

Atmospheric Chemistry of Nitrogen

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Reactive nitrogen compounds play key roles in chemical processes in both troposphere and stratosphere:

- NO_x is key to formation of tropospheric ozone
- HNO₃ is key ingredient in acid rain
- NO₃ is primary oxidant at night
- NO_x plays complex role in stratospheric ozone chemistry

We've learned a lot about the chemistry of inorganic nitrogen compounds.

We have a great deal to learn about the chemistry of organic nitrogen species and about heterogeneous chemistry in the troposphere.

Warning

Serious geek alert!

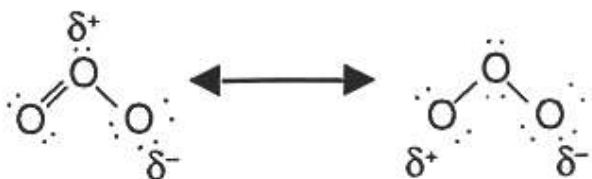
- Definitions
- Tropospheric Nitrogen Chemistry
 - focus on inorganic compounds - gas phase and PM 2.5 formation (discussed in greater depth this afternoon)
 - interaction with organic compounds and transformations to form organic nitrates
- Stratospheric Nitrogen Chemistry
 - Gas Phase NO_x - O_3 - Cl_x - Br_x
 - Heterogeneous Chemistry
- Factors Affecting Transformations
- ~~Quiz~~ Some things to consider ...

Definitions

- Radicals: chemical species having an unpaired electron ...high energy, great desire to be "paired" \longrightarrow highly reactive

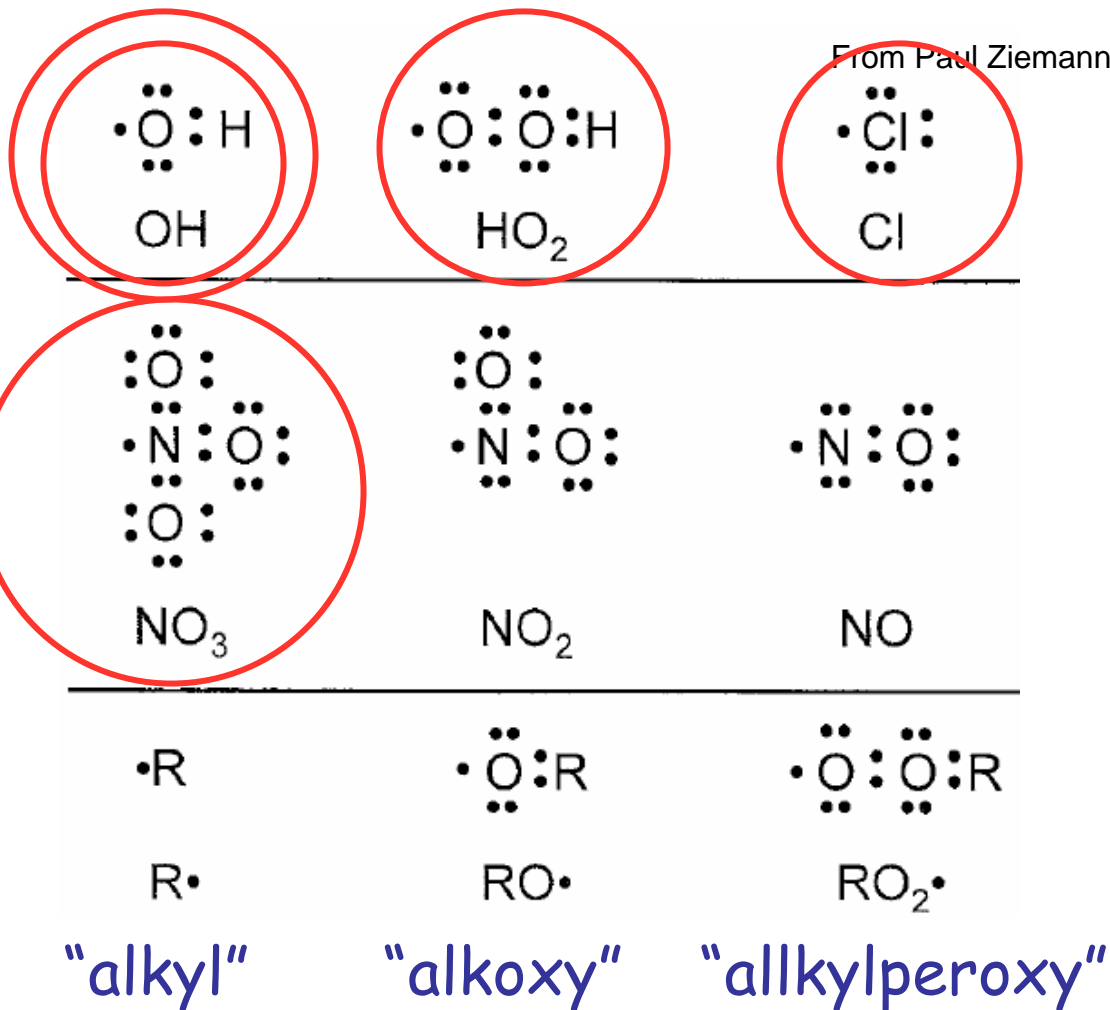


the primary oxidants:
and O_3 (a dipolar molecule)



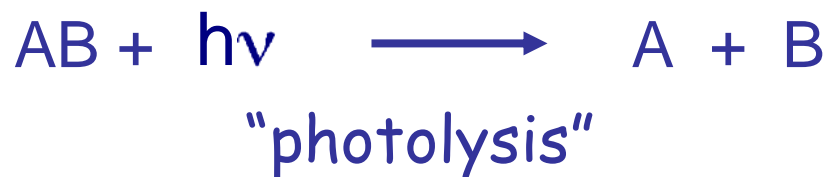
(slower reacting but high concentrations)

R is hydrocarbon chain C_xH_y



Definitions, continued

- photochemistry: chemical reactions involving radiation (e.g.,



- combination reactions that don't result in excited states require 3rd body (M) to take up excess energy of reaction



M typically N₂ or O₂

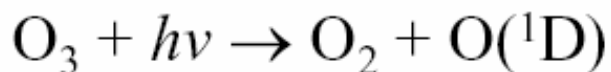
Context: we need a quantitative understanding of how the atmosphere's ability to cleanse itself of pollutants ("oxidizing capacity") is changing.

- the primary oxidants (mainly OH, HO₂, O₃, Cl, and NO₃) control the atmospheric lifetimes and abundances of reactive chemical species
- OH is by far the most reactive: lots of different compounds are competing to react with OH.
 - [OH] frequently < 1 pptv (part per trillion by volume)
 - OH lifetime = .01 - 1 second

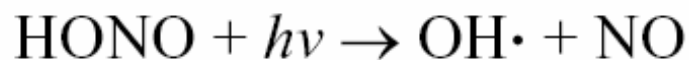
Roles of N species in Production of Tropospheric Oxidants

Hydroxyl Radical (OH)

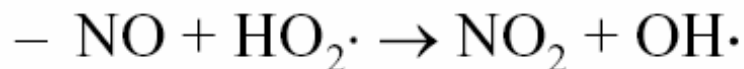
- Photodissociation of O₃



- Photodissociation of HONO



- From HO₂·



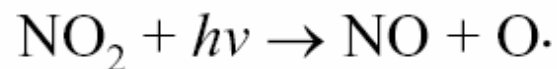
Nitrate Radical (NO₃·)

- Oxidation of NO₂



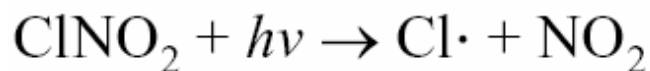
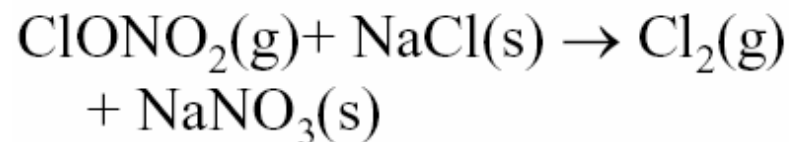
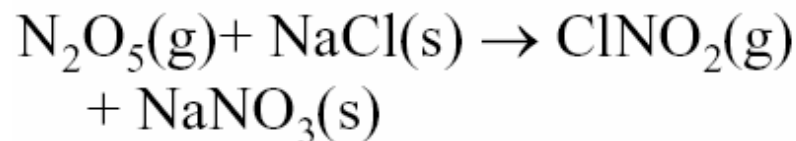
Ozone (O₃)

