Tropospheric Chemistry

Environmental Chemistry, vanLoon & Duffy – Chapter 4

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What is Smog?

Smog is a general term referring to forms of air pollution in which atmospheric visibility is partially obscured by a haze consisting of solid particulates and/or liquid aerosols.

The name originates from the combination of "smoke" and "fog".

Two types of smog are well-defined:
-Classical or London smog.
-Photochemical or Los Angeles smog.

Classical Smog

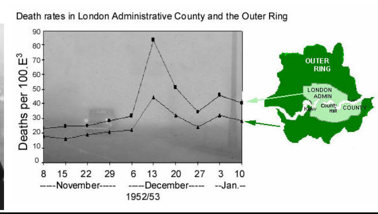
Classical smog is associated with the use of the traditional fuel, coal.

It's characterized by a high concentration of unburned carbon soot and elevated levels of SO_2.

Where the atmospheric is humid, the carbon particles serve as nucleation sites for the condensation of water droplets forming an irritating fog.

Classical smog was encountered in various cities in the 19th century.

In 1952, a severe smog lasted for week in London causing the death of more than 4000 persons.



Photochemical Smog

Photochemical smog is based on emissions form petroleum combustion, principally from motor vehicles, followed by a sequence of chemical and photochemical reactions occurring under specific conditions.

Photochemical smog contains high levels of oxidants (bad ozone and other oxidants) and carbon-containing reaction products.

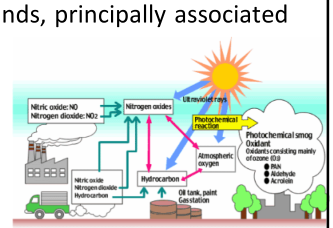
Conditions required for photochemical smog formation:

-Source of precursors, hydrocarbons and NO_x compounds, principally associated with internal combustion engines.

-A stable atmosphere to hold the reactants in place.

-High temperature to increase thermal reaction rates.

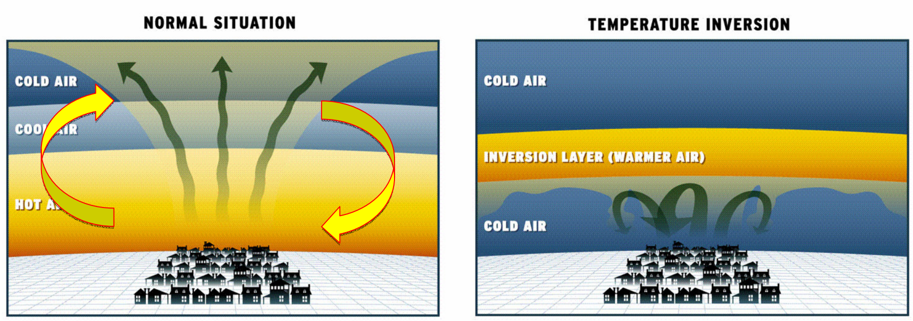
-Intense sunlight to facilitate photochemical reactions.



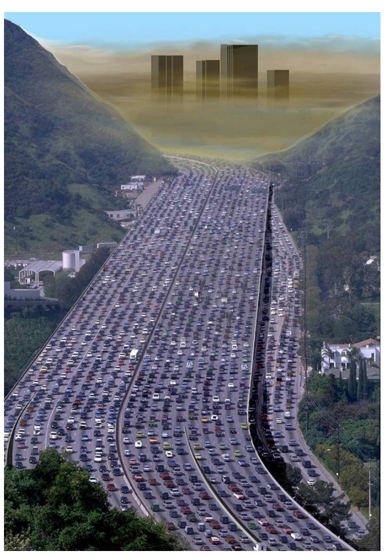
Photochemical Smog

A stable atmosphere ensures that the released gases remain in the same location where they are able to react.

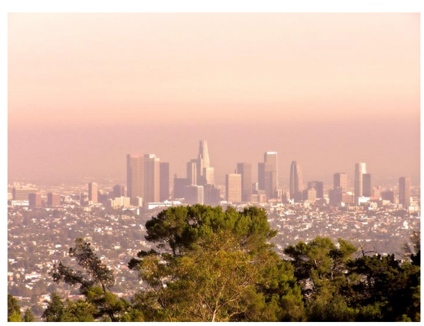
Stability is achieved where there is a temperature inversion in the troposphere.



