

iso TOC[®] cube

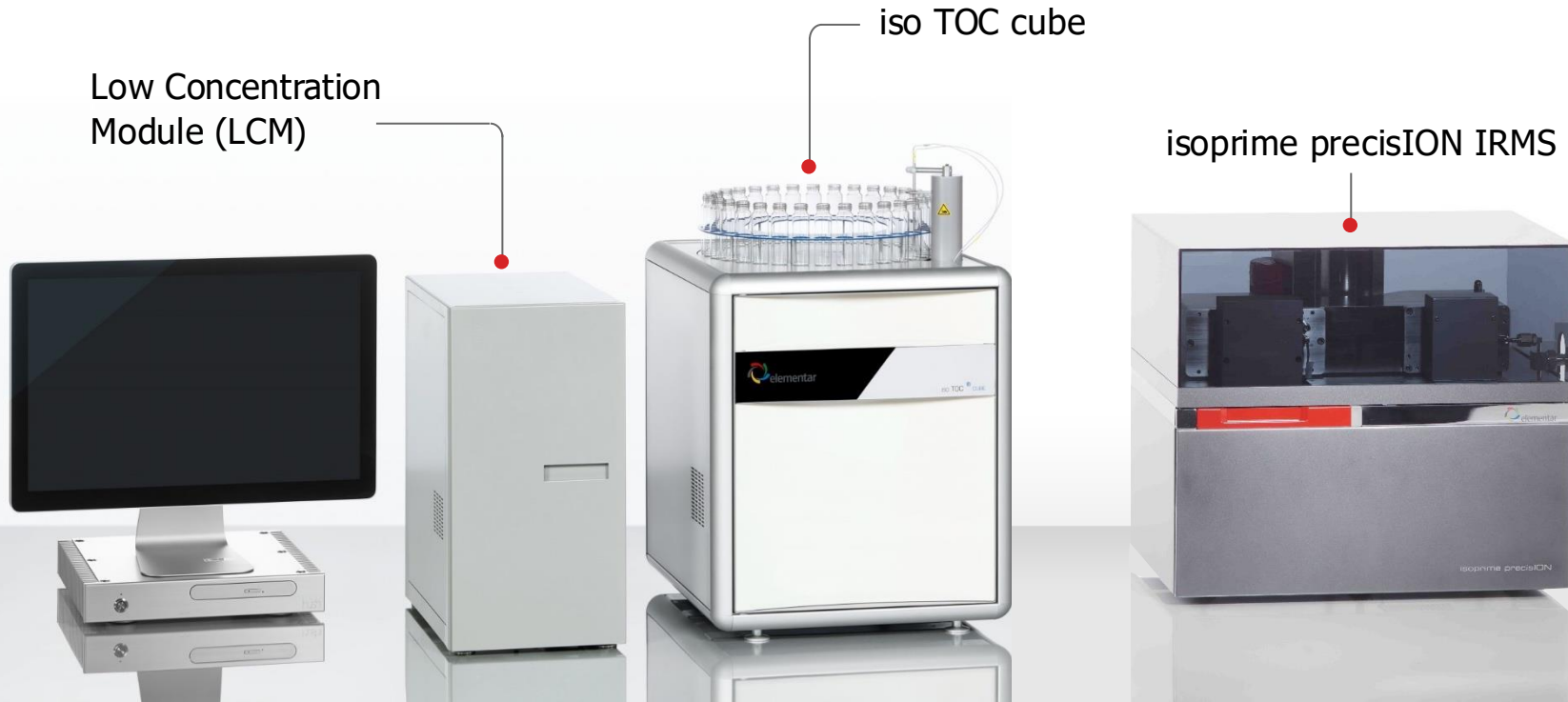
Isotopic analysis of dissolved TC, TOC, TIC and TNb

August 2024



Elementar: iso TOC cube

Uniquely single-manufacturer system for simultaneous isotope ratio analysis of dissolved C and N (TC / TOC / TIC / TN_b) in aqueous samples



TOC & TN_b Stable Isotope Applications

Identifying sources dissolved organic matter



Dissolved organic carbon controls the bioavailability of nutrients in soils and influences productivity in aquatic and terrestrial ecosystems.



Dissolved carbon and nitrogen are critical conduits for the global C & N cycles and constraining their transport and transformation process is essential



Precipitation and surface water leaches dissolved organic carbon (DOC) from vegetation and plant litter and percolates through the soil column



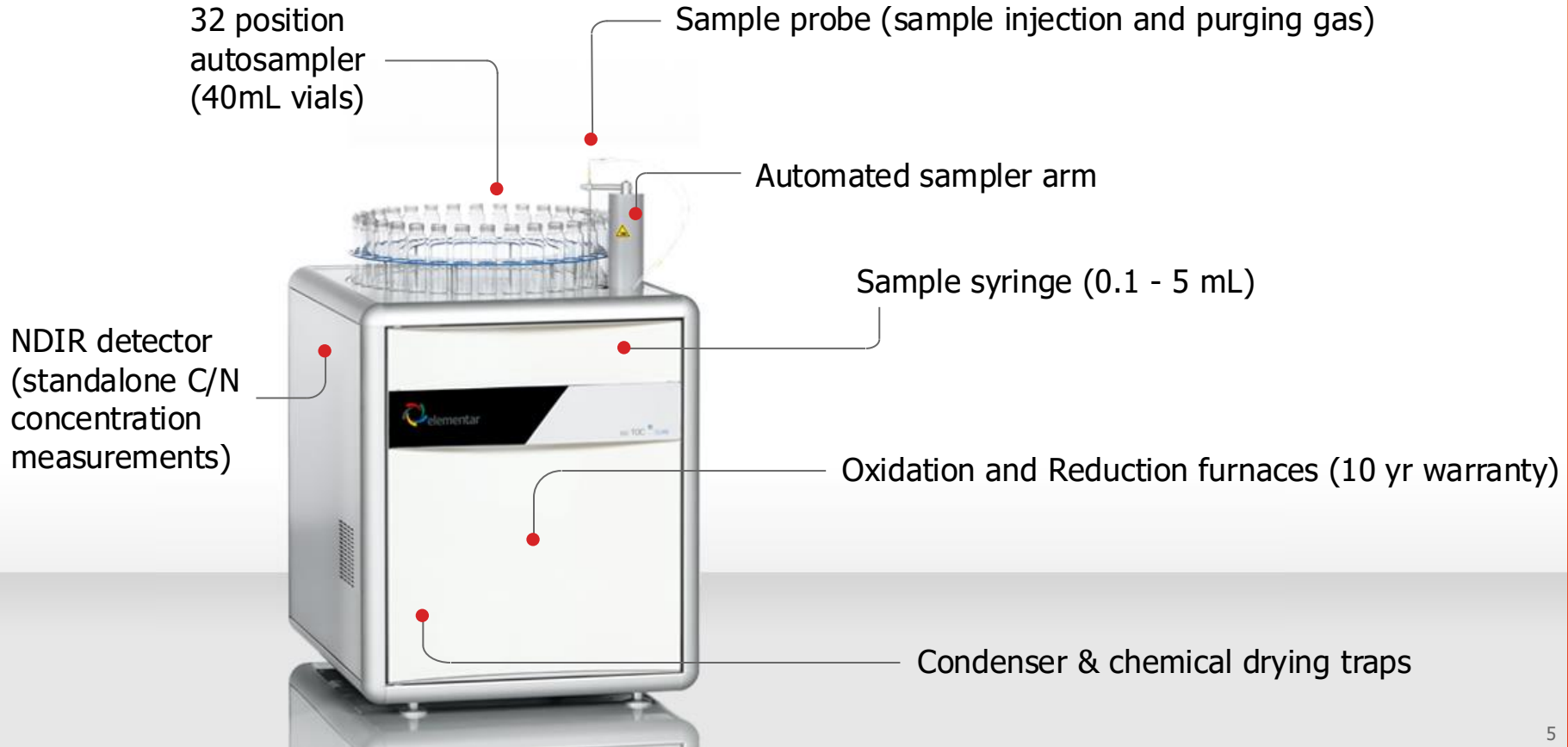
Aquatic systems account for the second largest reservoir sink of carbon on Earth behind forests

