Role of Nitrogen in Particulate Matter and Ozone Formation

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THE CO/VOC + NOx O_3-FORMATION THEORY

- **VOCs (Volatile Organic Compounds):**
  - **Sources:**
    - **biogenic (natural: e.g., trees)**
    - **anthropogenic (human activities: e.g., combustion**
      - **stationary (power plants)**
      - **mobile (automobiles)**

- **CO (carbon monoxide):**
  - **Sources:**
    - **primarily anthropogenic combustion**
      - **stationary (power plants)**
      - **mobile (automobiles)**

The CO/VOC + NOx O_3-Formation Theory, cont'd:

- **NOx ($NO + NO_2$):**
  - **Sources:**
    - **natural: lightning, biomass burning, soil microbial processes**
      - » ***INSIGNIFICANT* with respect to pollution-levels of ozone**
    - **anthropogenic (human activities: e.g., combustion**
      - » **stationary (power plants)**
      - » **mobile (automobiles)**

The CO/VOC + NOx O_3-Formation Theory, cont'd:

$$O_3 + h\nu \rightarrow O_2 + O(^1D)$$
$$O(^1D) + M \rightarrow O(^3P) + M$$
$$O(^3P) + O_2 + M \rightarrow O_3 + M$$

$M = N_2$ or O_2

$$O_3 + NO \rightarrow NO_2 + O_2$$
$$NO_2 + h\nu \rightarrow NO + O(^3P)$$

BUT!! When CO and VOCs are oxidized, HO_2 and RO_2 (highly reactive "radicals") are formed and can ALSO react with NO :

$$HO_2 + NO \rightarrow NO_2 + OH$$
$$RO_2 + NO \rightarrow NO_2 + OR$$

$$NO_2 + h\nu \rightarrow NO + O(^3P)$$
$$O(^3P) + O_2 + M \rightarrow O_3 + M$$

So, ozone is formed when carbon monoxide and reactive hydrocarbons (VOCs) are oxidized in the presence of NO.

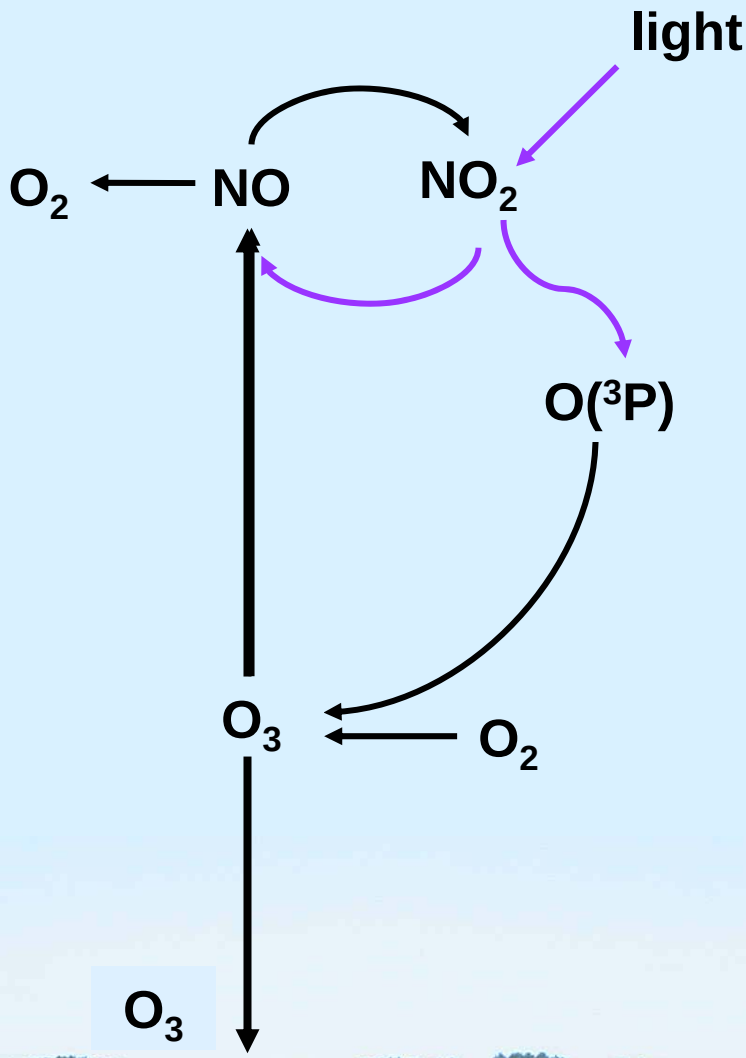
NOx and O_3 Formation

naturally-occurring ozone formation and loss:

primary source of $O(^3P)$ is NO_2 photolysis

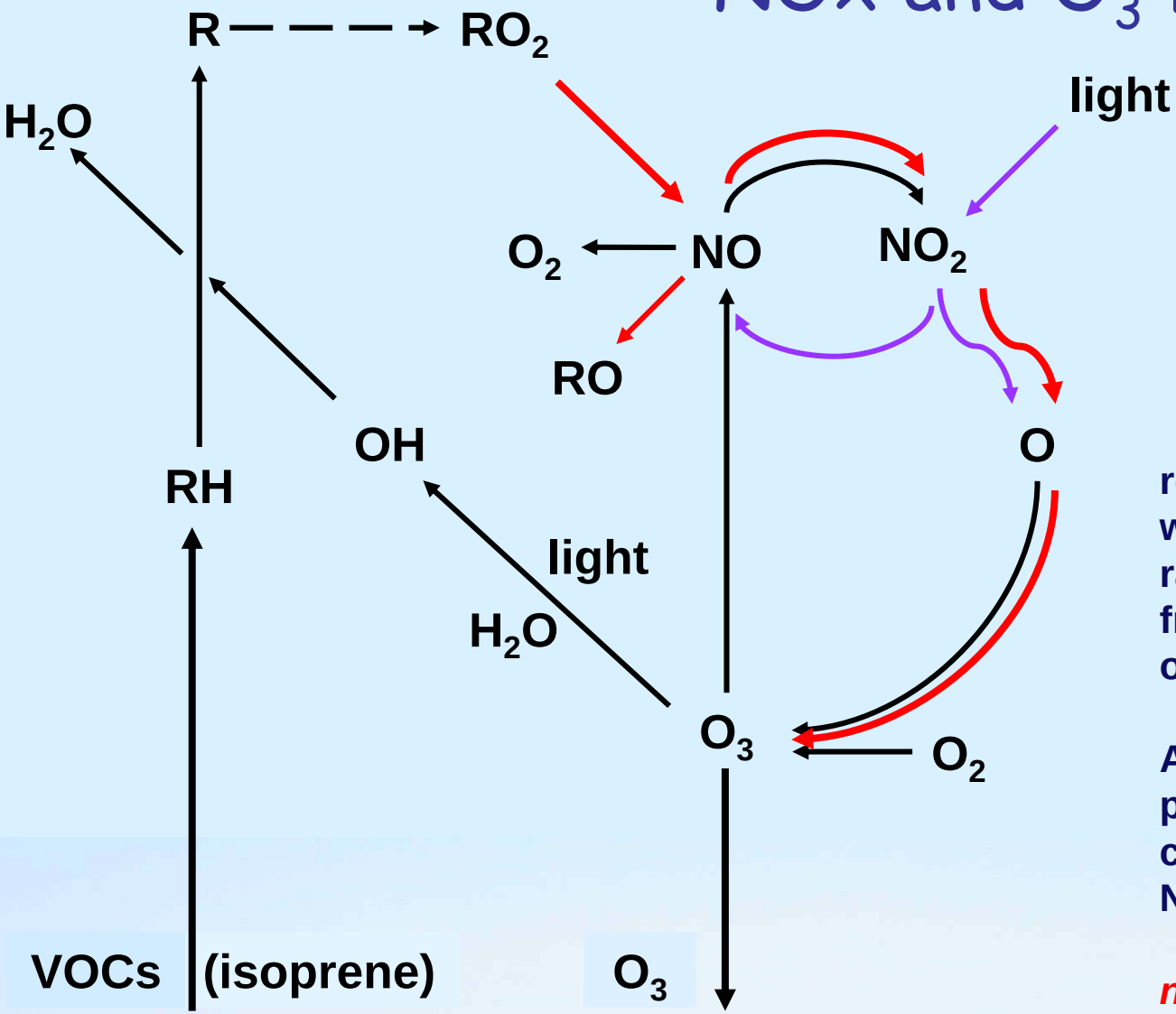
primary source of NO_2 is reaction of NO with O_3

a null cycle



after Harrison et al. 2000

NOx and O_3 Formation



reaction of NO with peroxy radicals resulting from hydrocarbon oxidation:

An *additional* pathway for conversion of NO to NO_2

net ozone formation

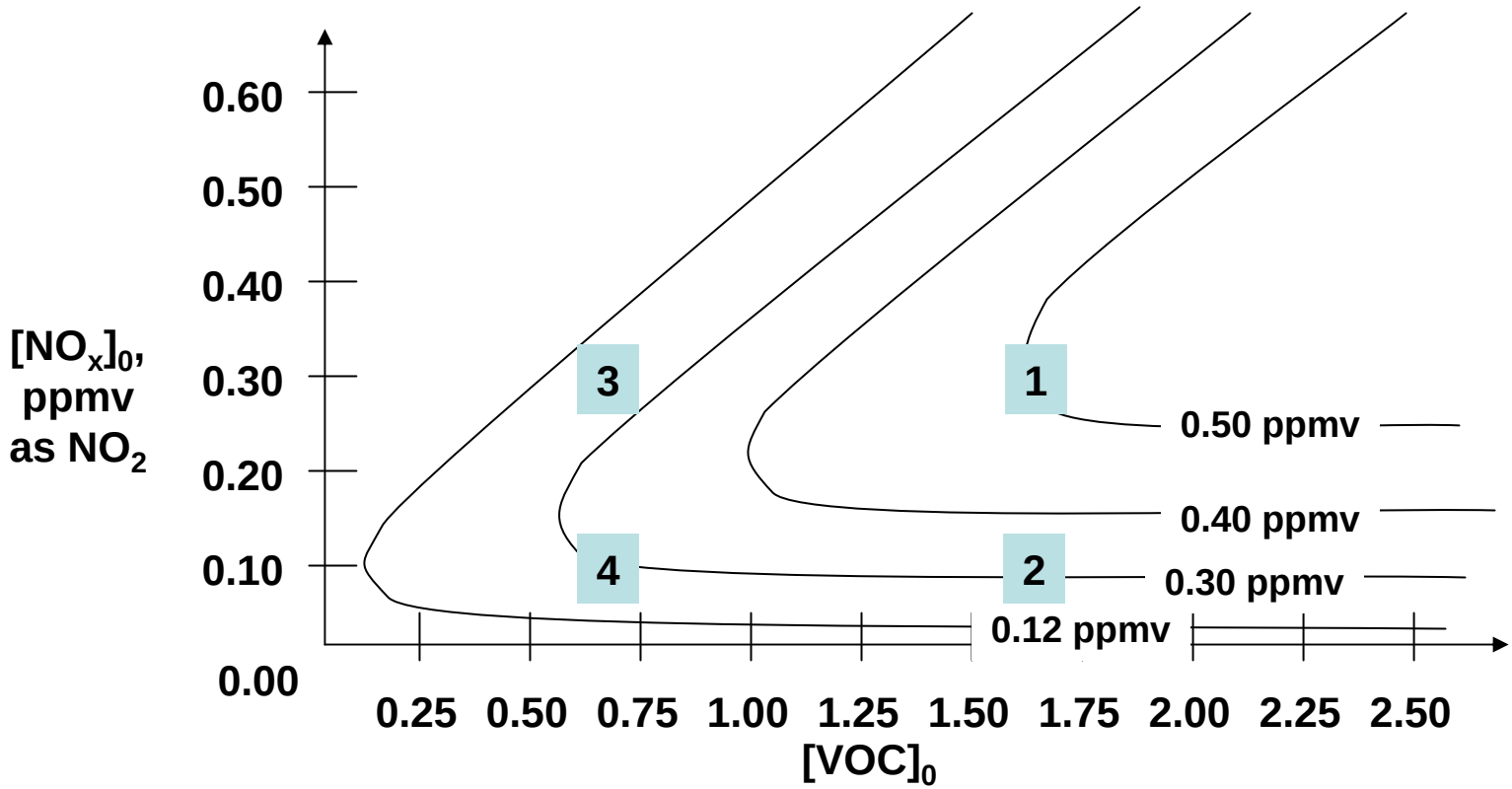
after Harrison et al. 2000

Evidence of Global Change

- Changes in atmospheric composition on local, regional, and global scales
  - O_3 at the surface has increased significantly:
    - Factor of 2 (global average)
    - Factor of 5 - 10 in Northern Hemisphere

- Hemispheric increases in tropospheric photochemical oxidants
  - Many areas that were previously regions of net O_3 destruction have become regions of net O_3 production (e.g. Atlantic ocean marine boundary layer). We understand this to be due to increasing NOx emissions.

