Environmental Aspects of Energy Production and Use

Mechanical Engineering 694C

Seminar in Energy Resources, Technology and Policy

Larry Caretto

September 11, 2001

California State University
Northridge

Remind students to turn in homework.

Hand out sign up sheet for student information. Please give your email and work phone. Also indicate if you want either of these items on the course web page.

Reading for this week is pages 226-234, 242-263 and 267-277 in Fay and Golomb.

Problems for this week, due next week: 9.1, 9.2, 9.4, and 9.9 in Fay and Golomb.

Also for next week: look at the EIA or USEPA web site to obtain the most recent data for emissions from electric power generation.

Main Ideas

- Multimedia impacts
  - Air pollution
  - Water pollution and ocean spills
  - Solid waste
- Impacts occur in extraction, refining, transportation, distribution and use
- Major impact is in air pollution
- Preliminary global warming discussion

California State University
Northridge

The impacts that energy production and use have on the environment start with the extraction of the basic resource. The mining of coal and uranium and the drilling and extraction of oil and natural gas.

Some energy resources, such as coal or natural gas, have minimal refining. Crude oil undergoes extensive refining to produce a range of produces that are used.

Both the initial fuel resource and refined products are transported by a variety of means. These include ships (for crude oil and petroleum products and some coal), rail (coal and some petroleum products), pipelines (crude oil, petroleum products, natural gas, and coal slurry), and trucks for local delivery of energy products to homes, commercial locations and retail gasoline distribution. Transportation has the possibility of accidental spills especially from tanker spills and pipeline ruptures.

Oil refinery processes also have a potential for accidents that can affect the environment, however the greatest potential for accidents comes from chemical plants that are preparing toxic compounds such as pesticides.

Electric power lines are another way of transporting energy from one point to another. This power transmission can remove the emissions associated with power production away from the point where the power is used. It can also remove the threat of accidents from nuclear power plants away from urban areas.

Much of these notes will examine air pollution which is the major environmental impact from energy production and use.

We will only have a preliminary discussion of global warming. An extensive discussion will be presented later in the course.

Air Pollution

- Most of energy production and use is from fossil fuels
- Most air pollution comes from the combustion of fossil fuels
- Overall policy and deadlines governed by Federal Clean Air Act
- Regulations and enforcement a combination of federal, state and local efforts

California State University
Northridge

Fossil fuels form the major link between energy resources and air pollution. The majority of energy used in both the US and the world comes from fossil fuels. The combustion of these fossil fuels produces the majority of air pollution in both the US and the world.

The regulation of air pollution started in the 17th century when the King of England directed that certain smoky coals known as sea coals should not be burned in the City of London. Until the 1950s air pollution regulations were directed at the reduction of smoke and air pollution control was known as smoke prevention.

In the last century, there were two dramatic air pollution incidents in which air pollution led to increased mortality over a short time period. These occurred in the Muese Valley in Belgum in 1936 and in London in 1948. The main contaminants in these incidents were particulate matter and sulfur oxides. During the early 1940s air pollution started to appear in Southern California and experiments by Aarie Haagen-Smidt at Cal Tech during the 1950s showed that the main component of this pollution ozone which was formed in the atmosphere from reactions of hydrocarbons and oxides of nitrogen.

Although local and state efforts were made to control pollution and Federal Clean Air Act legislation was passed in 1955, 1963, and 1967, the first stringent Federal law as passed in the 1970 amendments to the clean air act. Amongst other provisions, these amendments directed the federal Environmental Protection Agency to issue criteria and standards for air pollutants that came from “numerous or diverse … sources.” Such pollutants have become known as criteria pollutants.

Air pollution legislation and regulations deal separately with criteria pollutants and with toxic air contaminants.

Air Pollutants

- Criteria Pollutants
  - Come from “numerous or diverse mobile or stationary sources”
  - EPA administrator sets national ambient air quality standards (NAAQS)
    - Primary standards, “allowing an adequate margin of safety, are requisite to protect the public health”
    - Secondary standards to “protect the public welfare”

California State University
Northridge

The EPA administrator sets two kinds of ambient standards: primary standards to protect public health and secondary standards to protect public welfare. The latter standards include such items as visibility, ecosystem damage, material damage, and agricultural crop losses.

States that exceed the NAAQS must prepare plans known as state implementation plans or SIPs to meet the standards. Primary standards must be met by a fixed deadline. There is no deadline for secondary standards.

Historically many areas of the country have been unable to meet the primary standards leading to revisions in the Clean Air Act in 1977 and 1990. Because of the problems in meeting primary standards there has been little emphasis on secondary standards.

One exception to this is the acid deposition program that was explicitly written into the Act with the 1990 amendments. This program is designed to reduce ecosystem damage caused by acidic gases that are deposited into lakes and other fragile ecosystems through rain or dry deposition. The main sources of acid deposition are from reactions in the atmosphere where of sulfur and nitrogen oxides form sulfuric and nitric acid.

List of Criteria Pollutants

- Ozone (formed in atmosphere)
- Sulfur dioxide (primary pollutant)
- Nitrogen dioxide (direct and secondary)
- Particulate matter (direct and secondary)
- Carbon monoxide (direct)
- Lead (direct)

California State University
Northridge

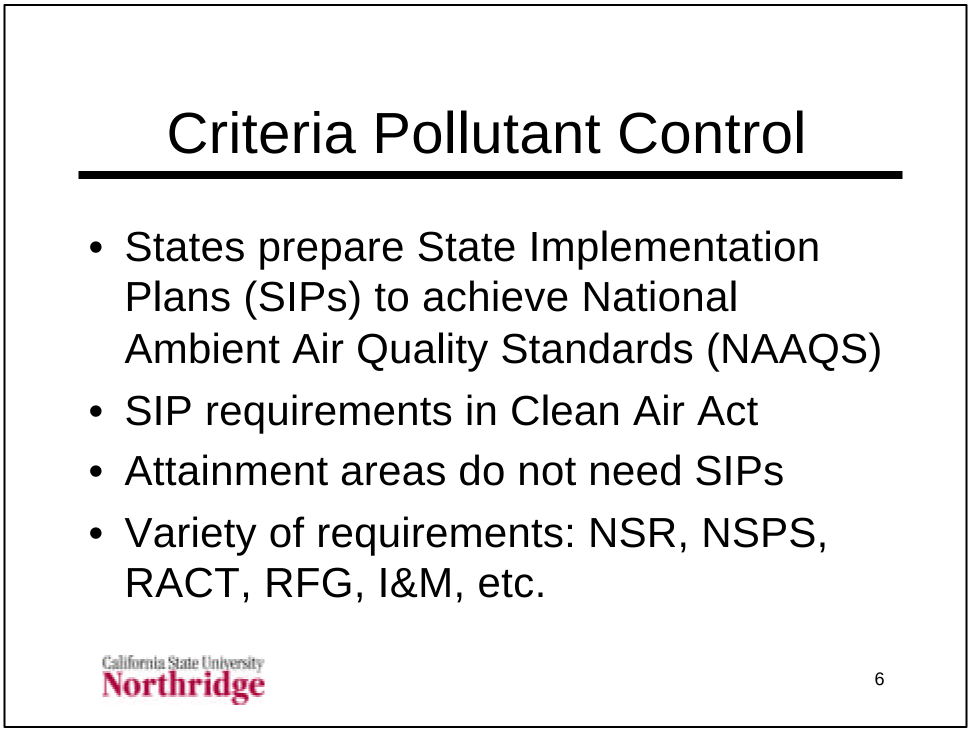
Ambient pollutants are either emitted directly from sources (so called primary pollutants) or formed by reactions in the atmosphere (so called secondary pollutants). Ozone is the main example of a secondary pollutant. It is formed by photochemical reactions between oxides of nitrogen and hydrocarbons typically called volatile organic compounds or VOCs.

Combustion sources emit two main oxides of nitrogen, nitric oxide, NO, and nitrogen dioxide, NO_2. The sum of these two compounds is written as NOx (and pronounced nocks.) The majority of the NOx emissions from combustion sources are NO. About 10% of the total NOx emissions are NO_2. However, NO can react to form NO_2 in the atmosphere. NO is not considered hazardous to health directly, but NO_2 is. Presently there are no areas in the US that exceed the NAAQS for NO_2.

Sulfur dioxide, SO_2, emissions come almost exclusively from the combustion of sulfur containing fuels. (Sulfur processing plants are an additional source of SO_2.)

The regulation of particulate matter is based on size of the particles. This is defined in terms of the mean aerometric diameter, the diameter of a sphere with equivalent drag characteristics. The NAAQS for particulate matter have changed from a standard for total suspended particulate matter (which has a mean aerometric diameter of 30 μm.) to the current standard for particulate matter with a mean aerometric diameter of 2.5 μm. (From about 1980 to 2000 the standard was for particulate matter with a mean aerometric diameter of 10 μm.) The finer particles are better able to penetrate deeper into the lung and have a greater impact on human health for this reason. In addition, finer particles tend to be those that have a greater chemical toxicity. Thus control of fine particles is thought to provide greater health protection. Particulate matter is directly emitted and is formed in the atmosphere from reactions of gaseous precursors.

CO and lead originate mainly from gasoline-powered automobiles. The elimination of lead from gasoline has eliminated lead as a pollution problem in almost all areas.



Criteria Pollutant Control

- States prepare State Implementation Plans (SIPs) to achieve National Ambient Air Quality Standards (NAAQS)
- SIP requirements in Clean Air Act
- Attainment areas do not need SIPs
- Variety of requirements: NSR, NSPS, RACT, RFG, I&M, etc.

California State University
Northridge

Since the 1970 amendments to the Act there have been several rounds of SIP submittals. SIPs that are prepared by states must be approved by EPA. To be approved the SIP must contain all the elements that Congress has required in the Act. In particular, it must show a plan of proposed regulations that will allow an area to meet the primary NAAQS by the required attainment date.

Among the various requirements are a preconstruction review and permit program for major new sources or major modifications to existing sources. This program is known as **N**ew **S**ource **R**eview or NSR. Permit programs are required in both attainment and nonattainment areas. In nonattainment areas the review must show that the new source will not degrade air quality. This requires the user to use equipment that achieves the **L**owest **A**chievable **E**mission **R**ate (LAER) and obtain emission reductions for other sources that are greater than the emission increases caused by the new source. In attainment areas, sources are required to use **B**est **A**vailable **C**ontrol **T**echnology which is less stringent than LAER.

Since the 1970 amendments to the Act, EPA has been required to set **N**ew **S**ource **P**erformance **S**tandards. These set minimum technology requirements for new sources.

