Transport and Fate of Contaminants in Surface Water

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This booklet is part of a series of educational brochures and slide sets that focuses on various aspects of water source protection. The series has been prepared jointly by the University of California Agricultural Extension Service and the California Department of Health Services.

For further information about this and other documents in the series, contact the project team leader (see below) or visit the following website:

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Several mechanisms exist for the transformation and transport of contaminants in water.

Knowledge of a contaminant's chemical form and of the chemical's ability to be sorbed, to precipitate, to dissolve, or to be degraded is necessary if the fate of the chemical is to be determined accurately.

Solids in water exist in two forms: either as particulate (filterable) solids or as dissolved (nonfilterable) solids. Within each group, further differentiation can be made between organic (volatile) solids and inorganic (nonvolatile, or fixed) solids.

The amount of a contaminant of concern (COC) found at a given location in the aquatic environment depends on the contaminant's rate of accumulation. That, in turn, depends on the rates of contaminant loading and transport (Tchobanoglous and Schroeder, 1987). Contaminant loading arises from an "input" (with respect to the water body) of allochthonous or autochthonous materials.

Allochthonous materials originate from within the watershed, but outside the water body. A few examples are: eroded soils and inorganic solids from weathered rocks, detritus imported from the catchment basin (e.g., leaves, twigs, grasses), fecal material, and organic and inorganic pollutants from road surfaces. Autochthonous material originates from within the water body. It includes ungrazed plant components such as cells and tissues, undigested plant materials within animal feces, and dissolved substances released by phytoplankton, macrophytes, and animals (Cole, 1994). Allochthonous loadings are usually less organic than autochthonous loadings (Chapra, 1997).