Photochemical Smog



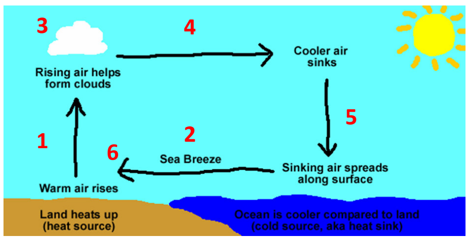
The requisite conditions for the formation of photochemical smog are available in automobile-rich cities (e.g. Los Angeles).

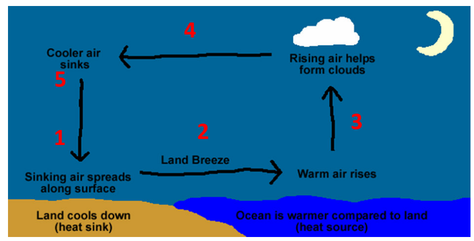


Photochemical Smog

Topography plays also a role in the concentration of the pollutants and thus the formation of the photochemical smog.

Air circulation flushes the smog (the Seawind/Landwind circulation is a local circulation driven by temperature/density gradients).



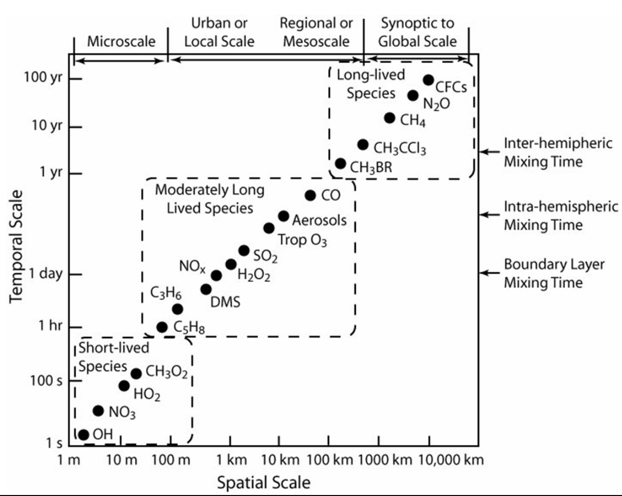


1. Warm air over land rises.
2. Sea Breeze moves inland as a mesoscale cold front.
3. Cumuli develop aloft and move seaward.
4. Upper level return land breeze.
5. Cool air aloft sinks over water.
6. Sea Breeze (meso-cold) Front.

1. Cool air over land sinks.
2. Land Breeze moves out over water.
3. Relatively warmer water heats air which then rises.
4. Upper level return sea breeze.
5. Cool air over land sinks.

Photochemical Smog

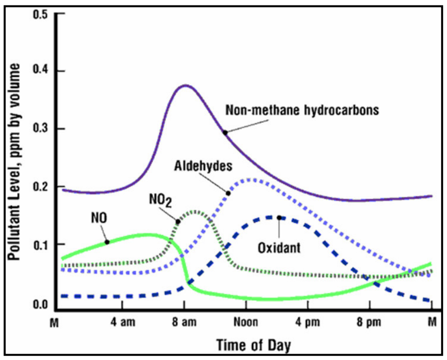
The lifetime of air pollutants depends very much on their chemical properties and ranges from seconds for •OH to several 10's of years for CO_2, N_2O.

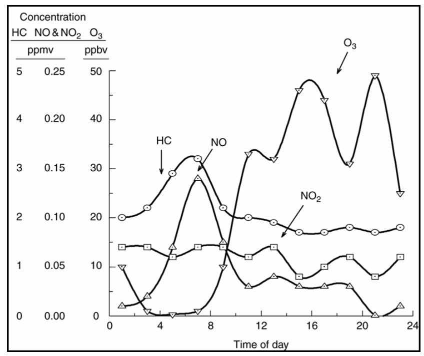


The Chemistry of Photochemical Smog

Photochemical smog contains high levels of oxidants (bad ozone and other oxidants) and carbon-containing reaction products.

The chemistry involved in the formation of photochemical smog has been studied in detail. It's summarized as follows:

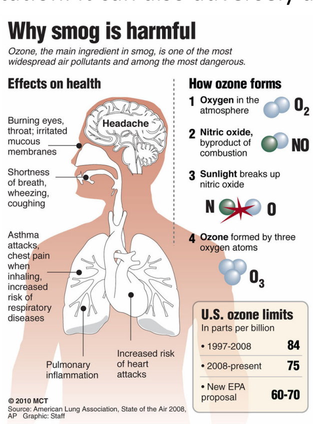




The Chemistry of Photochemical Smog

Photochemical smog is observable from midday to late afternoon.