In all SIPs states must include requirements that sources are retrofitted using **R**easonably **A**vailable **C**ontrol **T**echnology (RACT) as defined by EPA. Certain, more polluted, areas are required to use **r**e**f**ormulated **g**asoline (RFG).

States must implement vehicle **I**nspection and **M**aintenance (I&M) programs. There are two program levels, basic and enhanced. Enhanced programs, which are required in more polluted areas, test the vehicle under load. Basic programs use an idle test.

Stationary sources also have an operating permit program that is required under Title V of the 1990 amendments to the Act.

Toxic Pollutants

- 1970 amendments to the act called on EPA to control “hazardous air pollutants”
- Only seven were regulated by 1990
- In 1990 amendments to the Act, Congress specified 189 pollutants, one of which was subsequently removed from the list

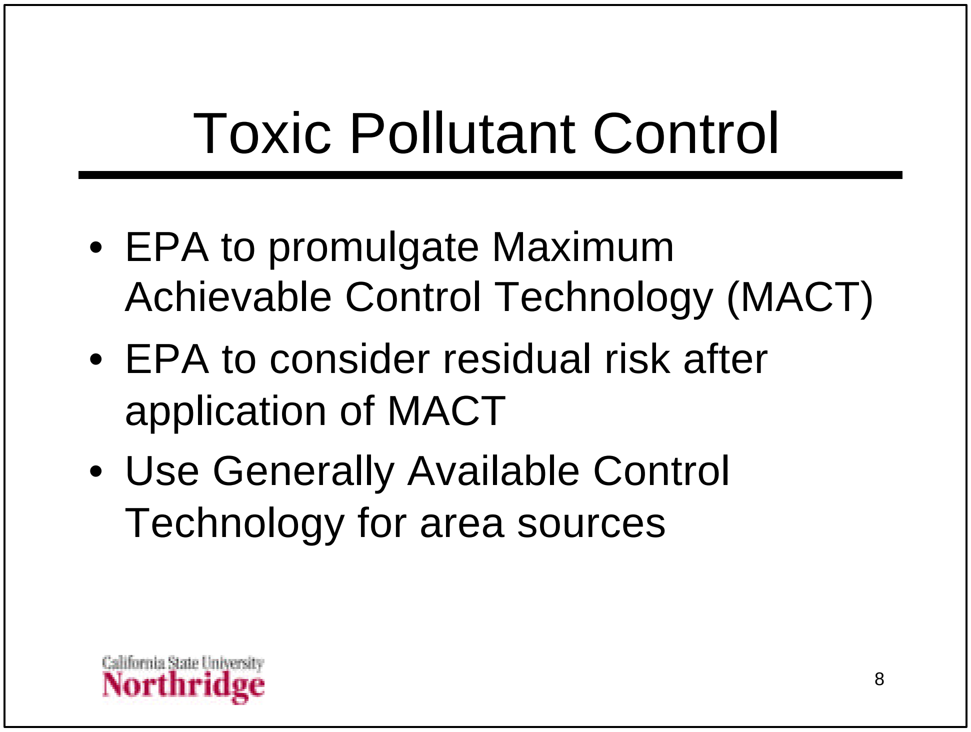
California State University
Northridge

In the 1970 amendments to the Act, hazardous or toxic pollutants were thought to be emissions that came from localized sources. This was in contrast to criteria pollutants that came from many and diverse sources. Thus hazardous pollutants were to be controlled under a separate regulatory scheme that did not make them part of SIPs or require NAAQS.

Another part of the reasoning for a separate control program was the idea that criteria pollutants have a threshold below which there are no health effects. Toxic pollutants, on the other hand, were considered to have no threshold. Thus toxic pollutants could not have a NAAQS that could be set with an adequate margin of safety. Recent research in standard setting has blurred the distinction between criteria pollutants and toxics in terms of health effects and the margin of safety.

The seven regulated toxic pollutants (under the program called NESHAPs for National Emission Standard for Hazardous Air Pollutants) were asbestos, benzene, beryllium, inorganic arsenic, mercury, radionuclides and vinyl chloride. The small number of regulated pollutants was due to the stringent requirements under the 1970 amendments for determining the risk of a hazardous pollutant prior to regulating it.

Noncancer risks are evaluated in terms of a reference concentration. This is an estimate (with uncertainty spanning perhaps an order of magnitude) of a continuous inhalation exposure to the human population (including sensitive subgroups which include children, asthmatics and the elderly) that is likely to be without an appreciable risk of deleterious effects during a lifetime. It can be derived from various types of human or animal data, with uncertainty factors generally applied to reflect limitations of the data used.(http://www.epa.gov/ttn/atw/nata/gloss1.html#hazardquotient)



Toxic Pollutant Control

- EPA to promulgate Maximum Achievable Control Technology (MACT)
- EPA to consider residual risk after application of MACT
- Use Generally Available Control Technology for area sources

EPA is required to establish Maximum Achievable Control Technology (MACT) standards for major sources that emit more than 10 tons per year of any listed HAP or 25 tons per year of a mixture of HAPs. For existing source categories, MACT standards must be at least as stringent as the degree of control achieved by the best-performing 12% of sources in source categories with more than 30 facilities, or by the best five sources in smaller source categories.

Standards may include operational improvements and implementation is done by individual states by permit requirements for the affected facilities.

Within eight years after a MACT standard is issued, EPA must assess the residual risk associated with the source category and issue additional standards adequate to provide an ample margin of safety to protect public health and, after considering costs and feasibility, the environment. EPA has begun residual risk assessments, but none have been completed.

EPA is also to set standards for area sources that require a lower level of controls. This level of control technology is known as GACT for generally available control technology.

Mobil sources have been found to he a major source of toxic emissions. These emissions include benzene, 1,3-butadiene, formaldehyde, acetaldehyde. EPA projects that future regulations to reduce VOCs form motor vehicles will reduce emissions of these toxic pollutants. Except for regulations to hold refineries to current levels of "overcompliance" with regulations for levels of toxic compounds in gasoline, EPA has proposed no further regulations on mobile source toxics.

List of Toxic Pollutants

- See notes for start of list
- Many compounds are listed here, but EPA is currently examining thirty compounds that contribute most of risk
- Toxic pollution was once associated with individual factories, but mobile sources produce a large amount of toxic pollutants

California State University
Northridge

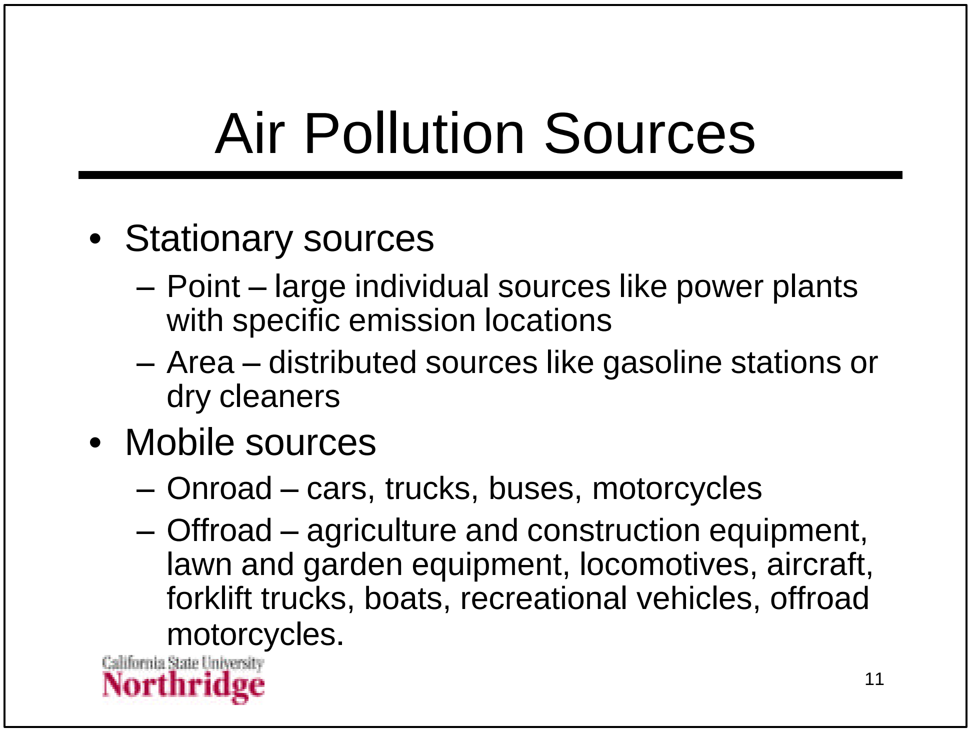
Acetaldehyde	Acetamide	Acetonitrile	Acetophenone	2-Acetylamino-fluorene
Acrolein	Acrylamide	Acrylic acid	Acrylonitrile	Allyl chloride
4-Aminobiphenyl	Aniline	o-Anisidine	Asbestos	Benzene (including
benzene from gasoline)		Benzidine	Benzotrichloride	Benzyl chloride
Biphenyl	Bis(2-ethylhexyl)phthalate (DEHP)		Bis(chloromethyl)ether	
Bromoform	1,3-Butadiene	Calcium cyanamide	Caprolactam	Captan
Carbaryl	Carbon disulfide	Carbon tetrachloride		Carbonyl sulfide
Catechol	Chloramben	Chlordane	Chlorine	Chloroacetic acid
2-Chloroacetophenone		Chlorobenzene	Chlorobenzilate	Chloroform
Chloromethyl methyl ether		Chloroprene	Cresols/Cresylic acid (isomers and mixture)	
o-Cresol	m-Cresol	p-Cresol	Cumene	2,4-D, salts and esters
DDE	Diazomethane	Dibenzofurans	1,2-Dibromo-3-chloropropane	
Dibutylphthalate	1,4-Dichlorobenzene(p)		3,3-Dichlorobenzidene	
Dichloroethyl ether (Bis(2-chloroethyl)ether)			1,3-Dichloropropen	Dichlorvos
Diethanolamine	N,N-Diethyl aniline (N,N-Dimethylaniline)			Diethyl sulfate
3,3-Dimethoxybenzidine		Dimethyl aminoazobenzene		3,3¬-Dimethyl benzidine
Dimethyl carbamoyl chloride		Dimethyl formamide	1,1-Dimethyl hydrazine	
Dimethyl phthalate	Dimethyl sulfate	4,6-Dinitro-o-cresol, and salts		2,4-Dinitrophenol
2,4-Dinitrotoluene	1,4-Dioxane (1,4-Diethyleneoxide)		1,2-Diphenylhydrazine	
Epichlorohydrin (l-Chloro-2,3-epoxypropane)			1,2-Epoxybutane	
Ethyl acrylate	Ethyl benzene	Ethyl carbamate (Urethane)		Ethyl chloride
(Chloroethane)	Ethylene dibromide (Dibromoethane)		Ethylene dichloride (1,2-Dichloroethane)	
Ethylene glycol	Ethylene imine (Aziridine)		Ethylene oxide	Ethylene thiourea
Ethylidene dichloride (1,1-Dichloroethane)			Formaldehyde	Heptachlor
Hexachlorobenzene		Hexachlorobutadiene		
Hexachlorocyclopentadiene		Hexachloroethane	Hexamethylene-1,6-diisocyanate	
Hexamethylphosphoramide		Hexane	Hydrazine	Hydrochloric acid
Hydrogen fluoride (Hydrofluoric acid)		Hydrogen sulfide	Hydroquinone	Isophorone
Lindane (all isomers)		Maleic anhydride	Methanol	Methoxychlor
Methyl bromide (Bromomethane)		Methyl chloride (Chloromethane)		Methyl chloroform (1,1,1-
Trichloroethane)	Methyl ethyl ketone (2-Butanone)		Methyl hydrazine	Methyl iodide
(Iodomethane)	Methyl isobutyl ketone (Hexone)		Methyl isocyanate	Methyl methacrylate

