ABB PROCESS AUTOMATION – MEASUREMENT AND ANALYTICS

ABB LGR-ICOS Stable Isotope Analyzers

Ecology Applications

DR FREDERIC DESPAGNE – LICA ISOTOPE SEMINAR – 15 APRIL 2021

ABB LGR-ICOS Stable Isotope Analyzers

Company and Technology Overview

ABB Group overview

A pioneering technology leader in digital industries

Digitalization: ABB Ability™

Electrification

Low/Medium voltage

Buildings & infrastructure

Electrification
#2

Automation

Measurement & analytics

Process control (DCS)

Process automation
#2

Motors & generators

Drives

Motion
#1

Robotization

Machine & factory

Robotics

Robotics & discrete automation
#2

33% Asia, Middle East and Africa

31% Americas

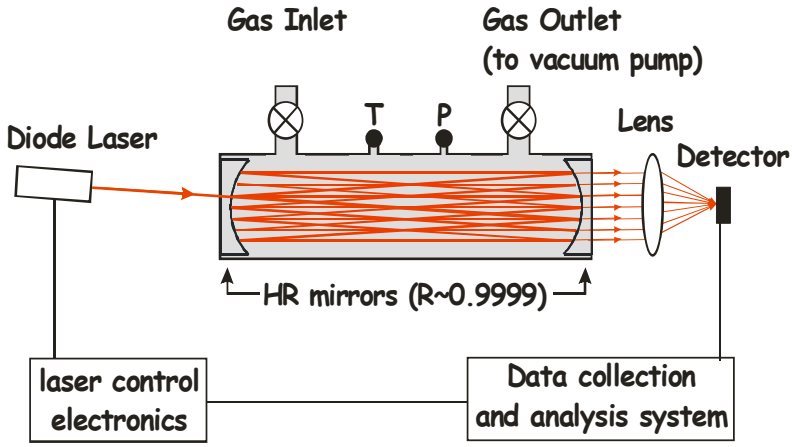
36% Europe

$410 bn market, growing at **3.5 – 4%** p.a. **$29 bn** revenues, **110,000** employees

Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS)

Technology and Main Environmental Applications

- OA-ICOS technology patented by Los Gatos Research in 2001.
- Laser light trapped into a cavity: effective pathlength >>km (sensitivity)
- Measures complete absorption peak area under: no sensitivity to matrix effects and wide dynamic range.
- Off-axis alignment of the beam leads to rugged optical system (control of parameters and alignment is not critical anymore).
- Mirrors can be cleaned in the field in a few minutes.
- 2 main applications of “LGR-ICOS” analyzers:
  - Real-time determination of trace gas concentration –in particular greenhouse gases (sensitivity down to ppb/ppt levels).
  - Real-time determination of stable isotope abundance in CO_2, H_2O, CH_4, N_2O.



Cavity mirrors easily serviced, if necessary.

ABB LGR-ICOS Isotopic Analyzers in Ecology

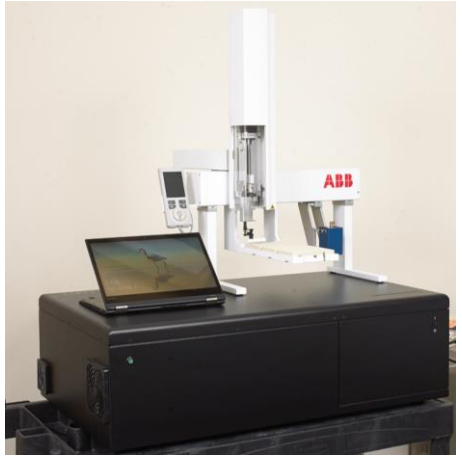
Isotopic H_2O Analysis

ABB LGR-ICOS Isotopic Analyzers in Ecology

Isotopic H_2O Analysis

ABB Solution: Principle

- LGR-ICOS isotopic water analyzers measure isotopic ratios in liquid and/or vapor phase.
- Liquid samples injected with autoloader (1µl samples in disposable glass vials).
- For liquid water, LGR-ICOS analyzers are equipped with Post-Analysis Software that calculates adjustments to measured isotopic ratios based on differences between known and measured values of water isotope IAEA-traceable standards, and reports a processed value.
- For vapor analyses, Water Vapor Isotope Standard Source (WVISS) accessory provides flows of water vapor with known concentration and isotope ratios over entire operating range of the analyzer, enabling comprehensive calibration of the response.
- LGR-ICOS isotopic water analyzers are available in different packages:
  - Ultraportable: GLA132 series.
  - Enhanced-Performance Rackmount: GLA331 series.
  - Enhanced-Performance Benchtop: GLA431 series.



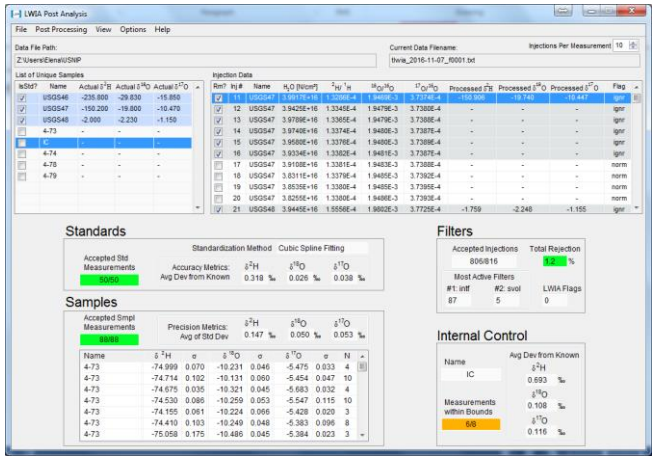


ABB LGR-ICOS Isotopic Analyzers in Ecology

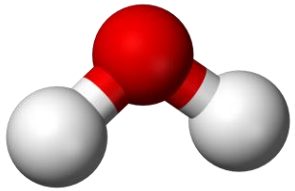
Isotopic H_2O Analysis

ABB Solution: Portfolio

- LGR-ICOS isotopic water analyzers portfolio and associated properties:

Model Name	Application - Isotopes	$\delta^{17}O$	$\delta^{18}O$	$\delta^{2}H$	^{17}O-excess	d-excess	H_2O
GLA132-LWIA	Ultraportable Liquid Water Isotopic Analyzer		X	X		X	X
GLA132-WVIA	Ultraportable Water Vapour Isotopic Analyzer		X	X		X	X
GLA331-TWVIA	Enhanced Performance Rackmount Triple Water Vapour Isotopes Analyzer	X	X	X			X
GLA331-WVIA	Enhanced Performance Rackmount Water Vapour Isotopic Analyzer		X	X			X
GLA431-LWIA	Enhanced Performance Benchtop Liquid Water Isotopic Analyzer		X	X		X	
GLA431-TLWIA	Enhanced Performance Benchtop Triple Liquid Water Isotopic Analyzer	X	X	X	X	X	
GLA431-IWA	Enhanced Performance Benchtop Isotopic Water Analyzer		X	X		X	
GLA431-TIWA	Enhanced Performance Benchtop Triple Isotopic Water Analyzer	X	X	X	X	X	

- Customers often use a liquid autoloader that allows to automatically analyze a large number of 1µl samples in disposable glass vials.
- With the typical operating procedure, 6 injections are performed per sample and the unknown samples are interleaved with certified standards to mitigate memory effects. Once the measurement run is set up, the system is fully autonomous and requires no consumable gases.



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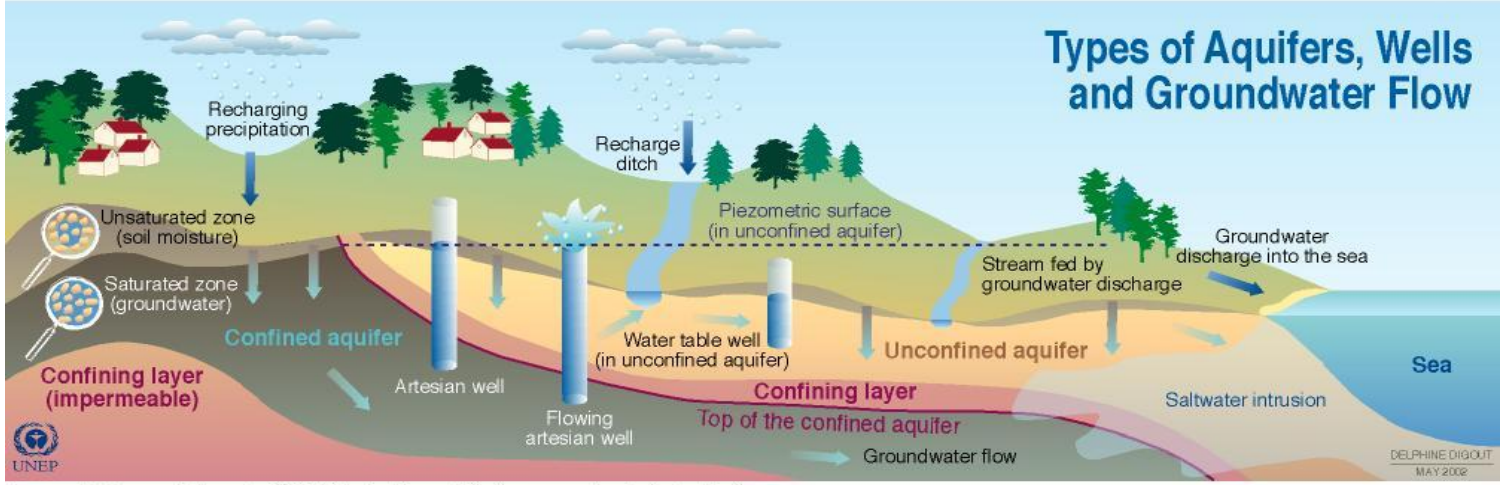
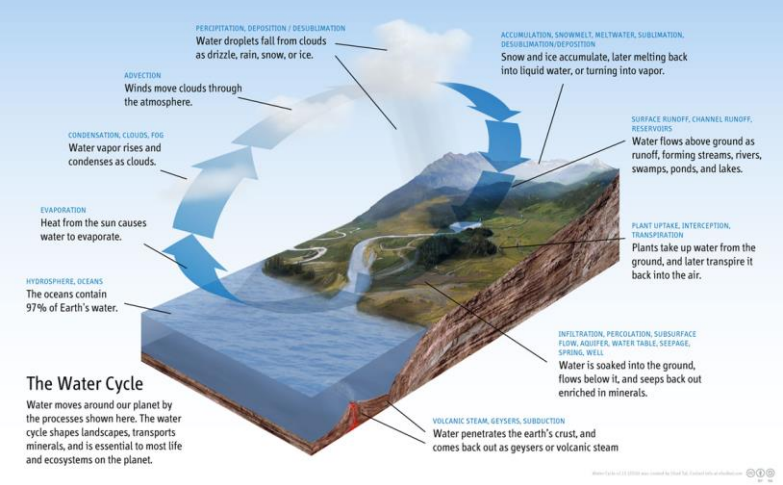
Isotopic H_2O Analysis

