

Chemistry of Inorganic Nitrogen Compounds

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Atmospheric Chemistry

CHEM-5151/ATOC-5151

Required Reading: Finlayson-Pitts and
Pitts Chapter 7

Other Possible Reading: Seinfeld and
Pandis Chapter 5

Outline

Introduction

- Oxidation of NO to NO₂ and the Leighton Relationship
- Oxidation of NO₂
- Atmospheric Chemistry of HONO
- Reactions of NO₃ and N₂O₅
- Atmospheric Chemistry of HNO₃
- “Missing NO_y”
- Ammonia

Bonus Material

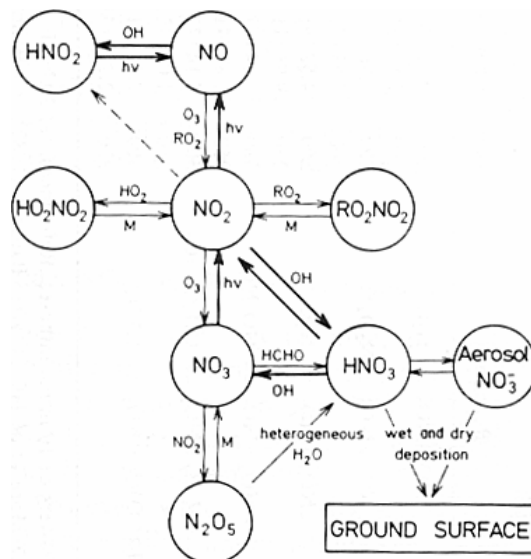
Motivation

- Inorganic nitrate compounds intimately involved in important chemical processes in both troposphere and stratosphere
 - NO_2 is key to formation of tropospheric ozone
 - Both in polluted and background troposphere
 - HNO_3 key ingredient in acid rain
 - NO_3 is primary night time oxidant
 - Participate with halogens in O_3 destruction chemistry in stratosphere
 - Regulate chain length of O_3 -destroying reactions
- Fascinating chemistry + unresolved issues

Intro

Diagram of NOy

- Stable species in circles
- Major pathways denoted by arrows
- Will use this diagram throughout



Intro

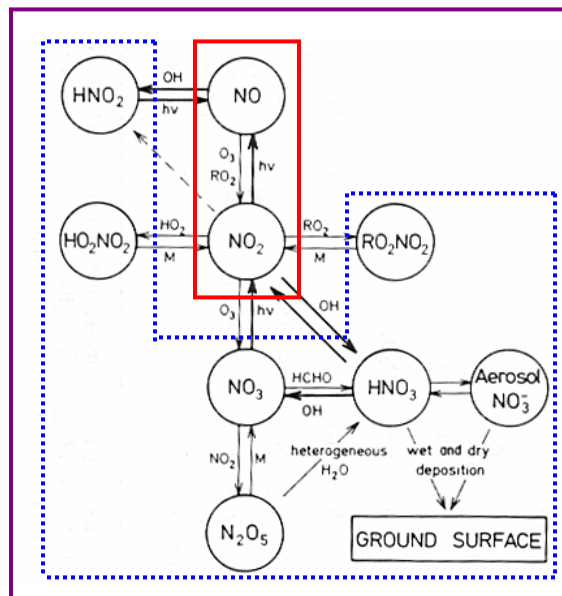
Definitions

- $\text{NO}_x = \text{NO} + \text{NO}_2$
 - These are the key nitrogen containing species
 - Rapid interconversion between NO & NO_2 in stratosphere and troposphere
- $\text{NO}_y = \text{NO} + \text{NO}_2 + \text{HNO}_3 + \text{PAN} + \text{HONO} + \text{NO}_3 + 2\text{N}_2\text{O}_5 + \text{organic nitrates (RNO}_3) + \text{particulate nitrate (pNO}_3^-) + \dots$
 - NO_x + all of its reservoir species
- $\text{NO}_z = \text{NO}_y - \text{NO}_x$
 - Just the reservoir species

Intro

Breaking Down NO_y

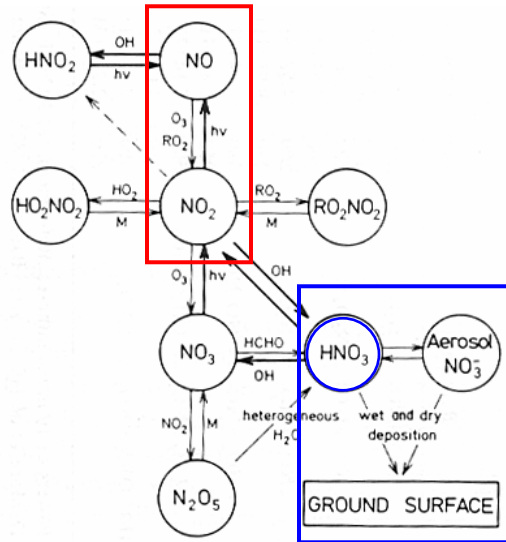
- $\text{NO}_x = \text{NO} + \text{NO}_2$
 - Rapid interconversion
- $\text{NO}_y = \text{NO}_x + \text{reservoir species}$
- $\text{NO}_z = \text{reservoir species}$



