

CIVE 3331 Environmental Engineering

CIVE 3331 - ENVIRONMENTAL ENGINEERING
Spring 2003

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Purpose: Lecture #13 CIVE3331

Criterion Pollutants

Six criteria pollutants that are the focus of CAA regulations are ozone, carbon monoxide, sulfur dioxide, particulates, oxides of nitrogen, and lead. Since 1970 there have been significant reductions in particulate materials and lead, some reduction in carbon monoxide and sulfur dioxide, and an increase in oxides of nitrogen (and ozone).

Carbon Monoxide – CO is a product of incomplete combustion. Oxygen starvation, burn temperature, combustion time, and chamber turbulence all impact the CO production. About 70% of CO is thought to be from automobile emissions.

CO competes with O₂ in blood, the hemoglobin in red cells is a very strong absorber of CO and CO essentially uses all the active heme-sites so that O₂ cannot enter the circulatory system. In high enough concentrations CO can easily kill the organism.

CO in the blood is usually expressed as a fraction of saturation %COHb (Carboxyhemoglobin). The amount of COHb is related to the CO concentration and exposure time.

$$\%COHb = (0.15\%)(1 - e^{-0.402t})[CO]$$

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Where $[CO]$ is the concentration in parts per million, and t is time in hours.

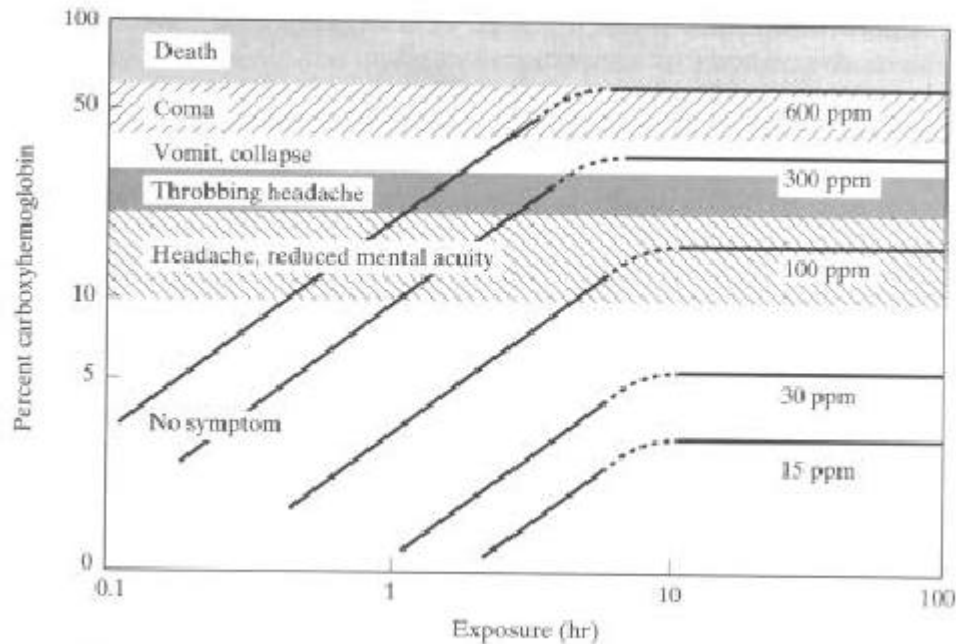


Figure 1. Chart of Health Impacts of CO exposure

Figure 1 is a copy of Fig 7.6 from the text. Note that 10% COHb causes headaches and an evening in a smoky bar, or a day at an indoor tractor pull can achieve these levels of blood CO. CO is rapidly expelled from the body in the presence of clean air. The half-life after exposure is on the order of 3-4 hours.

Oxides of Nitrogen

Seven oxides of nitrogen are known to exist, but only two are considered important in air pollution.

These two are NO and NO₂. Two sources are Thermal NO_x and Fuel NO_x.

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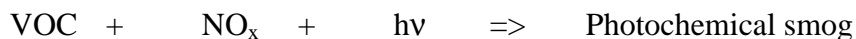
Thermal NO_x is created when N from air in high temperature combustion oxidizes. Fuel NO_x results from the oxidation of nitrogen compounds found in the fuel itself. Different fuels have different amounts of N in them ranging from none in natural gas to nearly 3% in some coals.

