High Speed, High Precision Laser Monitors for N_2O, CH_4, COS, NH_3, CO_2 Isotopes and More

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AsiaFlux Workshop
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Beijing, China

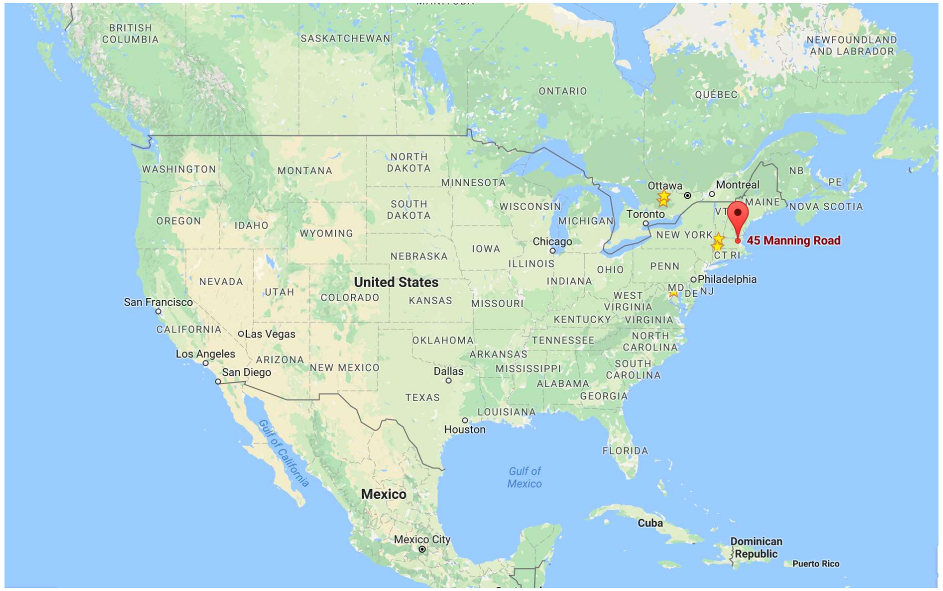
Outline

- Introduction to Aerodyne Research
- Measurement Technique
- Fast Nitrous Oxide Monitors for Eddy Flux Measurements
  - Monitor Versions with CO, CO_2 or CH_4
  - Performance
  - Eddy Flux Features
- Science Beyond Nitrous Oxide
  - CO_2 Isotope Fluxes
  - COS Fluxes
  - Ammonia Fluxes
  - Oxygen Fluxes?
  - More Molecules
- Surface Chambers with Eddy Covariance

Aerodyne Research, Inc.

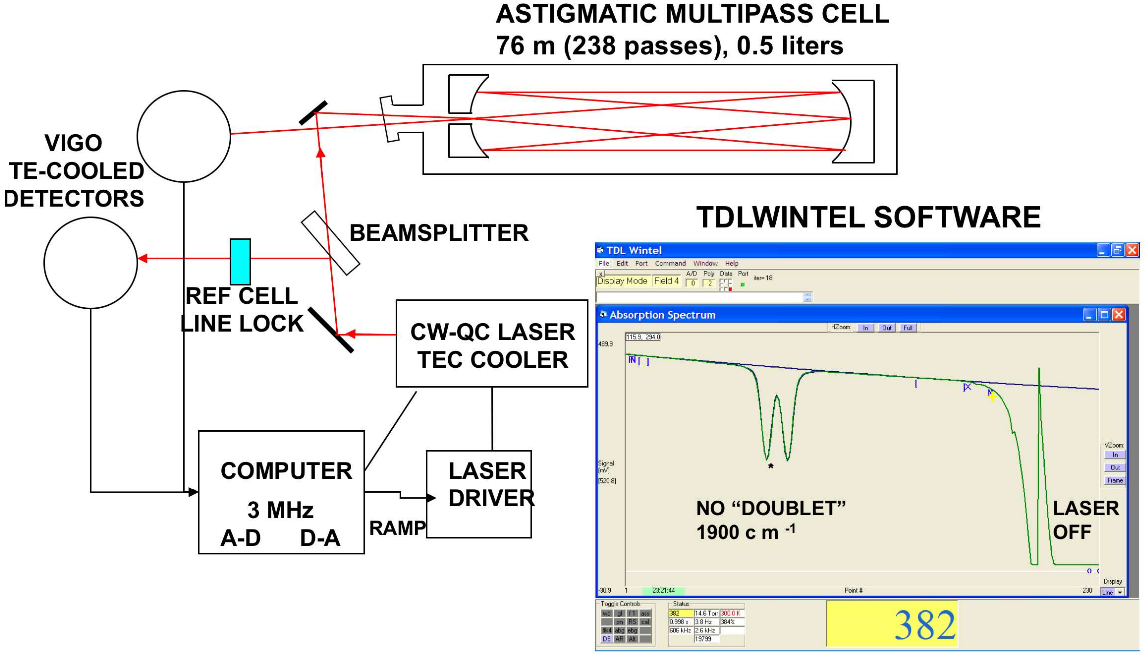
Small Business with R&D Focus

- Located just NW of Boston
- Founded in 1970
- Largely employee owned
- Organized into 6 Technology Centers
- 55 senior technical staff (45 Ph.D, 10 MS)
- 12 technical support, 9 business staff
- We are extremely collaborative!



