Lecture 7

Nitrogen and sulfur chemistry in combustion

Main mechanisms of NOx formation

- **Thermal NOx**: formed by reaction between N_2 and O_2 in the air; sensitive to temperature
  - Fast formation rate at high temperature
  - Fast cooling rate freezes formed NOx
- **Prompt NOx** :
  - NOx formation in the flame front zone mainly in the fuel-rich flames
- **Fuel NOx**: formed from combustion of fuels containing organic nitrogen in the fuel; dependent on local combustion conditions and nitrogen content in the fuel

Thermal NOx

O + N2 --> NO + N
N + O2 --> NO + O

Since the first reaction has very high activation energy it is a rate-determining step

Usually, the formation of NO stops when temperature drops, therefore amount of the formed NO is less than the equilibrium value. Thus, the amount of the NO formed can be calculated as follows:

$$NO_{formed} = \frac{dNO}{dt}\Delta t$$

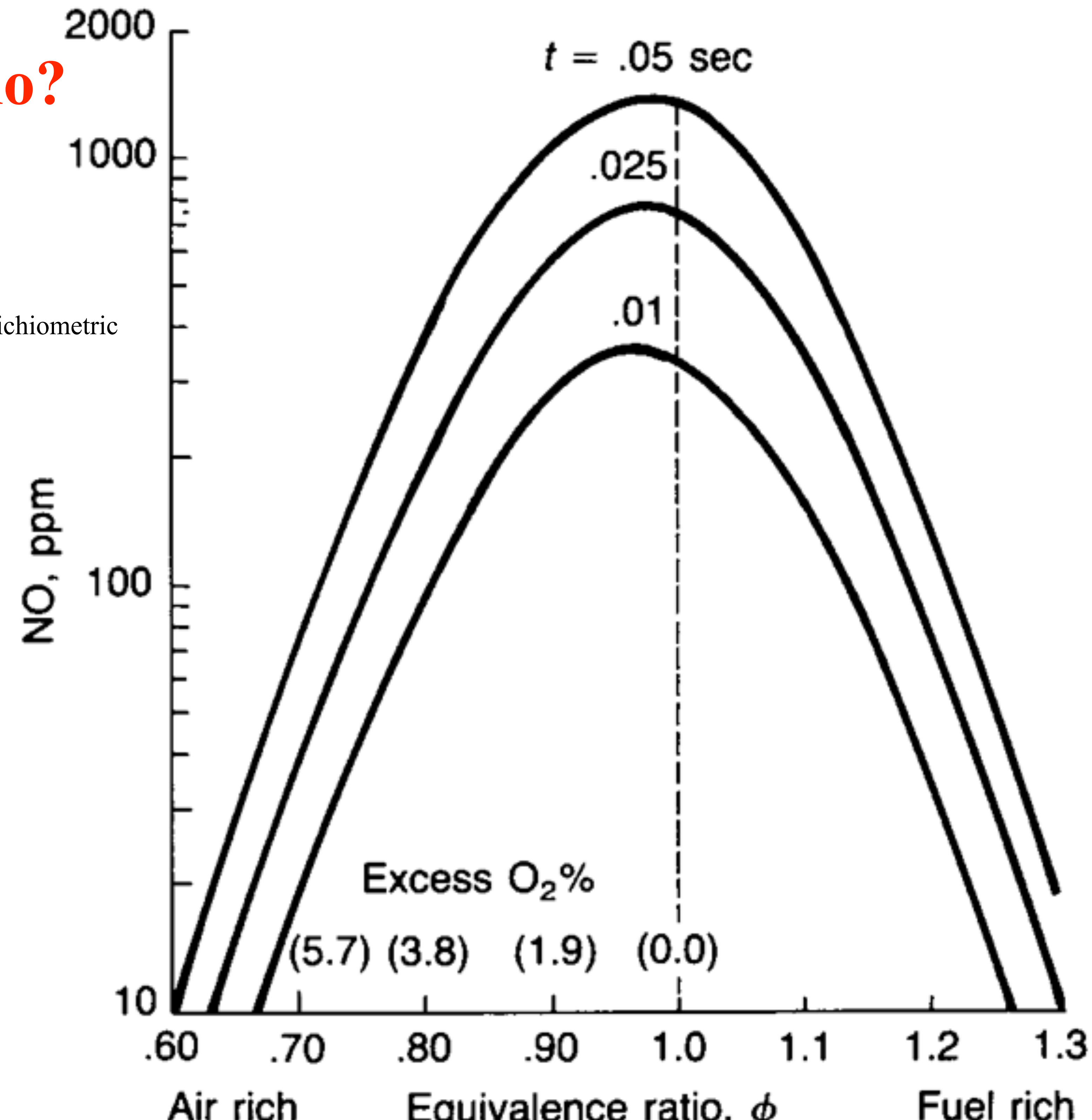
where Δt is a time the time during which the gases are at a high flame temperature

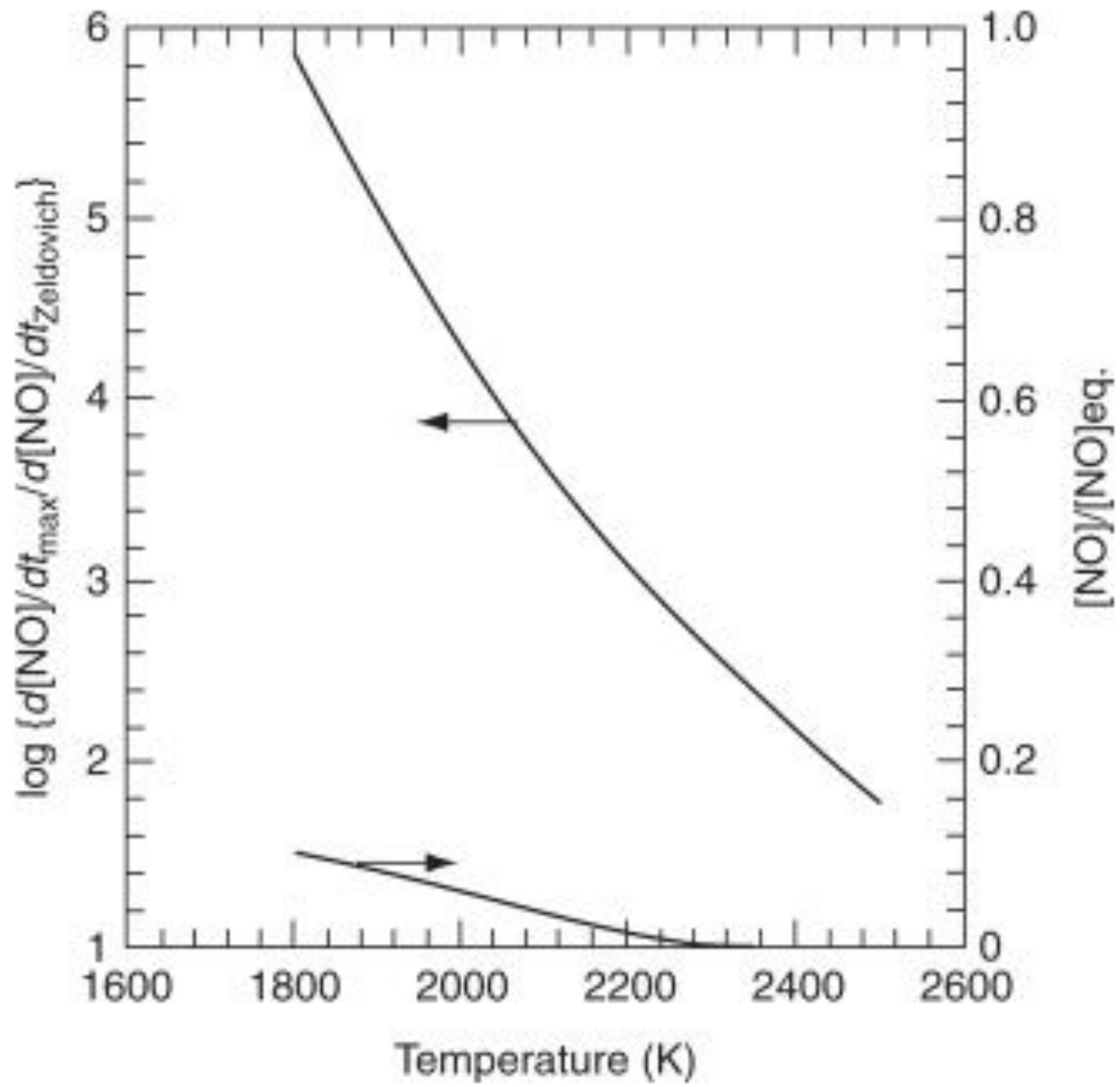
Strategies for Combustion Modification

Q: Temperature as a function of equivalent ratio?

