CONTAMINANT FATE AND TRANSPORT PROCESS

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Keywords: chemical fate, physical transport, chemical transport, transformation, surface waters, subsurface environment, atmosphere, biodegradation, biotransformation, photodegradation, hydrolysis.

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Summary

It is imperative that modern societies understand their environment in sufficient detail so that accurate assessments can be made about the environmental behavior and effects of chemicals that they use. This includes an understanding of both chemical transport and chemical reactions. This will protect both human health and the environment, while allowing human beings to enjoy the benefits of modern technology.

This article presents the principles that govern the fate and transport of many classes of chemicals in three major environmental media: surface waters, soil and groundwater (the subsurface), and the atmosphere. Although each medium has its distinct characteristics, there are also many similarities among them. Few chemicals are restricted in their movement to only one medium; thus chemical exchanges among the media must be

considered.

Despite their enormous variability, surface waters share many common features, including an interface with the atmosphere, a sediment layer capable of both retaining and releasing chemicals, active communities of living organisms, and the presence of sunlight. Through knowledge of these and other aspects of surface waters, it is possible to make reasonable judgments about the expected behavior of individual chemicals in specific surface water ecosystems.

Transport in the subsurface environment is slow compared with the other environmental media. Many organic compounds that would rapidly volatilize into the atmosphere from surface waters may reside in groundwaters for decades or longer. The subsurface environment also shares many processes with surface waters. Microbially mediated redox reactions and biodegradation processes are significant in each medium. The presence of particles, and their potential to absorb chemicals, also is common to both surface waters and groundwaters; when modeling surface transport, the high ratio of solid material to water requires special recognition of even moderate sorbing tendencies.

Chemical transport in the atmosphere has many parallels with transport in water; both advection and Fickian processes are important. However, the velocities and the Fickian transport coefficients tend to be larger in the atmosphere, and the distances over which pollutant sources have influence can be greater. Atmospheric chemical processes are dominated by the photochemical; biota, which compete with photochemistry as agents of chemical transformation in surface waters, are few in the air. Also light intensities in the atmosphere are higher than those in surface waters, and the presence of ultraviolet light of shorter wavelengths contributes to an expanded suite of photochemical reactions that may occur.

1. Introduction

Today, not only have the gross pollution effects of emissions from stacks, pipes, and dumps become evident, but more subtle and less predictable effects of chemical usage and disposal have also manifested themselves. Nevertheless, it is neither possible nor desirable for modern societies to stop all usage or environmental release of chemicals. Even in prehistoric times, tribes of troglodytes roasting hunks of meat over their fires were unknowingly releasing complex mixtures of chemicals into the environment. It is imperative, however, that modern societies understand their environment in sufficient detail so that accurate assessments can be made about the environmental behavior and effects of chemicals that they use. This includes an understanding of both chemical transport, referring to processes that move chemicals through the environment, and chemical fate, referring to the eventual disposal—either destruction or long-term storage—of chemicals. This will protect both human health and the environment, while allowing human beings to enjoy the benefits of modern technology.

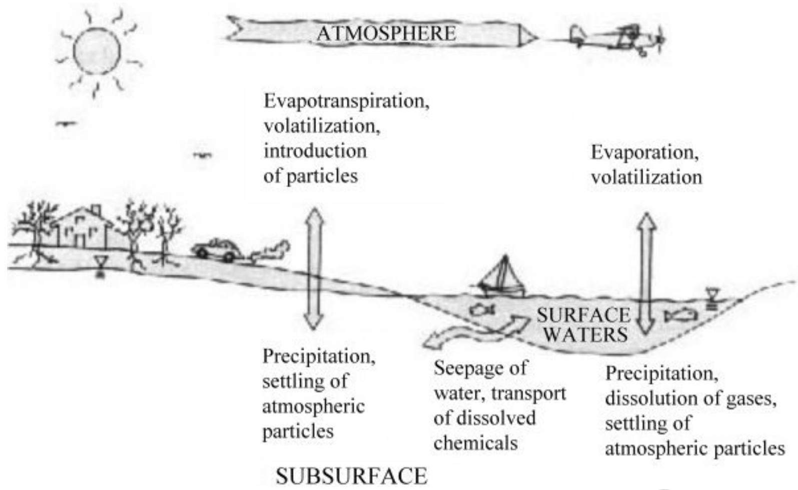

Figure 1. Three major environmental media
Source: Hemond H. and Fechner-Levy E. (2000). Chemical Fate and Transport in the Environment (Second Ed.).
San Diego: Academic Press.

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Knowledge of the principles underlying the fate and transport of chemicals in the environment allows problems ranging from local to global scales to be defined and analyzed. This first section presents fundamental concepts that apply universally to any environmental medium. The subsequent three sections focus on surface waters, the subsurface environment, and the atmosphere, respectively; see Figure 1 for a diagram of some of the interrelationships among these media. Because models of chemical fate and transport are necessary to compute the dose (concentration), frequency, and duration of chemical exposure to aquatic biota and humans, we will demonstrate briefly how to develop and solve mathematical models for a wide variety of chemical pollutants.

