

Week 10

Urban Pollution

Important concepts

- Sources and Sinks, Atmospheric variability
- Dry and Wet Deposition
- The Boundary Layer (stability, inversions)
- Transport in the Troposphere
- Oxidation
- Ozone Production and Nox
- Carbon monoxide and formaldehyde

Health and welfare effects of air pollution (p 403-407)

- Pollution episodes, Cause and effect relationships
- Human body
- Health effects of regulated pollutants
- Personal air pollution (smoking)
- Risk assessment and management
- Effects on agricultural crops, ornamental plants, and trees
- Effects on domesticated animals, Ecological effects
- Effects on materials
- Odor pollution

What are air pollution “episodes?”

Characterized by significant short-term increases in atmospheric pollutant concentrations above normal daily levels

Vary in intensity from mild (limited public health concern) to severe (widespread illness and mortality)

1952 – London, 4000 excess deaths attributed to pollution.

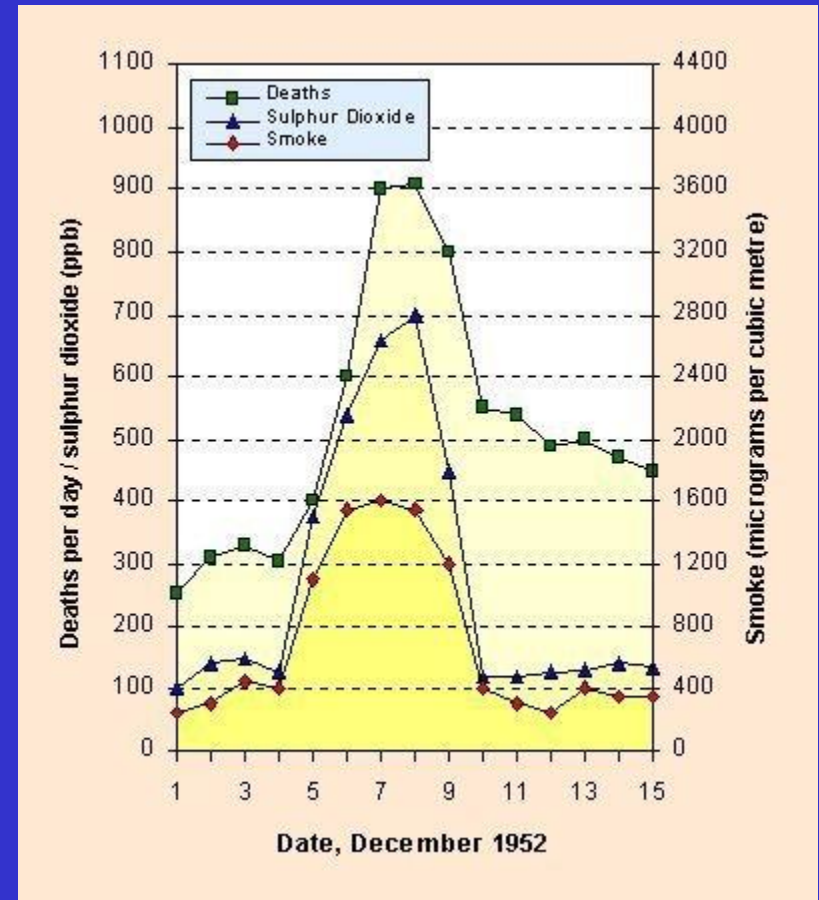
Many other examples that are less dramatic, but that provide solid evidence that elevated pollutant levels can cause illness and death

A problem for both developed and developing countries

London, December 1952 (see pages 414-416)



Primarily due to sulfur, tars (heavy hydrocarbons), and hydrocarbons from bituminous coal



Epidemiological Studies (p 141-149)

Statistical relationship between disease in a population and potential causal factors

Such studies become more important as the risk due to atmospheric pollutants becomes smaller and the duration of exposure required to produce effects becomes longer

Types

- Cross sectional (assess effects across a cross-section of population)
- Longitudinal (assess effects over a period of time)
- Case control (compare exposed group to an unexposed, control, group)

London, December 1952 (see pages 414-416)

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Primary
hydrocarbons
from bituminous coal

Date, December 1952

Smog was the term first used in 1905 to describe these smoke + fog events that were known to have a sulfurous smell and to cause acute respiratory illness.

Occur in areas with large primary pollutant emissions, typically from dirty burning (e.g., coal, wood, dung, etc.). Exacerbated by strong inversions, so typically worse in the cold season.

Although chemistry is involved (e.g., $\text{SO}_2 + \text{OH} \rightarrow \text{H}_2\text{SO}_4$), these are not typically photochemical events – more like acid rain, in that acids that are produced typically condense very quickly onto preexisting particles and these grow into larger ‘droplets’ that are highly acidic.



Painting of London by Claude Monet, ca 1899-1901

Kathmandu, Nepal, 2008

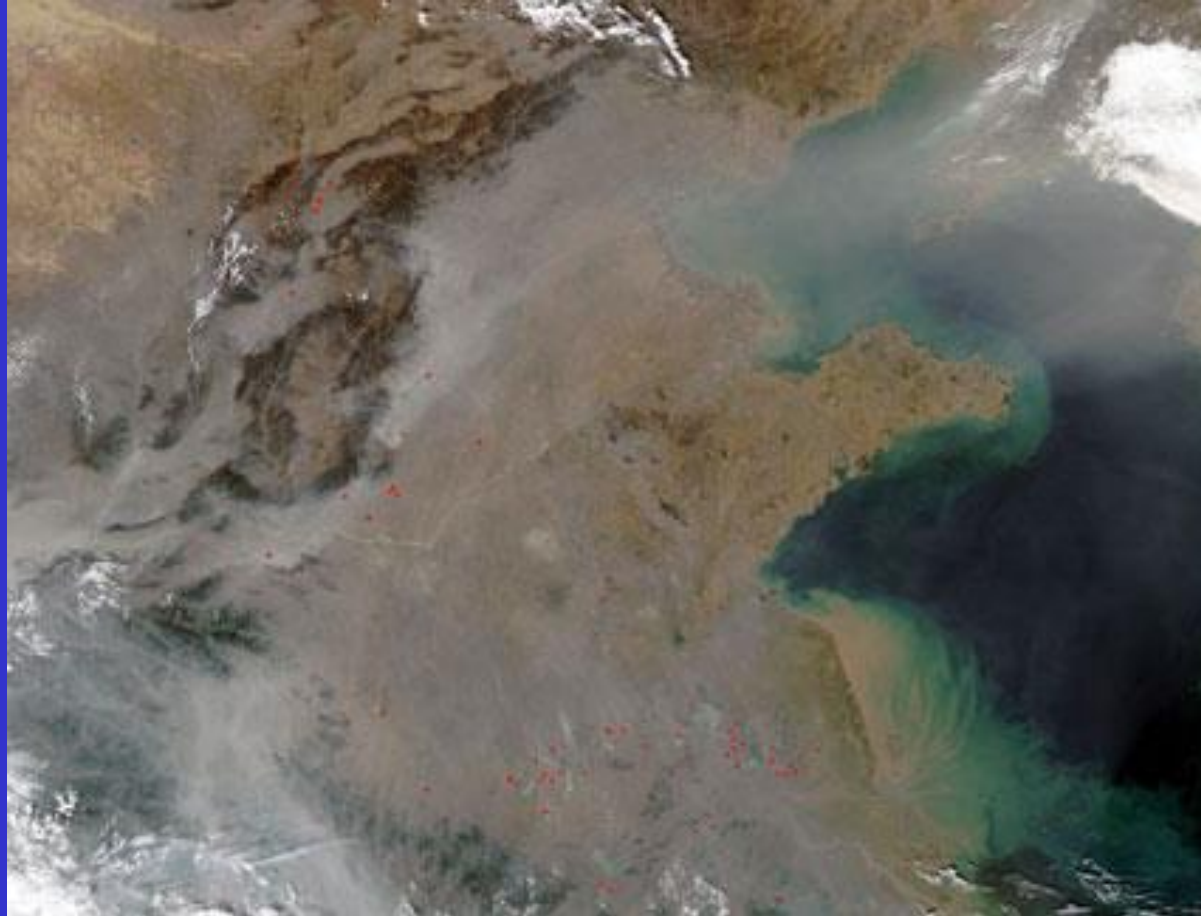
Mainly dust and aerosols due to vehicle traffic, HC incomplete combustion, and biomass burning



