Methods of pollution control and waste management

Lecture 6

The Earth's atmosphere and air pollution

Part 2

Carbon dioxide capture by chemical absorption

- **Chemical absorpion** $NaOH_{(aq)}$, $CH_3CH_2NH_{2(aq)}$ (Monoethylamine - MEA)

$$CO_2 + OH^- \rightleftharpoons HCO_3^-$$

$$HCO_3^- + OH^- \rightleftharpoons CO_3^{2-} + H_2O$$

$$CH_3CH_2NH_2 + CO_2 \rightleftharpoons CH_3CH_2NHCOO^- + H^+$$

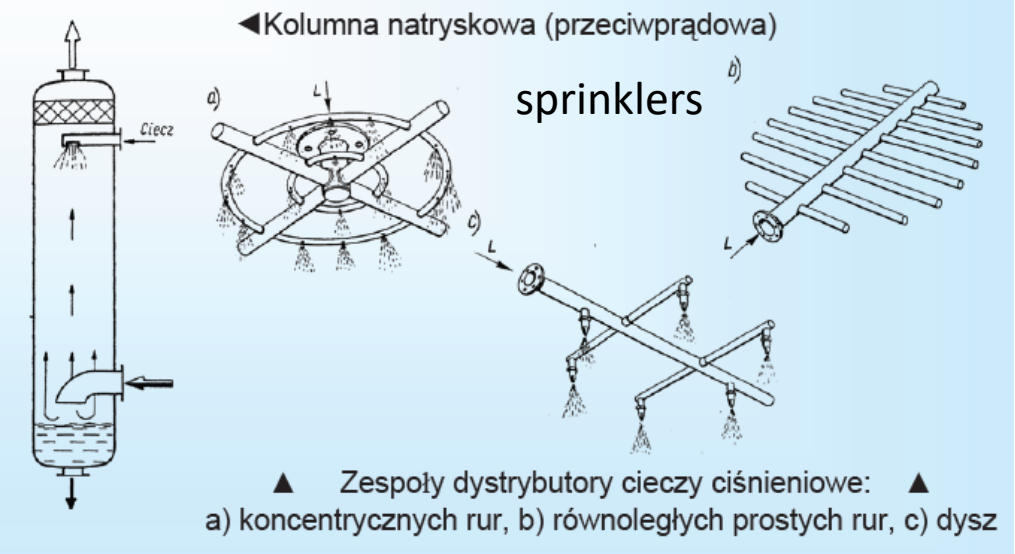
$$CH_3CH_2NH_2 + H^+ \rightleftharpoons CH_3CH_2NH_3^+$$

Gas absorption is the process whereby a pollutants (in gas or vapor form) are removed from air or another gaseous stream by contact with a flowing liquid phase.

Absorption is the process by which atoms, molecules, or ions enter a bulk phase (liquid, gas, solid).

Carbon dioxide capture by chemical absorption

- In order to increase the surface area available for mass transfer, the operation is almost always conducted inside a tower or column packed with high surface-area filling material
- Industrial-scale gas absorbers are often referred to as "scrubbers„



▲ Zespoły dystrybutory cieczy ciśnieniowe: ▲
a) koncentrycznych rur, b) równoległych prostych rur, c) dysz

