Inorganic Air Pollution

Sources and Types:

1. Carbon Oxides - Carbon Monoxide (CO), Carbon Dioxide (CO_2)

2. Sulfur Oxides - Sulfur Dioxides (SO_2) & Sulfur Trioxide (SO_3)
{contributor to ground level Ozone, (O_3)}

3. Nitrogen Oxides - Nitric Oxide (NO), Nitrogen Dioxide (NO_2), & Nitrous Oxide (N_2O)
{contributor to ground level Ozone, (O_3)}

4. Volatile Organic Compounds (VOCs) - Most organic compounds
Example: Methane (CH_4), Methanol (CH_3OH), Benzene (C_6H_6), Chlorofluorocarbons (CFCs), formaldehyde (CH_2O), Propane (C_3H_8).
{contributor to ground level Ozone, (O_3)}

5. Suspended Particulate Matter (SPM) - Solid and liquid particles both suspended in air. Example: dust, soot, pollen, asbestos, ash, conglomerates, soil, salts, etc.
{contributor to ground level Ozone, (O_3)}

6. Photochemical Oxidants - Ozone (O_3), Peroxide (H_2O_2), Complex interactions with VOCs and NOx. **Photochemical reactions**

7. Radioactive Isotopes - Radon - 222, Iodine - 131, Strontium - 90, Plutonium - 239, Potassium - 40,

8. Heat - Waste energy from fossil fuels; most energy sources and uses produce waste energy as heat, Ex.: cars, power, plants,

9. Noise - A byproduct of energy: airplanes, cars, industry, lawn mowers, mechanical, radios, wind, electrical power line discharge, etc.

10. Clorofluor carbons – Freons, etc.

Outdoor Air Pollutants

Primary Pollutants Anthropogenic, (Directly Emitted)

CO	Carbon Monoxide
CO_2	Carbon Dioxide
NO	Nitrogen Monoxide (Nitric Oxide)
NO_2	Nitrogen Dioxide
SO_2	Sulfur Dioxide
VOC	Volatile Organic Carbon
SPM,	Suspended Particulate Matter (PM-10)
CFCs	
NOx	
NH_3	
SiF_4	
Pb	
Radon (Rn)	

Secondary Pollutants (Transformed in the environment)

SO_3	Sulfite (Sulfur Trioxide)
HNO_3	Nitric Acid
H_2SO_4	Sulfuric Acid
H_2O_2	Hydrogen Peroxide
O_3	Tropospheric (not Stratospheric)

Acid Rain Solubility (Al) from Acid Rain

Cl_2

HOCl

Rn (Po)

Halocarbons

ClO

Acid Rain:

SO2 and NOx

Sulfur oxides enter mostly as fuel byproducts

NOx has been discussed below

One main effect is the change in soil of chemistry that promotes the dissolution of both Fe and Al at <pH 3

This then poisons the roots of trees and plants and kills forests and also lakes that are susceptible

$1/2O_{2(aq)} + SO_{2(aq)} + H_2O$ ¾¾→ $H_2SO_{4(aq)}$

$SO_{2(aq)} + H_2O_2$ ¾¾→ $H_2SO_{4(aq)}$

$4FeS_2 + 11O_2$ ¾¾→ $2Fe_2O_3 + 8SO_2$

NOx as Outdoor Air Pollutants

NO_2 & N_2O Emissions	1989	1980
North & Central Am.	21,600,000	22,300,000
Asia	1,400,000	?
Europe	~15,000,000	?
USSR	4,190,000	?

U.S. evaluation of sources

- Fuel combustion 46% of emissions
- Transportation 47% of emissions (specific fuel combustion)
- Industrial and other sources make up the remaining 7%

Principle **anthropogenic** source of NOx compounds is from fuel in **high temperature combustion processes:**

$$N_2 + O_2 + \text{heat } (>1{,}000\ °C) \rightleftarrows 2NO$$

Then NO combines with O_2 in air or other oxidants to convert NO to NO_2 within a few hours under normal conditions .

