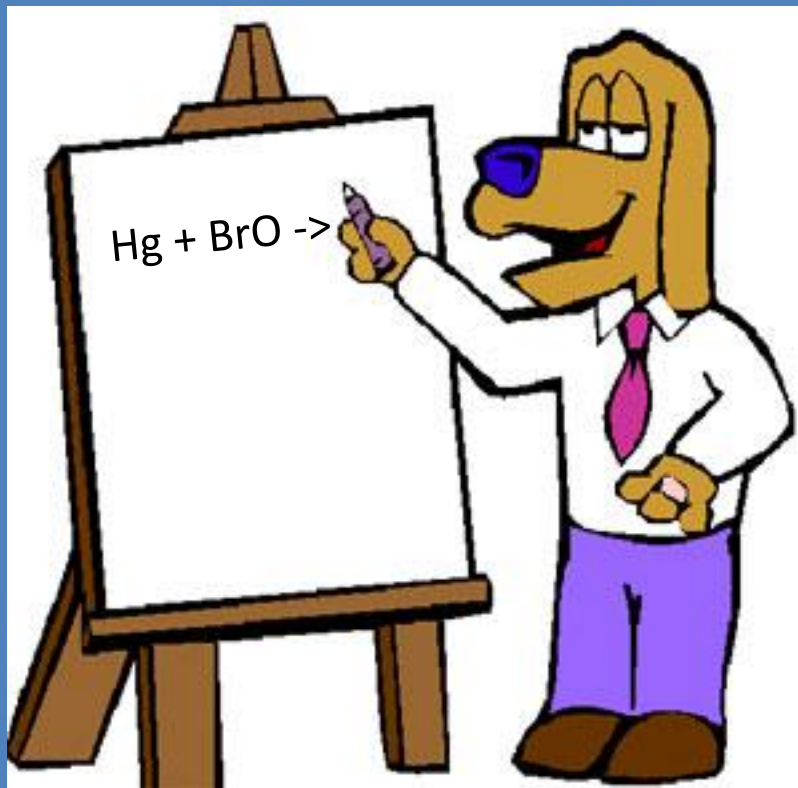


# Interesting points from presentations



The topics can be broken down, roughly, into the following categories

Emissions of NO<sub>x</sub>, CO, VOCs, and other gases that influence ozone (and, thus, OH)

- Electric Vehicles (shifting emissions from mobile sources to fixed sources)
- Methane capture on farms
- Hydraulic fracturing (Fracking)
- Lightning and NO<sub>x</sub>

Emissions of sulfur and formation of aerosols and acid rain

- Power plants (China)
- Sudbury and nickel processing (for batteries)
- Geoengineering by injections of SO<sub>2</sub>

Semi-volatile organic compounds aerosol formation

- The gulf oil spill
- Herbicides and crop (or drug) control
- Fracking
- The Japan nuclear reactor disaster (transport of aerosols)

Stratospheric ozone depletion

- Fertilizer, bacteria, and nitrous oxide (N<sub>2</sub>O)
- Fumigation and methyl bromide (CH<sub>3</sub>Br)
- Nuclear winter
- Geoengineering

## How green are electric vehicles?

It depends on what 'green' means. If one focuses on CO<sub>2</sub>, it's a bit of a mixed bag. You get about as much CO<sub>2</sub> emissions from a coal-fired power plant used to charge the batteries as you do from the gasoline that you would burn to go the same distance in a vehicle that gets about 40-80 mpg. So it's not a clear winner in this regard (unless you have cheap renewable energy, like solar or wind).



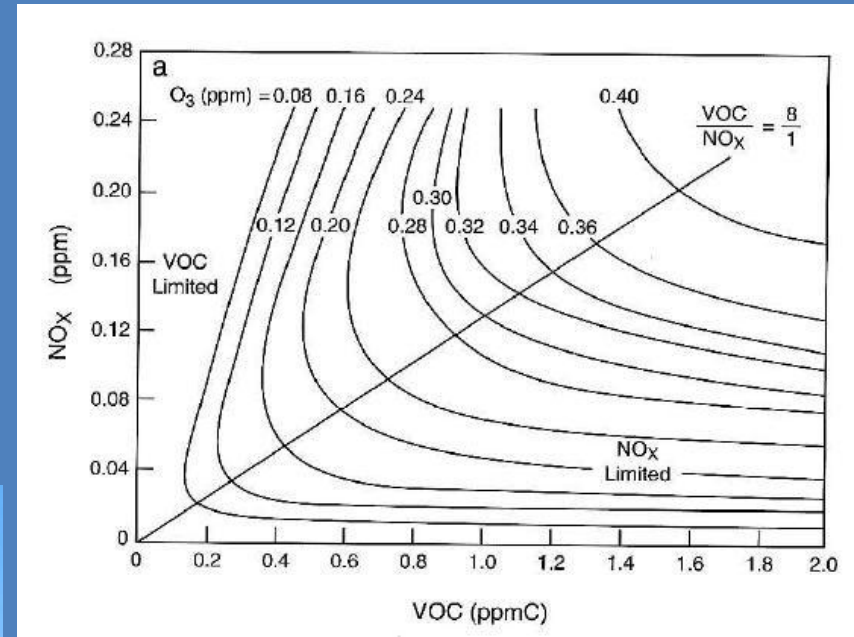
But one big advantage is that one can move the emissions of other harmful chemicals to a more rural environment, allowing for a cleaner urban area. Emissions like NO<sub>2</sub>, CO, particulates that are produced by combustion vehicles are shifted out of the urban centers and into the vicinity of the electricity generating power plants.