Introducing the iso TOC cube



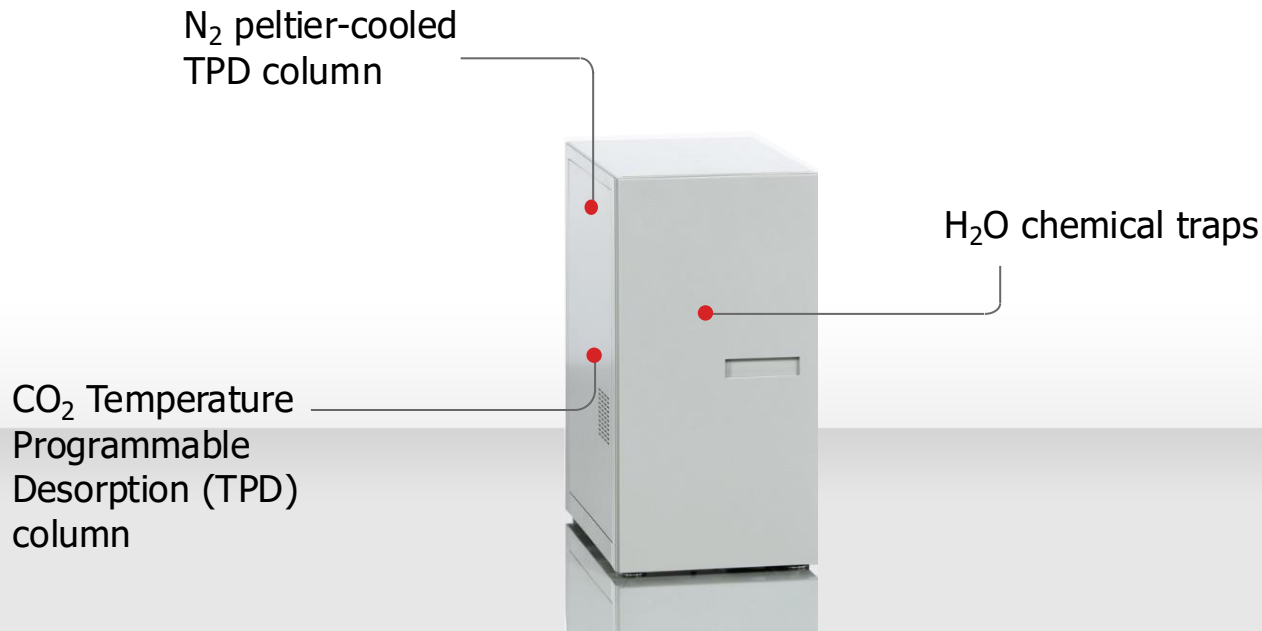
- Complete single-manufacturer solution for stable isotope analysis of dissolved organic matter in the liquid phase
- Uses high temperature (up to 850°C – furnace rated for 1200°C) rather than wet chemical oxidation
- High temperature oxidation exhibits less matrix effect (more quantitative combustion vs chemical oxidation)
- High temperature oxidation opens the possibility for analysing Total Organic Carbon $\delta^{13}\text{C}$ and Total bound nitrogen $\delta^{15}\text{N}$
- Using ramped GC chromatography allows lower detection limits and exceptional peak shapes
- Large liquid injection volume of up to 5 ml (*n.b. 3 ml more routine for maximum operating volume*)

iso TOC cube - components



Low Concentration Module (LCM) - components

“Optional” module to enable measurement of TN_b and improve sensitivity for low carbon abundances/saline samples



Improved sensitivity for low carbon analysis (LCM)

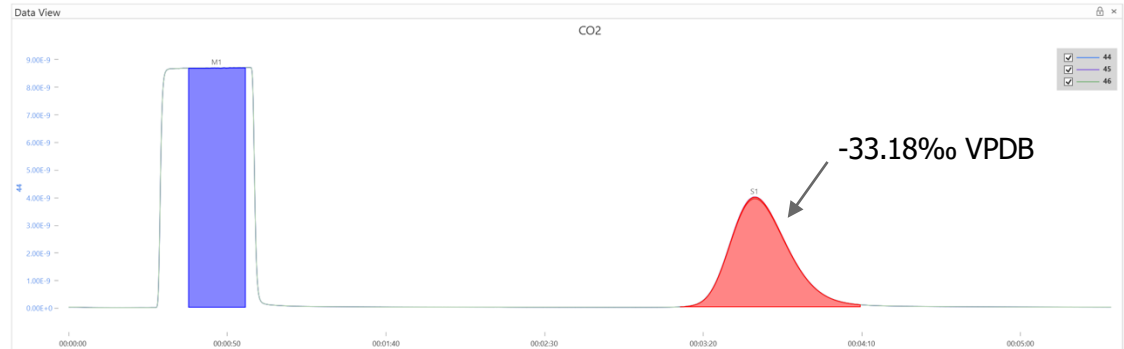
An example of a caffeine #04 internal lab standard diluted in DI water



No LCM

<6 minutes per sample

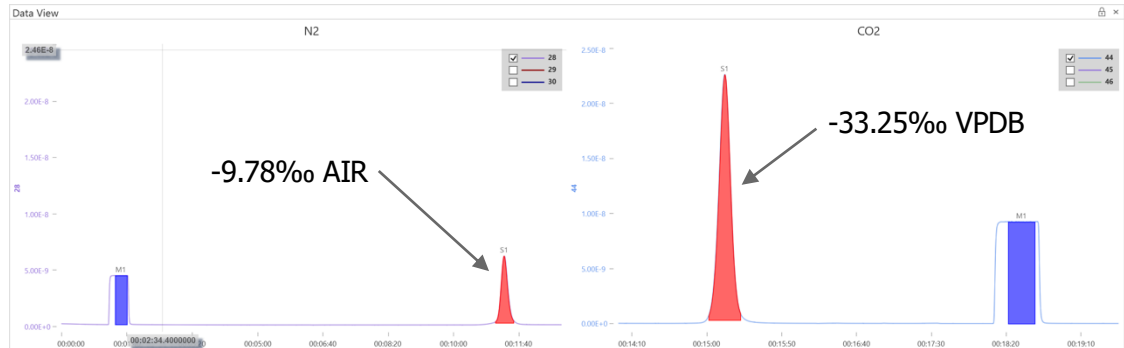
Fine for relatively high [C] in clean water, and gives fast analysis



With LCM

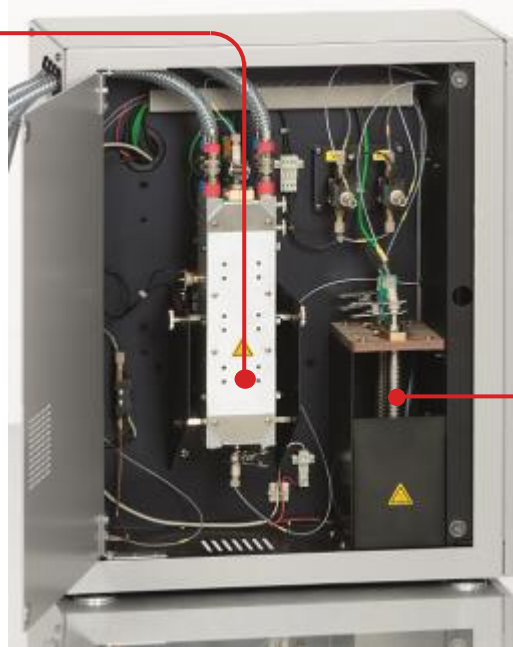
<20 minutes per sample

Gives both d13C & d15N, and needed for lower [C] and/or more challenging samples (e.g. saline)



Low Concentration Module (LCM) - components

N₂ peltier-cooled
TPD column



CO₂ TPD column

Total Dissolved Organic Matter – What is it?

Primarily produced from the decomposition of plants, bacteria and algae

Dissolved Organic Matter (DOM)

Total Bound Nitrogen (TN_b)

Inorganic N (DIN)



Organic N (DON)

Amino acids

Amino Sugars

Phytols

... anything C/N

Total Carbon (TC)

Inorganic C (DIC/TIC)



Organic C (DOC/TOC)

Sugars

Amino Acids

Lignin

... any organic
molecule

iso TOC cube vs EA-IRMS lyophilization

Sample analysis method

iso TOC cube

1. Collect sample
2. Filter <math><46 \mu\text{m}</math>
3. Acidify to $\text{pH} < 2$ for TOC
4. Analyse liquid by iso TOC[®] cube

EA-IRMS lyophilization

1. Collect sample
2. Filter <math><46 \mu\text{m}</math>
3. Acidify to $\text{pH} < 2$ for TOC
4. Freeze dry/oven dry overnight
5. Analyse residue by EA-IRMS

iso TOC cube  6-12 min/sample (direct liquid phase DOM measurement)

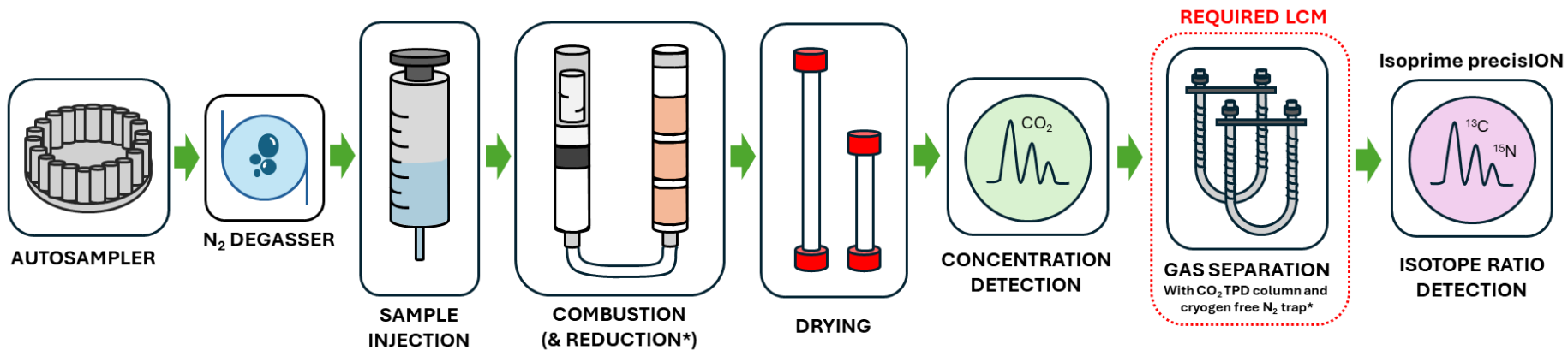
EA-IRMS
lyophilization



6-12hrs/sample (freeze-dry/oven dry)

