

Fate and Transport

Reading Packet EXA 404





EXA 404: Fate and Transport

READING PACKET

**Exposure Assessment (EXA)
Course Series**

EPA's Risk Assessment Training and Experience Program

EXA 404: Fate and Transport

The objective of this course is to give participants an overview of the factors that are important when assessing the fate of contaminants starting from their point of release until they reach “receptors” (i.e., adults, children, sensitive populations, and other exposure receptors). The important concepts of transfer of contaminants within media—advection, dispersion, and diffusion—and between media—air to soil, soil to plant, water to fish, and others—will be described to provide students a basis for later discussions on the application of environmental models. Concepts related to chemical transformation including transformation of inorganic and organic compounds and decay will also be discussed.

Table of Contents

1. Introduction to Fate and Transport.....	1
1.1 Transport	2
1.2 Transformation.....	3
1.3 Environmental and Exposure Media	3
2. Influences on Fate and Transport.....	5
2.1 Chemical Sources.....	5
2.2 Organic vs. Inorganic Chemical Contaminants.....	6
2.3 Vapor Pressure and Solubility.....	7
2.4 Contaminants for Which Physical Characteristics are Important	7
2.5 Environmental Characteristics	8
3. Physical Transport and Partitioning.....	9
3.1 Advective Transport.....	9
3.2 Diffusive and Dispersive Transport Processes.....	9
3.3 Partitioning Between Environmental Media.....	10
3.4 Partition Coefficients	10
3.5 Partitioning (and Other Transfer) into Biota.....	13
4. Chemical Transformation	14
4.1 Transformation of Organic and Inorganic Compounds	14
4.2 First-order Decay	14
5. Conclusion	16
6. References.....	17

List of Figures

Figure 1. Source-to-Effect Continuum.....	1
Figure 2. Transport: Movement Within and Between Environmental Media	2
Figure 3. Transformation: Chemical Changes within a Medium	3
Figure 4. Environmental and Exposure Media in a Hypothetical Exposure Scenario	4
Figure 5. Indoor Sources of Contaminants.....	5
Figure 6. Nanoparticles Viewed using Cryo-Electron Micrograph.....	7
Figure 7. Conceptual Illustration of Diffusion	9
Figure 8. Illustration of Henry's Law.....	11
Figure 9. Equation for First-order Decay	15

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1. INTRODUCTION TO FATE AND TRANSPORT

This course explores the major concepts behind fate and transport of chemical contaminants in the environment. Specific topics covered in this course include:

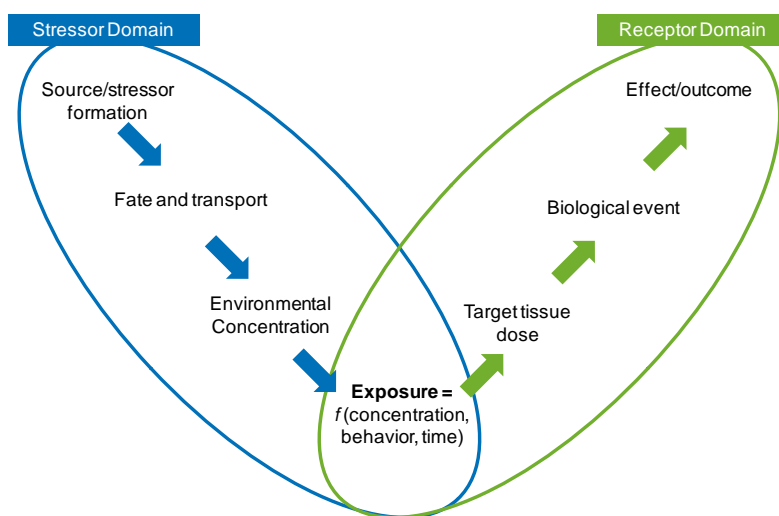
- How and why contaminant source, characteristics of the released chemical, and environmental conditions are important to fate and transport
- What can happen to a contaminant after it is released into the environment
- What chemical and physical processes are at play during contaminant movement through environmental media

The next course, EXA 405, discusses the application of these concepts in environmental monitoring and modeling. This course, like the rest of the EXA courses, is focused on chemical contaminants and does not cover nonchemical stressors such as noise and temperature.

When we perform an exposure assessment, we want to obtain the contaminant concentration at the point of contact with a receptor, in this case a human receptor. The phrase “fate and transport” refers to the processes that a contaminant undergoes between release from a source and contact with a receptor. When a contaminant is released from a source, it is subject to **transport** and **transformation** in the environment. This means, for example, that contaminants emitted from a smokestack can travel in the air and be transported by wind, fall to the ground or get washed out by rain, and accumulate in soil or surface water or on plants, where they could be taken up by animals living in the ecosystems. What begins as an airborne contaminant can end up in water, soil, or biota in the environment. The contaminants emitted from a smokestack or from cars could also be degraded, or they could be transformed through chemical reactions to entirely different substances ([U.S. EPA, 1998](#)).

The diagram in Figure 1 depicts a conceptual framework of exposure and effects beginning with release of the chemical from a source, chemical transport through environmental media, human exposure, and ultimately the effect or outcome that occurs from exposure. On the left side of this diagram, fate and transport processes “link” the formation or release of contaminants at a source with the resultant environmental concentrations to which people can be exposed. Where information is known about the source, environmental concentrations are sometimes estimated through modeling. Direct measurements of environmental concentrations or exposures can be obtained through monitoring ([Williams et al., 2010](#)).