- Various research areas but atmospheric chemistry and physics is at the core of much of our work.
- We provide many different types of atmospheric monitors:
  - Laser Trace Gas and Isotope Monitors (focus of this talk)
  - Aerosol Mass Spectrometers (AMS) and Aerosol Chemical Speciation Monitors (ACSM)
  - Chemical Ionization Mass Spectrometers (CIMS)
  - Cavity Attenuated Phase Shift (CAPS) Monitors for NO_2 or Optical Extinction

Measurement Technique – Tunable IR Laser Direct Absorption Spectroscopy (TILDAS)



- Fast scan of laser across absorption lines (1...3 kHz)
- Average 1000...3000 spectra per second
- Normalization and spectral fit to HITRAN
- We see the entire spectrum – no gaps
- Fast time response – 10 Hz in most cases
- Multipass absorption cell

Monitor Models – Single vs. Dual

Single Laser Instrument

Dual Laser Instrument

N_2O Monitor Versions – Species and Precision (@1 Hz)

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Single Laser Instrument

N_2O(60 ppt), CH_4(300 ppt) and H_2O(10 ppm)

N_2O(30 ppt), CO(100 ppt) and H_2O(10 ppm)

N_2O(30 ppt), CO_2^*(0.1 ppm), CO(1 ppb) and H_2O(10 ppm)

Dual Laser Instrument

N_2O (60 ppt), CH_4(300 ppt), CO_2(0.1 ppm), COS(10 ppt), CO(2 ppb) and H_2O(10 ppm)

N_2O(30 ppt), CH_4(200 ppt), CO_2^*(0.1 ppm), CO(1 ppb) and H_2O(10 ppm)

* CO_2 spectral line is due to $^{13}CO_2$. CO_2 emissions measurements are reliable using ^{13}C spectral lines, but high accuracy atmospheric concentration measurements are not recommended.

N_2O Monitor - Performance at 10 Hz

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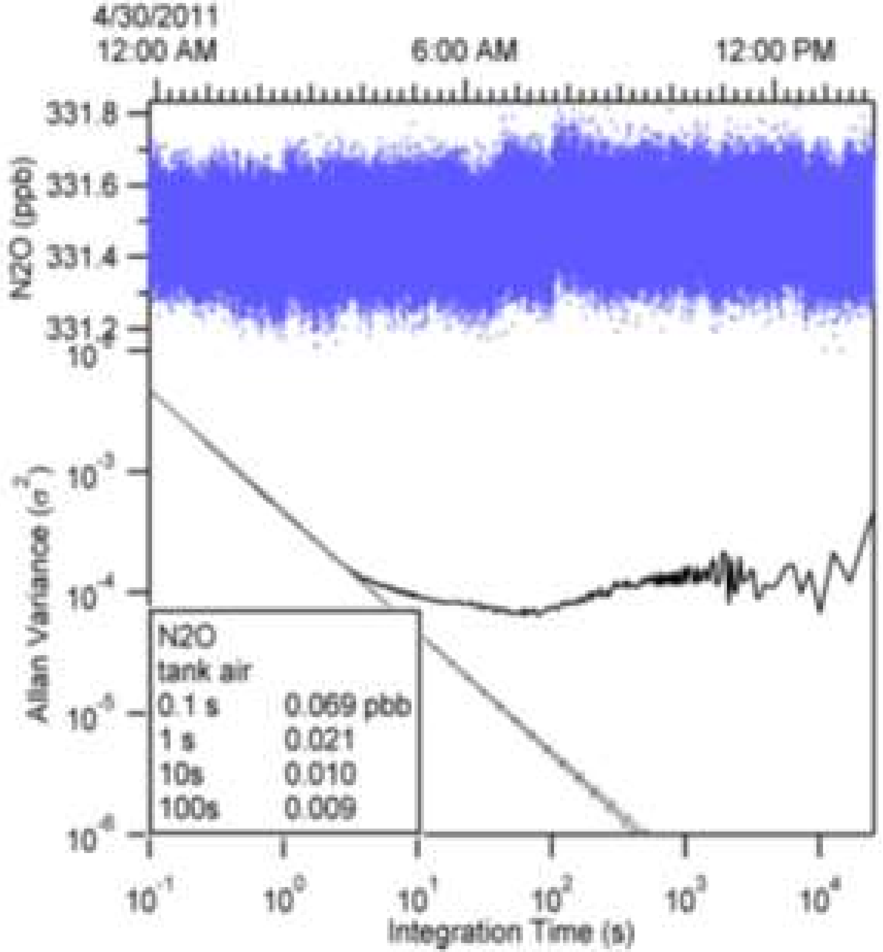

Figure 3. Allan plot for nitrous oxide generated from a reference cylinder. Data rate is 10 Hz.