- Photodissociation of NO₂

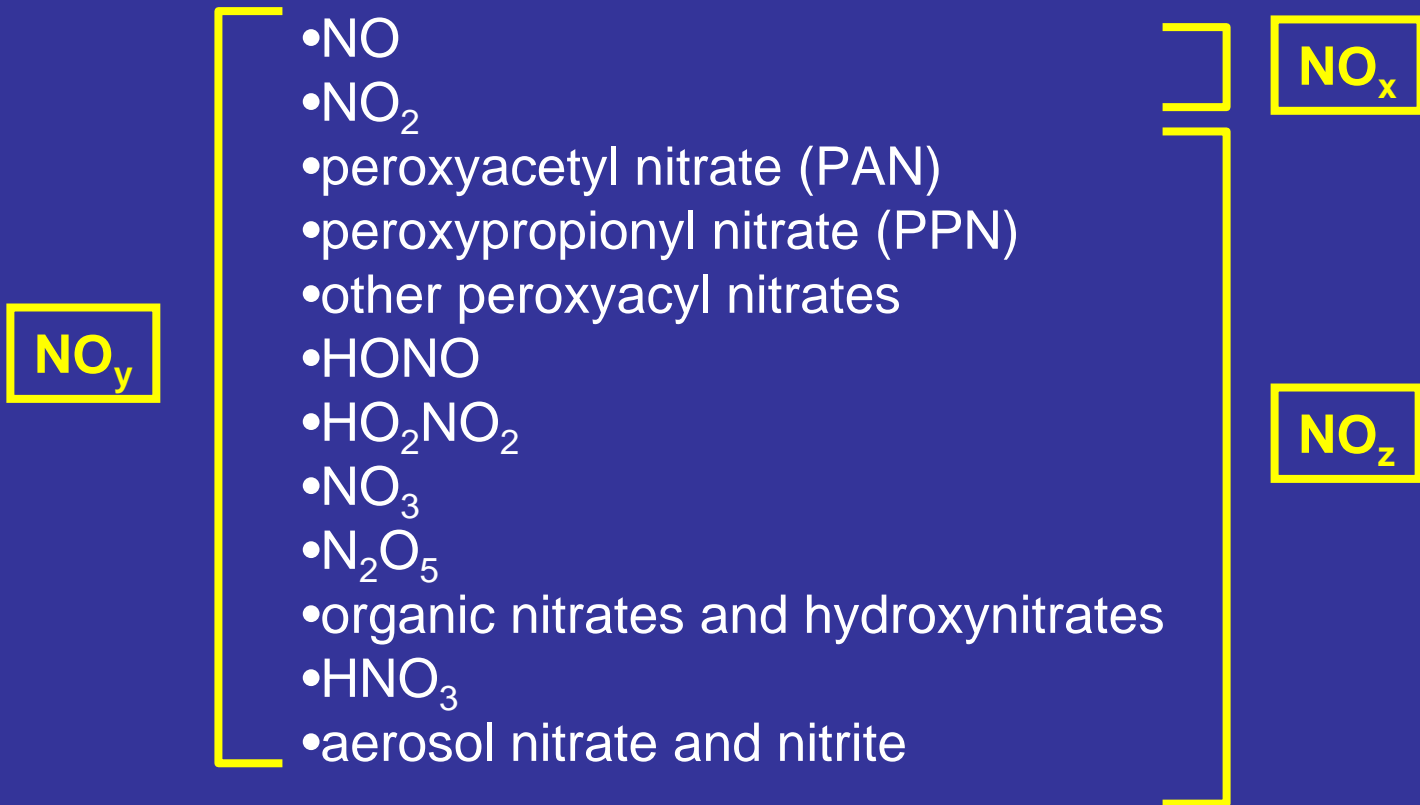


Chlorine (Cl)

- Sea-salt chemistry



Reactive Nitrogen Oxide Species: NO_x, NO_y, NO_z



- **$\text{NO}_x = \text{NO} + \text{NO}_2$ (both are radicals)**
 - Nitric oxide and nitrogen dioxide are closely tied through photolytic and chemical equilibria in the atmosphere; because of **rapid interconversion** the two species are often grouped together as NO_x
- **HNO_3 (nitric acid)**
 - One of the major oxidation products of NO_x , through reaction with OH or heterogeneous conversion of N_2O_5
 - subsequent **washout** and **dry deposition** are the **major sinks for atmospheric NO_x**
 - uptake on particles -> aerosol reservoir of NO_3^- ion (“particulate nitrate”) in the form of ammonium or other nitrate salt
- **HONO (nitrous acid)**
 - easily photolyzed and **a potentially important source of OH**

• $\text{RC(O)O}_2\text{NO}_2$: peroxyacyl nitrates

- formed by reaction of organic acyl radicals (RCO) with O_2 and NO_2
- important in the transport and recycling of NO_x
 - most abundant is PAN, peroxyacetyl nitrate ($\text{R}=\text{CH}_3$)

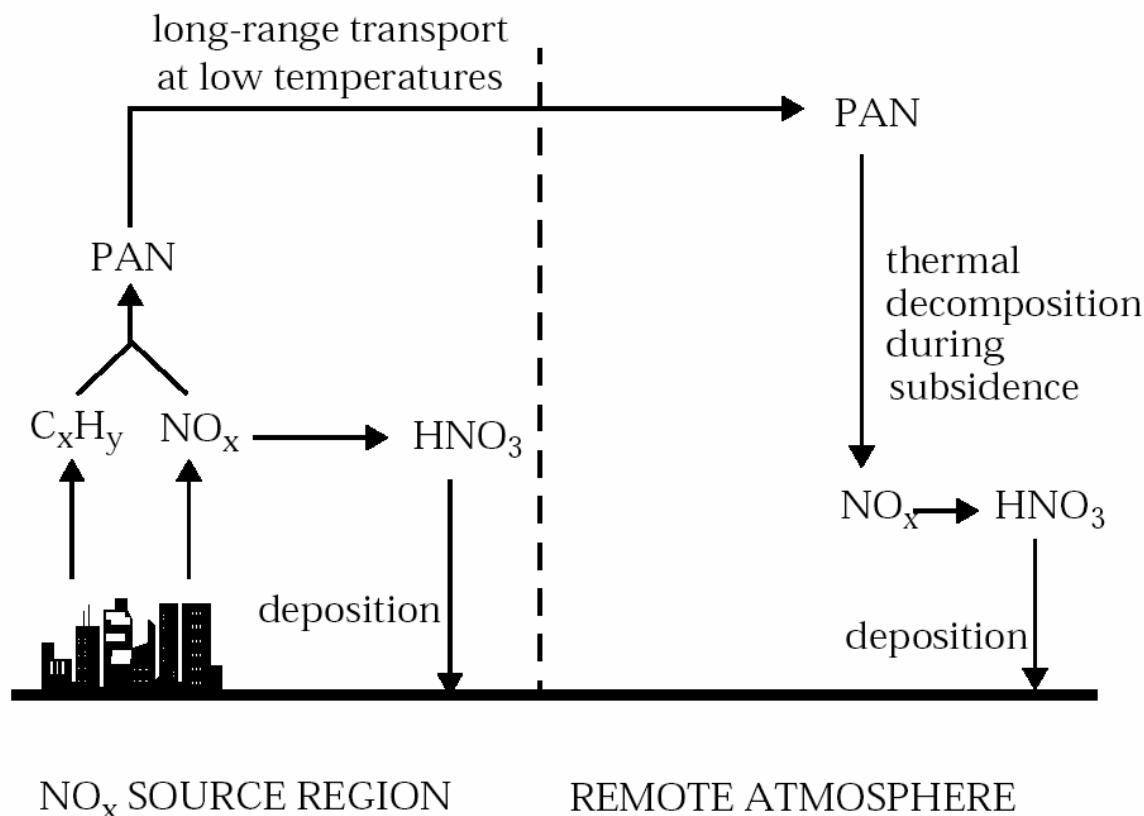


Figure 11-4 PAN as a reservoir for long-range transport of NO_x in the troposphere