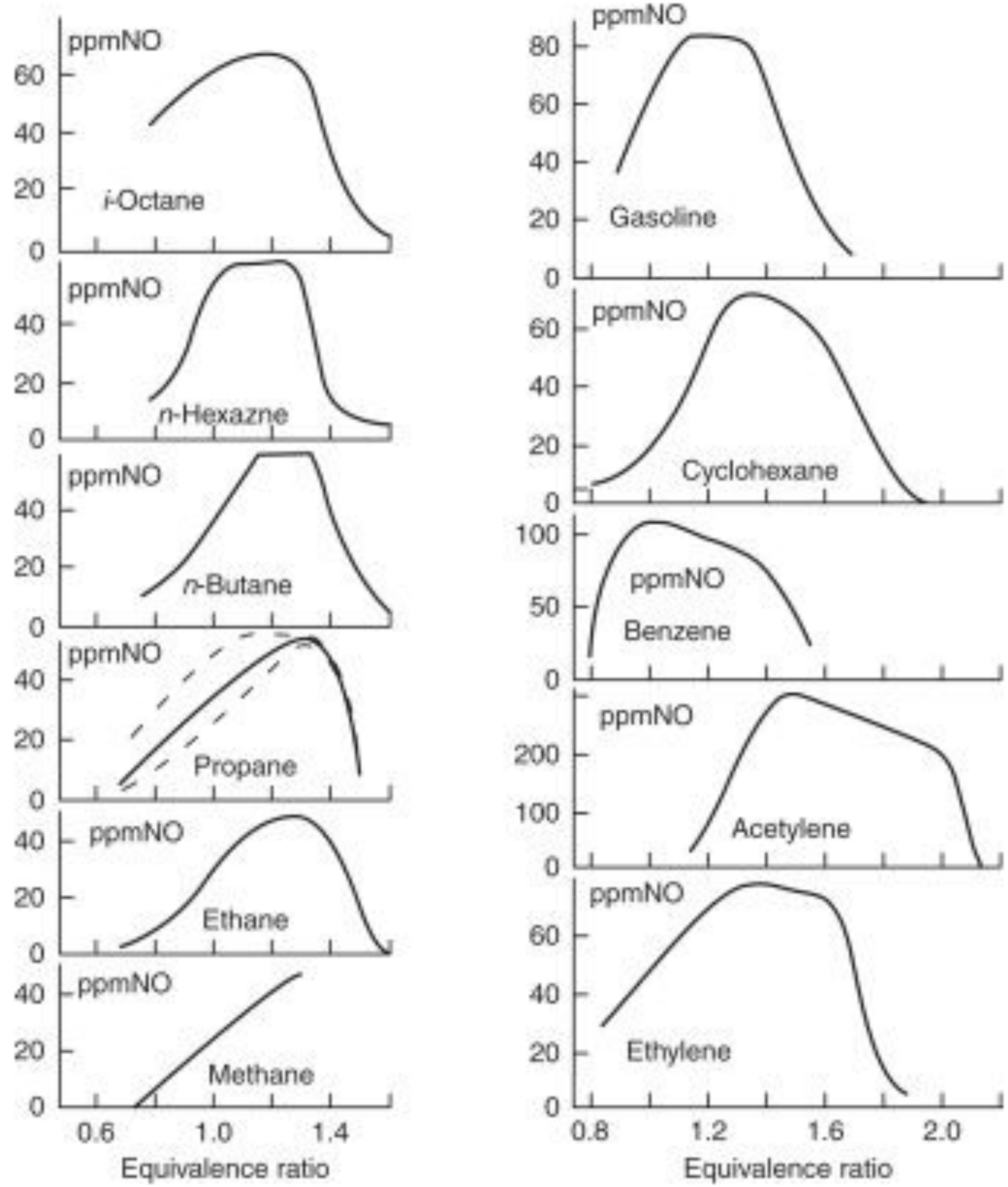
$$\text{Equivalent ratio } (\phi): \left(\frac{\text{fuel}}{\text{air}}\right) \Big/ \left(\frac{\text{fuel}}{\text{air}}\right)_{\text{Stoichiometric}}$$

- Reduce peak **temperatures** of the flame zone
- Reduce gas **residence time** in the flame zone

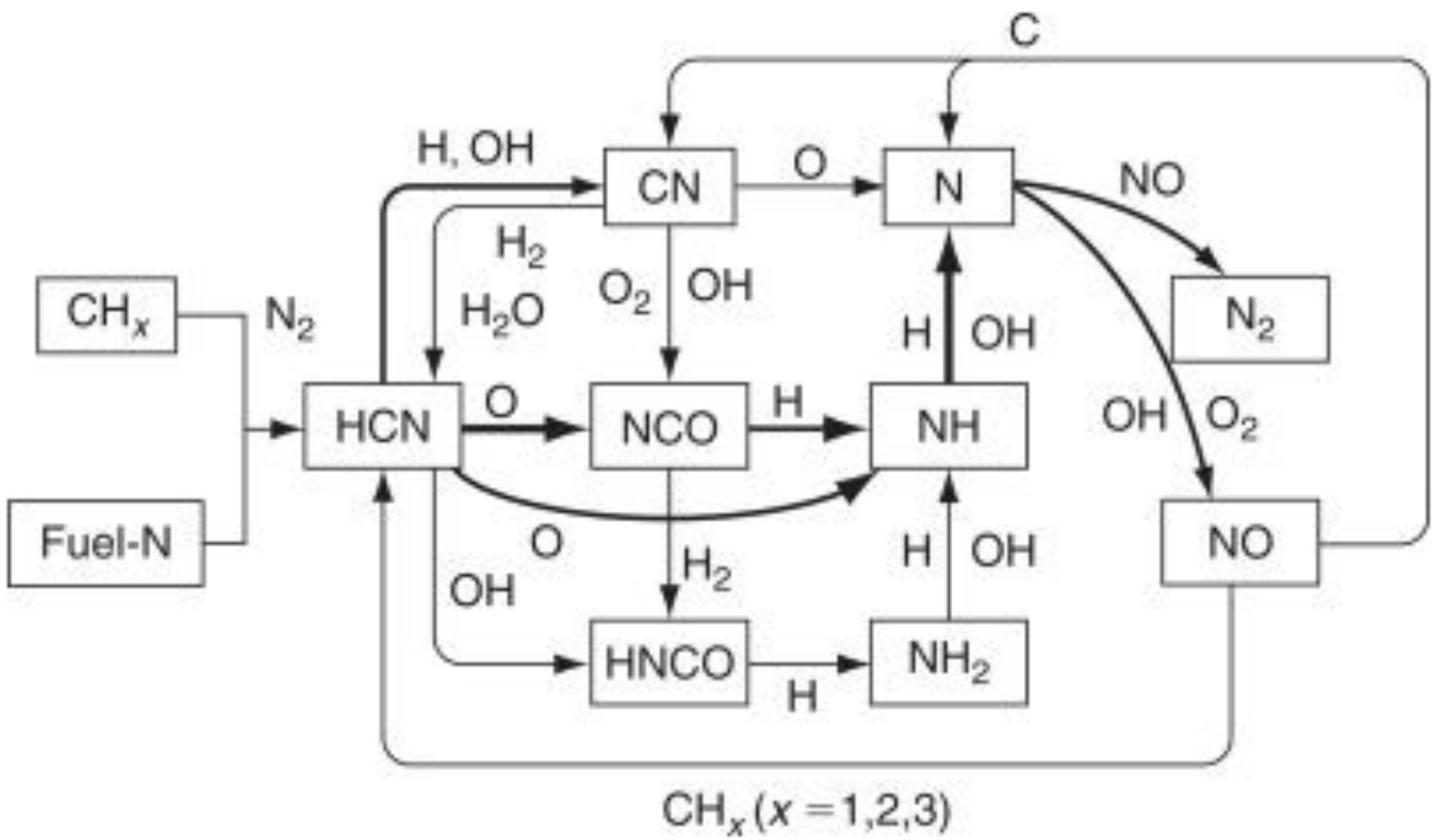




log {d[NO]/dt_max/d[NO]/dt_Zeldovich}
[NO]/[NO]eq.
Temperature (K)
1600
1800
2000
2200
2400
2600
1
2
3
4
5
6
0
0.2
0.4
0.6
0.8
1.0



