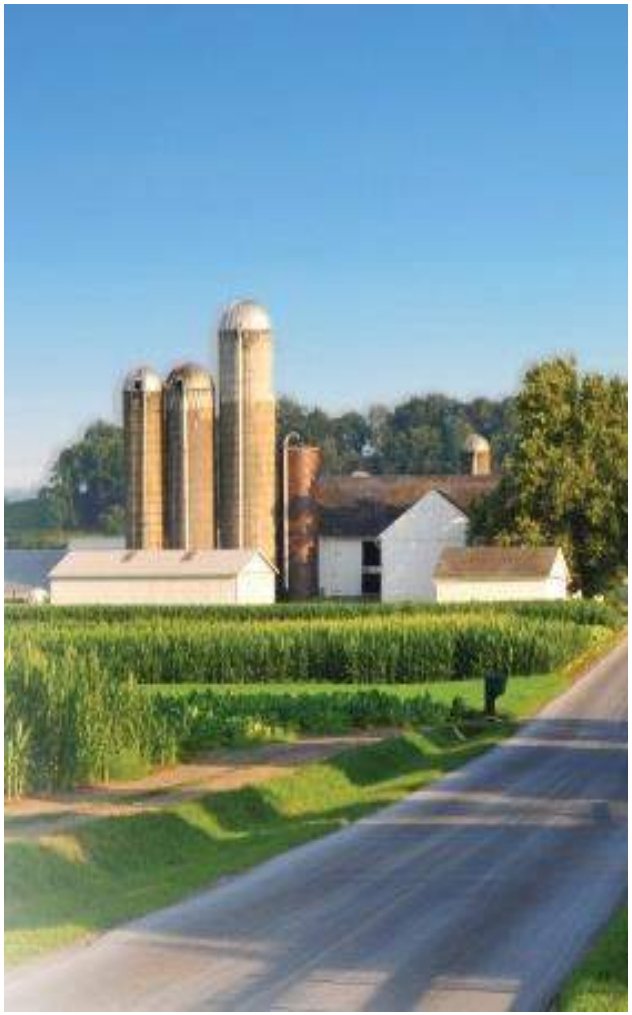
Picarro Green House Gas (GHG) analyzers



- Chosen by the world's most discerning scientists and accepted across federal and state agencies
- Featuring real-time continuous data streamed directly to your network
- Designed for easy deployment in remote locations
- Ruggedly built to require minimum maintenance

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Environmental testing of each analyzer

1. Thermal soak at -10 & 50 ºC (2 hrs)
   - Measure cylinder for 15 minutes after removal to check performance
2. Thermal ramp up and down between 20 & 40 ºC
   - Ramp 5º C / 10 min
   - Soak every 5 ºC for 20 min
   - Measure cylinder during thermal ramp & track drift

Picarro Environmental Test Chamber

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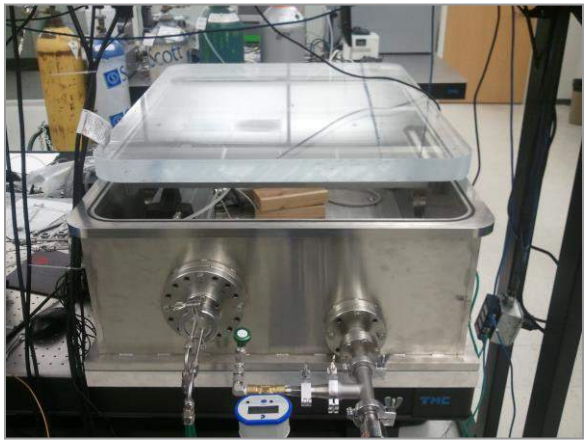
Tests for field conditions

- We stress-tests all instruments
  - Drop Test
  - Vibration test
  - Thermal test
- Flight analyzers undergo a pressure test to ensure proper function at altitude

Picarro Vibration Test



Picarro Pressure Test Chamber

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High precision data in real time

Example for G2301

Guaranteed Performance Specifications, in air	CO_2	CH_4	H_2O
Precision (1-σ of: Raw 5 sec / 5 min avg data) *Guaranteed over operating conditions specified below*	< 70 ppb / 25 ppb	< 0.5 ppb / 0.22 ppb	< 80 ppm / 30 ppm
Max Drift at STP (over 24 hrs / 1 month) *(peak-to-peak, 50-minute average) *Guaranteed over operating conditions specified below*	< 120 ppb / 500 ppb	< 1 ppb / 3 ppb	< 100 ppm ± 0.5% of reading
***Automated Determination of Dry Mol Fraction**	Included	Included	n/a
Operating Range	0 - 1000 ppm	0 - 20 ppm	0 - 7 %v (39 °C dew pt) non-condensing
Guaranteed Specifications Range	300 - 700 ppm	1 - 3 ppm	0 - 3 %v (25 °C dew pt) non-condensing
Measurement Interval (Data Rate)	< 5 seconds	< 5 seconds	< 5 seconds
Gas Response: Rise/Fall time (10-90 % / 90-10 %)	< 3 seconds	< 3 seconds	< 3 seconds
Measurement Cell Control	Temperature: +/- 0.005 °C & Pressure: +/- 0.0002 atm		

* Picarro calculates drift by subtracting the min from the max of 50 min averages taken over 30 hrs of testing

*Comparison between NOAA, LSCE, MPI, EMPA and FMI in Rella et al. 2012

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Picarro Green House Gas (GHG) analyzers

Advantages and Benefits

- High-precision, low drift measurements
- Multiple gas species in a single analyzer
- High reliability
- Easiest to use, up and running in minutes
- Requires no sample preparation
- Continuous measurements & sample flow
- Field & laboratory deployable

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Picarro GHG analyzers are present on all 7 continents

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Waliguan Station
Linan Station
2008/07/03
CMA Headquarters in Beijing
Great Wall of China
Longfengshan Station
Shangdianzi Station

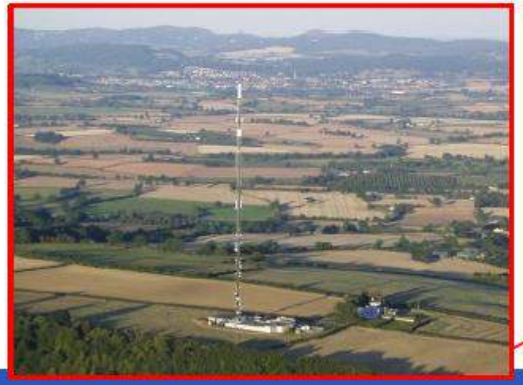
LSCE – CO & CO2 analysis – Eiffel Tower, Paris, France

UK Deriving Emissions linked to Climate Change Network

Mace Head

Angus

Ridge Hill



Tacolneston

University of BRISTOL

www.metoffice.gov.uk/atmospheric-trends

Met Office

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Picarro GHG analyzer family

Carbon Dioxide + Carbon Monoxide Analyzers

- G2302 → CO_2 **CO** H_2O precision analyzer
- G2401→ CO_2 **CO** CH_4 H_2O precision analyzer
- G2401-*m* → CO_2 **CO** CH_4 H_2O for flight

Carbon Dioxide + Methane Analyzers

- G2301→ CO_2 CH_4 H_2O precision analyzer
- G2301-*m* → CO_2 CH_4 H_2O for flight @ 1 Hz
- G2301-*f*→ CO_2 CH_4 H_2O for EC flux @ 10 Hz

Picarro GHG analyzers for flight measurements

Images courtesy
Huilin Chen
Max Planck Institute
Jena, Germany

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Three NASA deployments used to verify satellite measurements