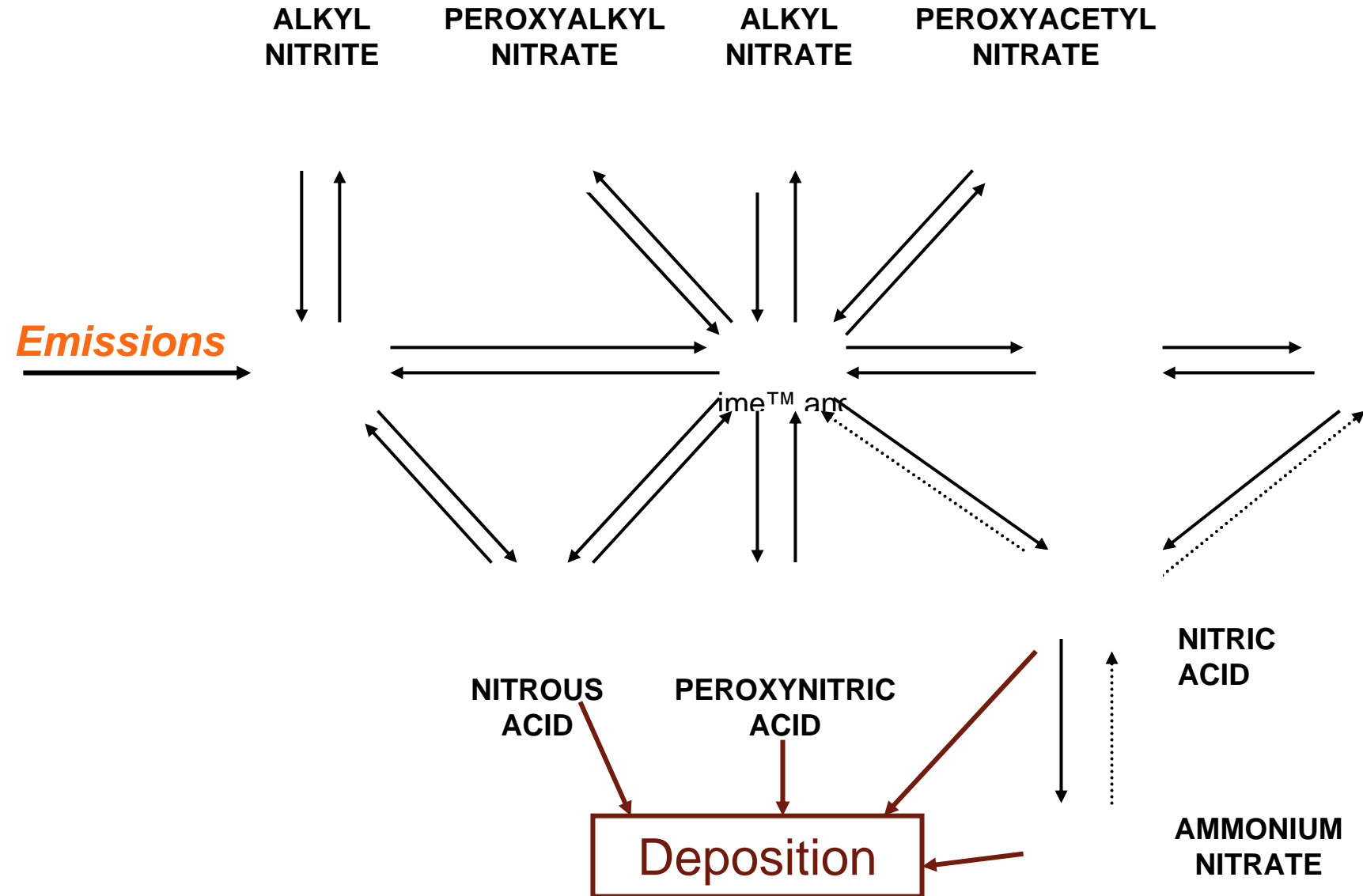
- **RONO₂ - alkyl nitrates**

- formed during the oxidation of most hydrocarbons by OH or NO₃; R is a simple alkyl chain or a multi-functional organic group, depending on parent HC
- *Fate? Significant sink for NO_x? (hydroxy group might impart high solubility in aqueous aerosols)*
- *Likely to dry deposition? (non-acidic source of reactive N to terrestrial ecosystems??)*

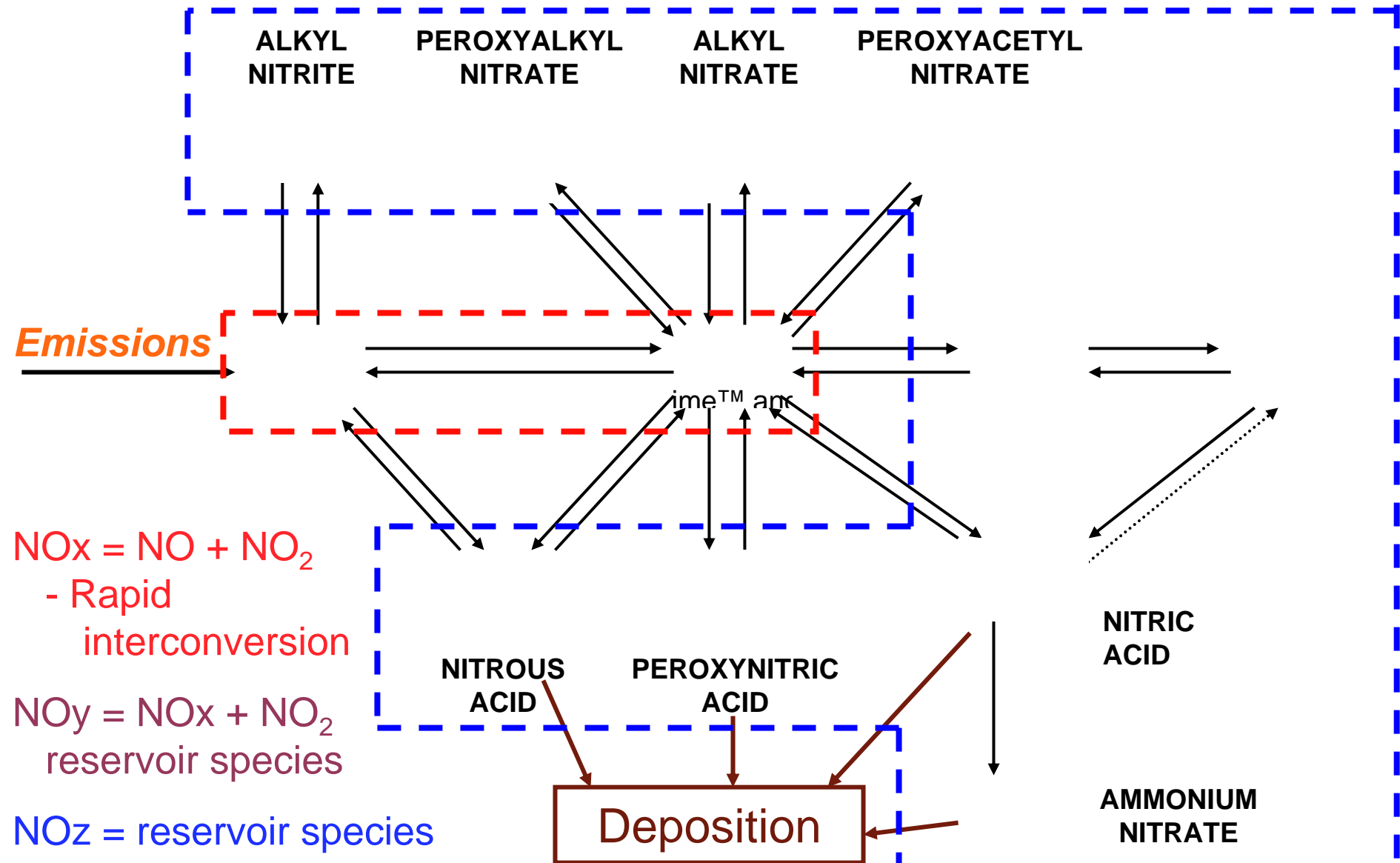
- **NO_y - total reactive oxidized nitrogen**

- N is in an oxidation state $\geq +II$; includes all species from above list; a more conserved quantity than NO_{yi} and thus useful when considering the **budget of reactive N** and in evaluating **speciation**

Chemical Transformations of Nitrogen Oxides in the Troposphere



Chemical Transformations of Nitrogen Oxides in the Troposphere



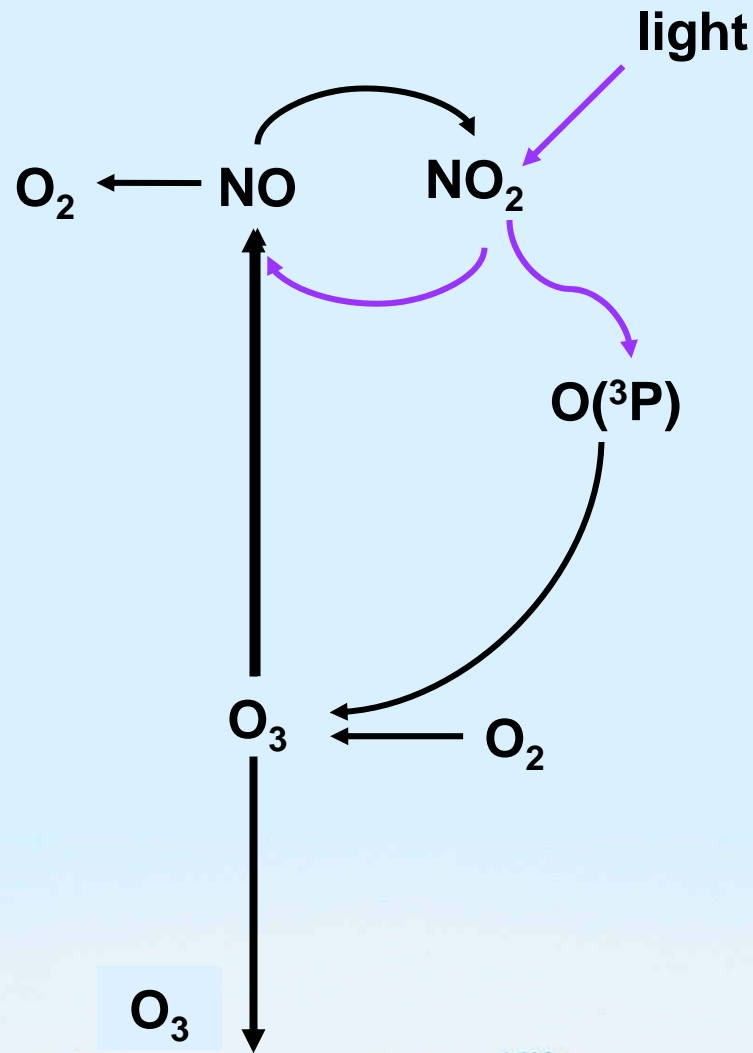
NO_x and O₃ Formation

naturally-occurring ozone formation and loss:

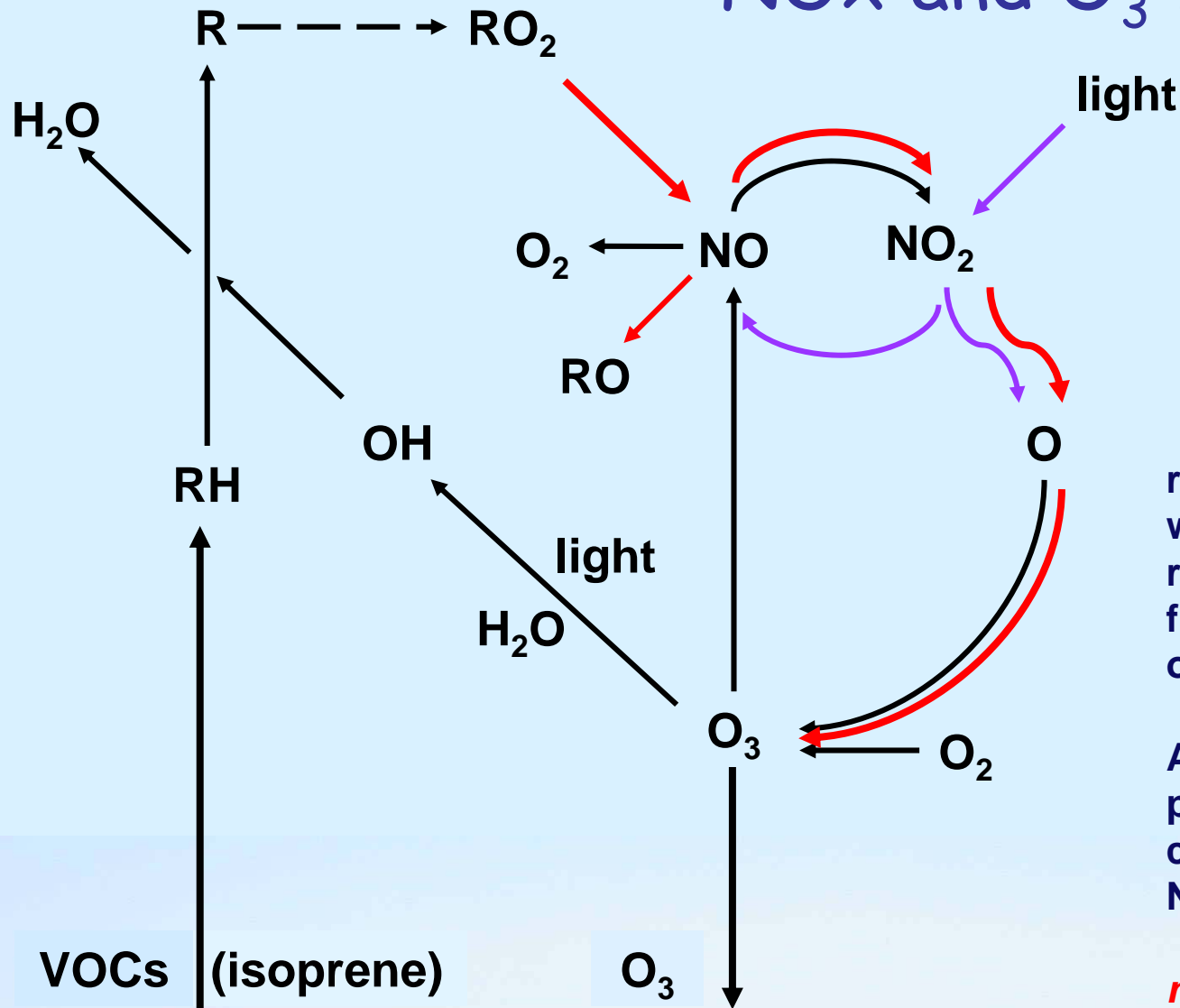
primary source of O(³P) is NO₂ photolysis

primary source of NO₂ is reaction of NO with O₃

a null cycle



NO_x and O₃ Formation



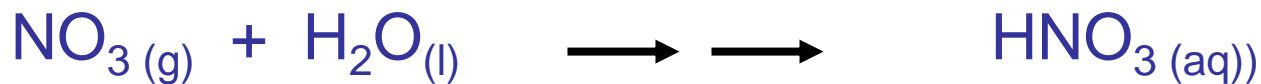
reaction of NO with peroxy radicals resulting from hydrocarbon oxidation:

An *additional* pathway for conversion of NO to NO₂

net ozone formation

Highly water soluble HNO_3 FORMATION

These transformations convert reactive N species into forms that affect terrestrial and aquatic ecosystems.



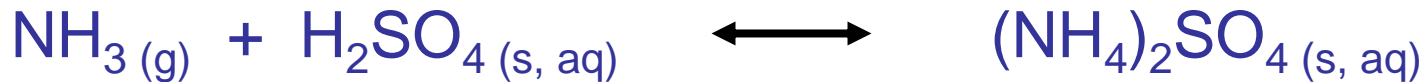
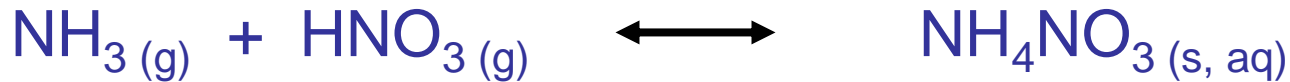
Caution: big-time violation of good speaker guidelines

FATE OF NH₃

Highly water soluble



Relatively
slow (~
72 days)



or NH₄HSO₄

or (NH₄)₃H(SO₄)₂

These transformations convert reactive N species into forms that affect human health and terrestrial and aquatic ecosystems.

Additional routes to nitrate aerosol formation:



NH_4NO_3 Formation: LA Example

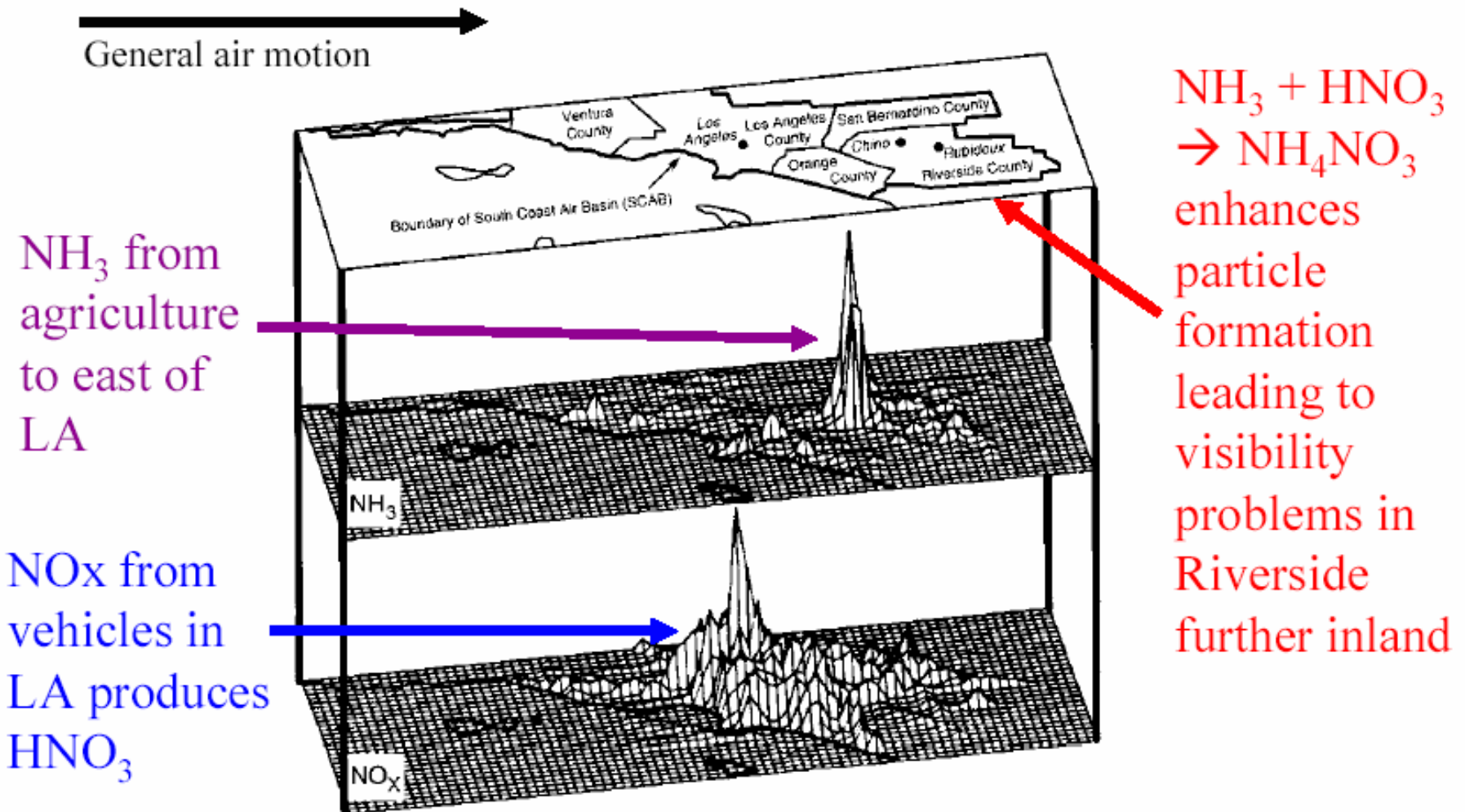


FIGURE 7.21 Estimated daily emissions of NH_3 and NO_x in the Los Angeles area in 1982 (adapted from Russell and Cass, 1986).