A contour map of O_3 mixing ratios that occur for different initial concentrations of NO_x and VOC at a fixed temperature and irradiation level



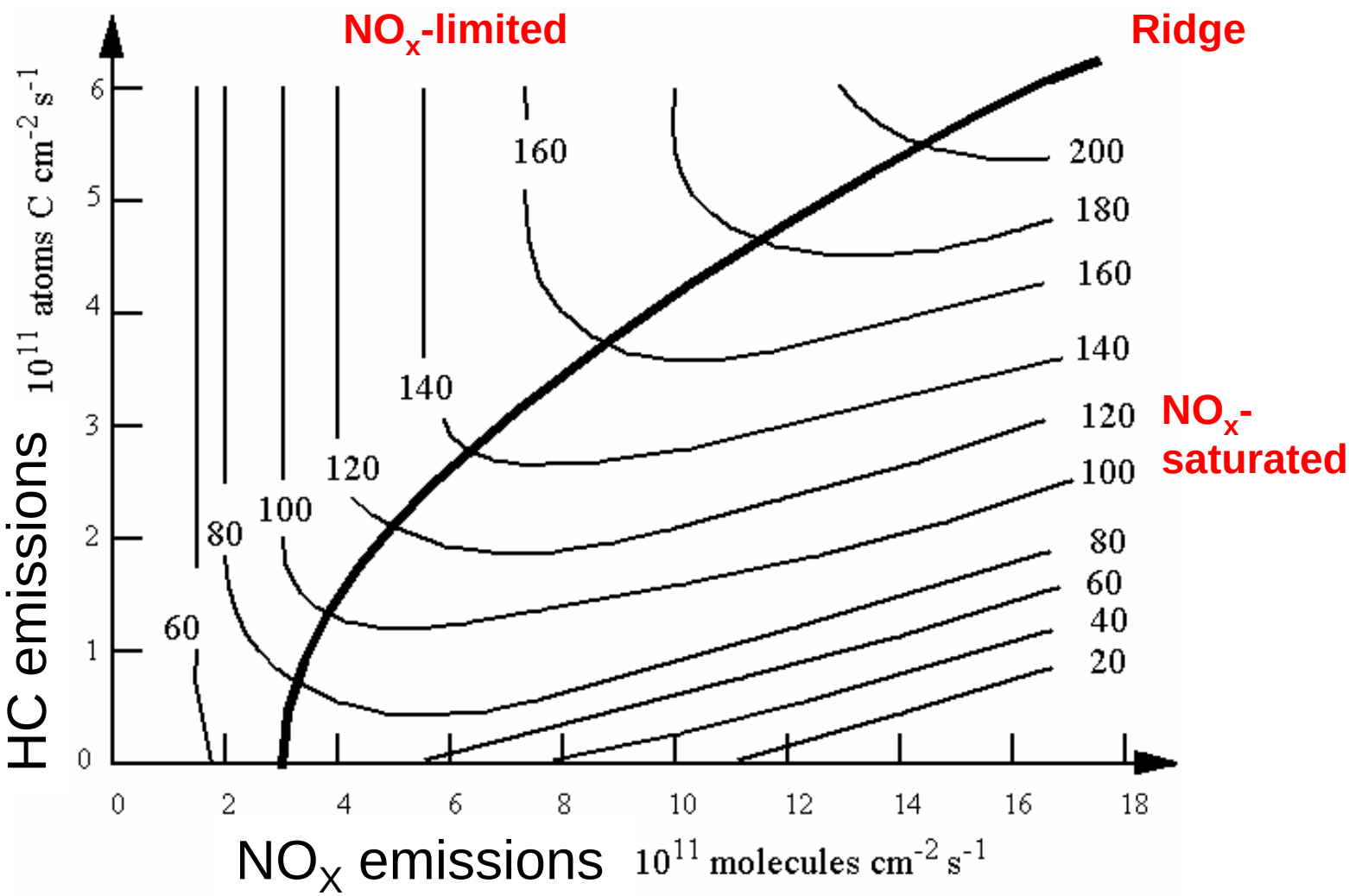
If your atmospheric conditions are similar to "1", you could reduce O_3 by reducing *either* NO_x or VOC. If you are at "3", reducing NO_x will actually *increase* O_3, but reducing VOC will reduce O_3. If you are at "2", reducing VOC will have no effect on O_3, but reducing NO_x will reduce O_3.

"2": Reduce NO_x, get a big drop in O_3. Reduce VOC, little change in O_3. NO_X Limited! Rural
"3": Reduce NO_x, get an increase(!) in O_3. Reduce VOC, get decrease in O_3. VOC Limited! Urban