1.1. Chemical Concentration

Perhaps the single most important parameter in environment fate and transport studies is chemical *concentration* (C). The concentration of a chemical is a measure of the amount of that chemical in a specific volume or mass of air, water, soil or other material. Not only is concentration a key quantity in fate and transport equations; a chemical's concentration in an environmental medium also in part determines the magnitude of its biological effect.

Most laboratory analysis methods measure concentration. The choice of units for concentration depends in part on the medium and in part on the process that is being measured or described. No matter which units are used, however, concentration is the relevant measure for predictions of the effect of a chemical on an organism or the environment. Concentration is also critical in one of the most important concepts of environmental fate and transport: the bookkeeping of chemical mass in the environment.

1.2. Mass Balance Approach

Three possible outcomes exist for a chemical present at a specific location in the environment at a particular time: the chemical can remain in that location, can be carried elsewhere by a transport process, or it can be eliminated through transformation into another chemical. This very simple observation is known as *mass balance*. Mass balance is a concept around which an analysis of the fate and transport of any environmental chemical can be organized. Mass balance also serves as a check on the completeness of knowledge of a chemical's behavior.

The key elements in a mass balance are:

- a clearly defined control volume
- a knowledge of inputs and outputs which cross the boundary of the control volume
- a knowledge of the transport characteristics within the control volume and across its boundaries
- a knowledge of the reaction kinetics within the control volume

A control volume can be as small as an infinitesimal thin slice of water in a swiftly flowing stream or as large as the entire body of oceans on the planet earth. The important point is that the boundaries are clearly defined with respect to their location (element i) so that the volume is known and mass fluxes across the boundaries can be determined (element ii). Within the control volume, the transport characteristics (degree of mixing) must be known either by measurement or an estimate based on the hydrodynamics of the system. Likewise, the transport in adjacent or surrounding control volumes may contribute mass to the control volume (much as smoke can travel from another room to your room within a house), so transport across the boundaries of the control volume must be known or estimated (element iii).

Knowledge of the chemical, biological, and physical reactions that the substance can undergo within the control volume (element iv) is the subject of next part of this section. If there were no degradation reactions taking place in aquatic ecosystems, every pollutant which was ever released to the environment would still be here to haunt us. Fortunately, there are natural purification processes that serve to assimilate some wastes and to ameliorate aquatic impacts. We must understand these reactions from a quantitative viewpoint in order to assess the potential damage to the environment from pollutant discharges and to allocate allowable limits for these discharges.

A mass balance is simply an accounting of mass inputs, outputs, reactions, and accumulation as described by the following equation.

$$\text{Accumulation within the control volume} = \text{Mass inputs} - \text{mass outputs} \pm \text{Reactions} \qquad (1)$$

If a chemical is being formed within the control volume (such as the combination of two reactants to form a product, $A + B \rightarrow P$), then the algebraic sign in front of the "Reactions" term is positive when writing a mass balance for the product. If the chemical is being destroyed or degraded within the control volume, then the algebraic sign of the "Reactions" term is negative. If the chemical is conservative (i.e. non-reactive or inert), then the "Reactions" term is zero.

$$\text{Accumulation} = \text{Inputs} - \text{Outputs} \pm \text{Reactions} \qquad (2)$$

If the system is at steady state (i.e. no change in concentration in the system and outputs are simply equal to inputs plus or minus reactions.

$$\text{Outputs} = \text{Inputs} \pm \text{Reactions} \qquad (3)$$

1.3. Physical Transport of Chemicals

Most physical transport of chemicals in the environment occurs in the fluids air and water. There are primarily two kinds of physical processes by which chemicals are transported in these fluids: bulk movement of fluids from one location to another, and random (or seemingly random) mixing processes within the fluids. Both types of transport processes are implicitly included in the input and output terms of Eqs. 1, 2, and 3.
The first type of process, *advection*, is due to bulk, large-scale movement of air or water, as seen in blowing wind and flowing streams. This bulk advective movement, resulting in chemical transport, passively carries a chemical present in air or water.

In the second type of transport process, a chemical moves from one location in the air or water where its concentration is relatively high to another location where its concentration is lower, due to random motion of the chemical molecules (*molecular diffusion*), random motion of the air or water that carries the chemical (*turbulent diffusion*), or a combination of the two. Transport by such random motions, also called *diffusive* transport, is often modeled as being *Fickian*. Sometimes the motions of the fluid are not entirely random; they have a discernible pattern, but it is too complex to characterize. In this situation, the mass transport process is called *dispersion*, and it is also commonly treated as a Fickian transport. In a given amount of time, the distances over which mass is carried by Fickian transport (molecular diffusion, turbulent diffusion, and dispersion) are usually not as great those covered by advection.

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Biographical Sketches

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