - marine, aquatic and terrestrial

d15N values reflect "island of fertility" development in the Mojave Desert

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Hillside slopes within the Mojave Desert are typically rocky with limited soil development. Here low soil nitrogen (N) contents typify soils between isolated shrubs, with higher d^{15}N values (~7‰) as denitrification processes exceed N_2 fixation by free-living bacteria. Yet, under shrubs nitrogen contents are higher, creating a phenomenon known as “islands of fertility”. Adult leaf d^{15}N values are lower (2-3‰). Here we describe leaf d^{15}N values in seedling, maturing, and adult *Encelia farinosa*, a common, drought-deciduous Mojave Desert shrub lacking any association with symbiotic N_2-fixing bacteria. As seedlings develop in bare soils and develop canopies over time, leaf d^{15}N values progressively decrease. It is hypothesized that leaf litter falling below shrubs decomposes, providing a carbon source to support free-living N_2 fixing bacteria and enrich shrub soils in N.

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Poster

Topics: 9 Ecology - marine, aquatic and terrestrial

Lipid hydrogen isotope ratios reflect phytoplankton community composition

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Phytoplankton play a key role in biogeochemical cycles, impacting atmospheric and aquatic chemistry, food webs, and water quality. However, it remains challenging to reconstruct past changes in algal community composition, as existing proxies are suitable only for a subset of taxa and/or influenced by degradation. Here, we demonstrate the potential of compound-specific hydrogen isotope ratios (δ^2H values) of common algal lipids (fatty acids, phytol, and phytosterols) to serve as (paleo)ecological indicators. We present data from (1) batch cultures of 20 species of algae, (2) large volume mesocosms that were manipulated with nutrient loading and the presence/absence of keystone species, and (3) a one-year time series from Rotsee, a small, eutrophic lake.

In our culturing data, water δ^2H values were constant but lipid δ^2H values ranged from -455 ‰ to -52 ‰, incorporating variability associated with chemical compound classes and taxonomic groups. Hydrogen isotope offsets among lipids of different compound classes (expressed as $\delta^2H_{Lipid1/Lipid2}$ values) are independent of source water δ^2H values and covary with changes in algal community composition. In our mesocosms and throughout the year in Rotsee, increases in the relative abundance of cyanobacteria and/or green algae relative to other eukaryotes are associated with high $\delta^2H_{C16:0/Phytol}$ values. High $\delta^2H_{C16:0/Sterol}$ values indicate increased abundance of green algae and dinoflagellates relative to diatoms, while high $\delta^2H_{Sterol/Phytol}$ values indicate increases in diatom abundance relative to other eukaryotic algae.

We suggest that measuring δ^2H values of multiple common lipids from sedimentary records and calculating $\delta^2H_{Lipid1/Lipid2}$ values can resolve changes in algal community composition from changes in source water isotopes. With an appropriate availability of sedimentary lipids, ideally including source-specific biomarkers limited to a single taxonomic group, this approach permits the reconstruction of both taxonomic variability and hydroclimate from diverse aquatic systems.

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Poster

Topics: 9 Ecology - marine, aquatic and terrestrial

Porpoise bone collagen as an indicator of North Sea ecosystem changes during the past 170 years

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Harbour porpoise (*Phocoena phocoena*) populations reside in one of the most heavily used shelf seas worldwide, the North Sea. In the last 200 years impacts occurred from hunting, fishing, shipping, chemical pollution, man-made underwater noise, eutrophication and climate change. Combined impacts caused a massive retreat of the population from the SE North Sea in the 1950's as well as a remarkable recovery through the late 1990's to early 2000's. Both trends cannot be clearly explained using available records, but food base alterations are a likely steering factor. To better understand North Sea harbour porpoise population dynamics, methods assessing long-term ecosystem health are needed, but gauging human impact on the ecosystem requires long-term records of ecosystem function that are extremely difficult to assemble. Here we show that molecular-level isotope measurements of amino acid carbon and nitrogen from harbour porpoise collagen allow for reconstruction of ecosystem status across ~170 years in the North Sea. We found increased reliance on high trophic position (TP) prey items (e.g. gadoids) from 1939 to 1969 which shifted towards lower TP demersal prey (e.g. gobies, sandeel) in 1970-1990. The trend of downward TP predation continued with reliance on smaller, abundant pelagic prey (e.g. herring, sprat, squid) through the 2010's as well as clear shift from dinoflagellate towards diatom support of the North Sea food web since 2008. These trends reflect a changing food base due to the combination of fisheries' pressure as well as climate warming in the North Sea and align with long-term regime shifts identified from fishery and plankton community records from the last 60 years. Additionally, porpoise feeding dynamics revealed a sex-based shift towards overlap of amino acid C records indicating development of competition for similar prey items that may explain increased stranding of juvenile males observed on the Dutch coast since 2005.

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Poster

Topics: 9 Ecology - marine, aquatic and terrestrial

Seasonal and Organ-Specific Variations in Nitrogen Dynamics of Lycopodium annotinum in Forest Ecosystems

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Mixed and coniferous forests are complex ecosystems with understory vegetation playing a vital yet often overlooked role in their functioning. Among the diverse understory plants are evergreen lycophytes such as *Lycopodium annotinum* L. (interrupted clubmoss), a protected species in the EU. Assessing long-term ecophysiological processes in this evergreen species is crucial to understand its interactions with its environment.

This study explores seasonal and organ-specific ecophysiological shifts in *L. annotinum* by using stable nitrogen isotopes ($^{15}N/^{14}N$) as integrators of ecophysiological processes. We hypothesized that $^{15}N/^{14}N$ ratios and nitrogen content (N%) in *L. annotinum* should vary across seasons and organs while being related with local plant diversity.

Plant specimens were collected in 2021-2022 during different seasons in Lithuania. Plant material was dried, separated into different organs (roots, plagiotropic stems and their leaves, orthotropic stems and their leaves), and ground into powder-like material. $^{15}N/^{14}N$ ratios and N% in bulk biomass were measured by employing isotope ratio mass spectrometry coupled with elemental analysis (EA-IRMS). $^{15}N/^{14}N$ ratios were expressed as $\delta^{15}N$ (‰) in relation with N-AIR.

The observed seasonal and organ-specific differences in nitrogen isotopic composition highlight adaptive ecophysiological responses of *L. annotinum*. Our results revealed significant seasonal shifts in $^{15}N/^{14}N$ ratios and N% of *L. annotinum*. Moreover, $^{15}N/^{14}N$ ratios and N% differed among different organs in *L. annotinum*. On the other hand, no significant relationships between neighbouring plant diversity and $^{15}N/^{14}N$ ratios and N% in *L. annotinum* were found, suggesting that nitrogen uptake in these plants might be independent from local plant diversity patterns. Our study contributes to understanding nitrogen dynamics in evergreen understory species and provides a foundation for further investigations into the nitrogen balance of *L. annotinum*.

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Poster

Topics: 9 Ecology - marine, aquatic and terrestrial

Kleptoplasty in Sacoglossan sea slugs: The role of algal donors

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Photosynthetic Sacoglossa sea slugs exhibit the remarkable ability to incorporate chloroplasts stolen from their algal prey—a process known as kleptoplasty. These algae organelles are then stored in the cells of the digestive diverticula, where, in some species, they can remain functional up to several months. The longevity of these kleptoplasts varies depending on the sea slug species and the algal donor. However, the extent to which the origin of the chloroplasts influences their contribution to the animal's metabolism remains unclear.

In this study, we incubated three species of sea slugs (*Elysia viridis*, *Elysia timida* and *Elysia crispata*) in seawater enriched with ^{13}C-bicarbonate and ^{15}N-ammonium under both light and dark conditions. The isotopic composition analysis using Isotope Ratio Mass Spectrometry (IRMS) allowed us to assess the incorporation of carbon and nitrogen, mediated by the stolen chloroplasts, into the animal tissues. The impact of the algal chloroplast donor (*Bryopsis* sp., *Acetabularia acetabulum*) on carbon fixation and nitrogen assimilation will be discussed, with evidence highlighting the significant role of chloroplast functionality in the metabolism of Sacoglossan sea slugs.

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Poster

Topics: 9 Ecology - marine, aquatic and terrestrial

More than one fish in the lake? Unexpected isotopic diversity in the endemic fish species Orestias chungarensis from Lake Chungará (4520 m asl), northern Chile.

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Orestias chungarensis is a small-bodied fish whose global distribution is limited to a single high-altitude (4520 m) Andean lake (Chungará) located in the Altiplano of northern Chile. Until the late 20th century *O. chungarensis* was the only fish species inhabiting the lake. The introduction of rainbow trout at this time led to the loss of Orestias from the River Chungará. Although of elevated conservation concern, little is known regarding *Orestias* ecology: the few studies conducted have relied on individuals captured from the shallow littoral. Here we analysed multi-tissue stable isotopes ($\delta^{13}C$, $\delta^{15}N$, $\delta^{34}S$) and stomach contents to study the trophic ecology of *Orestias* captured in different lake habitats.

Stable isotope values showed the existence of two putative groups of *Orestias*. A discriminant function analysis function supports the separation of two groups with a classification success of 98%. The *Orestias* included individuals belonging to a putative pelagic group (^{13}C-depleted, ^{15}N-enriched, ^{34}S-depleted) and a benthic /littoral group (^{13}C-enriched, ^{15}N-depleted and ^{34} S-enriched). Mixing models analysis showed the main contribution to the assimilated diet of the pelagic group *Orestias* in a short and longer time was pelagic zooplankton and benthic/littoral group amphipods and zooplankton from littoral indicating different foraging habitats.

Our stomach contents results showed that *Orestias* feed mainly on benthic macroinvertebrates (amphipods, chironomids, and gastropods.). However, the isotopic variation shown by *O. chungarensis* in Lake Chungará suggests that individuals forage across different habitats over time. Given the remarkable plasticity found in the genus, may reflect the existence of a previously unrecognized ecotype.

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Poster

Topics: 9 Ecology - marine, aquatic and terrestrial

Investigating physiological responses to wet and dry years of Norway spruce in Austrian forests with stable isotope methods (13C,18O)

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Norway spruce (*Picea abies* (L.) Karst) is a widespread tree species in Austria. Due to its economic importance and planting recommendations in the past, it can now also be found on sites that are close to the limits of suitability. Changing climate conditions affect plant growth and plant performance. Prolonged droughts and rising temperatures reduce the plant's resistance to pest insects but mild winters result in high insect populations. In recent years we see more regions where water availability is the limiting factor due to more frequent and longer droughts or changing precipitation patterns. Soil has a certain buffer function but only the water pools of the upper layers are accessible for spruce trees as they have shallow roots. Economic losses due to massive pests are becoming more common. To compare Norway spruce's strategies and resilience capacity we investigated sites all over Austria.

Stable isotope (^{13}C,^{18}O) data in tree rings is a very effective tool to investigate physiological responses to environmental and geomorphological conditions, specifically soil water availability and usage. It acts as an archive that provides insights into individual tree water status, temperature and source water use. We sampled 28 spruce plots all over Austria with 14 different soil types and linked the isotope data of selected dry and wet years with temperature and evaporation data as well as the precipitation amount during the growing season. We assessed radial growth through tree-ring width and intrinsic water-use efficiency (iWUE) for the individual site-specific conditions. This information should support forest management strategies to integrate specific environmental conditions, including soil properties and water status, to effectively mitigate impact of climate extremes and adapt our forests for future scenarios.

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Poster

Topics: 9 Ecology - marine, aquatic and terrestrial

Assessing Diachronic Shifts in Gilthead Seabream (Sparus aurata) Revealed by Amino Acid Compound Specific Isotope Analysis: Evidence Of Human Impacts In The Berre Lagoon, South Of France

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Compound-specific stable isotope analysis of amino acids (AA-CSIA) is increasingly used in ecological and archaeological studies, yet its data quality and interpretive power over time remain underexplored. This study applies both bulk and AA-CSIA to *Sparus aurata* remains from two archaeological sites—Font-aux-Pigeons (Neolithic, ~5000 BCE) and Saint Blaise Oppidum (13th century CE)—alongside modern samples from the nearby Berre Lagoon, to investigate diachronic shifts in trophic ecology and human exploitation of marine resources. Bivalves (*Ruditapes decussatus*) served as a proxy for baseline isotopic values. Collagen preservation was assessed through amino acid relative abundance, $\delta^{13}C$ and $\delta^{15}N$ patterns, and sum V. Finally, we further developed the ecological potential of these archives by measuring two proxies commonly used in ecological studies, i.e., Trophic level and the 13C and 15N Baseline, and compared their evolution across these different periods.

Significant temporal offsets were found in both trophic position and carbon source indicators. Neolithic fish exhibited lower trophic levels and more variable carbon sources, suggesting diverse habitats and potentially different fishing practices. Principal Component Analysis of $\delta^{13}C$ essential amino acids revealed a distinct reliance on phytoplankton in the medieval period. Overall, AA-CSIA, particularly $\delta^{15}N$, proved to be a robust tool for reconstructing ecological and anthropogenic patterns across time. These findings highlight shifts in resource use that may reflect broader socio-environmental changes and underscore the value of isotope analyses in archaeological ecology.