$2NO + O_2$ (or other oxidants, RO_2)¾¾→ $2NO_2$

All Oxides of nitrogen with water form nitric acid (HNO_3)

N_2O, NO, N_2O_3, NO_2, N_2O_4, N_2O_5 ~ = NOx

for reference:

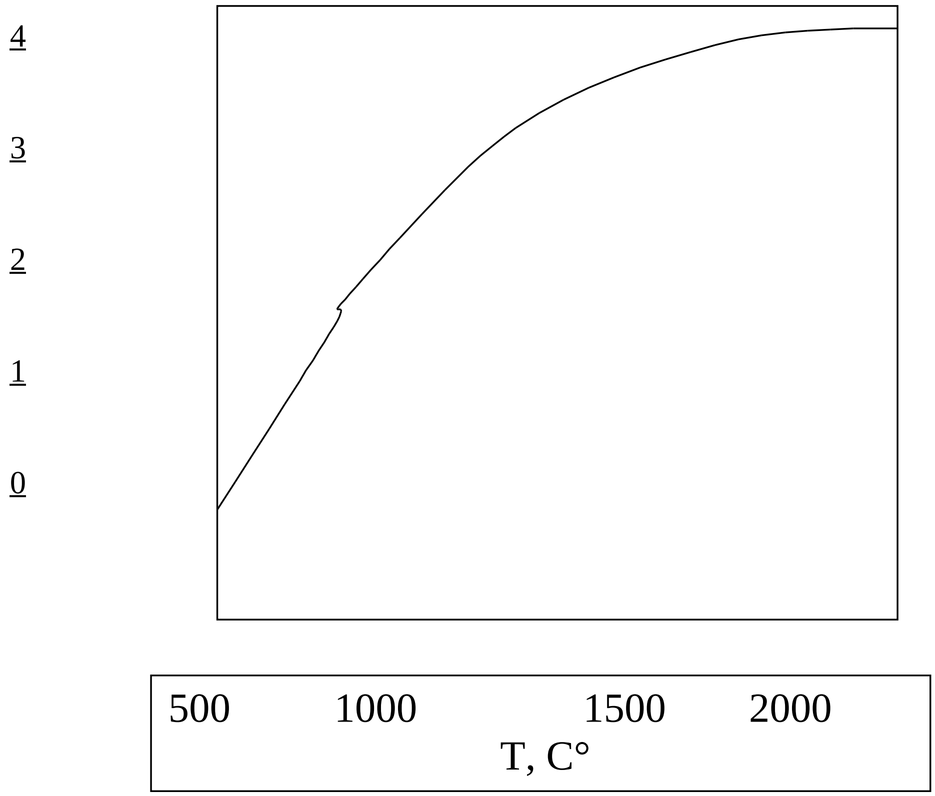
$2NO_2$ + H_2O ¾¾→ HNO_2 + HNO_3

Anthropogenic Prevention

Primary method of prevention is

1. reduced temperature of oxidation of fuel (or do not burn fuel) and
2. scrubbing with various bases can be used if the process permits

Log NO conc. ppm



$N_2 + O \longrightarrow NO + N$

$N + O_2 \longrightarrow NO + O$

$N_2 + O_2 \longrightarrow 2NO$

<u>Other species</u>

$RH + O \longrightarrow R\bullet + HO\bullet$

$N + HO\bullet \longrightarrow NO + H\bullet$

Other NOx as Outdoor Air Pollutants (Cont.)

Examples:

$NO + O_3$ ¾¾→ $NO_2 + O_2$

$NO_2 + O$ ¾¾→ $NO + O_2$

$NO_2 + NO_3$ ¾¾→ N2O5

$NO_3 + NO$ ¾¾→ $2NO_2$

N2O5 + H_2O ¾¾→ 2HNO3

NO_2 + HO• ¾¾→ 2HNO3

HNO_3 + HO• ¾¾→ H_2O + NO3

HNO_3 + hv ¾¾→ HO• + NO2

NO_2 + hv ¾¾→ NO + O

NO_2 + hv ¾¾→ NO_2*

Harmful effects of NO.
NO attaches to hemoglobin reducing Oxygen transport efficiency in the body.