Hydrology Applications: Background

- Specific ratio of water stable isotopes dictated by conditions associated with compound's formation, including biochemical formation processes and geographic place of origin.
- Water stable isotopes are ideal tracers for hydrological, analytical and biological applications that involve measurements of fresh water and seawater.
- Hydrology and hydrogeology studies aim at understanding origins and dynamics of groundwater and streamwater in various locations on planet.





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Isotopic H_2O Analysis

Hydrology Applications: Parameters of Interest

$^{18}O/^{16}O$ ($\delta^{18}O$) and $^{2}H/^{1}H$ ($\delta^{2}H$)

- Specific to different sources (*e.g.* rainfall, snowmelt, lakes, streams).
- Allow to identify components of water streams, understand specific water flow generation mechanisms, characterize the recharge rates and residence time of groundwater systems, predict the migration of contaminants and gauge the impact of climate change on water resources.

d-excess (deuterium excess)

- Reflects relationship between deuterium and ^{18}O: d-excess $=\delta^{2}H - 8\delta^{18}O$.
- Allows to measure environmental conditions of evaporation, identify vapour source regions and characterize climate and hydrological conditions in time.

$^{17}O/^{16}O$ ($\delta^{17}O$)

- Smaller variability than other stable isotope ratios but contains information about past humidity from ice cores and general evaporative regime from liquid water.

^{17}O-excess

- Relates to the environmental abundance of ^{17}O isotope -typically low. Discriminates effect of condensation versus evaporation on water isotopic composition.
- Complements $\delta^{17}O$ and $\delta^{18}O$ measurements and provides additional information on subtle variations in relative abundance of ^{17}O and ^{18}O isotopes in meteoric waters, seawater, leaf waters, and terrestrial rocks and minerals.
- Used for instance used for interpretation of glaciary profiles or variations in atmospheric humidity.

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Isotopic H_2O Analysis

Hydrology Applications: Challenges of Analytical Measurements

Groundwater/ Stream water

- May contain visible particulates and require sample preparation before analysis.

Sea water

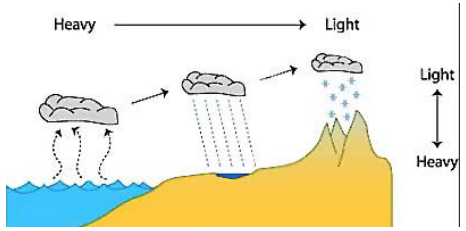
- Salt buildup can accumulate over time.

Glacier rivers

- Low temperatures could impact field deployments.

Precipitation

- Water isotopes are depleted. Heavy isotopes typically occur in liquid (or solid) phases and the light isotopes in the gaseous phase.



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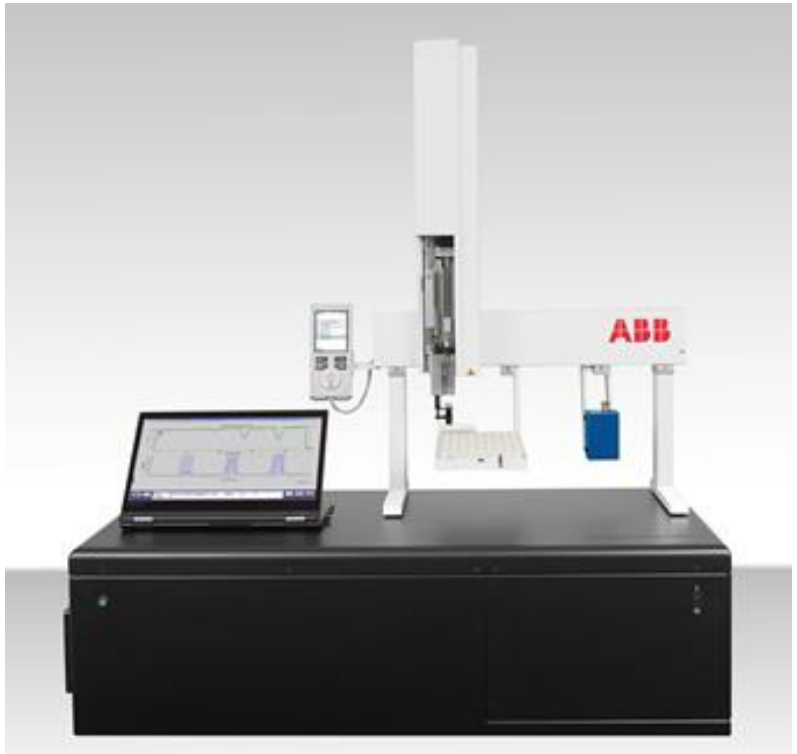
Isotopic H_2O Analysis

Hydrology Applications: Advantages of ABB Solution

- ABB offers a variety of rugged analyzer options, including:
  - Field-deployable portable analyzer
  - Temperature-stable benchtop model
  - Dual-modes for measuring liquid water and water vapor
- ABB LGR-ICOS instruments provide a number of customer benefits:
  - Fast: up to 800 injections-day.
  - Operation over a wide temperature range (0-45°C).
  - Remote instrument access.
  - Handle salt-water samples with salinities up to 0-4 g/L.
  - Wide range reference standards for depleted water samples up to highly enriched samples.
  - Sample preparation as simple as using a centrifuge or fine filter paper.
- Post Analysis Software simplifies analyses and enables highest performance:
  - Includes Spectral Contamination Identification module, which detects and accurately quantifies the presence of organic contaminants in water samples.



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Isotopic H_2O Analysis

Hydrology Applications: Injection Patterns

- Unknown samples interleaved with standards of a known isotopic value is the recommended configuration.
  - An interleaved run is defined as having standard and sample injection sets measured in alternating order.
- This image shows an example of an interleaved data set with rotating standards in between samples.
  - Each standard and sample injection group consists of 6 measurements:
    - 2 injections that will be ignored,
    - and 4 measured injections.
  - The run begins with 1 standard injection group, followed by 4 sample injection groups. This pattern continues with 3 standards of different isotopic compositions.
  - Ignored injections are the initial injections which will be excluded in the Post Analysis Software each time a standard or sample is changed in order to mitigate analyzer memory effects, regardless of any other issue with those injections.
    - They function as normal injections, but the measured data will be excluded by the Post Analysis Software.

		Ignored Injections		Measured Injections			
Standard 1		1	2	Inj 3	Inj 4	Inj 5	Inj 6
	Sample 1	1	2	Inj 3	Inj 4	Inj 5	Inj 6
	Sample 2	1	2	Inj 3	Inj 4	Inj 5	Inj 6
	Sample 3	1	2	Inj 3	Inj 4	Inj 5	Inj 6
	Sample 4	1	2	Inj 3	Inj 4	Inj 5	Inj 6
Standard 2		1	2	Inj 3	Inj 4	Inj 5	Inj 6
	Sample 5	1	2	Inj 3	Inj 4	Inj 5	Inj 6
	Sample 6	1	2	Inj 3	Inj 4	Inj 5	Inj 6
	Sample 7	1	2	Inj 3	Inj 4	Inj 5	Inj 6
	Sample 8	1	2	Inj 3	Inj 4	Inj 5	Inj 6
Standard 3		1	2	Inj 3	Inj 4	Inj 5	Inj 6
	Sample 9	1	2	Inj 3	Inj 4	Inj 5	Inj 6
	Sample 10	1	2	Inj 3	Inj 4	Inj 5	Inj 6
	Sample 11	1	2	Inj 3	Inj 4	Inj 5	Inj 6
	Sample 12	1	2	Inj 3	Inj 4	Inj 5	Inj 6