Pollution (sulfur from coal burning) over the Great Wall of China



This pollution from China can be readily seen from space!



Epidemiological Studies

Types

- Prospective (data to be collected)
- Retrospective (evaluation of existing data)

Confounding factors

- Multiple irritants make it difficult to isolate a single cause
- Coincidence of pollution episodes with particular meteorological conditions (e.g. temperature, humidity)
- Covariance of pollution with other exposures (eg. occupational, smoking)
- Relationships between pollution and infectious disease

Interaction Effects

Interactions between pollutants

Example – presence of particles facilitates the respiratory uptake of SO₂, which dissolves in water

Effects can be additive (irritations that are similar might simply add up), antagonistic (offsetting, such as the case for ammonium and sulfate), or synergistic (new response is significantly greater than the sum of individual effects, such as with radon with smoking)

Interaction Effects

Interactions between pollutants and meteorological factors

- Pollution episodes can be associated with meteorological extremes, such as cold, damp weather (London “fogs”), or heat waves

Interactions between different ‘types’ of pollution

- Smokers can be more susceptible to environmental pollution because their health is already compromised (e.g. heart disease)
- Occupational – people with different jobs may have different exercise/work habits. Americans typically spend ~2 hours per day outdoors. Someone with a job that requires them to be outdoors more frequently may experience higher levels of pollutants.

Assessing exposure

- Personal exposure meters (often tricky to make small, but can be quite effective at isolation of pollutants)
- Exposure models
- Personal diaries

Susceptibility

Different people are affected differently. Some are more sensitive to pollution than others:

- Elderly
- Children
- Smokers
- Those with preexisting health conditions
- Those with occupational exposure

Epidemiological studies are effective when:

- (1) Similar effects are observed in different populations
- (2) Incidence or severity of effects increases in severity with increased exposure
- (3) There is a plausible biological mechanism for the effect

Toxicity

Studies include:

- Carcinogenesis (cancer induction)
- Teratogenesis (induction of birth defects)
- Mutagenesis (production of mutations)
- Gametotoxicity (damage to sex cells)
- Endocrine disruption (hormone interference)

Usually performed on animals to minimize confounding factors

Human studies

- More definitive than those on animals
- Typically limited to acute (short term) exposure
- May not necessarily be realistic, so need to be interpreted with some caveats

ETHICS!!

Human Health Effects

Eye Irritation

Exposure to aldehydes and photochemical oxidants

Although ozone and NO_2 don't irritate eyes, other species covary with ozone, so its abundance is used as a gauge for other species. Eye irritation typically a problem when oxidant (i.e. ozone) levels exceed ~100-150 parts per billion

Cardiovascular disease

Appears to be due to exposure to small particles (PM 2.5), carbon monoxide (CO) and lead (Pb)

Respiratory Effects

Airway passageways and lungs are very susceptible to air pollution for obvious reasons

Large ($> 10 \mu\text{m}$) particles are removed in the upper airway (nasopharyngeal region) by hair and mucus. The large particles can't bend the corners of the air tract, so they impact the walls, where they are trapped and removed by cilia.

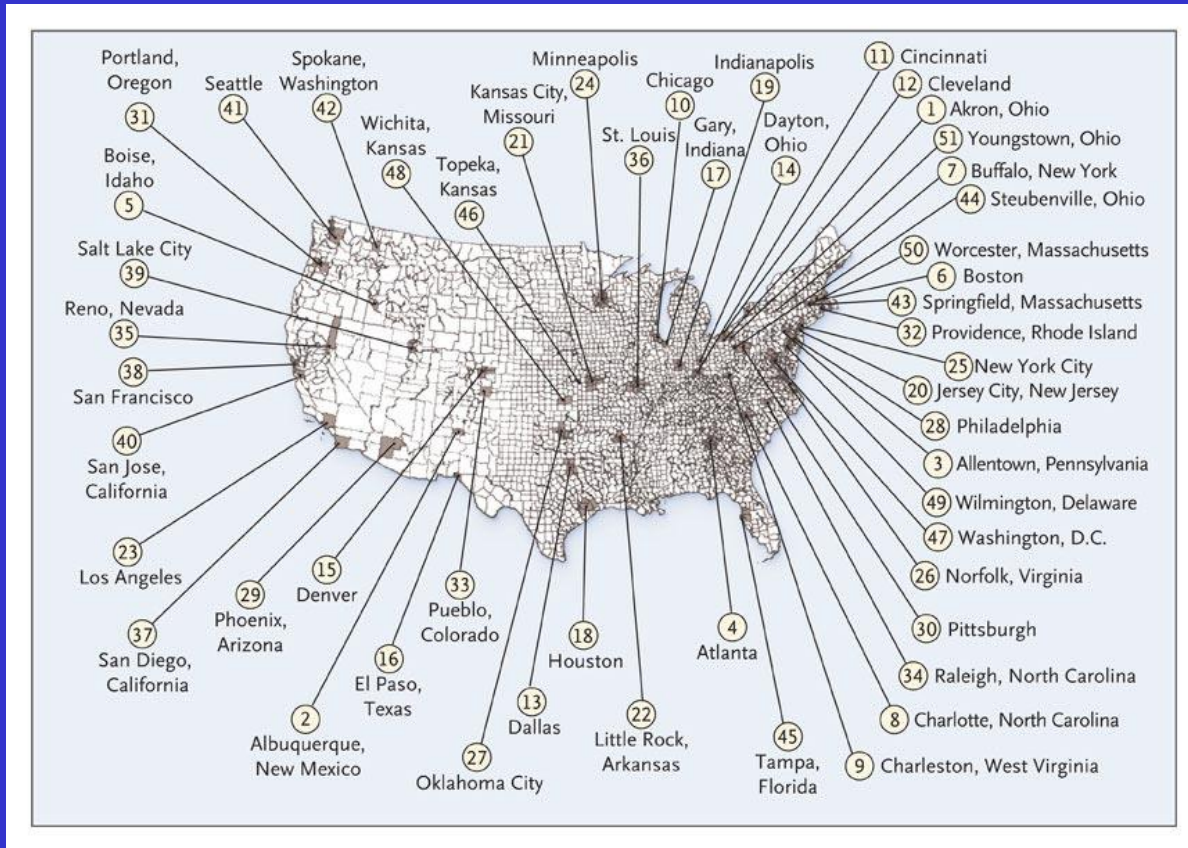
Gases (O_2 and CO_2) are exchanged in the lung tissue after traveling down the tracheobronchial region. There may be as many as 23-32 generations of branching as air travels from the trachea to the lung tissue. Cells are lined with mucus and cilia.