Of course, if a city has an abundance of solar or wind energy, it makes sense to use it to power electric vehicles.

# Methane Capture from farms – combustion generates smog

Primarily a  $\text{NO}_x$  issue from combustion

$\text{NO}_x$  leads to ozone formation via chemistry with VOCs

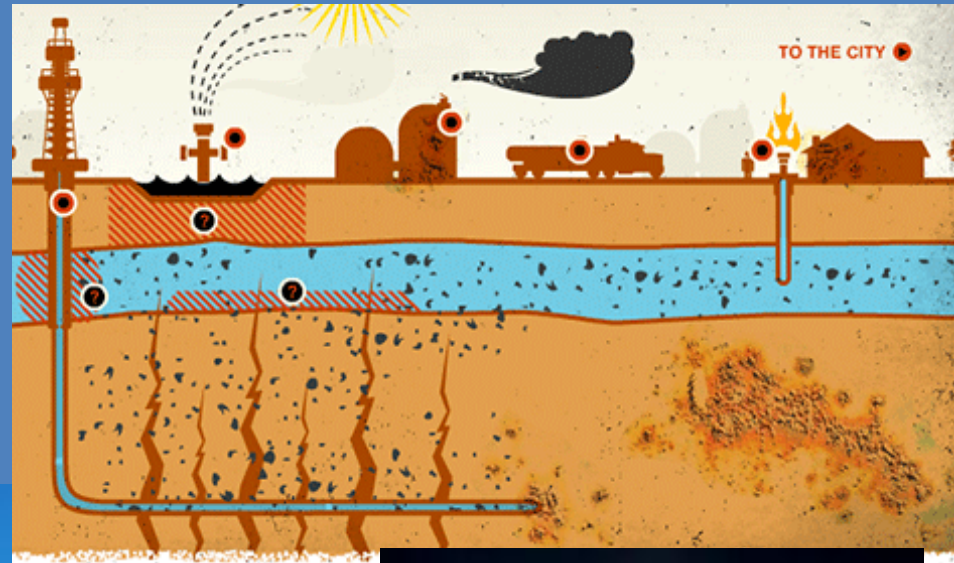


Probably can be mitigated by development of new technologies for cleaner combustion



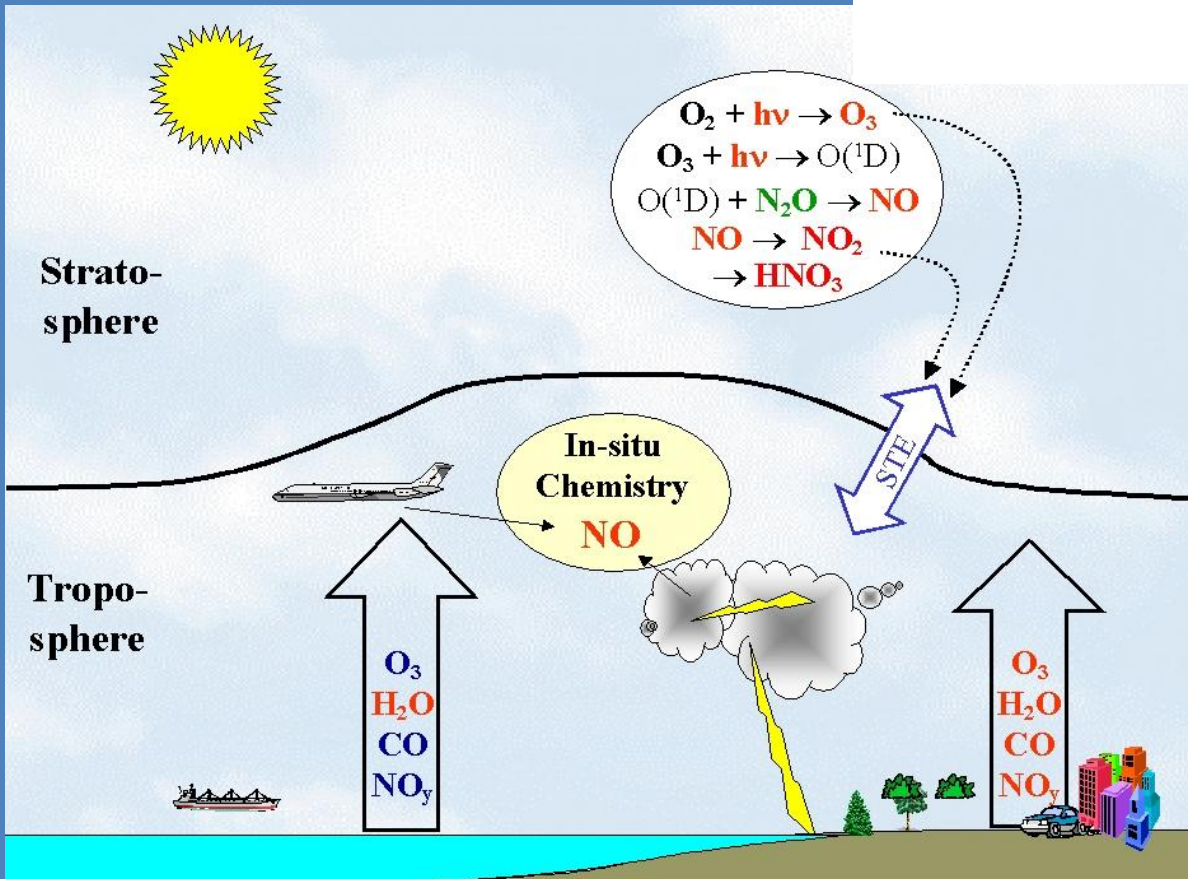
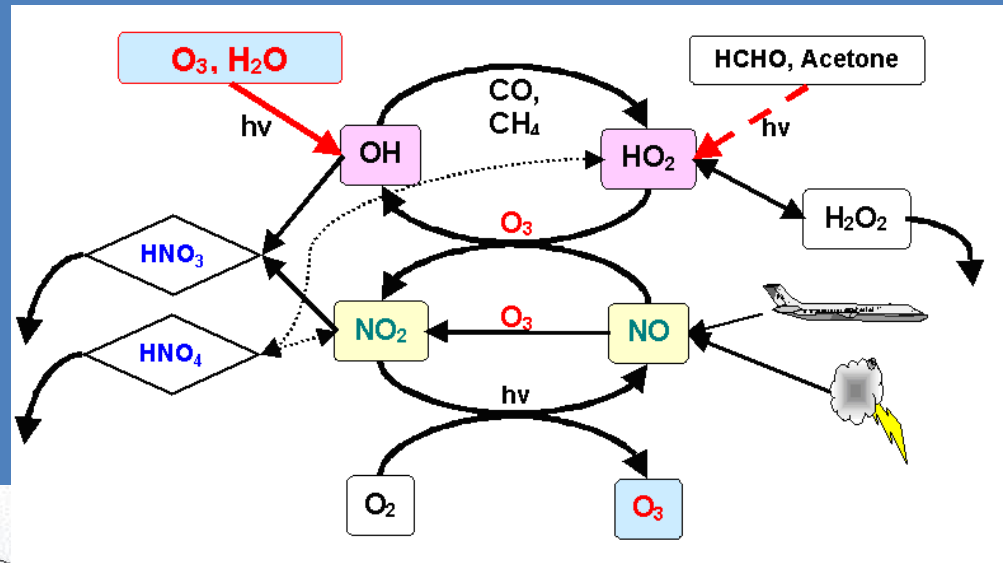
# Hydraulic fracturing ("Fracking")

