

Chapter 6

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Chemicals in the environment experience a variety of processes. For example, they may react with other chemicals, sorb onto surfaces, be transferred from air to water, or be transported by wind and water currents. Therefore, analyzing the fate of organic chemicals in the environment requires more than studying chemicals in the laboratory; it is a multidisciplinary task that incorporates knowledge of chemical properties as well as of the characteristics of the environment in which these chemicals are found. As we proceed through the book's chapters, our focus gradually moves from considerations of single processes acting on a chemical to more complex situations where several processes occur simultaneously. A common language is needed if we want to go beyond qualitative descriptions of the combined effects of processes like acid/base equilibrium, air–water exchange, turbulent mixing, and others. The common language is mathematics, and the translation of all these processes into that language is called mathematical modeling.

As we become familiar with concepts like the acidity constant for acid/base equilibrium (Chapter 4), Henry's law for air–water phase equilibrium (Chapter 9), or the ideal gas law, we easily forget that these simple mathematical expressions are *models* of phenomena that in reality are extremely complex. In environmental sciences, the expression “mathematical model” has over time acquired the meaning of something much more complicated than partitioning constants. We think of a mathematical tool that can describe a whole lake, the atmosphere, or even a combined atmosphere/ocean/land system, as in climate modeling. However, the transition from a partitioning constant to a climate model is gradual. Although the former is more fundamental than the latter, and thus often called a “law,” the same general idea is behind both models: when we describe an individual process or a whole natural system in terms of mathematical equations, we use a mathematical model by simplifying the infinite complexity of reality.

This chapter provides the reader with a basic toolkit for building mathematical models. We focus on models of whole systems that themselves are built by combining individual process models. The mathematical description (the modeling) of *individual* processes and more refined modeling tools are introduced in later chapters, where appropriate.

6.1 Systems and Models

Mathematical Models: Definition and Role

We define a *mathematical model* as a mathematical equation or a set of mathematical equations designed to imitate or reproduce one or several selected properties of a real system. Let us briefly focus on two aspects of this rather abstract definition. First, a model is intended to be a simplified picture (imitation) of a real system. Like in a caricature, simplification exaggerates certain properties, but, in doing so, renders clearer those aspects that are important for the model's specific purpose. Second, models are always designed to focus on a limited number of properties while all the others are overlooked. A model of everything is impossible; if one existed, it would be the real

world, not a model. Hence, one does not build a lake model without knowing what processes and data the model should reproduce; for instance, its wave patterns, water temperature, the concentration of benzene in the surface water, or its fish stock. In short, a model is never as complex and refined as the real system that it imitates, yet this shortcoming is advantageous as it allows us to identify properties of the real system that may not become apparent without focusing on a limited number of aspects.

What then are models good for in environmental sciences? Kleindorfer et al. (1993) distinguish between two fundamentally different goals of modeling, which they call inference and prediction. Inference means to bring some order to empirical data and to extract general rules from this order, that is, to develop models like the concept of the acidity constant to express the acid/base equilibrium. Once these rules have been extracted from real data by inference, the gained insight can be used to predict the outcome of a different experimental setup. Applied to environmental models, inference means to compare different models with real data to identify and quantify the major processes at work, whereas prediction means to extrapolate the development of a system into the future.

Environmental Systems and System Models

In order to explain what we mean with the term system, we have to highlight the difference between system and model. A system is a subunit of the world defined by the boundary that separates the system from the rest of the world (see Box 5.1 for the definitions of related terms). Examples of systems are the atmosphere, the ocean, a lake, a subsurface aquifer, and an algal cell. We can think of systems without defining a corresponding system model, but we cannot construct a model without having a system in mind, although this choice is often the consequence of an implicit, not a conscious act. A system can also include parts of the nonphysical world, like a country's politics or economy. In this respect, the term boundary in the preceding definition is not necessarily a physical boundary.

Let us now imagine a Roman architect who wants to build a new temple dedicated to Jupiter. The temple is his system. In order to better sell his idea to the Emperor, he has to build a model (*modulus*). When doing so, he must make several decisions: How detailed should the model be? Is it enough to represent the pillars by simple cylinders, or should the ornamentation be shown as well? Should colors be used? Should the interior of the temple also be shown and should it be furnished?

Of course, the goal here is not to build a Roman temple but a mathematical model of an environmental system such as a lake. But the decisions that need to be made to build the model are similar: How detailed should we make the description of the lake? Do we need water temperature to characterize the state of the lake? If yes, is a single mean temperature value good enough, or do we need to distinguish between surface and deep water (epilimnion and hypolimnion, see Fig. 5.7) or even among every cubic meter of the water body? Which chemical parameters do we need and at what spatial resolution, and what about biological parameters such as phytoplankton, zooplankton, and fish? Do we really need to impress the Emperor, or would something less and cheaper work?

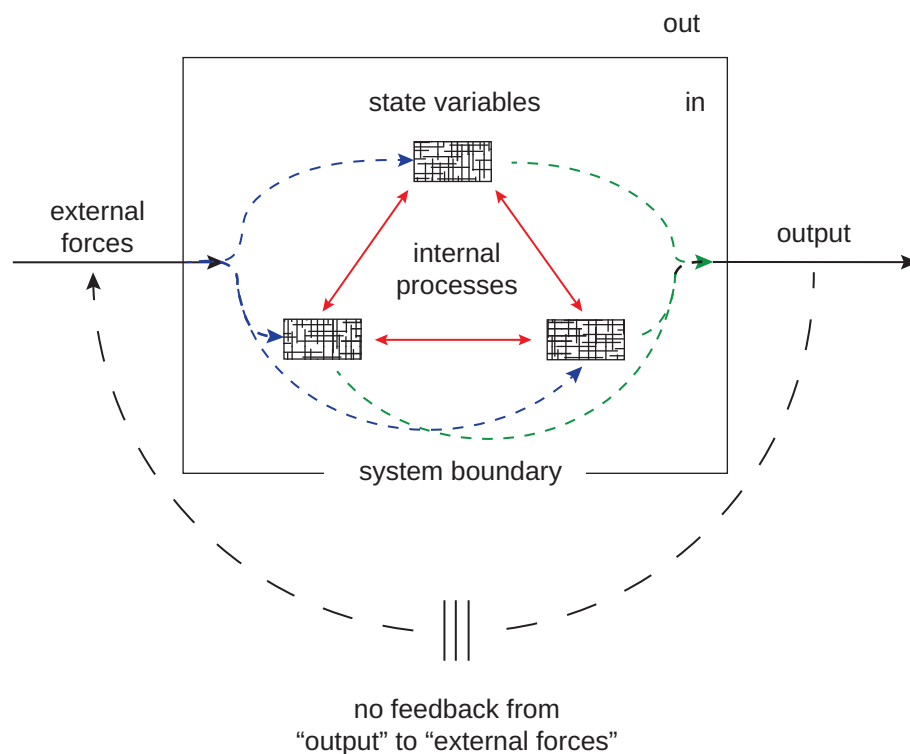
Box 6.1 Terminology for Dynamic Models of Environmental Systems

State variable	Quantity used in the model to describe the state of the system. A state variable usually depends on time t and (for some models) on one or more space coordinates x, y, z . <i>Example:</i> Concentration of chemical in a lake
Continuous state variable	State variable that depends on at least one space coordinate.
External force	Influence (constant or time-variable) that drives the state variables from outside. The term force is not restricted to its physical meaning. <i>Example:</i> Input of chemical into surface water of a lake
Output	Influence of state variables on the outside world, often a mass flux out of the system. <i>Example:</i> Flux of chemical from lake surface to the atmosphere
Internal process	Process occurring between state variables such as transport of a chemical or chemical transformation. <i>Example:</i> Vertical mixing of chemical between surface and deep water of a lake
Model parameter	Parameter used to describe modeled processes (external, output, and internal). <i>Example:</i> Lake volume

The answer to all these questions depends on the purpose of the model. Every lake model has its own set of properties that are used to characterize the system. Every property is represented by a mathematical variable (usually a function of time, often also of space) that we call a state variable (see Box 6.1 for terminology). The heart of the mathematical model is a set of equations that describes how these state variables are related to each other (the effect of internal processes) and how they are affected by external influences, which are influences from the world outside of the chosen system. Such external influences can be the intensity of solar radiation at the lake surface, the water discharge of the inlets into the lake and the concentrations of chemicals they carry, or the concentration of chemicals in the air. Since these influences drive the state variables, in the language of system analysis, they are called external forces (Fig. 6.1). Here, the term “force” is used more generally than a physical force, instead meaning influence. External indicates that the strength of the force is not reproduced by the model equations, like state variables are, but has to be fed into the model as a parameter such as lake volume, lake surface, or discharge rates. From a systemic point of view, the main difference between external forces and state variables is that the size and temporal change of the latter are *calculated by* the model while the size and temporal change of the former are known or assumed.

The system is *influenced* (driven) by the outside world, but may also *influence* the outside world. For example, as the result of the chemical degradation of an organic chemical in a lake, new chemicals can form that are then carried to the outside world by the outlet of the lake. These influences are called outputs. The external forces are not

Figure 6.1 A mathematical model is defined by a boundary (solid line) that separates a subunit of the world (IN) from the rest of the world (OUT). The state of the system is characterized by a set of variables (state variables). The dynamics of these variables is determined by internal processes and by external forces. The impacts of the system on the rest of the world are called outputs. An essential aspect of the representation of the world as IN and OUT is that the effect of the output on the external forces is neglected. The figure gives a general view of a system with three state variables. The lines with arrows show the interactions between the components; sometimes these interactions are negligible.



influenced by the output; external forces ignore the output. This is one of the essential simplifications of mathematical modeling. The infinite loop (everything influences everything else and is influenced by everything else) is transformed into a one-way street (driving forces influence the system state, but not *vice versa*) by cutting the feedback from system state to external forces (see Fig. 6.1).

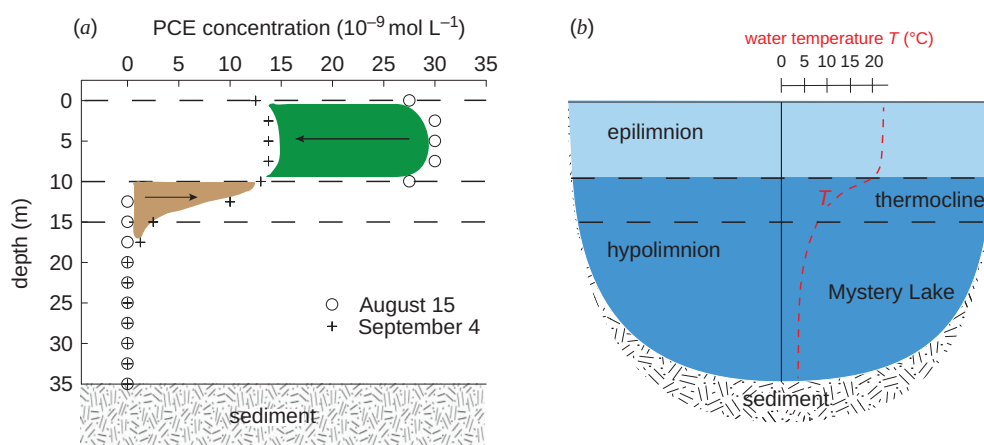
Model parameters are used to mathematically describe all processes that are part of the model (external, output, and internal). These parameters must be known or assumed and feed into the system. Therefore, they represent another kind of input for the model. Some model parameters can be taken from independent sources (e.g., values from chemical handbooks like a Henry's law constant or solubility) or from scientific publications (e.g., the relation between wind speed and air–water exchange). Other parameters have to be determined indirectly by comparing model calculations with data, a process called model calibration.

Incorporating all the newly defined elements, we can further refine the definition of a mathematical model: *A mathematical model of a system is defined by a specific choice of state variables, by the relations among the state variables (internal processes), by the action of the outside world on the state variables (external forces), and by the action of the model on the outside world (output). The feedback from the output to the external forces is neglected.*

A Case Study: Recipes for the Model Builder

In the following case study, we apply the defined terminology of Box 6.1 to build a concrete model. To do so, we will use a few basic recipes. The focus of the

Figure 6.2 (a) Concentrations of tetrachloroethene (PCE) as a function of depth measured in Mystery Lake, Cleanland on two consecutive sampling dates (August 15 and September 4). Maximum depth of the lake is 35 m. The water samples in the vertical are taken every 2.5 m (15 samples). The green area represents the PCE that disappeared from the epilimnion between the two sampling dates; the brown area represents the PCE that moved into the hypolimnion. (b) Schematic view of Mystery Lake and vertical temperature profile in August/September. The thermocline (boundary between epilimnion and hypolimnion, see Fig. 5.7), is between 10 and 15 m depth.



case is the contamination of a lake with tetrachloroethene (PCE), a chlorinated solvent and one of our companion compounds (see Chapter 3). We continually refer back to this case in following sections as more complexity is introduced into our modeling.

Case Study: Heidi and Paul, water chemists employed by the Public Water Authority of Cleanland, are responsible for the monitoring program conducted in Mystery Lake, located close to the capital of Cleanland. On August 15, they find dissolved tetrachloroethene (PCE) in water samples taken at several depths in the lake (Fig. 6.2). The PCE is only measured in the upper 10 m of the water column and is below the detection limit at lower depths. In water samples taken in the previous months, PCE concentrations had always been below the detection limit. Based on these new observations, Heidi and Paul decide to go to the lake again to measure another PCE concentration profile and to sample the major tributaries of Mystery Lake. The samples are taken on September 4, three weeks after the first sampling. They find that the PCE concentration in the top 10 m of the lake has dropped by about 50%, but they now detect some PCE in the lower water layers. PCE concentrations in the tributaries are below the detection limit. No indication of an accidental spill is found in drainage areas of places where PCE is used, such as dry cleaning businesses or car repair workshops.

The Water Authority is alarmed by the detection of PCE in the lake. Heidi and Paul are asked to predict the future development of PCE concentrations in the lake and how long it will take until the concentration has dropped below $1 \times 10^{-9} \text{ mol L}^{-1}$ everywhere in the lake. A colleague from the Engineering Section suggests to Heidi and Paul they should use one of the many lake models published in the scientific literature (e.g., Schnoor, 1996) in order to predict the further development of PCE concentrations in Mystery Lake. Heidi and Paul quickly realize that most of these models are fairly sophisticated and include all kinds of processes such as hydrodynamics of the lake driven by the wind, tributaries, and heat exchange at the water surface; the settling of suspended particles; air-water exchange at the water surface; growth and decomposition of various groups of phyto- and zooplankton; and more.

“Complexity has its price,” they say to each other. Heidi and Paul soon become aware that in order to run such a model for their lake, a large amount of information would

be needed (meteorological data, discharge rates of inlets and outlets as well as their chemical compositions, and much more), data that is not available for Mystery Lake. Fortunately, Heidi remembers a course on modeling she took a long time ago, in particular some simple rules for the design and use of models in environmental modeling. In her notes, she finds the following “Recipes for the Model Builder” (Imboden, 1986):

- (1) Build the model with a hypothesis in mind and begin with the simplest model that is compatible with the measured data set and suitable to test the hypothesis.
- (2) Do not introduce variables like concentrations of chemical species that are not measured.
- (3) Move from the simple to the more complex model and alter, if necessary, the hypothesis until the field data are reasonably explained.
- (4) Validate the model by applying it to a set of data that was not used to build and calibrate the model.

From her detailed notes during the lecture, Heidi finds that model calibration means to change the value of model parameters until optimal agreement between measured and calculated state variables is reached. Validation of a model means to run the model for another situation (e.g., further into the future) with the same parameter values that were determined by calibration and to compare the calculated state variables to an additional set of data. She remembers her teacher’s advice to proceed from the simple to the more complex model – but not *vice versa* – in order to check whether additional complexity would bring about an improved agreement between measurement and computation. Model complexity that goes beyond data complexity (Rule 3) could produce mathematical artifacts, that is, information that results from the mathematical structure of the model and not from the processes that are built into the model.

In order to formulate a first hypothesis for the future development of PCE in Mystery Lake, Heidi and Paul consult the scientific literature for information on the physico-chemical properties of PCE. They conclude that on a time-scale of weeks to months, PCE dissolved in water is fairly stable but would escape to the atmosphere at the water surface and would be flushed out of the lake at the outlet. Based on their knowledge about lake mixing (see Fig. 5.7), the scientists assume that although PCE is not homogeneously distributed in the vertical direction (Fig. 6.2), it is reasonable to assume homogeneity in the horizontal direction, so that the vertical profile measured at the center of the lake represents the vertical profile of PCE at any other location. Completing a back-of-the-envelope calculation, they conclude that the total amount of PCE in the lake has decreased by about 50% during the three weeks between the sampling dates. The scientists remember that in their survey of tributaries flowing into the lake, no PCE was found.