NO_2 harmful exposures:
50-100 ppm exposure of NO_2 for 1 hour causes lung tissue inflammation for 6-8 weeks.

150-200 ppm exposure of NO_2
produces “bronchiolitis fibrosa obliterans” and is fatal 3-5 weeks after exposure.

500 ppm 2-10 day death “Silofiller’s Disease”

Power plants emit 50-1000 ppm NO

CFCs

CFC's **-** chlorofluorocarbons
(Commercial name from DuPont - Freons)
(replaced sulfur dioxide (SO_2) and ammonia (NH_3)as refrigerants approximately 50 yrs. ago)

CFC's

Chemical Name	Formula	Commercial Name
trichlorofluoromethane	**CCl_3F**	**CFC-11 (Freon-11)**
dichlorodifluoromethane	**CCl_2F_2**	**CFC-12 (Freon-12)**
chlorodifluoromethane	**$CHClF_2$**	**CFC-22 (Freon-22)**
1,1,2-trichloro-1,2,2-trifluoroethane	**$Cl_2FCCClF_2$**	**CFC-113 (Freon-113)**

Naming of CFC's:

Units digit is # of F atoms
Tens digit is the # of H atoms plus 1
Hundredths digit is the # of C atoms minus 1

Ex. CFC-113 has 3 F atoms, 0 H atoms, and 2 C atoms.

CFC characteristics:

- stable
- odorless
- non corrosive
- nonflammable
- non toxic
- high heat of vaporization
- optimum vapor pressure

Hypotheses of effect on Ozone presented

The possible depletion of Ozone by Anthropogenic gases was first proposed by H. S. Johnson of the U. of CA, Berkeley in the 1960s.

Effect on ozone of CFCs was theorized in 1974 by two chemists, Sherwood Rowland and Mario Molina from the University of California, Irvine.

(ref. McQuarrie and Rock pg 630)

Uses of CFCs

Coolants in air conditioning and refrigerating
Propellants in aerosol spray cans
(not in US since 1978s)
Cleaning of electrical parts
Fumigants for granaries and cargo holds
Bubbles in polystyrene plastic foam packaging & insulation (DuPont - Styrofoam)

Other Sources of Halogenated Molecules in the Atmosphere as <u>Gaseous</u>

Bromine-containing compounds called halons for fire extinguishers

Carbon tetrachloride (extremely non-polar solvent)

1,1,1-trichloroethane solvent in products such as dry-cleaning and spray adhesives

<u>Demographics of CFCs</u>

MDCs (industrialized countries) use 84% of CFCs

US is 25% of global consumption of CFCs

Vehicle air conditioners account for about 3/4 of US CFC emissions

By year 2000, 75 countries will phase out all CFC use.

Why is Cl so devastating to Ozone?

How long does a CFC last in the atmosphere over 50-400 years?

Freons without any hydrogen atoms have an average life time of 100 years in the atmosphere.

Time is needed to drift up in the atmosphere to reach the Stratosphere

One Cl atom can convert 10,000 to 100,000 O_3 to O_2 and O

Hydrogen containing CFCs only last a relatively short time and probably never make it to the Stratosphere. CH_3CCl_3 and $CHClF_2$ only last 6-7 years.

Mechanism of Ozone Decomposition by CFCs

CFC travels just above the O3 layer in the Stratosphere.

$$CF_2Cl_2 \xrightarrow{\text{Ultraviolet - UV}} CF_2Cl + Cl \qquad \text{Eq-1}$$

It then drifts back into the lower Stratosphere where O_3 is in high concentrations

$$Cl + O_3 \longrightarrow ClO + O_2 \qquad \text{Eq-2}$$

Direct destruction of Ozone

$$ClO + O \longrightarrow Cl + O_2 \qquad \text{Eq-3}$$

Short circuit of Step a and c of Ozone UV protection cycle.

Life of Cl atom in atmosphere is 1-2 years.

In 1-2 years, one Cl atom will repeat Eq-2
100,000 times.

One Cl atom destroys ~ 10^5 the # of O_3 atoms.
(A very efficient reaction mechanism)

The new alternaive CFC compounds:

What is the difference between Hydrogen containing CFCs?

