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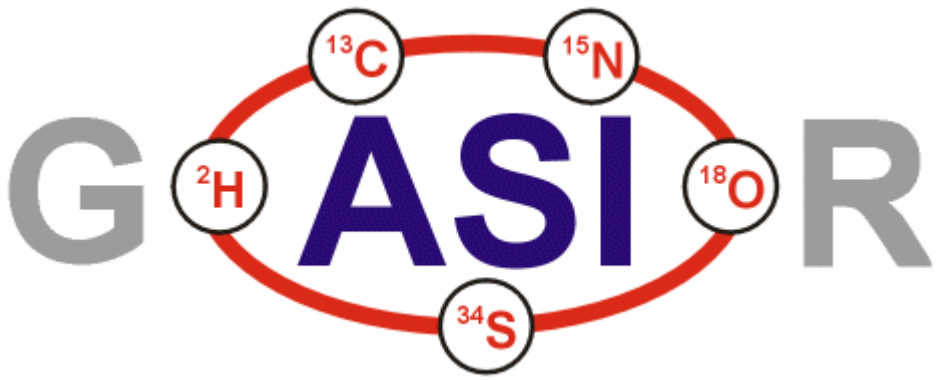

Jahrestagung 2005

Jena

10.-12. Oktober 2005

Jahrestagung der GasiR

10.-12. Oktober 2005, MPI-BGC Jena

Programm

Montag, 10. Oktober 2005

12.00 – 13.30	Anmeldung
13.30 – 14.00	Eröffnung und Begrüßung

Session 1: Stabile Isotope in Medizin, Sport und Lebensmittelkontrolle

14.00 – 14.20	U. Flenker, C. von Kuk, V. Gougoulidis, F.Hülsemann, W. Schänzer: Influence of dietary changes on the dynamics of $^{13}C/^{12}C$ in selected urinary steroids
14.20 – 14.40	K. D. Wutzke, I. Oetjens: ^{13}C- and ^{15}N-incorporation of doubly stable isotope labelled *Lactobacillus johnsonii* in humans
14.40 – 15.00	J. Jung, U. Hener, A. Münch, A. Mosandl: Authenticity Assessment of Glycerol in Wine
15.00 – 15.20	H.-L. Schmidt und A. Rossmann, H.-P. Sieper und H.-J. Kupka: Ein Meßsystem zur parallelen Isotopenverhältnis- und Elementaranalyse von vier Elementen in Lebensmitteln und anderem biologischem Material
	Kaffeepause

Session 2: Methoden, Entwicklungen und Referenzmaterialien

15.40 – 16.00	Simon Davis: Dual inlet precision ^{13}C analysis with multi-aliquot CF analysis
16.00 – 16.20	A. Hilkert, D. Juchelka, M. Krummen: New Applications by Isotope Ratio Monitoring LC/MS

16.20 – 16.40	E. Hettmann, F. Volders, and G. Gleixner: Compound specific Carbon isotopic ratios of metabolites determined by LC/MS-IRMS
16.40 – 17.00	M.Boner, K. Hecker, H. Förstel: Inertes Material zum Einsatz in der Hochtemperaturpyrolyse
17.00 - 18.00	Poster Session I
18.00 - 19.30	Mitgliederversammlung der ASI
ab 20.00	Users Meetings der ausstellenden Firmen (Ort und Termin werden von den Firmen bekanntgegeben)

Programm

Dienstag, 11. Oktober 2005

Session 2 (continued)

Methoden, Entwicklungen und Referenzmaterialien

8:40 - 9:00	W.A. Brand, M. Patecki, P. Ghosh and M. Rothe: J-RAS: A high precision reference for the isotopic composition of CO_2 in air

Session 3: Stabile Isotope in Pflanzen

9.00 - 9.20	Frank Keppler: Carbon isotope anomaly in the major plant C_1 pool and its biogeochemical implications
9.20 - 9.40	J. Seyfferth, A. Søe, M. Kunert, S. Bartram, W. Boland: Biosynthese von Blüten- und Blätterduftstoffen – verfolgt anhand stabiler Isotopen
9.40 - 10.00	A.R.B. Søe, A. Burse, S. Bartram, W. Boland: *De novo* biosyntheses versus sequestration of defense compounds in leaf beetles – a mechanistic approach by stable isotopes and molecular biological techniques

10.00 - 10.20	G.L.B. Wiesenberg, J. Schwarzbauer, and L. Schwark: Plant-internal variation of lipid composition and compound-specific isotopes of various crops
	Kaffeepause

Session 4: Ökosysteme I: Funktion und Schadstoffe

10.40 - 11.00	J. Gaye-Siessegger, U. Focken, H. Abel and K. Becker: Effect of dietary protein/energy ratio on trophic shift of C and N isotopes and on the activity of enzymes involved in the amino acid metabolism of Nile tilapia, *Oreochromis niloticus* (L.)
11.00 - 11.20	C. Pázmándi and M. Traugott: Calibration of isotopic turnover rates in wireworms, common agricultural pests
11.20 - 11.40	Gerhard Gebauer: Mundraub im Wurzelraum; Isotopenhäufigkeits-analysen und molekularbiologische Daten liefern neue Einblicke in die komplexe Ernährungsweise der Waldbodenvegetation
11.40 - 12.00	S.P. Sah, N. Lamersdorf and R. Brumme: Natural abundance of ^{15}N in different compartments of a spruce forest ecosystem under acid rain and manipulated clean rain field conditions
12.00 - 12.20	M. Voß, B. Deutsch, R. Elmgren, C. Humborg, P. Kuuppo, M. Pastuszak, C. Rolff, and U. Schulte: River biogeochemistry and source identification of nitrate by means of isotopic tracers in the Baltic Sea catchments
	Mittagspause
14.00 - 14.20	Böttcher M.E., Brumsack H.-J., Hetzel A. & Schipper A.: Isotope biogeochemistry of diagenesis caused by a black shale-fueled marine biosphere (ODP Leg 207)
14.20 - 14.40	C. F. Stange und N. Pekkarinen: Doppel Isotopen-Tracer Studie zur Validierung der Barometrischen Prozessseparation (BaPS)
14.40 - 15.00	Y. Oelmann, W. Wilcke und R. Bol: Quellencharakterisierung mit Hilfe von ^{15}N und ^{18}O Isotopen im Nitrat unter leguminosenhaltigem Grünland
15.00 - 15.20	N. Borges, M. Rode, J. Spindler, T. Neef, R. Meißner, G. Strauch: Identification of main nitrate sources in a lowland agricultural drainage system using stable isotopes analysis
	Kaffeepause

15.40 - 16.00	N. Stelzer, S. Weber, I. Nijenhuis, M. Kästner, H.-H. Richnow: Monitoring of in situ biodegradation of groundwater contaminants using a test system (BACTRAP) with ^{13}C-labelled substrates
16.00 - 16.20	J. Weihmann, U. Schulte und T. Mansfeldt: Stabile Isotope (C, N) zur Herkunftsbestimmung von Cyaniden in belasteten Böden
16.20 - 16.30	Vorstellung des Preisträgers der Karleugen Habfast Stiftung und Preisverleihung
16.30 - 17.00	Vortrag des Preisträgers
17.00 - 18.30	Postersession II
ab 20.00	Konferenz-Dinner (Restaurant 'zum Löwen')

Programm

Mittwoch, 12. Oktober 2005

9.00 - 9.30	Review: A. Augusti, T. Nicol, M. Öquist, T. Sparrman, J. Schleucher: NMR in Biogeochemistry

Session 5: Ökosysteme II: Stoffkreisläufe und Klima

9.30 - 9.50	A. Telz and G. Gleixner: Seasonal variations in the sources of soil CO_2 in a deciduous forest of the national park „Hainich", Germany
9.50 - 10.10	S. Steinbeiss, G. Gleixner: Variable contribution of soil and plant derived carbon to dissolved organic matter
10.10 - 10.30	R. Siegwolf, M. Saurer, J. Eitel, R. Vogt: $\delta^{13}C$ and $\delta^{18}O$ from Carbon Mono- and Dioxide, two proxies for tracing combustion sources
	Kaffeepause

11.00 - 11.20	A. Giesemann, S. Schrader, T.-H. Anderson, R. Manderscheid, S. Burkart, A. Pacholski, O. Heinemeyer, H.-J. Weigel: From atmosphere into soil – Carbon (C) translocation in an agro ecosystem under FACE conditions
11.20 - 11.40	M. Tichomirowa, F. Haubrich, K. Bombach, R. Liebscher: S and O isotope composition of the atmoshere in Saxony (Germany)
11.40 - 12.00	M. Saurer, C. Reynolds, P. Cherubini, K. Treydte, R. Siegwolf: Changing relation between CO_2- and water fluxes in Swiss forests
12.00 - 12.20	D. Sachse, J. Radke, I. Mügler and G. Gleixner: Compound specific hydrogen isotope rations of biomarkers reconstruct the palaeoclimate
12.20 - 12.30	Ende des Präsentationsteils der Jahrestagung
	Mittagspause
14.00 - 15.20	Workshop zur Datenauswertung
	Kaffeepause
15.50 - 17.00	Workshop zur Datenauswertung (Fortsetzung)
17:00	Ende der Jahrestagung GasiR 2005

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VORTRÄGE

Influence of dietary changes on the dynamics of $^{13}C/^{12}C$ in selected urinary steroids

U. Flenker, C. von Kuk, V. Gougoulidis, F.Hülsemann, W. Schänzer

Institute of Biochemistry, German Sport University Cologne, Carl-Diem-Weg 6, 50933 Cologne

The application of steroid hormones and correspondnig prohormones is prohibited in sport. In this regard the abuse of testosterone - the principal male sexual hormone - still is considerd the biggest problem. The detection of steroid administration relies on differences between $^{13}C/^{12}C$ of synthetic and biosynthesized steroids. Currently a difference exceeding 3 ‰ between $\delta^{13}C$ of testosterone or testosterone metabolites and any steroid coming from an independent pathway has been defined as criterion.

However the factors that control the carbon isotope ratios of endogenous steroids are relatively unknown. Geographic influences due to diverse contribution of C3- and C4-plants to human alimentation are straightforward indeed, but the characteristics of the propagation of dietary isotope signatures into steroid hormones require elucidation. In particular the effects of a rapid change of dietary $^{13}C/^{12}C$ is of interest, because different adaptation times of different steroids theoretically could effect false positive results.

Six subjects (four males, two females) changed from *ad-libitum* nourishment to a ^{13}C enriched diet for a period of 28 days. No animal products were consumed. The diet therefore was mostly free from cholesterol so that any observable change of $^{13}C/^{12}C$ in steroids must be due to *de-novo* synthesized compounds. $^{13}C/^{12}C$ of 5 urinary steroids relevant in doping control analysis was measured by GC/C/IRMS where samples were taken 5 times a day. Sampling also was perfomred during 8 days before and during two weeks after the diet changeover. Development of total body mass and of fat mass were monitored using a balance capable of impedance measurement.

In some subjects a parallel change of $^{13}C/^{12}C$ could be observed for all steroids. A close to perfect fit to these data can be achieved by a one compartment model, where the half lives' magnitudes are hundreds of hours. However different asymptotic values exist for different steroids, indicating that significant isotopic fractionation is present in the respective pathways. No evidence for time delay could be found here, suggesting that ingested foodstuff immediately is included into steroid biosynthesis. In contrast some subjects showed sigmoidal and strongly lagged increase of $^{13}C/^{12}C$. The actual existence of more than one compartment is hereby to be deduced. Furthermore different steroids exhibited different dynamics, but the ~~$\Delta\delta$ DID NOT EXCEED 3~~ ‰. Besides its relevance for doping control the study gives rise to some questions concerning the carbon sources of endogenous steroids.

^{13}C- and ^{15}N-incorporation of doubly stable isotope labelled *Lactobacillus johnsonii* in humans

K. D. Wutzke, I. Oetjens

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Rationale: Doubly labelled [^{13}C,^{15}N]Lactobacillus johnsonii (dlLa1) was prepared for oral administration in humans. The aim of the study was to investigate the metabolic fate of dlLa1, the $^{13}CO_2$-exhalation, the urinary and faecal ^{13}C-and ^{15}N-excretion in correlation to orocaecal transit time (OCTT) and the enrichment of blood plasma fractions.
Methods: Ten healthy adults aged 23-36 y received 87 mg/kg body weight wet vital dlLa1 cells and 10 g raffinose together with a continental breakfast. Expired air samples were taken over 14 h, whereas urine and faeces were collected over 2 days. A blood sample was taken 2 h after dlLa1 administration. ^{13}C- and ^{15}N-enrichments were measured by isotope ratio mass spectrometry (SerCon, Crewe, UK), H_2-concentations were measured by using an electrochemical detector (Stimotron, Wendelstein, Germany).
Results: Mean OCTT deriving from raffinose ingestion was reached after 3.7 h. After dlLa1 administration, 8.6% of ^{13}C was exhaled as $^{13}CO_2$. The resulting mean urinary excretion of ^{13}C and ^{15}N was 1.3 and 12.4%, respectively, whereas the faecal excretion was 39.9 and 37.6%, respectively. Two h after dlLa1 administration, ^{13}C- and ^{15}N-enrichment of fibrinogen amounted to 0.007 and 0.009 at%exc, respectively.
Conclusions: The ingestion of [^{13}C,^{15}N]Lactobacillus johnsonii in healthy adults led to a total excretion of approximately 50% of both stable isotopes. In comparison to OCTT of 3.7 h, both stable isotopes appear after 30 min in breath and urine, clearly indicating that dlLa1 is rapidly digested in the small bowel before reaching the caecum. This is confirmed by ^{13}C-and ^{15}N-enrichments of blood plasma fractions. Our combination of measuring the expiratory, urinary and faecal excretion of ^{13}C- and ^{15}N-enriched metabolic degradation products of vital doubly labelled *Lactobacillus johnsonii* in correlation to the orocaecal transit time is a novelty.
References: Wutzke KD, Oetjens I: Eur J Clin Nutr 2005, Jul 20 [Epub ahead of print], doi:10.1038/sj.ejcn.1602227.

Authenticity Assessment of Glycerol in Wine

Jung, J., Frankfurt a.M./D, Hener, U., Frankfurt a.M./D, Münch A., Frankfurt a.M./D, Mosandl, A., Frankfurt a.M./D

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The evaluation of natural isotope discrimination has become more and more important and, meanwhile it is well established in authenticity assessment of food.

Glycerol is an important by-product of wine fermentation and decisive for the full-bodied character of wines. So far, glycerol always received attention in the quality assessment of wine. Nowadays authentication of glycerol in wine is of special interest.

Different methods of glycerol authentication were published [1-4]. However, these methods are limited to measurements of highly pure glycerol, using off-line IRMS methods or the determination of stable isotope ratios via GC-IRMS after derivatisation. First reports about direct $\delta^{13}C$ GC-IRMS measurements concerning glycerol in wine have been published recently [5].

Due to their acidic character the hydrogen of the hydroxyl functions in the glycerol molecule are exchanged and equilibrated by the aqueous/alcoholic medium of wine. So far, direct $\delta^{2}H$-measurements of glycerol remain useless in view of authenticity assessment of glycerol. However, this paper presents the first multielement analysis ($\delta^{13}C$, $\delta^{18}O$) of glycerol via GC-C/P-IRMS. In order to prove that the extraction method takes place without any isotopic discrimination a model wine with two internal standards (1,4-butanediol, 2-methyl-1,3-propanediol), is analysed before and after extraction.

This investigation involves wines of different varieties and vintages, as well as the comparison of wines enriched with sucrose and the corresponding unchanged wines. After precipitation of sugars and organic acids with barium hydroxide and appropriate dilution the extract is ready for GC-C/P-IRMS-analysis [6].