Toxic Pollutants Continued

- Remainder of list in notes
- Toxic compounds do not have NAAQS
- Risk factors for some compounds based on cancer risk
  - Cancers per million people per μg/m^3
- Other toxic compounds based on critical concentration

California State University
Northridge

Methyl tert butyl ether 4,4-Methylene bis(2-chloroaniline)
Methylene chloride (Dichloromethane) Methylene diphenyl diisocyanate (MDI) 4,4¬-Methylenedianiline
Naphthalene Nitrobenzene 4-Nitrobiphenyl 4-Nitrophenol 2-Nitropropane
N-Nitroso-N-methylurea N-Nitrosodimethylamine N-Nitrosomorpholine
Parathion Pentachloronitrobenzene (Quintobenzene) Pentachlorophenol
Phenol p-Phenylenediamine Phosgene Phosphine
Phosphorus Phthalic anhydride Polychlorinated biphenyls (Aroclors) 1,3-Propane sultone
beta-Propiolactone Propionaldehyde Propoxur (Baygon) Propylene dichloride (1,2-Dichloropropane)
Propylene oxide 1,2-Propylenimine (2-Methyl aziridine) Quinoline Quinone
Styrene Styrene oxide 2,3,7,8-Tetrachlorodibenzo-p-dioxin 1,1,2,2-Tetrachloroethane
Tetrachloroethylene (Perchloroethylene) Titanium tetrachloride Toluene
2,4-Toluene diamine 2,4-Toluene diisocyanate o-Toluidine
Toxaphene (chlorinated camphene) 1,2,4-Trichlorobenzene 1,1,2-Trichloroethane
Trichloroethylene 2,4,5-Trichlorophenol 2,4,6-Trichlorophenol
Triethylamine Trifluralin 2,2,4-Trimethylpentane Vinyl acetate
Vinyl bromide Vinyl chloride Vinylidene chloride (1,1-Dichloroethylene)
Xylenes (isomers and mixture) o-Xylenes m-Xylenes p-Xylenes
Antimony Compounds Arsenic Compounds (inorganic including arsine)
Beryllium Compounds Cadmium Compounds Chromium Compounds
Cobalt Compounds Coke Oven Emissions Cyanide Compounds
Glycol ethers Lead Compounds Manganese Compounds Mercury Compounds
Fine mineral fibers Nickel Compounds Polycylic Organic Matter
Radionuclides (including radon) Selenium Compounds



Air Pollution Sources

- Stationary sources
  - – Point – large individual sources like power plants with specific emission locations
  - – Area – distributed sources like gasoline stations or dry cleaners
- Mobile sources
  - – Onroad – cars, trucks, buses, motorcycles
  - – Offroad – agriculture and construction equipment, lawn and garden equipment, locomotives, aircraft, forklift trucks, boats, recreational vehicles, offroad motorcycles.

Source classifications are used both for control regulations and for determination of source emissions. The process of determining emissions from all sources is known as obtaining an emissions inventory. This process has large uncertainties and is based on the use of emission factors.

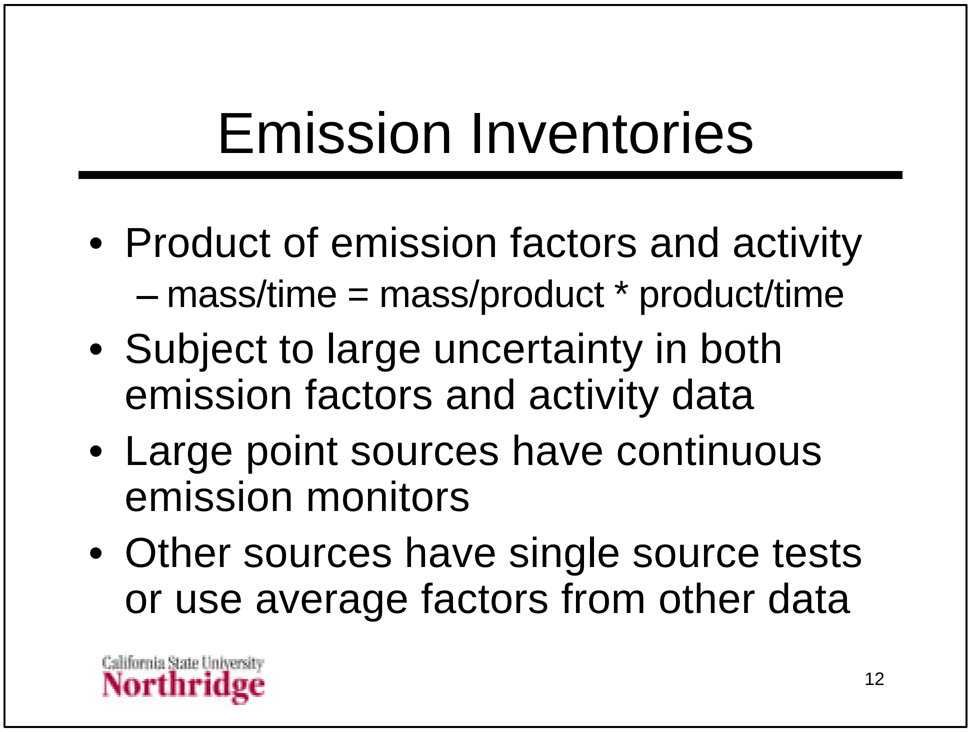
Regulations for stationary sources are usually set by state or local agencies. EPA has to approve regulations that are part of SIPs and may not approve regulations that are not stringent enough.

Mobile source regulations are done mainly by EPA. California is the only state that has the authority to set separate exhaust standards for mobile sources. States can regulate the fuel that is used by mobile sources and states are responsible for maintaining vehicle inspection and maintenance programs.

Emission controls for cars started in the 1960s with regulations that required crankcase ventilation gases to be recirculated back into the engine. Exhaust emission limitations started in California in 1966 and nationally in 1968. Controls on evaporation of fuel vapors from vehicles started in 1970.

Regulation of truck emissions started in the late 1970s and emission limitations on offroad sources started in 1990.

The sequence of regulation was based on the idea of starting on the largest problems first. As a result of the stringent control regulations, now and in the future, for cars and trucks, offroad sources are predicted to contribute an increasing amount to emissions.



Emission Inventories

- Product of emission factors and activity
  - – mass/time = mass/product * product/time
- Subject to large uncertainty in both emission factors and activity data
- Large point sources have continuous emission monitors
- Other sources have single source tests or use average factors from other data

California State University Northridge

The calculation of emission inventories is central to good air quality planning, regulation, and enforcement. Unfortunately, the calculation of inventories is fraught with uncertainties.

There are very few cases in which emissions are directly measured. Direct measurements are only required on large emission sources that use continuous emission monitors to obtain the mass emission rate of pollutants. In other cases emissions are estimated by emission factors that relate emissions to activity data that are more typically monitored.

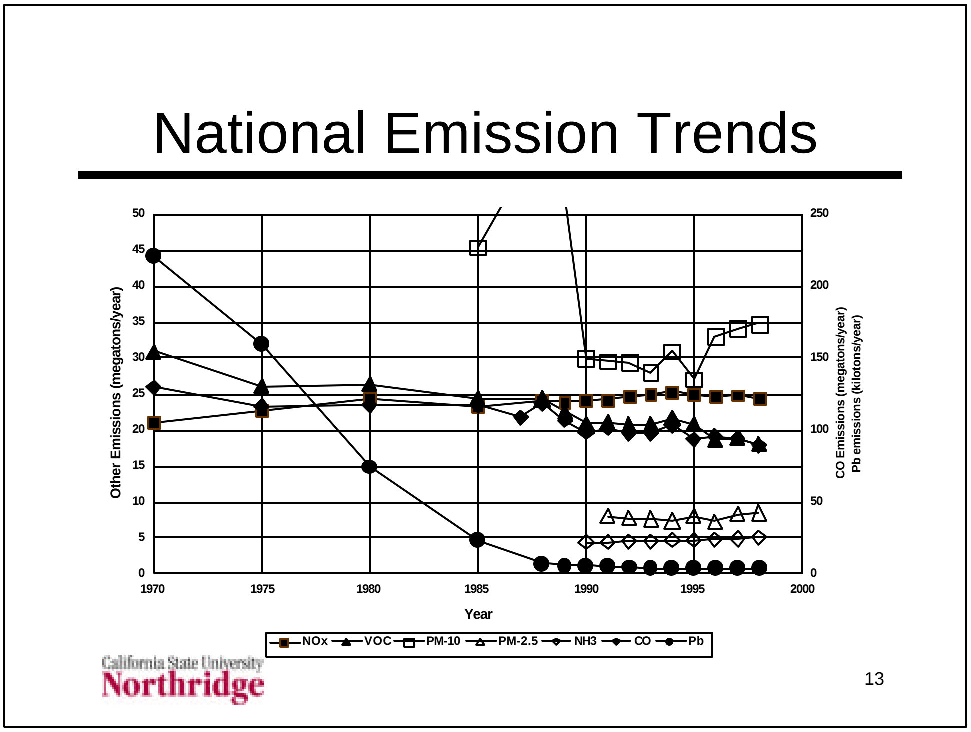
In combustion processes, many emission factors are linked to the heat input rate for the process. Since fuel flow rates are usually measured and the heating value of the fuel is reasonably well known, this provides an estimate of the emissions.

