Surface-Atmosphere Exchange of Ammonia in a Non-fertilized Grassland and its Implications for $PM_{2.5}$

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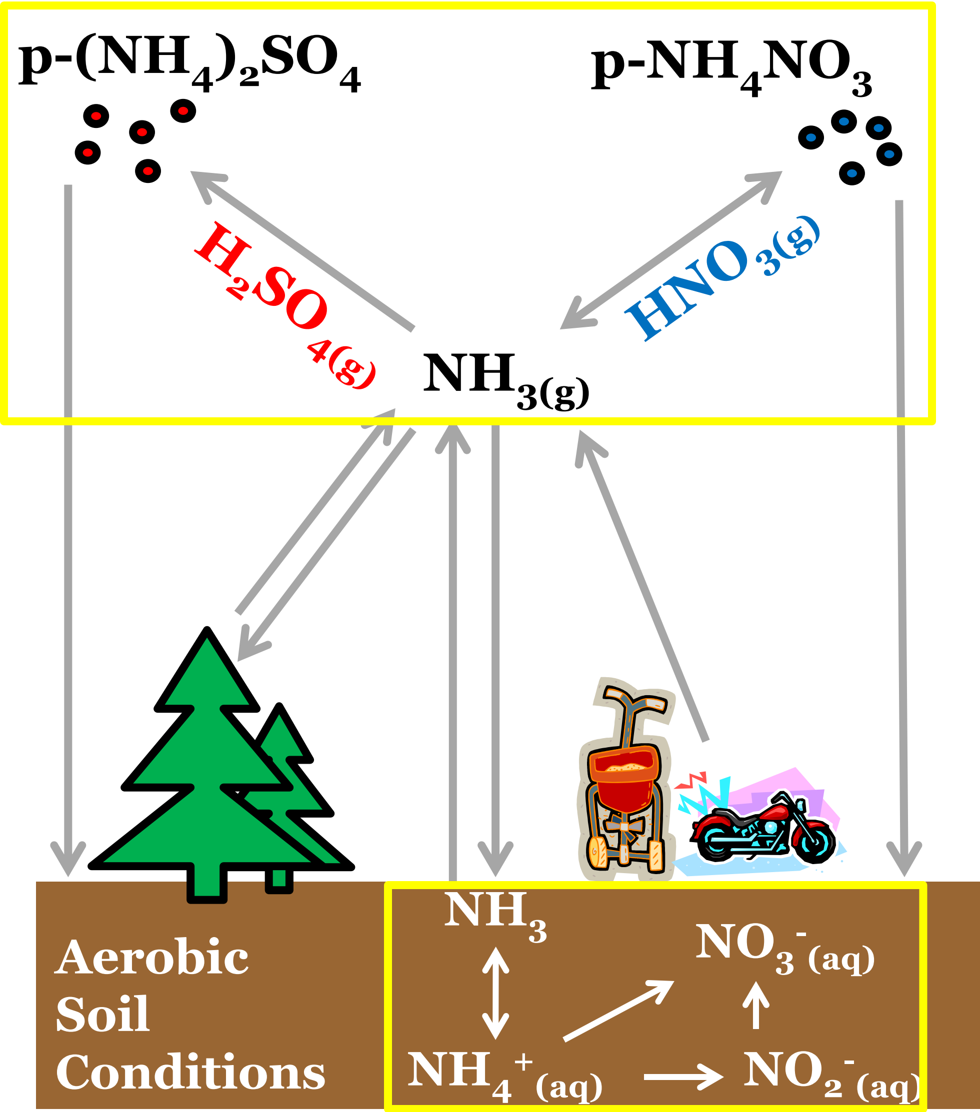
Ammonia in the Environment

- Atmosphere
  - Dominant alkaline gas
  - 2° aerosol formation
- Emissions
  - Mostly agricultural
- Deposition
  - Traditionally a "one-way street"
- Bidirectional Flux
  - "Two-way street"
  - Governed by compensation point (χ)
  - Poorly constrained
  - Lacking in most models