[1] D. Weber, H. Kexel, H.-L. Schmidt; J. Agric. Food Chem. **1997**, *45*, 2042

[2] A. Rossmann, H.-L. Schmidt, A. Hermann; Z Lebensm Unters Forsch A **1998**, *207*, 237

[3] G. Fronza, C. Fuganti, P. Grasselli; J. Agric. Food Chem. **1998**, *46*, 477

[4] G. Fronza, C. Fuganti, P. Grasselli, S. Serra, F. Raniero, C. Guillou; Rapid Commun. Mass Spectrom. **2001**, *15*, 763

[5] G. Calderone, N. Naulet, C. Guillou, F. Reniero; J. Agric. Food Chem. **2004**, *52*, 5902

[6] J. Jung; Dissertation Univ. Frankfurt/Main, in preparation

Ein Meßsystem zur parallelen Isotopenverhältnis- und Elementaranalyse von vier Elementen in Lebensmitteln und anderem biologischem Material

Hanns-Ludwig Schmidt und Andreas Rossmann, isolab GmbH, Schweitenkirchen
Hans-Peter Sieper und Hans-Joachim Kupka, Elementar Analysensysteme GmbH, Hanau

Zur Untersuchung der Herkunft und Authentizität von Lebensmitteln sowie von pflanzlichem und tierischem Gewebe wird heute in steigendem Maße die Multielement- und Multikomponenten-Isotopenverhältnisanalyse eingesetzt. Im Allgemeinen benötigt man hierzu wegen der verschiedenen Aufschlussverfahren zur Erzeugung der Messgasse und wegen häufig extremer Elementverhältnisse in den Proben mehrere Einwaagen, somit auch einen erheblichen Arbeitsaufwand.

Basierend auf Erfahrungen bei der Elementaranalyse von heterogenem biologischem Material wurde von uns ein Meßsystem entwickelt, mit dem aus einer einzigen Probe innerhalb von 20 Minuten neben der elementaren Zusammensetzung die Isotopenverhältnisse der Elemente Wasserstoff, Kohlenstoff, Stickstoff und Schwefel bestimmt werden können.

Die Probe (Bereich zwischen 10 und 200 mg) wird in einem Elementaranalysator vario EL III von elementar Analysensysteme bei 1150 ^{o}C im O_2/He-Strom an WO_3 verbrannt, NO_x wird mit Cu reduziert. Aus den Verbrennungsgasen werden die Elementkonzentrationen mittels eines WLD bestimmt. CO_2, H_2O und SO_2 werden durch reversible Bindung an spezifischen Adsorbern getrennt, H_2O wird bei 600 ^{o}C mittels Mg reduziert. Nacheinander erfolgt die Isotopenverhältnisanalyse an den Gasen in einem GVI Isoprime Massenspektrometer im Vergleich zu Laborstandards. Im gleichen Gerät sind an unabhängigen Proben auch Wasserstoff- und Sauerstoff-Isotopenverhältnisanalysen durch pyrolytischen Probenaufschluß möglich.

Prinzipieller Aufbau, Funktionsweise und Bedienungskomfort des Systems werden erläutert. Mittels Proben von Wasser(standards) werden Genauigkeit und Reproduzierbarkeit und anhand einer Korrelationskurve zu unabhängig gemessenen δ^2H-Werten biologischer Proben die Richtigkeit und Zuverlässigkeit der Wasserstoff-Isotopenverhältnisanalyse dargelegt. Vorteile und Grenzen der Anordnung in der Multielement-Isotopenanalyse, z.B. an Inhaltsstoffen von Obstsäften und Wein (Nachweis nicht-deklarierter Zusätze), von Casein aus Käse (Authentizitätsbestimmung) und von Pulpe aus Fruchtsäften (Herkunftsbestimmung) werden aufgezeigt. Anhand dieser Analysen und der Daten von anderen Lebensmitteln, z.T. mit extremen Elementverhältnissen, wird der weite Mess- und Anwendungsbereich des Systems demonstriert.

Dual inlet precision 13C analysis with multi-aliquot CF analysis

Simon Davis (www.massspecsolutions.com)

Despite the many benefits of continuous flow systems, standard CF peripherals still struggle to approach the precision and accuracy of dual inlet isotope ratio mass spectrometers. This is largely due to a function of the single sample nature and variable sample sizes encountered with CF techniques. This presentation will demonstrate how the use of volume controlled mutli-aliquot sampling can result in CF precisions exceeding 0.02 per mil, equaling the external precision of most commercially availably dual inlet systems.

New Applications by Isotope Ratio Monitoring LC/MS

A. Hilkert, D. Juchelka, M. Krummen
Thermo Electron (Bremen) GmbH, Barkhausenstr. 2, 28197 Bremen, Germany,

With the introduction of compound specific isotope analysis by isotope ratio monitoring GC/MS (irm-GC/MS) the immediate demand for similar applications using HPLC was created. Many compounds of biological, medical, pharmaceutical and environmental interest are not volatile or too polar. Consequently, they cannot be directly analyzed by gas chromatography.

In irm-GC/MS the carrier is helium, which does not interfere with the essential combustion step prior to isotope ratio mass spectrometry (IRMS). In opposite the LC mobile phase has inhibited a similar direct conversion up to now. All earlier irm-LC/MS approaches were based on the removal of the liquid phase prior to combustion risking fractionation of the isotope ratios of the eluted compounds.

The LC IsoLink uses a new concept for isotope ratio monitoring LC/MS. The liquid phase is not removed from the sample prior to oxidation. The sample is oxidized still in the aqueous, mobile phase followed by on-line separation of the CO_2 from the liquid phase and transfer into the isotope ratio MS. In marked contrast to former approaches the processes in the LC IsoLink are quantitative and fractionation-free.

This new approach opens up a whole new world in the application of gas isotope ratio mass spectrometry. The $^{13}C/^{12}C$ ratios of organic acids, amino acids, carbohydrates and nucleotides can now be measured. These components, typically within a complex matrix, are separated by liquid chromatography followed by on-line determination of the isotope ratios. The drawbacks of using derivatization and off-line preparation procedures can now be overcome.

The new access allows studying biochemical cycles, running tracer experiments and determining the origin of components.

Applications from different scientific areas such as biogeochemistry, molecular biology, and pharmacy as well as authenticity control of foods will be presented. Sensitivity, linearity and precision of the LC IsoLink have been evaluated and will be discussed.

Compound specific carbon isotopic ratios of metabolites determined by LC/MS-IRMS

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Sugars and organic acids play an important role in the metabolism of plants. They are involved in various anabolic and catabolic processes of metabolic pathways, such as photosynthesis, glycolysis, citrate cycle, synthesis of amino acids and fatty acids. Compound specific isotope analysis has been increasingly used to study metabolic pathways and their regulation. Thermodynamic and kinetic isotope effects discriminate isotopes in metabolic reactions and generate products with characteristic isotopic signatures (Schmidt, 2003). The new Finnigan LC IsoLink interface enables the on-line coupling of a liquid chromatograph to a stable isotope ratio mass spectrometer. It significantly reduces the preparation steps and the analysis time. We present an analytical method for the isotope ratio analysis of organic acids and sugars in different plants extracts. First results are reported and discussed.

Plant material was sampled from the "Jena Experiment" field. The low molecular weight metabolites were extracted, sugar and organic acid fractions were separated from the raw extract. The resulting isolates were analyzed by the Finnigan LC IsoLink Interface connected with a Finnigan Delta Plus XP. In the Finnigan LC IsoLink the sample is oxidized to CO_2 by wet combustion with sodium peroxidisulfate solution and transfer to the IRMS. The most abundant sugars (sucrose, glucose, fructose) and organic acids (malate, citrate) from plants were chosen as standards. Within optimal concentration range (250-1000 ng/µl) the standard deviation of the $\delta^{13}C$ values measured by LC/MS-IRMS was always below 0, 3‰ with mean 0,15‰ for sugars and 0,5‰ with mean 0,19‰ for acids.

For the whole separation train the standard deviation always below 0, 4‰ with mean 0,17‰ for sugars and 0,12‰ with mean 0,08‰ for organic acids.

For all plants the $\delta^{13}C$ values of sucrose was enriched by 3,95 ‰ and 4,16 ‰ in comparison to glucose and fructose respectively. Most samples showed a higher $\delta^{13}C$ value for malate than citrate. Our results are consistent with the results for potato leafs (Gleixner et al., 1998) and tobacco plants (Jamin et al., 1997). Possible metabolic reasons for the observations will be discussed.

Gleixner G, Scrimgeour C, Schmidt HL, Viola R. 1998 Stable isotope distribution in the major metabolites of source and sink organs of Solanum tuberosum L.: a powerful tool in the study of metabolic partitioning in intact plants 207: 241-245

Jamin E, Naulet N, Martin GJ. 1997 Stable isotope analysis of components from tobacco leaves. Phytochemical analysis 8: 105-109

Schmidt HL. 2003 Fundamentals and systematics of the non-statistical distributions of isotopes in natural compounds. Naturwissenschaften 90: 537-552

Inertes Material zum Einsatz in der Hochtemperaturpyrolyse

Inert material for high temperature pyrolysis

M. Boner[1], K. Hecker[2], H. Förstel[3]

[1]Agrisolab GmbH., [2]Hekatech GmbH., [3]Forschungszentrum Jülich

Die derzeit routinemäßig eingesetzte Hochtemperaturtechnik verwendet zum einen ein Keramikrohr-System mit einer Arbeitstemperatur von bis zu 1300°C oder ein Doppelrohraufbau mit einem äußerem Keramik- und einem innerem Classy-Carbon Rohr mit einer Arbeitstemperatur von bis zu 1450°C.

Beide Systeme haben Nachteile, so besteht beim ersteren durch die niedrige Temperatur immer die Gefahr einer unvollständigen Pyrolyse. Das zweite hat mit einer Arbeitstemperatur von bis zu 1450°C dieses Problem weitgehend gelöst. Jedoch führt der Systemaufbau zu einem mit der Temperatur stetig ansteigenden Untergrund auf der Masse 28. Oberhalb von 1450°C wird dadurch die Messung der Isotopenverhältnisse erheblich erschwert. Zudem führt die nur einfache federgelagerte Dichtung des Classy-Carbon-Rohres in Kombination mit dem geringen Innendurchmesser von ca. 8 mm gerade bei der Feststoffanalyse zur Restriktion des verwendeten Silberkapseln im Rohr, die sich wiederum in einer unzureichenden Pyrolyse äußert und eine Probenmessung von nur ca. 150 Proben erlaubt.

Es lag deshalb nahe, nach einem Material zu suchen, das einige der bisherigen Probleme löst. Siliciumcarbid bietet dabei durch den fehlenden Sauerstoff eine wesentliche Grundvoraussetzung für einem Rohraufbau. Es ist dazu chemisch inert, bis 1600º beständig, und gasundurchlässig. Der Untergrund liegt im direkten Vergleich um den Faktor 10 unterhalb des Classy-Carbon-Rohr-Aufbaus. Es wird mit einem Innendurchmesser von etwa 15 mm als Einrohrsystem verwendet und schließt damit die Restriktion durch das schmelzende Silber annähernd aus. Probenmessungen von 2000 bis 3000 Proben sind entsprechend möglich. Durch die Arbeitstemperatur von bis zu 1600º im Reaktionsbereich wird eine stetige vollständige Pyrolyse gewährleistet..

Das Reaktionssystem wird als Teil eines modifizierten Hochtemperaturofens der Firma Hekatech betrieben. Die Bestimmung des D/H-Verhältnisses erfordert etwa 5, die des $^{18}O/^{16}O$-Verhältnisses 10 Minuten, wobei diese Zeit gewählt wurde, um das CO mit Sicherheit vom N_2 zu trennen. Bei einer kombinierten Messung, unter Einsatz des Diluters, werden 12 Minuten benötigt. Die Messanordnung ermöglicht eine Reproduzierbarkeit von ± 0.1 bis 0.2 ‰ für $^{18}O/^{16}O$, das D/H-Verhältnis von unter ± 1 ‰.

J-RAS: A high precision reference for the isotopic composition of CO2 in air

W.A. Brand, M. Patecki, P. Ghosh and M. Rothe (MPI for Biogeochemistry Jena)

Due to the small changes that anthropogenic release of fossil carbon to the atmosphere leaves in the CO_2 isotopic composition its measurement in ambient air requires the highest precision obtainable. Moreover, measurements must be comparable between the different laboratory at the same high precision level. This has been a challenge in the past, in particular because the international 13C scale (VPDB) is based on a carbonate material and not on air, where the highest precision and accuracy are needed. Moreover, the scale must be stable over decades and more.

In order to generate a reliable and long lasting stable isotope ratio standard for CO_2 in samples of clean air, CO_2 is liberated from NBS 19 and other well characterized carbonate materials and mixed with CO_2-free air. For this purpose we have designed a dedicated *a*cid *r*eaction and *a*ir *mi*xing *s*ystem (*ARAMIS*). In the system, CO_2 is generated by a conventional acid digestion of powdered carbonate. Evolved CO_2 gas is mixed and equilibrated with a prefabricated gas comprised of N_2, O_2, Ar, and N_2O at close to ambient air concentrations. Distribution into glass flasks is made stepwise in a highly controlled fashion. The isotopic composition, established on automated extraction / measurement systems, varied within very small margins of error appropriate for high precision air-CO_2 work (about ± 0.015 ‰ for $\delta^{13}C$ and ± 0.025 ‰ for $\delta^{18}O$). For establishing a valid $\delta^{18}O$ relation to the VPDB scale, the temperature dependence of the reaction between 25°C and 47°C has been determined with a high level of precision.

CO_2-in-air mixtures were generated from a selection of reference materials

- the material defining the VPDB isotope scale (NBS 19, $\delta^{13}C$ = +1.95 ‰ and $\delta^{18}O$ = -2.2 ‰ exactly);
- a local calcite similar in isotopic composition to NBS 19 (‘MAR-J1’, $\delta^{13}C$ = +1.97 ‰ and $\delta^{18}O$ = -2.02 ‰)
- a natural calcite with isotopic compositions closer to atmospheric values (‘OMC-J1’, $\delta^{13}C$ = -4.24 ‰ and $\delta^{18}O$ = -8.71 ‰).

For quantitatively controlling the extent of isotope-scale contraction in the system during mass spectrometric measurement other available international and local carbonate reference materials (L-SVEC, IAEA-CO-1, IAEA-CO-8, CAL-1 and CAL-2) were also processed. As a further control pure CO_2 reference gases (Narcis I and II, NIST-RM 8563, GS19 and GS20) were mixed with CO_2-free synthetic air. Independently, the pure CO_2 gases were measured on the dual inlet systems of the same mass spectrometers. The isotopic record of a large number of independent batches prepared over the course of several months is presented. In addition, the relationship with other implementations of the VPDB-scale for CO_2-in-air (e.g. CG-99, based on calibration of pure CO_2 gas) has been carefully established.

A side result has been the discovery that most secondary standards in current use have suffered from scale contraction effects during the measurements underlying the consensus values. This is further confirmed by a new set of results involving carbonate, CO_2 and other stable isotope reference materials with a large number of measurements from four different laboratories. The measurements were made with a focus on avoiding scale contraction effects during measurement and appropriate correction. This recent set of data shows excellent agreement with the data generated from the CO_2 mixed into air experiment with $\delta^{13}C$ values covering a range of almost 50 ‰.

Carbon isotope anomaly in the major plant C_1 pool and its biogeochemical implications

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Stable isotope analysis has become a powerful tool for environmental scientists, plant biologists, ecologists and geochemists studying global elemental cycles or past climatic conditions. Thus most plant species have been photosynthetically characterised as Calvin cycle (C_3), Slack-Hatch cycle (C_4) and Crassulacean acid metabolism (CAM) categories using carbon isotope signatures. Moreover variations in the carbon isotope composition ($\delta^{13}C$) of compounds, produced and destroyed in the global carbon cycle, are often used to investigate biogeochemical cycles and global source-sink relationships, as well as the underlying mechanisms. Stable isotope techniques are increasingly applied to the study of atmospheric budgets of volatile organic compounds (VOCs).

In this presentation it is shown that methoxyl groups in terrestrial plants (in esters and aromatic ethers) have a unique carbon isotope signature exceptionally depleted in ^{13}C. Plant-derived C_1 volatile organic compounds (VOCs) are also highly depleted in ^{13}C compared with C_{n+1} VOCs. These observations suggest that the plant methoxyl pool is the predominant source of C_1 compounds of plant origin in the biosphere such as methanol, chloromethane, and bromomethane. Moreover this pool, which comprises *ca* 2.5% of carbon in plant biomass and represents an important substrate for methanogenesis, is likely to be a significant source of highly depleted methane entering the atmosphere.

The distinct ^{13}C depletion of methoxyl groups in plants which is reflected in isotope signatures of C_1 VOCs may provide a helpful tool in constraining complex environmental processes. These isotope anomalies have a tremendous potential to improve our understanding of the global cycles of atmospheric trace gases and the biochemical pathways involved. Furthermore methoxyl groups could act as markers for biological activity in organic matter of terrestrial and extraterrestrial origin.