Many unknowns – companies don't have to disclose their chemicals, but very likely emit VOCs to the atmosphere



# Lightning-produced NO<sub>x</sub>

Natural background sources are needed in order to attribute changes in chemistry due to human emissions, e.g. aircraft, ground level pollution.



## 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  $\text{SO}_2$  into  $\text{H}_2\text{SO}_4$  – it isn't necessarily simple

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

Important things to know:

$\text{SO}_2$  is rapidly oxidized into  $\text{H}_2\text{SO}_4$  by gas-phase reactions – e.g. with  $\text{OH}$  – 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 H<sub>2</sub>SO<sub>4</sub>



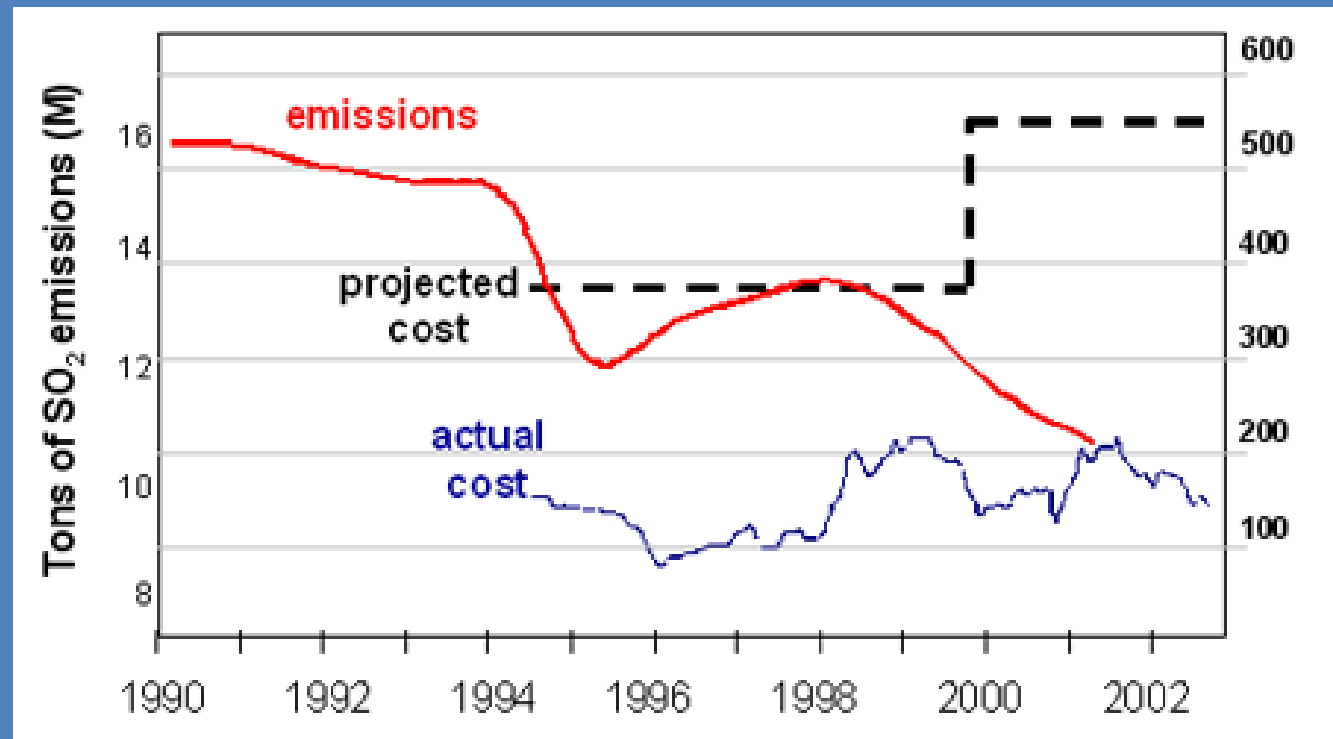
The equilibrium constant, K, for sulfuric acid is essentially infinite, meaning that H<sub>2</sub>SO<sub>4</sub> completely dissociates in water. We call this a 'strong acid,' and for every H<sub>2</sub>SO<sub>4</sub> that goes into water, two H<sup>+</sup> ions and one SO<sub>4</sub><sup>2-</sup> ions 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 SO<sub>2</sub> emissions from power plants in the Ohio/Tennessee areas in the 1980s. According to the Environmental Defense Fund, the actual cost of SO<sub>2</sub> allowances were less than ½ of the original projected costs – about \$100-200 per ton of SO<sub>2</sub>.

