ATOC 3500 – Fall 2006
Lectures for Weeks 3 and 4

Reading to accompany the lectures:

Chapter 2

Pages 23- 31 “What is Air Pollution and where does it come from?”
Pages 31-36 “Carbon dioxide and carbon monoxide”
Pages 36-38 “Sulfur compounds”
Pages 38-43 “Nitrogen compounds”
Pages 43-51 “Hydrocarbons”
Pages 51-54 “Oxidants”
Pages 54-55 “Ozone”
Pages 55-67 “Particles”

Note – this is a VERY detailed chapter. I don’t expect for you to understand every bit of every page. For now, read it in order to get a broad idea of the richness of atmospheric pollution. As the class progresses, we’ll deal with many of the details – so you will be referring to this chapter all semester!

ENN FULL STORY
County Plans to Vaporize Landfill Trash

September 11, 2006 — By Brian Skoloff, Associated Press

FORT PIERCE, Fla. — A Florida county has grand plans to ditch its dump, generate electricity and help build roads -- all by vaporizing garbage at temperatures hotter than parts of the sun. The $425 million facility expected to be built in St. Lucie County will use lightning-like plasma arcs to turn trash into gas and rock-like material. It will be the first such plant in the nation operating on such a massive scale and the largest in the world. Supporters say the process is cleaner than traditional trash incineration, though skeptics question whether the technology can meet the lofty expectations. The 100,000-square-foot plant, slated to be operational in two years, is expected to vaporize 3,000 tons of garbage a day. County officials estimate their entire landfill -- 4.3 million tons of trash collected since 1978 -- will be gone in 18 years. No byproduct will go unused, according to Geoplasma, the Atlanta-based company building and paying for the plant.

Synthetic, combustible gas produced in the process will be used to run turbines to create about 120 megawatts of electricity that will be sold back to the grid. The facility will operate on about a third of the power it generates, free from outside electricity. About 80,000 pounds of steam per day will be sold to a neighboring Tropicana Products Inc. facility to power the juice plant's turbines. Sludge from the county's wastewater treatment plant will be vaporized, and a material created from melted organic matter -- up to 600 tons a day -- will be hardened into slag, and sold for use in road and construction projects. "This is sustainability in its truest and finest form," said Hilburn Hillestad, president of Geoplasma, a subsidiary of Jacoby Development Inc.

For years, some waste-management facilities have been converting methane -- created by rotting trash in landfills -- to power. Others also burn trash to produce electricity. But experts say population growth will limit space available for future landfills. "We've only got the size of the planet," said Richard Tedder, program administrator for the Florida Department of Environmental Protection's solid waste division. "Because of all of the pressures of development, people don't want landfills. It's going to be harder and harder to site new landfills, and it's going to be harder for existing landfills to continue to expand."

The plasma-arc gasification facility in St. Lucie County, on central Florida's Atlantic Coast, aims to solve that problem by eliminating the need for a landfill. Only two similar facilities are operating in the world -- both in Japan -- but are gasifying garbage on a much smaller scale. Up to eight plasma arc-equipped cupolas will vaporize trash year-round, nonstop. Garbage will be brought in on conveyor belts and dumped into the cylindrical cupolas where it falls into a zone of heat more than 10,000 degrees Fahrenheit. "We didn't want to do it like everybody else," said Leo Cordeiro, the county's solid waste director. "We knew there were better ways." No emissions are released during the closed-loop gasification, Geoplasma says. The only emissions will come from the synthetic gas-powered turbines that create electricity. Even that will be cleaner than burning coal or natural gas, experts say. Few other toxins will be generated, if any at all, Geoplasma says.

But critics disagree. “We've found projects similar to this being misrepresented all over the country," said Monica Wilson of the Global Alliance for Incinerator Alternatives. Wilson said there aren't enough studies yet to prove the company's claims that emissions will likely be less than from a standard natural-gas power plant. She also said other companies have tried to produce such results and failed. She cited two similar facilities run by different companies in Australia and Germany that closed after failing to meet emissions standards. "I think this is the time for the residents of this county to start asking some tough questions," Wilson said.

Bruce Parker, president and CEO of the Washington, D.C.-based National Solid Wastes Management Association, scoffs at the notion that plasma technology will eliminate the need for landfills. "We do know that plasma arc is a legitimate technology, but let's see first how this thing works for St. Lucie County," Parker said. "It's too soon for people to make wild claims that we won't need landfills." Louis Circeo, director of Georgia Tech's plasma research division, said that as energy prices soar and landfill fees increase, plasma-arc technology will become more affordable. "Municipal solid waste is perhaps the largest renewable energy resource that is available to us," Circeo said, adding that the process "could not only solve the garbage and landfill problems in the United States and elsewhere, but it could significantly alleviate the current energy crisis." He said that if large plasma facilities were put to use nationwide to vaporize trash, they could theoretically generate electricity equivalent to about 25 nuclear power plants.

Americans generated 236 million tons of garbage in 2003, about 4.5 pounds per person, per day, according to the latest figures from the Environmental Protection Agency. Roughly 130 million tons went to landfills -- enough to cover a football field 703 miles high with garbage. Circeo said criticism of the technology is based on a lack of understanding. "We are going to put emissions out, but the emissions are much lower than virtually any other process, especially a combustion process in an incinerator," he said. Circeo said that both plants operating in Japan, where emissions standards are more stringent than in the U.S., are producing far less pollution than regulations require.