Intro

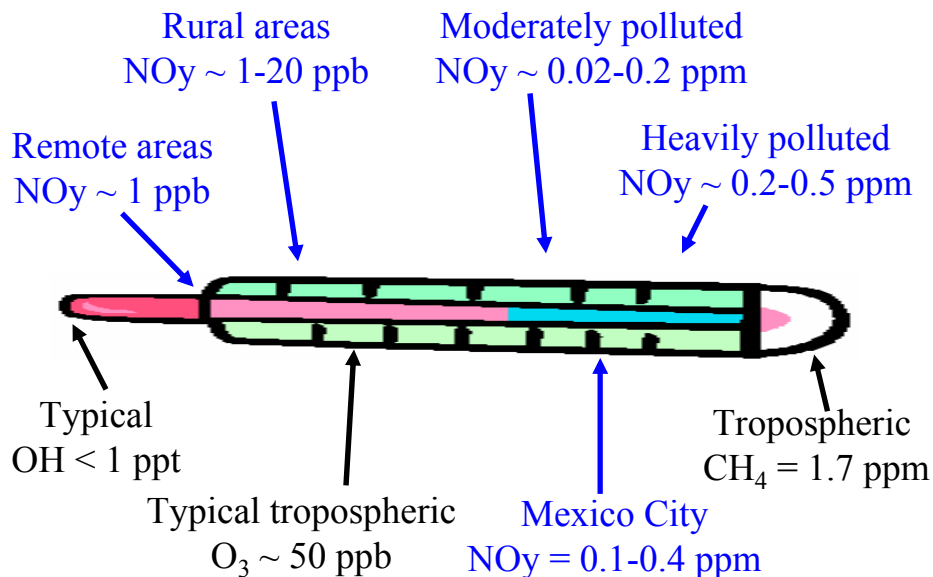
Sources and Sinks

- Sources of NO_y primarily directly emitted NO + NO₂
 - Combustion sources
 - Mobile – planes, trains and automobiles
 - Stationary - power plants, industrial
 - Natural – Biomass burning, lightning
- Sinks of NO_y lost through HNO₃
 - Washout of HNO₃
 - Dry deposition
 - Incorporation into aerosols as nitrate (pNO₃⁻) followed by loss of particles



Intro

Typical NO_y Concentrations



Intro

Overall Look at Oxidation

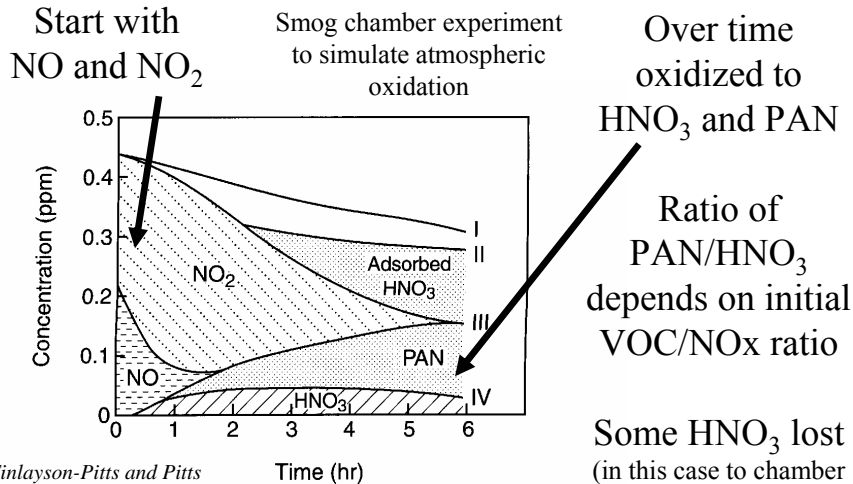


FIGURE 7.1 Cumulative plot of oxidized nitrogen compounds for a typical smog chamber run. Initial concentrations were 4.55 ppmC VOC, 0.21 ppm NO, and 0.23 ppm NO₂ (from Spicer, 1983).

Intro

Oxidation of NO to NO₂

- First guess in old days:
 - Reaction $2 \text{NO} + \text{O}_2 \rightarrow 2 \text{NO}_2$ responsible for NO oxidation in polluted urban areas
 - Not the case – too slow at typical [NO]
 - Does occur in power plant plumes with very high [NO]
- Now known: peroxy radicals responsible for NO oxidation
 - $\text{NO} + \text{HO}_2 \rightarrow \text{OH} + \text{NO}_2$
 - $\text{NO} + \text{RO}_2 \rightarrow \text{RO} + \text{NO}_2$
- Leighton relationship:
 - Assume hypothetical atmosphere – NO, NO₂ and air (no organics!)
 - Also called “photostationary state”
 - Continued on next slide...

A

“Photostationary State”

- $\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}$ (4)
- $\text{O} + \text{O}_2 \xrightarrow{M} \text{O}_3$ (5)
- $\text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2$ (6)

Photostationary state often close to reality

- In steady state:

$$\frac{[\text{O}_3][\text{NO}]}{[\text{NO}_2]} = \frac{k_4}{k_6}$$

$$\frac{k_6[\text{O}_3][\text{NO}]}{k_4[\text{NO}_2]} = 1$$

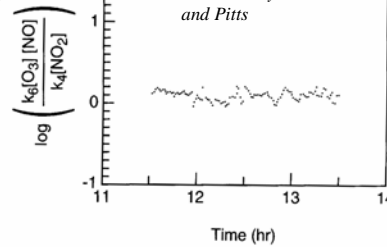


FIGURE 7.3 Test of photostationary state in rural Michigan on June 4, 1977, 11:30 to 13:30 hours (adapted from Ritter *et al.*, 1979).

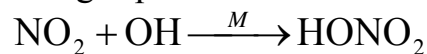
 Deviations from photostationary when there are significant organics present

$$\frac{[\text{NO}_2]}{[\text{NO}]} = \frac{1}{k_4} \{k_6[\text{O}_3] + k_{\text{HO}_2+\text{NO}}[\text{HO}_2] + \sum k_{\text{RO}_2+\text{NO}}[\text{RO}_2]\}$$

A

Oxidation of NO_2

- Daytime = gas phase reaction with OH



- Lifetime of $\text{NO}_2 \sim 16$ hr
 - At typical $[\text{OH}]$ of 2×10^6 molecule cm^{-3}
 - Competes with NO_2 photolysis during daytime
 - $\tau_{\text{photolysis}} \sim 2\text{-}3$ minutes
 - Reaction with OH important – converts $\text{NO}_x \rightarrow \text{NO}_y$
- Recent measurements for rate coefficients
 - Slightly smaller k_0 & k_∞
 - O_2 is $\sim 70\%$ as effective as N_2 as a quencher
 - See Brown *et al.*, 1999 recommendations and Dransfield *et al.*, 1999