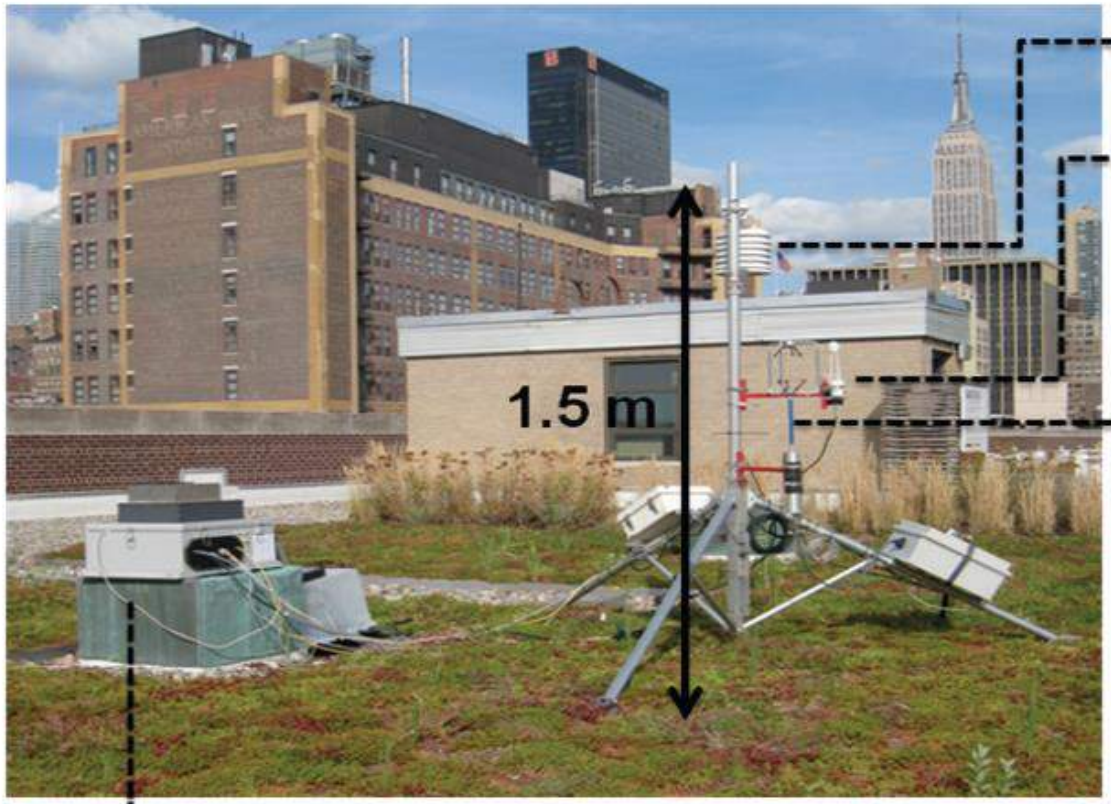
Inside a wing pod of the Alpha Jet

SIERRA UAV

Railroad Valley Playa, NV desert

Wade McGillis, Columbia University

Eddy Covariance measurements on a roof top in NYC



Vaisala RH/T

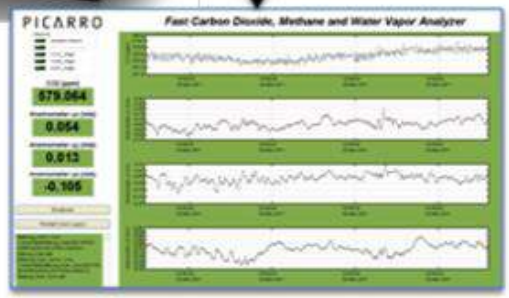
CO_2, & H_2O LiCOR 7500

Analog Signals

Gill WindmasterPro 3-D Sonic Anemometer

RS232

Sync Data



Picarro in a Peltier thermoelectric temperature box with 2m inlet tube

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Two other important GHG have come into focus:

Methane and N_2O have a high global warming potential (GWP) on a short term

GWP = Global Warming Potential

Gas	GWP 20 years	GWP 100 years	GWP 500 years	Radiative Forcing (W m^{-2})
CO_2	1	1	1	1.66
CH_4	72	25	7.6	0.48
N_2O	114	289	153	0.16

Important contribution !

Source: IPCC AR4, 2007

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Picarro (GHG) analyzer, including 5 species: The new G2508

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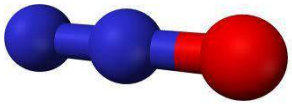
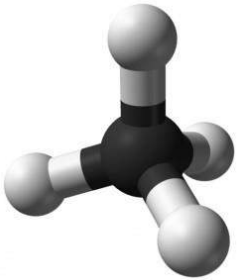
Measure critical greenhouse gases with one analyzer

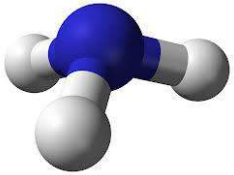


N_2O: < 5 ppb precision in 5 min

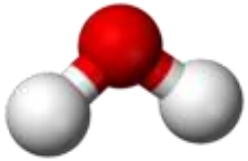


CH_4: < 5 ppb precision in 5 min

CO_2: < 200 ppb precision in 5 min



NH_3: < 1 ppb precision in 5 min



H_2O: < 100 ppm precision in 5 min

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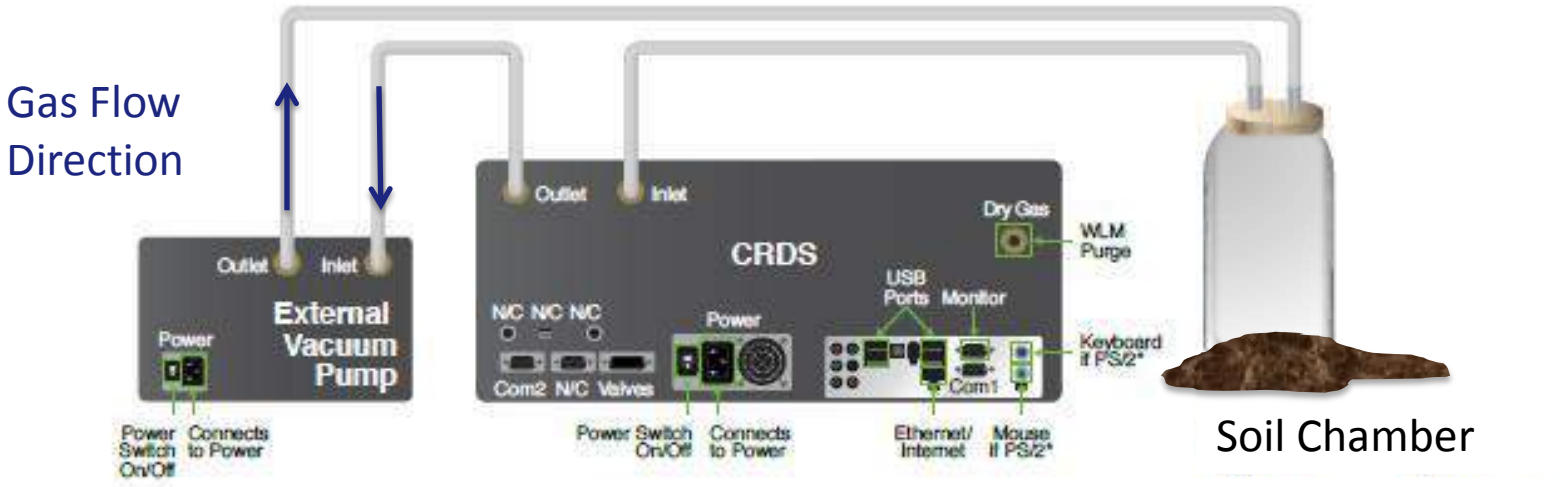
Experimental Set Up