Biosynthese von Blüten- und Blätterduftstoffen – verfolgt anhand stabiler Isotopen

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Bei vielen Pflanzen duften nicht nur die Blüten, sondern auch die Blätter. Dabei soll der Blütenduft häufig Bestäuber anlocken, während der Duft der Blätter der intra- und interspezifischen Kommunikation dient.
Als Duftstoffe werden von Pflanzen vor allem Terpene, aber auch Aromaten und Fettsäurederivate emittiert.
Für die Biosynthese der Vorstufen der Terpene in Pflanzen sind der cytosolische Mevalonat-Weg (MVA) und der plastidiäre Methylerythritolphosphat-Weg (MEP) bekannt. Aromaten werden über den Shikimisäureweg und Fettsäuren von AcetylCoA ausgehend synthetisiert.
Die auftretende Isotopendiskriminierung durch Enzyme und Diffusionsprozesse führt in der Pflanze zu spezifischen natürlichen Isotopenverhältnissen der produzierten Duftstoffe.
Bei dem Vergleich zwischen den emittierten Verbindungen von Blüten und Blättern lassen sich bei einigen Arten für die gleiche Substanz signifikante Unterschiede in den $\delta\ ^{13}C$ – Werten finden.
Diese Unterschiede können darauf beruhen, dass die Blätter im Gegensatz zu den Blüten photosynthetisch aktiv sind. Aber auch voneinander abweichende Transportprozesse oder die Beteiligung verschiedener Enzyme an der Biosynthese der Duftstoffe in Blüten beziehungsweise Blättern können eine Rolle spielen.

De novo biosyntheses versus sequestration of defense compounds in leaf beetles – a mechanistic approach by stable isotopes and molecular biological techniques

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Many insects defend themselves against enemies by oozing exocrine secretions from glands when attacked. Although the basic structure of their glandular systems are well described, the origin of the defense compounds and the biosynthetic mechanisms of these compounds are often poorly understood. Two terpenoid biosynthesis pathways (mevalonic acid (MVA) pathway and methylerythritol-4-phosphate (MEP) pathway) exist in nature. However, only the MVA pathway is present in animals. The localization of the biosynthetic enzymes was studied by molecular biology methods. Stable isotopes were used for labeling experiments with a precursor from the MEP pathway. Our data indicate that the leaf beetles, *Phaedon cochleariae* and *Gastrophysa viridula*, produce their defense-terpenes only *de novo*. However, by another species in the same taxonomic group (*Plagiodera versicolora*) we could show that a transport of compounds from the MEP pathway in the insects took place. These compounds were utilized for their defense mechanism. Such an uptake of terpene precursors in leaf beetles is in contradiction to the literature, claiming that the beetles – of the defense-terpene producing group - generate these terpenes only *de novo*.

Plant-internal variation of lipid composition and compound-specific isotopes of various crops

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Seasonal and plant-internal variations of lipid composition and compound-specific isotopic signatures were previously described for various plant groups [1], [2]. So far, no observations were documented concerning lipid variations of annual and perennial crops. In this study, we simultaneously applied biomarker and isotopic analysis to obtain information on compartmentalization of plant lipid distributions.

Plant samples were taken from several sites in Germany, where parallel cropping of C3-plants (rye, wheat) and C4-plants (maize) are practiced, whereby C3- and C4-crop plant samples were taken several times during the growing season. Plant samples were divided into leaf, stem and root biomass for each growth stage and analyzed separately, to obtain information on plant internal lipid and C-isotope variations. Extractable lipids of plant and soil samples were recovered by accelerated solvent extraction and separated into fractions of different polarity by automated liquid chromatography [3]. Fractions of aliphatic hydrocarbons and carboxylic acids were analyzed by GC-MS and GC-irmMS.

Within the total carboxylic acid fraction the short-chain (C_{12-18}) fatty acids, originating from various sources including bacteria, fungi, animalia, and crop plants, gave the highest concentrations. Amongst the crop lipid-derived *n*-carboxylic acids, however, the long-chain even carbon-numbered homologues (C_{22-26}) were most abundant. The aliphatic hydrocarbon fraction was dominated by long-chain (C_{29-33}) odd carbon-numbered *n*-alkanes. Compound-specific $\delta^{13}C$-compositions were determined for the most abundant alkanes and carboxylic acids and weighted averages calculated. Aboveground biomass (stems and leaves) of maize showed similar isotopic compositions for alkanes and carboxylic acids. During the growing season the plant parts became isotopically depleted, most likely due to successive incorporation of light carbon isotopes during biosynthesis. This isotopic depletion was similar for stems and leaves.

In terms of isotopic composition belowground biomass significantly differed from aboveground biomass. $\delta^{13}C$ values of belowground carboxylic acids remained fairly constant during the growing season. Root *n*-alkanes, however, became isotopically depleted in comparison to aboveground *n*-alkanes. Due to the difference in the isotopic signature of roots versus aboveground biomass, root lipids do not derive from photosynthates of aboveground biomass, which were then plant-internally translocated towards the roots. These lipids must be biosynthesized *in situ* by either (a) direct assimilation of soil organic carbon by root tissues, or (b) interaction with soil microbes growing on or within the roots as proposed by [4]. Compound-specific $\delta^{13}C$-signatures of long-chain carboxylic acids and alkanes are thus suitable for source apportionment of lipid production in different plant compartments.

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Calibration of isotopic turnover rates in wireworms, common agricultural pests

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Wireworms are the larvae of click beetles (Coleoptera: Elateridae). Some species, most notably of the genus *Agriotes*, are known as severe pests, especially in maize and potatoes. Previous investigations have shown that wireworms may also feed on weeds, their dietary choices in the field are not obligatory: either weeds or the crop might be eaten, or both, depending on environmental or genetic cues or a combination of these factors. Assessing the dietary choices of wireworms under field conditions is not a simple task as they are fluid feeders and leave no microscopically discernible food fragments to be found in gut dissection. Stable isotope analysis, however, can relate the composition of the tissues of the consumer to that of its diet by the ratio of different isotopes of the same element in each. A dietary switch does not show up immediately in the isotopic composition of the consumer because the isotopic turnover rate from an old food's signature to a new one has to be accounted for.

In a feeding experiment with laboratory-reared, late larvae of *Agriotes obscurus,* we fed them wheat, a C3-plant like weeds, and then switched half of the group to maize, a C4-plant and a common crop. Individuals were analyzed for their standardized isotopic ratio of ^{13}C and ^{12}C at days 2, 4, 8, 16, 32, 48, 64, 96, and 128 after the start of the experiment. From each specimen dried samples of the 9th abdominal segment as well as fat, obtained from centrifuged homogenates of the remaining body, were analyzed.
Within the first week the isotopic values of the maize-fed wireworms changed rapidly towards the isotopic value of maize and at slower rates thereafter. The curve towards the isotopic value of maize was hyperbolic and ascended slightly steeper for the fat component than for the all-components sample.
Isotopic turnover rates were found to be lower and more heterogeneous in a second feeding trial performed with individuals not raised in the laboratory but collected in the field. These results were similar to first trials with two other wireworm species common in Central Europe, the carnivorous *Agrypnus murinus* and the omnivorous *Hemicrepidius niger*.

Effect of dietary protein/energy ratio on trophic shift of C and N isotopes and on the activity of enzymes involved in the amino acid metabolism of Nile tilapia, *Oreochromis niloticus* (L.)

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The effect of dietary C/N ratios on the trophic shift of C and N isotopes ($\Delta\delta^{13}C$, $\Delta\delta^{15}N$) has been described in different species, e.g. in such diverse groups as crustaceans (Adams and Sterner 2000), birds (Pearson et al. 2003) and fish (Gaye-Siessegger et al. 2004). For an accurate back-calculation of diets using stable isotopes, an exact value for the trophic shift is indispensable. In order to test whether the measurement of the activities of enzymes involved in amino acid metabolism could be used to improve estimates of the trophic shift of C and N isotopes, Nile tilapia (*Oreochromis niloticus*) were fed semi-synthetic diets differing in their protein contents (37, 44 and 60%). The diets were formulated to be isolipidic and isoenergetic (on the basis of metabolizable energy) and were made from casein, wheat starch, corn germ oil supplemented with L-arginine, vitamins and minerals. The influence of the different diets on the trophic shift of C and N isotopes in the whole fish body and on the specific activity of aspartate aminotransferase (ASAT) and alanine aminotransferase (ALAT) in the liver was investigated.

The trophic shift of C and N isotopes decreased significantly while the activities of ASAT and ALAT increased significantly with increasing protein content in the diet. There was a strong positive correlation between the specific activities of ASAT and ALAT. The trophic shift of C and N isotopes decreased significantly with increasing specific activity of ALAT. The interactions between amino acid metabolism and trophic shift will be discussed as well as their implications for ecological studies.

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Mundraub im Wurzelraum: Isotopenhäufigkeitsanalysen und molekularbiologische Daten liefern neue Einblicke in die komplexe Ernährungsweise der Waldbodenvegetation

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Die meisten Pflanzen gehen mit Pilzen eine enge Partnerschaft ein – die Mykorrhiza. In der Regel versorgen dabei die Pflanzen den Pilzpartner mit Kohlenstoffverbindungen aus der Photosynthese und erhalten im Gegenzug mineralische Nährstoffe, die der Pilzpartner aus dem Boden effizienter aufnehmen kann. Diese mutualistische Beziehung wird weltweit von einigen hundert Pflanzenarten unterlaufen, die chlorophyllfrei sind und somit keine Photosynthese mehr betreiben. Diese Ernährungsweise auf Kosten des Pilzpartners wird als Mykoheterotrophie bezeichnet. Sie ist insbesondere bei Orchideen verbreitet. Trotz der bekanntermaßen mykoheterotrophen Ernährung mancher Orchideen wird für adulte, grünblättrige Orchideen eine vollständig autotrophe Ernährung angenommen. Häufigkeitsanalysen der stabilen Kohlenstoff- und Stickstoffisotope liefern neuerdings Hinweise, dass viele grüne Orchideen sich teilweise auch auf Kosten des Pilzpartners ernähren. Diese teilweise Mykoheterotrophie ist mit einem Wechsel des Pilzpartners verbunden und erlaubt den Orchideen ein Vordringen in den dunkelsten Schatten von Wäldern.

Pflanzen, die ihren Kohlenstoffbedarf aus der Photosynthese und ihren Stickstoffbedarf durch Aufnahme von Nitrat und Ammonium aus dem Boden decken, besitzen charakteristische Isotopenhäufigkeiten. Pilze dagegen unterscheiden sich auffällig in ihrer Isotopenhäufigkeit von der Mehrheit der Pflanzen. Chlorophyllfreie Orchideen, wie beispielsweise die in unseren Wäldern häufig anzutreffende Vogel-Nestwurz, besitzen Isotopenhäufigkeiten, die sie von grünen Begleitpflanzen grundlegend unterscheiden, die aber gleichzeitig den sie ernährenden Pilzen ähnlich sind. Scheinbar autotrophe Waldorchideen, wie etwa Vertreter aus den Gattungen Waldvögelein und Stendelwurz, weisen Isotopenhäufigkeiten auf, die eine auffällige Zwischenposition zwischen Nicht-Orchideen einerseits und offensichtlich mykoheterotrophen Orchideen andererseits einnehmen. Je lichtlimitierter der Standort dieser scheinbar autotrophen Orchideen ist, umso mehr nähert sich ihr Isotopenwert den mykoheterotrophen Orchideen an. Es liegt nahe, aus den Isotopendaten zu folgern, dass viele unserer einheimischen Waldorchideen ein für Pflanzen bisher unbekanntes Ernährungsverhalten besitzen. Je nach Lebensbedingung können sie offenbar zwischen Photosynthese (autotrophe Ernährung) und Pilzverdauung (mykoheterotrophe Ernährung) wechseln. Abschätzungen aus den Isotopendaten deuten darauf hin, dass der Beitrag aus der mykoheterotrophen Ernährung bis zu 85 % erreichen kann.

Die Interpretation der Isotopendaten wird durch zwei weitere Beobachtungen bestätigt: (1) Molekulargenetische DNA-Analysen belegen, dass der Übergang von autotropher zu fakultativ mykoheterotropher Ernährung mit einem Tausch des Pilzpartners im Wurzelraum der Orchideen einhergeht. Wahlweise oder obligat mykoheterotrophe Orchideen besitzen als Partner Pilzarten, die bekanntermaßen mit Bäumen eine Ektomykorrhiza eingehen. Es entsteht somit ein Stoffffluss vom Baum über den Pilz zur Orchidee. (2) Vereinzelt lassen sich in Wäldern weißblättrige Varietäten von eigentlich grünblättrigen Orchideenarten finden. Diese Albino-Varietäten unterscheiden sich in ihrem Wachstum nicht von grünblättrigen Individuen und besitzen Isotopenhäufigkeiten, die sie einer vollständig mykoheterotrophen Ernährung überführen.

Weiterführende Untersuchungen belegen neuerdings auch ein Auftreten der partiell mykoheterotrophen Ernährungsweise bei Waldbodenpflanzen außerhalb der Orchideen-Familie. Soweit bisher untersucht, ernähren sich auch Vertreter aus der Familie der Wintergrüngewächse (Pyrolaceen) teilweise auf Kosten ihres Pilzpartners.

Natural abundance of ^{15}N in different compartments of a spruce forest ecosystem under acid rain and manipulated clean rain field conditions

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Abstract

We analysed stable isotopes of N in a spruce forest both under ambient rainfall (no further manipulation of the atmospheric input) and the clean rain scenario, i.e. to the status after about 10 years of reduced inorganic N- and acid-constituent input (clean rain application). The objectives of the study were to assess whether or not the natural ^{15}N abundance will function as an indicator for the N-status of our forest ecosystems under above mentioned field conditions. For this purpose, natural 15N abundance values were measured in needles, litter fall, roots, soil, bulk precipitation, thoughfall and soil water of both plots. In the bulk precipitation, $\delta^{15}N$ values of NO_3-N were in the range reported from other studies (–16 to +23‰). In control plot of D2, the pathway of ambient rainfall through the canopy significantly influenced ^{15}N the abundance of nitrate; the throughfall was greatly depleted in ^{15}N compared to the bulk precipitation. The throughfall water after passing through the O-horizon (below 10 cm) and the upper mineral soil layers, the $\delta^{15}N$ abundance of nitrate increased in the 100 cm soil depth from -4.34 ‰ to –3.22‰ at D2 and from –6.29 ‰ to –2.04 ‰ at D1, i.e. the ^{15}N enrichment was significantly ($p \leq 0.05$) stronger at the clean rain plot D1. This stronger 15N enrichment in the soil water of clean rain plot of D1 has been explained by the presence of insignificant nitrification in clean rain D1 plot. ^{15}N enrichment of both green needles and litter fall was greater in the N-saturated control plot of D2 than in the clean rain plot of D1. In all soil depths, both living and dead fine roots were depleted in ^{15}N compared to the soil $\delta^{15}N$ in the respective depths. We found further positive correlation between $\delta^{15}N$ in soil and roots, leading us to believe that roots preferentially used N from the soil horizons they were in for their own biomass production. For the clean rain plot D1, a typical vertical gradient of the soil ^{15}N-enrichment was observed, whereas the roof control site D2 differs from the clean rain plot D1 with respect to the ^{15}N abundance trend in organic/humus soil layer. In the organic layer (0-6 cm depth) of plot D2, there is almost a trend of slight soil $\delta^{15}N$ depletion with increasing depth and this is explained by the presence of prominent nitrification at this plot. Our observations have concluded that the $\delta^{15}N$ natural abundance of undisturbed forest soil profiles can provide information about the N-status in forest ecosystems; comparatively low ^{15}N abundance in the surface layer than in the lower layers appears to indicate N limitation and low rates of nitrification, whereas a higher ^{15}N in the surface layer than in the deeper layers appears to indicate high rates of nitrification.

River biogeochemistry and source identification of nitrate by means of isotopic tracers in the Baltic Sea catchments

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Abstract

River nitrate input is largely controlled by the land use in its catchments. The information carried by the isotopic signatures in nitrate and particulate matter in relation to the vegetation cover is investigated in a comparative study of 12 rivers from the Baltic Sea catchments.

We found a wide range of isotope values in nitrate ranging from -2 to 14‰ for $\delta^{15}N$ and 8-25‰ for $\delta^{18}O$. These data and source isotope data from three major nitrate sources (farmland, nitrate from atmospheric deposition and from pristine soils) were used to theoretically estimate the shares. The results were compared to the same information from GIS data bases with good agreement.

