# Development of the Next Generation of Flux-Measurement Tools



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# Dry Deposition is an important contributor to acidification

- The EPA is considering changing future secondary National Ambient Air Quality Standards (NAAQS) for SO<sub>2</sub> and NO<sub>2</sub> based on acidification
- SO<sub>2</sub> dry deposition accounts for up to 50% of total sulfur deposition
- Dry deposition accounts for up to 40% of total nitrogen deposition
- There is a lot of uncertainty regarding dry deposition measurements and modeling

## Flux-measurement methods are costly or indirect



## **Inferential Method:**

### **Advantages:**

- basecexpensive thanteddy
- covariance Most accurate method available Less technically difficult

## **Disadvantages:**

- Essed grange of toto on't always
- agree with direct measurements, or lechnically difficult and
- other models computationally expensive Flux estimates between models can
- vary by a factor of 2 to 3

Burba (2005)

# Pape et al. demonstrated that flux chambers are an accurate tool for measuring dry deposition



- Dynamic flux chambers were used in combination with traditional pollutant monitors
- Measured CO<sub>2</sub> and methanol surface flux over grassland
- Demonstrated good agreement with eddy covariance systems

## Dynamic Flux Chambers could provide direct dry-deposition measurements



## Chamber outlet houses sensors and flow controls





## Dry deposition flux is calculated via a mass balance



$$C(t) = \frac{QC_{\text{out}}}{Q - v_{\text{d}}A_{\text{s}}} + (C_{\text{out}} - \frac{QC_{\text{out}}}{Q - v_{\text{d}}A_{\text{s}}})e^{\frac{-(Q - v_{\text{d}}A_{\text{s}})t}{V}}$$



## Inexpensive sensors enable low-cost measurements



#### CO<sub>2</sub> Sensor

- Non-dispersive infrared
- Costs about \$60
- Detection range of 0-5000 ppm
- 30 ppm resolution

#### Concerns

• Sensitive to temperature



## Inexpensive sensors enable low-cost measurements



### NO<sub>2</sub> Sensor

- Electrochemical Sensor
- Costs about \$80
- Detection range of 0-20,000 ppb
- < 20 ppb resolution</li>

#### Concerns

- Sensor resolution (ideally 1 ppb)
- NO emissions react with O<sub>3</sub> and rapidly produce NO<sub>2</sub>. This can diminish the magnitude of NO<sub>2</sub> deposition reading

### SO<sub>2</sub> Sensor

- Electrochemical Sensor
- Costs about \$80
- Detection range of 0-50,000 ppb
- < 100 ppb resolution</li>

#### Concerns

- Sensor resolution (ideally 1 ppb)
- SO<sub>2</sub> levels in the western US are low, so SO<sub>2</sub> deposition will be very difficult to measure

## **Summary & Future Plans**

- We developed a flux chamber that measures CO<sub>2</sub>, O<sub>3</sub>, RH, temperature, rainfall, and soil moisture.
- The crux of our project is finding inexpensive ways to take high-resolution NO<sub>2</sub> and SO<sub>2</sub> measurements.
- We will develop electronics and install the NO<sub>2</sub> and SO<sub>2</sub> sensors. We will also install high-resolution NO<sub>2</sub> measurement devices, which will enable us to calibrate and evaluate the inexpensive sensors.
- We will perform calibrations to explore the effects of temperature, RH, and cross-sensitivity on the O<sub>3</sub> sensors.
- We will compare our flux-chamber results to an eddy-covariance system.

# Questions?



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## References

EPA, Policy Assessment for the Review of the Secondary NAAQS for Oxides of Nitrogen and Oxides of Sulfur, United States Environmental Protection Agency, 2011.

Burba, G; Anderson, D. A Brief Practical Guide to Eddy Covariance Flux Measurements, Version 1.0.1; Licor, Inc.: Lincoln, 2005.

