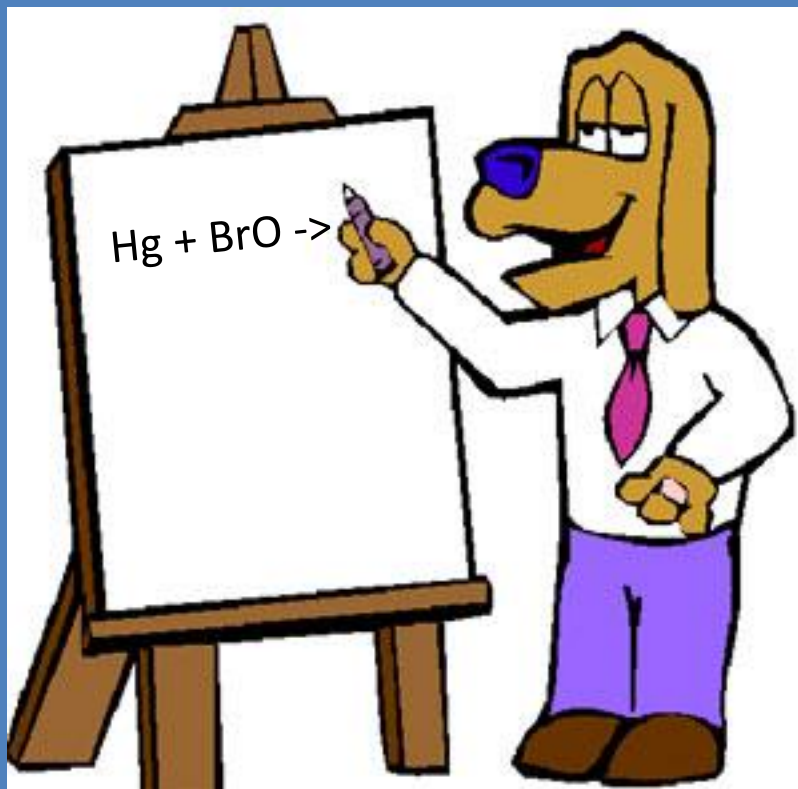


Interesting points from presentations



Atmospheric chemistry/air pollution topics can typically be broken down into the following categories:

Emissions of NO_x, CO, VOCs, and gases that influence criteria pollutants (like ozone)

- Air Pollution in India (Erin, Mercedes)
- Emissions from aircraft engines (Ryan)
- Trees and isoprene (Dayaam, James)
- Emissions from mobile sources (i.e. transportation) (Andrew)

Oxidation of sulfur and nitrates (NO_x) and formation of acid rain

- Flaring in Nigeria (Taylor)
- Acid rain in the Midwest (Haley)
- Influences from ammonia (Colby)

Semi-volatile organic compounds, sulfate, NO_x, and aerosol formation

- Air pollution in China (Dennis, Zhan)
- Trees and isoprene (Dayaam, James)