B

Oxidation of NO₂

- Nighttime = reactions with O₃ and NO₃
- $\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$ (1)
- $\text{NO}_2 + \text{NO}_3 \xrightleftharpoons{M} \text{N}_2\text{O}_5$ (2)
- k₁ relatively small, but [O₃] often high enough to make it important
 - NO₃ is primary nighttime oxidant of organics
- Several lab studies of k₂ range of factor of 2 in results
- N₂O₅ lost via hydrolysis (more in a few slides)
 - Sink of N₂O₅ = sink of NO₃

B

Oxidation of NO₂

- Uptake of NO and NO₂ into liquid water (clouds, fogs, etc.) too slow to be important under most atmospheric conditions
- “Heterogeneous” reaction of NO₂ + H₂O
$$2 \text{NO}_2 + \text{H}_2\text{O} \xrightarrow{\text{surface}} \text{HONO} + \text{HNO}_3$$
 - Variety of surfaces show HONO production (e.g. soot)
 - Mechanism still not understood
 - HONO observed but not equivalent HNO₃
 - Reaction enhanced by light
 - Isotope studies suggest multiple reaction pathways
 - Possible reduction of NO₂ by a surface group
 - Another possible pathway:
$$\text{NO} + \text{NO}_2 + \text{H}_2\text{O} \xleftarrow{\text{surface}} 2 \text{HONO}$$
- Reactions of NO₂ with alcohols, organics, sea salt particles, and mineral oxides all discussed, but none are atmospherically important

B

Atmospheric Chemistry of HONO

- Importance
 - Can be major OH source
 - Particularly at sunrise
 - Indoor air pollutant
- Sources
 - Heterogeneous reactions of NO₂ (discussed above)
 - $\text{OH} + \text{NO} \xrightarrow{M} \text{HONO}$
 - Hard to build up significant [HONO] during day though, owing to fast photolysis of HONO
 - Surface reactions of HO₂NO₂
 - Small source directly from combustion (autos with no catalytic converter)

Study in Long Beach shows HONO as dominant OH source in early morning and overall 2nd largest source of OH

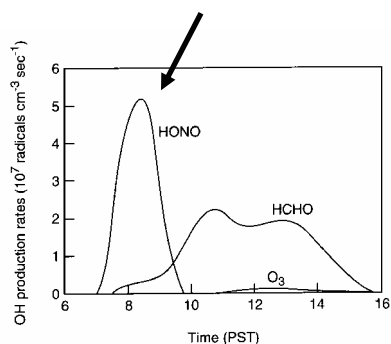


FIGURE 7.8 Calculated rates of formation of OH radical from photolysis of HONO, O₃, and HCHO at Long Beach, California, on December 10, 1987 (adapted from Winer and Biermann, 1994).

From Finlayson-Pitts and Pitts

C

Atmospheric Chemistry of HONO

Reminder of absorption cross section of HONO, gives OH + NO with $\phi = 1$ at $\lambda < 400$ nm

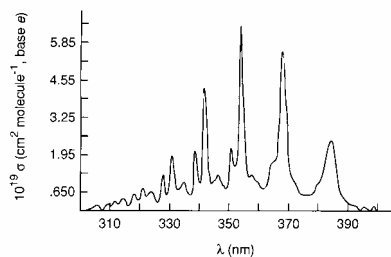


FIGURE 4.14 Absorption spectrum of HONO at 277 K (adapted from Bongartz *et al.*, 1991). Note that the absolute values of the cross sections shown here should be multiplied by 0.855 as recommended by Bongartz *et al.* (1994).

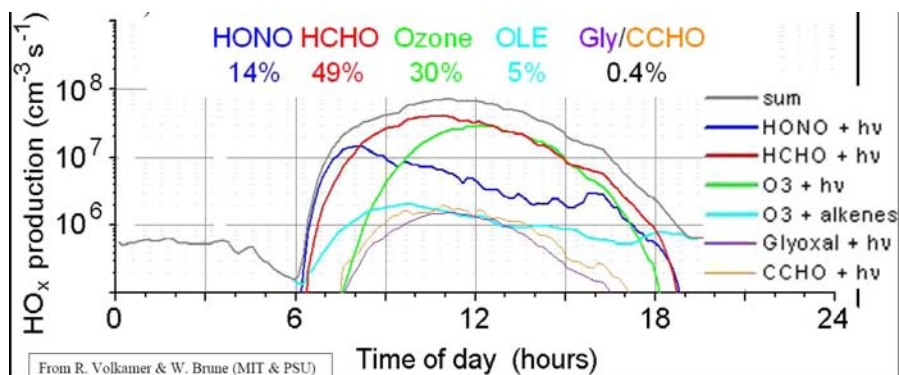
From Finlayson-Pitts and Pitts

- Atmospheric fates
 - Photolysis is major loss
 - Reaction of OH is fast, but not fast enough to compete
 - Uptake of HONO into liquid
 - Oxidation of NO₂⁻ to NO₃⁻
 - Greatly enhanced by freezing
 - Uptake onto ice
 - At T = 180 – 200K, $\alpha \sim 10^{-3}$
 - Deposition

C

HONO as Important OH Source

- Mexico City example (from photochemistry lectures)
- OH production from HONO dominates early morning photochemistry
 - Tails off later in day



Bonus

Peroxyacetyl Nitrate (PAN)

- Initially unknown product of photooxidation of organic/NO_x mixtures
 - Called “Compound X”
 - Strong eye irritant
 - Mutagenic & phytotoxic to plants
- Formed from RO₂ + NO₂ reaction
 - Competes with RO₂ + NO reaction
- Loss processes
 - Reverse of formation = thermal decomposition
 - Highly temperature dependent
 - Photolysis
 - Reaction with OH
- Concentrations as high as 70 ppb!
- Rapid vertical mixing leads to long lifetime → transport
 - Source of NO_x to remote areas

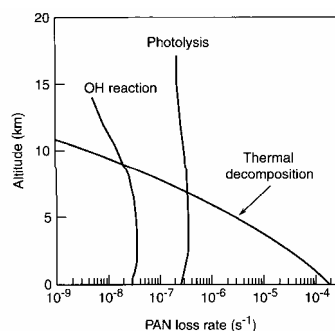
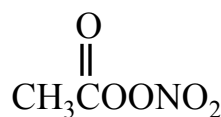
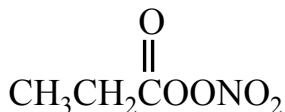


FIGURE 6.19 Calculated first-order loss rates of PAN due to thermal decomposition, OH reaction, and photolysis as a function of altitude (assuming diurnally averaged actinic fluxes for 30°N, July 4) (adapted from Talukdar *et al.*, 1995).