With this information, Heidi and Paul come up with the following first hypothesis about PCE in Mystery Lake.

First Hypothesis: Sometime prior to the sampling date in August, due to an accidental spill, an unknown amount of PCE has entered the surface layer of Mystery Lake. Before and after the accident, the input of PCE was not significant. The decrease of the total mass of PCE from the lake results from two processes: (1) loss through the outlet of the lake and (2) loss due to air–water exchange at the lake surface. The translation of the hypothesis into a model is shown in Figure 6.3, Model A.

Upon rethinking, Heidi and Paul realize that Model A may miss an important aspect of the dynamics of PCE in the lake, that is, the concentration difference between the surface water (epilimnion) and the deep water (hypolimnion), which is clearly shown in the data (Fig. 6.2). They guess that vertical mixing between the two water layers may be important for the development of the lake's PCE concentration since the removal processes identified in the first hypothesis, removal by flushing and air–water exchange, both probably depend on the surface concentration, not on the mean lake concentration. Thus, they formulate their second hypothesis.

Second Hypothesis: Two state variables are needed to describe PCE in the lake, the mean concentrations in the epilimnion and hypolimnion, respectively. In addition to

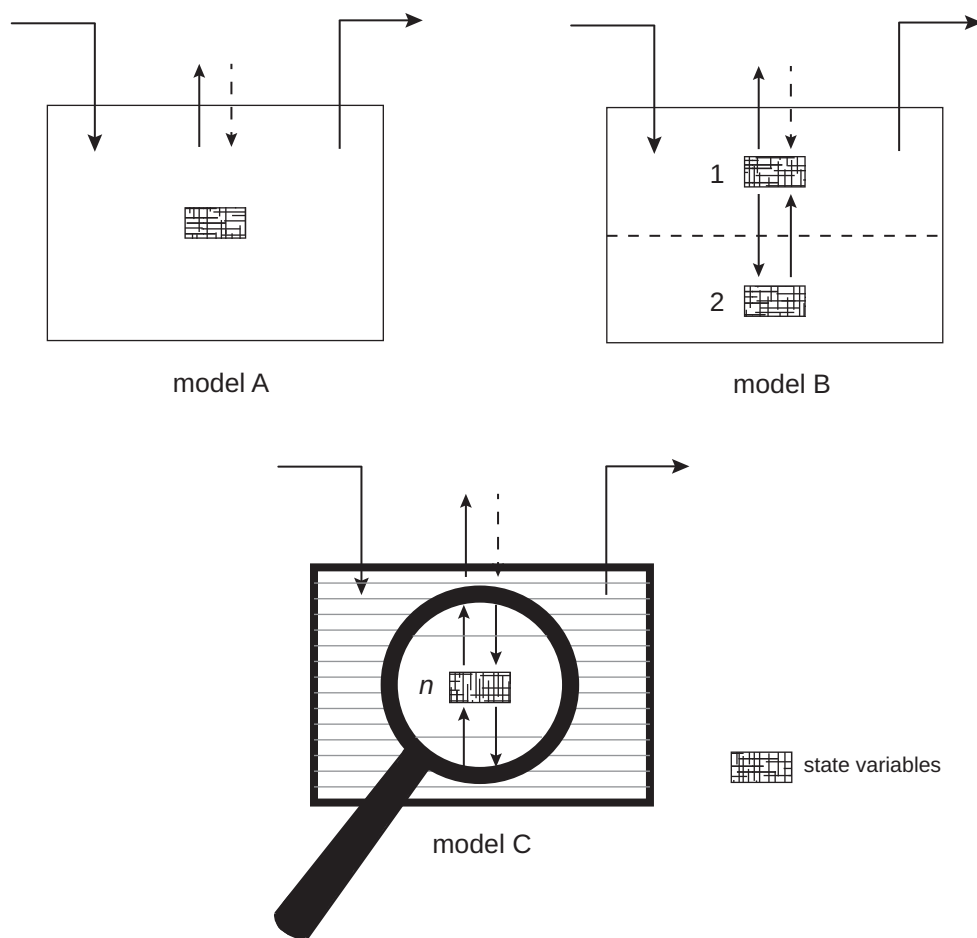


Figure 6.3 Three different models to describe tetrachloroethene (PCE) in Mystery Lake, Cleanland. Characteristic data of the models are given in Table 6.1. (a) Model A has one state variable (mean concentration of PCE in lake), (b) Model B has two state variables (mean concentrations of PCE in epilimnion and hypolimnion), and (c) Model C has 15 state variables (concentrations at 15 depths, each 2.5 m apart). The models have no external forces. Output processes are air–water exchange and flushing from the surface layer; internal processes are mixing between water layers.

Table 6.1 Characteristics of Different Models for PCE in Mystery Lake, Cleanland

Model Elements	Model A	Model B	Model C
System Boundary	whole lake	whole lake	whole lake
State variable(s)	1: mean concentration of PCE in lake	1: mean PCE conc. in epilimnion 2: mean PCE conc. in hypolimnion	1 to 15 mean PCE conc. at 15 depths 2.5 m apart
External force(s) ^a	<i>none</i>	<i>none</i>	<i>none</i>
Internal processes	<i>none</i>	vertical mixing between epilimnion and hypolimnion	vertical mixing between adjacent layers
Output	outlet flux to atmosphere	outlet flux to atmosphere	outlet flux to atmosphere

^a No external forces are considered since the accidental spill is assumed to have occurred before the first sampling date.

processes 1 and 2, another process has to be taken into account: (3) transport of PCE between the epilimnion and the hypolimnion by vertical mixing (Fig. 6.3, Model B).

Heidi is still not satisfied with the model. She points out to Paul that data from the second sampling date do not support the assumption of a completely mixed hypolimnion. She proposes to subdivide the water column into more than just two layers.

Third Hypothesis: The PCE in the lake is described as a quasi-continuous vertical concentration profile by modeling the PCE concentration at 15 depths, each 2.5 m apart. This results in 15 state variables that are coupled by vertical mixing. Further, only the uppermost layer is affected by flushing and air–water exchange (Fig. 6.3, Model C).

The three models are summarized in Table 6.1. The models have no external forces, since the water chemists assumed that after the accidental spill, occurring prior to the sampling on August 15, the input of PCE into the lake is zero.

Now, Heidi and Paul have everything they need in order to analyze the fate of PCE in Mystery Lake and to predict how PCE concentrations in the lake will further develop. They decide to follow the advice of Rule 3 of the recipes, beginning with the simplest model and then moving step by step to the more complex models. They lack just one small detail: the mathematical equations that describe the processes and temporal change of the state variables. “No problem,” Heidi says to Paul. “Everything we need to tackle Model A can be found in my lecture notes, go ahead.” She hands her notes over to Paul, “just start reading Section 6.2.”

6.2 Box Models: A Concept for a Simple World

In this section, we derive equations for describing the dynamics of the state variables of mathematical models. The basic premise of the derivation is a mass balance for

one or several compartments. By adding and subtracting all processes that affect the numerical value of the state variables in each compartment, we can determine the changes of the variables per unit time.

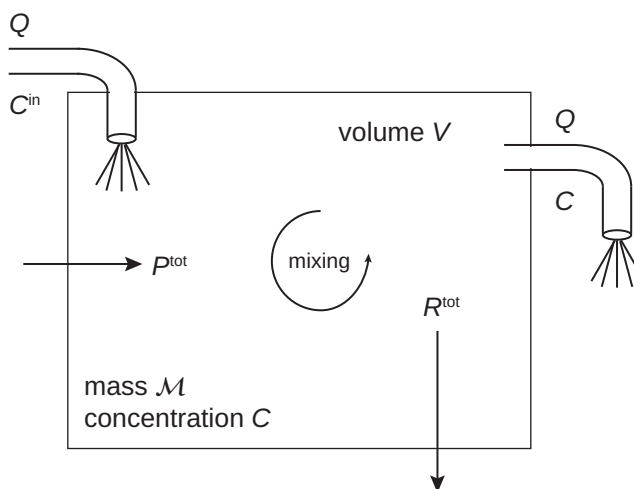
By the term compartments, we mean spatial subvolumes of the environment that are separated from their surroundings by a boundary (see Box 5.1). Examples are the troposphere, the water body of the Black Sea, the epilimnion of a lake (separated from the hypolimnion by the thermocline, see Fig. 5.7), or an algal cell. A compartment whose properties (e.g., concentrations, temperature, and density) are constant everywhere, is termed a completely mixed (homogeneous) box. The homogeneity of the box may be real or just assumed by averaging the property over the box volume. Boxes are the building blocks of many mathematical models. Every state variable is described by one single value per box. The simplest, and often most suitable, model is the one-box model. One-box models can have one or several state variables, such as the mean concentration of one or several chemicals.

The box-model concept can be extended to two or more boxes (two-box or n -box model), each box being described by one or several state variables. In addition to the external forces, multi-box models contain processes describing transport between the boxes that affect the state variables (exchange fluxes). In the terminology of Box 6.1, these are internal processes. Among the models introduced for PCE in Mystery Lake (Fig. 6.3), A is a one-box model, B is a two-box model, and C is a 15-box model. For the following mathematical derivations, the starting point is the simplest version of the box-model family, the linear one-box model with one state variable.

Linear One-Box Model with One State Variable

Let us consider a homogeneous (completely mixed) compartment (box) that is filled with a fluid (e.g., air or water). The box is connected to the outside world by an inlet and an outlet (Fig. 6.4). The flow rate, Q , into the box is equal to the flow rate out of the box; thus the total fluid mass and, provided that the fluid density is constant, the total

Figure 6.4 Schematic representation of a well-mixed box. A chemical is introduced into the system via the inlet and by production processes (total rate P^{tot} [MT^{-1}]) and removed via the outlet and by internal removal processes (R^{tot} [MT^{-1}]). Although P^{tot} and R^{tot} are *in situ* production and removal processes, the corresponding arrows are drawn across the system boundary to indicate that the chemical is added to or removed from the box. M [M] is the total mass of the compound in the volume V [L^3], C and C^{in} [ML^{-3}] are concentrations in the box and in the inlet, respectively, Q [L^3T^{-1}] is the flow rate through the box. The concentration in the outlet is equal to the concentration in the box, since the box is well mixed.



fluid volume, V , in the box remains constant. A chemical is added to the compartment as part of the inlet flow into the box (input concentration C^{in}). We assume this input is homogeneously mixed within the box, resulting in the mean box concentration C . The chemical is removed via the outlet flow. Since the box is homogeneously mixed, the output concentration and average box concentration are equal ($C^{\text{out}} = C$). We define only one state variable, either the total mass of the chemical in the box, \mathcal{M} , or its mean concentration, $C = \mathcal{M}/V$.

In addition to the fluid flow through the box, some *in situ* production and removal processes, P^j and R^k , may act on the compound while it is in the interior of the box. Their combined effects, P^{tot} and R^{tot} , are the sums of the single processes:

$$P^{\text{tot}} = \sum_j P^j; \quad R^{\text{tot}} = \sum_m R^m \quad [\text{MT}^{-1}] \quad (6-1)$$

The expression in the square brackets, $[\text{MT}^{-1}]$, gives the dimension of the equation as mass per time. For every dimension, we can choose specific units, for instance, kg for mass M and s for time T .

In order to arrive at an equation for the temporal change of the total mass of the compound in the box, $d\mathcal{M}/dt$, we take the sum of all processes that increase the mass in the box minus the sum of all the processes that decrease it (see Fig. 6.4):

$$\frac{d\mathcal{M}}{dt} = QC^{\text{in}} + P^{\text{tot}} - QC - R^{\text{tot}} \quad [\text{MT}^{-1}] \quad (6-2)$$

The first and third terms on the right-hand side of Eq. 6-2 describe the mass fluxes due to the flow of the fluid. Since the volume V is constant, we can rewrite the equation by dividing both sides by V and using $\mathcal{M}/V = C$, where C is the mean concentration in the box:

$$\frac{dC}{dt} = C^{\text{in}}k_w + \frac{P^{\text{tot}}}{V} - k_w C - \frac{R^{\text{tot}}}{V} \quad [\text{ML}^{-3}\text{T}^{-1}] \quad (6-3)$$

The flushing or dilution rate of the box, k_w , is then defined as:

$$k_w = \frac{Q}{V} \quad [\text{T}^{-1}] \quad (6-4)$$

That is, k_w gives the fraction per unit time of the fluid volume that enters and leaves the system. The inverse quantity, $\tau_w = 1/k_w$, is the mean residence time of the fluid in the box.

Equations 6-2 and 6-3 are two versions of the same one-box model; they differ in the choice of the state variable on the left side, \mathcal{M} for the former, C for the latter. On the right side of both equations are terms that we do not know how to relate to the state variable. Thus, we concentrate on Eq. 6-3 to analyze the meaning of these terms with the definitions that were introduced in Fig. 6.1 and Box 6.1. The first and second

terms are external forces. They are independent of the state variable C , can be constant or time-variable, and have to be fed into the model. The third and fourth terms are output processes (negative signs). The third term describes the loss from the system via the outflow; it is proportional to C . Mathematicians call such functions linear; in chemical kinetics, they are called first order. The fourth term describes the sum of removal processes that are not via the outflow from the box. They must somehow depend on the system variable C . For now, we assume that they are proportional to C , like the loss via the outlet:

$$R^{\text{tot}} = \sum_m R^m = \sum_m k^m C = k^{\text{tot}} C; \quad k^{\text{tot}} = \sum_m k^m \quad (6-5)$$

If in Eq. 6-3 we replace the first two terms by the total external force, J , given by:

$$J = C^{\text{in}} k_w + \frac{P^{\text{tot}}}{V} \quad [\text{ML}^{-3}\text{T}^{-1}] \quad (6-6)$$

and the fourth term using Eq. 6-5, we get a first-order linear inhomogeneous differential equation (FOLIDE):

$$\frac{dC}{dt} = J - (k_w + k^{\text{tot}})C = J - kC; \quad k = k_w + k^{\text{tot}} \quad (6-7)$$

The equation is first-order because it contains a first derivative of the variable C , but no higher ones; it is linear because of the term kC , and it is inhomogeneous because of the additional term J that describes the external forces. The first-order (or linear) rate constant k may be the sum of several first-order rate constants; in the specific example of Eq. 6-7, it is the sum of two such constants. Since the box has a constant volume V , \mathcal{M} and C are linearly related, and the same procedure can be easily applied to find a FOLIDE for Eq. 6-2.

The solution of Eq. 6-7 is given in Box 6.2. In the most general case, both J and k can be arbitrary functions of time. If J and k are constant and non-negative, we get:

$$C(t) = C^0 e^{-kt} + C^\infty (1 - e^{-kt}) = C^\infty + (C^0 - C^\infty) e^{-kt} \quad (6-8)$$

where C^0 is the initial value at $t = 0$ and $C^\infty = J/k$ is the steady-state value of C , that is, the value at which the concentration change becomes zero. The shape of $C(t)$ for different initial values and steady states is shown in Fig. 6.5.

Equation 6-8 tells us that the concentration decays from its initial value to its steady-state value at a rate given by e^{-kt} , where for the linear one-box model k is given by $k_w + k^{\text{tot}}$ (Eq. 6-7) and the steady-state concentration by:

$$C^\infty = \frac{J}{k} = \frac{k_w C^{\text{in}} + P^{\text{tot}}/V}{k_w + k^{\text{tot}}} \quad (6-9)$$

If the external force J is zero, C^∞ is zero and the solution Eq. 6-8 is reduced to the first term on the right-hand side (Box 6.2, case a).

