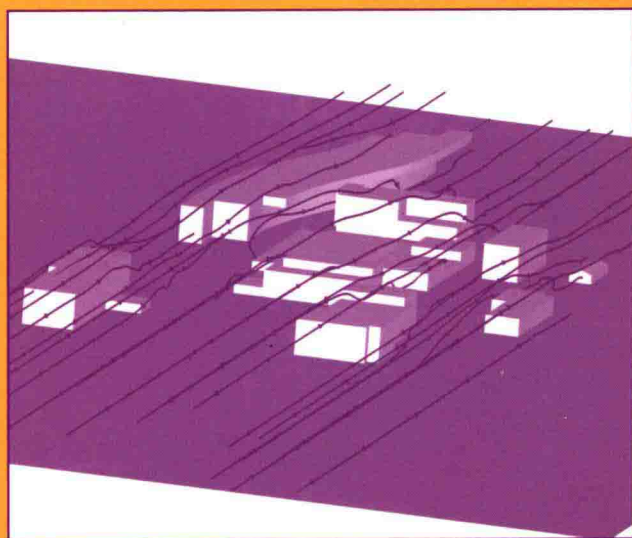


Introduction to Chemical Transport in the Environment



John S. Gulliver

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INTRODUCTION TO CHEMICAL TRANSPORT IN THE ENVIRONMENT

Estimating the transport and fate of chemicals released into the environment is an interesting and challenging task. The global environment is large on the chemical transport and fate scale. This text applies the mathematics of diffusion, turbulent diffusion, and dispersion to the atmosphere, lakes, rivers, groundwater, and oceans, as well as transport between these media. The book follows a new educational paradigm of textbooks, in that it is based on examples and case studies. The required theory is explained as a technique for solving the case studies and example problems. A large portion of the book is dedicated to examples and case studies, from which the important principles are derived.

Dr. John S. Gulliver is the Joseph T. and Rose S. Ling Professor of Civil Engineering in the Department of Civil Engineering at the University of Minnesota, with an educational background in chemical engineering and civil engineering. His major engineering interests are in environmental fluid mechanics, chemical transport in environmental systems, and flow and chemical transport at hydraulic structures, on which he has published 98 peer-reviewed articles. He has investigated the measurement and prediction of air–water mass transfer at hydraulic structures, in river systems, at aerating hydroturbines, and in sparged systems and membrane aeration in reservoirs. He has investigated turbulent mixing and dispersion in lakes, reservoirs, and rivers and the fate and transport of a spilled nonaqueous phase liquid. He has developed numerical models to predict chemical and thermal transport and fate in rivers, reservoirs, and lakes. Dr. Gulliver has also advised on the efforts to reduce dissolved nitrogen concentrations downstream of dam spillways, consulted on techniques to remediate low dissolved oxygen concentrations that can occur in hydroelectric releases, and worked on forensic analysis of water quality problems that occur during operation of power facilities. He is co-editor of the *Hydropower Engineering Handbook*, *Air–Water Mass Transfer: Selected Papers from the Second International Symposium on Gas Transfer at Water Surfaces*, and *Energy and Sustainable Development Sub-Theme D, Proceedings of the 27th Congress of the International Association for Hydraulic Research*. He is currently the Coordinator of the Hydropower Institute. Dr. Gulliver received the Rickey Medal in 2003 from the American Society of Civil Engineers. He has been a visiting professor at the University of Karlsruhe, the University of São Paulo–São Carlos, Louisiana State University, and the University of Chile, where he served as a Fulbright Scholar. He also served as a visiting research scientist at the Waterways Experiment Station of the U.S. Army Corps of Engineers.

Preface

This book is written as a text and reference for motivated seniors and first- or second-year graduate students in the area of chemical transport in the environment. The students in environmental sciences and engineering programs generally come from various backgrounds, such as chemical, civil, and mechanical engineering; chemistry; physics; biology; and environmental science. Courses are needed that focus on fundamentals of the environmental field, in this case environmental transport.

Emphasis is placed on developing the perspective and tools that will help students through graduate school and beyond. The diffusion equation is prevalent throughout environmental science and engineering, formulated to determine diffusion, turbulent diffusion, and dispersion of chemicals, in addition to convection. Learning about tools to solve this equation for different applications or boundary conditions is a task best undertaken early in one's career.

