Urban Air Pollution – "London" Smog

"London" smog:

- **fog**
- **soot particles**
- **sulfur dioxide**
- **tar**

This forms a highly acidic mist.

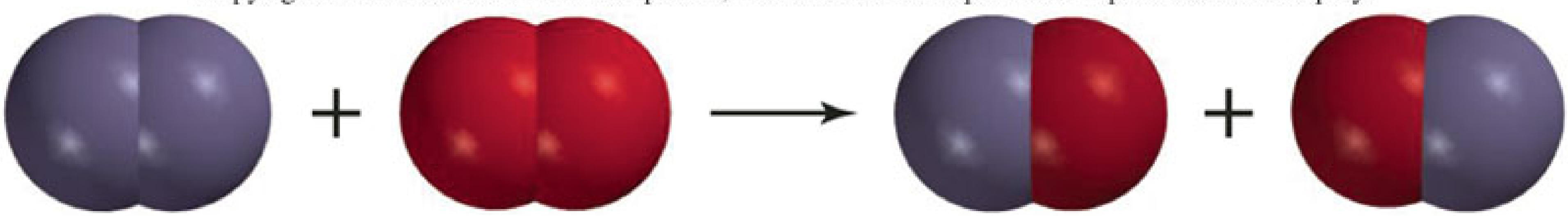
Some incidents of deaths associated with sulfurous smog:

1930	Meuse Valley, Belgium	63
1948	Donora, Pennsylvania	20
1952	London (5 days)	4000
1962	London	700

These deaths lead to a reduction in coal consumption and an increase in alternative fuels, such as gasoline...

NO_x Atmospheric Chemistry

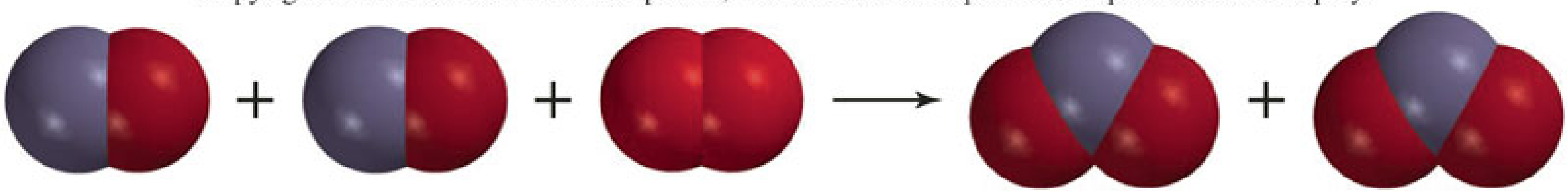
- Under very high temperature conditions, the normally stable nitrogen and oxygen in the air will react to form nitrogen monoxide