Additionally the annual variability of riverine isotope signatures is presented exemplarily from 3 rivers with contrasting vegetation cover and land uses. Nordic rivers with relatively pristine vegetation cover show not only low $\delta^{15}N$ –NO_3^- values and high $\delta^{18}O$ –NO_3^- but also lower annual variability than a river draining densely populated land. A seasonal signal could be found in all rivers but was most pronounced in the non regulated and high eutrophic rivers.

Isotope biogeochemistry of diagenesis caused by a black shale-fueled marine biosphere (ODP Leg 207)

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Sediments are carriers of proxy signals for present and past microbial activity. The presented study deals with diagenetic processes in the deep biogeochemical sulfur-carbon-metal cycles of sediments recovered from Demerara Rise (Leg 207) [1, 2]. We try to identify those reactions that may take part in the formation, alteration, or modification of proxy signals by means of inorganic and stable isotope geochemical pore water and solid phase investigations. The project focuses on the potential of the isotopic composition of sulfur-bearing authigenic minerals to reflect the history of biogeochemical reactions in deeply buried sedimentary sequences as well as early diagenetic reactions during black shale formation. Euxinic conditions during black shale formation are shown by the high ratios of reactive to total iron. Are authigenic sulfides useful paleo-proxies? Are deeply buried black shales acting as a bioreactor for driving ongoing diagenesis by a deep biosphere via methane as substrate? Associated with the reactions in the coupled carbon-iron-sulfur cycles is the development of authigenic barite enrichments. These serve as indicators for the evolution of dissolved sulfate-barium diffusion fronts in association with methane fluxes derived from deeply buried TOC-rich strata. Additionally, we extract informations about metabolic processes from the stable sulfur isotopes preserved in authigenic barites. From stable isotope analyses we deduce that extremely heavy authigenic pyrite and barite above the black shale sequence reflect different sulfate/sulfide pore water gradients caused by temporarily changing methane fluxes from underlying black shales. Isotopically heavy sulfur-bearing minerals seem to be indicative for anaerobic methane oxidation. Pyrites found within the black shales show a wide range of sulfur isotopic compositions essentially reflecting early diagenetic signals, that are within the range found at other Cretaceous black shale settings.

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Doppel Isotopen-Tracer Studie zur Validierung der Barometrischen Prozessseparation (BaPS)

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Aufgrund des hohen Aufwandes wird in vielen Untersuchungen, die sich mit dem N-Kreislauf im Boden beschäftigen nicht die eigentlich relevante Brutto-Nitrifikationsrate, sondern die einfacher zu bestimmende Netto-Nitrifikationsrate gemessen (z.B. ROWELL 1997). Die Netto-Nitrifikation lässt jedoch keinen Rückschluss auf die Höhe und die Dynamik der Nitrifikation (d.h. quantitative Umsetzung von NH_4^+ zu NO_3^-) im Boden zu (STARK & HART, 1997) und kann zur Interpretation mikrobieller N-Umsetzungen nur eingeschränkt herangezogen werden. Bisher konnte die Brutto-Nitrifikation nur mit der ^{15}N-pool dilution Technik bestimmt werden, die auf der Verdünnung zuvor homogen eingebrachten ^{15}N-Nitrat aufgrund der Nachlieferung von Nitrat durch die Nitrifikation in dem Boden beruht (MOSIER & SCHIMEL 1993).
Die BaPS-Methode (Ingwersen et al., 1999) bietet eine neue Möglichkeit die Brutto-nitrifikationsraten zu bestimmen, indem sie die Annahme, dass in einem mit Boden gefüllten, gasdichten System nur die folgenden Prozesse für eine Veränderung des Systemdruckes verantwortlich sind: Bodenatmung, Nitrifikation und Denitrifikation.
Die Bodenatmung ist annähernd druckneutral, da sich Sauerstoffverbrauch und CO_2-Produktion die Waage halten. Die Nitrifikation hingegen führt zu einer Druckabnahme im System, da 0,5 Mol molekularer Sauerstoff pro Mol Ammonium verbraucht werden, aber kein Gas produziert wird. Durch die Denitrifikation kommt es zu einer Druckzunahme, da kein Gas verbraucht, aber bei vollständiger Reduktion von 4 Mol Nitrat zu 2 Mol molekularem Distickstoff (N_2) neben dem N_2 zusätzlich 2,5 Mol CO_2 freigesetzt werden.
Durch vergleichende Messungen zur Bruttonitrifikation mittels dem BaPS-System und der ^{15}N-pool dilution Technik konnten wir zeigen, dass sich die Ergebnisse in Mineralböden teilweise um Größenordnungen unterscheiden. In einer zusätzlichen Studie mit Doppelmarkierung (^{15}N im Nitrat ^{13}C im CO_2) wurde versucht die Ursache für die Unterschiede zu identifizieren. In dem Beitrag sollen die beiden Methoden anhand der Versuchsergebnissen des Statischen Düngeversuchs in Bad Lauchstädt verglichen und Schwächen und Stärken der beiden Methoden anhand der Messergebnisse eingehen diskutiert werden.

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Quellencharakterisierung mit Hilfe von ^{15}N und ^{18}O Isotopen im Nitrat unter leguminosenhaltigem Grünland

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In der Landwirtschaft werden Leguminosen angesät, um die N-Verfügbarkeit zu verbessern. Damit steigt zugleich die NO_3^--Auswaschung in das Grundwasser. Um die Auswaschungs-gefahr zu verringern, muss der Beitrag der Leguminosen quantifiziert werden. Das Ziel unserer Arbeit ist daher die Beantwortung der Fragen: (1) Steigern Leguminosenwurzeln die N Mineralisation? (2) Kann der Anteil des Nitrats, der aus der Mineralisierung der Leguminosen stammt, mit Hilfe von ^{15}N und ^{18}O Isotopenanalysen berechnet und von anderen Quellen (z.B. organische Substanz im Boden, Niederschlag) unterschieden werden?

Wir entnahmen im August 2004 neun Bodenmonolithe (Ø 0,07 m; Tiefe 0,04 m) aus einer *Medicago x varia* Martyn Monokultur auf der Fläche des Jena-Experiments in der Saale-Aue. Jeweils drei Parallelen wurden (1) unbehandelt, (2) auf 2 mm gesiebt und (3) auf 2 mm gesiebt und die sichtbaren Wurzeln entfernt über zehn Wochen bei 20 °C inkubiert und wöchentlich mit einer Nährlösung gespült. Zur Quellencharakterisierung wurde zudem Freilandniederschlag und Bodenlösung verschiedener leguminosenhaltiger Mischungen untersucht. In den Lösungen bestimmten wir die NO_3^--Konzentrationen sowie die $\delta^{15}N$- und $\delta^{18}O$-Werte des Nitrats.

Die NO_3^--Mineralisierung unterschied sich nicht signifikant zwischen den gestörten Varianten mit und ohne Wurzeln. Alle drei Varianten zeigten außerdem denselben Verlauf der $\delta^{15}N$- Werte in NO_3^-. Nach 14 Tagen stiegen die $\delta^{15}N$ Werte in NO_3^- um 6 δ-Einheiten an und blieben danach bis zum Ende des Experiments konstant. Dies weist auf die Beteiligung von zwei verschiedenen N-Pools hin. Der erste N-Pool umfasste 6-39%, der zweite 15-52% des N-Gehaltes zu Beginn des Experiments. Aufgrund der niedrigen $\delta^{15}N$ Werte des ersten Pools gehen wir davon aus, dass es sich um leicht umsetzbare N-Verbindungen handelt, die Leguminosen entstammen. Der zweite Pool setzt sich vermutlich aus schwerer umsetzbaren N-Verbindeungen der (nicht-leguminosenbürtigen) organischen Bodensubstanz (SOM) zusammen. Somit ergeben sich drei Quellen für das Nitrat in der Bodenlösung: Niederschlag (P), Mineralisierung von Leguminosen (ML) und Mineralisierung nicht-leguminosenbürtiger SOM (MSOM). Mit Hilfe der ^{15}N und ^{18}O Isotopensignatur ergaben sich folgende Anteile der Quellen P: 12-17%, ML: 0-17% und MSOM: 71-81%. Durch optimiertes Management kann der Nitrataustrag unter *Medicago x varia* also maximal um 1/5 reduziert werden.

Identification of main nitrate sources in a lowland agricultural drainage system using stable isotopes analysis

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Diffuse nitrogen pollution in surface water is important especially in regions with intense agricultural land use. For improving the nutrient management in these catchments, the origin of different nitrate sources as well as their distribution in soil and groundwater has to be identified. Isotope analyses of nitrate can help to ascertain the origin and the fate of nitrate in soil and groundwater. We investigated the temporal variation of the nitrate sources and the role of hydrological factors controlling these variations. The factors may have considerable impact on the selection of measures for reducing high nitrate losses to lowland streams.

^{15}N and ^{18}O investigations of nitrate were carried out in the "Schaugraben" catchment (~25km²), a typical Pleistocene lowland located in the north of Saxony-Anhalt. Chemical parameters and discharge of the Schaugraben drain have been studied in weekly intervals since 1997 giving a mean discharge in winter with 93.8 l/s and mean N-nitrate content of 61 mg/l, and 20 l/s with N-nitrate of 6.4 mg/l in summer. Agriculture as grassland and pasture is the dominating landuse in the riverine area. The average total input of nitrate is 143 kg/ha*a on cropland; about 75% originate from inorganic fertilizer additions.

Extended measurements were conducted during in a 1 km measuring section of the Schaugraben drain since 2002. N- and C- compounds, main ions, and the isotope ratios of NO_3^--N and NO_3^--O were analysed in the water samples. The combined analysis of $\delta^{15}N$ and $\delta^{18}O$ signatures allows segregation of the different sources and enables estimation of nitrogen turnover.

The sampling periods represent different hydrologic conditions with wet and try periods which influence the flow regime and the input of nitrate into the surface water of the drain. We observed high variations of nitrate concentrations as well as NO_3^- isotopic signatures. In surface water $\delta^{15}N$ values range from +3 ‰ to +25 ‰, and from +4 ‰ to +17 ‰ in $\delta^{18}O$. Only two sources of nitrate are important in the surface water: soil organic matter and organic manure. The main sources vary in relation to the hydrological conditions: (i) during base flow conditions soil organic matter is the most important source of nitrogen, (ii) in periods with high ground water levels, nitrate seepage is influenced by organic manure.

A detailed discussion is given in the paper.

Monitoring of in situ biodegradation of groundwater contaminants using a test system (BACTRAP) with ^{13}C-labelled substrates

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To assess Natural Attenuation as a remediation strategy in contaminated sites, the proof of in situ biodegradation is needed, because the fate of contaminants is mainly governed by microbial processes. Except stable isotope fractionation approaches (Meckenstock et al. 2004) and labour intensive tracer experiments (Fischer et al. 2005) there are no tools available to monitor the in situ biodegradation within contaminated groundwater systems. Other methods to determine the biodegradation potential like ex situ laboratory microcosm studies are still questionable because the majority of microorganisms involved in the degradation of the organic contaminants have not been cultured yet and the laboratory conditions cannot completely reflect the natural aquifer system.

Our in situ microcosm system (BACTRAP®) allows to overcome these limitations (Geyer et al. 2005). The test system is based on the use of isotopically labelled tracer compounds. ^{13}C-labelled compounds (benzene, toluene, chlorobenzene and PAH) are loaded to an adsorption material. During the incubation in the contaminated aquifer, microorganisms will grow on the adsorption material by using the labelled substrate. The incorporation of the isotope label into microbial biomass will prove the in situ biodegradation of the test substrate. The transformation is assessed by means of carbon isotope analysis of fatty acids, which are major constituents of cell membranes of microorganisms.

The BACTRAP system was applied in different field studies. In a first approach we were able to prove the in situ biodegradation of benzene, toluene, chlorobenzene and PAH after the incubation within highly contaminated strictly anaerobic aquifers. After incubation, the isotope label was detected in fatty acids demonstrating the transformation of the ^{13}C-labelled carbon into biomass und thus proving in-situ biodegradation. The pattern and the isotope composition of fatty acids indicated that a complex microbial community settling on the in situ microcosms was involved in biodegradation of these compounds.

In the context of Natural Attenuation, this concept may have high potential to improve groundwater monitoring and remediation strategies.

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Acknowledgement

Financial support of Nicole Stelzer by the Deutsche Bundesstiftung Umwelt (DBU) is gratefully acknowledged (grant 20004/751).

Stabile Isotope (C, N) zur Herkunftsbestimmung von Cyaniden in belasteten Böden

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Im Bereich ehemaliger Kokereien oder Hochöfen treten häufig hohe Cyanidgehalte in Böden auf. Je nach Produktionsprozess liegen die Cyanide als $Fe_4[Fe(CN)_6]_3$ oder $K_2Zn_3[Fe(CN)_6]_2 \cdot 9\,H_2O$ vor. Beide Komplexe können über das Sickerwasser in das Grundwasser ausgetragen werden. Im Grundwasser liegt das Cyanid unabhängig von der ursprünglichen Bindungsform als $[Fe(CN)_6]^{4-}$ Komplex vor, so dass sich dessen Herkunft mit konventionellen physikalisch-chemischen Methoden nicht mehr identifizieren lässt. Letztere ist jedoch von Interesse, um Verursacher von Grundwasserkontaminationen zu identifizieren. Mit Hilfe der an Böden und Grundwasserproben unterschiedlicher Standorte durchgeführten Untersuchungen sollte daher geklärt werden, ob eine Herkunftsbestimmung über die stabilen Isotope ^{13}C und ^{15}N des Cyanidions möglich ist.

Die Bestimmung der C- und N-Isotopensignatur des Cyanidions erfolgt an dem Feststoff $Cu_2[Fe(CN)_6] \cdot 7\,H_2O$. Dieses Produkt erhält man entweder (i) über eine Extraktion des Hexacyanoferrat(II)-Komplexes aus dem Boden mit NaOH und nachfolgender Fällung im sauren Medium durch das entsprechende Kupfersalz oder (ii) durch die destillative Entfernung des Cyanids als Blausäure aus dem Boden. Anschließend wird das Cyanid mit Fe^{2+} komplexiert und mit Cu^{2+} in saurer Lösung gefällt. Der im Grundwasser gelöste $[Fe(CN)_6]^{4-}$ -Komplex wird an Ionenaustauschern angereichert, mit NaOH eluiert und durch Zugabe von Cu^{2+} -Salzen und Säure ebenfalls als $Cu_2[Fe(CN)_6] \cdot 7\,H_2O$ gefällt. Um zu belegen, dass Extraktion, Destillation und Fällung quantitativ erfolgen und nicht zu einer Isotopenfraktionierung führen, wurden zunächst 3 Reinsubstanzen (Berliner Blau, Gelbes Blutlaugensalz, $K_2Zn_3[Fe(CN)_6]_2$) mit bekannten $\delta^{13}C$- und $\delta^{15}N$-Werten in NaOH gelöst und anschließend destilliert bzw. gefällt. Die Wiederfindungsraten betrugen 79 – 104 %, die Abweichungen von den $\delta^{13}C$- bzw. $\delta^{15}N$-Werten der Ursprungssubstanz lagen unter 3 ‰.

Anschließend wurden ausgewählte Bodenproben unterschiedlicher Standorte (3 Gichtgasschlämme, 4 Gasreinigungsmassen) der Extraktion und der Destillation unterzogen. Dabei zeigte sich anhand der Wiederfindungsrate und Isotopenverhältnisse, dass die Wahl der geeigneten Aufschlussmethode von verschiedenen „Störstoffen“ abhängt: So lassen sich die in Kokereiböden enthaltenen PAKs und weitere organische Stoffe nur über die Destillation des Substrats aus dem Produkt fernhalten. Andererseits stören bei der destillativen Aufbereitung hohe Karbonatgehalte, wie sie in Gichtgasschlämmen auftreten. In diesem Fall ist die Extraktion der Destillation vorzuziehen.

Die Analysendaten der bisher untersuchten 20 Feststoffproben (14 Gichtgasschlämme, 6 Gasreinigungsmassen) zeigen signifikante Unterschiede in der C-Isotopensignatur. Die gemessenen $\delta^{13}C$-Werte der Gichtgasschlämme liegen im Bereich von –23 bis –30 ‰, die der Gasreinigungsmassen zwischen –5 und –16 ‰. Die N-Isotopensignatur der verschiedenen Proben variieren hingegen für beide Probenarten im Bereich zwischen 2 und 10 ‰.

