Acidity and Organic Aerosol Concentrations: An Analysis of Semi-Continuous OC and Acidity Field Measurements

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Introduction

- Jang and Kamens (2001) and others found that the presence of acidic seed particles can increase SOA formation

- Kalberer et al. (2004) reported that polymerization can proceed without pre-existing strong acid seed particles

- We use semi-continuous field measurements at PAQS from July 2001 to July 2002 to determine potential enhancements in SOA formation from inorganic acidity

2-4 hour OC and Sulfate
(Pittsburgh, July 2001- July 2002)

$r = 0.61$

OC ($\mu g/m^3$) vs Sulfate ($\mu g/m^3$)

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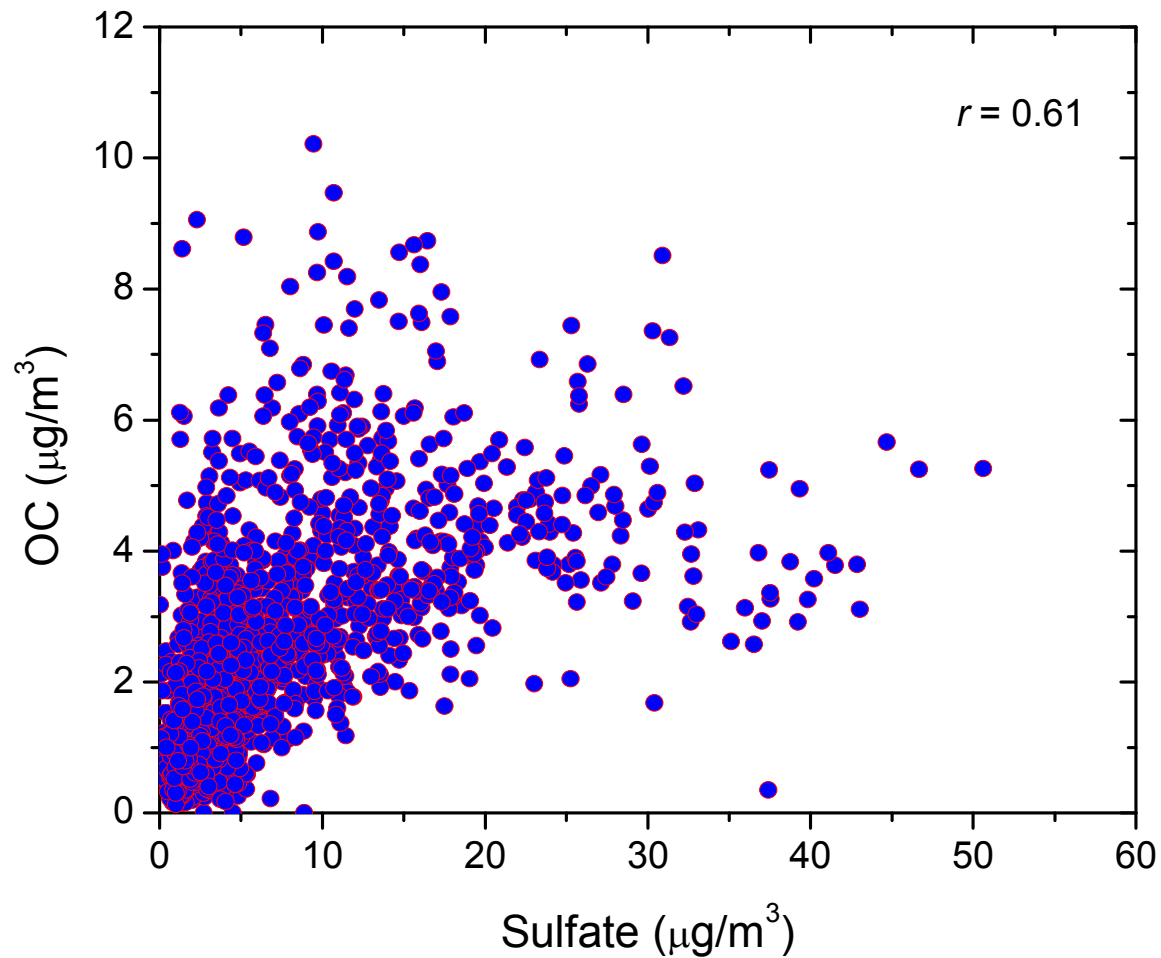
Metrics of Acidity and SOA