Driscoll, C.T.; Lawence, G.B.; Bulger, A.J.; Butler, T.J.; Cronan, C.S.; Eagar, C.; Lambert, K.F.; Likens, G.E.; Stoddard, J.L.; Weathers, K.C. Acidic Deposition in the Northeastern United States: Sources and Inputs, Ecosystem Effects, and Management Strategies. *Bioscience*. **2001**, *51*, 180-198.

Clean Air Status and Trends Network; 2010 Annual Report; U.S. Environmental Protection Agency: Washington, DC, 2010.

Seinfeld, John H.; Pandis, Spyros N. Atmospheric Chemistry and Physics - From Air Pollution to Climate Change, 2nd ed.; John Wiley and Sons: Hoboken, 2006.

Turnipseed, A.A; Burns, S.P.; Moore, D.J.P.; Hu, J.; Guenther, A.B.; Monson, R.K. Controls over ozone deposition to a high elevation subalpine forest. Agricultural and Forest Meteorology. 2009, 149, 1447-1459.

Baldocchi, D. D.; Hincks, B. B.; Meyers, T. P. Measuring Biosphere-Atmosphere Exchanges of Biologically Related Gases with Micrometeorological Methods. *Ecology.* **1988**, *69*, 1331-1340.

Schwede, D.; Zhang, L.; Vet, R.; Lear, G. An intercomparison of the deposition models used in CASTnet and CAPMoN networks. *Atmospheric Environment*. **2011**, *45*, 1337-1346.

Wesely, M. L.; Hicks, B. B. A review of the current status of knowledge on dry deposition. *Atmospheric Environment*. **2000**, *34*, 2261-2282.

Zhang, L.; Brook, J. R.; Vet, R. A revised parameterization for gaseous dry deposition in air-quality models. *Atmos. Chem. Phys.* 2003, *3*, 2067-2082.

Pape, L.; Ammann, C.; Nyfeler-Brunner, A.; Spirig, C.; Hens, K.; Meixner, F.X. An automated dynamic chamber system for surface exchange measurement of non-reactive and reactive trace gases of grassland ecosystems. *Biogeosciences Discuss.* **2008**, *5*, 3157-3219.

Jiang, Y.; Li, K.; Tian, L.; Piedrahita, R.; Yun, X.; Mansata, O.; Lv, Q.; Dick R.P.; Hannigan, M.P.; Shang, Li. *Papers and Notes*, 13th International Conference on Ubiquitous Computing, Beijing, China, September 17-21, 2011.

Myles, L.; Heuer, M.W.; Meyers, T.P.; Hoyett, Z.J. A comparison of observed and parameterized SO<sub>2</sub> dry deposition over a grassy clearing in Duke Forest. *Atmospheric Environment*. **2012**, *49*, 212-218.

Wu, Z.; Wang, X.; Chen, F.; Turnipseed, A.A.; Guenther, A.B.; Niyogi, D.; Charusombat, U.; Xia, B.; Munger, J.W.; Alapaty, K. Evaluating the calculated dry deposition velocities of reactive hitrogen oxides and ozone from two community models over a temperate deciduous forest. *Atmospheric Environment*. **2011**, *45*, 2663-2674.

D. Vaugn et al., *Characterization of Low-Cost NO*<sub>2</sub> Sensors; Sonoma Technology, Inc., 2010.

# Non-dispersive infrared radiation (NDIR)



- NDIR: Infrared light is directed through a sample chamber toward a detector.
- Each gas absorbs infrared radiation at a different wavelength (CO<sub>2</sub> absorbs 4.26μm).
- Concentration (density) can be calculated from measured voltage and optical path length.

[2] Environment Leading Technology Website, http://tccelt.co.kr/

## **Electrochemical Sensors**



• Measure concentration by oxidizing or reducing gas and measuring current.

#### Advantages:

- Output is linearly proportional to concentration
- Stable over time (less re-calibration)

### Disadvantages:

Cross-sensitive

# Relative contributions of N<sub>r</sub> species to total inorganic N dry deposition



\*Negative percentages for NH3 denote net NH3 emissions, which are expressed relative to the sum of dry deposition fluxes for the other four Nr species.

Flechard et al. (2011)

## Chemiluminescence

## **Nitrogen Chemistry**