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Poster

Topics: 6 Biogeochemistry - carbon, nitrogen, sulfur and other cycles

The nitrogen delta values of soil, grain and fertilizers from an agricultural field over a 20 year period

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The so-called crucial field is an agricultural test project west of Copenhagen since 2001, where various fertilizers (such as cattle manure, mineral fertilizer and organic household waste) have been applied on different sub-plots to study their long-term effects. Moreover, some sub-plots have been 'retired' and received only minimal fertilization after 2012. To investigate the numerous effects on C and N isotopes, I am analyzing stored fertilizer, soil and grain samples. The main points of investigation are

1. how the isotopic composition of the soil and the grain changes depending on the fertilizer treatment over time (caused by the fertilizer delta values or alternated soil processes due to fertilization);
2. how the isotopic delta values of the fertilizers themselves have changed since the beginning of the experiment and
3. how long the soil isotopic delta values take to reach pre-experimental values after 'retirement'.

In addition, it is intended to do GHG-flux measurements to investigate emissions of the sub-plots and examine whether high emissions can be linked to high delta values in the soil.

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Poster

Topics: 6 Biogeochemistry - carbon, nitrogen, sulfur and other cycles

A multiplexing set-up of aquatic biological chambers to study the isotopic fractionation of oxygen: application to the interpretation of the δ18O of O2 records found in deep ice cores.

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Earth atmospheric dioxygen is mainly produced by biosphere photosynthesis, biosphere respiration being one of its main consumers. Atmospheric O_2 evolution is thus linked to global biosphere productivity.

In ice cores we extract air from bubbles to study past atmosphere composition. However, as O_2 concentration in air bubbles is affected by close-off processes, it is difficult to reconstruct its past atmospheric variations. In turn, O_2 isotopic composition ($\delta^{18}O$ and $\delta\ ^{17}O$), is also modified by biological processes, but less influenced by close-off processes so this tracer should provide useful information on past biosphere activity.

Quantitative interpretation of O_2 past isotopic composition relies on robust estimate of oxygen fractionation coefficients associated with photosynthesis and respiration. In the past decades, some determinations of these biological fractionation coefficients were performed in uncontrolled large-scale environments or at the micro-organisms scale in conditions very different from the natural environment. There are thus inconsistencies in previous determinations of the O_2 fractionation coefficients limiting the interpretation of $\delta^{18}O$ and $\delta\ ^{17}O$ of O_2.

In order to come up with coherent estimates of oxygen fractionation coefficients during biological processes, we developed closed biological chambers as a biosphere replica, with controlled environment parameters (light, temperature, CO_2 concentration), which were used in combination with a newly designed optical spectrometer for continuous measurements of O_2 concentration and of its isotopic composition.

In this presentation, we show the design and realisation of our aquatic biological chambers as well as the associated development of the multiplexing system to be able to run parallel experiments with the same environmental conditions. Then, we show the results obtained for light and dark periods, and the corresponding fractionation coefficients calculated for photosynthesis and respiration. Finally, we use the newly determined fractionation coefficients to improve interpretation of O_2 $\delta^{18}O$ records in ice cores air bubbles.

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Poster

Topics: 6 Biogeochemistry - carbon, nitrogen, sulfur and other cycles

Changes in the carbon cycle of Lake Plateliai, Lithuania, over the past 130 years

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The present study focuses on how anthropogenic activities affected the carbon cycle and biological productivity in oligotrophic lake during the last 130 years. We analysed stable carbon isotopes and radiocarbon (^{14}C) distribution in two organic sediment fractions: alkali-soluble and alkali-insoluble was performed in lake sediments. Additionally, diatom analysis and organic matter content in sediments was performed. Over 130 years, the reservoir age (RA) in both organic sediment fractions in this ecosystem changed by 872.4 ± 80 years. In this lake ecosystem, during periods when the water level was maintained more or less constant (1885-1932 and after 1985), the ^{14}C specific activity values in both sediment fractions remained very similar, varying in the range of 1 pMC. Any changes in the plankton community that affect the stable carbon isotope ratio in the alkali-soluble fraction did not affect the redistribution of ^{14}C between both organic sediment fractions. Differences in RA up to 600 years changes between fractions were associated with the input of allochthonous substances into the lake.

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Poster

Topics: 6 Biogeochemistry - carbon, nitrogen, sulfur and other cycles

Modern carbonate sinter formation: Insights from trace element and multi-isotope partitioning

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Mineral formation from hard water creeks is sensitive to variations of physico-chemical boundary conditions, including climate change. Groundwaters saturated in $CaCO_3$ and supersaturated in CO_2 emerge from springs, degas CO_2, and after exceeding a critical supersaturation carbonate starts to precipitate. Lithology-dependent geogenic and anthropogenic loads with sulfate are observed, too. Trace element and stable isotope partitioning upon crystallization are controlled by non-equilibrium processes. Both may be used to estimate element sources, subterrestrial weathering, and surface precipitation, and degassing rates. The fresh waters will discharge to rivers or coastal waters and impact their buffer capacity with consequences for green-house gas levels and surface water acidification.

Examples for hard water creeks in the temperate climate zone showing recent active sinter formation were chosen from Mühlengrund and Kollicker Bach (Rügen), Nohn (Eifel), and Westerhof (Harz foreland). Westerhof has a well-documented long research history dating back to the 60s that allowing for anthropogenic impact identification.

The hydro- and stable isotope (H, C, O, S) geochemistry of dissolved and solid phases were analyzed. Carbonate precipitation rates are estimated from trace element distribution.

The systems are characterized by a two-stage development of the surface waters: An induction period with sol CO_2 degassing, and a stage where calcite formation drives further degassing. The liberation of CO_2 is associated with an enrichment of the heavy carbon isotope in the remaining dissolved inorganic carbon. Trace element discrimination between the aqueous solutions and fresh calcite precipitates along the flow path are compared of distribution coefficients derived in previous experimental studies and seasonal and spatial resolved field calcite-precipitation rates. Stable isotope signatures (H, C, O, S) allow water and element source identification and mechanistic interpretation of the processes controlling the carbonate system. Carbonate-associated-sulfate in sinter is a new proxy that allows for a source characterization of sulfate in fresh water carbonates.

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Poster

Topics: 6 Biogeochemistry - carbon, nitrogen, sulfur and other cycles

Can Isotopic Maps Reveal Soil N2O Hotspots?

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Soil N_2O emissions are laborious and difficult to quantify and upscale to larger areas due to high spatiotemporal variations. Nitrogen isotopes are gaining increasing attention as a potential tool for improving landscape-scale assessments of N_2O emissions. This is because biochemical processes in the nitrogen (N) cycle discriminate against the heavier N isotope, ^{15}N, resulting in distinct isotopic signatures in the product and residual substrate. Maps of the spatial distribution of isotopes, isoscapes, offer a promising approach for identifying spatial variability in N processes. However, integrating soil N isotopes into ecosystem models requires better understanding of the drivers behind their spatial variation.

Moist depressions in crop fields are known to be N_2O hotspots and represent key sites for exploring soil ^{15}N patterns associated with N_2O emissions. This study focused on spatial patterns of soil N isotopes across two rolling fields in Zealand, Denmark. A total of 148 topsoil samples (0-10 cm) were collected along multiple topographic transects and analyzed for soil N and carbon content and isotopic composition, with soil texture (at selected locations). Correlations between parameters were assessed using Spearman's Rank Correlation Coefficient.

Emitted N_2O is expected to be depleted in ^{15}N relative to its source substrate. Based on this, we hypothesized that soil N in N_2O hotspots (moist depressions) would show higher ^{15}N enrichment compared to adjacent soils, due to greater losses of ^{15}N depleted N. Contrary to this hypothesis, results showed a significant positive correlation between soil $\delta^{15}N$ and elevation, with the lowest $\delta^{15}N$ values observed in depressions. This suggests that processes other than N_2O emissions play an important role in shaping the isotopic patterns. The study revealed substantial spatial variability in soil $\delta^{15}N$ (3.8-9.8‰) underscoring the importance of sample location in determining isotope fractionation patterns and highlighting the need for further investigation to refine application of isoscapes.

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Poster

Topics: 6 Biogeochemistry - carbon, nitrogen, sulfur and other cycles

Is there evidence of significant contributions of fungal denitrification to nitrous oxide emissions in different soils?

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Information on fungal contribution to nitrous oxide (N_2O) emission from denitrification in soil is scarce. However, some fungal species were identified to produce substantial amounts of N_2O in controlled experiments and several soil incubation experiments even suggest that fungi may dominate N_2O emissions compared to bacteria. The present study aimed to answer the question, whether it is possible to identify soils with substantial contribution of fungal denitrification on N_2O emissions.

Repacked samples of eight arable and grassland soils and one artificial compost from different locations were incubated in a fully automated incubation system to investigate N_2O emissions and its origin. Two treatments without and with homogeneous straw incorporation were compared to vary the carbon availability and sources. Nitrate was added to allow denitrification. Three phases were established for a period of one week each, with varying experimental conditions. Initially, the water saturation was adjusted to 60% of water filled pore space (WFPS) with oxic conditions, followed by a second oxic phase with water saturation raised to 80% WFPS. During a third phase the oxygen was removed from the system. CO_2 and N_2O fluxes were measured continuously and gas samples for isotopic analysis of N_2O were collected manually at selected time points.

CO_2 fluxes decreased with the onset of a new phase, while CO_2 fluxes of treatments with straw exceeded the ones without straw. In contrast to that, N_2O fluxes increased from phase 1 to 3. Applying the FRAME model, which is used for N_2O source partitioning based on isotopic data taking into account mixing and fractionation effects, revealed bacterial denitrification or nitrifier denitrification being the dominant N_2O producing pathways. Thus, fungal denitrification played a minor role in N_2O production, although isotopic data of some soils indicated a fungal contribution by denitrification up to 0.4 %.

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Poster

Topics: 6 Biogeochemistry - carbon, nitrogen, sulfur and other cycles

Microbial communities and their role in the carbon cycle in groundwater remediation – synergistic impact of biofilm and biochar in PCE degradation

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Biochar as an alternative filter to activated carbon (AC) was tested for the removal of tetrachloroethene (PCE) from contaminated groundwater by means of sorption and biodegradation by organo-halide respiring bacteria in batch and column experiments. Besides quantifying PCE degradation and identifying the relevant bacteria, microbial biomass and its carbon isotope composition were determined using microbial phospholipid fatty acids (^{13}C-PLFA) analysis in order to allow a quantitative and functional observation of the microbial community.

PLFA analysis revealed that microorganisms and also those groups that can be assigned to the PCE-degrading organisms preferentially colonize biochar, while AC is avoided possibly due to the higher PCE sorption capacity of the activated charcoal and hence lower bioavailability of PCE. If pure PCE was added to AC to increase its concentration in the liquid phase, the microbial colonization of the AC still remained low, while the amount of floating microbial biomass increased. The carbon isotope value of the microorganisms (^{13}C PLFA) indicated the use of alternative carbon sources besides added lactate and acetate and/or the presence of strongly isotope-fractionating biochemical processes. This effect was especially strong on and under the presence of biochar and in gram positive bacteria. Besides incorporation of biochar, also the use of ethene (PCE degradation product) and methane (derived from methanogenesis) might be considered as carbon source.

Carbon cycling in this specific environment still need to be verified by further research. Nonetheless, we can conclude that it is advisable to choose the filter material not only on the basis of the sorption capacity, but above all on the synergy effects that leads to a permanently active microbial community and an extension of the filter life due to the continuous and complete degradation.

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Poster

Topics: 6 Biogeochemistry - carbon, nitrogen, sulfur and other cycles

Tracing the microbial assimilation of geogenic nitrogen using 15N amino sugars

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Nitrogen in soil is strongly influenced by anthropogenic activities, such as fertilization and atmospheric nitrogen deposition. Recent studies, however, show the possible importance of geogenic organic matter. Geogenic organic matter (also known as fossil, rock or petrogenic organic matter) consists of plant and microbial remains preserved in rocks. While typically inert due to deep isolation, it can be mobilized by human activities such as mining and construction or naturally by weathering. This makes it an active but understudied component of soil systems that enters the decomposer food chain.

Geogenic nitrogen can substantially affect nitrogen availability, which is a key factor shaping terrestrial ecosystems' responses to rising atmospheric CO2 levels. Quantifying this flux is essential for accurately modeling biogeochemical cycles and better understanding terrestrial ecosystem dynamics.

The study is set at post-mining sites in the NW Czech Republic, utilizing a unique chronosequence of spoil heaps with varying ages, developmental stages, and two types of reclamation approaches characterized by different vegetation. This setting allows us to investigate the integration of geogenic organic matter into soil processes and its utilization by microorganisms across the site development. By extracting amino sugars and determining their natural abundance nitrogen isotope ratio, we will gain insights into microbial assimilation of geogenic nitrogen as it is isotopically enriched compared to recent nitrogen sources. We will use a mixing model to assess the contribution of geogenic organic matter and recent nitrogen sources to microbial uptake.