Obtaining emissions for all sources in a region, particularly a large urban region, can be a data collection nightmare, with the need to obtain data from a large number of sources.

Accurate emission factors account for the operating conditions since emissions factors for many processes can change with load.

As discussed below the link between emissions and ambient concentrations is based on air quality models. Such models require the knowledge of how emissions vary over space and time in a particular region. Obtaining this information increases the requirements for inventory collection.

Mobile source emission inventories are a particular problem These inventories (using programs such as EPA's MOBILE6 or California's EMFAC 2000) as based on measurements of a sample of operating vehicles. However, research has found that a large proportion of vehicle emissions comes from a small percentage of the population that are high emitters. Obtaining a good measure of the distribution of vehicles as normal or high emitters has proven difficult.



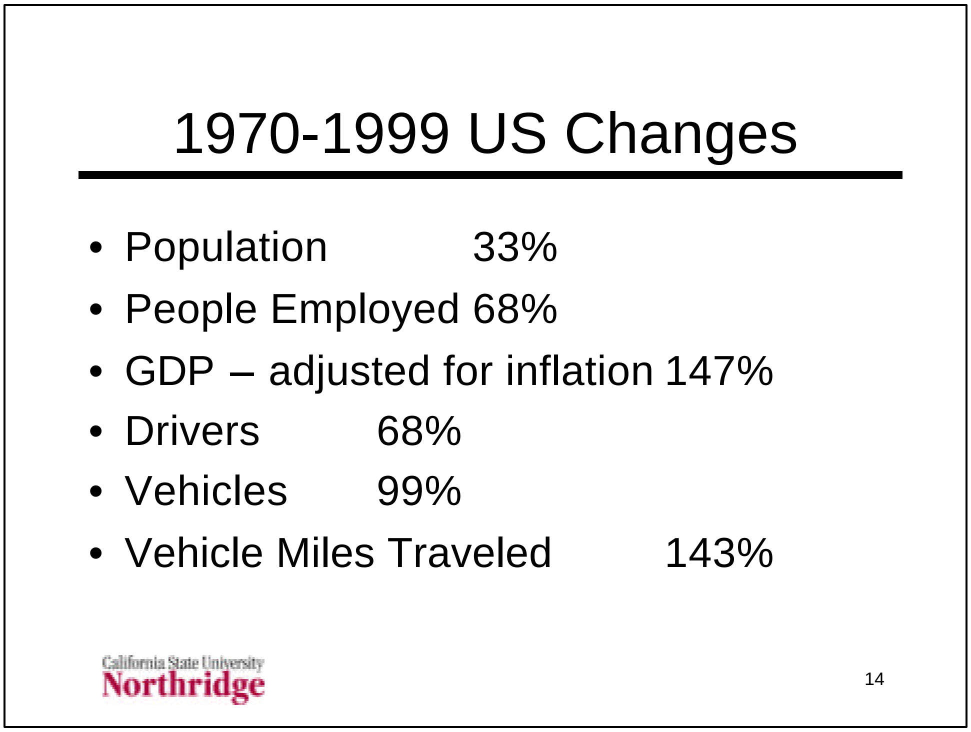
National Emission Trends

Despite all the caveats in the previous slide, emission inventories are produced and published. This chart shows the trends in national emissions between 1970 and 1998. Although significant reductions have been made in lead emissions, emissions of most other species have remained nearly constant.

National statistics are misleading. In some urban areas, like Los Angeles, significant reductions in emissions have occurred. However, in other areas emissions have increased. Thus the national emission trends look level, but the ambient air quality has improved in areas where it was particularly bad.

The graph above shows emissions for ammonia which is not regarded as a pollutant in its own right. However, ammonia can contribute to the formation of ammonium nitrate and ammonium sulfate what become particular matter. Although this role for ammonia has been known for several years, the potential need to control ammonia emissions has only been recently considered. Thus the inventory for this species starts in 1990.

The inventory for PM-2.5 is also relatively new; NAAQS for PM-2.5 were promulgated in 1997 and have become effective only recently following a court challenge to the original standards.



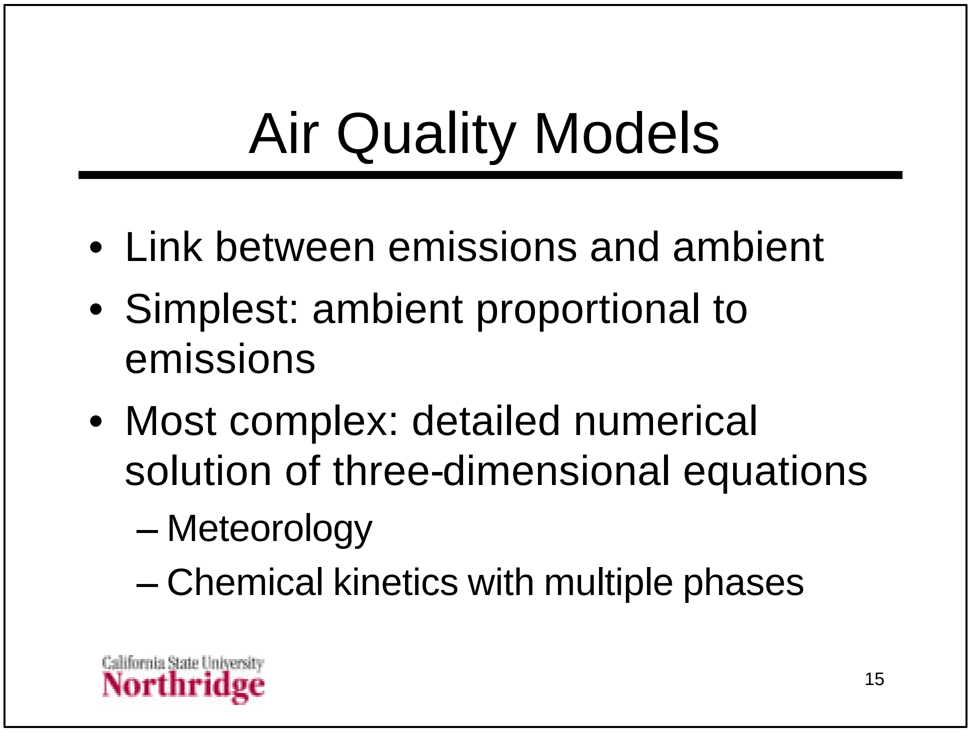
1970-1999 US Changes

- Population 33%
- People Employed 68%
- GDP – adjusted for inflation 147%
- Drivers 68%
- Vehicles 99%
- Vehicle Miles Traveled 143%

California State University
Northridge

Although the near constant level of national emissions makes it appear that air pollution control efforts have had little effect, this chart shows changes in the national picture that have occurred over the same time period. (These data, which are actually for 1970-1999 instead of 1997-1998, were taken from a US Department of Transportation web site: http://www.fhwa.dot.gov////environment/aqfactbk/factbk3.htm#t1)

The increased level of personal and economic activity shown here would be expected to increase emissions. The vehicle miles traveled (VMT) data indicate that in the absence of a motor vehicle control program, emissions from motor vehicles would have increased by 143% in the absence of a control program.



Air Quality Models

- Link between emissions and ambient
- Simplest: ambient proportional to emissions
- Most complex: detailed numerical solution of three-dimensional equations
  - Meteorology
  - Chemical kinetics with multiple phases

SIPs are planning documents that require a model which links the effects of emissions reductions to reductions in ambient concentrations. The simplest of these is a proportional model, called linear rollback. This model works reasonably well for pollutants which are directly emitted and are not formed by reactions in the atmosphere. CO is a good example of this. In this model the emissions, E, are proportional to the difference between the actual concentration, C, and the background concentration, C_b.

$$E = k(C - C_b)$$

If the present emissions and concentration are represented as E_p and C_p, respectively, and the future emissions and concentration are represented as E_f and C_f, the emissions reduction, $(E_p – E_f)/E_p = 1 – E_f/E_p$ is given by the following equation.

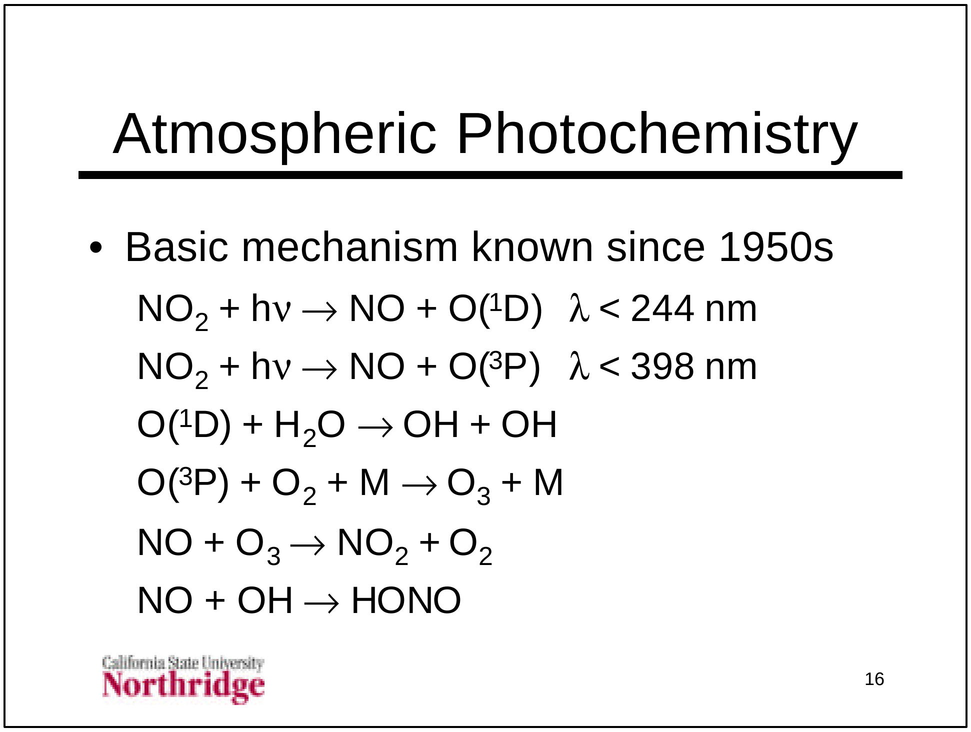
$$1 – E_f/E_p = 1 – [\ k(C_f - C_b)] / [k(C_p - C_b)] = \{ (C_p - C_b) - (C_f - C_b) \} / (C_p - C_b)$$

Thus, under linear rollback, the required emission reduction is found from the following equation

$$\text{Reduction} = 1 – E_f/E_p = (C_p - C_f) / (C_p - C_b)$$

This is a simple relationship between emissions and ambient concentrations. Unfortunately, it does not hold for pollutants that are formed by reactions in the atmosphere.

