Ammonia and Atmospheric Chemistry

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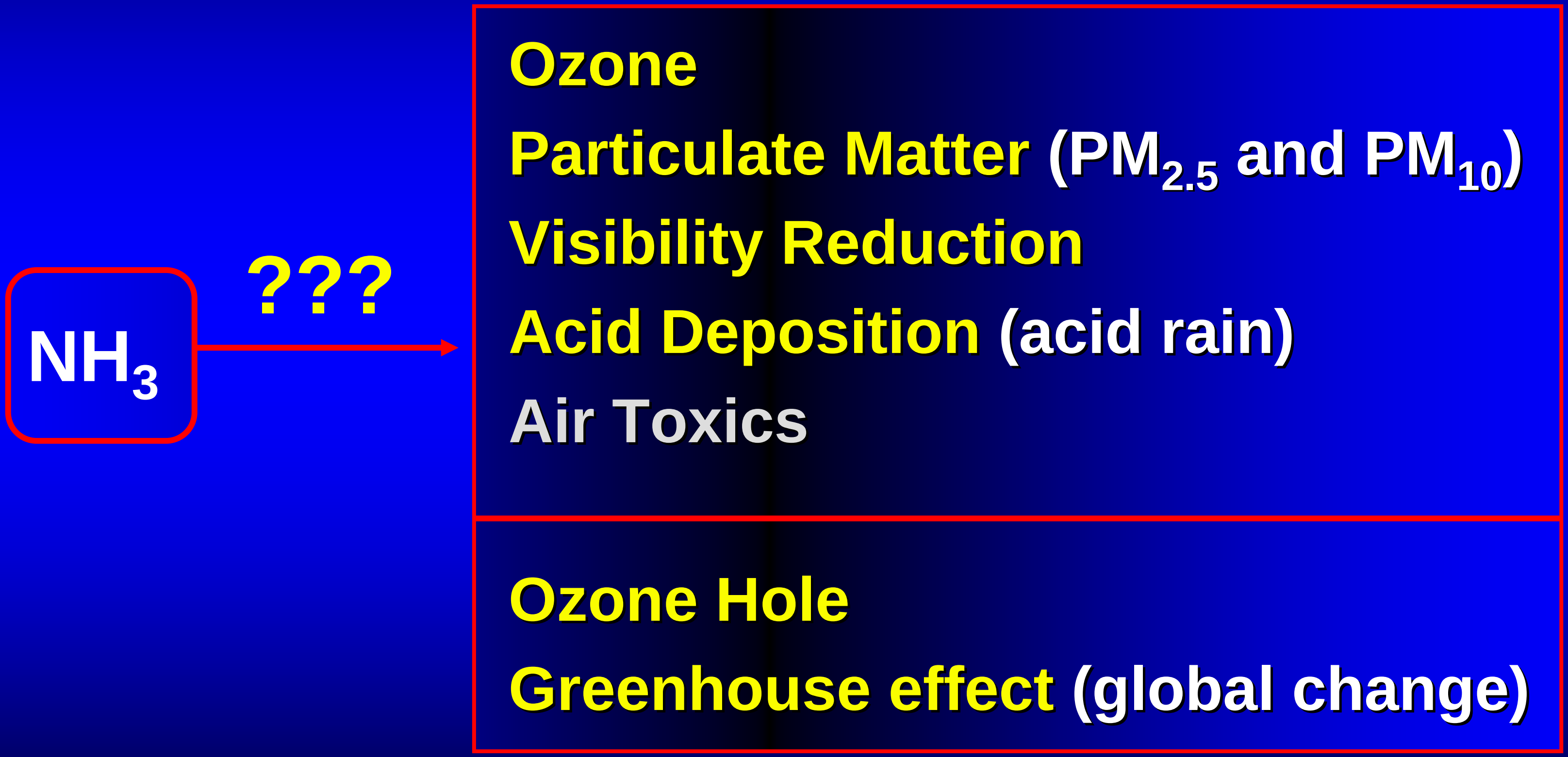
MAIN AIR QUALITY PROBLEMS



NH_3

???

Ozone

Particulate Matter ($PM_{2.5}$ and PM_{10})

Visibility Reduction

Acid Deposition (acid rain)

Air Toxics

Ozone Hole

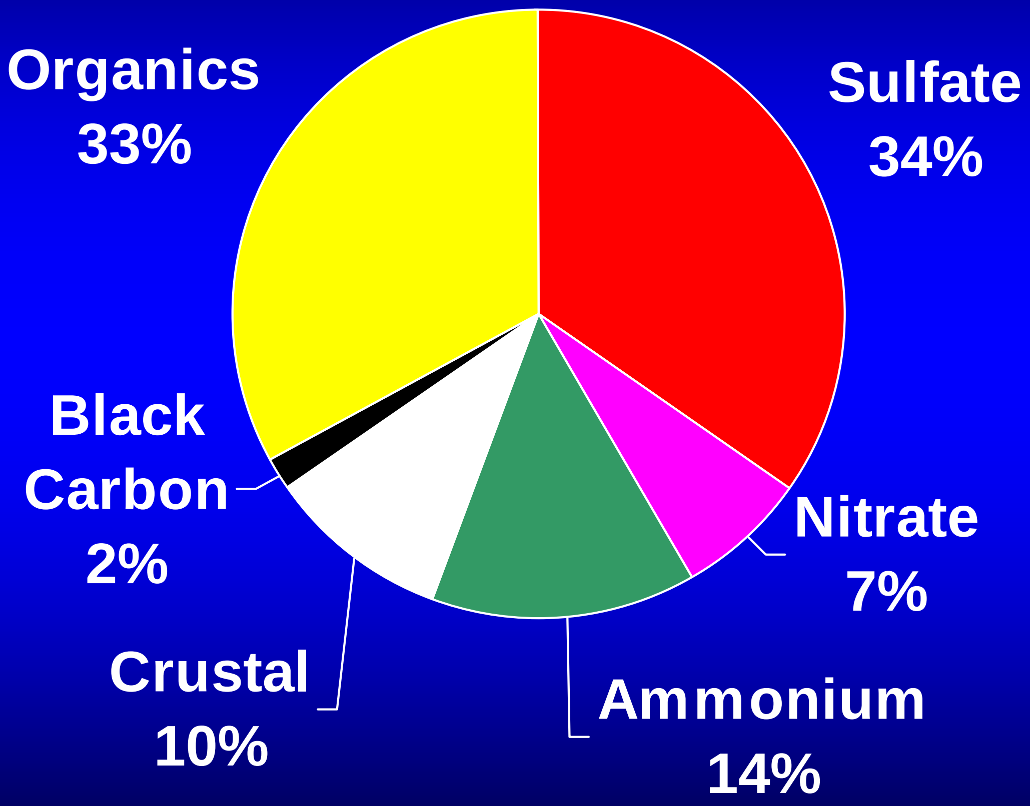
Greenhouse effect (global change)

Ammonia and Gas-Phase Chemistry

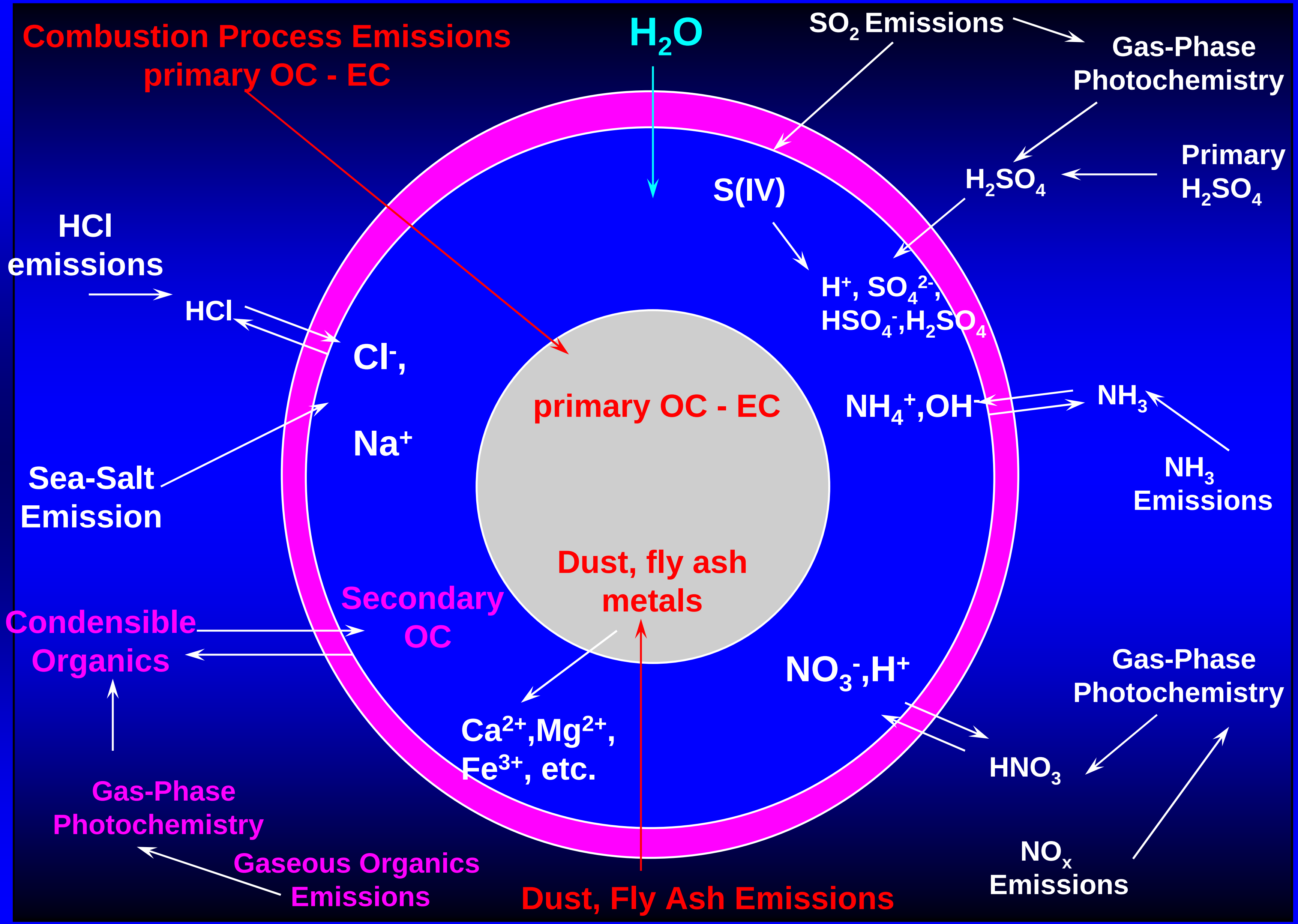
- Most species in the atmosphere react with the hydroxyl radical (OH)
    - These reactions remove the primary species, but initiate a complicated chain of radical reactions leading to the formation of ozone and other secondary pollutants
- The reaction of ammonia with OH is quite slow (2 months average lifetime)
    - Negligible importance for the atmospheric fate of ammonia
- Ammonia does not contribute directly to the atmospheric photochemistry
    - No role in the formation of ozone or other secondary gas-phase pollutants