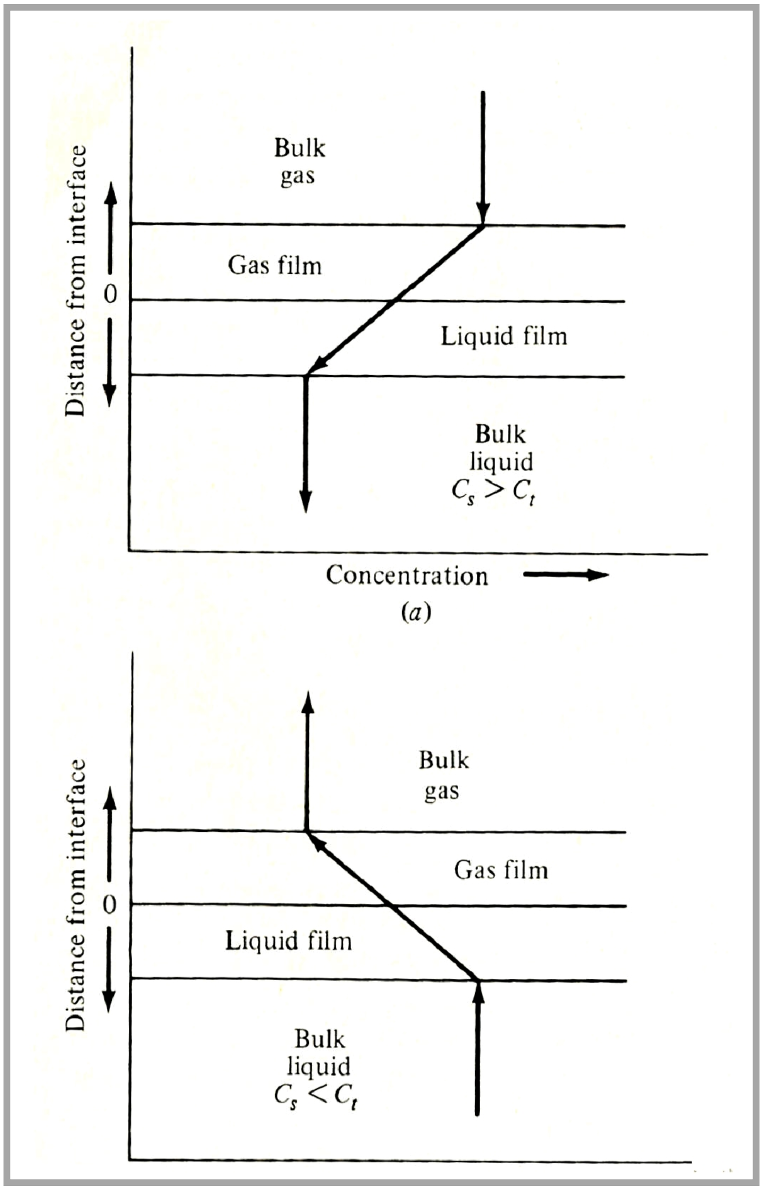

Figure 1: Gas transfer from water to air (and vice versa): (a) absorption and (b) desorption (Peavy et al., 1985).

Once a material is present in a surface body of water, it can be transported within the water body, volatilized or transported into the atmosphere, sorbed into the soil or solid matter in the water, precipitated or dissolved into and out of the water, degraded by photolysis, or transformed by biodegradation.

Water to Air

Many different contaminant transport processes occur in a water body at the boundary between water and air. These mechanisms include wind, hydraulic turbulence, and gas transfer.

Wind and hydraulic turbulence represent the transfer of airborne contaminants into water by mechanical means. Gas transfer is controlled by the difference in concentration of a gas in water and air. If the concentration of a gas in the atmosphere is greater than the concentration of that same gas in water, then the gas will tend to be absorbed into the water. The reverse is true, too: if the gas exists in the atmosphere at lower concentration than in water, it will tend to come out of solution. However, a gas film and water film in between the water body and atmosphere can limit the effect of the concentration gradient in gas transfer. Figure 1 shows absorption of a gas into a liquid, and desorption

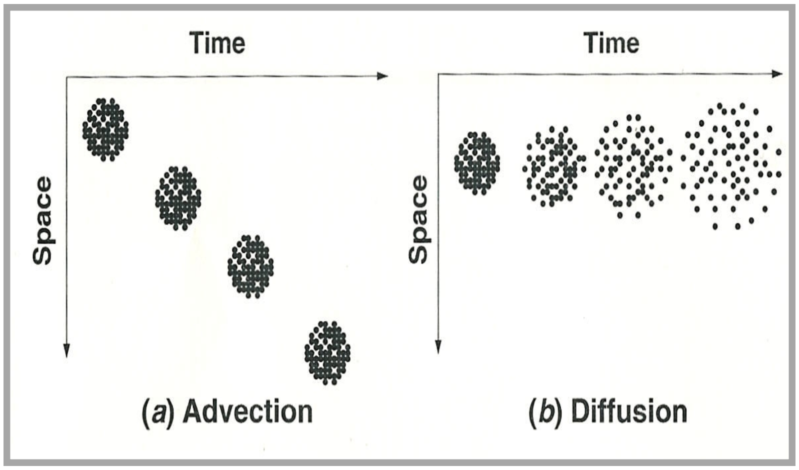

Figure 2: Transport of a contaminant in water: (a) advection and (b) diffusion (Chapra, 1997).

of a gas out of a liquid, resulting from a concentration gradient across a gas film and liquid film.

Water to Water

Within the water body itself, the possible modes of transport include advection and diffusion (Figure 2). Advection occurs when a COC moves as a result of fluid motion but the contaminant's concentration remains unchanged. Chapra (1997) defines advection as a flow that is unidirectional and does not change the identity of the substance being transported. Basic examples of advection are the downstream transport of a contaminant (1) in a river or (2) through a conduit.

Diffusion occurs when a COC is transported along a concentration gradient from a region of high concentration toward a region of lower concentration (Tchobanoglous and Schroeder, 1987). Diffusive transport occurs because of random mixing or motions in the water. Diffusion can be modeled by using Fick's First Law:

$J_x = -D(dc/dx)$

where:

J_x= mass flux in the x direction

D = the diffusion coefficient

dc/dx= the concentration gradient

Fick's First Law shows that the mass flux is proportional to the rate of change of the concentration of the contaminant. The diffusion coefficient is used to quantify the rate of the diffusive process. Therefore, if little or no mixing or turbulence occurs in a water body, the diffusion coefficient would be low. On the other hand, if mechanical mixers are present in a water body, then the diffusion coefficient would be high (Chapra, 1997).