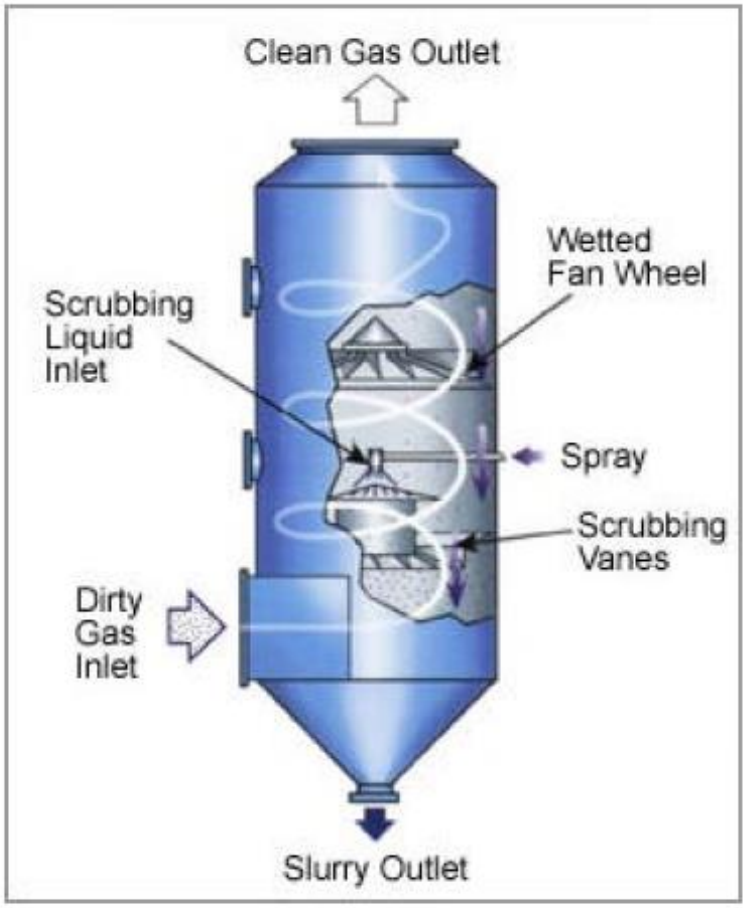
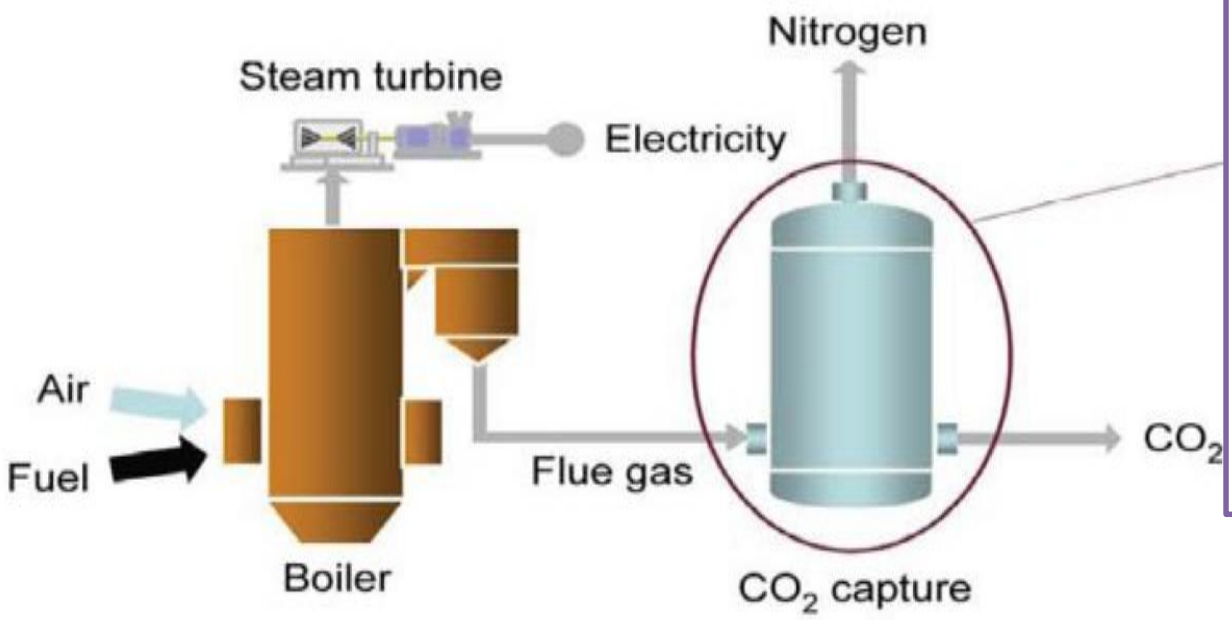


Figure 4: example of wet scrubber [ref. 34]

Carbon dioxide capture by chemical absorption

Electric plant



Flue gas from fuel combusting is directed to absorption tower where CO_2 is captured, nitrogen is directed to atmosphere and after absorption solution is heated with steam to reverse the CO_2 absorption reaction and afterwards CO_2 is compressed for transport.

Intergovernmental Panel on Climate Change, special report „**Carbon Dioxide Capture and Storage" 2005**

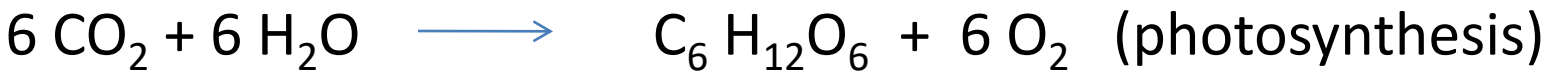
Carbon dioxide capture by chemical absorption

CO_2 post-combustion capture at a plant in Malaysia. This plant employs a chemical absorption process to separate 0.2 $MtCO_2$ per year from the flue gas stream plant for urea production (Courtesy of Mitsubishi Heavy Industries).

Intergovernmental Panel on Climate Change, special report „**Carbon Dioxide Capture and Storage" 2005**

Biological sequestration and biomass based fuels

- Plants can remove carbon dioxide from atmosphere or from water as they are growing. Biomass is organic material produced as the solid product.



Dry biomass can be used **as fuel** to provide energy. Biomass can be regard as **renewable resource** because energy of the Sun remains constant and crops can be grown and harvested year after year.

Categories of air pollutants

Pollutants - chemicals added to the atmosphere by natural events or human activities in high enough concentrations to be harmful

- **Primary pollutants** - resulting from combustion of fuels and industrial operations (precursors)
- **Secondary pollutants** - produced due to reaction of primary pollutants in the atmosphere