Figure 1. Source-to-Effect Continuum



1.1 Transport

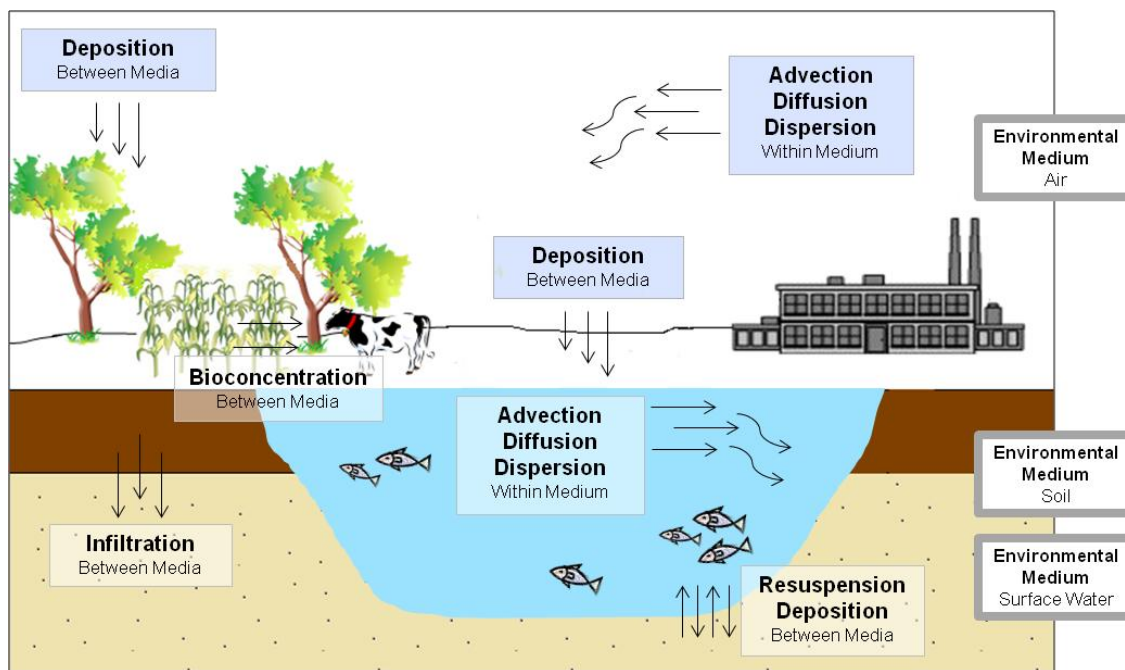
“Fate and transport” covers movement of substances in the environment and chemical reactions that affect the nature of the substance. Figure 2 shows some transport processes that might occur following release of a contaminant.

Transport can occur **within a medium**. For example, in Figure 2, the chemical released to the air is shown moving away from the stack via advective, dispersive, and diffusive processes. These same processes might also occur in the surface water. Transport can also occur at the interface **between two environmental media**. For example, chemicals present in the air as vapors or sorbed to particles can be transferred into the soil via a range of different processes occurring at and across the air-soil interface.

This brings up the concept of **equilibrium**. The addition of a chemical to a medium on one side of an interface will often result in some transfer of chemical to the medium on the other side of the interface through spontaneous chemical processes. More specifically, natural systems will have a tendency to move toward chemical equilibrium. This is an important concept because it drives many transport processes in the environment. Equilibrium is a condition where a forward reaction and the reverse of that reaction are occurring at rates where they balance each other out.

Transport of chemicals can also, of course, occur between abiotic and biotic media, as illustrated in Figure 2. In other words, people and wildlife, as part of the environment, can be exposed to chemicals released to environmental media ([Thibodeaux, 1996](#)).

Figure 2. Transport: Movement Within and Between Environmental Media



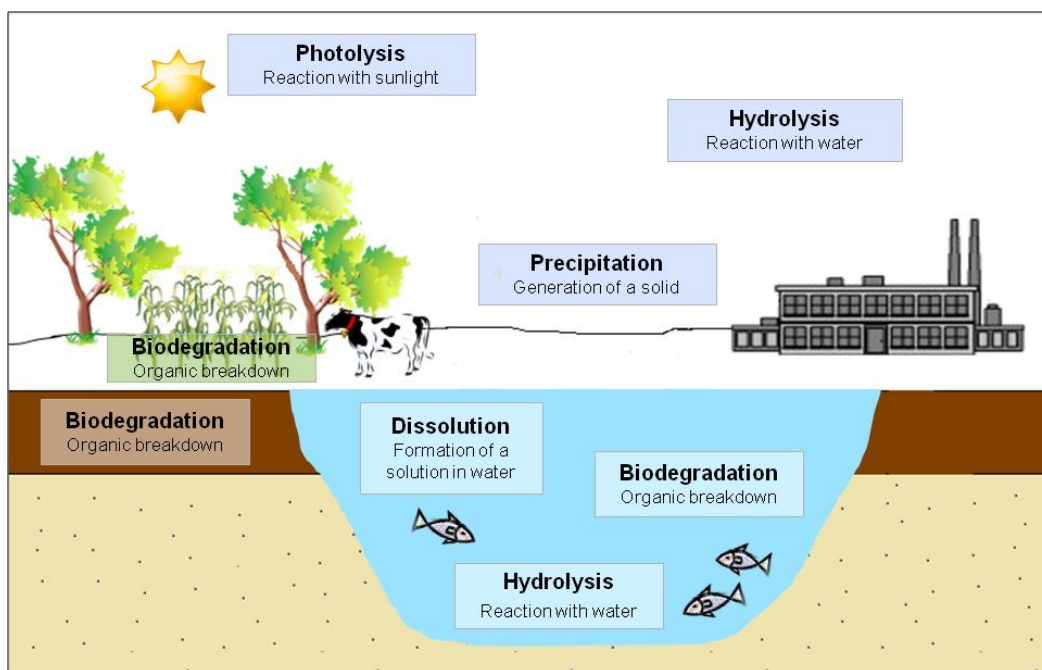
1.2 Transformation

The other part of “fate and transport” is chemical transformation of a contaminant in the environment. This is typically assumed to occur within a medium. Some of the types of transformations that can occur in the environment are shown in Figure 3.