Fine PM Composition in NE US

(Pittsburgh, 2001)



$PM_{2.5}$=20.1 μg m^{-3}



Combustion Process Emissions
primary OC - EC

H_2O

SO_2 Emissions

Gas-Phase
Photochemistry

H_2SO_4

Primary
H_2SO_4

S(IV)

H^+, SO_4^{2-},
HSO_4^-,H_2SO_4

HCl
emissions

HCl

Cl^-,

Na^+

Sea-Salt
Emission

primary OC - EC

Dust, fly ash
metals

NH_4^+,OH^-

NH_3

NH_3
Emissions

Condensible
Organics

Secondary
OC

Ca^{2+},Mg^{2+},
Fe^{3+}, etc.

NO_3^-,H^+

Gas-Phase
Photochemistry

HNO_3

Gas-Phase
Photochemistry

Gaseous Organics
Emissions

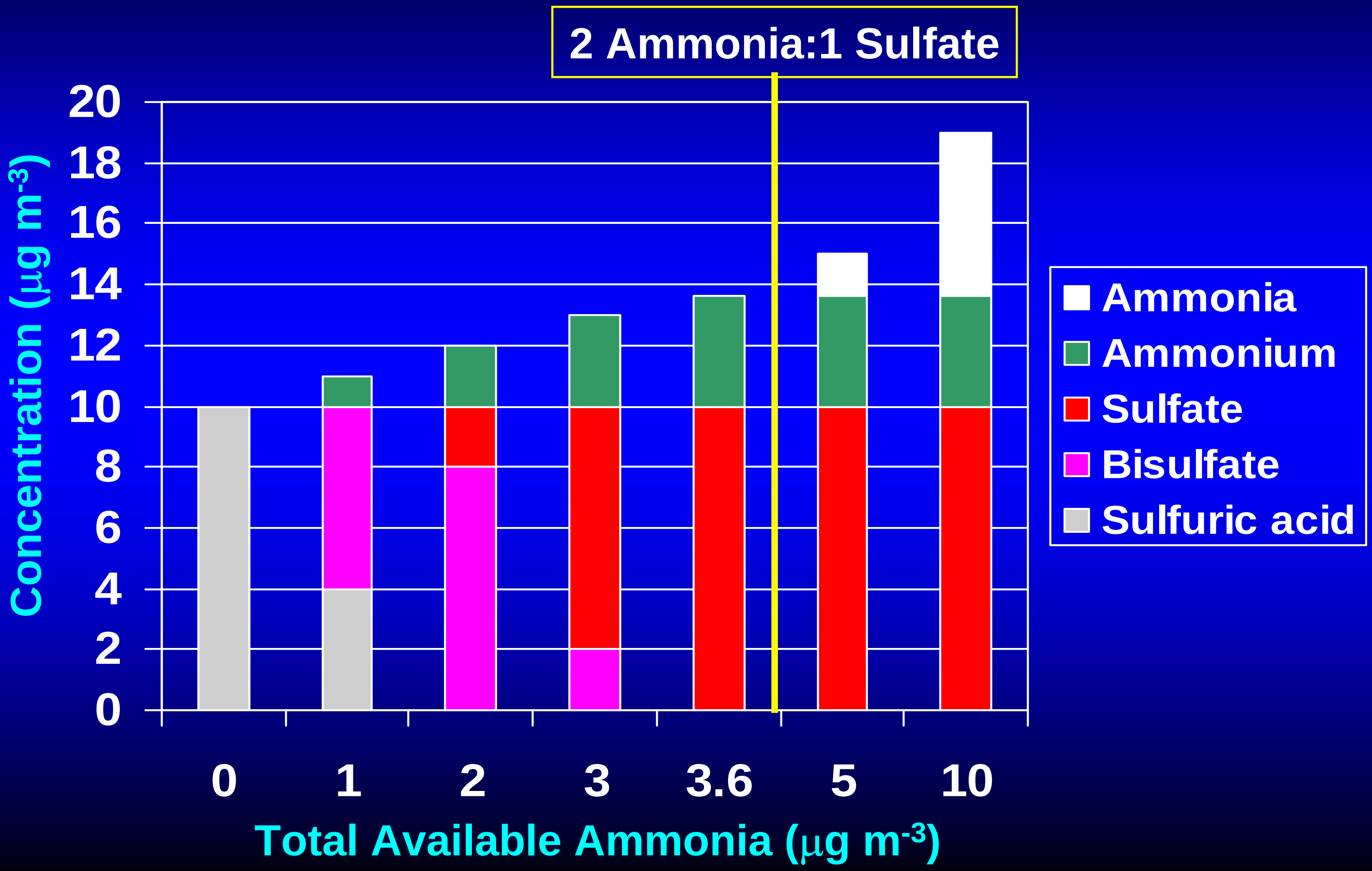
Dust, Fly Ash Emissions

NO_x
Emissions

Sulfuric Acid in the Atmosphere

- **Sulfuric acid in the presence of water vapor has an extremely low vapor pressure**
- **As soon as sulfuric acid vapor is formed in the atmosphere it is transferred to the particulate phase**
  - **Condensation on existing particles, or in-situ formation of new particles (nucleation)**
- **The preferred form of sulfuric acid in the aerosol phase is ammonium bisulfate $(NH_4)_2SO_4$**
  - **Each sulfuric acid molecule is looking for two ammonia molecules (neutralization)**
  - **If there is not enough ammonia present, sulfuric acid exists either as H_2SO_4(aq) or NH_4HSO_4**

