CHAPTER 3. SIMPLE MODELS

The concentrations of chemical species in the atmosphere are controlled by four types of processes:

- *Emissions.* Chemical species are emitted to the atmosphere by a variety of sources. Some of these sources, such as fossil fuel combustion, originate from human activity and are called *anthropogenic.* Others, such as photosynthesis of oxygen, originate from natural functions of biological organisms and are called *biogenic.* Still others, such as volcanoes, originate from non-biogenic natural processes.
- *Chemistry.* Reactions in the atmosphere can lead to the formation and removal of species.
- *Transport.* Winds transport atmospheric species away from their point of origin.
- *Deposition.* All material in the atmosphere is eventually deposited back to the Earth's surface. Escape from the atmosphere to outer space is negligible because of the Earth's gravitational pull. Deposition takes two forms: "dry deposition" involving direct reaction or absorption at the Earth's surface, such as the uptake of CO_2 by photosynthesis; and "wet deposition" involving scavenging by precipitation.

A general mathematical approach to describe how the above processes determine the atmospheric concentrations of species will be given in chapter 5 in the form of the *continuity equation.* Because of the complexity and variability of the processes involved, the continuity equation cannot be solved exactly. An important skill of the atmospheric chemist is to make the judicious approximations necessary to convert the real, complex atmosphere into a *model system* which lends itself to analytical or numerical solution. We describe in this chapter the two simplest types of models used in atmospheric chemistry research: *box models* and *puff models.* As we will see in chapter 5, these two models represent respectively the simplest applications of the Eulerian and Lagrangian approaches to obtain approximate solutions of the continuity equation. We will also use box models in chapter 6 to investigate the geochemical cycling of elements.

3.1 ONE-BOX MODEL

A one-box model for an atmospheric species X is shown in Figure 3-1. It describes the abundance of X inside a box representing a selected atmospheric domain (which could be for example an urban area, the United States, or the global atmosphere). Transport is treated as a flow of X into the box (F_{in}) and out of the box (F_{out}). If the box is the global atmosphere then $F_{in} = F_{out} = 0$. The production and loss rates of X inside the box may include contributions from emissions (*E*), chemical production (*P)*, chemical loss *(L)*, and deposition (*D)*. The terms F_{in}, *E,* and *P* are *sources* of X in the box; the terms F_{out}, *L,* and *D* are *sinks* of X in the box. The mass of X in the box is often called an *inventory* and the box itself is often called a *reservoir.* The one-box model does not resolve the spatial distribution of the concentration of X inside the box. It is frequently assumed that the box is well-mixed in order to facilitate computation of sources and sinks.
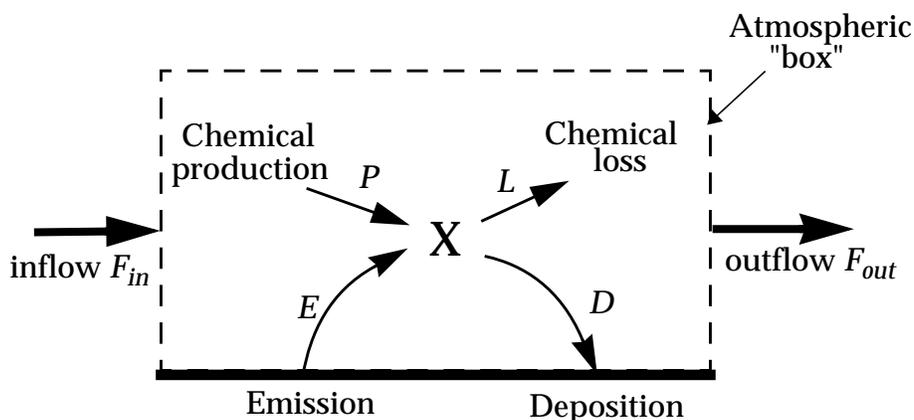

Figure 3-1 One-box model for an atmospheric species X

3.1.1 Concept of lifetime

The simple one-box model allows us to introduce an important and general concept in atmospheric chemistry, the *lifetime.* The lifetime τ of X in the box is defined as the average time that a molecule of X remains in the box, that is, the ratio of the mass *m* (kg) of X in the box to the removal rate $F_{out} + L + D$ (kg s^{-1})*:*

$$\tau = \frac{m}{F_{out} + L + D} \qquad (3.1)$$

The lifetime is also often called the *residence time* and we will use the two terms interchangeably (one tends to refer to *lifetime* when

the loss is by a chemical process such as *L,* and *residence time* when the loss is by a physical process such as F_{out} or *D*).