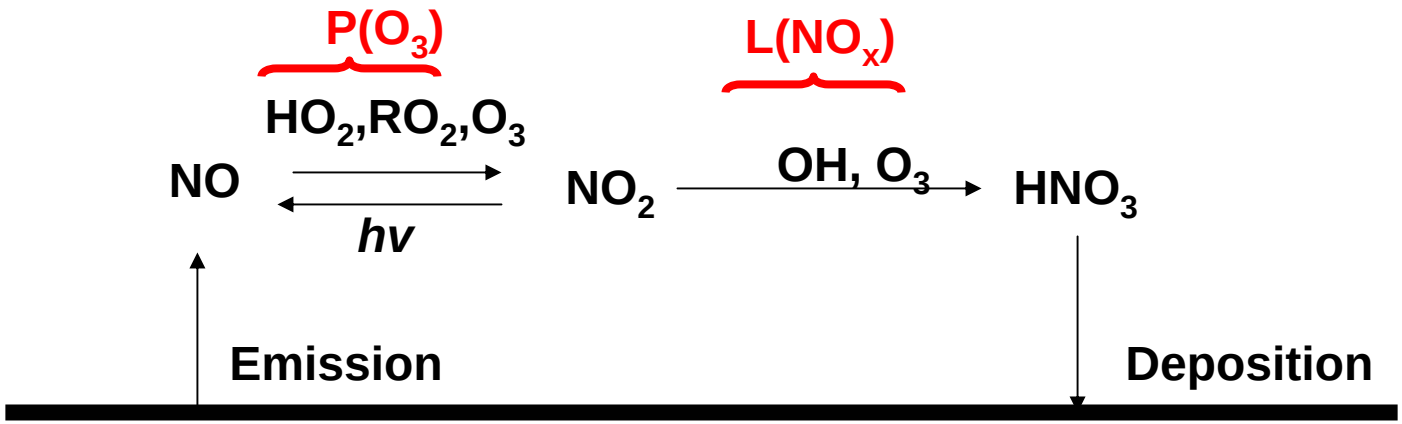
Credit due to unknown source!

Ozone Mixing Ratios vs. NO_x and VOC Emissions

Air pollution model calculation for a typical urban airshed



ALTHOUGH THE O_3 PRODUCTION RATE IS ~ $[NO_x]$, THE TOTAL O_3 PRODUCED IS HYDROCARBON-DEPENDENT AND $[O_3] = f(E_{NOx})$ IS STRONGLY NONLINEAR



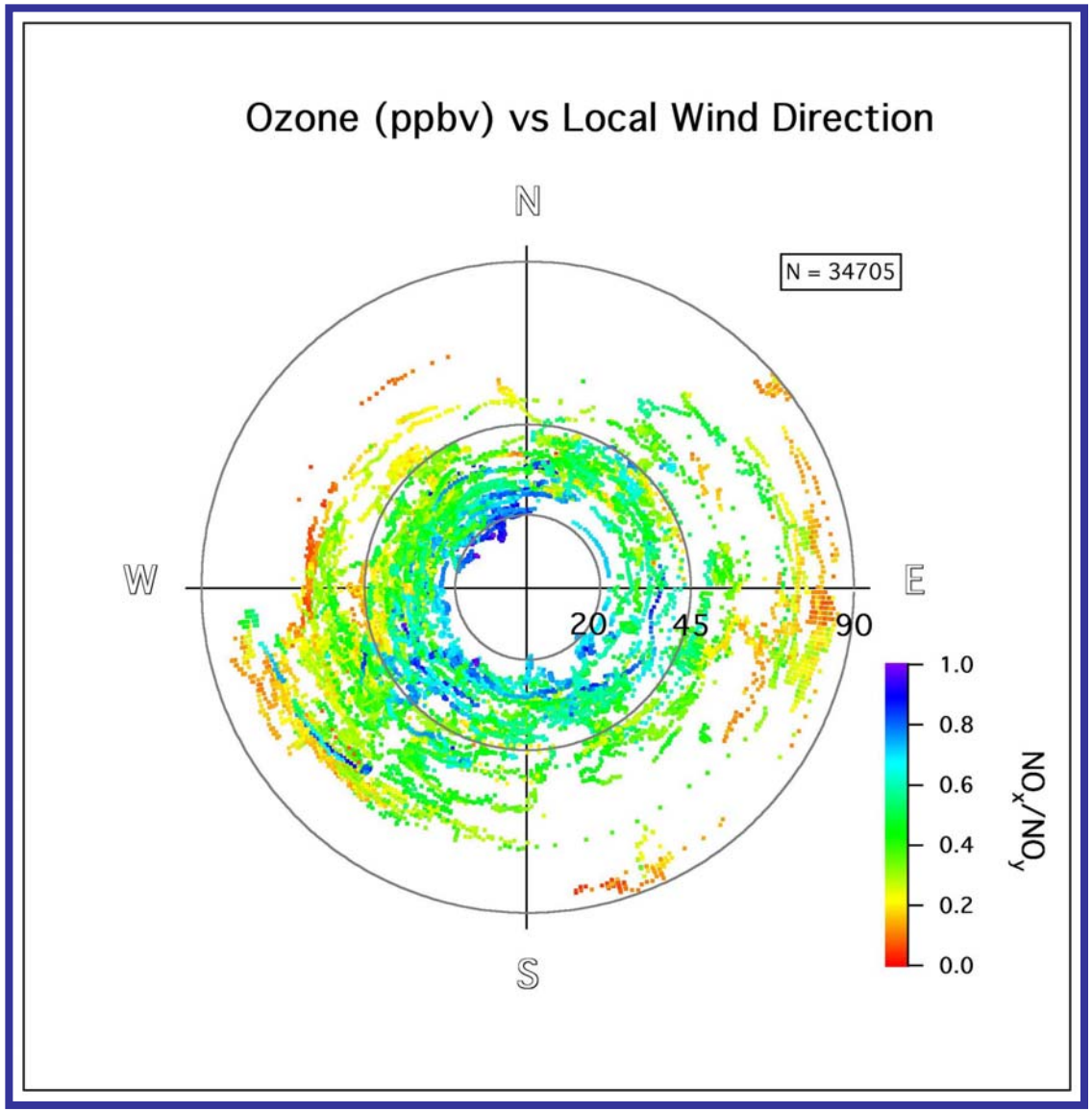
Define ozone production efficiency (OPE) as the total number of O_3 molecules produced per unit NO_x emitted (or oxidized!).

