

EXA 404: Fate and Transport

Instructor Notes

Course Description: 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 concept of transfer of contaminants within media – advection, dispersion, and diffusion – and between media – air to soil, soil to plant, water to fish, etc. – will be described to provide students a basis for later discussion of the application of environmental models. Concepts related to chemical transformation including transformation of inorganic and organic compounds and decay will also be discussed.

Expected Course Duration: Approximately 45 minutes

Terminal Learning Objective: Understand basic and important fate and transport concepts

Enabling Learning Objectives:

- Identify sources of chemicals in indoor and outdoor environments
 - Understand processes by which chemicals move within environmental media and the important concepts driving this movement
 - Understand how chemicals partition between environmental media, the important concepts driving partitioning, and general approaches for estimating partitioning
 - Understand key processes by which chemicals change within environmental media
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Course Materials

- Reading Packet

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TITLE SLIDE

- Welcome to EXA 404 on the basics of chemical fate and transport.

What You Can Expect to Learn from this Course (Slide 1)

- In this course, we'll review the major concepts behind fate and transport of chemical contaminants in the environment.
- We will discuss how and why the contaminant source, the characteristics of the released chemical, and the environment are important to fate and transport.
- We will also review what can happen to a contaminant after it is released into the environment.
- In the next course, EXA 405, we'll discuss 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 doesn't cover non-chemical stressors (such as noise and temperature).

KEY CONCEPTS AND DEFINITIONS (SLIDE 2)

- Let's start off by going over a few fundamental concepts and definitions.

Contaminant Fate and Transport (Slide 3)

- 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. 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 like the one in the picture can travel in the wind through the air, fall to the ground or get washed out by rain, and accumulate in soil or surface water, 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 this smokestack or from the cars could also be degraded, or they could be transformed through chemical reactions to entirely different substances.
- Although the range of possibilities for what happens to a contaminant in the environment is broad, there are some basic concepts that you should be aware of. We'll review these in this course.
- Source: ([U.S. EPA, 1998](#))

Source to Effect Continuum (Slide 4)

- Let's briefly review the source to effect continuum introduced in earlier EXA modules. This will help us see where fate and transport “fits” into exposure assessment.
- As you can see on the left side of this diagram, fate and transport processes “link” the formation or release of contaminant 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. We'll discuss both of these in the next course in the exposure series, EXA 405.
- Source: ([Williams et al., 2010](#))

Transport: Movement Within and Between Environmental Media (Slide 5)

- “Fate and transport” covers movement of substances in the environment and chemical reactions that affect the nature of the substance. Let's talk about transport first.
- This slide shows some transport processes that might occur following release of a contaminant.
- Transport can occur **within a medium**. For example, in this figure, 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.
 - 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.” We'll talk more about equilibrium in a few slides.
- Transport of chemicals can also occur between abiotic and biotic media, as shown in this figure. In other words, people and wildlife, as part of the environment, can be exposed to chemicals released to environmental media.
- Source: ([Thibodeaux, 1996](#))

Transformation: Chemical Changes within a Medium (Slide 6)

- 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 – in other words, it is separate from transport.
- Some of the types of transformations that can occur in the environment are shown on this figure. You may already know that some these changes are dependent on the environmental media.
 - 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 doesn’t 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.
- Source: ([Schwarzenbach, Gschwend, & Imboden, 2003](#))

Environmental and Exposure Media (Slide 7)

- Before we go into more detail on some of these processes, let’s briefly review two terms we use in this course and other EXA courses: environmental media 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, and air, plus the biota that reside in the environment.
 - 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.
- In the conceptual figure shown here, 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’s 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 is an environmental medium only. Chemical mass released from the pipe is transported to sediment by deposition in the water column and other processes, but we are assuming no direct dermal contact with the sediment occurs. Consequently, sediment is not an exposure medium.

- 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 eaten.
 - So, environmental media can be exposure media, but this is not always the case.
- Direct exposure to chemicals can also occur through other means, such as contacting consumer products containing chemicals or contacting pesticide residues on the surface of produce. Although these kinds of exposures are an important part of exposure assessment, the focus of this course is on environmental fate and transport, and we won't go into these kinds of exposure media in detail.
- Source: ([U.S. EPA, 2003](#))

INFLUENCES ON FATE AND TRANSPORT (SLIDE 8)

- 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. We'll review some common types of environmental sources in this next section. We'll also talk about chemical characteristics that affect how a chemical behaves once it's released into the environment as well as the characteristics of the environment.