Some transformation processes are specific to certain environmental media and depend on certain characteristics of the environment. For example, **photolysis** is a chemical process that occurs in the presence of visible light. As such, photolytic reactions do not typically occur in buried sediments where there is no light. **Hydrolysis**, a chemical process that occurs in the presence of water and results in components of the initial reactant associating with the hydrogen and hydroxide of a water molecule, is another example.

Transformation does not always mean degradation or conversion to an entirely different compound. Inorganic contaminants, such as metals and metal salts, undergo transformations that affect their physical state without changing their composition when they dissolve in water or precipitate out as solids. Speciation and complexation reactions are other important processes for inorganic chemicals. A few of the more common chemical transformation mechanisms will be covered later in this course ([Schwarzenbach et al., 2003](#)).

Figure 3. Transformation: Chemical Changes within a Medium



1.3 Environmental and Exposure Media

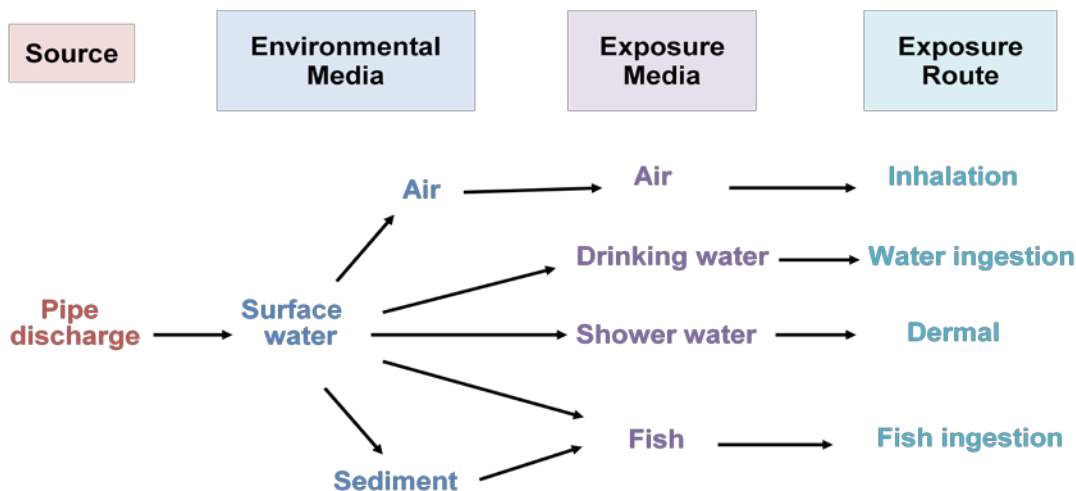
An **environmental medium** is the part, or phase, of the environment that holds a contaminant. The basic types of environmental media are soil, water (surface water and groundwater), and air; these are noted in Figure 2. The biota that reside in the environment can be considered another type of environmental medium. There are subparts to these media as well; for example, benthic sediments are an important “soil-like” medium found

below surface water. An **exposure medium** is the part of the environment that comes into contact with the receptor. Common exposure media for humans include air, water (for both drinking and showering), soil, indoor dust, and a range of plants and animals that are consumed ([U.S. EPA, 2003](#)).

Environmental media can also be exposure media, but this is not always the case. In Figure 4, water is both an environmental medium and an exposure medium. A chemical is assumed to be released from a pipe into surface water where it can be transported and perhaps transformed. So, surface water is an environmental medium. It is assumed that an individual is also drinking water that's derived from that surface water and is showering in it as well. The water being ingested and used for showering is an exposure medium. Sediment in this case would be an environmental medium only. Chemical mass released from the pipe is transported to sediment by deposition in the water column and other processes. Because we are assuming there is no direct dermal contact with the sediment, sediment is not an exposure medium in this case.

Direct exposure to chemicals can also occur through other means, such as contacting cleansers and other consumer products containing chemicals, or contacting pesticide residues on the surface of produce. Although these kinds of exposures can have an effect on public health and are therefore an important part of exposure assessment, the focus of this course is on fate and transport through environmental media. Consequently, these kinds of exposure media will not be discussed in detail.

Figure 4. Environmental and Exposure Media in a Hypothetical Exposure Scenario



2. INFLUENCES ON FATE AND TRANSPORT

Understanding where and how a contaminant is introduced to the environment provides information that can be helpful in determining where a contaminant will eventually end up. This section will review some common types of environmental sources, discuss chemical characteristics that affect how a chemical behaves once it is released into the environment, and review some of the characteristics of the environment that can influence fate and transport.

2.1 Chemical Sources

In an exposure assessment, it can often be useful to know how and where a contaminant is released. For instance, was the release a one-time event, intermittent, or a constant release over a long period of time? How much was released? What are the characteristics of the source? The answers to these questions can affect what happens to a chemical along that continuum from source to exposure and eventually to effect.

Location is often a critical component, and it is important to answer the question of “where.” In other words, to which environmental media are chemicals assumed to be released? A contaminant released directly to the air will, of course, behave differently than that same contaminant when released to surface water ([U.S. EPA, 2002](#)).