NO is relatively harmless, but it oxidizes into NO_2 which can irritate lungs, cause bronchitis, pneumonia and lower resistance to respiratory infections. NO_2 is the compound responsible for the reddish-brown color in the smog over (LA, Houston, etc. – most large polluted cities have pretty sunsets partly because of NO_2 in the air).

NO_x also reacts with VOCs in the presence of sunlight to form photochemical smog, including ozone, another criterion pollutant.

Volatile Organic Compounds (VOCs)

VOC produce photochemical smog. Some VOCs are toxic.



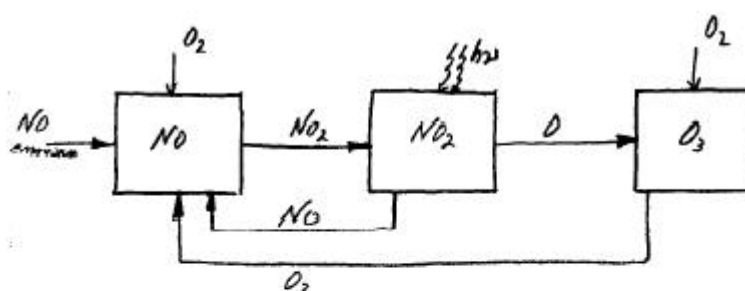
Photochemical smog irritates lungs and eyes. Scars lung tissue. O_3 (one component) damages plant and animal tissue.

The overall smog reactions are quite complex – The following figures are a simplification to illustrate the complex chemical steps thought to be involved.

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- (1) $N_2 + O_2 \rightarrow 2NO$ (thermal NO_x)
- (2) $2NO + O_2 \rightarrow 2NO_2$ (NO oxidizes to NO_2)
- (3) $NO_2 + h\nu \rightarrow NO + O$ (photolysis to split O from NO_2)
- (4) $O + O_2 + M \rightarrow O_3 + M$ (M is like a "catalyst" - needed to absorb excess energy from O+O₂ fusion)
- (5) $O_3 + NO \rightarrow NO_2 + O_2$ (NO_2 scavenges O_3)

Figure 2. Smog reactions (1 of 4)



free radicals initiated
by creation of OH^\bullet with
water vapor create VOC

radicals that slow down
reduction of O_3 thus VOC
help increase observed O_3 values

Figure 3. Smog Reactions (2 of 4)

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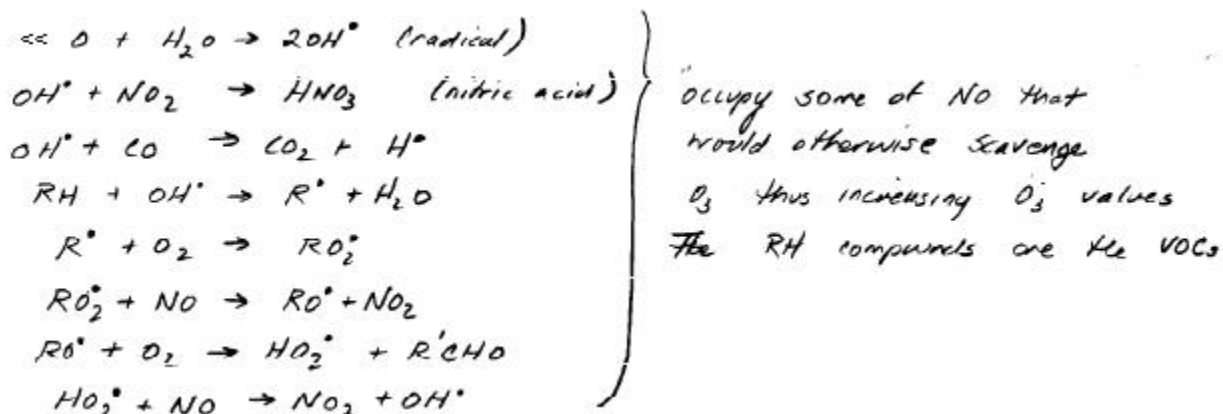


Figure 4. Smog Reactions (3 of 4)