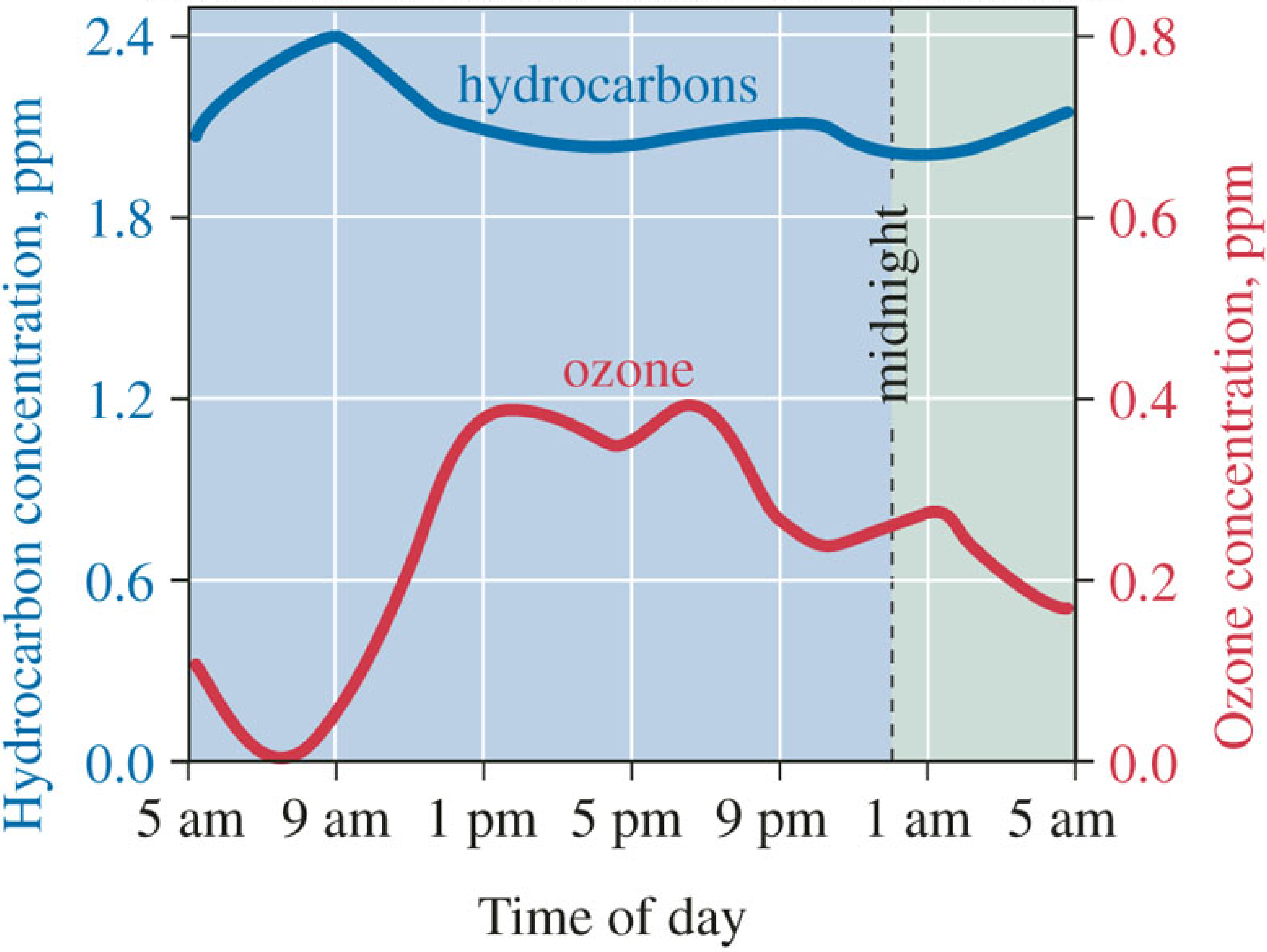
$$N_2 + O_2 \rightarrow NO + NO$$

NO_x Atmospheric Chemistry

- Nitrogen monoxide is very reactive and will react with oxygen to create nitrogen dioxide



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



hydrocarbons
ozone
midnight
Hydrocarbon concentration, ppm
Ozone concentration, ppm
2.4
1.8
1.2
0.6
0.0
0.8
0.6
0.4
0.2
0.0
5 am
9 am
1 pm
5 pm
9 pm
1 am
5 am
Time of day