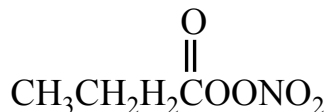
Bonus

PAN Homologs

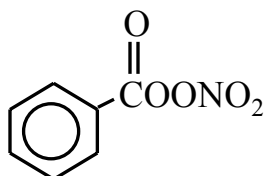
- General class of compounds = peroxyacyl nitrates
- Formed from different feedstock organics
 - Both natural and anthropogenic
 - PAN is most common of group



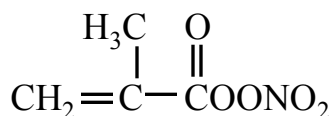
Peroxypropionyl nitrate (PPN)



Peroxy-n-butyryl nitrate (PnBN)



Peroxybenzoyl nitrate (PBzN)



Peroxyacryloyl nitrate (MPAN)

Bonus

Reactions of NO₃

- NO₃ present only at night
 - Very fast daytime photolysis
- Competition between NO₂ & NO
 - NO₃ + NO₂ ↔ N₂O₅
 - NO₃ + NO → 2 NO₂
 - At 1 ppb NO, τ_{NO₃} ~ 2 s
 - NO and NO₃ do not coexist
- Reactions with organics
 - Covered in Chapter 6
 - NO₃ = “OH of the night”
- Thermal decomposition
 - Not observed in atm
- Reaction with water
 - Evidence for uptake of NO₃ at high ambient RH
 - Difficult to separate from N₂O₅ uptake

Great review articles on NO₃
Wayne et al., 1991 &
Atkinson, 1991

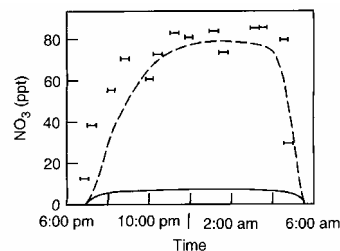


FIGURE 7.12 Comparison of measured (Platt *et al.*, 1984) and predicted nitrate radical concentrations at Edwards Air Force Base, California, May 23–24, 1982. The dashed line is the model prediction without the unimolecular decomposition of NO₃ and the solid line is that with the decomposition (adapted from Russell *et al.*, 1986).
From Finlayson-Pitts and Pitts

Later chapters cover aqueous
phase chemistry of NO₃

D

Reactions of N₂O₅

- Formation from NO₂ + NO₃
- Loss via hydrolysis
 - N₂O_{5(g)} + H₂O_(g) → 2 HNO_{3(g)}
 - N₂O_{5(g)} + 2 H₂O_(g) → 2 HNO_{3(g)} + H₂O_(g)
 - N₂O_{5(g)} + H₂O_(l) → 2 HNO_{3(aq)}
 - All three reactions important
 - Hydrolysis as much as 90% of HNO₃ production in atmosphere
 - Removal of NO₂ from system results in lower predicted O₃
- Loss via other reactions
 - Reactions with sea salt
 - NaX_(s,aq) + N₂O_{5(g)} → XNO_{2(g)} + NaNO_{3(s)}
 - X = Cl, Br, or I
 - Possibly important in marine boundary
 - Reactions with alkenes?

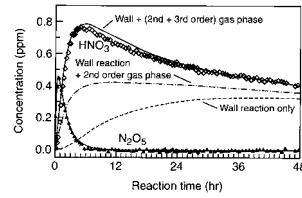


FIGURE 7.15 Measured loss of gaseous N₂O₅ in the presence of 8100 ppm H₂O and formation of HNO₃ as a function of reaction time in a large chamber (250 m³) and model-predicted HNO₃ for the heterogeneous wall hydrolysis of N₂O₅ for the combinations of wall loss plus bimolecular gas phase (N₂O₅ + H₂O) reaction and wall loss plus bimolecular and termolecular (N₂O₅ + 2H₂O) reaction (adapted from Wahner *et al.*, 1998a).

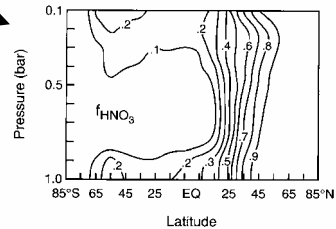
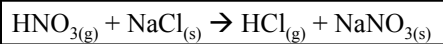
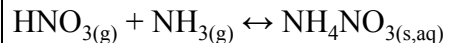
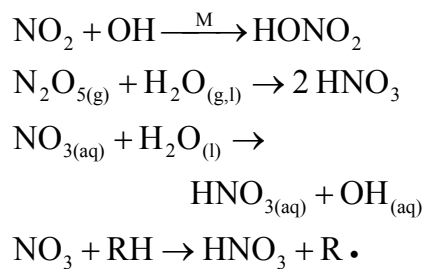


FIGURE 7.16 Model-predicted fraction of HNO₃ (f_{HNO_3}) produced by heterogeneous N₂O₅ and NO₃ hydrolysis in January (adapted from Dentener and Crutzen, 1993).

