November 7, 2005
Lecture 21   Mass Transfer (Transport) Phenomena

I. Mass Transfer Phenomena
  A. In part I of Environmental Chemodynamics, we discussed the movement of chemicals as they disperse from themselves (water solubility and vapor pressure) and as they move across compartmental interfaces (phase transfers or partitioning; e.g., K_H, K_{ow}, K_d or K_{oc}).
    1. Wherever the chemicals are as they approach equilibrium between one phase (or compartment) are and another, their biological effect will depend partly on their concentration.
    2. However, this concentration is quite dynamic rather than static.
    3. In this lecture we will discuss the processes that remove the chemical further away from their source points (mass transfer) and in the next lecture we will discuss the processes that lower a contaminants concentration in situ (degradation).
    4. First, we will differentiate molecular scale movement from mass transfer.
II. Molecular Diffusion--the **molecular scale movement** of a chemical within a medium (i.e., soil, air, water)
  A. Can be conceptualized as a spontaneous mixing process
    1. Loss of spatial unevenness in the distribution of mass (or concentration), heat, or other attributes of a system is a manifestation of the second law of thermodynamics, i.e., in the absence of an external energy source, entropy of a system increases until equilibrium is reached
      a. In other words, molecules will tend to rearrange themselves so that the system has the lowest energy.
      b. Molecules thus move from regions of high chemical potential to regions of low chemical potential.
    2. In the case of a mass of substance, the random movement of molecules is due to Brownian motion, the kinetic energy of the molecule that causes it to move and exchange places with other molecules
      a. The movement is directed from higher concentration of molecules to lower concentrations
  B. Visual Model (Figure 1)
    1. A dye is added to one end of a narrow tube filled with water
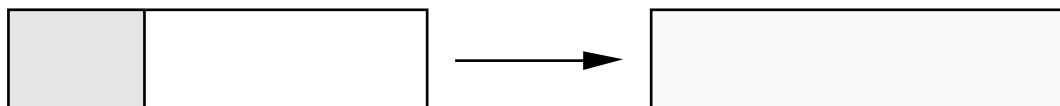   2. The dye will eventually spread throughout the tube (via diffusion)

Figure 1. Model for diffusion. At time $= 0$, a chemical is released into one end of the narrow tube filled with water. The time $= t$, the chemical will have moved through the water filled tube. No net movement occurs when

the system has reached equilibrium (entropy is maximized; free energy is minimized)

3. When the dye has become constant everywhere in the tube, net fluxes of dye across any section of the tube will be zero
4. As long as the dye distribution is not homogeneous, net fluxes will proceed across any interface such that transport is directed from the higher to the lower concentration
5. The net flux of dye is proportional to the concentration difference between any one point and an imaginary (or real) interface it crosses, or
   a. The flux term is given as mass (or moles) per square cm per unit of time (for example, moles/cm^2/sec

C. Diffusivity is related to **molecular size** and **viscosity** of the medium
1. Larger chemicals progress more slowly because the mean velocity of their thermal motion is reduced and their increased cross-sectional area reduces their mean free path, i.e., their ability to slip through a crowd of other molecules
2. Media exhibiting more crowding or viscosity will inhibit the Brownian movements of molecules
   a. Air is less densely packed than water, which means much higher diffusivities for a given chemical in air than in water
      1. General diffusivity (i.e., the diffusion coefficient) in air is about 0.1 cm^2/sec; for aqueous media, the general diffusivity is about 10^4 times less
3. Another variable affecting diffusivity is temperature
   a. Elevated temperatures result in more vigorous Brownian motion and consequently more rapid random movement
   b. Because heated media are less densely packed, "percolation" of chemicals through them is facilitated

III. Turbulent Diffusion
A. Molecular diffusion is important mainly on the microscopic scale; it brings reactants into contact with each other and causes transport of chemicals across boundaries (e.g., across a cell membrane; from water onto a particle surface; across the air-water interface)
1. On a macroscopic scale (rivers, lakes, aquifers), molecular diffusion is extremely slow in causing transport;
   a. Diffusion occurs very quickly (seconds or less) in water over distances less than 100 μm and in air across distances less than 1 cm; but to diffuse as far as a meter requires a long time
2. Over large distances, transport is caused by the motion of the fluid itself, i.e., **advection**; only at very short distances, where viscosity inhibits fluid motion, does transport by molecular diffusion become relevant (such areas exist in the pore space of sediments and at the various interfaces)
   a. There is a critical distance at which molecular diffusion and advection play equal roles in chemical transport