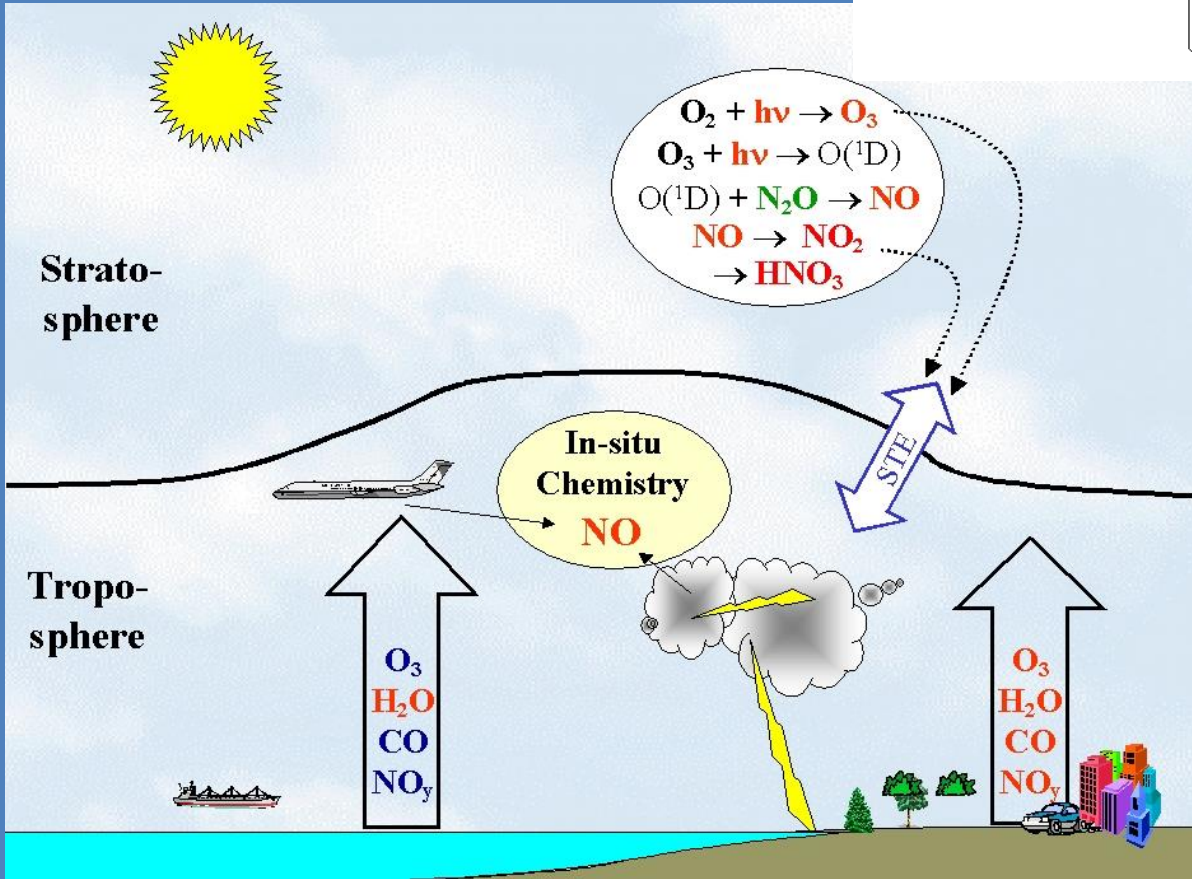
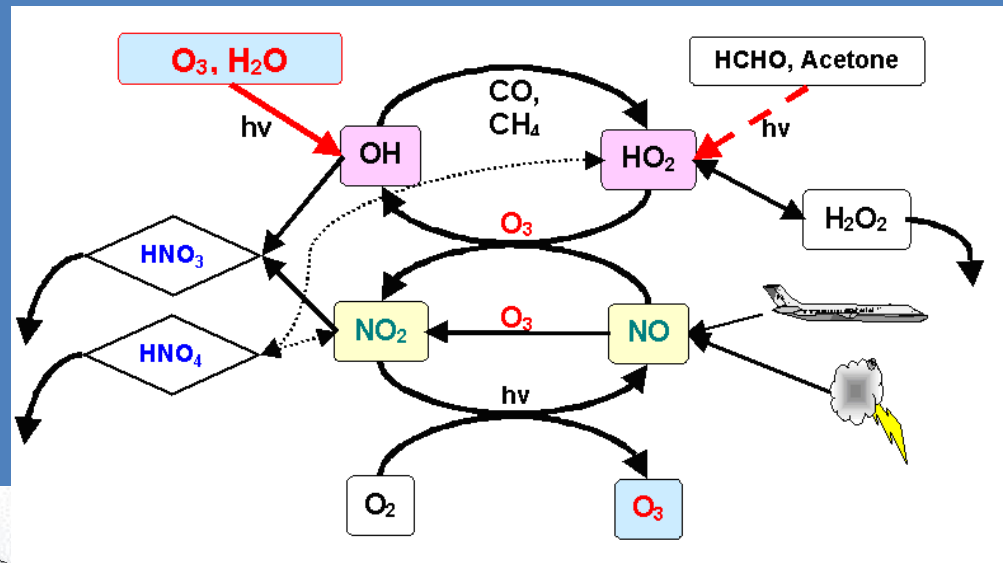
Primary aerosols and influences on chemistry

- Asian dust, heterogeneous chemistry, and buffering acid rain (Bailey)
- Sources of PM in Saudi Arabia (Nasser)
- Biomass burning (Angela, Maria, Catherine)
- Particulates from grilling (Lin)
- Ammonia (Colby)

Long-lived compounds, global warming, and stratospheric ozone depletion

- Methane, CH₄ (Hannah)
- Agriculture, bacteria, and nitrous oxide, N₂O (Lauren)
- Remote sensing (Jacob)

NOx emissions (multiple sources)