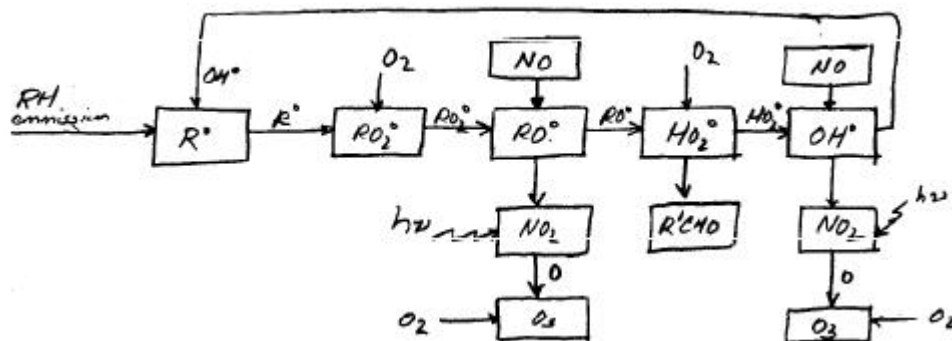


Figure 5. Smog Reactions (4 of 4)


*Ozone**Particulate Matter*

PM-100, PM-10, PM-2.5 etc. Size is based on aerodynamic diameter. Air purifying respirators

(NIOSH approved) can typically remove 99.8% of PM-100 or larger. Smaller sizes are much more difficult to remove and are a greater health threat – principally as vectors of toxic substances. Sizes range from 0.005 μm to 100 μm for particulates in air.

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Stokes law is used to define size.



$$F_r = m_g = \frac{\pi d^3 \rho g}{6}$$

Stokes Law $F_r = 3\pi\eta Vd$

can solve for velocity as

$$V = \frac{\pi g d^2}{18\eta}$$

$\eta = \text{viscosity}$

Aerodynamic size is the value d that satisfies the velocity equation for a particular particulate. Large particles settle faster than small particles (double d , 4X rate).

A useful concept in analysis is to determine the residence time of a contaminant in an environmental compartment. Consider a water drop, $2 \mu\text{m}$ in diameter. Its settling velocity in air is

$$V = \frac{g d^2}{18\eta} = \frac{(10^3/\text{m}^3)(9.8\text{m/s}^2)(2 \cdot 10^{-6}\text{m})^2}{18(0.01729/\text{m}\cdot\text{s})} = 1.27 \cdot 10^{-4} \text{m/s}$$

Now consider a 1000 m tall section of atmosphere. Assume the particles (water drops) are initially uniformly distributed throughout the column.

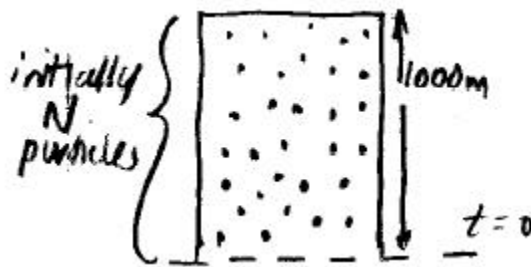


Figure 6. Initial particle distribution

We want to know how long until all the particles leave the box. Using classical settling theory we need to know how long a particle moving with speed v needs to traverse the entire length of the box

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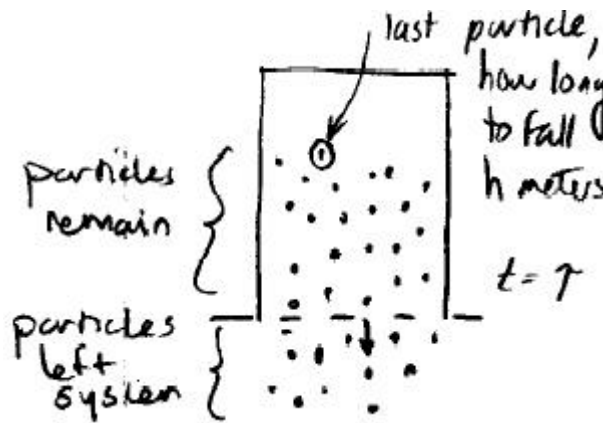


