Criteria Pollutants

Six criteria pollutants O_3, CO, SO_2, PM 10, NO_2, Pb
Since 1970 (Passage of CAA) have seen dramatic reduction in
PM10 & Pb, some reduction CO, SO_2, increase in NO_x.

- CO (Carbon monoxide) — product of incomplete combustion:
  oxygen starved; burn temperature, combustion time (at high temp), chamber turbulence (mixing).

~70% emmissions from motor vehicles

Competes with O_2 in blood. high concentrations can kill multi-cellular aerobic organisms. Expressed as · $\%COHb = 0.15\% (1 - e^{-0.402t/hr})[CO]$
where $[CO]$ = ppm CO in air. Outdoors 100 ppm is typical max value. Indoors 30 ppm typical max.

Physiological effects: 10% - headache; 30% - confusion; 60% - unconsious/death

- Oxides of Nitrogen

NO_x — Thermal NO_x from high-T combustion (N is from air); Fuel NO_x from chemical changes in fuel. (N is from fuel)
NO - no known effects at typ. conc.
NO_2 - irritates lungs, increases chance of respiratory infections. Reacts with OH (radical) to make HNO_3. Causes reddish-brown color in "smog"
Produces photochemical smog.

- Volatile Organic Compounds

VOC - produce photochemical smog; some components are toxic

$$VOC + NO_x + h\nu \rightarrow \text{Photochemical Smog}$$

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

"Smog reactions"

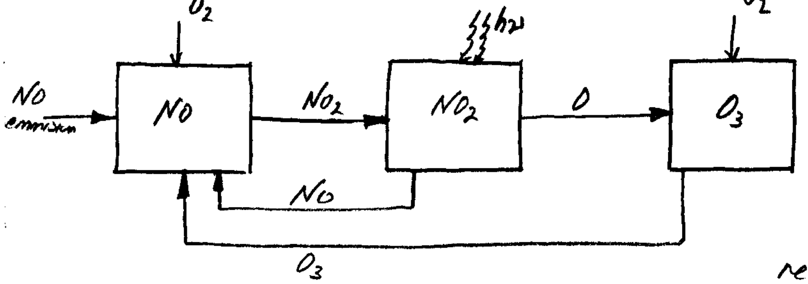
(1) $N_2 + O_2 \rightarrow 2NO$ (Thermal NOx)

(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 $O + O_2$ fusion)

(5) $O_3 + NO \rightarrow NO_2 + O_2$ (NO_3 scavenges O_3)



free radicals iniatiated by creation of OH° with water vapor create VOC radicals that slow down reduction of O_3 thus VOC help increase observed O_3 values

$O + H_2O \rightarrow 2OH^\circ$ (radical)

$OH^\circ + NO_2 \rightarrow HNO_3$ (nitric acid)

$OH^\circ + CO \rightarrow CO_2 + H^\circ$

$RH + OH^\circ \rightarrow R^\circ + H_2O$

$R^\circ + O_2 \rightarrow RO_2^\circ$

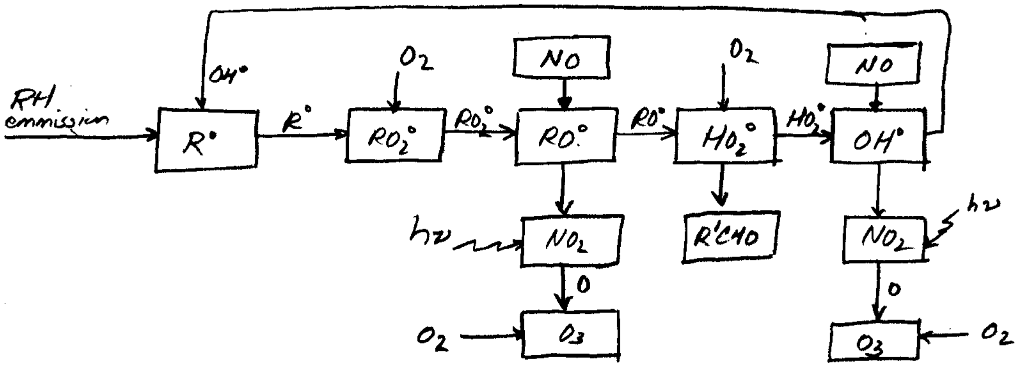
$RO_2^\circ + NO \rightarrow RO^\circ + NO_2$

$RO^\circ + O_2 \rightarrow HO_2^\circ + R'CHO$

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

"occupy some of NO that would otherwise scavenge O_3 thus increasing O_3 values

The RH compounds are the VOCs



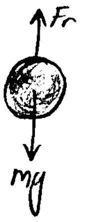
• **Particulate matter**

PM-100 , PM-10 , PM-2.5

Size is based on aerodynamic diameter. Air purifying respirators (typ. NIOSH approved) can remove 99.8% of PM-100 or larger. Smaller sizes are more difficult to remove and are a greater threat

Sizes range from 0.005μm – 100μm (Particulates)

Stokes Law used to define size



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

Stokes Law $F_r = 3\pi\eta V d$

can solve for velocity as

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

η = Viscosity

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

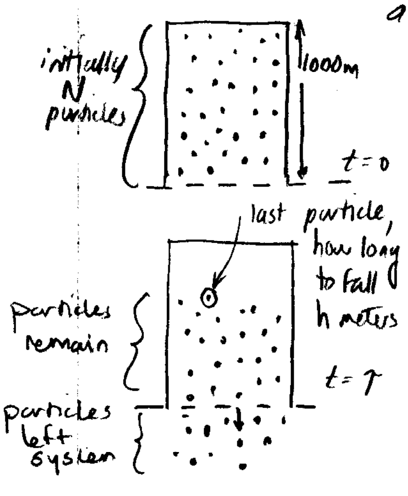
Residence time

Useful concept in analysis is to determine residence time of a contaminant in an environmental compartment.