Point and Nonpoint Sources

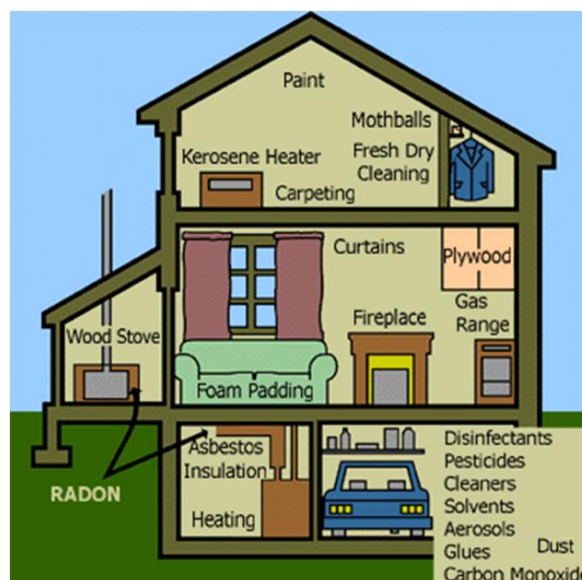
Sources of pollutants can be referred to as either **point** sources or **nonpoint** sources. A classic example of a point source is a smoke stack. The contaminant is emitted from a relatively small area, or point. In this example, the stack at the facility is a point source of emissions. The emissions are released directly to the air from the stack. Nonpoint sources are sources for which the location of release is difficult to define, perhaps because the chemical is released from many small sources or because the area from which the contaminant is released is large. Examples of nonpoint sources include automobiles in a metropolitan area and agricultural fields treated with pesticides ([Williams et al., 2010](#); [U.S. EPA, 2005b](#)).

Indoor Sources of Contaminants

We commonly think of environmental pollution as occurring outdoors. However, many contaminants enter buildings from outside or are generated inside (see Figure 5), and people spend a lot of time indoors. According to EPA’s 2011 Exposure Factor Handbook, an adult aged 18 to <65 spends on average 1,159 minutes, or a little more than 19 hours, indoors per day. An average child aged <18 spends even more time indoors per day. These estimates might differ from region to region and by season ([U.S. EPA, 2011](#)).

Indoor activities, such as cooking and heating, can add contaminants to the indoor air. Also, products brought into the home, such as furnishings, cleaning products, building materials, and personal care products can add or increase

Figure 5. Indoor Sources of Contaminants



contaminant concentrations. Outdoor pollution can also penetrate into a home; radon and ozone are examples of two pollutants formed outside the home that can travel to indoor living spaces. Radon is generated by certain types of rock and can accumulate in (or under) a home following emission from the ground. Indoor contaminants are primarily advected and dispersed on a relatively large scale by heating and air conditioning systems or natural ventilation. Contaminants can also be transported between exposure media. Dust is an important component of the indoor environment when considering potential exposures. In the case of indoor environments, carpet or dust, rather than soil or sediments, would typically be a solid exposure medium of interest ([U.S. EPA, 2008](#); [Weschler and Nazaroff, 2008](#); [ICF, 2004](#)).

Consumer Products as Sources of Contaminants

As noted previously, for certain classes of chemicals, exposures are associated with the use of consumer products rather than contact with environmental media. Examples of these include polybrominated flame retardants, plasticizers (e.g., phthalates, bisphenol A), and perfluorinated surfactants. Other contaminants are found in cleaning products, paint, degreasers and paint removers, and pesticides. Pharmaceuticals can also represent a source of exposure following use and elimination from the body or after disposal of unused drugs. Many of these chemicals comprise emerging classes of contaminants that have not historically been evaluated. Some of these are present in substances applied directly to the body, such as nanomaterials in lotions or sunscreens. Some are in direct contact with food. Others have been found at elevated concentrations in house dust, suggesting incidental ingestion might be an important exposure pathway.

Although exposure to these compounds is likely to occur, the important fate and transport processes for some of these classes of contaminants are not yet well understood. Exposure to them has been shown by their occurrence in indoor exposure media like air and house dust and in body burden measurements such as those taken from blood and urine samples ([Luoma, 2008](#); [Weschler and Nazaroff, 2008](#)).

Background Sources

Background can be important in an exposure assessment, especially for substances for which existing background levels are close to (or exceed) levels of concern. The term “background” can have different meanings. It could refer to naturally-occurring levels of a substance, such as arsenic that occurs naturally in groundwater. It could refer to exposures to contaminant concentrations that have resulted from distant sources and remained in the environment for a long period of time like PCBs, PAHs, or mercury.

In some cases, exposure resulting from one specific source, or perhaps one type of source, is all that is of interest, and background levels don’t need to be explicitly quantified. When this is the case, the assessor is only interested in what is termed the “incremental impact” from the source in question. This is the case in some exposure assessments EPA conducts for specific air toxics regulations. In other cases, the total exposure—inclusive of existing background, regardless of source—is estimated.

2.2 Organic vs. Inorganic Chemical Contaminants

Following release from a source, characteristics of the chemical of interest are important factors dictating fate and transport in the environment. One approach to categorizing environmental contaminants is as an organic or inorganic substance.

Organic compounds are carbon-based, and these include PCBs, dioxins, and many pesticides. The movement of organic contaminants through environmental media is controlled, in part, by sorption. Many organic contaminants are nonpolar and hydrophobic and, in the environment, have a strong preference to sorb to solid surfaces, such as soils and particles. In general, these contaminants are also more likely to be bioaccumulate—that is, be taken up by biota. Common **inorganic contaminants** of concern include many metals, such as cadmium, lead, and mercury, and compounds like nitrates and nitrites. These compounds are not carbon-based, and their movement through the environment is typically dictated by physical and chemical characteristics of the environment, such as soil structure and ionic transport.

Organic compounds can be chemically degraded or transformed in the environment to other compounds or to their constituent elements. Inorganic compounds can react in the environment—for instance, to a different valence state. They might also be transformed to a different inorganic species. However, the chemical element at the root of an inorganic compound cannot be degraded in the absence of radioactive decay. Knowledge of whether a contaminant of interest is organic or inorganic can be helpful in determining the dominant fate and transport mechanisms for that substance (Thibodeaux, 1996).

2.3 Vapor Pressure and Solubility

Two chemical characteristics that are important in determining chemical fate and transport are vapor pressure and water solubility. **Vapor pressure** is an indication of how likely a compound will evaporate or convert from a liquid phase to a gaseous phase. The higher a chemical's vapor pressure, the more likely that it will be found in the gas phase. **Water solubility** is a measure of the maximum amount of a chemical that will dissolve in pure water. Compounds with high solubility are likely to be mobile in the environment, given that water travels freely throughout our environment. However, these compounds are also less likely to sorb to other media or to bioaccumulate, and they are usually biodegradable. Both vapor pressure and water solubility are temperature-dependent parameters.