Chemical Source: The Beginning of the Continuum (Slide 9)

- 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 source to exposure (and eventually effect) continuum we saw earlier.
- 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.
- Source: ([U.S. EPA, 2002](#))

Point Sources and Non-Point Sources (Slide 10)

- Sources of pollutants are often referred to as "point" sources or "non-point" sources.
- A classic example of a point source is a smoke stack. The contaminant is emitted from a relatively small area, or point. In the example shown, the stack at the facility is a "point source" of emissions. The emissions are released directly to the air from the stack.
- "Non-point" 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 non-point sources include car exhaust and agricultural fields treated with pesticides.

Source: ([U.S. EPA, 2005](#); [Williams, et al., 2010](#))

Indoor Sources of Contaminants (Slide 11)

- We commonly think of environmental pollution as occurring outdoors. However, many contaminants enter or are generated indoors, 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. This estimate differs from region to region and can impact exposure to contaminants. ([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 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 typically 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 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, carpets or dust, rather than soil or sediments, would typically be a solid exposure medium of interest.
- Source: ([ICF, 2004](#); [U.S. EPA, 2008](#); [Weschler & Nazaroff, 2008](#))

Consumer Products as Sources of Contaminants (Slide 12)

- 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, such as phthalates and bisphenol A (or BPA), 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. Others are in direct contact with food. Others still have been found at elevated concentrations in house dust, suggesting incidental ingestion might be important.
- Although exposure to these compounds is likely to occur, the 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 in blood and urine.

- Source: ([Luoma, 2008](#); [Weschler & Nazaroff, 2008](#))

Background Sources (Slide 13)

- 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 result from distant sources, if the contaminant remains in the environment for a long period of time and can travel long distances from the original source like PCBs 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” or exposure from the source in question. This is the case in some exposure assessments EPA conducts for specific air toxics regulations.
- In many cases, the total exposure – inclusive of existing background, regardless of source – is estimated.

Organic vs. Inorganic Chemical Contaminants (Slide 14)

- 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 non-polar 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 taken up by biota, or bioaccumulate.
 - Common inorganic contaminants of concern include many metals, such as cadmium, lead, and mercury, as well as nitrates and nitrites. These compounds are not carbon-based, and their movement through the environment is more typically controlled 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 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.

- Source: ([Thibodeaux, 1996](#))

Vapor Pressure and Water Solubility (Slide 15)

- 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 is, the more likely that chemical 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 bioconcentrate, and usually they are biodegradable.
- Both vapor pressure and water solubility are temperature dependent.

Contaminants for which Physical Characteristics are Important (Slide 16)

- In some cases, we may be concerned with exposures to contaminants where physical attributes are one of or even *the* most important defining characteristic, rather than chemical composition – even though the contaminants are still made up of chemicals. Two examples of such contaminants 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 compositions and influence particle behavior and persistence.
- But this doesn't mean that the composition of particulate matter is not a concern. For example, environmental tobacco smoke is more harmful than wind-blown dust because of the chemical composition of tobacco smoke, even when the particle sizes are comparable.
- Nanoparticles are a class of emerging contaminants that are not fully understood in which physical characteristics are important. They can be engineered to behave differently from larger particles, for instance, by staying suspended in water, rather than settling. Nanoparticles are also small enough to pass through human skin or even cell walls, which can confer different exposures compared to the traditional, non-nanoscale form of a contaminant.
- Source: ([Luoma, 2008](#); [U.S. EPA, 2004](#))

Environmental Characteristics (Slide 17)

- Finally, it's clear that the characteristics of the environment can also impact fate and transport. 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 covers properties like wind speed, evaporation, and rainfall amounts;
 - Surface water and groundwater properties, including flow, temperature, and pH; and
 - Other properties of the ecosystem, including microbial populations, topography, and indigenous species.
- ? What other environmental characteristics could impact fate and transport?
- Source: ([Thibodeaux, 1996](#))

PHYSICAL TRANSPORT AND PARTITIONING (SLIDE 18)

- Now, let's talk about how contaminants move in the environment. We'll first talk about movement of chemicals within an environmental phase (like soil, water, or air) and then discuss movement between phases.

Advective Transport (Slide 19)

- 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, either via dry or wet processes. An example of this is rain-out of suspended particulate matter by precipitation.
 - Downstream movement of contaminants dissolved in a river through flow of the river water.
- 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.