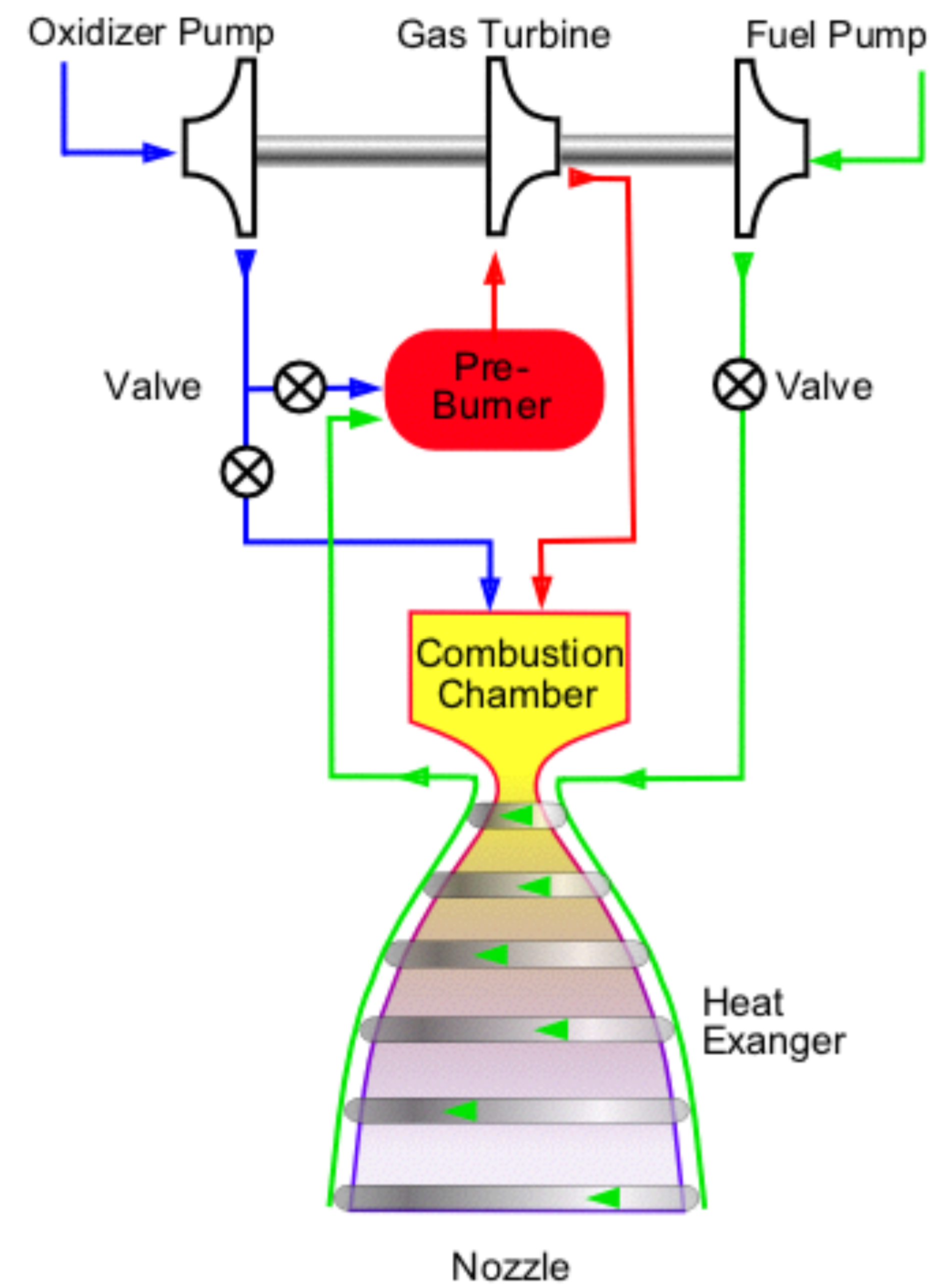
ppmNO
i-Octane
n-Hexazne
n-Butane
Propane
Ethane
Methane
0.6
1.0
1.4
Equivalence ratio
Gasoline
Cyclohexane
Benzene
Acetylene
Ethylene
0.8
1.2
1.6
2.0
Equivalence ratio


C
H, OH
CN
O
N
NO
H_2
H_2O
O_2
OH
CH_x
N_2
H
OH
N_2
HCN
O
NCO
H
NH
OH
O_2
Fuel-N
O
H_2
H
OH
NO
OH
HNCO
NH_2
H
CH_x (x = 1,2,3)

Modification of Operating Conditions

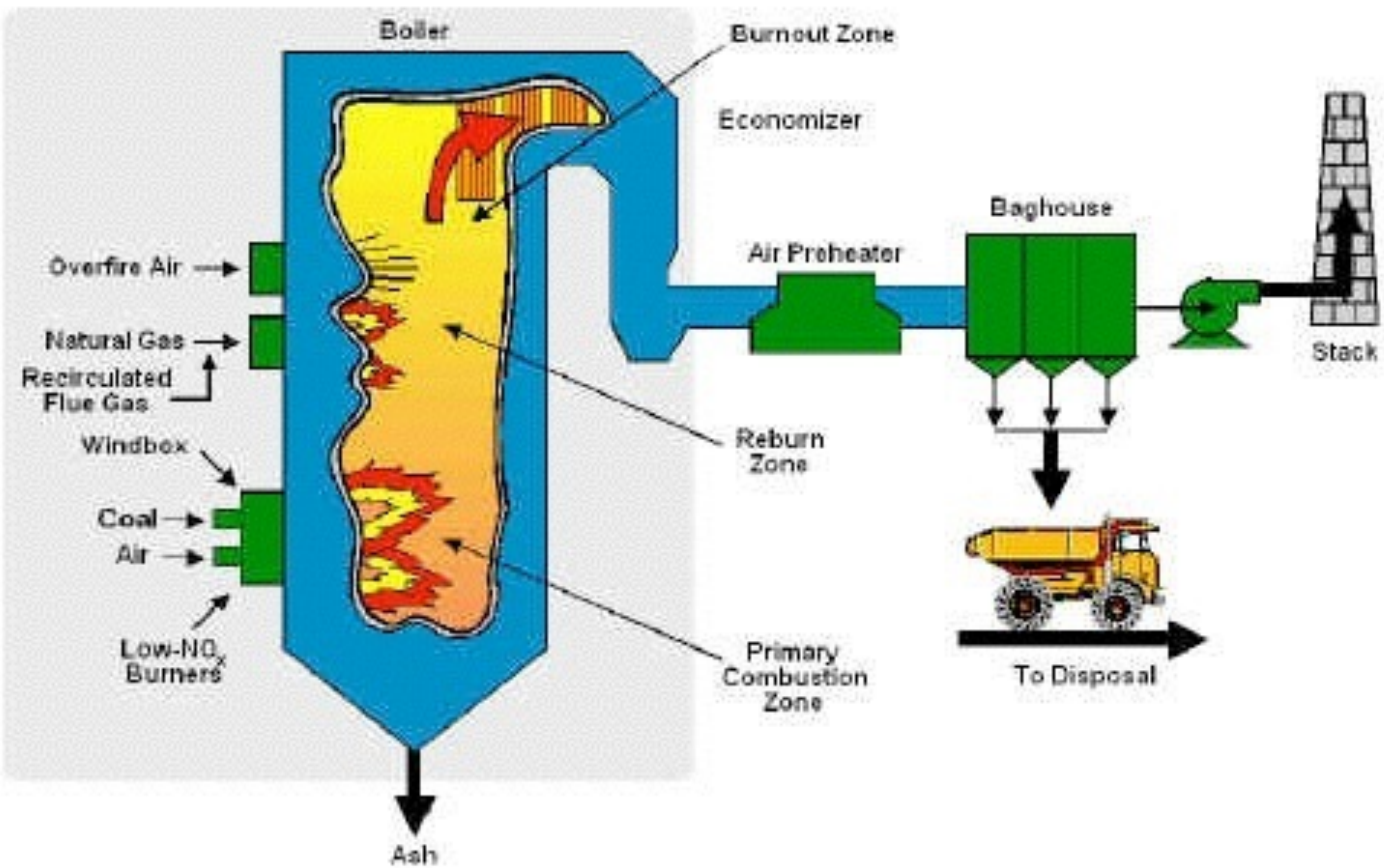
- **Off-Stoichiometric Combustion/ Staged combustion**: combusting the fuel in two or more steps. Fuel rich then fuel lean.

- **Flue gas recirculation**: reroute some of the flue gas back to the furnace; lower O_2 and allow NOx to proceed the "frozen" reactions
- **Water injection**: reduce flame temperature; energy penalty

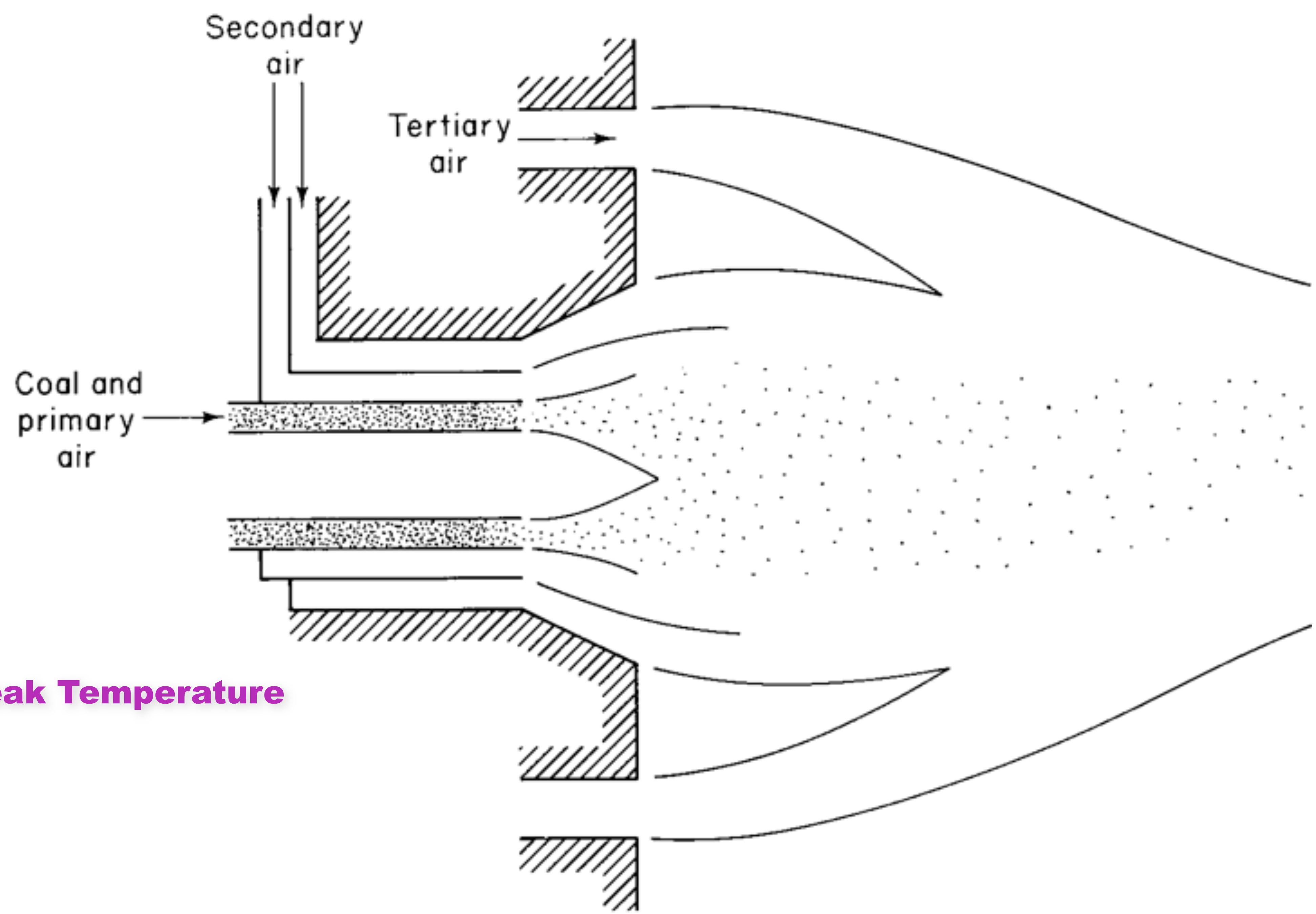


http://en.wikipedia.org/wiki/Staged_combustion_cycle_(rocket)