In addition to producing a visible haze, it also causes eye and other membrane irritation. It can also adversely affect plant growth.



Hydroxyl Radical Production

Hydroxyl-radical formation takes place via a reaction sequence that begins with the production of nitric oxide.

$$N_2 + O_2 \Leftrightarrow 2NO$$

Because the right-to-left reaction is endothermic, nitric oxide is produced at significant high-energy conditions (like engines of the cars).

In air, NO is oxidized to nitrogen dioxide by oxygen or other oxidants.

$$2NO + O_2 \rightarrow 2NO_2 \quad \text{(slow)}$$

A second and more important mechanism for the oxidation of NO is:

$$NO + O_3 \rightarrow NO_2 + O_2$$

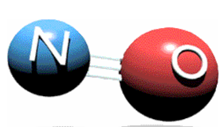
A third route for the oxidation of NO involves reaction with peroxyl radicals:

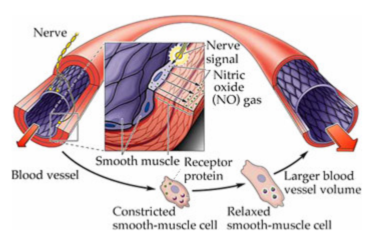
$$ROO\bullet + NO \rightarrow RO\bullet + NO_2$$

Hydroxyl Radical Production

NO

- Cellular inflammation at very high concentrations.
- May be incorporated into hemoglobin in the blood to interfere with the transport of oxygen around the body.





NO_2

- irritate the lungs.
- lower resistance to respiratory infection such as influenza.

$NO_2 \xrightarrow{h\nu,\ \lambda < 400\ nm} NO + O(^3P)$

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

Major reaction to forming ozone in the Troposphere

$O_3 \xrightarrow{h\nu,\ \lambda < 315\ nm} O^* + O_2^*$

$O^* + H_2O \rightarrow 2\ \bullet OH$

$NO_2 + H_2O \rightarrow NO + 2\ \bullet OH$

One NO_2 can produce two •OH; most important means.

Another mechanism (in heavily polluted atmospheres)

$NO + NO_2 + H_2O \rightarrow 2HONO$

$2HONO \xrightarrow{h\nu,\ \lambda < 400\ nm} 2NO + 2\ \bullet OH$

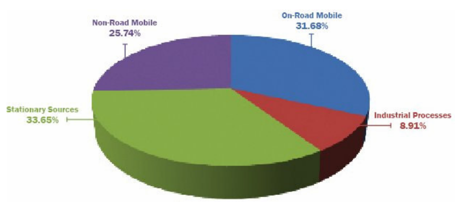
$NO_2 + H_2O \rightarrow NO + 2\ \bullet OH$

Also one NO_2 can produce two •OH.

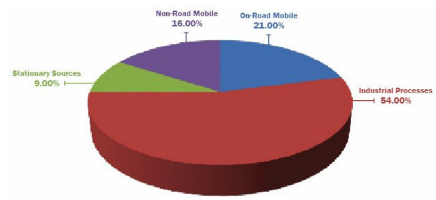
The production of •OH in urban atmosphere is a function of the presence of NO_2 in an internal combustion engine.

[•OH] in a polluted urban environment = 2.5×10^6 molecules cm^{-3}
[•OH] in a relatively clean rural area = 1.0×10^5 molecules cm^{-3}

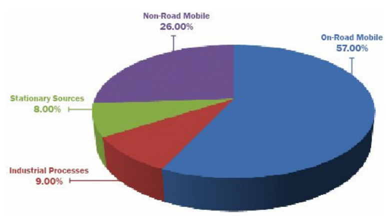
NO_x Emissions 2008



VOC Emissions 2008



CO Emissions 2008



From the website of the US Department of Transportation – Federal Highway Administration.

AUB The Chemistry of Photochemical Smog

Oxidation Hydrocarbons - Alkanes

Besides being a source of NO, internal combustion engines simultaneously emit unburned volatile hydrocarbons and these are oxidized through reactions initiated by the highly reactive hydroxyl radical.