N_2O and CH_4 Fluxes at Grassland

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Global Change Biology
celebrating 20 years

Global Change Biology (2014) **20**, 1913–1928, doi: 10.1111/gcb.12518

Greenhouse gas budget (CO_2, CH_4 and N_2O) of intensively managed grassland following restoration

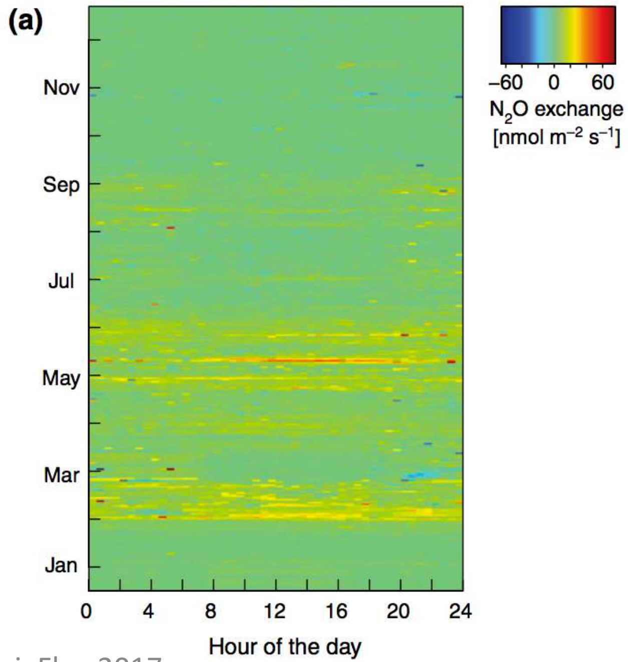
LUTZ MERBOLD[1], WERNER EUGSTER[1], JACQUELINE STIEGER[1], MARK ZAHNISER[2], DAVID NELSON[2] and NINA BUCHMANN[1]

[1]*Department of Environmental Systems Science, ETH Zurich, Universitaetsstr. 2, Zurich 8092, Switzerland,* [2]*Aerodyne Research Inc., 45 Manning Rd, Billerica, MA 01821, Massachusetts, USA*

Full year of N_2O and CH_4 fluxes measured using Aerodyne N_2O/CH_4 monitor

Nearly continuous data coverage

Plot at right shows N_2O flux by hour of day and by day of year.



CO_2 Isotopic Eddy Covariance
at Harvard Forest

U of AZ: **Rick Wehr**
Scott Saleska
Harvard: **Bill Munger**
Steve Wofsy
ARI: **Barry McManus**
Dave Nelson
Mark Zahniser

SHACK

TOWER

Wehr, R., Munger, J.W., McManus, J.B., Nelson, D.D., Zahniser, M.S., Davidson, E.A., Wofsy, S.C. and Saleska, S.R., 2016. Seasonality of temperate forest photosynthesis and daytime respiration. *Nature*, *534*(7609), pp.680-683.

Science Beyond N_2O Fluxes: CO_2 Iso-Flux at Harvard Forest

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Isotopes of carbon dioxide (^{13}C and ^{18}O) can be measured with high precision and high speed (0.07 per mil at 1 Hz, 0.2 per mil at 10 Hz) enabling measurement of iso-fluxes.

Rick Wehr's recent Nature paper shows how measurements of ^{13}C-CO_2 iso-fluxes can be used to constrain the partitioning of NEE at ecosystem level.

LETTER

doi:10.1038/nature17966

Seasonality of temperate forest photosynthesis and daytime respiration

R. Wehr[1], J. W. Munger[2], J. B. McManus[3], D. D. Nelson[3], M. S. Zahniser[3], E. A. Davidson[4], S. C. Wofsy[2] & S. R. Saleska[1]

We are also developing measurements of the clumped isotopes of carbon dioxide and of oxygen 17 excess. Results coming soon.

Challenge: Measuring CO_2 Isotopes for NOAA Global Flask Network

BACKGROUND:

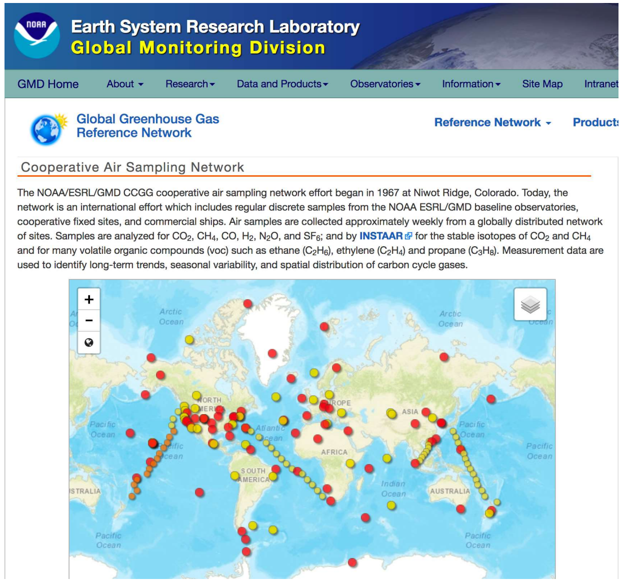
-Greenhouse gas (GHG) emissions drive global climate change