Method of destruction in Troposphere.

$$CHClF_2 + OH\bullet \longrightarrow H_2O + CClF_2\bullet$$

The hydroxyl radical is the natural air cleanser of the Troposphere.

This path is not available to fully saturated cloro and fluoro CFCs.

“Scientific Basis of Good and Bad Ozone”

(Review) The Sun - The Atmospheric Energy Driver

All energy driven reactions on Earth are a result of large amounts of energy form the Sun.

The atmosphere has different temperatures at different heights due to chemical reactions driven by the Sun’s energy of **~1 Kw/m^2/ day at surface** and **~1,340 watts/m^2/ day** in the upper atmosphere perpendicular to the Sun.

What wavelengths are involved with the conversion of energy?
The sun is our only source of energy. It transmits ~ 86 % of this energy at 400-700 nm (0.4 to 0.7 {µm} micrometers)
The visible light spectrum. [400 nm blue and 700 nm red]
~7 % is transmitted at < 400 nm or as ultraviolet (UV).
(remember O_3)
~7 % is transmitted at > 700 nm or as Infrared (IR).

Outdoor Air Pollutants

Sources and Types: (bold for those that participate in Tropospheric ozone)

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7. Radioactive Isotopes - Radon - 222, Iodine - 131, Strontium - 90, Plutonium - 239, Potassium - 40,

8. Heat - Waste energy from fossil fuels; most energy sources and uses produce waste energy as heat, Ex.: cars, power, plants,

9. Noise - A byproduct of energy: airplanes, cars, industry, lawn mowers, mechanical, radios, wind, electrical power line discharge, etc.

Methane (CH_4) {a primary VOC}, Contributor to Photochemical Smog and Greenhouse Gas Emissions from <u>Anthropogenic</u> Sources

World 270,000,000 metric tons

By World Region

Asia	130,000,000
North and Central America	45,000,000
Europe	26,000,000

USSR	34,000,000
Africa	19,000,000
South America	18,000,000
Oceannia (Australia, Fiji, etc.)	6,200,000

Outdoor Air Pollutants

Pollution Emissions

Anthropogenic compositional alterations to the atmosphere:

From 1989 Compilation (from United Nations Reference)

Emissions of Chlorofluorocarbons (CFCs)

World 580,000 metric tons

By World Region

Asia	140,000
North and Central America	150,000
Europe	180,000
USSR	67,000
Africa	16,000
South America	15,000
Oceannia (Australia, Fiji, etc.)	9,000

Ozone depletion is the main effect, remember on average each Cl atom destroys 100,000 (10^5) O_3 molecules (4 per molecule of CFC).

Pollutant Trends

From 1900 to 1970 the U.S. had a dramatic increases in some pollutants

NO_x	690%
VOC	260%
SO_2	210%

From 1986-1995 U.S. concentrations of key pollutants decreased by

NO_x	14%	
Ozone	6%	
PM-10	22%	(Particulate Matter, <10 µm)
SO_2	37%	
lead	78%	
CO	37%	

From 1986-1995 U.S. Emissions of key pollutants decreased by

NO_x	3%	
VOC	9%	
PM-10	17%	(Particulate Matter, <10 µm)
SO_2	18%	
lead	32%	
CO	16%	

While you can measure Troposhperic Ozone, it is not (generally) a direct emission but is the result of reactions catalyzed or caused by other pollutants.

Smog & Acid Deposition Concentration

Photochemical smog is the interaction of electromagnetic radiation from the Sun and Primary Pollutants to form photochemical smog.