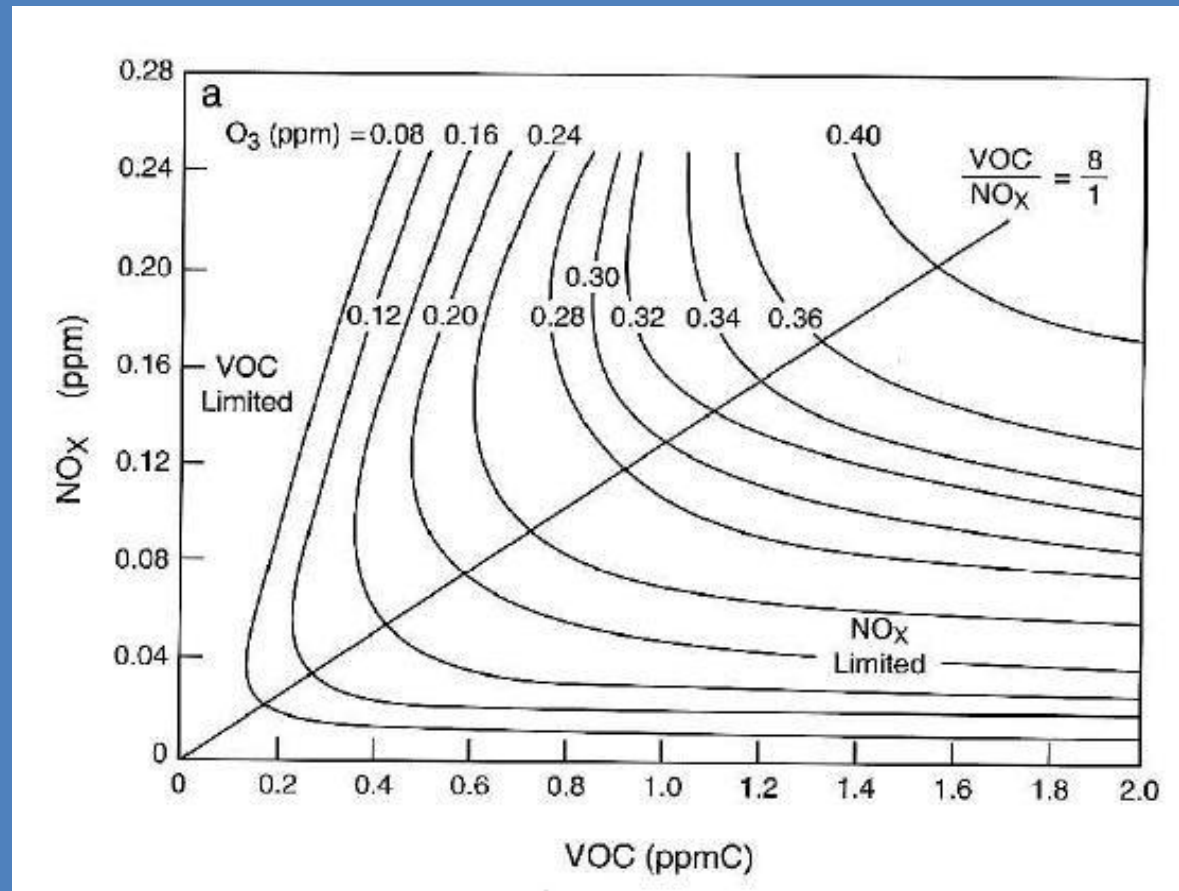


Combustion always generates some smog

NO_x is primarily from combustion

NO_x leads to ozone formation via chemistry with VOCs

EKMA



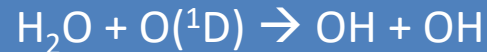
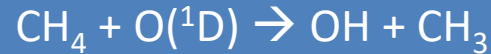
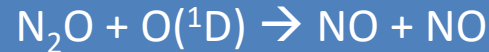
Agricultural and livestock emissions – ammonia, methane, N₂O

Probably can be mitigated, by finding ways to “clean up”, or capture emissions (in this case, methane capture by rancher in California)



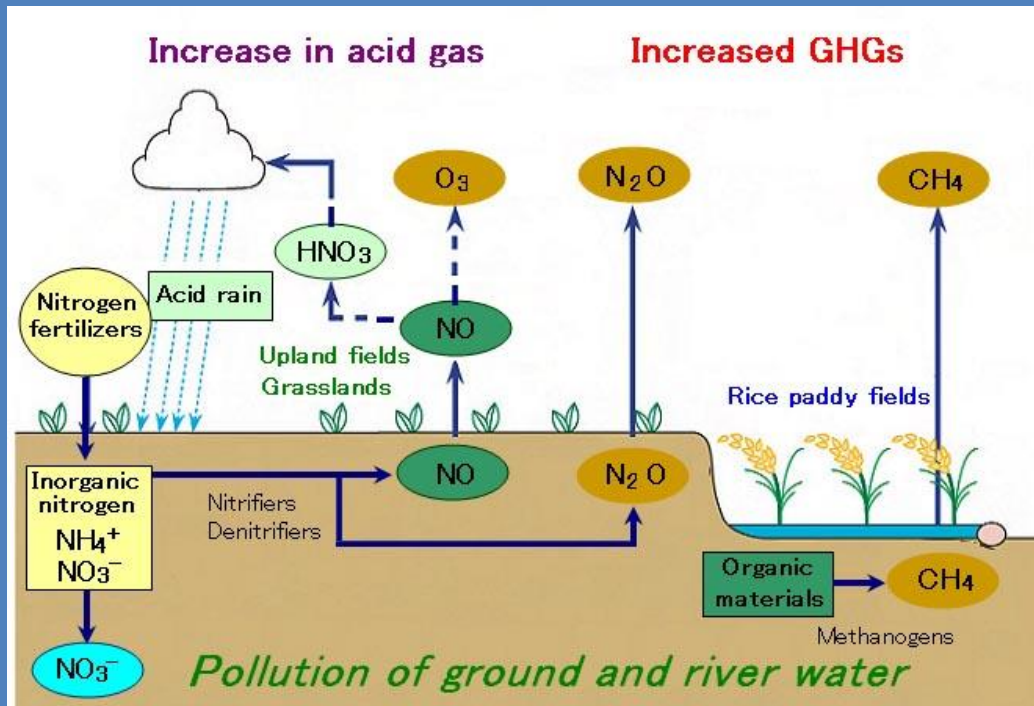
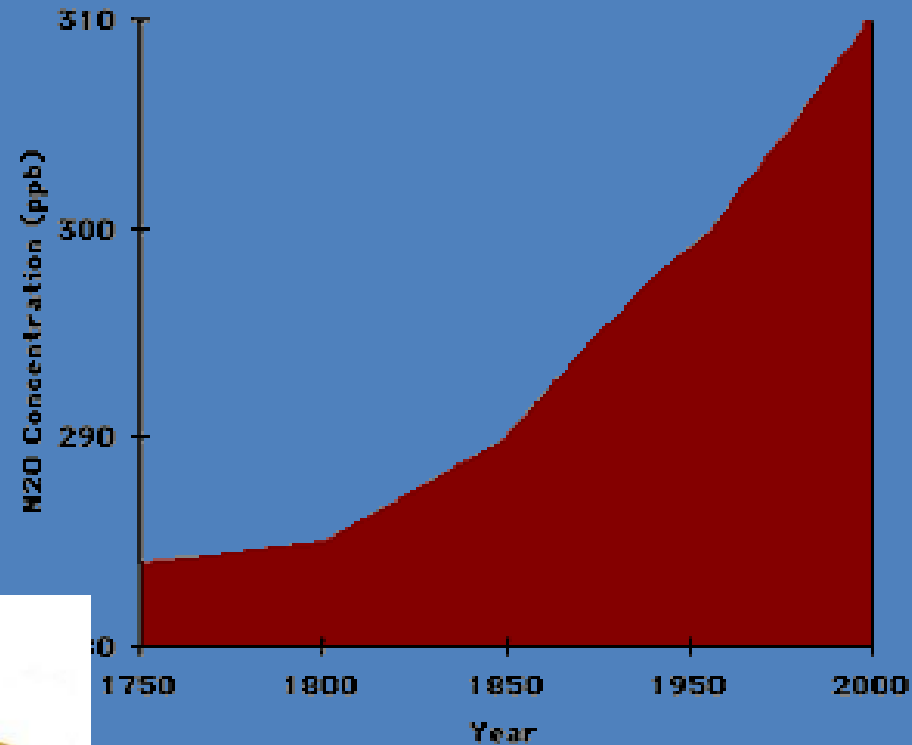
N₂O and CH₄ from agriculture/anaerobic bacterial metabolism