From Finlayson-Pitts and Pitts D

Atmospheric Chemistry of HNO₃

Formation reactions previously discussed:



More discussion on these during aerosol section

- Tropospheric fates
- Fast wet and dry deposition
 - HNO₃ is “sticky”
- Photolysis is slow
- OH rxn relatively slow
 - Interesting kinetics → some complex formation
 - Temp dependence of $k =$ positive or negative?
- Reaction with NH₃
 - Acid – base reaction
 - NH₄NO_{3(s)} formation requires water
 - Equilibrium strongly dependent on temperature
- Reactions with sea salt
 - Possible importance in marine boundary layer

E

NH₄NO₃ Formation: LA Example

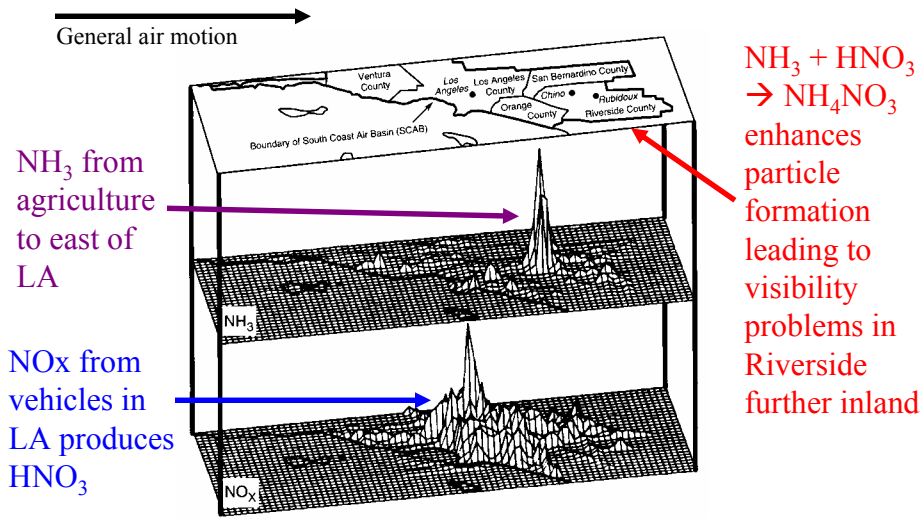


FIGURE 7.21 Estimated daily emissions of NH₃ and NO_x in the Los Angeles area in 1982 (adapted from Russell and Cass, 1986).

From Finlayson-Pitts and Pitts

E

“Missing NO_y”

- Compare measurement of total NO_y with sum of measurements of individual nitrogen containing compounds
 - Shortfall → not all of NO_y accounted for
 - See FP&F p.570 - 573
- Problem in numerous field campaigns in past
 - As of FP&P printing in 1999, still very much a mystery

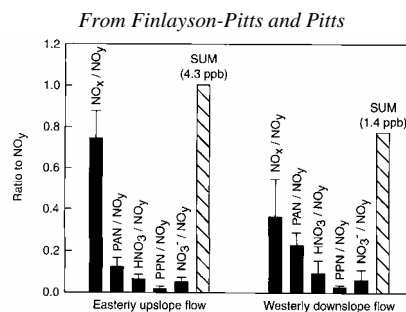


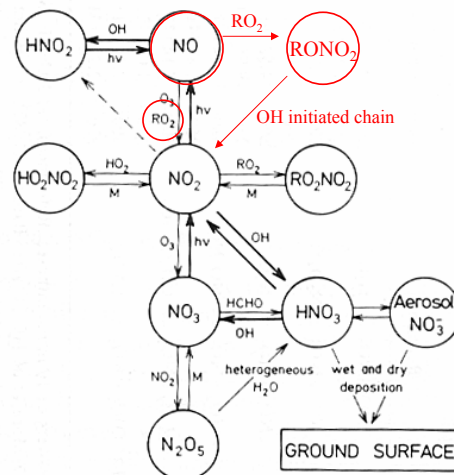
FIGURE 11.29 Ratio of measured individual compounds of NO_x to total NO_y at Idaho Hill, Colorado, with easterly winds (more polluted air) and with westerly winds (cleaner but more aged air), respectively (data from Williams *et al.*, 1997).

- Measurements by NOAA folks right here in Colorado
- Poor agreement with cleaner westerly winds from mountains
- Better agreement with easterly winds from Boulder/Denver metropolitan area
- Deficit correlated with O₃ indicating photochemical source

F

Alkyl Nitrates

- Missing NO_y = alkyl nitrates?
- Mystery possibly solved by Cohen et al. at UC Berkeley
 - Measurements show larger than expected amounts of alkyl nitrates (RNO₃)
 - See Day et al., JGR, 108, 4501, 2003
 - Recent development – jury is still out
- Determined by branching ratio in reaction RO₂ + NO
 - RO₂ + NO → RO + NO₂
 - RO₂ + NO → RONO₂



F / Bonus

What do cows, raw sewage, and a brand new Nissan have in common?

Ammonia!

NH₃ is only significant gaseous base in atmosphere



Photos courtesy of B. Knighton



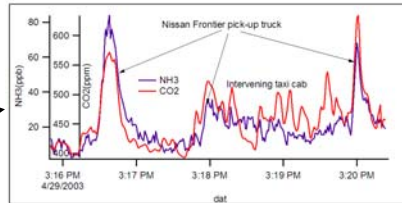
- Sewage and livestock known sources
- Neutralizes atmospheric acids (HNO₃, H₂SO₄, etc.)
- NH₃ contributes to particle growth
- Also lost via dry deposition
- Reaction with OH is slow

G

NH₃ from Vehicles During Mexico City Field Campaign

AMMONIA EMISSIONS FROM NISSAN FRONTIER in MEXICO CITY

Can see large plumes of NH₃ while following new truck



Proof that signal is truly NH₃, not interference

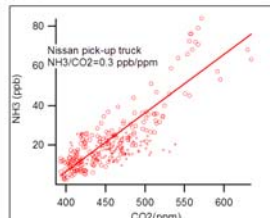
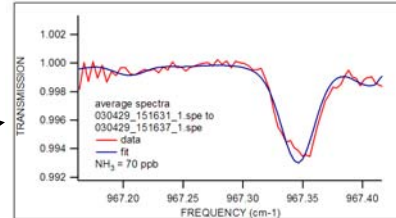
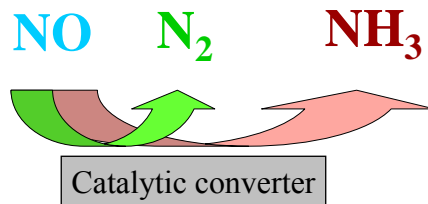