C & CN Mode for IRMS

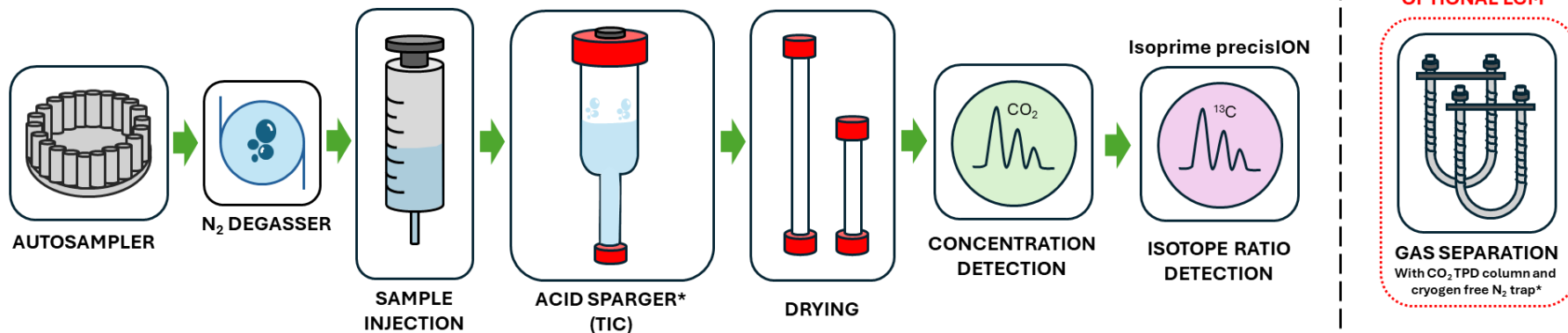
- The LCM includes both a CO₂ TPD column and the required cryogen free Peltier N₂ column for trapping and focusing the released nitrogen
- The CO₂ TPD column is essential for low ppm C and/or saline samples
- The N₂ degasser is essential for CN mode
- Measures DOC as CO₂ and DON as N₂



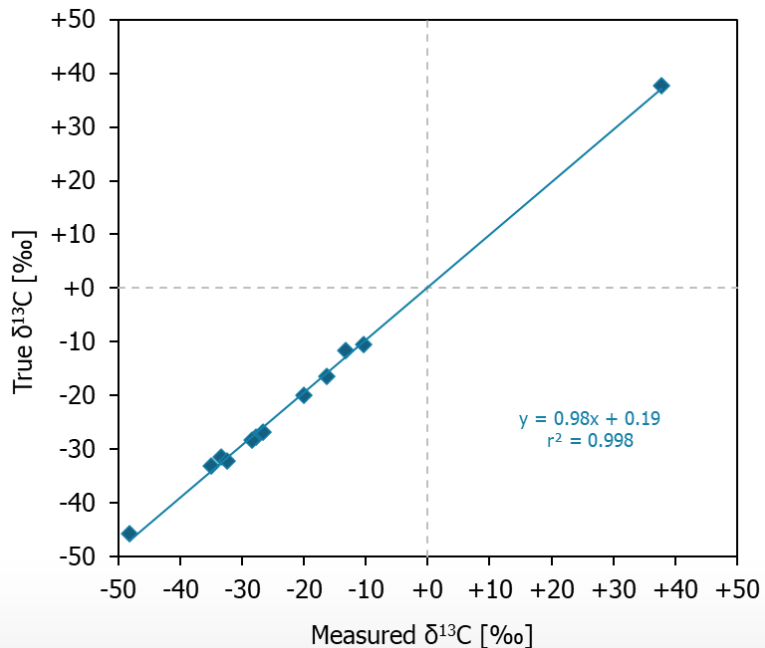
C Mode (TIC)

The iso TOC cube also has an inbuilt acid sparger which can be used to measure TIC from samples

The acid sparger is connected to a bottle of H_3PO_4 acid
Sparger is held at ambient temperature



iso TOC cube $\delta^{13}\text{C}$ performance

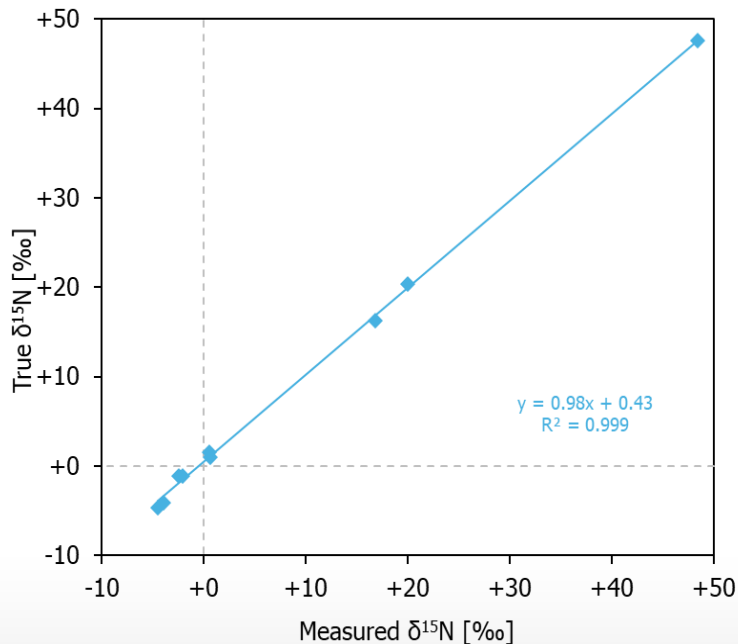


Compound	ID	Known $\delta^{13}\text{C}$ [‰]	Measured $\delta^{13}\text{C}$ [‰]	1 S.D.
Sucrose	IAEA-CH-6	-10.45	-10.40	0.09
Glutamic Acid	USGS41	+37.63	+37.70	0.40
Caffeine	IAEA-600	-27.77	-27.77	0.04
Citric Acid	EAS 13 005	-16.42	-16.32	0.05
Glutamic Acid	EAS 12 004	-26.77	-26.64	0.05
Glucose	EAS 14 003	-11.57	-13.31	0.02
Urea	EAS 13 003	-45.64	-48.16	0.10
Caffeine	EAS 16 001	-31.44	-33.30	0.09
Caffeine	EAS 16 002	-33.13	-35.01	0.08
Caffeine	EAS 16 003	-32.21	-32.46	0.10
Fructose	EAS 16 004	-19.93	-20.01	0.12
L leucine	EAS 18 004	-28.35	-28.33	0.14

Standards with EAS prefix are internal RMs calibrated back to internationally accepted CRMs

iso TOC cube $\delta^{15}\text{N}$ performance

Requires optional Low Concentration Module (LCM)

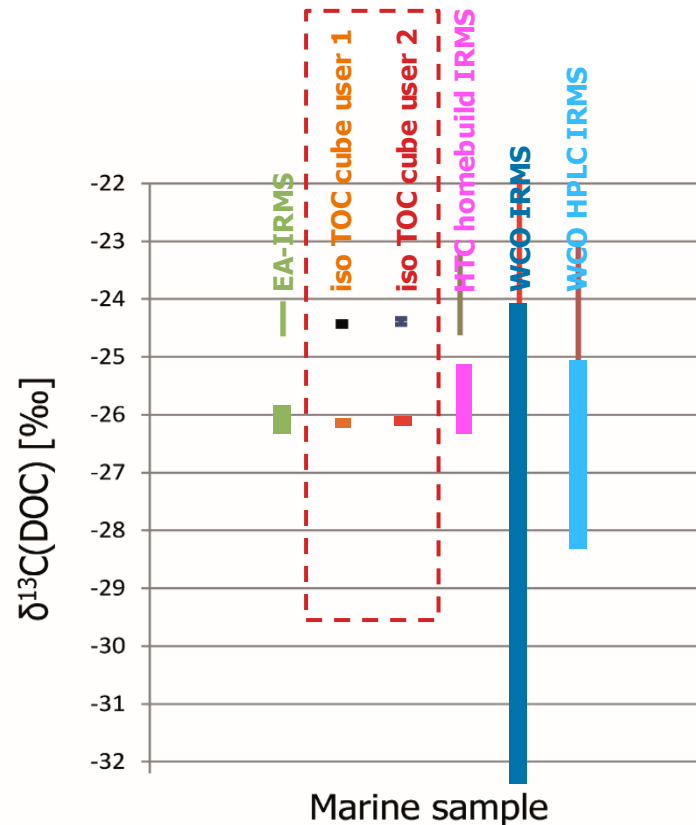
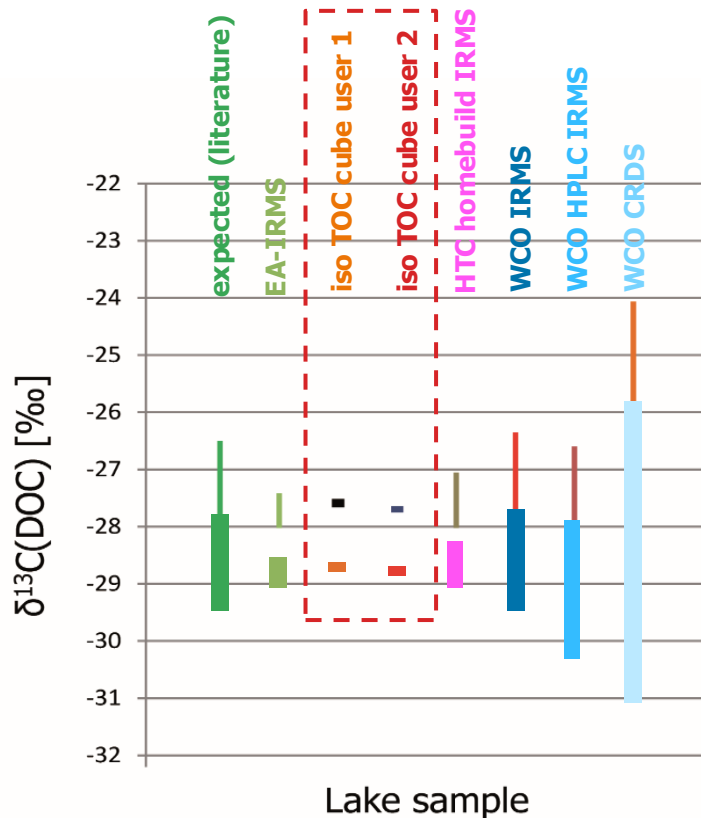