Table of Atmospheric Trace Gases in Dry Air Near Ground Level

Gas or Species	Volume Percent	Major Source	Process for Removal
CH_4	$1.6x10^{-4}$	Biogenic	Photochemical
CO	$\sim1.2x10^{-5}$	Photochemical, Anthro.	Photochemical
N_2O	$3x10^{-5}$	Biogenic	Photochemical
NO & NO_2	10^{-10}-10^{-6}	Photochemical, Lightning, Antho.	Photochemical
HNO_3	10^{-9}-10^{-7}	Photochemical	Precipitation, rain
NH_3	10^{-8}-10^{-7}	Biogenic	Photochemical, rain
H_2	5x10-5	Biogenic, Photochem.	Photochemical
H_2O_2	10^{-8}-10^{-6}	Photochemical	Precipitation
HO•	10^{-13}-10^{-10}	Photochemical	Photochemical
HO_2•	10^{-11}-10^{-9}	Photochemical	Photochemical
H_2CO	10^{-8}-10^{-7}	Photochemical	Photochemical
SO_2	$\sim2x10^{-8}$	Anthropogenic, Photochem., volcanic	Photochemical
CCl_2F_2	$2.8x10^{-5}$	Anthropogenic	Photochemical
H_3CCCl_3	$\sim1 x 10^{-8}$	Anthropogenic	Photochemical

Good Ozone

Hypotheses of CFC Effect on Ozone Presented

The possible depletion of Ozone by Anthropogenic gases was first proposed by H. S. Johnson of the U. of CA, Berkeley in the 1960s.

Effect on ozone of CFCs was theorized in 1974 by two chemists, Sherwood Rowland and Mario Molina from the University of California, Irvine.
(Noble Prize for this contribution)

Uses of CFCs

Coolants in air conditioning and refrigerating
Cleaning of electrical parts
Fumigants for granaries and cargo holds
Bubbles in polystyrene plastic foam packaging & insulation (DuPont - Styrofoam)
Propellants in aerosol spray cans (not in US since 1978s)

Demographics

By year 2000, 75 countries will phase out all CFC use.

MDCs (industrialized countries) use 84% of CFCs
US is 25% of global consumption of CFCs

Vehicle air conditioners account for about 3/4 of US CFC emissions

Why is Cl from CFCs so devastating to Stratospheric Ozone?

How long does a CFC last in the atmosphere?

Over 50-200 years.

Freons without any hydrogen atoms have an average life time of 100 years in the atmosphere.
Time is needed to transcend the Troposphere thermal barrier and get into the Stratosphere reach the Ozone layer and enter it.

One Cl atom can convert 10,000 to 100,000 O_3 to O_2 and O.

Hydrogen containing CFCs only last a relatively short time and probably never make it to the Stratosphere. CH_3CCl_3 and $CHClF_2$ only last 6-7 years. This is the change in CFC formulation.

What is the difference between hydrogen containing (H)CFCs and halogen saturated CFCs?

Method of destruction in Troposphere.

$$CHClF_2 + OH\bullet \longrightarrow H_2O + CClF_2\bullet$$

The hydroxyl radical is the natural air cleanser of the Troposphere and can work on (H)CFCs (not CFCs).

Mechanism of Ozone Decomposition

CFC travels just above the O3 layer in the Stratosphere.

$$CF_2Cl_2 \xrightarrow{\text{Ultraviolet - UV}} CF_2Cl + Cl \qquad \text{Eq-1}$$

It then drifts back into the lower Stratosphere where O_3 is in high concentrations

$$Cl + O_3 \longrightarrow ClO + O_2 \qquad \text{Eq-2}$$

Direct destruction of Ozone

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Short circuit of Step a and c of Ozone UV protection cycle.

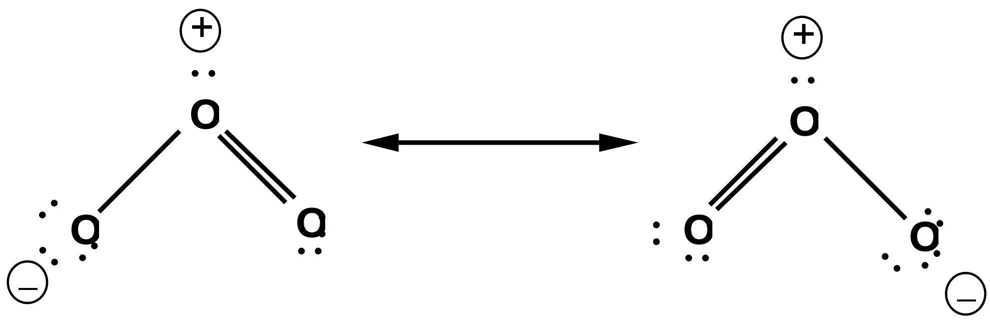
Life of Cl atom in atmosphere is 1-2 years.