Dispersion is a third possible mode of transport within a water body. Dispersion is related to diffusion in that it will mix a contaminant in a water body. However, whereas diffusion mixes contaminants in water due to random motions in the water over time (i.e., wind, waves, turbulance), dispersion mixes contaminants in water due to velocity differences in a given space (Chapra, 1997).

Figure 3 shows an example of dispersion in a pipe. The velocity near the walls of the pipe are less than the velocities in the center of the pipe. The difference in these velocities results in a gradual mixing of the water along the axis of the pipe. The figure also demonstrates diffusive mixing, which is completely random in nature.

Most mixing that occurs in narrow conduits of rapidly flowing water, such as a river or pipe, is a result of dispersion. Most long-term mixing that occurs due to wind action, such as in a lake or bay, is a result of diffusion (Chapra, 1997).

Water to Soil

Water-to-sediment transport mechanisms include sorption (adsorption and desorption), precipitation, and dissolution. Sorption describes a contaminant's attachment to and movement within the soil. The term is often used to refer to the transfer of organics in surface waters to a solid surface (Chapra, 1997; Sawyer, *et al.*, 1994). Sorption can occur either by the compound *ad*sorbing chemically onto the surface of the solid or by the compound *ab*sorbing (penetrating into) the solid's surface (Chapra, 1997).

Several factors affect a chemical's potential to adsorb to soil. These include: (1) the chemical and physical characteristics of the soil, (2) whether or not adsorption will be chemical or physical, (3) the type of bonding that will occur between the COC and the soil, and (4) such characteristics of the environment as pH and temperature (Tchobanoglous and Schroeder, 1987).

Adsorption is evident when there is an accumulation of material at the water-soil interface. Desorption can occur when the conditions resulting in adsorption reverse, causing a release of the contaminant from the soil back to the water column (Tchobanoglous and Schroeder, 1987).

Precipitation and Dissolution

Precipitation is the removal of a chemical species from water by formation of solid mineral(s). This can occur when the concentrations of the mineral-forming chemical species exceed the solubilities of the minerals they form. In such situations, the solution is said to be supersaturated with respect to those minerals.

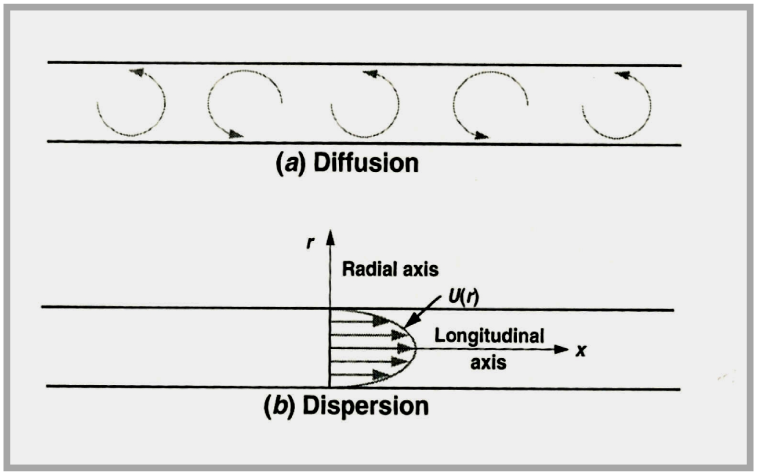

Figure 3: Contrast between (a) diffusion and (b) dispersion. Diffusion is caused by random motions over time; dispersion is caused by differential movement of water over a space (Chapra, 1997).

Dissolution—essentially the reverse of precipitation—typically occurs when the water is undersaturated. The net result, assuming reaction kinetics are favorable, is the diffusion of ionic species away from the solid(s). The rate of dissolution is affected by several factors: (1) the saturation concentration, (2) the actual concentration of the limiting ion, (3) the rate constant for the reaction, and (4) the surface area available for precipitation (Snoeyink and Jenkins, 1980).