We aim to quantify quantify the amount of geogenic nitrogen assimilated by soil microorganisms, as determined by the isotopic composition of nitrogen in their amino sugars, across the chronosequence and assess how the developmental stage of the sites and the type of reclamation influence this assimilation.

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Poster

Topics: 6 Biogeochemistry - carbon, nitrogen, sulfur and other cycles

Biofilters, a self-sustaining system for the purification of contaminated groundwater?

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The biofilter, represented by a microbially active biochar filter, has been explored as a potential tool for groundwater remediation, offering the prospect of self-renewal of the sorbent's sorption capacity through the microbial degradation of introduced contaminants, as well as the utilisation of eco-friendly filter materials, such as biochar.

Utilising tetrachloroethene (PCE, C_2Cl_4), a prominent groundwater contaminant, as a model substance, a comprehensive experimental approach was adopted, encompassing batch and column studies in the laboratory. These experiments involved the use of different biochars and activated carbon in conjunction with two organohalide respiring microbial communities. The fate and behaviour of PCE and its daughter products were monitored using a combination of compound specific isotope analysis (CSIA) and sorption/desorption analysis. Additionally, molecular biological and biochemical methods were employed to analyse the composition and proliferation of microbes.

The results obtained provided compelling evidence for the complete dechlorination of PCE and its daughter products to ethene. Furthermore, the results indicated that microorganisms may proliferate more readily on biochar compared to activated carbon. In essence, a functional biofilter requires both an adaptable microbial community and a corresponding filter medium. The outcome of a recently completed project will be presented, along with the plans for a follow-up project that is currently in its initial stages. The objective of this subsequent project is to enhance the biofilter approach to a technical level and to conduct a pilot study in a field setting.

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Poster

Topics: 6 Biogeochemistry - carbon, nitrogen, sulfur and other cycles

Application of Compound-Specific Stable Isotope Analysis in Isotopic Mixing Models to Decipher the Effect of Priming in Coastal Sediments

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The priming effect (PE) refers to the enhanced remineralization of recalcitrant organic carbon (OC) driven by the respiration of labile OC, potentially increasing CO_2 fluxes from aquatic ecosystems. Investigating PE dynamics requires precise methods to trace the fate of organic matter sources and their transformation within sedimentary environments. In this study, we apply compound-specific stable isotope analysis (CSIA) within an isotopic mixing model framework to quantify the contribution of priming to the degradation of hydrocarbons (C_{15}–C_{30}) in coastal sediments. By integrating stable isotope data with concentration profiling, we assess how the remineralization of recalcitrant OC is influenced by fresh organic inputs. To achieve this, we conducted controlled microcosm experiments using coastal sediments ($\delta^{13}C$_bulk = −25.26 ± 0.06 ‰, 1.63 ± 0.07% OC) spiked with isotopically distinct marine and terrestrial OC sources such as Nannochloropsis phytoplankton ($\delta^{13}C$ = −43.18 ± 0.31 ‰) and C_4 corn leaves ($\delta^{13}C$ = −13.90 ± 0.09 ‰). The temporal variations in isotopic composition of respired OC were tracked by difference through CSIA at multiple time points across 30 microcosms, allowing us to resolve source-specific degradation pathways. Our results demonstrate that stable isotope values effectively capture the acceleration of recalcitrant OC remineralization following the addition of fresh, labile OC. The protein/peptide-rich Nannochloropsis and polysaccharide-rich corn leaves both enhanced OC degradation compared to sediment incubated alone under identical conditions. Additionally, CSIA revealed a decline in fractionation over time, indicating stabilization of the degradation process within the sedimentary matrix. These findings highlight the power of CSIA in isotopic mixing models as a robust tool for quantifying OC transformations and source contributions in complex sedimentary systems. Understanding these dynamics is crucial for refining global carbon cycle models, particularly in the context of increasing atmospheric CO_2 levels, eutrophication, and enhanced terrestrial OC fluxes to marine environments.

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Poster

Topics: 6 Biogeochemistry - carbon, nitrogen, sulfur and other cycles

Real-time in situ monitoring of biogeochemical processes in aquatic ecosystems: Nitrous oxide and methane concentrations and isotopic signatures

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Coastal ecosystems are dynamic regions rich in diverse biological and geochemical interactions. However, major gaps exist in our knowledge of these biogeochemical processes and the factors regulating their relative importance. The study of nitrogen and carbon cycling in aquatic systems is important for understanding these biogeochemical processes and the impact of human and natural inputs to the ecosystems. Nitrous oxide (N_2O) and methane (CH_4) have important roles in the nitrogen and carbon biogeochemical processes as they are produced or externally introduced and then cycled within coastal and ocean environments. The gaps in our understanding of the distribution and dynamics of the underlying processes controlling these N and C cycles can be filled with the development and deployment of high-resolution spatial-temporal measurement methods.

We have developed a real-time, *in situ* system to quantify dissolved greenhouse gases (N_2O and CH_4 and their isotopologues) in aquatic ecosystems including coastal wetlands. This measurement system consists of i) an array of permeable, hydrophobic probes to passively sample dissolved gases; ii) a collection protocol for efficiently transferring dissolved gases without isotopic fractionation; and iii) an interface of the probe array and sampling system with an Aerodyne tunable infrared laser direct absorption spectrometer (TILDAS). The TILDAS provides real time determination of concentration and isotopic abundances of N_2O and CH_4.

In laboratory studies, we have compared dissolved gases extracted from a variety of collected water samples including different tap water sources, ocean water, and wetland “swamp” water. A field deployment of the system is planned for Spring 2025 at a coastal site on Cape Cod, MA with an array of 16 probes to be deployed in the coastal ecosystem. Dissolved N_2O and CH_4 concentrations and isotopic signatures will be measured continuously over several weeks at the site. Preliminary results and the biogeochemical implications will be discussed.

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Poster

Topics: 6 Biogeochemistry - carbon, nitrogen, sulfur and other cycles

Sulfamethoxazole Transformation by Heat-Activated Persulfate: Linking Transformation Products Patterns with Carbon Compound-Specific Isotope Analysis

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Sulfamethoxazole (SMX) is a frequently detected sulfonamide antibiotic in surface and groundwater, raising environmental concerns about its fate. Oxidative treatments, such as persulfate application, are commonly used for micropollutant removal. To investigate and differentiate SMX transformation by various radicals from other SMX dissipation processes, SMX transformation experiments were conducted using heat-activated persulfate at pH 3, 7, and 10. SMX hydroxylamine (TP269a) and TP178 were identified as the dominant transformation products across all pH levels. The exclusive formation of 4-nitroso-SMX, 4-nitro-SMX, and TP518 at pH 3 highlighted the role of $SO_4^{\bullet-}$ in attacking the amino group. At pH 7 and pH 10, 3A5MI emerged as the dominant TP. Normal carbon isotope fractionation ($\Delta\delta^{13}C$ from 1.9‰ to 2.3‰), with consistent isotopic values across pH levels, was attributed to the formation of TP178, which involves C-S bond cleavage. An inverse nitrogen isotope fractionation at pH 3 ($\varepsilon_N = +0.68 \pm 0.11$‰) was linked to $SO_4^{\bullet-}$-induced single-electron transfer, leading to the formation of N-centered SMX radicals. Conversely, normal nitrogen isotope fractionation at pH 10 ($\varepsilon_N = -0.27 \pm 0.04$‰), was associated with multiple bond cleavages, including N-H bond cleavage initiated by H abstraction through HO• and N-S bond cleavage leading to the formation of 3A5MI. The inverse nitrogen isotope fractionation observed at pH 7 indicated that the dominant pathway involved $SO_4^{\bullet-}$ reactions, accounting for 76% of the overall transformation. Overall, the results highlight the potential of CSIA to elucidate SMX persulfate oxidation pathways and evaluating the natural attenuation of SMX through radical reactions in aquatic systems.

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Poster

Topics: 6 Biogeochemistry - carbon, nitrogen, sulfur and other cycles

A trans-European decomposition study, focusing on the impact of plant diversity using a common 13C-labelled litter in arable soils.

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Root carbon has been shown to be one of the most dominant forms of soils carbon inputs in agricultural systems. New paradigms in soil organic matter theory suggest the role of root derived soil carbon in its influence on carbon storage and decomposition may have been overlooked.

Mixed species systems are currently gaining traction Europe providing opportunities for sustainable intensification of agriculture and other ecosystem-service co-benefits. In Mix&Max-Root-C we aimed to gain a management-oriented understanding of the effect of mixed-species root systems on carbon flows and organic matter accumulation across a European gradient

We conducted pan-European in-situ field experiments to measure decomposition rates and the fate of carbon using labelled litter. Treatments included:((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 goal was to determine the impact of increased plant diversity organic matter breakdown to develop a trans-European decomposition index. Using a hub spoke design, a common ^{13}C-labelled material was supplied to each participant and was mixed in a similar manner with the soil from the local treatments, packed into mesh bags and buried in the treatment plots. This was done at the start of the growing season and excavated at the end of the growing season and returned to Tulln for a suite of carbon pool analysis.

The experiment, covered eight sites, diverse climates and cropping systems. We tested the null hypothesis that increased plant diversity does not increase the decomposition rate in the field. Initial results suggest that decomposition rates were 40-65% across sites and that diverse cover-cropping mixtures did not lead to lower decomposition rates. These data and results will be used to guide model predictions.

Keywords* Mixed cropping, Diversity, ^{13}C labelled, Maize litter, Monoculture, Carbon

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Topics: 6 Biogeochemistry - carbon, nitrogen, sulfur and other cycles

Isotopic Analysis of Organic Matter in a Stratified Marine Lake: Evaluating Environmental Shifts and Eutrophication Drivers

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Rogoznica Lake – Dragon Eye (RL) is a highly eutrophic, stratified euxinic marine system on the Adriatic coast, significantly affected by environmental changes, including water column warming, deoxygenation, accumulation of toxic sulfides and ammonia, and an increased frequency of anoxic holomictic events. These factors strongly influence the dynamics and properties of organic matter (OM).

Long-term data on OM reveal the accumulation of particulate (POC) and dissolved (DOC) organic carbon, particularly in the anoxic hypolimnion, with DOC ranging from 0.809 to 7.16 mg L^{-1} and POC from 0.572 to 10.5 mg L^{-1}. Qualitative changes in OM are assessed using DOC-normalized surfactant activity (NSA = SAS/DOC), determined by monitoring DOC levels and its surface activity, i.e., surface-active substances (SAS). Further characterization of OM is conducted through the analysis of stable isotopes of light elements ($^{13}C/^{12}C$, $^{15}N/^{14}N$, $^{34}S/^{32}S$) and the C:N ratio in the POC fraction, providing insights into phytoplankton community structure, OM sources and origins, and its role in biogeochemical cycles. These analyses are performed using isotope-ratio mass spectrometry (IRMS).

Preliminary seasonal isotope data ($\delta^{13}C$, $\delta^{15}N$, $\delta^{34}S$) from the RL water column reveal values ranging from -20.89‰ to -32.30‰ for $\delta^{13}C$, -8.07‰ to 7.24‰ for $\delta^{15}N$, and -10.83‰ to 21.74‰ for $\delta^{34}S$, with noticeable seasonal shifts along the water column driven by variable physico-chemical parameters (salinity, oxygen saturation, atmospheric deposition). The position of the chemocline, which separates the surface oxic and bottom anoxic water layers, is distinctly observable in the $\delta^{34}S$ values, showing pronounced seasonality.

These findings indicate that OM in the RL water column is predominantly autochthonous, largely derived from phytoplankton activity, with occasional allochthonous inputs, as suggested by the C:N ratio (ranging from 1.09 to 6.51), contributing to eutrophication. During holomictic events, when the water column becomes entirely mixed and anoxic, isotope ratios suggest a significant presence of bacterially-produced OM.

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Topics: 6 Biogeochemistry - carbon, nitrogen, sulfur and other cycles

Clumped isotope measurements reveal aerobic oxidation of CH4 below the Greenland ice sheet

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Clumped isotopes of methane (CH_4), specifically $\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$, provide additional information to constrain its sources and sink processes. These isotopes complement interpretations of CH_4 provenance based on bulk isotopes. However, interpreting the origin of CH_4 using isotopes becomes challenging when the isotopic signature is altered by post-generation processes. In this study, we measured, for the first time, the bulk and clumped isotopic composition of sub-glacial CH_4 samples. These samples were collected from the air-filled headspace of the glacier portal (ice cave) at the edge of the Isunnguata Sermia glacier (ISG), located at the western margin of the Greenland ice sheet (GrIS). Our goal was to identify the processes underlying the sub-glacial production and potential processing of CH_4. The $\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$ values of the samples measured in this study are 3.7 ± 0.3 ‰ and 39.7 ± 2.0 ‰, respectively (95 % confidence interval). The $\Delta^{12}CH_2D_2$ values are close to those of atmospheric CH_4. The elevated $\Delta^{12}CH_2D_2$ values can be attributed to the alteration of the source's isotope signal by aerobic oxidation. This conclusion is supported by previous studies at this site, which reported the presence of methanotrophic bacteria and dissolved oxygen close to saturation in the meltwater. Our results confirm that the correlation between $\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$ is a useful tool for deciphering oxidation pathways. Our results support the inference that aerobic CH_4 oxidation can strongly modify the $\Delta^{12}CH_2D_2$ isotope signal, which must be considered when determining the source signatures of environmental samples.