Hydrogen abstraction: $RCH_3 + \bullet OH \rightarrow RCH_2\bullet + H_2O$
alkyl

Dioxygen addition: $RCH_2\bullet + O_2 + M \rightarrow RCH_2OO\bullet + M$
per oxyalkyl

Oxygen abstraction by NO: $RCH_2OO\bullet + NO \rightarrow RCH_2O\bullet + NO_2$
alkoxyl

Formation of aldehyde: $RCH_2O\bullet + O_2 \rightarrow RCHO + HOO\bullet$
aldehyde *hydro peroxyl*

NO_2 regeneration: $HOO\bullet + NO \rightarrow NO_2 + \bullet OH$

$$RCH_3 + 2O_2 + 2NO \rightarrow RCHO + 2NO_2 + H_2O$$

Hydrocarbon reactivity increases with size and number of double bonds

Oxidation Hydrocarbons - Alkanes

A cascade of reactions increases the number of •OH radicals:

$$RCH_3 + 2O_2 + 2NO \rightarrow RCHO + 2NO_2 + H_2O$$

$$2NO_2 + 2H_2O \rightarrow 2NO + 4 \bullet OH$$

$$RCH_3 + 2O_2 + H_2O \rightarrow RCHO + 4 \bullet OH$$

NO as "Catalyst"

Finally the •OH has a limited lifetime – termination reactions:

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

Removed by precipitation

$$HOO\bullet + HOO\bullet \rightarrow H_2O_2 + O_2$$

$$\bullet OH + HOO\bullet \rightarrow H_2O + O_2$$

The products of each of these reactions are relatively stable.

Secondary Reactions

There are secondary reactions that occur simultaneously with the oxidation of hydrocarbons.

$$NO_2 \xrightarrow{h\nu,\ \lambda < 400\ nm} NO + O(^3P)$$

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

Other very important reactions involve the aldehyde product of oxidation of hydrocarbons.

$$CH_3CHO + \bullet OH \rightarrow CH_3CO\bullet + H_2O$$

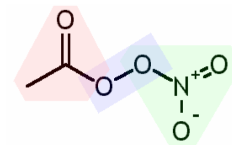
$$CH_3CO\bullet + O_2 + M \rightarrow CH_3C(O)OO\bullet + M$$

acetylperoxy

$$CH_3C(O)OO\bullet + NO_2 \Leftrightarrow CH_3C(O)OONO_2$$

Peroxyacetic Nitric Anhydride (PAN)
a storage-product for NO_2

About PANs

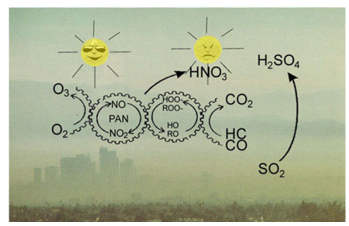


✓PANs are the major eye irritants in a photochemical smog.

✓PANs are reservoirs of NO_x.

✓PANs is a relatively stable molecule, especially at low temperatures Lifetime 20 days at 263K) → may be transported over long distances by air currents.

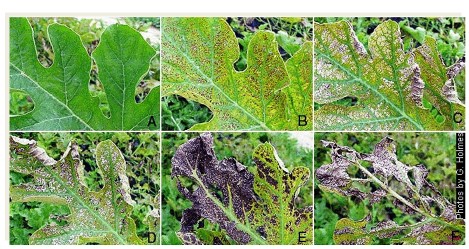
✓In warmer locations, PAN decomposes to produce NO_2 → additional photochemical ozone and •OH radicals.



About PANs

Ozone and PAN Damage

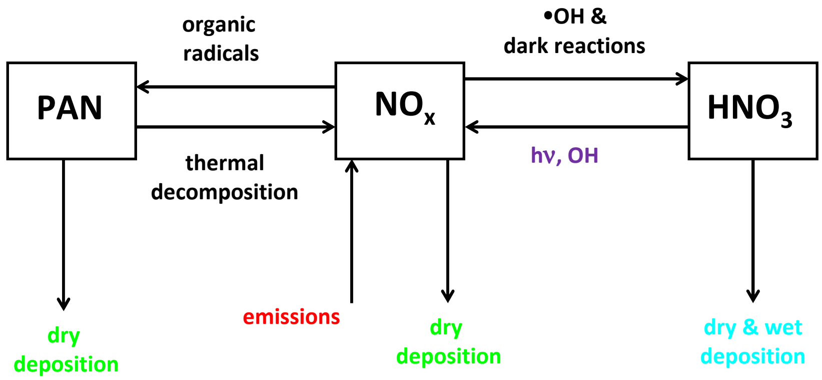
- To right: Leaf severe damage due to ozone exposure.