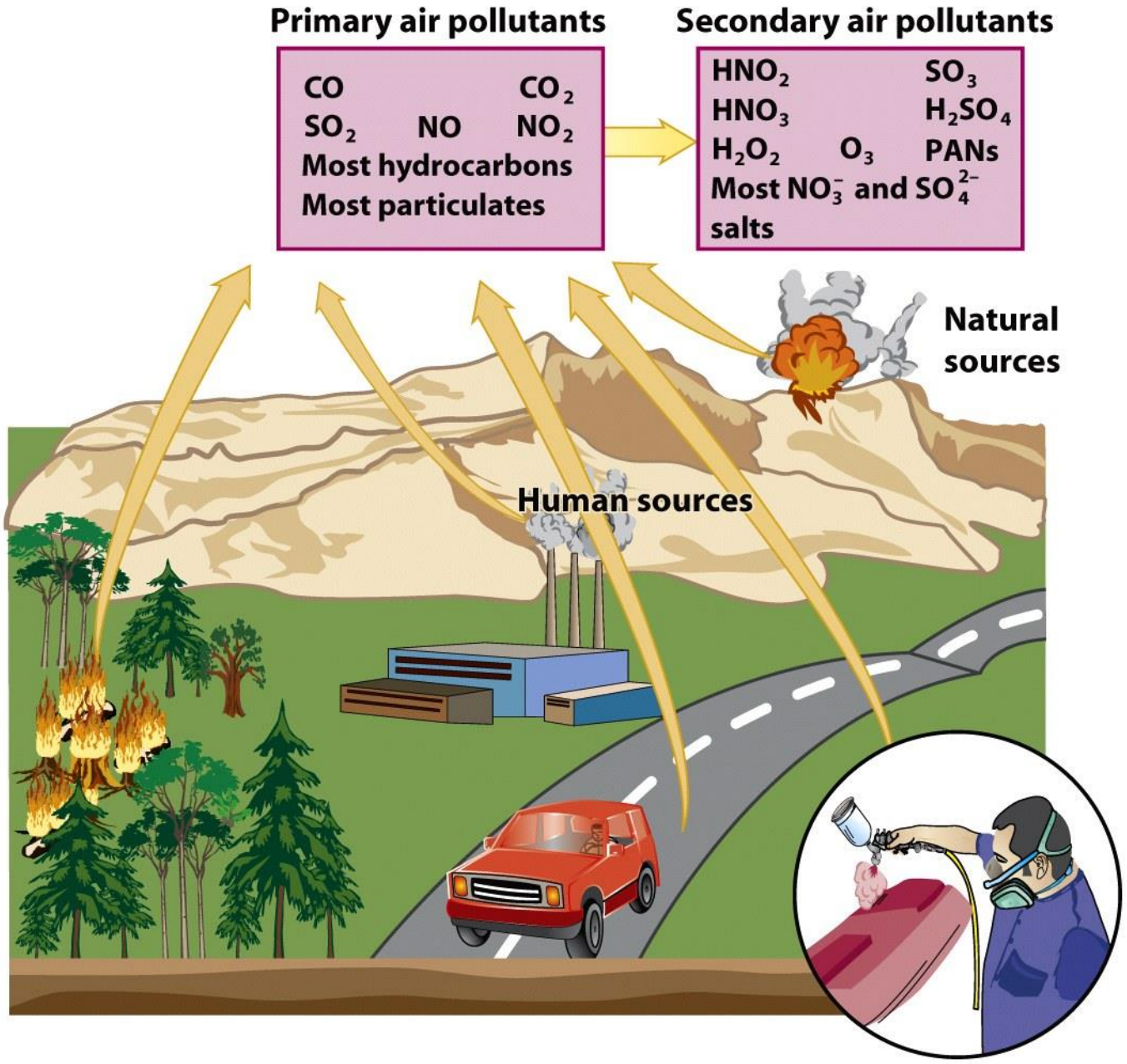

Primary air pollutants
CO
CO_2
SO_2
NO
NO_2
Most hydrocarbons
Most particulates
Secondary air pollutants
HNO_2
SO_3
HNO_3
H_2SO_4
H_2O_2
O_3
PANs
Most NO_3^- and SO_4^{2-} salts
Natural sources
Human sources

Table 1: Common pollutants and their sources.

Pollutants	Sources
Suspended particulate Matter, SPM[a]	Automobile, power plants, boilers, Industries requiring crushing and grinding such as quarry, cement.
Chlorine	Chlor-alkali plants.
Fluoride	Fertilizer, aluminum refining
Sulphur dioxide	Power plants, boilers, sulphuric acid manufacture, ore refining, petroleum refining.
Lead	Ore refining, battery manufacturing, automobiles.
Oxides of nitrogen,[a] NO, NO_2 (NO_X)	Automobiles, power plants, nitric acid manufacture, also a secondary pollutant
Peroxyacetyl nitrate, PAN	Secondary pollutant

Table 1: Common pollutants and their sources.

Pollutants	Sources
Formaldehyde	Secondary pollutant
Ozone[a]	Secondary pollutant
Carbon monoxide[a]	Automobiles
Hydrogen sulphide	Pulp and paper, petroleum refining.
Hydrocarbons	Automobiles, petroleum refining
Ammonia	Fertilizer plant

a- Criteria pollutants

- Criteria air pollutants are six major pollutants defined by EPA (Environmental Protection Agency) for which ambient air standards have been set to protect human health and welfare.

Criteria pollutants (defined by EPA):

1. Ozone, O_3.
2. Carbon monoxide, CO.
3. Sulfur dioxide, SO_2.
4. Nitrogen oxides, NO_x.
5. Lead, Pb.
6. Particulates, PM10.