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Topics: 6 Biogeochemistry - carbon, nitrogen, sulfur and other cycles

Carbon sequestration in vineyards: Isotopic evidence of management impacts on SOC stock

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Soil organic carbon (SOC) is fundamental to both climate regulation and agricultural sustainability. Enhancing SOC stocks is recognized as an effective strategy for mitigating climate change, promoting soil fertility, and ensuring ecosystem sustainability. Perennial crops, such as vineyards, have received more attention due to their ability to store SOC. In contrast to annual cropping system, vineyards may contribute to SOC accumulation through permanent root systems, substantial biomass input, and long-term organic matter inputs into the soil. However, vineyard soils are managed in diverse ways that can either enhance or reduce SOC stocks. Management strategies range from maintaining permanent ground cover between the rows to biannual tillage that eliminates vegetation, considered as competing for water resources. Yet, the impact of these practices on SOC turnover and stabilization remains poorly understood. This study aims to assess the impact of ground cover and tillage on soil carbon storage using δ13C and Δ14C isotopic analysis. Soil samples collected from two adjacent vineyard plots in center Spain. One has maintained spontaneous vegetation cover, whereas the other has undergone tillage. Samples were taken down to 90 cm, with a 5 cm step down to 20 cm, 10 cm step down to 50 cm and 20 cm step thereafter. C and N contents, δ13C and Δ14C were analysed to trace carbon sources and access carbon dynamics and stabilization.

The findings of this research will offer valuable perspectives on how different soil management practices affect soil carbon storage in vineyards. By analysing isotopic signatures under contrasted practices, this work aims to deepen our understanding of soil carbon dynamics and support more sustainable practices. The findings support conversations on improving soil health, adapting land management to climate change, and mitigating climate change by minimizing soil carbon loss and boosting storage and sequestration.

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Topics: 3 Atmospheric Sciences - Greenhouse and Other Tracer Gases, Air Quality and Aerosols

Development of an Aerosol Collector to Investigate Non-Mass-Dependent S Isotopic Fractionation Mechanisms in the Stratosphere

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The sulfur mass-independent fractionation (S-MIF) anomaly in sulfate records from ice cores, marine, and terrestrial archives has become a valuable geochemical tracer. However, significant uncertainties remain about the mechanisms that generate S-MIF, which complicates the interpretation of these measurements. The most widely invoked mechanism involves the exposure of sulfur gases to high levels of UV radiation. In this study, we present the development of a balloon-borne aerosol sampler, StratoPart, designed to collect sulfate on filters in the stratosphere - an environment with high UV radiation where the largest S-MIF anomalies in sulfate are expected to be found. The goal is to analyse the collected stratospheric sulfate to investigate and test the various proposed mechanisms for terrestrial sulfate S-MIF anomalies. StratoPart was flown during two balloon campaigns in the summer of 2024: one operated by CNES in Kiruna, Sweden, and the other by the TiFR balloon facility in Hyderabad, India. We will share preliminary results from the chemical analysis of some of the filters collected during these campaigns and discuss their implications.

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Topics: 3 Atmospheric Sciences - Greenhouse and Other Tracer Gases, Air Quality and Aerosols

Comparative Analysis of Isotopic Composition of Aerosols from Biomass and Coal Burning under Controlled and Uncontrolled Conditions

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Keywords: biomass burning, aerosol, isotopic analysis.

Biomass burning contributes to atmospheric aerosols, emitting a variety of particles and gases that impact both local and global air quality, as well as climate systems. This research examines aerosols produced from different wood species and coal, focusing on their isotopic signatures for total carbon under both controlled and uncontrolled experimental conditions. The study involved two distinct setups. First experiment was designed to simulate typical domestic heating practices during winter (in Lithuania). Second experiment was set up with controlled conditions as well as assessing the mass and humidity of biomass material and coal before monitoring of O_2, CO_2, temperature, airflow, pressure, η, λ, NO , CO and NO_2 levels of the smoke. A high flow (0.5 m3/min) sampler „DIGITEL DH-77" with a pre-separator "DPM 10/30/00" was used to collect biomass burning organic aerosol (BBOA) from the smoke on Whatman QM-A pure quartz fiber filters "Pallflex Tissuquartz 2500QAT-UP" of 150 mm diameter. The $\delta^{13}C$ values of bulk material ($\delta^{13}C_{TC}$) and total carbon of OA were determined at Center for Physical Sciences and Technology, Vilnius, Lithuania. The analysis was conducted using an elemental analyzer ("Flash EA 1112") coupled to an isotope ratio mass spectrometer ("Thermo Finnigan Delta Plus Advantage") via a "ConFlo III" interface (EA–IRMS system). A 1cm diameter round punch of the filter containing aerosol particles was wrapped in a tin capsule and introduced into the EA–IRMS system for measurement. The isotopic signatures and fractionation factors were observed to vary between controlled and uncontrolled settings, providing insights into how variations in environmental factors affect aerosol composition. This study enhances understanding of the aerosol formation under idealized conditions and real-world burning scenarios, thus providing deeper insights into the environmental effects of biomass burning.

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Topics: 3 Atmospheric Sciences - Greenhouse and Other Tracer Gases, Air Quality and Aerosols

Continuous methane isotope measurements in Lindenberg, Germany

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Methane (CH_4) mitigation is crucial for climate change mitigation, as it is a potent greenhouse gas with a shorter lifetime compared to CO_2. This, however, requires a solid understanding of the CH_4 sources. Isotopic analysis can aid in source partitioning.

CH_4 isotopic source signatures obtained through mobile measurements are limited to short durations and often fail to capture smaller or previously unknown emissions. In contrast, continuous CH_4 measurements cover longer periods and can detect inaccessible or unknown sources. These continuous measurements are unfortunately costly and it is more challenging to identify the source.

Researchers at Utrecht University developed an isotope ratio mass spectrometer system that measures CH_4 mole fraction, δD and $\delta^{13}C$ at high precision ($\delta^{13}C$ ± .2 ‰ δD ± 1 ‰) with a 40-minute resolution. This system was deployed from 15 April 2022 until 8 January 2023 in Lindenberg, Germany. Measurements were initialised at 40 meters and later continued at 98 meters. The station is part of the Integrated Carbon Observation System (ICOS), providing mole fraction measurements of CO, CO_2, and CH_4. The CH_4 measurements were also compared with simulations from EMPA. These simulations include the CH_4 emissions for each category, allowing us to assign an isotopic source signature to each emissions category, thereby simulating the δD and $\delta^{13}C$ of CH_4.

In the isotopic measurements, we observed 169 peaks related to diurnal elevations. This corresponds to 67% of the deployment days. Most source signatures indicate a microbial fermentation source. Additionally, we identified 19 multi-day elevations. Eight multi-day elevations displayed isotopic signatures similar to those of the diurnal peaks, while the remaining multi-day peaks were more distinct.

In short: this dataset with continuous CH_4 δD and $\delta^{13}C$ measurements enables the characterization of diurnal elevations and multi-day emissions and can show the quality of transport models.

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Topics: 3 Atmospheric Sciences - Greenhouse and Other Tracer Gases, Air Quality and Aerosols

Overcoming sulphate isotopologues measurement challenges in Electrospray-Orbitrap using Higher-energy Collisional Dissociation

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The oxidative capacity of the atmosphere and its implication in past and present climate changes remain poorly understood. In that perspective, better understanding the chemistry of atmospheric oxyanions like nitrate and sulphate is key, as they are the stable end products of oxidation reactions. In oxyanions, isotope clumping —the likelihood of multiple isotopic substitutions in the same molecule— is anticipated to be sensitive to the oxidation pathway involved in molecule formation. Accessing clumping information requires measuring the scarce doubly-substituted isotopologues.

The recent Orbitrap mass spectrometers combined with electrospray ionisation allow measurements on intact ions at high mass resolution, conserving the intra-molecular clumping information and discriminating the doubly-substituted isotopologue peaks. While this novel method provides promising results for nitrate isotopologues, measuring sulphate isotopologues remains challenging.

One way to measure sulphate isotopologues with ESI-Orbitrap is to analyse them as HSO4- anions. However, the isobaric interference between DSO4- and HS17OO3- isotopologues leads to inconsistent results for 17O or requires a drastic increase in resolution, which is detrimental to the precision of all sulphate isotopologue measurements. An alternative approach involves breaking the HSO4- anions into SO3- fragments, which eliminates this issue and requires lower mass resolution. This can be achieved by using higher-energy collisional dissociation —where the accelerated ions collide with nitrogen molecules— converting 90% of HSO4- into SO3- fragments which keep a satisfactory base peek intensity. We applied this method to several standards and natural samples and found that it provides better results both in terms of precision and accuracy for singly-substituted isotopologues, including 17O, compared to the previous method. We also measured doubly-substituted isotopologues, yet the question of which method is best for this purpose remains open.

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Topics: 3 Atmospheric Sciences - Greenhouse and Other Tracer Gases, Air Quality and Aerosols

Implementing a setup for continuous, long-term, high-frequency flux measurements of CO2 and H2O isotopologues using eddy covariance

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Monitoring greenhouse gas exchange between land ecosystems and the atmosphere using the eddy covariance technique has become standard practice in many flux observation networks. However, studies on stable isotope fluxes remain scarce and are typically limited in their temporal extent, despite their importance at contributing to accurate partitioning of fluxes. As part of the ISOMONEAE project, we designed a setup for eddy covariance measurements of CO_2 and H_2O stable isotopologues, which will be active over a two-year period from 2025 to 2027 in a managed beech forest in central Germany. The primary objective of the project is to investigate whether and how continuous, long-term, high-frequency isotopologue flux measurements can provide valuable additions to existing flux observation networks such as ICOS or FLUXNET.

Here, we present a novel setup for CO_2 and H_2O isotopologue eddy covariance measurements, utilizing an Aerodyne quantum cascade laser absorption spectrometer (Aerodyne Research Inc.) for CO_2 and an LGR absorption spectrometer (Los Gatos Research (ABB Inc.)) for H_2O. Ongoing work includes characterizing and enhancing instrument performance and designing automated calibration systems necessary for accurate long-term measurements. The instruments were characterized based on their drift behavior, time response, and measurement linearity. Through these investigations we identified temperature and pressure fluctuations as major sources of drift. To mitigate these effects, we designed automated calibration systems that perform hourly calibrations to maintain accuracy and precision.

We believe our projects outcome represents a significant step towards the implementation of large-scale, continuous, long-term, high-frequency isotopologue eddy covariance measurements into existing flux observation networks. The results will enhance our understanding of ecosystem-atmosphere exchange processes by disentangling greenhouse gas sources and sinks in ecosystems.

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Topics: 3 Atmospheric Sciences - Greenhouse and Other Tracer Gases, Air Quality and Aerosols

Rapid MIR laser spectroscopy for methane clumped isotopes: development and first applications

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The methane clumped isotope approach measures differences in abundances of doubly substituted species, i.e. $^{13}CH_3D$ and $^{12}CH_2D_2$, relative to the expected stochastic distribution of atoms. The resulting $\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$ serve as proxy for formation temperature under thermodynamic equilibrium, while departure from equilibrium indicates contributions of kinetically controlled CH_4 formation and consumption mechanisms, as well as other post-generation processes. Due to the extremely low abundance of doubly substituted isotopologues, highly advanced techniques are required.

In recent years, we established a spectroscopic platform based on quantum cascade laser absorption spectroscopy (QCLAS), with optimized spectral windows for clumped isotope analysis and a custom-built gas inlet system. The developed technique offers the feasibility of reducing sample size down to 3–7 mL CH_4 gas while achieving precision levels comparable to HR-IRMS. Samples larger than 10 mL can be quantified in a single run in under 20 min.

By leveraging this rapid, high-throughput QCLAS method, we explored several prototype applications. In a comprehensive technical study, we optimized the selection and use of cryogenic adsorbents for CH_4 storage targeting conservation of bulk and clumped isotopic signatures. As an illustrative and relevant geological application, we extract thermogenic CH_4 entrapped in the porosity of the source rocks to test whether CH_4 has formed under thermodynamic equilibrium. CH_4 clumped signatures of bubble gases collected from various mud volcanoes and hybrid systems in Italy and Indonesia can provide valuable insights into the mixing of thermogenic CH_4 with secondary microbial CH_4 and enzyme-catalyzed isotope exchange. We also investigate the clumped isotopic fingerprint of CH_4 originating from iron-oxido mediated formation of methyl radicals from methyl-substituted substrates, which might be a common abiotic source for C1 and C2 compounds. Our presentation will showcase the potential of the spectroscopic technique to be a more practical tool for analyzing methane clumped isotope signatures.