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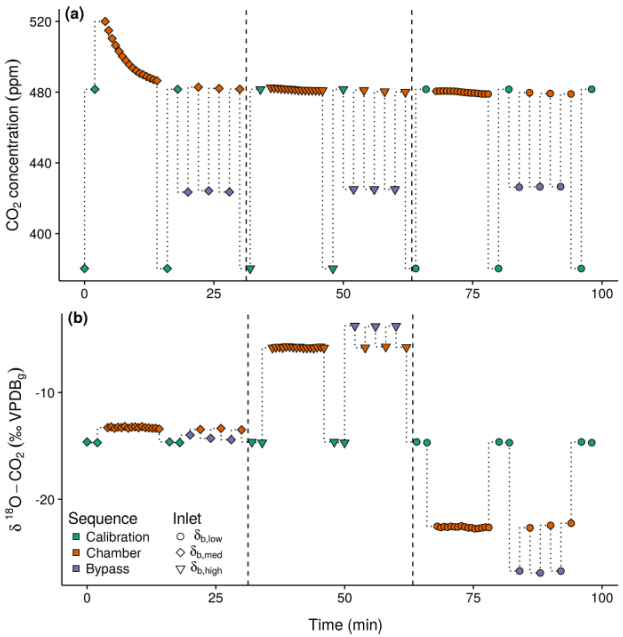
Isotopic H_2O Analysis

Hydrology Application Example: Determination of Hydrogen Composition of Soil Waters

- Understanding relative contribution of photosynthesis and soil respiration to net atmospheric CO_2 budget. Focus on understanding the activity of carbonic anhydrases (CA) enzymes that catalyse the hydration of CO_2 in soils and plants.
- Parallel assessments of CA activity from various soils and oxygen isotope composition ($\delta^{18}O$) of soil waters enable differential estimation of leaves and soils contribution to atmospheric CO_2 budget.
- Cryogenically extracted water samples from the soil of coniferous (pine) forest was analyzed with the ABB LGR-ICOS and liquid autoinjector to provide $\delta^{18}O$ profile of soil waters.
- Estimated rates of CO_2 hydration 6.8–14.6 times greater than theoretical uncatalysed rate of hydration, indicating that CA were active in these soils.



- *The role of soil pH on soil carbonic anhydrase activity*, Sauze et al., **Biogeosciences**, 15 (2018) 597–612.
- *The interaction of soil phototrophs and fungi with pH and their impact on soil CO_2, $CO^{18}O$ and OCS exchange*, Sauze *et al.*, **Soil Biology & Biochemistry**, 115 (2017) 371-382.
- *Non-destructive estimates of soil carbonic anhydrase activity and associated soil water oxygen isotope composition*, Jones *et al.*, **Hydrol. Earth Syst. Sci.**, 21 (2017) 6363–6377.

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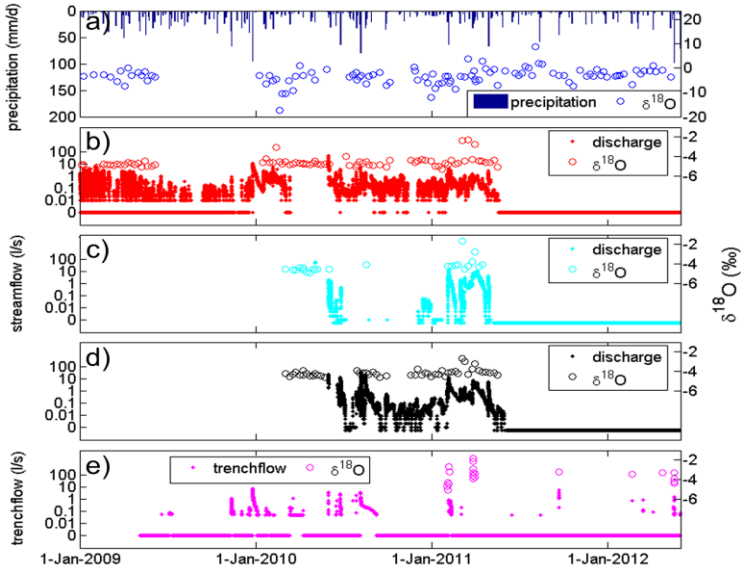
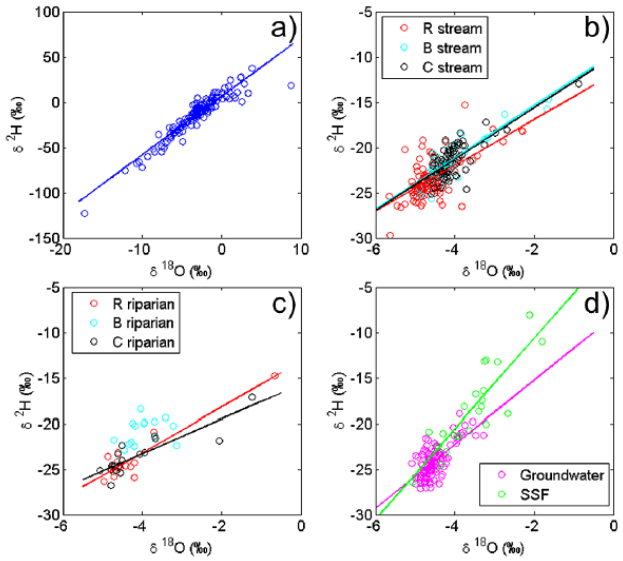
Isotopic H_2O Analysis

Hydrology Application Example: Determination of Streamwater Source Components

- Determination of streamwater source components near a river site: hydrologists combined a dual-isotope approach (δ^2H, $\delta^{18}O$) with the flow versus time charts (hydrographs) at various runoff sources around the river to build a conceptual model of streamflow generation in a low-angled terrain.
- Established link between various H_2O cycle components and identified unique hillslope, riparian, deep groundwater and streamflow compositions.





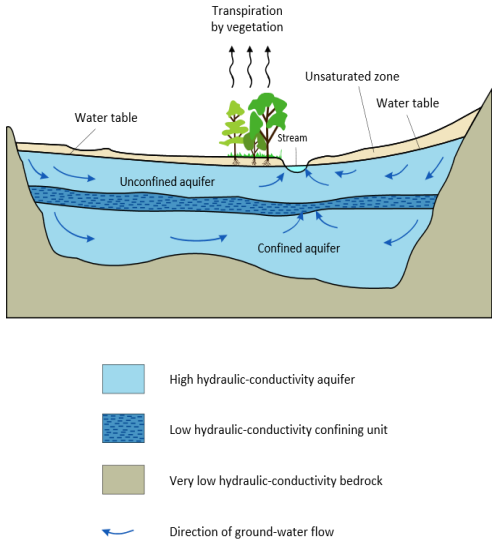
➢ *Where does streamwater come from in low-relief forested watersheds? A dual-isotope approach*, Klaus *et al.*, **Hydrol. Earth Syst. Sci.**, 19 (2015) 125–135.

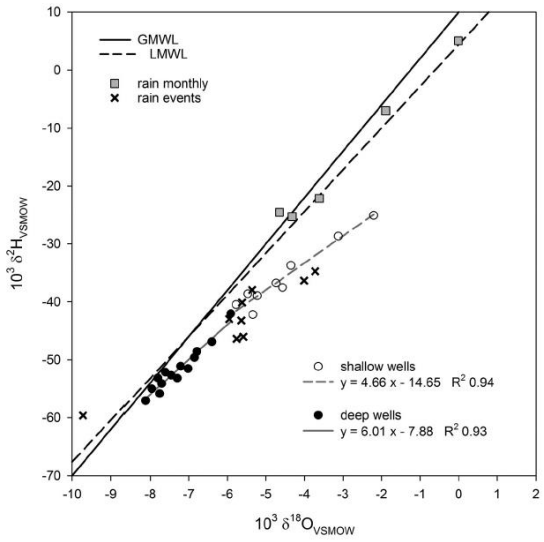
ABB LGR-ICOS Isotopic Analyzers in Ecology

Isotopic H_2O Analysis

Hydrology Application Example: Identification of Aquifer Recharge Mechanisms

- Dual-isotope study to characterize groundwater and identify possible recharge mechanisms of underground layers of water-bearing rocks (”aquifers”) in Namibia.
- Plots of δ^2H versus $\delta^{18}O$ regression lines in various shallow wells and deep wells against the Global Meteoric Water Line (GMWL) and the Local Meteoric Water Line (LMWL) provide mean isotopic composition of parent rainwater and propose aquifer differential water recharge mechanisms .
- Collected groundwater samples plot below both the LMWL and the GMWL, reflect a relative enrichment of heavier isotopes. Most groundwater samples, particularly those from deep wells plot close to the LMWL which indicates that they originated from modern precipitation infiltration.
- Isotopic composition of the deep wells suggests distinguishing between two recharge processes:
  1. Water that is affected by evaporation either before or after infiltration, in shallow wells.
  2. Water that infiltrates through fast preferential paths for deep groundwater wells.





➢ *Hydrogeochemical and isotope study of perched aquifers in the Cuvelai-Etosha Basin, Namibia*, Hamutoko *et al.*, **Isotopes in Environmental and Health Studies** (2017).

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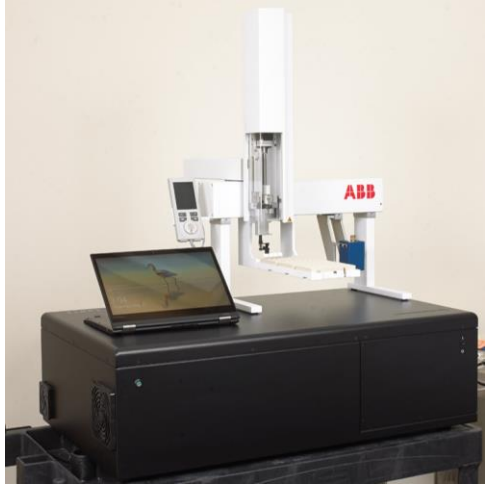
Isotopic H_2O Analysis

Hydrology Application Example: Intercomparison Study for Natural Waters Analysis

- IAEA organized an international water isotope intercomparison (WICO) for laboratory performance assessment of stable isotope determination ($\delta^{18}O$, $\delta^{2}H$) in natural waters.
- Analysis of 8 challenging samples in liquid mode. Reference isotope values of samples determined by consensus of four dual-inlet IRMS international reference labs and were *unknown* to participants.