We are often interested in determining the relative importance of different sinks contributing to the overall removal of a species. For example, the fraction *f* removed by export out of the box is given by

$$f = \frac{F_{out}}{F_{out} + L + D} \tag{3.2}$$

We can also define sink-specific lifetimes against export ($\tau_{out} = m/F_{out}$), chemical loss ($\tau_c = m/L$), and deposition ($\tau_d = m/D$). The sinks apply in parallel so that

$$\frac{1}{\tau} = \frac{1}{\tau_{out}} + \frac{1}{\tau_c} + \frac{1}{\tau_d} \tag{3.3}$$

The sinks F_{out}, *L,* and *D* are often *first-order*, meaning that they are proportional to the mass inside the box ("the more you have, the more you can lose"). In that case, the lifetime is independent of the inventory of X in the box. Consider for example a well-mixed box of dimensions l_x, l_y, l_z ventilated by a wind of speed *U* blowing in the x-direction. Let ρ_X represent the mean mass concentration of X in the box. The mass of X in the box is $\rho_X l_x l_y l_z$, and the mass of X flowing out of the box per unit time is $\rho_X U l_y l_z$, so that τ_{out} is given by

$$\tau_{out} = \frac{m}{F_{out}} = \frac{\rho_X l_x l_y l_z}{\rho_X U l_y l_z} = \frac{l_x}{U} \tag{3.4}$$

As an another example, consider a first-order chemical loss for X with rate constant k_c. The chemical loss rate is $L = k_c m$ so that τ_c is simply the inverse of the rate constant:

$$\tau_c = \frac{m}{L} = \frac{1}{k_c} \tag{3.5}$$

We can generalize the notion of chemical rate constants to define rate constants for loss by export ($k_{out} = 1/\tau_{out}$) or by deposition ($k_d = 1/\tau_d$). In this manner we define an overall loss rate constant $k = 1/\tau = k_{out} + k_c + k_d$ for removal of X from the box:

$$F_{out} + L + D = (k_{out} + k_c + k_d)m = km \tag{3.6}$$

Exercise 3-1. Water is supplied to the atmosphere by evaporation from the surface and is removed by precipitation. The total mass of water in the atmosphere is 1.3×10^{16} kg, and the global mean rate of precipitation to the Earth's surface is 0.2 cm day^{-1}. Calculate the residence time of water in the atmosphere.

Answer. We are given the total mass *m* of atmospheric water in units of kg; we need to express the precipitation loss rate *L* in units of kg day^{-1} in order to derive the residence time $\tau = m/L$ in units of days. The mean precipitation rate of 0.2 cm day^{-1} over the total area $4\pi R^2 = 5.1 \times 10^{14}$ m^2 of the Earth (radius $R = 6400$ km) represents a total precipitated volume of 1.0×10^{12} m^3 day^{-1}. The mass density of liquid water is 1000 kg m^{-3}, so that $L = 1.0 \times 10^{15}$ kg day^{-1}. The residence time of water in the atmosphere is $\tau = m/L = 1.3 \times 10^{16}/1.0 \times 10^{15} = 13$ days.

3.1.2 Mass balance equation

By mass balance, the change with time in the abundance of a species X inside the box must be equal to the difference between sources and sinks:

$$\frac{dm}{dt} = \Sigma\text{sources} - \Sigma\text{sinks} = F_{in} + E + P - F_{out} - L - D \qquad (3.7)$$