Diffusive and Dispersive Transport Slide 20)

- Dispersion and diffusion are two similar processes.
- Diffusion is movement of a substance that results from a concentration gradient. 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 an equilibrium is reached. This can happen relatively quickly – for example, think about how a drop of dye spreads through a cup of water – or more slowly in other types of media.

- Dispersion is typically described as the spreading out of chemical within an environmental medium, and 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 as shown here on the slide 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 discussed on the previous slide, are typically intraphase transfers. In other words, each of these types of processes 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.
 - Biota can also be considered a different sort of environmental phase that we’ll discuss in a bit.
- Source: ([Thibodeaux, 1996](#); [U.S. EPA, 2002](#))

Partitioning between Environmental Media (Slide 21)

- Another critical aspect of a chemical’s behavior in the environment involves transfer **between** these environmental phases – in other words, partitioning of chemical mass between 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; we’ll talk about this more on the next slide.
- 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 (between two immiscible liquids, such as water and oil).
 - [Instructor note: Gas-to-gas interfaces are rare in the natural environment.]
- Solid-solid interfaces also exist, but partitioning at this type of interface is much less important in considering distribution of most of the chemicals we will be dealing with.
- Chemicals can also partition between environmental media and biota, but we’ll discuss this later on.
- Let’s go over the important partitioning behaviors in the next few slides and talk about the relationships that have been derived for these behaviors.

Equilibrium: A State of No (Observable) Change (Slide 22)

- 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 that 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.”
- Equilibrium conditions are useful in predicting chemical transport because the relationship between concentrations of a chemical on either side of an interface depend on properties of the chemical and properties of the media (and temperature too). This relationship dictates the **equilibrium constant** for a substance.
 - A capital K is used as a symbol for an equilibrium constant, 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.
- Let's talk about some kinds of equilibrium constants that have been developed for different environmental interfaces.

Air-Water Partitioning: Henry's Law (Slide 23)

- First, let's talk about the partitioning of a chemical between water and the atmosphere (that is, the air) above the surface of the water. A chemical's preference for being either dissolved in water or present in air as a vapor will 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 constants are temperature dependent as well.
- The figures on the left illustrate 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's 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.

- Note that neither of these vessels is at saturation, and they are 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 have to pay attention to units. The units shown here (atmosphere-liters per mole) are typical, but others are used too – including a unitless K_H that uses mole or mass concentrations.
- Source: ([Schwarzenbach, et al., 2003](#); [Thibodeaux, 1996](#))

Octanol-Water Partition Coefficient: K_{ow} (Slide 24)

- A related concept is the partitioning of organic chemicals between octanol and water. Octanol is a non-aqueous, non-polar 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 non-aqueous and non-polar – 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 doesn't change as the total chemical mass in the system increases (assuming we're below the saturation point and all chemical mass stays in dissolved).
- So, what does the magnitude of K_{ow} mean?
 - A higher K_{ow} , which indicates more of the chemical partitioning into octanol, tends to correspond to higher bioconcentration potential (at least up to a certain point) because chemicals that partition to fat tend to be metabolized and/or eliminated from the body more slowly.
 - A low K_{ow} value correlates with a high water solubility, and this 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.
- Source: ([Schwarzenbach, et al., 2003](#))

Soil-Water Partitioning: K_d (Slide 25)

- Now, let's talk about how chemicals in the environment partition between the soil and water phases. This is a bit more complicated.
- 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.
 - As a side note: when we're talking here about soil-water partitioning, we are also generally talking about partitioning between the water column and suspended or benthic sediment. So, even though the matrices that make up surface soils and

benthic sediments are different, the same basic principles generally apply to partitioning behavior.

- 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, or the ratio of [milligrams of chemical per kg sorbent] to [milligrams of chemical per L of solute], which can be reduced to L/kg.
- The physical and chemical composition of soil is highly variable and complex, and partitioning 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 chemical. In addition, the relationship between concentration in soil and concentration in water within a single environment is not necessarily linear.
- In some cases, K_d can be estimated based on certain properties associated with a site, such as the amount of organic matter, mineral content, soil surface charge, soil surface area, and other characteristics. But in general, it is difficult to accurately predict soil-water partition coefficients without taking site-specific measurements.
- 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.