Atmospheric particulate matter with diameter 10 μm and less (can be easy respirable)

Primary and secondary pollutants

Nitrogen oxides

$3\ NO_2 + H_2O \longrightarrow 2\ HNO_3 + NO$

$2\ NO_2 + H_2O \longrightarrow HNO_3 + HNO_2$

$N_2O_5 + H_2O \longrightarrow HNO_3$

In stratosphere:

$\cdot OH + NO_2 \longrightarrow HNO_3$

4. Secondary Air Pollutants

Secondary pollutants form when primary pollutants react in the atmosphere. Table 1 summarizes common forms of atmospheric reactions.

Table 1. Chemical kinetics in the atmosphere.

Type of reaction	Process	Notation
Bimolecular	Two reactants combine to produce two products.	$A + B \rightarrow C + D$
Three-body	Two reactants combine to form one new product. A third, inert molecule (M) stabilizes the end product and removes excess energy.	$A + B + M \rightarrow AB + M$
Photolysis	Solar radiation photon breaks a chemical bond in a molecule	$A + hv \rightarrow B + C$
Thermal decomposition	A molecule decomposes by collision with an inert molecule (M)	$A + M \rightarrow B + C$

Secondary air pollutants

Produced in the atmosphere when certain chemical reactions take place among primary pollutants

- **Atmospheric sulfuric acid** is one example of a secondary pollutant.
- Air pollution in urban and industrial areas is often called **smog**.
- **Photochemical smog**, a noxious mixture of gases and particles, is produced when strong sunlight triggers **photochemical reactions** in the atmosphere. The major component of photochemical smog is **ozone**.

Table 1. Nitrogen Oxides (NOx)

Formula	Name	Nitrogen Valence	Properties
N_2O	nitrous oxide	1	colorless gas water soluble
NO	nitric oxide	2	colorless gas
N_2O_2	dinitrogen dioxide		slightly water soluble
N_2O_3	dinitrogen trioxide	3	black solid water soluble, decomposes in water
NO_2	nitrogen dioxide	4	red-brown gas
N_2O_4	dinitrogen tetroxide		very water soluble, decomposes in water
N_2O_5	dinitrogen pentoxide	5	white solid very water soluble, decomposes in water

Nitrogen oxides NO_x

Nitrogen oxides NO_x : N_2O, NO, N_2O_3, NO_2, N_20_4, N_2O_5, NO_3

Natural: N_2O, NO, NO_2

Nitrous oxide N_2O – forms in soil and water by microbiological process (denitrification in nitrogen cycle)

$$2\ NO_3^- + 2\ CH_2O + 2\ H_3O^+ \longrightarrow N_2O + 2\ CO_2 + 5\ H_2O$$

N_2O relatively unreactive in troposphere

In stratosphere photochemical reactions:

$$N_2O + h\nu \longrightarrow N_2 + O$$

$$N_2O + O \longrightarrow 2\ NO$$

Influences on depletion of the ozone layer

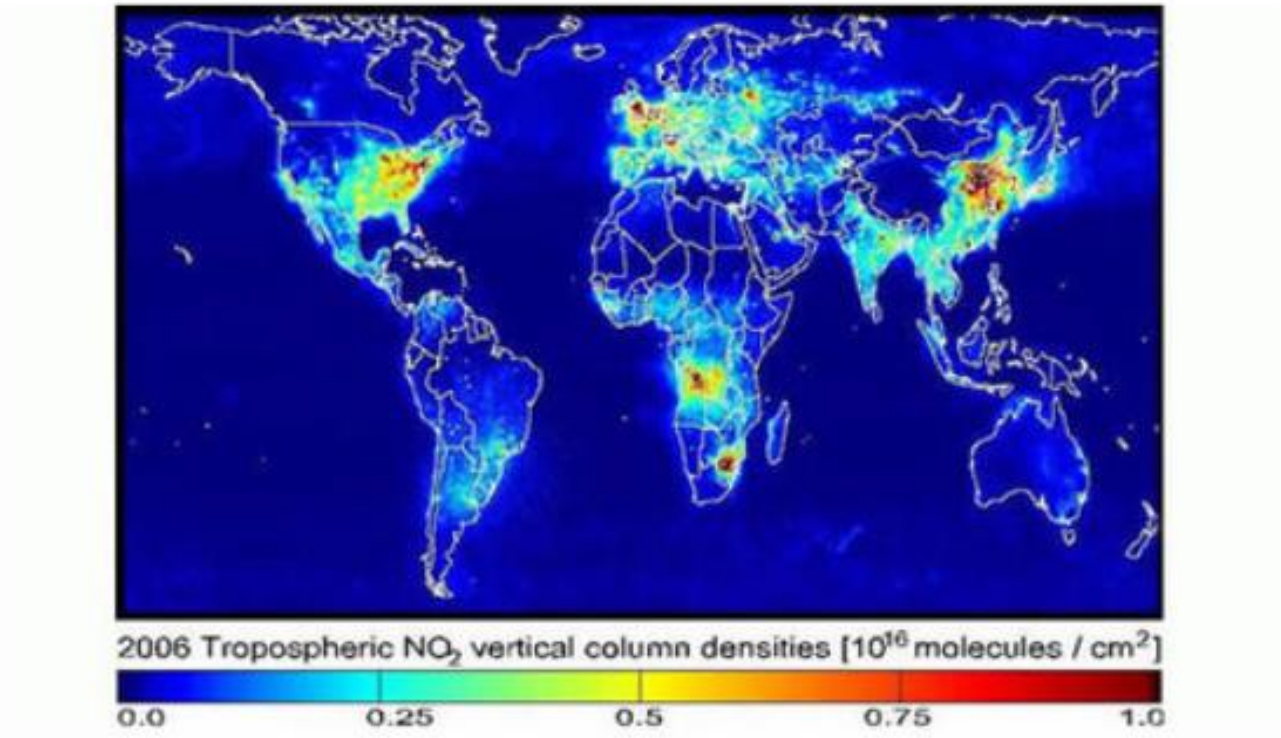


Figure 4. Satellite observations of tropospheric NO2, 2006

Courtesy Jim Gleason, USA and Pepijn Veefkind, KNMI, National Aeronautics and Space Administration.