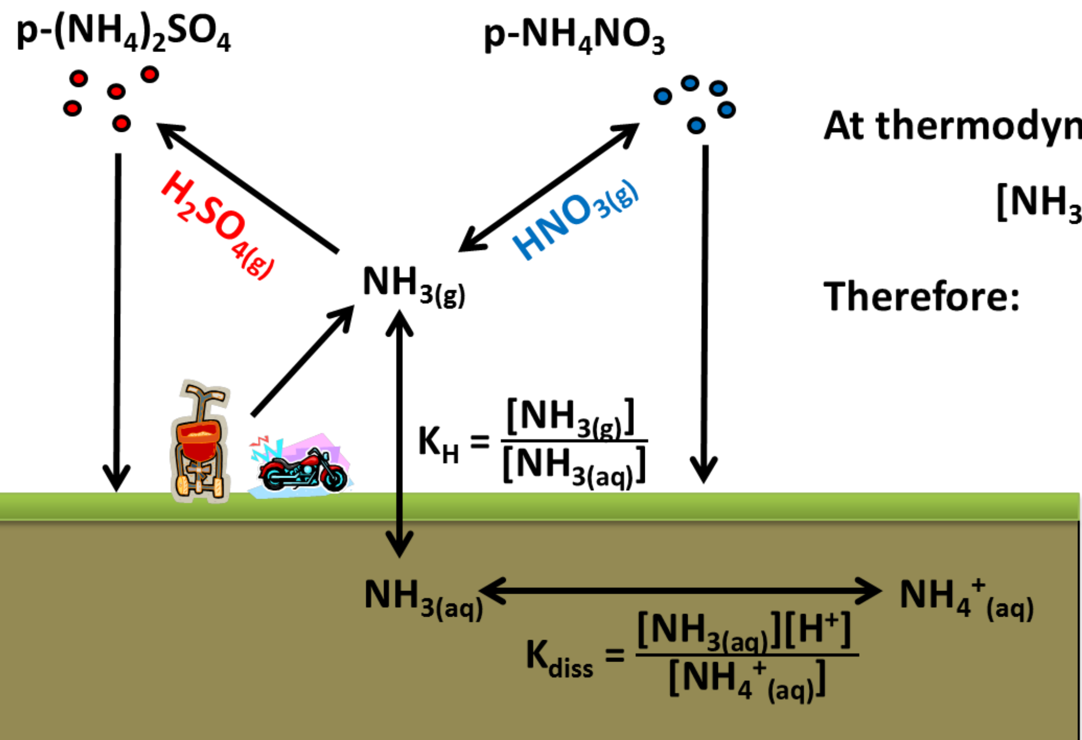


Zhang et al. (2010) *J. Geophys. Rev.*, **115**, D20310.

Ellis et al. (2011) *Atmos. Chem. Phys.*, **11**, 133.

NH_3 Soil Compensation Point (χ_{soil})

- Equilibrium between $NH_{3(g,\ atmo)}$ and $NH_4^+{}_{(aq,\ soil)}$
  - Dependent on soil temperature, pH and $[NH_4^+]$
- If $NH_{3(g)} < \chi_{soil}$, then soil emission
- Bash *et al.* included bi-directional flux in CMAQ
  - 10% increase in NH_3, 45% decrease in NH_3 dry deposition



At thermodynamic equilibrium:

$$[NH_{3(g)}] = \frac{K_{diss}[NH_4^+{}_{(aq)}]}{K_H[H^+]}$$

Therefore:

$$\chi = \frac{K_{diss}[NH_4^+{}_{(aq)}]}{K_H[H^+]} e^{\left(\frac{\Delta H_{vap}+\Delta H_{dis}}{R}\right)\left(\frac{1}{298.15K}-\frac{1}{T_{soil}}\right)}$$

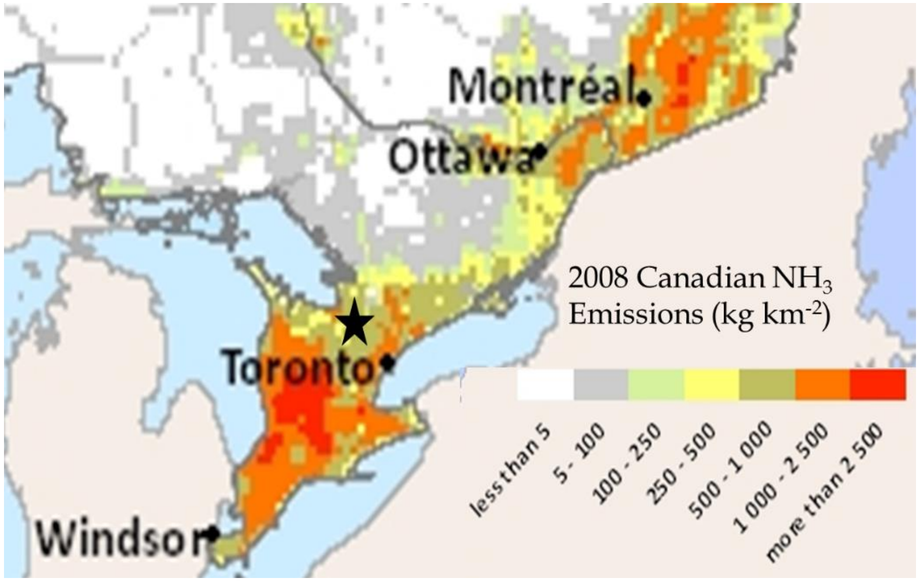
$$\chi = 13{,}587 \frac{[NH_4^+{}_{(aq)}]}{[H^+]} e^{\frac{-10{,}396K}{T_{soil}}} \times 10^9 \text{ ppb}$$

Bash et al. (2013) *Biogeosciences*, **10**, 1625.
Nemitz et al. (2004) *Atmos. Chem. Phys.*, **4**, 989.