3. Fluids are turbulent, making description of transport by currents complicated; turbulence can be thought of as the fine structure of the fluid motion, as opposed to the flow pattern of large-scale currents (i.e., small scale motion within large scale motion)
4. Differences between molecular diffusion coefficient (called D) and turbulent (eddy) diffusion coefficient (called E_x):
    a. E_x depends only on the fluid motion (turbulence structure of the fluid) and not on the substance described by the concentration C; D depends on the physicochemical properties of the substance and the medium (e.g., the medium's viscosity)
        1. Because the intensity of turbulence must strongly depend on forces like wind, solar radiation, river flow, etc., driving the currents, the coefficients of turbulent diffusion constantly vary in space and time
    b. Visual model (Figure 2)--a dye is placed at a single point in a body of turbulent water; large scale fluid motion moves the dye patch center of mass to a new location; at the same time, the patch grows in size because of small (turbulent) eddies (i.e., eddies with size similar to or smaller than the dye patch size) (remember that molecular diffusion is also causing the molecules to spread out in a normal distribution over small distances);
        1. With increasing time, the growth of the patch will continue at an increasing rate since larger and larger eddies will contribute to the spreading while the mean motion becomes more and more restricted to the very large scales. Eventually, the dye patch extends over the whole water body; then no significant mean motion is possible any more, and all mixing has become turbulent (small scale fluid motion)

pesticide spill in water

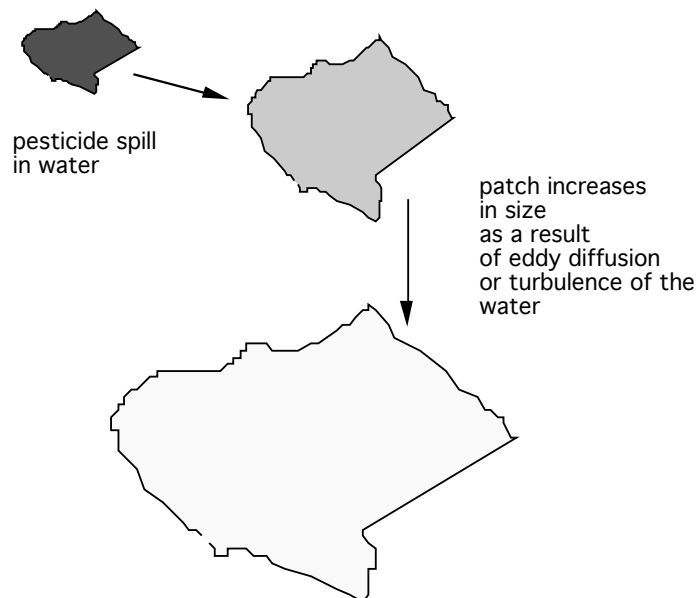patch increases in size as a result of eddy diffusion or turbulence of the water

Figure 2. Patch size of a spilled chemical in a body of water will spread owing to turbulence (a.k.a. eddy diffusion). Thus, it is the movement of the fluid itself, not diffusion, that carries the chemical away from its point source.

5. In the surface water of the ocean, turbulent diffusivities (i.e., E_x) vary by several orders of magnitude (10^2 - 10^8 cm^2 • sec^{-1}, the lower value is still 10^7 times larger than molecular diffusivity); since the shear stress of wind acting at the water surface is one of the most important sources of turbulent movement, diffusivities in the deeper parts of oceans and lakes are usually smaller by 1-2 orders of magnitude (volume of water is less affected by shear stress).
6. Atmospheric turbulence > Oceans > Lakes
    a. Lakes are less exposed to wind than oceans, therefore less turbulence
    b. Lakes don't have long-lasting current systems
    c. Deep parts of lake are less turbulent than shallower parts