Gas exchange occurs in the alveoli – 300 million air sacs.

Fine-Particulate Air Pollution and Life Expectancy in the United States

C. Arden Pope, III, Ph.D., Majid Ezzati, Ph.D., and Douglas W. Dockery, Sc.D.

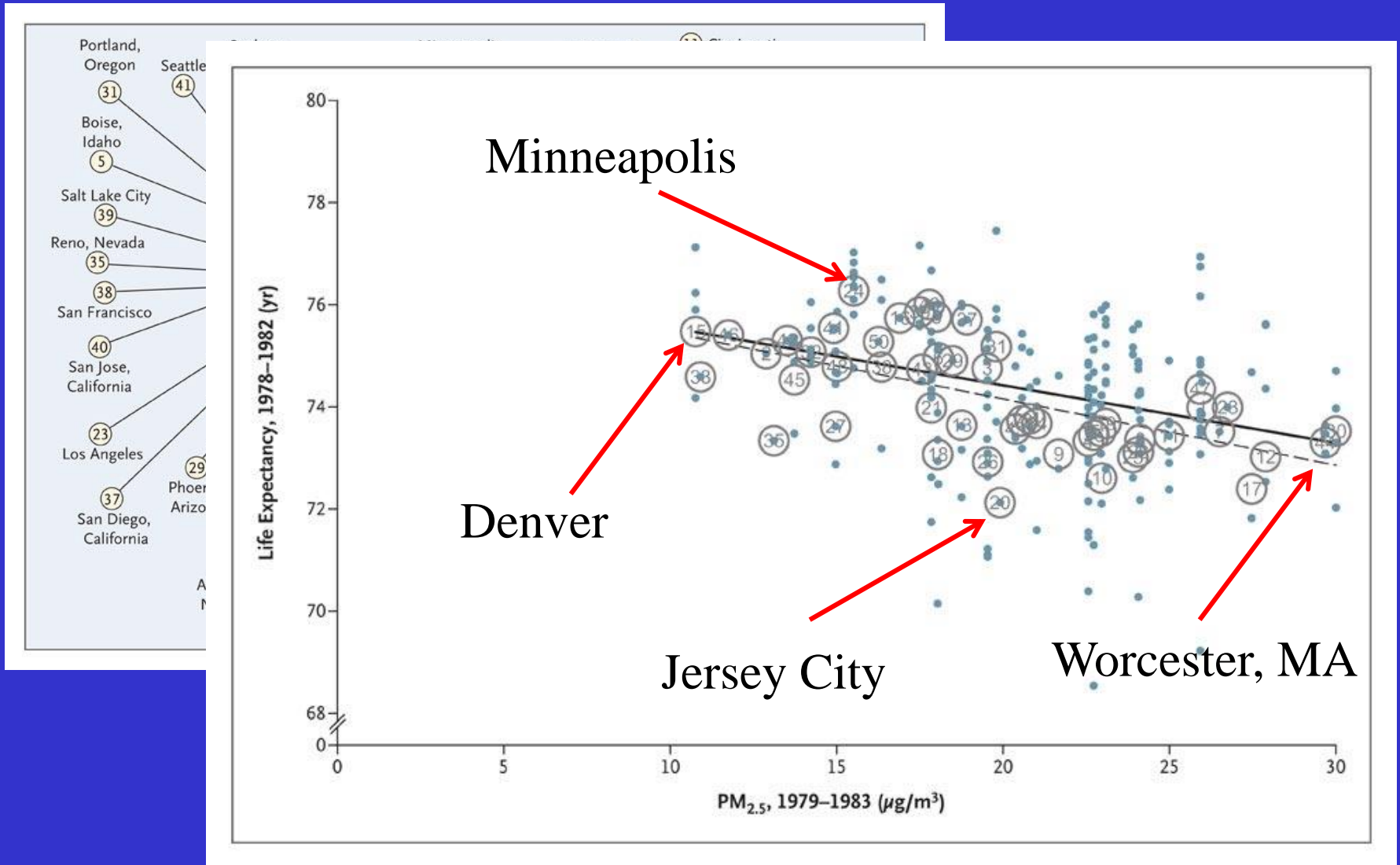
New England Journal of Medicine, Volume 360, p 376-386, Jan. 22, 2009



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Exposure to fine-particulate air pollution has been associated with increased morbidity and mortality, suggesting that sustained reductions in pollution exposure should result in improved life expectancy. This study directly evaluated the changes in life expectancy associated with differential changes in fine particulate air pollution that occurred in the United States during the 1980s and 1990s.

Methods We compiled data on life expectancy, socioeconomic status, and demographic characteristics for 211 county units in the 51 U.S. metropolitan areas with matching data on fine-particulate air pollution for the late 1970s and early 1980s and the late 1990s and early 2000s. Regression models were used to estimate the association between reductions in pollution and changes in life expectancy, with adjustment for changes in socioeconomic and demographic variables and in proxy indicators for the prevalence of cigarette smoking.

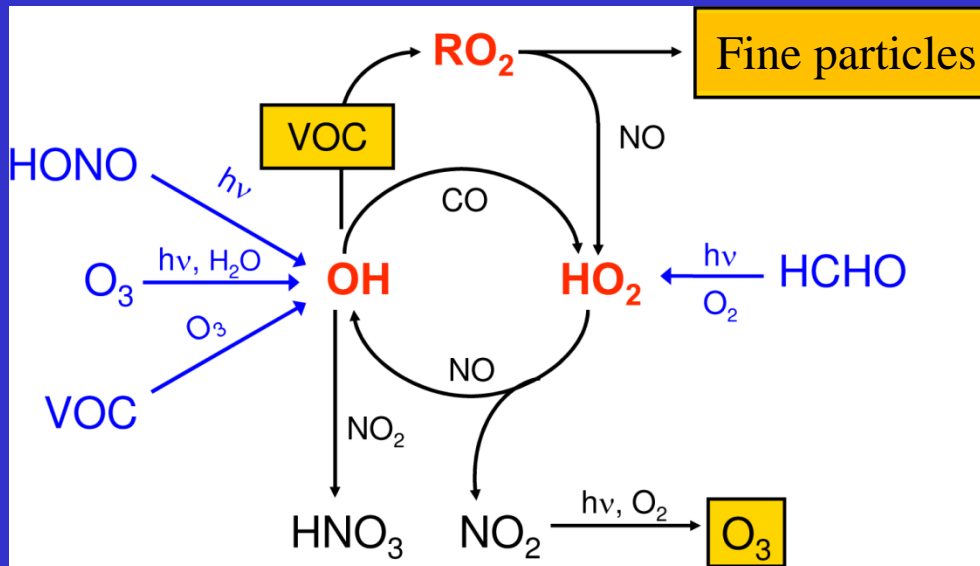
Results A decrease of 10 μg per cubic meter in the concentration of fine particulate matter was associated with an estimated increase in mean ($\pm\text{SE}$) life expectancy of 0.61 ± 0.20 year ($P=0.004$). The estimated effect of reduced exposure to pollution on life expectancy was not highly sensitive to adjustment for changes in socioeconomic, demographic, or proxy variables for the prevalence of smoking or to the restriction of observations to relatively large counties. Reductions in air pollution accounted for as much as 15% of the overall increase in life expectancy in the study areas.