Figure courtesy of S. Herndon, Aerodyne

- NH₃ correlates with CO₂
- CO₂ is marker for combustion, in this case, from auto
- Thus, NH₃ definitely from vehicles

G

Ammonia From Mobile Sources



- Over-functioning catalytic converters reduce nitrogen oxides to ammonia
 - Possibly associated with cars running fuel-rich
- NH₃ from vehicles observed in previous studies
 - LA NH₃ emissions from vehicles estimated as high as emissions from livestock (Fraser and Cass, 1998)
- Observations in Mexico City
 - Higher than expected levels of ambient NH₃ observed
 - Observed correlation with CO₂ plumes directly from exhaust
 - Observed newer cars as highest NH₃ emitters

G

Real Data from Mexico City

CO = Morning traffic emissions
Late morning boundary layer rise
Evening boundary layer reforms

O₃ = Afternoon photochemistry

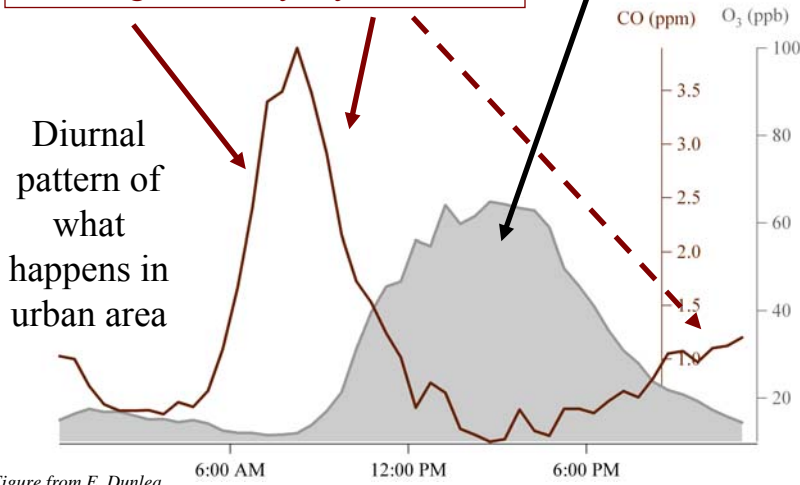


Figure from E. Dunlea

Bonus

Mexico City NO_x Diurnal Patterns

NO = Morning traffic
Boundary layer +
 $\text{NO} + \text{RO}_2 \rightarrow \text{NO}_2$

NO₂ = Afternoon
Photochemistry
Boundary layer reform

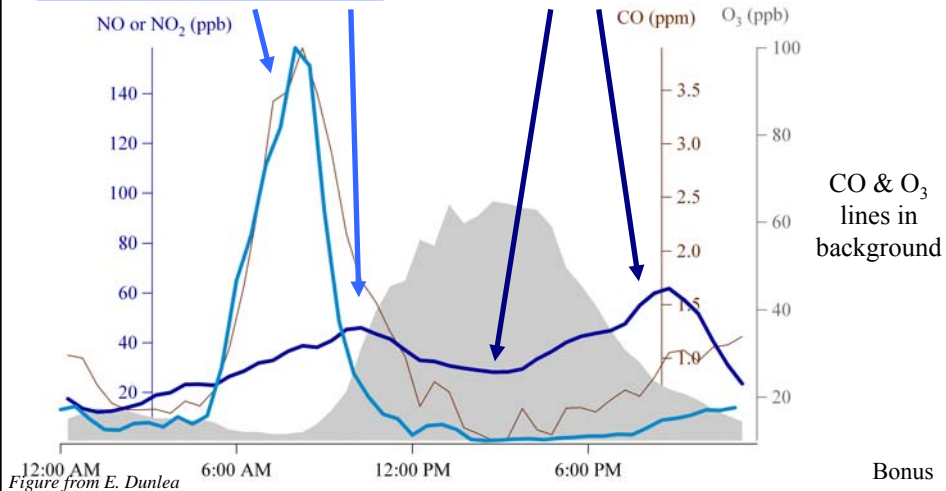
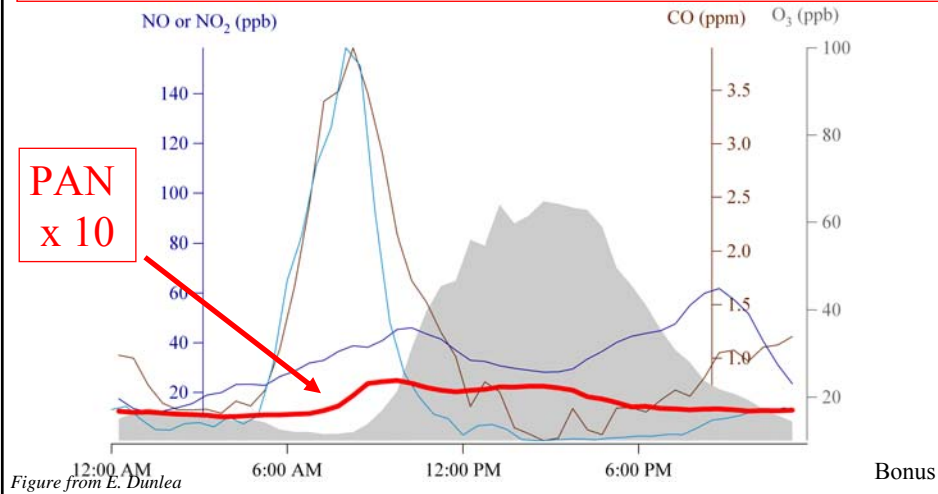