IV. **Volatilization: Physical Models Describing "Structural Aspects" of Volatilization from Air to Water** (or vice versa)--note that the models indicate that molecular diffusivities in both air and water are necessary to describe the air-water mass transfer process
    A. Four layers arranged in series at the contact of air and water interface (Figure 3)
        1. Turbulent air
        2. Quiescent layer ("skin") of air about 1 mm thick (**boundary layer**)
        3. A quiescent layer of water ~0.1 mm thick (**boundary layer**)
        4. Well-mixed (turbulent) bulk water below the interface of (2) with (3)
            a. It is at the interface between (2) and (3) that the molecules of air and water contact one another
            b. Bubbles, aerosol droplets, and oily surface films are not included in this particular physical model
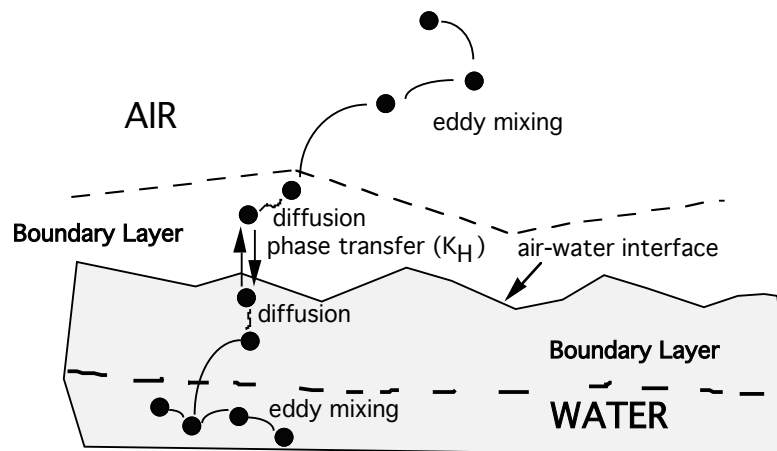

Figure 3. Model of volatilization showing the boundary layers at the interface of the water and the air. Below the boundary layers are the turbulent layers of air and water.

B. Assumption of homogeneous chemical concentration in the turbulent air and water layers as a result of bulk fluid motions (turbulence); thus, vertical transport through these layers is not rate limiting for volatilization

C. Boundary layers are established because eddy mixing is reduced in a thin zone just at the water or soil surface as a result of diminished wind flow from frictional forces opposing wind movement;
   1. Also, fluids become increasingly viscous on smaller and smaller length scales, requiring more energy than is available to drive eddies less than 100 μm (water) or 1 mm (air);
      a. Thus the boundary layers are stagnant or intermittently mixed in contrast to the bulk volume just above (air) or underneath (water)

D. Chemicals must move through the **boundary layers** where eddies or turbulence is absent; thus **molecular diffusion predominates**, and movement through the boundary layers is therefore rate-limiting to volatilization

E. The contact boundary (i.e., interface) is presumed to be a gas in equilibrium with the adjacent surface water, or in the case of soil with the soil water;
   1. Regardless of the speed of transport through the bulk layers, the molecular equilibrium at the interface is established fast enough to compensate immediately for concentration changes in the bulk volumes

V. Volatilization From Soil

A. Chemicals must diffuse to the surface of the soil, or at least be in a position where there is good atmospheric contact for exchange of chemical. Volatilization will still proceed through a surface boundary layer (stagnant air boundary) and wind speed or turbulence will enhance flux
   1. Temperature and moisture content of the soil will also influence flux
   2. Must consider effects of adsorption and degradation

B. Volatilization from soil involves desorption of the chemical from soil, movement to the soil surface in the water or air phase, and vaporization into the atmosphere; mechanisms and factors affecting volatilization can be grouped into three categories:
   1. Those that affect vapor pressure or vapor density of the pesticide at the soil surface (or in other words at the interface where evaporation will take place)
   2. Those that affect movement away from the evaporating surface (e.g., turbulence)
   3. Those that affect rate of movement of the pesticide to the evaporating surface (e.g., mass transfer in water and air)