Des weiteren wurden zwei Grundwasserproben eines Kokereistandortes und drei einer Gichtgasschlammdeponie entnommen und untersucht. Die C-Isotopenverhältnisse der aus dem Grundwasser extrahierten Cyanide fallen jeweils in den oben genannten standortspezifischen Wertebereich.

Damit scheint das C-Isotopenverhältnis ein geeigneter Indikator für die Herkunft von Cyaniden in Böden und Grundwässern zu sein.

NMR IN BIOGEOCHEMISTRY

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Stable isotope abundance in atmospheric gases and biochemical metabolites constrain current greenhouse gas fluxes, and can trace long-term plant-climate interactions. For symmetric molecules, like most atmospheric trace gases, IRMS is the method of choice to measure stable isotope abundances. In contrast, plant metabolites are non-symmetric molecules, and their stable isotope abundance is not fully described by δ values, because they can carry stable isotopes in several non-equivalent intramolecular positions. The variation in the abundances of these isotopomers can be larger than the δ variation, therefore more detailed information is present in the isotopomer abundances than in δ.

Isotopomer abundances can be measured by several techniques, including specialized IRMS techniques, light spectroscopy, and nuclear magnetic resonance (NMR). For most molecules of interest, no standard procedures exist for isotopomer measurements. This contribution will compare strengths and limitations of the techniques. The principles of isotopomer measurements by NMR and its prospects for ^{2}H, ^{13}C, ^{15}N and ^{17}O will be discussed and illustrated with recent applications.

1. We use ^{2}H NMR to measure the abundances of the seven ^{2}H isotopomers of plant glucose, isolated from primary photosynthate and tree rings. A ^{2}H labeling experiment shows that individual isotopomer abundances carry physiological [1] and climate signals [2]. These signals allow studying long-term plant-climate interactions using tree rings, to predict tree responses to ongoing climate change. We use the same approach to understand the ^{2}H abundances of persistent environmental toxins.
2. The heavy isotopes ^{13}C and ^{15}N are challenging targets for measurements of isotopomer abundances by NMR, mainly due to the smaller abundance variations and technical difficulties. In spite of this, it appears that ^{13}C isotopomers can be measured with sufficient precision, and in favorable cases also ^{15}N. ^{13}C NMR is a very powerful tool to track the bioconversion of ^{13}C-labelled substrates, for example by cancer cells [3] or soil microorganisms.
3. The *current* N_2O flux has natural and anthropogenic parts, among them biological activity *in frozen soils*. To assess biological activity in frozen soils, the fraction of liquid water in soil pores must be known. Solid-state ^{2}H NMR is a reliable method to measure this fraction, and that humus-rich soils can contain over 10% of their dry weight of liquid water at -5 °C [4].

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Seasonal variations in the sources of soil CO_2 in a deciduous forest of the national park „Hainich“, Germany

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During the last years we measured concentration and the ^{13}C and ^{14}C content of CO_2 in soil air and dissolved inorganic carbon. This will identify sources and dynamics of CO_2 in soil. Additionaly these measurements will contribute to our understanding of carbon storage in soil organic matter.
We collected soil air biweekly in 5, 10 and 20 cm depth in a beech forest on a limestone basement.
CO_2 concentrations in the cold season depended on temperature, while during summer and fall soil moisture controls CO_2 dynamics. The concentrations were up to 10 times higher in the wet season (October to May), than in the dry season (June to September). Decreasing $\delta^{13}C$ values in the growing season suggest root and microbial origin of soil CO_2. Most interestingly in summer after drying of the soil this carbon source seem aprubtly to end as indicated by a 2 – 3 ‰ shift of the gases. Increasing $\delta^{13}C$ values at this phase indicated decomposition of SOM or microbial carbon as major carbon source. After rewetting in fall the $\delta^{13}C$ values finally decreased and indicatet the importance of litter decomposition as carbon source for soil CO_2. Our result suggest that sources of2soil CO_2 derive from different sources over the year and that stable isotopes are able to partition these different fluxes.

Variable contribution of soil and plant derived carbon to dissolved organic matter

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The seasonal variation in the amount and sources of dissolved organic matter (DOM) in soil profiles was investigated. In general DOM in soil solution can evolve from the decomposition and mobilization of soil organic matter (SOM), dissolution of dead microbial cells or from the input of plant material such as root exudates or decomposing litter. Here we used vegetation change from C3 to C4 plants to quantify the plant derived carbon in DOM.
In 2002 an agricultural field was converted to an experimental grass land. The average $\delta^{13}C$ value of SOM was -26.5 ‰ (sd = 0.2) for the plough horizon. On two independent plots, each 10 x 20 m, we used Amaranthus retroflexus as C4 plant with a carbon isotope label of -13.0 ‰ to distinguish unlabeled SOM and plant derived carbon sources. To quantify the contribution of litter input on DOM formation we applied a split plot design. One half had no litter and the other half double amount of above ground litter. Soil water was collected in 10, 20 and 30 cm depth biweekly and DOM concentrations in solution and carbon isotope ratios of the freeze dried and decarbonized material were investigated.
During winter uniform concentrations of DOM of about 7 mg/l were measured throughout all depth and treatments. In spring when soil temperatures increase and water availability decreases DOM concentrations increased with similar rates in all depth. Even in the second year of Amaranth growth the carbon isotope ratios of DOM in winter and spring had no C4 signal. The $\delta^{13}C$ values of -26 to -27 ‰ suggest SOM as carbon source and contradict a contribution of root exudates to the DOM pool. During summer almost no soil solution was collected. After rewetting in fall DOM concentrations up to 50 mg/l in 10 cm depth and up to 35 mg/l in deeper layers were found. These high concentrations held carbon isotope signals from -25 to -26.5 ‰ contradicting carbon input from plant material. With ongoing wetting of the soil the carbon isotope ratios suddenly increased up to -21.7 ‰ on the double litter plots and to -24 ‰ on no litter plots. However, this signal was not detected in 30 cm depth. Keeling plots proved that the major part of the DOM comes from SOM. In fall and early winter only 36 % and 19 % of plant derived carbon were found in the double litter and no litter plots, respectively.
Our results suggest that carbon of the SOM pool is the major source for carbon in DOM. In the spring season root exudates seem to be completely respired by soil organisms suggesting that root and rhizosphere respiration are the same respiratory pool. Only in fall the decomposition of plant litter contributed to carbon in DOM. However, this carbon source is already exhausted in the next spring. In consequence our results may indicate that stored soil carbon is more active than thought and that DOM transport might be a key process to understand carbon sequestration.

$\delta^{13}C$ and $\delta^{18}O$ from Carbon Mono- and Dioxide, two proxies for tracing combustion sources

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Combustion processes still present a considerable load of pollution on the environment. Catalyzers, filters for diesel engines, optimizations of heating and industrial energy conversion systems have helped improving the air quality considerably, due to specific law enforcements. However, an effective enforcement strongly depends on the verification of the specific measures. Therefore it is important to identify the sources of the emissions. Here the use of the stable C and O isotopes prove to be an important tool. Measurements of the $\delta^{18}O$ from CO reveal a very distinct pattern whether the combustion processes are highly oxygen supplied or lack oxygen. Industrial energy conversion systems or modern cars are optimized for a complete fuel combustion, which is which occurs under oxygen surplus. On the other hand wood or biomass burning undergoes often strongly oxygen starved combustion processes, resulting in a more ^{18}O depleted CO molecule.

In a case study in the southern part of Switzerland air samples were collected in two differently exposed sites. In Moleno most emissions were traffic derived, while in Roveredo the emission of CO originated predominantly form wood burning for heating the houses. The $\delta^{18}O$ values from Roveredo followed a strong diurnal course, which was well synchronized with the wood burning. Little fluctuation in $\delta^{18}O$ was found in Moleno, a site near a motorway. In this particular study we found a similar but less pronounced trend in the $\delta^{13}C$ of CO_2 as we found for the $\delta^{18}O$ from CO. Another data set from the city of Basel revealed a more difficult picture, where we assume higher atmospheric chemical activity and a considerable transport of air masses. The results shown from both study sites are quite contrasting and possible interpretations are discussed.

From atmosphere into soil – Carbon (C) translocation in an agro ecosystem under FACE conditions

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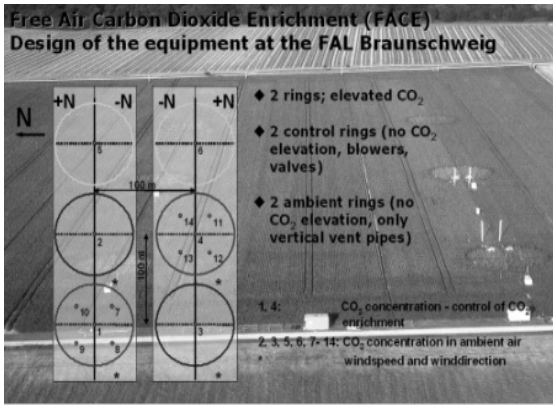
Translocation of C was analyzed in a typical North German agro ecosystem cropped in a three year crop rotation (winter barley, sugar beet, winter wheat) under elevated CO_2 conditions (Free air carbon dioxide enrichment, FACE). Particular emphasis of the investigations was laid on the trophic chain within this system.

The study site is located within the experimental area of the Federal Agricultural Research Centre, Braunschweig. It consists of experimental plots designed as rings of 20 m diameter, two of which are equipped with fumigation facilities to increase atmospheric CO_2 concentration ("elevated plots") and two with blowers only ("control plots"). The atmospheric CO_2 concentration of the treatment plots is elevated to 550 ppm during daylight hours (T>5°C) and the CO_2 applied to these plots is depleted in ^{13}C. The plots are divided into two halves. One half is fertilized with nitrogen (N) at the locally common level (100 %); the other half receives 50 % of this amount of N. All other management treatments are carried out according to local farming practices.

Investigations covered aboveground biomass parameters (e.g. crop growth rate), root growth and gas exchange (H_2O, CO_2) throughout the whole of a three year period of crop rotation. Soil fauna included in the study comprised collembolans and enchytraeids. In addition soil microbial biomass, microbial respiration coefficient, soil respiration and soil water content were monitored.

We were aiming at evaluating in how far elevated CO_2 influenced different compartments in the agro ecosystem by analysis of changes in the trophic chain within this system. The stable isotope labelling of the CO_2 used for enrichment allowed tracing of the C applied and hence of translocated newly formed C-compounds. C isotopic measurements also gave insight into C turnover rates in different compartments of the system.

The presentation will give an overview over the relationships between aboveground and belowground biomass, soil C and organisms considering effects on different temporal levels. Results presented here were achieved from the plots fully supplied with N.



C isotopic composition in different compartments of an agorecosystem (mean $\delta^{13}C$ values over a three year crop rotation period)

Sample	Ambient air	Elevated CO_2
atmospheric CO_2	-8.7 ‰	$-21_{(calc.)}$ ‰
plants – green leaves	-29.4 ‰	-40.4 ‰
plant – roots	-27.9 ‰	-38.7 ‰
soil (mean of 0-30 cm)	-26.4 ‰	-26.8 ‰
collembolans*	-26.7 ‰	-33.6 ‰
Enchytreids	-24.1 ‰	-30.5 ‰

*determined only during one growing season

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Sulfur and oxygen isotope composition of the atmosphere in Saxony (Germany)

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Introduction

Sulfate from atmospheric precipitation (wet deposition) was sampled monthly or for two-month periods at different locations in Saxony from 1997 until 2004 and analysed for its $\delta^{34}S$ and $\delta^{18}O$ composition. In addition, the sulfur and oxygen isotope composition was obtained from atmospheric SO_2 at the location Freiberg from 1997 until 1999 (Klemm & Siedel, 1999; Walter, 2000; Haubrich, 2001). Haubrich (2001) investigated atmospheric dust from the Freiberg location for its $\delta^{34}S$. Further data for sulfate from atmospheric precipitation and/or SO_2 are published in Klemm & Siedel (1999) and Knief (1998) for various locations in Saxony and adjacent regions. This dataset enables a discussion on the sulfur and oxygen isotope composition of Saxonian atmosphere during the last years.

Results on $\delta^{34}S$ values

The compilation of mean $\delta^{34}S$-values reported in the literature shows, that the $\delta^{34}S$-value of sulfate of precipitation is relatively homogenous over wide areas of Saxony in the range between 3 and 6‰. These mean values are lower than those reported in Novak et al. (2001) for the Czech Republic measured from 1993 until 1996. Obvious deviations from Saxonian mean values are reported by Klemm (2005) for the region around Schkopau (50 km south of Halle/Saale), where the usage of coal with different $\delta^{34}S$-values in fuel industry results in much lower $\delta^{34}S$-values of –4‰ and +1‰ for sulfate crusts on monuments in and around the city of Halle. The lower mean $\delta^{34}S$ value of Bad Lauchstädt may result from some contribution of this local anomaly. Without the value of Bad Lauchstädt the range of mean values is even smaller (from 4.0‰ to 5.4‰) with a higher mean value for the region of Dresden (6.3‰). Long-term comparison is possible for the location Freiberg (1997 – 2002). No obvious change of the mean $\delta^{34}S$ value is obtained although the scatter of monthly $\delta^{34}S$ values decreased for 2000 – 2002 compared to 1997 – 1999. The sulfur isotope composition of SO_2 is always lower compared to sulfate from the same location (mean values from 1.5 to 3.4‰ which are similar to values from the Czech Republik after Novak et al., 2001). The dust has the highest $\delta^{34}S$ value from atmospheric components. Haubrich (2001) and Haubrich & Tichomirowa (2004) explained the higher sulfur isotope composition in sulfate from precipitation with a higher contribution of dust in it. The difference in the sulfur isotope composition between SO_2 and sulfate seem to be smaller in summer. This is the reason why Tichomirowa et al. (2004) argue for fractionation processes between SO_2 and sulfate causing their sulfur isotope difference.

Sulfur and oxygen fractionation processes in atmospheric sulfate and SO_2

Tichomirowa et al. (2004) have shown that oxygen isotope composition of sulfate from precipitation and of SO_2 should be used to distinguish between mixing of different sources (e.g. contribution of dust) and fractionation processes. Saisonal variations are found for both sulfate and SO_2 for oxygen isotopes confirming the existence of fractionation processes. SO_2 is usually deposited on alkaline filters where during sampling a small sulfur isotope fractionation can occur (e.g. Torfs et al., 1997). There seem to be a week correlation of $\delta^{34}S$-values of the sulfate from precipitation with higher SO_2 concentrations in colder heating periods pointing to usage of fuels which contribute the high $\delta^{34}S$ value to the atmosphere. One possible high $\delta^{34}S$-source can be SO_2 generated by burning processes of brown coal which should produce $\delta^{34}S$ similar to the high values reported for gypsum from desulfurisation of fumes (Klemm & Siedel, 1999).

Changing relation between CO_2- and water fluxes in Swiss forests

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Global change and increasing carbon dioxide in the atmosphere do not only affect the CO_2-, but also the water fluxes. These two matter fluxes are tightly linked at the biosphere-atmosphere interface, as both fluxes pass through the stomatal openings of plant leaves. The relation between carbon uptake and water release can be monitored by the carbon isotope ratio of organic matter and reconstructed through time from tree-rings. In this study, we analysed 11 tree ring chronologies from Switzerland including three wide-spread conifer species (*Abies alba*, *Picea abies*, *Pinus sylvestris*) and three deciduous species (*Quercus petraea*, *Fagus sylvatica*, *Fraxinus excelsior*). Diverse site conditions were covered, from dry to humid, with altitudes ranging from 480m to 1400m a.s.l. Each $\delta^{13}C$-series was established as an average of 4 to 6 trees. The isotope data were analysed with the Farquhar-isotope fractionation model to derive changes in the intercellular CO_2-concentration and the water-use efficiency, i.e., the water used per unit carbon gained at the leaf level. The results for the last 200 years show strongly increasing water-use efficiency of 41.6% (when averaging all species), while the increase from 1800 until 1900 was only 12.5%. The conifers in general had higher water-use efficiency, but the increase in the last century for the conifers was not significantly different from the deciduous trees. Our results indicate that trees transpire less water today for the same amount of biomass production than two centuries ago, with an acceleration of the observed change in the last century. These observations may have implications for the water cycle, leading, for instance, to more water-saturated soils with less capacity to absorb heavy rains and increased potential for flooding.