- Acidity: free acidity (H^+)
  - H^+ calculated for every 1-2 hours by GFEMN

    (Ansari and Pandis, 1999) from measurements of temperature, RH, sulfate, total nitric acid, total ammonia (total = gas + $PM_{2.5}$)

- SOA: OC/EC ratio
  - OC and EC measured by in-situ analyzer in 2-4 hour sampling periods (Lim and Turpin, 2002)
  - Increases with SOA formation
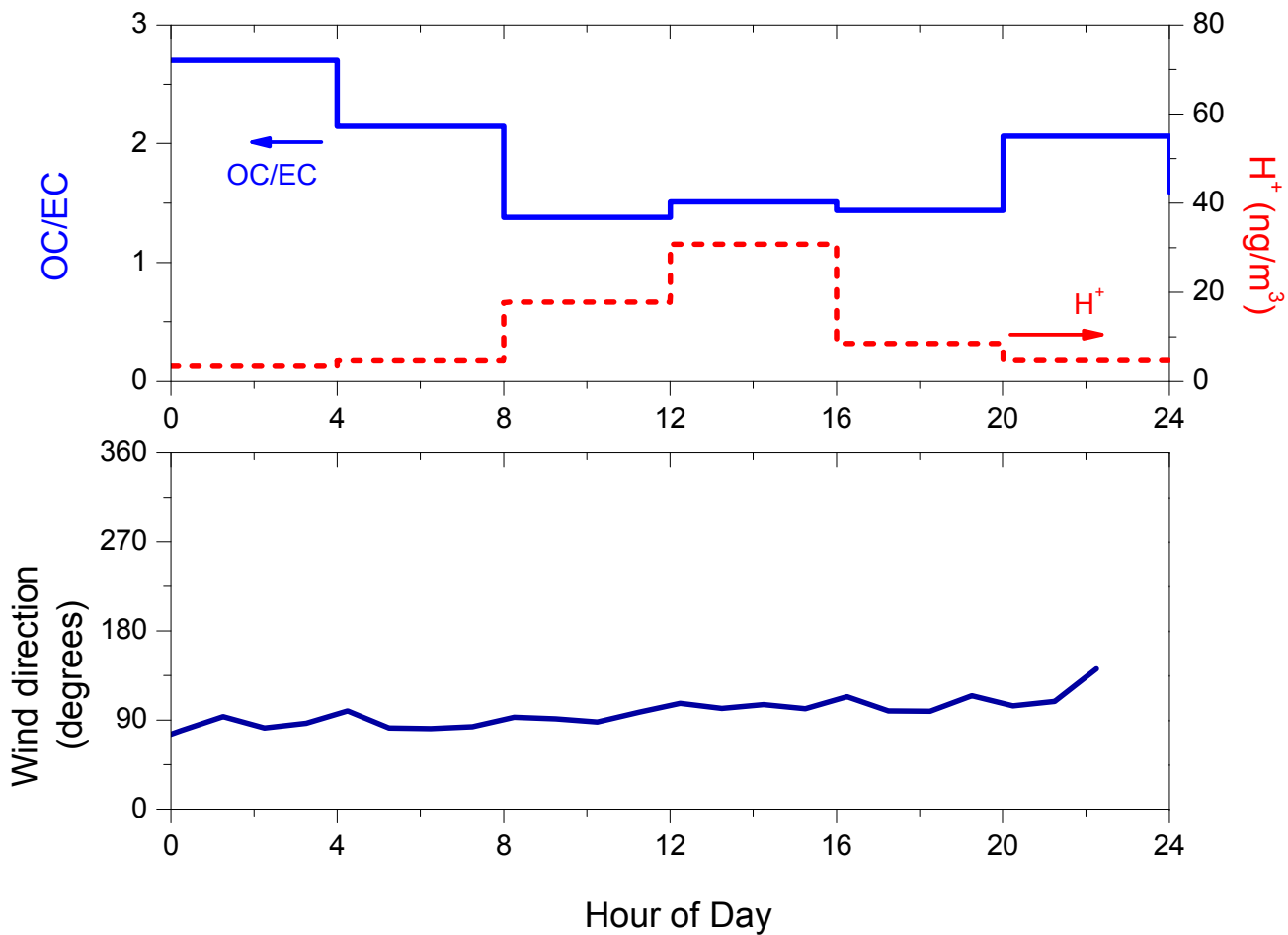 - Robust with respect to atmospheric mixing
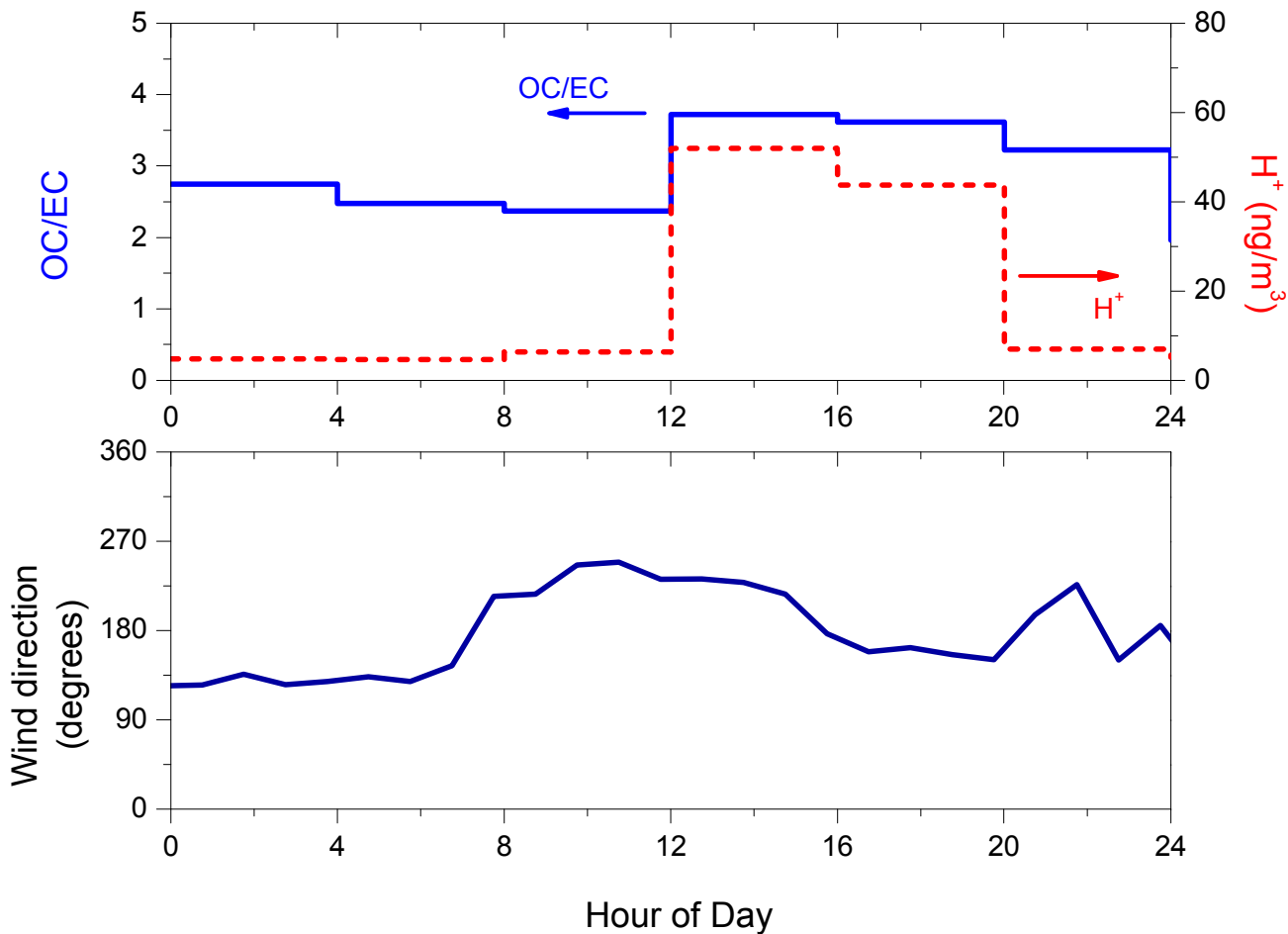
Seasonal variation of H⁺
(Pittsburgh)