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Topics: 3 Atmospheric Sciences - Greenhouse and Other Tracer Gases, Air Quality and Aerosols

Temporal trends in δ13C- and δD-CH4 and C2H6 / CH4 in ambient air at a suburban site in Switzerland

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The dual isotopic composition of CH_4 ($\delta^{13}C$-CH_4, δD-CH_4) holds potential to differentiate between fossil fuel-related, microbial and pyrogenic sources. Separation between thermogenic and biogenic processes can be supported by the analysis of co-emitted species, such as ethane (C_2H_6), which is formed during thermal cracking of sedimentary organic matter, while microbial formation practically lacks ethane emissions.

In this study, we present high-resolution measurements of $\delta^{13}C$- and δD-CH_4 by a customized preconcentration (TREX) - laser spectroscopy (Aerodyne Research Inc.) system, $\delta^{13}C$-CH_4 by commercial cavity ring-down analyzer (G2201-I, Picarro Inc.) and C_2H_6 / CH_4 by a compact laser spectrometer (Aeris Technologies Inc.) in ambient air sampled at a suburban site close to Zürich, Switzerland. We show performance characterization, i.e. temporal resolution, precision, repeatability and comparability of techniques in relation to WMO/GAW (Word Meteorological Organization/Global Atmosphere Watch) requirements for monitoring atmospheric composition in regions with significant local fluxes. Furthermore, the temporal variations in CH_4 isotopic composition and C_2H_6 / CH_4 are interpreted by using the Keeling-plot or mixing-model approach.

We use atmospheric transport modelling and a sectorial CH_4 emission inventory to simulate CH_4, its isotopic composition and C_2H_6 / CH_4 at the site. We compare analytical results with these simulations with a focus on validating the applied regional emissions. By analyzing individual events, we identify periods and regions where isotopic observations can inform emission estimates.

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Topics: 3 Atmospheric Sciences - Greenhouse and Other Tracer Gases, Air Quality and Aerosols

Long-Term Trends in PM2.5 and Nitrogen Isotope Ratios of Water-Soluble Ions in Dhaka, Bangladesh: Implications for Source Contributions

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The COVID-19 pandemic led to significant air quality changes due to lockdowns. While $PM_{2.5}$ reductions were observed in many regions, long-term trends and variations in sources remain unclear, especially in Dhaka, Bangladesh, which records some of the highest $PM_{2.5}$ levels globally. Understanding $PM_{2.5}$ sources is essential for air quality management, pollution mitigation, and public health, as exposure to fine particulate matter is linked to severe respiratory diseases and cardiovascular problems.

This study analyzed $PM_{2.5}$ samples collected in Dhaka after COVID-19 to examine trends in water-soluble ions and nitrogen stable isotope ratios of ammonium ($\delta^{15}N\text{-}NH_4^+$) and nitrate ($\delta^{15}N\text{-}NO_3^-$, $\delta^{18}O\text{-}NO_3^-$). $PM_{2.5}$ concentration data were obtained from EPA AirNow. Water-soluble anions (Cl^-, NO_2^-, NO_3^-, SO_4^{2-}) and cations (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) were analyzed using ion chromatography. $\delta^{15}N\text{-}NH_4^+$ was measured using solid-phase extraction and the bacterial denitrification method (Kawashima et al., 2021), while $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ were analyzed via bacterial denitrification method.

$PM_{2.5}$ concentrations increased annually from 86.2 μg/m³ (2019) to 103.6 μg/m³ (2023). During the lockdown (March–May 2020), $PM_{2.5}$ levels (69.8 μg/m³) were lower than in 2019 (53.7 μg/m³, a 23% reduction), indicating a temporary decline in emissions. However, post-pandemic, $PM_{2.5}$ rebounded due to resumed economic activities, increased industrial output, and biomass burning. The $\delta^{15}N\text{-}NH_4^+$ values decreased (21.3‰ in 2019 to 12.3‰ in 2022), suggesting increased agricultural contributions, particularly from fertilizer and livestock waste.

Similarly, $\delta^{15}N\text{-}NO_3^-$ values declined slightly, indicating changes in NO_3^- sources, while $\delta^{18}O\text{-}NO_3^-$ remained stable. These shifts may be linked to environmental policies, such as converting Fixed Chimney Kilns to ZigZag Kilns, reducing emissions. This study highlights the importance of stable isotope analysis in pollution source identification. Future research should investigate seasonal variations and meteorological influences on nitrogen isotopes to improve air quality policies and public health interventions.

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Topics: 3 Atmospheric Sciences - Greenhouse and Other Tracer Gases, Air Quality and Aerosols

Tracing the sources and dynamics of SO2 and PM1 sulfate in Vilnius, Lithuania through stable sulfur isotope analysis

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Sulfur compounds are vital to Earth's climate and air quality, with sulfate aerosols contributing to atmospheric cooling by scattering solar radiation. Their radiative effects are influenced by SO_2 oxidation pathways, which determine their properties. Since the 1980s, sulfur pollution in Lithuania has steadily declined, with SO_2 emissions decreasing at a faster rate than sulfate emissions. However, the sources and formation mechanisms of atmospheric sulfate remain uncertain. In this study, we analyzed the concentrations and sulfur isotopic compositions of SO_2 and PM_1 sulfate over a two-year period to identify pollution sources and sulfate formation pathways in Vilnius, Lithuania.

Distinct seasonal patterns were observed in the $\delta^{34}S$ values of SO_2 and sulfate, with lower $\delta^{34}S$ values during wintertime and higher $\delta^{34}S$ values in summer. Source apportionment of major regional pollution sources revealed, that biomass burning was the primary contributor to sulfur pollution in summer, while coal combustion emissions from neighboring countries were dominant in winter. During the winter of 2022–2023, heavy fuel oil (HFO) replaced natural gas at the local thermal power station in Vilnius, making HFO emissions a significant source of SO_2 and PM_1 sulfate during this period. Additionally, during the 2022-2023 winter period, the predominant sulfate production mechanisms were evaluated, revealing that SO_2 oxidation by O_2, catalyzed with transition metal ions, was the primary mechanism, accounting for 79 ± 7 %, while oxidation by OH radicals and H_2O_2 contributed 5 ± 5 % and 16 ± 7 %, respectively.

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Topics: 3 Atmospheric Sciences - Greenhouse and Other Tracer Gases, Air Quality and Aerosols

Semi-continuous Δ17O measurements of atmospheric CO2 from the North coast of the Netherlands

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We present semi-continuous stable isotope composition measurements of atmospheric CO_2, including the triple oxygen isotope composition or $\Delta^{17}O$, in a record spanning the end of 2024 until spring 2025. Measurements are conducted with an Aerodyne dual-laser absorption spectrometer which was installed at the Lutjewad atmospheric measurement station, located at the North coast of the Netherlands. Atmospheric air coming from the 60 m high tower is measured as discrete samples, continuously alternated with measurements of a working gas for drift correction. Reference cylinders covering the range of CO_2 amount fractions occurring in the atmospheric samples are measured for calibration of the isotopologue amount fraction measurements.

The $\Delta^{17}O$ measurements typically have a standard deviation of 0.06 ‰ for a single gas measurement, and the long-term stability is 0.04 ‰. Multiple tracers are measured at the Lutjewad station, including CO_2, H_2 and N_2O amount fractions as well as the $\delta^{13}C$ and $\delta^{18}O$ composition of atmospheric CO_2. This gives us the opportunity to explore the potential of the $\Delta^{17}O$ of atmospheric CO_2 for carbon cycle research, for instance by studying the coupling with biosphere activity and fossil fuel combustion. In this project we have a special focus on the potential correlation between positive $\Delta^{17}O$ anomalies and stratospheric intrusions, and first results of these analyses will be presented on the poster.

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Poster

Topics: 3 Atmospheric Sciences - Greenhouse and Other Tracer Gases, Air Quality and Aerosols

Assessing the impact of uncertainties in prior sector level flux and atmospheric transport models on modelling of methane in regional scale

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Quantification of greenhouse gas (GHG) emissions are required for the mitigation strategies to be effectively made. Top-down methods, one of the efforts to improve our estimation, utilise ambient GHG measurements and atmospheric transport models (ATMs) on top of the prior flux estimates. A network of isotopic measurements of methane (δ13C-CH4 and δ2H-CH4) across Europe is starting to get developed, which has been identified as tracers to allow us to differentiate different sources categories within regional scale.

This work aims to show how the two components of the top-down methods, ATMs and prior flux estimates contribute towards uncertainties in the initial modelled observations to compare it with the uncertainties in our measurements. We model for 6 European sites (Heathfield, UK; Heidelberg, Germany; Lindenberg, Germany; Lutjewad, Netherlands; Mace Head, Ireland; and Tacolneston; UK), some of which have high frequency isotope measurements, using two ACTMs and their associated meteorology: NAME with the UK Met Office Unified Model; and FLEXPART with ECMWF IFS analysis and short-term forecasts, and an ensemble of prior fluxes created from their assigned uncertainties.

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Poster

Topics: 3 Atmospheric Sciences - Greenhouse and Other Tracer Gases, Air Quality and Aerosols

Measurement and Source Determination of Particulate Matter, and CO2 in Air Quality Studies: Insights from Stable Isotope Analysis and Black Carbon Observations

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Particulate air pollution, particularly carbonaceous aerosols like black carbon (BC), significantly impacts urban air quality and human health. BC, emitted from incomplete combustion of carbonaceous fuels, is a key indicator of anthropogenic sources and CO_2 emissions. While spectrally resolved aerosol absorption measurements help distinguish between traffic and biomass burning sources, stable carbon isotope analysis of CO_2 provides insights into gaseous CO_2 sources.

This study combines stable carbon isotope analysis of CO_2 with highly time-resolved BC measurements to distinguish between different sources, providing valuable insights into the contributions and timings of various sources, gas and particles, to air pollution

Method for air CO_2 stable isotope composition using Continuous Flow IRMS approach developed as part of the SIRS project was compared with the “golden standard” in atmospheric researches Dual Inlet IRMS approach compared with measurements performed during the CCQM P-204 pilot study. A real-world application was tested in the STRAP project.

From July to September, CO_2 concentrations and BC from wood-burning and traffic sources revealed distinct daily patterns. Traffic emissions caused morning BC peaks, while midday atmospheric mixing reduced BC and CO_2 concentrations, followed by pollutant accumulation in the afternoon. A two-hour lag was observed between BC and CO_2 morning peaks, reflecting their distinct emission dynamics. Ultrafine particles (UFP) mirrored BC’s behaviour, indicating a combustion origin. Lower $\delta^{13}C$ values (down to −15 ‰) during high CO_2 concentrations further confirmed anthropogenic sources.

These findings highlight the importance of continuous monitoring and advanced analytical methods to better understand and address air pollution in urban and rural settings.

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Poster

Topics: 3 Atmospheric Sciences - Greenhouse and Other Tracer Gases, Air Quality and Aerosols

Revising the 13C KIE and D KIE values for the CH_4-OH Sink

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Methane (CH_4) plays a crucial role in the global carbon cycle and is the second most significant anthropogenic greenhouse gas after CO_2. The current global methane mole fraction in the atmospheric is 2.5 times higher than pre-industrial levels. The isotopic signatures of methane, $\delta^{13}C$-CH_4 and δD-CH_4, are valuable tools for identifying sources and tracking its atmospheric pathway. However, discrepancies persist between measured and simulated $\delta^{13}C$-CH_4 values, with a wide uncertainty being the kinetic isotope effect (KIE) associated with the reaction between CH_4 and hydroxyl radicals (OH·)—the primary atmospheric sink for methane. Reported KIE values for this reaction vary, with previous studies reporting ^{13C}KIE ranging from 1.0054 to 1.0039, and ^{D}KIE ranging from 1.294 to 1.25. These variations contribute to significant uncertainty in the global methane isotope budget, underscoring the need for more precise KIE determinations to improve CH_4 source attribution.

To address this, this study aims to refine KIE measurements by conducting controlled laboratory experiments in which CH_4 reacts with OH· radicals. The hydroxyl radicals are produced via the photolysis of hydrogen peroxide (H_2O_2) using a deep-UV light source (200–380 nm). The reactions occur in a triple-quartz-layered reactor under stable pressure and temperature conditions, with secondary products removed via low-temperature trapping. The reactor is directly connected to two Isotope Ratio Mass Spectrometers (IRMS), allowing for continuous, high-precision measurements of $\delta^{13}C$, δD, and $\delta^{18}O$ in the remaining CH_4 and CO throughout the photochemical experiments.