2.4 Contaminants for Which Physical Characteristics are Important

In some cases, we may be concerned with exposures to types of contaminants for which physical attributes are one of the most or even *the* most important defining characteristic that affects fate and transport and exposure. Two examples of such contaminant types are particulate matter and nanomaterials. For these contaminants, **size** is a critical attribute affecting their toxicity and their fate and transport.

Particles behave differently according to their size. Larger particles will tend to deposit from air faster than smaller particles due to gravitational settling. Smaller particles, particularly those less than 2.5 microns in diameter, are small enough to penetrate to the alveolar region of the lung and are associated with increased adverse health effects. Particles can also have surface coatings, which can consist of various chemical

Figure 6. Nanoparticles Viewed using Cryo-Electron Micrograph



Magenta circles are gold nanoparticles situated on an array of enzymes.

Source: Brookhaven National Laboratory.
http://www.bnl.gov/bnlweb/pubaf/pr/PR_display.asp?prID=07-73

compositions and influence particle behavior and persistence. But, this does not mean that the chemical composition of these particulates is not of concern. For example, environmental tobacco smoke is more harmful than wind-blown dust because of the chemical composition of tobacco smoke, even if the particle sizes are comparable.

Nanoparticles are a class of emerging contaminants that are not fully understood in which physical characteristics are important (see Figure 6). They can be engineered to behave differently from larger particles. For example, they may be engineered with surface coatings to stay suspended in water rather than settling. Nanoparticles are also small enough to pass through human skin or even cell walls. This behavior can confer different exposures compared to the traditional, non-nanoscale form of a contaminant ([Luoma, 2008](#); [U.S. EPA, 2004](#)).

2.5 Environmental Characteristics

It is clear that characteristics of the environment can also impact fate and transport ([Thibodeaux, 1996](#)). Some categories of characteristics that can influence contaminant fate and transport include:

- Soil and sediment properties, such as particle size and porosity
- Climate and meteorology, which cover properties like wind speed, evaporation rates, and rainfall amounts
- Surface water and groundwater properties, including flow, temperature, and pH
- Other properties of the ecosystem, including microbial populations, topography, and indigenous species

The specific influences that environmental characteristics can have on chemicals' fate and transport patterns are wide and varied. Some of the important properties are referenced in this reading packet; in general, a comprehensive discussion of this is beyond the scope of this introductory course.

3. PHYSICAL TRANSPORT AND PARTITIONING

This section explores how contaminants move in the environment. Movement of chemicals within an environmental phase (like soil, water, or air) is covered first, followed by movement between phases.

3.1 Advective Transport

Advection is movement of a contaminant that occurs as a result of bulk movement of the environmental phase containing the contaminant. This can be thought of as the contaminant “piggybacking” on a material that is moving, generally for reasons unrelated to the contaminant. Examples include:

- Smoke being blown by the wind.
- Deposition of solid particles (with chemicals sorbed to the particles) from air to surface soil via dry or wet processes. An example of this is rain-out of suspended particulate matter by precipitation.
- Downstream movement (flow) of contaminants dissolved in a river.

To estimate how much chemical is advected through these processes, we need to know how much chemical is in the medium and how quickly that medium is moving. Advective transport processes are typically responsible for much of the mid- to long-range transport of chemicals in the environment.

3.2 Diffusive and Dispersive Transport Processes

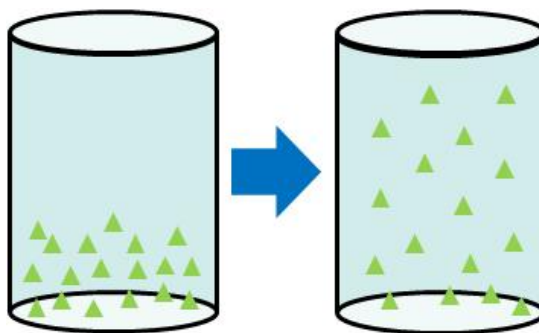
Dispersion and diffusion are two similar processes.

Diffusion is movement of a substance that results from a concentration gradient as shown in Figure 7. When a contaminant is not evenly distributed in a medium, molecules from the more concentrated area tend to diffuse to areas of lower concentration until equilibrium is reached. This can happen relatively quickly depending on the medium—for example, think about how a drop of dye spreads through a cup of water compared with the same drop in a cup of vegetable oil.

Dispersion is typically described as the spreading out of chemical within an environmental medium, and it is a process that can occur during advective transport. Dispersion occurs as a result of collisions between molecules of the contaminant and the medium of interest; it can be partially explained by Brownian motion of molecules. Dispersion of a substance in air as it is blown away from a stack is a typical example of this phenomenon. An air contaminant will “spread out” in directions perpendicular to the direction of the wind, so that the plume gets wider and taller as it gets further from the source.

Both of these processes, as well as advective transport, commonly occur as intraphase transfers. In other words, each of these types of processes typically occurs *within* one of the three main phases of the environment: soil, water, or air. These more or less correspond to the three primary chemical phases: solid, liquid, and gas ([U.S. EPA, 2002](#); [Thibodeaux, 1996](#)).

Figure 7. Conceptual Illustration of Diffusion



3.3 Partitioning Between Environmental Media

Another critical aspect of a chemical's behavior in the environment involves transfer (partitioning) of chemicals between environmental phases. Partitioning between environmental phases can often be described and predicted using known chemical relationships and equations that depend on chemical-specific properties. The letter K is typically used to describe partitioning ratios. Considering the three abiotic phases, there are four types of interfaces important to environmental behavior of chemicals:

- Between air and water
- Between air and soil
- Between soil and water (or other liquid)
- Between liquid and liquid (two immiscible liquids, such as water and oil)

Solid-solid interfaces also exist, but partitioning at this type of interface is much less important for most of the chemicals we might consider. Gas-to-gas interfaces also occur, but are rare in the natural environment. Chemicals can also partition between environmental media and biota; this phenomenon will be discussed later.