Compound specific hydrogen isotope rations of biomarkers reconstruct the palaeoclimate

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We determined the compound specific isotope ratios of alkanes in order to test whether these isotope ratios are suitable to reconstruct the palaeoclimate. Therefore terrestrial and aquatic n-alkanes were extracted from lake sediments to estimate the isotopic composition of lake water and precipitation. This was done for lakes covering the climatic gradient from north Finnland to south Italy showing consistent results. In addition we compared sediments from closed lake sediments from humid and arid regions and found the isotopic difference between terrestrial and aquatic makers suitable to distinct between both systems. Finally we elaborated a correction function for thermally altered sediments in order to extent the reconstructions to the geological past. Our results suggest that compound specific isotope ratios of n-alkanes are a new proxy for the palaeoclimate.

POSTER

Isolierung von Kreatin und Kreatinin aus dem Urin für die $^{13}C/^{12}C$ und $^{15}N/^{14}N$ Isotopenanalyse

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Kreatin-Monohydrat ist ein im Amateur- und Spitzensport sowie in der Fitnessbewegung weit verbreitetes Nahrungsergänzungsmittel. In der Vergangenheit gab es wiederholt Diskussionen um die Dopingrelevanz von Kreatin-Supplementierungen und über die Herkunft des im Urin gefundenen Kreatins und Kreatinins. Da sich die $^{13}C/^{12}C$- und die $^{15}N/^{14}N$-Isotopenverhältnisse von synthetischem Kreatin-Monohydrat ($d^{13}C_{VPDB}$ zwischen -28 und -45 ‰ und $d^{15}N_{AIR}$ zwischen -5 und 2 ‰) deutlich von den Werten für körpereigenen Stoffe unterscheiden, sollte eine Differenzierung zwischen endogenem und exogenem Kreatin im Urin möglich sein. Kreatinin, der Metabolit von Kreatin, wird mit Konzentrationen von ca. 1,5 g/d über den Urin ausgeschieden. Da Kreatinin auf Grund seiner geringen Volatilität nicht per GC-C-IRMS gemessen werden kann, ist eine hinreichende Isolierung und Aufreinigung für eine Messung mittels EA-IRMS aus der urinären Matrix notwendig.

Die Isolierung von Kreatinin aus dem Urin für EA-IRMS erfolgt mit Hilfe der Kationenaustauschchromatographie über einen starken Kationenaustauscher in stark verdünnter Lösung. Für die Bestimmung der $^{13}C/^{12}C$- und $^{15}N/^{14}N$-Isotopenverhältnisse des urinären Kreatinins genügt die Aufreinigung von 1 ml Urin. Das bei kreatinreicher Ernährung und bei Kreatin-Supplementierung im Urin neben dem Kreatinin auftretende Kreatin kann ebenfalls durch Kationenaustauschchromatographie vom Kreatinin und den restlichen Hauptbestandteilen des Urins hinreichend getrennt und bestimmt werden.

Determination of the origin of urinary norandrosterone-traces by gas chromatography combustion isotope ratio mass spectrometry

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The steroid 19-norandrosterone (19NA) is anongoing problem in doping control: On the one hand it is the most abundant metabolite of the potent synthetic anabolic steroid 19-nortestosterone (19NT). The presence of 19NA in urine is therefore considered a doping offense. On the other hand small ammounts are biosynthesized by pregnant women and further evidence exists for physiological origin of this compound. A threshold concentration of 2 ng per ml urine therefore was introduced to discriminate 19NT abuse from biosynthetic origin.

Recently it could be shown however that formation of 19NA resulting in concetrations above the threshold level might be due to demethylation of urinary androsterone (A). This steroid is excreted in milligram ammounts per day by healthy persons. We therefore tried to elucidate the origin of urinary 19NA in doping control samples by means of .$^{13}C/^{12}C$ analysis.

Initially we added deuterated androgens such as D_5-androsterone (D_5A) to urines that were suspected to have demethylation activity. This in fact resulted in formation of demethylated analogues, e.g. deuterated 19NA. In a second step a cleanup-procedure was developed which allowed to validly measure $^{13}C/^{12}C$-ratios of urinary 19NA down to concentrations of 2 ng per ml urine. Several routine urine samplesshowing presence of 19NA in various ammounts were investigated, where$^{13}C/^{12}C$-ratios of A and Etiocholanolone (E) served as reference values. Indeed two groups could be clearly identified. One showed an isotope signature typical of synthetic steroids and the other showed values close to those of E and A.

Der Einfluss einer vegetarischen Kost mit niedrigem und hohem Oxalatgehalt auf die intestinale Oxalatabsorption und Oxalatausscheidung im Urin

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Einführung

Die Ausscheidung von Oxalat mit dem Urin steigt bei einer vegetarischen Kost [1] im Vergleich zu einer gemischten Kost. Eine Unterscheidung zwischen dem exogen zugeführten Oxalat und dem endogen gebildeten Oxalat ist normalerweise nicht möglich. Diese Studie wurde durchgeführt, um mit Hilfe des stabilen Isotops ^{13}C den Effekt je einer vegetarischen Kost mit niedrigem und mit hohem Oxalatgehalt auf die intestinale Oxalatabsorption und Oxalatausscheidung im Urin zu quantifizieren.

Methode

8 gesunde freiwillige Probanden nahmen an der Studie teil. Die Probanden wiederholten den [$^{13}C_2$]Oxalat-Absorptionstest jeweils dreimal unter Standardbedingungen [2] mit der Aufnahme einer gemischten Kost mit geringem Oxalatgehalt (63 mg Oxalat/Tag), einer vegetarischen Kost mit niedrigem Oxalatgehalt (70 mg Oxalat/Tag) und einer vegetarischen Kost mit hohem Oxalatgehalt (300 mg Oxalat/Tag). Bei jedem [$^{13}C_2$]Oxalat-Absorptionstest hatten die Probanden die jeweils vorgegebene Kostform mit konstanter Nährstoff- und Flüssigkeitsmenge über zwei Tage zu befolgen. Beide vegetarischen Kostformen enthielten dieselbe Menge an Nährstoffen, besonders Calcium, und Flüssigkeiten. An beiden Tagen wurde der 24-h-Urin gesammelt. Am Morgen des zweiten Tages wurde eine Kapsel mit 50 mg Natrium[$^{13}C_2$]oxalat eingenommen. Aus der wiedergefundenen Menge an markiertem Oxalat im 24-h-Urin wurde die prozentuale Absorption berechnet.

Ergebnisse

Oxalatausscheidung: Unter der gemischten Kost mit geringem Oxalatgehalt schieden die Probanden im Mittel 0,319 ± 0,049 mmol Oxalat/Tag mit dem Urin aus. Diese Ausscheidung stieg unter der vegetarischen Kost mit hohem Oxalatgehalt auf 0,347 ± 0,051 mmol/Tag und bei der vegetarischen Kost mit niedrigem Oxalatgehalt signifikant auf 0,414 ± 0,076 mmol/Tag.
Oxalatabsorption: Unter der gemischten Kost mit geringem Oxalatgehalt betrug die mittlere intestinale Oxalatabsorption der Probanden 9,2 ± 4,0 %. Unter beiden vegetarischen Kostformen stieg die intestinale Oxalatabsorption der Probanden im Mittel auf 13,4 ± 4,2 % (hoher) bzw. 15,8 ± 2,7 % (niedriger Oxalatgehalt).

Diskussion

Beide vegetarische Kostformen verursachten einen Anstieg der intestinalen Oxalatabsorption und der Oxalatausscheidung im Urin. Da Oxalatabsorption und Oxalatausscheidung im Urin unter beiden vegetarischen Kostformen steigen, sollte eine vegetarische Kost nicht für Patienten mit Calciumoxalat-Steinen empfohlen werden.

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Bestimmung der $\delta^{13}C_{V\text{-}PDB}$ und $\delta^{15}N_{V\text{-}AIR}$-Werte von Cocain aus einer Großsicherstellung in Hessen

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Bei der kriminaltechnischen Untersuchung illegaler Drogen wird die Bestimmung der Stabilisotopenverhältnisse sowohl zur herkunftsbezogenen Analyse [1-3] als auch zu vergleichenden Messungen herangezogen [4].
Im Jahr 2002 konnten in Kassel durch das Hessische Landeskriminalamt 1,2 Tonnen Cocain sichergestellt werden. 132 Proben wurden im Bundeskriminalamt auf ihre $\delta^{13}C_{V\text{-}PDB}$ und $\delta^{15}N_{V\text{-}AIR}$-Werte hin mittels EA-IRMS untersucht. Zur Herkunftsbestimmung lagen Proben definierter Herkunft aus Kolumbien, Peru und Bolivien vor. Zusätzlich konnten Literaturwerte authentischer Proben zur Interpretation der Ergebnisse herangezogen werden.

Das sichergestellte Cocain war in branchenübliche 1kg-Pakete verpackt. Die innenliegenden, in Buchform gepressten, Cocainplatten waren durch 20 verschiedene eingeprägte Symbole (Logos) gekennzeichnet. Im Zuge der Untersuchung wurde daher u.a. die Möglichkeit einer Zuordnung von Proben gleichen Logos zu Gruppen geprüft.
Die Cocainproben weisen $\delta^{15}N_{V\text{-}AIR}$-Werte im Bereich von –17,5 bis –1,8 ‰ auf. Ein Anteil von 73 % der Proben kann aufgrund der Stickstoffisotopenverhältnisse Kolumbien als Herkunftsland zugeordnet werden. Bei den restlichen Proben sind überwiegend Werte wie bei definierten Cocainvergleichsproben aus Bolivien und Peru erkennbar. Die bestimmten $\delta^{13}C_{V\text{-}PDB}$-Werte liegen in einem Bereich von –35,4 bis –33,9 ‰, der keine weitere Differenzierung der Proben ermöglicht.

Die Analyse von 67 Proben eines Logos ergab für 63 Proben $\delta^{15}N_{V\text{-}AIR}$-Werte im Bereich von –4,3 bis –5,9 ‰, die weiteren 4 Proben dieses Logos lagen im Bereich bis –7,1 ‰ und waren damit von der Gruppe zu unterscheiden. Die weiterhin untersuchten Proben konnten aufgrund der Stickstoffisotopenwerte keinen logospezifischen Gruppen zugeordnet werden.

Diese Ergebnisse zeigen, dass für Großtransporte wahrscheinlich Produkte unterschiedlicher illegaler Laboratorien und Herkunftsländer zusammengefasst werden und in der Regel keine Korrelation der Prägung mit den Stabilisotopenwerten feststellbar ist.

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A practical guide to the reliability of simultaneous $\delta^{13}C$ and $\delta^{15}N$ measurement at different C/N ratios

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The simultaneous measurement of $\delta^{13}C$ and $\delta^{15}N$ values of solid materials in one single sample is handy to reduce analysis costs or necessary if sample amount is limited. However, the accuracy and reliability of the results especially for ^{15}N are uncertain. We therefore analysed samples from our daily routine covering a wide range of provenances, C/N ratios and sample amounts to give a guide under which circumstances simultaneous $\delta^{13}C$ and $\delta^{15}N$ measurements give reliable results.

Correction strategies in deuterium analysis using chromium reduction

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Introduction

High precision deuterium isotope analysis (D/H) of water is routinely carried out by using a hot chromium reactor. One crucial point is to observe and correct for the machine drift. Consequently, different strategies for drift correction were proposed (e.g. Nelson and Dettman, 2001; Werner and Brand, 2001). In this study different correction approaches were tested for their influence on quality control and their usability in day to day analysis. Measurements were carried out on a H/Device coupled to a Delta S mass spectrometer.

Results and Discussion

Different reactor types (standard packing and alternative mix proposed by Nelson and Dettman, 2001 for longer reactor life) were tested for differences in drift behavior. Provided that all other parameters are identical, the results show a strict linear drift for the standard packing and a polynomial drift for the alternative packing of the reactor.

Miscellaneous correction functions, including polynomial, linear point-to-point and Rayleigh fractionation were evaluated. Results show that a simple second order polynomial regression to the drift of the signal from the standard bellow yields the best results. Two quality control standards treated as unknowns were measured in each run. After this correction external reproducibility - defined as standard deviation of the control standards during all runs - was 0.5 ‰ and 0.7 ‰, respectively.

Reactors with different packing were reheated several times and the results of different runs were compared. It turned out that reheating of reactors has no influence on the quality of the data, a fact that is generally worried about. The influence of an additional memory correction applied to the raw data prior to drift correction was evaluated, too.

Conclusions

The results show that an external precision of 0.5 ‰ is reachable in routine analysis if this standardized polynomial drift correction is applied.

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UV-Laser-Ablation-Combustion-GC-IRMS
a tool for on-line analysis of intra-annual variation of $\delta^{13}C$ in tree rings

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For high special resolution in $\delta^{13}C$ tree ring analysis we use a UV-Laser-Ablation-Combustion-GC-IRMS.
Precision and repeatability is around 0.2 ‰. Compared to single sample preparation tedious cutting and weighing are avoided. Moreover, the original tree core sample can be used for documenting the location from where a particular isotope ratio was measeured as well as for further analysis.

A UV-Laser (266nm Nd-YAG, Merchantec / New Wave) is connected with an isotope mass spectrometer Delta$^+$XL (Thermo-Finnigan MAT, Bremen) via a home-made* combustion interface. The system is continuously purged with a He-carrier-gas flow (~10 ml/min). Every 8.5 minutes woody dust particles are ablated from a tree core. The resulting material is swept to the interface where it is combusted to CO_2 (+ H_2O) at 700°C. Inside the reactor an oxidized copper wire provides the oxygen for the combustion. The resulting CO_2 is separated from other gases in a GC-column (Haysep Q) and transferred to the mass spectrometer via an open split after water removal using a Nafion trap.

The measurements are calibrated and checked with external CO_2 standard gas, injected in the open split region, and in addition with internal cellulose standards which are also ablated by laser shots and combusted in the interface.

CO_2 standard gas for mass spectrometer control is needed throughout the long run-times, sometmes exceeding 5 hours. Small instabilities of the mass spectrometer within a run can be corrected in hindsight by applying a drift correction as a function of retention time.

An independently calibrated internal cellulose standard (ICS; $\delta^{13}C$ = -24.50 ‰) is important to correct for altering conditions inside the interface and for the final positioning of the isotopic results onto the VPDB scale.

*The donation of the Laser-Interface breadboard from Finnigan is greatfully acknowledged.

Hoch-präzise Continuous Flow δ^2H und $\delta^{18}O$ Analyse von Wasserproben

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Hintergrund:
Die Online-Bestimmung von δ^2H und $\delta^{18}O$ Werten organischer Proben bei Temperaturen über 1300°C unter Verwendung eines He-Trägergases und eines Kohlenstoffpools in der Reaktionszone hat wachsendes Interesse gefunden. Das Hauptproblem der Methode bestand in der geringen Präzision der ConFlo Technik vor allem für $\delta^{18}O$, die im Wesentlichen durch Memory Effekte bedingt war. Messungen konnten nur mit einer Genauigkeit von 0,2 - 0,3 ‰ durchgeführt werden, was für Wasserproben zu gering ist.

Zielsetzung:
Das Hauptziel der hier vorgestellten Experimente bestand darin, eine Routinemethode zur Analyse stabiler Isotope in Wasserproben zu entwickeln und dabei die Meßgenauigkeit durch signifikante Verringerung des Memory Effekts zu erhöhen.

Experimenteller Aufbau:
Der Originalaufbau ist ein Hochtemperatur-Reaktor (TC/EA), der on-line über ein ConFlo III Interface mit einem Delta+XL IRMS verbunden ist (Thermo-Finnigan MAT). Die wichtigsten Veränderungen dieses Systems bestehen in der Modifizierung des Reaktordesigns und einer Umleitung des Trägergasstroms.

Ergebnisse:
Durch die Veränderung des experimentellen Aufbaus wurde die Messgenauigkeit für $\delta^{18}O$ durchgängig auf ein Niveau von 0,1 ‰ verbessert. Memory Effekte innerhalb des Hochtemperaturreaktors wurden reduziert, indem durch eine Flussumkehr das Zurückschlagen von Wasser bei der Injektion vermieden wurde. Die verbleibenden Memory Effekte werden in der Auswertung analysiert und korrigiert. Diese Memory-Korrektur berücksichtigt bis zu acht der aktuellen Probe vorausgehende Messungen.

irm-EAMS routine – measurements: high precision; high accuracy; high throughput

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Since about six years we analyse $\delta^{13}C$ and $\delta^{15}N$ of bulk organic and inorganic sample material with high precision. Hence, these measurements, which are made using an EA-IRMS system, are daily routine in BGC-IsoLab. More than 25000 measurements in 2004 demonstrate, that the interest in stabile isotope analyses inside the institute as well as from outside partners has remained strong and has even increased over time.