"For the amount of energy produced, you get significantly less of certain pollutants like sulfur dioxide and particulate matter," said Rick Brandes, chief of the Environmental Protection Agency's waste minimization division. Geoplasma expects to recoup its $425 million investment, funded by bonds, within 20 years through the sale of electricity and slag. "That's the silver lining," said Hillestad, adding that St. Lucie County won't pay a dime. The company has assumed full responsibility for interest on the bonds. County Commissioner Chris Craft said the plasma process "is bigger than just the disposal of waste for St. Lucie County. It addresses two of the world's largest problems -- how to deal with solid waste and the energy needs of our communities," Craft said. "This is the end of the rainbow. It will change the world."

Back to the Atmosphere

TABLE 3-2

Major Constituents of Earth's Atmosphere Today

Name and Chemical Symbol	*Concentration (% by volume)*
Nitrogen, N_2	78
Oxygen, O_2	21
Argon, Ar	0.9
Water vapor, H_2O	0.00001 (South Pole)–4 (tropics)
Carbon dioxide, CO_2	0.037*

*In 2002

Compare to Table 1.1 of text

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Variations in abundances of gases with their lifetimes (or ‘residence time’)

Recall that the ‘lifetime’ of a compound is defined as the ratio of the size of the reservoir with the loss rate (or, equivalently, the production rate, if the reservoir is in steady-state).

Junge (1974) noted that the variability of atoms and compounds in the earth’s atmosphere varied ~monotonically with lifetime. By looking at a variety of compounds with widely varying abundances and distributions in the atmosphere he developed the following simple formula relating the variability of a gas with the lifetime in the atmosphere (i.e. how long the molecules spend in the atmosphere before being incorporated into another form, such as dissolved in the oceans, taken up by vegetation, destroyed by reactions, etc.).

$$RSD = 0.14\ \tau^{-1}$$

RSD = “relative standard deviation”, a measure of variability in the atmosphere
τ = approxomate lifetime in years

Junge, C.E., Residence time and variability of tropospheric trace gases, *Tellus*, *26*, 477-488, 1974.

Here is an example of some measurements of the variability of different short-lived hydrocarbons versus their lifetimes

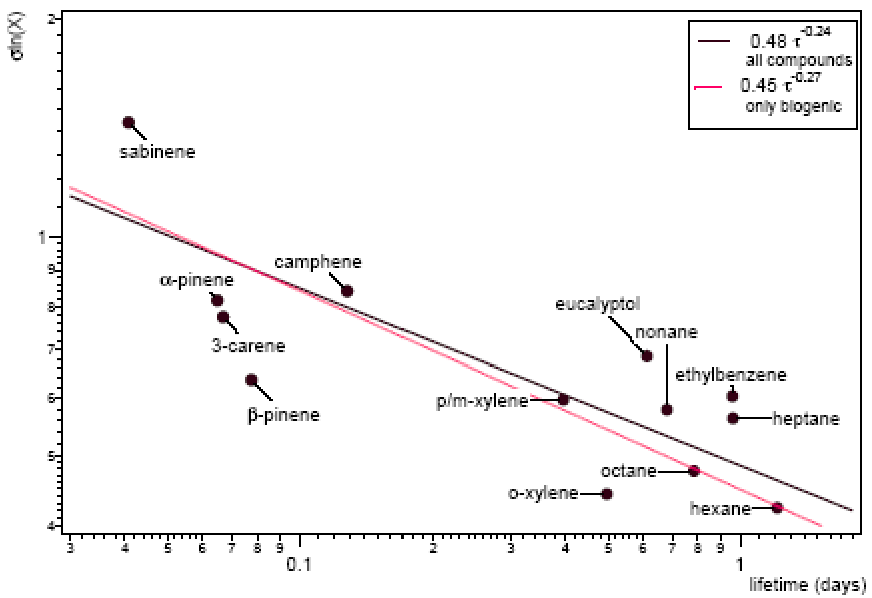

Fig. 6. Logarithmic graph showing the variability of measured short-lived VOCs. The black line is a fit through all VOCs, the dotted line with biogenically emitted compounds only. Assumed concentration for HO is 1.7×10^{6} molecules cm^{-3} (0.071 pmol mol^{-1}) and for O_3 1.0×10^{12} molecules cm^{-3} (42.0 nmol mol^{-1}).

In-situ measurement of reactive hydrocarbons at Hohenpeissenberg with comprehensive gas chromatography (GCxGC-FID): use in estimating HO and NO_3

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Chemical ‘roles’ of gases

Major constituents

N_2 (nitrogen) – contains an important element for life, but is very inert, so N is limiting. Ultimate source for nitrogen oxides (NO, NO_2, … HNO_3) from lightning and ammonia (NH_3) from *nitrogen-fixing* bacteria. From the early outgasing period

More on nitrogen a bit later…

O_2 (oxygen) – precursor for critical species like ozone (O_3), nitrogen oxides, organic acids (CH_3OOH). Produced by photosynthesis in the consumption of CO_2 to make green plants.

What do you suppose would happen to atmospheric O_2 if we were to burn all the plant material on the surface of the earth?

Chemical ‘roles’ of gases

What do you suppose would happen to atmospheric O_2 if we were to burm all the plant material on the surface of the earth?

Chemical ‘roles’ of gases

O_2 (oxygen)

What do you suppose would happen to atmospheric O_2 if we were to burm all the plant material on the surface of the earth?

Atmospheric oxygen would drop 0.03%…

Why not 100%?