Organic Carbon-Water Partitioning: K_{oc} (Slide 26)

- Let's talk about solid-liquid partitioning in soil a little more.
- Most (though not all) soil has some organic matter in it. Natural organic matter includes substances like 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.
- This is a convenient fact, because you can use this assumption to estimate the ratio of chemical sorbed to organic carbon to the chemical concentration dissolved in the surrounding water. This ratio is 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 what the total concentration of chemical is. This is also true regardless of what else might be in the soil. (Once again, this assumes we are below the saturation point.)
 - Furthermore, for soils that have very low organic carbon, the amount of sorbed organic chemical will also be very low.
- Source: ([Schwarzenbach, et al., 2003](#); [Thibodeaux, 1996](#); [U.S. EPA, 2003](#))

Using K_{oc} (and K_{ow}) to Estimate Soil Partitioning (Slide 27)

- 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.
- We can use these relationships to obtain a new expression for K_d : $K_d = f_{oc} \times K_{oc}$
- It's also true that K_{oc} and K_{ow} are typically directly proportional for a chemical.
- Although we won't go into the details right now, 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. This is convenient, 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.
- Source: ([Schwarzenbach, et al., 2003](#); [Thibodeaux, 1996](#); [U.S. EPA, 2003](#))

Partitioning (and Other Transfer) into Biota (Slide 28)

- Compounds can transfer from an environmental medium to biota, a process referred to as bioaccumulation.
- **Bioconcentration** is a specific term that refers only to direct transfers of the chemical from the surrounding environmental medium to the animal – it does not account for uptake by ingestion. It's usually used for fish and other aquatic organisms.
- **Bioaccumulation** is the uptake of a substance from an environmental medium through all routes.
 - 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). An example bioaccumulation factor 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's an empirical partitioning ratio relating concentration in sediment to the concentration in aquatic organisms, including benthic organisms and higher trophic level fish.
- Yet another term related to transfer of chemicals into biota is the biotransfer factor (or 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 the biota is exposed to 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 (for example, mg of chemical ingested per day due to incidental soil ingestion). For example, biotransfer factors have been developed to estimate contaminant concentrations in beef for cattle that graze on land with contaminated soil.
- Source: ([U.S. EPA, 2003](#), [2005](#))

Interactive Discussion: How will this chemical behave in the environment? (Slide 29)

- Presented here are several characteristics of a chemical.
 - It is an organic chemical released by combustion.
 - It has low water solubility.
 - It has a high organic carbon partitioning coefficient.
- Where would you expect to find the chemical in the environment? In what media? Do you expect it to bioaccumulate?
 - Allow class discussion; prompt class that chemical is dioxin if they are having trouble.
- When ready to discuss, **click on slide** to make “answers” appear.

Interactive Discussion: Answers

- This organic chemical released by combustion with a low water solubility and high K_{oc} is dioxin. We would expect to find it sorbed to airborne particles, soils, and sediments.
- We would also expect it to bioaccumulate.
- Because dioxin is released to the air, we expect to find it there. It will also be transported throughout the environment, and due to its affinity to sorb to organic carbon (high K_{oc}), we expect to find dioxin sorbed to particles, soils, and sediments. Compounds with low water solubility are associated with a higher bioaccumulative potential, and dioxin is no exception.

CHEMICAL TRANSFORMATION (SLIDE 30)

- In addition to being transported through the environment, contaminants also chemically react with their environment. We'll present an overview of these processes in this section.

Transformation of Organic and Inorganic Compounds (Slide 31)

- 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.
- Many organic compounds degrade through biotic processes (though some are very slow to do so). 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 VOCs in the atmosphere can lead to the formation of formaldehyde, which is associated with adverse health effects.
 - As another, different 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 can also undergo transformation reactions, including some similar to the chemical and biological reactions that involve organic compounds – for example, reactions with light, water, and oxygen.
- As we mentioned earlier in this class, though, 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, and sometimes higher toxicity to organisms living in the water as a result.
- 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.
- Source: ([U.S. EPA, 1997](#), [2002](#); [Williams, et al., 2010](#))

First-order Decay (Slide 32)

- 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 is because the contaminant of concern is reduced exponentially. The greater the concentration of the compound, the more rapidly it is reduced; likewise, at lower concentrations, the decay occurs more slowly.
- The equation for first order decay is presented on this slide. This allows you to 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 one over time. Note that this is a lower-case k (unlike the upper-case K that we use to represent an equilibrium constant).
- In other words, the concentration of a contaminant at time, t , is a function of the original concentration multiplied by the exponential of the rate constant k multiplied by time.
- 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 relationship between rate constant and half life is also shown here below the chart. 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 dark blue box, and then solve for k .
- Source: ([U.S. EPA, 2002](#))

First-order Decay Exercise – Ozone (Slide 33)

- Let’s look at an example of a first-order environmental fate reaction.
- Assume that an air cleaning machine that generates ozone is used in an indoor environment and has been running for a while. When the air cleaner is switched off, the indoor ozone concentration is 600 ppb. If the removal of ozone from the indoor environment occurs through a first-order reaction, and the half life of ozone indoors is 10 minutes, how long will it take to reach the 8-hr ozone standard of 75 ppb?
 - The conversion between half life and k is shown here again (note that the natural log of 2 is about 0.693).