This mass balance equation can be solved for *m(t)* if all terms on the right-hand-side are known. We carry out the solution here in the particular (but frequent) case where the sinks are first-order in *m* and the sources are independent of *m*. The overall loss rate of X is *km* (equation *(3.6)*) and we define an overall source rate $S = F_{in} + E + P$. Replacing into *(3.7)* gives

$$\frac{dm}{dt} = S - km \qquad (3.8)$$

Equation *(3.8)* is readily solved by separation of variables:

$$\frac{dm}{S - km} = dt \qquad (3.9)$$

Integrating both sides over the time interval [0, *t*], we obtain

$$\left(-\frac{1}{k}\right)\ln(S - km)\Big|_0^t \;=\; t\Big|_0^t \tag{3.10}$$

which gives

$$\left(-\frac{1}{k}\right)\ln\left(\frac{S - km(t)}{S - km(0)}\right) \;=\; t \tag{3.11}$$

and by rearrangement,

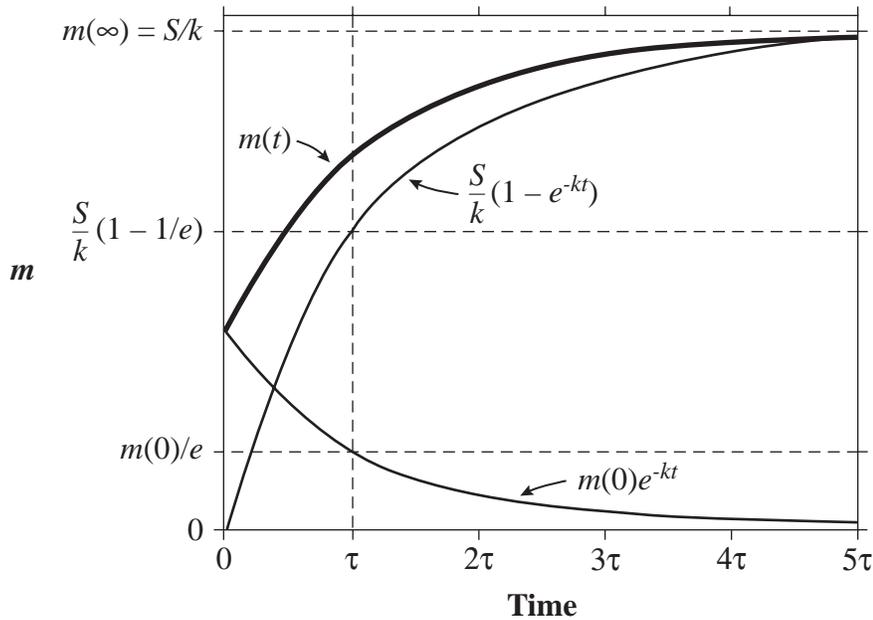$$m(t) \;=\; m(0)e^{-kt} + \frac{S}{k}(1 - e^{-kt}) \tag{3.12}$$

.

Figure 3-2 Evolution of species mass with time in a box model with first-order loss

A plot of *m(t)* as given by *(3.12)* is shown in Figure 3-2. Eventually *m(t)* approaches a *steady-state* value $m_\infty = S/k$ defined by a balance between sources and sinks ($dm/dt = 0$ in *(3.8)*). Notice that the first term on the right-hand-side of *(3.12)* characterizes the decay of the initial condition, while the second term represents the approach to steady state. At time $\tau = 1/k$, the first term has decayed to $1/e = 37\%$ of its initial value while the second term has increased to $(1\text{-}1/e) = 63\%$ of its final value; at time $t = 2\tau$ the first term has decayed to $1/e^2 = 14\%$ of its initial value while the second term has increased to 86% of its final value. Thus τ is a useful *characteristic time* to measure the time that it takes for the system to reach steady state. One sometimes refers to τ as an "*e*-folding lifetime" to avoid confusion with the "half-life" frequently used in the radiochemistry literature.

We will make copious use of the steady-state assumption in this and subsequent chapters, as it allows considerable simplification by reducing differential equations to algebraic equations. As should be apparent from the above analysis, one can assume steady state for a species as long as its production rate and its lifetime τ have both remained approximately constant for a time period much longer than τ. When the production rate and τ both vary but on time scales longer than τ, the steady-state assumption is still applicable even though the concentration of the species keeps changing; such a situation is called *quasi steady state* or *dynamic equilibrium*. The way to understand steady state in this situation is to appreciate that the loss rate of the species is limited by its production rate, so that production and loss rates remain roughly equal at all times. Even though *dm/dt* never tends to zero, it is always small relative to the production and loss rates.