The Sulfuric Acid/Ammonia System



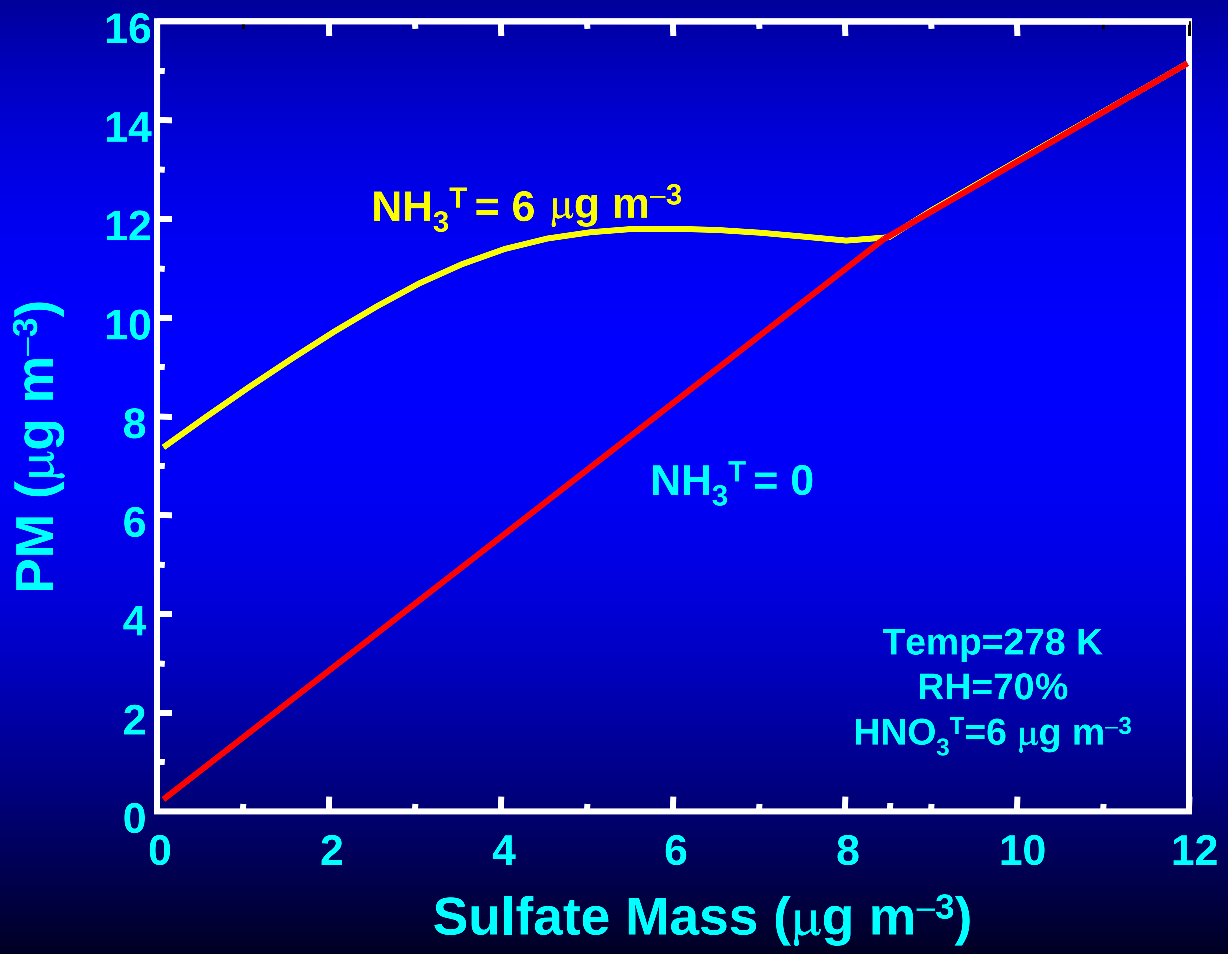
Ammonium Nitrate Formation

$$NH_3\,(g) + HNO_3\,(g) \leftrightarrows NH_4NO_3\,(s) \qquad \text{(low RH)}$$

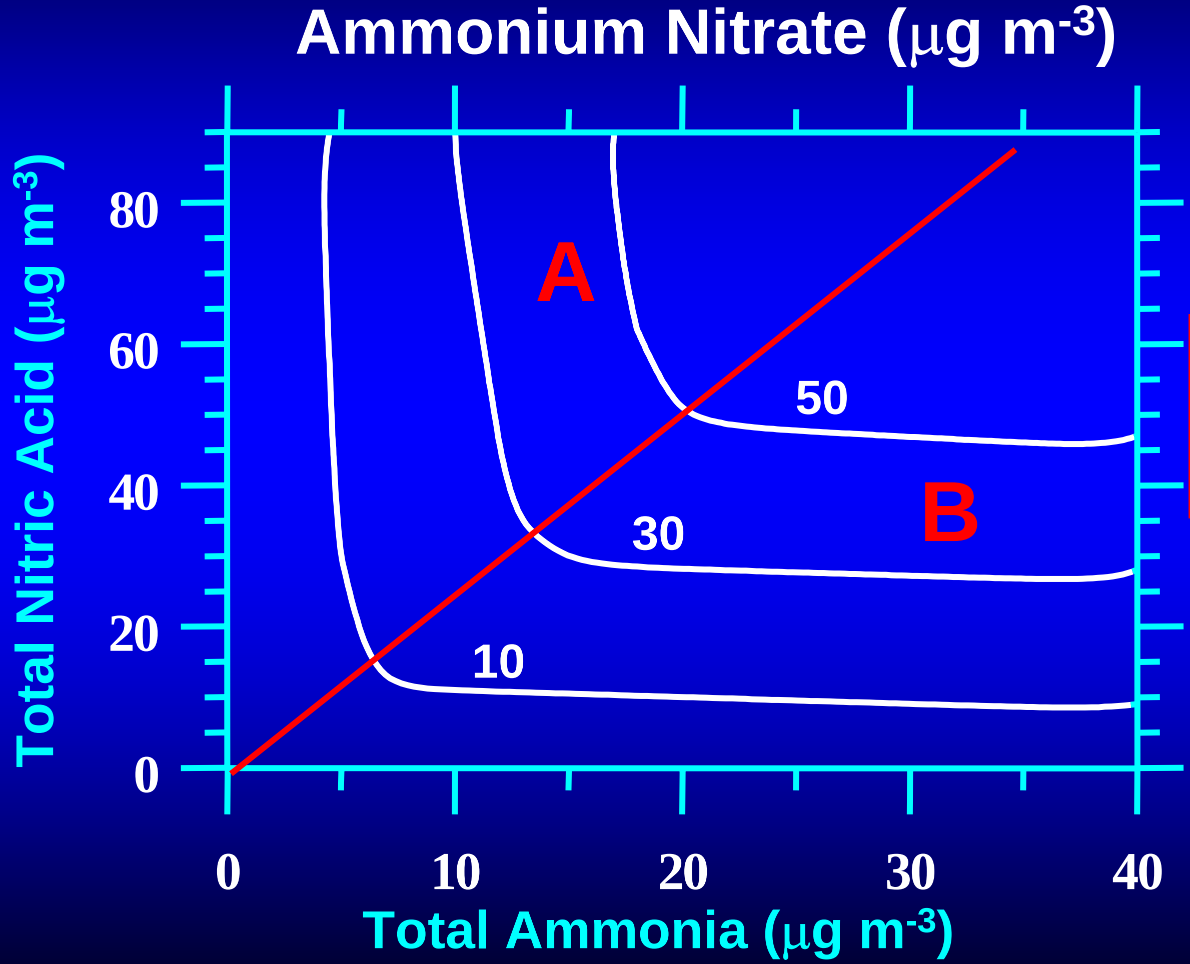
$$NH_3\,(g) + HNO_3\,(g) \leftrightarrows NH_4^+\,(aq) + NO_3^-\,(aq) \quad \text{(high RH)}$$

- The formation of ammonium nitrate requires
  - Nitric acid (major sources of NOx in the US are transportation and power plants)
  - Free ammonia (ammonia not taken up by sulfate)
- The formation reaction is favored at:
  - Low temperatures (night, winter, fall, spring)
  - High relative humidity

Linear and Nonlinear Behavior of Inorganic PM



Limiting Reactant: Ammonia or Nitric Acid?



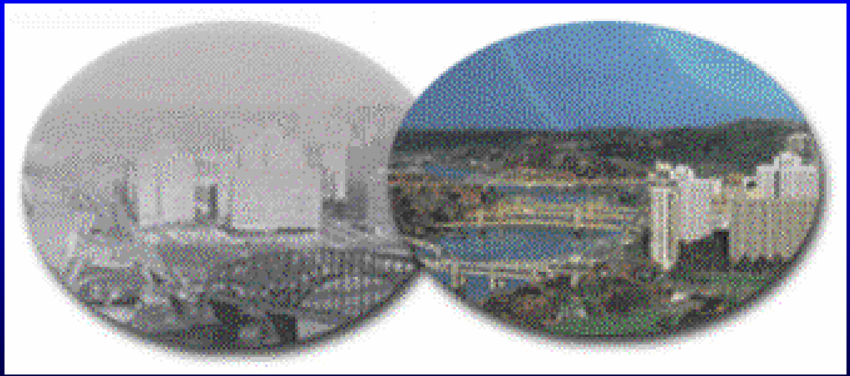
A:Ammonia limited

B: Nitric acid limited

Pittsburgh Air Quality Study (PAQS)

Carnegie Mellon University

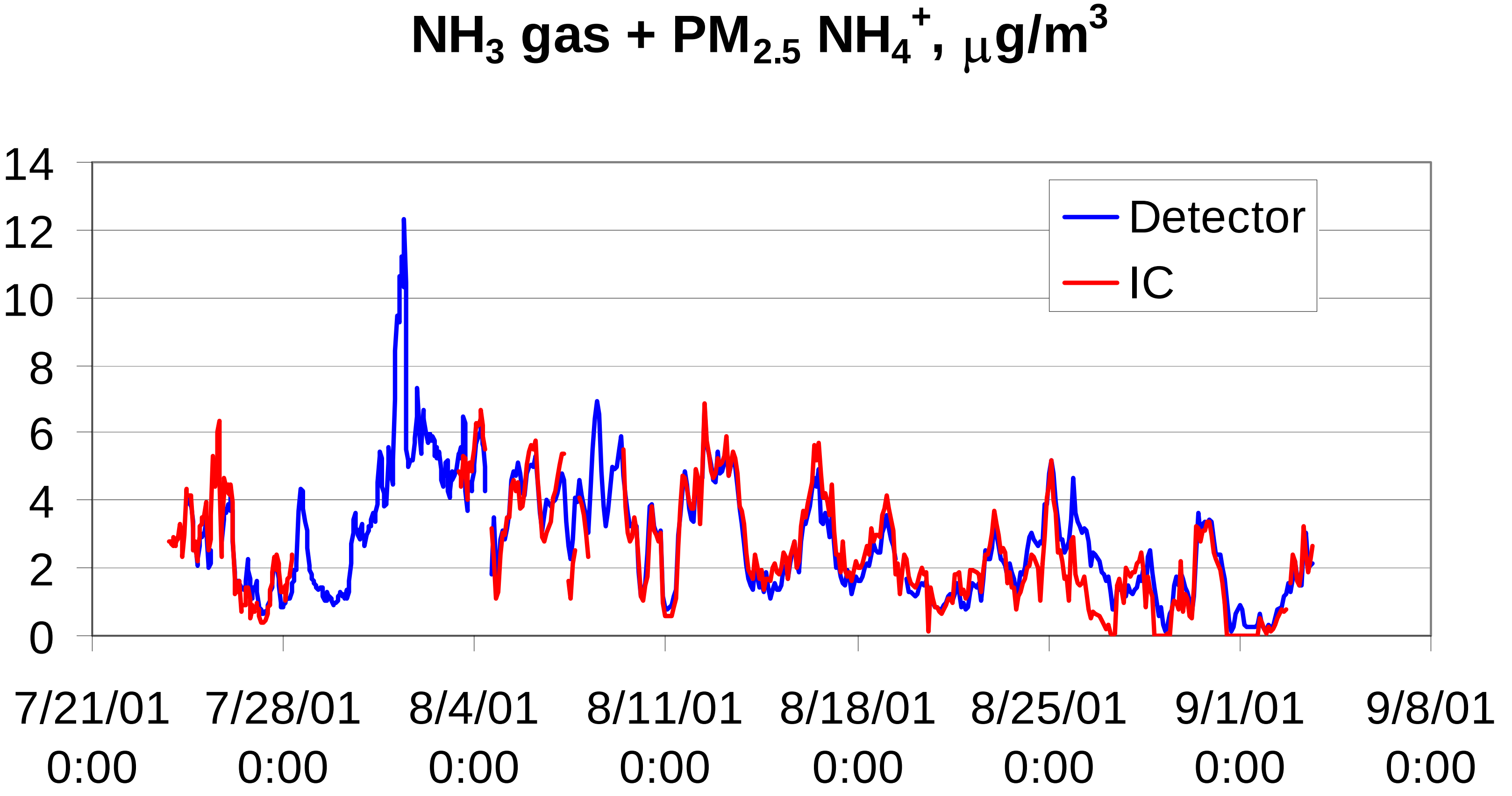
A Multidisciplinary Research Consortium for Atmospheric Aerosol Research
Funded by EPA and DOE/NETL