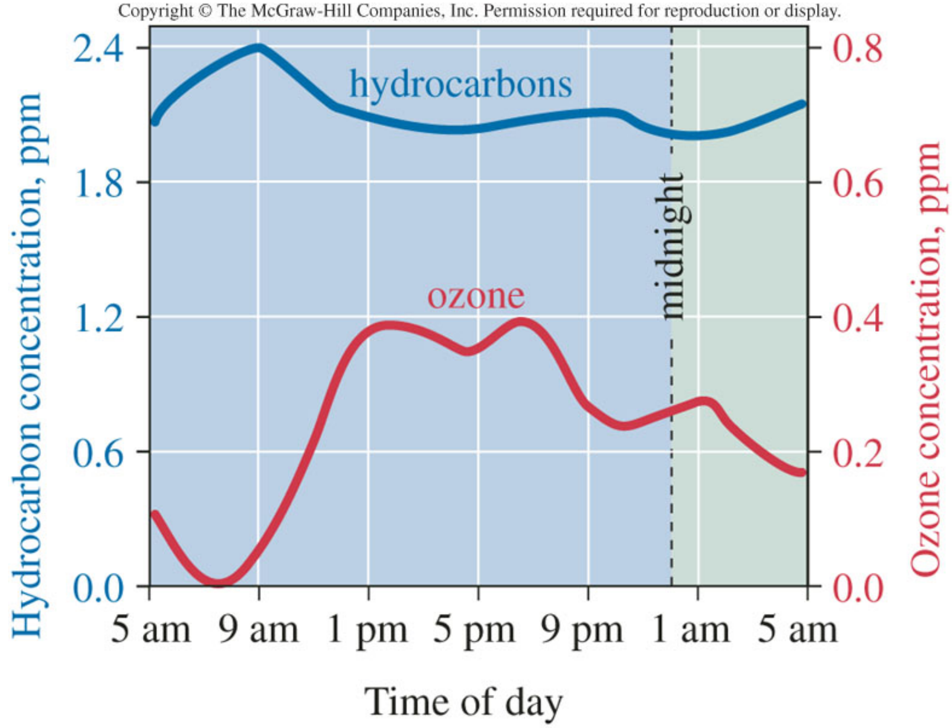
Your Turn 1.32

This figure shows how hydrocarbon and ozone concentrations might vary over time in a metropolitan area.

a. At what time of day are the ozone levels at their highest? Assuming that the sun rises at 6 am and sets at 8 pm, what are the ozone levels like when it's dark?

b. Why would you expect hydrocarbon levels to rise in the morning rush hour?

c. Name a compound that could be contributing to the hydrocarbon increase.