Primary pollutants

Nitrogen oxides

Arises at very high temperature in furnaces and in combustion engines (> 1200^0C)

$N_2 + O_2 \longrightarrow 2\,\underline{NO}$

Mechanism: $N_2 + O \longrightarrow NO + N$

$N_2 + O_2 \longrightarrow NO + O$

Breakage of the oxygen bond requires 118 kcal/mol, breakage of the nitrogen bond requires 225 kcal/mol

Rapid reactions in troposphere:

$NO + O_3 \longrightarrow 2NO_2 + O_2$

$NO_2 + O_3 \longrightarrow NO_3 + O_2$

$NO_3 + NO_2 \longrightarrow N_2O_5$

Classical and photochemical smog

Figure 3. Smog over Los Angeles

Smog (smoke and fog) – forms of air pollution in which atmospheric visibility is partially obscured by solid particles and/or liquid aerosols

Fog - the dispersed in air water drops

- Classical smog – associated with the use of traditional fuel – coal
- Photochemical smog – associated with use of petroleum fuels

Classical and photochemical smog

- **Sulfurous smog** („London-type" smog) results from a high concentration of sulfur oxides in the air and is caused by the use of sulfur-bearing fossil fuels, particularly coal.
- **Photochemical smog** ('Los Angeles-type' smog) occurs most prominently in urban areas that have large numbers of automobiles, requires neither smoke nor fog. This type of smog has its origin in the nitrogen oxides and hydrocarbon vapors emitted by automobiles and other sources, which then undergo photochemical reactions in the lower atmosphere.

Classical smog (London-type smog)

$C_{(soot)}$, $SO_{2,}$

High concentration of carbon soot and sulfur dioxide (SO_2), chemical properties are reducing and acidic. Carbon particles may serve as nuclei for condensation of water droplets forming irritating fog. First observed in nineteenth-century in industrial centres (London).

In 1952 in London smog being several weeks led to the death of more than 4000 persons (mostly by the pre-existing respiratory problems)

The chemistry of photochemical smog

- **Oxidation of hydrocarbons (combustion engines emit unburned volatile hydrocarbons)**