Assuming NO_x steady state, efficient HO_x cycling, and loss of NO_2 by reaction with OH:

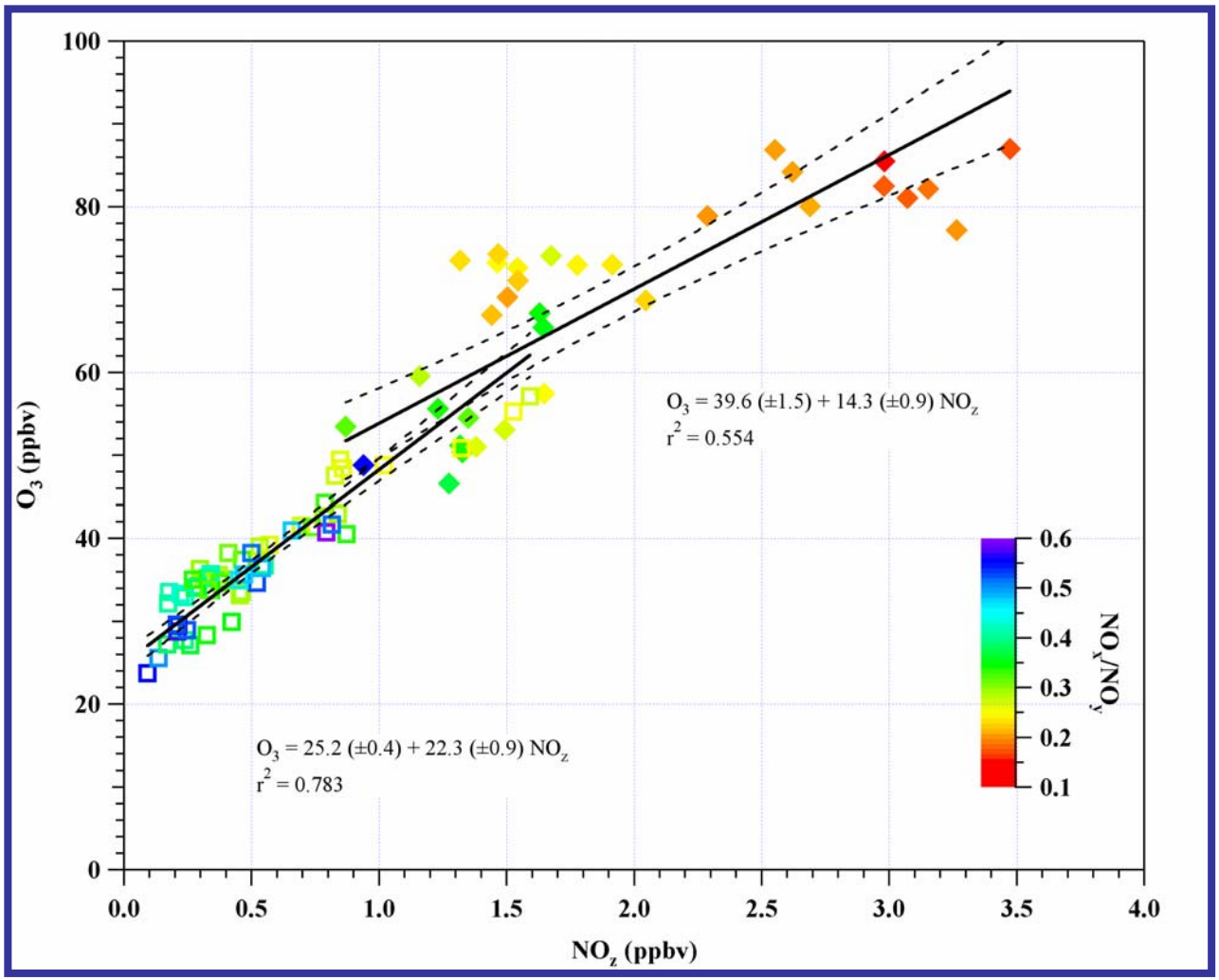
$$\mathbf{OPE} = \frac{P(O_3)}{L(NO_x)} = \frac{2k_7[HO_2][NO]}{k_9[NO_2][OH]} = \frac{2k_4[RH]}{k_9[NO_2]}$$

OPE ↘ as NO_x ↗ ⇨ strong nonlinearity

Ozone and Reactive Nitrogen Summer 1998



Background Ozone and OPE Summer 1998



Background O_3

~ 25 ppbv in northerly flow

~ 40 ppbv in southerly flow

OPE

~ 22 in no. flow

~ 14 in so. flow

$O_3 = 55 + 8.7*NO_z$ (r^2=0.61) for southerly data filtered for NOx/NOy < 0.25

Role in PM Formation?

… as previously noted,

$$NH_{3\,(g)} + HNO_{3\,(g)} \longleftrightarrow NH_4NO_{3\,(s,\,aq)}$$

$$NH_{3\,(g)} + H_2SO_{4\,(s,\,aq)} \longleftrightarrow (NH_4)_2SO_{4\,(s,\,aq)}$$