In 1-2 years, one Cl atom will repeat Eq-2
100,000 times.

One Cl atom destroys ~ 10^5 the # of O_3 atoms.
(A very efficient reaction mechanism)

Why Ozone absorb UV energy?

Ozone is a resonance structure.



This resonance gives it the unique UV energy (< 308 nm) absorbing property.

Photochemical Formation of Ozone in the Stratosphere and Its Interaction with UV light

Photodissociation Reaction

Step a

Ultraviolet

O_2(g) ¾¾¾¾¾→ 2O(g) Free Radical

120 Kcal/Mol

Step b

240 - 300 nm
Ultraviolet

O(g) + O_2(g) + M(g) ¾¾¾¾¾→ O_3(g) + M(g)

where M(g) is another molecule such as O_2 or N_2 or particle to carry away thermal energy
(unchanged chemically)

How Ozone absorbs ultraviolet light

Step c

< 308 nm
Ultraviolet

O_3(g) ¾¾¾¾¾→ O_2(g) + O(g)* + 636, 630, 558 nm

26 Kcal/mol (yellow to red light)

Back to Step b again to be regenerated if no pollutants are present

Smog and Acid Deposition

Photochemical Smog is the interaction of electromagnetic radiation from the Sun and Primary Pollutants to form photochemical smog.

Sulfate particles are a major cause of haze and smog.

pH

pH of rain is 5.0 to 5.6 due to CO_2 and water interaction as previously described, recall carbonate equilibrium.

Average eastern US precipitation is 4.3 with pHs < 3 and 2.5.

What are the consequences of "Acid Rain"?

Toxic: It Kills - fish, plants aquatic and terrestrial, microorganisms

Damage to - Soil and Buildings (Limestone, $CaCO_3$), Oxidizes metal and pits finishes like paint and coatings.

Shifts Equilibrium in soil leaching Ca, Mg, K, and other cations.

Weakens species making them susceptible to disease
(AIDS type effect)

Stunts growth of crops

Proposed to be the third largest cause of lung disease in US after smoking and radon.

Figure 22-10 Effects of air pollution including acid rain.

Effects may cross borders and thus are exported to other countries.

Indoor Air Pollution

This is the source of one of the most significant pollution exposures facing humans.

Why?

Duration of exposure
We spend 70 to 90% of our time indoors.

Intensity of exposure
Levels reach 10 to 40 times those of outdoor air concentrations.

Estimates of ≥ 6,000 excess cancer deaths each year (excluding radon)
and ≥ 20,000 excess cancer deaths from Radon alone.

Industrial exposure is estimated by the author and EPA to be 100,000 to 200,000 premature deaths each year to workers from indoor air in industrial settings.

Specific indoor air problems

- Radon
- Asbestos
- Formaldehyde
- Smoke
- Fumes (ever been to a dry-cleaning shop) ("nose analysis")
- Secondary Smoke
- Buildup of toxic fumes

Figure 22- 4 Identifies some sources

Relationships between

- Vapor pressure
- Formaldehyde and building materials
- Particulate matter
- Building air exchange (Outdoor air "dilution", Why?)

What is the "Sick Building Syndrome"?
Why does it exist?

Effect of Air Pollution on Living Organisms

Humans

Cumulative effect of all of these pollutants is:

- Emphysema
- Respiratory tract irritation from gas and particles
- Asthma
- Heart trouble
- Lung cancer
- Irritation

Estimates:

Office of Technology Assessment estimates 50,000 premature deaths in US each year from respiratory or cardiac problems as result of air pollutants

American Lung Association estimates 120,000 US deaths each year from air pollution

EPA estimates air pollution costs $150 billion yearly in health care

- $100 billion from indoor air pollution
- $40 billion from automobiles

Plants

Chronic exposure to ozone, acid rain, sulfur, and nitrogen oxides may be most significant and synergistic.