Box 6.2 Solution to the First-Order Linear Inhomogeneous Differential Equation (FOLIDE)

$$\frac{dY}{dt} = J - kY \quad (1)$$

Y : State variable; J : inhomogeneous term; k : linear rate constant

Solutions:

a. Homogeneous case with constant coefficient. $J = 0$, $k = \text{constant}$

$$Y(t) = Y^0 e^{-kt}, Y^0: \text{value of variable } Y \text{ at } t = 0 \text{ (initial value)} \quad (2)$$

b. Inhomogeneous case with constant coefficients. $J, k = \text{constant}$

$$Y(t) = Y^0 e^{-kt} + Y^\infty (1 - e^{-kt}) = Y^\infty + (Y^0 - Y^\infty) e^{-kt} \quad (3)$$

For $k > 0$, Eq. (3) has the steady state

$$Y^\infty = \frac{J}{k} \quad (4)$$

c. Variable input $J(t)$, $k = \text{constant}$

$$Y(t) = Y^0 e^{-kt} + \int_0^t e^{-k(t-t')} J(t') dt' \quad (5)$$

d. Variable coefficients $J(t)$ and $k(t)$

$$Y(t) = Y^0 e^{-\phi(t)} + e^{-\phi(t)} \int_0^t e^{+\phi(t')} J(t') dt' \quad (6)$$

where

$$\phi(t) = \int_0^t k(t') dt' \quad (7)$$

Time-to-Steady State. Next, we address the question of how long it takes for C to reach its steady state. Since the time dependence of $C(t)$ is described by exponential functions of the form e^{-kt} , strictly speaking, steady state is only reached if $k > 0$ and time t is infinitely large. But since exponential functions quickly become very small with the growing negative exponent (e.g., $e^{-1} = 0.37$, $e^{-3} = 0.050$, $e^{-5} = 0.0067$), we define a critical adjustment time, $t_{5\%}$, at which the time-dependent terms of Eq. 6-8 have dropped to 5% of their original value. Using $e^{-kt_{5\%}} = 0.05$ and taking the natural logarithm on both sides, we get:

$$t_{5\%} = \frac{-\ln 0.05}{k} = \frac{3}{k} \quad (6-10)$$

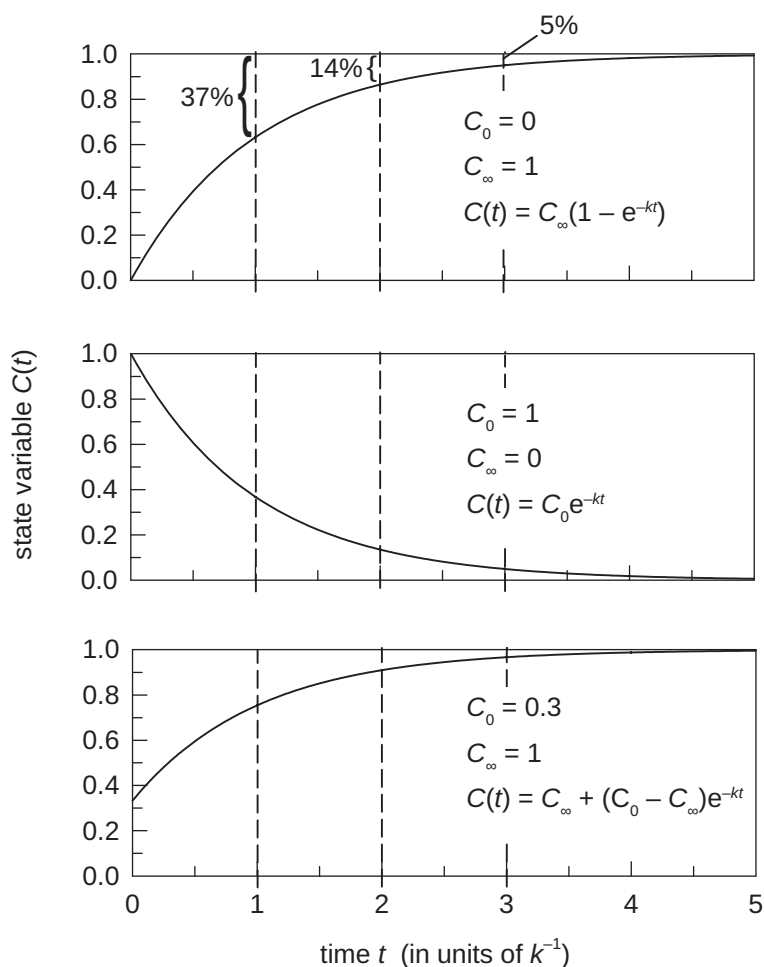


Figure 6.5 Solution to the first-order linear inhomogeneous differential equation (FOLIDE) (Eq. 6.7). C^0 = initial value at $t = 0$, $C^\infty = J/k$ is the steady-state value. (a) Growth curve for $C^0 = 0$; (b) Decay curve for $C^0 = 1$, $J = 0$; (c) general case for $C^0 = 0.3$. The time axis is in units of $1/k$. The remaining difference to steady state drops from 37% at $t = 1/k$ to 14% and 5% for each additional time interval $1/k$.

Instead of 5% of the original value, we could choose any other adjustment criterion, for instance, 10% or 1%. Our choice only influences the numerical value in the numerator of Eq. 6-10 but does not alter the fact that the adjustment time is inversely related to the rate constant, k . For the one-box model (Eq. 6-7):

$$t_{5\%} = \frac{3}{k_w + k^{\text{tot}}} \quad (6-11)$$

The denominator consists of the sum of the flushing rate and all reaction rate constants. We can assess the relevance of the different removal processes by looking at the relative size of the different k -values. One single, large k -value is sufficient to make the response time of the system short, even if the other k -values are small or zero. If k^{tot} (or just one single k^{m}) is much larger than k_w , time-to-steady state is primarily determined by *in situ* removal processes (or just by one of them) while removal through the outlet is negligible. Conversely, flushing is the dominant removal mechanism if $k_w \gg k^{\text{tot}}$. Finally, if all the rates k are of similar size, then all the removal processes are about equally important.

A similar analysis can be made for the size of C^∞ (Eq. 6-9). If the internal production processes P^{tot} are zero and the input occurs exclusively via the inlet, then, $J = k_w C^{\text{in}}$, and Eq. 6-9 becomes:

$$C^\infty = \frac{k_w}{k_w + k^{\text{tot}}} C^{\text{in}} \quad (6-12)$$

This expression for the steady-state concentration of the linear one-box model without internal production (Eq. 6-12) is extremely useful. By comparing C^∞ and C^{in} , we can find out whether internal removal processes exist or whether the chemical is stable (conservative) in the box. In the latter case, C^∞ and C^{in} are equal; in the former, C^∞ is smaller than C^{in} . In turn, $C^\infty > C^{\text{in}}$ points to an additional internal source ($P^{\text{tot}} > 0$ in Eq. 6-9).

We should bear in mind that the concept of steady state only makes sense if J and k are constant over time. Of course, Eq. 6-9 remains valid if J or k varies with time, but then C^∞ becomes a moving target for which the concept of “time-to-steady state” (Eq. 6-11) has no meaning.

With the introduced equations for a one-box model, we now have everything needed to tackle Model A for tetrachloroethene (PCE) concentrations in Mystery Lake (see Table 6.1 and Fig. 6.3). Heidi and Paul decide to use the PCE concentrations measured on August 15 as initial values and assume that after this date the PCE input to the lake is zero. Box 6.3 gives the outcome of their modeling attempt. According to their approach, it takes 100 days until the mean concentration of PCE in Mystery Lake, C , has dropped below $1 \times 10^{-9} \text{ mol L}^{-1}$. Since C is the only state variable, the model cannot tell us whether the mean concentration is indeed a good approximation or whether the real distribution of PCE is heterogeneous with areas where C remains clearly above the mean.

Since Heidi and Paul do not want to run the risk that such areas exist, they decide to move one rung up the ladder of model complexity and to make a second attempt with Model B (Table 6.1 and Fig. 6.3). Model B adds a little bit of heterogeneity by treating the lake as a two-box model. Heidi must go back to her lecture notes and study the chapter dealing with multi-box models.

From One-Box to Multi-Box Models

When constructing multi-box models for environmental systems, we must define more than one state variable. These variables can either be added chemical species to the box or added boxes for the one selected species. For organic chemicals, the first case is only relevant for very special situations for which no additional mathematical tools are needed. Although many different organic chemicals are usually simultaneously present in natural systems, in most cases, these chemicals do not interact. They can be mathematically treated as if the other species were not present, that is, like the one-species case.

Box 6.3 Tetrachloroethene (PCE) in Mystery Lake: One-Box Model (Model A)

Lake characteristics

Total Volume (V_{tot})	$2 \times 10^8 \text{ m}^3$
Volume top 10 m (V_E)	$0.9 \times 10^8 \text{ m}^3$
Surface (A)	$1 \times 10^7 \text{ m}^2$
Water through-flow (Q)	$10 \text{ m}^3 \text{ s}^{-1}$

In the course of a monitoring program conducted in Mystery Lake, on August 15 dissolved tetrachloroethene (PCE) was detected in water samples taken at different depths (Fig. 6.2). No PCE had been measured in the previous month. On September 4, the PCE-concentration in the top 10 m has dropped by about 50%, whereas below that depth, the concentration has increased. Use a one-box model (Fig. 6.3, Model A) to estimate how long it takes until the mean PCE concentration in the system has dropped below $1 \times 10^{-9} \text{ mol L}^{-1}$.

Mean concentration and total mass of PCE in total lake estimated from Figure 6.1

	mean lake $C_{\text{mean}}^{(*)}$	total mass \mathcal{M}
August 15	$13.5 \times 10^{-9} \text{ mol L}^{-1}$	2,700 mol
September 4	$8.0 \times 10^{-9} \text{ mol L}^{-1}$	1,600 mol

(*) Calculated as volume-weighted mean from concentrations in surface and deep layer, respectively.

Definition of model

System: Total lake volume, V_{tot}

State variable: average PCE concentration in total lake volume, C_{mean}

Processes to be considered: (1) removal via outlet; (2) removal by air/water exchange (R^{aw})

No input via inlets ($C^{\text{in}} = 0$), *no in situ production* ($P^{\text{tot}} = 0$).

Solution

Equation 6-3 is reduced to:

$$\frac{dC_{\text{mean}}}{dt} = -k_w C_{\text{mean}} - \frac{R^{\text{tot}}}{V_{\text{tot}}} \quad (1)$$

Assumption: Removal by air-water exchange is first-order (linear) with rate constant k^{aw} , see Eq. 6-5 and Chapter 19. Inserting into Eq. 1 yields:

$$\frac{dC_{\text{mean}}}{dt} = -k_w C_{\text{mean}} - k^{\text{aw}} C_{\text{mean}} \quad (2)$$

According to Box 6.2 (Eq. 2), the solution is an exponential function where $C_{\text{mean}}^0 = 13.5 \times 10^{-9} \text{ mol L}^{-1}$ is the initial mean concentration in the total lake volume:

$$C_{\text{mean}}(t) = C_{\text{mean}}^0 e^{-(k_w + k^{\text{aw}})t} \quad (3)$$

or in logarithmic form:

$$\ln C_{\text{mean}}(t) = \ln C_{\text{mean}}^0 - (k_w + k^{\text{aw}})t \quad (4)$$

If we choose $t = 0$ on August 15 and evaluate Eq. 4 for $t = 20$ d (September 4), we can solve Eq. 4 for the sum of the two first-order rate constants, $k_w + k^{aw}$:

$$k_w + k^{aw} = \frac{1}{t} [\ln C_{\text{mean}}^0 - \ln C_{\text{mean}}(t)] = \frac{1}{20\text{d}} [\ln 13.5 - \ln 8] = 0.026\text{d}^{-1} \quad (5)$$

The flushing rate of the total lake (Eq. 6-4) is $k_w = 10 \text{ m}^3 \text{ s}^{-1} / 2 \times 10^8 \text{ m}^3 = 5 \times 10^{-8} \text{ s}^{-1} = 0.0043 \text{ d}^{-1}$, thus the major fraction of the removal appears to be due to air-water exchange; $k^{aw} = 0.022 \text{ d}^{-1}$ (84% of total removal).

The time t_1 until $C_{\text{mean}}(t)$ has dropped below $1 \times 10^{-9} \text{ mol L}^{-1}$ is calculated from Eq. 3 by setting $C_{\text{mean}}(t) = 1 \times 10^{-9} \text{ mol L}^{-1}$, $k_w + k^{aw} = 0.026 \text{ d}^{-1}$ and by solving for $t = t_1$:

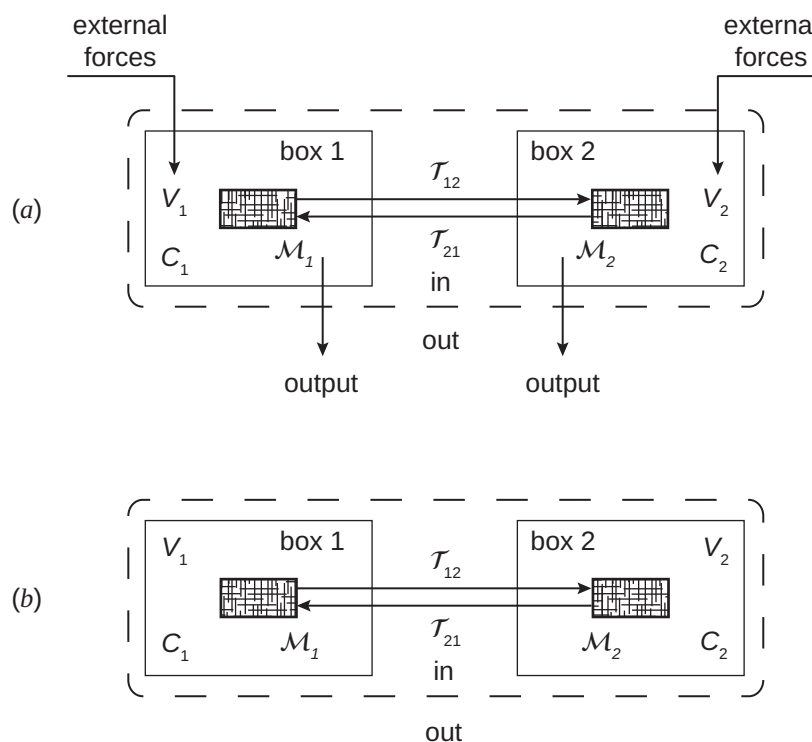
$$t_1 = \frac{1}{0.026\text{d}^{-1}} [\ln 13.5 - \ln 1] = 100 \text{ d} \quad (6)$$

If they do interact, they often do so fast compared to other processes like flushing or air-water exchange, so we can consider the reaction partners to be in equilibrium. For instance, this is usually the case for a process like sorption, so it can be assumed that the concentrations of all forms of the chemical (dissolved, sorbed on solids, and sorbed on colloids) are proportional to each other. Therefore, we can simply model one species and then calculate the concentrations of the other species by making use of the corresponding proportionality constants. Furthermore, organic chemicals in the environment can be transformed, for instance, by biological degradation (Chapters 26). Since such reactions commonly do not run backwards in a given environment, we can again model the original chemical by simply introducing the corresponding reaction rates of degradation without explicitly treating the products of the degradation process. Examples are given in Chapter 28.

Therefore, we restrict the following modeling discussion to the extension of the one-box model to two or more boxes. Boxes could be the gas and water volume in a sealed glass flask, the epilimnion and hypolimnion of a lake, different basins of a lake, or the troposphere and the stratosphere. Each box can be modeled by a mass balance equation like Eq. 6-7. The boxes are coupled by mass fluxes (\mathcal{T}_{12} and \mathcal{T}_{21} , if there are two boxes, see Fig. 6.6a). Examples of mass fluxes are the transport of a chemical from the water into the air and *vice versa*; the flux of dissolved chemicals by turbulent mixing from the surface layer into the deeper parts of a lake; the downward transport of chemicals sorbed to particles sinking to the deep-sea; and the transport of a dissolved chemical in the water of a river flowing from one lake to another lake further downstream. Without such fluxes, the differential equations would not be coupled and could be solved separately. The multi-box model would then be reduced to a couple of one-box models.

Most fluxes between boxes are two-way fluxes; therefore, they are also called exchange fluxes. The equilibrium between two phases (e.g., air and water) is the result of exchange fluxes. Whether we add a chemical to the water, the air, or both, if one waits long enough, the concentrations attained in the two phases will reach a constant

Figure 6.6 (a) System consisting of two boxes (two-box model) described by one state variable in each box (total mass, \mathcal{M}_1 and \mathcal{M}_2 , or mean concentration C_1 and C_2). V_1 and V_2 are the volumes of the boxes. In addition to the usual processes of the one-box model (external forces, outputs), mass fluxes τ_{12} and τ_{21} exist between the boxes. (b) Same as (a), but all processes are zero except the mass fluxes between the boxes (pure exchange model). Since there are no fluxes between the system (IN) and its environment (OUT), total mass, $\mathcal{M}_{\text{tot}} = \mathcal{M}_1 + \mathcal{M}_2$, is constant with time (Eq. 6.13), but the sum of the concentrations, C_1 and C_2 , is not constant, unless the box volumes are equal.



ratio that is independent of the original concentration distribution (see Chapter 9). In contrast, if the flux occurs only in one direction (e.g., $\tau_{12} > 0$, $\tau_{21} = 0$), one speaks of a directed flux. The examples of particles sinking and a river flowing between two lakes are directed fluxes. As we will see, directed fluxes are fundamentally different from exchange fluxes; they introduce an asymmetry into the model (Box 1 influences Box 2 but not *vice versa*), which is also reflected in the mathematical structure of the model equations.