Exercise 3-2 . **What is the difference between the e-folding lifetime τ and the half-life $t_{1/2}$ of a radioactive element?**

Answer. Consider a radioactive element X decaying with a rate constant k (s^{-1}):

$$\frac{d}{dt}[X] = -k[X]$$

The solution for $[X](t)$ is

$$[X](t) = [X](0)e^{-kt}$$

The half-life is the time at which 50% of *[X](0)* remains: $t_{1/2} = (ln\ 2)/k$. The e-folding ifetime is the time at which $1/e = 37\%$ of *[X](0)* remains: $\tau = 1/k$. The two are related by $t_{1/2} = \tau\ ln\ 2 = 0.69\ \tau$.

Exercise 3-3 The chlorofluorocarbon CFC-12 (CF_2Cl_2) is removed from the atmosphere solely by photolysis. Its atmospheric lifetime is 100 years. In the early 1980s, before the Montreal protocol began controlling production of CFCs because of their effects on the ozone layer, the mean atmospheric concentration of CFC-12 was 400 pptv and increased at the rate of 4% yr^{-1}. What was the CFC-12 emission rate during that period?

Answer. The global mass balance equation for CFC-12 is

$$\frac{dm}{dt} = E - km$$

where m is the atmospheric mass of CFC-12, E is the emission rate, and $k = 1/\tau =$ 0.01 yr^{-1} is the photolysis loss rate constant. By rearranging this equation we obtain an expression for E in terms of the input data for the problem,

$$E = \left(\frac{1}{m}\frac{dm}{dt} + k\right)m$$

The relative accumulation rate $(1/m)dm/dt$ is 4% yr^{-1} or 0.04 yr^{-1}, and the atmospheric mass of CFC-12 is $m = M_{CFC}C_{CFC}N_a = 0.118\text{x}400\text{x}10^{-12}\text{x}1.8\text{x}10^{20} = 8.5\text{x}10^9$ kg. Substitution in the above expression yields $E = 4.2\text{x}10^8$ kg yr^{-1}.

3.2 MULTI-BOX MODELS

The one-box model is a particularly simple tool for describing the chemical evolution of species in the atmosphere. However, the drastic simplification of transport is often unacceptable. Also, the model offers no information on concentration gradients within the box. A next step beyond the one-box model is to describe the atmospheric domain of interest as an assemblage of N boxes exchanging mass with each other. The mass balance equation for each box is the same as in the one-box model formulation *(3.7)* but the equations are coupled through the F_{in} and F_{out} terms. We obtain in this manner a system of N coupled differential equations (one for each box).

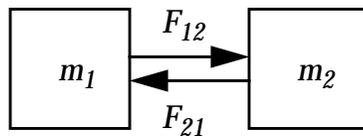As the simplest case, consider a two-box model as shown in Figure 3-3:

Figure 3-3 Two-box model

Let m_i (kg) represent the mass of X in reservoir i; E_i, P_i, L_i, D_i the sources and sinks of X in reservoir *i*; and F_{ij} (kg s^{-1}) the transfer rate of X from reservoir i to reservoir j. The mass balance equation for m_1 is

$$\frac{dm_1}{dt} = E_1 + P_1 - L_1 - D_1 - F_{12} + F_{21} \qquad (3.13)$$

If F_{ij} is first-order, so that $F_{ij} = k_{ij}m_i$ where k_{ij} is a *transfer rate*

constant, then *(3.13)* can be written

$$\frac{dm_1}{dt} = E_1 + P_1 - L_1 - D_1 - k_{12}m_1 + k_{21}m_2 \qquad (3.14)$$

and a similar equation can be written for m_2. We thus have two coupled first-order differential equations from which to calculate m_1 and m_2. The system at steady state $(dm_1/dt = dm_2/dt = 0)$ is described by two coupled algebraic equations. Problems 3.3 and 3.4 are important atmospheric applications of two-box models.