-Measurement of the isotopic variants of GHG's can be used to constrain sources/sinks

-But this demands the highest possible accuracy

- This can be achieved with IRMS but it is labor intensive and ^{17}O is difficult

- Global flask networks require high accuracy measurements of relatively small samples



GOALS:

-Provide high accuracy, laser based measurement of $\delta^{13}C$ (0.01‰), $\delta^{18}O$ (0.01‰) and $\delta^{17}O$ (0.02‰) in ambient air samples

-Small sample consumption (<100 ml of air at STP)

-Fast measurement time (<15 minutes)

Standard CO_2 Isotopes with Sample/Reference Switching

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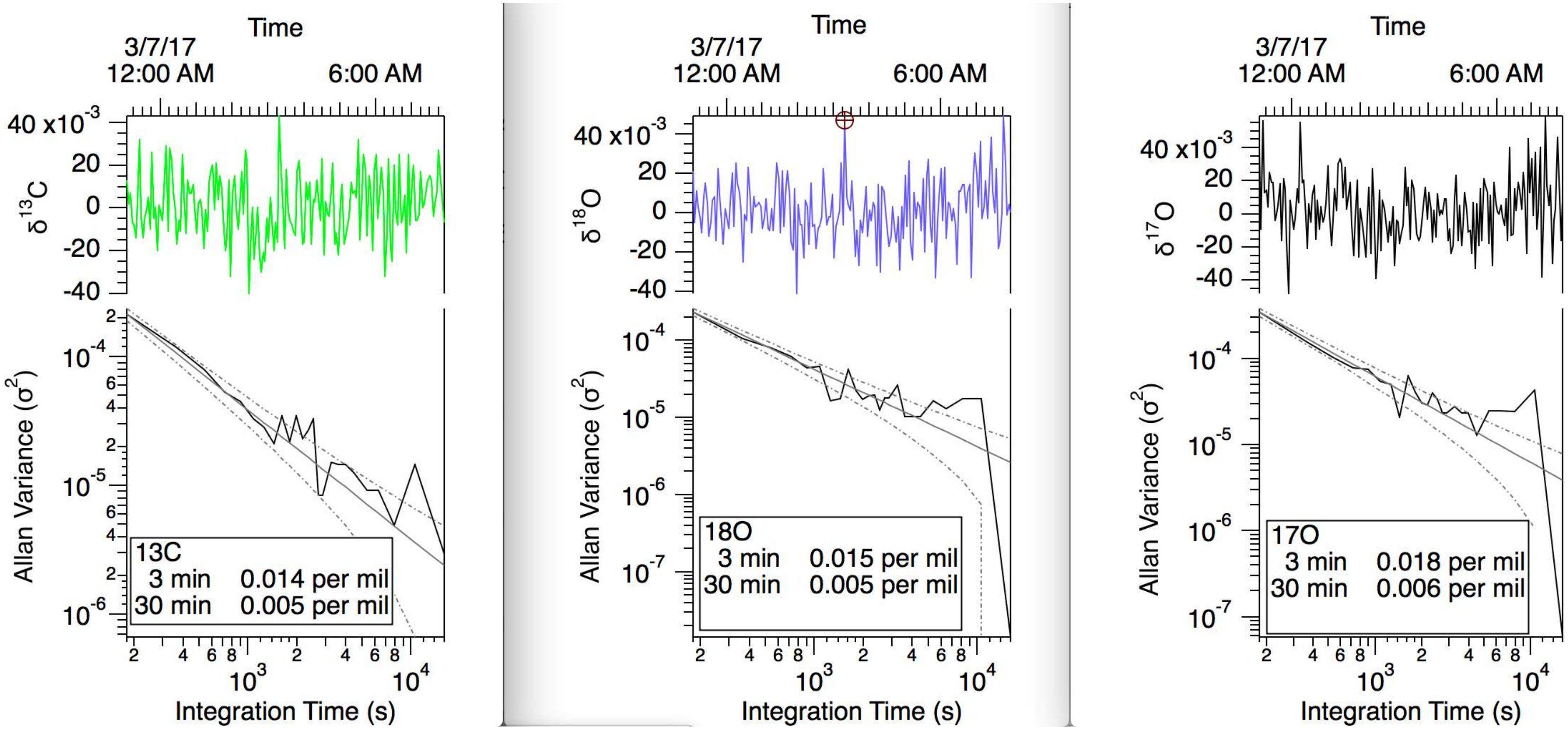

By comparing the sample to a working reference on an ~1 minute time scale, we are able to eliminate long term span drift in ^{13}C-, ^{18}O- and ^{17}O- CO_2

- **15 per meg precision for a three minute measurement**
- **Small sample size: only 12 ml air or 200 nmoles CO_2 (36 meter cell)**
- **Signal averaging effective for many hours**
- **5 per meg precision for 10 samples over 30 minutes (2 μmoles CO_2)**
- **Best results require sample concentration ~ reference concentration**

COS Measurements to Constrain Gross Primary Productivity (GPP)

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COS is a major source of S to the atmosphere and is being investigated as a surrogate for GPP