CONTACT 2012

Characterizing **O**ntario **N**itrogen **T**ransport **A**nd **C**hemical **T**ransformation

- Primary Objective
  - Provide observational constraints on χ_{soil} and NH_3 fluxes
- Motivation
  - Lack of studies over ***non***-fertilized grasslands[‡]
  - Minimal field measurements of χ_{soil}
- Egbert, ON (★)
  - August 13 to October 2



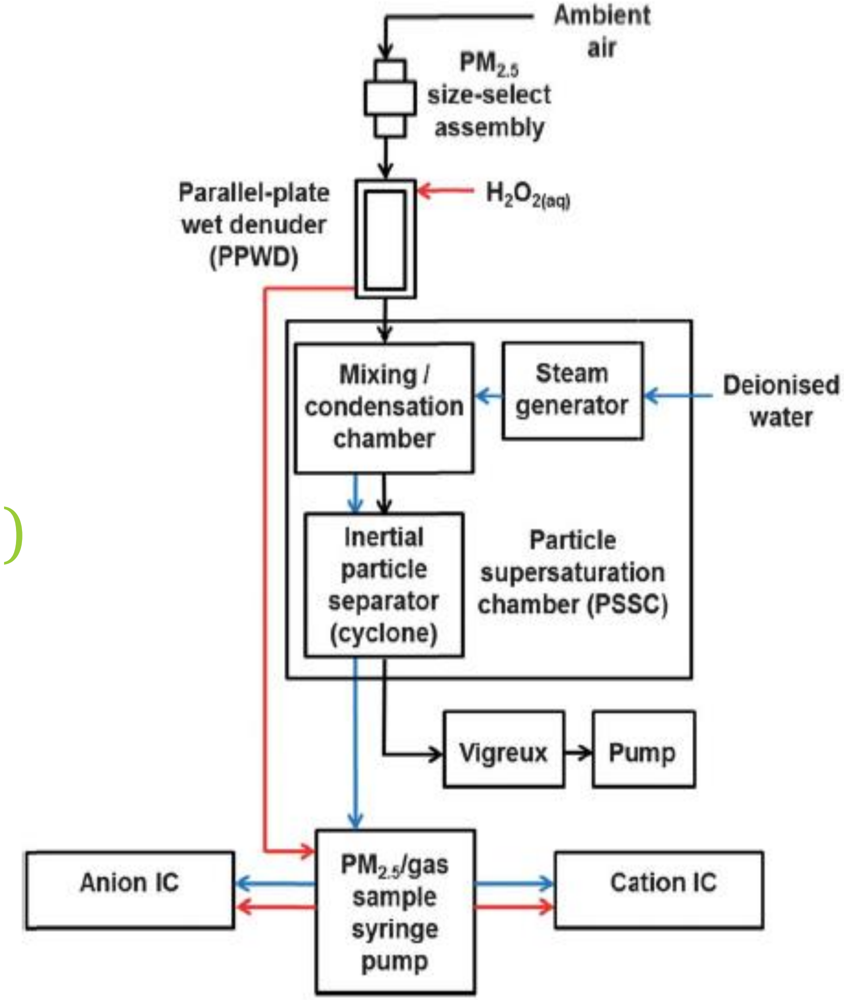
‡ Zhang et al. (2010) *J. Geophys. Rev.*, **115**, D20310.

Methodology – Atmospheric Sampling

- Ambient Ion Monitor-Ion Chromatograph (AIM-IC)

- Simultaneous on-line quantification (via Ion Chromatography) of water soluble:
  - Gas-phase species (**NH_3**, HNO_3, SO_2, HCl, HONO, etc…)
  - Ions in $PM_{2.5}$ (NH_4^+, SO_4^{2-}, NO_3^-, Cl^-, NO_2^-, etc…)

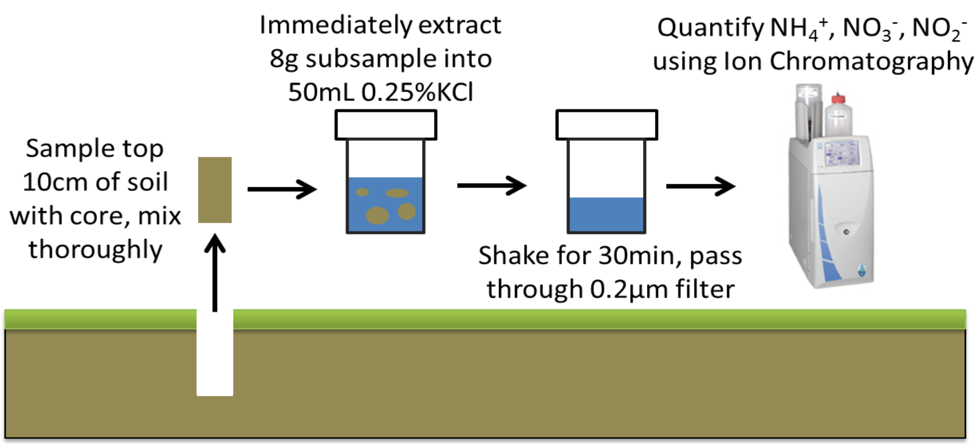
- Hourly time resolution



Markovic et al. (2012) *J. Environ. Monit.*, **14**, 1872.