$\bullet OH + RCH_3 \longrightarrow RCH_2\bullet + H_2O$

$RCH_2\bullet + O_2 \longrightarrow RCH_2OO\bullet$

$RCH_2OO\bullet + NO \longrightarrow RCH_2O\bullet + NO_2$

$RCH_2O\bullet + O_2 \longrightarrow RCHO + HOO\bullet$

Formation of aldehyde

$HOO\bullet + NO \longrightarrow NO_2 + HO\bullet$

Nitrogen dioxide regeneration

The chemistry of photochemical smog

- Secondary reactions

$NO_2 \xrightarrow{h\nu,\ \lambda<400\ nm} NO + O^*$

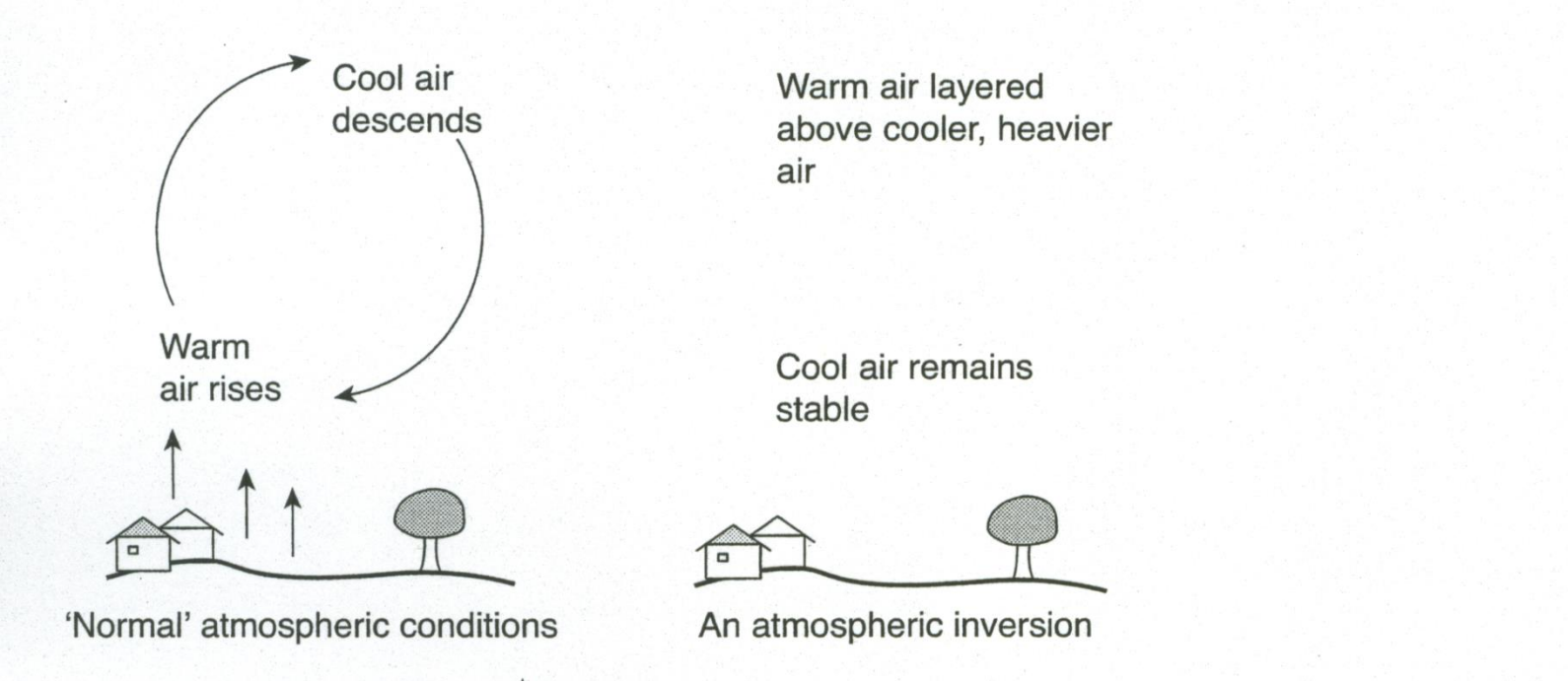
$O^* + O_2 \longrightarrow O_3$

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

$CH_3CO\bullet + O_2 \longrightarrow CH_3C(O)OO\bullet$

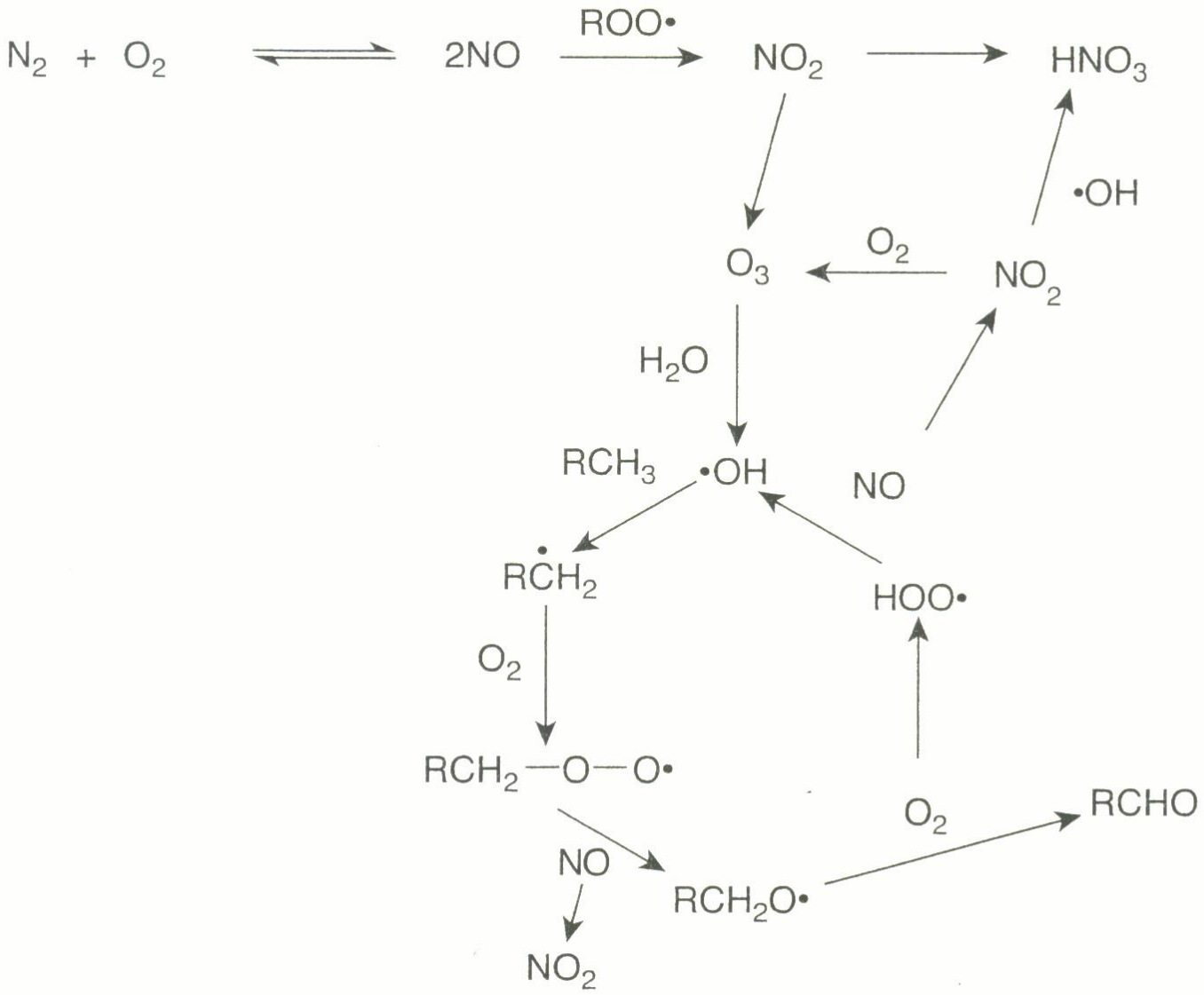
$CH_3C(O)OO\bullet + \bullet NO_2 \longrightarrow CH_3C(O)OONO_2$