C. Vapor pressure (V.P.) or vapor density (V.D.) of the pesticide within the soil
   1. Using the fugacity approach, volatilization can be seen as starting with a concentration of pesticide at the inner layer of the stagnant or laminar boundary layer (remember that crossing of this layer is dominated by molecular diffusion)
      a. The concentration of chemical can be expressed as a vapor pressure or as a vapor density (i.e., the weight of the chemical per unit volume)--this is equivalent to the pure compounds vapor pressure (i.e., the saturation or equilibrium vapor pressure) only if--

1. The residues are present as a continuous exposed layer on the soil or plant surfaces
2. The fugacity is not reduced by chemical or physical adsorption reactions
3. The rate of vapor formation is fast enough to keep the inner surface of the laminar or boundary layer saturated

b. The V.P. values for most pesticides are very low compared to common environmental chemicals like gases, alcohols, aldehydes, terpenes (derived from plants), and thus would predict that volatilization would be low;
   1. However, keep in mind that the background vapor pressure in the atmosphere is essentially zero (i.e., the pesticides do not naturally exist there) which makes the system equivalent to evaporation into a vacuum

c. Note that there is a tremendous range of vapor pressures and thus vapor densities for contaminants; for example, 2800 mPa for the herbicide EPTC to 0.00074 mPa for picloram;
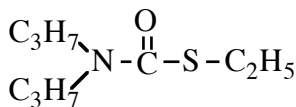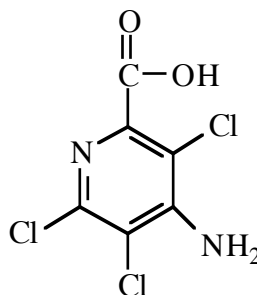
EPTC (Eradicane)   picloram (Tordon)

   1. Take-home lesson--don't lump contaminant behavior as if it's all the same; the physicochemical properties tell you that the behavior is different for each chemical

2. Vapor density is greatly decreased by sorption
  a. Influenced by soil water content, pesticide properties, and soil properties
    1. Sorption or dissolution in water or plant cuticle (waxy) reduces the vapor pressure below the equilibrium value of the pure compound
    2. Note in the data for dieldrin below (Taylor and Spencer, 1990), that vapor density decreases generally as organic matter increases and moisture decreases (i.e., dry soil). (Figure 4)
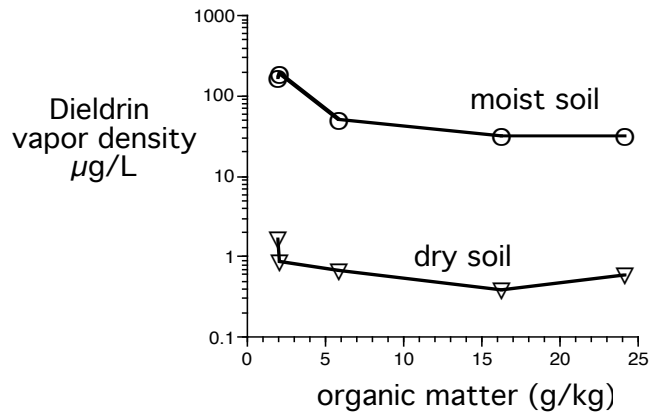
Figure 4. Vapor density of dieldrin relative to soil OM content (graph drawn from data in Taylor and Spencer 1990)

    a. Note that if sorption is linear, and Kd is constant regardless of solution concentration, then as concentration increases, relatively more is in solution and relatively more can escape into the vapor phase; this process proceeds until at some solution concentration, movement from water to air is at equilibrium (i.e., the process is in accordance with Henry's Law, and at equilibrium, distribution between water and air is defined by K_H;)