Equilibrium Partitioning

We will focus in particular on the partitioning behavior and relationships present at equilibrium conditions. These concepts can be described as “equilibrium partitioning.” When we talk about equilibrium with respect to phases that meet at an interface, we are referring to “dynamic equilibrium.” This means there is no net change in concentrations on either side of the interface. This doesn't necessarily mean that there's no movement of chemical mass across the interface—only that the net change, or total sum of the changes, is zero.

When a system is in a state of “dynamic equilibrium,” it will also be in a condition referred to as steady state. Steady state refers to a system in which masses are constant over time. A steady state system might not include reversible processes and, therefore, will not necessarily be in “dynamic equilibrium.”

3.4 Partition Coefficients

Equilibrium conditions are useful in predicting chemical transport because the relationship between concentrations of a chemical on either side of an interface depends on properties of the chemical and properties of the media. Temperature is also an important factor. This relationship dictates the **partition** or **distribution coefficient** for a substance. A capital K is used as a symbol for this coefficient, with a subscript denoting the type of interface. In short, the value for K is the concentration ratio of a two-phase system at equilibrium. In the remainder of this section, we will review some of the important partition coefficients used to describe chemical behavior in the environment.

Air-Water Partitioning: Henry's Law

A chemical's preference for being either dissolved in water or present in air as a vapor will

$$\text{Henry's Law constant: } H, \text{ or } K_H = \frac{\text{Partial pressure in air}}{\text{Concentration in water}}$$

depend on both its solubility in water and its vapor pressure. For dilute solutions, the ratio of vapor pressure to water solubility can be used to calculate a Henry's Law constant (H or K_H). In other words, Henry's Law constant is an index of partitioning for a compound between the atmospheric and the aqueous phases. Because

both vapor pressure and water solubility are temperature dependent, Henry's Law constants are temperature dependent as well.

Figure 8. Illustration of Henry's Law

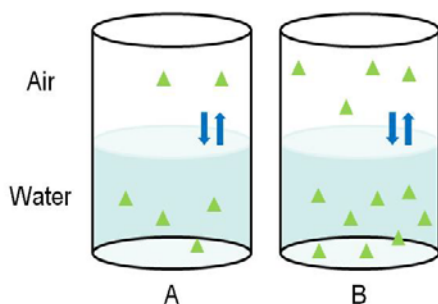


Figure 8 illustrates conceptually what happens in air-water partitioning. The chemical, represented by the green triangles, is distributed between air and water. This system is assumed to be at equilibrium. In both vessels A and B, the ratios of chemical in the air to chemical in the water are the same, even though there is more total chemical in B. In other words, even though the mass of chemical is greater within the air-water system on the right (vessel B), the ratios of chemical masses in air and water are the same for A and B. The Henry's law constant for this "green triangle" chemical is constant—it's the same in system A and in system B. It is assumed that neither of these vessels is at saturation, and they are also assumed to be at the same temperature.

Higher values of H are associated with compounds that preferentially partition to air rather than to water. One important point: you must pay attention to units. Atmosphere-liters per mole are typical units, but other types of units are also possible—including a unitless K_H that uses mole or mass concentrations ([Schwarzenbach et al., 2003](#); [Thibodeaux, 1996](#)).

Octanol-Water Partition Coefficient: K_{ow}

A related concept is the partitioning of organic chemicals between octanol and water. Octanol is a nonaqueous, nonpolar solvent. The dissolution and partitioning of chemicals into octanol is of interest because this chemical is a reasonable surrogate for various environmental and physiological media that are nonaqueous and nonpolar, including lipids, or fat. Strictly speaking, the K_{ow} describes a compound's behavior if allowed to equilibrate between phases in a solution of octanol and water. The K_{ow} for a given chemical does not change as the total chemical mass in the system increases, assuming the system is below the saturation point and all chemical mass stays dissolved.

$$K_{ow} = \frac{\text{Concentration in octanol}}{\text{Concentration in water}}$$

A higher K_{ow} indicates that more of the chemical partitions into octanol. Higher K_{ow} tends to correspond to higher bioconcentration potential (up to a point), because chemicals that partition to fat tend to be metabolized and/or eliminated from the body more slowly. A lower K_{ow} value typically correlates with a higher water solubility and suggests the compound partitions preferentially to water. Because the values for K_{ow} vary over a rather wide range for environmental contaminants, the log of this coefficient, or "log K_{ow} ," is often used and referenced ([Schwarzenbach et al., 2003](#)).

Soil-Water Partitioning: K_d

A chemical associated with the solid phase of soil will typically be sorbed to the surface of soil particles. The aqueous phase that comes in contact with the soil can take the form of surface water, precipitation, or water located in the interstitial or pore spaces of the soil.

The solid-water distribution ratio (K_d) is the ratio of the sorbed concentration to the concentration of the chemical dissolved in the

aqueous solution. This is typically expressed as a ratio of concentrations, such as the ratio of [milligrams of chemical per kg sorbent] to [milligrams of chemical per L of solute], which can be reduced to L/kg.

$$K_d = C_s / C_w = \frac{\text{Concentration in soil}}{\text{Concentration in water}}$$

The physical and chemical composition of soil is highly variable and complex, and partitioning behavior will depend on the components of the soil or other solid matrix, the physical complexities of soils and the pore spaces within soil, and other factors. As a result, K_d is **highly variable** across different environments, even for the same concentrations of the same chemical. In addition, the relationship between concentration in soil and concentration in water within a single environment is not necessarily linear.