Exchange Fluxes and Equilibrium. In order to demonstrate how the one-box model is modified due to the interactions with another box, we utilize the case of a chemical that moves between two boxes. First, we disregard all other processes (external forces, output) and just look at the effect of the exchange fluxes between the boxes (Fig. 6.6b). For reasons soon becoming clear, we use the total mass of the chemical in Box 1 and Box 2, \mathcal{M}_1 and \mathcal{M}_2 , as the state variables. The mass transfer fluxes are described by τ_{12} , the transfer of chemical from Box 1 to Box 2, and τ_{21} , the transfer of chemical from Box 2 to Box 1. The mass balance equations for the two boxes are:

$$\frac{d\mathcal{M}_1}{dt} = -\tau_{12} + \tau_{21}; \quad \frac{d\mathcal{M}_2}{dt} = \tau_{12} - \tau_{21} \quad [\text{MT}^{-1}] \quad (6.13a)$$

$$\frac{d\mathcal{M}_1}{dt} + \frac{d\mathcal{M}_2}{dt} = 0 \quad (6.13b)$$

where the total mass of the chemical in the two boxes, $\mathcal{M}_{\text{tot}} = \mathcal{M}_1 + \mathcal{M}_2$, is constant with time. This reflects the law of mass conservation in a two-box system that has neither inputs nor losses but only fluxes between the boxes. To relate the exchange

fluxes to the concentrations in the boxes, we assume that the fluxes are proportional to the concentration in the box from which the flux originates (linear exchange flux):

$$\mathcal{T}_{12} = \varphi_1 C_1; \quad \mathcal{T}_{21} = \varphi_2 C_2 \quad [\text{MT}^{-1}] \quad (6-14)$$

The coefficients φ_1 and φ_2 relate a concentration (dimension $[\text{ML}^{-3}]$) to a mass flux $[\text{MT}^{-1}]$ and thus have the dimension of a volume flux $[\text{L}^3\text{T}^{-1}]$. Their meaning are discussed in the following section.

If the difference between the fluxes, \mathcal{T}_{12} and \mathcal{T}_{21} , called the net flux, $\mathcal{T}_{12,\text{net}} = \mathcal{T}_{12} - \mathcal{T}_{21}$, is zero, the masses in the boxes become constant, meaning they reach a steady state. Eq. 6-14 then becomes:

$$\left(\frac{C_1}{C_2} \right)_{\text{exchange equilibrium}} = \frac{\varphi_2}{\varphi_1} \quad (6-15)$$

Equation 6-15 is called the exchange equilibrium. In Chapter 4 we have used the same mathematical concept to describe partitioning between two or more phases of a chemical, for instance, between the concentration in air and in water, or in an organic solvent and water.

Exchange Fluxes by Fluid Motion. To illustrate the meaning of the coefficient φ , we consider the special case where the exchange process is caused by the movement of a fluid (air or water) in which the chemical is embedded. As an example, consider boxes that represent the epilimnion and hypolimnion of a lake (recall Mystery Lake, Fig. 6.2). The exchange fluxes between the water layers is by turbulent motion of the water that results in the random exchange of water parcels between the upper and lower layers of the lake. Since the volumes of the epilimnion and hypolimnion are assumed to remain constant, the volumes of the downward flowing parcels per unit time must be equal to the volumes of the upward flowing parcels. Each volume carries with it the concentration of the layer from which it originates. According to the concept of completely mixed boxes, once the parcel has arrived in the other box, it is instantaneously mixed into the surrounding water. The φ 's represent the exchanged water volumes per unit time, Q^{ex} , hence the dimension $[\text{L}^3\text{T}^{-1}]$. By replacing the φ 's by Q^{ex} , we get from Eq. 6-14:

$$\mathcal{T}_{12} = Q^{\text{ex}} C_1; \quad \mathcal{T}_{21} = Q^{\text{ex}} C_2; \quad \mathcal{T}_{12}^{\text{net}} \equiv \mathcal{T}_{12} - \mathcal{T}_{21} = Q^{\text{ex}}(C_1 - C_2) \quad [\text{MT}^{-1}] \quad (6-16)$$

In other words, if the exchange fluxes are by fluid motion, φ_1 and φ_2 are equal, and the exchange equilibrium (Eq. 6-15) is given by $C_1 = C_2$.

Other Exchange Processes. Equation 6-16 does not always apply. If the exchange fluxes occur between different phases, for instance, between a gaseous and a liquid phase, the exchange mechanism cannot be by the exchange of fluid parcels. In fact, we have not specified the physico-chemical mechanism that drives the fluxes between the boxes, except for the specific case previously discussed. The only assumption we have made is the linear relationship between concentration and mass flux (the first-order

flux assumption, Eq. 6-14). In Chapters 17 to 20 of the book, different mass transfer processes are discussed such as air–water exchange and sorption between water and sediment beds or air and soils. For all of them, the first-order transport assumption (Eq. 6-14) is valid, at least as a first approximation, but the ϕ 's are not necessarily identical and thus the concentrations C_1 and C_2 are not equal at equilibrium. For instance, for air–water exchange, the concentration ratio at equilibrium, is the nondimensional Henry's Law constant (Chapter 9).

Dynamic Solution of Linear Exchange Model. We now want to derive the dynamic equations of the linear exchange model and discuss their solution. By inserting the first-order transport equations (Eq. 6-14) into Eq. 6-13, we get two coupled differential equations. In order to arrive at expressions in which the state variables on both sides are the same, we replace C by \mathcal{M}/V in both equations:

$$\begin{aligned}\frac{d\mathcal{M}_1}{dt} &= -k_{11}^{\text{ex}}\mathcal{M}_1 + k_{22}^{\text{ex}}\mathcal{M}_2 \\ \frac{d\mathcal{M}_2}{dt} &= k_{11}^{\text{ex}}\mathcal{M}_1 - k_{22}^{\text{ex}}\mathcal{M}_2\end{aligned}\tag{6-17}$$

The exchange rates, $k_{11}^{\text{ex}} = \phi_1/V_1$; $k_{22}^{\text{ex}} = \phi_2/V_2$, have the dimension $[T^{-1}]$. Equation 6-17 is a system of two coupled linear homogeneous differential equations. As for Eq. 6-13, the right-hand sides are identical except for the signs, thus the sum of the two variables, $\mathcal{M}_1 + \mathcal{M}_2$, is constant with time (mass conservation).

The general solution of the homogeneous system with mass conservation (Eq. 6-17) is given in Box 6.4. By substituting the general variable Y , the masses in the two boxes as a function of time can be calculated. At this point, we highlight two properties of the solution. First, according to Eq. 6 of Box 6.4, the exchange equilibrium between the boxes is characterized by:

$$\left(\frac{\mathcal{M}_1}{\mathcal{M}_2}\right)_{\text{exchange equilibrium}} = \frac{k_{22}^{\text{ex}}}{k_{11}^{\text{ex}}} = \frac{\phi_2 V_1}{\phi_1 V_2}\tag{6-18}$$

By dividing both sides by the volume ratio (V_1/V_2), we get the expression for the corresponding concentration ratio at equilibrium that had been derived before (Eq. 6-15).

Second, we note from Eq. 7 of Box 6.4 that the time to reach exchange equilibrium is characterized by the inverse of the sum of the two rate constants:

$$t_{5\%} = \frac{3}{k_{11}^{\text{ex}} + k_{22}^{\text{ex}}}\tag{6-19}$$

As is characteristic for linear differential equations, their solutions are built from exponential functions that from a mathematical point of view need an infinite amount of time to reach steady state. So again we must choose some fractional approach to equilibration (e.g., 5%) as a practical metric of this time.

Box 6.4 Solution of Two Coupled First-Order Linear Homogeneous Differential Equations with a Conservation Law (see Imboden and Pfenninger, 2013, Example 5.4)

We consider two first-order linear homogeneous differential equations for the state variables Y_1 and Y_2 of the form:

$$\begin{aligned}\frac{dY_1}{dt} &= -k_{11}Y_1 + k_{22}Y_2 \\ \frac{dY_2}{dt} &= k_{11}Y_1 - k_{22}Y_2\end{aligned}\quad (1)$$

The sum of the two equations is zero, thus:

$$\frac{dY_1}{dt} + \frac{dY_2}{dt} = \frac{d(Y_1 + Y_2)}{dt} = \frac{dY_{\text{tot}}}{dt} = 0 \Rightarrow Y_{\text{tot}} = Y_1 + Y_2 = Y_1^0 + Y_2^0 \quad (2)$$

By replacing Y_2 by $Y_{\text{tot}} - Y_1$ in the first Eq. 1, we get a differential equation for Y_1 alone:

$$\frac{dY_1}{dt} = k_{22}Y_{\text{tot}} - (k_{11} + k_{22})Y_1 \quad (3)$$

with the solution (Box 6.2, Eq. 3):

$$Y_1(t) = Y_1^\infty + (Y_1^0 - Y_1^\infty)e^{-(k_{11}+k_{22})t} \quad (4)$$

and the steady states:

$$Y_1^\infty = \frac{k_{22}}{k_{11} + k_{22}}Y_{\text{tot}}^0; \quad Y_2^\infty = \frac{k_{11}}{k_{11} + k_{22}}Y_{\text{tot}}^0 \quad (5)$$

Note that:

$$\frac{Y_1^\infty}{Y_2^\infty} \equiv \left(\frac{Y_1}{Y_2} \right)_{\text{exchange equilibrium}} = \frac{k_{22}}{k_{11}} \quad (6)$$

According to Eq. 6-19, time-to-steady state is characterized by:

$$t_{5\%} = \frac{3}{k_{11} + k_{22}} \quad (7)$$

The Complete Linear Two-Box Model. We now derive the dynamic equations of the complete linear two-box model, that is, the model that includes external forces and outputs as well as internal fluxes. For each box, we write down the differential equation for concentration of the linear one-box model (Eq. 6-7) and then add the linear transfer fluxes (Eq. 6-14) divided by the corresponding box volumes. The results are a coupled system of two linear inhomogeneous differential equations:

$$\begin{aligned}\frac{dC_1}{dt} &= J_1 - (k_{w1} + k_1^{\text{tot}} + k_{11}^{\text{ex}})C_1 + k_{12}^{\text{ex}}C_2 \\ \frac{dC_2}{dt} &= J_2 + k_{21}^{\text{ex}}C_1 - (k_{w2} + k_2^{\text{tot}} + k_{22}^{\text{ex}})C_2\end{aligned}\quad (6-20)$$

where the rate constants of exchange are:

$$k_{11}^{\text{ex}} = \varphi_1/V_1; \quad k_{12}^{\text{ex}} = \varphi_2/V_1; \quad k_{21}^{\text{ex}} = \varphi_1/V_2; \quad k_{22}^{\text{ex}} = \varphi_2/V_2 \quad (6-21)$$

The terms of the first equation of Eq. 6-20 represent external input, loss through the outlet, loss by internal processes, loss by transfer to Box 1, and gain by transfer from Box 2. For the second equation, the terms mean external input, gain by transfer from Box 1, loss through the outlet, loss by internal processes, and loss by transfer to Box 2.

In contrast to Eq. 6-17, all linear exchange rates (Eq. 6-21) are different. When writing the mass balance equations for concentrations instead for masses, the fluxes φ must be divided by the volume of the receiving box. If the fluxes are due to fluid motion (Eq. 6-16), then Eq. 6-21 is reduced to:

$$k_{11}^{\text{ex}} = k_{12}^{\text{ex}} = Q^{\text{ex}}/V_1; \quad k_{21}^{\text{ex}} = k_{22}^{\text{ex}} = Q^{\text{ex}}/V_2 \quad \Rightarrow \quad k_{22}^{\text{ex}} = \frac{V_1}{V_2} k_{11}^{\text{ex}} \quad (6-22)$$

The solution of the system of two linear, inhomogeneous differential equations is given in Box 6.5, Eq. 2. Again, it is composed of exponential functions, this time with rate constants, q_1 and q_2 , that are called the eigenvalues of the linear system. The time-to-steady state is determined by the smaller of the two eigenvalues (Box 6.5, Eq. 6).

The temporal evolution of the state variables depends on their initial values (Box 6.5, Eqs. 2 and 5), but the steady state does not (Box 6.5, Eq. 4). The steady state of Eq. 6-20 is:

$$C_1^\infty = \frac{(k_{w2} + k_2^{\text{tot}} + k_{22}^{\text{ex}})J_1 + k_{12}^{\text{ex}}J_2}{(k_{w1} + k_1^{\text{tot}} + k_{11}^{\text{ex}})(k_{w2} + k_2^{\text{tot}} + k_{22}^{\text{ex}}) - k_{12}^{\text{ex}}k_{21}^{\text{ex}}} \quad (6-23)$$

$$C_2^\infty = \frac{k_{21}^{\text{ex}}J_1 + (k_{w1} + k_1^{\text{tot}} + k_{11}^{\text{ex}})J_2}{(k_{w1} + k_1^{\text{tot}} + k_{11}^{\text{ex}})(k_{w2} + k_2^{\text{tot}} + k_{22}^{\text{ex}}) - k_{12}^{\text{ex}}k_{21}^{\text{ex}}}$$

If the rate constants are such that the denominators in the preceding equations are zero, Eq. 6-23 is not valid. This is the case if the equations have the special form of Eq. 6-17, that is, if the sum of the two state variables is constant with time (mass conversation).

With these mathematical tools at hand, Heidi and Paul from the Public Water Authority of Cleanland have everything they need to develop a two-box model for PCE in Mystery Lake (Fig. 6.3, Model B). The outcome of their modeling exercise is given in Box 6.6.

Box 6.5 Solution of Two Coupled First-Order Linear Inhomogeneous Differential Equations (Coupled FOLIDEs) (see Imboden and Pfenninger, 2013, Appendix C and D)

Note: The following derivations are not valid if the rate constants of Eq. 1 have the special property $k_{11} = k_{21}$ and $k_{12} = k_{22}$ (the linear exchange model). Then the solution given in Box 6.4 applies.