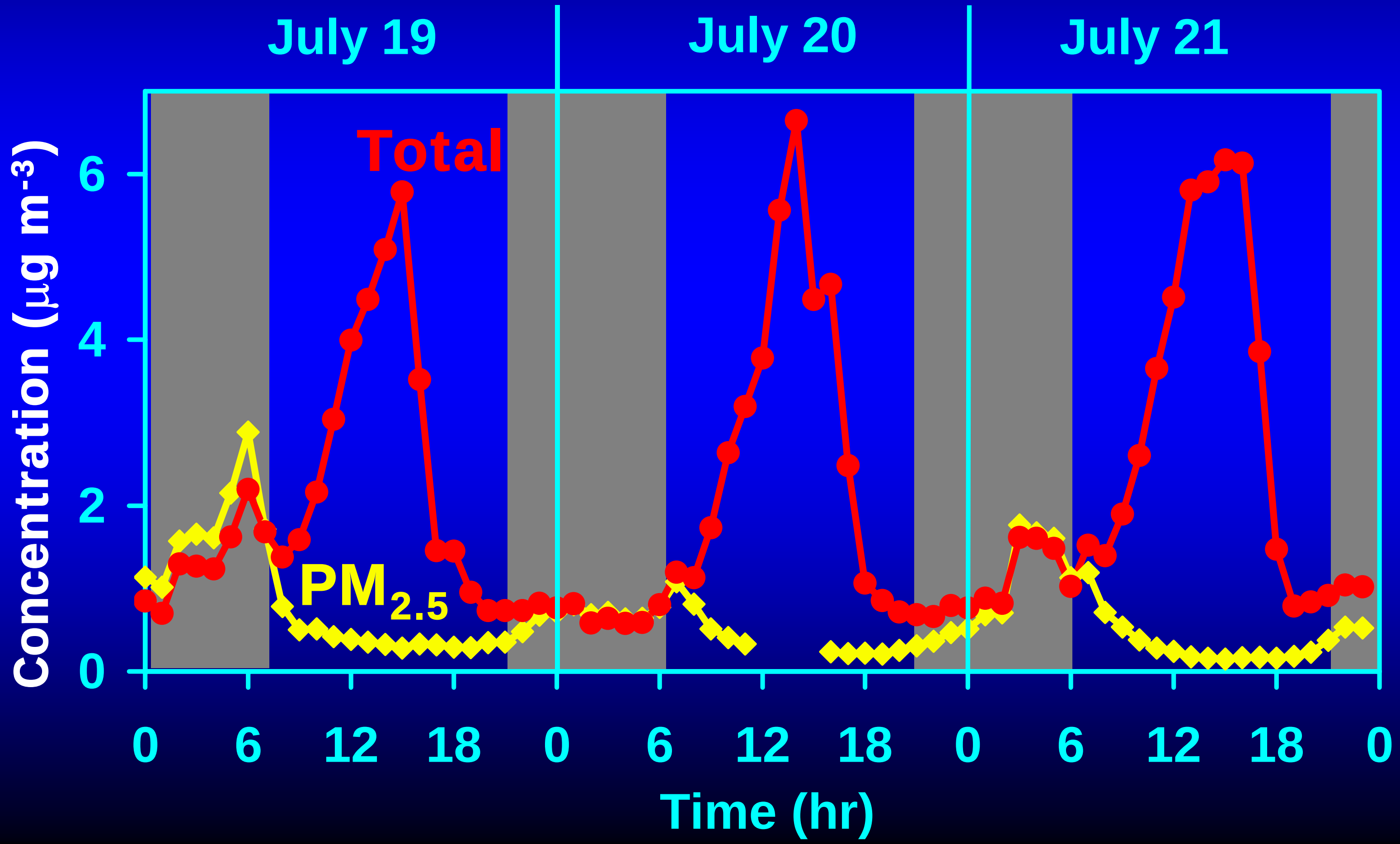
Aerosol Nitrate, Ammonia and Inorganic $PM_{2.5}$ Control

- **Motivation:** What is the response of fine $PM_{2.5}$ when the emissions of SO_2 are reduced? What about changes in NOx or NH_3 emissions?
- **Hypothesis:** A significant fraction of the sulfate reduced will be replaced by nitrate when SO_2 emissions are reduced.
- **Approach:** High resolution measurements of aerosol sulfate, nitrate, and total (gas+aerosol) nitrate and ammonium. Use of numerical models.

On-line (detector) vs. off-line (IC)

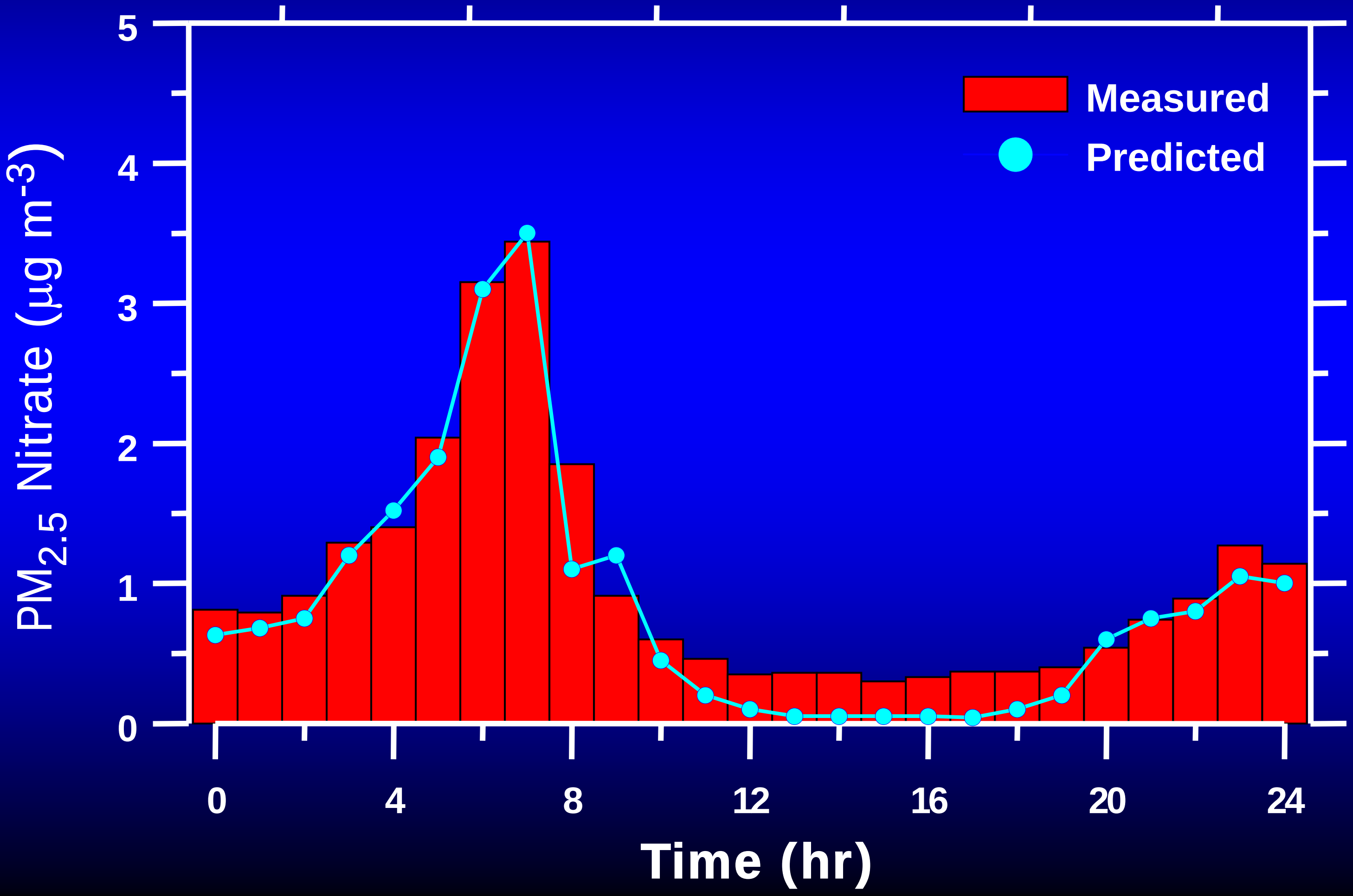


Partitioning of $PM_{2.5}$ Nitrate
(Pittsburgh, 2001)