Ozone Solution (Slide 34)

- The 8 hr ozone standard is 75 ppb. If the original concentration is 600 ppb and the half life is 10 minutes, it will take three half lives to reduce the ozone concentration to 75 ppb (12.5% of 150 ppb), or 30 minutes.
- The relationship between k and half-life is important to remember, because decay in the environment is often expressed in terms of half-life and the assessor needs to convert this half-life to a k value for use in this equation.

CONCLUSION (SLIDE 35)

- Now we have covered many of the processes that affect fate and transport. Let's briefly review these and conclude by discussing how we put it together.

Key Concepts (Slide 36)

- We started by reviewing 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.
- We covered some important fate processes of interest, including processes that move a chemical 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.
- We also discussed the principles behind interphase partitioning, such as Henry's law, soil-water partitioning, and K_{ow} or octanol-water partitioning.
- Finally, we briefly reviewed the importance of chemical transformations and discussed how many transformations in the environment can be described using first-order reaction kinetics.

Applying Fate and Transport Concepts for Exposure Assessment (Slide 37)

- 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 be 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 potentially occur.
- We'll want to consider:
 - 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? (K_{ow} , K_d , K_{oc} , etc. are useful here.)
 - What does the chemical change into, and are the degradation products chemicals of concern?
- Flow charts and exposure pathway analysis can be helpful in conceptualizing the behavior of a chemical in the environment.
- In the next course, EXA 405, we'll discuss how we can use monitoring to determine the environmental concentrations that result from these processes, and we'll also talk about how we can use mathematical models to estimate the concentrations that result from these processes.

REFERENCES

- ICF. (2004). Air toxics risk assessment reference library: Volume 1: Technical resource manual. Research Triangle Park, NC: U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards.
- Luoma, S. N. (2008). Silver nanotechnologies and the environment: Old problems or new challenges. Washington, DC: Project on Emerging Nanotechnologies.
- Schwarzenbach, R. P., Gschwend, P. M., & Imboden, D. M. (2003). *Environmental Organic Chemistry* (2 ed.). Hoboken, New Jersey: John Wiley & Sons.
- Thibodeaux, L. J. (1996). *Environmental Chemodynamics* (2 ed.). New York: John Wiley & Sons.
- U.S. EPA. (1997). Mercury Study Report to Congress. Washington, DC: U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards.
- U.S. EPA. (1998). Methodology for assessing health risks associated with multiple pathways of exposure to combustor emissions. Washington, DC.
- U.S. EPA. (2002). Total risk integrated methodology TRIM.FaTE technical support document [Computer Program]. Retrieved from <http://www.epa.gov/ttnatw01/urban/trim/trimpg.html>
- U.S. EPA. (2003). Exposure and human health reassessment of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) and related compounds National Academy Sciences (NAS) review draft. Part I: Estimating exposure to dioxin-like compounds. Volume 3: Site-specific assessment procedures. Washington, DC.
- U.S. EPA. (2004). Air quality criteria for particulate matter. Research Triangle Park, NC: U.S. Environmental Protection Agency, National Center for Environmental Assessment.
- U.S. EPA. (2005). Human health risk assessment protocol for hazardous waste combustion facilities: Volume 1. Washington, DC: US Environmental Protection Agency, Office of Solid Waste and Emergency Response (OSWER).
- U.S. EPA. (2008). Care for your air: A guide to indoor air quality.
- U.S. EPA. (2011). Exposure factors handbook 2011 edition (final).
- Weschler, C. J., & Nazaroff, W. W. (2008). Semivolatile organic compounds in indoor environments. *Atmospheric Environment*, 42, 9018-9040.
- Williams, P., Hubbell, B. J., Weber, E., Fehrenbacher, C., Hrdy, D., & Zartarian, V. (Eds.). (2010). *An overview of exposure assessment models used by the U.S. Environmental Protection Agency* (Vol. II). Hertfordshire, UK: ILM Publications.