or NH_4HSO_4

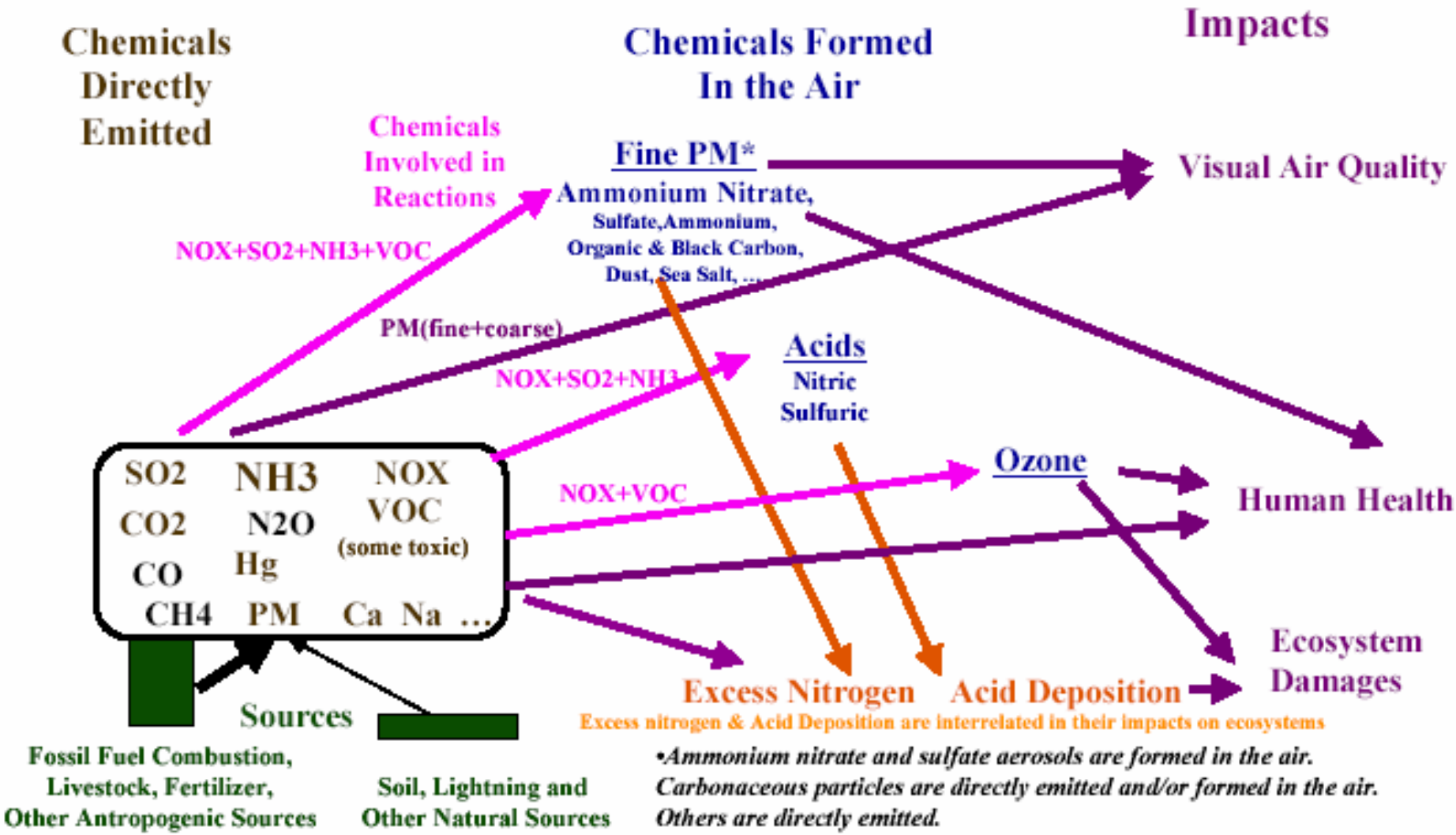
or $(NH_4)_3H(SO_4)_2$

Additional routes to nitrate aerosol formation:

$$NaCl_{\,(s)} + 2\,NO_{2\,(g)} \longrightarrow ClNO_{\,(g)} + NaNO_{3\,(s)}$$

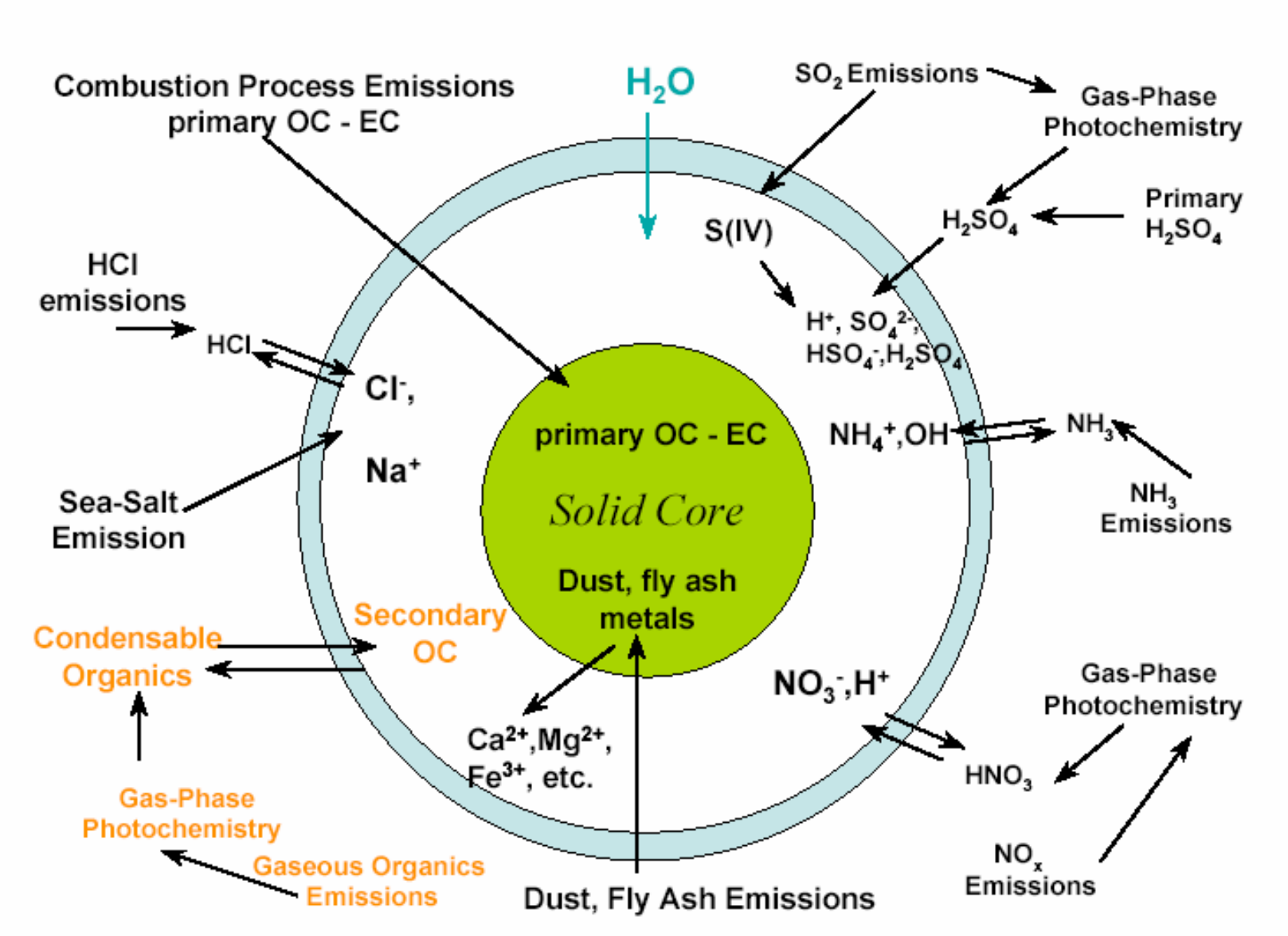
$$NaCl_{\,(s)} + HNO_{3\,(g)} \longrightarrow HCl_{\,(g)} + NaNO_{3\,(s)}$$

Overview of Roles Played by NH_3 and NOx in the Formation of Fine Particles (PM 2.5)