- Analyzer: Picarro G2508
- Gas flow rate: 100 sccm
- Data measurement rate: 7 seconds
- Configuration: The analyzer was attached to a glass sample chamber with two modified VCR stainless steel attachments in a closed-system configuration as shown below
- Total system volume = 495 mL



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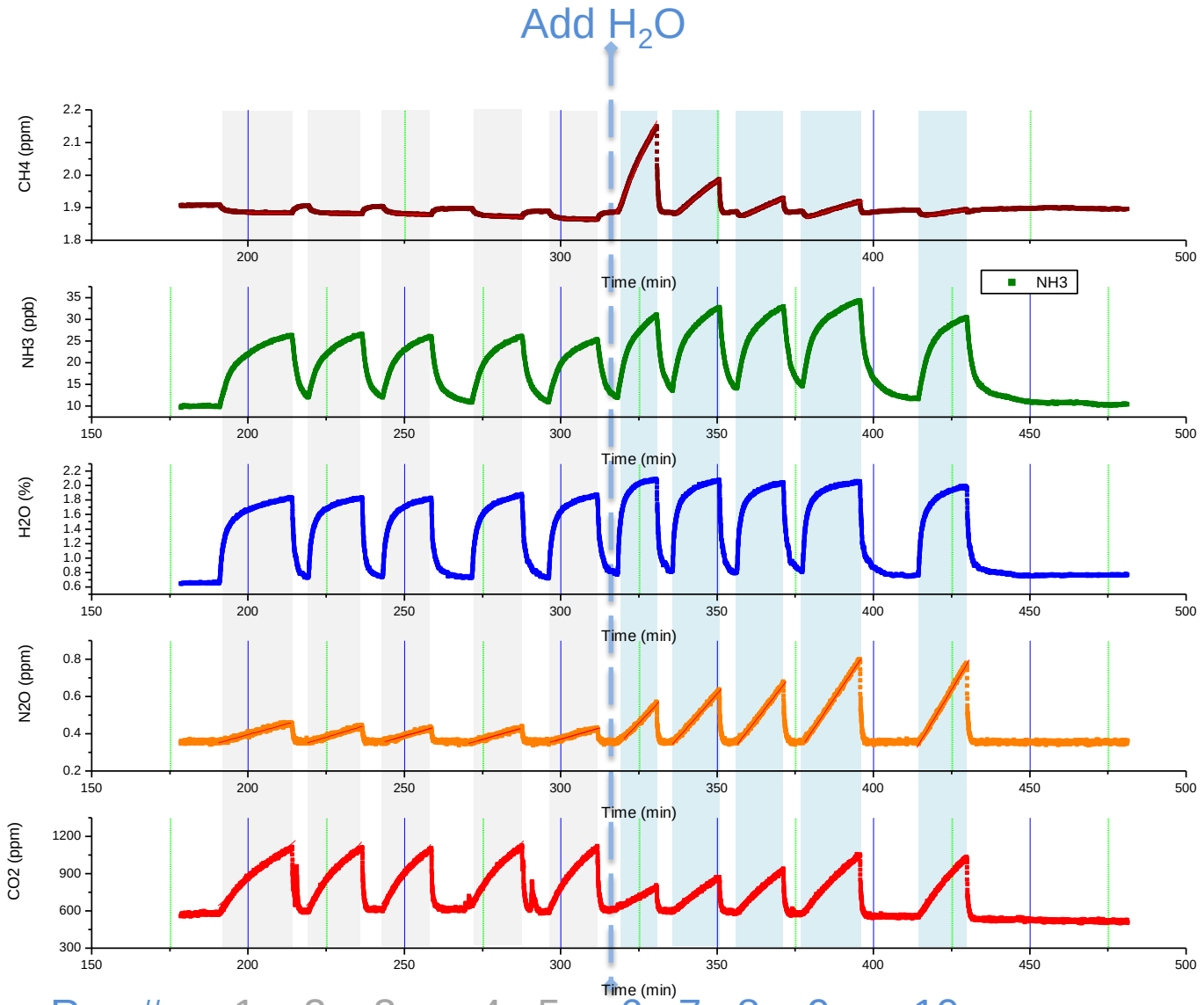
Laboratory Soil Flux: CH_4, NH_3, H_2O, N_2O, CO_2

Shaded areas indicate periods where chamber was closed



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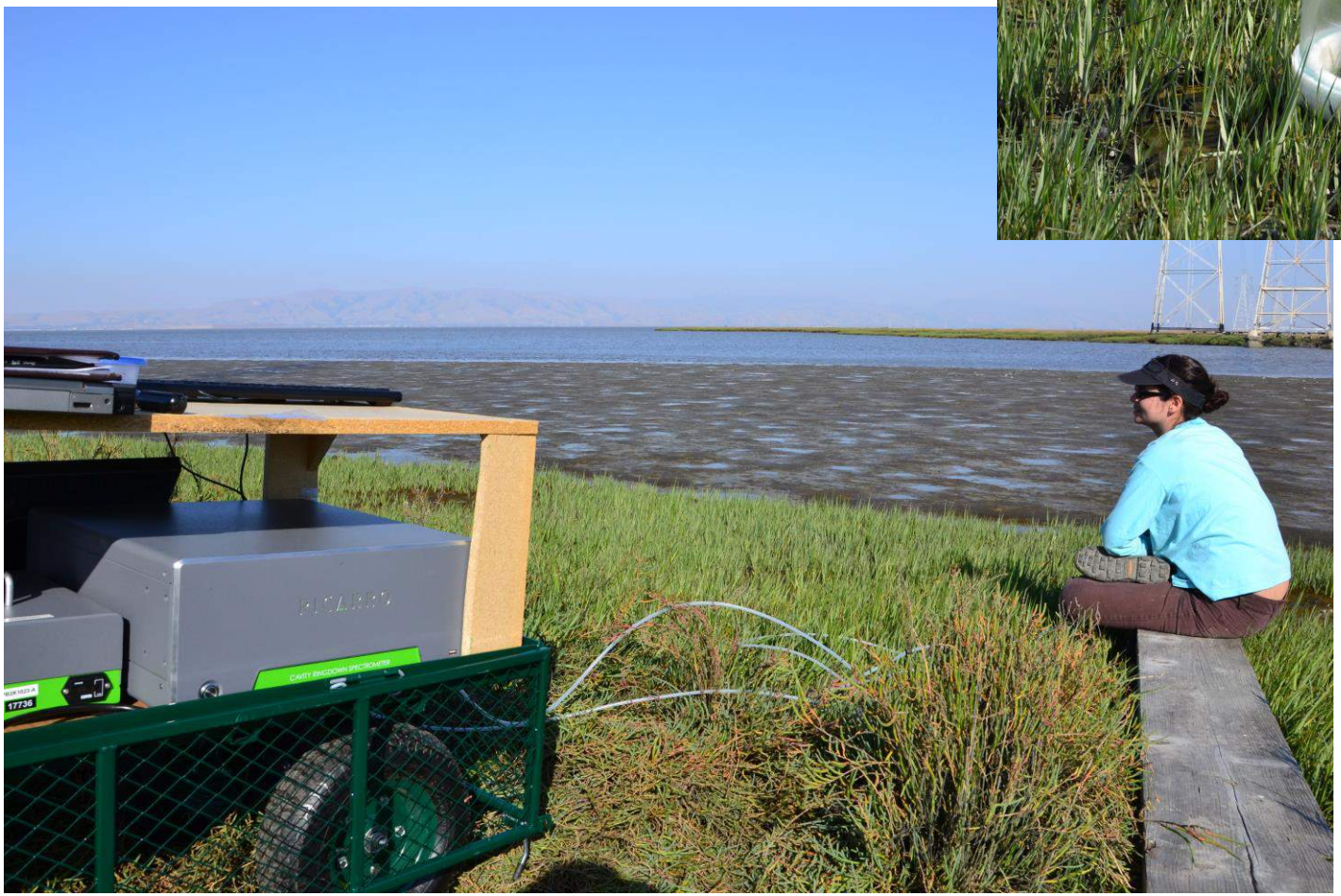
Measuring GHG from a Salt Marsh in Palo Alto, CA
Serena Moseman from Univ. of Rhode Island