Compound	ID	Known $\delta^{15}\text{N}$ [‰]	Measured $\delta^{15}\text{N}$ [‰]	1 S.D.
Caffeine	IAEA-600	+1.00	+0.66	0.09
Glutamic Acid	USGS 41	+47.57	+48.41	0.08
Ammonium Sulfate	IAEA-N-2	+20.41	+20.03	0.07
Urea	EAS 13 003	-1.12	-2.46	0.10
Acetanilide	EAS 12 001	+1.57	+0.60	0.15
Glutamic Acid	EAS 12 004	-4.66	-4.51	0.05
Glutamic Acid	EAS 12 005	-4.06	-3.96	0.17
Sodium Nitrate	EAS 13 002	+16.31	+16.87	0.05
Ammonium Chloride	EAS 13 001	-1.05	-2.07	0.11
Caffeine	EAS 13 015	-1.78	-2.02	0.02

Standards with EAS prefix are internal RMs calibrated back to internationally accepted CRMs

Comparison with other methods

WCO = Wet chemical oxidation, HTC = High Temperature Combustion, CRDS = Cavity Ring down spectroscopy, EA = Elemental Analyzer, HPLC = High-Performance Liquid chromatography



iso TOC cube - Specifications

Specification	TC / TOC / TIC	TN _b
Standalone mode (abundance)		
Measuring range	0-60,000 ppm	0-60,000 ppm ¹
LOeD	6 ppb	500 ppb
Relative standard deviation	< 2%	< 2%
IRMS mode		
External precision	$\delta^{13}\text{C}_{\text{CO}_2}$ 0.1‰ ²	$\delta^{15}\text{N}_{\text{N}_2}$ 0.2‰ ^{2,3}
LOiD	1 ppm (<i>0.5 ppm</i>)	15 ppm
LOiQ	5 ppm	25 ppm

¹Measured as NO, bypasses reduction furnace, cannot measure $\delta^{15}\text{N}$ at same time

²For a standard solution with > LOQ concentrations, **Installation specification**

³Requires LCM and measured as N₂

LOeD = Limit of Elemental Detection

LOiD = Limit of Isotopic Detection

LOiQ = Limit of Isotopic Quantification

iso TOC cube sample types



Freshwater



Seawater



Drinking water



Wastewater



Soil Leachate

TOC in freshwaters

- In these data, water samples from the River Dart, Devon, UK were collected along an estuarine transect with a salinity gradient from 2 g/L to 25 g/L.
- Samples were filtered (<45um) and acidified on collection to a pH < 2 to remove TIC.
- **These data show good isotopic precision for challenging low concentration 1-3ppm C samples across a freshwater gradient**

Sample	n	Analysis volume (ml)	Salinity (g/L)	NPOC (mg/L)*	CO ₂ peak height (nA)	δ ¹³ C _{VPDB} (‰)
Dart 2	4	1	2	1.89 ± 0.06	1.20 ± 0.05	-29.53 ± 0.32
Dart 3	4	1	5	2.26 ± 0.18	1.33 ± 0.03	-29.01 ± 0.16
Dart 4	4	1	10	2.20 ± 0.02	1.33 ± 0.04	-28.61 ± 0.22
Dart 5	4	1	15	3.06 ± 1.45	1.38 ± 0.02	-27.74 ± 0.20
Dart 6	4	1	25	1.77 ± 0.06	1.21 ± 0.01	-27.26 ± 0.17

TOC in seawater



Whilst inorganic carbon in the form of bicarbonate is dominant in seawaters, an ability to undertake a range of direct measurements of Total Carbon (TC), Total Inorganic Carbon (TIC) and Total Organic Carbon (TOC) is vital for achieving a better understanding of the ocean carbon cycle.



Seawater samples were pre-acidified to a pH < 2 offline to remove TIC. It is recommended to use a lower combustion temp of 680° C for salty waters to reduce salt corrosion. SALTTRAP technology can also be used to improve system lifetimes.



Analysis of seawater samples on the iso TOC cube shows excellent isotopic precision for replicate analyses of seawater TOC.

Sample	n	Analysis Volume (ml)	NPOC (mg/L)*	CO ₂ Peak Height (nA)	δ ¹³ C _{VPDB} (‰)
Croatian Seawater 1	4	1	10.6 ± 0.1	10.06 ± 0.41	-31.84 ± 0.15
Croatian Seawater 2	4	1	8.7 ± 0.4	8.35 ± 0.35	-30.37 ± 0.10
Croatian Seawater 3	4	1	5.5 ± 0.1	5.59 ± 0.15	-28.82 ± 0.07
Croatian Seawater 4	4	1	5.0 ± 0.1	5.09 ± 0.30	-24.35 ± 0.17
Croatian Seawater 5	4	0.1	>100*	34.56 ± 4.53	-21.62 ± 0.06

Soil DOM extracts

- Dissolved Organic Matter (DOM) in soil affects fundamental biogeochemical processes, including carbon and nutrient circulation.
- DOM is a mixture of soluble organic compounds derived from terrestrial and autochthonous sources, including decaying root and leaf, root exudates, and microbial metabolism
- Traditional lyophilization EA-IRMS methods are complex and time consuming.
- **The iso TOC cube offers a much more rapid and direct analysis of the extracted DOM, without sacrificing accuracy or precision**

SAMPLE* (DOM EXTRACT)	TOC-IRMS $\delta^{13}\text{C}$ (‰ VPDB)	EA-IRMS $\delta^{13}\text{C}$ (‰ VPDB)
BLACK HUMUS LAYER (H, FIMIC ANTHROSOL)	-26.29 ± 0.03	-26.39 ± 0.03
SUBSOIL (HAPLIC CAMBISOL)	-26.50 ± 0.08	-26.54 ± 0.01
ERODED SEDIMENT (PETRIC CALCISOL)	-25.28 ± 0.07	-25.30 ± 0.01
BURIED ILLUVIAL HORIZON (ZBC, HAPLIC PODZOL)	-26.61 ± 0.03	-26.69 ± 0.12
ASH LEAVES	-29.37 ± 0.07	-29.36 ± 0.02
PINE NEEDLES	-30.77 ± 0.08	-30.87 ± 0.04
SPRUCE NEEDLES	-31.72 ± 0.07	-31.78 ± 0.02
RICE STRAW	-29.43 ± 0.11	-29.44 ± 0.05
MOSS	-27.56 ± 0.01	-27.60 ± 0.07
HUMIC ACID	-32.66 ± 0.03	-32.69 ± 0.02

*0.5 mL liquid injection

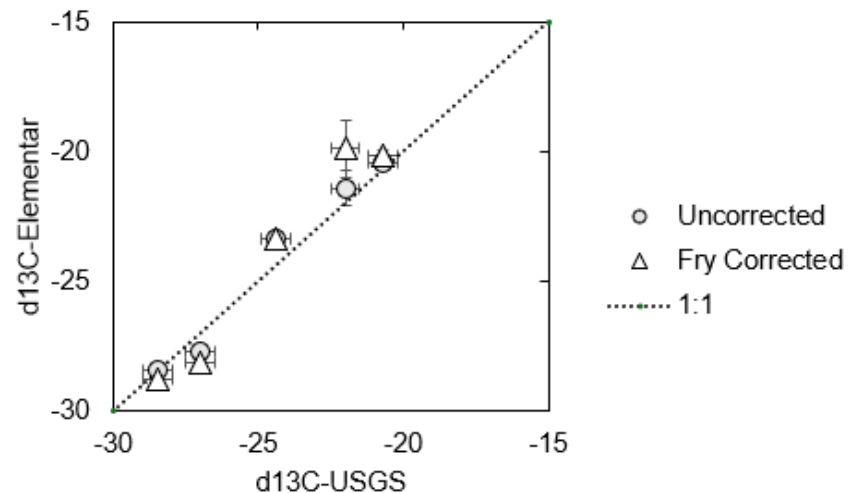
Comparison between $\delta^{13}\text{C}$ values determined by TOC-IRMS and by conventional EA-IRMS of lyophilized DOM extracts.

Recent Demo Lab Analysis

Table 1: TOC and $\delta^{13}\text{C}$ results of second batch of analyzed water samples.