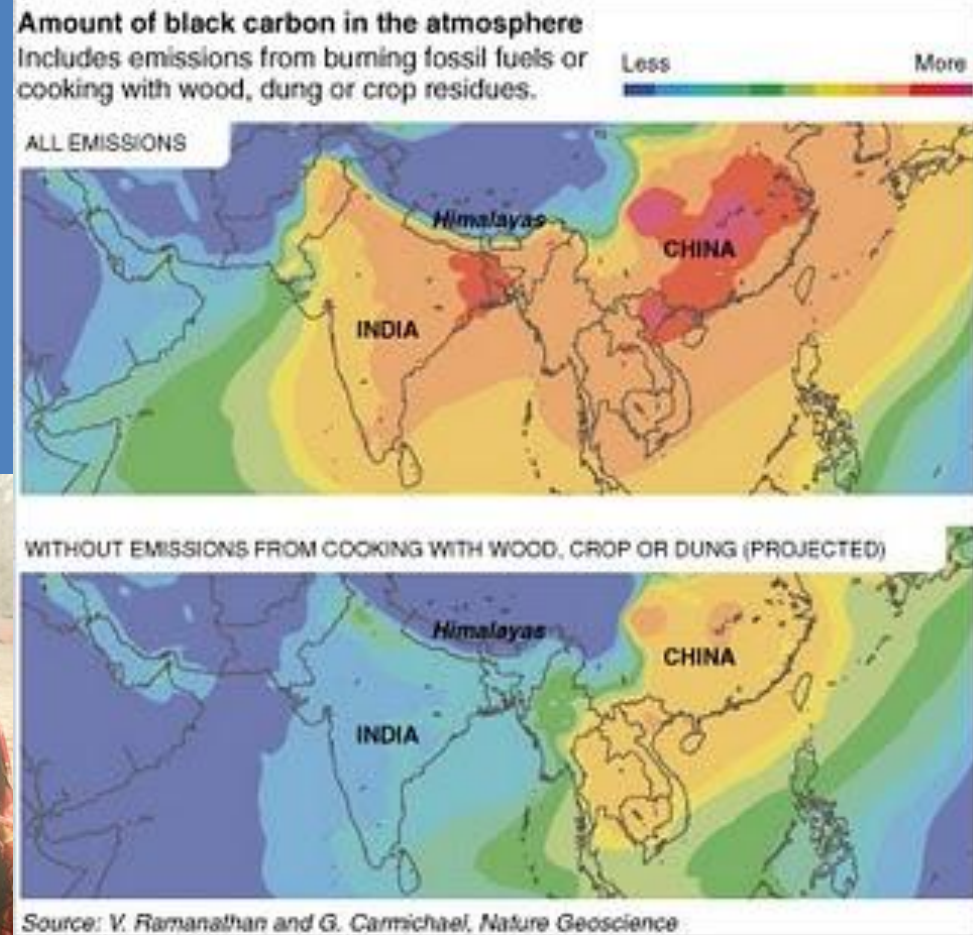
Note that a ton of coal produces about 2500 kWhr of electricity. At \$0.10 per kWhr, this is \$250. Note that in high sulfur coals (that appear yellowish in color) sulfur can be as high as 10% by weight. Assume, at worst, burning 1 ton of coal produces 0.1 ton of SO<sub>2</sub>. The SO<sub>2</sub> allowance 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.