Ozone Atmospheric Chemistry

$$NO_2 \xrightarrow{sunlight} NO + O$$

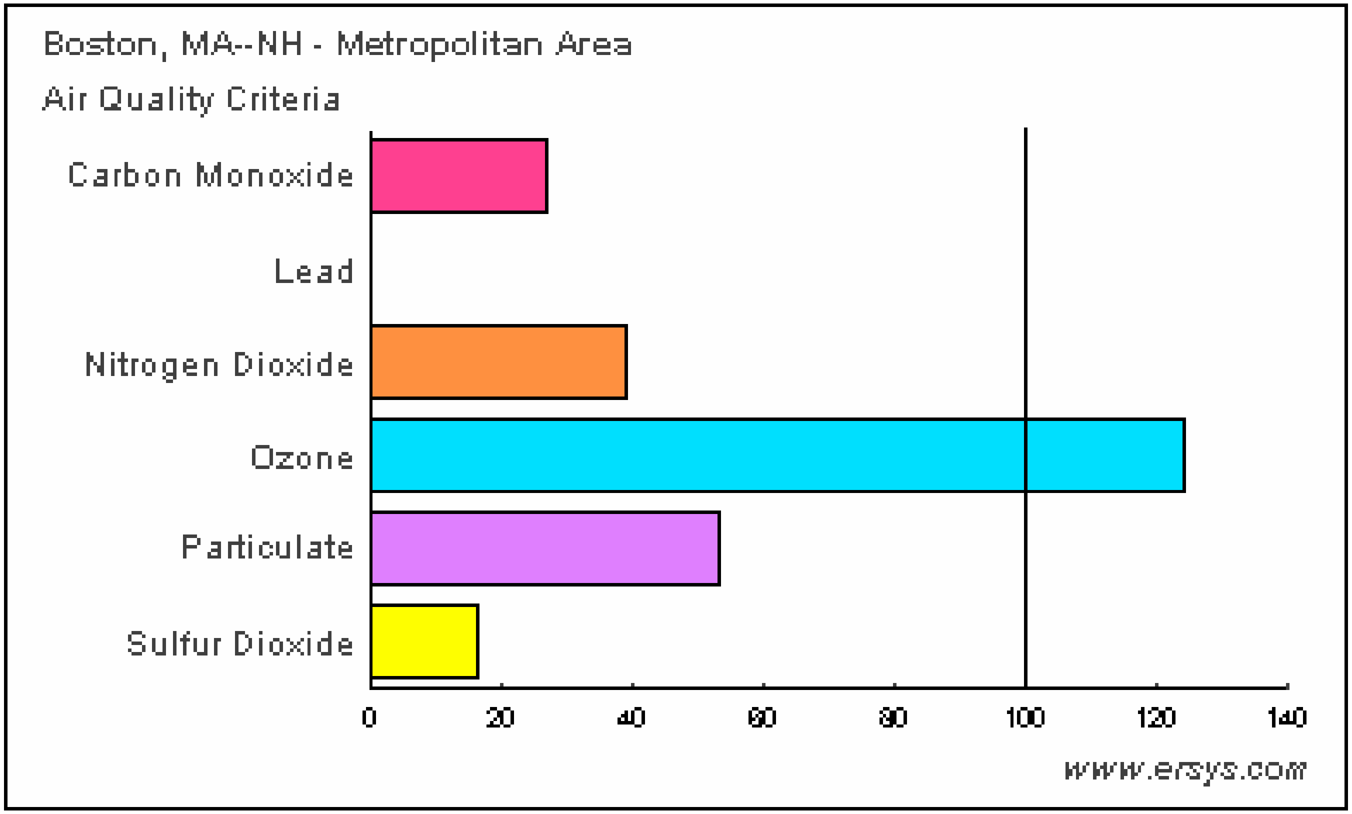
$$O + O_2 \rightarrow O_3$$

- NO is emitted from an automobile.
- NO reacts with VOCs and •OH radicals to form NO_2.
- NO_2 reacts with visible light to form a highly reactive oxygen atom.
- The oxygen atom reacts with molecular oxygen to form ozone.

Smog

- This mixture of O_3, NO_2 and VOCs is called "**photochemical smog**" or "**Los Angeles smog**" to distinguish it from "sulfurous smog" or "London smog"

The following chart shows the ranking of the 5 major air pollutants monitored by the EPA. The chart shows the quantity of pollutant as a percentage to the minimum allowed (before it is considered a serious health risk) by the EPA. It is interesting to note that in the majority of cases Ozone is the major pollutant facing most cities. Sources: EPA - Air Quality Trends 2001



http://www.ersys.com/usa/25/2507000/air.htm

- Ozone is readily formed in the atmosphere by the reaction of VOCs and NO_x in the presence of sunlight, which is most abundant in the summer.
- VOCs are emitted from a variety of sources, including motor vehicles, chemical plants, refineries, factories, consumer and commercial products, other industries, and natural (biogenic) sources.
- Nitrogen oxides (a precursor to ozone) are emitted from motor vehicles, power plants, and other sources of combustion, as well as natural sources including lightning and biological processes in soil.

- Changing weather patterns contribute to yearly differences in O_3 concentrations.

- Ozone and the precursor pollutants that cause O_3 also can be transported into an area from pollution sources located hundreds of miles upwind.

So – how to solve the smog problem?

- Ozone production requires both NOx and VOCs
- The obvious solution is to limit the emission of NOx and VOCs, but how?

Solving the smog problem

- The first step is to limit auto exhaust

  This is an ongoing process – the EPA regularly tightens the emissions requirements (catalytic converters)
- But this only applies to **new** cars: older vehicles are grandfathered in under the previous emissions standards