Sample	ppm C Known	ppm C (by IR)		Uncorrected $\delta^{13}\text{C}$ (VPDB)		Fry Corrected $\delta^{13}\text{C}$ (VPDB)	
		ppm C	%RSD	$\delta^{13}\text{C}$	SD	$\delta^{13}\text{C}$	SD
NOM	2.8	2.7	0.6%	-27.69	0.05	-28.12	0.06
GC05 465.5	5.5	4.6	1.5%	-20.42	0.17	-20.15	0.19
WHLA 24	4.2	4.5	0.3%	-28.45	0.05	-28.80	0.06
WHLA 05	2.8	2.7	0.8%	-23.37	0.08	-23.34	0.10
Hansell_DSR_12_08	0.5	0.5	1.4%	-21.40	0.66	-19.88	1.11

- “Blind” samples sent to Elementar demo lab – mix of salinities, and 0.5 – 5 ppm TOC
- Compared to OI-IRMS results from origin lab
- Very good agreement – and on uncorrected, rather than “Fry Corrected”
- Excellent precisions for the most part too – horizontal is origin lab precisions, most iso TOC precision error bars end up almost invisible!



Post-ASITA Workshops!

Post-ASITA Elementar Workshop: Registration



Wed PM: 1:30 PM - 5:30 PM
2 parallel sessions

- Source Maintenance
- LyticOS Data Processing

Thu AM: 08:30 AM - 1:00 PM (*workshops start at 9:00*)
Possibly 2 parallel sessions (depending on final numbers for source workshop)

- Source Maintenance
- EA & EA-IRMS

Thu PM: 1:30 PM - 5:30 PM
2 parallel sessions

- Source Maintenance
- iso FLOW GHG for N2/N2O

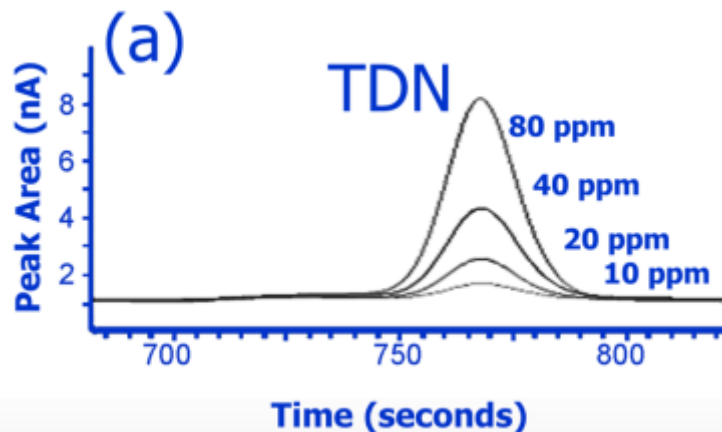


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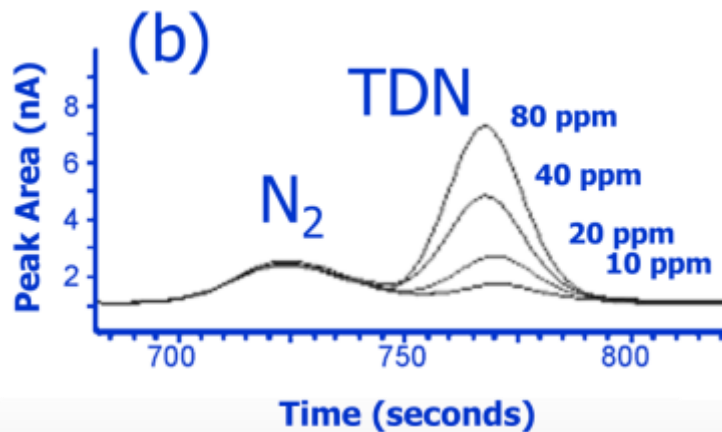
Need for degassing for ^{15}N analysis

Membrane degassing unit rapidly and efficiently removes N_2 from the sample prior to combustion
 (a). Without degassing (b), the equivalent of 20 ppm N_2 would contribute to the TDN signal

Degassed sample



No degassing of sample



Influence of monsoons on DOC in a river estuarine environment

[Kumar et al. \(2022\)](#)



Tracing terrestrial versus marine sources of dissolved organic carbon in the largest monsoonal Godavari estuary in India using stable carbon isotopes

B.S.K. Kumar^a, V.V.S.S. Sarma^{a,b,*}, D. Cardinal^c

^a CSIR-National Institute of Oceanography, Regional Centre, 176 Lawsons Bay Colony, Visakhapatnam, India

^b Academy of Scientific and Innovative Research, Ghaziabad, India

^c LOCEAN UMR 7159 Sorbonne Université/CNRS/IRD/MNHN, 4 Place Jussieu - Boite 100, F-75255 Paris, France

- ① Monsoonal rains occur for 3-4 months (July-Sept) every year across the Indian subcontinent
- ① The Godavari river is the largest monsoonal river in the Indian subcontinent.
- ① The terrestrial organic carbon flux from the continent to the ocean is an important component of the global organic carbon cycle.
- ① This study performs a time series analysis monthly to evaluate the impact of monsoonal rains on C fluxes.



Influence of monsoons on DOC in a river estuarine environment

[Kumar et al. \(2022\)](#)

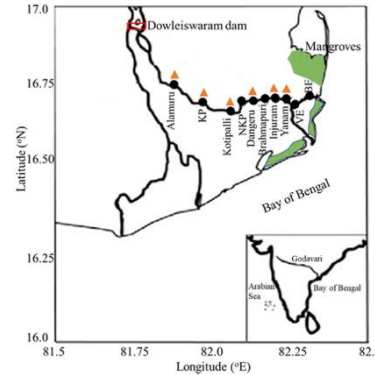
IRMS instrumentation

- ⊗ DOC/TNb concentrations and $\delta^{13}\text{C}_{\text{DOC}}$ were measured on an iso TOC cube with LCM
- ⊗ Samples were acidified to a pH <2 to remove DIC
- ⊗ Samples were purged with He to remove purgeable organic carbon
- ⊗ DON was estimated by subtracting dissolved inorganic nitrogen (DIN) from TNb.
- ⊗ DOC conc precision < 3%
- ⊗ $\delta^{13}\text{C}_{\text{DOC}}$ precision < 3‰



Influence of monsoons on DOC in a river estuarine environment

Kumar et al. (2022)



- The relation between DOC and $\delta^{13}\text{C}_{\text{DOC}}$ displayed a negative (inverse) relationship during both wet and dry periods suggesting the removal of DOC during estuarine mixing.

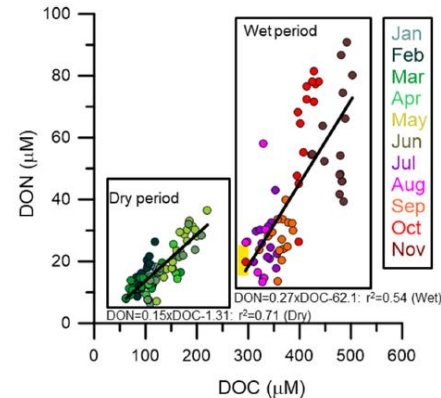


Fig. 6. Relationship between DOC and DON in the Godavari estuary during the dry and wet periods.

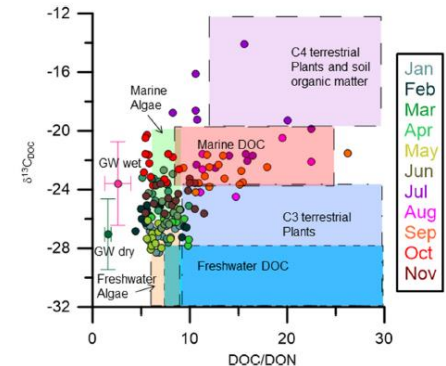


Fig. 7. The relationship between DOC/DON ratio and $\delta^{13}\text{C}_{\text{DOC}}$ in the Godavari estuary during 2019. The ranges of C/N and $\delta^{13}\text{C}_{\text{DOC}}$ of different end-members are shown. The mean $\delta^{13}\text{C}_{\text{DOC}}$ during wet (August) and dry (March) periods on the bank of the river is also given.



Tracing DOC across a glacio-fluvial transition in the Tibetan Plateau freshwaters

2022



Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

The glacial–terrestrial–fluvial pathway: A multiparametrical analysis of spatiotemporal dissolved organic matter variation in three catchments of Lake Nam Co, Tibetan Plateau

Philipp Maurischat ^{a,*}, Lukas Lehnert ^b, Vinzenz H.D. Zerres ^b, Tuong Vi Tran ^c, Karsten Kalbitz ^d, Åsmund Rinnan ^e, Xiao Gang Li ^f, Tsechoe Dorji ^g, Georg Guggenberger ^h



- ⊙ The Tibetan Plateau (TP) is a sensitive alpine environment of global importance, being Asia's water tower, featuring vast ice masses and comprising the world's largest alpine grasslands.
- ⊙ Sensitive high-altitude ecosystems such as the TP are under pressure by several threats such as intensified land-use and pronounced global warming
- ⊙ Gaining knowledge on biogeochemistry processes within the TP is an essential component for understanding current challenges.