- **Gas reburning**: injection of natural gas into the boiler above the main burner to create a fuel-rich reburn zone; hydrocarbon radicals react with NOx to reduce NOx to N_2.



- **Low-NOx burner**: inhibit NOx formation by controlling the mixing of fuel and air; lean excess air and off-stoichiometric combustion



Avoid Peak Temperature

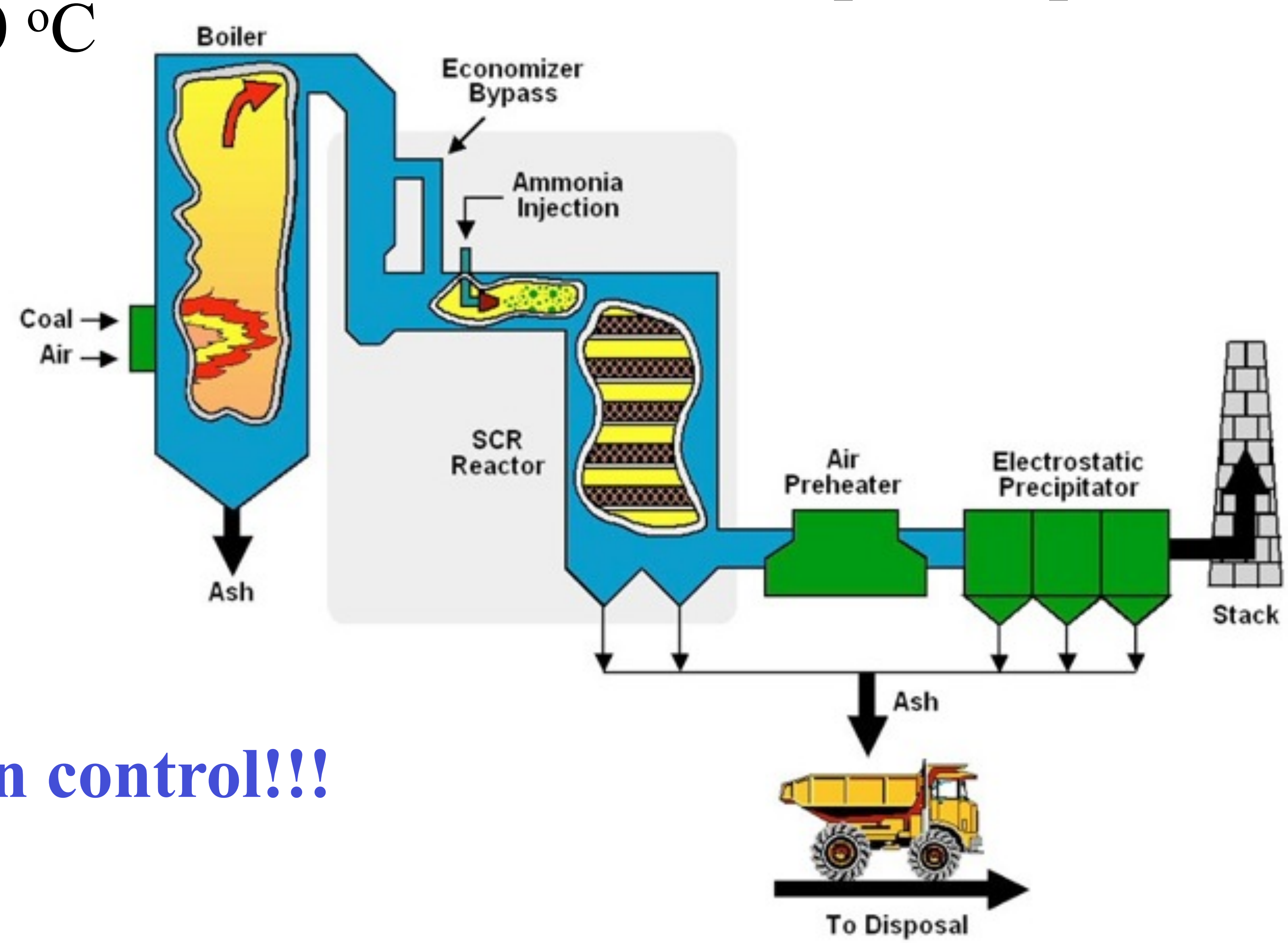
Flue Gas Treatment

- **Selective Catalytic Reduction (SCR)**

$$4NO + 4NH_3 + O_2 \xrightarrow{\text{TiO}_2 \text{ or } \text{V}_2\text{O}_5 \text{ supported catalyst}} 4N_2 + 6H_2O$$

$$2NO_2 + 4NH_3 + O_2 \xrightarrow{\text{TiO}_2 \text{ or } \text{V}_2\text{O}_5 \text{ supported catalyst}} 3N_2 + 6H_2O$$

Temperature ~ 300 - 400 ^{o}C



Also good for Hg emission control!!!

- **Selective Noncatalytic Reduction (SNR)**

$$4NH_3 + 4NO + O_2 \text{ ® } 4N_2 + 6H_2O$$

Temperature ~ 800 - 1000 ^oC

$$4NH_3 + 5O_2 \text{ ® } 4NO + 6H_2O$$

Above 1000 ^oC

- **Wet Absorption**: generally good for only NO_2 because NO is insoluble. Need to oxidize NO first.

$$H_2O_2 \Leftrightarrow 2OH$$

$$\left\{ \begin{array}{l} OH + NO \Leftrightarrow HONO \\ OH + NO_2 \Leftrightarrow HNO_3 \\ OH + H_2O_2 \Leftrightarrow HO_2 + H_2O \end{array} \right.$$

$$\left\{ \begin{array}{l} HO_2 + NO \Leftrightarrow HNO_3 \\ HO_2 + OH \Leftrightarrow H_2O + O_2 \end{array} \right.$$

- **Dry Sorption**
  - **Activated carbon** (220 ~ 230 ^{o}C): reduce NOx to N_2; oxidize SO_2 to H_2SO_4 if NH_3 is injected, and carbon is thermally regenerated to remove concentrated H_2SO_4
  - **Shell Flue Gas Treating System** (~ 400 ^{o}C)

$$CuO + 0.5O_2 + SO_2 \circledR\ CuSO_4$$

$$4NO + 4NH_3 + O_2 \xrightarrow{\text{CuO or CuSO}_4\text{ as catalysts}} \circledR\ 4N_2 + 6H_2O$$

$$CuSO_4 + 2H_2 \circledR\ Cu + SO_2 + 2H_2O$$

$$Cu + 0.5O_2 \circledR\ CuO$$

Figure 5.2
Nitrogen Oxides Concentrations in the Air, in General Stations in Jerusalem, Annual Averages, 2000-2008