Without an environmental application, the material in this text may be perceived as dry and tedious. For that reason, much of the development of solution techniques is contained in examples of applications to environmental transport. Chapter 2, titled "The Diffusion Equation," is essential to the remainder of the text, which uses the examples provided in Chapter 2 to further develop solutions for other applications.

There are three reasons to develop analytical solutions to the diffusion equation during this age of numerical solutions. First, numerical solutions do not provide a good physical understanding of how diffusion works and what diffusion is. The insight gained through a serious study of the diffusion equation is difficult to achieve through another means. Second, it is handy to be able to perform back-of-the-envelope solutions to determine if a detailed numerical solution is justified. This can save a great deal of time. Third, numerical solutions are far from perfect. In fact, they are always wrong due to the need to discretize the solution domain into well-mixed cells in which the computer can add, subtract, multiply, and divide numbers to find an approximate solution to our boundary conditions. The question is not "what is the acceptable error" but "what is the error" in a numerical solution. The answer is best determined through developing an analytic solution to the diffusion equation with boundary conditions that are close to the application of interest and then solving the

same problem computationally. The difference between the two is the true error in the numerical solution. At that point, a decision can be made about what error is acceptable.

This text is therefore designed to develop insight into the diffusion, turbulent diffusion, and dispersion problems that present themselves in chemical transport through the environment. It is also designed to provide skills that can be used to develop quick solutions to simplified boundary conditions for environmental transport problems. Finally, it is designed to test and verify computational solutions to the diffusion equation in situations that are similar to those to be modeled computationally.

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1 The Global Perspective on Environmental Transport and Fate

Estimating the transport and fate of chemicals released into the environment is an interesting and challenging task. The environment can rarely be approximated as well mixed, and the chemicals in the environment often are not close to equilibrium. Thus, chemical transport and fate in the environment require a background in the physics of fluid flow and transport, chemical thermodynamics, chemical kinetics, and the biology that interacts with all of these processes. We will be following chemicals as they move, diffuse, and disperse through the environment. These chemicals will inevitably react to form other chemicals in a manner that approaches – but rarely achieves – a local equilibrium. Many times these reactions are biologically mediated, with a rate of reaction that more closely relates to an organism being hungry, or not hungry, than to the first- and second-order type of kinetics that we were taught in our chemistry courses.

To which environmental systems will these basic principles be applied? The global environment is large, on the chemical transport and fate scale. We will attempt to apply the mathematics of diffusion techniques that we learn to the atmosphere, lakes, rivers, groundwater, and oceans, depending on the system for which the material we are learning is most applicable. To a limited extent, we will also be applying our mathematics of diffusion techniques to transfer between these media. Volatilization of a compound from a water body, condensation of a compound from the air, and adsorption of a compound from a fluid onto a solid are all interfacial transport processes. Thus, the transport and fate of chemicals in the environmental media of earth, water, and atmosphere will be the topic. In this text, we will attempt to formulate transport and fate problems such that they can be solved, regardless of the media or the transport process, through the mathematics of diffusion.

A. Transport Processes

A transport process, as used herein, is one that moves chemicals and other properties of the fluid through the environment. *Diffusion* of chemicals is one transport process, which is always present. It is a spreading process, which cannot be reversed

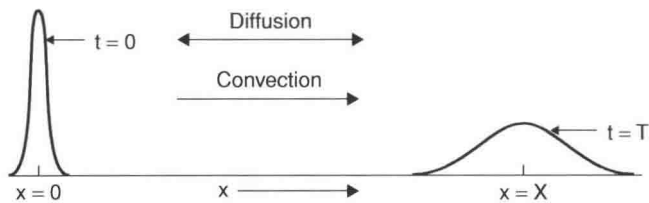


Figure 1.1. Illustration of convection and diffusion of a chemical cloud along the x -space coordinate (x -axis).

(without the involvement of another media such as in reverse osmosis). *Convection* or *advection* is the transport of chemicals from one place to another by fluid flow. The convection and diffusion of a chemical cloud, as represented in Figure 1.1, are the movements of the cloud and spreading of the cloud over time.

Turbulent diffusion is actually a form of advection, but the turbulent eddies tend to mix fluid with a random characteristic similar to that of the diffusion process, when viewed from enough distance. The representation given in Figure 1.1 could also be used to represent convection and turbulent diffusion, except that the pace of turbulent diffusion is normally more than one order of magnitude greater than diffusion. This higher pace of turbulent diffusion means that diffusion and turbulent diffusion do not normally need to be considered together, because they can be seen as parallel rate processes, and one has a much different time and distance scale from the other. If two parallel processes occur simultaneously, and one is much faster than the other, we normally can ignore the second process. This is discussed further in Section 1.D.