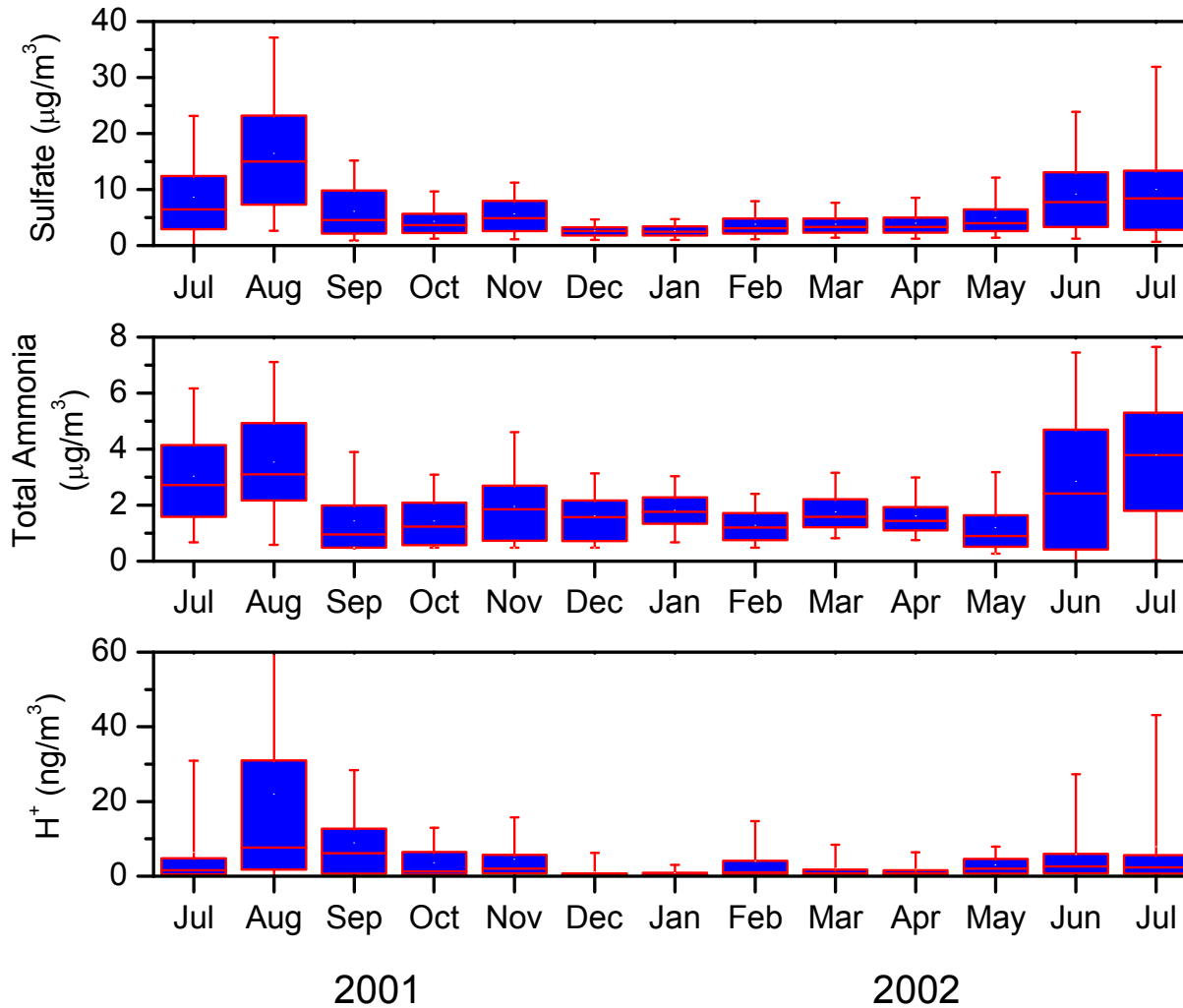
Diurnal variation of H$^+$
(Pittsburgh)
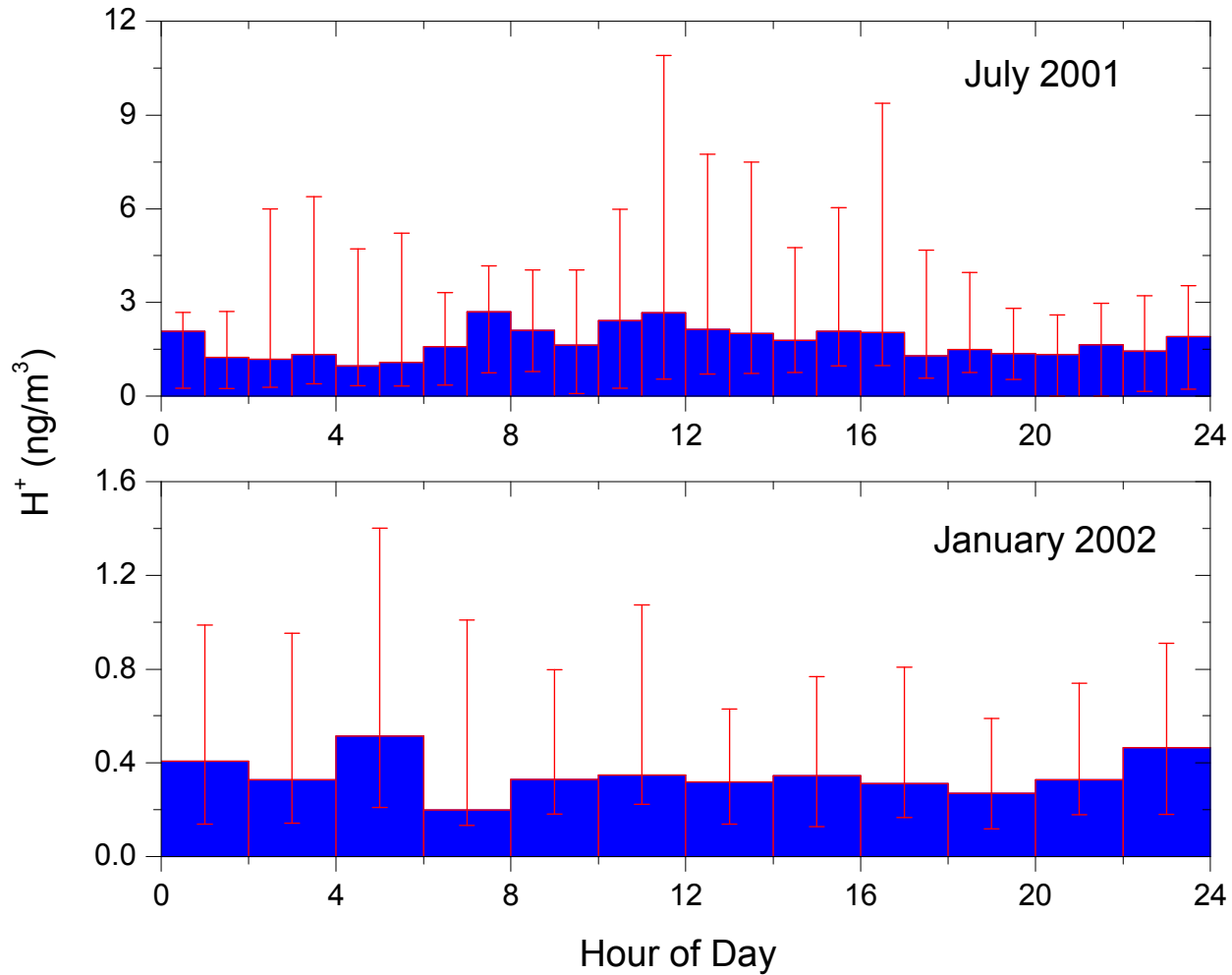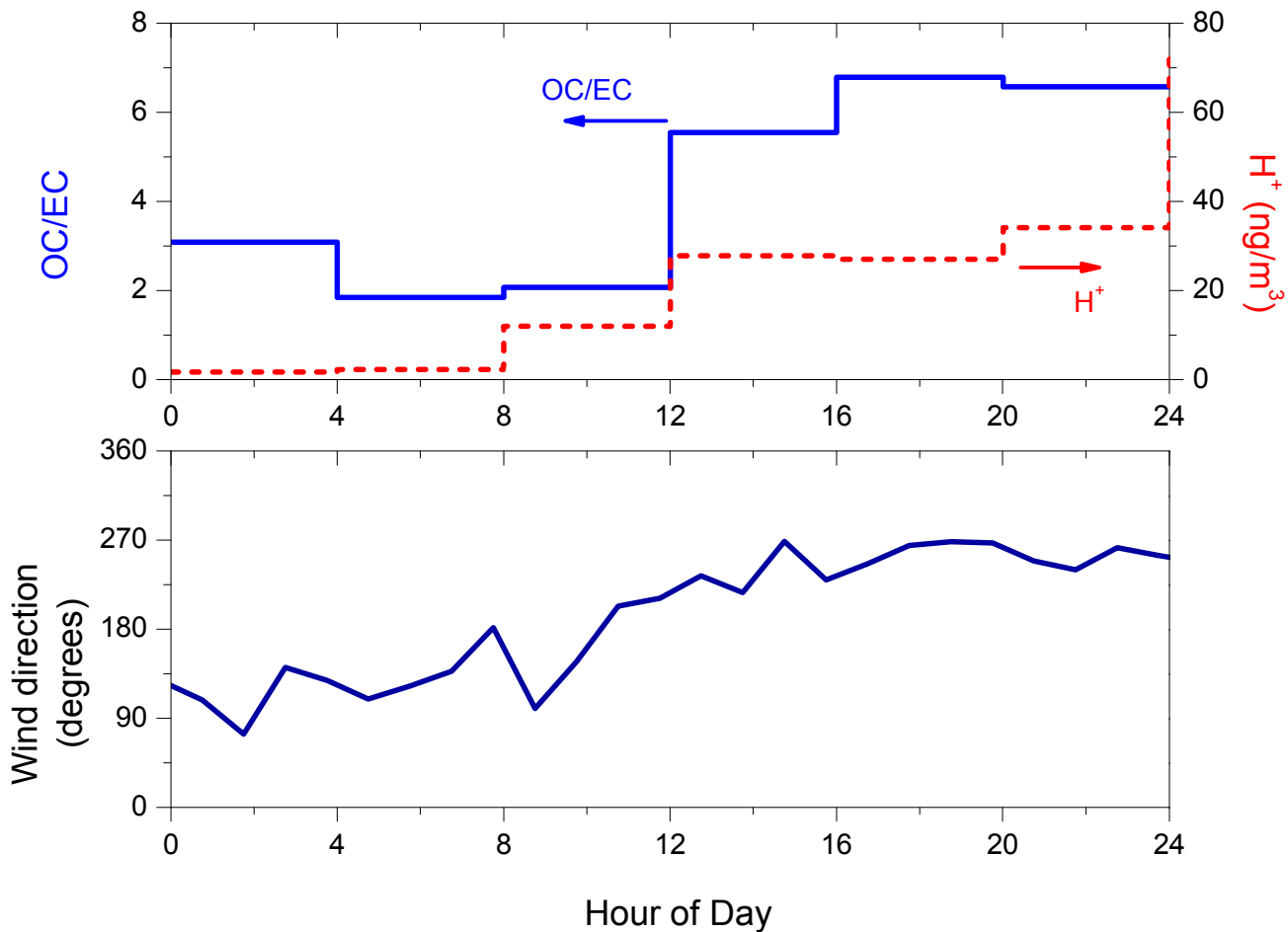
Organic PM and Acidity
June 25, 2002