In addition to planning models that cover an entire urban area, there are point source models that are used to determine the impact of single sources on the areas around the source. Such models are used in decisions about construction permits for new sources or major source modifications.



Atmospheric Photochemistry

- Basic mechanism known since 1950s

$NO_2 + h\nu \rightarrow NO + O(^1D)$ $\lambda < 244$ nm

$NO_2 + h\nu \rightarrow NO + O(^3P)$ $\lambda < 398$ nm

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

$O(^3P) + O_2 + M \rightarrow O_3 + M$

$NO + O_3 \rightarrow NO_2 + O_2$

$NO + OH \rightarrow HONO$

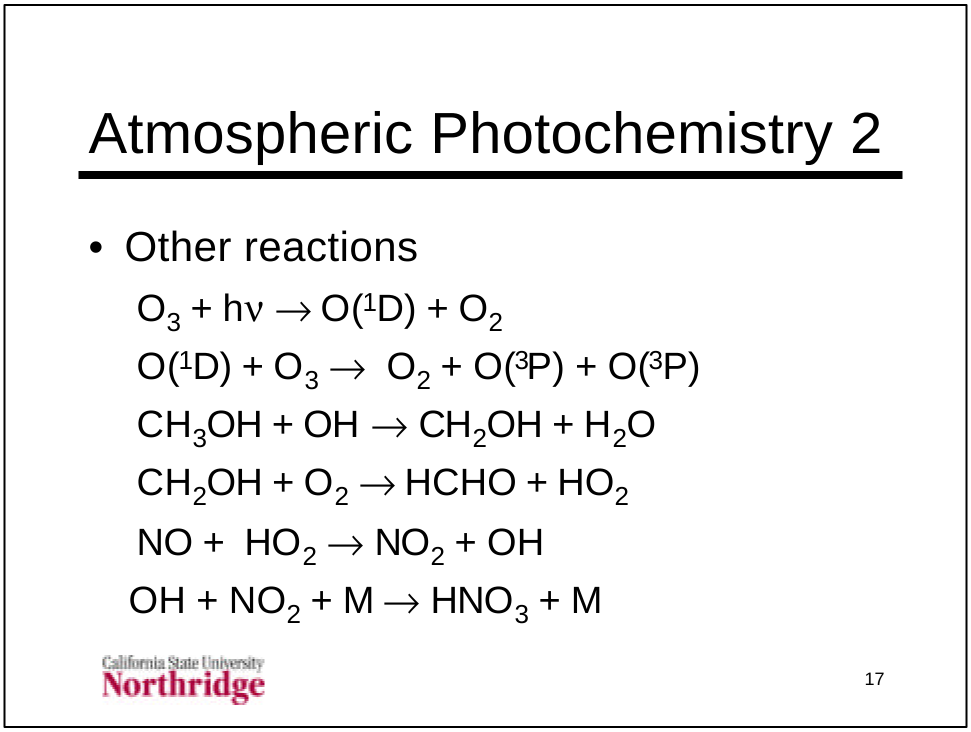
California State University Northridge

Photochemical reactions (chemical reactions in the presence of sunlight) produce photochemical smog. The criteria pollutant associated with photochemical smog is ozone. Ozone is produced by a complex series of reactions a small number of which are shown on this and the next slide.

The reaction steps on the chart are the reactions that are regarded as the start of the mechanism for photochemical smog formation. In these reactions the symbol $h\nu$ represents the photochemical energy that splits a molecule. Such a reaction is known as photolysis. The (^1D) and (^3P) indicate the electronic energy states of the oxygen atoms that are formed in the reactions. Recall that the visible part of the spectrum lies between 300 and 700 nm and shorter wavelengths mean higher frequencies that correspond to greater energy in the photon participating in the reaction.

The symbol M represents a collusion partner, sometimes called a third body. This means that an another molecule must participate in the reaction to absorb energy. The presence of this third body affects the form of the equation used to model the rate of the reaction.

Compounds like O atoms, hydroxyl (OH), and HONO are called free radicals. These are highly reactive atoms or molecules that have an unbound electron. (They are not ions because they have the same number of protons and electrons, but the bonding structure of the radicals makes them want to enter into reactions with other molecules.



Atmospheric Photochemistry 2

- Other reactions

$O_3 + h\nu \rightarrow O(^1D) + O_2$

$O(^1D) + O_3 \rightarrow O_2 + O(^3P) + O(^3P)$

$CH_3OH + OH \rightarrow CH_2OH + H_2O$

$CH_2OH + O_2 \rightarrow HCHO + HO_2$

$NO + HO_2 \rightarrow NO_2 + OH$

$OH + NO_2 + M \rightarrow HNO_3 + M$

Additional reactions are shown in this slide. This reaction shows the participation of additional free radical reactions and additional photolysis reactions.

These reactions show how intermediate products such as formaldehyde (HCHO) and nitric acid (HNO_3) can be produced.

There is a general set of hydrocarbon reactions that have not been shown here. One such reaction is shown below.

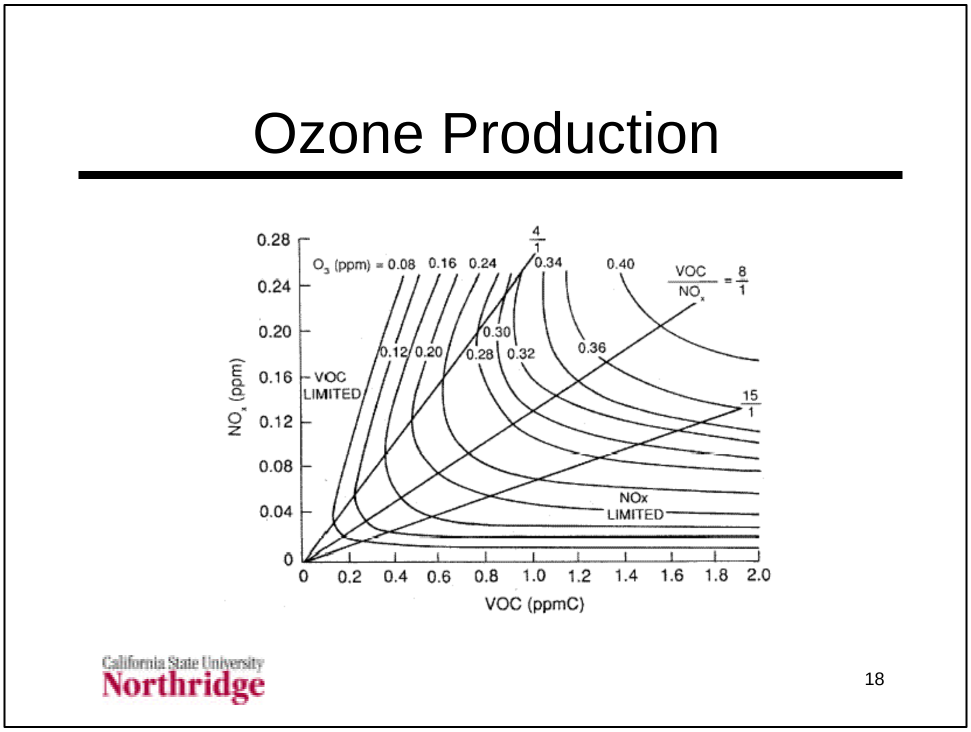
$$CH_4 + O(^1D) \rightarrow CH_3 + OH$$

This is called a chain branching reaction because there is one free radical in the products and two free radicals in the products. Other hydrocarbons can participate in similar reactions. The general reaction equivalent to the one shown above for methane, may be written as follows.

$$RH + O(^1D) \rightarrow R + OH$$

In this general reaction, R represents some radical containing hydrogen and carbon atoms. For example, in the methane reaction $R = CH_3$.

The wide range of reactions that can take place lead to different amounts of ozone. Detailed chemical kinetic models are required to simulate the entire mechanism.



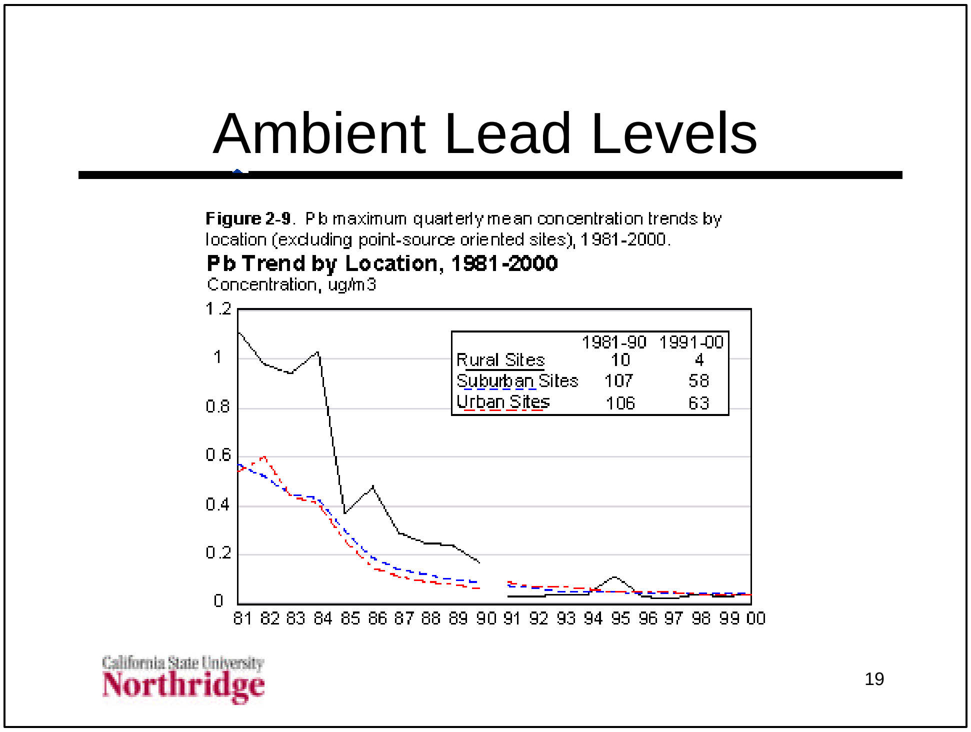
Ozone Production

The diagram shown here, called an EKMA diagram, is taken from National Academy of Sciences, *Rethinking the Ozone Problem*, 1991, which says that the diagram was adapted from a 1977 reference to Dodge. (EKMA stands for **E**mpirical chemical **K**inetics **M**odeling **A**pproach.) This diagram formed the basis for air quality planning the the late 1970s and early 1980s. The basic point of this diagram – the need to choose controls over hydrocarbons or NOx as a way to control ozone – remains true today even when more sophisticated models are used.