Figure from E. Dunlea

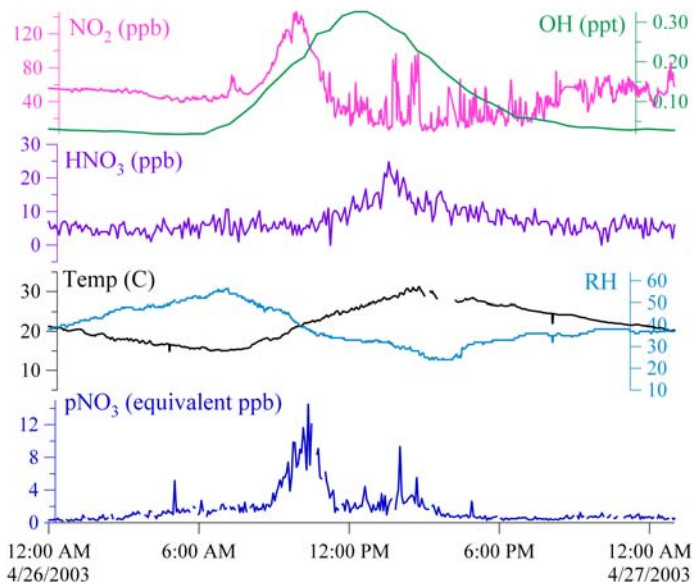
Bonus

Mexico City PAN Diurnal Pattern

NO_z levels much less than NO_x levels
 2003 PAN levels lower than previous (max = 10 ppb)
 Indication of changing chemical environment in Mexico City

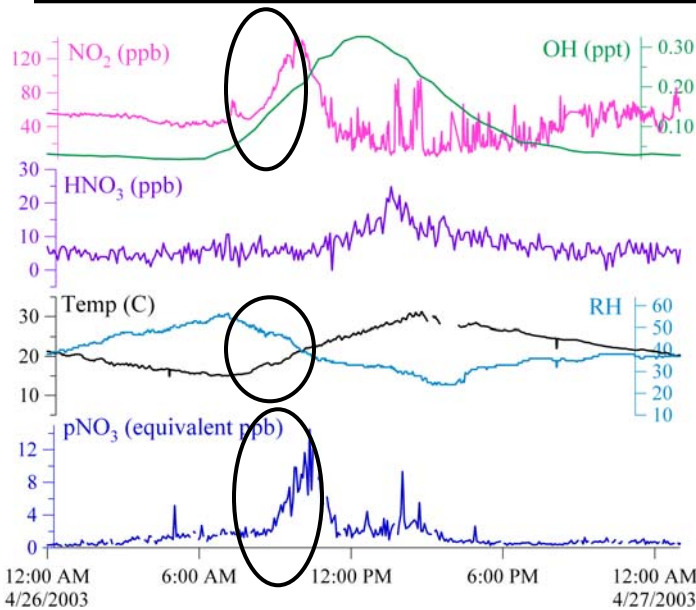


Mexico City HNO₃ Budget Example



- Data taken during 2003 Mexico City field campaign at La Merced fixed site
- Downtown location near market & traffic corridor
- Data from several groups (Aerodyne Research, RAMA Monitoring network, Penn State, UNAM University)

Mexico City HNO₃ Budget Example



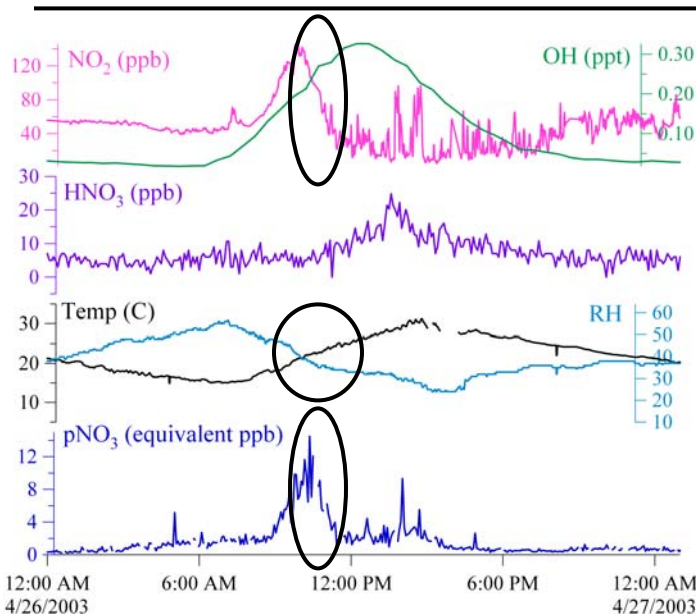
Early morning

- $\text{OH} + \text{NO}_2 \rightarrow \text{HNO}_3$
- No gas phase $[\text{HNO}_3]$
- Low temp, high RH
- HNO_3 partitions to particles

Figure from E. Dunlea

Bonus

Mexico City HNO₃ Budget Example



Late morning

- Boundary layer rise \rightarrow NO_2 decrease
- Temp increase, RH decrease
- HNO_3 repartitioning to gas phase