Any system of two first-order linear differential equations for the state variables Y_1 and Y_2 can be transformed to arrive at the following form:

$$\begin{aligned}\frac{dY_1}{dt} &= J_1 - k_{11}Y_1 + k_{12}Y_2 \\ \frac{dY_2}{dt} &= J_2 + k_{21}Y_1 - k_{22}Y_2\end{aligned}\quad (1)$$

where J_1 and J_2 are the inhomogeneous terms, and k_{mn} ($m, n = 1$ or 2) are the linear (or first-order) rate constants. If the k_{mn} -matrix is not singular (i.e., $(k_{11}k_{22} - k_{12}k_{21}) \neq 0$), then the solutions are composed of the steady-state values, Y_1^∞ and Y_2^∞ , and of two exponential functions with rates q_1 and q_2 :

$$\begin{aligned}Y_1(t) &= Y_1^\infty + A_{11}e^{-q_1t} + A_{12}e^{-q_2t} \\ Y_2(t) &= Y_2^\infty + A_{21}e^{-q_1t} + A_{22}e^{-q_2t}\end{aligned}\quad (2)$$

The rate constants, q_1 and q_2 , are the *negative eigenvalues* of the linear system. If Eq. 1 describes a mass balance model, the values of all coefficients k_{nm} and q_n are positive or zero.

$$\begin{aligned}q_1 &= \frac{1}{2}[k_{11} + k_{22} - r]; \quad q_2 = \frac{1}{2}[k_{11} + k_{22} + r] \\ r &= [(k_{11} - k_{22})^2 + 4k_{12}k_{21}]^{1/2}\end{aligned}\quad (3)$$

The steady-state values of the system are:

$$Y_1^\infty = \frac{k_{22}J_1 + k_{12}J_2}{k_{11}k_{22} - k_{12}k_{21}}; \quad Y_2^\infty = \frac{k_{21}J_1 + k_{11}J_2}{k_{11}k_{22} - k_{12}k_{21}}\quad (4)$$

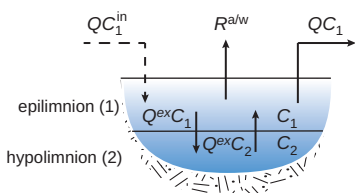
The coefficients A_{mn} introduced in Eq. 2 are:

$$\begin{aligned}A_{11} &= 1/r[-(k_{11} - q_2)(Y_1^0 - Y_1^\infty) + k_{12}(Y_2^0 - Y_2^\infty)] \\ A_{21} &= 1/r[(k_{11} - q_1)(Y_1^0 - Y_1^\infty) - k_{12}(Y_2^0 - Y_2^\infty)] \\ A_{12} &= 1/r[k_{21}(Y_1^0 - Y_1^\infty) - (k_{22} - q_2)(Y_2^0 - Y_2^\infty)] \\ A_{22} &= 1/r[-k_{21}(Y_1^0 - Y_1^\infty) + (k_{22} - q_1)(Y_2^0 - Y_2^\infty)]\end{aligned}\quad (5)$$

where Y_1^0 and Y_2^0 are the initial values at $t = 0$. Since q_1 is the smaller of the two eigenvalues, time-to-steady state is (see Eq. 6-11)

$$t_{5\%} = \frac{3}{q_1} = \frac{6}{k_{11} + k_{22} - r}\quad (6)$$

Box 6.6 Tetrachloroethene (PCE) in Mystery Lake: Two-Box Model (Model B)



Two-Box Model of Mystery Lake

Lake characteristics

Total Volume (V_{tot})	$2 \times 10^8 \text{ m}^3$
Volume top 10m (V_{10})	$0.9 \times 10^8 \text{ m}^3$
Surface (A)	$1 \times 10^7 \text{ m}^2$
Water discharge (Q)	$0 \text{ m}^3 \text{ s}^{-1}$

Problem

As an improvement of Model A (Box 6.2) a two-box model for PCE in Mystery Lake can be developed to describe the dynamics of PCE in the lake. From Fig. 6.2, the following mean can be estimated from the concentration in the two boxes, the epilimnion and the hypolimnion:

Mean PCE concentration and total mass in the epilimnion and hypolimnion of lake

	Epilimnion		Hypolimnion	
	mean conc. C_{Epi}	total mass \mathcal{M}_{Epi}	mean conc. C_{Hypo}	total mass $\mathcal{M}_{\text{Hypo}}$
August 15	$30 \times 10^{-9} \text{ mol L}^{-1}$	2,700 mol	0	0
September 4	$13 \times 10^{-9} \text{ mol L}^{-1}$	1,170 mol	$4 \times 10^{-9} \text{ mol L}^{-1}$	440 mol

Solution

In order to apply Eq. 6-20 and the solution of the system of differential equations given in Box 6.5, the following definitions are used:

- Box 1 = Epilimnion, $V_1 = V_{10}$; Box 2 = Hypolimnion, $V_2 = V_{\text{tot}} - V_{10}$
- Processes to be considered (see Eq. 6-20 for notation):
 - Box 1: (1) removal via outlet ($k_{w1} = Q/V_{10} = 1.1 \times 10^{-7} \text{ s}^{-1} = 0.0096 \text{ d}^{-1}$);
 - (2) removal by air–water exchange ($k_1^{\text{tot}} = k_1^{\text{aw}}$)
 - (3) exchange with Box 2 by mixing ($k_{11}^{\text{ex}}, k_{12}^{\text{ex}}$)
 - Box 2: (1) exchange with Box 1 by mixing ($k_{21}^{\text{ex}}, k_{22}^{\text{ex}}$)
- No inputs: $J_1, J_2 = 0$

Putting the processes into the mass balance equations for C_1 and C_2 yields:

$$\begin{aligned} \frac{dC_1}{dt} &= -(k_{w1} + k_1^{\text{aw}} + k_{11}^{\text{ex}})C_1 + k_{12}^{\text{ex}}C_2 \\ \frac{dC_2}{dt} &= k_{11}^{\text{ex}}\frac{V_1}{V_2}(C_1 - C_2) \end{aligned} \quad (1)$$

where we have made use of Eq. 6-22 in order to express all exchange rates by k_{11}^{ex} .

Since k_{w1} and the volumes V_1 and V_2 are known, only two adjustable parameters remain in Eq. 1: k_1^{aw} and k_{11}^{ex} . Since the measurements from August 15 will be used

as the initial values C_1^0 and C_2^0 , there are just two data points to be fitted by the model, the mean concentrations in the two subvolumes on September 4. Generally, a unique choice exists for the two model parameters to force the concentrations as a function of time exactly through the data points. Numerous procedures and computer programs are available to best-fit models to a given set of data. For didactic reasons, we rely on a simple back-of-the-envelope procedure to determine the size of the unknown model parameters.

Because initially the incident PCE is confined to the epilimnion (Box 1), the back-mixing from Box 2 can at first be disregarded. The first line of Eq. 2 then reduces to:

$$\frac{dC_1}{dt} \approx -(k_{w1} + k_1^{aw} + k_{11}^{ex})C_1 \quad (2)$$

As for Model A (Box 6.2, Eqs. 3–5), the solution of Eq. 2 is a pure exponential function that can be used to determine the sum of the three linear rate constants from the mean concentration in the epilimnion at the two sampling dates:

$$(k_{w1} + k_1^{aw} + k_{11}^{ex}) = \frac{1}{t} (\ln C_1^0 - \ln C_1(t = 20 \text{ d})) = \frac{1}{20 \text{ d}} (\ln 30 - \ln 13) = 0.042 \text{ d}^{-1} \quad (3)$$

The flushing rate of the surface layer, $k_{w1} = 0.0096 \text{ d}^{-1}$, amounts to 23% of the total removal rate. Seventy-seven percent of the removal must occur by exchange to the atmosphere and by downward mixing. The two removal rates can be further split by comparing the amount of PCE found below 10 m (440 mol) on September 4 with the total loss of PCE from the surface in this period (1530 mol). Thus, downward mixing accounts for 29% of total removal from the surface layer ($k_{11}^{ex} = 0.29 \times 0.042 \text{ d}^{-1} = 0.0122 \text{ d}^{-1}$, thus $k_{22}^{ex} = (V_1/V_2)k_{11}^{ex} = 0.0100 \text{ d}^{-1}$), and the rest (48%) must be due to air–water exchange ($k_1^{ex} = 0.0202 \text{ d}^{-1}$).

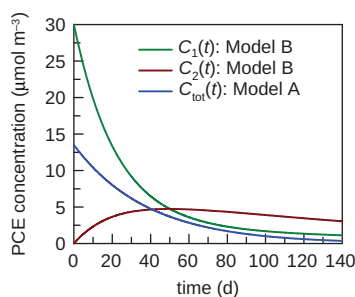
Now, we can solve the system of differential equations (Eq. 1) with the help of Box 6.5. Since the external forces, J_1 and J_2 , are zero, the steady-state concentrations are zero (Box 6.5, Eq. 4). The rate constants of the exponential functions appearing in the solutions (the negative eigenvalues, see Box 6.5, Eq. 3) are:

$$q_1 = 0.0066 \text{ d}^{-1}; \quad q_2 = 0.0455 \text{ d}^{-1} \quad (4)$$

Inserting all these coefficients into Eq. 2 of Box 6.5 yields the numerical solution (C is in units $10^{-9} \text{ mol L}^{-1}$ or in $\mu\text{mol m}^{-3}$; t is in days):

$$\begin{aligned} C_1(t) &= 2.7e^{-0.0066t} + 27.3e^{-0.0455t} \\ C_2(t) &= 7.7e^{-0.0066t} - 7.7e^{-0.0455t} \end{aligned} \quad (5)$$

The solution of Eq. 5 over time is shown in the figure in the margin. To test the applicability of Eq. 5, we use the data from August 15 to calculate the



PCB modeling results for Mystery Lake.

concentrations in the two boxes for September 4 ($t = 20$ d) and compare them with the actual measurements (about 13 and $4 \mu\text{mol m}^{-3}$, respectively):

$$C_1(20 \text{ d}) = 13.4 \times 10^{-9} \text{ mol L}^{-1}; \quad C_2(20 \text{ d}) = 3.6 \times 10^{-9} \text{ mol L}^{-1} \quad (6)$$

Fundamental differences between the one-box model (Model A) and the two-box model (Model B) become apparent when looking at the solutions (figure in margin). For $t > 50$ d, in Model B, the concentration in the deep layer (C_2) becomes larger than C_1 and the net flux between the boxes changes sign indicating an upward flux from the hypolimnion to the epilimnion. The time until the concentration has dropped below $1 \times 10^{-9} \text{ mol L}^{-1}$ (about 300 days) is much larger than calculated from Model A, since the long-term memory of the lake is in the deep water while all removal processes occur in the surface layer. Model B has its shortcomings as well, because it assumes that the sizes of the two boxes remain constant over time, which means the same degree of the lake's stratification lasts during the whole year. During the winter, this is not the case in temperate climates (see Chapter 5, Section 5.3).

So far, we have only discussed linear box models. Although natural processes are not always linear, even nonlinear phenomena can often be approximately modeled using linear equations, especially if the state variables vary only within a narrow range. Therefore, linear equations are frequently ideal tools for a first simple analysis of a system, which is why we make extensive use of them in this book.

But simplicity has its price. As shown in Boxes 6.2, 6.4, and 6.5, the solutions of linear differential equations all have the same mathematical form, that is, they are exponential functions or sums of exponential functions. As a consequence, linear models always tend to the same steady state (if it exists), independently of the initial conditions. The steady states of nonlinear models may depend on the initial state of the system. An example of a nonlinear biodegradation process in a reactor is given in Problem 6.8.

6.3 When Space Matters: Transport Processes

Deterministic *versus* Random Motion: A Thought Experiment in a Train

Imagine sitting in the dining car of a train that takes you through the steep mountains of eastern Switzerland to St. Moritz. While you travel uphill along the winding track, through loop-tunnels and narrow valleys, you order a cup of coffee. You add some milk and stir the coffee with your spoon. Then you lift the cup and take the first sip. Though in this wonderful setting it may seem nerdy, you ask yourself the question: How is the milk moving? You begin to analyze the situation. First, relative to the ground outside, the milk, together with the cup, your arm and the dining car, travel along the



A thought experiment in a train.
Photo: Böhringer (2013).

tracks toward St. Moritz. The motion can be described by a three-dimensional velocity vector, which is a set of three numbers comprising velocity's components along the three axes of a Cartesian coordinate system: $\mathbf{v} = (v_x, v_y, v_z)$. The car and its content move in a common direction, like the flow of water in a river. The flow is determined by the railway tracks or by the riverbed. Therefore, this type of motion is characterized by the expressions: deterministic, directed, or advective.

How does the situation change when you move the cup with your arm? Most objects in the car do not experience the movement of your arm, but the movement is still directed and shared by all the fluid elements in the cup and by the cup itself. A velocity vector can still describe the movement, although the vector is not identical with the dining car's velocity vector. The combined effect of different advective motions is described by the sum of the respective velocity vectors: $\mathbf{v}_{\text{tot}} = \mathbf{v}_{\text{car}} + \mathbf{v}_{\text{cup}}$.

How can we characterize the motion of the milk that results from stirring the coffee cup? At first glance, the motion of the fluid produced by the spoon may look like advection as well, since it sets the coffee into a rotational motion. If this were all that stirring does, we could never produce a homogeneous mix of milk and coffee. The essence of stirring is to add enough kinetic energy to the liquid to make the flow turbulent. Although the movement of the spoon is not really random, it triggers a random process called turbulent diffusion. If you could look closer, you would observe that the coffee has little eddies in it after stirring, and these work to distribute the milk throughout the coffee. This process is called turbulent diffusion. Finally, at the molecular level, if one could see it, the random motion of the molecules acts to distribute the molecules originally in the milk into the molecules that were initially in the coffee. This process is called molecular diffusion. In contrast to the deterministic nature of advective motion, these diffusive motions are random processes dependent on the relative motions of the materials.

To make things even more complex, you perform another experiment in the dining car. For a moment you forget all your manners, and you put salt in the sugar bowl and mix the contents with your spoon. Not concerned about the possibility that a later customer may not be very happy about your experiment, you ask yourself whether your action is an advective or a diffusive process. After some thought, you realize that the answer depends on the scale at which you are looking. At the scale of the sugar bowl, you have randomly mixed the individual sugar and salt grains to reach a homogeneous mixture of particles of both kinds. This is a diffusive process. However, at the level of the individual grains, the picture looks different. The molecules contained in an individual crystal were advectively, or jointly, moved around. The distinction between advective and diffusive motion is scale-dependent.

Environmental transport processes are composed of all the phenomena encountered in the dining car: advective motion, turbulent diffusion, and molecular diffusion. As an example, large-scale ocean currents, such as the Gulf Stream, are like the dining car. Within the Gulf Stream travel parcels of water, so-called turbulent eddies, that move relative to each other. Where eddies collide, a series of ever smaller eddies is produced until the eddies become so small that their motion dissolves in the molecular movement of the water molecules.

It is impossible to model the whole spectrum of water movement from the global scale of the Gulf Stream down to the molecular movement of the molecules. Models of fluid systems (atmosphere, ocean, lake, or river) are characterized by their scale of spatial resolution, that is, by the “grain size” of our observations and descriptions. Motion patterns that are larger than our spatial resolution are deterministically modeled by advective motion; patterns smaller than the spatial resolution are modeled as a random or diffusive process. Randomness means that the movement of an individual fluid parcel cannot be described deterministically. But the combined effect of many individual random processes results in simple macroscopic laws that depict the mean effect of the random system.

In box models, the scale size below which advective transport is neglected, is determined by the size of the boxes. Since a box is assumed to be completely mixed, modeling a lake by one single box means completely disregarding the effect of internal water currents. At the same time, turbulent diffusive transport is assumed to be intense enough to keep the box well mixed. This assumption of complete diffusive mixing is an extreme method to account for transport and mixing. Sometimes such a description is not justified. In this section, we show how models can be further modified to describe systems that are not completely mixed since mixing is not fast enough or the system is too big.

Mathematical Description of Transport Processes

We now aim to derive mathematical expressions for diffusive and advective transport in environmental systems. To do so, we seek a mathematical description of advective and diffusive transport in a model, based on the equations derived for first-order (linear) transport by fluid motion between boxes (Eq. 6-16), in which the boxes become smaller and smaller until the boxes are replaced by continuous space coordinates. Let's begin building the model using an illustrative example.

A lake is separated into two basins linked by a shallow channel (Fig. 6.7). The modeling procedure for this system is the same as before: Two state variables are introduced and linked by an exchange flux Q^{ex} [L^3T^{-1}] (Eq. 6-16). In addition to the symmetric exchange of water at the channel, we add the effect of an inlet into Basin 1 with discharge rate Q^{ad} [L^3T^{-1}] and of an outlet from Basin 2 with the same discharge rate. A chemical is entering Basin 1 via the inlet (concentration C^{in}). We assume that

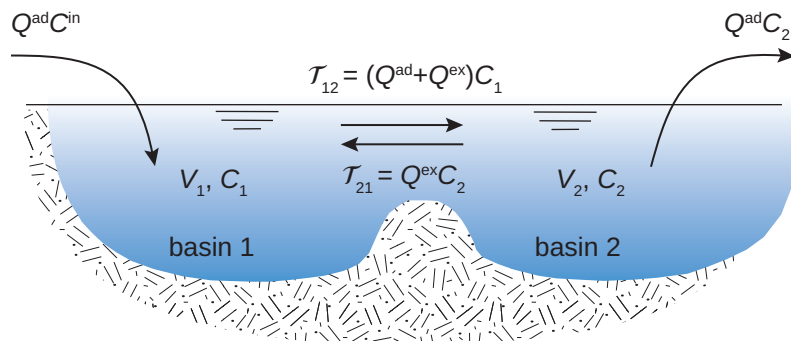


Figure 6.7 Water exchange between two lake basins that are separated by a channel. If the channel gets long and shallow, the backward flux T_{21} becomes zero. The flow from Basin 1 to Basin 2 is then purely advective, the influence from Basin 2 on Basin 1 disappears and the system becomes hierarchical.

except for the outlet, no other removal or *in situ* transformation processes affect the concentration in the two separately mixed lake basins. The dynamic equations of the concentrations, C_1 and C_2 , are:

$$\begin{aligned}\frac{dC_1}{dt} &= k_1^{\text{ad}} C^{\text{in}} - (k_1^{\text{ad}} + k_{11}^{\text{ex}}) C_1 + k_{12}^{\text{ex}} C_2 \quad \text{with } k_{11}^{\text{ex}} = k_{12}^{\text{ex}} = \frac{Q^{\text{ex}}}{V_1}; \quad k_1^{\text{ad}} = \frac{Q^{\text{ad}}}{V_1} \\ \frac{dC_2}{dt} &= (k_2^{\text{ad}} + k_{21}^{\text{ex}}) C_1 - (k_2^{\text{ad}} + k_{22}^{\text{ex}}) C_2 \quad \text{with } k_{21}^{\text{ex}} = k_{22}^{\text{ex}} = \frac{Q^{\text{ex}}}{V_1}; \quad k_2^{\text{ad}} = \frac{Q^{\text{ad}}}{V_2}\end{aligned}\quad (6-24)$$

The steady-state concentrations are $C_1^\infty = C_2^\infty = C^{\text{in}}$. As before, all rates k have dimension $[\text{T}^{-1}]$.