Conclusions A reduction in exposure to ambient fine-particulate air pollution contributed to significant and measurable improvements in life expectancy in the United States.

Note – study does not go lower than $\sim 10 \mu\text{g m}^{-3}$

Loss of about 0.6 year of life expectancy for an increase in average exposure of $10 \mu\text{g m}^{-3}$ for PM_{2.5} (particles smaller than $2.5 \mu\text{m}$)

Week 10 - Introduction to Tropospheric Photochemistry



Reading

Chapter 8 – the following pages are critical!

- 99-100 – Introduction, Boundary layers (review stability and the adiabatic lapse rate!)
- 101-104 – VOC oxidation, chain initiation by OH, photolysis of NO_2 in the visible, and oxidation steps forming ozone
- 104-105 – Importance of NO_x

Additional material to read:

- 105-110 – oxidation of more complex hydrocarbons
- 110-115 – the roles of NO_3 and O_3

What is the fate of an organic compound in an oxidizing atmosphere?

Let's consider methane, CH₄

Naively, we would expect slow “combustion” of methane in an atmosphere loaded with oxygen.



The problem is that oxygen doesn't really react with methane in a single step – combustion is a process that involves multiple ‘intermediate’ reactions that eventually will oxidize methane to CO₂ and water, but there are some interesting products that pop up along the way, and these can have important implications – for health, visibility, and the chemical state of the atmosphere.

So what does the 'oxidation' of methane look like, and what are the important intermediates? First, we note that methane is a fairly stable molecule, so it doesn't react with just any old molecules. In fact, it reacts only with radicals (atoms or molecules with an unpaired electron). The hydroxyl (OH) is the most important species that initiates the oxidation of methane (and most other organic compounds in the atmosphere);



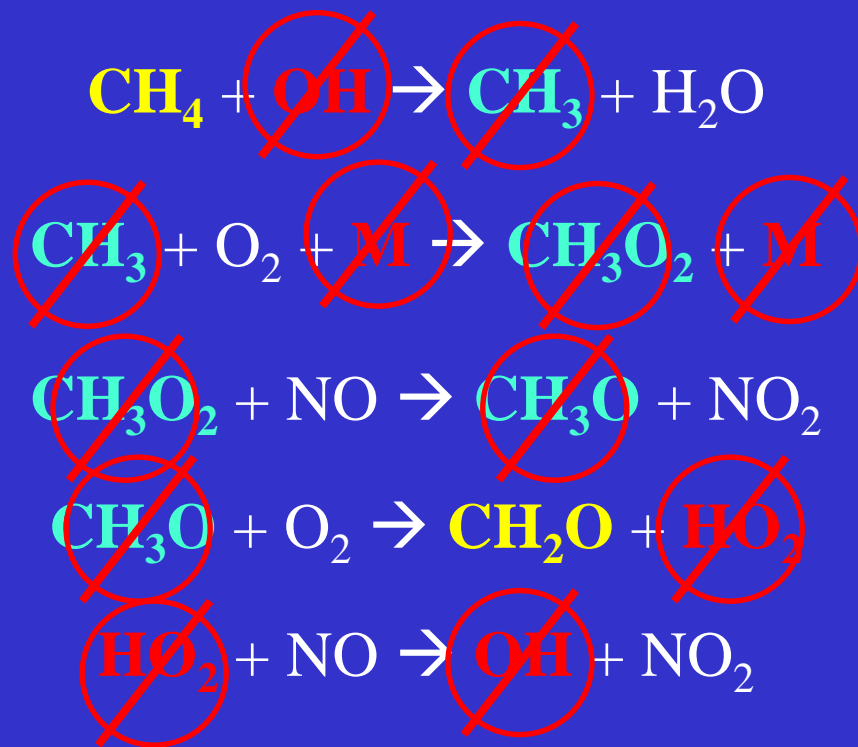
Let's take a closer look – note that some reactions produce species that are consumed in the next step – we call these ‘intermediates’. The aqua color below tracks the evolution of the hydrocarbon intermediates as they are progressively oxidized. Note, even after four steps, we are still a few steps away from carbon dioxide!



Red colors below identify species that are critical to the reaction scheme, but are themselves not consumed. We call these species “catalysts,” since they are important for the overall reaction cycle to continue, but are themselves not consumed, so they are present for the next round of reactions. Notice our ‘friend’ M. This is simply “air” (mainly N₂ and O₂). We will see that M is a bit different than the other catalysts OH and HO₂ because it doesn’t ever change forms.

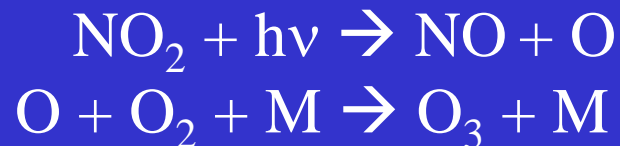


To determine the over 'net' result of these five reactions, we can cancel out species that appear on both sides of the overall reaction.





This net reaction is a bit more interesting than the simple formation of CO_2 and H_2O . It leaves behind a new hydrocarbon, formaldehyde, which is more toxic than methane and one that survives long enough in the atmosphere to be of concern for air quality. However, perhaps even worse, it converts two molecules of nitric oxide (NO) into nitrogen dioxide (NO_2). Nitrogen dioxide itself is highly toxic (although so is NO !), but what NO_2 does next is highly problematic:



The photolysis of NO_2 (a process that can only take place in sunlight) thus rereleases NO so that it can participate in another series of reactions with other hydrocarbons (and essentially converts it into a catalyst for additional oxidation reactions).



We now have the makings of photochemical smog! Nature has taken a single – mainly harmless – molecule of methane and turned it into formaldehyde, a toxic molecule, and two ozone molecules. Ozone is very harmful for living things (as a molecule, it is toxic, but it's also important for absorbing ultraviolet light, so we like ozone to stay put in the stratosphere where it is too far from the surface to be harmful, but provides a shield to protect us from harmful UV radiation).

Urban Pollution Control Strategies

Reading – pages 213-219

Important concepts (with reading from text, where available)

Aerosols/Particulate matter – p 5-6

- Hydrocarbons and VOCs – p 87-90
- Health effects of air pollution – p206-209
- Primary and secondary pollutants – p 209-210
- Federal Monitoring Requirements
- Air Quality Monitoring Networks
- Air Quality Index – p 217
- Regulation and Public Policy
- Regulatory Strategies and Tactics
- Federal Legislative History
- Air Pollution Control 1970-1990

In the case of ozone depletion in the stratosphere, the world decided to simply ban all production and sales of chlorofluorocarbons and any other compounds with similar properties that would live long enough in the troposphere to reach the stratosphere, releasing atoms that could initiate catalytic cycles that destroy ozone.

As noted in class last time, this was a rare example of the world's sovereign nations coming together to avoid a threat before any evidence existed to prove that the threat was real. As it turned out, the ozone hole was a warning – in fact, these chemicals could deplete ozone, and it was a good thing countries agreed to ban CFCs and other ODS (ozone depleting substances).