    b. As expected, note in the graph below that temperature greatly affects vapor density; remember that V.P. is a function of temperature; thus increases in temperature would greatly increase volatilization (Figure 5).
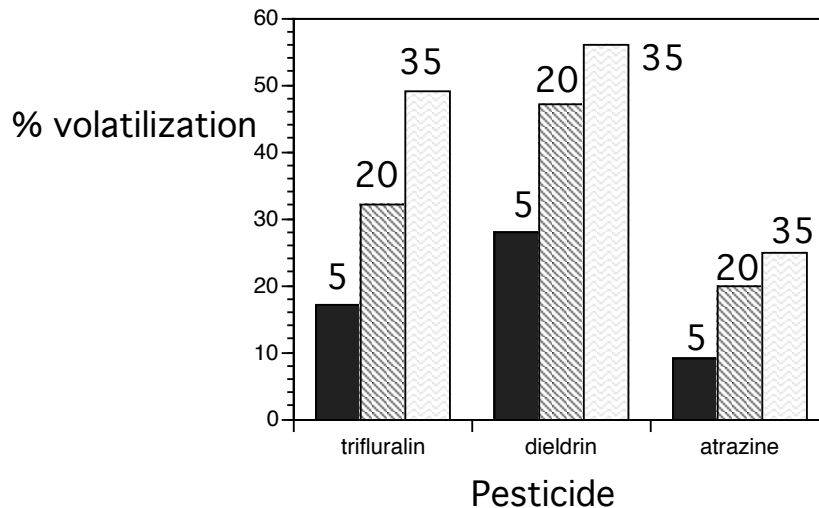

Figure 5. Effect of temperature on proportional volatilization of three pesticides

   3. Practical significance of relationship between contaminant concentration in soil and vapor density:

    a. If a pesticide is sprayed at a rate of 1.25 kg/ha to the surface of an uncultivated bare soil and remains within the top 1-mm layer, the

local concentration may be expected to be about 75-100 mg/kg (assuming a bulk density of 1.25 g/cc); according to the graph above (i.e., Vapor density of dieldrin…), the vapor densities will be close to or at saturation (if the moisture content is also adequately high); thus volatilization would be facilitated
   b. If the pesticide is incorporated to a greater depth, for example 75 mm, the average soil concentration will be reduced to 1 - 1.25 mg/kg, the relative vapor densities are likely to be reduced to 10% or less; thus volatilization will be reduced

   D. Volatilization in the Field
      1. Studies of pesticides intentionally applied to fields show some definitive patterns of volatilization; these patterns could be generalized to any chemical present in the soil. (A good review article: Taylor, A. W., and W. F. Spencer. 1990. Volatilization and vapor transport processes. pp. 213-269 in Pesticides in the Soil Environment. Soil Science Society of America, Madison, WI)
         a. Most rapid volatilization losses are found where materials with the highest vapor pressures are exposed on the surface of moist soils
            1. Incorporation into the soil reduces volatility
         b. Volatilization from moist soils show marked diurnal changes with maximum rates in the early afternoon (assuming moisture content is adequate as it might be with a clay or silt loam soil)
      2. If soil has a propensity to dry out (like a sandy or sandy loam soil), then volatilization flux probably greatest in morning or evening when moisture would be highest
         a. Vegetation on surface and consequent interception of a spray results in greater overall volatilization (may be due to larger surface area of vegetation; also, air circulation and transfer is probably much greater in the turf or vegetation than on the soil surface)
         b. Volatilization from soil and/or plant surfaces followed by redeposition can be a significant factor in causing occurrence of contaminants on plants

VI. Effect of Surface Films on Volatilization from Surface Water
   A. Surface Films
      1. Oily liquids or amphiphilic substances often accumulate at air-water interfaces. A surface film or microlayer is formed that may slow rate of exchange from water to air.
         a. Equivalent to adding a third stagnant boundary layer in series
         b. And/or equivalent to the damping of mixing and turbulence, thereby increasing diffusion lengths or slowing renewal rates
      2. Effect of Kow: if a compound has a large Kow, then can neglect the effect of film's transport resistance (i.e., resistance to transport into the film), unless the diffusivity of the volatilizing compounds through the film was especially low (for example, in highly viscous oil)

a. Gas exchange (gases would tend to have low Kow) is little affected by oil films; but could be due to dampening of surface layer mixing

3. Addition of organic material (like oil) to sea surface causes wave action to decrease yielding a "glassy" slick appearance; wind speed effects on volatilization will be correspondingly decreased.

B. In addition to volatilization from water solely in the gas phase, other mass transfer processes can result in transfer from water to atmosphere and vice versa; for example, bubble formation and/or emission.

