Atmos. Chem. Lecture 19, 11/20/13: Aerosol chemistry (inorganic)

Chemical composition of fine PM

$HNO_3 + NH_3 + H_2O$ mixtures

$H_2SO_4 + NH_3 + H_2O$ mixtures

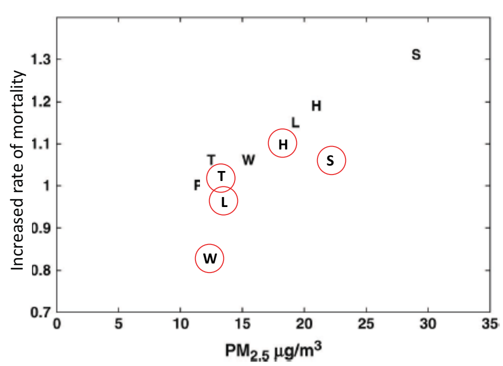
$H_2SO_4 + HNO_3 + NH_3 + H_2O$ mixtures

PSet 4 due Mon Nov 25

Health effects of particulate matter

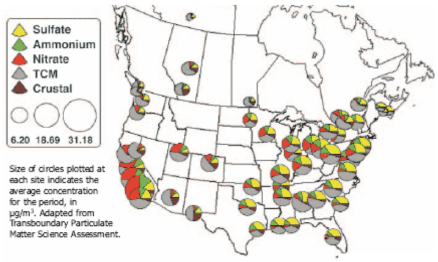
Fine particles can travel deep into the lungs

"Harvard Six Cities Study": fine particle loading correlates with increased mortality; associated with lung cancer and cardiopulmonary disease



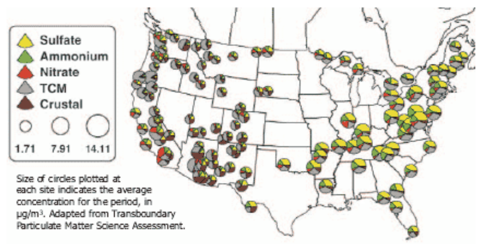
D. W. Dockery et al., *New Engl. J. Med.* 329, 1753-1759 (1993) and F. Laden et al., *Am. J. Resp. Crit. Care Med.*, 173, 667-672 (2006)

Chemical composition of fine particulate matter

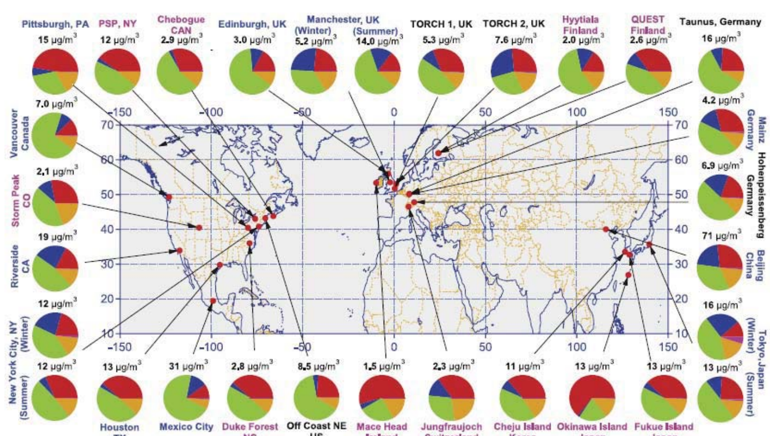


urban US: STN, NAPS networks

rural US: IMPROVE network



Chemical composition of fine particulate matter



organic sulfate nitrate ammonium

Zhang et al. 2007

General sources of aerosol

Coarse mode (>2.5 μm): Mechanically-generated aerosol
- sea-spray
- wind-blown dust (crustal material)

Fine mode (<2.5 μm): Gas-to-particle conversion
- nitrate (NO_3^-)
- sulfate (SO_4^{2-})
- ammonium (NH_4^+)
- chloride (Cl^-)
- organics