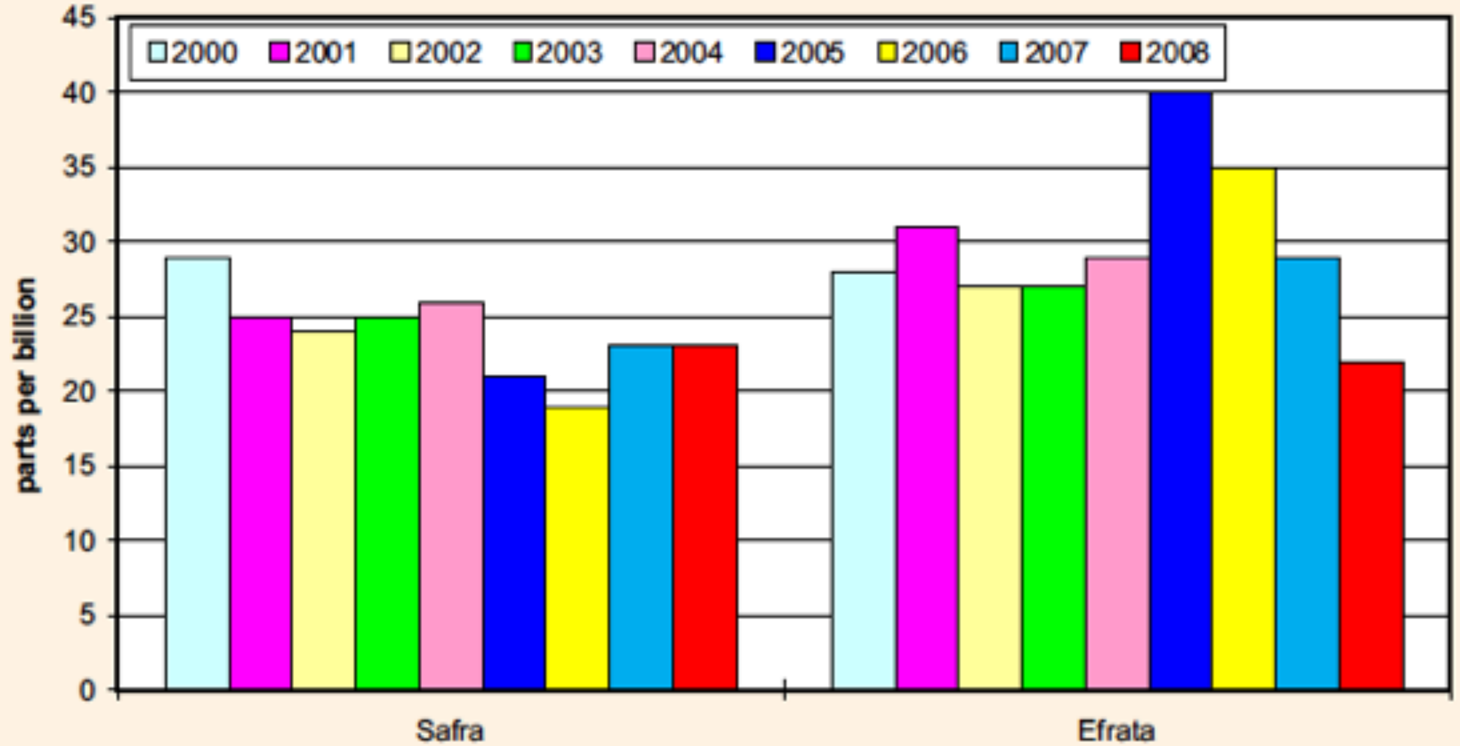


Figure 5.3
Nitrogen Oxides Concentrations in the Air, in Transportation Stations in the Tel Aviv Metropolitan Area, Annual Averages, 2000-2008

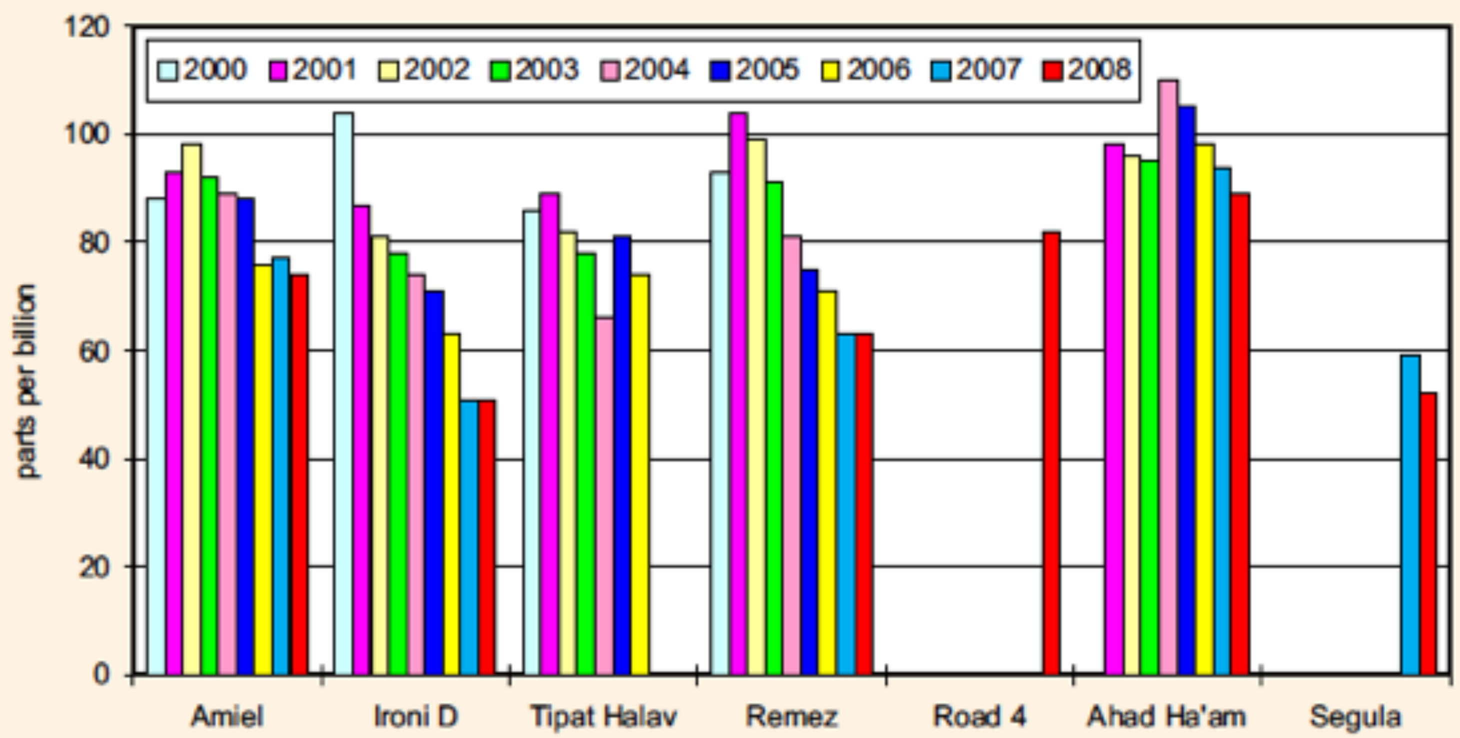


Figure 9.1
Electricity Production,1998-2008

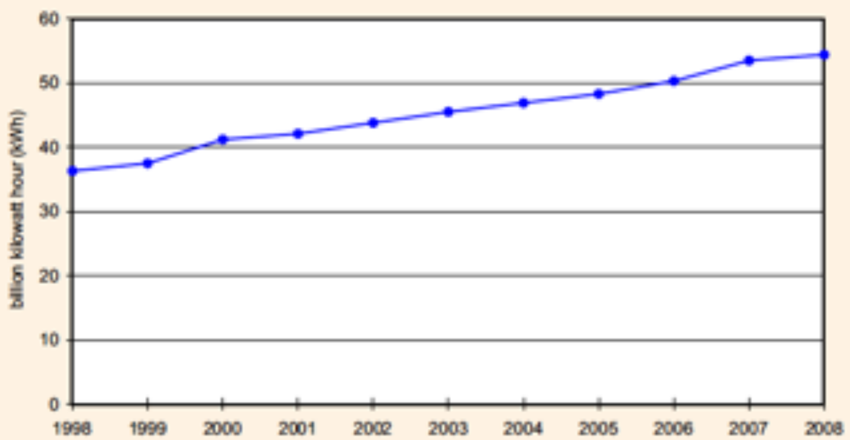


Figure 9.2
Annual Emission and Specific Emission of Sulfur Dioxide (SO_2) to the Air during Electricity Production, 1998-2008