Peroxyacetyl nitrate (PAN) and related compounds are the major eye irritants in photochemical smog



A well mixed atmosphere occurs when warm air at the surface of the Earth rises and is replaced by cooler air descendig from above. In less-common situation the atmosphere is stable during an inversion event, when the surface air is cooler and more dense then that above.

G. W. vanLoon, S. J. Duffy Environmental Chemistry, Oxford Press, 2011



Reaction series during a photochemical smog event

G. W. vanLoon, S. J. Duffy Environmental Chemistry, Oxford Press, 2011

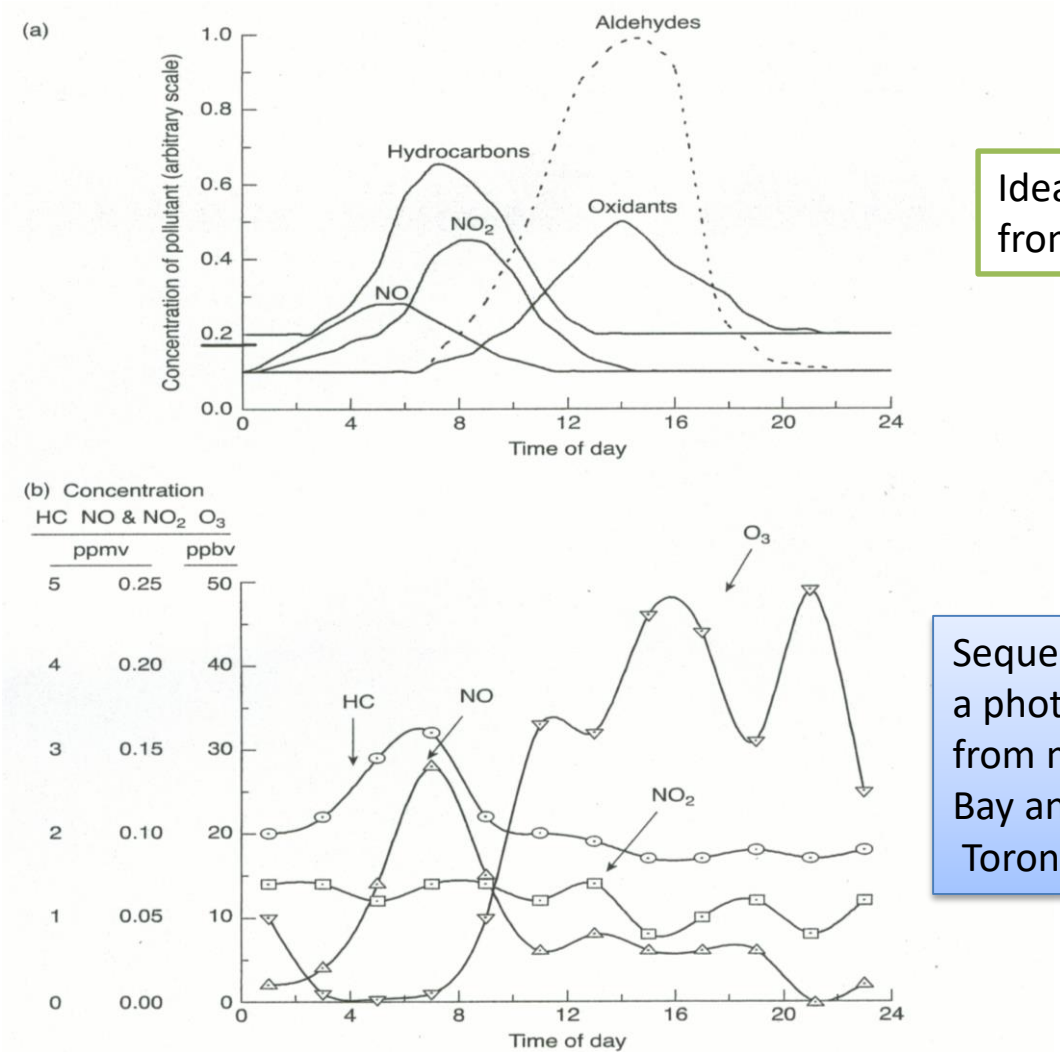
Photochemical smog

- *Based on emissions* resulting from the *combustion* of *petroleum*-based products

Conditions required for photochemical smog formation:

- Precursors: hydrocarbons, NO_x
- A stable atmosphere to hold the reactants in place
- High temperature to increase thermal reaction rates
- Intense sunlight to facilitate photochemical reactions

The chemistry of photochemical smog



Idealized plot based on results from laboratory studies

Sequence of chemical species during a photochemical smog event from measurements on the corner of Bay and Grosvenor Streets in Toronto, May 21, 1992

