Aerosol Acidity in the New England Coastal Atmosphere During Summer 2002

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NEW ENGLAND AIR QUALITY STUDY
2002 Campaign
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Abstract

Aerosol pH controls important multiphase chemical pathways in the atmosphere but absolute values are poorly constrained. As part of the New England Air Quality Study, aerosol pH was quantified based on multiple independent approaches and results were intercompared for consistency. Soluble, reactive trace gases with pH-dependent solubilities (HNO_3, NH_3, HCl, HCOOH, and CH_3COOH) were sampled with mist chambers. Size-segregated aerosols were sampled in parallel with cascade impactors and analyzed for major ionic constituents. H^+ was measured directly in minimally diluted, 5-µL spots on surfaces of impaction substrates with a flat-surface, field-effect transistor. Aerosol liquid water contents (LWCs) were calculated with hygrospocity models. Aerosol pHs required to sustain the measured phase partitioning of each analyte were inferred based on corresponding thermodynamic properties and direct pH measurements were extrapolated to ambient LWCs. The ensemble of approaches yielded coherent results. Sea-salt pHs ranged from about 2 to the mid 4s and sub-µm aerosol pHs ranged from <1 to the mid 3s. The $H^+ + SO_4^{2-}$ HSO_4^- equilibrium strongly buffered aerosol pH in all size fractions.

Science Questions

- What are the pHs of aerosols as functions of particle size over coastal new England?
- What is the degree of "closure" in aerosol pH based on multiple independent approaches?

Measurements – Gases

(HNO_3, NH_3, HCl, HCOOH, CH_3COOH)

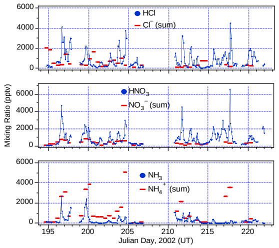
- Tandem mist chamber technique; deionized H_2O mist
- 2-hour samples; flow rate ~ 20 standard liters per minute
- Inertial inlet removed super-micrometer aerosols
- In-line Teflon filter removed sub-micrometer aerosols
- Inlet passing efficiencies for HCl ~100% (Keene et al., 1993) and >86% for HNO_3 (see below)
- Gases trapped quantitatively
- Mist solutions analyzed by ion chromatography aboard ship
- Precisions from paired measurements ~ ±10 to ±15%
- Detection limits ~ 10 to 25 pptv

Measurements – Soluble Particulate-Phase Species

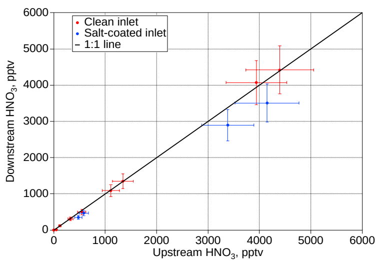
- Anions: NO_3^-, Cl^-, Br^-, SO_4^{2-}, $CH_3SO_3^-$, $HCOO^-$, CH_3COO^-, $C_2O_4^{2-}$
- Cations: H^+, NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+}

- Hi-volume (~1.1 m^3 min^{-1}) impactor deployed over ~12-hr (day or night) intervals
- Polycarbonate impaction substrates and quartz-fiber back-up filter
- Average GMDs: 24, 13, 6.0, 2.8, 1.5, 0.75, 0.38 µm
- On ship, replicate 5-µL H_20 droplets added to exposed areas
- pH measured with flat-surface, field effect transistor
- Remaining sections stored frozen
- Anions and other cations quantified by ion chromatography after cruise

Temporal Variability of Soluble Gases and Associated Aerosol Ions



Inlet passing efficiency for HNO_3 (Laboratory experiments)



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Estimating Aerosol pH from Thermodynamics

$$\mathrm{HNO_{3g}} \overset{K_H}{} \{\mathrm{HNO_{3aq}}\} \overset{K_a}{} \{\mathrm{H^+}\} + \{\mathrm{NO_3^-}\}$$

$$\{\mathrm{HNO_{3aq}}\} = K_H * \mathrm{HNO_{3g}}$$

$$\{\mathrm{HNO_{3aq}}\} = (\{\mathrm{H^+}\} * \{\mathrm{NO_3^-}\}) / K_a$$

$$\{\mathrm{H^+}\} = K_H * K_a * \mathrm{HNO_{3g}} / \{\mathrm{NO_3^-}\}$$

$$\{\mathrm{NO_3^-}\} = \mathrm{NO_3^-}_{meas} / LWC * AC$$

- Based on RH, temperature, and GMD
- LWC for sea salt from Gerber (1985) and Gong et al. (1997)
- LWC for S aerosol from Tang and Munkelwitz (1994)
- Activity coefficients (AC) from Pitzer (1991)
- Independent estimates based on HCl / Cl^- and NH_3 / NH_4^+

Estimating Aerosol pH from Measurements

$$[H_{tot}]_{aer} = [H_{tot}]_{spot} * (LW_{spot} / LW_{samp})$$

where:

$$[H_{tot}]_{spot} = [H^+]_{meas} + [HSO_4^-] - [H^+]_{CO_2}$$

$$LW_{spot} = 5\ \mu L + LW_{samp}$$

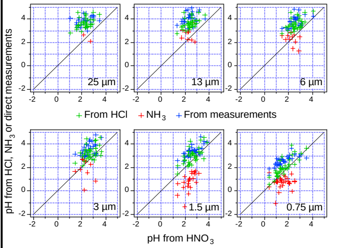
$$LW_{samp} = LWC_{aer} * Vol_{air} * f$$

f = fraction of exposed substrate covered by spot

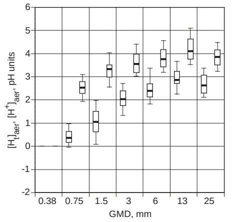
$$[H^+]_{aer} = [H_{tot}]_{aer} - [HSO_4^-]_{aer}$$

where $[HSO_4^-]_{aer}$ is calculated from $[H_{tot}]_{aer}$, SO_4^{2-}, K_a, and LWC_{aer}

(Keene et al., 2002)

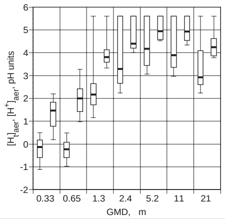


Total and Ambient Aerosol Acidity from Direct Measurements



Bermuda, May 1997

(Keene et al., 2002)



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Conclusions

- Ensemble of approaches yields coherent results
- Sea-salt aerosol pHs range from about 2 to mid 4s
- Sub-µm aerosol pHs range from <1 to mid 3s
- Total acidities are 20 to 200 times higher than free
- Relative to Bermuda
  - Sea-salt aerosol pHs are lower
    - Due to higher concentrations of acidic gases
    - Significant NH_4^+ partitions in larger aerosols
  - Sub-µm aerosol pHs are higher
    - Due to higher concentrations of NH_3

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