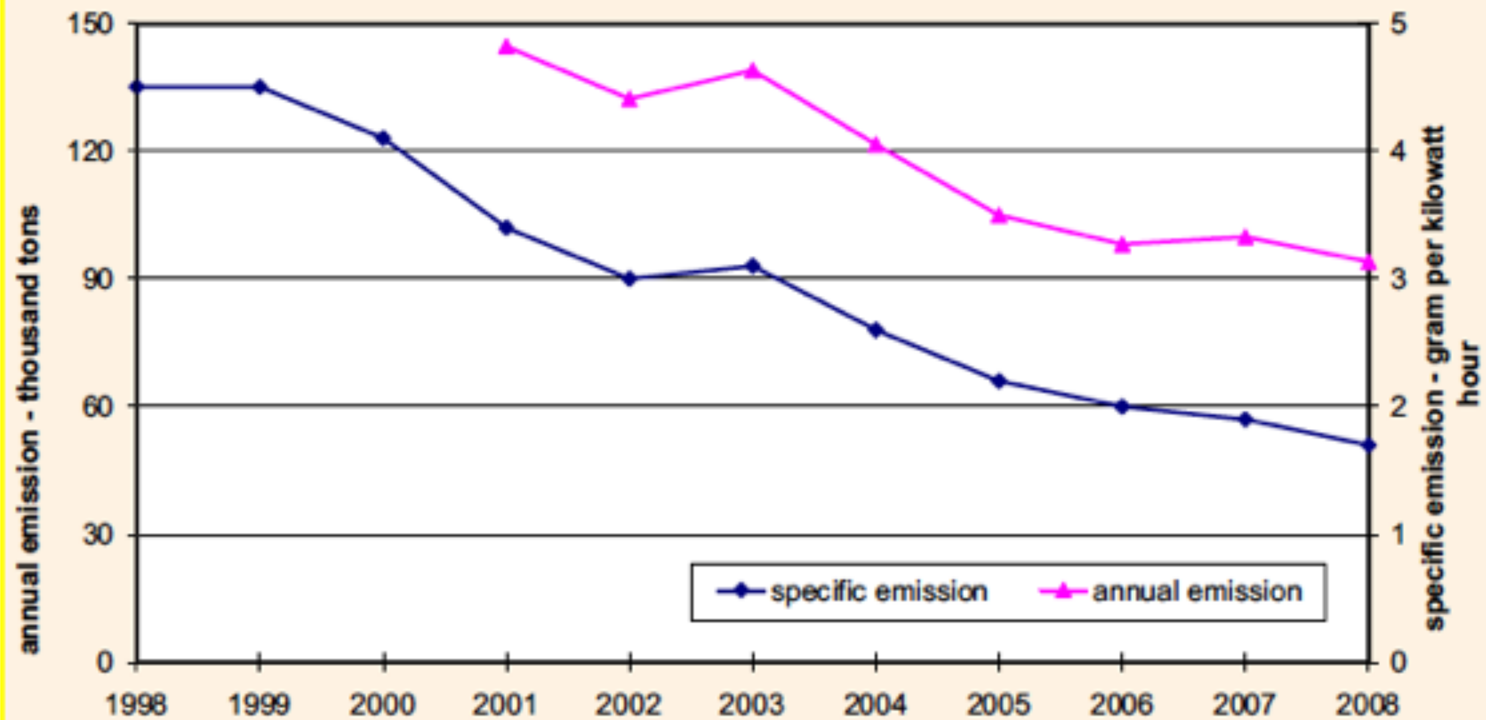
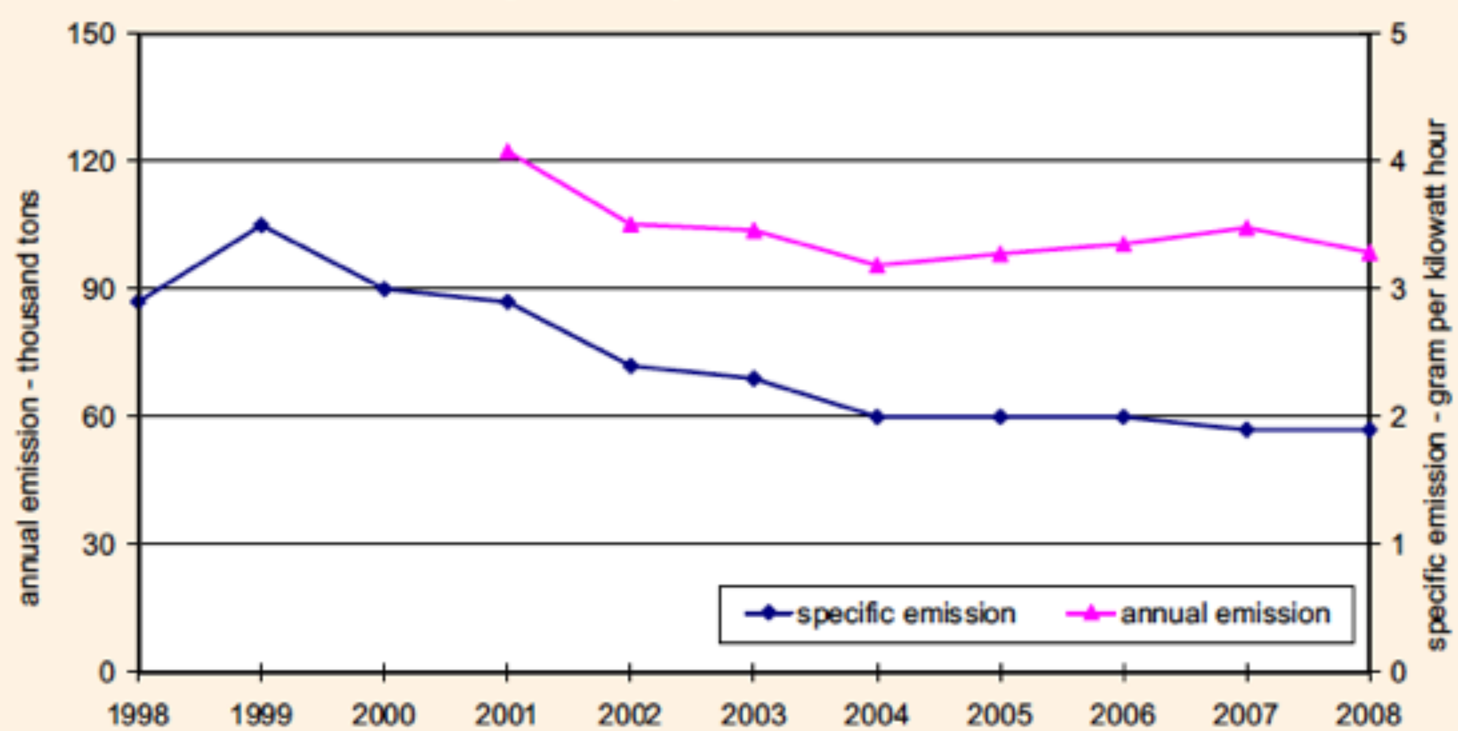


Figure 9.3
Annual Emission and Specific Emission of Nitrogen Oxides (NOx) to the Air during Electricity Production, 1998-2008



Sulfur dioxide emission from flames

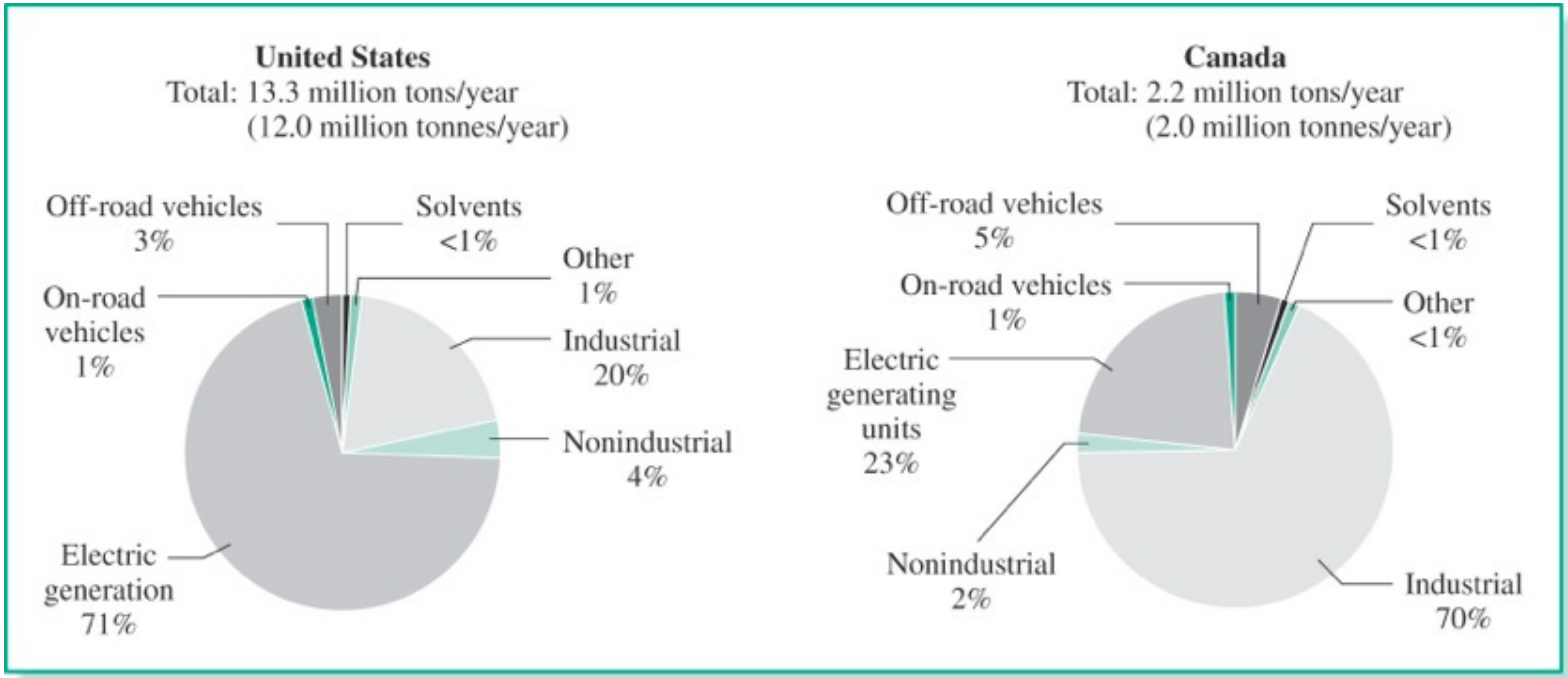
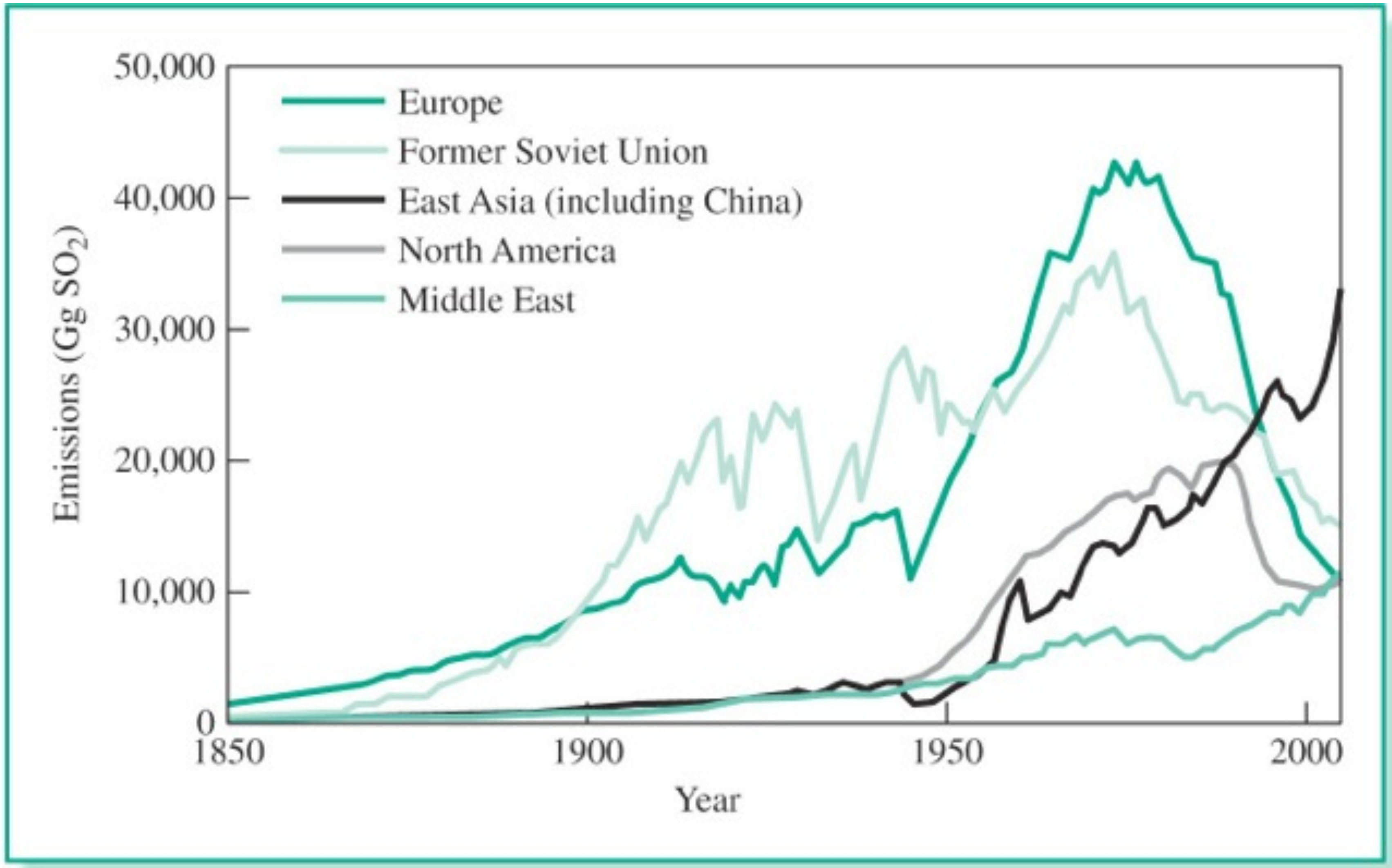