Soil vs. Sediment

The discussion in this course regarding soil-water partitioning also applies generally to partitioning between the water column and suspended or benthic sediment. Even though the matrices that make up surface soils and sediments are different, the same basic principles generally apply to partitioning behavior between solids and water.

The magnitude of K_d will vary not just on chemical properties but also on certain properties associated with soil at a site, such as the amount of organic matter, mineral content, soil surface charge, soil surface area, and other characteristics. In general, it is difficult to accurately predict soil-water partition coefficients without taking site-specific measurements, and the relationship between partitioning and these various

characteristics can be complex. So, although in theory K_d is useful for predicting fate and transport, in practice it can be very difficult to obtain values for this constant using chemical data we can find in common reference materials.

Partitioning between Organic Carbon and Water (K_{oc})

Most (although not all) soil has some organic matter in it. Natural organic matter includes substances such as cellulose, humic and fulvic acids, and other organic compounds. A similar term is organic carbon. Natural organic matter is made up of roughly half carbon—therefore, the mass fraction of organic carbon in the soil is approximately equal to half of the mass fraction of organic matter.

The ratio of chemical sorbed to organic carbon to the chemical concentration dissolved in the surrounding water can be

$$K_{oc} = \frac{\text{Concentration sorbed to organic carbon}}{\text{Concentration in water}}$$

measured to obtain the partition coefficient K_{oc} . The relationship between K_{oc} and the dissolved concentration in water is **linear** for a fixed level of organic carbon, or f_{oc} (fraction of organic carbon in the soil). In other words, K_{oc} is constant for a given type of soil regardless of the total concentration of chemical (assuming we are below the saturation point) and what else might be in the soil. Furthermore, it turns out that the partitioning of chemical between water and organic carbon drives the overall partitioning of organic chemical between the water and the soil. Thus, for soils that have very low organic carbon, the amount of sorbed organic chemical will also be low ([Schwarzenbach et al., 2003](#); [U.S. EPA, 2003](#); [Thibodeaux, 1996](#)).

Using K_{oc} (and K_{ow}) to Estimate Soil Partitioning

Based on what we just discussed, the soil-water partitioning behavior, or K_d , of organic chemicals depends on:

- The fraction of organic carbon in the soil or sediment sorbent (f_{oc}), which is a soil property, and

- The partitioning behavior of the organic chemical between organic carbon (K_{oc}) and water, which is a constant chemical-specific property.

Based on these relationships, the product of f_{oc} and K_{oc} will be equal to K_d . K_{oc} and K_{ow} are typically directly proportional for a chemical, and although details regarding this relationship are not provided here, this means that we can use K_{ow} to predict or estimate K_{oc} . In other words, we can use f_{oc} and K_{oc} (or even just K_{ow}) to predict behavior of organic chemicals in many soil-water or sediment-water systems. These relationships are useful because the fraction of organic carbon can be determined or estimated based on the soil type at a location, and K_{ow} can often be found in reference materials, at least for many organic compounds ([Schwarzenbach et al., 2003](#); [U.S. EPA, 2003](#); [Thibodeaux, 1996](#)).

$$K_d = f_{oc} \times K_{oc}$$

3.5 Partitioning (and Other Transfer) into Biota

Compounds can transfer from an environmental medium to biota, a process referred to as bioconcentration or bioaccumulation. **Bioconcentration** is a specific term that refers only to direct transfers of the chemical from the surrounding environmental medium into the animal—it does not account for uptake by ingestion. It is usually used in reference to fish and other aquatic organisms. **Bioaccumulation** is the uptake of a substance from an environmental medium through all routes, including food chain transfers. For example, for a fish, bioaccumulation of a substance in the water includes both uptake from water through gills (which is direct uptake) and accumulation of that substance through ingestion of contaminated plants or animals (which might be considered indirect food chain uptake).

In natural environments, the ratio of the chemical concentration in an animal to the chemical concentration in its environment generally is referred to as a **bioaccumulation factor**, or **BAF**. This is typically expressed as L/kg, which is what you get when you divide mg/kg (the concentration in the fish) by mg/L (the concentration in the water). For example, BAF could relate the concentration of a contaminant in fish tissue to the concentration in the natural water body where the fish is found. A **bioconcentration factor (BCF)** can be measured, but must be evaluated under controlled situations to avoid indirect uptake through the food chain. This is also typically expressed as L/kg. A **biota-sediment accumulation factor**, or **BSAF**, is analogous to a BAF. It is an empirical partitioning ratio relating concentration in sediment to the concentration in an aquatic organism, including benthic organisms and higher trophic level fish.

Yet another term related to transfer of chemicals into biota is the **biotransfer factor (BTF)**. BTF is an empirical ratio relating the chemical concentration in biota, such as produce, livestock, or animal products (such as eggs), to the amount of chemical to which the plant or animal is exposed in soil or feed (or other media). The units of BTF are specific to the situation. A common BTF relates the concentration in the animal's body (usually expressed as mg chemical/kg in body weight) to the mass of chemical to which an animal is exposed (e.g., mg of chemical ingested per day due to incidental soil ingestion). For example, BTFs have been developed to estimate contaminant concentrations in beef for cattle that graze on land with contaminated soil ([U.S. EPA, 2005a, 2003](#)).

4. CHEMICAL TRANSFORMATION

In addition to being transported through the environment, contaminants also chemically react with their environment (i.e., experience chemical transformation). This section presents an overview of some important transformation processes.