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Topics: 3 Atmospheric Sciences - Greenhouse and Other Tracer Gases, Air Quality and Aerosols

Isotope evidence for increasing biogenic methane emissions at high northern latitudes

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Methane (CH_4) is the second most important anthropogenic greenhouse gas, with a global warming potential 84 times greater than carbon dioxide (CO_2) over a 20-year period. In recent years, atmospheric CH_4 concentrations have accelerated rapidly, with $\delta^{13}CH_4$ measurements indicating a notable shift towards biogenic emissions. However, significant uncertainties persist regarding the relative contributions of sinks and sources to observed CH_4 and $\delta^{13}CH_4$ trends, complicating efforts to pinpoint the drivers of methane growth and improve predictions of the methane budget under future climate change scenarios.

In this study, we employ the Miller-Tans method to determine the $\delta^{13}CH_4$ source signature for regional methane emissions, utilizing long-term atmospheric CH_4 and $\delta^{13}CH_4$ observations from the NOAA Global Monitoring Laboratory (GML) sampling network and optimised CH_4 and $\delta^{13}CH_4$ model fields from a latest global inverse model. We conduct detailed analysis of the spatial distribution, seasonal variations, and long-term trends of the $\delta^{13}CH_4$ source signature time series. Our analysis reveals a significant trend towards lower source signature from tropical to high northern latitudes. A clear seasonal cycle in source signature is observed at the high latitude stations. Our analysis also shows that this is not limited to a single site but represents a common and persistent feature at high northern latitudes. These results suggest that biogenic emissions are increasingly influential in driving atmospheric methane levels at high northern latitudes. These findings provide new insights into the processes governing atmospheric CH_4 and $\delta^{13}CH_4$ variations and assess how accurately contemporary inverse models reproduce these observed changes.

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Topics: 3 Atmospheric Sciences - Greenhouse and Other Tracer Gases, Air Quality and Aerosols

Utilizing tropospheric CO isotope observations from a low-latitude Atlantic sampling network to constrain the oxidative chlorine sink

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The isotopic composition of CO can be used to detect enhanced oxidation of methane by atomic chlorine due to the strong kinetic isotope effect related to this reaction (KIE_{CH4+Cl} = 66 per mil). Importantly, this detection method has demonstrated the presence of a large ground-level North Atlantic chlorine source for the years 1996-1997, linked to the geographic distribution of iron-rich Sahara dust within the marine boundary layer (Mak et al., 2003; van Herpen et al., 2023). Here, we present 2023-2024 $d^{13}C_{CO}$ and $d^{18}O_{CO}$ data from an air sampling network established across the low-latitude Atlantic Ocean, including bi-weekly measurements from Tenerife (IEO and IZO), Cape Verde (CVAO), Barbados (RPB), and northern Brazil (ATTO). In addition, the network includes intermittent flask samples taken aboard commercial shipping vessels as they complete trans-Atlantic routes. Our analysis supports the existence of a large chlorine sink of methane in dust-associated regions, which varies seasonally. Underestimates in the occurrence of chlorine oxidation propagate to isotope-constrained top-down global methane models, shifting predicted contributions away from fossil fuels and towards biological sources. Ultimately, our results provide an opportunity to reconcile missing chlorine sources, which may have significant implications for global methane source estimations.

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Poster

Topics: 3 Atmospheric Sciences - Greenhouse and Other Tracer Gases, Air Quality and Aerosols

High-precision measurements of the atmospheric δ13C(CO2) and δ18O(CO2) using Tunable Infrared Laser Direct Absorption Spectroscopy

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Quantifying the sources and sinks of CO_2 is crucial to constrain the global carbon budget, where very precise measurements of the mole fraction and isotopic composition of carbon dioxide are required. Additionally, global monitoring by analysing air samples from various locations is necessary to monitor (regional) trends. An increasingly used technique for measuring isotopic composition is laser spectroscopy, which is fast and precise.

In this study, an Aerodyne TILDAS Compact Single Laser CO_2 Isotope Analyzer was characterized and calibrated. As part of this, different measurement conditions, such as measurement pressure and time, were tuned to achieve the highest precisions. During the past year a measurement procedure was developed to analyse air samples. The samples were collected at various ground stations worldwide and along the Atlantic transect using ships and the mole fraction and isotopic composition of CO_2 ($\delta^{13}C$ and $\delta^{18}O$) were measured. The ground-based sampling stations include Cape Verde, Tenerife (IEO and IZO), Barbados (RPB), the Amazon Tall Tower Observatory (ATTO), Zeppelin Observatory (ZEP) and Monte Cimone (ICOS station). The measurements achieved mean precisions of 0.03‰ and even up to 0.01‰ for $\delta^{13}C$ and $\delta^{18}O$, comparable to gas source isotope ratio mass spectrometry, and 0.08 ppm for CO_2 mole fraction.

Our time series reveal a clear seasonal trend, with bigger seasonal variations in poleward regions (e.g. ZEP), where photosynthesis and respiration processes exhibit the greatest fluctuations seasonally. In contrast, smaller variations are recorded near the equator (e.g. Cape Verde), where vegetation coverages remains relatively stable throughout the year. Similarly, we observe a latitudinal gradient in CO_2 mole fraction and isotopic composition obtained from the ship transects.

To reduce uncertainties in the global carbon cycle, further long-term measurements are needed to extend the dataset and improve our understanding of seasonal and spatial CO_2 variations.

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Poster

Topics: 3 Atmospheric Sciences - Greenhouse and Other Tracer Gases, Air Quality and Aerosols

Atlantic Meridional Transect of polyisotopic carbon dioxide: Challenges of ship-based laser spectroscopy and implications for atmosphere-biosphere exchange

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During the AMT31 research cruise (RRS James Cook, Southampton/UK to Montevideo/Uruguay, 27 November–December 2024), we measured CO_2 polyisotopologues using a tuneable infrared laser direct absorption spectrometer (Aerodyne TILDAS-FD-L2). Dried marine air from an inlet at the bow of the ship was alternated with a working reference every 2 min to correct for instrument drift. Compared with land-based measurements, ship motion (roll, pitch, heave) was found to deteriorate isotope ratio precision by a factor of 3 to 10 (depending on the sea state). However, after averaging over hourly intervals, precisions better than 0.05 $\mu\mathrm{mol\ mol}^{-1}$ for $y(CO_2)$ and better than 0.03 ‰ for $\delta(^{13}C)$, $\delta(^{18}O)$ and $\delta(^{17}O)$ were achieved. For the ^{17}O isotope excess, $\Delta(^{17}O)$, hourly precision was often better than 10 ppm (0.01 ‰), but unfortunately, target tank results showed unexplained day-to-day variability of the order of ±35 ppm. Preliminary corrections for this day-to-day variability indicate that southern hemisphere $\delta(^{18}O)$ is 1.2–1.8 ‰ higher and $\Delta(^{17}O)$ is (70±22) ppm higher than northern hemisphere marine background air. This interhemispheric $\Delta(^{17}O)$ gradient is more than twice as high as predicted by atmosphere-biosphere exchange models (Koren et al., 2019) and could indicate a stronger than expected influence of the ^{17}O-enriched stratospheric return flux in austral spring or a stronger biospheric exchange signal in boreal autumn.

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Topics: 3 Atmospheric Sciences - Greenhouse and Other Tracer Gases, Air Quality and Aerosols

Laser absorption spectrometry measurements of polyisotopic carbon dioxide at Weybourne Atmospheric Observatory (north Norfolk, United Kingdom)

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Polyisotopic elements have more than one minor stable isotope (e.g., ^{17}O and ^{18}O next to the most abundant ^{16}O). The UK Natural Environment Research Council-funded project POLYGRAM (POLYisotopologues of GReenhouse gases: Analysis and Modelling) makes targeted observations of polyisotopologues, which includes variants of molecules with polyisotopic elements as well as so-called ‘clumped isotopes’.

Carbon dioxide (CO_2) polyisotopologue budgets allow estimating gross primary productivity (GPP) but require leaf and soil water isotope ratios and isotopic fractionations associated with transport and uptake. Simultaneous measurements of ^{18}O/^{16}O and ^{17}O/^{16}O isotope ratios, expressed as relative isotope ratio differences $\delta(^{18}\mathrm{O})$ and $\delta(^{17}\mathrm{O})$, simplify these requirements since $\delta(^{17}\mathrm{O})$ variations are correlated with $\delta(^{18}\mathrm{O})$. The deviation of $\delta(^{17}\mathrm{O})$ from a mass-dependent correlation with $\delta(^{18}\mathrm{O})$ is expressed as the ‘triple oxygen isotope excess’, $\Delta(^{17}\mathrm{O})$. Variability in $\Delta(^{17}\mathrm{O})$ only depends weakly on the $\delta(^{18}\mathrm{O})$ of soil and leaf water, simplifying productivity estimates.

We present a 2.5-year in-situ record (2021–24) of simultaneous $\delta(^{13}\mathrm{C})$, $\delta(^{18}\mathrm{O})$, $\delta(^{17}\mathrm{O})$ and CO_2 amount fraction measurements using an Aerodyne tuneable infrared laser direct absorption spectrometry (TILDAS) instrument at Weybourne Atmospheric Observatory on the north Norfolk coast (UK). The reproducibility of the measurement system was sufficient to clearly resolve variability on seasonal and diurnal scales. The reproducibility for $\Delta(^{17}\mathrm{O})$ was 4 ppm over 30 min.

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Topics: 4 Paleoclimatology and Archaeology

δ18O Measurements on Tree Ring Cellulose at the Centre for Isotope Research, University of Groningen

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Tree rings provide annual records of environmental and climatic conditions. These records can be interpreted through the physical characteristics of tree rings or the isotopic composition of their structural elements. Oxygen isotope chronologies are created by combining data from overlapping-aged trees, reflecting tree-environment interactions in the $\delta^{18}O$ of tree-ring cellulose. The abundance of ^{18}O in tree-ring cellulose is closely linked to hydroclimate, influenced by source water $\delta^{18}O$ and atmospheric humidity. Long sequences of annually resolved tree-ring $\delta^{18}O$ measurements have been used, to good effect, in the dating of archaeological timbers and as proxies in the reconstruction of climatic variables. In this research we have established a working methodology for producing and measuring $\delta^{18}O$ in tree-ring α-cellulose at the Centre for Isotope Research. We have demonstrated an average precision of roughly 0.2‰ standard deviation under a variety of conditions, which exceeds the expected performance of continuous flow IRMS techniques. Difficulties were encountered during the correction of tree-ring cellulose $\delta^{18}O$ measurements using non-cellulose, organic reference materials. Measurements of cellulose standards alongside water reference materials and an independent quality control standard proved successful, resulting in a number of cellulose standards being accurately placed on the VSMOW-SLAP scale, including the intercomparison and de facto reference material IAEA-C3 holocellulose.

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Poster

Topics: 4 Paleoclimatology and Archaeology

Isotopic approach to study the provenance and growth media of flax fibres produced in Ancient Egypt: first steps of the ISOPALIN project with a focus on modern linen

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The abundant quantities of well-preserved flax found in Egypt make this material a unique source of investigation for reconstructing the history of ancient Egyptian techniques and life. As a yearly-grown plant, it can be used as a reliable paleoclimatic archive. The ISOPALIN project proposes a multi-isotopic study of flax fibres found in archaeological contexts in Egypt, to document the growth media associated with this fibre through time. This project combines two different methodologies:

- A multi-isotopic study (^{2}H, ^{13}C, ^{18}O) of flax cellulose using isotopic ratio mass spectrometry (IRMS), which is conducted at the Institute for Analytical Sciences (Lyon, France)
- An innovative study focused on ^{13}C from flax cellulose using CO_2 laser spectroscopy (*Off Axis Integrated Cavity Output Spectroscopy* or *OA-ICOS*) to be implemented at the French Institute of Oriental Archaeology (Cairo, Egypt)

This combined methodology addresses several issues, including the link between post-burial degradation of linen artefacts and isotopic fractionation, the possibility for studying fibres provenance based on water isotopes, and ultimately, it allows us to document the growth environments associated with flax in ancient Egypt. Thanks to our two different approaches, this work will be articulated through isotope ratio mass spectrometry (IRMS) and CO2 laser spectroscopy, between France and Egypt, between fibre and sediment, and between modern linen samples, fragments from European museum collections and archaeological textiles found during recent excavations in Egypt. In this communication, the methodology and preliminary results will be detailed, and the importance of using isotopic instrumentation in Egypt will be highlighted.

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Poster

Topics: 4 Paleoclimatology and Archaeology

High precision stable isotope analysis of carbonate and water samples for paleoclimate applications using the Elementar iso DUAL INLET

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Paleoclimate research is important for understanding past, current and future climate, providing the data needed to model and predict current and future climate change scenarios. Stable isotope analysis provides an essential tool for gathering past climate information from natural archives such as waters including ice-cores, ground waters, and biological waters; and carbonate materials such as foraminifera and other fossilized carbonates. Due to the often limited and small sample sizes available for stable isotope analysis it is vital that highly precise and accurate analysis can be carried out on the smallest of sample sizes.

Dual inlet technology remains the most precise, accurate and sensitive technique for pure gas, carbonate and water analysis. The Elementar iso DUAL INLET is a valuable tool for paleoclimate applications, enabling the analysis of pure gas samples within an incredibly compact footprint via our powerful lyticOS software suite. The 14-ultra low dead volume valves with bodies machined from a single block of high purity stainless steel and dedicated turbomolecular pump for the changeover valve guarantees zero residual memory effects between reference and sample gas.