Remember my 2012 lecture at the U.S. Department of State for more on this issue.

In the case of smog formation in the troposphere, the problem is far more complex, and every city/region has its own unique mix of chemicals (from various sources of emissions) and meteorology (winds and transport) that makes regulating the problem very difficult. A different set of regulations is probably needed for each unique environment. Therefore, a framework was established in the 1980s and 1990s to address these differences, and rather than simply “ban” emissions of compounds such as volatile organic compounds (VOCs), nitrogen oxides (NO_x), carbon monoxide (CO), and particulate matter (PM), a partnership-like approach was adopted, where scientists worked together with local industries and civic leaders to establish a rational set of rules to reduce the most important pollutants, called “criteria pollutants.” Specialized, but highly constrained models are used to assess the impacts of all the individual pollutants, and rules address those that have the greatest impact on reducing smog.

Urban Pollution Control Strategies

What we know so far:

- Different regions have different issues, but two types of ‘smog’ stand out
 - London-type (cold, damp, smoke, fog, sulfur)
 - Los Angeles-type (photochemical) (sunny, warm, NO_x, HCs, ozone, CO)
- Pollution is made worse by meteorological conditions called “inversions”
- In all cases, it’s important to *reduce emissions*, but in the case of the photochemical pollution, there are primary and secondary pollutants to be concerned with – e.g. ozone. One doesn’t ‘reduce emissions’ of these secondary pollutants. Rather, one identifies the mechanism of formation and goes after the primary pollutants that are responsible for the formation of the secondary pollutants.

Urban Pollution Control Strategies

What we know so far:

- Generic scheme for photochemical smog:



Urban Pollution Control Strategies

What we know so far:

Primary pollutants: NO, hydrocarbons (RH), CO

Secondary pollutants: NO₂, R'CHO (HCs), O₃

HC = hydrocarbon

VOC = volatile organic compound

We typically call species that appear on both sides of a series of reactions “intermediates”, although we call those intermediates that speed up the overall reaction scheme “catalysts”.

We know that the catalyst OH is formed by the reaction of H₂O with O(¹D) (which comes from ozone photolysis)

Let's examine the evolution of photochemical smog on a typical day in Los Angeles

Early morning (6 – 9 am): Automobile traffic and industrial emissions begin. Largest concentrated emissions of CO, RH, and NO. Winds generally slack and air is relatively stagnant, with a low inversion layer.

Midday (9 am – 2 pm): Primary emissions continue. Photochemical transformations take place. Sea breeze picks up and transports pollutants inland. Maximum sun intensity around noon.

Late afternoon (3 – 5 pm): Ozone concentrations peak. Inversion usually broken, so vertical transport moves pollutants upward and sometimes out of region.

Evening (5 – 7 pm): More primary emissions from traffic. Low sun angles, so difficult to make secondary pollutants. Primary pollutants can accumulate. Ozone concentrations begin to fall.

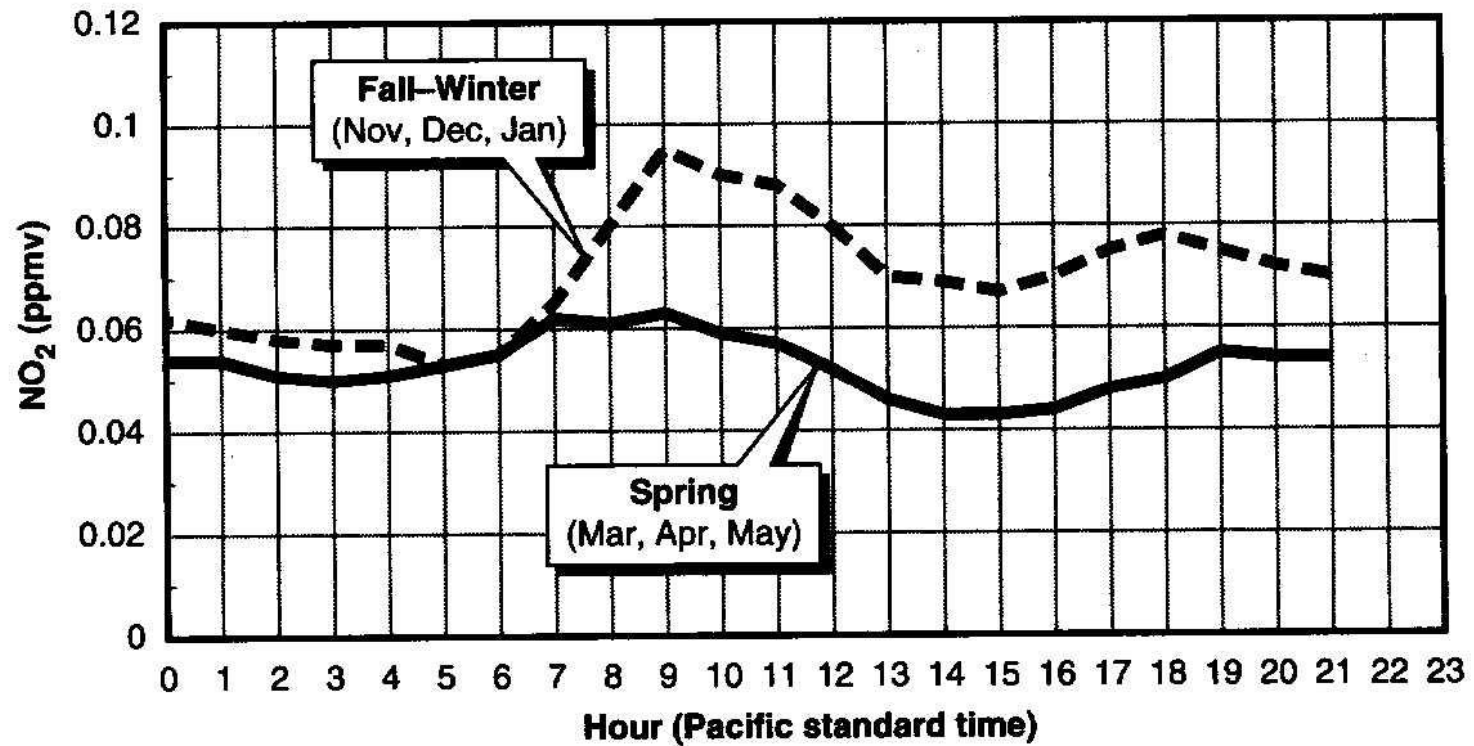
Late evening (7 – 9 pm): Sea breeze dies. Temperature inversion reforms, usually leaving day's pollution above (accounts for layered structure of multiple day's smog).

Overnight (9 pm – 6 am): Pollutants are converted to reservoir species, such as HNO_3 and peroxy acetyl nitrate (PAN = $\text{CH}_3\text{C}(\text{O})\text{O}_2\text{NO}_2$).