Organic PM and Acidity
# July 17, 2002

# Organic PM and Acidity
March 27, 2002

Changes in OC/EC with increases in H^+

- 343 days examined
- Identified 104 days during which acidity increased significantly
  - 13 days in which OC/EC decreased when wind direction was steady
  - 22 days in which OC/EC increased when wind direction was steady (strong evidence)
  - 38 days in which OC/EC increased when wind direction was unsteady (weak evidence)
  - 31 days when there was no significant change in OC/EC

Correlations of H⁺ with ΔOC/EC
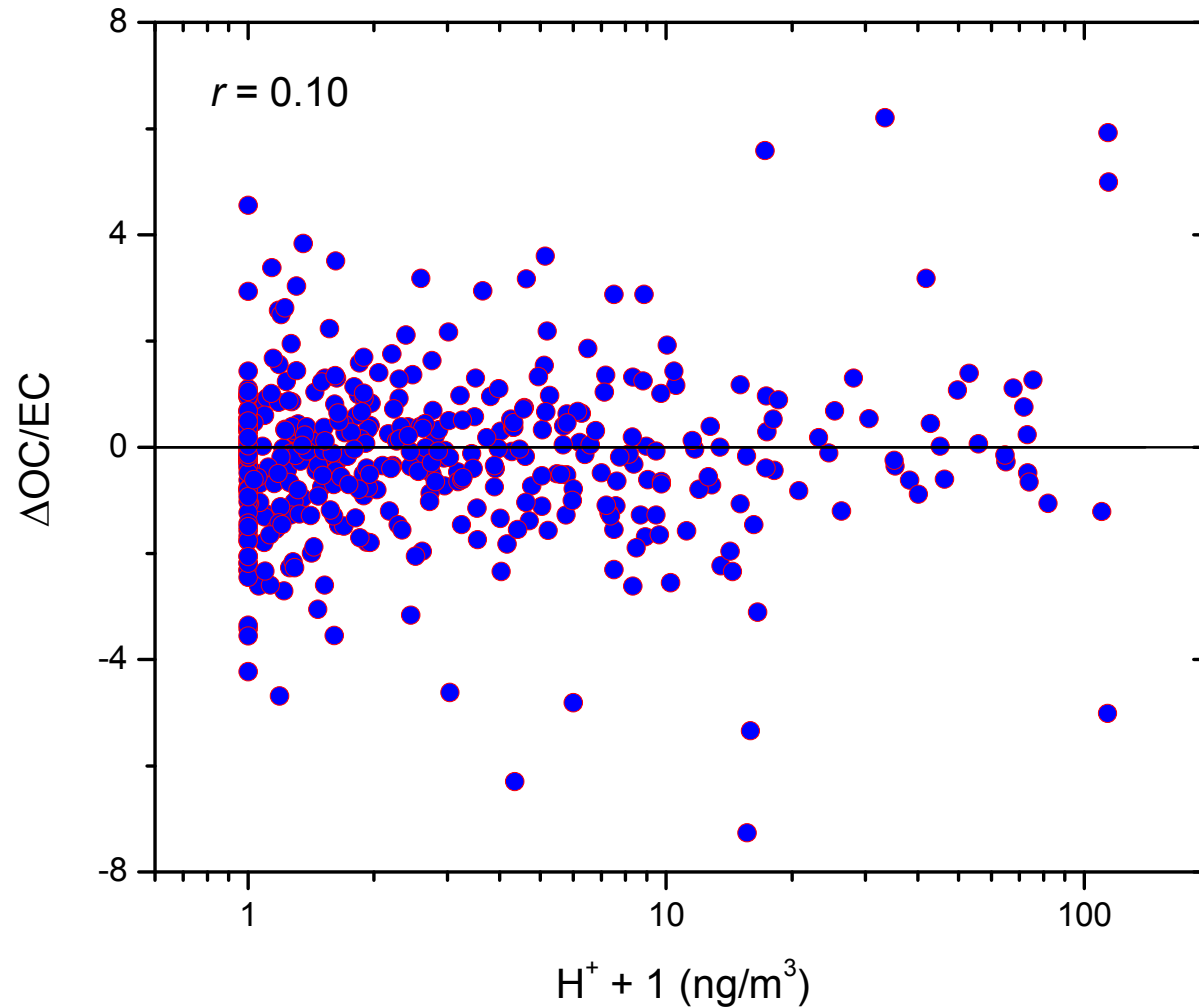
Correlations of various metrics of acidity with ΔOC/EC
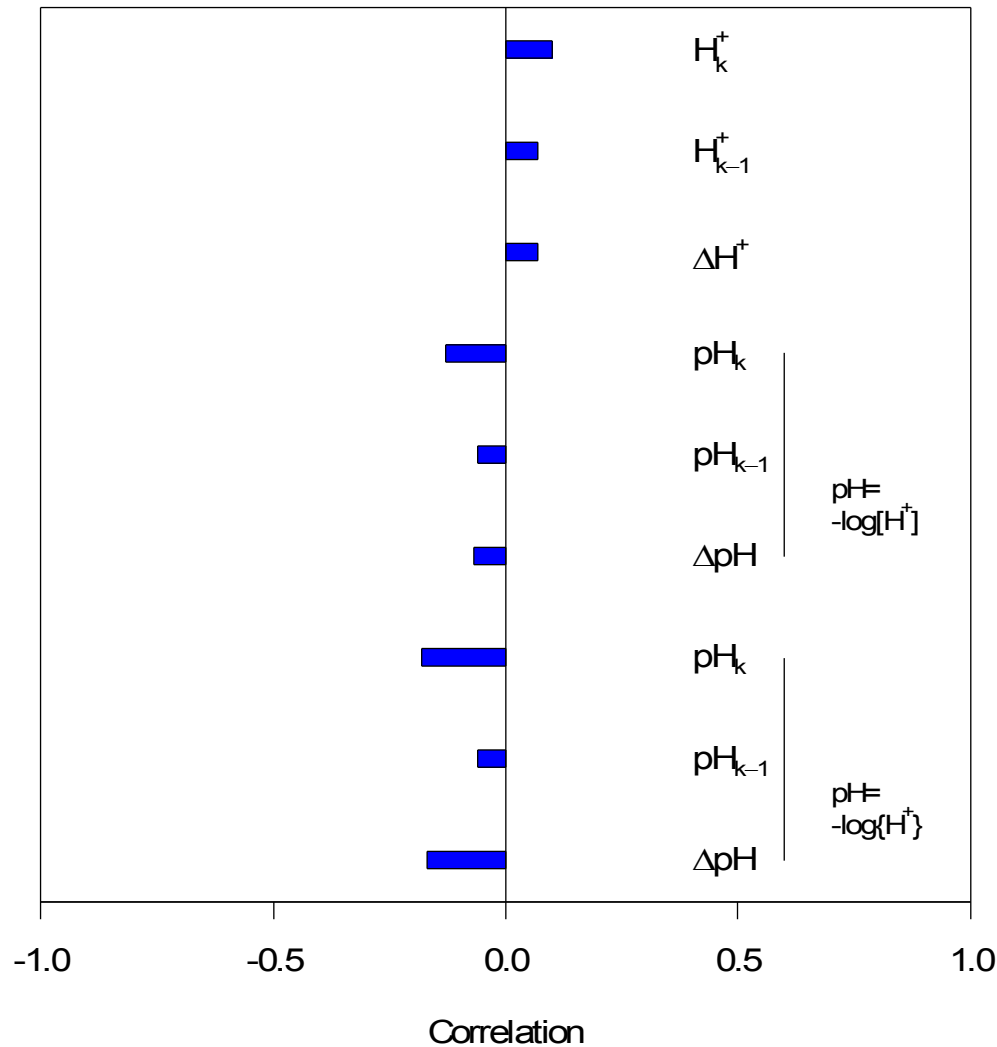
Regression Analysis