Research article — 29 Feb 2016

Continuous and high precision atmospheric concentration measurements of COS, CO_2, CO and H_2O using a quantum cascade laser spectrometer (QCLS)

Linda M. J. Kooijmans[1], Nelly A. M. Uitslag[1], Mark S. Zahniser[2], David D. Nelson[2], Stephen A. Montzka[3], and Huilin Chen[1,4]
[1]Centre for Isotope Research (CIO), University of Groningen, Groningen, The Netherlands
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[3]NOAA Earth System Research Laboratory, Boulder, Colorado, USA
[4]Cooperative Institute for Research in Environmental Sciences (CIRES), University of Colorado, Boulder, CO, USA

Review status
A revision of this discussion paper is under review for the journal Atmospheric Measurement Techniques (AMT).

High precision (<5 ppt at 1 Hz) measurements of COS are necessary due to its low atmospheric abundance (~500 ppt)

JOURNAL OF GEOPHYSICAL RESEARCH: ATMOSPHERES, VOL. 118, 8001–8009, doi:10.1002/jgrd.50581, 2013

Carbonyl sulfide in the planetary boundary layer: Coastal and continental influences

R. Commane,[1] S. C. Herndon,[2] M. S. Zahniser,[2] B. M. Lerner,[3] J. B. McManus,[2] J. W. Munger,[1] D. D. Nelson,[2] and S. C. Wofsy[1]

Received 31 January 2013; revised 10 June 2013; accepted 14 June 2013; published 22 July 2013.

Eddy covariance flux measurements are being performed by several groups.

The biosphere-atmosphere exchange and global budget of carbonyl sulfide WORKSHOP

2016
September 5-9
Finland

Contact Kukka-Maaria Erkkilä, at (kukka-maaria.erkkila at helsinki.fi) and Cc Timo Vesala (timo.vesala at helsinki.fi)

Location: Hyytiälä Forestry Field Station, Finland

Abstract:

The coupled vegetation uptake of carbonyl sulfide (COS) and CO2, and the potential to use this coupling to study large-scale photosynthesis, has prompted exciting new research into the biosphere-atmosphere exchange of COS recently. Aided by new measurement capabilities, information on leaf, soil and ecosystem COS fluxes is now being collected in order to develop COS-based estimates of gross primary production (GPP). These recent investigations complement more established research on the role of COS in atmospheric chemistry and the sulfur cycle, signifying the importance

Recent workshop on COS at Hyytiälä

Ammonia Flux Measurements

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N emissions can be a major driver of environmental change

NH_3 emissions can be crucial to atmospheric particle formation

However direct measurements of NH_3 flux are difficult due to stickiness of NH_3

Recent papers show progress

Active surface passivation promises even more freedom from surface interactions

Atmos. Chem. Phys., 16, 11283–11299, 2016
www.atmos-chem-phys.net/16/11283/2016/
doi:10.5194/acp-16-11283-2016

Atmospheric Chemistry and Physics
Open Access
EGU

Surface–atmosphere exchange of ammonia over peatland using QCL-based eddy-covariance measurements and inferential modeling

Undine Zöll[1,*], Christian Brümmer[1], Frederik Schrader[1], Christof Ammann[2], Andreas Ibrom[3], Christophe R. Flechard[4], David D. Nelson[5], Mark Zahniser[5], and Werner L. Kutsch[6]

Agriculture, Ecosystems and Environment 219 (2016) 1–13
Contents lists available at ScienceDirect
Agriculture, Ecosystems and Environment
journal homepage: www.elsevier.com/locate/agee
ELSEVIER

Dynamics of ammonia volatilisation measured by eddy covariance during slurry spreading in north Italy

Rossana Monica Ferrara[a], Marco Carozzi[b,*], Paul Di Tommasi[c], David D. Nelson[d], Gerardo Fratini[e], Teresa Bertolini[f], Vincenzo Magliulo[c], Marco Acutis[g], Gianfranco Rana[a]

THE JOURNAL OF PHYSICAL CHEMISTRY A
Article
pubs.acs.org/JPCA

New Approaches to Measuring Sticky Molecules: Improvement of Instrumental Response Times Using Active Passivation

J. R. Roscioli,* M. S. Zahniser, D. D. Nelson, S. C. Herndon, and C. E. Kolb

Wide Variety of Molecules

- Infrared spectroscopy is a general technique – with the right laser, we can detect any small molecule with a vibrational dipole moment. For example:
  - CO, CO_2, H_2CO, HCOOH, CH_4, C_2H_2, C_2H_4, C_2H_6, acrolein, butadiene
  - H_2O, HOOH, HO_2, O_3, O_2
  - NO, NO_2, N_2O, NH_3, HNO_3, HONO, N_2H_4, HCN
  - HF, HCl, HOCl, HBr, HI
  - COS, SO_2, SO_3, H_2S, H_2SO_4
- Isotopes of several of the above species as well
- Eddy flux measurements for most of these species