Figure 7. Particles leaving the column

In the current example this time is:

$$h = vt$$

solve for $t = \frac{h}{v} = \frac{1000}{1.27 \cdot 10^{-4} \text{ m/s}} = 7.9 \cdot 10^6 \text{ s} \approx 90 \text{ day.}$

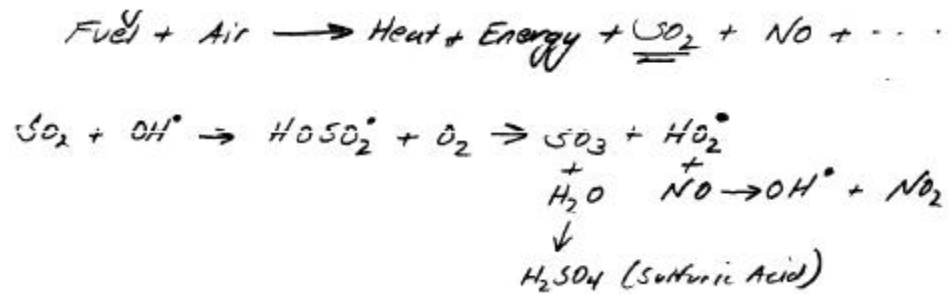
Since half the particles are above 500m and half below the mean residence time is about 45 days.

In general small particles settle slowly. Particles smaller than $10 \mu\text{m}$ can defeat the body's natural defenses. Current regulations track $10 \mu\text{m}$ particles (PM-10) but regulations are beginning to include $2.5 \mu\text{m}$ particles, because of this size particles' ability to do health damage.

Oxides of Sulfur

SO_x result from combustion of fuel, mostly stationary sources (85% from power production).

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SO_3 combines with water vapor in the atmosphere to produce a strong acid (low pH) that precipitates with rainfall (acid rain). These sulfate aerosols (SO_4) can travel large distances before deposition so that impact may be many miles from the source of pollution.

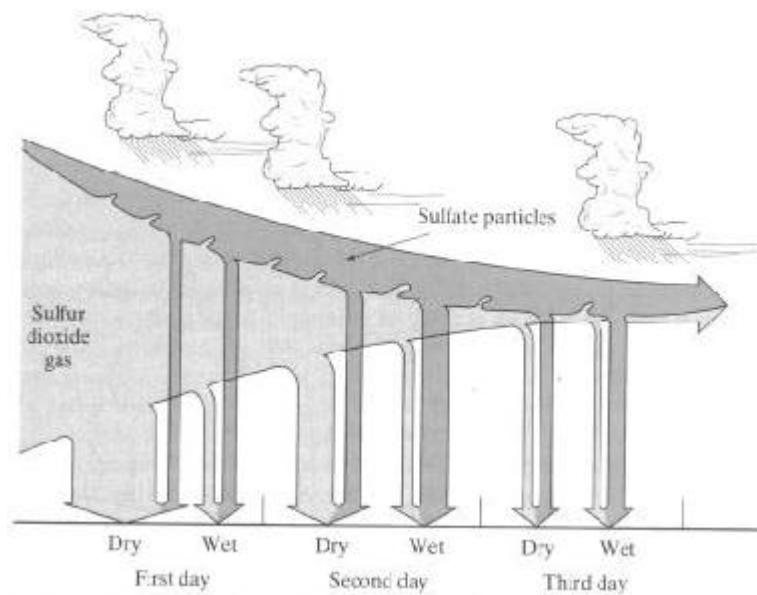


Figure 8. SOx Travel as particulates

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**Figure 9. pH rainfall map of USA***Lead*

Originally tetraethyl lead $\text{Pb}(\text{C}_2\text{H}_5)_4$ was added to motor fuel to reduce pre-ignition in internal combustion engines. Elimination of lead in fuels in late 1980s has practically eliminated motor fuel as a source of lead in the environment in the USA and some other developed nations. Remaining sources are paint, metal smelters, lead-acid battery manufacture and recycling.

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Lead enters the body by inhalation and ingestion. Pb attacks the CNS and higher brain functions – it is nearly impossible to remove from the body although there has been limited success with chelating therapy (EDTA).