A 3-box model is already much more complicated. Consider the general 3-box model for species X in Figure 3-4:
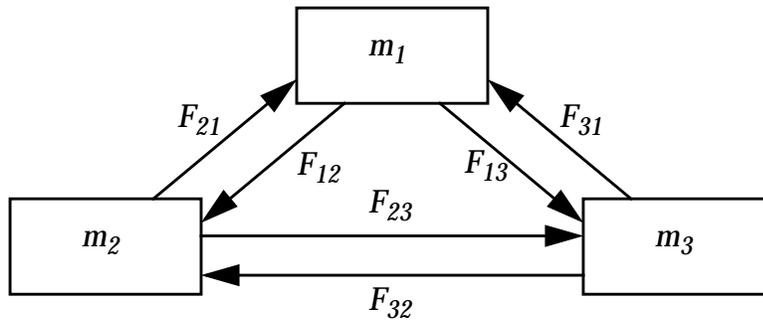

Figure 3-4 Three-box model

The residence time of species X in box 1 is determined by summing the sinks from loss within the box and transfer to boxes 2 and 3:

$$\tau_1 = \frac{m_1}{L_1 + D_1 + F_{12} + F_{13}} \qquad (3.15)$$

with similar expressions for τ_2 and τ_3. Often we are interested in determining the residence time within an ensemble of boxes. For example, we may be interested in knowing how long X remains in boxes 1 and 2 before it is transferred to box 3. The total inventory in boxes 1 and 2 is $m_1 + m_2$, and the transfer rates from these boxes to box 3 are F_{13} and F_{23}, so that the residence time τ_{1+2} of X in the ensemble of boxes 1 and 2 is given by

$$\tau_{1+2} = \frac{m_1 + m_2}{L_1 + L_2 + D_1 + D_2 + F_{13} + F_{23}} \qquad (3.16)$$

The terms F_{12} and F_{21} do not appear in the expression for τ_{1+2} because they merely cycle X between boxes 1 and 2.

Analysis of multi-box models can often be simplified by isolating different parts of the model and making order-of-magnitude approximations, as illustrated in the Exercise below.

Exercise 3-4.   Consider a simplified 3-box model where transfers between boxes 1 and 3 are negligibly small. A total mass m is to be distributed among the three boxes. Calculate the masses in the individual boxes assuming that transfer between boxes is first-order, that all boxes are at steady state, and that there is no production or loss within the boxes.

Answer. It is always useful to start by drawing a diagram of the box model:
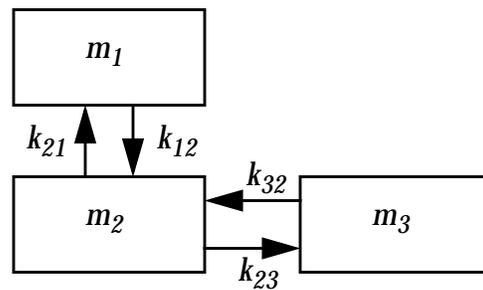
We write the steady-state mass balance equations for boxes 1 and 3, and mass conservation for the ensemble of boxes:

$$k_{12}m_1 \; = \; k_{21}m_2$$

$$k_{23}m_2 \; = \; k_{32}m_3$$

$$m \; = \; m_1 + m_2 + m_3$$

which gives us three equations for the three unknowns m_1, m_2, m_3. Note that a mass balance equation for box 2 would be redudant with the mass balance equations for boxes 1 and 3, i.e., there is no fourth independent equation. From the system of three equations we derive an expression for m_1 as a function of m and of the transfer rate constants:

$$m_1 \; = \; \cfrac{m}{1 + \cfrac{k_{12}}{k_{21}}\left(1 + \cfrac{k_{23}}{k_{32}}\right)}$$

Similar expressions can be derived for m_2 and m_3.

3.3 PUFF MODELS

A box model describes the composition of the atmosphere within fixed domains in space (the boxes) through which the air flows. A

puff model, by contrast, describes the composition of one or more fluid elements (the "puffs") moving with the flow (Figure 3-5). We define here a fluid element as a volume of air of dimensions sufficiently small that all points within it are transported by the flow with the same velocity, but sufficiently large to contain a statistically representative ensemble of molecules. The latter constraint is not particularly restrictive since 1 cm^3 of air at the Earth's surface already contains ~10^{19} molecules, as shown in chapter 1.
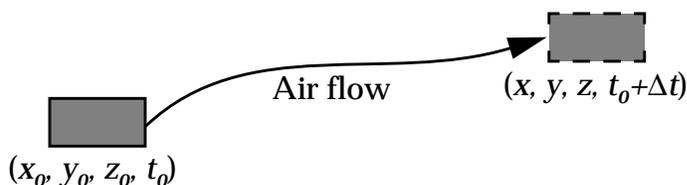