Chemical ‘roles’ of gases

Ar – nothing much to tell us, except that we can learn something about the history of the atmosphere and the rate of radioactive decay in the lithosphere, especially if we examine it’s isotopes – $^{40}K \rightarrow {}^{40}Ar$…see page 24

Minor gases

TABLE 3-3

Important Atmospheric Greenhouse Gases

Name and Chemical Symbol	***Concentration (ppm by volume)***
Water vapor, H_2O	0.1 (South Pole)–40,000 (tropics)
Carbon dioxide, CO_2	370
Methane, CH_4	1.7
Nitrous oxide, N_2O	0.3
Ozone, O_3	0.01 (at the surface)
Freon-11, CCl_3F	0.00026
Freon-12, CCl_2F_2	0.00054

Chemical ‘roles’ of gases

H_2O

Besides the hydrologic cycle?

$$H_2O + O(^1D) \rightarrow OH + OH$$

O *singlet* D (means that the electrons in the oxygen atom have opposite spins, which is not the most stable configuration. The ground state of oxygen is called triplet, where the two spins are in the same direction). We’ll hear more about this species later

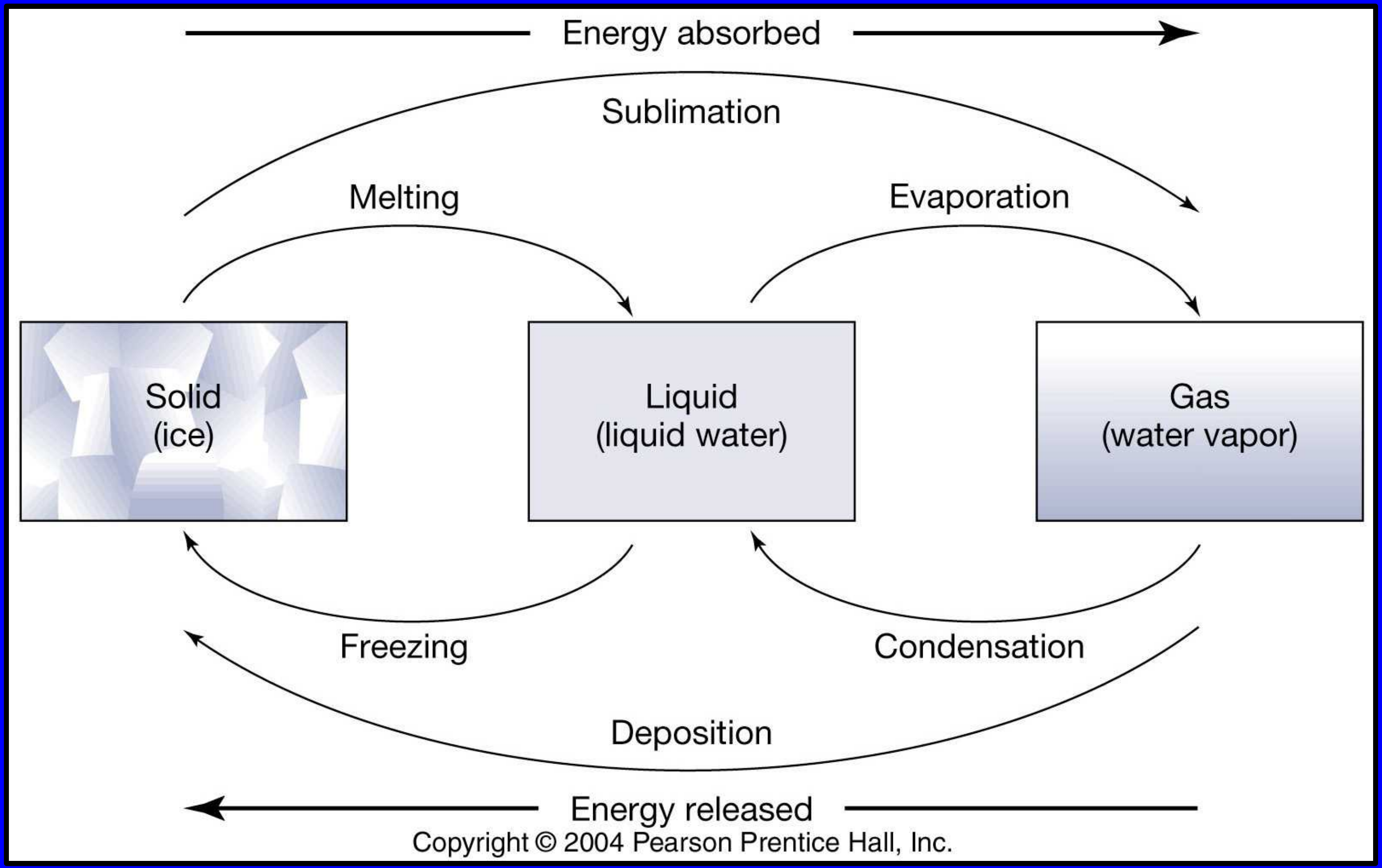
OH, or the *hydroxyl* radical, is the main oxidant in the atmosphere, reacting with many species to form compounds that eventually are scavenged out by particles and rain