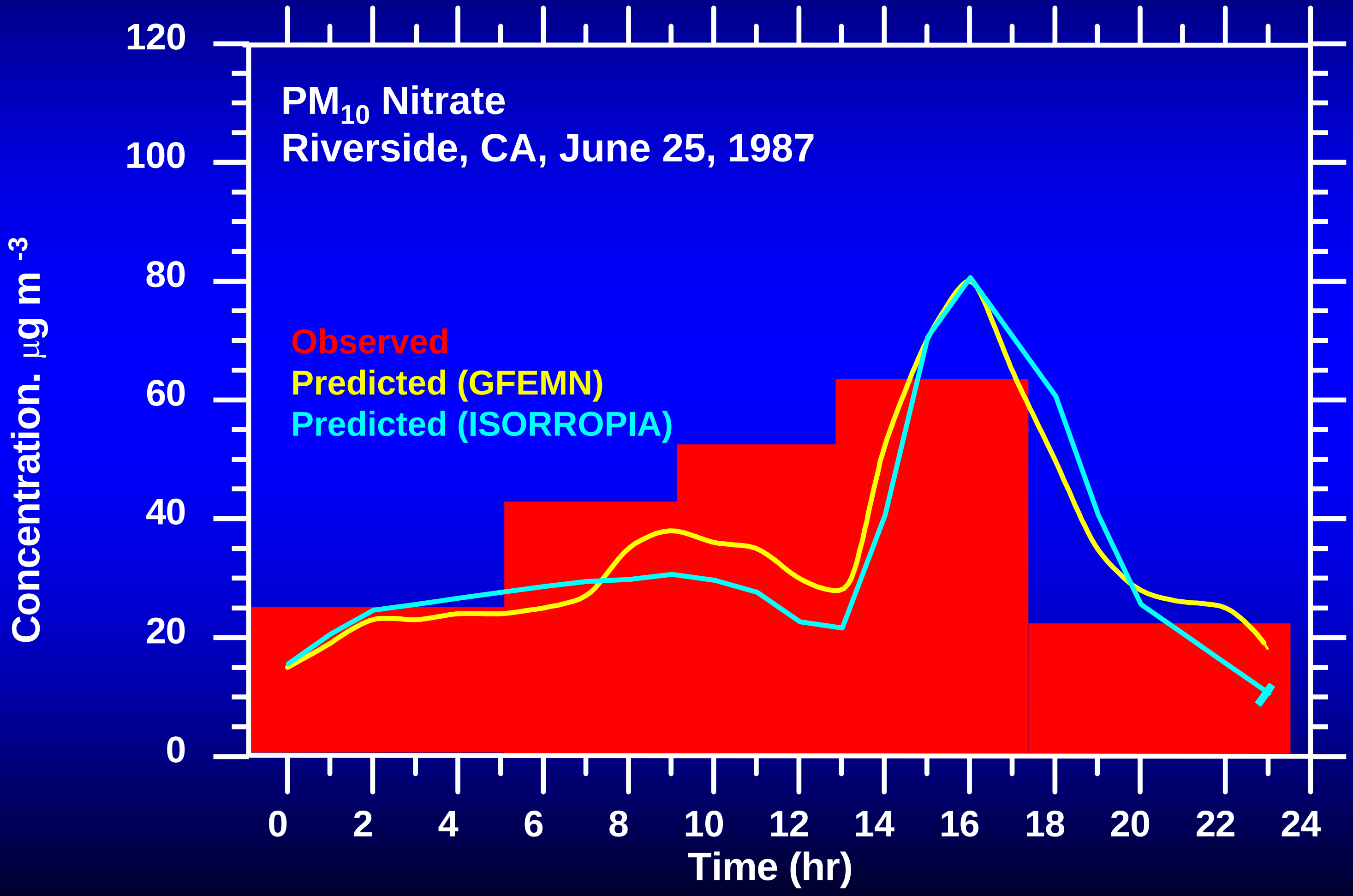


GFEMN Evaluation: Nitrate Partitioning

(July 19, 2001)

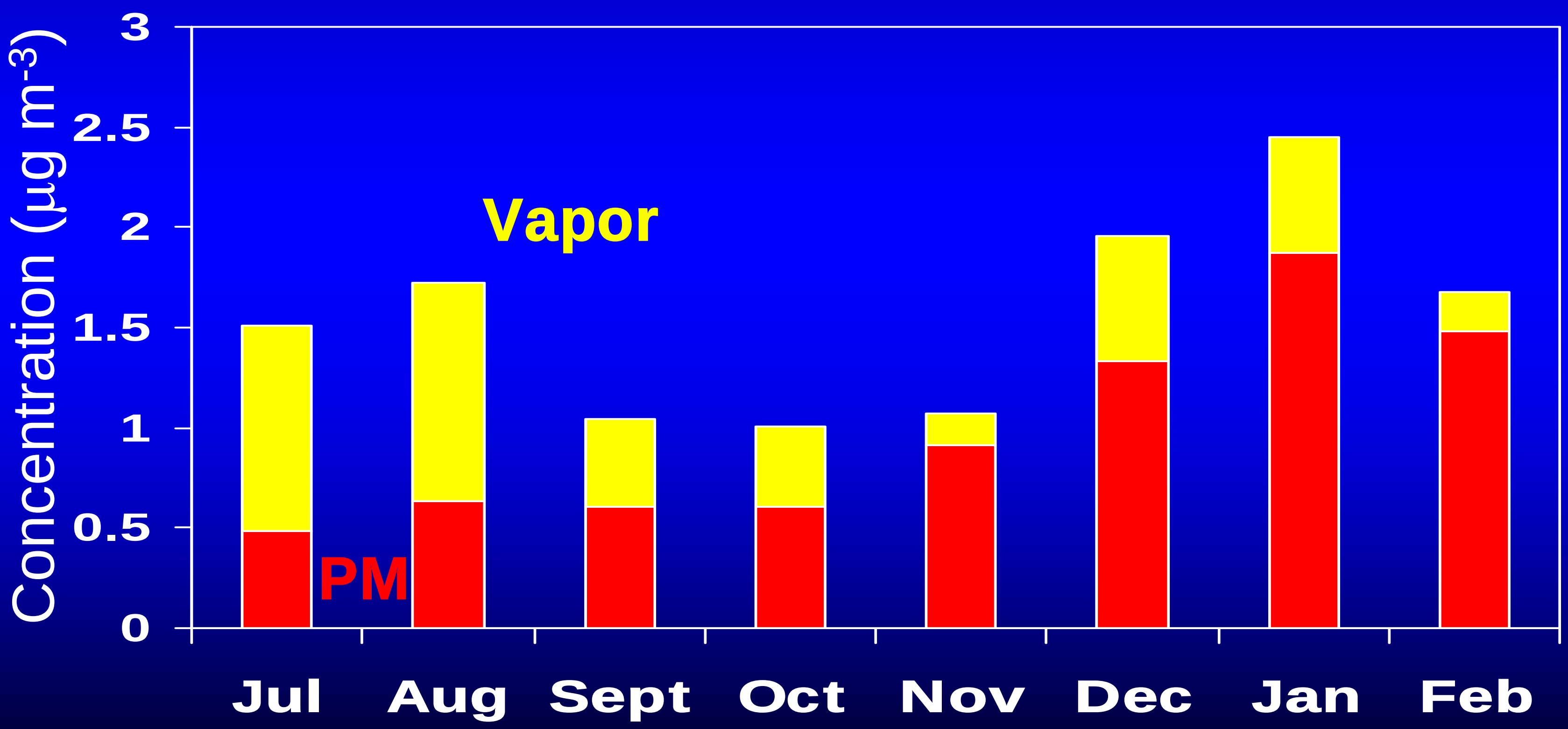


Evaluation of ISORROPIA and GFEMN

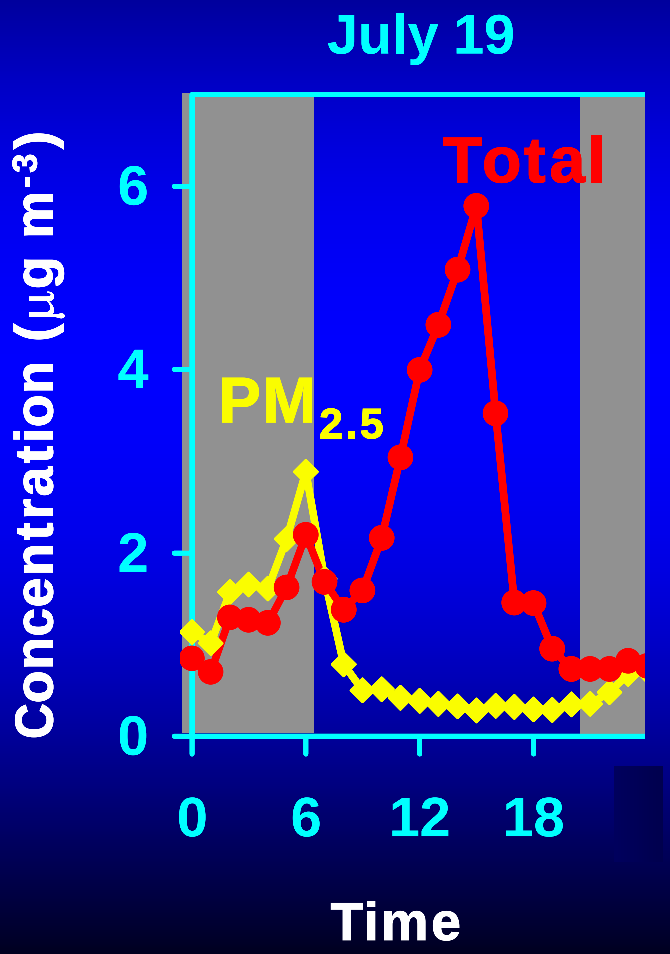


Availability of Nitric Acid/Nitrate

(Pittsburgh 2001-02)



Where does the HNO_3 go?



- The HNO_3 declines rapidly every afternoon with an average rate of around 30% per hour.

- Dry removal can explain rates of 10-30% per hour.

- Net contribution of horizontal transport should be small because of the relatively spatial homogeneity in the area.