Sample	Description
WICO-1	Danube River Water, Austria, filtered
WICO-2	Neusiedler See (lake water), Austria, filtered
WICO-3	Bow River Water, Canada, filtered
WICO-4	Ground Water Mix, Egypt, Austria, filtered
WICO-5	Vienna tap water and WICO-6 mix, research-grade methanol was added gravimetrically to produce a 0.05 % methanol/water volumetric ratio of contaminated water sample
WICO-6	Depleted Greenland Ice Sheet fern melt, unfiltered
WICO-7	Enriched Vienna groundwater w/ 99% D_2O and 99.9% $H_2{}^{18}O$ mixed to ensure a normal d-excess, isotopically enriched result, unfiltered
WICO-8	Synthetic seawater to 30 g/L (commercial Red Sea salt), mixed with WICO-6 to produce a slightly depleted result with a normal d-excess, unfiltered



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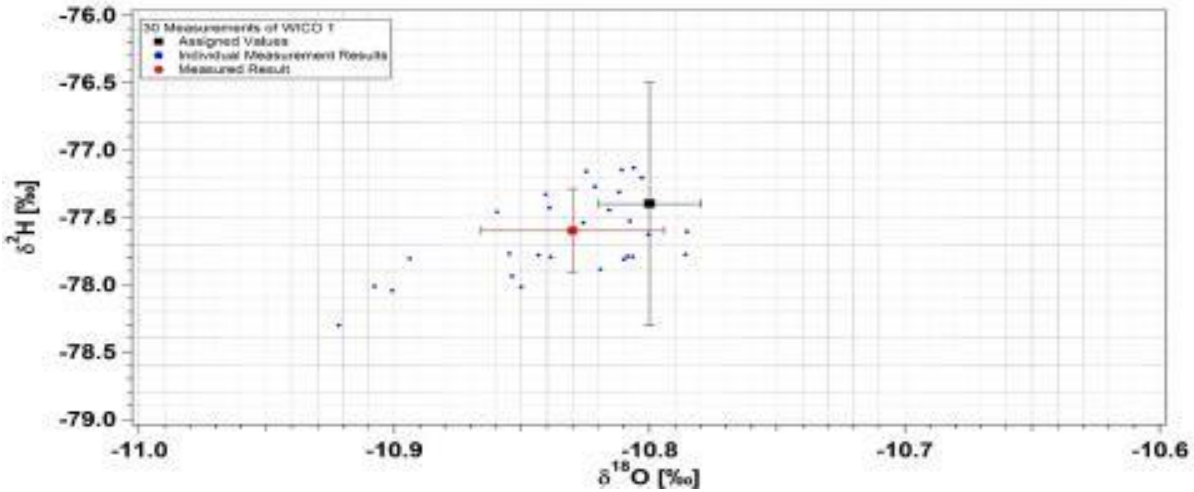
Isotopic H_2O Analysis

Hydrology Application Example: Intercomparison Study for Natural Waters Analysis



- Example: 30 individual δ^2H and $\delta^{18}O$ measurements of WICO-1 recorded with LGR-ICOS triple isotopic water analyzer (TIWA).
- Average measured value is very precise and in excellent agreement with the assigned value to within the error bars that represent the 1σ standard deviation per measurement.

	Assigned Values			TIWA Measured Values		
Sample	δ^2H [‰]	$\delta^{18}O$ [‰]	d-excess [‰]	δ^2H [‰]	$\delta^{18}O$ [‰]	d-excess [‰]
WICO-1	-77.4 ± 0.9	-10.80 ± 0.02	9.0	-77.6 ± 0.1	-10.83 ± 0.01	9.0
WICO-2	-41.7 ± 1.1	-5.11 ± 0.03	-0.8	-42.3 ± 0.1	-5.13 ± 0.02	-1.3
WICO-3	-168.3 ± 1.0	-22.01 ± 0.05	7.8	-168.9 ± 0.0	-22.07 ± 0.02	7.6
WICO-4	0.5 ± 1.1	-0.50 ± 0.05	4.5	-0.1 ± 0.2	-0.55 ± 0.08	4.3

- Each measurement of sample or standard involved 10 injections to account for memory effects and to improve measurement precision.
- Differences between values assigned by IRMS and TIWA are within the convoluted measurement uncertainties.
- TIWA measures all three isotope ratios simultaneously, faster and with substantially less maintenance than IRMS.

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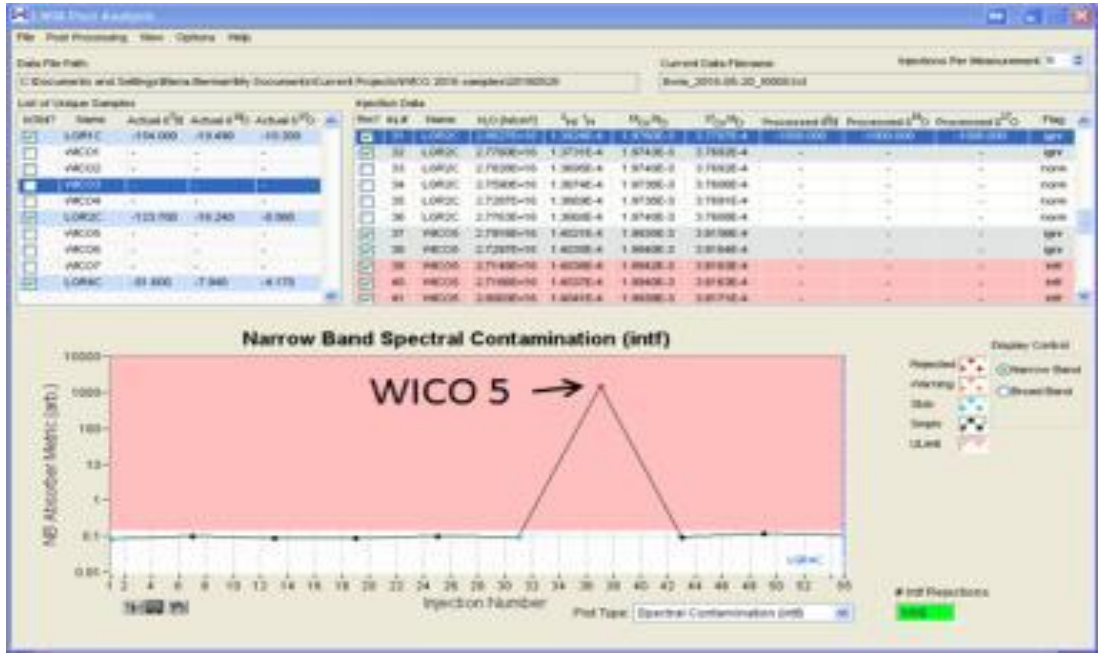
Isotopic H_2O Analysis

Hydrology Application Example: Intercomparison Study for Natural Waters Analysis

- ABB TIWA Post-Analysis Software features a Spectral Contaminant Identifier to flag and discard contaminated samples.
- SCI metrics can be used to correct measured values for spectral contamination.
- SCI module clearly flagged WICO-5 sample as contaminated. The large narrowband metric and minimal broadband metric suggested that the contaminant was methanol.
- WICO-5 was measured multiple times, a correction function was applied to each measurement, and the corrected measurements were averaged to get a final value in agreement with the assigned value.

	Assigned (‰)	Raw Measured (‰)	Corrected (‰)
δ^2H	-114.3 ± 1.1	-100.1 ± 0.3	-114.0 ± 0.2
$\delta^{18}O$	-15.68 ± 0.02	-6.36 ± 0.06	-15.42 ± 0.21
d-excess	11.1	-49	9.4



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Isotopic H_2O Analysis

Hydrology Application Example: Intercomparison Study for Natural Waters Analysis

- Intercomparison results also very good for highly depleted sample (WICO-6), enriched sample (WICO-7) and sea-salted sample (WICO-8).
- Differences between IAEA assigned values and TIWA are within the convoluted uncertainties.
- Results demonstrate that sample-to-sample memory effects were appropriately mitigated.

	Assigned Values			TIWA Measured Values		
Sample	**δ^2H, ‰**	**$\delta^{18}O$, ‰**	**d-excess ‰**	**δ^2H, ‰**	**$\delta^{18}O$, ‰**	**d-excess ‰**
WICO-6	-323.7 ± 0.9	-41.41 ± 0.04	7.6	-323.7 ± 0.0	-41.44 ± 0.01	7.9
WICO-7	55.7 ± 1.6	5.61 ± 0.08	10.8	54.6 ± 0.1	5.63 ± 0.03	9.5
WICO-8	-17.6 ± 1.2	-3.45 ± 0.10	10.0	-18.8 ± 0.1	-3.50 ± 0.04	9.2

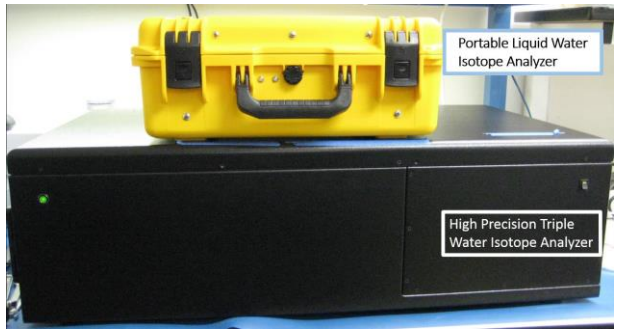
➢ *ABB LGR TIWA Performance - IAEA WICO Intercomparison,* **Application Note**, 2017.