From Finlayson-Pitts and Pitts

FATE OF NO₃

These transformations convert reactive N species into forms that affect human health and terrestrial and aquatic ecosystems.



Daytime
fast



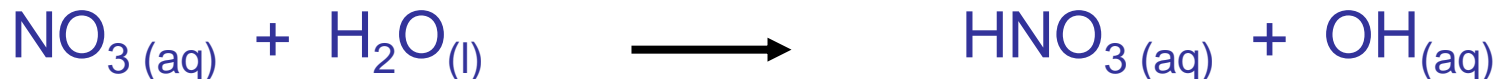
Daytime
fast



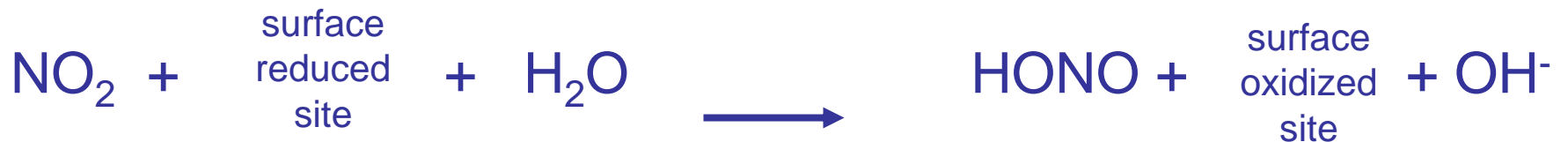
Nighttime
fast



Nighttime
fast



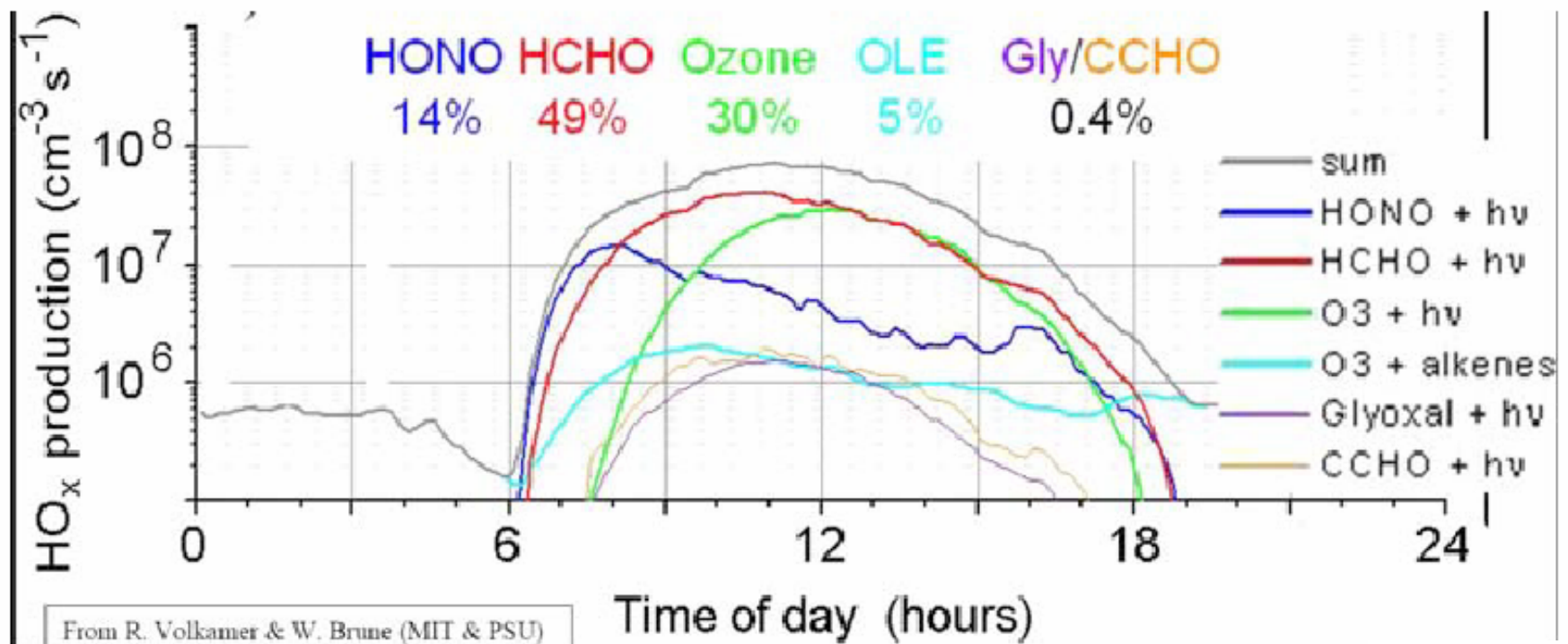
HONO Formation



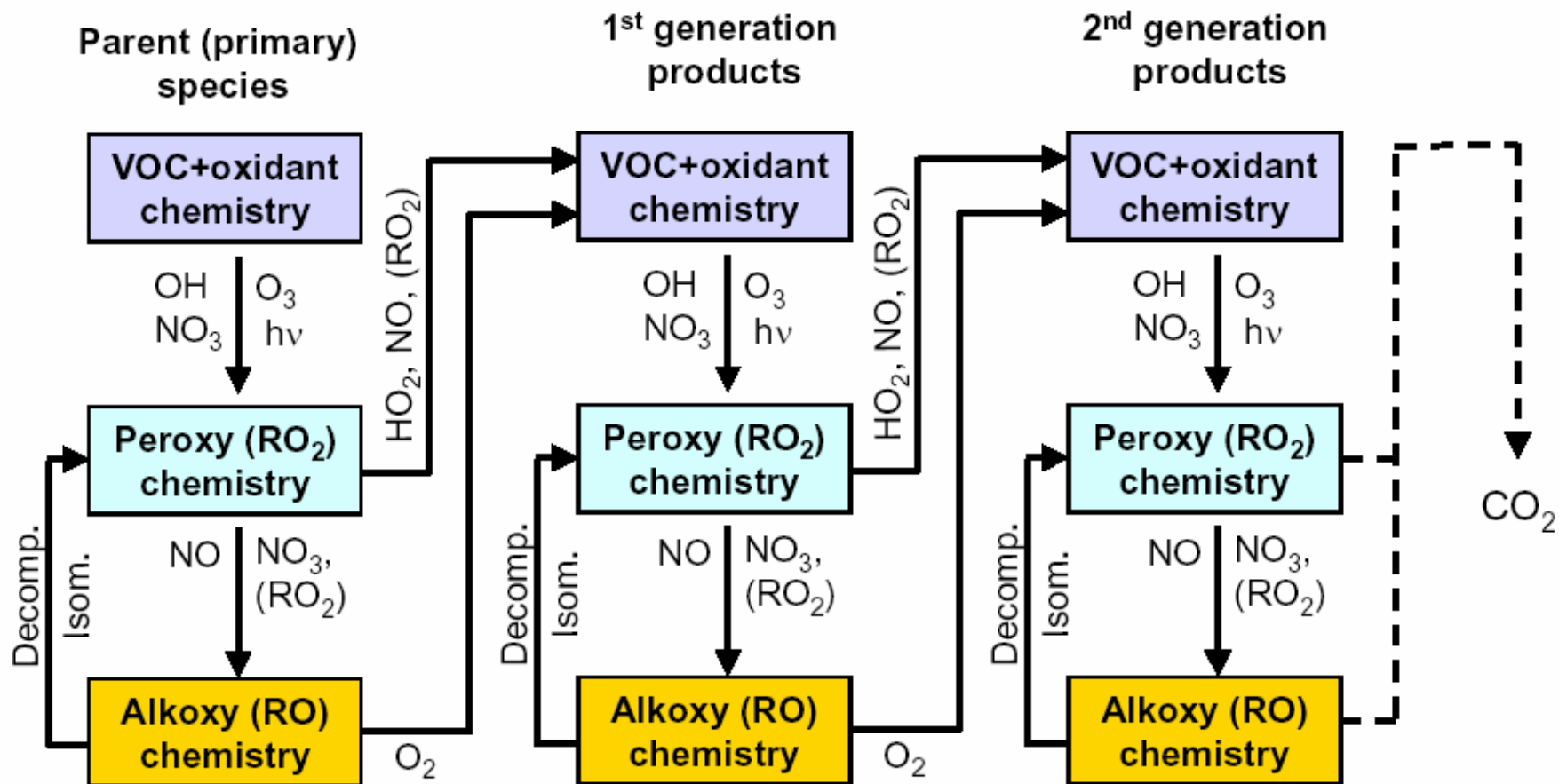
This transformation converts reactive N into a form that affects terrestrial and aquatic ecosystems.