Tracing DOC across a glacio-fluvial transition in the Tibetan Plateau freshwaters

2022

IRMS instrumentation

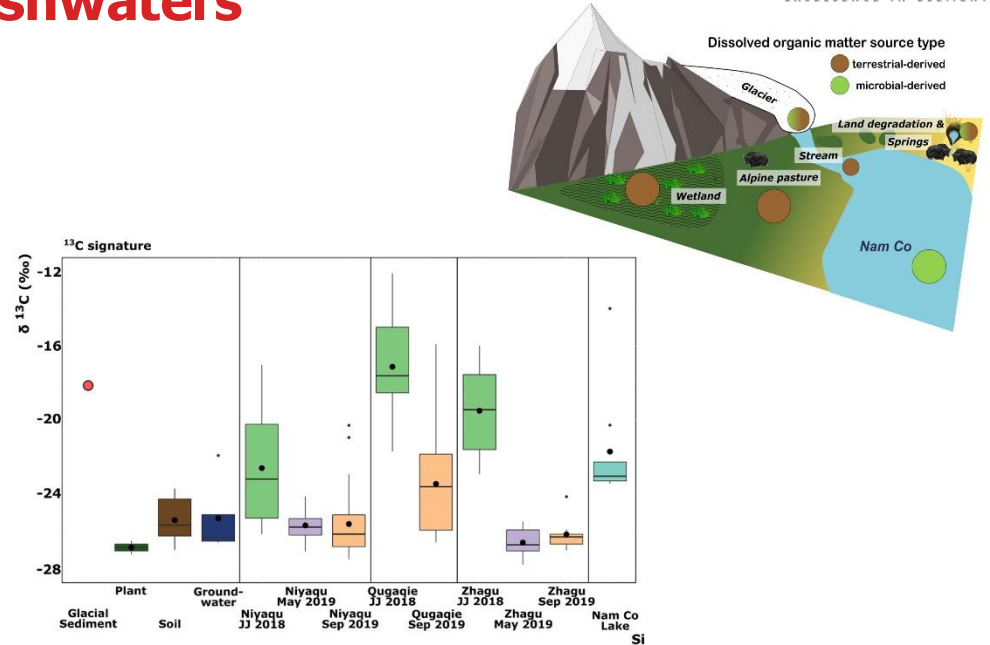
- ④ DOC concentrations measured on vario TOC cube, $\delta^{13}\text{C}_{\text{DOC}}$ measured on iso TOC cube
- ④ Samples were filtered $<45\mu\text{m}$ (PES membrane) and acidified to a $\text{pH} < 2$ with HCl
- ④ When the DOC concentration was below $1.6\text{mgL}^{-1}\text{C}$, 1 mL of caffeine standard (reference material IAEA-600) was added. Sample $\delta^{13}\text{C}$ was calculated using the common mixing equation.





Tracing DOC across a glacio-fluvial transition in the Tibetan Plateau freshwaters

2022



- Stream samples were strongly influenced by terrestrial signatures, inherited from glaciers, alpine wetlands, and groundwater sources. Lakewaters are however dominantly influenced by microbial DOM. Study measured a wide range of fresh waters (lake, brackish, wetland, glacial, stream and spring waters) and DOC concentrations from 0.63 to 12.46 mg/L-1



Tracing C uptake in plants from soils through enriched ^{13}C doping experiments

2021

Received: 28 June 2021 | Accepted: 16 October 2021

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RESEARCH ARTICLE



Above- to belowground carbon allocation in peatlands shifts with plant functional type and temperature[#]

Lilli Zeh¹ | Claudia Schmidt-Cotta¹ | Juul Limpens² | Luca Bragazza³ | Karsten Kalbitz¹



- ⊙ Peatlands store one-third of the global soil carbon on only 3% of the land surface area.
- ⊙ Vascular plants with root systems expanding coverage and dominating sphagnum moss. Concern that this will impact the ability to sink C in peatlands.
- ⊙ Experimental setup using ^{13}C labelled water to quantify how vascular plants assimilate and store carbon in the field.



Tracing C uptake in plants from soils through enriched ^{13}C doping experiments

2021



IRMS instrumentation

- ④ DOC concentrations measured on vario TOC cube, $\delta^{13}\text{C}_{\text{DOC}}$ measured on iso TOC cube
- ④ Pore waters were collected in syringes connected to mini-rhizons protected from UV light with foil. Water was extracted by vacuum extraction the day after sampling.
- ④ Pore waters were pre acidified to a pH <2
- ④ Injection volume 0.5mL
- ④ Combustion at 850°C





Tracing C uptake in plants from soils through enriched ^{13}C doping experiments

2021

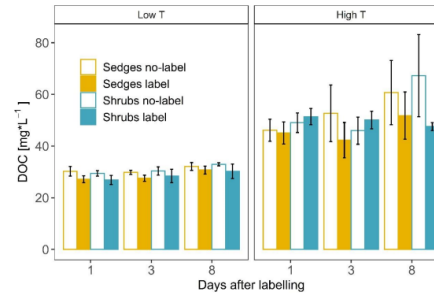


Figure S2 DOC concentrations for the label and no-label plots of shrubs (*C. vulgaris*) and sedges (*E. vaginatum*) at two peatland sites (high and low temperature site, high T and low T, respectively) on the first day after labelling, day 3 and day 7 after labelling. Bars give means with SE.

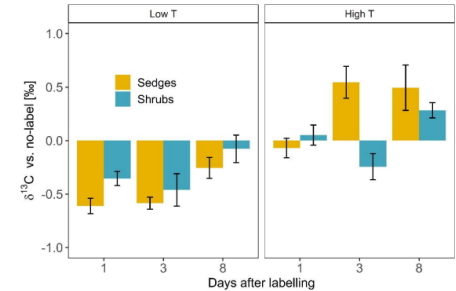


Figure S3 $\delta^{13}\text{C}$ in DOC of the label plots of shrubs (*C. vulgaris*) and sedges (*E. vaginatum*) at two peatland sites (high and low temperature site, high T and low T, respectively) on the first day after labelling, day 3 and day 7 after labelling. The numbers represent $\delta^{13}\text{C}$ of label plots after subtraction of no-label plot values. Positive values indicate an enrichment of ^{13}C in the respective treatment sample relative to the no-label plot. Negative values mean that no enrichment in ^{13}C was found. Bars give means with SE.

- ⊗ Above- to below- ground C allocation in peatlands differs between sedges and shrubs and that this C allocation is dependent on temperature. Under climate change, root-driven C-cycling in peatlands might become less important compared to the direct effects associated, for example, to an increase of peat aeration.



Carbon and nitrogen in seawater photic zone from the Bay of Bengal

2024



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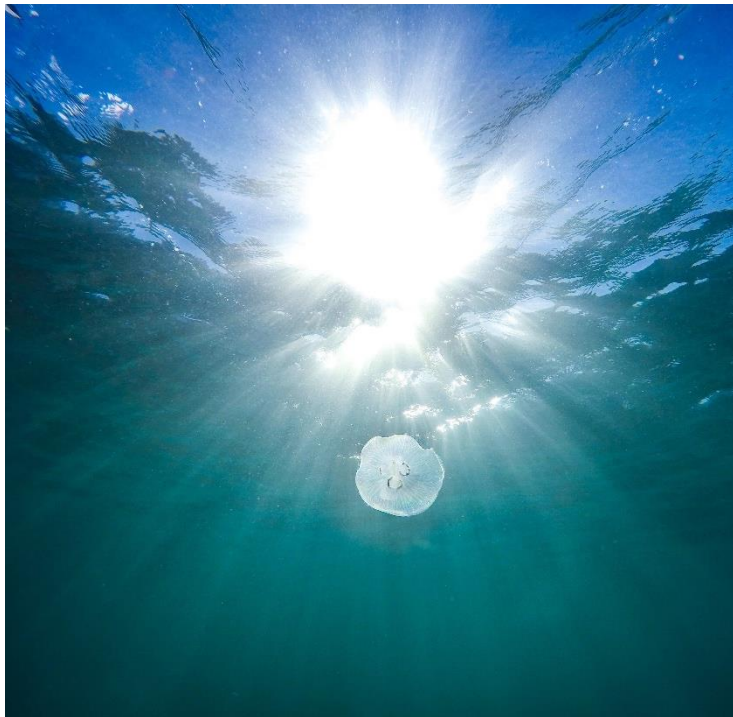


Accumulation of dissolved organic carbon and nitrogen in the photic zone in the nitrogen-depleted waters of the Bay of Bengal



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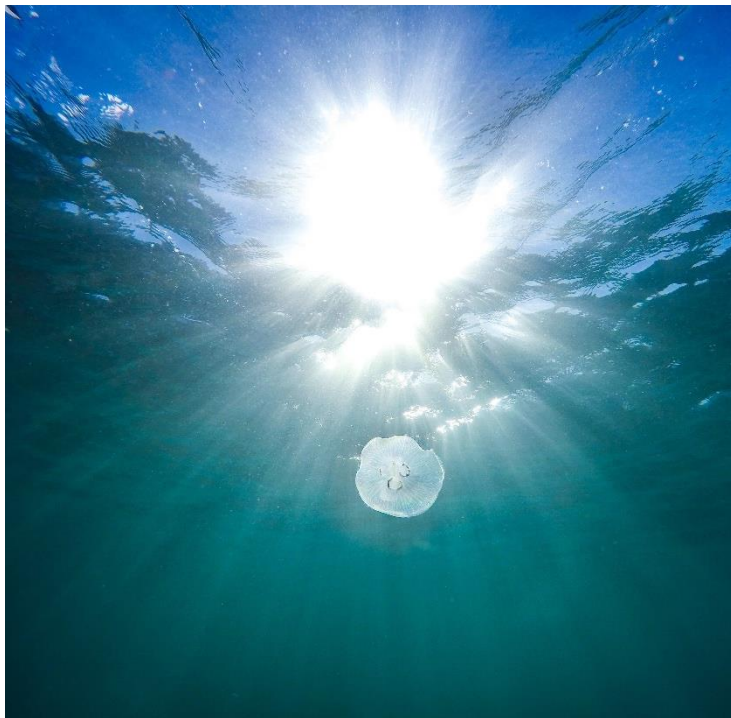