Methodology – Soil Sampling

- Nitrogen Speciation



- Temperature/Water Content
  - Hourly averages with commercial sensors
- pH
  - pH electrode in 1:1 slurry of soil and deionized water
- Vegetation not sampled
  - Small N-pool relative to soil

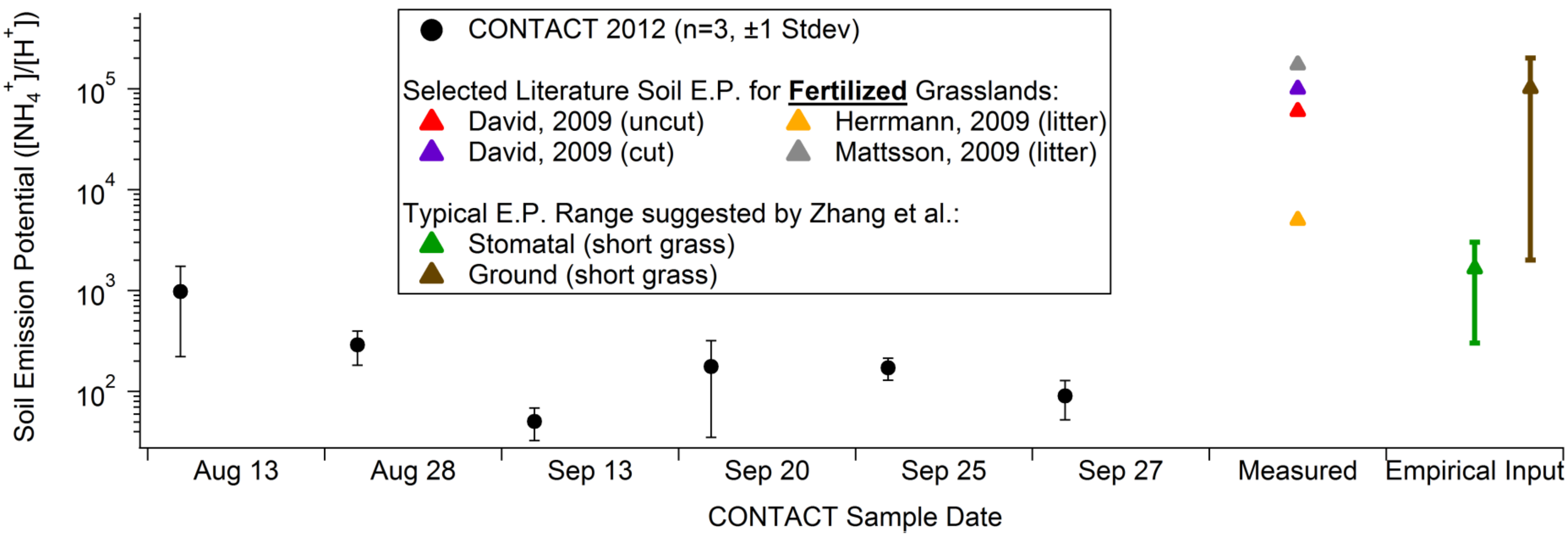
Li et al. (2012) *Commun. Soil Sci. Plan.*, **43**, 571.

Van Miegroet. (1995) *Soil Sci. Soc. Am. J.*, **59**, 549.

Results - Soil Emission Potential (Γ_{soil})