Dispersion is the combination of a nonuniform velocity profile and either diffusion or turbulent diffusion to spread the chemical longitudinally or laterally. Dispersion is something very different from either diffusion or turbulent diffusion, because the velocity profile must be nonuniform for dispersion to occur. The longitudinal dispersion of a pipe flow is illustrated in Figure 1.2. While there is diffusion of the chemical,

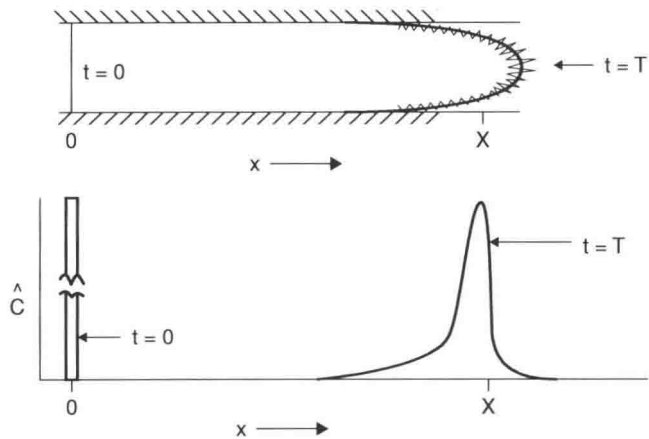


Figure 1.2. Illustration of longitudinal dispersion of a tracer “plane” at $t = 0$ to a dispersed “cloud” at $t = T$. \hat{C} is the cross-sectional mean concentration.

the nonuniform velocity profile creates a dispersion that is much greater than would occur with diffusion alone. The other important difference is that *dispersion reflects the spreading of a cross-sectional mean concentration*, while diffusion represents the spreading of a local concentration. In some contexts, typically in atmospheric applications, turbulent diffusion is also considered to be a form of dispersion. This is only a semantic difference, and herein we will continue to distinguish between turbulent diffusion and the dispersion of a mean concentration.

Interfacial transfer is the transport of a chemical across an interface. The most studied form of interfacial transfer is absorption and volatilization, or condensation and evaporation, which is the transport of a chemical across the air–water interface. Another form of interfacial transfer would be adsorption and desorption, generally from water or air to the surface of a particle of soil, sediment, or dust. Illustration of both of these forms of interfacial transfer will be given in Section 1.D.

Finally, there is *multiphase transport*, which is the transport of more than one phase, usually partially mixed in some fashion. The settling of particles in water or air, the fall of drops, and the rise of bubbles in water are all examples of multiphase transport. Figure 1.3 illustrates three flow fields that represent multiphase transport.

Mass transport problems are solved with the *diffusion equation*, often represented as

$$\frac{\partial C}{\partial t} + \underset{1}{u} \frac{\partial C}{\partial x} + \underset{2}{v} \frac{\partial C}{\partial y} + w \frac{\partial C}{\partial z} = D \left[\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2} \right] + S \quad (1.1)$$

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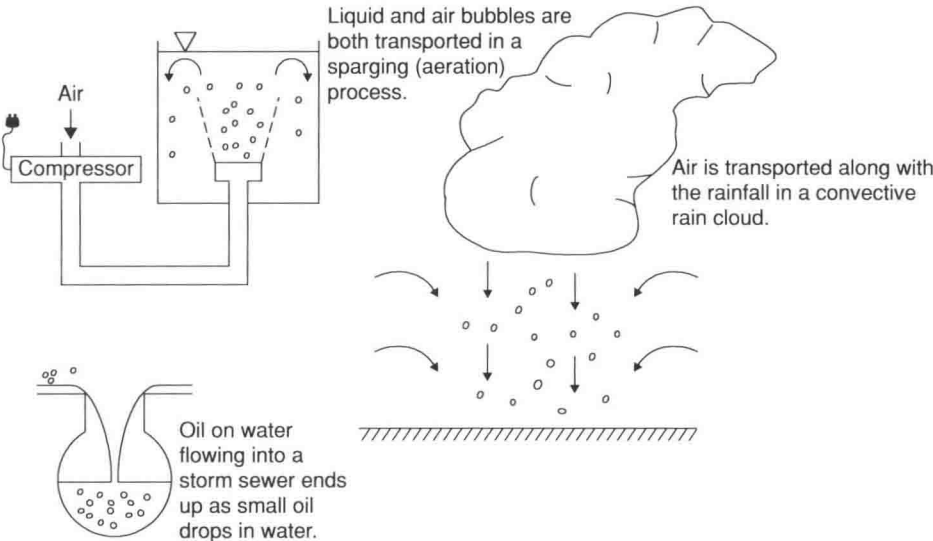