Figure from E. Dunlea

Bonus

Mexico City HNO₃ Budget Example

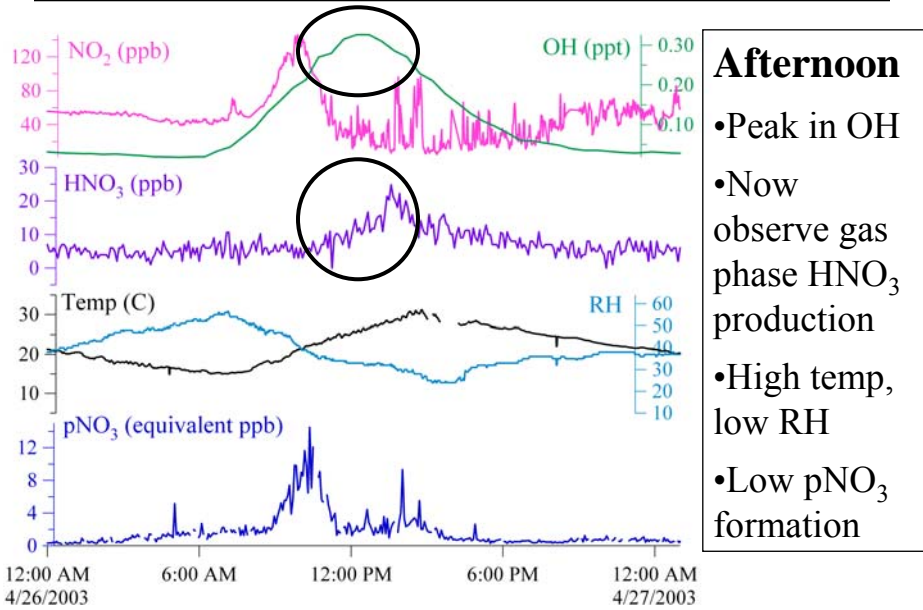


Figure from E. Dunlea

Bonus

Mexico City HNO₃ Budget Example

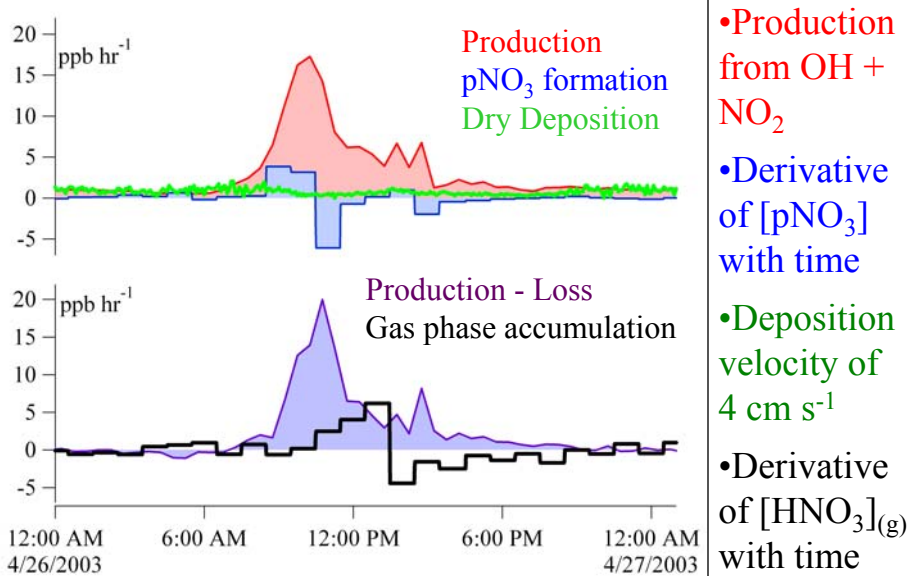
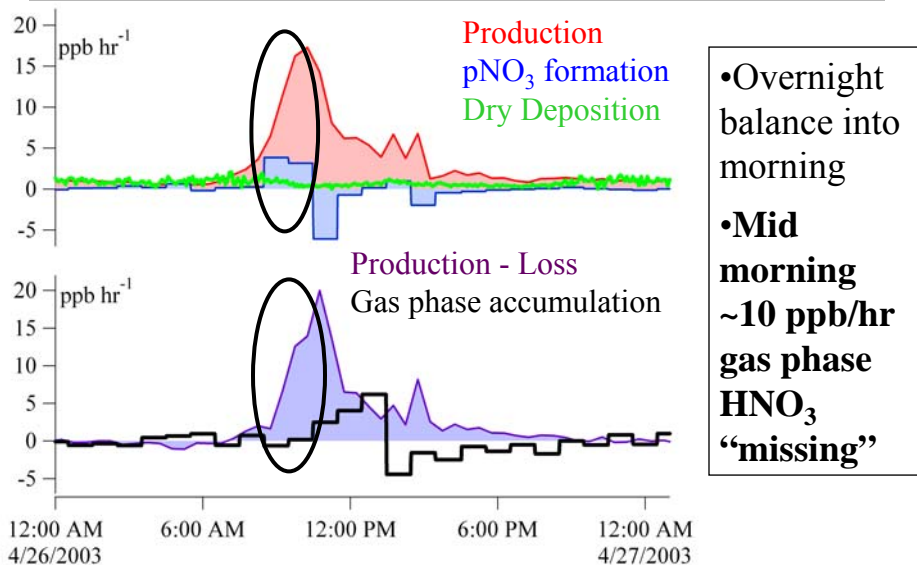


Figure from E. Dunlea

Bonus

Mexico City HNO₃ Budget Example



Bonus

Summary – What Have We Covered

- NO_y = NO_x + reservoir species
- Sources → NO; Sinks → HNO₃
- Daytime story = NO ↔ NO₂ interconversion
 - Photostationary state = good 1st approximation
- Nighttime story = NO₃ ↔ N₂O₅ interconversion
- Details on specific compounds:
 - NO, NO₂, HONO, NO₃/N₂O₅, HNO₃, PAN
 - Missing NO_y
- Real life examples from Mexico City on NH₃ and HNO₃

Another NO_y Schematic

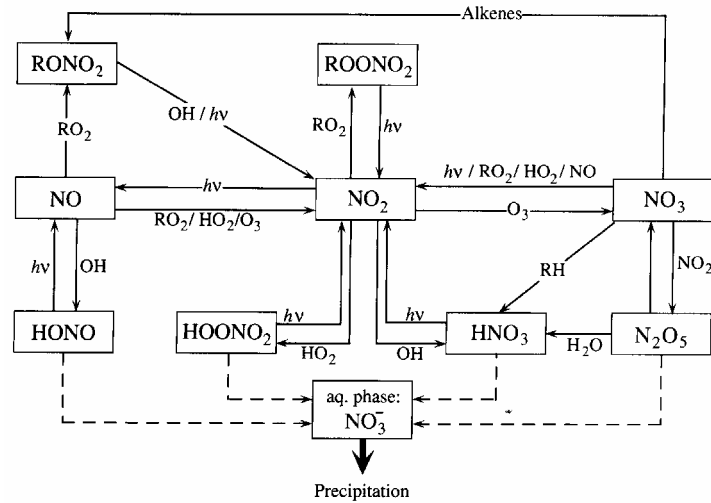


FIGURE 5.16 Schematic of NO_x chemistry.

From Seinfeld and Pandis