The reaction that occurs when a precipitate dissolves in water to form its constituent ions ($AzBy_{(s)} = zA^{y+} + yB^{z-}$) is described by the equilibrium constant as follows:

$K_{so} = [A^{y+}]^z [B^{z-}]^y$

where:

K_{so} = the solubility product

A = the cation

B = the anion

This relationship can be used to determine whether a solution will precipitate ions, forming a solid, or result in the dissolution of ions from a solid.

Biodegradation

Biodegradation processes typically result from microorganism activity that causes the transformation or breakdown of organic materials. Chemical conversions associated with biodegradation include: (1) organics to inorganics; (2) toxic compounds to innocuous compounds; and (3) non-toxic compounds to toxic compounds (Chapra, 1997).

Biodegradation of organic substances can be carried out by aerobic or anaerobic organisms. Aerobic organisms utilize oxygen to metabolize organics. Anaerobic organisms do not use oxygen to metabolize organics. Figure 4 outlines the aerobic and anaerobic processes that degrade organics composed of nitrogen, sulfur, and carbon.

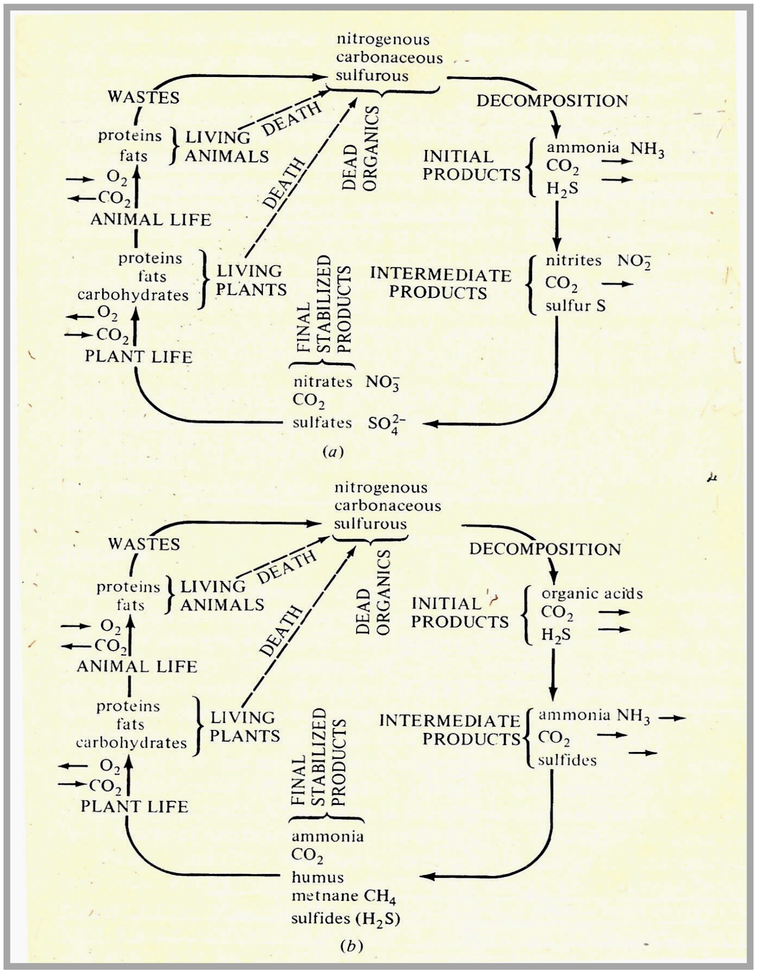

Figure 4: Nitrogen, carbon, and sulfur cycles: (a) aerobic and (b) anaerobic (Peavy et al., 1985).