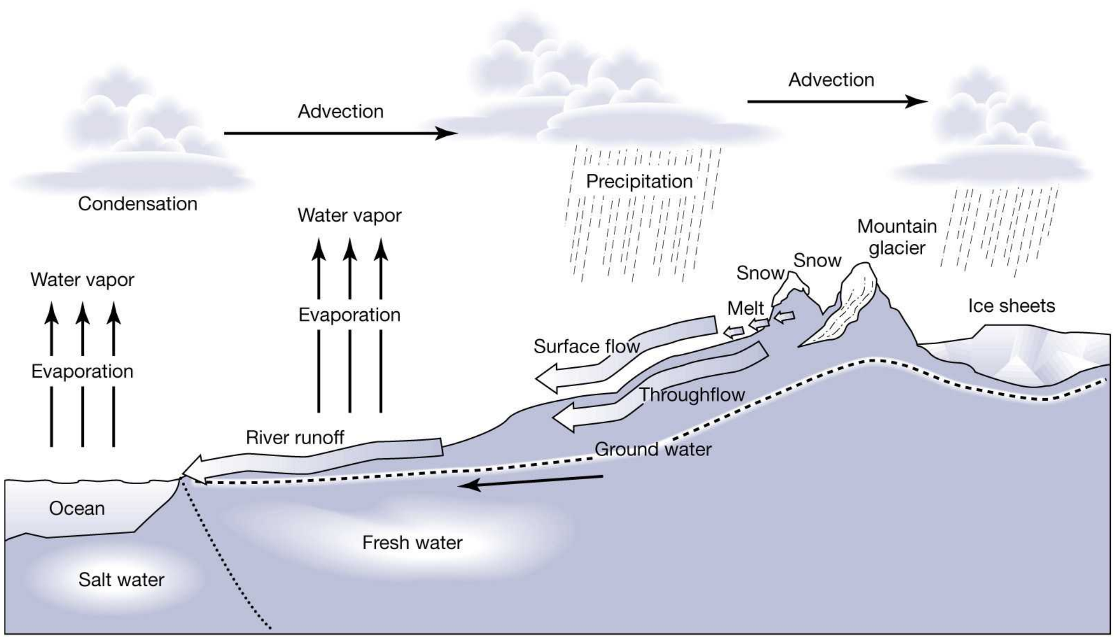
Chemical ‘roles’ of gases

H_2O

Water molecules serve as a cage that can surround and isolate charged spcecies (e.g. ions) in solution, thereby *dissolving* them. Of course, this often results in acid precipitation.

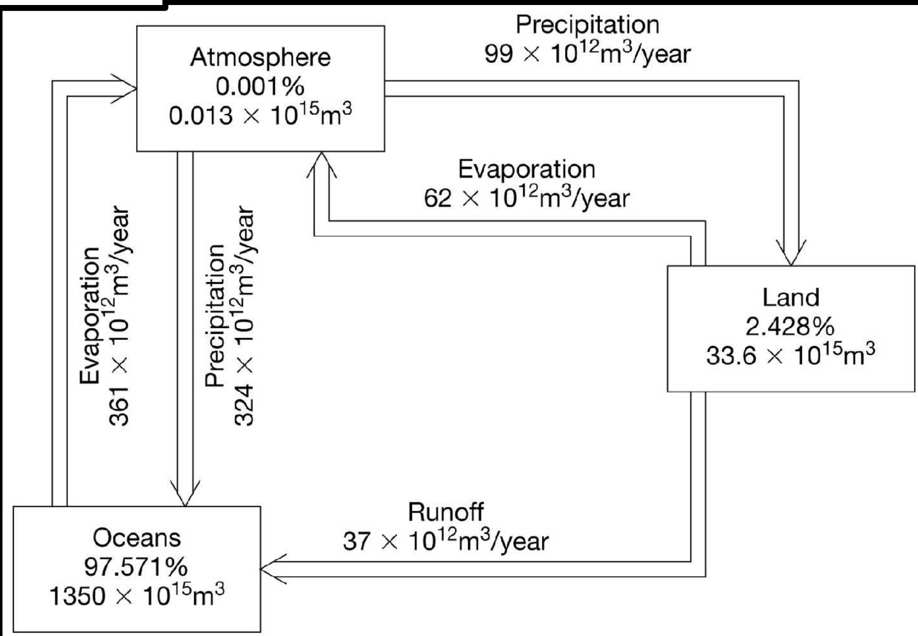
Three phases of water





(a)