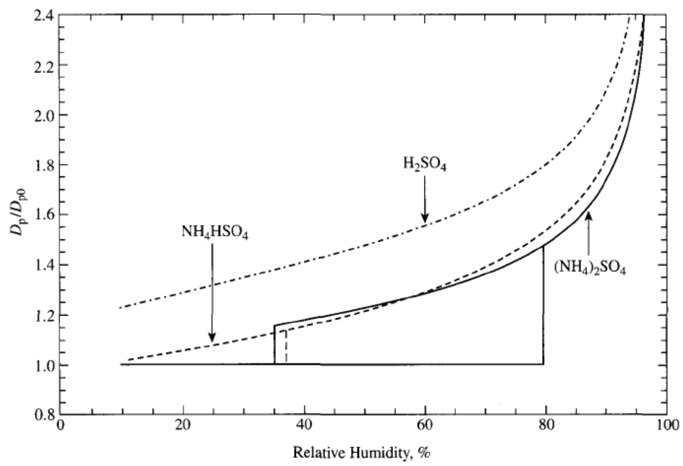
Inorganic gas-particle partitioning

H_2SO_4: very low in volatility (10^{-5} Torr), mostly in condensed phase

NH_3: vapor pressure of ~7600 Torr – highly volatile
H* of 2.6 x 10^5 M/atm – very soluble

HNO_3: vapor pressure of ~50 Torr – volatile
H* of 2.5 x 10^6 M/atm – very soluble

Interaction of liquid water with inorganic ions

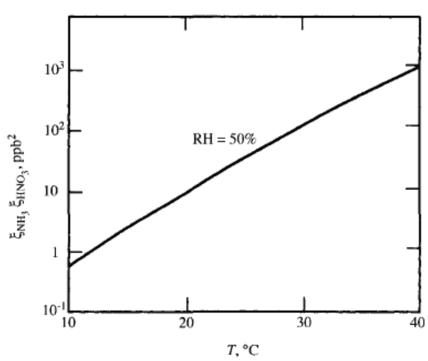


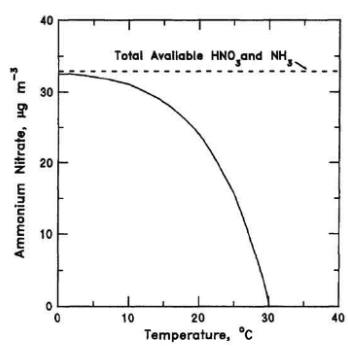
S&P

Ammonium nitrate (s): $HNO_3 + NH_3$

Below the DRH (61.8% at 298K)

$NH_4NO_3(s) \leftrightarrows NH_3(g) + HNO_3(g)$





S&P

Stelson and Seinfeld 1982a (*Atm. Env.* 16:993)
Mozurkewich 1993 (*Atm. Env.* 27A:261)

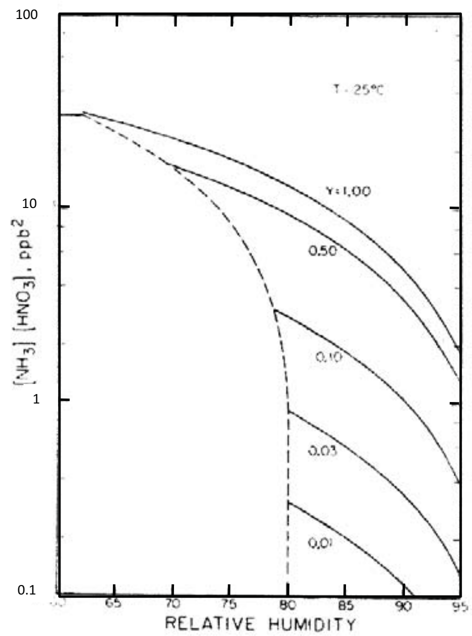
Ammonium nitrate (aq): $HNO_3 + NH_3 + H_2O$

Above the DRH (61.8% at 298K)

$NH_4^+(aq) + NO_3^-(aq) \leftrightarrows NH_3(g) + HNO_3(g)$

Stelson and Seinfeld 1982b (*Atm. Env.* 16:2507)

Use this (*not* S&P Fig 10.21!) for NH_4NO_3 equilibrium constants



$H_2SO_4 + NH_3 + H_2O$ system

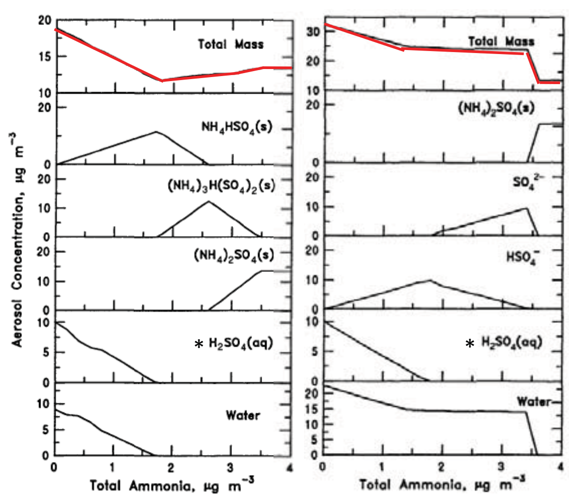
gaseous species:
H_2SO_4 (g), NH_3 (g), H_2O (g)

aqueous species:
HSO_4^- (aq), SO_4^{-2} (aq), NH_3(aq), NH_4^+ (aq), H^+ (aq)

solid species:
NH_4HSO_4 (s), $(NH_4)_2SO_4$ (s), $(NH_4)_3H(SO_4)_2$ (s)

liquid species:
H_2O (l)