HONO as Important OH Source

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

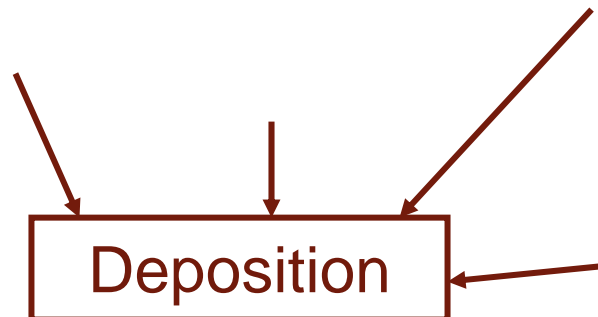


Big Picture of Organic Oxidation



Chemical Transformations of Nitrogen Oxides in the Troposphere

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.



**NITRIC
ACID**

In summary, this is what happens in photochemical smog formation

- 1) Nitrogen dioxide photolysis generates oxygen atoms, which combine with molecular oxygen to form ozone.
- 2) Ozone photolysis generates excited oxygen atoms, which react with water vapor to form hydroxyl radicals.
- 3) Hydroxyl radicals generate hydrocarbon radicals.
- 4) Hydrocarbon radicals form hydrocarbon peroxides.
- 5) Hydrocarbon peroxides form aldehydes.
- 6) Aldehydes form aldehyde peroxides.
- 7) Aldehyde peroxides form peroxyacyl nitrates.

A Brief Look at Stratospheric N Chemistry

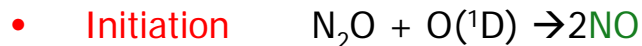
- Primary source: ~ 90% of stratospheric NO_x comes from tropospheric N₂O (nitrous oxide).
 - a greenhouse gas (GWP = 310, lifetime = 120 years)

N₂O is transported upward into the stratosphere mainly through the tropical tropopause by the lifting of the Brewer-Dobson Circulation.

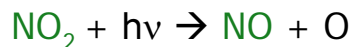
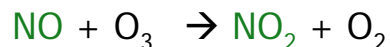
A typical distribution of N₂O in the stratosphere as seen by the Cryogenic Limb Array Etalon Spectrometer (CLAES) instrument aboard the Upper Atmospheric Research Satellite (UARS) in January 1993.

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.

Gas Phase NO_x-O₃ Photochemistry

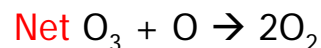
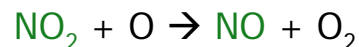
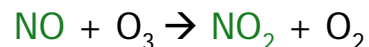
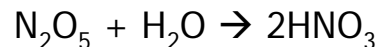
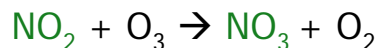


- **Propagation**

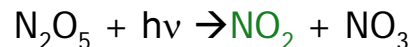
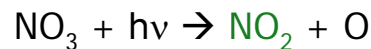
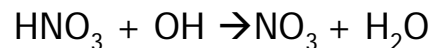
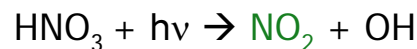


Null cycle

- **Termination**



Recycling



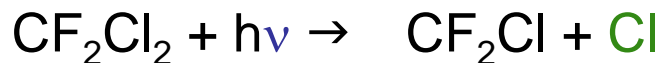
O₃ loss rate:

$$-\frac{d[\text{O}_3]}{dt} = 2[\text{NO}_2][\text{O}]$$

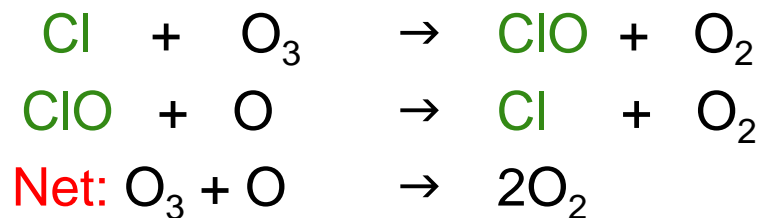
NO_x is a catalyst for O₃ loss

... And NO_x plays a key role as "terminator" for ClO

- Initiation:



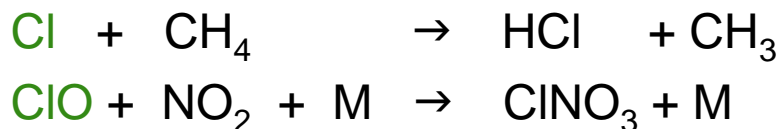
- Propagation:



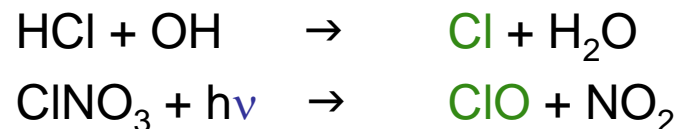
O₃ loss rate:

$$-\frac{d[\text{O}_3]}{dt} = 2[\text{ClO}][\text{O}]$$

- Termination:

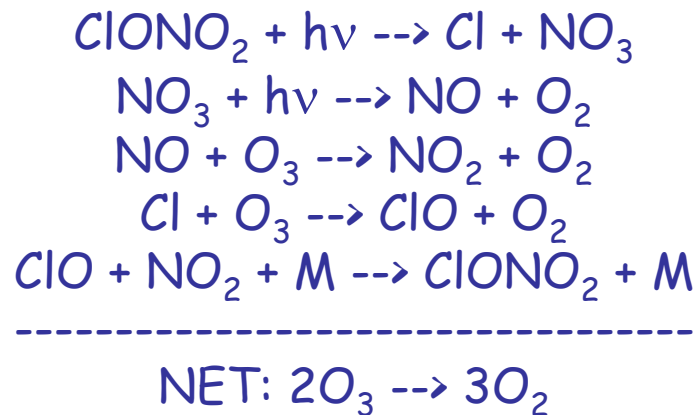


Recycling:



Cl_x is a catalyst for O₃ loss

In the lower stratosphere, several other catalytic cycles involving chlorine have important effects on the ozone balance. One of these catalytic cycles involves the photolysis of NO_3 and ClONO_2 :

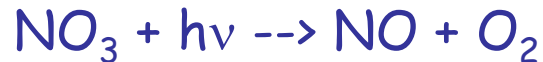


The net effect of this set of reactions involving both reactive and nonreactive forms of chlorine and nitrogen is to convert two molecules of ozone into three molecules of O_2 .

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.

NO_x also plays a role in the cycling of Bromine leading to loss of stratospheric O₃

Br_x - NO_x - O_x Reaction Cycle



Polar Stratospheric Clouds

Reactive nitrogen oxides also play an important role in the heterogeneous chemistry leading to severe O₃ loss over the Antarctic pole in spring.

Type I PSC:

Formation Temp:
Particle diameter:
Altitudes:
Settling rates:

Nitric acid trihydrate (HNO₃·3H₂O)
Ternary solution (H₂O, H₂SO₄, HNO₃)
195 K
1 μm
1024 km
1 km/30 days

Type II PSC:

Formation Temp:
Particle diameter:
Altitudes:
Settling rates:

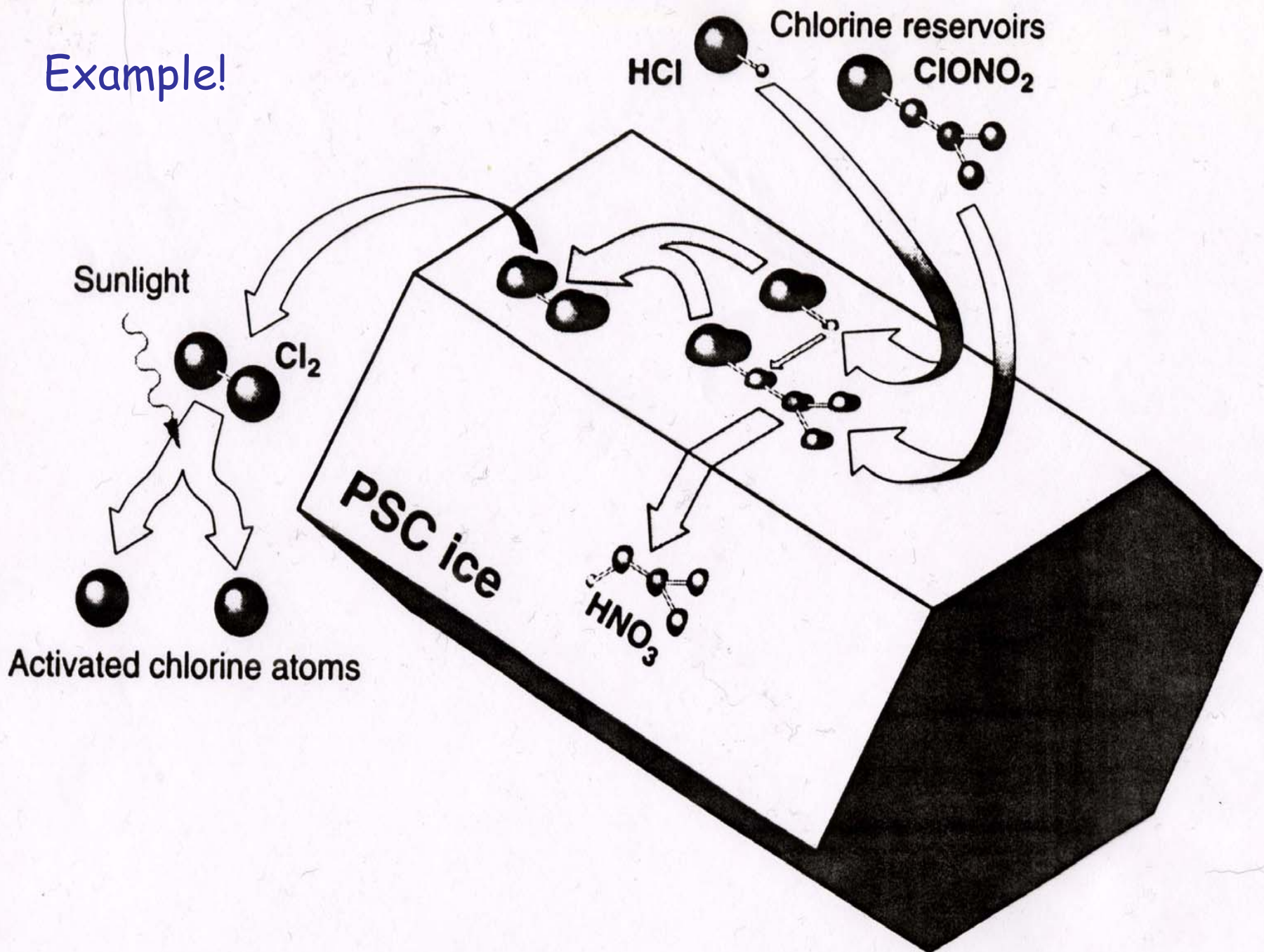
Water Ice
188 K
> 10 μm
1024 km
> 1.5 km/day