$$\Gamma_{soil} = \frac{[NH_4^+]}{[H^+]}$$

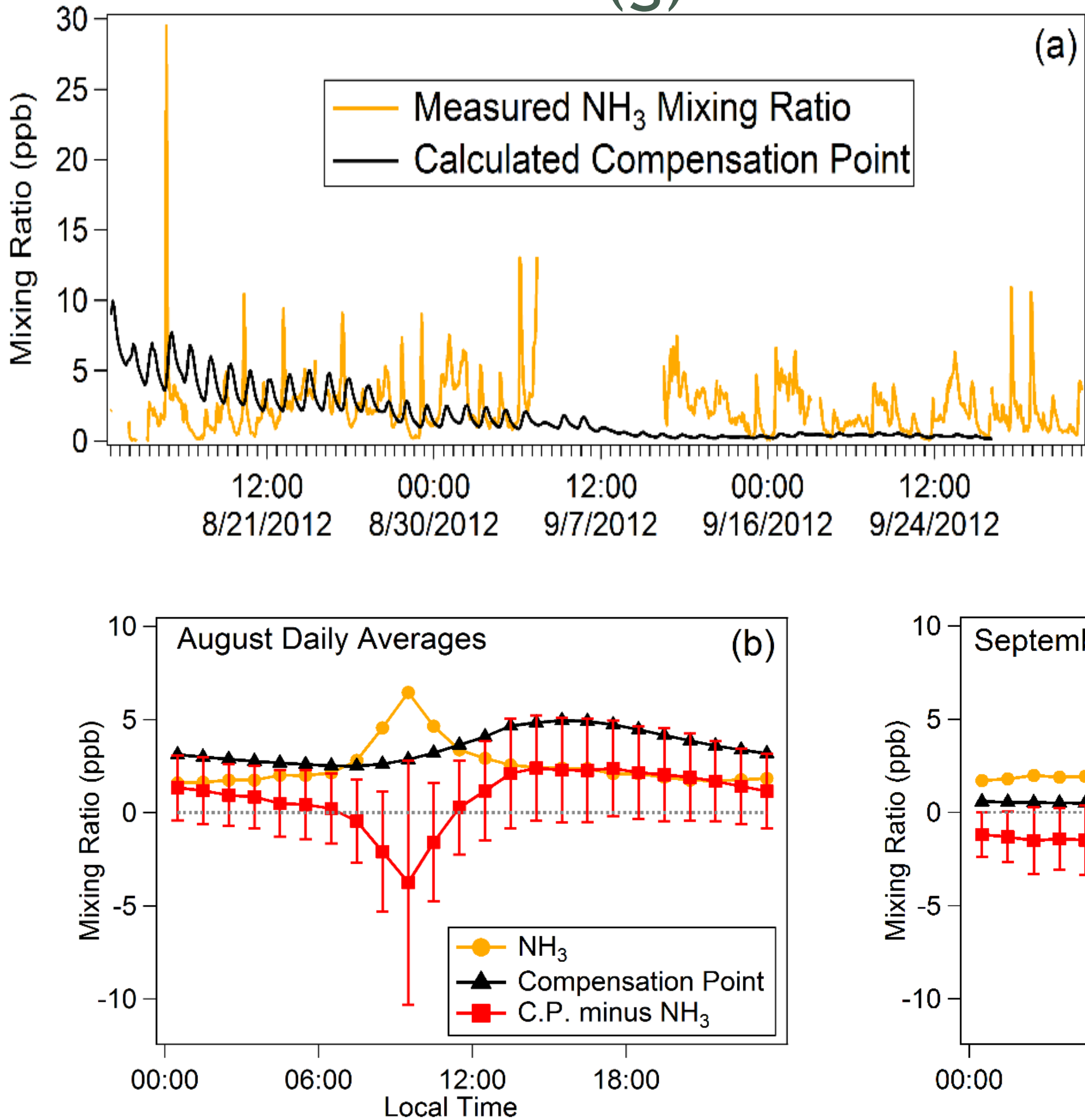
$$\chi = 13{,}587 \frac{[NH_4^+{}_{(aq)}]}{[H^+]} e^{\frac{-10{,}396K}{T_{soil}}} \times 10^9 \text{ ppb}$$



- First *measured* Γ_{soil} in a *non*-fertilized grassland
- Lower end of literature value for grasslands

Zhang et al. (2010) *J. Geophys. Rev.*, **115**, D20310.

Results – $NH_{3(g)}$ and Calculated χ_{soil}



- Temporal trends in χ:
  - Seasonal (lower values in autumn)
  - Daily (lower values at dawn)

Results – Estimated Fluxes

- Assumptions:
  - z_0 is 0.05m
  - Soil resistance and vegetation are negligible
- Previously *measured* fluxes†:
  - 4 ng $m^{-2}s^{-1}$ in summer
  - -24 ng $m^{-2}s^{-1}$ in autumn