Species like PAN can be very toxic, so regulations are often established to reduce their buildup in urban regions

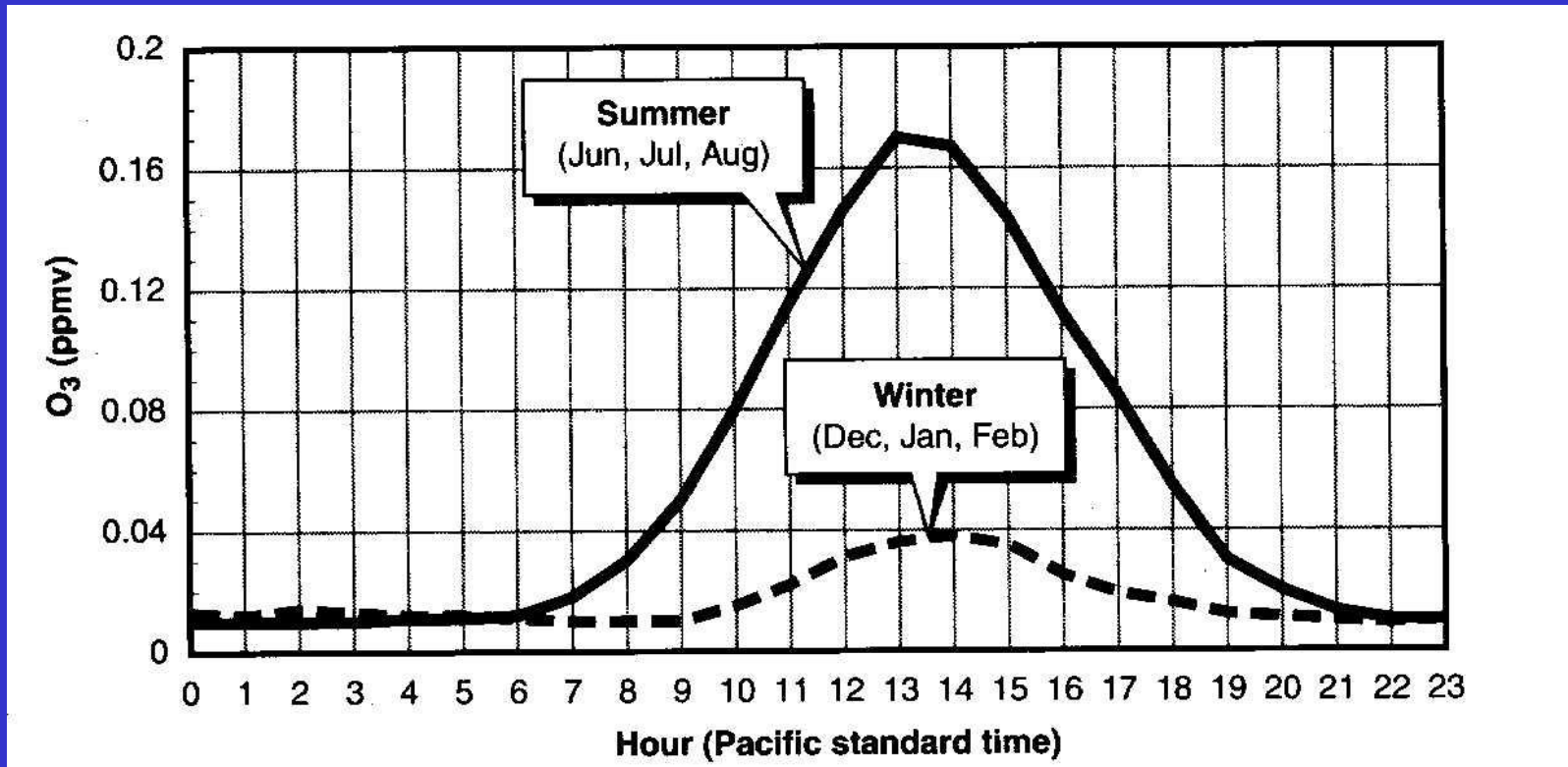
Diurnal Behavior of Various Species

Nitrogen dioxide (NO₂)



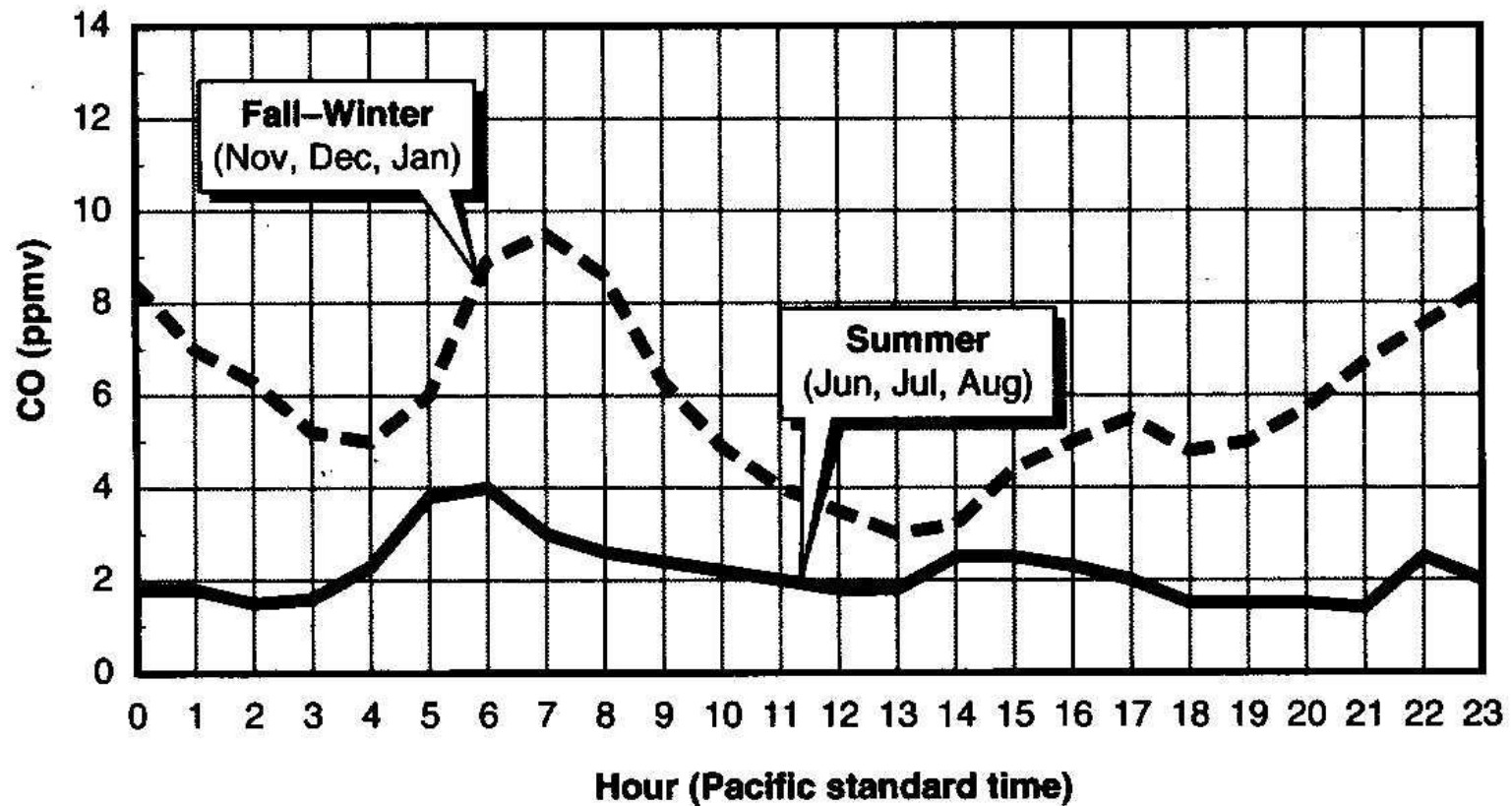
Diurnal Behavior of Various Species

Ozone (O_3)