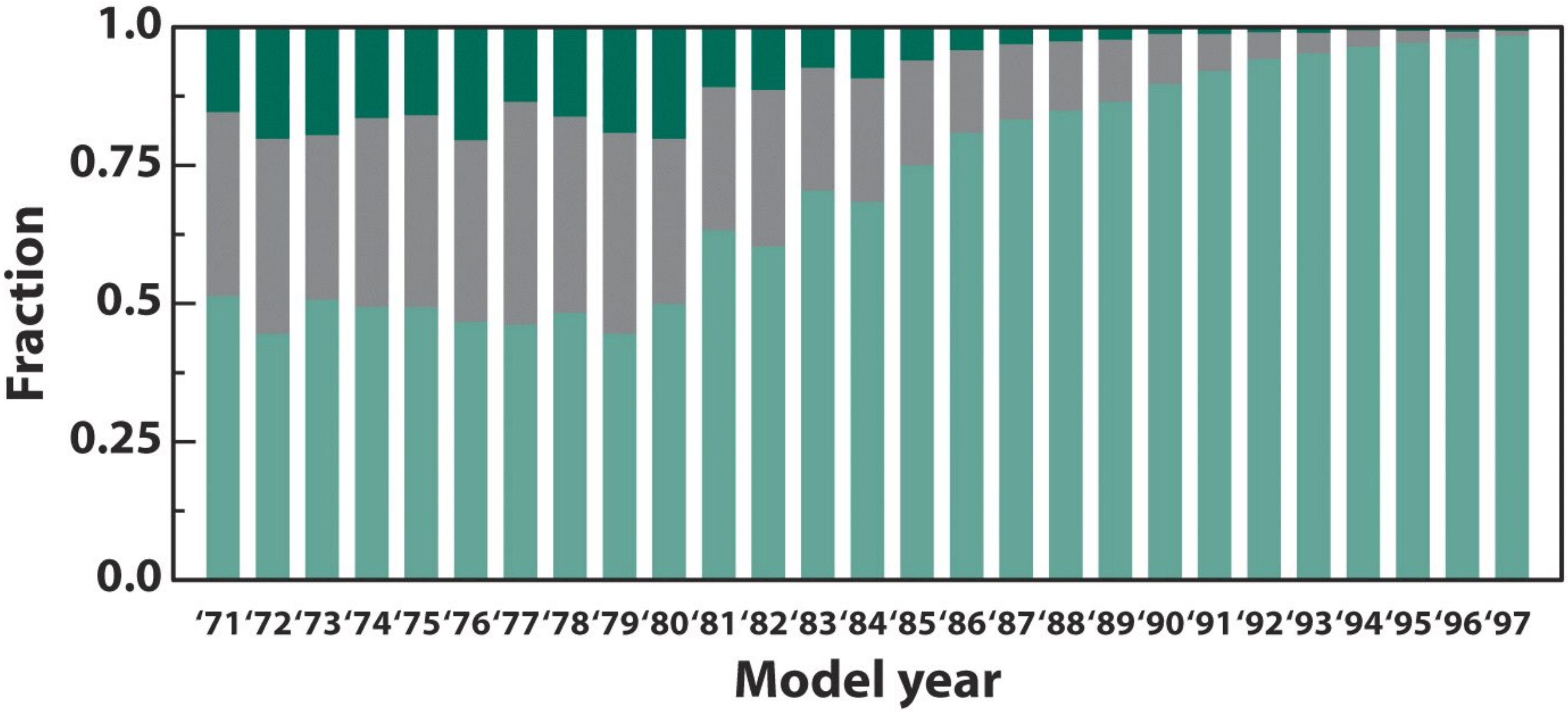


Figure 2-8a
Environmental Chemistry, Third Edition

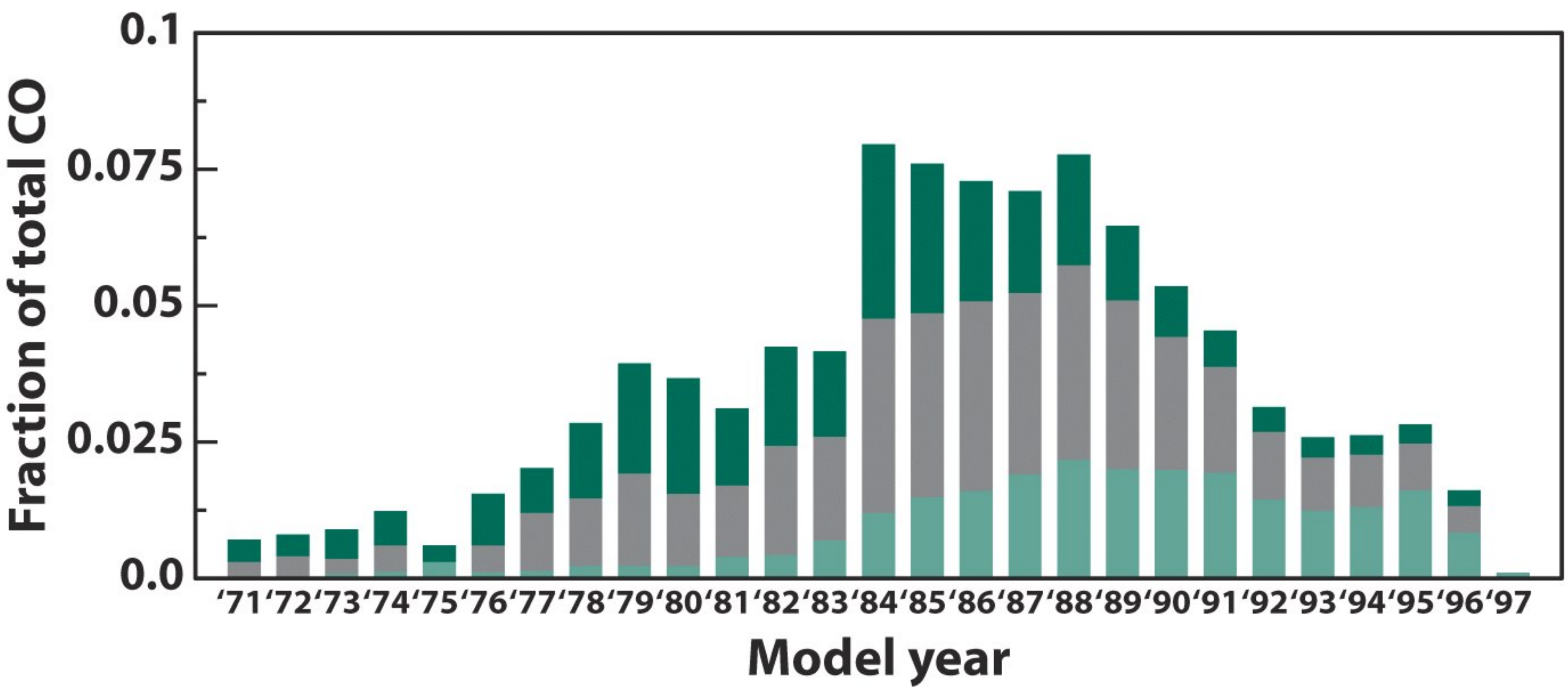


Figure 2-8c
Environmental Chemistry, Third Edition

50% of hydrocarbon and CO emissions are released by 10% of the fleet

Solving the smog problem

- Is limiting auto exhaust enough?

  NO. Car exhaust is not the **only** source for either VOCs or for NOx.
- Recall that NOx can be produced in any high temperature process: power plants, large fires, refineries, industrial plants
- Efforts must be made to clean up the smoke plumes from all such plants and to remove NOx from the air stream
- Much like older cars, older plants are exempt from the EPA's newer regulations, and in recent years the EPA has not had the power to force change

Solving the smog problem

- Is limiting auto exhaust enough?

  NO. Car exhaust is not the **only** source for either VOCs or for NOx.
- VOCs come from a variety of sources:
- Paint thinners
- Solvents
- Natural gas leaks
- Gasoline and oil processing and storage
- **Natural sources:** trees, bushes

Solving the smog problem

- VOCs come from a variety of sources:
- Paint thinners
- Solvents
- Natural gas leaks
- Gasoline and oil processing and storage