- During the night the dry deposition becomes very slow because the HNO_3 goes to the aerosol phase

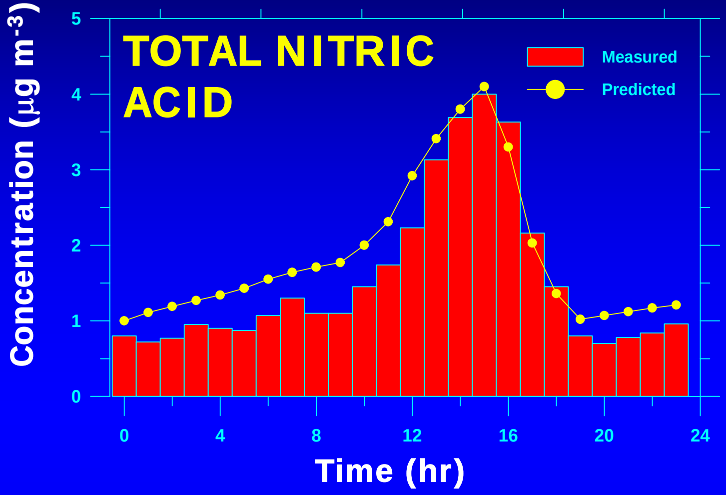
Some potential implications

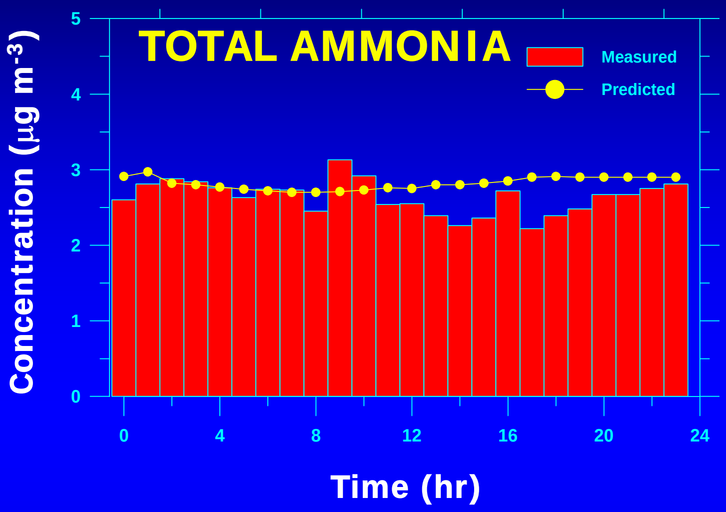
- During the summer there is 1-2 μg m^{-3} of HNO_3(g) on average (and as much as 10 μg m^{-3}) that could be transferred to the aerosol phase.
- The lifetime of nitric acid vapor is only a few hours
  - Reaction with ammonia will increase its lifetime
- Decreasing sulfate or increasing ammonia will transfer nitric acid to the particulate phase, increase its lifetime, and its concentration levels.
- During the fall and winter months in Pittsburgh most of the available nitric acid appears to be already in the aerosol phase.

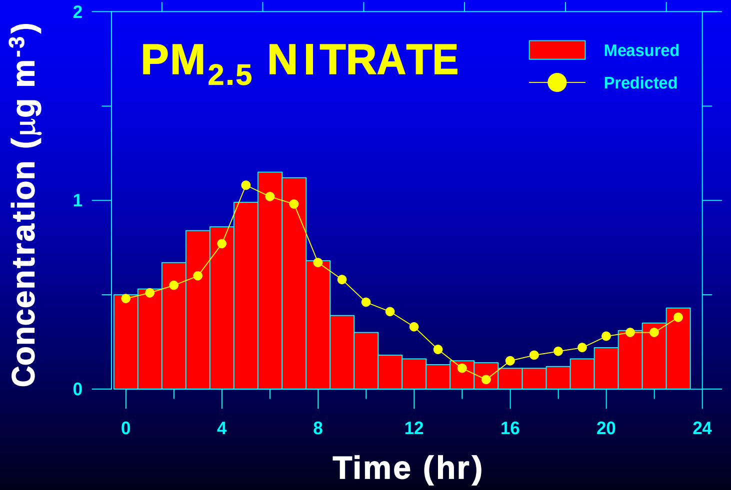
Modeling of the $H_2SO_4/HNO_3/NH_3/H_2O$ System

- **Processes:** Partitioning (with GFEMN), removal (dry deposition velocities), emission/production
- **Framework:** Box model (Pandis and Seinfeld, 1991).
- Gas-phase production fitted to the observations (reasonable rates).
- July 2001 and January 2002 periods. Use of average diurnal concentrations.
- **Inputs:** Sulfate concentrations, meteorology.