# Cooking stoves

Primarily a problem with black carbon, but other emissions include  $\text{NO}_x$ ,  $\text{CO}$ ,  $\text{N}_2\text{O}$ , 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

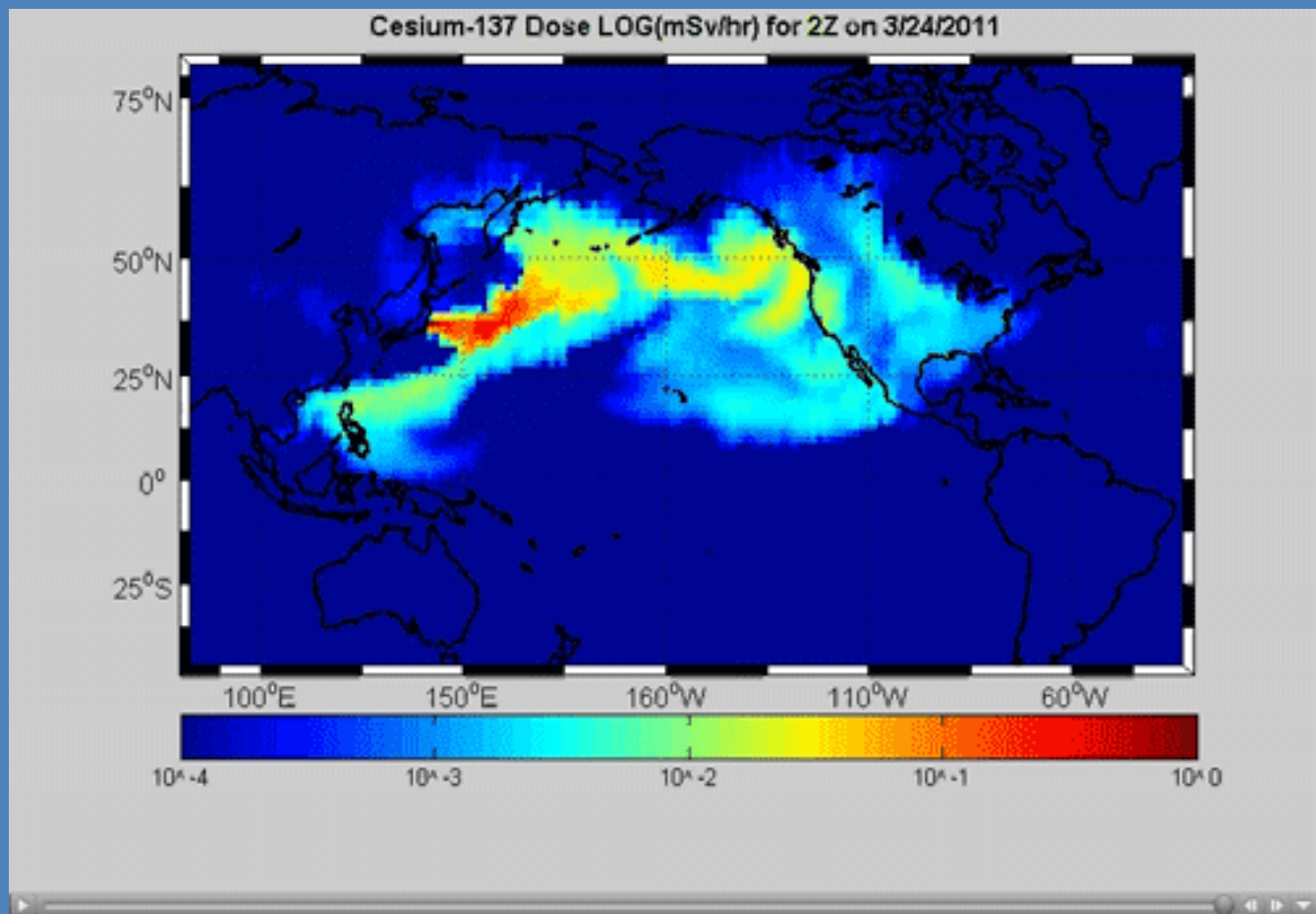
## Biomass burning



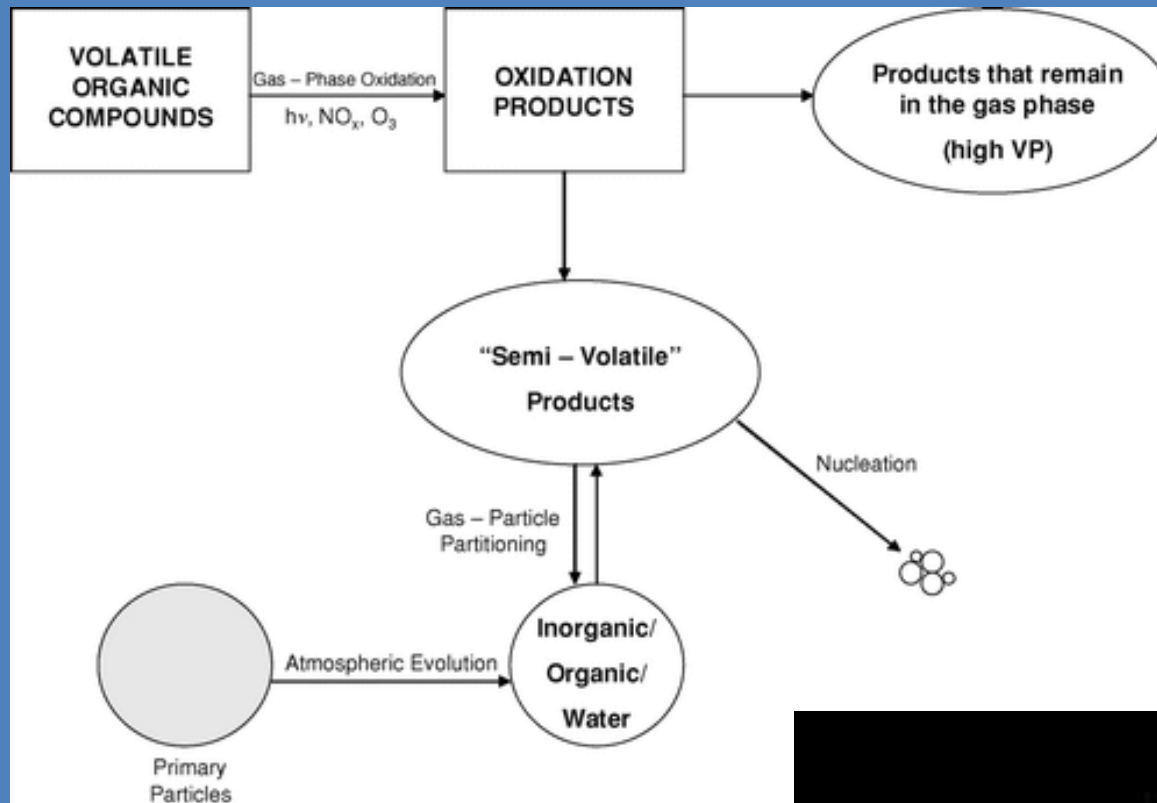
Produces toxic compounds  
Also very important for visibility