30% RH　　75% RH



S&P

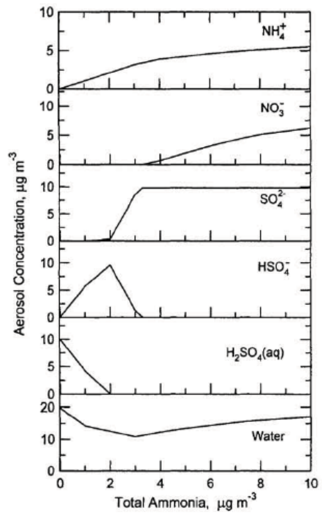
$NH_3 + H_2SO_4 + HNO_3 + H_2O$ system

gaseous species:
H_2SO_4, NH_3, HNO_3, H_2O

aqueous species:
HSO_4^-, SO_4^{-2}, NH_3, NO_3^-, NH_4^+, H^+

solid species:
NH_4HSO_4, $(NH_4)_2SO_4$, NH_4NO_3,
$(NH_4)_3H(SO_4)_2$, $(NH_4)_2SO_4 \cdot 2NH_4NO_3$,
$(NH_4)_2SO_4 \cdot 3NH_4NO_3$

liquid species:
H_2O (l)



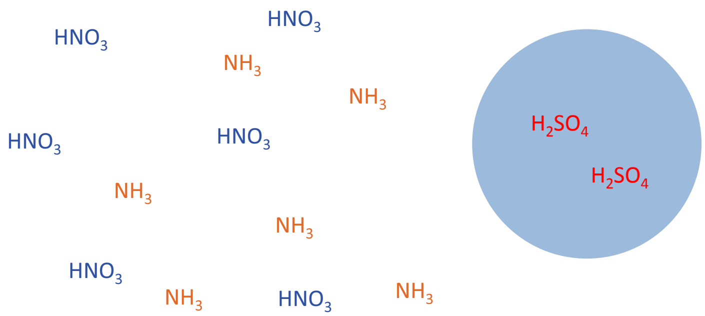
S&P: RH 70%

Online calculators

Extended Aerosol Inorganic Model (E-AIM) *Clegg, Brimblecombe, Wexler*
http://www.aim.env.uea.ac.uk/aim/aim.php/

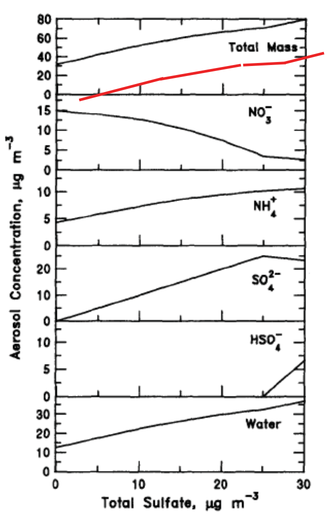
ISORROPIA *Nenes*
http://nenes.eas.gatech.edu/ISORROPIA/

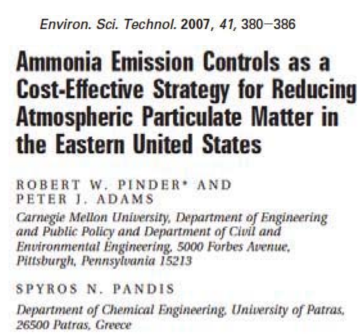
$NH_3 + H_2SO_4 + HNO_3 + H_2O$ system



[*Note: Additional material is discussed here during lecture.*]

Decreasing PM: SO_2, NO_X, or NH_3?




Environ. Sci. Technol. 2007, *41*, 380–386

Ammonia Emission Controls as a Cost-Effective Strategy for Reducing Atmospheric Particulate Matter in the Eastern United States

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S&P: 70% RH

1.84J / 10.817J / 12.807J Atmospheric Chemistry
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