Toxic Pollutants

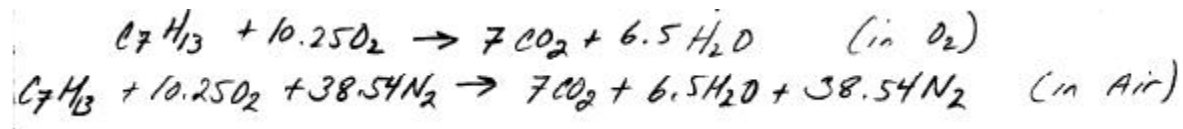
Arsenic, mercury, radionuclides, benzene, beryllium etc.

Some of these materials are directly inhaled and toxic, while others are probably more of a problem as a depositional concern.

[Add health effects and env. Compartments]

Pollutant Sources

About 1/3 of all emissions is from motor vehicles. Major concern is incomplete combustion.



Too little air => fuel in exhaust => wastes fuel, produces VOCs.

Too much air => excess O₂ and heat => increases NO_x

Legislation

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~ 1969 specified certain emissions standards. By 1996 nearly 90% reduction in per vehicle CO and VOCs.

~1979 Corporate Average Fuel Economy (CAFE) - high economy vehicles (in response to oil embargos) tend to emit fewer pollutants.

~1990 SUV and light trucks represent about 40% of fleet. Lower economy and less strict tailpipe standards.

Economy/efficiency

4-stroke (Otto cycle)

2-stroke – pass a lot of fuel to exhaust, run hot and produce lots of thermal NOx.

Diesel – produce lots of particulates , NOx.

Controls –

Recirculation, afterburners, catalytic converters, fuel modification.

Clean fuels – add oxygen to fuels (MTBE, Ethanol) to compensate for oxygen starved combustion.

Emulsions – add water to fuel to increase compression and lower operating temperature.

Alternative fuels – natural gas, propane, alcohol, hydrogen.

Alcohol is a low energy fuel (relative to gasoline). It attacks synthetic rubber in conventional fuel systems.

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Hydrogen is perceived to be dangerous, (its really not). Storage is a problem, gaseous hydrogen always leaks a little. Current hope is absorbtion/despobtion on metal hydrides (kind of like a chemical sponge, a deltaT is used to store and release the hydrogen)

ULEV,ZEV Ultra low emissions vehicles, Zero emissions vehicles. Hybrid (gasoline+battery electric)
Battery and fuel cell based. Range and AC is a challenge.

The other half of emissions($\frac{1}{2}$) is stationary sources. Produce similar emissions as motor vehicles.
Management is somewhat simpler because base load management can be used (don't have to start-stop).

Controls

Pre-combustion – fuel selection

Combustion-chamber geometry, heat transfer, fuel feed

Post combustion-off gasses and exhaust

Fuel type -

Fuel phase - (solid, liquid, gaseous) dictates chamber design.

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Gassification (steam reforming)

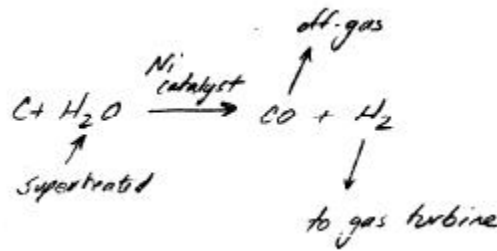


Figure 10. Steam reforming

Low NO_x combustion

Limit air to stoichiometric needs only.

Stratified charge (2 stage combustion)

Off-gas treatments

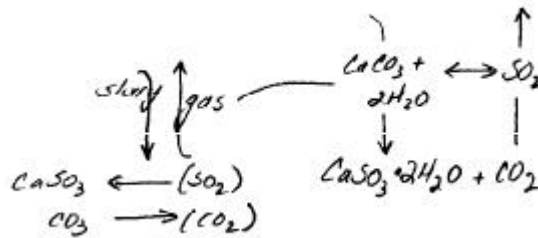


Figure 11. Wet Scrubbing

Wet scrubbers – particulate control

Hydrocyclone precipitation

Filtration

Electrostatic precipitation

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Fuel cell – direct conversion to electricity by RedOx reactions in cell.

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