Eddy Flux Measurements Around the World

Clockwise from top, left corner:
NH_3 fluxes in Beijing, China
N_2O and CH_4 fluxes in Czech Republic
N_2O fluxes in Sweden
SO_2 and NO_2 fluxes in South Africa

High Precision Oxygen Measurements

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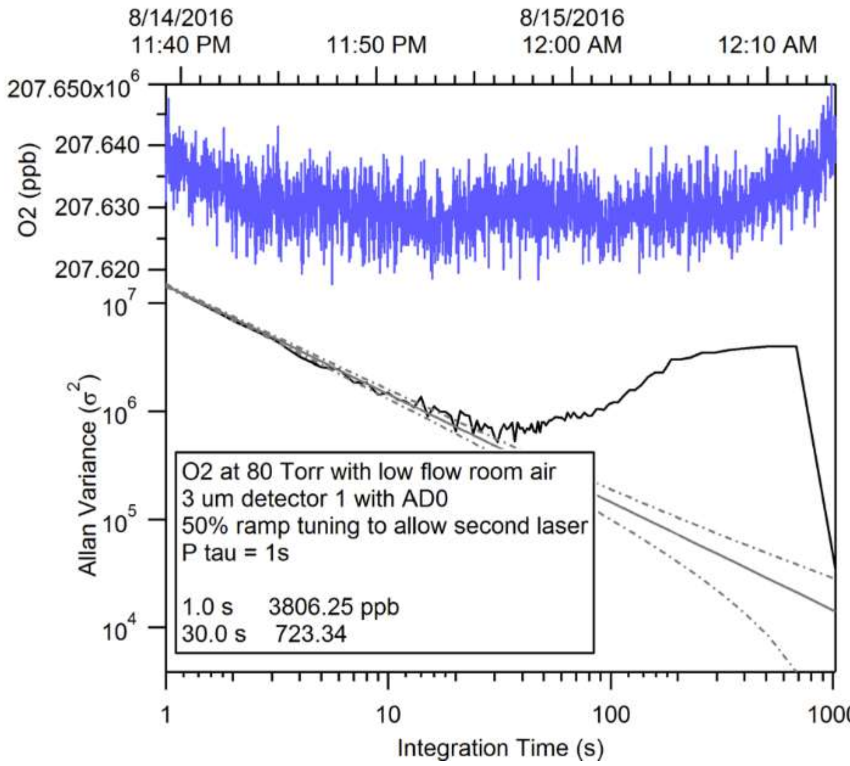
New instrument measures oxygen with extremely high precision (3.8 ppm at 1 Hz) offering the hope of direct oxygen flux measurements.

Oxygen measurements can reveal stoichiometery of local ecosystem processes.

New instrument will also measure CO_2 simultaneously and perform real time water vapor corrections.

Oxygen measurements may be able to constrain GPP at local level [Ishidoya, 2015]:



Ecol Res (2015) 30: 225–234
DOI 10.1007/s11284-014-1241-3

SPECIAL FEATURE

Long-term and interdisciplinary research on forest ecosystem functions: Challenges at Takayama site since 1993

Shigeyuki Ishidoya · Shohei Murayama
Hiroaki Kondo · Nobuko Saigusa ·
Ayaka W. Kishimoto-Mo · Susumu Yamamoto

Observation of O_2:CO_2 exchange ratio for net turbulent fluxes and its application to forest carbon cycles

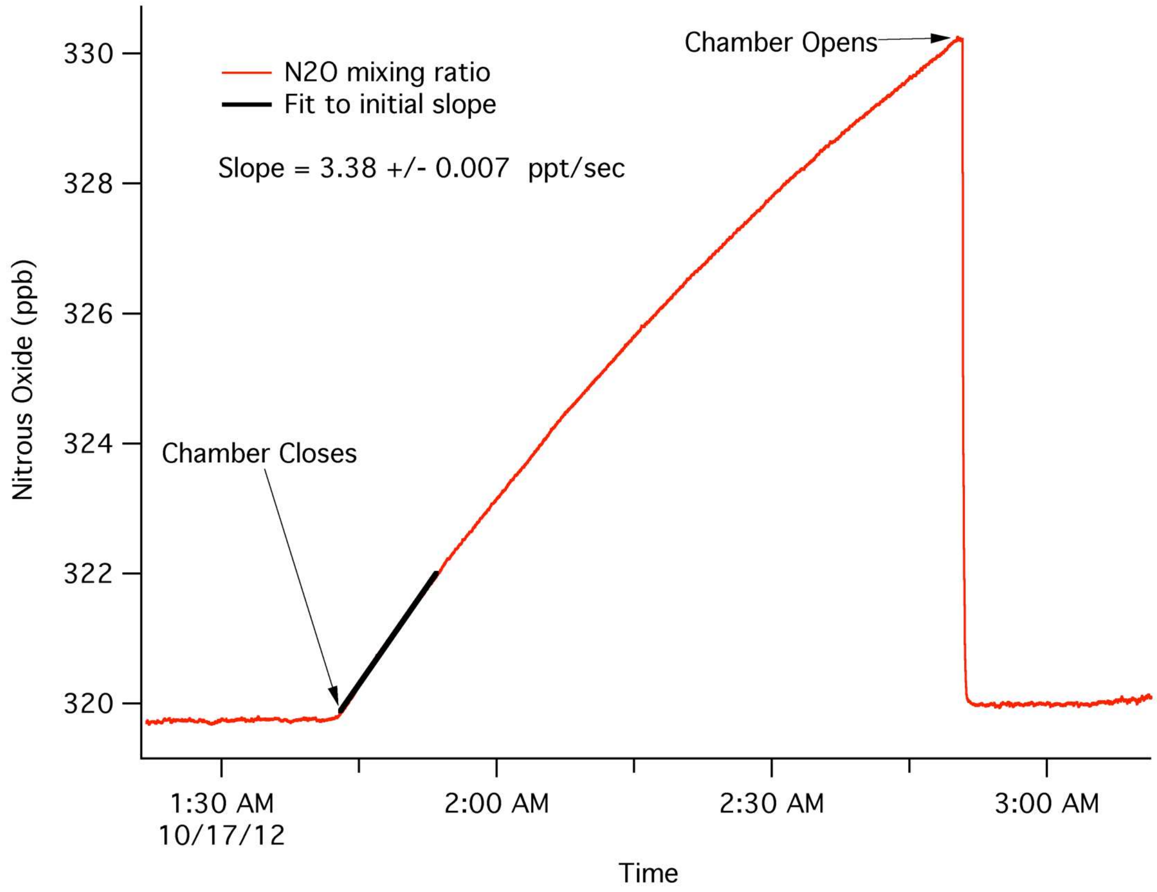
Measurements with Surface Chambers Can Detect Very Small Fluxes