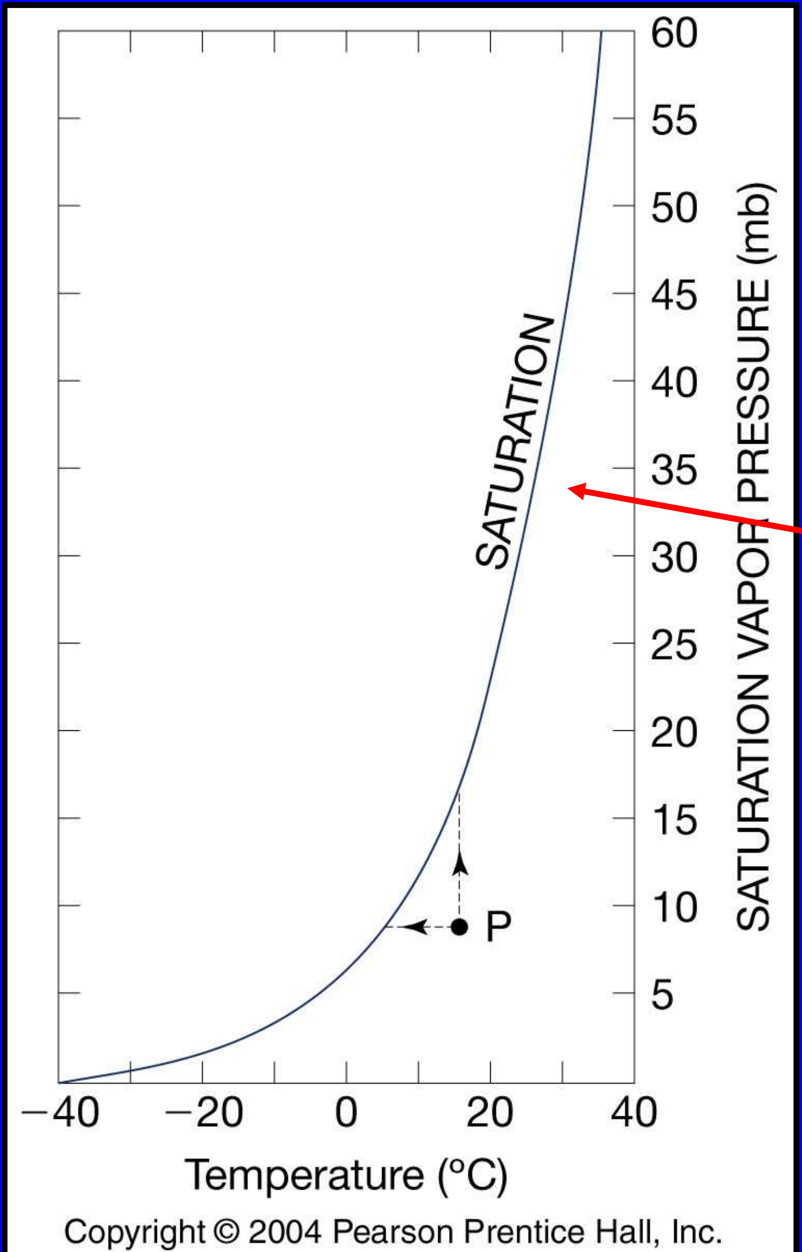
The hydrologic cycle



(b)

Water vapor pressure

(Clausius Clapeyron curve)



warmer air can hold more water vapor

Chemical ‘roles’ of gases

CO_2

Carbon dioxide, at 380 parts per million, is one of the most important anthropogenic greenhouse gases on Earth (remember, water is the most important greenhouse gas)

It is relatively inert chemically, but does dissolve in water to form carbonic acid that plays a bit of a role in ion chemistry. That chemistry is especially important in seawater (e.g. formation of shells…calcium carbonate

Important in photosynthesis

Public Doesn't Understand Global Warming
(ENN Full Story)

August 16, 2006 — By Dr. David Suzuki, David Suzuki Foundation

Have you ever been to a focus group? They're very odd. Often used in marketing research, these small selections of randomly chosen people are brought together as a sampling of public opinion to gauge how folks feel about a particular product or issue. Recently, my foundation conducted a focus group about global warming to see where people are at in their understanding of this complex and challenging problem. The results? Let's just say they were disconcerting, to say the least. Simply put, most people don't have a clue. The majority felt that global warming was a pretty important problem and they were concerned about it. But when pressed as to why it was a problem or what caused the problem, all heck broke loose. Apparently, according to the average Joe, global warming is happening because we've created a hole in the ozone layer, allowing the sun's rays to enter the atmosphere and heat up the earth -- or something like that. The cause of the problem is cars, or airplanes, or aerosol cans. No one really knows for sure.

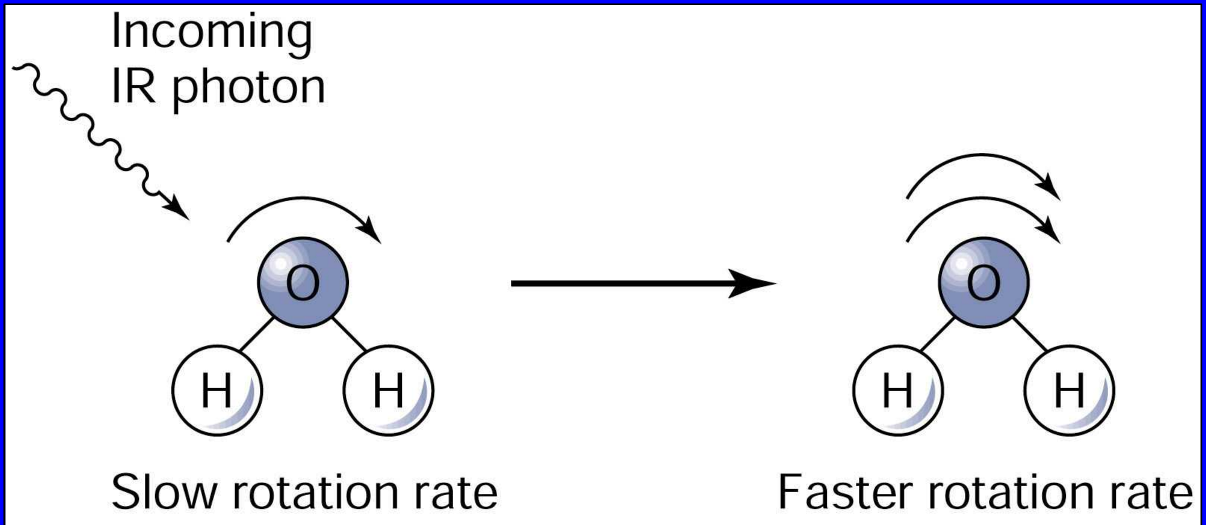
This is really quite remarkable. I would have thought that such confused understandings of the issue would have been commonplace five or six years ago, but with global warming being in newspapers on practically a daily basis this spring, on the front cover of magazines, in theatres (*An Inconvenient Truth*), and a hot political issue as well, surely people would get it by now. Apparently I was wrong. People don't get it. This is a big problem, because if people don't get it, then they don't really care, so politicians and CEOs don't really care, and status quo rules the day. And blindly we march into the sunset. But while science magazines are all talking about carbon sequestration and climate-forcing mechanisms, the average person is still trying to decipher the nature of the problem itself. True, few citizens need to understand the complicated nuances of atmospheric science or the various mechanisms of the Kyoto Protocol, but people cannot care about things they do not understand. If our leaders are to take the issue seriously, the public must have at least a basic understanding of it.