In order to cope with the increased request for measurements we have acquired a second EA combustion unit in the second half of 2004. With this additional capacity, which we activate during times of high sample backlog, we have been able to shorten the average dwell time of submitted samples considerably.

Typical samples we analyse derive from plants or from soil, but these are by no means the only sources. Special attention of the operator is required for some soil samples, when the C and / or N content is very low, or for samples with a high volatility like methanol or alkanes, which we measure as a service for other techniques like GC-combustion.

A considerable effort went into new reference materials or into round robin checks of existing reference materials. The latter activities have been in collaboration with the IAEA in Vienna, with the USGS and other international partners. It is within this context that we have made a large number of $\delta^{13}C$ analyses on carbonates, oils, sugars, cellulose samples etc.

All measurements are routinely controlled using QA-standards as well as internal working reference materials. High precision data require that the signals of working reference materials and measured samples are of comparable size. Hence, the carbon or nitrogen content of the materials must be known a priori and weighing of samples and standards must be made with utmost care.

Analysis of low concentration ground water contaminants from sample head space vials using automated Cryo-Focusing GC-C-IRMS

Neil Wallace (www.massspecsolutions.com)

Legislation has driven the use of isotopic analysis of ground water contaminants, such as VOC's, to determine the source of the pollution and whether remediation activities have proved effective. Typically, the head space of sample flasks is injected directly into a GC for standard GC-C-IRMS analysis. However, this technique is limited by the volume the GC injection port can handle, typically 2ml making it difficult to analyze low concentration compounds. This technique also results in N2 and other non condensable gases being injected onto the column along with H2O and the sample. The results of this often manifest themselves as poor chromatography and analytical results.

To avoid these problems an economical GC front end device is presented where headspace samples can be automatically injected into a cryo-focusing system that is capable of removing water and none condensable gases and injecting the sample directly into the GC. The poster will demonstrate the resultant improvement in isotopic analysis.

Bedeutung N-haltiger Wurzelabscheidungen in Mischkulturen von Nichtleguminosen mit Leguminosen

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Einführung

Leguminosen geben durch Knöllchenabbauprozesse und Exsudation wurzelbürtiger organischer Substanzen ständig C- und N-Verbindungen (Rhizodeposition) an den Boden ab (Hütsch *et al*., 2002). Die N-Rhizodeposition, die im Gegensatz zur C-Rhizodeposition nicht veratmet wird, kann zur N-Versorgung von Nichtleguminosen in Mischkulturen beitragen. Über den Stellenwert dieses N-Transfers besteht noch Unklarheit. Ziel dieser Untersuchungen war, den N-Transfer von Luzerne/Futterwicke indirekt durch Ermittlung der Verdünnung von aufgenommenen ^{15}N-markierten Dünger in Gras/Gerste zu erfassen.

Material und Methoden

Es wurden Gefäßversuche mit Quarzsand bzw. Kies als Substrat zur Anzucht der Pflanzen in Rein- oder Mischkultur durchgeführt, wobei den Pflanzen ^{15}N als Dünger ($K^{15}NO_3$ oder $^{15}NH_4{}^{15}NO_3$) über das Substrat verabreicht wurde. Nur die Pflanzen mit hohen ^{15}N-Gaben wurden nach 5-6 Wochen zur Bestimmung der N-haltigen Wurzelabscheidungen bzw. des N-Transfers in Gefäße ohne ^{15}N umgesetzt. Nach der Ernte wurden Trockensubstanz-, N- und ^{15}N-Gehalte in Spross, Wurzel und Wurzelexsudaten bestimmt.
Der Stickstoff aus der N_2-Fixierung der Leguminosen (N-Transfer) in den Nichtleguminosenwurde nach folgender Formel berechnet: N_2-Fixierung (N-Transfer) = Gesamt-N - (Dünger-N + Samen-N + atmosphärische N-Deposition).

Ergebnisse und Schlussfolgerungen

- Bei einer Mischkultur von Gras- mit Luzernepflanzen wurde ein signifikanter Beitrag des N-Transfers von ~50% (~ 5 kg N ha^{-1}) zur N-Ernährung der Graspflanzen bei sehr niedrigen N-Düngergaben (< 10 kg N/ha) innerhalb von 3 Monaten festgestellt (Beschow *et al*., 2000). In der Literatur werden N-Transfermengen von 3-5 kg N ha^{-1} angegeben (Hardason *et al*., 1988).
- Syrische Wickenpflanzen hatten zu ~30% innerhalb von nur 2 Wochen zur N-Ernährung von Gerstenpflanzen beigetragen (~ 10 kg N ha^{-1}).
- Es wird angenommen, dass während der frühen Vegetationsphase der N-Transfer hauptsächlich über die Aufnahme von N-haltigen Abscheidungen der Leguminosenwurzeln durch Nichtleguminosenwurzeln erfolgt. Der N-Transfer ist vom N-Angebot im Substrat, vom Leguminosen-Nichtleguminosen-Verhältnis und von der Pflanzenart abhängig.
- Auch Graspflanzen geben N-haltige Wurzelabscheidungen an das Substrat ab. Dieser Beitrag muss in weiteren Versuchen ebenfalls berücksichtigt werden.

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Potential of nitrogen isotopic analysis in crops for the discrimination of agricultural systems

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Many studies used the ratios of stable isotopes of several elements for origin assignment and the authenticity control of various food products and crops. The nitrogen isotopic ratio is affected by many factors such as climate, soil characteristics and primary nitrogen sources. Consequently, the $^{15}N/^{14}N$ ratio in the biomolecules of the plants depends also on the type of fertiliser used for growing the crops.
The technique of stable isotopic ratio measurement of nitrogen addresses whether the reported differences between the stable nitrogen isotope ratios of mineral and organic nitrogenous fertilisers are retained by plants and can be exploited to differentiate organic versus conventional agricultural production of crops.
The present study involved 4 different crops: potato, carrot, horsebean and winter wheat, grown in two neighbouring fields (similar environment). Samples at different growth stages where taken of the plants grown in a conventional agricultural system, i.e. using mineral fertiliser, on the one hand and in an organic system, i.e. using fertiliser of organic origin on the other. Samples were lyophilised and ground. The method for isotope ratio measurement was EA-IRMS (an elemental analyser coupled to an isotope ratio mass spectrometer). In this method bulk materials are converted to gasses (N_2 for nitrogen isotopic analysis) by oxidation and reduction steps in a constant flow of helium. The gasses are then introduced in the source of the IRMS on-line with the EA.
The results show significant differences for all 4 crops in nitrogen isotopic ratio (t-test) comparing results in samples taken at the same growth stage of the plants, thus reflecting the difference between mineral and organic fertiliser. Horse bean presented an opposite difference, which could be explained by its capability to bind nitrogen from air.
The complete study was set up to investigate the potential use of several parameters, not only nitrogen isotopic ratio, in the discrimination of both investigated agricultural systems. The presented results do certainly show nitrogen isotopic ratio measurements in crops to be a major potential contributor in a multivariate approach to achieve such discrimination in the support of European food and agricultural policies.

Verbleib von ^{15}N-Harnstoff ohne und mit Zusatz eines Ureaseinhibitors im System Boden-Pflanze

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Bei der Düngung mit Harnstoff kann die Ammoniakverflüchtigung als N-Verlustquelle eine besondere Rolle spielen. Zur Reduzierung bzw. Vermeidung eines solchen N-Verlustes können Ureaseinhibitoren herangezogen werden. Bei deren Prüfung wurde ^{15}N-markierter Harnstoff eingesetzt, um den Verbleib des Dünger-N exakt zu quantifizieren.
Die Untersuchungen erfolgten in einem Mikroparzellenversuch (Anlage = 1 m^2, Ernte = 0,5 m^2) auf lehmigen Sandboden mit Sommerweizen (Thasos). Es wurden die Varianten 1. ohne N-Düngung ohne Ureaseinhibitor, 2. mit N-Düngung ohne Ureaseinhibitor und 3. mit N-Düngung mit Ureaseinhibitor mit je 4 Wiederholungen geprüft. Die N-Düngung betrug 80 kg N/ha als Harnstoff mit 20 at-%^{15}N zum 2-Blattstadium. Die Ernte erfolgte zur Milchreife getrennt nach Ähren und Stroh bei gleichzeitiger Entnahme von Bodenproben bis 60 cm Tiefe.
Zur Ernte lagen im Boden bedeutsame Restmengen an Dünger-N vor, die bei Inhibitoreinsatz im Vergleich zur Variante ohne Ureaseinhibitor erhöht waren. Die Nitrat-N-Menge im Boden und die Anteile des Dünger-Nitrat-N an der Gesamt-Nitratmenge und an der Düngermenge waren zur Ernte nur sehr gering.
Der Einsatz eines Ureaseinhibitors zur Harnstoffdüngung führte nicht zur Erhöhung der Trockenmassebildung der Pflanzen, jedoch zu einer geringfügigen Erhöhung der Aufnahme und Ausnutzung des Dünger-N durch die Pflanzen. Insgesamt war bei Inhibitoreinsatz eine deutliche Verringerung des Bilanzdefizits des eingesetzten Stickstoffs zu verzeichnen.
Als Ursachen für die Verringerung des Bilanzdefizits bei Anwendung des Ureaseinhibitors kommen vor allem eine Verringerung von gasförmigen N-Verlusten und eine erhöhte N-Festlegung im Boden in Betracht.

Impact of Drainage Water Nitrate on Adjacent Surface Waters: A stable isotope approach

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A dual isotope approach with $\delta^{15}N$ and $\delta^{18}O$ values of nitrate in drainage water from a conventionally managed field, the adjacent ditch and the brook was carried out 6 weeks during the main discharge period of the hydrological year 2003/2004. The $\delta^{15}N\text{-}NO_3$ values in the drainage water varied between 8.5 and 15.0 ‰ and well reflected the fertilizing practice, carried out with organic as well as inorganic fertilizers. The low $\delta^{18}O\text{-}NO_3$ values between 1.8 and 4.3 ‰ indicated, that - as expected - most of the nitrate derived from the nitrification process. In the adjacent ditch and the brook similar $\delta^{15}N\text{-}NO_3$ values (7.2 – 12.1 ‰) and $\delta^{18}O\text{-}NO_3$ values (2.4 - 9.1 ‰) compared to the tile drain outlet indicated, that the drainage water nitrate is the major N source for the adjacent surface waters. A linear mixing model estimated a contribution of the drainage water nitrate to the nitrate in the ditch and brook of 76 %.

Isotopomer signatures of N_2O emitted from an arable loess soil under different process conditions - a soil microcosm study.

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Abstract:
Stable isotope signatures of N_2O can be used to constrain the atmospheric N_2O budget and to characterize N_2O turnover processes. The aim of our study is to evaluate the use of isotopomer analysis of N_2O (site-specific and average ^{15}N, ^{18}O) (i) as a tool to identify N_2O production processes in soils and (ii) to constrain the isotopic fingerprint of soil-derived N_2O. Microcosm studies were conducted arable loess soil fertilized with $^{15}NO_3$-labeled or non-labeled N-fertilizer. Soils were incubated at varying moisture conditions in order establish different levels of nitrification and denitrification. Further experiments were conducted to study the NO_3^--to-N_2O step and the N_2O-to-N_2 step of denitrification separately. Analysis of soils and emitted gases was conducted in order to quantify gross rates and N_2O production of nitrification and denitrification, respectively, N_2O reduction of denitrification, isotope fractionation associated with these processes, and the isotopic fingerprint of emitted N_2O. Headspace gas samples were collected and analyzed for N_2O, CO_2, and N_2O isotopomer signatures. ^{15}N- and ^{18}O-signatures of NH_4^+ and NO_3^- were analyzed in soil extracts. Selected results of the study will be presented.

^{15}N site preference of N_2O produced by fungal denitrification

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The production of N_2O is typically attributed to bacterial activity in soils and waters, but it has been suggested that fungal denitrification can play an important role in N_2O emissions in some environments. In order to determine the proportion of N_2O produced by fungal denitrification it is necessary to find a method of differentiating N_2O produced by bacterial processes and fungal denitrification. Our previous work has demonstrated that the intramolecular distribution of nitrogen isotopes (isotopomers) within N_2O can be used to distinguish N_2O produced by denitrification and nitrification (0 and 33 ‰, respectively). Here, we investigate whether site preference can be used to distinguish N_2O produced by fungal denitrification and bacterial denitrification. The two best-studied fungal denitrifiers, *Fusarium oxsporum* and *Cylindrocarpon tonkinense* were grown aerobically for 5 days and then purged with N_2 to stimulate denitrification. Nitrite was added to each culture and incubated for an additional 12 hours before the first headspace sample was collected. Samples were analyzed immediately for $\delta^{15}N$, $\delta^{15}N^{\alpha}$ and $\delta^{18}O$ on a Trace Gas system interfaced to a multicollector Isoprime that allowed for analysis of the molecular and fragment ion in a single run. The site preference of N_2O produced by F. *oxsporum* and C. *tonkinense* was 36.7 ± 3.2 ‰ and 36.1 ± 3.2 ‰, respectively. The results indicate that isotopomers can be used as a basis for differentiating bacterial denitrification from fungal denitrification. This work reveals the step in denitrification responsible for producing the site preference of N_2O since the mechanisms of fungal nitric oxide reductases is different than bacterial nitric oxide reductases.

Biomonitoring of atmospheric CO_x and NO_x in urban and rural areas using carbon and nitrogen isotopes as proxy parameters. Part I: method development

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Continuing concern about present atmospheric pollution demands improvement in monitoring and control of air quality, especially in densely populated areas. Therefore, EU-regulation 1999/30/EG, specifically addressing fine particulate matter, has become effective in January 2005. In order to account for the spatial heterogeneity and variable sources of atmospheric pollutants it is of prime importance to establish large scale continous sampling grids.
The comprehensive study includes investigation of airborne PAH and heavy metal loads accumulated on pine needles. We here discuss magnetic properties as proxy for PM (particulate matter) pollution and $\delta^{13}C$ and $\delta^{15}N$ composition of pine needles for CO_x- and NO_x-concentration in air. *Pinus nigra* was selected as passive sampler, due to its frequent use as ornamental tree and resulting good availability in urban as well as rural areas. Needle ages of up to five years give a time-integrated record of atmospheric pollution and at the same time offer a cost-effective monitoring method.

Climatic, nutritional and physiological factors are known forces to determine the isotopic composition of plants. Additionally, N- and C-oxide concentration of ambient air is assumed to be the main agent influencing the isotopic composition of pine needles via stomatal uptake and incorporation into biosynthate in urban areas (see parallel poster by Lehndorff et al. *Part II: The Cologne Conurbation*).
In this part of the study the use of $\delta^{13}C$, $\delta^{15}N$ of pine needles as a proxy for atmospheric CO_x- and NO_x-concentration shall be discussed. Therefore, six locations representing urban and rural areas with variable emission background have been chosen, displaying spatial variation in isotopic composition of pine needles.
It is of key importance to demonstrate that variability in proxy data determined for the entire measuring network is significantly higher than at any given sampling point. Local consistence of biomonitoring data at one point is verified by separate sampling of three trees and up to five needle ages.

Magnetic analyses of needles of varying age (1-5 y) show that these reach equilibrium with pollution in ambient air after 3 years. Thereby, each location approximates to a state typical for the respective emission background. Magnetic properties of different needle ages represent particle accumulation with time. The relationship of $\delta^{13}C$ to the magnetic PM proxy is highly significant and linear, whereby $\delta^{13}C$ decreases with increasing PM. The ^{13}C enrichment is assumed to be controlled by needle aging (reduced photosynthesis activity) and/or environmental stress (e.g. pine reacts to pollution with stomata aperture). The question which factor is dominating will be discussed in this presentation.

In addition to differentiate local variance it is necessary to ascertain whether $\delta^{13}C$ and $\delta^{15}N$ of pine needles is predominantly affected by the isotopic composition of soil substrate or atmospheric signatures. Therefore, we compared the interrelation between carbon and nitrogen isotopes of pine needles, litter, humus layer and mineral soil at 4 of the above mentioned locations.