- ④ 90% of marine life lives in the photic zone and Oceanic DOC is equivalent to the total amount of atmospheric carbon.
- ④ The Bay of Bengal is a tropical basin and receives a significant amount of freshwater through major rivers, such as Ganges, Brahmaputra, Irrawady and Salween riverine systems, leading to strong salinity stratification
- ④ DOM source can be identified using stable isotopes (C & N)



Carbon and nitrogen in seawater photic zone from the Bay of Bengal

2024



IRMS instrumentation

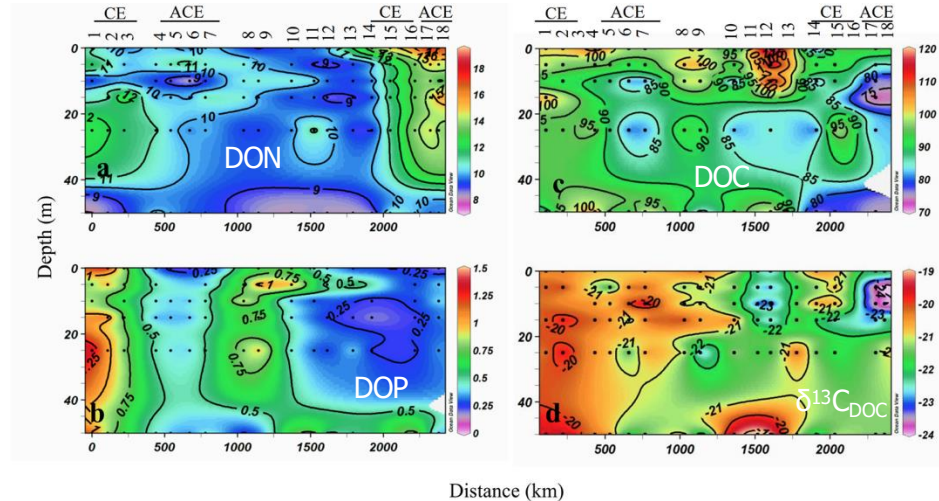
- ⊙ DOC/TNb concentrations and $\delta^{13}\text{C}_{\text{DOC}}$ were measured on an iso TOC cube with LCM
- ⊙ Seawater samples collected from top 20-40m of seawater across a cruise transect of over 2500km across Bay of Bengal
- ⊙ Seawaters were pre acidified to a pH <2 and purged with high purity helium to remove inorganic carbon
- ⊙ DON is estimated by subtracting dissolved inorganic nitrogen (DIN) from TNb





Carbon and nitrogen in seawater photic zone from the Bay of Bengal

2024



- ⊙ The strong relationship of DOC with Chl-a, POC and DOC exudation rates, DOC: DON, DON: DOP ratios and $\delta^{13}\text{C}_{\text{DOC}}$ suggested in situ production is the major source of DOC and DON in the Bay of Bengal. DOM acts as an energy source to the plankton and contributes to the food web dynamics and C-cycling in the Bay of Bengal



Mineral – soil carbon exchange experiments using ^{13}C enriched DOM

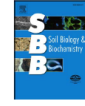
2018



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Multiple exchange processes on mineral surfaces control the transport of dissolved organic matter through soil profiles

T. Leinemann^{a,*}, S. Preusser^b, R. Mikutta^c, K. Kalbitz^d, C. Cerli^e, C. Höschel^f, C.W. Mueller^f, E. Kandeler^b, G. Guggenberger^a

^a Institute of Soil Science, Leibniz Universität Hannover, Herrenhäuser Straße 2, 30451 Hannover, Germany

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- ④ Dissolved organic matter (DOM) mobilized in topsoil and transported to subsoil horizons is an important source of carbon (C) throughout the soil profile.
- ④ Adsorption of carbon by reactive minerals such as clays reduces the concentration of dissolved organic carbon in soil pore water.
- ④ The objective of this study was to experimentally test whether changes in amounts and composition of DOM within soil profiles are due to sorption processes alone or to additional stepwise exchange of OM on mineral surfaces.





Mineral – soil carbon exchange experiments using ^{13}C enriched DOM

2018



IRMS instrumentation

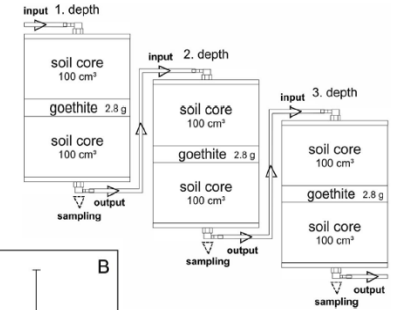
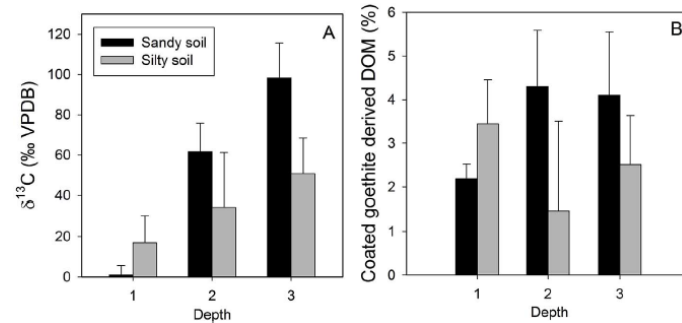
- ⊙ Goethite covered with ^{13}C (12.3 atom %) labelled organic matter
- ⊙ Water with define DOC and known $\delta^{13}\text{C}$ ratio pumped through soil at 5.5mL/hr and sampled over days-weeks.
- ⊙ Soil eluate measured for DOC on vario TOC cube, and $\delta^{13}\text{C}_{\text{DOC}}$ on an iso TOC cube
- ⊙ Samples acidified to pH <2
- ⊙ Injection volumes between 0.2 and 1mL





Mineral – soil carbon exchange experiments using ^{13}C enriched DOM

2018



- ⊙ Exchange processes at mineral surfaces due to simultaneous adsorption and desorption of OM thus play a crucial role in DOM transport, as well as in the fate and properties of mineral-associated OM. Adsorbed OM can be mobilized and replaced by DOC over an entire soil profile even at depth, thus confirming the importance of mineral – soil carbon exchange.



DOC cycling in modern redox stratified lakes

2023

The hidden role of dissolved organic carbon in the biogeochemical cycle of carbon in modern redox-stratified lakes

Robin Havas¹, Christophe Thomazo^{1,2}, Miguel Iniesto³, Didier Jézéquel^{4,5}, David Moreira³, Rosaluz Tavera⁶, Jeanne Caumartin⁷, Elodie Muller⁷, Purificación López-García³, and Karim Benzerara⁷

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⁷Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie (IMPMC), CNRS,

Muséum National d'Histoire Naturelle, Sorbonne Université, 75005 Paris, France



- ⊗ This study characterizes the DOC reservoir of four modern redox-stratified alkaline crater lakes from the Trans-Mexican Volcanic Belt.
- ⊗ Although many studies have explored C cycling in modern redox-stratified environments, very few have measured the stable isotope signature.
- ⊗ The production and fate of the DOC reservoir in these modern analogues is used to discuss the potential role of DOC in past perturbations of the sedimentary C isotope record from the Neoproterozoic and Phanerozoic.



DOC cycling in modern redox stratified lakes

2023



IRMS instrumentation

- ⊙ DOC concentrations measured on vario TOC cube, $\delta^{13}\text{C}_{\text{DOC}}$ measured on iso TOC cube
- ⊙ Samples were filtered $<0.22\mu\text{m}$ (Filtropur S filters) and acidified to a pH $\sim 1-2$
- ⊙ Injection volume of 1mL (four replicates, 1st measurement discarded)
- ⊙ Combustion temperature 850°C
- ⊙ Six injections of DI water between samples to minimise memory effect





DOC cycling in modern redox stratified lakes

2023

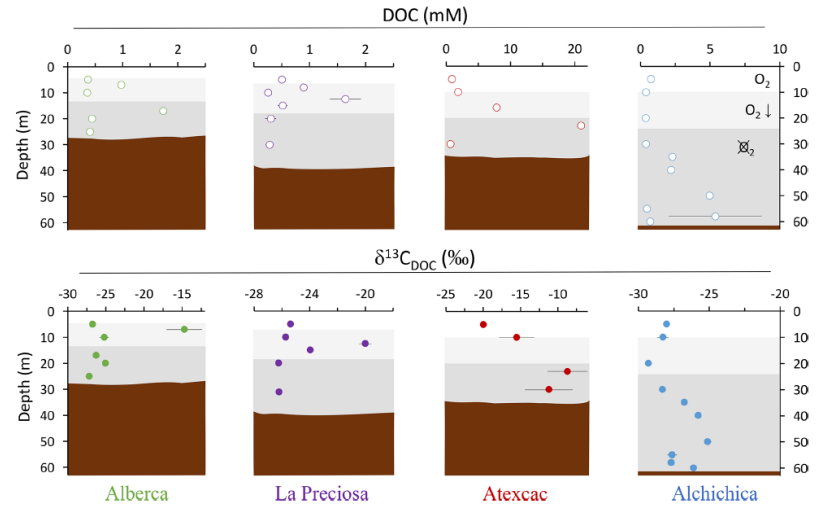


Figure 3. Vertical profiles of concentration and isotopic composition of dissolved organic carbon (DOC) throughout the water columns of the studied lakes: Alberca de los Espinos, La Preciosa, Atexcac, and Alchichica. Concentration is in mmol L^{-1} (mM), and isotopic composition is in ‰ vs. VPDB. The white, gray, and dark-gray shading are as in Fig. 2. The brown shading symbolizes the presence of sediment at the bottom of the water columns (showing the greater water depth in Lake Alchichica).