- To right: Potato leaves showing bronzing due to PAN exposure.

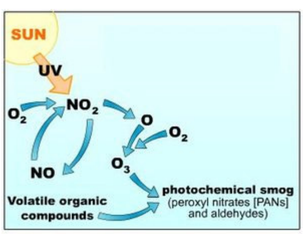
The Chemistry of Photochemical Smog

Simplified Schematic of NO_x Chemistry in the Troposphere

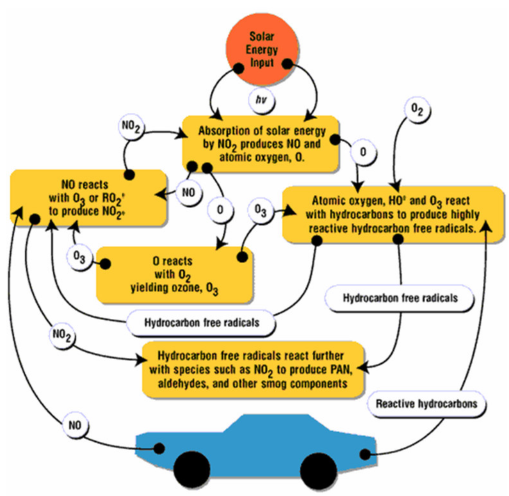


The Chemistry of Photochemical Smog

Summary: Photochemical Smog



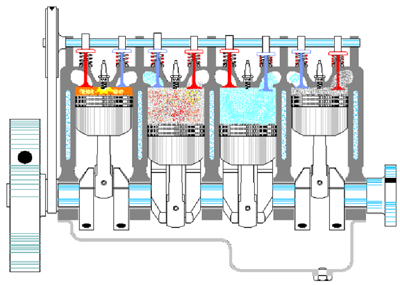
FORMATION OF PHOTOCHEMICAL SMOG



The Internal Combustion Engine as Source of CO and NO_x

$$\Delta G = \Delta H - T\Delta S$$

$$\ln K_{eq} = \frac{-\Delta G_T^{\,0}}{R\,T}$$



$N_2 + O_2 \Leftrightarrow 2\,NO$ is this reaction likely to occur?

Compound	ΔG_f^0 (kJ mol^{-1})	ΔH_f^0 (kJ mol^{-1})	ΔS^0 (J mol^{-1} K^{-1})
N_2	0	0	191.6
O_2	0	0	205.1
NO	86.55	90.25	210.8

The Internal Combustion Engine as Source of CO and NO_x

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N_2	0	0	191.6
O_2	0	0	205.1
NO	86.55	90.25	210.8

$\Delta G^0 = \Sigma\Delta H_p^0 - \Sigma\Delta H_r^0 - T\,(\Sigma S_p^0 - \Sigma S_r^0)$

ΔG_{25}^0 = 2x90250 – 298 (2x210.8 - 191.6 - 205.1) J mol^{-1} = 173 kJ mol^{-1}

ΔG_{2500}^0 = 2x90250 - 2773 (2x210.8 - 191.6 - 205.1) J mol^{-1} = 111 kJ mol^{-1}

$\ln K_{eq}(25)$ = -69.8 $K_{eq} = 4.7\times10^{-31}$

$\ln K_{eq}(2500)$ = -4.68 $K_{eq} = 9\times10^{-3}$

$$\Delta G = \Delta H - T\Delta S$$

$$\ln K_{eq} = \frac{-\Delta G_T^{\,0}}{R\,T}$$

AUB

The Internal Combustion Engine as Source of CO and NO_x

$$N_2 + O_2 \Leftrightarrow 2\,NO$$

$$K_{eq} = \frac{[NO]^2}{[O_2][N_2]}$$

$$[NO] = \sqrt{K_{eq}[O_2][N_2]}$$

$$mixing\ ratio\ NO = p_{NO} / p_{tot}$$

At ambient temperature

T=25°C, P_{O2}=21 kPa P_{N2}=79 kPa

$$P_{NO} = \sqrt{4.7\times10^{-31}\times0.79\times0.21}\ atm = 2.8\times10^{-16}\,atm$$

P_{NO} = 2.8×10^{-11} Pa **P_{NO}/P_{tot} = 2.8 ×10^{-16} or 2.8 ×10^{-7} ppbv**

At 2500°C (precise calc. see book)