G. W. vanLoon, S. J. Duffy Environmental Chemistry, Oxford Press, 2011

The chemistry of photochemical smog

- The chemical reactions that lead to smog formation center around the hydroxyl radical

$N_2 + O_2 \longrightarrow 2\,NO$

In high energy conditions
(internal combustion engines)

$2NO + O_2 \longrightarrow 2NO_2$

$NO + O_3 \longrightarrow NO_2 + O_2$ (rapid)

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

$NO_2 \xrightarrow{h\nu,\ \lambda<400\ nm} NO + O^*$

peroxyls radicals are generated
in oxidation of hydrocarbons

$\mathbf{O^* + H_2O \longrightarrow 2\ \bullet OH}$

Hydroxyl radicals are highly reactive species

Formation of Photochemical Smog

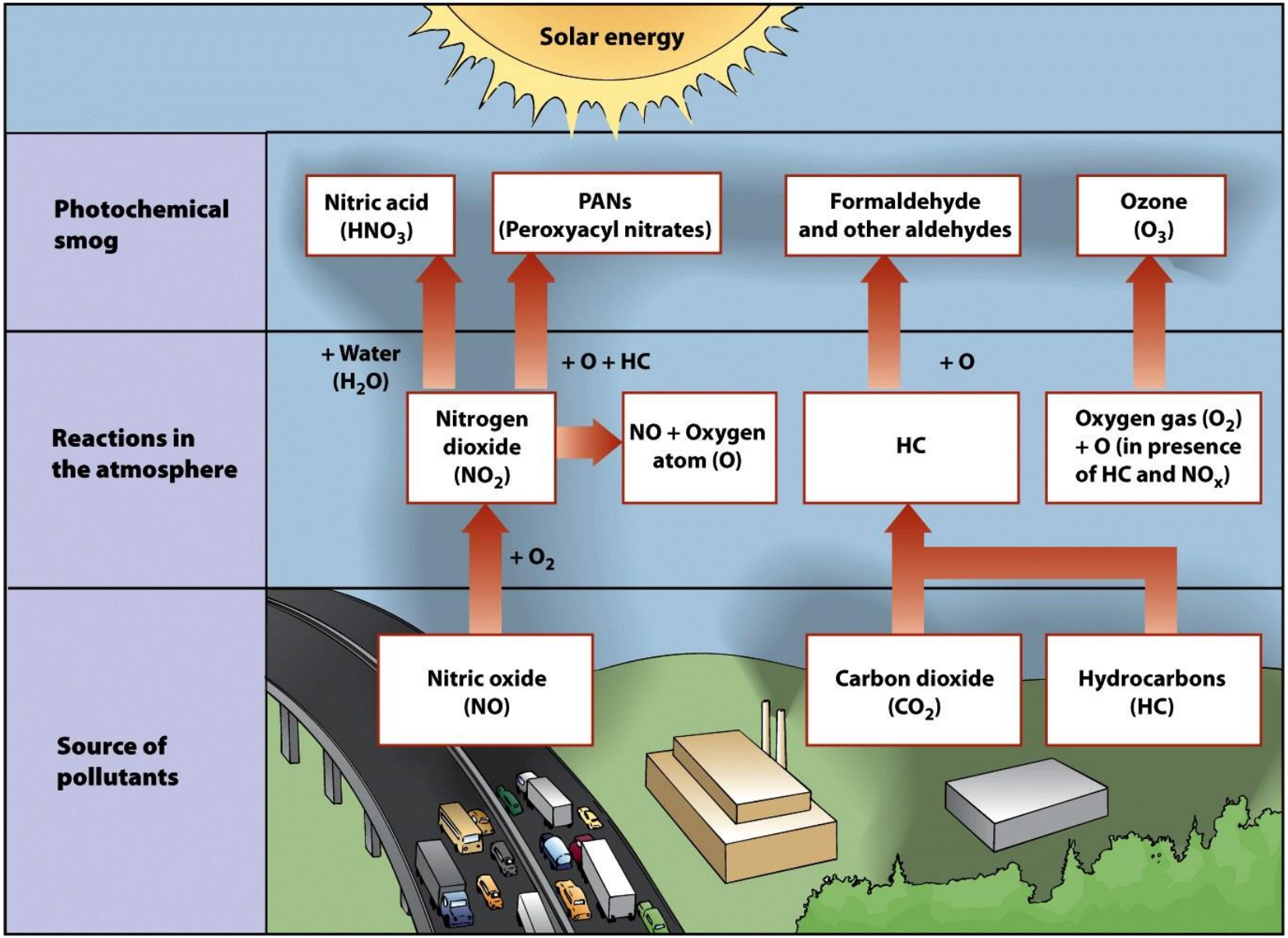


Table 4.1 Typical atmospheric concentrations of selected species characteristic of a photochemica smog[a].

Species	Concentration / ppbv	
	Polluted area	Unpolluted area
Carbon monoxide	10 000–30 000	<200
Nitric oxide plus nitrogen dioxide (NO_x)	100–400	<20
Hydrocarbons (excluding methane)	600–3000	<300
Ozone	50–150	<5
PANs	50–250	<5

[a] Most values are estimates based on data in *Air quality in Ontario 1991*, Environment Ontario, Queen's Printer for Ontario; 1992.

G. W. vanLoon, S. J. Duffy Environmental Chemistry, Oxford Press, 2011