

**Lecture 20. Urban photochemical smog.**  
**Part 2: Evolution of smoggy air.**

Objectives:

1. Lifetimes of air pollutants.
2. A typical polluted day in Los Angeles.
3. Time evolution of smoggy air.

Readings: Turco: p. 155-163,165-166, 172-174

**1. Lifetimes of air pollutants.**

**Lifetime,  $\tau$** , of a species in a chemical reaction is defined as the time it takes for the species concentration to fall to  $1/e$  of its initial value ( $e$  is the base of natural logarithms, 2.718).

NOTE: recall half-life time of a species discussed in Lecture 7, and reaction rates, reaction rate constant, order of reactions discussed in Lecture 6.

**Another way to define lifetime of a species A:**

$$\tau = [A] / \text{Rate}$$

where **[A]** is the species concentration, and **Rate** is the rate of the reaction.

NOTE: Recall that the rate of a chemical reaction shows how rapidly a chemical change take place.

**Relationships between the rate constant and the lifetimes for first-, second-, and third-order reactions:**

**First-order reaction with the reaction constant  $k_1$ :**

A  $\rightarrow$  products

$$\text{Rate} = -dA/dt = k_1 [A]$$

For first-order reaction the lifetime of species A is

$$\tau = [A] / \text{Rate} = 1 / k_1$$

**Second-order reaction with the reaction constant  $k_2$ :**

A + B  $\rightarrow$  products

$$\text{Rate} = -dA/dt = k_2 [A] [B]$$

For second-order reaction the lifetime of species A is

$$\tau = [A] / \text{Rate} = [A] / k_2 [A] [B] = 1 / k_2 [B]$$

**Third-order reaction with the reaction constant  $k_3$ :**

A + B + C  $\rightarrow$  products

$$\text{Rate} = -dA/dt = k_3 [A] [B] [C]$$

For third-order reaction the lifetime of species A is

$$\tau = [A] / \text{Rate} = [A] / k_3 [A] [B] [C] = 1 / k_3 [B] [C]$$

Important to remember:

- The lifetimes defined above are valid only for the specified reaction; if there are other competing processes, they must be taken into account.
- In two- and three body reactions, the lifetime depends on the concentration of other reactants.

## Problem.

Calculate the lifetime of carbon monoxide using the reactions below.

$$[\text{O}_3] = 2 \cdot 10^{12} \text{ molec cm}^{-3}; [\text{CO}] = 3 \cdot 10^{12} \text{ molec cm}^{-3}; [\text{HC}] = 4 \cdot 10^{10} \text{ molec cm}^{-3}$$



## Solution.

The lifetime of CO is

$$\tau_{\text{CO}} = [\text{CO}] / k_3 [\text{OH}] \quad [\text{CO}] = 1 / k_3 [\text{OH}]$$

Assume steady-state condition for OH. Thus,

$$d[\text{OH}]/dt = 0 \quad \text{or}$$

$$2k_1 [\text{O}({}^1\text{D})] [\text{H}_2\text{O}] - k_2 [\text{OH}] [\text{HC}] - k_3 [\text{OH}] [\text{CO}] = 0$$

$$\text{Therefore, } [\text{OH}] = 2k_1 [\text{O}({}^1\text{D})] [\text{H}_2\text{O}] / \{ k_2 [\text{HC}] + k_3 [\text{CO}] \}$$

Then assume steady-state condition for O(<sup>1</sup>D):

$$d[\text{O}({}^1\text{D})] / dt = 0 \quad \text{or}$$

$$J[\text{O}_3] - k_1 [\text{O}({}^1\text{D})] [\text{H}_2\text{O}] = 0$$

$$\text{Therefore, } [\text{O}({}^1\text{D})] = J[\text{O}_3] / k_1 [\text{H}_2\text{O}]$$

Thus,

$$[\text{OH}] = 2k_1 [\text{O}({}^1\text{D})] [\text{H}_2\text{O}] / \{ k_2 [\text{HC}] + k_3 [\text{CO}] \} = 2 J[\text{O}_3] / \{ k_2 [\text{HC}] + k_3$$

$$[\text{CO}] \} =$$

$$= 1.9 \cdot 10^7 \text{ molec cm}^{-3};$$

Finally, the lifetime of CO is

$$\tau_{\text{CO}} = 1 / k_3 [\text{OH}] = 1 / \{ 1.5 \cdot 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \cdot 1.9 \cdot 10^7 \text{ molec cm}^{-3} \} =$$

$$= 3.5 \cdot 10^5 \text{ s or about 4 days}$$

⇒ Recall that under the steady-state condition, we defined residence time (or lifetime) as  $\tau = Q / S = Q / P$ , where **Q** is the mass (or concentration) of a species, **S** is its production rate, and **P** is its removal (or loss) rate by **any** process. Thus, we can compare the lifetime of a species by any removal process and the lifetime of the species by chemical transformation.