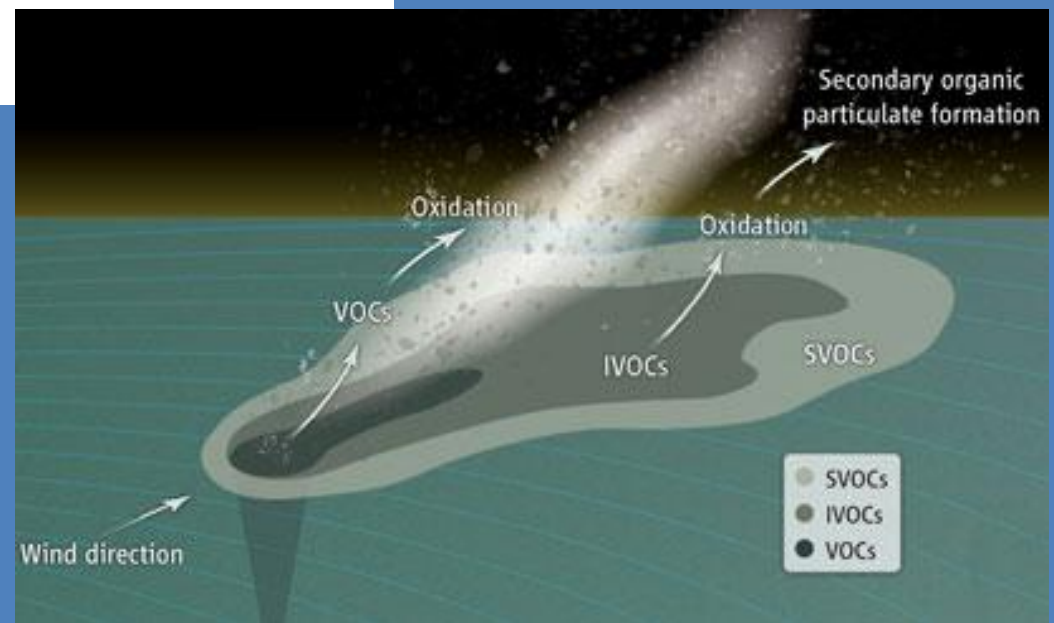
The Japan nuclear incident can be useful for testing atmospheric chemical transport models (CTMs). This is because the radioisotopes that were released have no known sources, so detecting them downwind is a sensitive way to 'trace' them back to the original source without ambiguity. If the model can reproduce the observations, it is useful confirmation of model processes that are important for other problems, like ozone transport.