P_{O2}= 1 kPa P_{N2}= 650 kPa

N_2	+ O_2	$\longleftrightarrow$ $2NO$
650	1	0
$650-x$	$1-x$	$2x$

$$K_{eq} = \frac{P_{NO}^2}{P_{N2}P_{O2}} = \frac{(2x)^2}{(650-x)(1-x)}$$

$$\approx \frac{4x^2}{650(1-x)} = 9\times10^{-3}$$

x is negligible compared to 650

P_{NO} = 2x = 1.3 kPa

P_t= 650+1 ≈ 650 kPa **P_{NO}/P_{tot} = 1.3/650 = 2 ×10^{-3} or 2000 ppmv**

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The Internal Combustion Engine as Source of CO and NO_x

P_{NO}/P_{tot} at 2500°C: 2000 ppmv

P_{NO}/P_{tot} at 25°C: 2.8 ×10^{-7} ppbv

But NO doesn't disappear at room temperature!

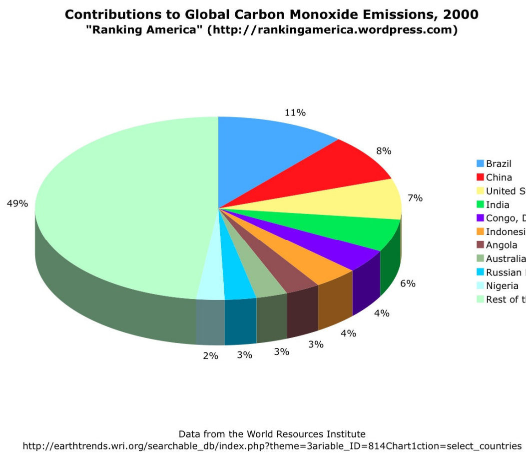
Kinetics control the concentration rather than thermodynamics:

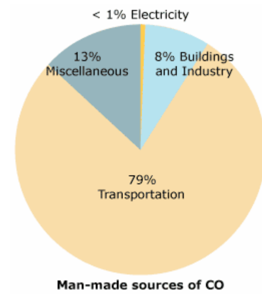
At high T – high reaction rate
($E_{a\text{-}forward}$ provided thermally)

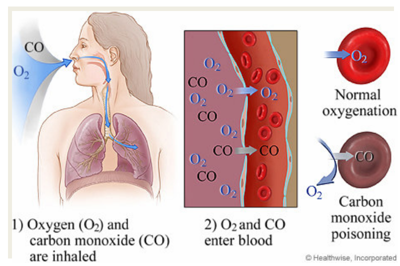
At low T – no reaction rate
(no source for $E_{a\text{-}reverse}$)

Thus combustion engines feed NO into the Troposphere

Carbon Monoxide: Sources and Sinks







Carbon Monoxide: Sources and Sinks

Sources

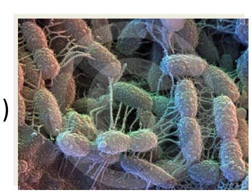
- Incomplete combustion (internal engine)
- Biomass burning
- Methane oxidation
- Oxidation of non-methane hydrocarbon
- Decay of plant matter

Sink

- Reaction with •OH radical:

$$\bullet OH + CO \rightarrow CO_2 + H\cdot$$
$$H\bullet + O_2 + M \rightarrow HOO\bullet + M$$

- Removal by soil microorganism (enzymatic oxidation)



Carbon Monoxide: Atmospheric Chemistry

$CO + \bullet OH + O_2 \rightarrow CO_2 + HOO\bullet$

$HOO\bullet + NO \rightarrow NO_2 + \bullet OH$

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

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

Net: $CO + 2\,O_2 + h\nu \rightarrow CO_2 + \mathbf{O_3}$

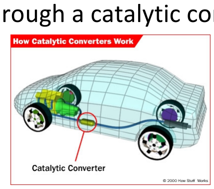
The net reaction can be viewed as a catalytic oxidation of CO to CO_2. Net formation of O_3 occurs.

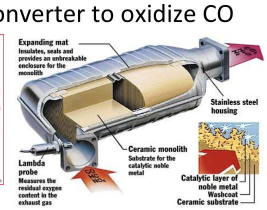
Carbon Monoxide: Control Strategies on the Automobile Source

Employ a leaner air/fuel mixture (higher air/fuel ratio)

Employ catalytic exhaust reactors

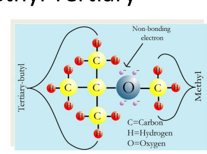
- Excess air is pumped into the exhaust pipe.
- Air-exhaust mixture pass through a catalytic converter to oxidize CO to CO_2.