Nitrous oxide flux measured with an automatic chamber at Thunen Institute in Braunschweig, Germany.

Flow rate only 1 slpm.

Observed rise rate is 3.4 ppt/sec

Same instrument simultaneously observed CO consumption by soil.



This rise rate corresponds to a small flux: 8 micro grams N_2O-N /m^2/hour or 0.08 nano-moles/m^2/s.

Measurements with Surface Chambers Can Detect Very Small Fluxes

Biogeosciences, 11, 2709–2720, 2014
www.biogeosciences.net/11/2709/2014/
doi:10.5194/bg-11-2709-2014

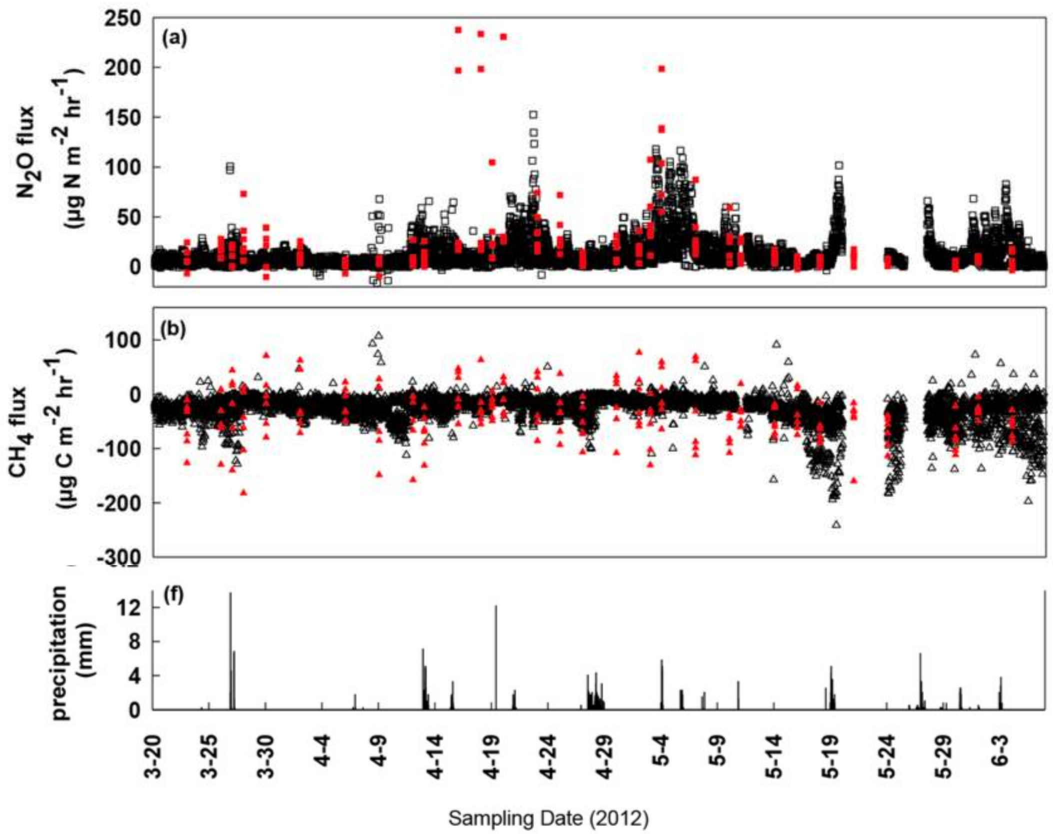
Biogeosciences

High temporal frequency measurements of greenhouse gas emissions from soils

K. Savage[1], R. Phillips[2], and E. Davidson[1]
[1]The Woods Hole Research Center, 149 Woods Hole Rd, Falmouth, MA 02540, USA
[2]Landcare Research, Riddett Road, Massey University, Palmerston North, 4472, New Zealand