Overall lifetime of a species that is removed by several independent processes is

$$1/\tau = 1/\tau_1 + 1/\tau_2 + \dots + 1/\tau_i$$

where  $\tau_i$  can be thought of as the lifetime of the species if the only removal process is process i.

Example:

Consider a species A in the atmosphere that is removed by two independent processes. Process 1, for example, could be dry deposition and process 2 chemical reaction. For each process we can find the lifetimes of the species A, which are  $\tau_1$  and  $\tau_2$ , using the removal rates for these processes as

$$\tau_1 = [A] / \text{Rate1} \text{ and } \tau_2 = [A] / \text{Rate2}.$$

However, the overall lifetime of species A is

$$\tau = [A] / \{ \text{Rate1} + \text{Rate2} \}$$

Thus

$$1/\tau = 1/\tau_1 + 1/\tau_2$$

or

$$\tau = \tau_1 \tau_2 / \{ \tau_1 + \tau_2 \}$$

If  $\tau_1 \gg \tau_2$ , the lifetime associated with removal process 1 is much longer than that associated with process 2, therefore process 2 is more effective removal mechanism, and

$$\tau = \tau_2$$

Thus, when there are several competing removal paths, in order to estimate the overall lifetime (or residence time) of a species, focus should always be on improving estimates for the fastest removal rate.

Example:

In photochemical smog, ozone can react with organics ( $\tau_{\text{chem}}$ ), can be destroyed by photolysis ( $\tau_{\text{phot}}$ ), can be removed by dry deposition ( $\tau_{\text{dep}}$ ). What is the lifetime of  $\text{O}_3$ ?

The lifetime of ozone is

$$1/\tau = 1/\tau_{\text{chem}} + 1/\tau_{\text{phot}} + 1/\tau_{\text{dep}}$$

## 2. A typical polluted day in Los Angeles.

### I. Early morning (6 to 9 am):

Heavy morning traffic causes high emissions of CO, NO, and RH.

Inversion layer is often very low.

Pollution left over from the previous day may be trapped in narrow layers close to the surface.

## **II. Midday (9 am to 2 pm):**

The primary emissions continue, with a small boost around lunchtime.

After 9 am through 2 pm, primary pollution is photochemically transformed into the secondary pollutants (NO<sub>2</sub>, O<sub>3</sub>, and HC).

In the late morning, the sea breeze picks up and transports the coastal pollution inland.

Near noon, the intensity of the sun maximizes, and secondary pollutants are generated rapidly. Ozone peaks in the afternoon hours.

## **III. Late afternoon (2 to 5 pm):**

Ozone concentrations have accumulated to their highest levels.

Sea breeze is strong, pushing a cloud of smog far inland against mountains.

If air pollutants can be lofted through mountain passes onto the high plateau beyond. From there, the pollution can travel hundreds of miles across the desert regions. (Enjoy Los Angeles smog in the Four Corners!!!).

## **IV. Evening (5 to 7 pm):**

Traffic again builds up, and more primary pollutants are released into the smoggy air. However, the sun is low, and so insufficient radiation is available to generate much photochemical smog. The primary pollutants themselves accumulate. The ozone concentration begin to fall (because no sunlight). The sea breeze continues to sweep the pollutants inland, diluting their effects closer to the coast.

## **V. Late evening (after 7 pm):**

Sea breeze dies, and a weaker land breeze may develop. Radiative cooling creates temperature inversion. Most of previous day's pollution is left above this inversion and is dispersed by prevailing regional winds (advection).

Under the temperature inversion, primary pollutants can accumulate.

### 3. Time evolution of smoggy air.

Photochemical smog in Los Angeles shows diurnal and seasonal variations.

#### **Diurnal variations:**

##### **CO (primary pollutant):**

maximum concentrations are during the morning rush hours, and secondary peak is in the late evening; minimum concentrations are around noon.

##### **NO<sub>2</sub> (secondary pollutant):**

maximum concentrations are in the late morning, and later times, concentrations decrease.

##### **O<sub>3</sub> (secondary pollutant):**

maximum concentrations are in mid- or late afternoon.

#### **Seasonal variations:**

##### **CO:**

monthly concentrations in summer are lower than in winter.

##### **NO<sub>2</sub>:**

small seasonal variations.

##### **O<sub>3</sub> (secondary pollutant):**

monthly concentrations in summer are higher than in winter.

Smog may have different characteristics at different locations, owing to the following main factors:

- 1) Sources of primary pollutants;
- 2) Timing of emissions;
- 3) Distribution of sources;
- 4) Prevailing winds;
- 5) Regional topology;
- 6) Geographical character;
- 7) Season of the year;
- 8) Urban demographics.