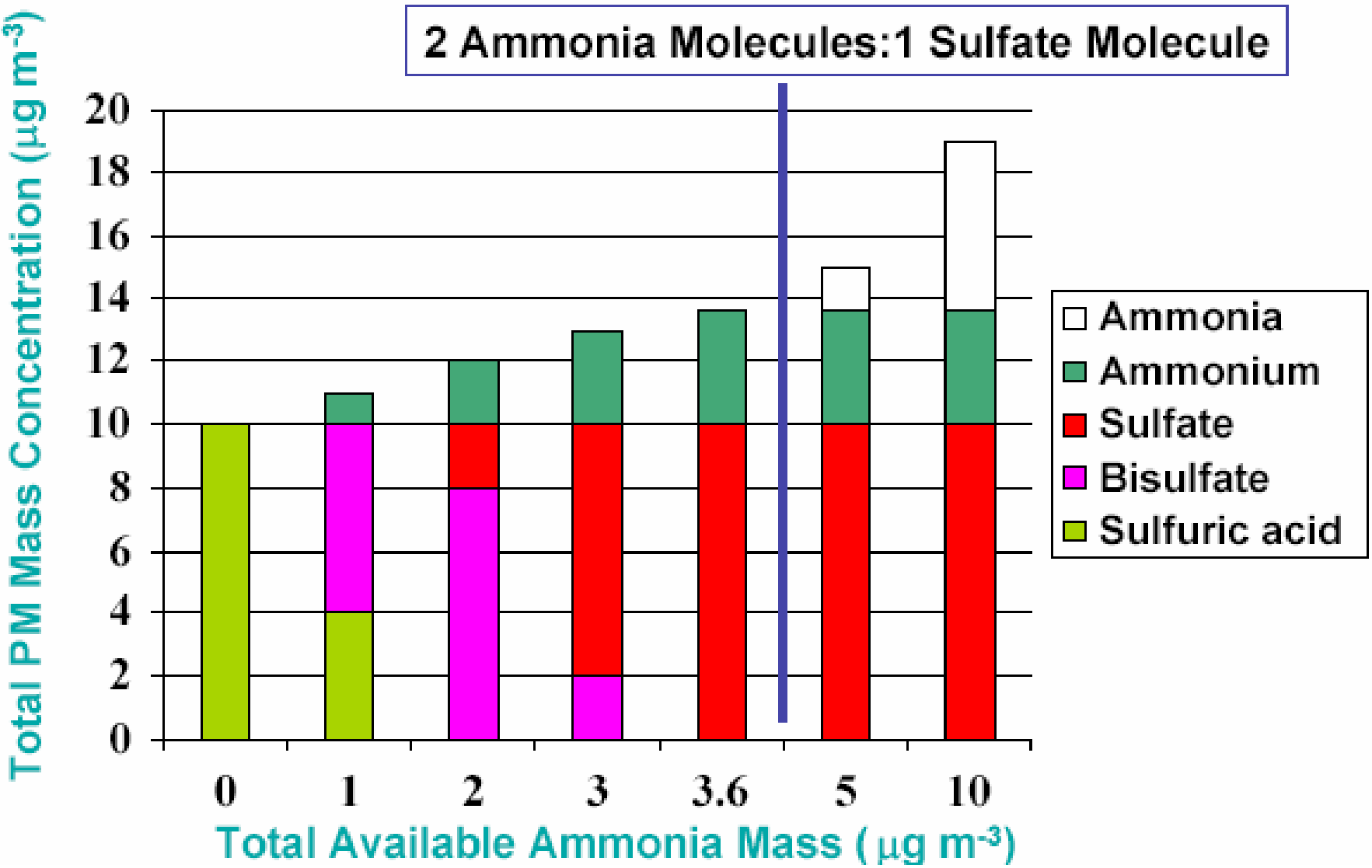
Ammonia Contribution to Fine Particles, Panorama Pathways 2004

Role of NOx and NH_3 in the Formation of Fine Particles



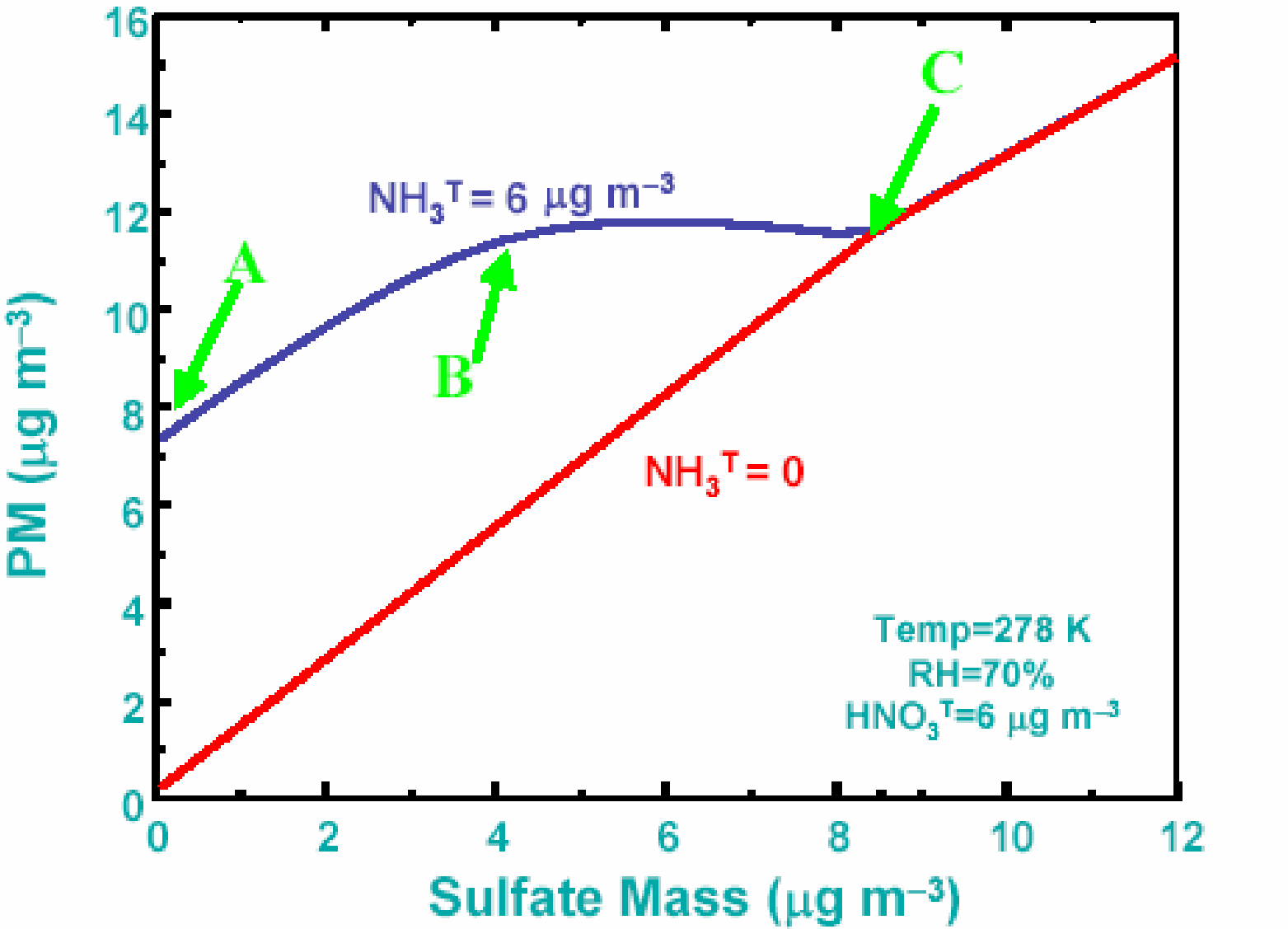
Ammonia Contribution to Fine Particles, Panorama Pathways 2004, adapted from Pandis 2003