N₂O and CH₄ have long lifetimes in the troposphere so that they can be carried into stratosphere, where they break down to form ozone-destroying radicals:



Nitrous oxide could become the largest contributor to human-influenced ozone depletion

Recall – N_2O lifetime in troposphere is > 100 years



Power plants in China

Did you know that China is outpacing the US in the building of ‘cleaner’ coal-fired power plants? Still, only half of the power plants have sulfur emissions controls.



See page 210-213 for discussion of sulfur emissions and acid rain

Page 118-121 describes the chemistry that converts SO_2 into H_2SO_4 – it isn't necessarily simple

“smog” was a word coined in 1905 to describe smoke and fog in London

Important things to know:

SO_2 is rapidly oxidized into H_2SO_4 by gas-phase reactions – e.g. with OH – and heterogeneous reactions. Sulfuric acid then condenses into small particles which are hygroscopic (take up water). So this tends to be a regional problem, although it can lead to very contentious arguments if emissions are near state or national borders, as is often the case.

Chemistry of H₂SO₄

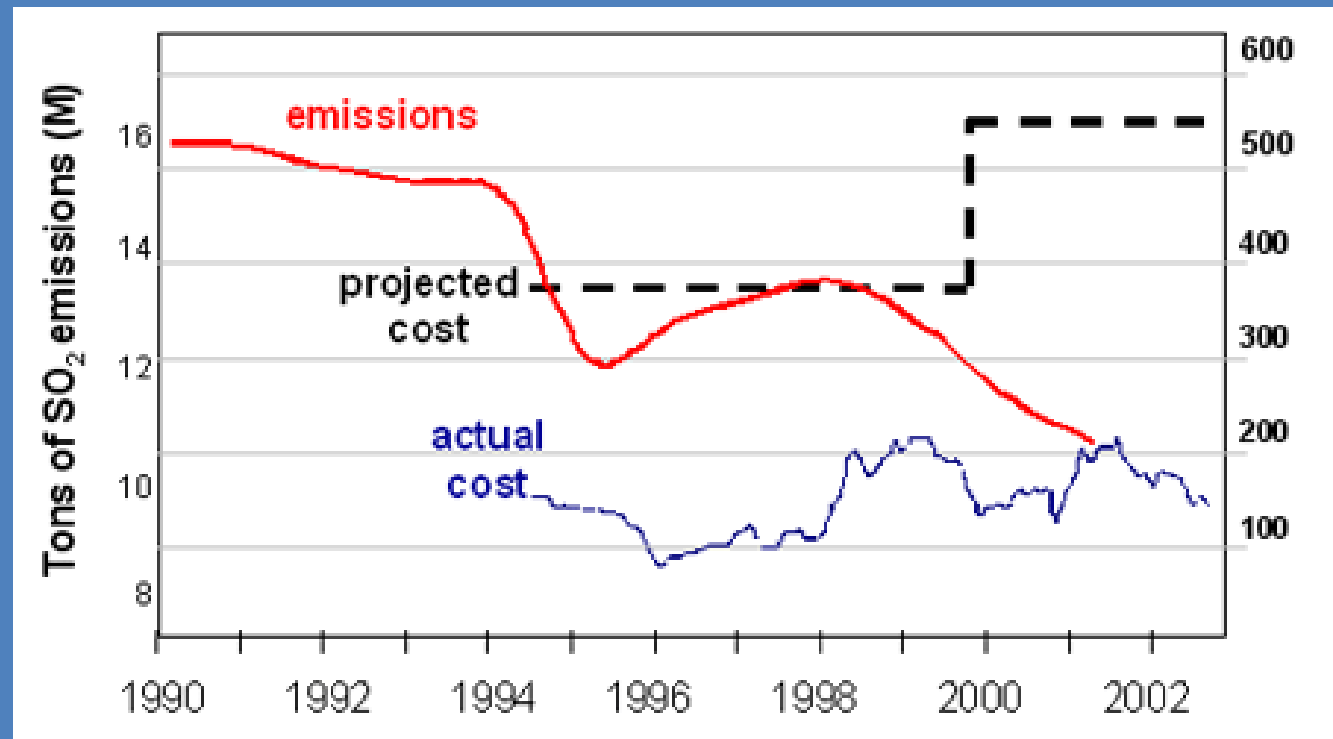


The equilibrium constant, K, for sulfuric acid is essentially infinite, meaning that H₂SO₄ completely dissociates in water. We call this a 'strong acid,' and for every H₂SO₄ that goes into water, two H⁺ ions and one SO₄²⁻ ions are formed.

$$K_{\text{eq}} = [\text{H}^+]^2[\text{SO}_4^{2-}]/[\text{H}_2\text{SO}_4] = \text{infinity}$$

In the US, Cap and Trade was a policy that was successful in reducing SO₂ emissions from power plants in the Ohio/Tennessee areas in the 1980s. According to the Environmental Defense Fund, the actual cost of SO₂ allowances were less than ½ of the original projected costs – about \$100-200 per ton of SO₂.