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Picarro stable isotopes analyzers

- Nitrogen isotope ^{15}N, and its isotopomers
- Carbon isotope ^{13}C on carbon dioxide and methane
- Water isotopologues $H_2{}^{18}O$ and $HD^{16}O$

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Nitrogen isotopomers $\delta^{15}N^{\alpha}$ and $\delta^{15}N^{\beta}$ and N_2O measurements at ambient concentrations

Analyzer: Picarro G5101-i (Mid-IR Laser source)

Guaranteed Performance Specifications			
Target Species	**Precision 1-σ**		**Concentration Range**
	10 min avg	**100 sec avg**	(ppm N_2O in Air)
N_2O (Concentration)	< 0.05 ppb	< 0.1 ppb	0.3 - 2
$\delta^{15}N$, $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$	< 0.5 ‰	< 1 ‰	0.3 - 2

Big advantage compared to IRMS

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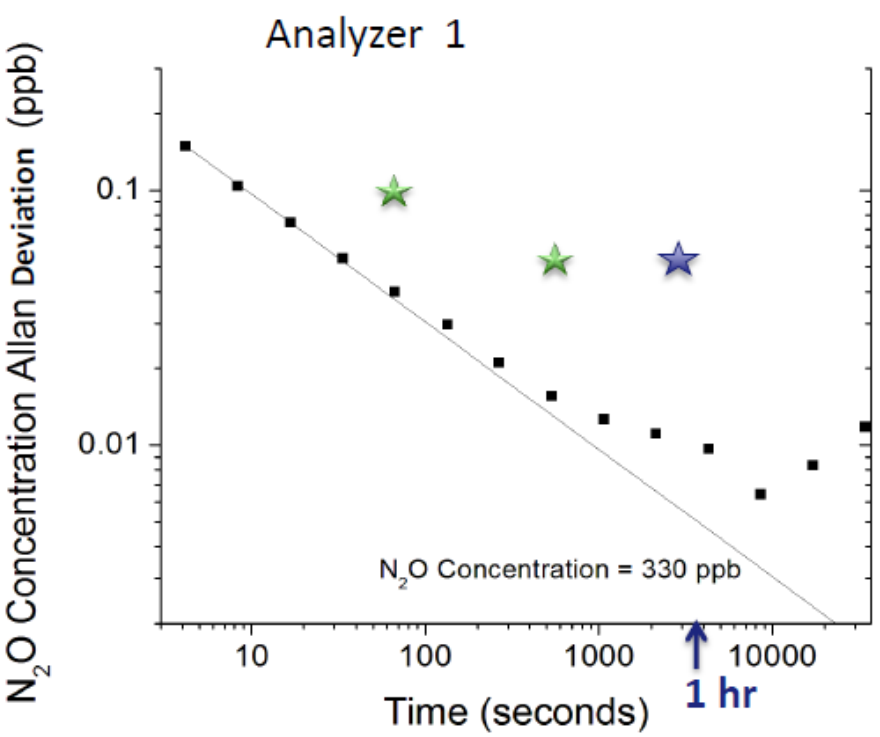
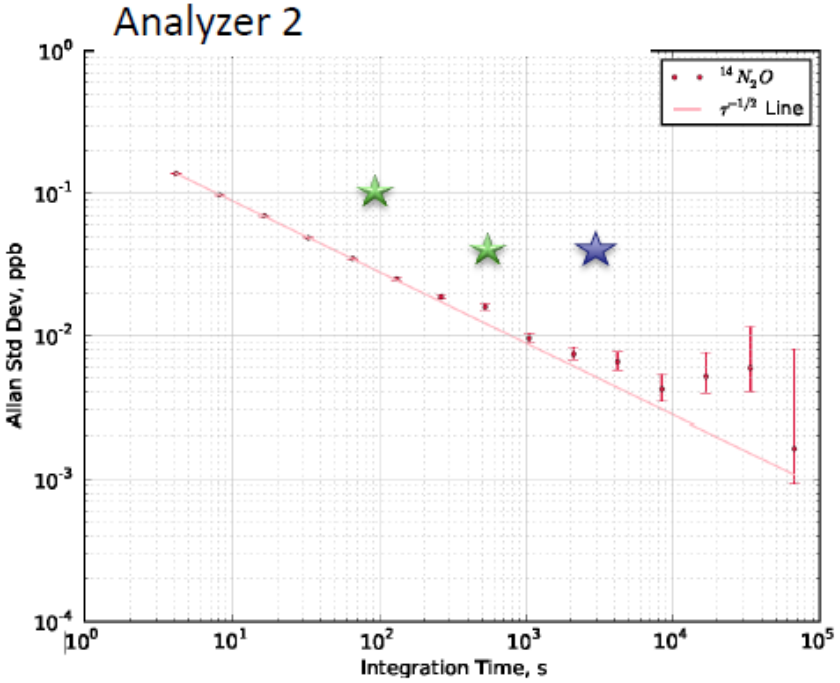
Allan deviation for ambient N_2O measurements





Both analyzers perform better than the Picarro specifications and the GAW inter-laboratory uncertainty recommendations

Picarro Guaranteed Specification

GAW Specification

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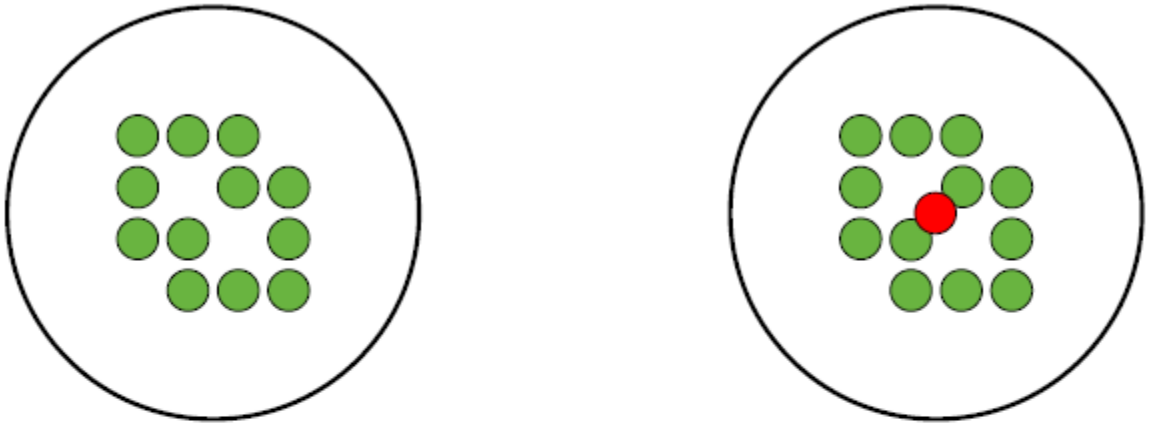
Carbon Isotopes



Naturally occurring

Safe, non-radioactive

One is heavier than the other

Different behaviors – simple tracers

Measure Precise Enough – Spot the difference!