ABB LGR-ICOS Isotopic Analyzers in Ecology

Isotopic H_2O Analysis

Hydrology Application Example: Antarctic Glacier Ice Composition Analysis

- Collaboration University of Ottawa / NASA / ABB using 2 LGR-ICOS instruments for measurements of δ^2H and $\delta^{18}O$ from samples of antarctic lake and glacier ice:
  1. Benchtop GLA431-TIWA.
  2. Portable GLA132-LWIA (15 kg , 18cm x 36cm x 47cm).
- Traditionally, discrete water samples are collected and transported to a laboratory for isotope analysis. Due to associated labor and expense, isotope studies have generally been limited in scope and time-resolution.
- Increased time resolution of field sampling with portable instrument illuminates substantially greater short-term variability than generally observed during discrete sampling. It also opens possibility to rapidly identify which water samples would be particularly interesting for further laboratory investigation.



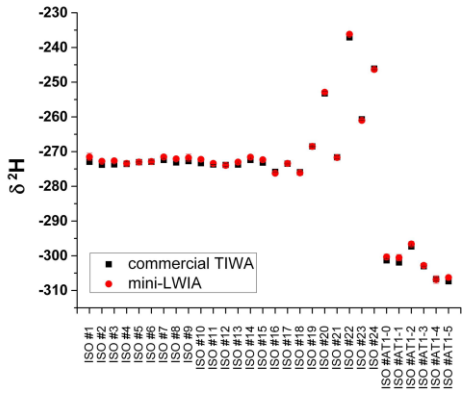
➢ *A Portable, Field-Deployable Analyzer for Isotopic Water Measurements*, Berman *et al.*, **American Geophysical Union**, Fall Meeting 2015, abstract id. H43I-1648.

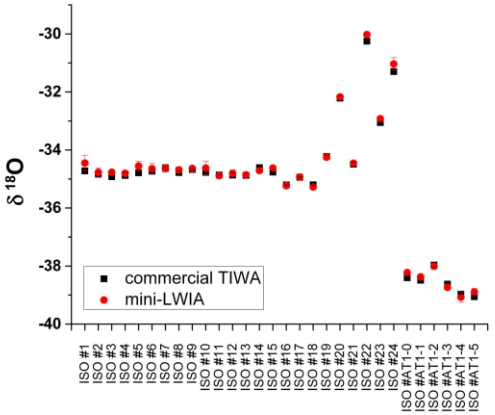
ABB LGR-ICOS Isotopic Analyzers in Ecology

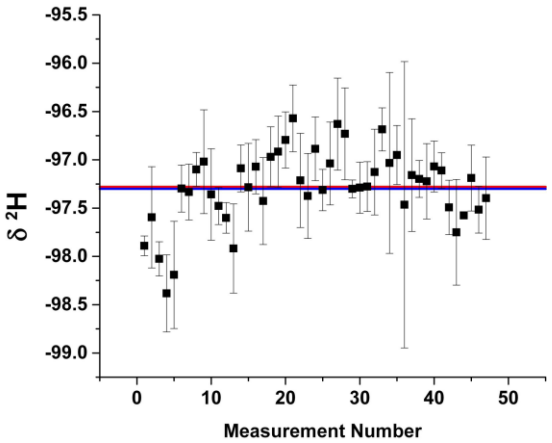
Isotopic H_2O Analysis

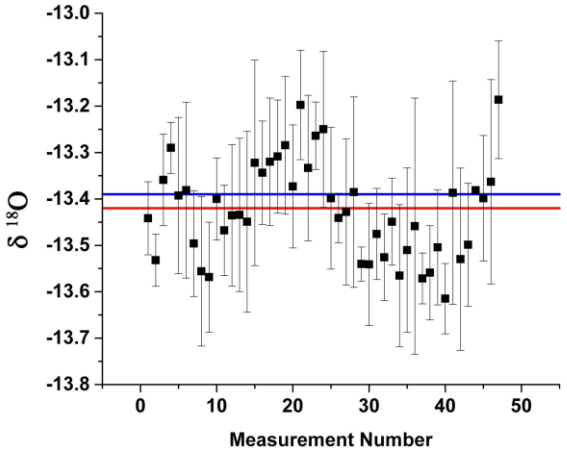
Hydrology Application Example: Antarctic Glacier Ice Composition Analysis

- Comparative isotopic measurements of field samples show that portable LGR-ICOS instrument provides accuracy comparable to benchtop instrument.
- Repeat measurements (47) of distilled water sample with known isotope ratio show a measured precision (1σ) of 0.4‰ for δ^2H and 0.1‰ for $\delta^{18}O$.
- The laboratory accuracy is well within the laboratory precision.









➢ *A Portable, Field-Deployable Analyzer for Isotopic Water Measurements*, Berman *et al.*, **American Geophysical Union**, Fall Meeting 2015, abstract id. H43I-1648.

ABB LGR-ICOS Isotopic Analyzers in Ecology

Isotopic N_2O Analysis

ABB LGR-ICOS Isotopic Analyzers in Ecology

Isotopic N_2O Analysis

ABB Solution: Portfolio

- LGR-ICOS isotopic nitrous oxide analyzers portfolio and associated properties (gas samples only):

Model Name	Application - Isotopes	$\delta^{17}O$	$\delta^{18}O$	$\delta^{15}N$	$\delta^{15}N^{\alpha}$	$\delta^{15}N^{\beta}$	H_2O	N_2O
GLA451-N2OI2	Enhanced Performance QC Benchtop Isotopic Nitrous Oxide Analyzer		X	X	X	X	X	X
GLA451-N2OI3	Enhanced Performance QC Benchtop Isotopic Nitrous Oxide Analyzer - Advanced	X	X	X	X	X	X	X

- N_2O: 3rd most important long-lived greenhouse gas. LGR-ICOS isotopic N_2O analyzers provide continuous and precise analysis of the site-specific isotopic ratios $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$, $\delta^{17}O$ and $\delta^{18}O$ of N_2O directly to elucidate processes in soil and wastewater incubation experiments (*e.g.* bacterial denitrification) as well as in ambient air for N source allocation.
- LGR-ICOS "Enhanced Performance" (EP) series of isotopic N_2O analyzers incorporate proprietary internal thermal control and provide ultra-stable measurements with unsurpassed precision, accuracy and drift.
- Intramolecular distribution of ^{15}N in N_2O (site preference S_P) is an indicator of the microbial origin and geochemical cycle of N_2O because many biological and chemical processes have distinct isotopic signatures.
- ^{17}O measurement capability of model GLA451-N2OI3 allows to better understand mass-independent O isotope atmospheric fractionation mechanisms and source apportionment for nitrates and NO_x species.

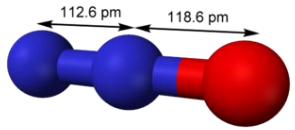
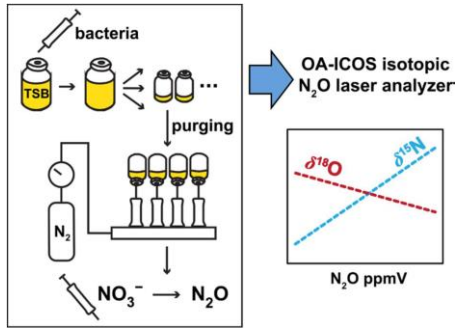


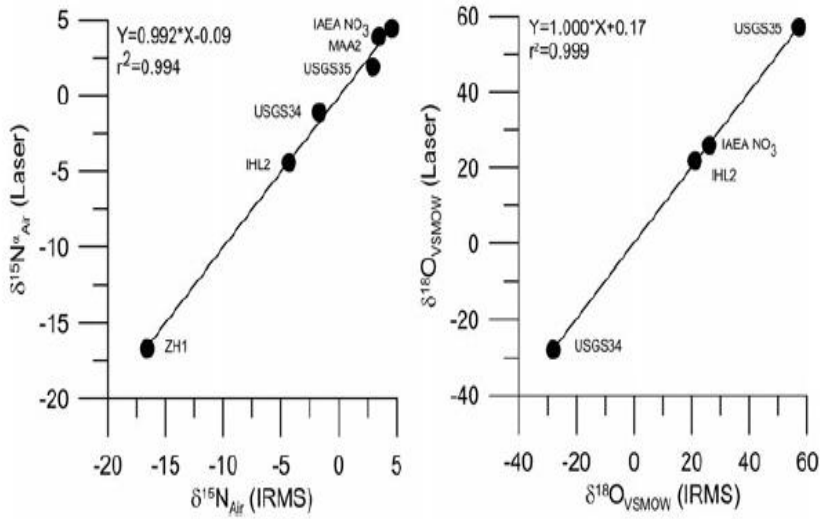
ABB LGR-ICOS Isotopic Analyzers in Ecology

Isotopic N_2O Analysis

Nitrate Analysis Application Example: Identification of Nitrogen Sources and Dynamics in Aquatic Systems

- Excessive concentrations of nitrate (NO_3^-) stemming from agriculture runoff and municipal wastewater entering rivers, lakes, groundwater, and marine estuaries have negative impacts that include eutrophication, dead zones in coastal oceans, and drinking water deterioration in many worldwide aquifers.
- Stable isotopes of nitrate are crucial tracers of nutrient N sources and dynamics in aquatic systems. Several methods such as bacterial denitrification, Cd-azide reduction or the new one-step Ti(III) chloride reduction method developed by IAEA and University of Massachusetts enable to reduce NO_3^- to N_2O and perform fast nitrate analysis by measuring $\delta^{15}N$, $\delta^{18}O$, and $\delta^{17}O$ with an LGR-ICOS analyzer as an interference-free, faster and cheaper alternative to IRMS.