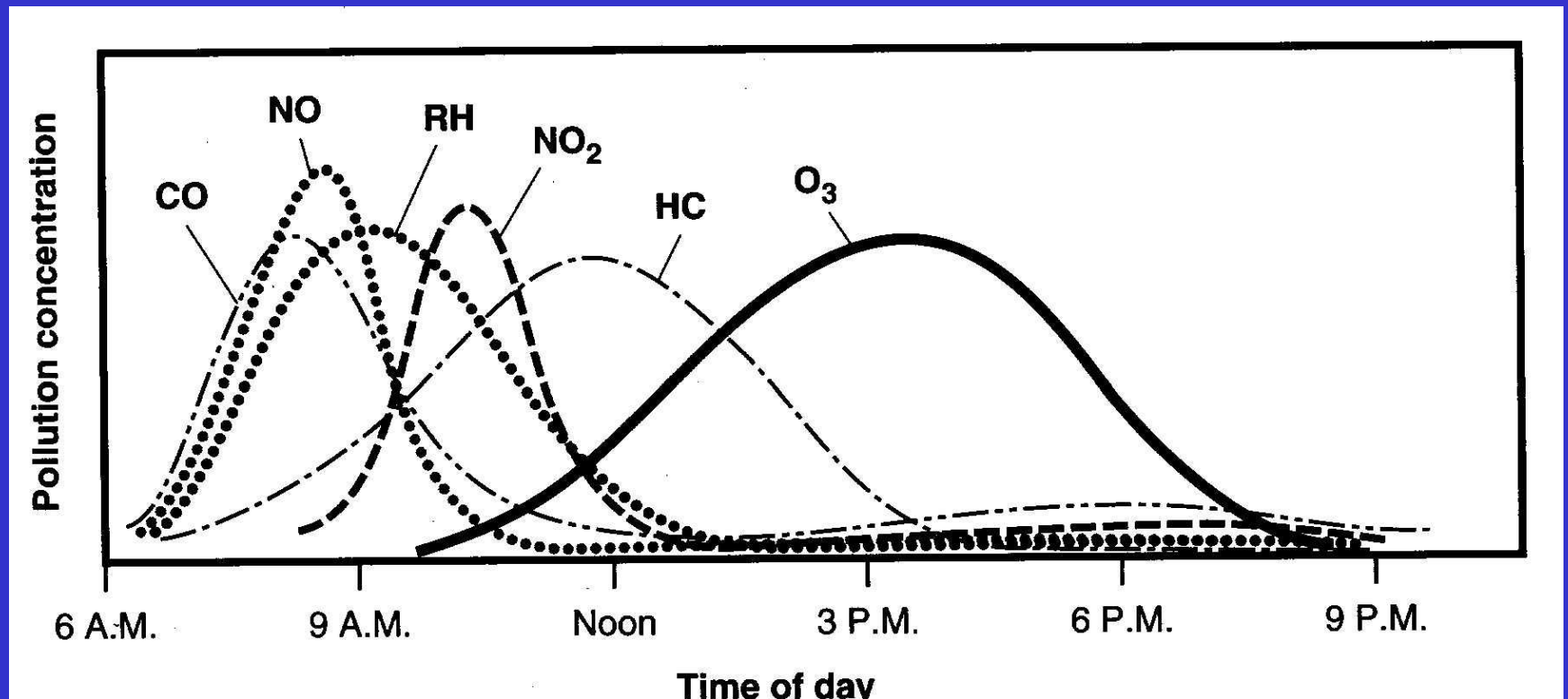
Diurnal Behavior of Various Species

Carbon Monoxide (CO)



Diurnal Behavior of Various Species

Putting it all together:

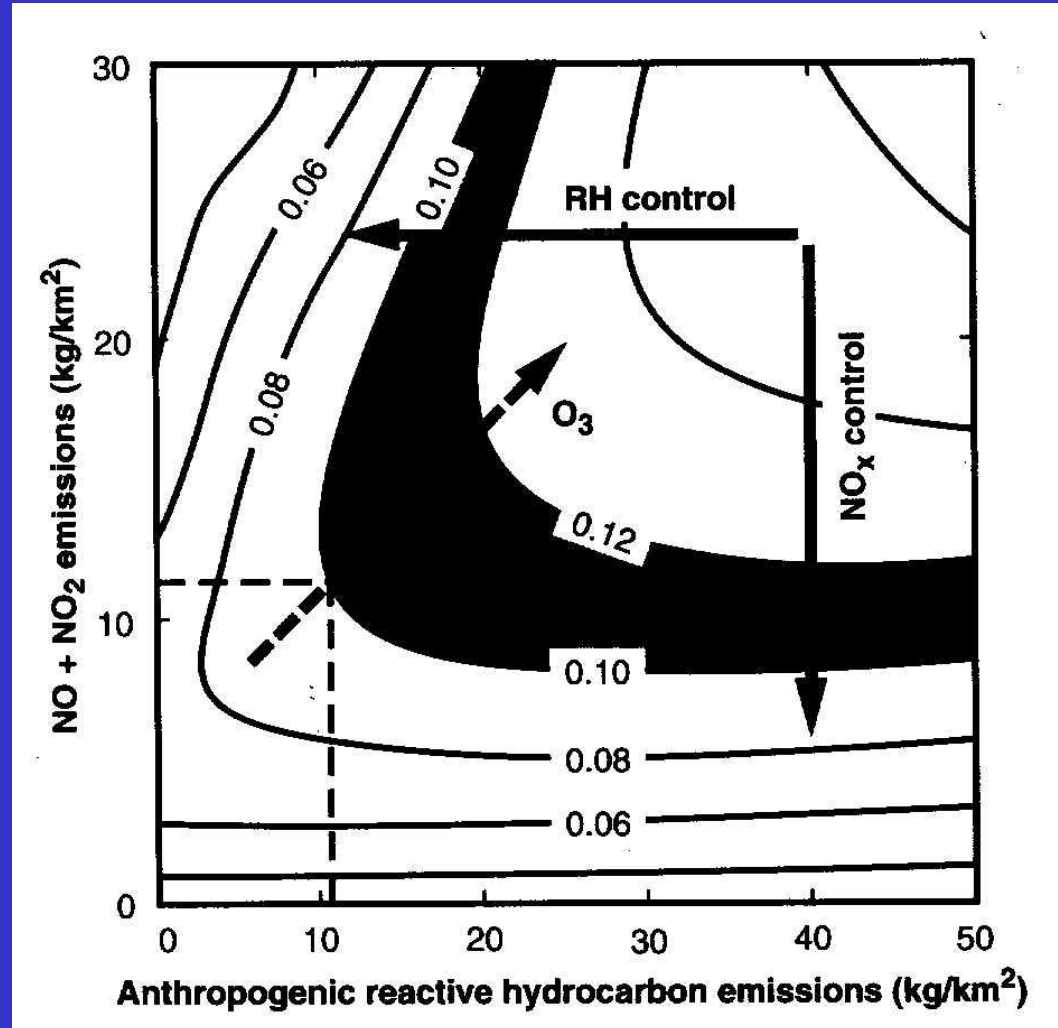


Controlling Smog

Requires a combination of RH and NO_x controls

In regions with relatively high VOCs (e.g. near forests), reductions in NO_x are effective in reducing O_3 .