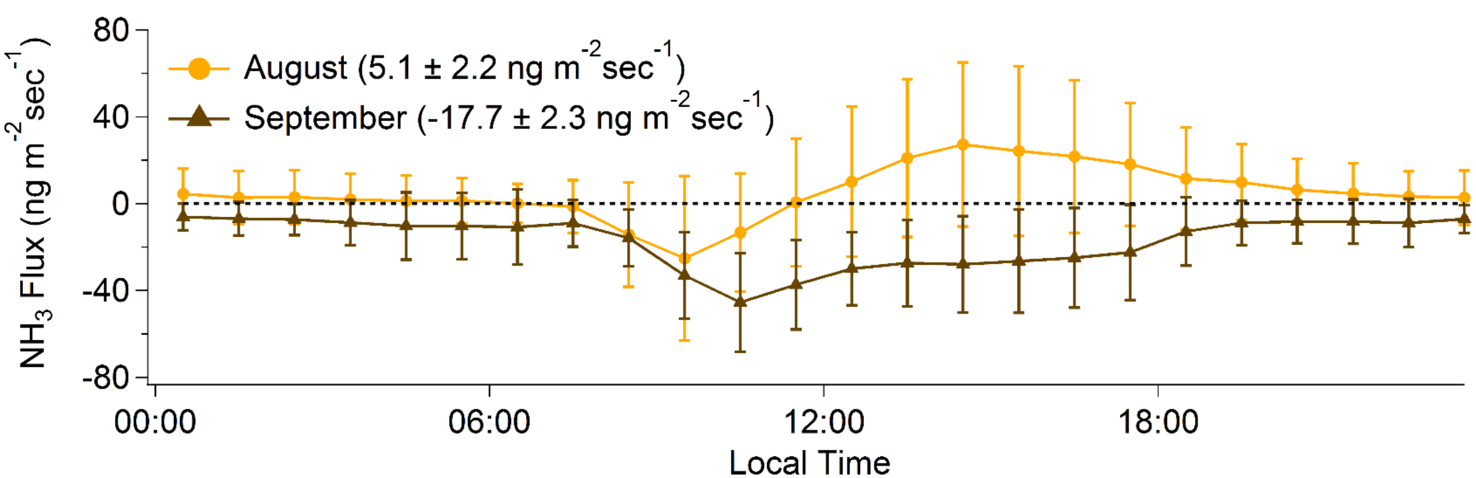
$$\text{Flux} = V_{exchange} * (\chi - NH_{3(g)})$$

$$V_{exchange} \approx \frac{1}{R_a + R_b}$$

$$R_a = \frac{ln(z_{ref}) - ln(z_0)}{\kappa u_*}$$

$$R_b = \frac{2}{\kappa u_*}\left(\frac{Sc}{Pr}\right)^{\frac{2}{3}}$$

$V_{exchange}$ = exchange velocity
R_a = aerodynamic resistance
R_b = quasi-laminar resistance
z_{ref} = AIM-IC inlet height
z_0 = 0.05m for uncut grass
κ = 0.4
u_* = friction velocity
Sc = 1.07
Pr = 0.72