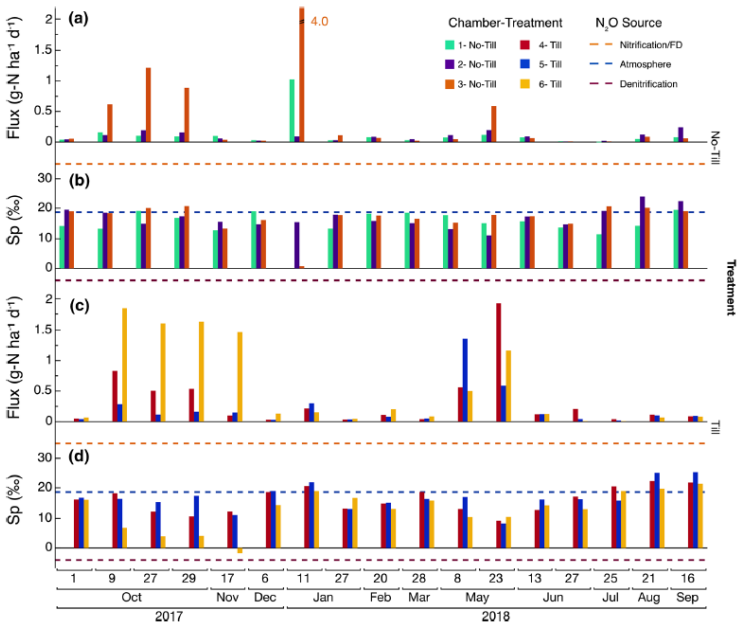
- *Combining Denitrifying Bacteria and Laser Spectroscopy for Isotopic Analyses ($\delta^{15}N$, $\delta^{18}O$) of Dissolved Nitrate*, Soto *et al.*, **Anal. Chem.**, 87 (2015) 7000–7005.
- *N and O isotope ($\delta^{15}N\alpha$, $\delta^{15}N\beta$, $\delta^{18}O$, $\delta^{17}O$) analyses of dissolved NO_3^- and NO_2^- by the Cd-azide reduction method and N_2O laser spectrometry*, Waseenaar *et al.*, **Rapid Commun Mass Spectrom.**, 32 (2018) 184–194.
- *A Ti(III) reduction method for one-step conversion of seawater and freshwater nitrate into N_2O for stable isotopic analysis of $^{15}N/^{14}N$, $^{18}O/^{16}O$ and $^{17}O/^{16}O$*, Altabet *et al.*, **Rapid Commun Mass Spectrom.**, 33 (2019) 1227–1239.

ABB LGR-ICOS Isotopic Analyzers in Ecology

Isotopic N_2O Analysis

Nitrate Analysis Application Example: Influence of Tillage and Fertilization on Grassland N_2O Emissions

- Agriculture: largest cause of N_2O emissions as a consequence of alteration of soil microbial activity, fertilization, cultivation of N fixing plants and various management practices. Microbial nitrification and denitrification are the primary sources of N_2O and *Sp* is an indicator affected by those processes.
- Understanding soil microbial processes and response of N_2O production pathways to tilling and fertilization that influence soil aerobicity, carbon availability and inorganic nitrogen enables development of guidelines to manage and mitigate agricultural N_2O emissions.
- Scientists used LGR-ICOS isotopic N_2O analyzer to measure N_2O flux and evaluate microbial sources of N_2O using concentration and S_P values in flux chambers from a grassland tilling and agricultural fertilization experiments.
- Temporal and spatial variability of N_2O flux and S_P results suggest influence of different soil microbial processes on atmospheric N_2O emissions in different ecosystems.



➢ The *influence of tillage and fertilizer on the flux and source of nitrous oxide with reference to atmospheric variation using laser spectroscopy*, Ostrom *et al.*, **Biogeochemistry**, 152 (2021) 143-159.

ABB LGR-ICOS Isotopic Analyzers in Ecology

Isotopic CO_2 Analysis

ABB LGR-ICOS Isotopic Analyzers in Ecology

Isotopic CO_2 Analysis

ABB Solution: Portfolio

- LGR-ICOS isotopic carbon dioxide analyzers portfolio and associated properties (gas samples only):

Model Name	Application - Isotopes	$\delta^{13}C$	$\delta^{17}O$	$\delta^{18}O$	H_2O	CO_2
GLA132-CCIA2	Ultraportable Carbon Dioxide Isotopic Analyzer	X		X	X	X
GLA331-CCIA1	Enhanced Performance Rackmount Carbon Dioxide Isotopic Analyzer - Elevated	X		X		X
GLA331-CCIA2	Enhanced Performance Rackmount Carbon Dioxide Isotopic Analyzer	X		X	X	X
GLA351-CCIA3	Enhanced Performance QC Rackmount Carbon Dioxide Isotopic Analyzer	X	X	X		X
GLA431-CCIA2	Enhanced Performance Benchtop Carbon Dioxide Isotopic Analyzer	X		X	X	X
GLA431-CCIA1	Enhanced Performance Benchtop Carbon Dioxide Isotopic Analyzer - Elevated	X		X		X

- ABB portfolio comprises several instruments to report isotopic ratios $\delta^{13}C$, $\delta^{17}O$, $\delta^{18}O$ and [CO_2] simultaneously and in real time.
- GLA132-CCIA2 ultraportable analyzer designed for field studies, can be integrated in complete measurement suite.
- GLA331-CCIA1 and GLA431-CCIA1 “elevated CO_2” models designed for analysis of samples containing high levels of CO_2 (2%-100%).
- For laboratory-based analysis, GLA331/GLA351/GLA431 “Enhanced-Performance (EP)“ series incorporate proprietary internal thermal control for ultra-stable measurements with unsurpassed precision, accuracy and drift.
- OA-ICOS analyzers can perform isotopic CO_2 measurements either in continuously flowing air samples (at up to 1 Hz frequency) or in discrete samples, using gas-tight syringe.

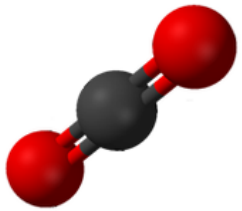


ABB LGR-ICOS Isotopic Analyzers in Ecology

Isotopic CO_2 Analysis

Soil Respiration Applications: Background

- Soil respiration refers to the CO_2 flux released from the soil surface to the atmosphere as a result of microbial and root respiration. It is the second largest terrestrial carbon flux.
- Analysis of soil respiration is needed for:
  - Agricultural management: practices that optimize soil organic carbon sequestration as well as water and nutrient
  - Efficiency enhancement for food security and sustainable agriculture.
  - Climate-smart agriculture: by making soils and plants more resilient to climate change and by reducing greenhouse gas emissions.

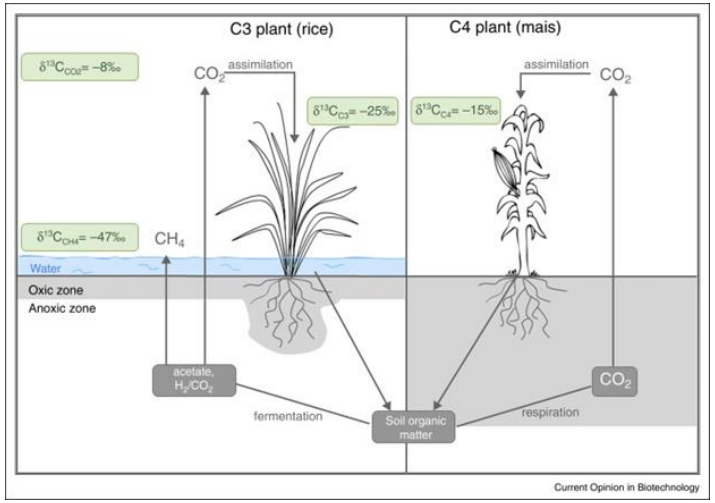


ABB LGR-ICOS Isotopic Analyzers in Ecology

Isotopic CO_2 Analysis

Soil Respiration Applications: Parameters of Interest

- Stable CO_2 isotopes are indicators to study biogeochemical processes and fluxes that occur at the soil-plant-atmosphere interface.
- The $\delta^{13}C$ measurements provide information on physiological history of soil carbon and help identify the sources of CO_2 soil emissions such as photosynthesis, natural gas combustion, fossil fuels, landfills or other sources.
- Oxygen isotopes aid in inferring interaction between CO_2 and soil waters as $\delta^{18}O$ and $\delta^{17}O$ ratios of soil CO_2 are determined by its hydrological cycle.
- The soil respiration parameters are often measured using chamber-based, “mini-tower”, and soil-gas-well-based methods.
- Traditional sampling of soil-produced CO_2 done at specific time intervals, $\delta^{13}C$ and $\delta^{18}O$ analysed offline with isotope ratio mass spectrometry (IRMS).