Figure 3-5 Movement of a fluid element ("puff") along an air flow trajectory

The mass balance equation for a species X in the puff is given by

$$\frac{d}{dt}[X] = E + P - L - D \qquad (3.17)$$

where *[X]* is the concentration of X in the puff (for example in units of molecules cm^{-3}) and the terms on the right-hand side are the sources and sinks of X in the puff (molecules cm^{-3} s^{-1}). We have written here the mass balance equation in terms of concentration rather than mass so that the size of the puff can be kept arbitrary. A major difference from the box model treatment is that the transport terms F_{in} and F_{out} are zero because the frame of reference is now the traveling puff. Getting rid of the transport terms is a major advantage of the puff model, but may be offset by difficulty in determining   the trajectory of the puff.   In addition, the assumption that all points within the puff are transported with the same velocity is often not very good.   Wind shear in the atmosphere gradually stretches the puff to the point where it becomes no longer identifiable.

One frequent application of the puff model is to follow the chemical evolution of an isolated pollution plume, as for example from a smokestack (Figure 3-6):
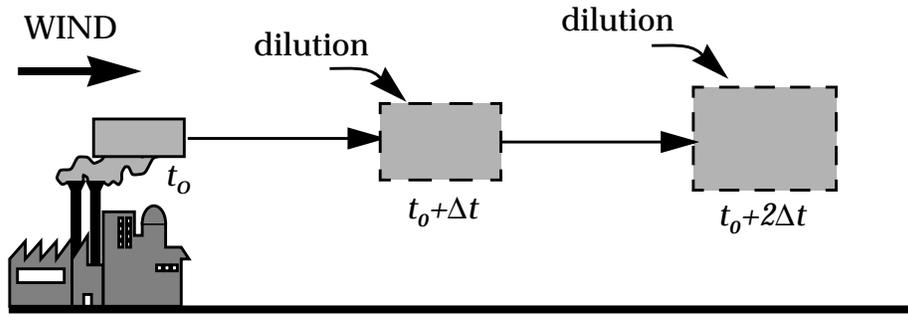
Figure 3-6 Puff model for a pollution plume

In the illustrated example, the puff is allowed to grow with time to simulate dilution with the surrounding air containing a background concentration $[X]_b$. The mass balance equation along the trajectory of the plume is written as:

$$\frac{d}{dt}[X] = E + P - L - D - k_{dil}([X] - [X]_b) \tag{3.18}$$

where k_{dil} (s^{-1}) is a *dilution rate constant* (also called *entrainment rate constant*). The puff model has considerable advantage over the box model in this case because the evolution in the composition of the traveling plume is described by one single equation *(3.18)*.

A variant of the puff model is the *column model,* which follows the chemical evolution of a well-mixed column of air extending vertically from the surface to some *mixing depth h* and traveling along the surface (Figure 3-7). Mass exchange with the air above *h* is assumed to be negligible or is represented by an entrainment rate constant as in *(3.18)*. We will see in chapter 4 how the mixing depth can be defined from meteorological observations.
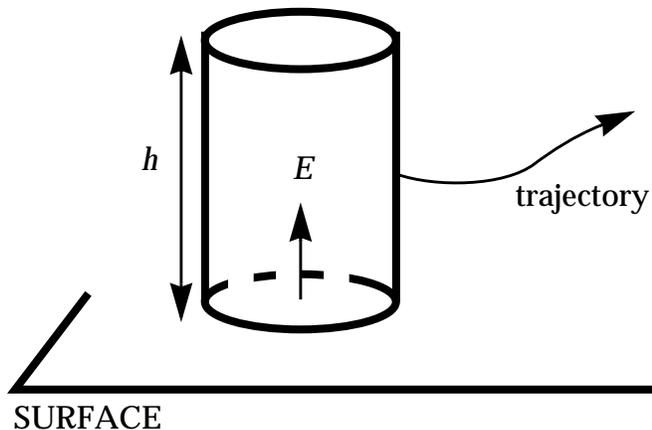

Figure 3-7 Column model

As the column travels along the surface it receives an emission flux E of species X (mass per unit area per unit time) which may vary with time and space. The mass balance equation is written:

$$\frac{d}{dt}[X] = \frac{E}{h} + P - L - D \qquad (3.19)$$

The column model can be made more complicated by partitioning the column vertically into well-mixed layers exchanging mass with each other as in a multi-box model. The mixing height h can be made to vary in space and time, with associated entrainment and detrainment of air at the top of the column.