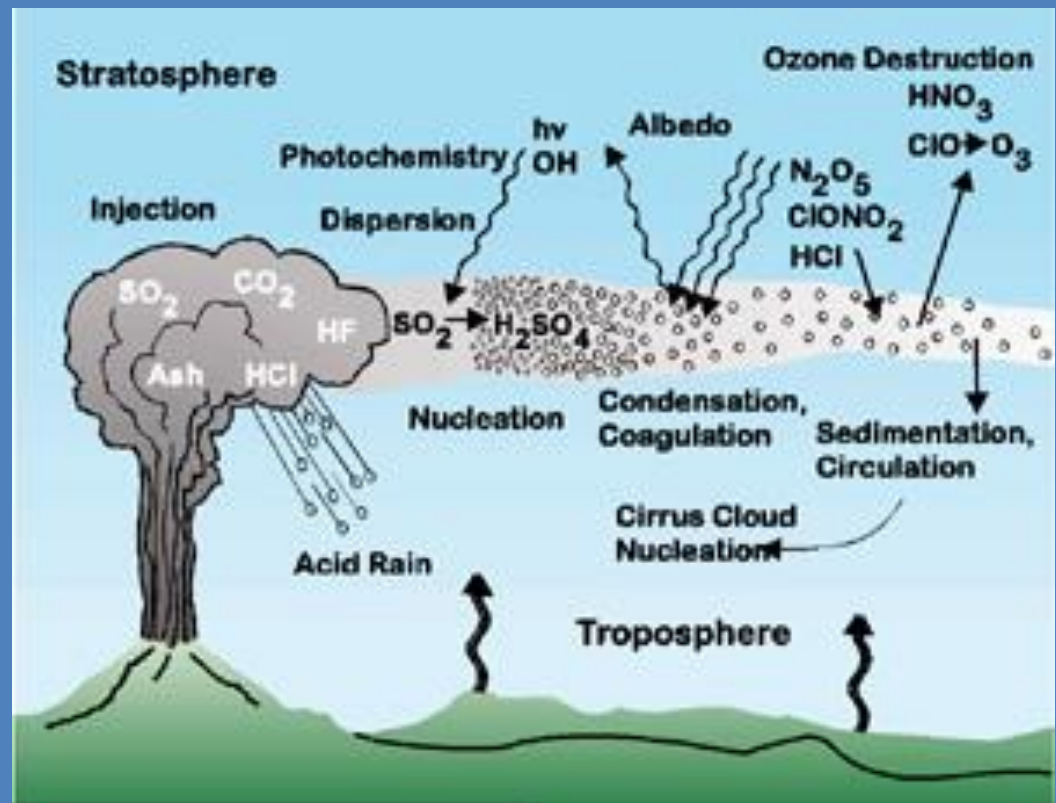
Note that a ton of coal produces about 2500 kWhr of electricity. At \$0.10 per kWhr, this is \$250. Note that in high sulfur coals (that appear yellowish in color) sulfur can be as high as 10% by weight. Assume, at worst, burning 1 ton of coal produces 0.1 ton of SO₂. The SO₂ allowance would add 4-8% to the cost of electricity generation. The cost is less than 1% for cleaner coals found in western states like Wyoming.



Geoengineering by solar radiation management

Analogy to volcanic emissions of SO_2 directly to stratosphere, cooling the planet by forming sulfuric acid aerosols

The catch – as we saw in class (see page 149-150, 155-159), particles like sulfuric acid can lead to activation of halogens (mainly chlorine) which destroys ozone. This isn't a theoretical threat. Ozone destruction was observed after several volcanoes. The main issue is one of the ability to mitigate ozone losses by controlling the properties of the clouds. It may not be possible, so one would be trading one environmental problem for another.