In regions of low VOCs, reducing NO_x can actually increase ozone (although this isn't necessarily a bad thing because it could reduce products like PAN!).



Unlike acid rain, can't really fix or forestall damage once pollutants are emitted. Instead, need to control emissions (sources)

Culprit #1: Old cars ("heaps" or "junks")

- emit much more than newer cars
- 10%/90% issue
- identifying worst polluters?

Culprit #2: Industry

- concept of waivers or allowances
- advantage of always reducing pollution
- does it send a bad message?

Culprit #3: Energy usage

- alternative fuels
- population; lifestyles

How large are rate constants for reactions?

Reactions between charged species (“ion-ion” reactions) are incredibly fast if the charges are opposite.

Reactions between charged species and neutral species (“ion-molecule” reactions) are also pretty fast, as the neutral species becomes polarized (i.e. charge within the molecule begins to separate and the molecule looks somewhat charged) as the ion approaches.

Reactions between two radicals (“radical-radical” reactions) can also be very fast because the two unpaired electrons would like to form a new covalent bond. Usually, these reactions occur on every collision. However, these reactions are not as fast as those involving ions, because the ions actually attract each other or other molecules, whereas radicals act more ‘neutral’ – they react IF they hit each other, but they don’t tend to pull other species towards them.

Reactions between radicals and molecules (“radical-molecule” reactions) can be fast, but usually less so than reactions between two radicals. They don’t typically occur on every collision – maybe only in one-in-ten or one-in-100 collisions.

Molecules rarely react with each other (i.e. “molecule-molecule” reactions are the slowest of them all).

We call the fastest rates for any two reactants “gas kinetic”, meaning that a reaction occurs on every collision. Ion reactions have larger gas-kinetic rate coefficients. We don’t worry about these in the lower atmosphere, since there are so few ionic species present in the gas phase.

For a radical-radical or radical-molecule reaction, a ‘gas-kinetic’ rate coefficient will be no larger than about

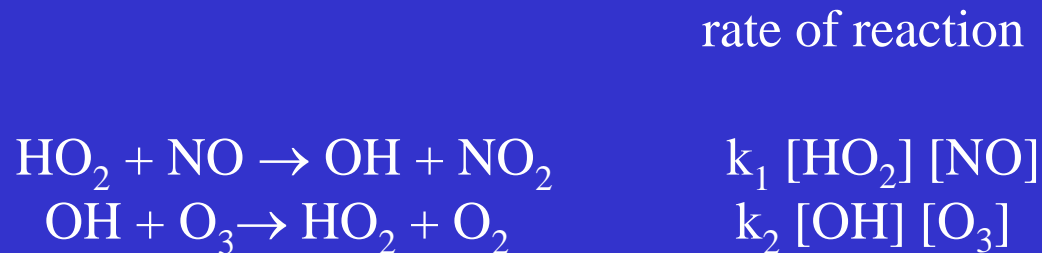
$$k \sim 1 \times 10^{-10} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$$

Most bimolecular reactions have rates between 10^{-11} and $10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$

Steady-State Approximation

Very often in atmospheric chemistry, we are not interested in a single reaction, but rather in a coupled set of reactions, where the products of one reaction are the reactants in the next. We make the assumption that these gases are in "steady-state"; that is, that their concentrations do not change with time.

For example:



In this pair of reactions, we need to consider what is causing OH and HO₂ to change.

First, let's look at OH. It is produced by the first reaction and consumed by the second one. The rate of the first reaction is

$$\text{Rate1} = k_1[\text{HO}_2][\text{NO}]$$

and the rate of the second is

$$\text{Rate2} = k_2[\text{OH}][\text{O}_3].$$

If the concentration of OH is not changing, it must be produced as fast as it is consumed. Thus:

$$d[\text{OH}]/dt = 0 = k_1[\text{HO}_2][\text{NO}] - k_2[\text{OH}][\text{O}_3]$$

We can make the same argument for HO₂:

$$d[\text{HO}_2]/dt = 0 = k_2[\text{OH}][\text{O}_3] - k_1[\text{HO}_2][\text{NO}]$$

In the not-too-distant past, accurate measurements of OH and HO₂ were not possible in the atmosphere. People would use relationships like these to assess both their observations and chemical models.

It is easy to rearrange either of the above expressions:

$$0 = k_1[\text{HO}_2][\text{NO}] - k_2[\text{OH}][\text{O}_3]$$

$$k_1[\text{HO}_2][\text{NO}] = k_2[\text{OH}][\text{O}_3]$$

$$[\text{OH}]/[\text{HO}_2] = k_1[\text{NO}]/k_2[\text{O}_3]$$

Thus, with measurements of ozone and nitric oxide (which are both relatively easy) and temperature (to get the rate constants right), one can estimate the ratio of OH to HO₂.

Sample Problem: The production of ozone in the troposphere requires the photolysis of NO_2 , followed by reaction of an oxygen atom with molecular oxygen:



If the NO_2 concentration is $2.46 \times 10^{10} \text{ molec cm}^{-3}$ and the density, $[\text{M}]$, is $2.46 \times 10^{19} \text{ molec cm}^{-3}$, what is the steady-state production rate of ozone?

The only species that we can create a steady-state approximation for here is O, as it is the only one with both production and loss processes.

$$d[\text{O}]/dt = J[\text{NO}_2] - k[\text{O}][\text{O}_2][\text{M}] = 0$$

The production rate of ozone is: $d[\text{O}_3]/dt = k[\text{O}][\text{O}_2][\text{M}]$

But, we don't know $[\text{O}]$.

However, we can substitute from the steady-state expression for $[\text{O}]$:

$$\begin{aligned} d[\text{O}_3]/dt &= J[\text{NO}_2] = 1 \times 10^{-2} \text{ s}^{-1} * 2.46 \times 10^{10} \text{ molec cm}^{-3} \\ &= 2.46 \times 10^8 \text{ molec cm}^{-3} \text{ s}^{-1} \end{aligned}$$

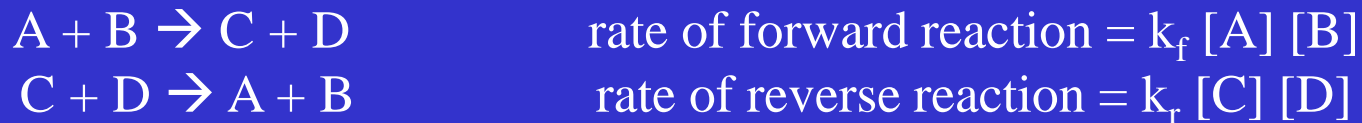
How do equilibrium constants relate to rate coefficients?

We'll come back to this when we deal with acid rain

We write an equilibrium expression, with equilibrium constant K_{eq} , as:



We can break this into a forward reaction and reverse reaction:



At equilibrium, the rates of forward and reverse reactions are equal (or else the concentrations of the species would change). So

$$k_f [A] [B] = k_r [C] [D]$$

Rearranging:

$$[C] [D] / [A] [B] = k_f / k_r = K_{\text{eq}}$$

So $K_{\text{eq}} = k_f / k_r$, the ratio of two reaction rate coefficients!