Biomonitoring of atmospheric CO_x and NO_x using carbon and nitrogen isotopes as proxy parameters. Part II: The Cologne Conurbation

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It is of critical importance for assuring environmental health to understand the distribution of atmospheric pollutants at high temporal and spatial resolution. New legislation effective January 2005 (EU-regulation 1999/30/EG) necessitates German city councils to monitor and control urban air quality, e.g. PM_{10}, CO_x, and NO_x. Passive sampling using artificial devices or natural vegetation biomonitoring allows acquisition of well-defined samples at affordable costs. Method development and verification for our approach is shown in the parallel poster by Lehndorff et al. *Part I: Method development*.

This contribution presents results from a biomonitoring study conducted in the conurbation of Cologne, Germany based on airborne pollutants accumulated on and in needles of *Pinus nigra*. Pine is an evergreen conifer ubiquitous throughout the study area with needle generations representing a time range up to three years.
Our integrated study of atmospheric pollution so far has addressed distribution and origin of particulate matter, carcinogenic organic compounds (PAH) and heavy metals (Urbat et al. 2004, Lehndorff and Schwark, 2004). The gaseous atmospheric pollutants CO_x and NO_x, primarily resulting from fossil fuel combustion, have previously been monitored in vegetation by their respective isotopic proxies $\delta^{13}C$ (Lichtfouse et al., 2003) and $\delta^{15}N$ (Jung et al., 1997; Amman et al., 1999). $\delta^{13}C$ and $\delta^{15}N$ analysis of pine needles accompanied by electron microscopy of needle surfaces from 43 locations in the Cologne Conurbation, integrated in a GIS-database, are shown in this study.

REM-analysis indicates that particles accumulated on needle surfaces and within stomata are mostly <2.5 µm in diameter and comprise organic pollen or spores, irregular-shaped mineral dust and silica-glassy or metallic spheroids. The latter derive from combustion of coal in power plants or fuel in vehicular engines. Additionally, damage of epicuticular waxes due to increased ozone exposure or acid precipitation can be observed.
Beside climatic, nutritional and physiological factors, the N- and C-oxide concentration of ambient air is assumed to be the main agent influencing the isotopic composition of pine needles via stomatal uptake and incorporation into photosynthetic biosynthate. This is shown by a good correlation of urban atmospheric NO_x-concentration determined by the City of Cologne with our $\delta^{15}N$ analysis of pine needles. Hereby, higher NO_x-loads result in heavier $\delta^{15}N$ signatures. Particle load and wax affection lead to interference of stomatal uptake of CO_x and NO_x, which may exert a secondary influence on isotopic composition of needle biomass.
The dominant sources of C- and N-oxides are emissions from road traffic (esp. diesel engines) and industry. Park and forest areas show the lowest levels of pollution by CO_x and NO_x, followed by residential areas. This implies that traffic emissions with short transportation distances are dominant in the Cologne Conurbation.

Active air quality control by the City of Cologne ceased beginning of 2004 due to budget restrictions. Cost effective biomonitoring of pine needle $\delta^{15}N$ and $\delta^{13}C$ enables reconstruction of time-integrated and spatially highly-resolved CO_x- and NO_x-concentrations in urban environments.

Abiotic hydrolysis or microbial disproportionation of elemental sulfur? An experimental sulfur and oxygen isotope study

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In the sulfur cycle of natural environments a wide variety of processes take place both by abiotic reaction and induced by microorganisms. Besides reduction and oxidation of sulfur species in sediments also the simultaneous production of sulfide and sulfate from elemental sulfur by microbial disproportionation may occur. However, in experimental studies also the abiotic hydrolysis of elemental sulfur has been demonstrated. As both processes leads to the same products, they cannot be distinguished by quantification of the reaction products alone. This needs the implementation of stable isotope discrimination.

It has been reported that microbial sulfur disproportionation leads to a significant enrichment in the heavy isotopes ^{34}S and ^{18}O in the newly formed sulfate and therefore to a depletion of ^{34}S in the produced sulfide (Canfield et al., 1998; Böttcher et al., 2001, 2005). In the present study, abiotic sulfur hydrolysis at 50°C in the presence of Cu leads to a $^{34}S/^{32}S$ fractionation between elemental sulfur and sulfate as well as sulfide, and $^{18}O/^{16}O$ fractionation between water and sulfate of less than 0 to 1 ‰. This indicates that abiotic hydrolysis is associated with completely different stable isotope effects compared to microbial disproportionation which is likely caused by different reaction pathways. The relevance of the abiotic processes under low-temperature natural conditions is small, as also seen from our and preceding studies demonstrating that at low temperatures hydrolysis rates need to be enhanced by the presence of catalysts, like copper or zinc. Dual-isotope fractionation is a very valuable tool to distinguish abiotic from microbial sulfur disproportionation.

Sulfur isotope biogeochemistry of microbial sulfate reduction by the deep biosphere off Peru (ODP Leg 201)

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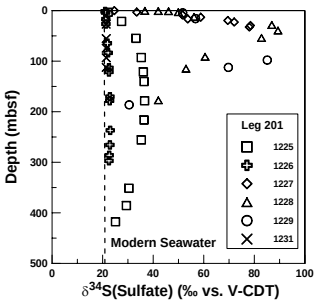
A deep biosphere was found in long sediment cores recovered during Leg 201 in the Pacific Ocean off Peru. Microbial sulfate reduction leads to changes in the pore water sulfate concentrations and is associated with characteristic mass-dependent sulfur isotope discrimination. We have measured concentrations and the stable sulfur isotopic composition of dissolved sulfate and sulfide in the pore water-sediment system of ODP Sites 1225 to 1231 [1]. Besides tracing the *in-situ* microbial activity in the deep biogeochemical sulfur cycle, stable isotope signatures help to identify the sources of brines occuring at some sites at depth. Results are discussed in terms of the activity of the deep biosphere, availability of substrates and other sediment properties, and fluid transport.

As a synthesis a combination with oxygen isotope measurements on dissolved sulfate [2] is currently carried out, and sulfur isotope discrimination will be subjected to a transport-diagenesis modeling approach.



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Isotope geochemistry of sedimentary sulfur in hypersulfidic carbonates of the Great Australian Bight (ODP Leg 182)

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Carbonates with hypersulfidic pore waters from the Great Australian Bight were recovered during ODP Leg 182 [1, 2]. In the present study, total reduced inorganic sulfur (TRIS; essentially pyrite) as a product of microbial sulfate reduction was quantified and isotopically characterized for 9 sites (1126 to 1134). POC and PIC contents were measured, too. Stable isotope measurements gave $\delta^{34}S$ values between –12 and -51‰ (Figure) similar to results of [3] without a relation to the isotopic composition of coexisting dissolved sulfide [2]. This indicates pyrite formation close to the sediment-water interface without further significant later diagenetic contributions or isotope exchange reactions under iron-limited conditions of the carbonate sediments. Maximum isotope fractionation between TRIS and modern seawater sulfate range up to 72 per mil. This indicates that a near-surface sulfur cycle responsible for pyrite formation including oxidative reactions leads to a similar overall maximum isotope discrimination as the single-step *in-situ* sulfate reduction by a deep biosphere in the hypersulfidic pore water system as reported by [2]. Higher variabilities in the isotopic composition of pyrite are only observed in sediments younger than about 7 million years.

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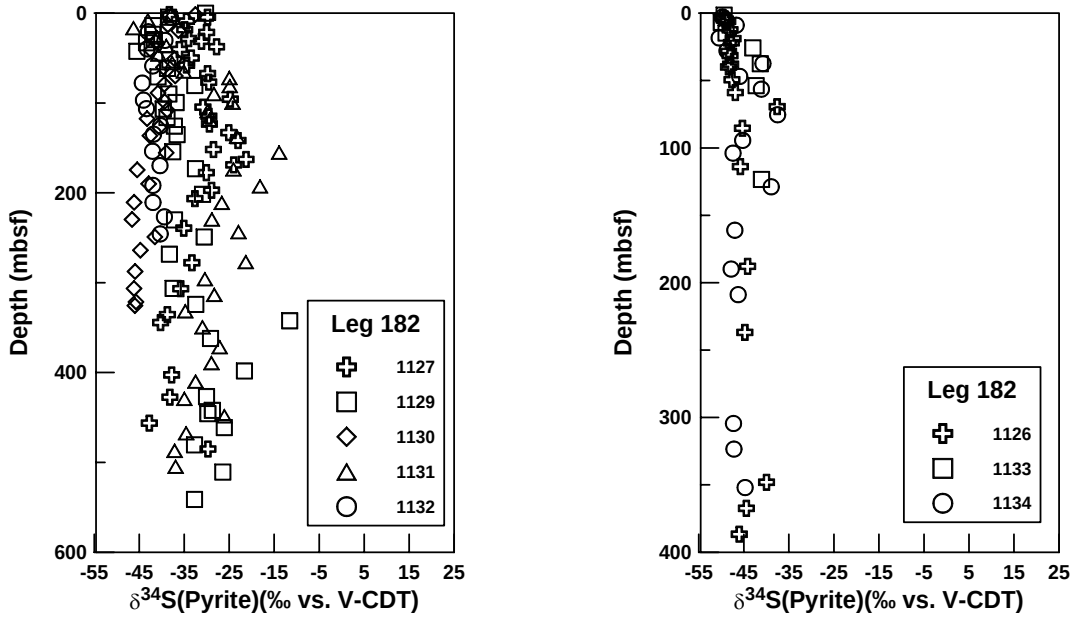

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Carbon, oxygen, and hydrogen isotope fractionation during experimental formation of pirssonite

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The mineral pirssonite ($Na_2Ca[CO_3]_2{*}2H_2O$) occurs in oil shales and sediments of evaporated lacustrine lakes as the Green River formation (Milton & Fahey, 1960) and Searkes lake (Smith 1979). The stable isotopes of carbon, oxygen and hydrogen are extremely usefull in deducing carbonate formation conditions and may preserve informations about the paleoenvironment. For a correct interpretation of natural isotopic signals, however, a carefull experimental calibration is fundamental. Less work has been done on hydrated carbonate minerals, so far. The present study is an extension of previous work, where stable carbon isotope fractionation during pirssonite formation was studies experimentally at 60 and 90°C (Böttcher, 1994).

In the present study, stable carbon, oxygen and hydrogen isotope fractionation was investigated during experimental formation of pirssonite at 86±3°C. Pirssonite was formed via the transformation (dissolution-precipitation) of anhydrous calcium carbonate (natural aragonite, synthetic calcite) or natural gaylussite in aqueous sodium carbonate solution. This approach is similar to the one described by Bury & Redd (1930).

The newly formed solid was enriched in ^{13}C and 18O compared to the dissolved carbonate ion (essentially the carbonate ion and the sodium carbonate ion pair), and in 18O compared to water. Deuterium, on the other hand, was depleted in the hydrate molecules of the pirssonite lattice compared to the aqueous solution.

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New insight into the atmospheric chloromethane budget gained using stable carbon isotope ratios

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Atmospheric chloromethane (CH_3Cl) plays an important role in stratospheric ozone destruction, but many uncertainties still exist regarding strengths of both sources and sinks and the processes leading to formation of this naturally occurring gas. Recent work has identified a novel chemical origin for CH_3Cl, which can explain its production in a variety of terrestrial environments: The widespread structural component of plants, pectin, reacts readily with chloride ion to form CH_3Cl at both ambient and elevated temperatures (Hamilton et al., 2003). It has been proposed that this abiotic chloride methylation process in terrestrial environments could be responsible for formation of a large proportion of atmospheric CH_3Cl. However, more information is required to determine the global importance of this new source and its contribution to the atmospheric CH_3Cl budget.

A potentially powerful tool in studying the atmospheric CH_3Cl budget is the use of stable carbon isotope ratios. It is now reported that the reaction of CH_3Cl with OH radical, the dominant sink for atmospheric CH_3Cl, is accompanied by an unexpectedly large fractionation factor (Gola et al., 2005). Another recently published study shows that CH_3Cl formed by the abiotic methylation process at ambient temperatures has a unique stable carbon isotope signature, extremely depleted in ^{13}C, unequivocally distinguishing it from all other known sources (Keppler et al., 2004). Using these findings together with data existing in the literature, we present three scenarios for an isotopic mass balance for atmospheric CH_3Cl. Our calculations provide strong support for the proposal that the bulk fraction of atmospheric CH_3Cl (1800 to 2500 Gg yr^{-1}) is produced by an abiotic chloride methylation process in terrestrial ecosystems, primarily located in tropical and subtropical areas, where turnover of biomass is highest. Furthermore our calculations also indicate that the microbial soil sink for CH_3Cl is likely to be much larger (> 1000 Gg yr^{-1}) than that previously assumed.

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Is the atmospheric Suess-effect reflected in arable soils of urban areas?

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Fossil fuel burning led to an increase in atmospheric CO_2 and a depletion in atmospheric stable carbon isotopic composition ($\delta^{13}C$) since the beginning of the industrial revolution [1], the so-called Suess-effect. Plants and especially annual crop plants have been strongly affected by the atmospheric Suess-effect with respect to their biomass production and stable carbon isotopic composition [2]. Within larger cities massive local increases in CO_2-concentrations are observed [3] producing a so-called "urban dome effect". This urban dome effect should lead to enhanced carbon isotopic fraction in (crop) plants. In this study, we present a time-series of isotopic composition of archived arable soil samples covering four decades. We then discuss, how the atmospheric Suess-effect may influence the stable carbon isotopic composition of arable soils.

Arable soil samples were derived from the 'Eternal Rye' trial in the urban area of the city of Halle/Saale (Germany). Archived soil samples were available since 1958 for rye cropped soil. After introduction of silage-maize monoculture cropping on a part of the trial parallel samples of rye and silage-maize cropped soils were taken at twelve times since 1961 until 2004. During the last four decades an isotopic depletion of wheat plant biomass of approximately 2.5‰ V-PDB could be expected, according to [2]. This isotopic development must result in an isotopic depletion of approximately 0.5‰ V-PDB in monoculture rye cropped soil, assuming an annual turnover of 0.5% of the total soil organic carbon.

Maize and other C4 plants are less influenced by the atmospheric Suess-effect than C3-plants [4]. C4 plants directly reflect the atmospheric isotopic composition with minor photosynthetic fractionation depending on the internal versus external CO_2-concentration. The maize cropped soil became successively isotopically enriched since introduction of maize monoculture cropping.

After four decades of parallel silage-maize and rye cropping an isotopic difference of 2.0‰ V-PDB occurs. Increases in plowing depth will dilute the Ap-horizon with ^{13}C-enriched soil organic matter. If plowing depth had not been increased during the last 40 years, we would expect an isotopic difference of 3.0‰ V-PDB. Calculations assuming an annual turnover of 0.5% of total soil organic carbon indicate a reduction of 0.2‰ V-PDB in isotopic difference of both soils due the atmospheric Suess-effect. When assuming higher turnover rates, the atmospheric Suess-effect will lead to an underestimation of the isotopic difference of up to 1.0‰ V-PDB between both soils.

In contrast to previous observations in rural areas [5] this study detects a stable carbon isotopic changes in arable soils of urban areas caused by the atmospheric Suess-effect.

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About the characteristics of delta^{18}O in combustion derived CO_2

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From the ratio of $^{18}O/^{16}O$ in atmospheric CO_2 one can distinguish different exchange processes, in which the background value is determined by the oxygen exchange with oceanic water. With focus on environmental conceptual formulations delta^{18}O in CO_2 can be used to quantify the gross carbon flux of the terrestrial biosphere, because of different signals obtained from assimilation and respiration. Furthermore, the release of CO_2 from the combustion of fossil fuel and from biomass burning contributes also to the atmospheric CO_2 content with distinct regional attributes.

We assumed that by the ratio of the stable oxygen isotopes in combustion derived CO_2 the formation process, and at least partially also the origin, of the sampled air can be identified, due to two characteristic complexes. 1) The oxygen involved in the CO_2 formation emanates from different sources, namely from the atmosphere and from the burned material itself. 2) Depending on the kind of fire, i.e. smoldering/low temperature combustion compared to a high temperature burning with open flame, and on fractionation processes coming along with this, different conditions are affecting the ^{18}O content in the formed CO_2.

We validated these hypotheses by laboratory experiments, presented by examples from fossil fuel combustion (car exhaust and house heating) and from biomass, that involves plant material from a transect stretching from west Europe to central Asia.

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