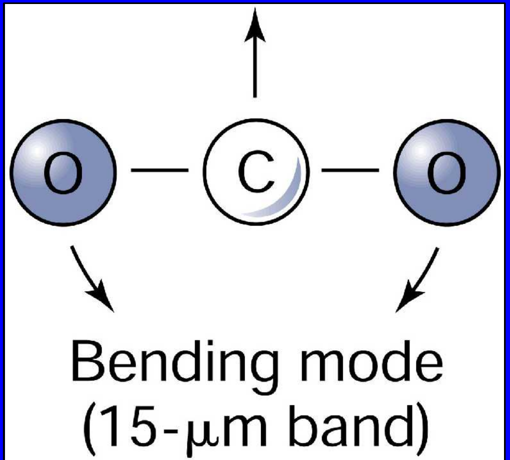
So, to clarify

-- the ozone layer is a part of the atmosphere way up high that helps shield the earth from the sun's most harmful rays. A couple of decades ago, scientists realized that some of the chemicals we were using in our industries and homes were finding their way into the upper atmosphere, reacting with the ozone and destroying it. Scientists were concerned that if this continued, it would thin the vital protective layer, leading to increased skin cancers and crop damage. They sounded the alarm bell, the international community responded with the Montreal Protocol to phase out ozone-depleting substances, and today the ozone layer is gradually healing itself.

Global warming is a quite different phenomenon. Again, it's a human-made problem, but this time it's due to the heat-trapping gases we are putting into the atmosphere from our industries, cars and homes. These gases act like a blanket, keeping more heat near the earth's surface. More heat also means more energy in the atmosphere, which means more frequent or severe extreme weather events like droughts, storms and floods. With each new piece of research, the expected effects of global warming become clearer, more urgent and more disturbing. Scientists say this will be one of the biggest challenges humanity will face this century. Right now we are not tackling the issue fast enough or direct enough to escape the most severe consequence. So if you understand what global warming is, and what it isn't, please tell your friends. Please speak up and help ensure that we don't continue to grope blindly into the future, searching in the darkness for a light switch. Because at this rate, by the time we finally reach it, it may no longer work.

How molecules interact with infrared light





How absorption of infrared light emitted by the earth varies with wavelength

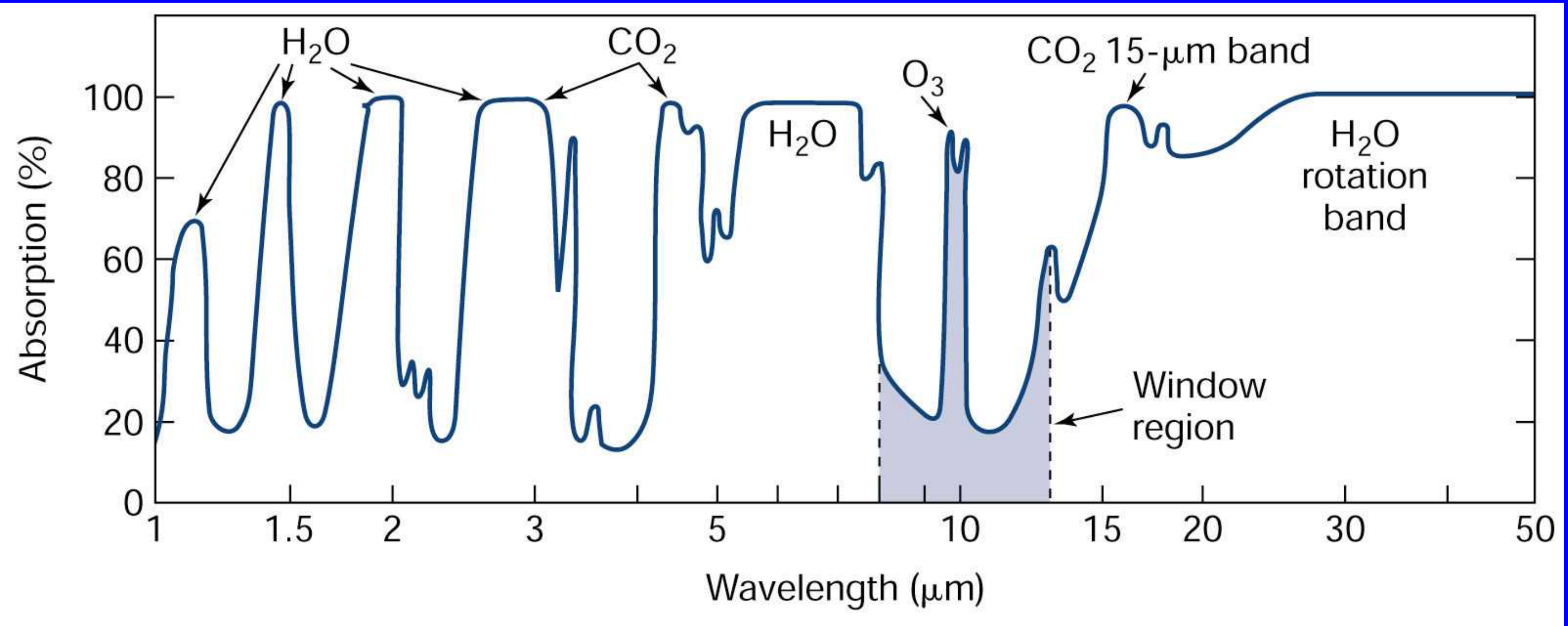
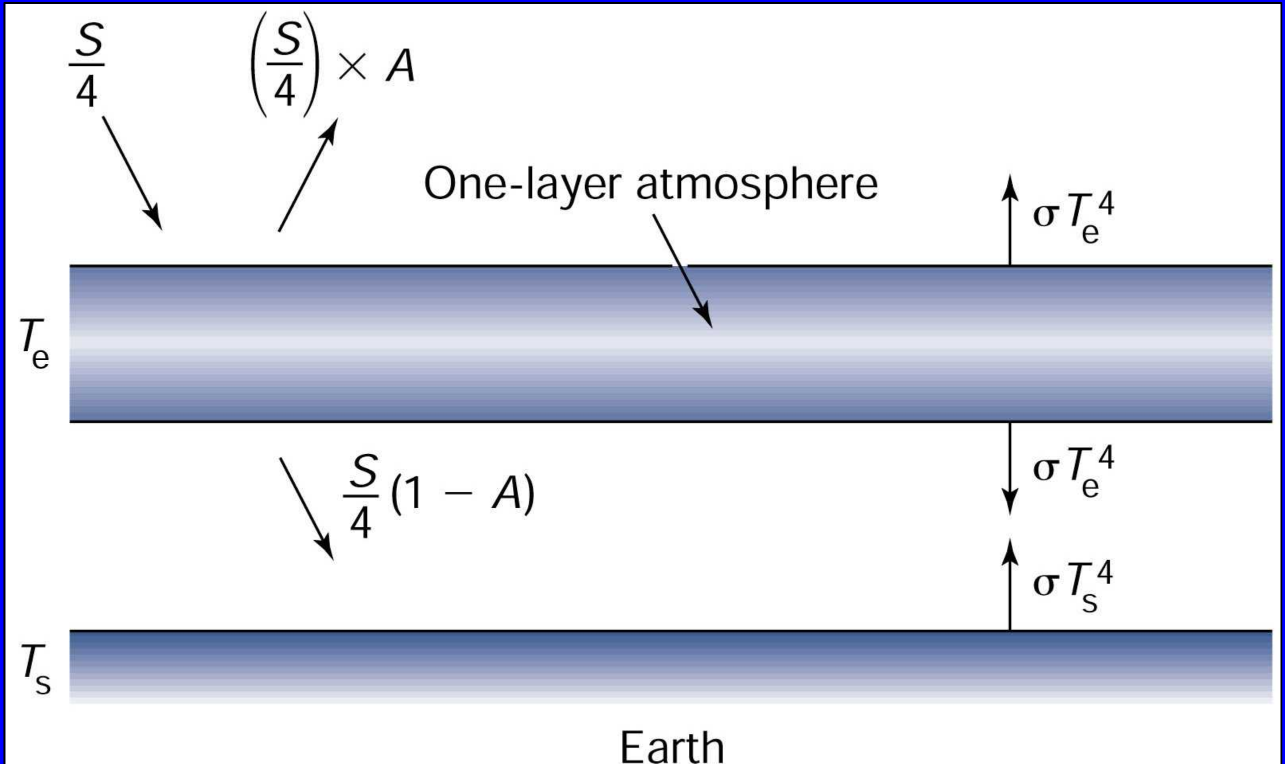