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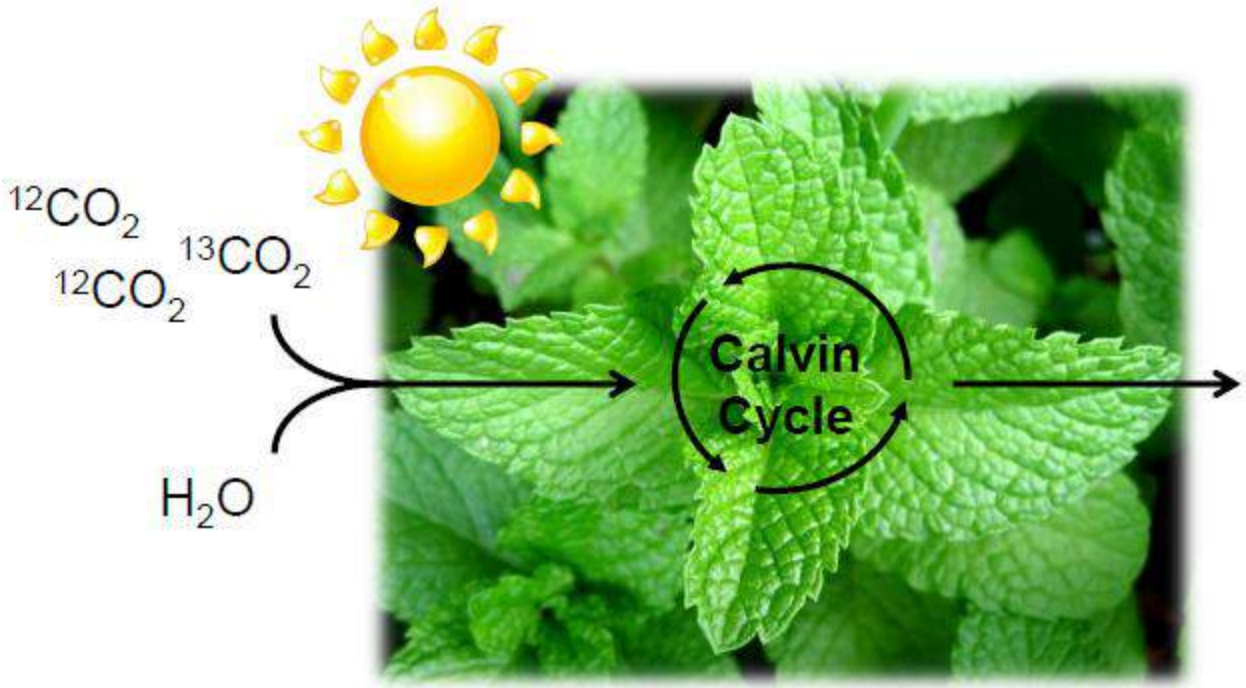
Photosynthesis: ^{12}C is biochemically preferred



Plant ^{13}C values depend on:
-Metabolic Pathway (C3 or C4)
-Species
-Environment

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Carbon isotopes: $\delta^{13}C$ in CO_2 and CH_4

- **Excellent precision** for both d13C measurements simultaneously.
- **Most stable results**: Excellent temperature, pressure stability.
- Two d13C-CH4 modes**:** High Precision for the best results for near-ambient applications and High Dynamic Range for higher concentrations.
- Know all the concentrations: 12CO2, 13CO2, 12CH4, 13CH4, H2O
- No drying needed. No CO2 removal needed for d13C-CH4 measurement.
- **Get a complete isotopic picture of your samples for maximum carbon cycle insight.**

CRDS Analyzer for Isotopic Carbon in CO_2 and CH_4

Model G2201-*i*

PICARRO

ChemDetect™ and interferences

Detect interference in complex gas matrix often found in oil & gas operations

ChemDetect™ is a new layer of analysis to detect any species that influences the optical spectrum. ChemDetect™ looks at three types of spectral distortion

- Abnormally large fit residuals
- Changes in the baseline level
- Changes in the baseline slope

The purpose of ChemDetect™ is to alert a user to the possibility that the measurements are being affected by unexpected gas matrixes.

Picarro G2201-i :
One Analyzer with many applications and solutions

Costech EA or CM	Closed System	SSIM2	OI 1030W	Mobile Kit
				
Bulk sample analysis for isotope labs	Ecology, soil & agriculture Science	Small, high-concentration samples	Oceanography hydrology	Fugitive emissions, energy exploration

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Picarro Combustion Module + CRDS : Measures Bulk $\delta^{13}C$ in CO_2 in everything that burns

- Portable – easily moved from lab to field
- Unique combination of high precision and ease-of-use
- High throughput – 148 samples in 24 hours
- Fix costs are 2x to 3x less than EA-IRMS,
- Continuous costs 5x to 10x less

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Picarro Combustion Module + CRDS application: Honey Fraud detection

Honey is one of a number of natural products that are regularly tested for adulteration with lower cost sweeteners such as High Fructose Corn Syrup (HFCS) and cane sugar. Such frequent adulteration poses a problem for scrupulous honey producers and importers who end up operating at a cost disadvantage. The problem is significant enough that U.S. Customs and Border Protection agents regularly test for adulteration in honey shipments.

- Carbon isotopic fractionation is related to CO_2 uptake and enzymatic processes (C3 or C4 plants)
- Bees feed on C3 plants with a $\delta^{13}C$ of approx. – 27 permil and produce a protein, that is found in the honey
- Corn is a C4 plant with a $\delta^{13}C$ of approx. – 11 permil

→ adding corn syrup to honey will lead to an increase in $\delta^{13}C$

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Process

- 6 honey samples and the protein extracted from each sample were sourced from a honey importer for analysis
- The CO_2 resulting from combustion of samples was collected via Picarro's Liaison high throughput interface
- $\delta^{13}C$ was measured on the Picarro CM-CRDS

Sample	Protein (‰)	Honey (‰)	C4 Sugars (%)
Sample 1	-26.57	-27.35	-4.6
Sample 2	-26.79	-27.57	-4.6
Sample 3	-26.27	-25.45	5.0
Sample 4	-26.21	-27.84	-9.8
Sample 5	-26.55	-26.19	2.1
Sample 6	-27.80	-27.45	1.9

Comments

- These results show that an AOAC method can be run on a Picarro CM-CRDS
- Negative values should be reported as 0%
- Values above 7% are indicative of significant amounts of C4 sugars
- All six honey samples were unaltered following these criteria

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Another example: Sparking waters, is the CO_2 really natural?

- Problem: Sparkling waters advertised as “Natural” are not
- Question: Is this sparkling water natural?
- Several waters, labeled as “Natural” and “Artificial” were measured for their carbon isotopes to test a single isotope detection method.