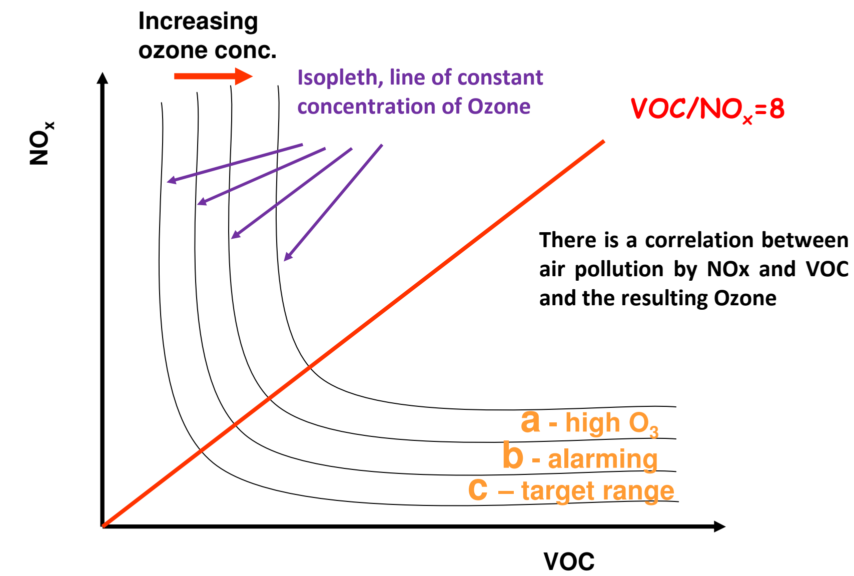




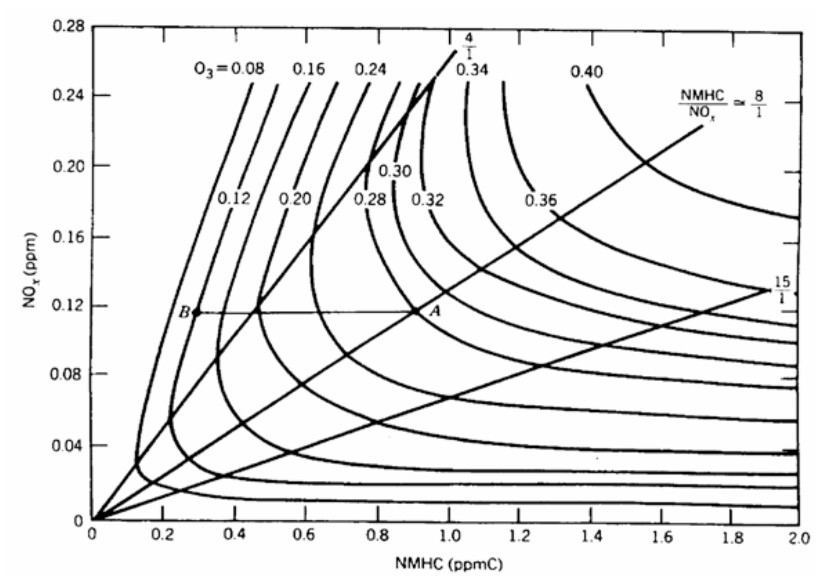
Addition of oxygenates to gasoline

- Examples of oxygenates: methanol, ethanol, MTBE (Methyl Tertiary Butyl Ether)





There is a correlation between air pollution by NOx and VOC and the resulting Ozone



AUB

VOC & NO_x - Ozone Isopleths

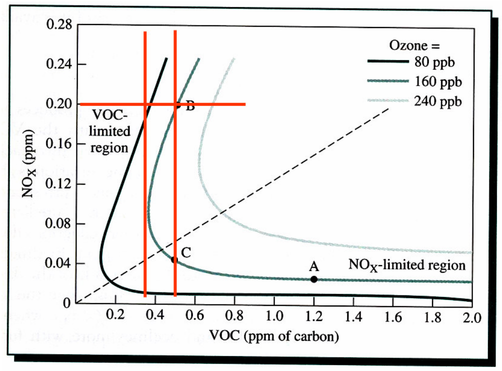
Three chemicals required:

Ozone, NO_x, and VOC

As illustrated in this figure, ozone concentration is a function of NO_x and VOC.