1. For example an experiment reported by Sodergren and Larsson (1982; Transport of PCBs in Aquatic Laboratory Model Ecosystems from Sediment to the Atmosphere via the Surface Microlayer; Ambio 11:41-45) measured PCBs on jet impactors situated above a column of sediment and water containing PCBs. PCBs were also measured in the surface microlayer. (Table 1)

a. Presumably, bubbles of air arising from metabolism in the sediment can carry PCBs through the water column, deposit in the surface microlayer, and then move into the air.

b. Biota in the sediment can disturb the sediment causing a release of PCBs;

c. Thus, in the following table, when animals are present, perturbation of the sediment as well as air bubbles results in measurable PCB concentration in the sample surface microlayer as well as volatilized PCBs collected on the jet drop impactor. However, in sterile soil, PCBs did not move from the point of origin (the sediment).

Table 1. PCB concentrations recovered after biotic perturbation of sediments (Adapted from Sodergren and Larsson, 1982

System	sediment (ng/g) 0-5 mm depth	water (ng/L)	surface microlayer ng/cm²	jetdrop impactor ng/cm²
w/ midges	123	0	92	16
w/ worm & midges	37	6	76	8
sterile	56	0	0	0
no animals	145	0	0	0

VII. Pesticide Spray Drift

A. Represents a direct emission of pesticide residues in the atmosphere. However, any chemical that is deliberately applied into the environment (i.e., a nonclosed system) is subject to the same principles affecting movement and possible contamination due to eventual deposition of residues.

B. See the accompanying article by Felsot (2005), Evaluation and Mitigation of Spray Drift in Proc. International Workshop on Crop Protection Chemistry in Latin America; Harmonized Approaches for Environmental Assessment and Regulation, 14-17 February, 2005, San Jose, Costa Rica

VIII. Mechanisms of Surface Transport
   A. Note that many examples will involve pesticides because these are applied yearly and will be at much higher concentrations than other chemical contaminants; thus, much research with pesticides has elucidated principles about transport that would have been difficult to obtain by just examining contaminants in soil that are at very low concentrations and are not intentionally added yearly; uncontrolled hazardous waste might be an exception, but I have seen very few studies where hazardous waste has been studied from the perspective of elucidating principles of surface transport; more studies are available for leaching, however).
   B. Runoff is a term used to describe the movement in surface drainage of water and any dissolved or suspended matter it contains from a plot, field, or small watershed (Leonard 1990 definition, "Movement of Pesticides into Surface Water, p. 303 in H. H. Cheng, ed. Pesticides in the Soil Environment. Soil Sci. Soc. Am., Madison, WI).
      1. However, agricultural engineers prefer to consider surface drainage as consisting of the runoff phase (water movement) and the eroded or erosion phase (particulate, sediment, or soil movement)
      2. Chemical runoff includes dissolved, suspended particulate, and sediment-adsorbed chemical
      3. Although runoff is commonly used in the sense of the definition above, i.e., including water and soil, it is also informative to follow the definition of agric. engineers because of the quantitative differences in pesticide movement in each phase;
         a. Furthermore, because runoff & erosion can be managed (and thus provide the potential to control chemical surface transport), it is useful to treat "runoff" as two phases (but obviously they are occurring together and the water is carrying the sediment)
   C. Chemical extraction into runoff may be described as mechanisms of:
      1. Diffusion and turbulent transport of dissolved pesticide from soil pores to the runoff stream; (runoff)
      2. Desorption from soil particles into the moving liquid boundary; (runoff)
      3. Dissolution of stationary chemical particulates; (runoff)
      4. Scouring of chemical particulates and their subsequent dissolution in the moving water; (runoff)
      5. Entrainment in runoff while attached to suspended soil particles (erosion)
   D. General Description of the Runoff Process
      1. After a chemical is released to soil, whether by a spill, application of granular formulations or sprays of pesticides, or atmospheric deposition, there will be a strong tendency toward the sorbed state.
      2. If precipitation exceeds rate of water infiltration, water may pond on the surface, and if the slope is significant (could be anything measurable given an intense enough rainfall), than water will begin to move across the surface. If chemical desorbs in the water phase, it will be carried by the surface flow.
      3. Precipitation impacts the soil surface with a characteristic energy, loosening silt and clay particles; if the rainfall is hard enough and the soil in the near surface becomes saturated, then particles can be carried (i.e., eroded) with the

horizontal movement of water across the soil surface. The faster the flow of water, then the greater the transport of sediment. If chemical is adsorbed on the sediment, then it is carried by the moving water.