The Sulfuric Acid / Ammonia System



Ammonia Contribution to Fine Particles, Panorama Pathways 2004

Relationship between NH_3, NOx, and $SO_4^=$ in PM Formation



Ammonia Contribution to Fine Particles, Panorama Pathways 2004, adapted from Pandis 2003

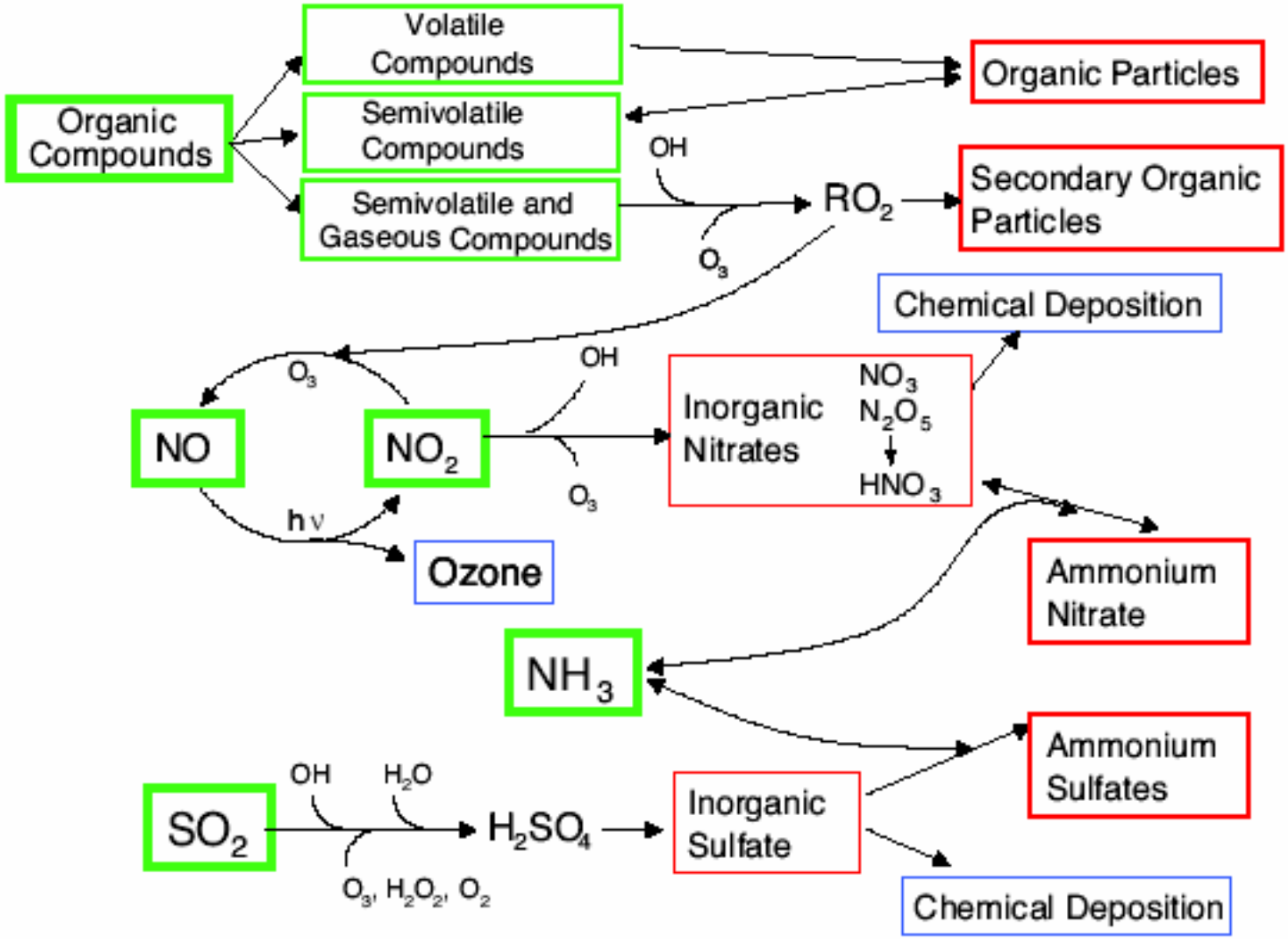


Figure 3.16. Chemical links between the ozone and PM formation processes. The major precursors are shown in green squares. The VOC can be gaseous (always in the gas phase), non-volatile (always in the condensed phase), and semivolatile ((partitioned between the gas and condensed phases (adapted from MSC, 2001)).

COMPOSITION OF PM2.5 (EPA/NARSTO PM ASSESSMENT, 2003)