As mentioned above, aerobic organisms require oxygen to function. Therefore, when an organic waste is discharged into an aquatic system, a biological oxygen demand (BOD) is created. BOD is a measure of the oxygen required to break down organic compounds (Tchobanoglous and Schroeder, 1987). High BOD levels significantly deplete the amount of dissolved oxygen (DO) in a surface water. Consequently, high

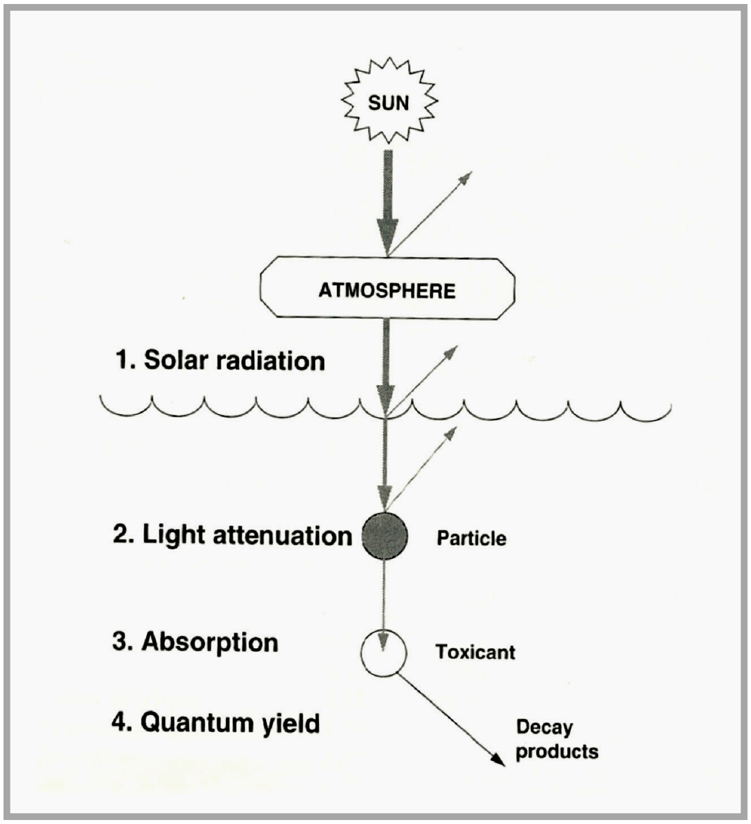

Figure 5: A simplified schematic of photodegradation in natural waters (Chapra, 1997).

BOD levels can have a detrimental effect on the health of aquatic species that require elevated DO levels, such as fish. This happens, for example, when algae reproduce rapidly within a reservoir in response to input of phosphorus or other contaminants that happen to be nutrients for algae. The algae biodegrade the nutrients, at the same time decreasing the amount of available oxygen. Thus, the increased amount of algae creates a high BOD, which depletes the DO, possibly resulting in the death of fish in the reservoir.

Dilution

Contaminants of concern in the aquatic environment can be reduced by dilution, a natural self-cleaning mechanism in many surface waters. In the past, dilution was considered a viable method for disposal of wastewater. However, steady increase in the world's human population, paired with an increase in the per-capita volume of wastewater to be discharged, has precluded dilution as a solution in many water bodies. The net result is increased constraints on disposal into many surface waters.

According to Peavy *et al.* (1985), the capacity of a stream to receive a waste discharge with a known contaminant concentration can be calculated using the following equation:

$$C_sQ_s + C_wQ_w = Q_mC_m$$

where:

C is the concentration in mass per unit volume,

Q is the flow rate in volume per unit time,

s refers to the stream conditions,

w refers to the waste conditions, and

m refers to the mixed conditions.

This equation can be used to determine whether compliance with regulatory standards, guidelines, and goals is being achieved.

Photodegradation

Chemical degradation due to the radiant energy of light is referred to as photodegradation or photolysis. It typically occurs when a compound absorbs light. This type of degradation depends on the amount of sunlight available, the physical water characteristics that allow the sunlight to penetrate the water, the degree to which the chemical will absorb sunlight, and many other factors.

COCs near the water surface are particularly vulnerable to solar radiation and resulting photodegradation (Chapra, 1997). Figure 5 shows a schematic of the photodegradation process. The figure shows that solar radiation is absorbed by a toxicant, which then undergoes a chemical reaction that results in decay of the toxin.

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