This diagram was based on experimental data which showed that the amount of ozone formed in photochemical smog depended on the initial concentration of reactants, volatile organic compounds (VOC) and oxides of nitrogen (NOx). When the VOC/NOx ratio is about 4/1 or less, the reaction is VOC limited. This region is on the left side of the diagram. Here ozone is reduced by controlling VOC. In this region, controls on NOx will actually increase ozone.

When the ratio of VOC/NOx is about 15/1 or more, as shown in the lower right side of the diagram, the control of NOx is the best way to reduce ozone. Between these limits, reductions in either NOx or VOC will reduce ozone.

The limitation of the EKMA model is that it gives a single value for an urban area. Recent models use the full integration of partial differential equations to examine photochemical reactions with variation of emissions and wind over space and time.

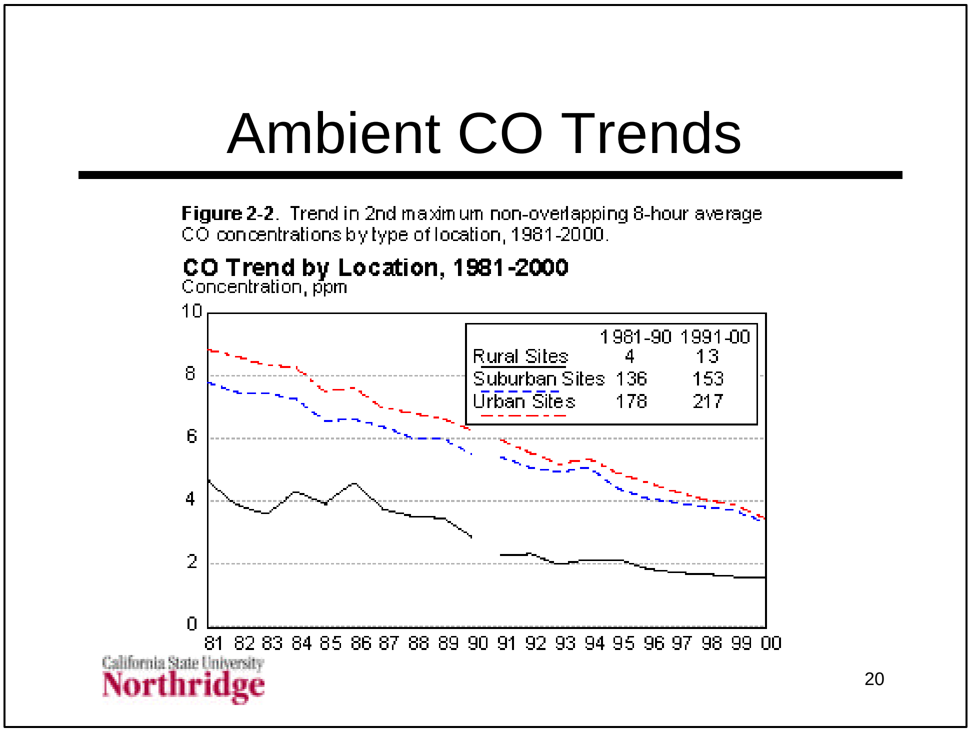


Ambient Lead Levels

Figure 2-9. Pb maximum quarterly mean concentration trends by location (excluding point-source oriented sites), 1981-2000.

	1981-90	1991-00
Rural Sites	10	4
Suburban Sites	107	58
Urban Sites	106	63

The greatest success in air pollution control has been the reduction in lead emissions and the resulting lead concentrations in the atmosphere. Almost all of this reduction has come from the removal of lead from gasoline. At present, most lead emissions come from facilities that process lead or use it. Battery plants are a common source of lead emissions in many urban areas. You will sometimes see Proposition 65 warnings from lead plants in newspapers. Based on a negotiated settlement of a lawsuit, these warnings show a map of the likely high concentration regions around the plants.



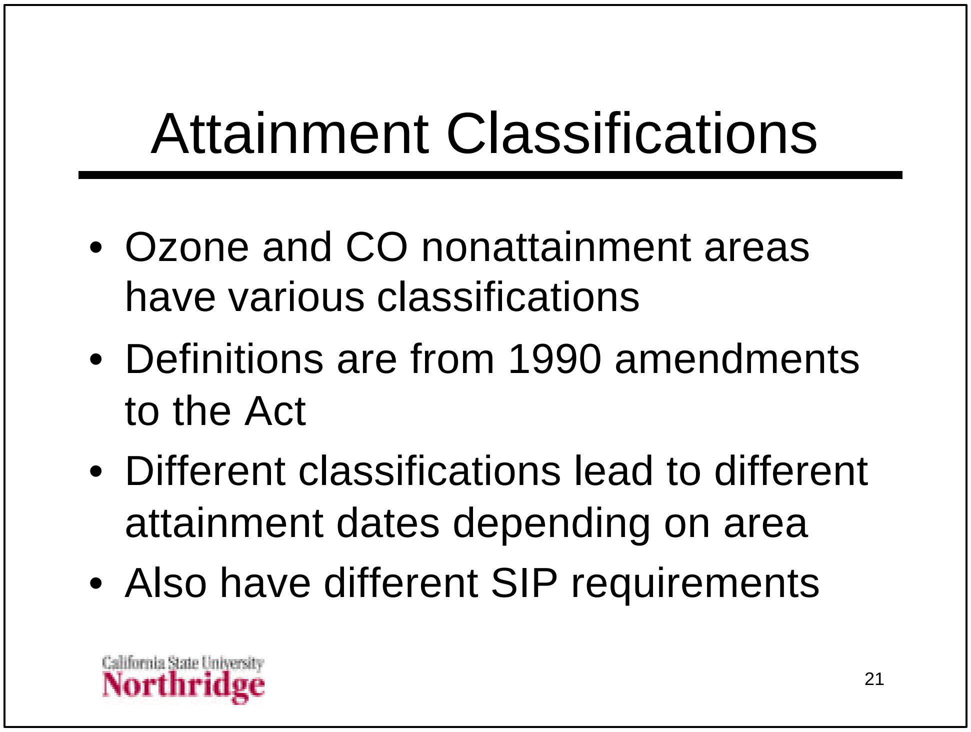
Ambient CO Trends

Figure 2-2. Trend in 2nd maximum non-overlapping 8-hour average CO concentrations by type of location, 1981-2000.

CO Trend by Location, 1981-2000

California State University Northridge

Although the total national CO emissions showed very change over a thirty-year period, the ambient concentrations of CO have been decreasing. This is mainly due to the reduction in mobile source emissions near monitors. In particular there are reductions in urban areas where there are concentrations of motor vehicles.



Attainment Classifications

- Ozone and CO nonattainment areas have various classifications
- Definitions are from 1990 amendments to the Act
- Different classifications lead to different attainment dates depending on area
- Also have different SIP requirements

California State University Northridge

Classification of Nonattainment Areas for Ozone and Carbon Monoxide

Ozone Nonattainment Areas

Area classification	Design value	Attainment date*
Marginal	0.121 up to 0.138 ppm	November 15, 1993
Moderate	0.138 up to 0.160 ppm	November 15, 1996
Serious	0.160 up to 0.180 ppm	November 15, 1999
Severe–15**	0.180 up to 0.190 ppm	November 15, 2005
Severe–17**	0.190 up to 0.280 ppm	November 15, 2007
Extreme	0.280 ppm and above	November 15, 2010

Carbon Monoxide Nonattainment Areas

Area classification	Design value	Attainment date
Moderate (low)***	9.1 up to 12.7 ppm	December 31, 1995
Moderate (high)***	12.8 up to 16.4 ppm	December 31, 1995
Serious	16.5 ppm and above	December 31, 2000

*The primary standard attainment date for ozone is measured from the date of the enactment of the Clean Air Amendments of 1990.

**Severe–15 and severe–17 ozone nonattainment areas have no difference in requirements except for the attainment dates.

***Moderate CO nonattainment areas with design values of 12.7 ppm or less have reduced SIP requirements compared to those areas with design values above 12.7 ppm.

The attainment dates for ozone are in section 181 of the 1990 Clean Air ActAmendments; those for CO are in section 186.

Attainment Status

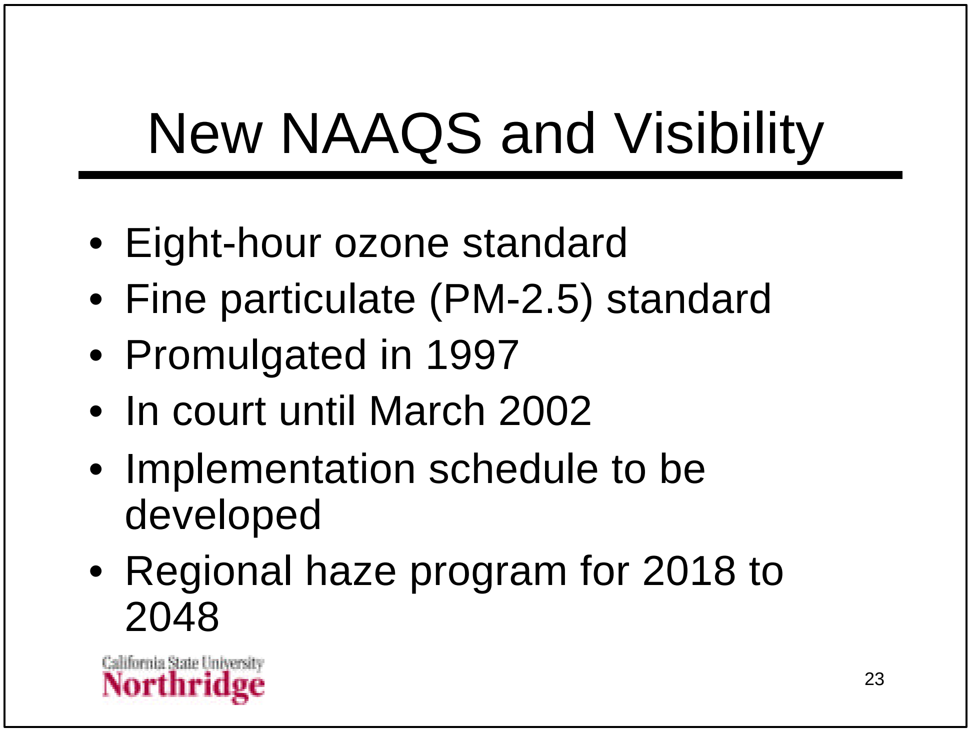
- Notes show problems with attainment
- Severe and extreme ozone areas not due for attainment until 2005-2010
- Section 185A areas are transitional between attainment and nonattainment
- No serious ozone areas which should have attained by 1999 have done so

Areas Classified as Nonattainment in 1992 that are Nonattainment as of July 1, 2001*

Pollutant	Classification	1992	2001
Ozone	Extreme	1	1
	Severe-17	5	5
	Severe-15	4	4
	Serious	14	14
	Moderate	31	10
	Marginal	42	21
	Section185A	11	4
	Other	2	1
	Incomplete Data	23	15
CO	Moderate<=12.7ppm	32	8
	Moderate>12.7ppm	4	2
	Not Classified	34	11
	Serious	7	7
Lead	N/A	13	4
NO2	N/A	1	0
PM10	Moderate	76	62
	Serious	8	8
SO2	Primary	48	26
	Secondary	6	6

Obtained from data on nonattainment history provided by EPA at http://www.epa.gov/oar/oaqps/greenbk/anay.html.