$$\log\left(OC\!/EC\right)_k = \beta_0 + \beta_1 \log\left(OC\!/EC\right)_{k-1} + \beta_2 H_k^+ + \beta_3\left(1\!/NO_x\right)_k + \beta_4 CO_k + \beta_5 O_{3k} + \varepsilon_k$$

- Solve with generalized least squares
- n = 1200+
- Correlation of fitted v. observed values = 0.75
- β_2 = 2.1±0.8
- If H$^+$ → 0, average reductions in OC estimated to be 1±3%

Estimate of Upper Bound

- Maximum enhancement of SOA due to acidity under atmospheric conditions estimated to be 40% (Iinuma et al., 2004)
- For our calculations
  - When acidity was present ($H^+ > 0$) estimates of secondary organic carbon (SOC) reduced by 40%
  - SOC contribution to OC estimated by EC-tracer method (Cabada et al., 2004)
  - SOC is ~35% of OC (Cabada et al., 2004)
- Reductions in OC calculated for July 2001 to July 2002 was on the order of 5%. This is a upper bound estimate.

Conclusions

- We were not able to detect significant enhancements of SOA production due to inorganic acidity in Western Pennsylvania.
  - Its effect may be lost in the noise of the system.
- Upper range of OC reductions resulting from reductions in acidity estimated to be on the order of 5% for Pittsburgh.

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