Figure 1.3. Illustration of multiphase transport. In these cases, air bubbles create a water flow and rain drops create an air flow. The oil drops do not have a significant rise or fall velocity in water and are simply transported.

where C is the concentration of a chemical; t is time; u , v , and w represent the temporal mean velocity in the x , y , and z directions, respectively; and D represents a diffusion coefficient. The first term (1) on the far left of equation (1.1) represents the rate of accumulation of chemical concentration. The second terms (2) represent the mean convection of the chemical. The third terms (3), to the right of the equal sign, represent either diffusion or turbulent diffusion of the chemical. The fourth term (4) represents the multitude of reactions that are possible in a fluid in environmental media.

We will be solving equation (1.1), or a similar equation, for various applications.

B. Chemical Fate

Chemical fate is the eventual short-term or long-term disposition of chemicals, usually to another chemical or storage. Some examples that fit the concept of short-term and long-term fate are given in Table 1.1. If a polychlorinated biphenol (PCB) compound is in groundwater, the media are soil and water. The short-term fate will be that the PCB will primarily adsorb to the soil. The long-term fate is that the chemical will desorb, when the PCB-laden water has left, and eventually be bioremediated by microbacteria looking for carbon sources. If this PCB is in the atmosphere, it will be adsorbed primarily to aerosols and particles in the short term, whereas its long-term fate will probably be photocatalyzed degradation.

There are as many or more examples of short-term and long-term fate as there are chemical-media combinations. An important consideration for this topic is whether we are interested in short-term or long-term fate. This is often a question to be answered by toxicologists. We will, for example, take the results of their computations and experiments and track the more toxic forms of a spill. Sometimes this involves a short-term fate, and sometimes this involves a long-term fate. The time scale of the calculations is important in determining how we deal with the problem or how we set up our solution.

Table 1.1: *Examples of short-term and long-term fates*

Chemical	Media	Short-term fate	Long-term fate
PCB	Soil and water	Adsorbed to soil	Biomediated degradation
PCB	Atmosphere	Adsorbed to aerosols	Photocatalyzed degradation
CO ₂	Water	Reactions to carbonate and bicarbonate	Photosynthesis to oxygen and biomass
Benzene	Water	Adsorbed to suspended particles	Bioremediated degradation
Ammonia	Soil and water	Reaction to ammonium	Bioremediated degradation to nitrogen

PCB, polychlorinated biphenyl.

C. The Importance of Mixing

Mixing is a rate-related parameter, in that most rates of reaction or transport are dependent on mixing in environmental systems. When mixing is dominant (the slowest process), the first-order rate equation can be described as

$$\text{Rate of process} = \text{Mixing parameter} \times \text{Difference from equilibrium} \quad (1.2)$$

Thus, we need two items to compute the rate of the process: the equilibrium concentrations for all species involved and the mixing rate parameter. A common example would be dissolved oxygen concentration in aquatic ecosystems.

One of the most common chemicals of concern in water bodies is oxygen. Without sufficient oxygen, the biota would be changed because many of the “desirable” organisms in the water body require oxygen to live. The rate of oxygen transfer between the atmosphere and a water body is therefore important to the health of the aquatic biota. For air–water oxygen transfer, equation (1.2) can be formulated as