Damage to leaves, roots, microorganisms (nitrogen fixing bacteria) etc. all weaken plant resistance to insects, frost, fungi, mosses, and disease.

Equilibration shifts in nutrients, aluminum ions, etc.

Radon (Rn)

Estimates of ≥ 6,000 excess cancer deaths each year (excluding radon)
and ≥ 20,000 excess cancer deaths from Radon alone.

Why:

$^{238}_{92}U_{(s)}$ ¾¾¾¾¾→ $^{234}_{90}Th + {}^{4}_{2}He$ … $^{222}_{86}Rn_{(g)}$

$^{222}_{86}Rn_{(g)}$ ¾¾¾¾¾→ $^{218}_{84}Po_{(s)} + {}^{4}_{2}He$

3 Alpha particles in 3 days

20,000 Deths/yr. Du to Rn

EPA in 1984 had “Zero” interest in Radon

US House of Representatives 1995
authorized 1st $3 million after 2 sets of congressional hearings into Radon in US homes.

1. Measurable
   4 pci/L EPA Action Level

2. Engeneerable fix or barriers

3. Epidemiological data on U miners for Rn.

Aquatic Organisms Are Also At Risk

Acid precipitation is a major threat.

Low buffering capacity permits acid shock.

Why?

Hint: What is physiological pH and what does it control?

Aluminum soil leached by acid precipitation
kills fish by interfering with gill oxygen exchange

Liming is a temporary fix.

> ~ 75,000 lakes or streams world wide have been acidified to a substantial loss of aquatic life or are stressed.

Air Pollution Control and
Clean Air Act of 1977 as revised in 1990

Established national ambient air quality standards (NAAQS) for 7 outdoor pollutants:

- suspended particulate matter
- sulfur oxides
- carbon monoxide
- nitrogen oxides
- ozone
- hydrocarbons
- lead

Why is nitrogen oxide unchanged and lead reduced?

Toxic Air Pollutants

A list of 600 toxic air pollutants was proposed

EPA has emission standards of 7 of the 600 toxic air pollutants:

- arsenic
- asbestos
- benzene
- beryllium
- mercury
- vinyl chloride
- radioactive isotopes

Goals for CFCs, CO_2, NOx, Auto emission Standards etc.

Methods of Pollution Control

Control of
- Pollutants in general
- Sulfur dioxide
- Nitrogen oxides
- Particulate matter emissions
- Motor vehicle emissions
- Troposphere ozone
- Indoor air pollutants
- + 600 other pollutants (189 prime)

Prevention General (Text Pgs 585-590)

Set limits, provide technology, provide incentive

Conservation of energy use in general and recycling and mass transit

Cleaner (low S fuel) and alternative Fuels and electric motors as alternative (batteries), Nuclear (fission, fusion?)

Modifying industrial plants and the engines for cleaner burning
lower operating temperatures for NO_x for example or collection devices in conjunction with reduced emission processes

Convert coal to gas first (eliminate particulate and S at same time)

Eliminating SO_2 and NO_x will reduce O_3 in Troposphere from Photochemical reactions

Control Population?

Prevent indoor air pollutant buildup using air-to-air heat exchangers

Materials evaluation prior to use as building materials (indoor +)

<u>Methods of Pollution Control</u>

Cleanup & Dispersion (Text Pgs. 585-590)

Introduction of CaO (lime) into burning chamber for industrial burning

why?

To form Ca salts with SO_4^{-2} and NO_3^- (<u>chemical modification</u>, neutralization & conversion to salts and products {gypsum $CaSO_4$}) {$CaSO_4 \cdot H_2O$ used in plaster and wall board}

Higher smoke stacks to get above the inversion layer reduce local particulate, smog and pollution but let it fall elsewhere

Capture particulate and some pollutants using
Electrostatic Precipitators, Baghouse Filters,
Cyclone Separators, Wet Scrubbers.

Chemical Modification - example NOx and HCNO (isocyanic acid converts 99% of NOx to N_2 and water {not yet technically feasible commercially}.

☞ "Rule of Thumb"

Cleanup vs. Prevention - Prevention is always cheaper in the long run.