Biomass burning



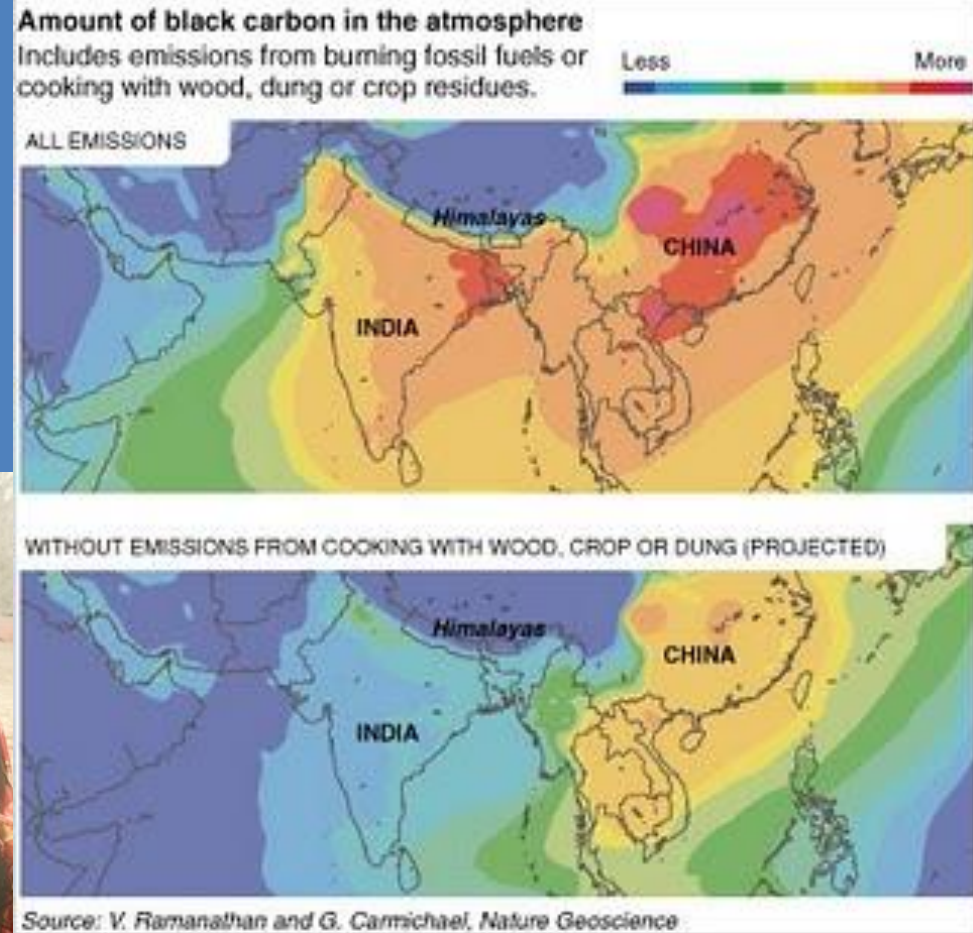
Produces toxic compounds
Also very important for visibility



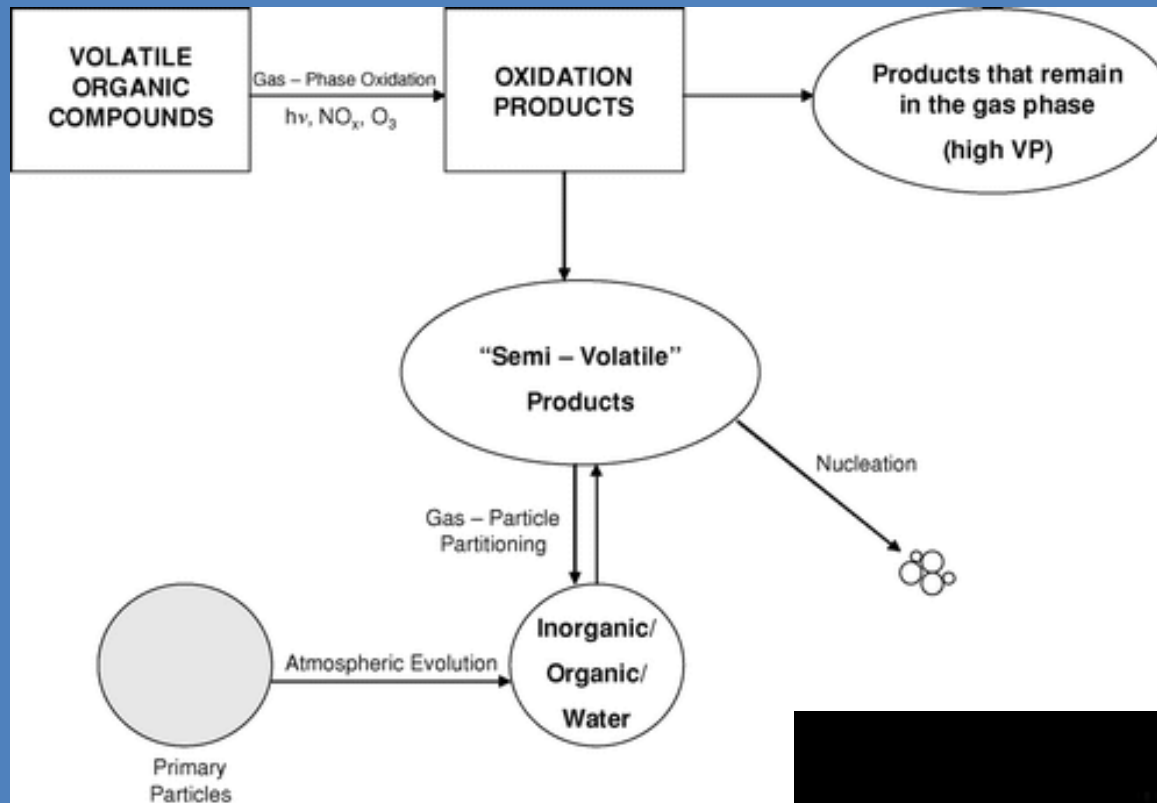
Cooking stoves

Primarily a problem with black carbon, but other emissions include NO_x , CO, N_2O , polycyclic aromatic hydrocarbons.