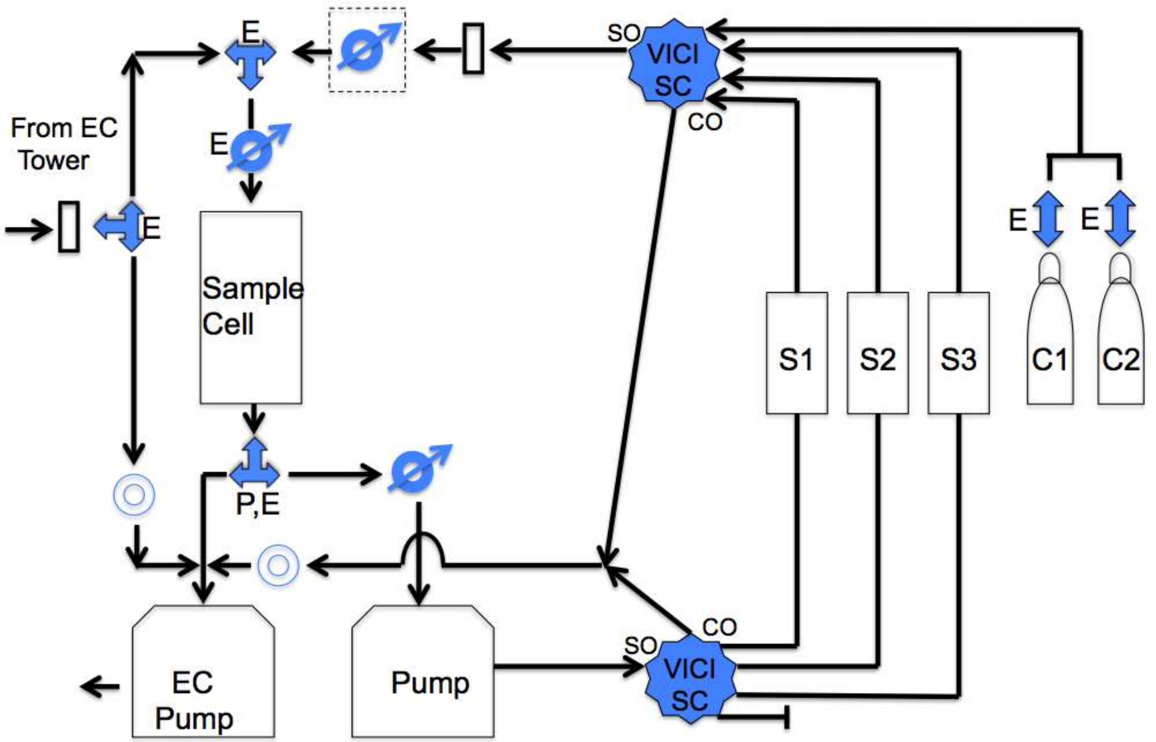
N_2O and CH_4 fluxes measured using Aerodyne N_2O/CH_4 analyzer with automated surface chambers

Measurements performed at North Dakota alfalfa cropland.



Automatic Switching Between Eddy Covariance and Surface Chambers

EC/Chambers/Cylinders with Recirculation (2 Pumps), with Continuous Flow



A system to automatically switch between

(1) fast flow mode for eddy covariance and

(2) a slow flow mode for measuring up to 16 automatic chambers and/or calibration gas cylinders.

Automatically switches inlet flow rate, pumping speed, data rate, data processing, sample chamber flows, etc…

Conclusions: Aerodyne's Laser Trace Gas and Isotope Monitors

Our laser monitors are used by many research groups including at ICOS ecosystem sites

Excel at fast (10 Hz) and highly sensitive (tens of ppt) measurements but also do high sensitive background measurements

Aerodyne is highly collaborative and provides excellent support

Continuous flow and trapped sample modes

Customized sampling systems allow the control of several automated tasks. For example, eddy covariance fluxes part of the day and chamber measurements at other times.

Many molecules and isotopes can be measured. A few examples of popular instruments are shown at right.

Mini Monitor:
single laser, 76 meter path

- N_2O, CH_4 and H_2O
- N_2O, CO, CO_2 and H_2O
- COS, CO_2, CO and H_2O
- NH_3
- CO_2 isotopes (including ^{17}O and clumped)
- CH_4 isotopes
- H_2CO and HCOOH

Questions?

Aerodyne Laser Monitor Team

Mark Zahniser	Christoph Dyroff	Joanne Shorter
Scott Herndon	Tara Yacovitch	Rob Roscioli
Mike Agnese	Mike Moore	Stanley Huang
Paula Sar-Kroeung	Bill Brown	Bill Rundgren
Shrid Ambady	Greg Genecin	Frank Hills
Conner Daube	David Nelson	Barry McManus

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