*For areas designated as “Not Classified”, the number in the final column represents the number of areas that have not yet been designated as attainment areas.



New NAAQS and Visibility

- Eight-hour ozone standard
- Fine particulate (PM-2.5) standard
- Promulgated in 1997
- In court until March 2002
- Implementation schedule to be developed
- Regional haze program for 2018 to 2048

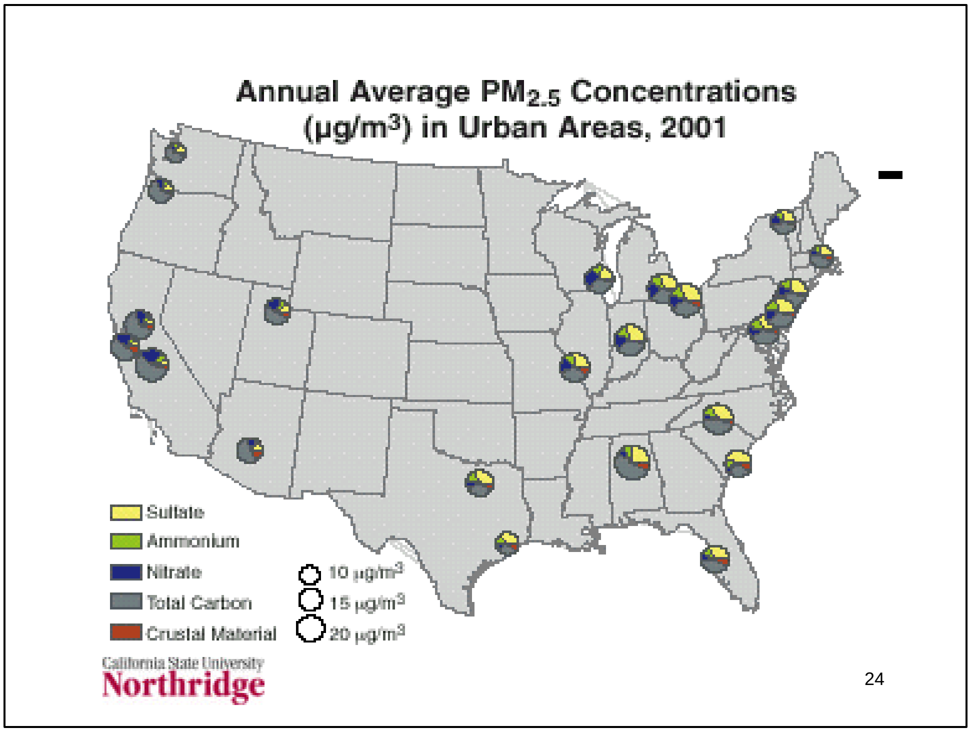
California State University
Northridge

The new 8-hour ozone standard is 0.08 parts per million (ppm). This standard applies to the 3-year average of the annual 4th-highest daily maximum 8-hour ozone concentrations. It replaces the old one-hour standard which was 0.12 ppm with a probability that it would not be exceeded more than once a year over a three-year period. EPA set the 8-hour standard at 0.08 ppm because it concluded that there is no discernible threshold below which no adverse health effects occur. Accordingly, no level would eliminate all risk. EPA further concluded that a zero-risk standard was neither possible nor required by the Clean Air Act. They selected the 0.08 ppm level based on their judgment that at this level public health will be protected with an adequate margin of safety. (paraphrased from text at http://www.epa.gov/ttn/oarpg/t1/fact_sheets/o3fact.pdf

The new PM-2.5 standards are set at 15 µg/m , annual arithmetic mean, and 65 µg/m , 24-hour average The annual average standard is based on a three-year average of all the “community-based” monitoring stations in an area. The new 24-hour PM standard, the form is based on the 98th percentile of 24-hour PM-2.5 concentrations in a year (averaged over 3 years), at the 2.5 population-oriented monitoring site with the highest measured values in an area. (paraphrased from http://www.epa.gov/ttn/oarpg/t1/fact_sheets/pmfact.pdf

The regional haze program is a separate initiative intended to improve visibility over national parks and monuments known as Class I areas. This is a long-range program in which the first compliance date is 2018 and periodic reviews and improved regulations are scheduled, in ten-year periods, from then to 2048.

.

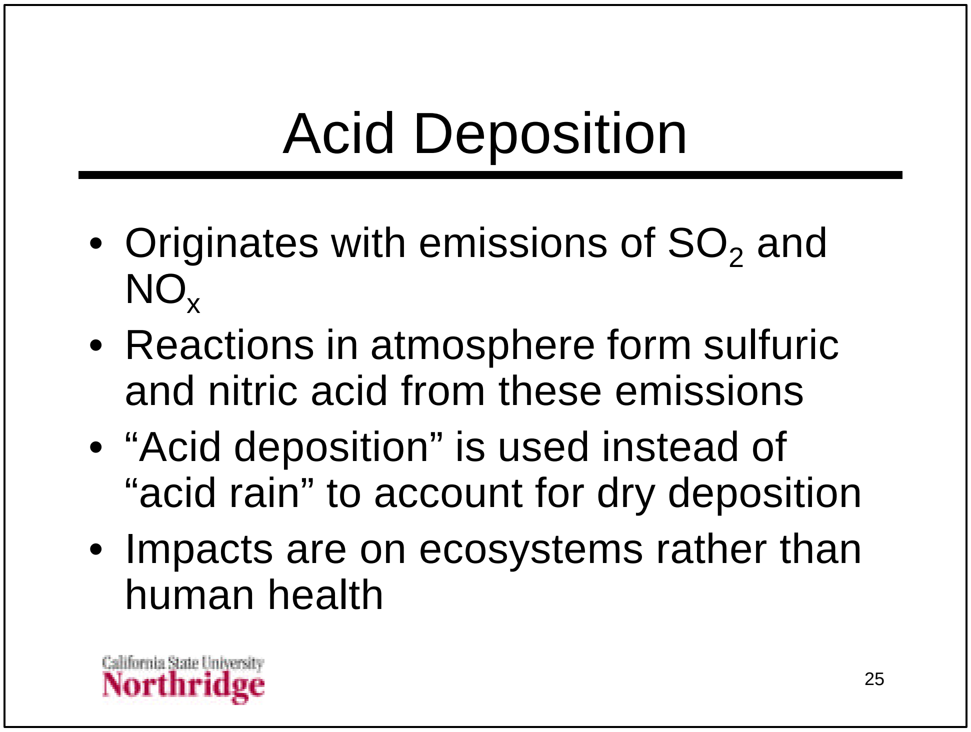


Annual Average $PM_{2.5}$ Concentrations ($\mu g/m^3$) in Urban Areas, 2001

California State University
Northridge

This figure is taken from http://www.epa.gov/airtrends/pm.html. It shows the size and species distributions for PM in a variety of regions of the country. A major difference between the eastern and western parts of the US is the larger sulfate concentrations in PM in the east.

With the PM-2.5 standard, almost none of the fine particulate matter is “crustal” material (i.e., dirt). Much of the PM is carbon coming from carbon particulate and condensed hydrocarbons. Some part of the PM-2.5 is nitrate. These compositing data imply that methods used to control ozone (VOC and NOx control) will also have an impact on particulate matter.



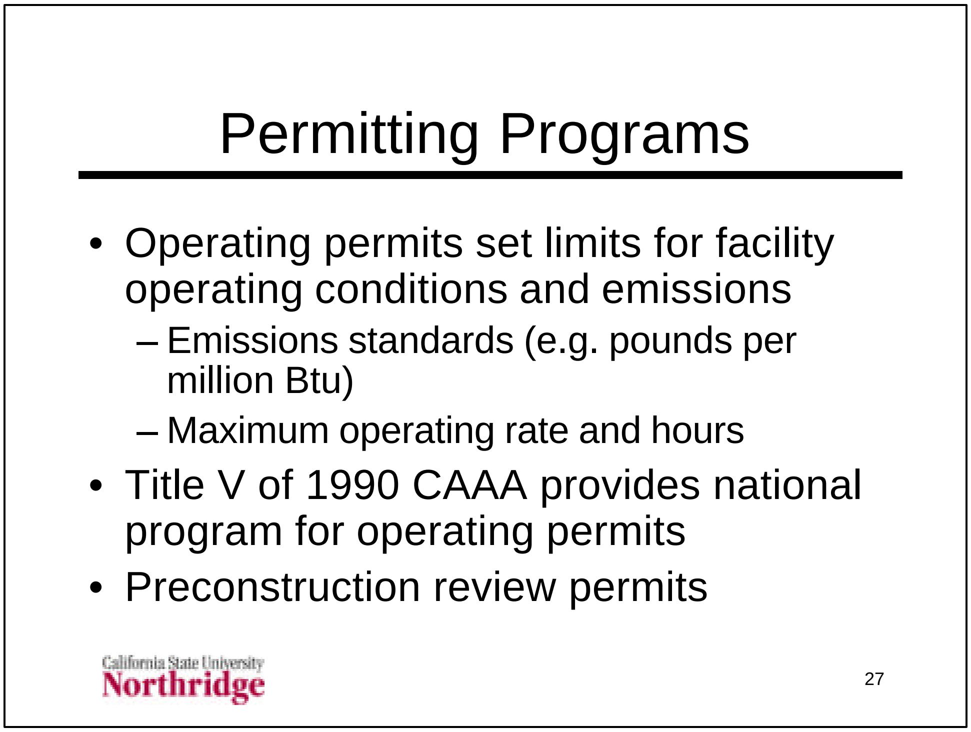
Acid Deposition

- Originates with emissions of SO_2 and NO_x
- Reactions in atmosphere form sulfuric and nitric acid from these emissions
- “Acid deposition” is used instead of “acid rain” to account for dry deposition
- Impacts are on ecosystems rather than human health