FIGURE 3-16 Anthropogenic SO_2 emissions by sources in North America in 2006. [Source: International Joint Commission, *Canada–United States Air Quality Agreement: 2008 Progress Report*, Washington, D.C. and Ottawa, Ontario, 2008.]

FIGURE 3-17 Global anthropogenic SO_2 emissions by region. [Source: S. J. Smith et al., *Atmospheric Chemistry and Physics* 10 (2010): 16111–16151.]



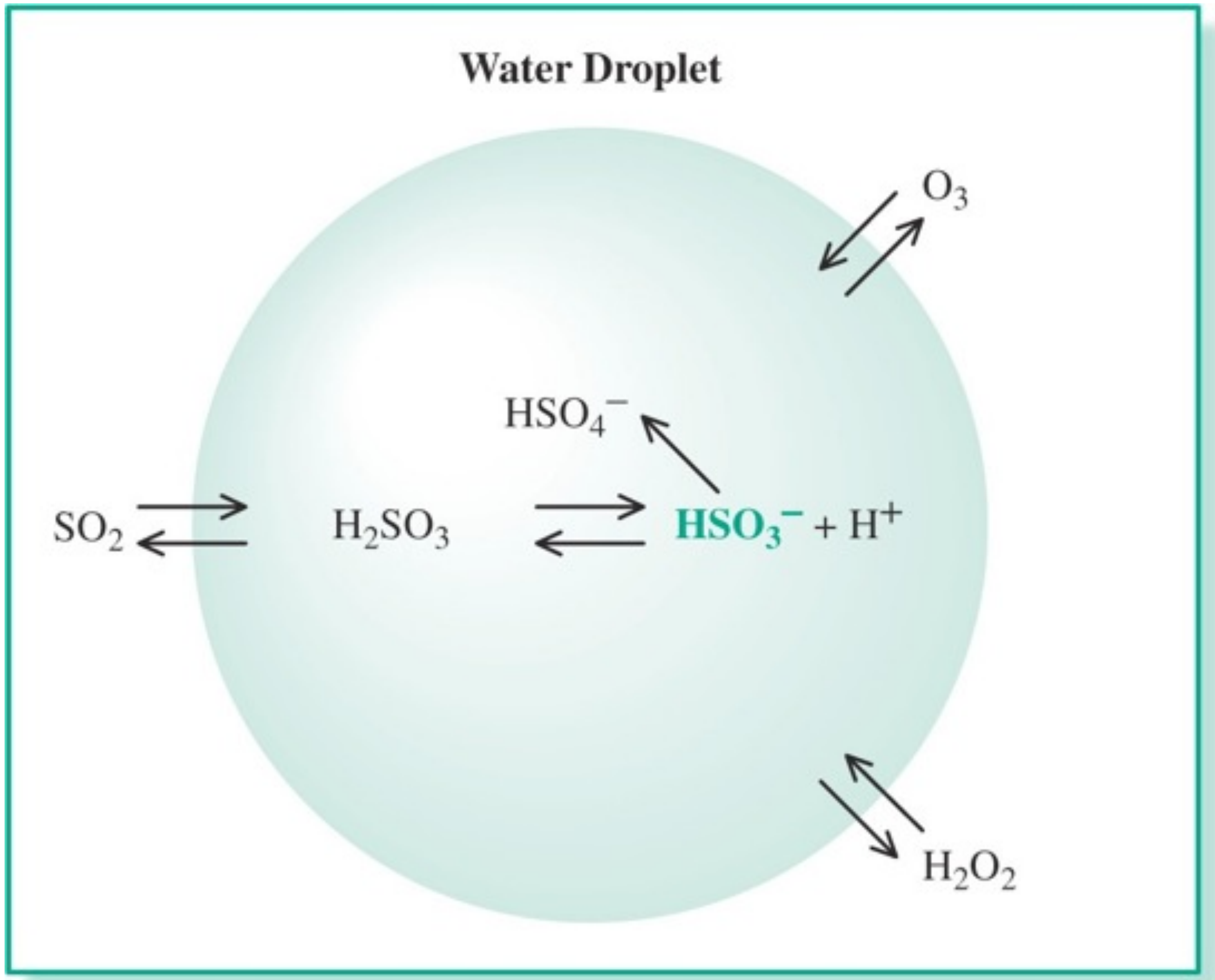
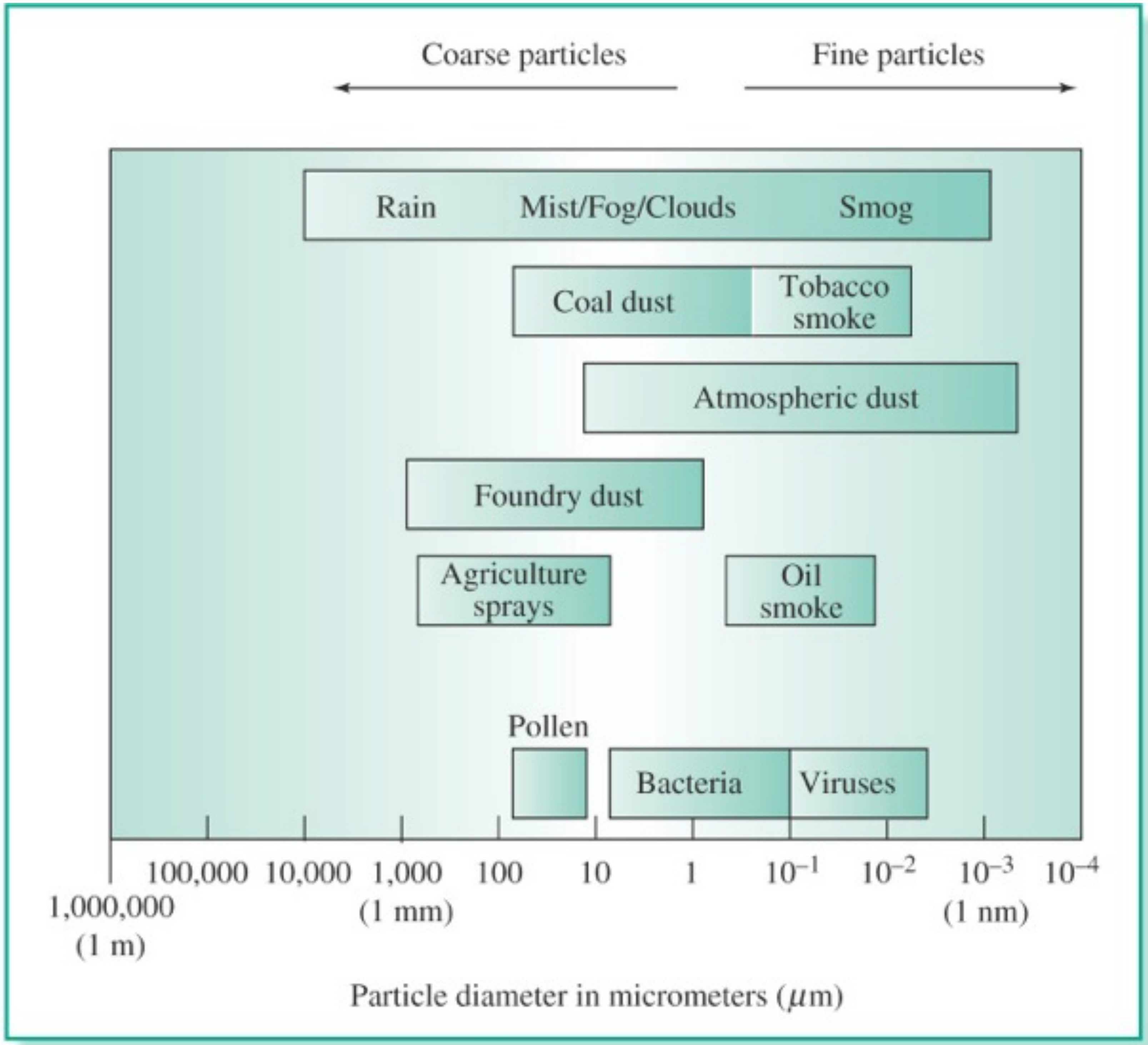
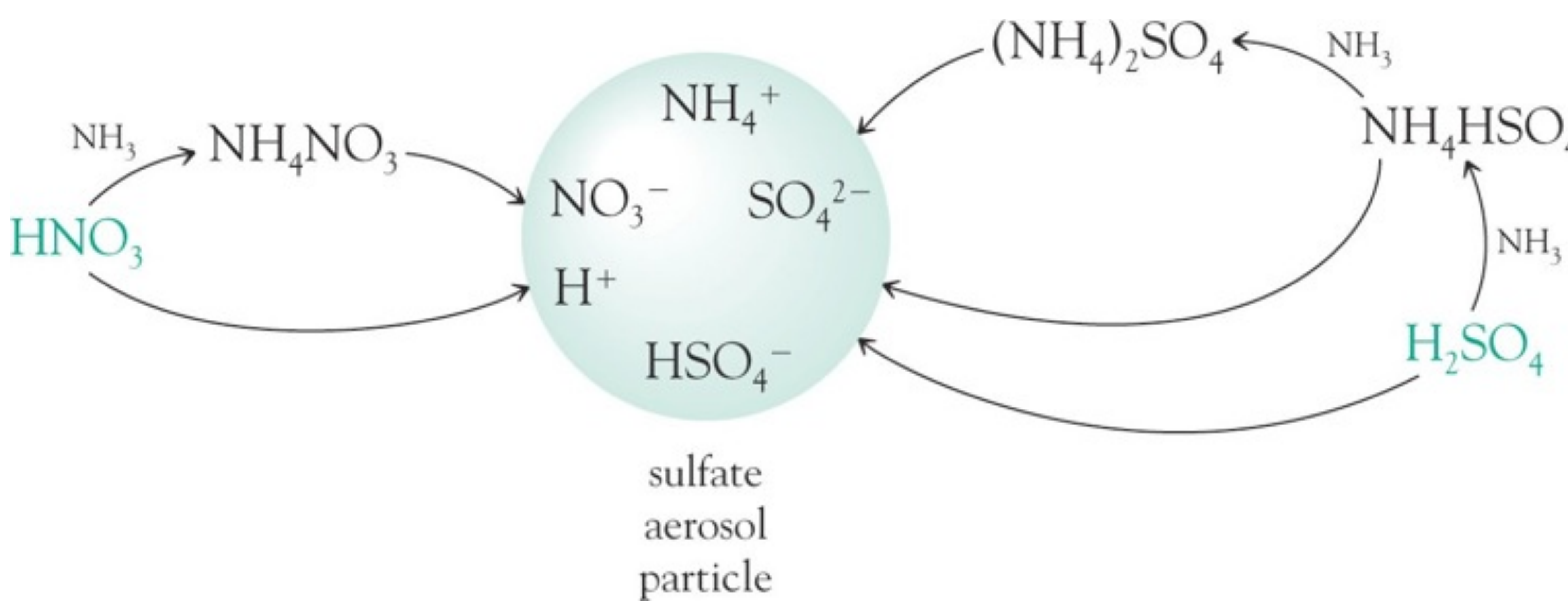