- **Natural sources:** trees, bushes
- Efforts must be made to limit the release of solvents, etc., but even in the best case scenario, VOCs will **always** be present – **even in a purely natural environment**

Table 1.9 Air Quality in Megacities Around the World

City	SO_2	PM	Lead	CO	NO_2	O_3
Bangkok, Thailand	Low	Serious	Moderate to heavy	Low	Low	Low
Beijing	Serious	Serious	Low	…	Low	Moderate to heavy
Cairo	…	Serious	Serious	Moderate to heavy	…	…
Jakarta, Indonesia	Low	Serious	Moderate to heavy	Moderate to heavy	Low	Moderate to heavy
London	Low	Low	Low	Moderate to heavy	Low	Low
Mexico City	Serious	Serious	Moderate to heavy	Serious	Moderate to heavy	Serious
Moscow	…	Moderate to heavy	Low	Moderate to heavy	Moderate to heavy	…
São Paulo, Brazil	Low	Moderate to heavy	Low	Moderate to heavy	Moderate to heavy	Serious
Tokyo	Low	…	Low	Low	Serious	…

Source: Atmospheric Research and Information Centre, Manchester Metropolitan University, Manchester, England (1992 data).

… Data not available

Low pollution: normally meets World Health Organization (WHO) guidelines (on occasion may exceed guidelines short-term).

Moderate to heavy pollution: WHO guidelines exceeded up to twice as much (short-term guidelines regularly exceeded at certain locations).