- ⊗ In each of the four lakes, diverse photosynthetic planktonic communities release greater or smaller amounts of DOC, depending strongly on environmental factors such as nutrient and DIC availability, and transfer most of the inorganic C to DOC rather than POC.




Tracing labile versus nonlabile organic matter degradation in aquatic systems

2023



Evidence for a Temporary Positive Priming Effect in Aquatic Systems With Certain Substrates and Isotopic Discrimination of DOM Sources

Wafa Laffet¹, Andrea Prentice¹, and Luc Tremblay¹ 

¹Department of Chemistry and Biochemistry, Université de Moncton, Moncton, NB, Canada

- ⊗ The majority of DOM in fresh or saline aquatic systems is labile and rapidly consumed by microorganisms and converted to CO₂. Yet, a small fraction of it is less reactive and persists for months and years, contributing to a huge reservoir of nonlabile dissolved organic carbon, similar in size to atmospheric CO₂.
- ⊗ Experiments were performed to test the priming effect (PE) of labile organic substrates on nonlabile dissolved organic matter degradation.



Tracing labile versus nonlabile organic matter degradation in aquatic systems

2023



IRMS instrumentation

- ⊗ DOC concentrations and $\delta^{13}\text{C}_{\text{DOC}}$ measured on iso TOC cube with LCM
- ⊗ Samples were filtered (precombusted GFF) and acidified to a pH < 2
- ⊗ Samples purged of purgeable organics with He gas
- ⊗ Injection volume of 1mL (four replicates, 1st measurement discarded)
- ⊗ Combustion temperature 850°C
- ⊗ DOC conc precision < 5%
- ⊗ $\delta^{13}\text{C}_{\text{DOC}}$ precision < 0.4‰





Tracing labile versus nonlabile organic matter degradation in aquatic systems

2023

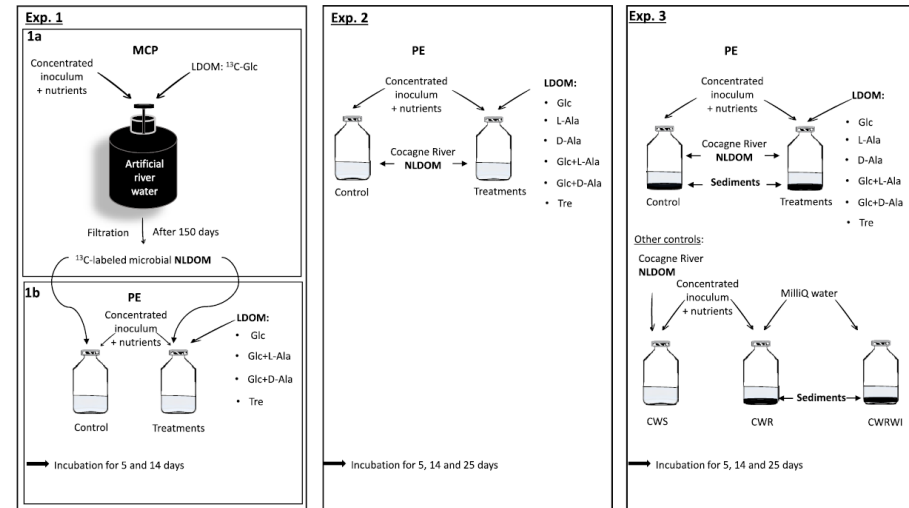
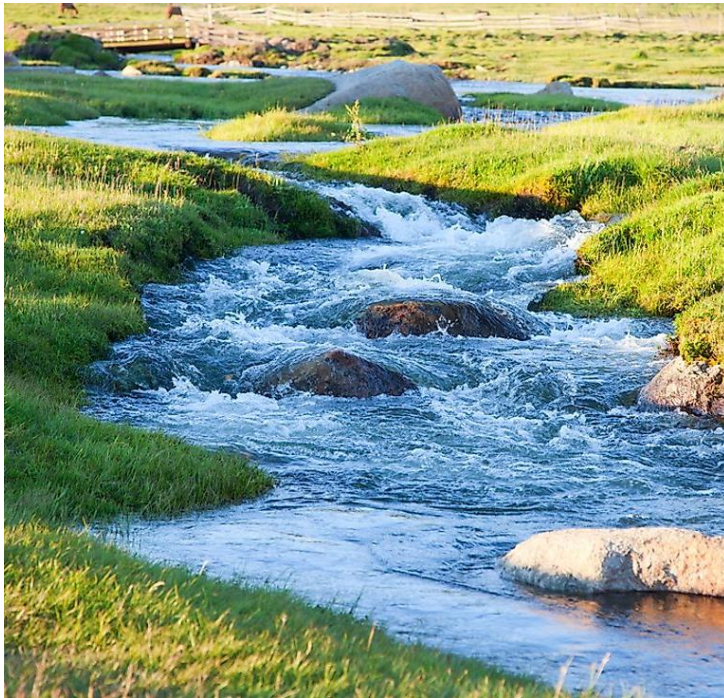


Figure 1. Experimental setup for the three priming effect (PE) experiments (Exp. 1, 2, 3). Control and treatment bottles were prepared in replicates. MCP, microbial carbon pump; LDOM, labile dissolved organic matter; NLDOM, nonlabile dissolved organic matter; Glc, glucose; L-Ala, L-alanine; D-Ala, D-alanine; Tre, trehalose; CWS, control without sediments; CWR, control with river water replaced by ultrapure water; CWRWI, control with river water replaced by ultrapure water and no inoculum.

- ④ The main goal of this study is to evaluate the occurrence of PE in aquatic environments using different experimental conditions and stable isotope analysis of DOC. Microbial DOM was always produced from the added labile substrate. This contribution is often overlooked but must be discriminated for accurate estimates of the PE.



Tracing dissolved nitrogen in tropical forest waterways

2024

Sources and Sinks of N in Ecosystem Solutions Along the Water Path Through a Tropical Montane Forest in Ecuador Assessed With $\delta^{15}\text{N}$ Values of Total Dissolved Nitrogen

Pablo Alvarez^{1,2}, Andre Velescu¹, Kerstin Pierick³, Juergen Homeier^{4,5}, and Wolfgang Wilcke¹

¹Institute of Geography and Geoecology, Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany, ²Faculty of Agriculture and Renewable Natural Resources, Universidad Nacional de Loja, Loja, Ecuador, ³Spatial Structures and Digitization of Forests/Silviculture and Forest Ecology of the Temperate Zones, Georg August University Göttingen, Göttingen, Germany, ⁴Faculty of Resource Management, University of Applied Sciences and Arts, Göttingen, Germany, ⁵Department of Plant Ecology and Ecosystem Research, Georg August University Göttingen, Göttingen, Germany



- ⊗ Tropical forests are biodiverse ecosystems
- ⊗ Tracking N input from atmospheric deposition, through surface runoff and leaf litter leaching to the record in soil profiles is important to understand the processing of N in N limited ecosystems.
- ⊗ The $\delta^{15}\text{N}$ value of total dissolved nitrogen (TDN) provides useful information about the sources and sinks of N in forest ecosystems.



Tracing dissolved nitrogen in tropical forest waterways

2024



IRMS instrumentation

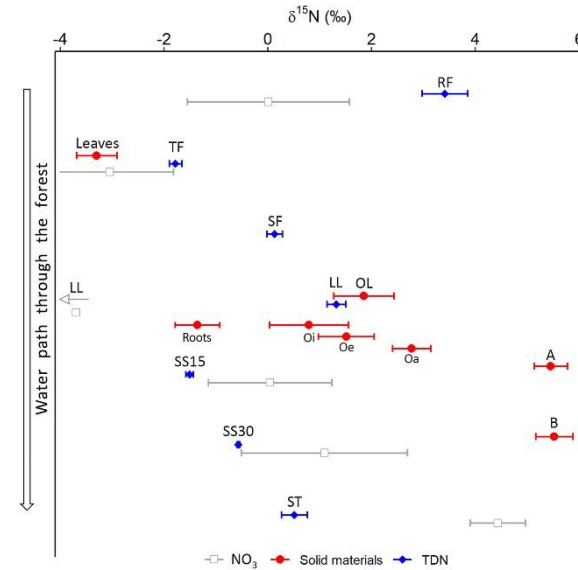
- ⊙ $\delta^{15}\text{N}_{\text{DON}}$ measured on iso TOC cube with LCM
- ⊙ Samples were filtered with ashless folded filters of 4–7 μm pore size (Type 392)
- ⊙ Injection volume of 1–2.5 mL
- ⊙ Combustion temperature 850°C
- ⊙ LCM N_2 trap held at -38°C
- ⊙ $\delta^{15}\text{N}_{\text{DON}}$ precision < 0.4‰





Tracing dissolved nitrogen in tropical forest waterways

2024



- ⊙ Isotopically heavy nitrogen input via rainfall is enriched by isotopically lighter nitrogen from plants and nitrogen turnover during the water passage through the canopy. The direct measurement of $\delta^{15}\text{N}$ values provides a tool to monitor the changing nitrogen cycle in ecosystems.