4.1 Transformation of Organic and Inorganic Compounds

Organic contaminants can be transformed in the environment in a variety of ways. Some compounds chemically react and degrade in the environment through reactions initiated or assisted by exposure to light, water, or oxygen, although some are very slow to do so. Many organic compounds also degrade through biotic processes. **Biodegradation** refers to the breakdown of the chemical in an abiotic environment, such as soil, by a biotic organism, such as bacteria. In some cases, transformation reactions result in degradation products that are inert or benign. But in other cases, the reaction or degradation products can themselves be a contaminant of concern. For example, the oxidation of some volatile organic compounds (VOCs) in the atmosphere can lead to the formation of formaldehyde, which is associated with adverse health effects. As another example, oxidation reactions in the atmosphere involving ozone can lead to the formation of fine particulate matter; both ozone and PM_{2.5} are criteria pollutants.

Inorganic compounds also undergo transformation reactions, including some similar to the chemical and biological reactions that involve organic compounds—for example, reactions with light, water, or oxygen. One difference between organic and inorganic compounds is that inorganic compounds cannot be broken down beyond the metal or other species that is the basis of the compound—that is, they cannot be “completely” degraded.

Changes in speciation and complexation reactions are important for inorganic compounds and species. These can result from reduction/oxidation reactions (redox reactions) that change the valence of the inorganic species and can affect the solubility, mobility, or other characteristics of the substance. Precipitation and dissolution of inorganic compounds in water are important processes that directly affect the subsequent fate and transport of metal salts and other compounds. For example, acidic conditions in surface water tend to increase the solubility of metal salts that might otherwise precipitate out of solution. So, acidic conditions can lead to higher dissolved concentrations of some metals, sometimes resulting in more toxic conditions for organisms living in the water. Another example is mercury. Burning coal leads to emissions of elemental mercury and divalent mercury. Divalent mercury can deposit to surface water, where it can be transformed to methyl mercury by anaerobic microbes. This chemical transformation is of particular concern because methyl mercury readily bioaccumulates in fish (unlike divalent mercury), and methyl mercury is a potent neurotoxin in humans ([Williams et al., 2010](#); [U.S. EPA, 1997](#)).

4.2 First-order Decay

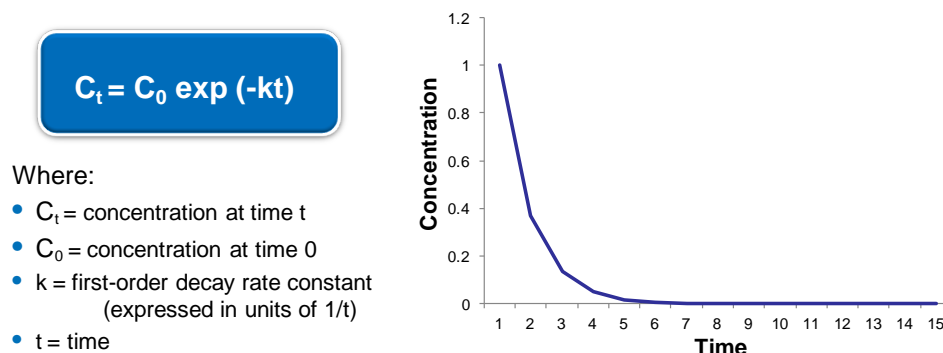
Regardless of the mechanism, many environmental transformations can be modeled as a first order reaction. A **first order reaction**, or first order decay (where the original chemical species “decays” as it degrades or is transformed to another species), is also known as **exponential decay**. This term is used because the contaminant of concern is reduced exponentially at a rate proportional to the concentration of the reactant chemical. The greater the concentration of the compound, the more rapidly it is reduced; likewise, at lower concentrations, the decay occurs more slowly. This type of reaction is referred to as first order because the rate

of reaction depends on the concentration of reactant raised to the first power. There are also higher-order reactions, but first-order reactions are used most frequently in describing environmental fate and transport reactions.

The equation for first-order decay is presented in Figure 9. Using this equation, one can calculate the concentration at a time (t), given a certain starting concentration (C_0) and a rate constant (k). The rate constant, k , has units of $1/t$. Note that this is a lower-case k (unlike the upper-case K that we use to represent a partition coefficient). The concentration of a contaminant at time t (C_t) is a function of the original concentration (C_0) multiplied by the exponential of the rate constant multiplied by time ($-kt$).

The half life, represented by $t_{1/2}$, is the time it takes for a substance to react by first-order decay to the point where half of the original substance remains. The rate constant is equal to the natural log of 2 divided by the half life. You can see this relationship if you substitute 1 for C_0 and 0.5 for C_t in the first-order decay equation shown in the box below and then solve for k ([U.S. EPA, 2002](#)).

Figure 9. Equation for First-order Decay



5. CONCLUSION

This course reviewed some of the important characteristics that influence chemical fate and transport, including source properties, properties of the chemical of interest, and characteristics of the environment to which the chemical is released. It also covered some important fate processes of interest, including processes that move chemicals within an environmental phase, such as advective transport in moving air and surface water as well as chemical dispersion that can occur in these phases. The principles behind interphase partitioning, such as Henry's Law, soil-water partitioning, and K_{ow} or octanol-water partitioning were discussed. Finally, this course briefly reviewed the importance of chemical transformations and discussed how many transformations in the environment can be described using first-order reaction kinetics. These fate and transport principles are the foundation for understanding modeling and monitoring approaches and their role in exposure assessment.

In applying these concepts to gain an understanding of a particular exposure situation, it's helpful to build a clear mental picture of where a contaminant is expected to occur in the environment before beginning monitoring or modeling. This includes reviewing the chemical of interest and the possible linkages between environmental media, and then considering what environmental processes might occur. Factors to consider include:

- Source characteristics—where is a pollutant released, to what media, how much, how long?
- Principal mechanisms responsible for change or removal in media.
- Chemical behavior—does it bioaccumulate or biodegrade?
- What is the potential for intermedia transfer (what are the K_{ow} , K_d , K_{oc} , etc.?)
- What does the original chemical transform or degrade into? Do additional chemicals of concern result?

Flow charts and exposure pathway analysis can be helpful in conceptualizing the behavior of a chemical in the environment.

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