Serious pollution: WHO guidelines exceeded at greater than twice as much.

Megacity = city with a population larger than 10 million people

Megacity

http://en.wikipedia.org/wiki/Megacity

- **Megacity**, **megapolis**, or **megalopolis** is a general term for cities together with their suburbs or recognized metropolitan areas usually with a total population in excess of 10 million people.
- In 1950, London and New York were the only such areas
- There were 26 as of 2006, an increase from 19 in 2004 and only nine in 1985.
- The ten largest megacities according to this criterion are, in declining order of population: Tokyo (~32,000,000); Mexico City (24,340,000); Seoul, South Korea (23,100,000); New York (21,800,000); Mumbai (Bombay), India (21,100,000); Delhi, India (20,800,000); São Paulo, Brazil (20,300,000); Shanghai, China (18,600,000); Los Angeles (17,900,000); and Jakarta, Indonesia (16,900,000).

Indoor Air Quality

- Nearly a thousand substances typically are detectable at the parts per billion level or higher.
- Some are familiar
  - VOCs, NO, NO_2, SO_2, CO, ozone, radon, and PM
- Less familiar pollutants
  - Formaldehyde, benzene and acrolein
- Some are brought in from outside, others are generated indoors.

Your Turn 1.35

Name five indoor activities that generate pollutants.

What's in Cigarette Smoke?

There are over 4,000 identified chemicals in cigarette smoke. Listed here are 109 of the more toxic chemicals. Those proven to cause **cancer** are in **boldface** type (carcinogenic). Those proven to cause *birth defects* are in *italic* type. (http://www.ashline.org/ASH/cigsmoke/index.html)

A
Acetaldehyde
Acetic Acid
Acetone
Acetylene
Acrolein
Acrylonitrile
Aluminum
Aminobiphenyl
Ammonia
Anabasine
Anatabine
Aniline
Anthracenes
Argon
Arsenic

B
Benz(a)anthracene
Benzene
Benzo(a)pyrene
Benzo(b)fluoranthene
Benzo(j)fluoranthene
Butadiene
Butane

C
Cadmium
Campesterol
Carbon Monoxide
Carbon Sulfide
Catechol
Chromium
Chrysene
Copper
Crotonaldehyde
Cyclotenes

D
DDT/Dieldrin
Dibenz(a,h)acridine
Dibenz(a,h)anthracene
Dibenz(a,j)acridine
Dibenzo(a,l)pyrene
Dibenzo(c,g)carbazole
Dimenthylhydrazine

E
Ethanol
Ethylcarbamate

F
Fluoranthenes
Fluorenes
Formaldehyde
Formic Acid
Furan

G
Glycerol

H
Hexamine
Hydrazine
Hydrogen cyanide
Hydrogen sulfide

I
Indeno(1,2,3-c,d)pyrene
Indole
Isoprene

L
Lead
Limonine
Linoleic Acid
Linolenic Acid

M
Magnesium
Mercury
Methane
Methanol
Methyl formate
Methylamineethylchrysene
Methylamine
Methylnitrosamino
Methylpyrrolidine

N
n-Nitrosoanabasine
n-Nitrosodiethanolamine
n-Nitrosodiethylamine
n-nitrosodimethylamine
n-Nitrosoethyl methylamine
n-Nitrosomorpholine
n-Nitrosopyrrolidine
Naphthalene
Naphthylamine
Neophytadienes
Nickel
Nicotine
Nitric Oxide
Nitrobenzene
Nitropropane
Nitrosamines
Nitrosonomicotine
Nitrous oxide phenols
Nomicotine

P
Palmitic acid
Phenanthrenes
Phenol
Picolines
Polonium-210
Propionic acid
Pyrenes
Pyrrolidine

Q
Quinoline
Quinones

S
Scopoletin
Sitosterol
Skatole
Solanesol
Stearic acid
Stigmasterol
Styrene

T
Titanium
Toluene
Toluidine

U
Urethane

V
Vinyl Chloride
Vinylpyridine

Indoor Pollutants - VOCs

- Paint
- Nail polish
- Nail polish remover
- Paint thinner
- Hairspray
- Just about anything with a smell is releasing something into the air.