Evaluation of Box Model



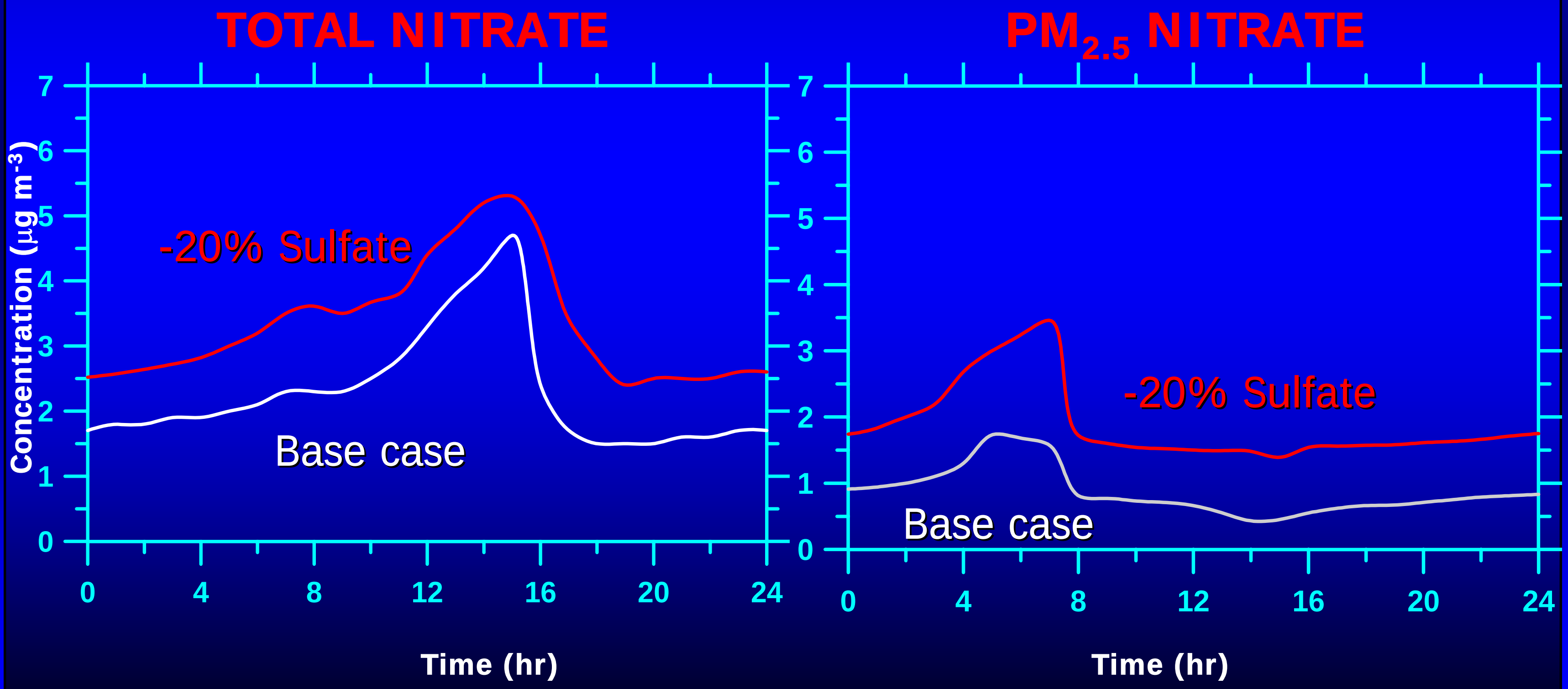




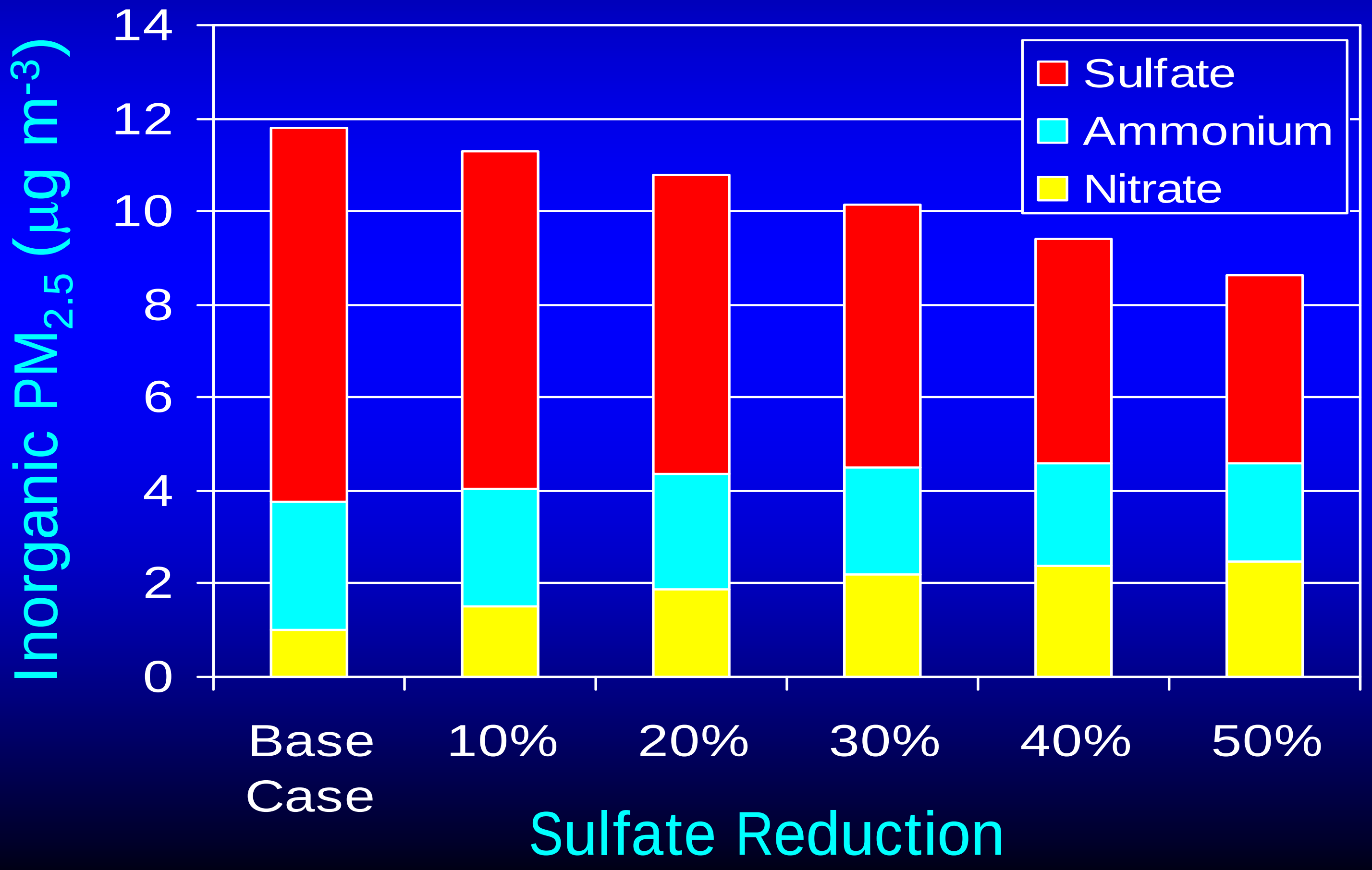
PITTSBURGH
July 2001

Effect of 20% Reduction of the Sulfate Concentration on Nitrate Levels

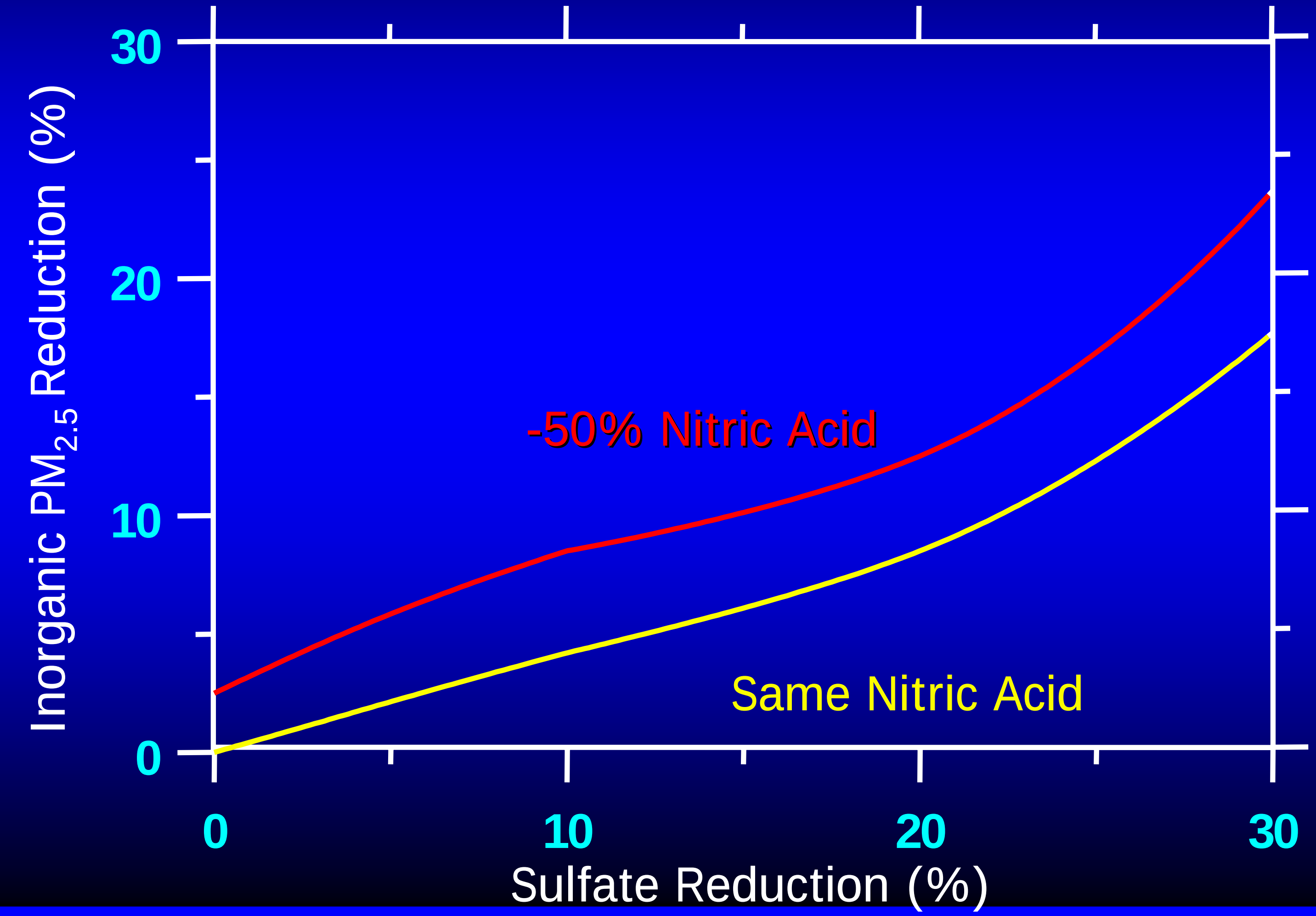
(Pittsburgh, July 2001)



Effect of Sulfate Concentration Changes on Inorganic $PM_{2.5}$

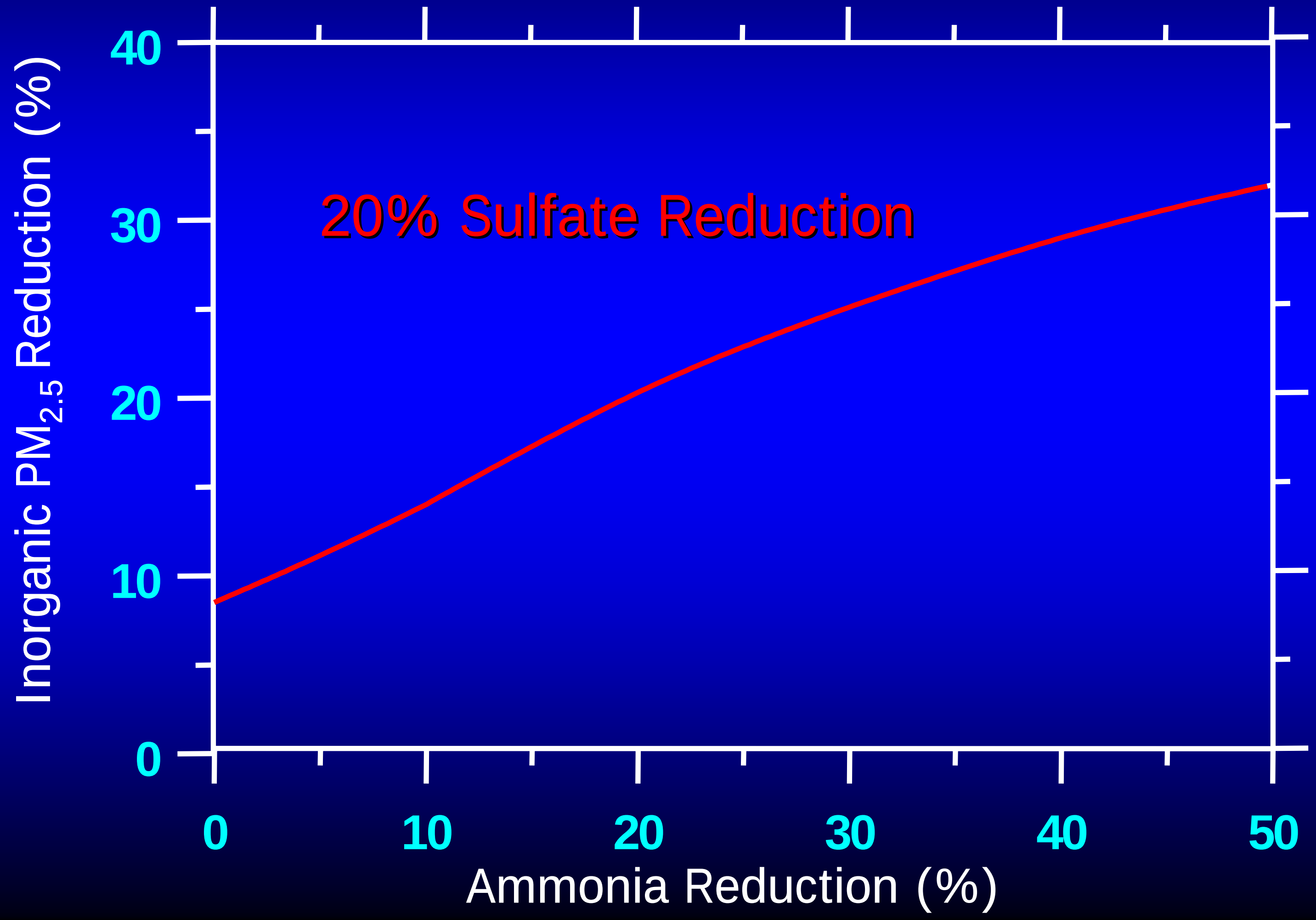


Reductions of Sulfuric and Nitric Acid (Pittsburgh, July 2001)