Fig. 3.13

The Layer Model



Chemical ‘roles’ of gases

CH_4

Methane, at 1.8 parts per million, is the second most important anthropogenic greenhouse gas on Earth. Although it is 1/50 the abundance of CO_2, it absorbs in a region of the infrared that is relatively transparent, so it blocks that radiation from exiting to space (we call that region a *window*)

Abundance expected in balance with 21% O_2 is approximately 10^{-148} ppb (would be oxidized to CO_2) – so must be a major source, in this case biological (microbes)

Reacts readily with OH, such that its residence time is relatively short compared to the major gases (about 9 yr)

Stratospheric Sulfur Could Stall Global Warming
September 15, 2006 — By Deborah Zabarenko, Reuters

WASHINGTON — To stall global warming for 20 years, one climate scientist Thursday proposed lobbing sulfur dioxide into the stratosphere, which would work in concert with cuts in greenhouse gas emissions. The sulfur dioxide, a pollutant on Earth, would form sulfate aerosol particles to shade the planet, much as the ash clouds from a major volcanic eruption do, said Tom Wigley of the National Center for Atmospheric Research. Wigley used computer models to determine that injecting sulfate particles at intervals from one to four years would have about the same cooling power as the 1991 eruption on Mount Pinatubo in the Philippines. His research, published in the journal *Science*, indicates this approach would work together with cutting emissions of greenhouse gases, which are produced by the burning of fossil fuels.

The idea of injecting sulfates into the stratosphere, some 10 miles above the Earth's surface, was first proposed and quickly rejected three decades ago as a dangerous tinkering with natural processes. But Wigley said he was prompted to pursue this angle when Paul Crutzen, a Nobel-winning atmospheric chemist, recently suggested a new look at the notion of geoengineering, as this notion is known.

COST-EFFECTIVE? "I'm not suggesting we don't reduce our dependence on fossil fuels for energy," Wigley said in a telephone interview. "I think that that's the only long-term solution to the problem of global warming, we definitely have to do that. "But ... can we make it economically and technologically easier by doing something that's also technology, which may be cost-effective?"

It would not be cheap, according to Wigley's estimates. The most sensible way to get sulfur dioxide into the stratosphere would be to send numerous planes -- more than the world's current commercial airline fleet -- to take it there. This might cost hundreds of millions of dollars, he said. The sulfur dioxide would form small sulfuric acid aerosol droplets. Another method to get these aerosols into the air is the possible addition of sulfur compounds to airplane fuel, which would then form sulfur dioxide, Wigley said. On Earth, sulfur dioxide contributes to respiratory illness, aggravates heart and lung disease and contributes to acid rain. Power plants and other factories are the biggest producers. But Wigley said the amount of sulfur dioxide needed for the geoengineering project would probably cause negligible pollution down on Earth's surface, because his model called for less than 10 percent additional sulfur dioxide than is emitted by the burning of fossil fuels. The technology exists now to put this plan into effect, but studies of economic feasibility are needed, he said. It has the potential to stall global warming for 20 years, to buy time for solutions to the problem, according to Wigley. "We've got to consider it very seriously because otherwise we might be in for much worse things just due to emission of carbon dioxide and other greenhouse gases," he said.