The iso DUAL INLET can be enhanced for automated analysis of carbonates and water samples. The iso AQUA PREP module analyzes up to 180 water samples with high precision for $\delta^{18}O$ and $\delta^{2}h$. The iso CARB PREP module analyzes up to 180 micro-fossil samples for ^{13}C and ^{18}O, even with small sample sizes. The iso MULTI PREP module allows for both carbonate and water analysis with a simple needle change. The system can also be upgraded for "clumped isotope analysis" of carbonates.

We will highlight the performance of the iso DUAL INLET with carbonate and water functionality across a range of sample types for paleoclimate applications, supporting researchers building a detailed understanding of the past to better inform policy makers for the future.

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Poster

Topics: 4 Paleoclimatology and Archaeology

Effect of sodium hypochlorite pretreatment on carbonate isotopic values (δ13C and δ18O) in lacustrine and wetland sediment, and laboratory standards.

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Geochemical and biological records from lake and wetland sediments can be used to reconstruct past environmental conditions, providing insight into long-term climate variability and informing future climate predictions. Palaeoclimatic records produced in this way can also improve our understanding of how climate may affect landscapes and influence human behaviour both in the past and into the future.

Carbon and oxygen stable isotope measurements ($\delta^{13}C$ and $\delta^{18}O$) of lacustrine carbonate are often used as a proxy to reconstruct past climate. Changes in lake systems can impact the amount of carbonate and organic matter (OM) preserved in the bulk sediment. Previous studies have documented that volatile components released from OM during phosphoric acid digestion of bulk sediment may impact the carbonate stable isotopic values. A commonly used method to remove OM from bulk sediment is pretreatment with sodium hypochlorite (‘bleach’), however care must be taken with sample pretreatment steps applied before carbonate stable isotope analysis, as the pretreatment itself may induce a bias in the carbonate $\delta^{13}C$ and $\delta^{18}O$ values. Previous studies have recommended that the suitability of pretreatment methods for OM removal be evaluated on a case-by-case basis.

Two small sets of sediment samples (from Loch Balnagowan in Scotland, and Gortnacrannagh wetland in Ireland) were pretreated for OM removal. Additionally, carbonate laboratory standards with different $\delta^{13}C$ and $\delta^{18}O$ values were pretreated, including across a series of pretreatment times. We report the carbon and oxygen stable isotope values following these pretreatment tests and discuss the implications of sodium hypochlorite pretreatment on bulk sediment from these systems.

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Topics: 4 Paleoclimatology and Archaeology

Using CNOS isotopes to fingerprint the Messinian Salinity Crisis in the South Asian Monsoon

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Carbon, nitrogen, oxygen and sulphur isotopes in marine sediments have been widely used to study past environmental and climatic changes providing insights into biogeochemical cycles, oceanographic changes, and ecosystem responses. In this study, we utilize a suite of organic carbon CNS as well as bulk carbonate C and O isotope data in marine sediment cores from the Maldives archipelago to study local palaeoenvironmental, oceanographic and atmospheric changes related to past variability of the South Asian Monsoon (SAM). Our study focusses on a 6.2- and 5.1-million-year-old sedimentary sequence recovered from International Ocean Discovery Program (IODP) Site U1467. The recovered sediments were deposited during the time of the Messinian Salinity Crisis (MSC). The MSC was a significant hydrological event that occurred between 5.97 and 5.33 million years ago (Ma). During this period, the Mediterranean basin gradually dried out, leading to the formation of thick evaporite deposits as the connection to the Atlantic Ocean progressively closed.

The desiccation of the Mediterranean Sea during the MSC had a significant impact on regional Mediterranean climate dynamics and is further hypothesized to have even influenced global atmospheric circulation patterns, such as the position of the Intertropical Convergence Zone (ITCZ). Our study thus aims to test if SAM - a key global ocean-atmospheric system directly related to the ITCZ – was influenced by shifts in northern hemisphere pressure patterns, during the MSC.

Preliminary data shows elevated and muted $\delta^{18}O_{blkcarb}$ values from ~5.8 Ma to the end of the MSC suggest strong evaporation and/or higher temperatures in the region. These findings provide new insights into the climatic and oceanographic response of the Maldives to MSC-driven shifts in monsoon dynamics.

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Poster

Topics: 4 Paleoclimatology and Archaeology

Advancing stable isotope dendrochronology for dating historic timbers in the continental Euro-Atlantic region

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Stable oxygen isotope (δ18O) dendrochronology has recently emerged as a groundbreaking method for dating historic timbers that contain few tree rings or exhibit complacent growth (i.e., minimal year-to-year variation). In the continental Euro-Atlantic façade (from northwest Spain to northwest Germany), approximately 70% of timbers in historic buildings possess these characteristics, making them undatable with conventional ring-width dendrochronology. As a result, existing tree-ring datasets in this macro-region are predominantly composed of timbers with over 100 rings, as these are more likely to yield dates using traditional methods. This bias in dendrochronological records distorts studies on historical deforestation and construction activities, exaggerating building hiatuses and overemphasizing the role of timber trade in sustaining construction.

The ERC WoodCulture project (2025–2029) addresses this issue through the development of δ18O reference chronologies along the continental Euro-Atlantic façade for the period 1300–1600 CE. Preliminary results from the Netherlands demonstrate that δ18O can successfully date timbers with as few as 30 rings. Additionally, the first δ18O chronology for northwest Germany exhibits strong teleconnections with δ18O data recently produced in Belgium, though this correlation diminishes with the English δ18O chronology. These findings demonstrate the great potential of δ18O dendrochronology to date previously unstudied and undated timbers and highlights the need to expand reference chronologies across the continental Euro-Atlantic region.

This presentation will showcase these recent advances and the progress in developing δ18O reference chronologies for dating purposes, discussing several case studies. By enabling the study of wood from buildings, shipwrecks, and archaeological structures that were previously undatable, this research marks a crucial step toward redressing biases in dendrochronological databases and reshaping our understanding of past timber use and trade.

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Poster

Topics: 4 Paleoclimatology and Archaeology

Decoupling of oxygen and hydrogen isotope ratios in tree ring cellulose: Why and when?

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Oxygen and hydrogen isotope ratios (d18O and d2H) are highly correlated in water sources, like precipitation and soil water, as they share the same isotopic fractionation processes, in particular evaporation. This water signal is in principle transferred to the cellulose of tree rings, which is the basis for climatic reconstructions using this archive. However, it has been observed that d2H variation in tree rings are often less well related to climate variations compared to d18O. Even sometimes an opposite pattern of the isotope ratios was observed – a decoupling. Recent studies have demonstrated that d2H is strongly influenced by biological processes and may be a proxy for physiological changes in carbon utilization, reflecting shifts between autotrophic and heterotrophic processes. These processes may be responsible for a decoupling occurring under certain situations. We highlight some of known decoupling examples, like the defoliation effect by the larch budmoth, an insect that regularly impacts larch (Larix decidua) trees in the Alps. We discuss how d2H variations may be a useful proxy for deciphering past environmental factors affecting the carbon metabolism of trees.

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Topics: 4 Paleoclimatology and Archaeology

Zooarchaeology and trophic ecology of wild and domestic animals in Neolithic Istanbul, around 8.2 kya event

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Archaeologists often seek cause-effect relations between (pre-)historica phenomena and episodes of Rapid Climate Change (RCC). The 8.2 kya event is one of the most debated RCC in prehistoric archaeology of Western Asia and Europe, because it coincides with the expansion of agriculture and animal husbandry into Europe, facilitated through human migrations. If and how this momentous change in production economies, landscape use and demography, coinciding with a significant RCC, impact trophic ecosystems of terrestrial and marine fauna can, in theory, be addressed using the stable isotope analysis of animal remains from archaeological sites. The archaeological record, however, is not perfect. In this paper, we present the results of our research on a submerged anthropopogenic site at the border of the Aegean and the Black Sea, with stratigraphic layers dating to ca 8.2 kya event, and possibly of the establishment of the connection between the Black Sea and the Bosporus. We report on the combined results of zooarchaeological analysis and nitrogen, carbon, sulfur, and oxygen stable isotopic ratios on stratified animal bones and teeth.

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Holocene variability of the Southern Hemisphere Westerly Winds on Amsterdam Island (37°S) reconstructed from peat records

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The Southern Hemisphere Westerly Winds (SHW) play a key role in the global climate system, by regulating climate variability in Southern Hemisphere mid- and high-latitudes and by controlling deep water ventilation in the Southern Ocean (SO). The vigorous SHW strengthened and shifted poleward during the last decades of the 20th century, contemporary with an increase in atmospheric temperatures, and enhanced SO CO_2 upwelling. This flux of 'natural' CO_2 to the atmosphere forms a potential amplification of human-induced global warming, as the strength of the SO CO_2 sink will weaken. In addition, a more poleward position of the wind belt, directly impacts human society as large areas on the three mid-latitude austral continents are exposed to droughts. Despite substantial research efforts during the last decades, our understanding of proxy-based knowledge on the strengthening and/or latitudinal shifts of the SHW is still fragmentary and sometimes contradicting. Here we present data on the Holocene evolution of the SHW from Amsterdam Island (37°S, Indian Ocean), located at the current northern edge of the SHW wind belt and part of a latitudinal transect of peat sequences from SO islands with Kerguelen and Crozet Islands at 49° and 46°S respectively. Rain-fed peat bogs occur on Amsterdam Island providing unique paleo-environmental archives. From those we will study the Holocene SHW variability in effective precipitation (precipitation minus evaporation) through bog surface wetness (BSW) proxies. We analysed stable hydrogen (δ^2H) isotopes of plant derived n-alkanes to reconstruct water table depth and thus BSW. This isotopic record will be complemented with a macrofossil analysis, to assess possible species dependence of the δ^2H record. Here we present preliminary results of this isotopic record and macrofossil analysis, along with a temperature record derived from the relative abundance of branched glycerol dialkyl glycerol tetraethers (brGDGTs), bacterial membrane lipids.

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Topics: 5 Food Authenticity, Forensics and Isoscapes

Accelerating the Sample Preparation of Sports Drug Testing Samples Employing Supercritical Fluid Chromatography for Sample Clean-up

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Doping control samples showing elevated urinary concentrations of testosterone or testosterone metabolites are forwarded to isotope ratio mass spectrometry-based determinations in order to differentiate between naturally elevated concentrations and doping offenses. The sample preparation encompasses liquid-liquid and solid phase extraction steps and enzymatic deconjugation of steroid glucuronides. In order to separate all steroid of interest from the biological matrix and to obtain sufficiently clean urinary extracts, high performance liquid chromatography (HPLC) with fraction collection is currently employed in routine doping controls. This preparation step is very time consuming as each HPLC run takes approx. 45 min and the evaporation of collected fractions containing water and acetonitrile lasts for up to 90 min.

Supercritical fluid chromatography (SFC) employs liquid carbon dioxide as eluent combined with other organic solvents like methanol or acetonitrile as modifiers. The unique physiochemical properties of liquid carbon dioxide enable to accelerate the chromatographic separation of different compounds and subsequently collected fractions only contain the modifier and additional methanol as make-up solvent which enables a very fast evaporation within 10 minutes.

Considering the potential benefits, a method was developed and validated in-line with current World Anti-Doping Agency-based regulations for doping control purposes encompassing testosterone, epitestosterone, dehydroepiandrosterone, androsterone, etiocholanolone, 5α- and 5β-androstanediol as target analytes and cholesterol, pregnanediol, 16-androstenol, and 11-oxo-etiocholanolone as endogenous reference compounds. An additional focus was set on potential isotopic fractionation during the SFC-based separation and the fraction collection process. Investigations into reference population derived carbon isotope ratios especially of cholesterol are still ongoing as this steroid has not been implemented into sports drug testing so far.

Keywords: supercritical fluid chromatography, fraction collection, chromatographic isotopic fractionation, doping controls, urinary steroids

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Applications of Stable Isotope Ratio Analysis and Site-Specific Natural Isotope Fractionation-Nuclear Magnetic Resonance in Discriminating Between Synthetic and Natural Analogs

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Consumers today are increasingly seeking products containing molecules of natural origin, as these are often perceived as healthier compared to their synthetic or semi-synthetic counterparts. However, the higher costs associated with the production of plant-based raw materials, as well as the extraction and purification of these natural substances, create opportunities for counterfeiting. This often involves the addition of cheaper, chemically indistinguishable synthetic forms. Techniques such as Stable Isotope Ratio Mass Spectrometry (SIRA) and Site-Specific Natural Isotope Fractionation by Nuclear Magnetic Resonance (SNIF-NMR) are valuable tools for distinguishing molecules of natural, biosynthetic, or synthetic origin across various categories, including flavorings, essential oils, foodstuffs, dietary supplements, pharmaceuticals, and steroids. While both methods are expensive and require specialized equipment, SNIF-NMR is less accessible and more complex than SIRA. However, it provides more detailed, site-specific molecular information. Despite the high precision and sensitivity of SNIF-NMR, SIRA offers broader scientific applications but is challenged by complex data interpretation and the limited availability of reference materials. Among isotopic parameters, $\delta^{2}H$ measured by IRMS or (D/H)n determined via SNIF-NMR has demonstrated the greatest ability to discriminate, generally showing lower values in natural molecules and more positive ones in their synthetic counterparts. Although $\delta^{13}C$ is the most extensively studied parameter, it does not always provide significant discrimination between natural and synthetic fossil-derived products. Nevertheless, it is particularly effective for differentiating natural molecules extracted from specific plants and their biosynthetic analogs, which are synthesized from C4 substrates such as sugarcane and corn (e.g., red yeast rice or L-theanine). In specific cases, $\delta^{15}N$ (e.g., for caffeine) and $\delta^{18}O$ (e.g., for Serenoa repens extract) have shown excellent potential for characterization.