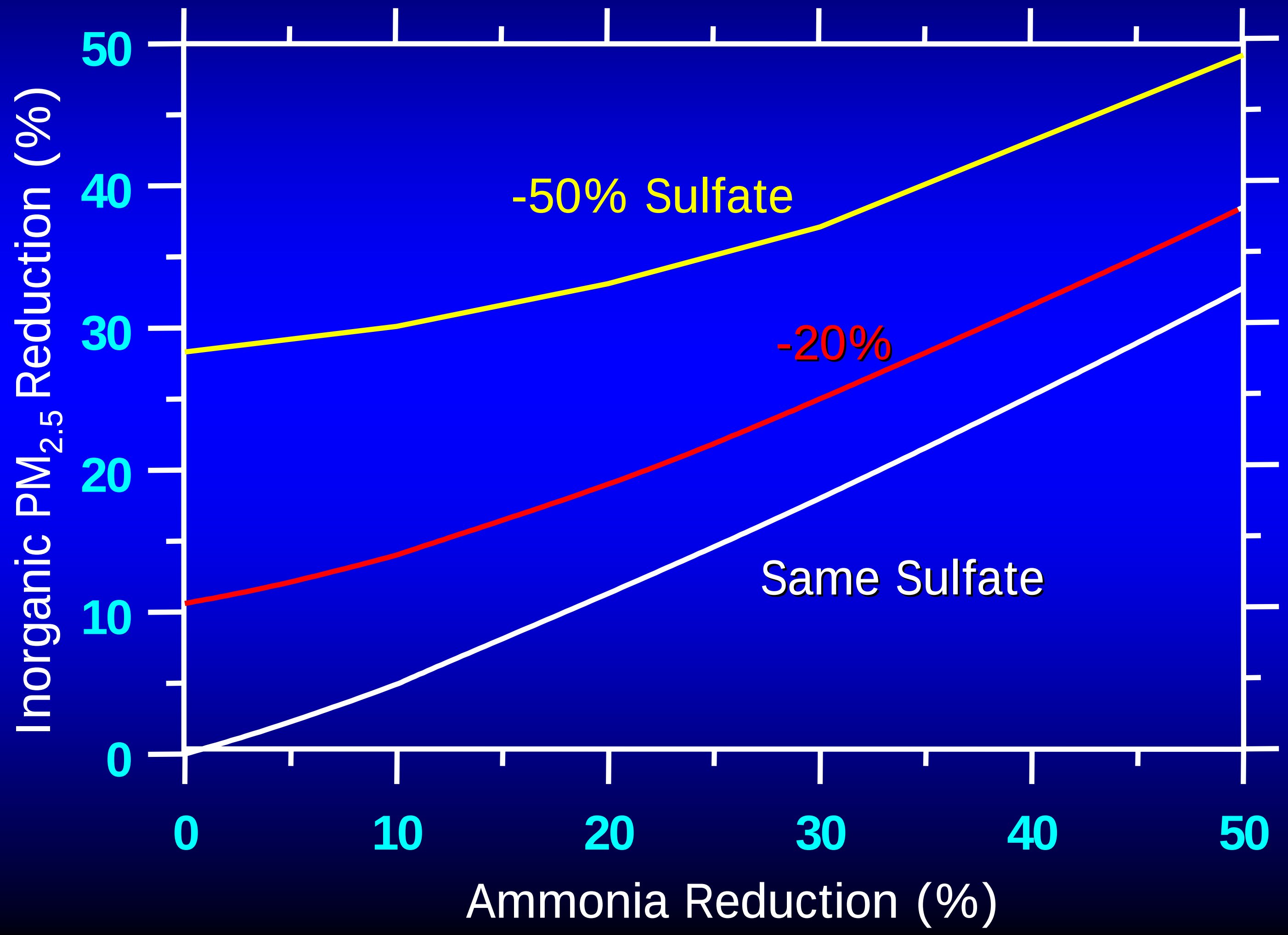
Reductions in Ammonia

(Pittsburgh, July 2001)

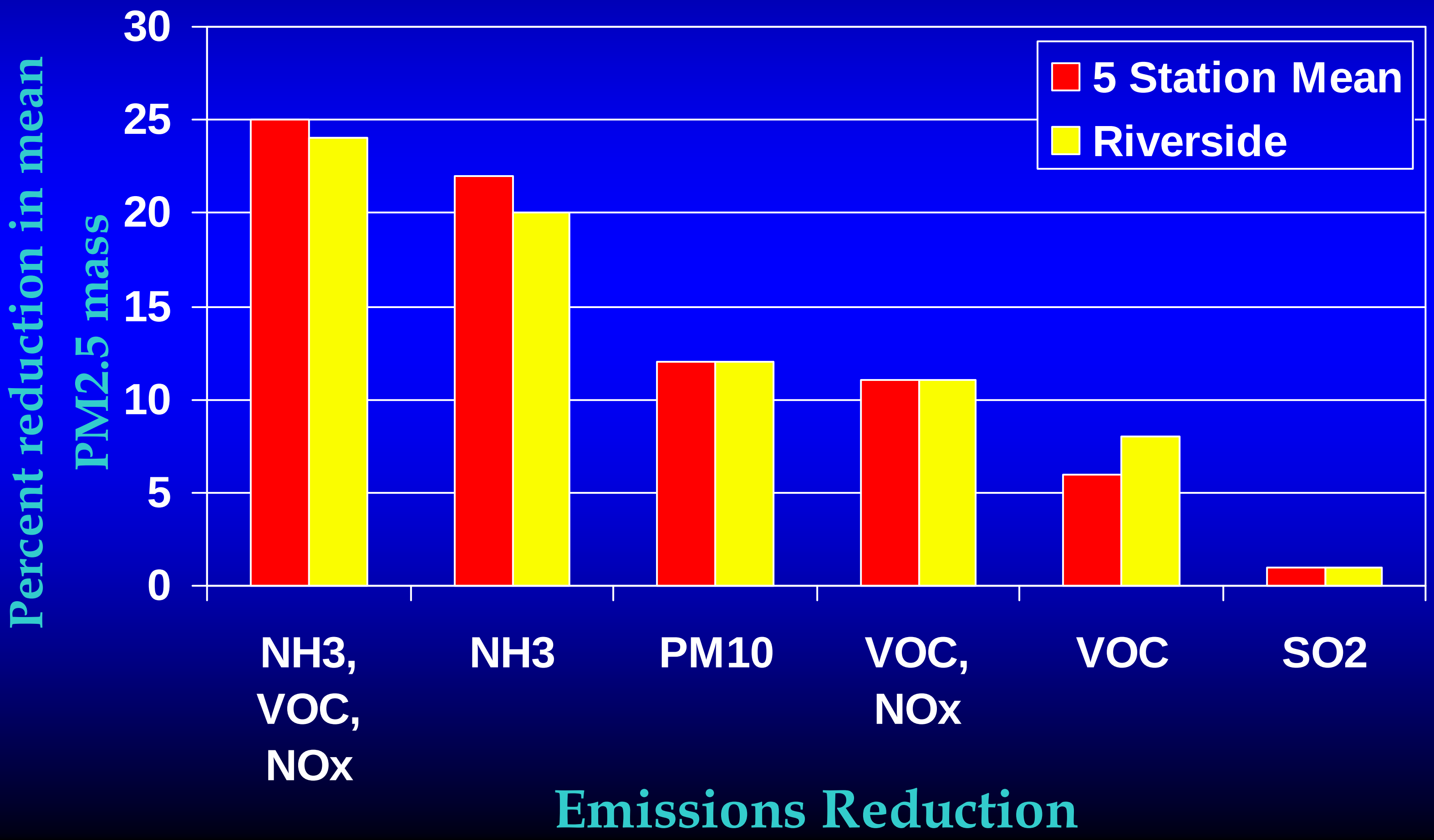


Reductions in Ammonia

(Pittsburgh, January 2002)



Effect of 50% Emissions Change on 24-hr Average PM$_{2.5}$ mass



Ammonia and Global Change

- Increases in ammonia concentrations will result in increases of the fine aerosol mass
  - Visibility reduction
  - Cooling of the planet
- The role of ammonia is expected to become more important in the coming years as SO_2 emissions decrease
- The lifetime of ammonia in the troposphere is only a few days so it does not have enough time to make it to the stratosphere
  - no effect on stratospheric ozone

Conclusions

- Continuous measurements of the major inorganic ions and the corresponding gas-phase species allow us
  - to evaluate our understanding of the system
  - provide insights about important processes
- Existing models (GFEMN) reproduce well the partitioning of nitric acid in Western Pennsylvania both during the summer and the winter
- Sulfate reductions result in nitrate level increases (change of partitioning, lifetime increase).

Conclusions (continued)

- Ammonia, is controlling the ammonium nitrate formation both during the summer and the winter.
- $PM_{2.5}$ control efficiencies (for Pittsburgh)
  - July: Sulfate > Ammonia > Nitric Acid
  - January: Ammonia >= Sulfate >= Nitric Acid
- Ammonia is not involved in the ozone formation in the troposphere and its destruction in the stratosphere
- Increases in ammonia levels result in cooling of the planet, decreases of the acidity of particles and clouds, but increases of the fine particulate matter concentrations and reductions of visibility