New stoves can make a big difference, and they aren't that expensive (~\$100)

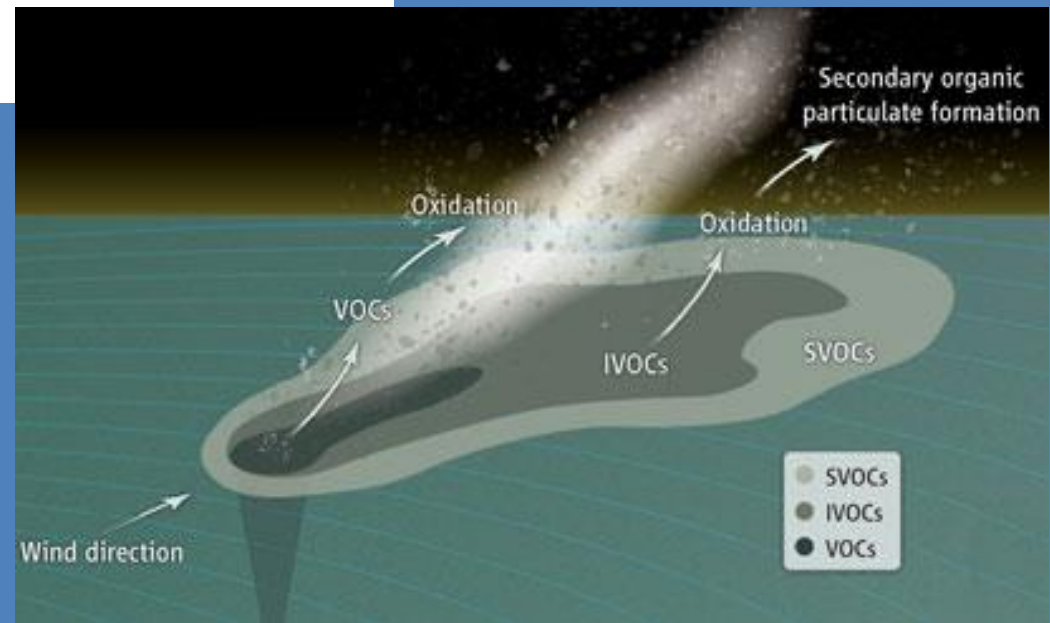


Black carbon is thought to be contributing to melting glaciers in Himalayas

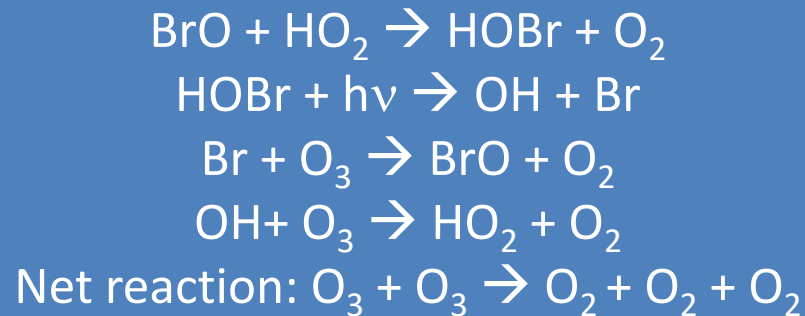
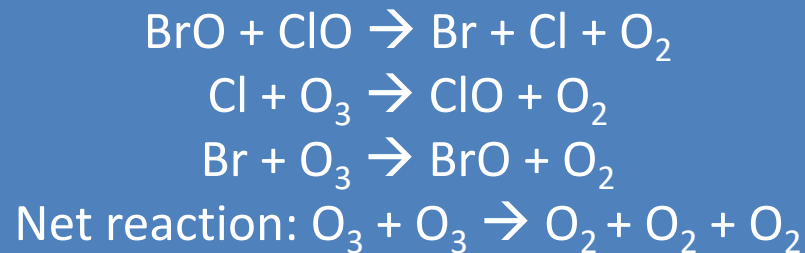


VOCs and aerosol formation (an example from the 2010 oil spill, but one that applies to any VOC emissions)

The gulf oil spill provided a test of this understanding

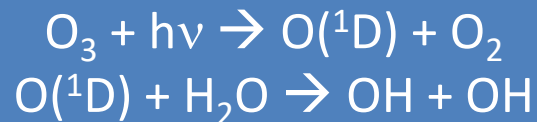


I noted in class that there is another issue related to “natural” sources of halogens – depletion of surface ozone in the Arctic (and, to a lesser extent, the Antarctic). Bromine is released from sea salt (see pages 124-125) when it is wicked upward through sea ice. Heterogeneous reactions on aerosols in the air can convert sodium bromide to reactive forms of bromine, which then destroy ozone:



These reactions are about 50 times faster than chlorine reactions alone, so bromine is 50 times more effective at destroying ozone. Fortunately, there isn't much bromine in the stratosphere (20 ppt of bromine vs. 2000 ppt of chlorine). Even so, bromine is still nearly as important as chlorine, so regulations are just as important for Br as for Cl.

Boundary layer ozone is important for producing OH – through the following reactions:



And, recall that OH is the main oxidant in the troposphere, and is instrumental in determining the reactive lifetimes of most short-lived compounds. So if ozone is destroyed in the boundary layer, this reduces OH, which, in turn, increases the lifetimes of many compounds, some of which are important greenhouse gases.

There is another interesting chemical feedback involving bromine. As noted on page 128 of the textbook, bromine (in particular, BrO), converts elemental mercury (Hg) into a more toxic, bio-active form (HgO). It is known that elemental mercury becomes depleted when ozone is depleted. What isn't known is whether the bio-active form increases in plants and animals that are then consumed by other animals and, ultimately people, and whether or not changing patterns in sea ice, which affect levels of BrO, also impact this mercury chemistry. This is an active field of scientific study.