FIGURE 3-18 Dissolution of atmospheric gases SO_2, O_3, and H_2O_2 into a water droplet and their subsequent reactions.

FIGURE 3-19 Sizes of common airborne fine and coarse particulates. [Source: Adapted from J. G. Henry and G. W. Heinke, *Environmental Science and Engineering* (Upper Saddle River, NJ: Prentice Hall, 1989).]




NH_3
NH_4NO_3
HNO_3
NH_4^+
NO_3^-
SO_4^{2-}
H^+
HSO_4^-
$(NH_4)_2SO_4$
NH_3
NH_4HSO_4
NH_3
H_2SO_4
sulfate aerosol particle

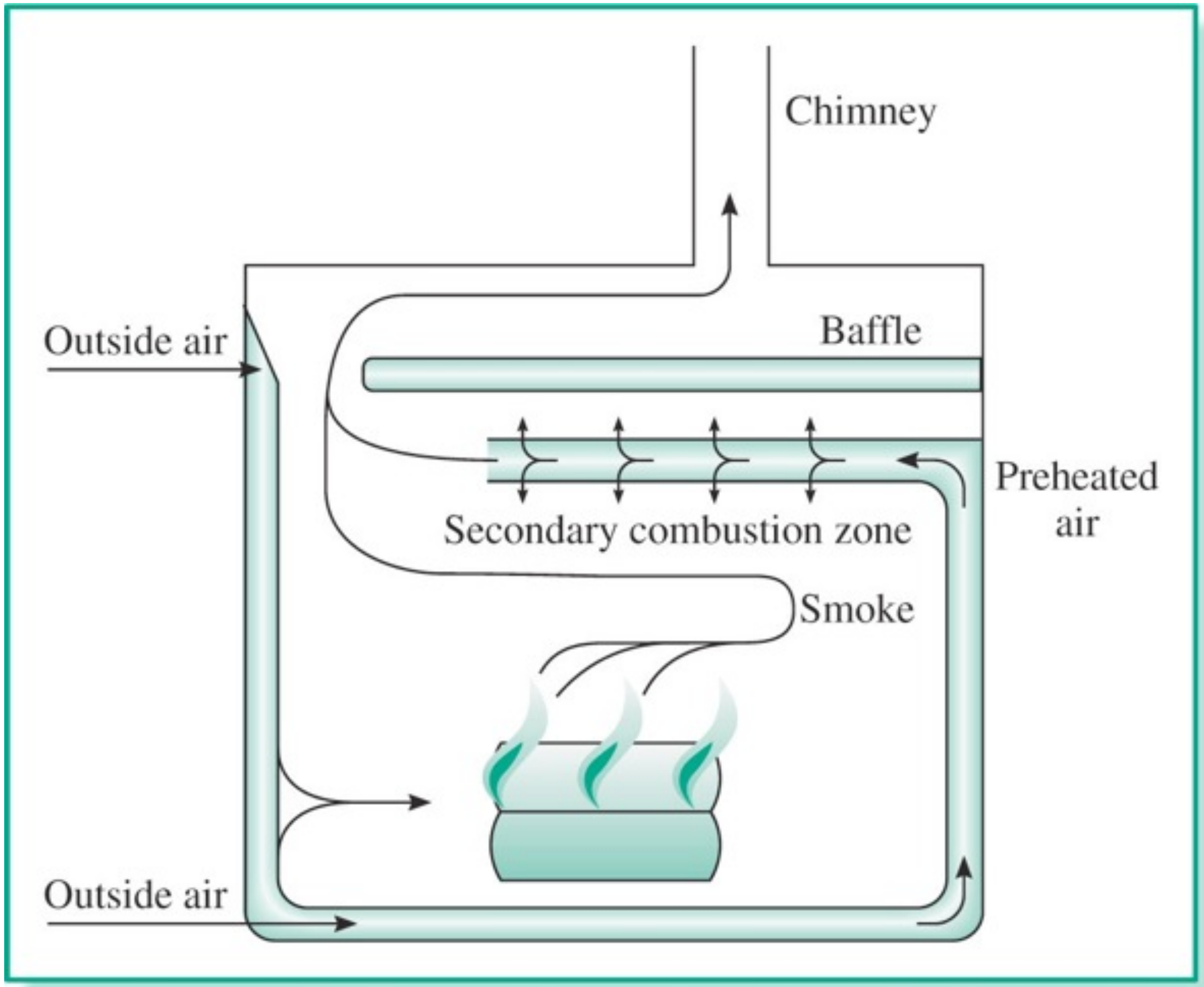


FIGURE 3-20 Noncatalytic wood stove (schematic) with preheated air and baffle for more complete combustion.

FIGURE 3-21 Particulate air quality in major world cities *Note*: Values are annual PM_{10} means. The green horizontal line is the WHO air quality guideline for this parameter. [Source: D. D. Parish and T. Zhu, *Science* 326 (2009): 674–675.]