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Isotopic CO_2 Analysis

Soil Respiration Applications: Challenges of Analytical Measurements

- Challenges of traditional method based on IRMS:
  - High sampling costs.
  - Excessive time consumption for sampling and analysis.
  - Increased sampling error and low temporal resolution.
  - Non steady-state conditions may arise within the chamber due to increased CO_2 concentrations, which in turn hinders the diffusion of $^{12}CO_2$ more strongly than that of heavier $^{13}CO_2$.
  - It has also been found that ^{18}O of the CO_2 inside a chamber is significantly influenced by the ^{18}O of the surface soil water, as an equilibrium isotopic exchange happens during the upward diffusive movement of soil CO_2.

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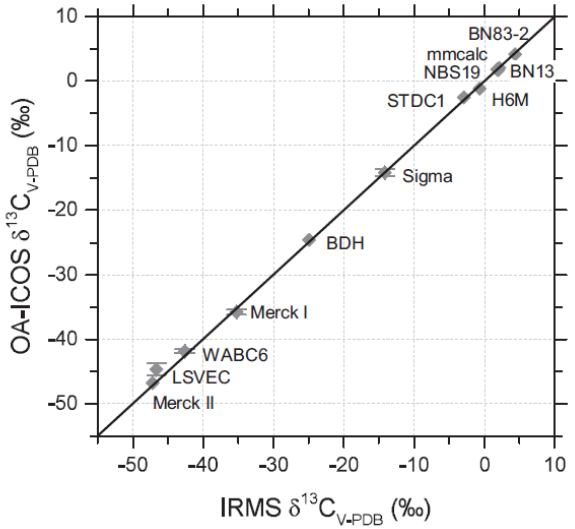
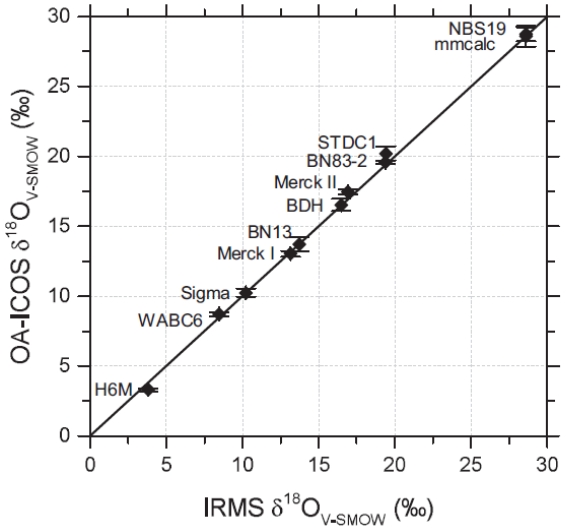
Isotopic CO_2 Analysis

Soil Respiration Applications: Advantages of ABB Solution

- Laser-based CO_2 carbon isotope analysis using ABB LGR–ICOS analyzers is a recent alternative approach to IRMS with similar accuracy.
- Simpler and faster approach that provides robust data for real-time, *in situ* measurements of CO_2 concentration and isotopic ratios.
- Enables detection of vertical CO_2 concentration profiles, analysis of temporal dynamics of soil CO_2 concentration, and isotopic signature of soil CO_2 across different soil layers, aiding in identifying and quantifying various sources of CO_2 across depth profile.





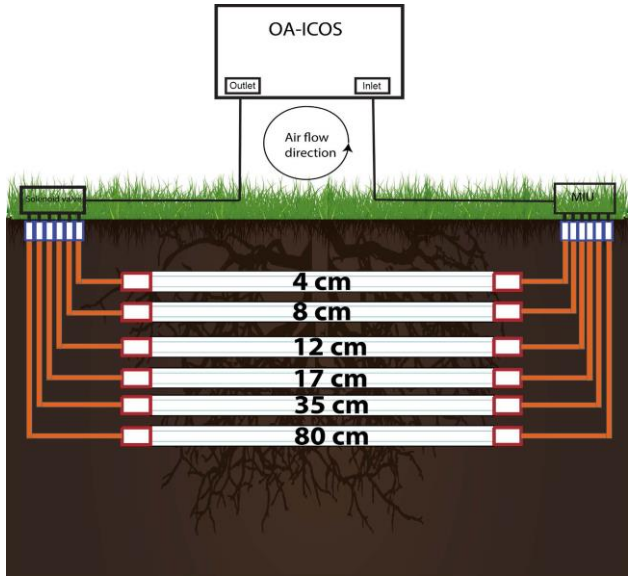
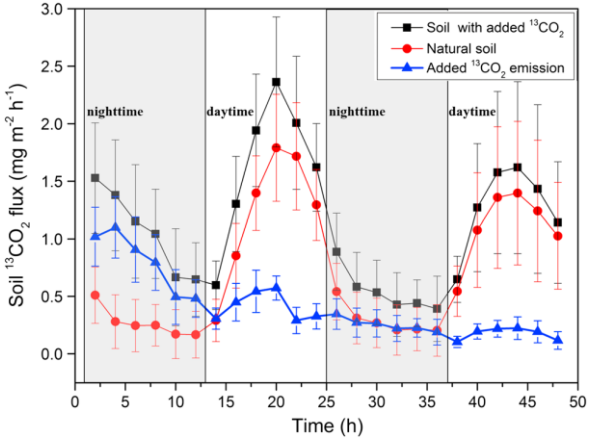


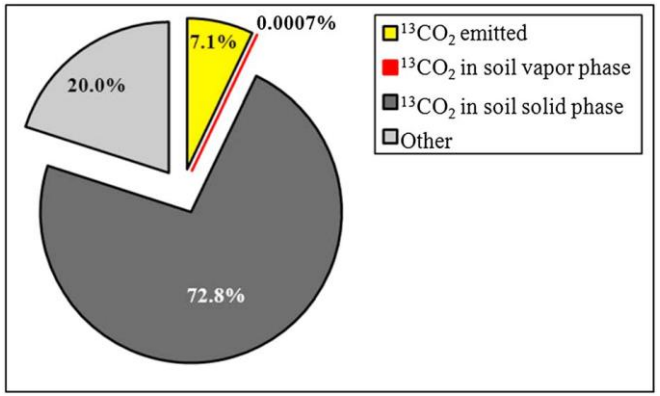
ABB LGR-ICOS Isotopic Analyzers in Ecology

Isotopic CO_2 Analysis

Soil Respiration Application Example: Elucidation of CO_2 Absorption Mechanisms in Desert Soils

- Over 40% of earth land surface consists of dry lands. Amount of CO_2 fixed in desertic regions exceeds productivity of desert plants or biological soil crusts. To understand that discrepancy and mechanisms of CO_2 uptake and partitionining in deserts, Beijing Forestry University scientists have quantified CO_2 fluxes in Mu Us desert.
- Inserted steel boxes in desert soil and injected controlled amounts of ”labelled” $^{13}CO_2$. After one day, $^{13}CO_2$ fluxes over the boxes were measured using LGR-ICOS Isotopic CO_2 Analyzer connected to soil flux chamber.
- Also studied partitioning of CO_2 between soil solid and vapor phases by measuring relative $\delta^{13}C$ for gas samples extracted from soil and solid soil samples.
- Results indicate that atmospheric CO_2 enters soil and dissolves in soil water. Most of dissolved CO_2 returns to atmosphere when temperature increases. Remaining dissolved CO_2 reacts with some matters in soil and is stored in soil solid phase.





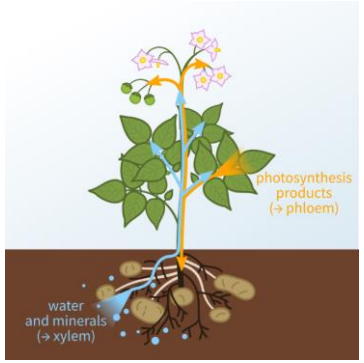
➢ *Abiotic CO_2 uptake from the atmosphere by semiarid desert soil and its partitioning into soil phases*, Liu *et al.*, **Geophys. Res. Lett.**, 42 (2015) 5779–5785.

ABB LGR-ICOS Isotopic Analyzers in Ecology

Isotopic CO_2 Analysis

Plant Respiration Application Example: Understanding Dynamics of Organic Energy Transport in Trees

- Assessing the effect of K and water deficit on phloem transport of photosynthates in eucalypt trees using ^{13}C labelling and isotopic analysis to monitor CO_2 uptake and organic compounds dynamics though trees.
- Scientists applied different K/H_2O supply treatments to trees and estimated the velocity of C transfer by comparing time lags between uptake of $^{13}CO_2$ and its recovery in trunk CO_2 efflux recorded at different heights. Also analyzed dynamics of labelled photosynthates recovered in foliage and in phloem sap extracted from trees inner bark. Appearance of ^{13}C in trunk and root CO_2 effluxes was determined by LGR-ICOS isotopic CO_2 analyzer connected to 48 chambers (two trunk chambers and two root chambers on each tree).
- Results suggest that K deficiency leads to reductions in photosynthetic C supply and velocity, and in C demand by sink organs. They also showed that a large part of labelled assimilates are exported out of the phloem and replaced by unlabelled C.



➢ *In situ $^{13}CO^2$ pulse labelling of field-grown eucalypt trees revealed the effects of potassium nutrition and throughfall exclusion on phloem transport of photosynthetic carbon*, Epron *et al.*, **Tree Physiology**, 36 (2015) 6-21.