Imagine that the channel between the two basins gets shallower and longer. At one point, water can no longer flow back from Basin 2 (where the outlet of the lake is located) to Basin 1. The corresponding backward flux becomes zero: $Q_{\text{ex}} = 0$. Then, Eq. 6-24 is reduced to:

$$\frac{dC_1}{dt} = k_1^{\text{ad}} (C^{\text{in}} - C_1); \quad \frac{dC_2}{dt} = k_2^{\text{ad}} (C_1 - C_2) \quad (6-25)$$

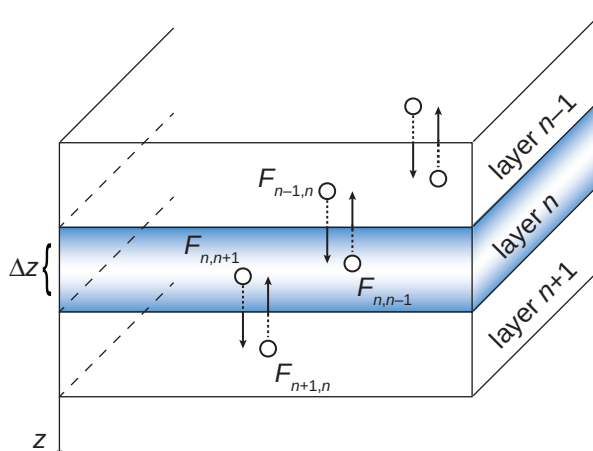
With the elimination of the exchange flux, Q_{ex} , the mathematical structure of the two coupled differential equations (Eq. 6-24) undergoes a fundamental change. The influence from the state variable C_2 on the differential equation of the state variable C_1 disappears so the model becomes hierarchical. In hierarchical models, the state variables can be ordered such that the variable with the lower number influences the one with the higher number but not reversely. A series of lakes that are connected by channels in which the flow is unidirectional, that is, in which back mixing is excluded, represents a hierarchical system. The solution of such models is straightforward: First, the equation of the variable with the lowest number (the one on top of the hierarchy) is solved; the solution is inserted as an external force into the next equation and so forth.

If we compare Eqs. 6-24 and 6-25 in terms of advective *versus* diffusive transport, Eq. 6-24 represents a system in which the coupling between the two boxes is due to both types of transport (advection and diffusion), while in Eq. 6-25, diffusion is suppressed, and transport becomes purely advective (unidirectional). A river can be modeled as a purely advective system. Although in rivers turbulence is important, turbulent transport cannot act against the current, unless the flow velocity is extremely small or the river is dammed to become a lake. Therefore, we can be rather sure that water pollution in New Orleans does not affect water quality in St. Louis upstream, but the reverse is easily possible.

Continuous Models

Let us now go one step further. We drop the concept of real compartments (lake basins or well-defined horizontal water layers) and subdivide the system into a large number of virtual boxes, which are boxes that do not physically exist but are just imagined. As an example, we imagine the water column of a lake or the ocean to consist of m

Figure 6.8 Schematic picture showing how a m -box model consisting of m horizontal layers (boxes) turns into a model with a continuous description of concentration C along the spatial axis under consideration (in this case, it is the z -axis). $F_{n,n+1}$ and $F_{n+1,n}$ are the downward and upward fluxes, respectively, across the boundary between layer n and layer $n+1$.



horizontal layers that are connected to their neighboring layers by vertical exchange fluxes (Fig. 6.8). We divide the total flux between the layers, \mathcal{T} [MT^{-1}], by the area A , and get the normalized flux per unit area, $F = \mathcal{T}/A$ [$\text{ML}^{-2}\text{T}^{-1}$]. For the flux from layer n to layer $n+1$, we write:

$$F_{n,n+1} = \frac{\mathcal{T}_{n,n+1}}{A} = \frac{Q_{n,n+1}}{A} C_n = v_{n,n+1} C_n \quad [\text{ML}^{-2}\text{T}^{-1}]; \quad v_{n,n+1} \equiv \frac{Q_{n,n+1}}{A} \quad [\text{LT}^{-1}] \quad (6-26)$$

The flow rate Q divided by the area across which the flow occurs is the transport velocity across the interface between layer n and layer $n+1$, $v_{n,n+1}$. Let us assume that $v_{n,n+1}$ is larger than the reverse velocity. We split the velocities into a symmetric part that is the diffusive exchange velocity, $v_{n,n+1}^{\text{diff}} = v_{n+1,n}^{\text{diff}}$, and the excess velocity from layer n to layer $n+1$ that we call the advection velocity, $v_{n,n+1}^{\text{ad}} = v_{n,n+1} - v_{n+1,n}$:

$$v_{n,n+1} = v_{n,n+1}^{\text{diff}} + v_{n,n+1}^{\text{ad}}; \quad v_{n+1,n} = v_{n+1,n}^{\text{diff}} = v_{n,n+1}^{\text{diff}} \quad (6-27)$$

For thin layers, the concentration difference between two adjacent layers can be approximated by the slope of the concentration profile, which is the vertical derivative of $C(z)$, dC/dz , multiplied by the vertical spacing of the layers, Δz , where z is the vertical coordinate:

$$C_{n+1} - C_n \approx \Delta z \frac{dC}{dz} \quad (6-28)$$

Let us first look at the situation of pure diffusive exchange ($v^{\text{ad}} = 0$). Since the diffusive velocities are equal in both directions, the net flux across the interface between layer n and $n+1$ is:

$$F_{n,n+1}^{\text{diff,net}} \equiv F_{n,n+1}^{\text{diff}} - F_{n+1,n}^{\text{diff}} = v_{n,n+1}^{\text{diff}} (C_n - C_{n+1}) = -v_{n,n+1}^{\text{diff}} \Delta z \frac{dC}{dz} \quad (6-29)$$

where we have approximated the concentration difference by Eq. 6-28. The product of the diffusive exchange velocity and the layer thickness is the diffusion coefficient, D :

$$D \equiv v_{n,n+1}^{\text{diff}} \Delta z \quad [\text{L}^2\text{T}^{-1}] \quad (6-30)$$

We can now drop the subscripts $(n, n+1)$ because they refer to virtual layer numbers that were only introduced to show how one can extrapolate the concept of finite layers (or finite boxes) to the continuous space. However, we need to remember that F^{diff} and D may not be constant along the chosen axis. That is, they may depend on the coordinate z , $F^{\text{diff}}(z)$ and $D(z)$, although we do not usually explicitly write down the z -dependence.

Fick's First Law. Inserting Eq. 6-30 into Eq. 6-29 yields *Fick's first law*:

$$F^{\text{diff}} = -D \frac{dC}{dz} \quad (6-31)$$

The law states that a flux resulting from a random process is proportional to the negative gradient of the concentration, that is, directed from the zone of higher concentration to the one of lower concentration. Depending on the physical nature of the flux, D either reflects molecular or turbulent diffusion. As long as the underlying process is random, the resulting flux always has the general form of Eq. 6-31.

Finally, we want to calculate the net flux for the situation of pure advection ($v^{\text{diff}} = 0$). Since the backward advection velocity is zero (Eq. 6-27), the net advective flux is:

$$F_{n,n+1}^{\text{ad,net}} = v_{n,n+1}^{\text{ad}} C_n \quad \text{or simply} \quad F = v^{\text{ad}} C \quad (6-32)$$

Models in which space is described continuously (along one or several space coordinates) are mathematically more complex than box-models; their solutions demand partial differential equations. We come back to such models in Section 6.4.

6.4 Models in Space and Time

This chapter has given us a first glimpse at mathematical modeling of environmental systems so as to fill our basic mathematical toolkit. We started with the concept of a mass balance applied to simple compartments of the environment called boxes. When moving from one- to two- and to multi-box models, we learned about how these boxes are connected by transport processes. Two distinct modes of transport were identified: diffusive transport, which we relate to random processes, and directed transport, which we relate to advective flow. By making the boxes smaller and smaller, we saw how the box models naturally develop into models in which space is described as a continuous coordinate. We learned how advective and diffusive fluxes are described in these new spatial models. For the latter, we utilized the well-known *Fick's first law* (Eq. 6-31). We will now create a sketch of how these elements can be put together into continuous time-space models.

Gauss' Theorem

The final mathematic tool is an equation for the local concentration changes due to the combined action of transport and reaction in a three-dimensional system (e.g., lake, ocean, atmosphere etc.). We do not fully derive this equation but make use of *Gauss' theorem*. The theorem states that the mass balance in an infinitesimally small control volume can be calculated by looking at all input and output fluxes at the surface of the cube (Fig. 6.9):

$$\left(\frac{\partial C}{\partial t}\right)_{\text{transport}} = -\frac{\partial F_x^{\text{tot}}}{\partial x} - \frac{\partial F_y^{\text{tot}}}{\partial y} - \frac{\partial F_z^{\text{tot}}}{\partial z} = -\text{div} F^{\text{tot}} \quad [\text{ML}^{-3}\text{T}^{-1}] \quad (6-33)$$

Some further explanation may help to fully understand this equation. First, since concentration C now depends on four coordinates (time t , space coordinates x , y , z), the normal derivatives (i.e., dC/dt) have become partial derivatives ($\partial C/\partial t$). The notation indicates that we are looking at the change of C with time while all other coordinates (x, y, z) are held constant. Likewise, $\partial C/\partial x$ would mean the change of concentration along the x -axis while y , z and time t are kept constant. Second, in the three-dimensional space, the total flux of the chemical described by concentration C is a vector F^{tot} (written as bold symbol) composed of the three Cartesian components F_x^{tot} , F_y^{tot} , and F_z^{tot} . The specific 'diagonal' sum of the three partial derivatives in the

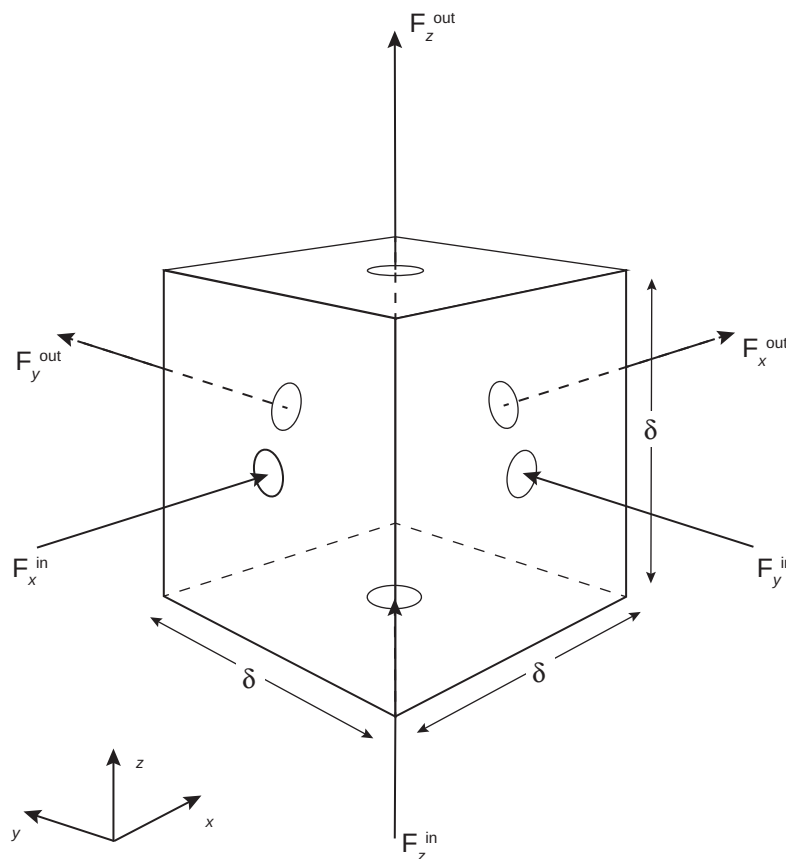


Figure 6.9 A cube with dimension δ (control volume) illustrates Gauss' theorem (Eq. 6-33). The concentration change within the cube results from the differences between input and output fluxes, $F_j^{\text{in}} - F_j^{\text{out}}$, calculated for the three Cartesian coordinates $j = x, y, z$.

middle part of Eq. 6-33 is called *divergence* (div). In the specific case of $\text{div } \mathbf{F}$, it measures how the flux field diverges (moves apart). If the flux is constant in space, the three partial derivatives are zero and $\text{div } \mathbf{F} = 0$. Thus, we can describe the essence of *Gauss' theorem* as follows: The local concentration change due to a sum of fluxes is given by the divergence of the flux.

For the derivation of Eq. 6-33, the physical nature of the flux did not matter, meaning whether the flux is due to diffusion, advection, or any other process. Now let us use the equation for the two types of flux that we have derived in the previous section. We restrict the discussion to just one spatial dimension (x -axis) and assume that the fluxes along the y - and z -axis are zero. For the remaining flux along the x -axis, we use Eq. 6-32 for advection and Eq. 6-31 for diffusion (*Fick's first law*). The subscript x is added to v to indicate that we consider the x -component of the three-dimensional velocity vector:

$$\left(\frac{\partial C}{\partial t}\right)_{\text{advection}} = -\frac{\partial F_x^{\text{adv}}}{\partial x} = -\frac{\partial(v_x C)}{\partial x} = -v_x \frac{\partial C}{\partial x} \text{ if } v_x = \text{constant with } x \quad (6.34a)$$

$$\left(\frac{\partial C}{\partial t}\right)_{\text{diffusion}} = -\frac{\partial F_x^{\text{diff}}}{\partial x} = -\frac{\partial}{\partial x} \left(-D \frac{\partial C}{\partial x}\right) = D \frac{\partial^2 C}{\partial x^2} \text{ if } D = \text{constant with } x \quad (6.34b)$$

Equation 6-34b is called the Fick's second law.

The mathematical descriptions for either flux or change of concentration due to advection or diffusion can be summarized by a two-dimensional scheme that helps one remember these relationships (Table 6.2). In the scheme, every move to the right (from flux to concentration change) or downward (from advection to diffusion) involves a sign change as well as an additional differentiation of C with respect to x . The simple form of the scheme is helpful to qualitatively determine the direction of transport and the accompanying concentration changes due to advection and diffusion. A graphical explanation is given in Fig. 6.10.

Table 6.2 Scheme to Describe Flux and Temporal Concentration Change Due to Advection and Diffusion

	Flux F [ML ⁻² T ⁻¹]	Concentration Change $\partial C / \partial t$ [ML ⁻³ T ⁻¹]	Transport Distance L [L]
Advection	$v_x C$	$-v_x \frac{\partial C}{\partial x}$	$v_x t$
Diffusion ^a	$-D \frac{\partial C}{\partial x}$	$D \frac{\partial^2 C}{\partial x^2}$	$(Dt)^{1/2}$ ^b

v_x : advection velocity [LT⁻¹], D : diffusivity coefficient [L²T⁻¹], C : concentration [ML⁻³], t : time [T]

^a The expressions for diffusion are called *Fick's first and second laws*.

^b Relation by Einstein and Smoluchowski (Einstein, 1905), numerical factor omitted.