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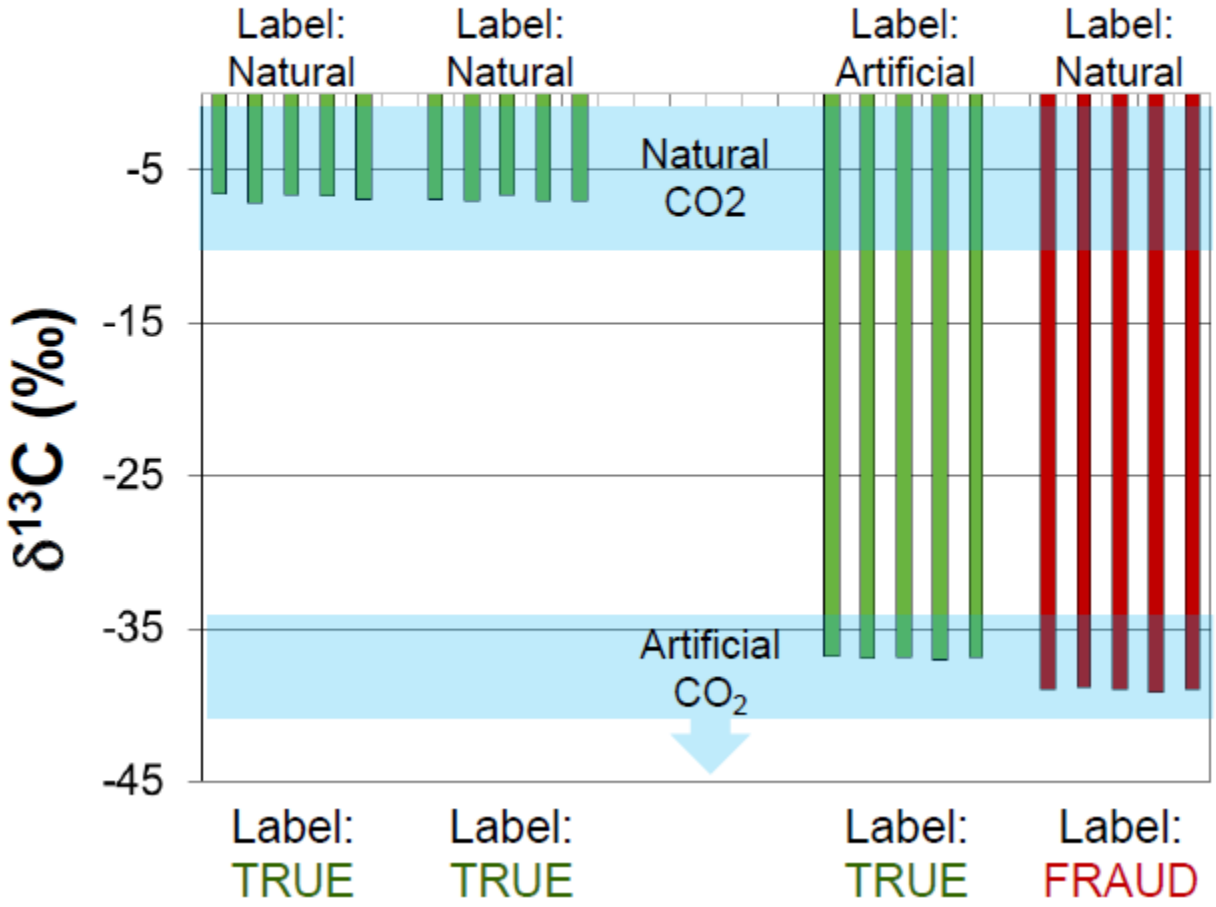
Not in all the cases…

- Single isotope measurement compared to known natural ranges proves label fraud in a sparkling water



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B2221: Simultaneous δD and $\delta^{13}C$:

World's First and Only Integrated Solution for Simultaneous Bulk ^{13}C + D Isotope Analysis

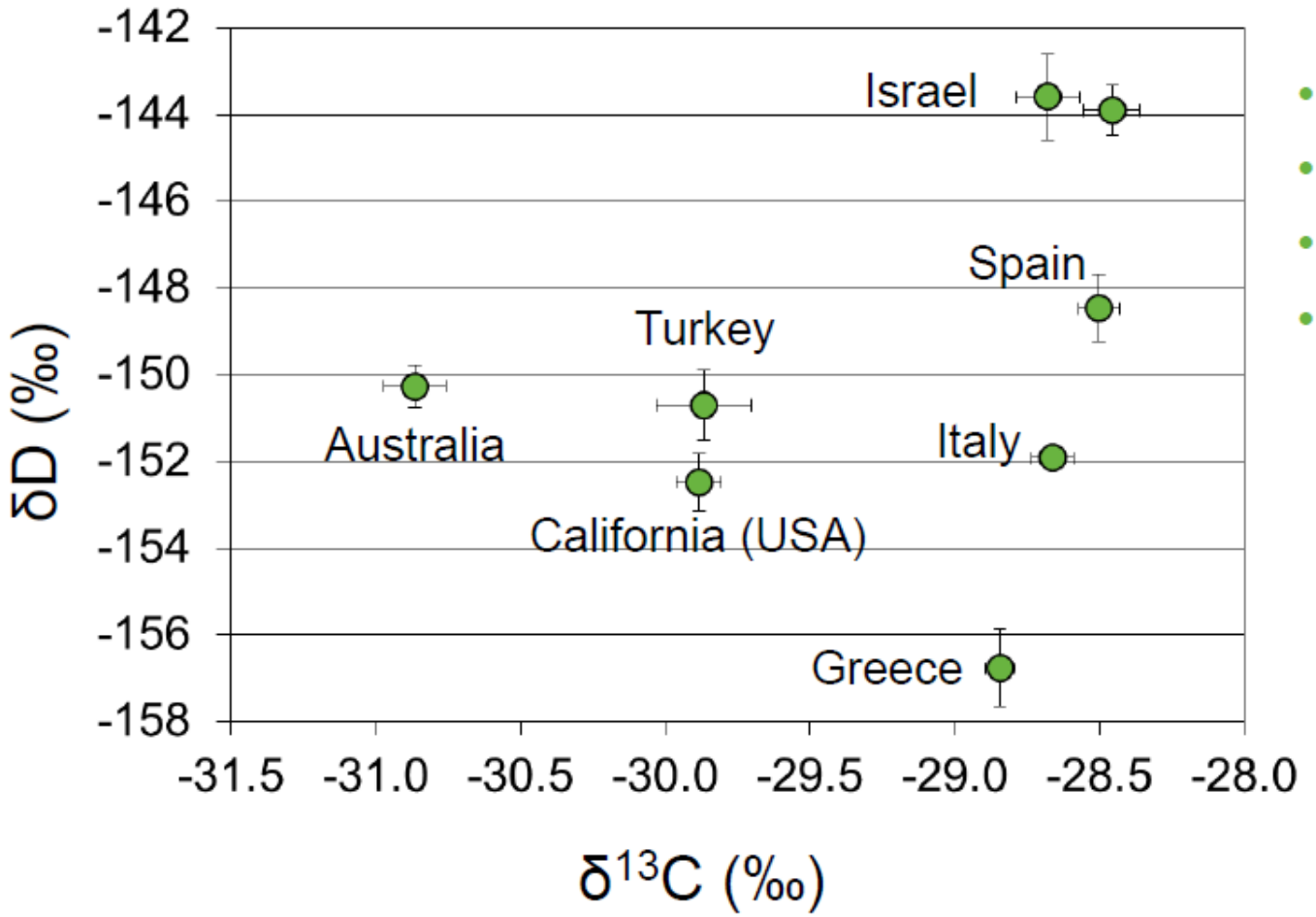
- Combust one sample. Measure both ^{13}C + D ratios.
- Comparable precision to IRMS at one-third the upfront investment.
- Much faster than IRMS. 20 minutes for both ^{13}C + D analyses.
- One analyzer replaces two IRMS systems.
- Easy sample prep. Runs 99 replicates unattended in 33 hours.