$$\frac{dM}{dt} = K_L A \left(\frac{C_a}{H} - C \right) \quad (1.3)$$

where dM/dt is the rate of mass transfer into the water, K_L is a bulk oxygen transfer coefficient, A is the surface area for transfer, C_a is the concentration of oxygen in the air, H is a coefficient that partitions oxygen between the air and water at equilibrium (called Henry’s law constant for liquid and gas equilibrium), and C is the concentration of oxygen in the water. Air is approximately 20.8% oxygen, so the concentration of oxygen in the atmosphere is determined primarily by atmospheric pressure. Henry’s law constant for oxygen is a function of pressure as well as temperature. Thus, the equilibrium concentration of oxygen is influenced by the thermodynamic variables: pressure and temperature. The rate parameter is $K_L A$, which has units of volume per second. The difference from equilibrium partitioning is represented by $C_a/H - C$. It is C that we typically need to bring as close to equilibrium with the atmosphere as possible, and the means to do it is by having a large dM/dt . This usually means a large $K_L A$ because it would be difficult to alter either C_a or H in the atmosphere. While the surface area is often established by the boundary conditions, K_L is determined by turbulence and diffusion coefficient (i.e., mixing) close to the water surface and represents the rate of mixing per unit surface area. Thus, the primary variable that can be changed in order to increase dM/dt is the mixing parameter represented by K_L . Some further examples of mixing rate and equilibrium parameters in environmental processes are given in Table 1.2.

D. Resistance to Transport

An important concept for environmental transport is *resistances*. The inverse of a rate parameter is a resistance to chemical transport. Or, in equation form:

$$1/\text{Rate parameter} = \text{Resistance to chemical transport} = R \quad (1.4)$$

Table 1.2: *Examples of important mixing rate and equilibrium parameters in environmental process*

Process	Mixing rate-related parameter	Equilibrium parameter
1. Treatment Processes		
Coagulation/flocculation	Size of coagulation and flocculation basins and proper mixing (residence time)	Dose of coagulants (alum)
Softening	Design of softening tank to increase mixing	Dose of softening agent (lime)
Settling	Design of settling basin to reduce mixing	→ 0
Chlorination	Design of chlorination and dechlorination chambers for proper mixing and residence time	Dose of chlorine
Filtration	Size of filter bed	Length of time before backflushing
2. Surface Waters		
Oxygen transfer	Diffusion and turbulent mixing	Atmospheric concentration of oxygen and Henry's law constant
Volatilization of pollutants	Diffusion and turbulent mixing	→ 0
Toxic spills	Diffusion and turbulent mixing	Spill-water equilibrium
Internal loading of nutrients	Hypolimnetic mixing	Oxygen concentration in hypolimnion
Sorption onto suspended sediments	Turbulent mixing exposes chemicals to sediment	Sediment–water partitioning
3. Atmosphere		
Greenhouse gases (CO ₂ , CH ₄)	Turbulent mixing	Atmospheric concentrations
Volatilization of spills	Turbulent mixing–dispersion	→ 0
Aerosols	Turbulent mixing – dispersion – settling	None
4. Groundwater and Sediments		
Spills	Advection – dispersion	→ 0
Oxygen	Diffusion – advection	Atmospheric concentration of oxygen
Sorption of soil	Advection – diffusion	Equilibrium soil–water partitioning

Figure 1.4 gives an example of the adsorption of a compound to suspended sediment, modeled as two resistances in series. At first, the compound is dissolved in water. For successful adsorption, the compound must be transported to the sorption sites on the surface of the sediment. The inverse of this transport rate can also be considered as a resistance to transport, R_1 . Then, the compound, upon reaching the surface of the suspended sediment, must find a sorption site. This second rate parameter is more related to surface chemistry than to diffusive transport and is considered a second resistance, R_2 , that acts in series to the first resistance. The second resistance cannot

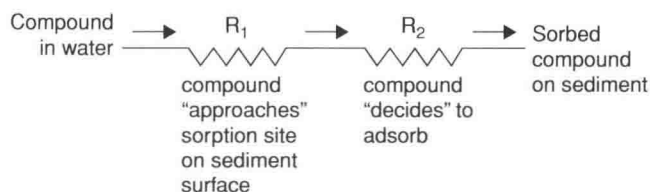


Figure 1.4. Adsorption analogy to two resistors in a series: adsorption of an organic compound to sediment.

occur without crossing the first resistance of transport to the sorption site; so, they must occur in series.

Now, if R_1 is much greater than R_2 , we can assume that R_2 is zero without compromising the accuracy of the rate calculation. In electric circuits, two resistances applied in series are simply added together in calculating the line resistance. The same is true for resistance to chemical transport. If R_1 is 1,000 resistance units and R_2 is 1 resistance unit, we can ignore R_2 and still be within 99.9% of the correct answer. For most environmental transport and fate computations, it is sufficient to be within 99.9% of the correct answer.