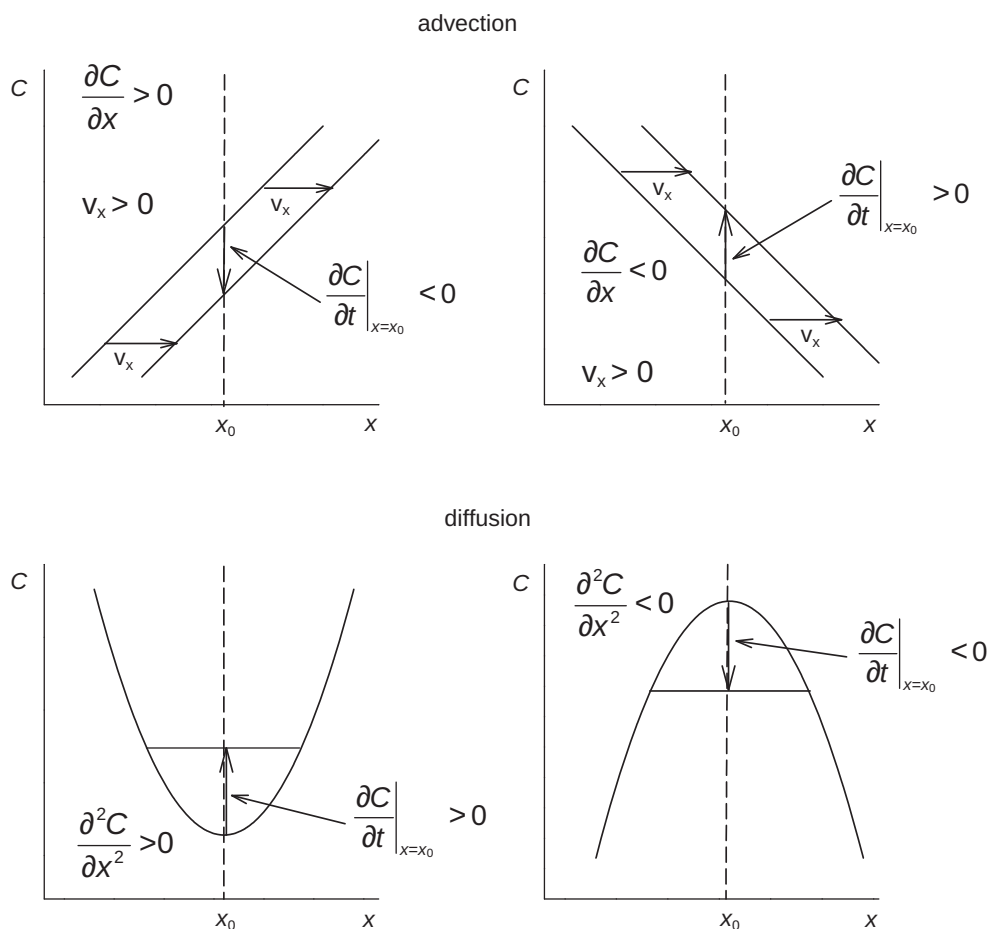


Figure 6.10 Qualitative relations between the sign of concentration change at location x_0 due to advection and diffusion, respectively. Advection (upper panels): A concentration profile along the x -axis is shifted to the right (thin line) due to advection in the positive x -direction ($v_x > 0$). This leads to a decrease of C at x_0 if the slope of $C(x)$ is positive (left panel), and to an increase of C if the slope is negative (right panel). Diffusion (lower panels): According to Fick's second law (Eq. 6.34b), diffusion always shifts a concentration profile to its concave side.

In Table 6.2, we have included the transport distance, L , for advection and diffusion; it gives an average distance over which a chemical moves during time t . For advection, L is given by:

$$L_{\text{ad}} = |v_x|t \quad (t = \text{transport time}) \quad (6-35)$$

For diffusive transport in one dimension, the average distance is given by the Einstein-Smoluchowski Law (Einstein, 1905):

$$L_{\text{diff}} = (2Dt)^{1/2} \quad (6-36)$$

For diffusion in two and three dimensions, the factor 2 changes. It is omitted for the following order-of-magnitude considerations. Comparing Eqs. 6-35 and 6-36 (without factor 2) yields the critical time t_{crit} , the time at which for a given set of v and D , diffusive transport is overpowered by advective transport:

$$t_{\text{crit}} = D/v_x^2 \quad (6-37)$$

Table 6.3 Critical Times t_{crit} (s) at which Transport Distance by Advection Becomes Larger than Transport Distance by Diffusion (Eq. 6-37)^a

Diffusivity D (m ² s ⁻¹) ^b			Advection Velocity $ v_x $ (m s ⁻¹)				
			10 ⁻⁴	10 ⁻²	1	10 ²	10 ³
Molecular	in water	10 ⁻⁹	10 ⁻¹	10 ⁻⁵	10 ⁻⁹	10 ⁻¹³	10 ⁻¹⁵
	in air	10 ⁻⁵	10³	10 ⁻¹	10 ⁻⁵	10 ⁻⁹	10 ⁻¹¹
Turbulent	in water						
	vertical	10 ⁻⁶	10²	10 ⁻²	10 ⁻⁶	10 ⁻¹⁰	10 ⁻¹²
	horizontal	1	10⁸	10⁴	1	10 ⁻⁴	10 ⁻⁶
Turbulent in atmosphere		10 ²	(10¹⁰) ^c	(10⁶) ^c	10²	10 ⁻²	10 ⁻⁴

^a Note: Values larger than 10² s are marked in bold. 10⁵ s \approx 1 day, 3×10^7 s \approx 1 year

^b Typical sizes of (molecular and turbulent) diffusivities are taken from Table 17.3.

^c Such small advection velocities do not occur in a turbulent atmosphere.

For times smaller than t_{crit} , diffusive transport reaches farther. t_{crit} is listed for different values of D and v_x in Table 6.3. The table shows that molecular diffusion only plays a role if advection is absent. Such situations occur at interfaces (water–air, water–solid) or where the size of the system is very small, like in the pore water of sediments. In contrast, turbulent diffusion in fluid systems (water, atmosphere) is relevant over the time scale of minutes to days.

Diffusion/Advection/Reaction Modeling

To conclude this chapter, we apply Eqs. 6-34 to a one-dimensional concentration profile (e.g., in the atmosphere or the ocean) that is influenced by the simultaneous action of advection, diffusion, and transformation. We assume that transformation (reaction) consists of an input term J and a first-order removal rate ($-kC$). Putting everything together yields the following one-dimensional linear transport-reaction equation:

$$\frac{\partial C}{\partial t} = \left(\frac{\partial C}{\partial t} \right)_{\text{reaction}} + \left(\frac{\partial C}{\partial t} \right)_{\text{adv}} + \left(\frac{\partial C}{\partial t} \right)_{\text{diff}} = J - kC - v_x \frac{\partial C}{\partial x} + D \frac{\partial^2 C}{\partial x^2} \quad (6-38)$$

Equation 6-38 is a one-dimensional second order linear partial differential equation. Second order means that the highest derivative, the one describing the effect of diffusive transport, is of second order. The meaning of the terms on the far right-hand side of the equation are input per unit volume and time, J , first-order degradation reaction with rate constant k , advection with velocity v_x , and diffusion with diffusivity D .

Here, we do not deal with the general solution of this equation (see Crank, 1975). We restrict the following discussion to the steady-state case for Eq. 6-38 (i.e., $\partial C/\partial t = 0$). Steady state means that the combined effect of all individual processes (diffusion, advection, and reaction) is such that at every location along the x -axis,

the concentration C remains constant. Since at steady state, time no longer matters, we can simplify $C(x,t)$ to $C(x)$ and replace the partial derivatives by ordinary ones:

$$0 = J - kC - v_x \frac{dC}{dx} + D \frac{d^2C}{dx^2} \quad (6-39)$$

In contrast to the differential equations resulting from box models, the state variable C is not treated as a function of time t but of space x . Eq. 6-39 is an inhomogeneous linear differential equation of second order. The term J makes it inhomogeneous, the second derivative (last term on right-hand side of equation) makes it second order. Since the equation is linear, based on our experience with FOLIDE (Box 6.2), we expect the solutions to be composed of exponential functions. The difference from FOLIDE is related to the boundary conditions. FOLIDE just needs one condition, called the initial condition C^0 that is usually defined for $t = 0$. Since Eq. 6-39 is second order, it requires two boundary conditions; that is, we need to know two values of concentration, $C(x)$, or concentration gradient, dC/dx , at some specific point along the x -axis. Box 6.4 gives the explicit solution for just one possible combination of boundary conditions, the case with fixed concentrations at $x = 0$ (C_0) and $x = L$ (C_L). The general solution of Eq. 6-39 is given, for instance, in Schwarzenbach et al., (2003) and Imboden and Pfenninger (2013).

As shown in Box 6.4, the inhomogeneous term J can be eliminated by a simple transformation to a new variable $C^* = C - J/k$. The remaining terms of Eq. 6-39 describe the processes first order reaction, advection, and diffusion. Their relative importance, that is, their influence on the shape of the steady-state concentration profile $C^*(x)$, can be analyzed by two non-dimensional numbers. The first, the Damköhler Number, Da , compares the critical time, t_{crit} (Eq. 6-37), with the individual ‘clock’ of the reactive species, $t_r = 1/k$. This means one considers the time at which transport by advection becomes dominant over transport by diffusion with the mean lifetime of the chemical with respect to linear transformation:

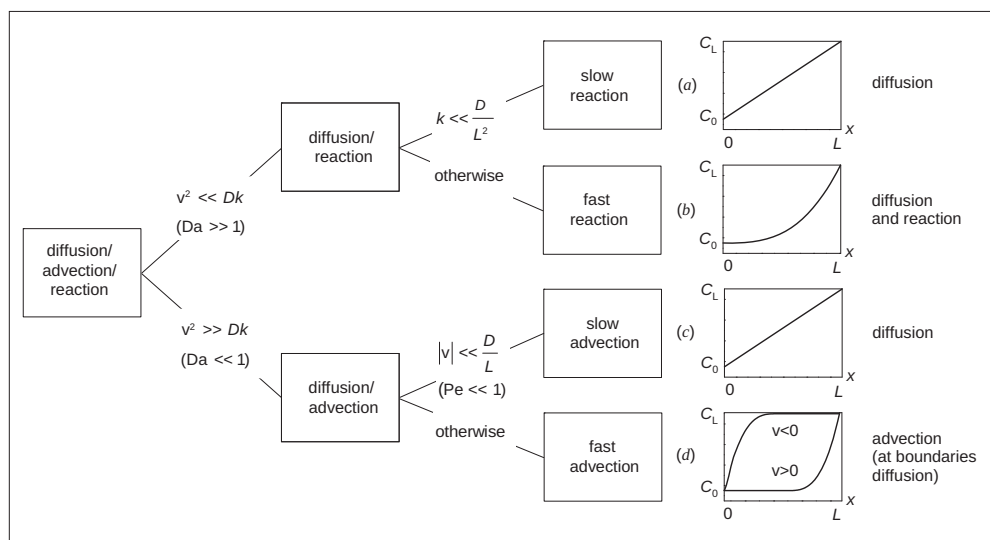
$$Da \equiv \frac{t_{crit}}{t_r} = kt_{crit} = \frac{Dk}{v_x^2} \quad (6-40)$$

If $Da \gg 1$, reaction has significantly reduced C before advection becomes the dominant transport process. Thus, only diffusion and reaction are relevant while advection can be neglected. By comparing the reaction time $t_r = 1/k$ with the diffusion time along a system of size L , $t_{diff} = L^2/D$ (see Eq. 6-36 and drop the factor 2), we can further subdivide the diffusion/reaction regime into the case of slow reaction ($k \ll D/L^2$, only diffusion matters) and fast reaction ($k \gg D/L^2$, both diffusion and reaction matter). The shape of the resulting profiles are qualitatively shown in Fig. 6.11.

If $Da \ll 1$, the reactivity of the chemical can be neglected (diffusion/advection regime). We just have to check which of the two processes dominates in a system of size L . To do so, we compare the diffusion time, $t_{diff} = L^2/D$, (again a factor of

Figure 6.11

Schematic one-dimensional concentration profiles resulting from the diffusion/advection/reaction equation at steady state (Eq. 6-39) for different parameter values D (diffusion coefficient), v_x (advection velocity along the x -axis), and k (first-order reaction rate constant). The profiles obey the boundary conditions $C_0 = C(0)$, $C_L = C(L)$. The four 'pure' situations are determined by the size of the Damköhler Number, Da (Eq. 6-40), and the Peclet Number, Pe (Eq. 6-41).



2 has been omitted from Eq. 6-36) with the advection time, $t_{ad} = L/|v_x|$. The ratio between the two times is called the Peclet Number, Pe :

$$Pe = \frac{t_{diff}}{t_{ad}} = \frac{L|v_x|}{D} \quad (6-41)$$

If $Pe \ll 1$, the profile is diffusion-controlled, otherwise, it is advection-controlled ($Pe \geq 1$), except close to the boundaries (see Fig. 6.11).

Box 6.7 One-Dimensional Diffusion-Advection-Reaction Equation at Steady State

$$0 = J - kC - v_x \frac{dC}{dx} + D \frac{d^2C}{dx^2} \quad (6-39)$$

With the new concentration variable $C^* = C - J/k$, the equation becomes homogeneous:

$$D \frac{d^2C^*}{dx^2} - v_x \frac{dC^*}{dx} - kC^* = 0 \quad (1)$$

Solution for:

$$C^*(x) = A_1 e^{\lambda_1 x} + A_2 e^{\lambda_2 x} \quad (2)$$

where λ_i are the eigenvalues of the differential equation (Eq. 6-39) given by

$$\lambda_i = \frac{1}{2D} [v_x \pm (v_x^2 + 4Dk)^{1/2}] = \frac{|v_x|}{2D} [\text{sgn}(v_x) \pm (1 + \text{Da})^{1/2}] \quad (3)$$

Da is the Damköhler Number (Eq. 6-40) and $\text{sgn}(v_x) = \pm 1$ is the sign of the specific value of v_x . The λ 's differ by the sign in front of the square root. For any choice of the parameters k , v_x , $D > 0$, the eigenvalues λ_i have the following sign: $\lambda_1 > 0$, $\lambda_2 < 0$.

The coefficients A_1 and A_2 of Eq. 2 are determined from the boundary conditions $C(0) = C_0$, $C(L) = C_L$:

$$A_1 = \frac{\left(C_L - \frac{J}{k}\right) - \left(C_0 - \frac{J}{k}\right)e^{\lambda_2 L}}{e^{\lambda_1 L} - e^{\lambda_2 L}}; \quad A_2 = \frac{-\left(C_L - \frac{J}{k}\right) + \left(C_0 - \frac{J}{k}\right)e^{\lambda_1 L}}{e^{\lambda_1 L} - e^{\lambda_2 L}} \quad (4)$$

Backward transformation of Eq. 2 gives:

$$C^*(x) = \frac{J}{k} + A_1 e^{\lambda_1 x} + A_2 e^{\lambda_2 x} \quad (5)$$

Special case $v_x = 0$:

$$C(x) = \frac{J}{k} + \frac{\left(C_0 - \frac{J}{k}\right) \sinh[\lambda(L-x)] + \left(C_L - \frac{J}{k}\right) \sinh[\lambda x]}{\sinh[\lambda L]}; \quad \lambda = \left(\frac{k}{D}\right)^{1/2} \quad (6)$$

Special case $L \rightarrow \infty$:

$$C(x) = \frac{J}{k} \left(C_0 - \frac{J}{k}\right) e^{\lambda_2 x}; \quad \lambda_2 < 0 \quad (\text{see Eq. 3}) \quad (7)$$

6.5 Questions and Problems

Special note: Problem solutions are available on the book's website. Solutions to problems marked with an asterisk are available for everyone. Unmarked problems have solutions only available to teachers, practitioners, and others with special permission.

Questions

Q 6.1

What is the purpose of models?

Q 6.2

Give a short definition for each of the following terms: *system*, *model*, and *mathematical model*

Q 6.3

What is implied with the statement “The relation between a system and its environment is asymmetrical”?

Q 6.4

What are important decisions to make before building a mathematical model?

Q 6.5

Explain the difference between model calibration and model validation. How are these terms related to Kleindorfer’s (1993) definition of *interference* and *prediction* of outcomes?

Q 6.6

When constructing a model, why should one consider the relationship between available data and model complexity?

Q 6.7

Explain the difference between homogeneous and inhomogeneous linear differential equations.

Q 6.8

How do the solutions of linear one-box models vary with time?

Q 6.9

What requirements must a linear differential equation fulfill to have a finite steady state?

Q 6.10

Why do we have to introduce a *convention*, such as $t_{5\%}$, to define time-to-steady state of a linear model?

Q 6.11

Explain the difference between exchange flux and directed flux. Explain the consequences for solving the equations of a two-box model in which the boxes are coupled by a directed flux rather than by an exchange flux.

Q 6.12

You have constructed a *linear* two-box model for tetrachloroethene (PCE) in a lake. In your model, the only input of PCE into the lake is from the outlet of a sewage treatment plant. The model includes several internal and output processes such as vertical mixing between the epilimnion and hypolimnion, air–water exchange, and outflow from the water surface. How does the steady-state concentration in the epilimnion of the lake change if the input from the sewage treatment plant is reduced by 50%?

Q 6.13

You measure the increase of the molecular oxygen (O_2) concentration in a constantly mixed, open-top beaker. The water in the beaker had been completely purged of O_2 beforehand. How can you find out from your time series of O_2 -concentrations in the beaker whether the air–water exchange of O_2 is a linear process?

Q 6.14

How many model parameters are needed to describe the most general linear two-box model?

Q 6.15

Using examples, explain the meaning of the sentence “The distinction between advective and diffusive motion is scale-dependent.”