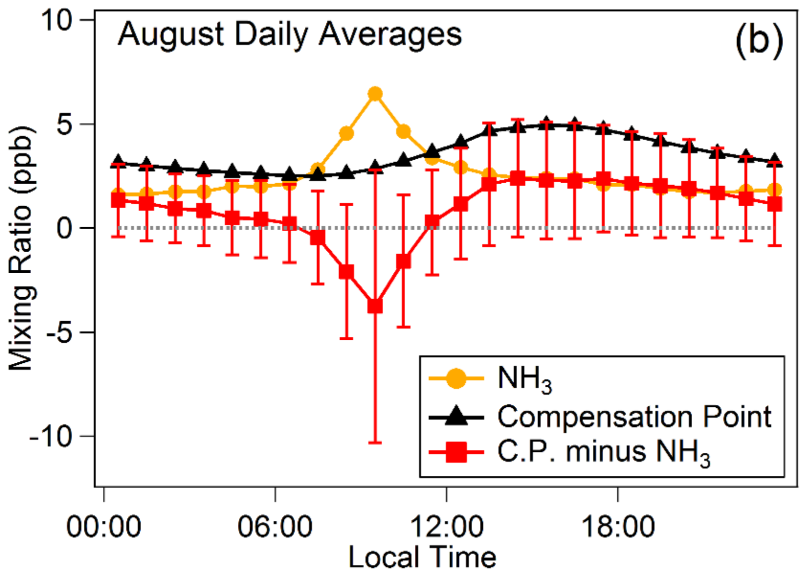


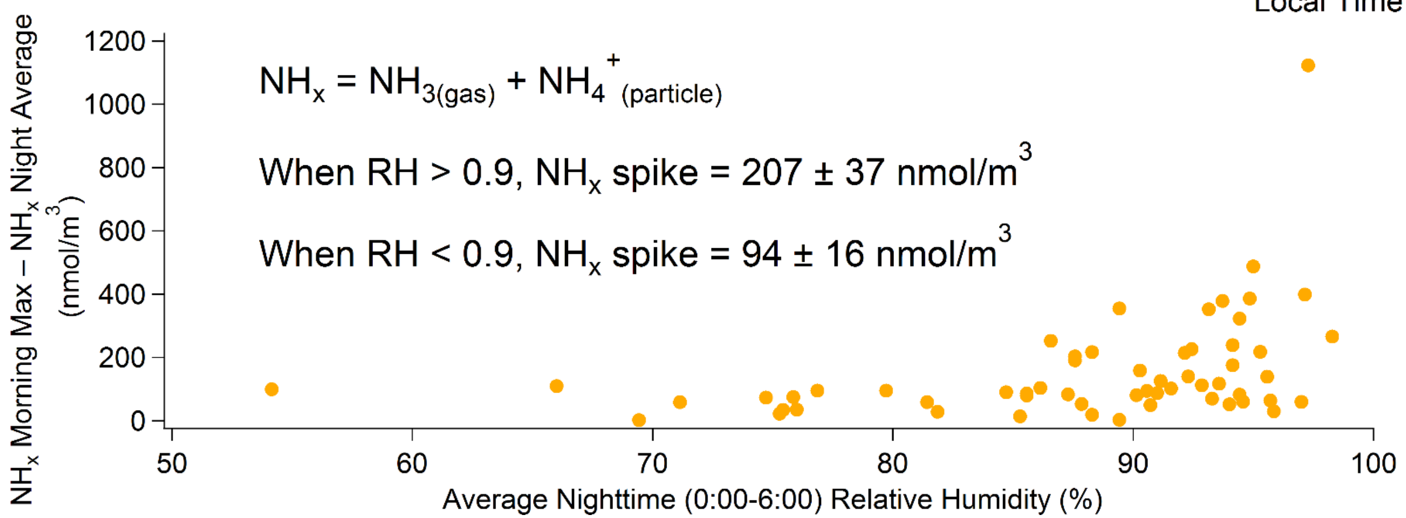
Seinfeld, J.H., Pandis, S.N. *Atmospheric Chemistry and Physics*. (Wiley, New York, 2006).

†Kruit et al. (2007) *Atmos. Environ.*, **41**, 1275.

Results – NH_3 Morning Spike

- Previous studies (i.e. Ellis *et al.*) observe morning peak of NH_3 at ~10:00
- Possibly due to:
  - Volatilization of dew/fog
  - Plant/soil emissions
  - Nocturnal BL break up

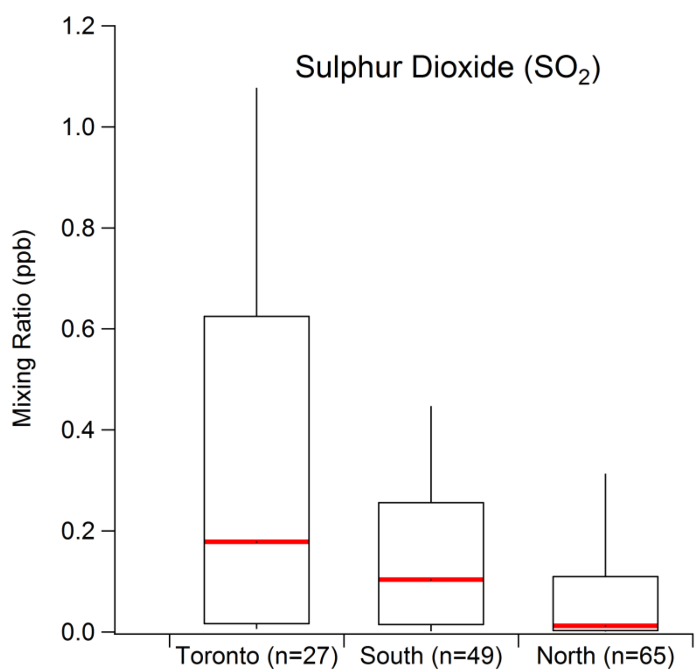


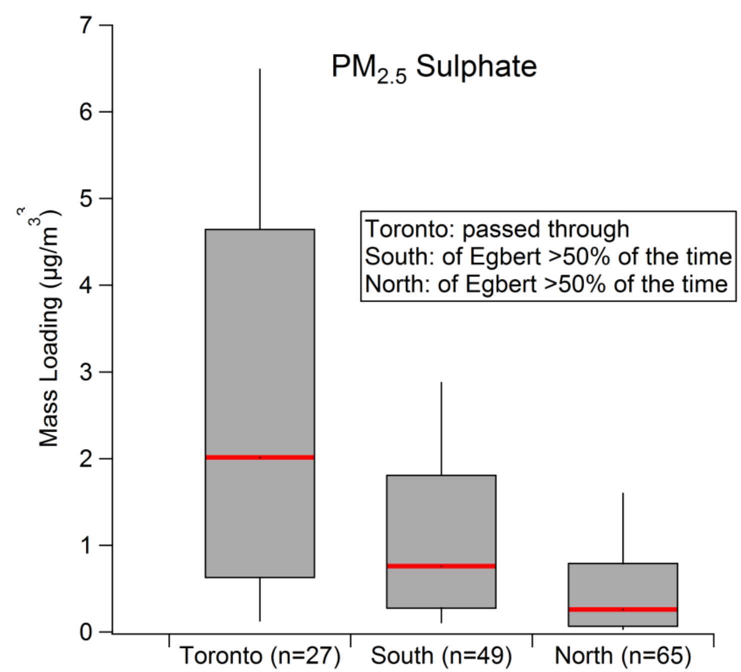


Ellis et al. (2011) *Atmos. Chem. Phys.*, **11**, 133.