Acid Deposition Controls

- Title IV of 1990 Clean Air Act Amendments
- Market-based, cap-and-trade program
- SO_2 allowances initially assigned to coal-fired power plants
- NOx controls also required

California State University
Northridge



Permitting Programs

- Operating permits set limits for facility operating conditions and emissions
  - Emissions standards (e.g. pounds per million Btu)
  - Maximum operating rate and hours
- Title V of 1990 CAAA provides national program for operating permits
- Preconstruction review permits

California State University
Northridge

New Source Review

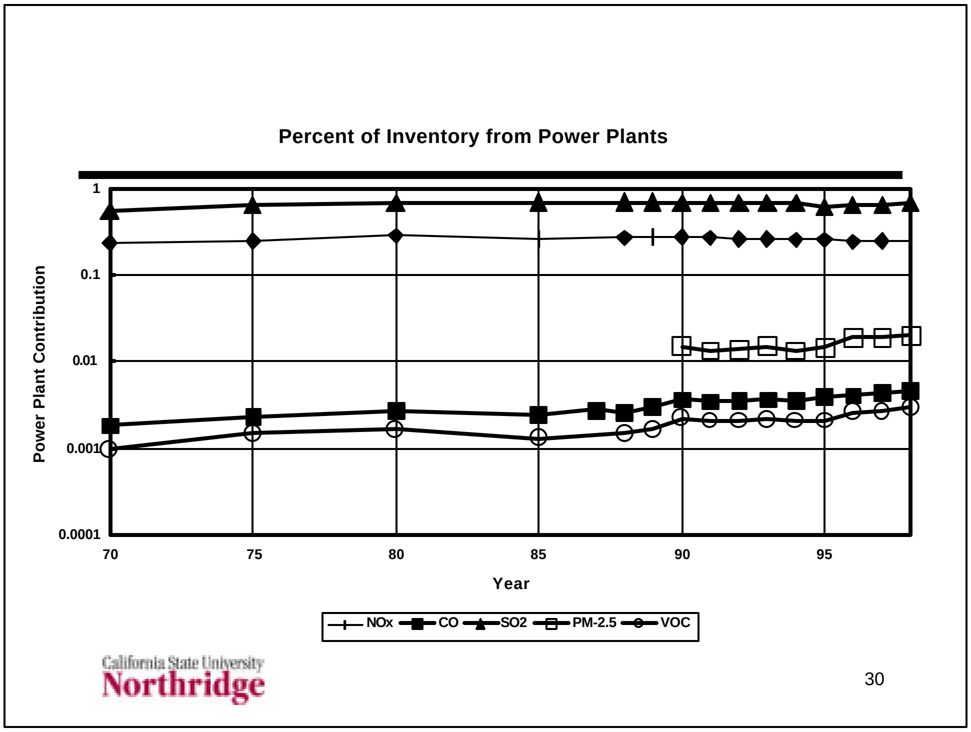
- Permits required prior to start of
  - Constructing major new source
  - Major modification
- Applies in attainment (PSD) and nonattainment areas
- Issue in 2001 energy study
- Pending enforcement issues
- Proposed changes to program

California State University Northridge

Clear Skies Initiative

- Proposed by White House/USEPA
- Applies to electric power plants
- Controls SO_2, NOx and mercury
- Implementation schedule until 2018
- Would replace NSR for power plants
- EPA report shows benefits
- Environmentalists question schedule

California State University
Northridge



This chart shows that electric power plants contribute a significant fraction to the emissions of NOx and SO_2 in the United States. The contributions of other emissions are small to negligible.

Although it is not shown on this chart, the majority of the power plant emissions come from coal-fired power plants. Coal accounts for about 90% of the NOx emissions from power plants and about 95% of the SO_2 emissions.

Mercury, which is another significant pollutant from power plants, is not shown on this slide. Mercury in the mineral matter of coal is vaporized in the combustion process and exits partially as recondensed mercury and partially as mercury vapor. Mercury is a toxic pollutant and is regulated as such.

Climate Issues

- Planetary energy balance
  - Greenhouse effect
  - Stratospheric ozone
- Provide introduction now, cover later
- Stratospheric ozone has general agreement
- Greenhouse effect still controversial

California State University
Northridge

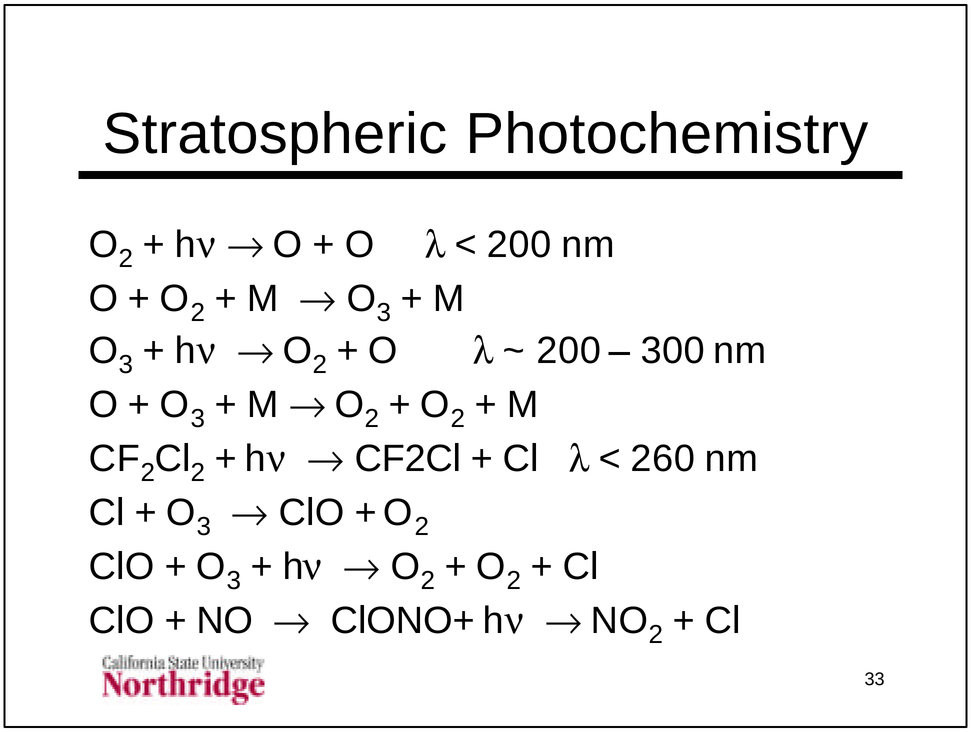
The planetary energy balance between incoming solar radiation and outgoing infrared radiation is affected by two main sources. The first is the ozone layer in the stratosphere. This layer is formed by photochemical reactions that can be disturbed by human emissions that reach there.

“the balance of evidence suggests that there is a discernible human influence on global climate,” the Third Assessment Report states the influence of human activities on climate in even starker terms. It concludes that, “[I]n light of new evidence and taking into account the remaining uncertainties, most of the observed warming over the last 50 years is likely to have been due to the increase in greenhouse gas concentrations” (IPCC 2001).

Stratospheric Ozone

- Ground level (tropospheric) ozone is a pollutant
- Stratospheric ozone reduces UV radiation reaching planet’s surface
- Cl atoms that reach the stratosphere can destroy ozone there
- Chlorofluorocarbons (CFCs) good for ground-level, bad for stratosphere

California State University
Northridge



Stratospheric Photochemistry

$O_2 + h\nu \rightarrow O + O \quad \lambda < 200\ \text{nm}$

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

$O_3 + h\nu \rightarrow O_2 + O \quad \lambda \sim 200 - 300\ \text{nm}$

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

$CF_2Cl_2 + h\nu \rightarrow CF2Cl + Cl \quad \lambda < 260\ \text{nm}$

$Cl + O_3 \rightarrow ClO + O_2$

$ClO + O_3 + h\nu \rightarrow O_2 + O_2 + Cl$

$ClO + NO \rightarrow ClONO + h\nu \rightarrow NO_2 + Cl$

The first two reactions provide for the production of ozone; the second two for the destruction of ozone. These four reactions lead to a natural equilibrium concentration of ozone in the stratosphere.

The ozone concentration peaks in a region between 20 and 30 km above the earth's surface and the concentration there is over ten times that at the earth's surface.

CFC's that reach the stratosphere can be photolyzed releasing Cl atoms. These atoms can react with ozone creating a new equilibrium that reduces the normal ozone concentration by as much as 60% in artic regions (the so-called ozone hole.)

The Montreal protocol of 1987 as revised in 1992 calls for the complete elimination of CFCs by the beginning of 1996 in developed countries.

Greenhouse Gases

- Incoming solar radiation mainly in UV and visible
- Outgoing terrestrial radiation infrared
- Atmospheric gases absorb different amounts at different wavelengths
- Greenhouse gases: CO_2, CH_4, N_2O
- Equivalent tons of carbon measure

California State University
Northridge

The impact of greenhouse gases has been hypothesized for many years. In particular, anthropogenic emissions of CO2 have increased ambient CO2 levels and continued CO2 emissions are forecast in the future. Since CO2 is a strong absorber of IR radiation, it will reduce the energy leaving the earth's surface as it increases.

The main concern over greenhouse gases is the uncertainty about the ultimate impact. There are may interactions to consider. For example a warmer climate will allow more water vapor in the air. This may lead to the formation of more clouds. The additional clouds will scatter more incoming radiation and absorb (and scatter) outgoing radiation. What will the net effect of this interaction be?

Climate models project that the mean annual global surface temperature will increase by 1–3.5°C by 2100, that global mean sea level will rise by 15–95 cm, and that changes in the spatial and temporal patterns of precipitation would occur. The average rate of warming probably would be greater than any seen in the past 10,000 years, although the actual annual to decadal rate would include considerable natural variability, and regional changes could differ substantially from the global mean value. for damage or take advantage of opportunities created, due to a given change in climate). (IPCC summary report)