Consider a water drop 2μm in diameter. Its settling velocity is

$$V = \frac{\rho g d^2}{18\eta} = \frac{(10^6 g/m^3)(9.8 m/s^2)(2\cdot10^{-6} m)^2}{18(0.0172 g/m\cdot s)} = 1.27\cdot10^{-4} m/s$$

Now consider a 1000m tall section of atmosphere



assume particles are initially uniformly distributed throughout column.

Want to know how long until all particles leave box. Using classic settling theory we simply need to know how long a particle moving with speed v needs to traverse the distance h?

$h = vt$ solve for $t = \frac{h}{v} = \frac{1000}{1.27\cdot10^{-4} m/s} = 7.9\cdot10^6 s \approx 90$ day.

In general small particles settle slowly. Particles smaller than 10μm can defeat body's natural defenses.
Current regulations track 10μm particles (PM-10) but regulation of PM-2.5 will become important, as the smaller particles appear to have significant health affects.

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

$$\text{Fuel} + \text{Air} \longrightarrow \text{Heat} + \text{Energy} + \underline{\underline{SO_2}} + NO + \cdots$$

$$\begin{array}{lcl} SO_2 + OH^\bullet \rightarrow HOSO_2^\bullet + O_2 \rightarrow & SO_3 & + \; HO_2^\bullet \\ & + & \;\;\; + \\ & H_2O & \;\;\; NO \rightarrow OH^\bullet + NO_2 \\ & \downarrow & \\ & H_2SO_4 \text{ (Sulfuric Acid)} & \end{array}$$

SO_3
Combines with water vapor in 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 source of pollution.

Lead Pb

Orginally tetraethyl lead $Pb(C_2H_5)_4$ 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 environment in USA and some other developed nations.
Remaining sources are paint, metal smelters, lead-acid battery manufacture.

Lead enters body by inhalation & ingestion. Pb attacks CNS and higher brain functions — nearly impossible to remove from body although some success with EDTA cheleating

Air toxics

arsenic, mercury, radionuclides, benzene, beryllium, etc.

Sources of pollutants

Motor vehicle emmissions, Stationary sources (factories, powerplants)

Motor Vehicles

About 1/2 of all emmissions. Incomplete combustion

$$C_7H_{13} + 10.25O_2 \rightarrow 7CO_2 + 6.5H_2O \quad (\text{in } O_2)$$

$$C_7H_{13} + \underbrace{10.25O_2 + 38.54N_2}_{} \rightarrow 7CO_2 + 6.5H_2O + 38.54N_2 \quad (\text{in Air})$$

too little air ⇒ fuel in exhaust → wastes fuel + VOC

too much air ⇒ excess O_2 & heat → increases NOx

Legislation ~1969 specified certain emmissions standards

by 1996 nearly 90% reduction in per vehicle CO & VOC

1973 Corporate Average Fuel Economy (CAFE) - high economy vehicles tend to emit less pollutants

1990's SUV & light trucks represent about 40% of fleet - lower economy & less strict tailpipe standards.

Economy/efficiency

4-stroke engine (otto cycle)

2-stroke engine - pass a lot of fuel to exhaust. Run hot and produce a lot of thermal NOx

diesel - produce a lot of thermal NOx & particulates

Controls - recirculation, afterburner, catalytic converters

- clean fuels: add "oxygen" to fuel by modifying chemistry; reformulated gasoline (RFG)

6/6

Alternative fuels

- CH_3OH (methanol) ⇒ formaldehyde in exhaust
  low energy content; attacks synthetic rubber in conventional fuel systems

ULEV, ZEV   hybrid, battery-electric, fuel cell - range, speed, AC

Stationary sources

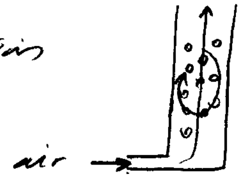
About 1/2 of all emmissions. Produce similar emmisions as motor vehicles. Can be managed better using base-load concepts (eg. don't have to start/stop)

Controls: pre combustion - fuel
combustion - chamber geometry, heat transfer, fuel feed
post-combustion - off gasses & exhaust

fuel type: solid (coal), liquid (diesel, fuel oil, hydrocarbon slurry)
gas (natural, propane etc.)

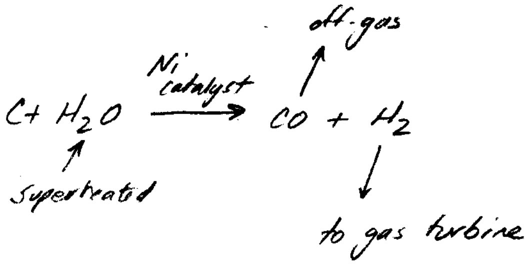
fuel type (phase) dictates combustion chamber design

Fluidized bed combustion



"porous medium combustion"

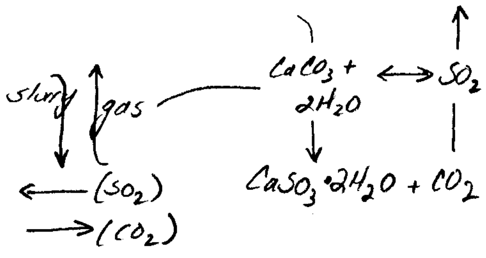
Gassification (steam reforming)



low NO_x combustion

1) limit air to reduce fuel NOx
2) Stratified charge (2-stage) combustion

Off gas treatments - wet scrubbers



particulate control
- hydrocyclone separation
- electrostatic precipitation
- filtration

Fuel cell - direct conversion fuel to electricity by redox reactions