Bi-directional Exchange in Action?

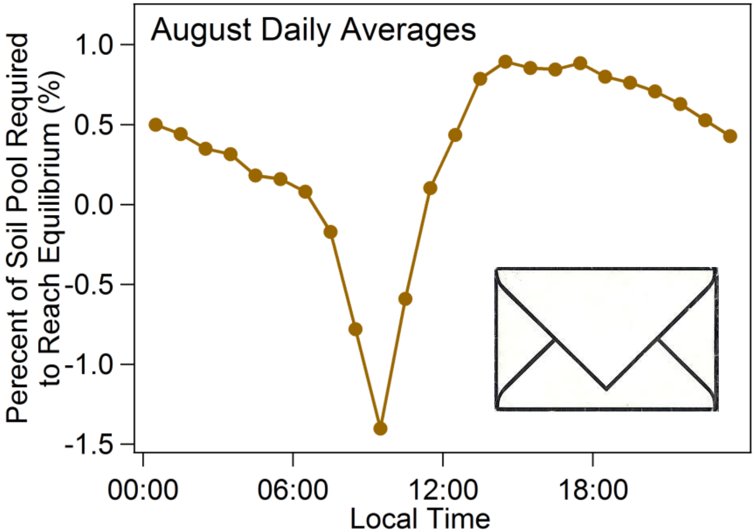
- Used HYSPLIT to determine 48 hour back-trajectories
  - Calculated every 6 hours during CONTACT
  - Clear directional bias for $PM_{2.5}$ and precursor gases
  - ***Except*** NH_3
    - Spatial homogeneity of local sources or evidence for bi-directional exchange?





Bi-directional Exchange in Action?

- Is the soil pool big enough?
  - Average fluxes during August
  - Boundary layer is 1000m
  - Top 10cm of soil exchanges
  - Soil is 1.5 g/cm^3



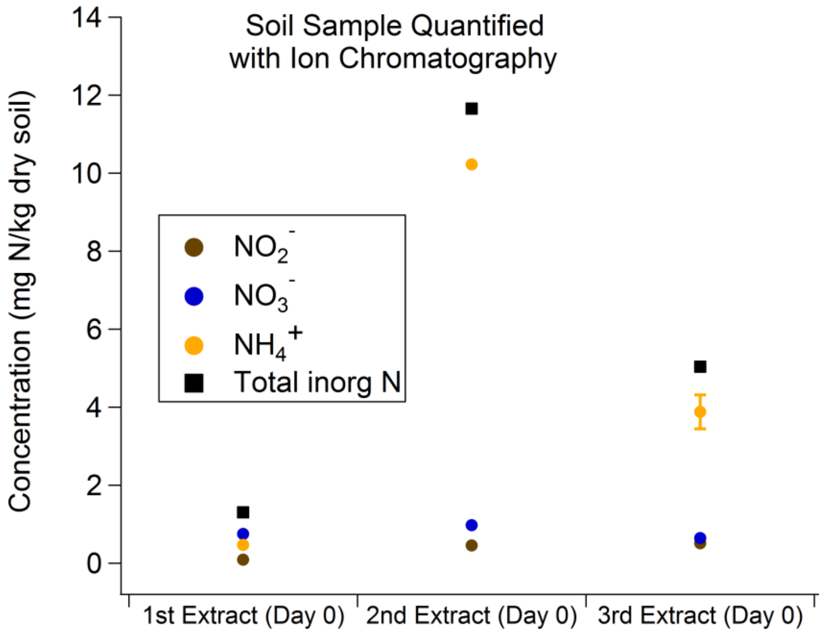
- Is the exchange fast enough (how long to reach 50% equilibrium)?
  - Using v_{ex} and (χ_{soil} – NH_3) from August

Height (m)	14:00 (fast)	01:00 (slow)
1000	~11 hours	~37 hours
3	~2 min	~7 min

Difficulties in Studying NH_3 Fluxes

1. Measure Fluxes
   - Typically requires intensive field work (unrealistic over large area)

2. Estimate Fluxes from surface and atmospheric properties (i.e. T, $[NH_4^+]$, pH, μ, NH_3, etc...)
   - Logistically easier
   - Complicated by heterogeneity
   - What methods are most representative of available NH_4^+ and H^+?



Conclusions

1. Γ_{soil} (non-fertilized grassland) is well below previous measurements for fertilized grasslands

2. Estimated Soil Fluxes:
   - Exhibit clear diurnal and seasonal trend
   - 5 and -18 ng $m^{-2}s^{-1}$ for Aug and Sept, respectively
   - Consistent with previous measurements from Kruit *et al*.

3. Evidence that emissions from non-fertilized grasslands could sufficiently modulate *near-surface* NH_3 despite low Γ_{soil}

4. Morning Spike of NH_3 is likely related to dew/fog

Kruit et al. (2007) *Atmos. Environ.*, **41**, 1275.

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