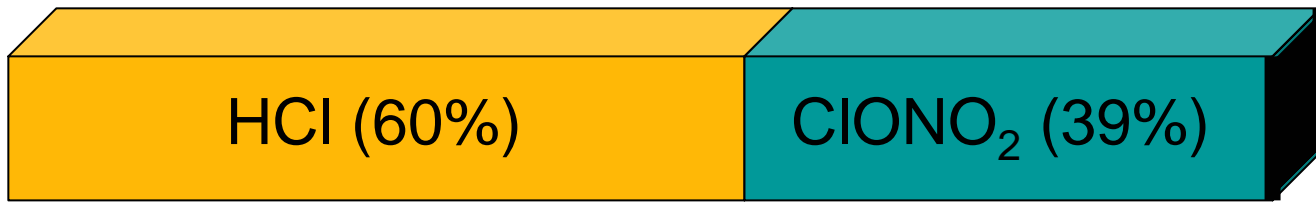
Type II PSC cloud



Heterogeneous reactions take place on PSCs, releasing chlorine from HCl and ClONO₂ into reactive forms (ClO) that can rapidly destroy ozone.

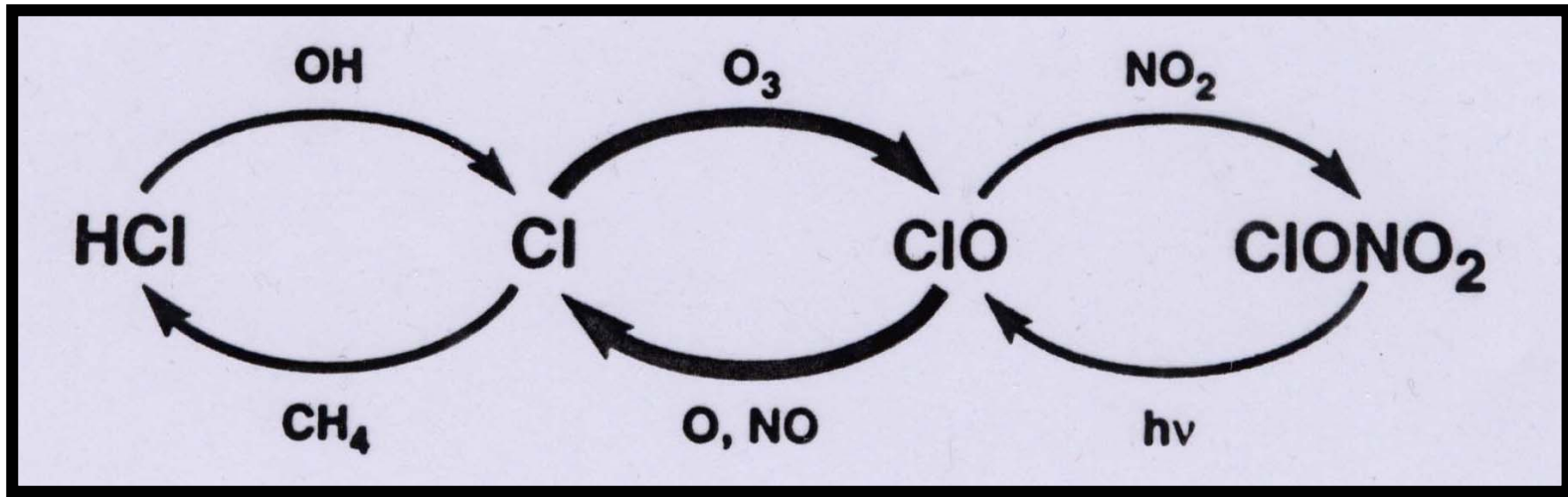
Example!



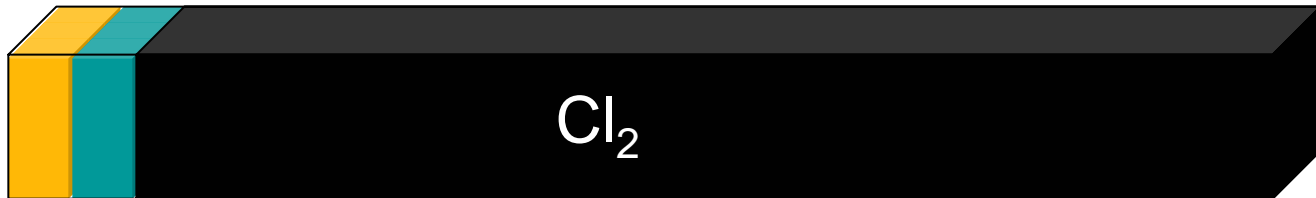


Without PSCs

"active" / "reactive chlorine (Cl, ClO) ~1%



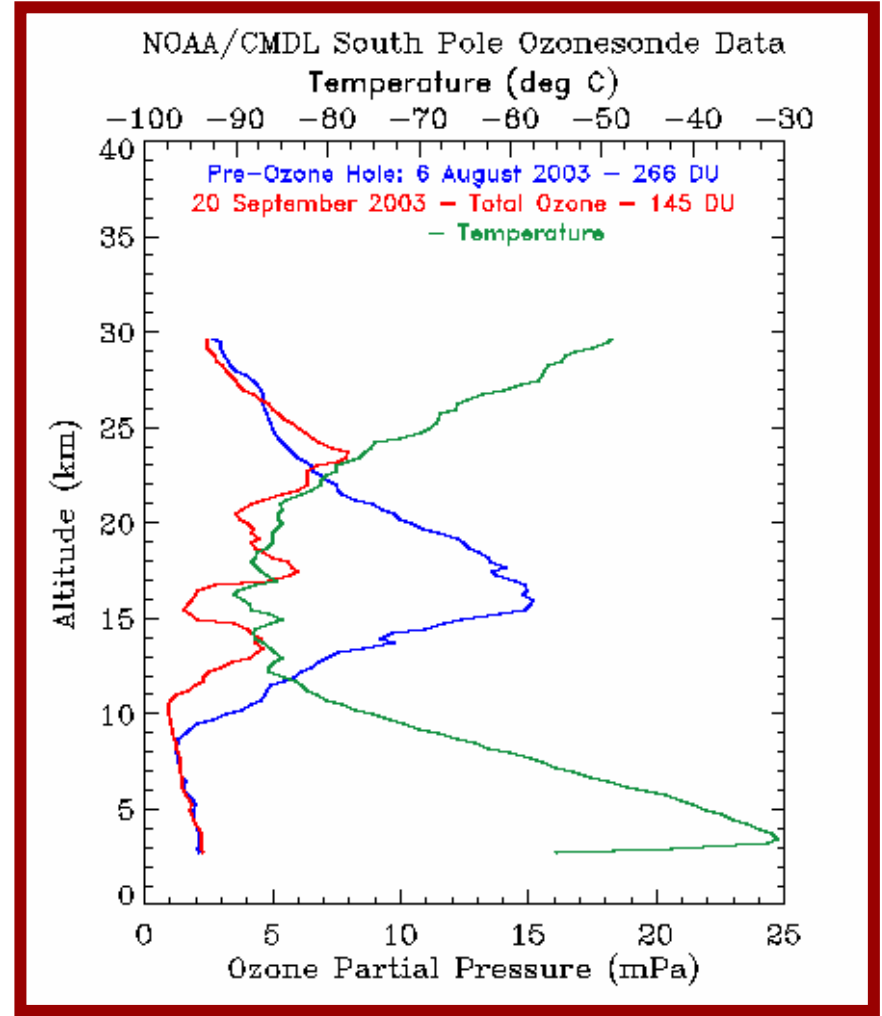
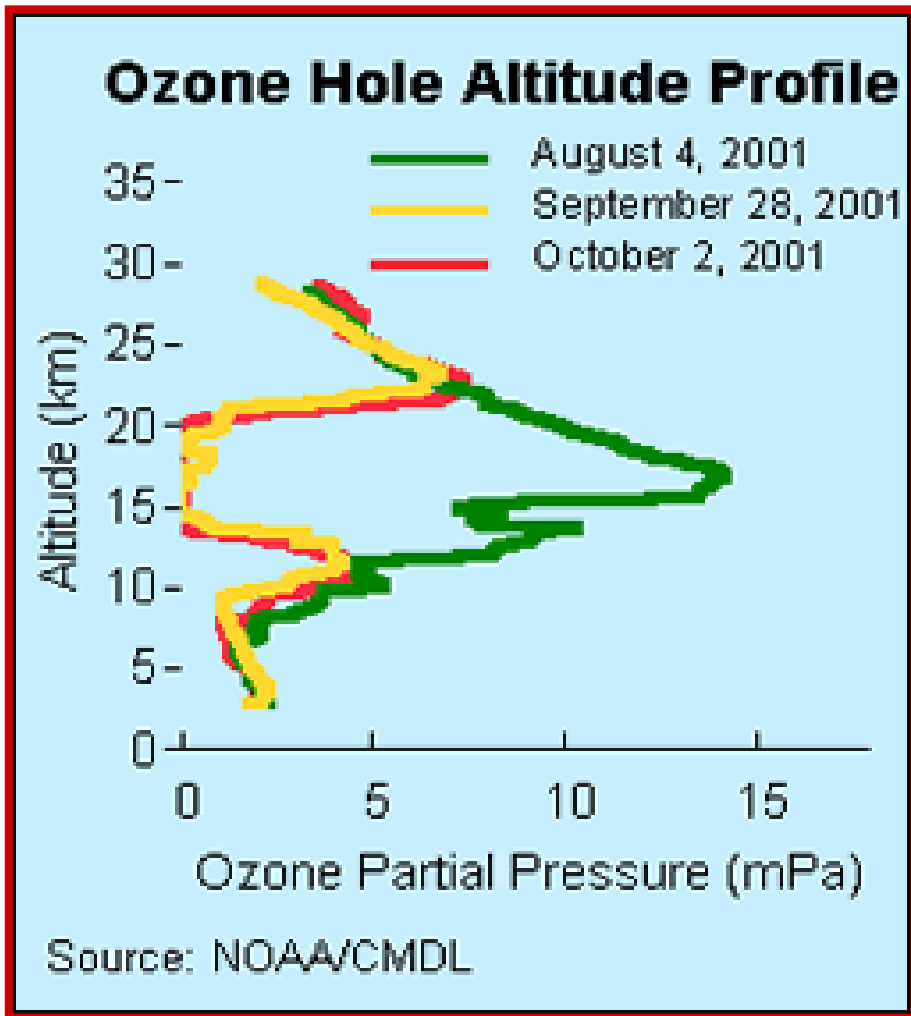
Potentially "active" chlorine increased by a factor of 100