Additional points raised in presentations

Forests and trees have a major impact on atmospheric chemistry. In particular, isoprene and other emissions (terpenes) are VOCs, and when mixed with sources of nitrogen oxides, they produce ozone. In addition, forests affect ground water, which has an impact on bacteria in soils, which produce methane and nitrous oxide (N_2O). These species are long-lived in the lower atmosphere, which allows them to mix upward, where they enter the stratosphere, releasing radicals that destroy ozone.

I also noted in class that trees typically release compounds that have C=C double bonds, which are highly reactive with ozone. This chemistry is described in the textbook on pages 87-91 and 114-115. There are lots of consequences of these emissions and subsequent reactions, the most obvious being (1) under high VOC emissions (such as inside the canopy) ozone is destroyed rapidly by reactions with VOCs, (2) above the canopy in sunlight and in the presence of NO_x , ozone is formed rapidly by smog photochemistry, and the levels of ozone can be quite high, adding to background levels, and (3) formation of aerosols that contribute to particulate matter (PM) as well as assisting in the formation of clouds (acting as cloud condensation nuclei).

I also noted that forests and trees can be a source of methyl chloride (especially when there are large forest fires), and this is an ozone depleting substance. CH_3Cl is the largest natural source of chlorine to the stratosphere.

Additional points raised in presentations

I also noted after Dayaam's presentation that changes in CO₂ in the stratosphere can have important impacts on ozone depletion. CO₂ doesn't deplete ozone directly. Rather, thermal (infrared) radiation to space from CO₂ is the primary means of cooling the stratosphere. Absorption of ultraviolet radiation by ozone is the primary means by which the stratosphere warms. So when CO₂ abundances increase in the stratosphere, the additional cooling reduces temperatures. This, in turn, changes the reaction rate constants of important ozone-destroying processes and increases formation of polar stratospheric clouds. Consequently, more ozone is destroyed, and this further reduces the warming that comes from absorption of UV by ozone. This represents a positive feedback loop. So as CO₂ abundances have increased due to human activities, the ozone layer has thinned. This is in addition to the thinning due to releases of ozone-depleting substances.

So even though CO₂ isn't an "ozone depleting substance", it has an indirect effect on ozone in the stratosphere that is important.

Additional points raised in presentations

Jacob talked about remote sensing. One of the points I made is that global observations of O_3 and H_2O are critical for estimating the production rate of OH.

OH is very difficult to measure because concentrations are so small. There are currently no methods for measuring it from space. So atmospheric chemists use detailed models along with observations of precursor gases to estimate the abundance, and they compare these calculations to limited observations of OH that are obtained from aircraft. These “reconstructed” global abundances of OH are then used to estimate the lifetimes of most gases that react with OH.

Observations of water and aerosols are also important for determining the global distribution of clouds and particulate matter, which in turn are important influences on atmospheric chemistry (by acting as surfaces for heterogeneous reactions and as scrubbers – removers – of pollutants).

Bailey noted that dust from China can be an important contributor to particulate matter downwind (like in South Korea). Dust tends to have a neutralizing effect on acid rain, which can be good. But it also acts as a surface for heterogeneous reactions. Currently, the impact of dust on atmospheric chemistry via such reactions isn't well understood.

Additional points raised in presentations

Anna talked about ocean acidification. The main issue is with emissions of CO_2 (I've provided a question that I used to require having to deal with calculating the pH of "pure" water exposed to present-day abundances of CO_2). Because ATOC has several new courses that address ocean acidification, I have discontinued these questions, but it is important to note that there are circumstances where the pH of water is influenced by carbonate chemistry, and it is believed that there are regions on Earth (mainly near very large coastal cities) where acid rain can influence the nearby ocean, and this can impact life (like coral reefs). This is an area of ongoing research, one that is likely to gain more attention as CO_2 levels continue to rise in the atmosphere.

Carbonate chemistry is also important for schemes to remove CO_2 from the atmosphere. These are called "carbon capture and storage" (or CCS), and very little is currently known how large-scale attempts to remove CO_2 from the atmosphere could also have impacts on local air pollution.

Additional points raised in presentations

Hannah talked about methane, and I noted that one issue we didn't examine this term was the formation of formaldehyde from oxidation of methane. Formaldehyde is highly soluble in water, which at first glance would seem like a good thing – that it would dissolve in water and rain out. But there is an important process in clouds where small droplets are lofted by updrafts to the tops of clouds, and these droplets contain formaldehyde, which is released to the upper atmosphere when the droplets evaporate. Formaldehyde is a source of OH radicals in the presence of sunlight. Thus, the formation of OH above convective clouds could represent an important source of OH in addition to the process we already know about – photolysis of ozone followed by reaction of $O(^1D)$ with H_2O . Because formaldehyde is difficult to measure, scientists are still assessing the importance of this mechanism.

I also commented that when methane oxidizes in the stratosphere, it forms two H_2O molecules. Currently, methane is about 2 parts per million in the troposphere. Thus, it produces about 4 parts per million of water in the stratosphere. This represents about half of the total water vapor in the upper atmosphere. Methane is an important source of OH, which destroys ozone, but it also reacts with chlorine, reducing its effectiveness in destroying ozone. These competing effects are still being studied by atmospheric scientists.

Additional points raised in presentations

As we saw in other presentations, there are still many things that we don't understand, especially in parts of the globe where there aren't a lot of measurements and observations. But we can use the same tools to study those problems, and hopefully solve them!