Another example is the air–water transfer of a compound, illustrated in Figure 1.5. This example will be used to explain volatile and nonvolatile compounds. There is resistance to transport on both sides of the interface, regardless of whether the compound is classified as volatile or nonvolatile. The resistance to transport in the liquid phase is given as $R_L = 1/K_L$. If we are describing chemical transfer through an equation like (1.3), the resistance to transfer in the gas phase is given as $R_G = 1/(HK_G)$. The equilibrium constant is in the R_G equation because we are using the equivalent water side concentrations to represent the concentration difference from

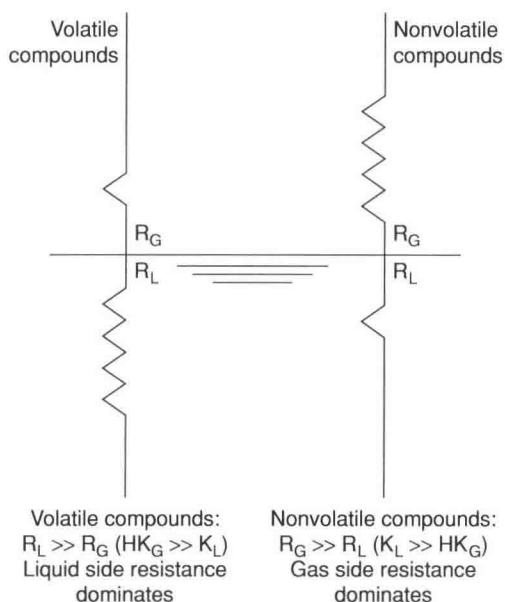


Figure 1.5. Air–water transfer analogy to two resistors in a series.

equilibrium, and the gas phase resistance needs to be a resistance to an equivalent water concentration.

The gas phase and the liquid phase resistances are applied in series. In general, gas film coefficients are roughly two orders of magnitude greater than liquid film coefficients. It is also true that Henry's law constant, H , varies over many orders of magnitude as the transported compounds are varied. Nitrogen gas, for example, has a Henry's law constant of approximately 15, using mass concentrations. The herbicide atrazine has a Henry's law constant of 3×10^{-6} . Thus, the ratio R_G/R_L would vary by seven orders of magnitude between nitrogen gas and atrazine (see Appendix A-5).

If we put these orders of magnitude into a series resistance equation

$$R = R_L + R_G = \frac{1}{K_L} + \frac{1}{HK_G} \quad (1.5)$$

Because of Henry's law constants, we can see that, for nitrogen gas, $R \cong R_L$, and for atrazine, $R \cong R_G$. If the ratio of $K_G/K_L \sim 100$ is applied (Mackay and Yuen, 1983), $R_G = R_L$ when $H = 0.01$.

Now, the mass transfer between phases is given as

$$\frac{dM}{dt} = \frac{A}{R} \left(\frac{C_a}{H} - C \right) \quad (1.6)$$

or

$$\frac{dM}{dt} = \frac{A}{\frac{1}{K_L} + \frac{1}{HK_G}} \left(\frac{C_a}{H} - C \right) \quad (1.7)$$

Nitrogen gas would be a volatile compound, because the equilibrium is strongly to the gas phase, and there is little gas phase resistance to its transfer (that is, $1/K_L \gg 1/(HK_G)$). For that reason, nitrogen is generally called a gas, as are many other volatile compounds, such as methane, oxygen, and propane.

Atrazine, however, would be a nonvolatile compound – $1/(HK_G) \gg 1/K_L$ – because equilibrium is strongly to the liquid phase due to the small Henry's law constant. There is also a strong gas phase resistance to the transfer. Atrazine was manufactured to remain in the liquid phase, where it will act as a herbicide, rather than in the gas phase, where farm personnel will be breathing this toxic chemical. If you were going to pick a compound that is *not* made by humans from the list of those that are a gas or liquid in our environment, a good guess is that it would be a volatile or semivolatile compound. There are only a few nonionic environmental compounds that are nonvolatile. Remarkably, one of them is water. While the atmosphere may be as much as 3% water, the water bodies in the world are very close to 100% water. The equilibrium is strongly to the liquid side because of the small Henry's law constant.

One theme of this discussion can now be stated as follows: when transport processes occur in series, it is the slower transport processes that are important for chemical transport calculations, because the *resistance* to transport is large, just as the large resistors of a series in an electronic circuit are the most important.

Now we are ready for the second theme: when transport processes *occur in parallel*, the fast transport process with the low resistance dominates. The result is the