4. From the above discussion, it follows that the total amount of chemical lost by runoff and erosion is equal to the product of the carrier phase (i.e., water or sediment) times the concentration of the chemical in each phase.

E. Because the pesticide, which is largely in the sorbed state, essentially has to undergo phase transfer into the runoff water, or alternatively, leaves in the sorbed state as erosion, the total amount available for transport becomes a question of the effective depth of soil or surface soil mass that interacts with runoff.

1. Estimates of the effective interacting depth have varied from 3 mm to 10 mm (this is also called the **mixing zone**)

a. The degree of interaction decreases exponentially with depth

b. Effective depth of interaction is related to the degree of soil aggregation and it increases with soil slope, kinetic energy of raindrops, and rainfall intensity

2. Note that if rills form (i.e., surface channels caused by erosion of soil), the effective depth of interaction of runoff with soil is much deeper

a. Rills form where water flow becomes concentrated because of topography (steeper slopes, i.e., more hilly, have greater propensity for rill formation), tillage patterns (plowing up-and-down slope rather than across slope causes more rills), or other irregularities affecting water flow patterns

b. The concentrated flows detach and transport soil from a limited part of the land surface

c. Although varying in size and depth, rills are by definition limited to depths that can be crossed by farm machinery and filled in by tillage (Figure 6).
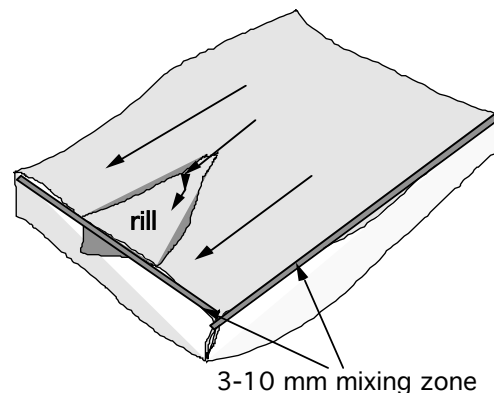

Figure 6. Rill on soil surface. Note that the rill exposes deeper soil layers to direct runoff.

3. Shallow interflow is another mechanism by which runoff can interact with soil at an effectively deeper depth

a. Shallow interflow is defined as water that has infiltrated the soil surface, but returns to the surface as seepage downslope or into rills, furrows (the spaces in between seed rows created by plowing), and other surface depressions.

F. Chemical can be surface transported while in the sorbed state (i.e., eroded) as well as while dissolved in runoff water; whether one mode of transport dominates will depend on the compound's K_d
   1. Wauchope (1978) has found that pesticides with WS < 5 ppm are transported primarily by sediment (i.e., erosion phase) (Journal of Environmental Quality vol. 7, pp. 459-472; 1978)
   2. Baker and Johnson (1983) have characterized runoff phase and potential relative to K_d; K_d>50 favors runoff in erosion phase (Ag. Management & Water Quality, pp. 281-304; 1983)
G. Factors Affecting Surface Runoff of Pesticides (i.e., what controls the amount of surface runoff)
   1. **Rainfall timing and intensity**: because the pesticide is subjected to so many dissipation pathways, including degradation, volatilization, leaching, and plant uptake, the timing between application and the first runoff-producing rainfall is critical.
       a. The shorter the interval between chemical application and a rain event, then the greater the pesticide runoff
       b. Wauchope (1978) considered that the bulk of runoff over the season was determined by critical runoff events and catastrophic events
           1. Critical runoff events were defined as occurring within 2 weeks of pesticide application, had at least one cm of rain, and runoff volume was 50% or more of precipitation amount
               a. "These events almost always produce the bulk of the runoff losses observed for an entire season unless the chemical is incorporated or is extremely persistent."
       c. Catastrophic events are defined in terms of pesticide losses; rainfall amount and intensity is high enough to cause losses of 2% or more of the applied pesticide
   2. Amount of runoff is affected by **where pesticide application is directed** (i.e., to the target; e.g., is the pesticide applied directly to soil or is it intercepted by a plant canopy or a layer of plant residue on the ground)
       a. Wash off from these surfaces must occur prior to transport in runoff; the tenacity with which pesticides are sorbed by vegetation surfaces will thus affect total pesticide mass available for runoff
   3. **Pesticide properties**: affect sorption as well as degradation
       a. Baker and Johnson (1983) pointed out that chemicals with "intermediate" K_d's are most susceptible to greatest runoff losses
           1. If Kd is real high, runoff will be largely in sediment, but amount of sediment running off is orders of magnitude lower than amount of water runoff
           2. Very low Kd pesticides will be lost through subsurface flow (i.e., leaching)
       b. Intermediate Kd pesticides are still quite adsorbed and thus trapped in the surface, but soluble enough to become entrained in runoff (i.e., they are likely to desorb fast enough in the mixing zone)
   4. Topography, soil characteristics, surface roughness