Table 1.10 Selected Indoor Air Pollutants and Their Sources

Form	Source	Pollutants
Solid/particulate	Floor tile, insulation	Asbestos
	Pets	Pet dander, dust
	Plants	Molds, mildew, bacteria, viruses
Liquid/gas	Carpet	Styrene
	Cigarette smoke	CO, benzene, nicotine
	Clothes	Dry-cleaning fluid, moth balls
	Electric arcing	Ozone
	Unvented space heaters	CO, NO, NO_2
	Furniture	Formaldehyde
	Glues and solvents	Acetone, toluene
	Paint, paint thinners	Methanol, methylene chloride
	Soils under house	Radon

Radon

- Noble gas – colorless, odorless, tasteless and chemically unreactive
- RADIOACTIVE
- It is generated as part of the radioactive decay of uranium.
- Extended inhalation of radon can result in lung cancer.

Green Chemistry

- Green chemistry is the designing of chemical products and processes that reduce or eliminate the use or generation of hazardous substances.
- “Benign by Design”
- An obvious way to reduce pollutants is not to have them in the first place.
- The use of green chemical principles has led to cheaper, less wasteful, and less toxic production of the following:
  – Ibuprofen
  – Pesticides
  – New materials for disposable diapers and contact lenses
  – New dry-cleaning methods
  – Recyclable silicon wafers for integrated circuits.

Table 1.5 National Ambient Air Quality Standards, 1999

Pollutant	Standard (ppm)	Approximate Equivalent Concentration of Standard ($\mu g/m^3$)
Carbon monoxide		
8-hr average	9	1×10^4
1-hr average	35	4×10^4
Nitrogen dioxide		
Annual average	0.053	100
Ozone		
1-hr average	0.12	235
8-hr average	0.08	157
Lead		
Quarterly average	…	1.5
Particulates*		
PM_{10}, 24-hr average	…	150
PM_{10}, annual average	…	50
$PM_{2.5}$, 24-hr average	…	65
$PM_{2.5}$, annual average	…	15
Sulfur dioxide		
Annual average	0.03	80
24-hr average	0.14	365
3-hr average	0.50	1300

… Data not available

* PM_{10} refers to airborne particles 10 μm in diameter or less, and $PM_{2.5}$ to those less than 2.5 μm. These two categories are monitored separately, and the standards for $PM_{2.5}$ are still controversial.

A Breath of Air

- If air contains on average 8 ppm of CO it is considered safe.
  - For every one million molecules of air there can only be eight molecules of CO.
- In one breath, we inhale 500 mL of air
  - This corresponds to 2×10^{22} molecules and/or atoms
  - That's 20,000,000,000,000,000,000,000 molecules of air.

A Breath of Air

- So in one breath, how many molecules of CO do we breath in at a ‘safe’ concentration of 8 ppm of CO?

\# molecules of CO = # molecules of air in breath x concentration of CO

$$\# \text{ molecules of CO} = 2\times10^{22} \text{ molecules of air} \times \frac{8 \text{ molecules of CO}}{1\times10^{6} \text{ molecules of air}}$$

$$\# \text{ molecules of CO} = 1.6\times10^{17} \text{ molecules of CO in a single breath}$$

Using ‘significant figures’ this gives us an answer of 2×10^{17} molecules of CO brought into our body with every breath.

Significant Figures

- Defined as a number that correctly represents the accuracy with which an experimental quantity is known.
- The accuracy of a calculation is **limited by the least accurate piece of data** that goes into it.
- You cannot improve the accuracy of experimental measurements by ordinary mathematical manipulations.

Is zero pollutants an achievable goal?

- NO
- Why?
- We wouldn’t even be able to tell if it had happened.
- Limits of Detection ~ 1ppt
  - This corresponds to moving 6 inches in the 93 million mile trip to the Sun.
  - A single breath can still contain 2×10^{10} molecules of a pollutant at a concentration of less than 1 ppt and thus ‘undetectable’

Molecules in the Air

- Natural is not necessarily good.
- Human-made is not necessarily bad.
- Even with cleaning up all the human emissions, there are still pollutants in the air.
- Nonetheless, human-made emissions may overwhelm the atmosphere’s ability to clean itself.