Precision from replicate to replicate:

- $1\sigma < 0.3$ permil for $\delta^{13}C$, and < 3 permil for δD

Application:
Isotopic δD and $\delta^{13}C$ can be used to determine the origin of Olive Oil

Simultaneous δD and $\delta^{13}C$ Results



- 8 Olive Oils
- 7 Locations
- n = 4
- 15 minutes each rep.

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PICARRO L2130-*i* $\delta D/\delta^{18}O$ Ultra High-Precision Isotopic Water Analyzer

The quantum leap to per meg level precision

- One analyzer for solids, liquids, and vapor: lab precision and field robustness
- Typical precision of 11 per meg for $\delta^{18}O$ and 38 per meg for δD simultaneously for liquid samples
- Allan variance of 10's per meg for averaged $\delta^{18}O$ and δD vapor measurements
- Calibrate once per day while measuring with sub per mil certainty

A0211: High Precision Vaporizer

A0212: High Throughput Vaporizer

A0325: Autosampler for liquid injection

A0101: Standards Delivery Module

A0214: Micro-Combustion Module™

A0213: Induction Module

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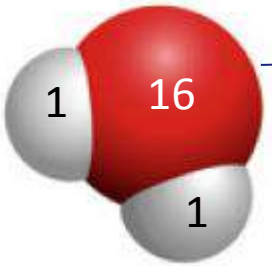
Stable water isotopologues:

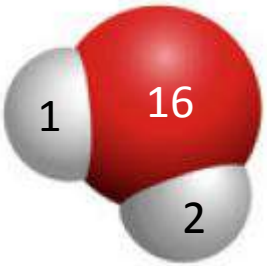
Tool to understand the hydrological cycle of the Present and Past and its link with climate

Light

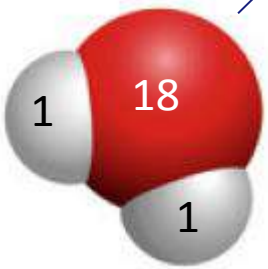
Most abundant
≈ 99.7 % of all water



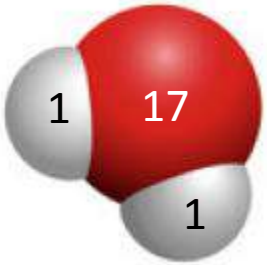
Three rare heavy isotopologues



0.018 %



0.204 %



0.037 %

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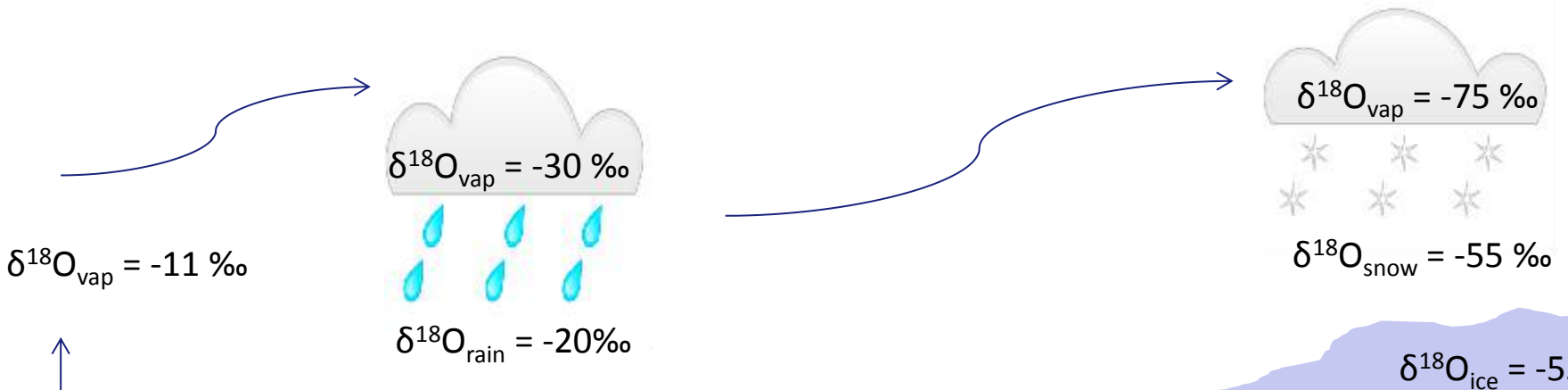
Isotopic fractionation:

Heavy water isotopologues are preferably condensing from vapour to liquid water (rain) or ice crystals (snow)

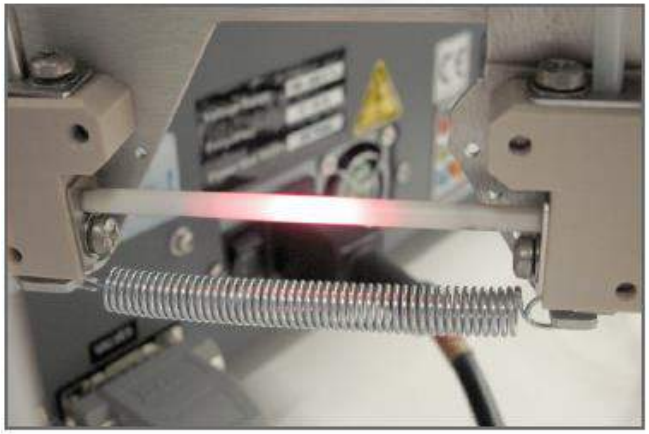
Thus, leaving the remaining water vapour depleted in heavy isotopologues with respect to Ocean water

$\delta = \frac{R_{sample}}{R_{reference}} - 1$ expressed in ‰ relative to a reference Ocean water, R = atomic ratio



Picarro Peripherals for L2130-i:

Micro-Combustion-Module



High precision vaporizer

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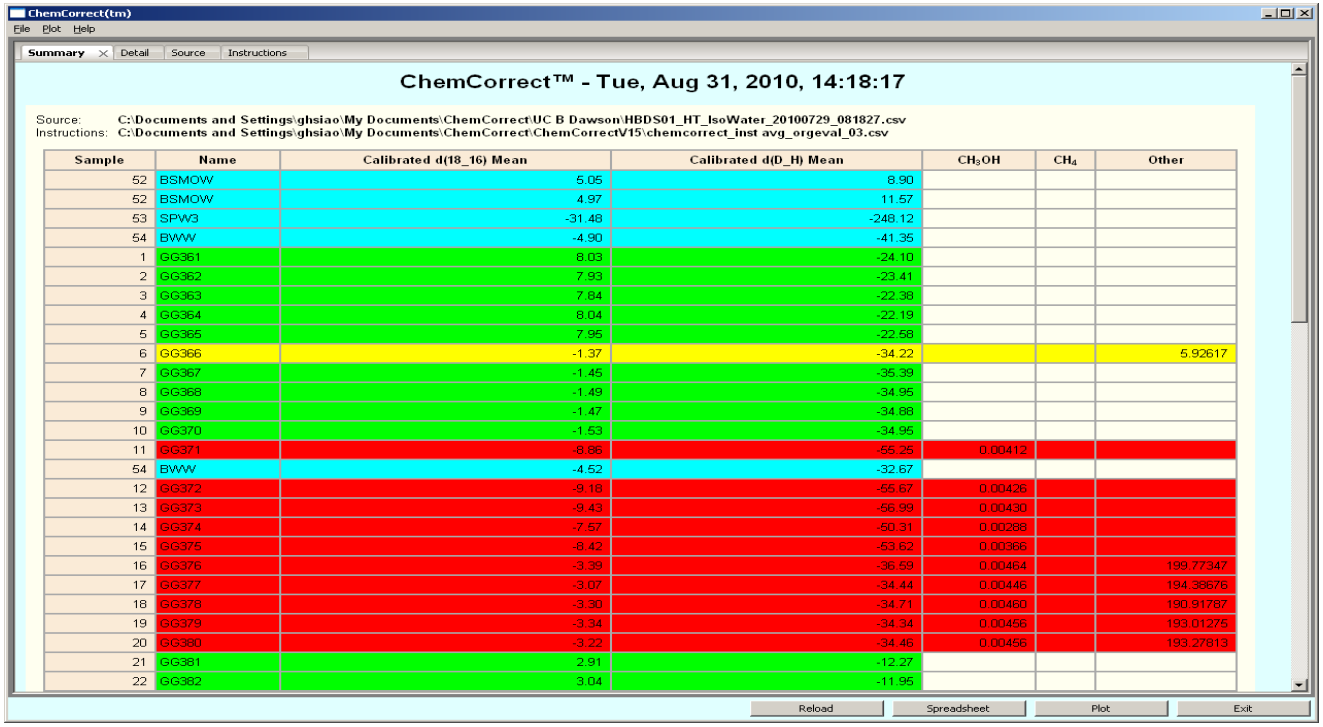
ChemCorrect™: identifies contaminated samples