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Integrating Metabolomics and Stable Isotope Ratios (δ13C and δ15N) in Blood Fractions to Assess Dietary Changes in Iberian Pigs

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This study is focused on the integration of stable isotope ratios of carbon (δ13C) and nitrogen (δ15N) from blood plasma and erythrocytes, combined with metabolomic profiling, as a powerful tool to trace the dietary background of Iberian pigs. This approach enhances the capacity to authenticate this sustainable production system within the DEHESA ecosystem, ensuring the product quality and preventing fraud. The castrated Iberian pigs were initially fed maternal milk and commercial feed until the montanera period, during which they were divided into different groups according to the feeding regime followed: only acorns; acorns + concentrates; only concentrates. Blood samples were collected and subjected to stable isotope analysis of δ13C and δ15N using an EA-C-IRMS, while untargeted metabolomic profiling was performed using an UHPLC-HRMS/MS.

Stable isotope analysis revealed significant dietary effects on δ13C and δ15N values blood samples. ANOVA demonstrated significant impacts of sampling time on δ13C data. Metabolomic profiling identified distinct metabolic signatures associated with the diet. Acorn-fed pigs showed elevated levels of oleic acid and polyphenols related metabolites, while concentrate-fed pigs displayed markers linked to formulated feed, including altered lipid profiles and amino acid derivatives.

In summary, combining stable isotope analysis and metabolomics provides a robust approach to verify dietary practices in Iberian pig production. δ13C values on blood detects dietary shifts in short time, and metabolomics offers a detailed biochemical fingerprint of feed intake. Together, these methods could contribute to the fraud prevention, ensure product quality, and support sustainable dehesa ecosystem practices.

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Detection of synthetic urea in a specimen provided as human urine sample

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Manipulation of urine samples for drug testing or doping control analysis is a well-known problem, including dilution of urine, chemical adulteration or substitution by other liquids. Different analytical strategies have been developed to identify diluted or adulterated urine samples, as well as the identification of urine samples substituted with other liquids such as apple juice, alcohol-free beer, water or synthetic urine. Synthetic urine may contain different substances, including creatinine, uric acid and urea and show a specific gravity and pH similar to natural human urine samples. Several methods have been evolved within the last years to identify synthetic urine samples with routine analytical methods. These methods are based either on the identification of substance solely present in synthetic, but not natural urine, or on the identification of the absence of typically present urinary biomolecules.

In doping control analysis, the total absence of naturally occurring endogenous steroids (markers of the steroid profile) in a urine sample is strong evidence for a manipulated e.g. highly diluted or substituted sample. However, additional information supporting the assumption of a substitution of the original sample by synthetic urine can be particularly interesting.

A suspicious doping control urine sample without detectable amounts of endogenous steroids, a specific gravity of 1.014 and a pH of 8.3 revealed significant amounts of urea and protein. The urine sample was analyzed per EA/IRMS and the nitrogen and carbon isotopic composition of urea and total urine indicated a synthetic origin, similar to commercially available urea standards and synthetic urine. Compared to nitrogen and carbon stable isotope ratios of urine samples from a human reference population from Germany the suspicious doping control urine sample was clearly distinguishable.

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Authentication of essential oils using multi-isotopic approaches and molecular quantification used to highlight complex adulterations

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For a long time, isotopic investigations are done to determine and guarantee the naturalness of commercial compounds claimed to be natural, such as flavours, essential oils, which are widely used in various industries (aromatherapy, cosmetics, food…). However, some suppliers are tempted to adulterate these expensive products by adding components of other origins to increase their financial profit. To address this issue, analytical controls are routinely carried out to guarantee authenticity, as consumers are sensitive to the origin of these products and are willing to pay more for natural origin.

While many forms of adulterations are well-known, fraud is still progressing in new areas where knowledge is quite limited, and identifying them requires increasingly complex solutions.

Here, we present 3 different studies that demonstrate how combinations of multi-isotopic approaches and molecular quantification can detect new types of adulterations in essential oil (EO):

- 1. Authentication of wintergreen EO: The naturalness of wintergreen EO was confirmed using a combination of hyphenated, ^{13}C isotopic and molecular indicators. By comparing GC chromatograms, ^{13}C and ^{14}C measurements, a novel form of adulteration was identified, resulting from the addition of synthesised ^{14}C-enriched molecule to mimic a natural raw material.

- 2. Differentiation of Neroli and Petitgrain EOs: Both EOs are derived from the bitter orange tree, with neroli obtained from its flowers and petit grain from its leaves. Although their molecular compositions are similar, their market prices differ significantly. Isotopic and molecular analyses were used to distinguish between them and identify potential adulterations.

- 3. Detection of semi-synthetic molecules: Semi-synthetic molecules, are natural equivalent molecules produced by chemical reactions. Limonene from sweet orange EO, cheaper to produce, is oxidised to carvone, which is the main component of spearmint EO. The most effective method to detect adulteration involves ^{18}O GC-IRMS analysis unlike ^{14}C dating or chiral methods.

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Investigation of Oxidative Aminopolyphosphonate Degradation via LC-IRMS/HRMS

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Aminopolyphosphonates (APPs) are strong chelating agents have therefore been used since the 1980s to remove cations from reverse osmosis concentrates, as bleach stabilizers in detergents, and in paper and textile industries. However, possible risks of APP use such as eutrophication of natural waters, remobilization of heavy metals and formation of toxic transformation products (TPs) during degradation are not sufficiently known.

Therefore, we plan to investigate the oxidative degradation of three commonly used APPs – Aminotris(methylphosphonic acid) (ATMP), Ethylenediaminetetra(methylenephosphonic acid) (EDTMP), and Diethylenetriaminepenta(methylenephosphonic acid) (DTPMP) – via ozonation, persulfate oxidation, and percarbonate oxidation by coupling Liquid Chromatography-Isotope Ratio Mass Spectrometry (LC-IRMS) and LC-High Resolution Mass Spectrometry (HRMS) with a flow-splitter after LC-separation. This method was successfully developed for ATMP and its photolysis products by Marks et al.

To measure the isotopic fractionation of carbon during degradation, the LC-IRMS is used. By measuring isotopic fractionation of the educts, Rayleigh-plots that are characteristic for each degradation pathway can be obtained. Moreover, the extent of isotopic fractionation provides insight into the reaction mechanism as pronounced isotopic fractionation indicates a reaction at a carbon atom. To gain further insights into the degradation pathways and to identify TPs, a LC-HRMS system is needed as for LC-IRMS measurements all analytes are mineralized to CO_2.

Of the few well-known TPs, (Aminomethyl)phosphonic acid (AMPA) is of particular interest as it is genotoxic and more stable than the APPs. It is a TP of all APPs as well as of the herbicide glyphosate so that the origin of AMPA can likely be determined by LC-IRMS due to its isotopic composition. Moreover, glyphosate itself was proposed to be a TP of EDTMP and DTPMP. Therefore, the coupling method can be used to identify glyphosate in case it is formed and to distinguish between different degradation pathways and industrially produced glyphosate.

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Stable carbon isotope ratios for ascorbic acid in dietary vitamin C supplements

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Stable isotope ratios have been used to authenticate and trace various food products. In the 2000s, liquid chromatography combined with isotope ratio mass spectrometry (LC/IRMS) was developed, enabling the measurement of stable carbon isotope ratio ($\delta^{13}C$) of highly polar and non-volatile analytes without derivatization. LC/IRMS has been applied to authenticate and trace products such as honey, wine, lemon juice, and alcohol beverage.

As health awareness grows, health foods and dietary supplements have become readily available online. However, fraudulent activities, such as the mislabeling of geographical origin or ingredients, have been reported. In particular, naturally derived vitamin C supplements are several times more expensive than synthetic ones, resulting in mislabeling of ingredients. Vitamin C supplements can be derived from two main sources: those synthesized industrially from sugarcane or corn, and those extracted from fruits (e.g., acerola, camu-camu). Therefore, a reliable method is needed to determine the origin of vitamin C supplements. In this study, we analyzed the $\delta^{13}C$ values of ascorbic acid in vitamin C supplement products using LC/IRMS.

First, we tested various types of analytical columns, eluents, pH levels, and column flow rates to establish a highly accurate analytical method of LC/IRMS. The optimized conditions were as follows: analytical column – Inert Sustain AQ-C18 (GL sciences inc.), column flow rate – 0.5 mL/min, and eluent – 0.1% phosphoric acid solution. We then applied the optimized method to more than 20 vitamin C supplement products. It was observed that natural vitamin C supplements products were more than 10‰ lighter than synthetic ones, providing a clear distinction. These results indicate that LC/IRMS is a powerful method for distinguishing synthetics from natural ascorbic acid in vitamin C supplements products.

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Combining GC/MS and GC/IRMS for the Authentication of High-Value Natural Products

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GC/MS is a well-established technique that has been used in analytical laboratories for many decades, while GC/IRMS is a more recent method widely applied in the field of food traceability. In this work, we present the application of these two techniques in combination to assess the authenticity of certain high value food products.

Lavender essential oil is a high-value commodity used as a fragrance in cosmetics, as a flavoring component, and as a preservative in food and beverages. Due to its economic value, it is often substituted or blended with cheaper oils such as spike lavender, French lavender, and especially lavandin oils. The combination of these two techniques not only enables the distinction between lavender essential oil and lavandin oil based on VOC composition but also facilitates the identification of commercial samples adulterated with synthetic compounds through stable isotope analysis.

A similar approach was used to characterize menthol-based products: a wide variety of commodities were investigated in terms of their volatile/aromatic profile and stable isotope ratios in order to identify markers for distinguishing between synthetic and natural products. First, VOC extraction was carried out on several peppermint samples to establish reference isotopic values for natural products. Subsequently, various commercial products containing menthol were analyzed to verify the synthetic or natural origin of the menthol present in them. Samples like mint essential oils, toothpaste, mouthwash, candies, chewing gum, and syrups were considered in this study.

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Nitrogen Isotope characteristics of vegetables for traceability of organic and conventional productions

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The demand of organic vegetables is mainly explained by consumers' concerns about safety and perception that organically produced vegetable is safer and healthier than conventional vegetables. The aim of the study is to assess the preliminary data on stable nitrogen isotope as a screening tool to differentiate between organic and conventional growing vegetables. In this study, 180 samples of organically and conventionally grown vegetables that were obtained from various farms in Thailand were analyzed in order to determine if there are any differences in $\delta^{15}N$ values. The results showed that there are significant differences ($P < 0.001$) in mean of $\delta^{15}N$ values between organically and conventionally grown vegetables (8.99‰ ± 41%, n = 108 versus 0.44‰ ± 499%, n = 72). It is concluded that nitrogen isotope fingerprinting has the potential to enable authentication of organic vegetables.

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Identification of provenance of Thai Hom Mali rice grown in different regions in the Thung Kula Rong Hai area based on C, N, O, H, S stable isotopic and elemental compositions

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Thai Hom Mali rice or Thai Jasmine rice, which has been registered under the European Protected Geographical Indication (PGI), is the most famous rice in the Thung Kula Rong Hai area in the northeast of Thailand. This is because of its unique characteristics, such as fragrant and smell like pandan leaves, especially if the rice was grown in the Thung Kula Rong Hai area in the northeast of Thailand. Thus, Thai Hom Mali rice has become a target for the unscrupulous producers to increase profits by mislabeling rice. In this study, the stable isotopic and elemental compositions including $\delta^{13}C$, $\delta^{15}N$, $\delta^{18}O$, $\delta^{2}H$, $\delta^{34}S$, %C, %N %O, %H, and %S in Thai Hom Mali rice were analyzed using elemental analyzer isotope ratio mass spectrometer (EA-IRMS). Discrimination of the geographical origin of Thai Hom Mali rice cultivated in 5 provinces located in the Thung Kula Rong Hai area using stable isotopic and elemental compositions combined with multivariate analysis was demonstrated. The LDA for classification of the geographical origin of rice cultivated in 5 provinces in the Thung Kula Rong Hai area was achieved with 97.2% correct classification of their original groups and 72.2%.