ABB LGR-ICOS Isotopic Analyzers in Ecology

Isotopic CH_4 Analysis

ABB LGR-ICOS Isotopic Analyzers in Ecology

Isotopic CH_4 Analysis

ABB Solution: Portfolio

- LGR-ICOS isotopic methane analyzers portfolio and associated properties (gas samples only):

Model Name	Application - Isotopes	$\delta^{13}C$	CH_4
GLA431-MCIA1	Enhanced Performance Benchtop Methane Carbon Isotopic Analyzer	X	X
GLA631-MCIA2	Carbon Isotopic Ratio in Methane Deep Water Gas Analyzer	X	X

- LGR-ICOS instruments report fractions of $^{12}CH_4$ and $^{13}CH_4$ and thus the isotopic ratio $\delta^{13}C$ and CH_4 concentration simultaneously and in real time.
- GLA431-MCIA1 benchtop analyzer provides highly sensitive and stable measurements for measurements of CH_4 concentrations expected in ambient air near landfills and natural gas leaks (10-500 ppm).
- GLA631-MCIA2 Deep Water Gas Analyzer submarine system combines membrane separation with LGR-ICOS technology to provide *in situ* measurements of $\delta^{13}C$ and CH_4 at depths to 2500 meters, for applications in which higher levels of CH_4 may be encountered (500-10,000ppm) such as mud logging and oil and gas exploration.

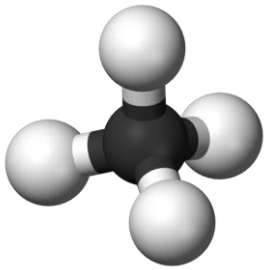
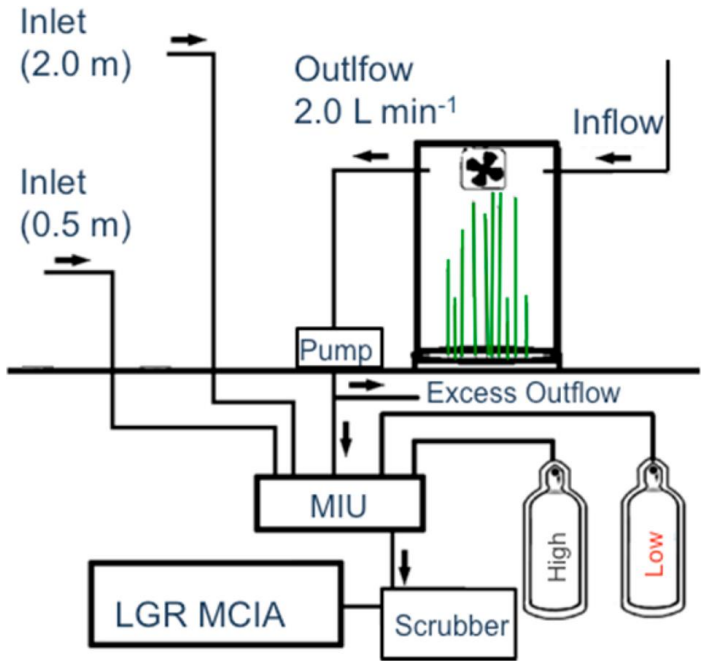


ABB LGR-ICOS Isotopic Analyzers in Ecology

Isotopic CH_4 Analysis

Application Example: Understanding Origin and Dynamics of CH_4 Emissions at Tidal Marsh

- It is challenging to quantify magnitude of emissions and separate influence of anthropogenic activities from climate variability on CH_4 concentrations. Stable isotopes can help distinguishing methanogenic pathways (*e.g.* CO_2 reduction, acetate fermentation) of CH_4 sources to the atmosphere.
- Sampling frequency using IRMS is limited, instrument size and operational requirements pose challenges for field deployment.
- Deployment of LGR-ICOS Isotopic CH_4 Analyzer connected to removable chambers at tidal marsh over multiple days to study flux variations. Instrument operates over wide dynamic range of CH_4 concentration and is accurate to <±0.5‰ (within accuracy of IRMS) with minimal dependence of measured $\delta^{13}C$ on CH_4 concentration (<1‰) .
- Study demonstrates how CH_4 fluxes vary by one order of magnitude over 2-day deployment periods, and shows 17‰ variability in $\delta^{13}CH_4$ of emitted CH_4 during growing season.



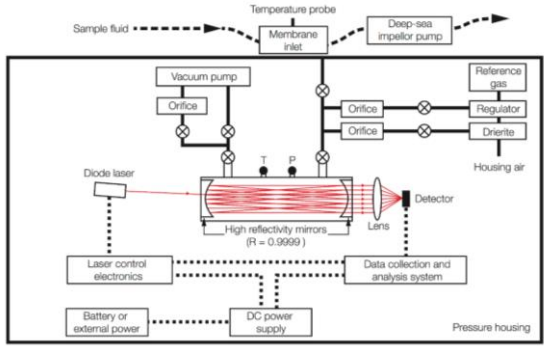
➢ *Validation and Application of Cavity-Enhanced, Near-Infrared Tunable Diode Laser Absorption Spectrometry for Measurements of Methane Carbon Isotopes at Ambient Concentrations*, Mortazavi *et al.*, **Environ. Sci. Technol.**, 47 (2013) 11676–11684.

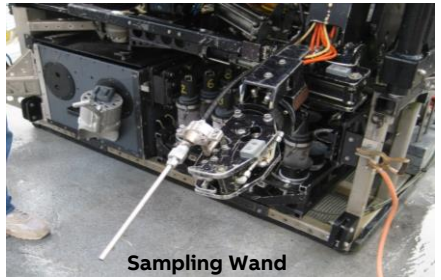
ABB LGR-ICOS Isotopic Analyzers in Ecology

Isotopic CH_4 Analysis

Application Example: *In Situ* Characterization of Methane Sources in Deep Ocean

- Deployment of GLA632-MCIA2 onboard research vessel Point Lobos by a group of marine scientists from Harvard University to CH_4 seeps in Monterey Bay (-962m) provided the first *in situ* stable isotope-based characterization of how anaerobic methane oxidation affects CH_4 flux from seep sediments.
- Data gathered demonstrate efficacy of LGR-ICOS analyzer as an effective platform for analysis of $\delta^{13}C_{CH4}$ within deep-sea environments.
- Monitoring of changes in $\delta^{13}C_{CH4}$ can provide a more sensitive means for early detection of important changes in subsurface tectonic activity to predict earthquakes and eruptions.





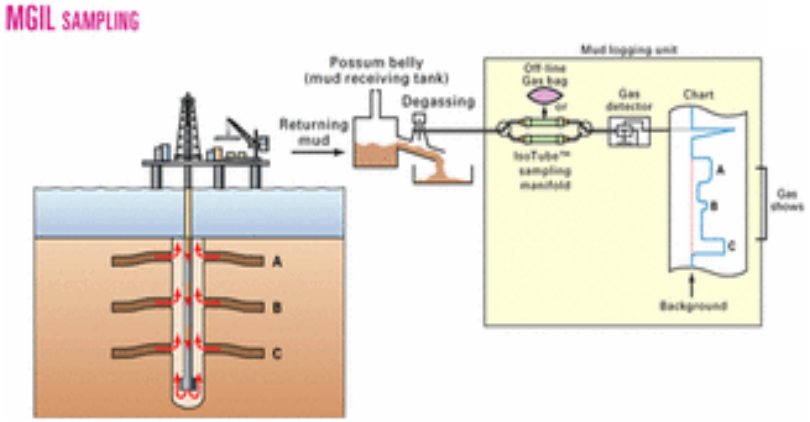
➢ *Characterizing the Distribution of Methane Sources and Cycling in the Deep Sea via in Situ Stable Isotope Analysis*, Wankel *et al.*, **Environ. Sci. Technol.**, 2013, 47 (2013) 1478–1486.

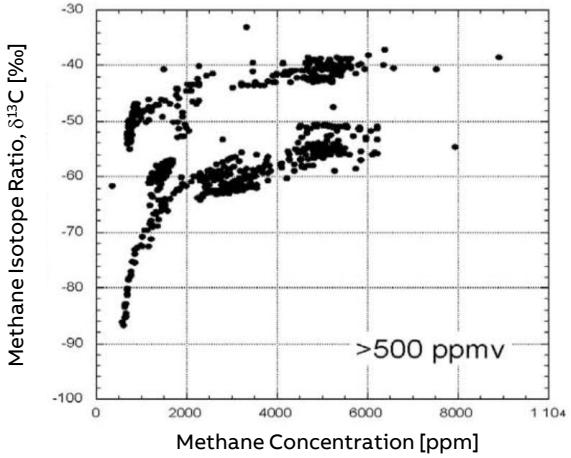
ABB LGR-ICOS Isotopic Analyzers in Ecology

Isotopic CH_4 Analysis

Application Example: Mud Logging Analysis

- Mud logging involves rig-site monitoring and assessment of information that comes to surface while drilling. Provides well owners and producers with information about the lithology and fluid content of the borehole.
- Traditionally people would utilize degassing and GC to measure concentrations of hydrocarbons, and determination of $^{13}C/^{12}C$ isotope ratios in CH_4 requires shipping samples to shore for IRMS measurements.
- LGR-ICOS Methane Carbon Isotope Analyzer reports $\delta^{13}CH_4$ ratio as well as $[CH_4]$ continuously and without sample preparation, as a faster, simpler and on-site alternative to IRMS.
- Used in over 60 units in the field for energy (oil & gas) exploration and optimization of the drilling process.





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