Q 6.16

Is it possible that the spatial concentration distribution of two organic chemicals along a water-filled canal is such that the chemicals' direction of net transport by advection points in opposite directions? If yes, what do the concentration profiles look like? Answer the same questions for transport by diffusion.

Q 6.17

How can you estimate the molecular diffusion coefficient of a chemical in air from its mean free path and its mean velocity of molecular thermal motion?

Q 6.18

Water temperature along a water-filled pipe increases linearly between two points A and B. The water in the pipe does not flow. Does a heat flow exist between the points, and if yes, in what direction does heat flow and how would water temperature change between A and B due to a possible heat flow, provided that the temperatures at A and B are kept constant?

Q 6.19

From Fig. 5.1, we learned that the temperature of air has a maximum in the stratopause (height about 50 km). Given the fact that there is always turbulent diffusion in air, also in the vertical, what kind of physical processes must be at work in order to sustain the temperature maximum?

Q 6.20

Derive analytical expressions for the flux F and the temporal concentration change $\partial C/\partial t$ for the following one-dimensional concentration distributions:

- (a) $C(x) = a + bx$; (b) $C(x) = a - bx - cx^2$; (c) $C(x) = C_0 \exp(-ax)$;
(d) $C(x) = a \sin(bx)$.

The parameters a , b , c and diffusivity D are constant and positive.

Q 6.21

Why does the incorporation of advection and diffusion into a model lead to partial differential equations? For what conditions do these equations become normal differential equations again?

Q 6.22

Explain Gauss' theorem in words.

Q 6.23

Nondimensional numbers like the Reynolds Number always measure the relative importance of two different processes. Which processes are compared by the Damköhler Number and the Peclet Number?

Q 6.24

What is the difference between the diffusive-advective and the diffusive-reactive regime of a space/time model?

Problems**P 6.1 Half-Life of a Chemical in a Reactor**

In a completely mixed chemical reactor, the concentration of a chemical is measured to be $60 \mu\text{g L}^{-1}$. Two hours later, the concentration has dropped to $54 \mu\text{g L}^{-1}$. You have no idea what could have caused this decrease. As a hypothesis, you assume that all the processes that were responsible for the concentration change would remain in action during the hours to come. Furthermore, you assume that the sum of all the processes results in a first-order elimination process.

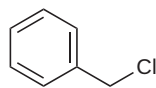
(a) Using the simplest linear model, calculate the total linear elimination rate constant k^{tot} from the two measurements.

(b) Estimate the uncertainty of the rate constant k^{tot} by assuming that the concentration measured 2 hours after the first one is $(54 \pm 1) \mu\text{g L}^{-1}$. (Of course, for a more precise error analysis, one has to take into account the uncertainty of both concentration measurements, but as a first estimate, the simple procedure is sufficient.)

(c) Further observations show that after about two days the concentration in the reactor approaches the value $30 \mu\text{g L}^{-1}$ and then remains approximately constant for the next few days. This makes you to re-analyze your answer to the first question (a). How could you fix the problem without giving up the linear modeling approach and how would this affect the value of k^{tot} estimated before?

Hint: From the measurements it seems that in the solution of the linear one-box model (Eq. 6-8), C^∞ is not zero. It may help to rewrite Eq. 6-8 in the form:

$$C(t) - C^\infty = (C^0 - C^\infty) e^{-kt}$$



benzyl chloride

Pond characteristics

Volume (V)	10^5 m^3
Surface (A)	$2 \times 10^4 \text{ m}^2$
Water through-flow (Q)	$10^3 \text{ m}^3 \text{ d}^{-1}$

P 6.2* A Benzyl Chloride Spill into a Pond

Due to an accident right before Christmas, an unknown amount of benzyl chloride (BzC) is introduced into a small, well-mixed pond used as a drinking water reservoir. Working for the State Water Authority, you are asked to estimate how much BzC has entered the pond, and, more importantly, how long it will take before the concentration drops below $1 \mu\text{g L}^{-1}$. Because of the Christmas holiday, you need five days until you can take the first water sample. Five days after the spill you measure a BzC concentration in the pond of $50 \mu\text{g L}^{-1}$. A second measurement five days later shows that the concentration has dropped to $23.6 \mu\text{g L}^{-1}$. Assume that all relevant parameters remain constant over time.

P 6.3 Investigating the Elimination Process of a Chemical in a Well-Mixed Reactor with Throughflow

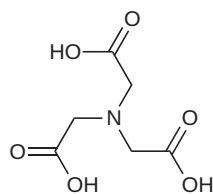
The behavior of a chemical in a well-mixed reactor (volume $V = 500 \text{ L}$, flow rate $Q = 100 \text{ L h}^{-1}$) is investigated by measuring the outflow concentration C^{out} at steady state for different input concentrations C^{in} . The results are given in the table below.

(a) Determine the order of the elimination process and formulate the differential equation that describes the chemical concentration in the reactor.

(b) How long does it take for the outflow concentration to drop from 40 mmol L^{-1} to 2 mmol L^{-1} , if at time t_1 , C^{in} drops to zero instantaneously?

Concentrations in reactor

$C^{\text{in}} (\text{mmol L}^{-1})$	$C^{\text{out}} (\text{mmol L}^{-1})$
10	8
25	20
40	32
65	52



nitrilotriacetic acid (NTA)

Characteristics of Greifensee

Volume (V)	
Total	$150 \times 10^6 \text{ m}^3$
Epilimnion	$50 \times 10^6 \text{ m}^3$
Hypolimnion	$100 \times 10^6 \text{ m}^3$
Surface (A)	$8.6 \times 10^6 \text{ m}^2$
Water through-flow (Q)	$0.34 \times 10^6 \text{ m}^3 \text{ d}^{-1}$

P 6.4* Nitrilotriacetic Acid (NTA) in a Lake

Around 1983, typical concentrations of nitrilotriacetic acid (NTA) in Greifensee (Switzerland) were found to be $3.7 \times 10^{-9} \text{ mol L}^{-1}$. NTA is a complexation agent which at that time was mainly used in detergents. Based on measurements made in 1982 and 1983 on the major rivers and sewage inlets of Greifensee, total NTA loading was estimated as $J_{\text{NTA}} = 13 \text{ mol d}^{-1}$. At that time, NTA degradation experiments for concentrations between $2 \times 10^{-8} \text{ mol L}^{-1}$ and $5 \times 10^{-6} \text{ mol L}^{-1}$ (Larson and Davidson, 1982; Barthomolew and Pfaender, 1983) yielded first-order rate constants between 0.02 and 1 d^{-1} . No data were available for concentrations below $2 \times 10^{-8} \text{ mol L}^{-1}$. Use the information on NTA concentrations in Greifensee to estimate the first-order degradation rate of NTA in natural waters at concentrations below this value.

P 6.5 One-Box Models are Everywhere: Cars in a Parking Lot

In a downtown parking lot, 300 cars enter per hour. Fifteen percent of them immediately leave again, having found no free spot. The individual length of stay

of parked cars varies. An observer notes that per minute, 1% of the parked cars leave the parking lot.

- (a) How many parking spots does the parking lot have?
- (b) How long does a car stay in the parking lot on average (not counting the 15% unsuccessful visitors)?
- (c) Assume that the parking lot is open at 6 A.M. and is completely empty at that time. The parking behavior remains exactly as previously described: 300 cars enter per hour (of course, initially, all of them will find a free spot), 1% parked cars leave every minute. When is the parking lot full?

P 6.6 Another Kind of Linear Exchange Equilibrium

In a museum, a separate room A showcases a famous Roman treasure of gold coins. The room is only reachable from the neighboring room B. Custodians have studied the behavior of the visitors. They found that (1) each minute, 30% of visitors in room B decide to enter the treasure chamber A and (2) each minute, 10% of visitors inside the treasure chamber A decide to leave and walk back to room B. Since on weekends the treasure room may sometimes be overcrowded, the museum's director decides to take measures such that no more than 30 people will ever be in room A. Since the door between room B and A cannot be closed, he asks the custodian in room B to close the entrance to room B as soon as the occupancy in room B reaches a critical level. What is this critical level (number of people in room B) in order to keep the occupancy in room A below 30 people?

P 6.7* Two-Box Model for NTA in Greifensee

In Problem 6.4, we analyzed the fate of nitrilotriacetic acid (NTA) in Greifensee (Switzerland), especially its degradation rate. Now we want to refine the analysis by using the two-box model developed in Box 6.6. During the stagnation period (the period when a thermocline separates the epilimnion at the surface from the hypolimnion underneath), the following NTA-concentrations are found in Greifensee:

$$C_E = 5.2 \times 10^{-6} \text{ mol m}^{-3}; C_H = 2.1 \times 10^{-6} \text{ mol m}^{-3}$$

Assume that the input of NTA into the lake, $J_{\text{NTA}} = 13 \text{ mol d}^{-1}$, is to the epilimnion only. Assume steady-state conditions and calculate the linear degradation rate constants in the epilimnion (k_{TE}) and hypolimnion (k_{TH}) that would reproduce the measured NTA-concentrations. The necessary data on Greifensee are given in P 6.4. Use $Q^{\text{ex}} = 0.375 \times 10^6 \text{ m}^3 \text{ d}^{-1}$ for the exchange rate of water across the thermocline (see Eq. 6-16).

P 6.8* Nonlinear Biodegradation in a Reactor

A chemical is continuously added to a well-mixed reactor (input concentration C^{in} , water throughflow rate Q , reactor volume V). The chemical is biodegraded and also flushed into the outlet of the reactor. If the concentration of the chemical in the reactor

becomes too large, biodegradation halts. The degradation rate can be approximated by:

$$\left(\frac{dC}{dt}\right)_{\text{biodegradation}} = \begin{cases} k_r C \left(1 - \frac{C}{C_{\text{crit}}}\right) & \text{if } 0 \leq C \leq C_{\text{crit}} \\ 0 & \text{if } C > C_{\text{crit}} \end{cases}$$

(a) Write down the dynamic equation of the system and calculate all steady-state concentrations by setting the left-hand side of the equation zero and solve the resulting algebraic expression for C . Use the numbers of the parameters listed on the margin. *Hint: Do not forget the effect of the inflow and outflow on the mass balance of the chemical in the reactor.*

Reactor characteristics

$$V = 900 \text{ L}$$

$$Q = 100 \text{ L h}^{-1}$$

$$k = 0.5 \text{ h}^{-1}$$

$$C_{\text{crit}} = 100 \text{ mg L}^{-1}$$

$$C^{\text{in}} = 110 \text{ mg L}^{-1}$$

(b) In case there are several steady states, to which steady state does the system move? *Hint: Make a qualitative analysis by just looking at the size of dC/dt for different C -values.*

(c) What happens with C when the input concentration C^{in} is either increased to 150 mg L^{-1} or lowered to 50 mg L^{-1} ?

P 6.9 Diffusive Fluxes and Concentration Changes

Consider the concentration profile $C(x) = C_0 e^{-ax}$ along the positive x -axis ($0 \leq x < \infty$), where C_0 and a are constant positive parameters. (a) Calculate the size and direction of the diffusive flux as a function of x produced by the constant diffusivity D . (b) Calculate the corresponding *in situ* concentration change, $\partial C/\partial t$, due to diffusion.

$$\begin{aligned} \text{Numbers: } C_0 &= 1 \text{ mmol L}^{-1} \\ a &= 0.02 \text{ m}^{-1} \\ D &= 1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1} \end{aligned}$$

Evaluate flux F and concentration change, $\partial C/\partial t$, at $x = 0, 10 \text{ m}, 100 \text{ m}, 1 \text{ km}$.

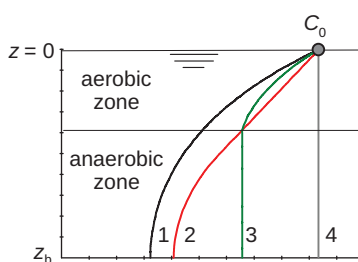
P 6.10 Diffusive and Advective Fluxes

Consider the same profile as in P 6.9. In addition to diffusion, an advective velocity, v , acts on the profile. (a) Calculate the corresponding additional contributions to the flux F and the concentration change, $\partial C/\partial t$. (b) Determine the relation between v and the other parameters (D, a, C_0) such that the profile given in P 6.9 for the range $0 \leq x < \infty$ corresponds to a steady state. Is such a steady state possible if $v > 0$?

Note: The solution to Problem 6.10b may yield a velocity $v(x)$ that varies along the x -axis. For incompressible flow (water is hardly compressible), $v(x)$ cannot vary with x if the flow is one-dimensional, yet in two or three dimensions this is possible.

P 6.11 * Diffusion and Reaction in a Lake's Water Column

The measurement of four different volatile chemicals in a lake results in distinct vertical steady-state concentration profiles (see the following figure). Based on physics and chemistry studies of the lake, the following simplifying assumptions can be made: (a)



vertical transport of the chemical is by turbulent diffusion with an approximate constant diffusion coefficient, D , while the mean vertical advection velocity, v_z , is zero; (b) the lake consists of an oxic upper layer and an anoxic lower layer; (c) all chemicals enter the lake by air–water exchange at the water surface and are at equilibrium with the constant air concentrations; and (d) the lake bottom acts like an impermeable boundary, that is, the chemicals can neither enter the sediment column nor is there any flux out of the sediment.

The four chemicals A, B, C, and D have the following specific properties: A is not reactive at all in the water; B is degraded in the anoxic part by a first-order reaction but is nonreactive in the oxic layer; C is degraded by a first-order reaction in the oxic layer but nonreactive in the anoxic layer; and D is degraded in both layers by a first-order reaction with an equal rate constant in both layers.

Identify the concentration profiles of the four different volatile chemicals A to D marked in the figure (in margin) by 1, 2, 3, and 4. Derive an analytical solution for the curves of chemical A and D.

P6.12* *Tetrachloroethene (PCE) in Mystery Lake*

In Boxes 6.3 and 6.6, we discussed two different models to describe and interpret the PCE concentrations measured in Mystery Lake (Fig. 6.2). A third model could describe Mystery Lake as a multi-box model (Fig. 6.3, Model C). Given the number of samples taken in the vertical profile (15 samples, spaced 2.5 meters), the best we can do is to develop a 15-box model consisting of 13 layers, each 2.5 m thick, and a top and bottom layer, each only 1.25 m thick. In the following questions, you are asked to analyze the situation qualitatively. For quantitative solutions, you need a computer and the appropriate software tools. (a) Develop a 15-box model for PCE in Mystery Lake. Assume that PCE is conservative in the water column and that inlets, outlets, and air–water exchange affect the top layer only. (b) What is the problem with such a general model? What kind of additional assumptions (e.g., regarding vertical mixing) have to be made in order to get reasonable results? (c) How does the model change if it is assumed that all the inlets enter the lake at 9 m depth while the outflow occurs from the top layer? (d) Should lake bathymetry, specified by the depth-depending lake cross-section $A(z)$, be taken into account to answer the above questions? If yes, how?

P6.13* *Vertical Distribution of Dichlorodifluoromethane (CFC-12) in a Small Lake*

Dichlorodifluoromethane (CCl_2F_2 , CFC-12) enters a small lake (surface area $A_0 = 2 \times 10^4 \text{ m}^2$, maximum depth $z_m = 10 \text{ m}$) from the atmosphere by air–water exchange. The top 2 m of the lake are well mixed. Vertical turbulent diffusivity between 2 and 10 m is estimated to be $E_z = 1 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$. Groundwater infiltrates at the bottom of the lake adding fresh water at the rate of $Q_{\text{gw}} = 100 \text{ L s}^{-1}$. The only outlet of the lake is at the surface. The CFC-12 concentration in the mixed surface water is $C_0 = 10 \times 10^{-12} \text{ mol L}^{-1}$ and below the detection limit in the infiltrating groundwater.

(a) Write down the appropriate one-dimensional equation and calculate the eigenvalues λ_1 and λ_2 (Box 6.4, Eq. 3), the Damköhler Number Da , and the Peclet Number Pe in order to sketch the shape of the vertical profile of CFC-12 between 2 and 10 m

depth at steady state provided that all relevant processes (turbulent mixing, discharge rate of groundwater, and mixed-layer concentration) remain constant.

(b) Estimate how long it would take for the profile to reach steady state.

(c) Somebody claims that CFC-12 might not be stable in the water column. To check this possibility, you compare your model with a vertical CFC-12 profile measured in the lake. How big would a hypothetical first-order reaction rate constant, k , have to be in order to be detected by your model? Assume that the absolute accuracy of your CFC-12 analysis is $\pm 10\%$. Hint: The non-dimensional numbers Da and Pe may help.

Note: Disregard the depth-dependent cross section of the lake. Assume that the area of the lake is A_0 at all depths.

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