Aerosols

(suspension of particles in air)

For now, note that there are three main 'modes' of particles suspended in air

- *Course* mode – particles larger than about 1 micrometer (μm) in diameter. Usually suspended by mechanical processes (e.g. windblown dust)

- *Fine* mode – particles between ~0.05-1 μm. Also called accumulation mode. Usually produced by condensation of water and other volatile materials on smaller particles (something like condensation, but better called *deliquescence* when water and sticking and dissolution on when talking about other species. This mode is responsible for *haze* (e.g. poor visibility).

Aerosols

(suspension of particles in air)

Ultrafine mode – smaller than 0.05 μm, formed exclusively from condensation (e.g. new particle growth). *Condensation nuclei* (CN) are particles that are particularly good at aiding in the formation of larger particles, and *cloud condensation nuclei* (CCN) are particles that eventually form water droplets. Usually small particles (~ few nm) form by homogeneous nucleation ("out of gas phase into liquid phase") of low-volatility gases like sulfuric acid, ammonia, and nitric acid. This typically requires neutralization (that is, positive charges, other than water, equal negative charges).

Aerosols – what they do

Scavenge materials out of the atmosphere – ultimately, raining them out. Organics (hydrocarbons), soot, acids, bases, salts, just about everything that can't be broken down to O_2, N_2, CO_2, H_2O

Absorb and scatter sunlight, and radiate heat, thereby affecting radiative balance – changing the albedo and alterting the distribution of heating throughout the atmosphere (e.g. haze, smoke and soot).

Provide surfaces for chemical reactions that do not occur in the gas-phase (*heterogeneous* reactions).

Transport of nutrients

China proposes plan to curb emissions

Trading scheme could finally lower sulphur dioxide levels.

David Cyranoski

China is renewing its promise to reduce sulphur dioxide emissions, with a plan that would see power plants paying for, and trading, the right to emit the pollutant. A similar trading market in the United States, established under the country's Environmental Protection Agency, has had a huge impact, reducing emissions of the acid-rain-causing gas by 31% between 1993 and 2002.

So far, China's attempts to lower pollution emissions have failed, according to a government report released on 26 August. Instead of the 10% sulphur dioxide reduction they had planned for 2001 to 2005, emissions jumped up 27% over this period.

That makes China the world's largest sulphur dioxide emitter, pumping out 25.5 million tonnes of the gas in 2005 (compared to US emissions of roughly 15 million tonnes). According to Xinhua News Service, the official government news provider, one-third of the country "was bathed in acid rain last year". The State Environmental Protection Agency estimated RMB500 billion (US$63 billion) in related economic losses.

Now the country is taking a shot at a revised goal, hoping to reduce emissions by 10% from 2006 to 2010. Cutting sulphur dioxide emissions could have a warming effect on the planet — these particles currently reflect sunlight back into space. But fears about respiratory and cardiovascular disease, ecological impact, and harm to crops are deemed to outweigh this concern.

Chemical ‘roles’ of gases

CH_4

Photochemically active – producing ozone and CO

$$CH_4 + OH \rightarrow CH_3 + H_2O$$

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M$$

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2$$

$$CH_3O + O_2 \rightarrow CH_2O + HO_2$$

$$HO_2 + NO \rightarrow OH + NO_2$$

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Chemical 'roles' of gases

CH_4

Photochemically active – producing ozone and CO

$CH_4 \rightarrow H_2O$

$O_2 \rightarrow$

$NO \rightarrow NO_2$

$O_2 \rightarrow CH_2O$

$NO \rightarrow NO_2$

$CH_4 + 2NO + 2O_2 \rightarrow CH_2O + 2NO_2 + H_2O$

Chemical 'roles' of gases

CH_4

$$NO_2 + h\nu \rightarrow NO + O(^3P)$$

$$O + O_2 + M \rightarrow O_3 + M$$

$$CH_4 + 2NO + 2O_2 \rightarrow CH_2O + 2NO_2 + H_2O$$

$2O_3$

Chemical 'roles' of gases

CH_4

$$NO_2 + h\nu \rightarrow NO + O$$

$$O + O_2 + M \rightarrow O_3 + M$$

$$CH_4 + 4O_2 + h\nu \rightarrow CH_2O + 2O_3 + H_2O$$

Chemical ‘roles’ of gases

CH_4

$CH_2O + OH \rightarrow HCO + H_2O$

$HCO + O_2 \rightarrow HO_2 + CO$

$HO_2 + NO \rightarrow OH + NO_2$

$CH_4 + 4O_2 + h\nu \rightarrow CH_2O + 2O_3 + H_2O$

$\searrow$

CO

$$CH_4 + 5O_2 + h\nu \rightarrow CO + 3O_3 + 2H_2O$$

Atmospheric oxidation – also like incomplete combustion

occurs at low temperature, unlike a flame

From IUPAC (International Union of Pure and Applied Chemistry)

mixing ratio (in atmospheric chemistry)

In meteorology, the dimensionless ratio of the mass of a substance (such as water vapour) in an air parcel to the mass of the remaining substances in the air parcel. For trace substances, this is approximated by the ratio of the mass of the substance to the mass of air. However, in the case of water vapour the mass of dry air is used. In atmospheric chemistry, mixing ratios (molecular, molar, by volume, as well as by weight) are used to describe relative concentrations of atmospheric trace gases and impurities.