With PSCs

September 28, 2001

September 20, 2003



Skin Cancers

- **More than 90% of non-melanoma skin cancers are related to UV-B exposure**
- **1% ozone decrease produces a ~2% increase in UV-B**
- **2% increase in UV-B**
 - > 2-5% increase in basal-cell cancer cases**
 - > 4-10% increase in squamous cell cancer cases**
- **In 1990, there were ~500,000 cases of basal cell cancer and ~100,000 cases of squamous cell cancer in the US.**
- **A 1% depletion of ozone --> ~ 20,000 new cases per year**

The same increase would be expected if the U.S. population moved ~12 miles closer to equator (on average)

Factors affecting N species chemical transformations, hydroxyl levels, and air quality:

Temperature, UV, [H₂O], composition of upstream air, whether you are in a NO_x-limited or VOC-limited regime with respect to O₃ production.

Different meteorological flow regimes bring different mixes of temperature, relative humidity, biogenic / anthropogenic VOCs, NO_x, SO₂, NH₃: Ozone levels and primary driver(s) for ozone formation may differ significantly!

- In some cases, different AQ management strategies are needed to address different flow regimes / different seasons.

Findings from the Texas 2000 Air Quality Study: Chemical Processes that Control Urban Ozone Production *T.B. Ryerson et al.*

During summer, the Houston urban area routinely experiences highly elevated levels of ozone exceeding the EPA air quality limits for ozone of 120 ppbv. Airborne measurements obtained in the Houston-Galveston metropolitan area during the 2000 TEXAQS field campaign identify the chemical mechanisms leading to these major ozone exceedences. Petrochemical industrial sources located along the ship channel emit large amounts of highly reactive hydrocarbons and NO_x to the atmosphere; in the summertime, such co-located emissions are shown to consistently result in rapid and efficient ozone formation downwind. Routine emissions of the alkenes, propene (C₃H₆) and ethene (C₂H₄), by the petrochemical industrial sources result in the high initial hydrocarbon reactivity and, consequently, high ozone formation rates and yields per NO_x molecule emitted from petrochemical industrial sources when compared to rates and yields observed in urban or rural power plant plumes. This information will aid state regulators in formulating new control strategies for bringing Houston into compliance with EPA air quality standards.

The mitigation plan proposed by the state of Texas to tackle the pollution by reducing nitrogen oxide (NO_x) emissions up to 90% percent by 2007 would not have addressed this problem.

Factors that would most likely be most relevant in an Alberta context:

- Contribution from biogenic VOCs
- Contribution from NO_x and anthropogenic VOCs from Oil Sands
- Increasing NH₃ emissions (along with decreasing SO₂ emissions): increasing NH₄NO₃ aerosol formation expected and concomitant health effects from increasing PM 2.5
- Warmer temperatures.... Will conditions be drier? (This will affect VOC emissions and OH levels, and nitrate aerosol formation.)

Regarding the importance of fully accounting for biogenic VOC emissions:

Noting President Ronald Reagan's notorious 1980 reference to trees causing pollution (Reagan said: "Approximately 80 percent of our air pollution stems from hydrocarbons released by vegetation."), the authors conclude: "The results reported here call for *a wider recognition that an understanding of recent, current and anticipated changes in biogenic VOC emissions is necessary to guide future air-quality policy decisions*; they do not provide any evidence that responsibility for air pollution can or should be shifted from humans to trees."

Emission of smog ingredients from trees is increasing rapidly: □ Changes in forestry and agriculture affecting ozone pollution - Purves et al.

Good advice! Land use change, plantation farming, changing temperatures (species migration), natural succession, ecosystem response to environmental stresses...

Influence of Biogenic Emissions Uncertainties on Ozone Predictions in the Oil Sands Region

Dave Fox, Karen McDonald, and Ron Goodson

CONCLUSIONS The influence of biogenic emission uncertainties on predicted ozone concentrations is significant in the Athabasca Oil Sands region. Depending on the selection of biogenic emission factors, the model results range from ozone being a relatively small issue (Run 1 -lowest isoprene emissions) to being a major problem (Run 4 -highest isoprene emissions). Model results for each of the biogenic emission scenarios indicate that ozone formation will increase with the additional NO_x emissions from proposed developments. Ozone concentrations are predicted to exceed the hourly 82 ppb guideline for all biogenic emission scenarios. The predicted SUM60 index indicates that there is potential for vegetation damage from long-term ozone exposure northeast of the oil sands developments. Terrestrial effects monitoring should be focused in this area.

Some things to consider:

- lessons learned regarding importance of developing a quantitative understanding of heterogeneous chemistry...
 - pre mid-1980's, stratospheric chemistry models contained only gas phase reactions... we did not predict the ozone hole!
 - we have have a great deal to learn about heterogeneous chemistry in the troposphere.....

“Hydrolysis of N_2O_5 to HNO_3 in aqueous aerosols and heterogeneous conversion of NO_2 to HONO in the surface layer should be included in models.”

-Heterogeneous Chemistry and Tropospheric Ozone, D. Jacob, 1999

Continued:

- In the past (and present?) tropospheric chemistry and deposition/ecosystem impacts models treated (treat) deposited HNO_3 as a permanent sink from the atmosphere.
- In the last decade we've learned that photolysis of deposited NO_3^- in ice, snow, and dew leads to the re-emission of NO and HONO (an important source of OH).
- We know very little about the role of surfaces (including canopies) in the remobilization of deposited N

Multiple environmental stresses affect ecosystem processes which affect atmospheric composition and chemistry

“Natural, managed, and socio-economic systems face multiple environmental influences that can potentially interact and cause additional, unexpected stresses. The dynamics of interactions across multiple environmental stresses are currently poorly understood. Understanding the impacts of a suite of environmental stresses is required to develop a robust predictive capability and response strategies for ecosystems, agricultural lands, and human settlements to current and future changes.

In addition to gaps in the scientific understanding of multiple environmental stresses, there is a lack of understanding of how to devise wise management and policy decisions to address suites of problems, in particular, institutional and management options that make sense in the face of uncertainty. Options to enhance resiliency and reduce vulnerability to multiple environmental stresses, effective communication between researchers and stakeholders, and tools to evaluate potential management responses are also critically needed.”

The message?

NOT that it's too complicated to do anything about it!

Instead, that what's needed - in parallel with current efforts - is the development of integrated, process-focused modeling capabilities and infrastructure for complex, multi-variable studies.

And, the involvement of stakeholders and the training of young scientists to work at the interface of the related disciplines.

I applaud the recommendations made by Julian Aherne.

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.

my pet-therapists