Problem: Assuming a NO_x concentration of 0.20 ppm, estimate ozone levels by reducing VOC concs. from 0.5 to 0.35 ppm.

Is this "VOC-limited?" i.e., when you change VOC concentration a small amount, do you have a large effect on ozone concentration?



Yes, this combination is VOC-limited. The ozone concentration is reduced from 160 ppb to 80 ppb when VOC reduced.

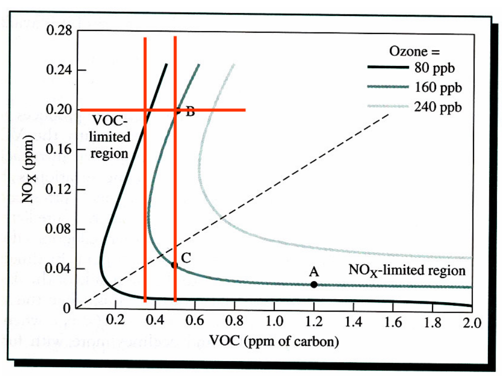
AUB

VOC & NO_x - Ozone Isopleths

How can you manage a change in VOC?

•So how do you get to 0.08 ppm or 80 ppb if the concentrations for NO_x, O_3, and VOC indicate your city to be at point "A"?

•This might represent the situation in Atlanta which has a large number of southern pines that give off terpenes.



Without terpenes *(a large and varied class of hydrocarbons, produced primarily by a wide variety of plants, particularly conifers)* you might find the city at point "B".
Do you cut down the trees?

Issues in O_3 Pollution Control

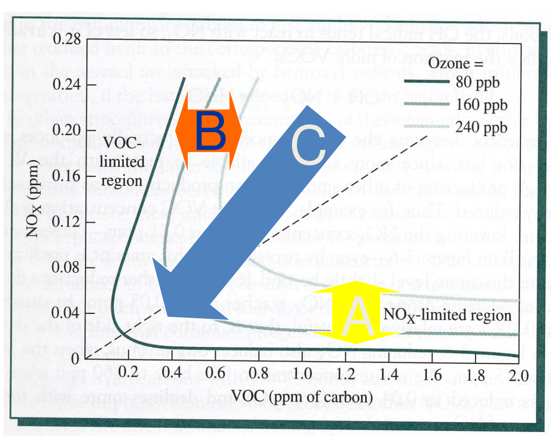
Questions:

- NO_x or HC (VOC) emission controls or combination.
- Degree of emission controls – How much O_3 do we accept?

Uncertainties

- Reliability of emission inventories (e.g. natural hydrocarbon inventories).
- Reliability of air quality models (e.g. local vs transported NO_x/HC/O_3).

Manage Air Pollution



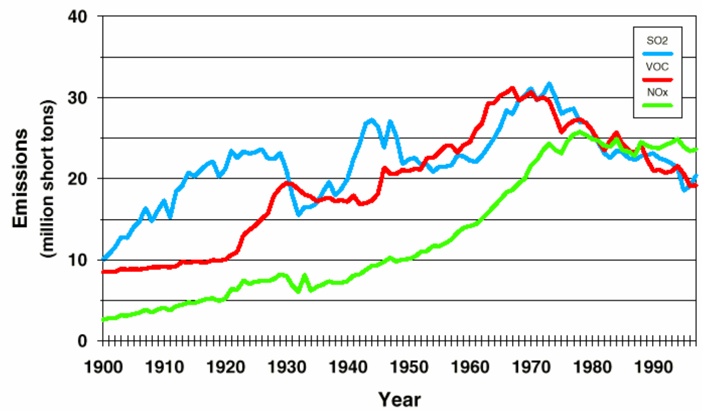
A) NO_x is the critical issue

B) VOC is the critical issue

C) The situation is out of control with regard to NO_x and VOC

Did we learn a lesson in atmospheric pollution control?

Figure 15. Trend in National Emissions, SULFUR DIOXIDE, VOLATILE ORGANIC COMPOUNDS, and NITROGEN OXIDES (1900 to 1997)



Did we learn a lesson in atmospheric pollution control?

Figure 16. Trend in National Emissions, CARBON MONOXIDE (1940 to 1997), LEAD (1970 to 1997)