# VOCs and aerosol formation

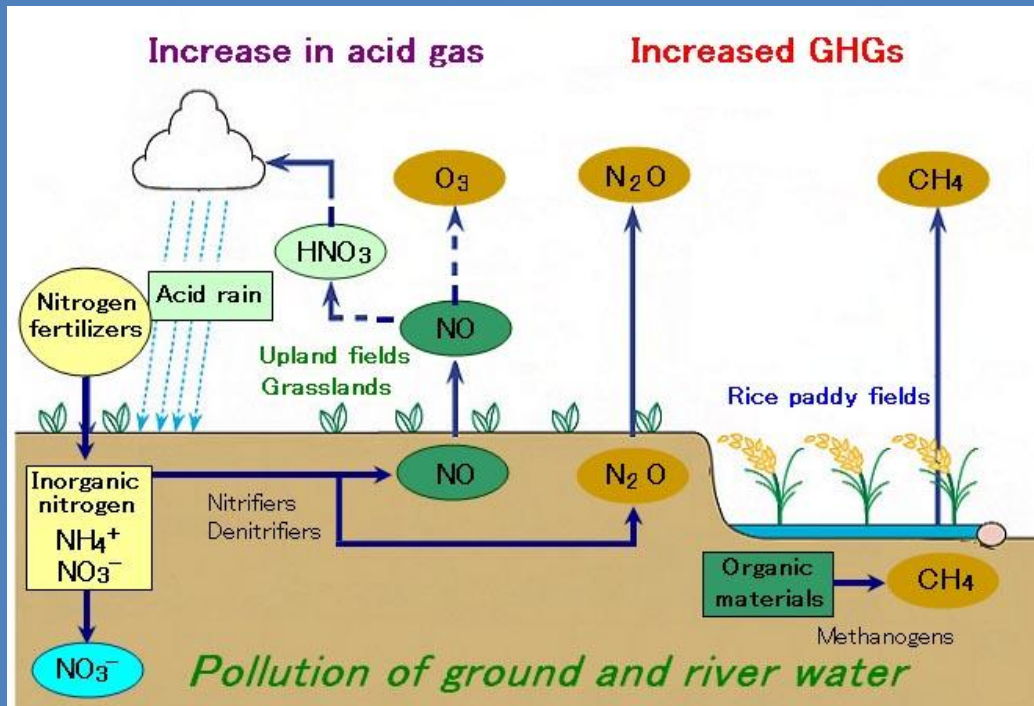
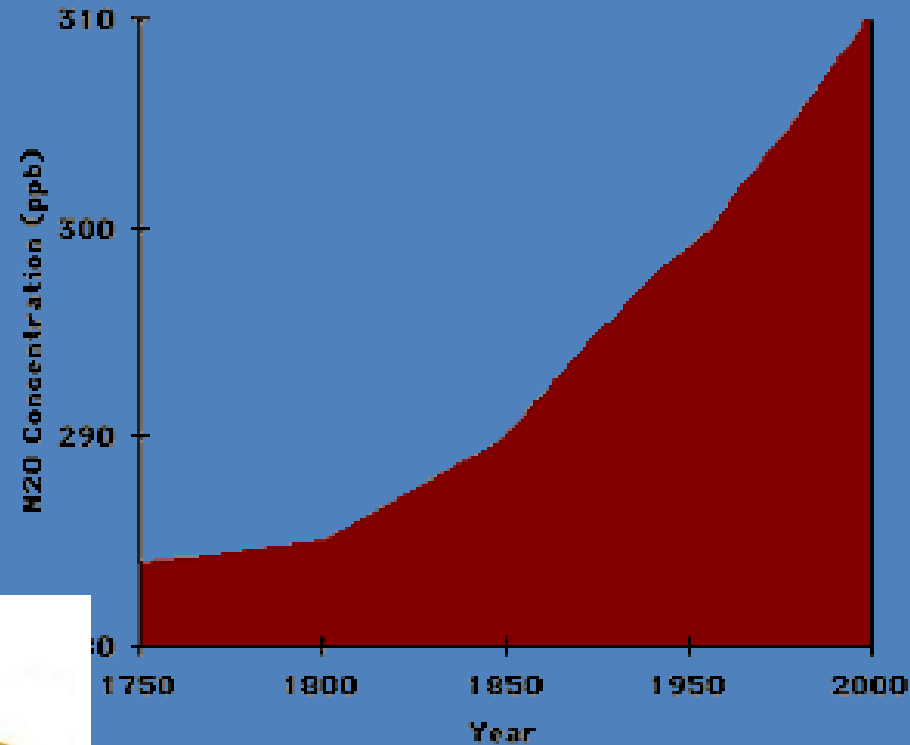


The gulf oil spill provided a test of this understanding

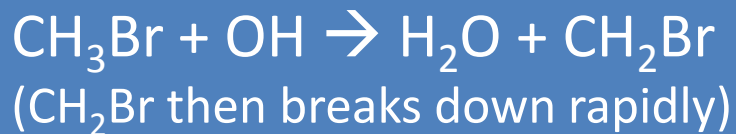
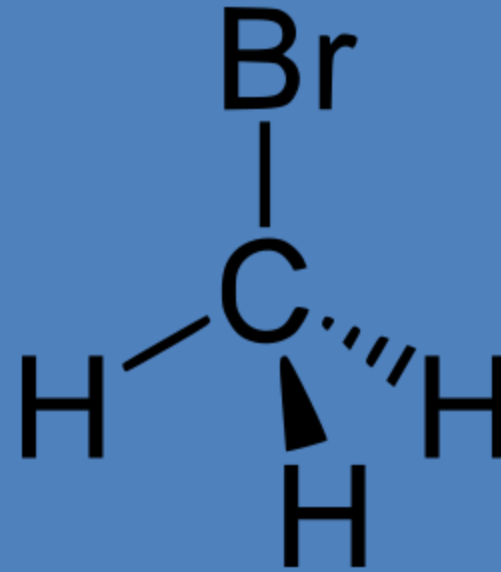
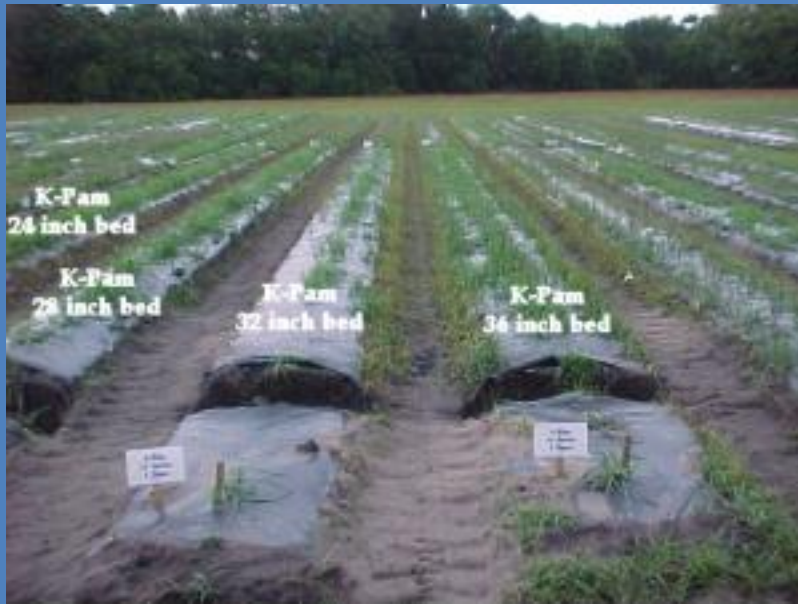