- ChemCorrect™:
  - Identifies and flags contaminated samples with absorption features in the same region as the water spectra, e.g., methanol and ethanol



ChemCorrect(tm)

File Plot Help

Summary | Detail | Source | Instructions

ChemCorrect™ - Tue, Aug 31, 2010, 14:18:17

Source: C:\Documents and Settings\ghsiao\My Documents\ChemCorrect\UC B Dawson\HBDS01_HT_IsoWater_20100729_081827.csv
Instructions: C:\Documents and Settings\ghsiao\My Documents\ChemCorrect\ChemCorrectV15\chemcorrect_inst avg_orgeval_03.csv

Sample	Name	Calibrated d(18_16) Mean	Calibrated d(D_H) Mean	CH_3OH	CH_4	Other
52	BSMOW	5.05	8.90			
52	BSMOW	4.97	11.57			
53	SPW3	-31.48	-248.12			
54	BWW	-4.90	-41.35			
1	GG361	8.03	-24.10			
2	GG362	7.93	-23.41			
3	GG363	7.84	-22.38			
4	GG364	8.04	-22.19			
5	GG365	7.95	-22.58			
6	GG366	-1.37	-34.22			5.92617
7	GG367	-1.45	-35.39			
8	GG368	-1.49	-34.95			
9	GG369	-1.47	-34.88			
10	GG370	-1.53	-34.95			
11	GG371	-8.86	-55.25	0.00412		
54	BWW	-4.52	-32.67			
12	GG372	-9.18	-55.67	0.00426		
13	GG373	-9.43	-56.99	0.00430		
14	GG374	-7.57	-50.31	0.00288		
15	GG375	-8.42	-53.62	0.00366		
16	GG376	-3.39	-36.59	0.00464		199.77347
17	GG377	-3.07	-34.44	0.00446		194.38676
18	GG378	-3.30	-34.71	0.00460		190.91787
19	GG379	-3.34	-34.34	0.00456		193.01275
20	GG380	-3.22	-34.46	0.00456		193.27813
21	GG381	2.91	-12.27			
22	GG382	3.04	-11.95			

Reload | Spreadsheet | Plot | Exit

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Collecting rain isn’t hard
but how do you measure it in real time?

Research Article

Rapid Communications in Mass Spectrometry

Received: 24 August 2011 Revised: 3 October 2011 Accepted: 3 October 2011 Published online in Wiley Online Library

Rapid Commun. Mass Spectrom. **2011**, *25*, 3706–3712
(wileyonlinelibrary.com) DOI: 10.1002/rcm.5282

Continuous analysis of $\delta^{18}O$ and δD values of water by diffusion sampling cavity ring-down spectrometry: a novel sampling device for unattended field monitoring of precipitation, ground and surface waters

Niels C. Munksgaard*, Chris M. Wurster and Michael I. Bird

James Cook University, Earth and Environmental Sciences, MacGregor Road Building A2, Smithfield, Cairns, Queensland 4878, Australia

PICARRO

High-Precision and High-Throughput Vaporizers

	High-Precision Vaporizer (A0211)	High-Throughput Vaporizer (A0212)
$\delta^{18}O$ precision (1σ) by injection/sampe	0.1 ‰ / 0.05 ‰*	0.2 ‰ / 0.1 ‰
δD precision (1σ) by injection/sample	0.5 ‰ / 0.3 ‰*	0.6 ‰ / 0.4 ‰
δ18O/δD Drift (peak to peak, in 24 hrs)	< 0.6 ‰ / < 1.8 ‰	< 0.2 ‰ / 0.8 ‰
Volume by injection/sample**	≤ 2 µL / ≤ 12 µL	≤ 5 µL / ≤ 30 µL
Maximum TDS	≤ 200 g/kg	≤ 40 g/kg
Analysis time per injection	4 or 9 minutes	< 2 minutes
Analysis time per sample	24 or 54 minutes	< 12 minutes
Daily throughput (per 24 hrs)	360 or 160 injections	750 injections

*Precision and drift are specified for the high-precision mode.
**By sample calculations are based on running 6 injections, with the first 2 discarded and standard deviation calculated for the last 4.

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Performance Specifications	CO_2 Isotope-only mode	CH_4 Isotope-only mode	Simultaneous mode
$\delta^{13}C$ Precision (1-σ, 1 Hr window, 5 min. average)			
$\delta^{13}C$-CO_2	< 0.12 ‰	-	< 0.16 ‰
$\delta^{13}C$-CH_4	-	High Precision mode: < 0.8 ‰ High Dynamic Range mode: < 0.4 ‰	High Precision mode: < 1.15 ‰ High Dynamic Range mode: < 0.55‰
$\delta^{13}C$ Maximum Drift (peak-to-peak, 1 hr average interval average over 24 hrs at STP)			
$\delta^{13}C$-CO_2	< 0.6 ‰	-	< 0.6 ‰
$\delta^{13}C$-CH_4	-	High Precision and High Dynamic Range modes: < 1.5 ‰ at 10 ppm CH_4	High Precision and High Dynamic Range modes: < 1.5 ‰ at 10 ppm CH_4
Concentration Precision (1-σ, 30 sec. average)			
CO_2	200 ppb + 0.05 % of reading (^{12}C) 10 ppb + 0.05 % of reading (^{13}C)	1 ppm + 0.25 % of reading (^{12}C)	0-2.2 %
CH_4	50 ppb + 0.05 % of reading (^{12}C)	High Precision mode 5 ppb + 0.05 % of reading (^{12}C) 1 ppb + 0.05 % of reading (^{13}C) High Dynamic Range mode: 50 ppb + 0.05 % of reading (^{12}C) 10 ppb + 0.05 % of reading (^{13}C)	High Precision mode 5 ppb + 0.05 % of reading (^{12}C) 1 ppb + 0.05 % of reading (^{13}C) High Dynamic Range mode: 50 ppb + 0.05 % of reading (^{12}C) 10 ppb + 0.05 % of reading (^{13}C)
H_2O	100 ppm		

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