Column models are frequently used to simulate air pollution in cities and in areas downwind. Consider as the simplest case (Figure 3-8) an urban area of mixing height h ventilated by a steady wind of speed U. The urban area extends horizontally over a length L in the direction x of the wind. A pollutant X is emitted at a constant and uniform rate of E in the urban area and zero outside. Assume no chemical production ($P = 0$) and a first-order loss $L = k[X]$.
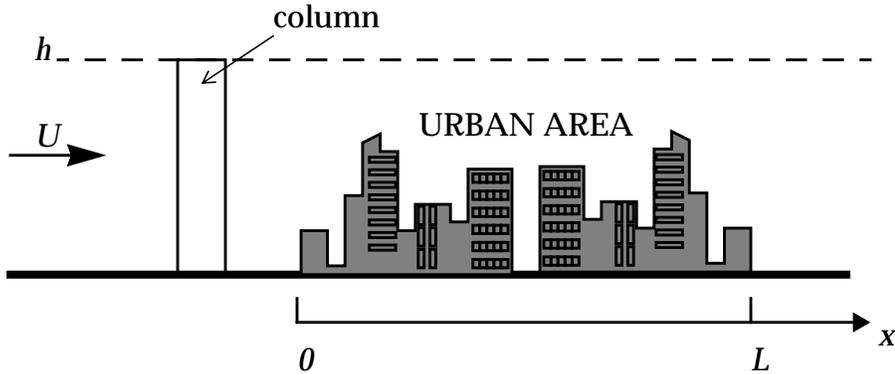

Figure 3-8 Simple column model for an urban airshed

The mass balance equation for X in the column is

$$\frac{d[X]}{dt} = \frac{E}{h} - k[X] \qquad (3.20)$$

which can be reexpressed as a function of x using the chain rule:

$$\frac{d[X]}{dt} = \frac{d[X]}{dx}\frac{dx}{dt} = U\frac{d[X]}{dx} = \frac{E}{h} - k[X] \qquad (3.21)$$

and solved with the same procedure as in section 3.1.2:

$$[X] = 0 \qquad x \le 0$$

$$[X] = \frac{E}{hkU}\left(1 - e^{-\frac{kx}{U}}\right) \qquad 0 \le x \le L \tag{3.22}$$

$$[X] = [X](L)e^{-\frac{k(x-L)}{U}} \qquad x \ge L$$

A plot of the solution is shown in Figure 3-9. The model captures gradients in pollutant levels across the city and also describes the exponential decay of pollutant levels downwind of the city. If good information on the wind field and the distribution of emissions is available, a column model can offer considerable advantage over the one-box model at little additional computational complexity.
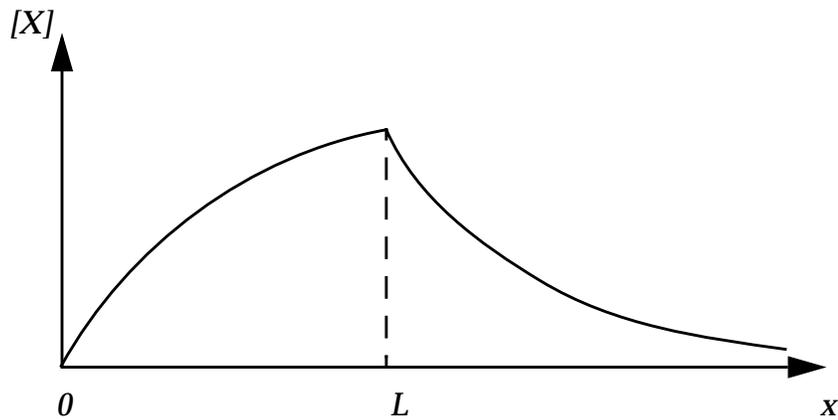

Figure 3-9 Evolution of pollutant concentrations within and downwind of an urban area in the column model