Nitrous oxide could become the largest contributor to human-influenced ozone depletion

Recall –  $N_2O$  lifetime in troposphere is  $> 100$  years



# Methyl bromide and stratospheric ozone depletion

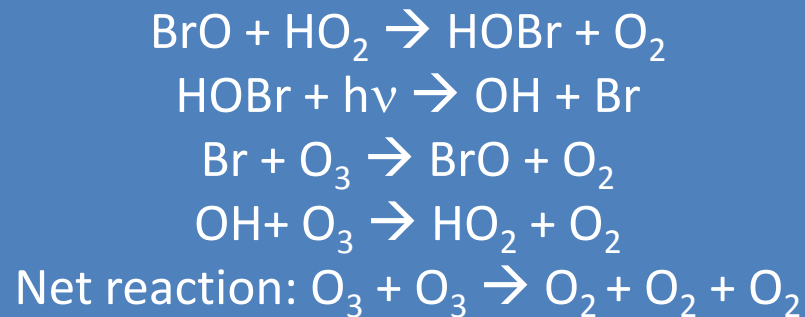
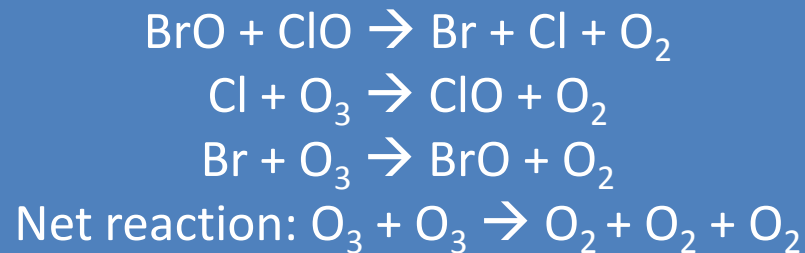


Lifetime =  $1/k[\text{OH}] = 1.7$  years

Other processes (dry deposition)  
reduce the total lifetime to  $< 1$  y



Not all of the methyl bromide that is released reaches the stratosphere, but a significant fraction does - say about 1/3 (since it takes year or so for air to reach the stratosphere). Once bromine atoms are formed, the following reaction cycles destroy ozone:



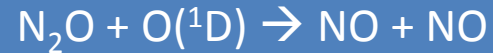
These reactions are about 50 times faster than chlorine reactions alone, so bromine is 50 times more effective at destroying ozone. Fortunately, there isn't much bromine in the stratosphere (20 ppt of bromine vs. 2000 ppt of chlorine). Even so, bromine is still nearly as important as chlorine, so regulations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



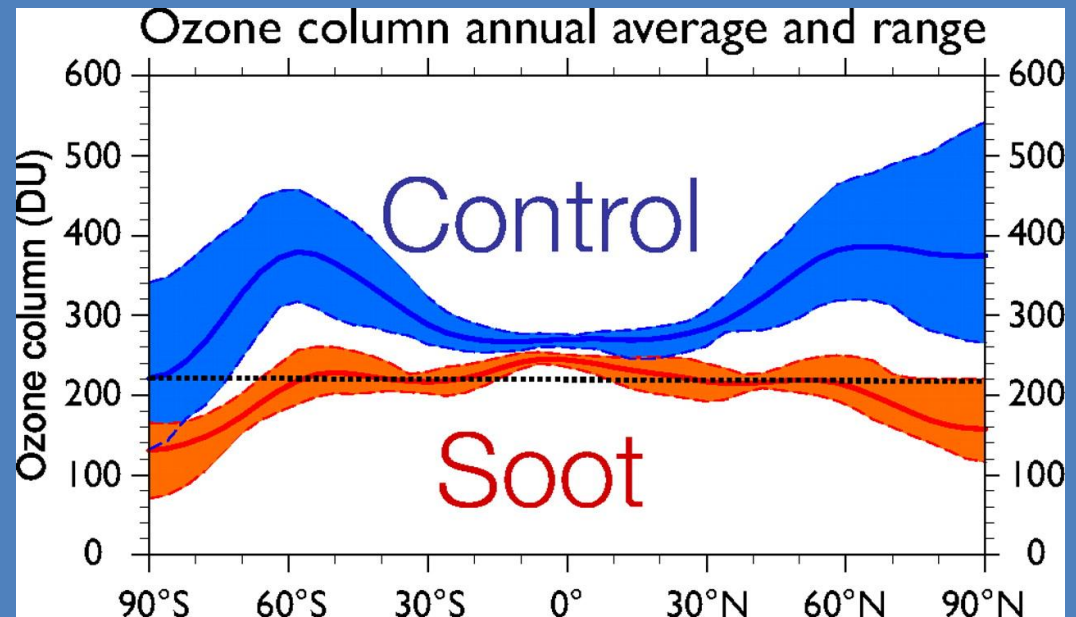
# Nuclear conflict and ozone depletion



$\text{N}_2\text{O}$  carried into stratosphere by plumes



Circulation slows down due to soot,  
which leads to longer residence  
times of ozone-depleting  $\text{NO}_x$



# Geoengineering by solar radiation management

Analogy to volcanic emissions of  $\text{SO}_2$  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.