   a. Runoff volumes greater from steeper slopes
   b. Soil characteristics:
    1. Organic matter content (affects sorption);
    2. Soil texture affects infiltration rate
     a. Greater rates of infiltration with comparatively higher rainfall intensities will result in less runoff then slow rates of infiltration
     b. Sandy soils generally have greater infiltration rates than finer textured silt loams and clay loams
     c. Surface roughness can slow the movement of water, allowing more time for infiltration
 H. Spatial and Temporal Relationships
  1. The greatest concentration of chemical will be found in the earliest stages of runoff; this observation has been noted from small plot research
  2. However, the concentration in runoff is much more variable when large or field-sized watersheds are considered
  3. The concentration of pesticide in sediment is actually higher than in water; however, except for compounds with extremely high K_d's, water runoff will be the main transport mechanism for most pesticides
   a. Consider that over time, the volume (or mass) of water running off a field is several orders of magnitude greater than the sediment eroding.

IX. **Magnitude of Pesticide Losses in Runoff** (Natural rainfall-driven seasonal losses and losses based on simulated rainfall)
 A. **Cropland** (Wauchope 1978; i.e., "edge-of-field" losses does not account for amount of pesticide that actually reaches the streams; in other words there are further attenuation processes between the edge of the field and the stream)
  1. 1% of applied amount--foliar-applied emulsifiable concentrates
  2. 2-5% of applied amount--wettable powders (includes herbicides, fungicides, insecticides)
  3. 0.5% of applied amount--other formulations, like emulsifiable concentrates and incorporated pesticides
  4. Note that simulated runoff studies (i.e., using rainfall simulation machines in the field on small plots) tend to show larger percentage losses than studies under natural rainfall conditions
 B. Losses from **forests and rangelands** (bulk of pesticides used are herbicides)
  1. Generally less than 1%; rule of thumb is that runoff losses are much less than from agricultural land because:
   a. Partial area contribution to runoff, that is, all areas of the watershed do not contribute runoff equally
   b. Herbicides tend to be sufficiently mobile to penetrate the soil surface before runoff begins and be translocated below the surface that is in contact with runoff (of course there are exceptions)
    1. Forest floor is covered with detritus contributing to high infiltration rates
 C. Field-to-Stream Losses (Attenuation in Overland Transport)

1. Runoff losses at the edge of the field may reach several percent of the application and concentrations in runoff may reach several mg/L if runoff occurs soon after application;
    a. However, runoff from large scale watersheds is usually much lower, and concentrations in receiving streams are much lower than in runoff; implication is attenuation during overland transport
    b. Attenuation by dilution, deposition, and trapping of sediments, adsorption by stream bottom and bank materials, and infiltration along the various flow paths

X. **Best Management Practices for Prevention of Pesticide Runoff** (based on Baker & Johnson (1983; pp. 281-304 in Agricultural Management and Water Quality. F. W. Schaller and G. W. Bailey, eds. Iowa State University Press, Ames, IA)
    A. Strategy--because surface transport of pesticides are quantitatively the product of the pesticide concentration in the carrier phase (i.e., the runoff water or eroding soil) and the mass or volume of carrier phase, then one can either reduce the concentration of the pesticide or the mass/volume of carrier phase; (Figure 7)
        1. Control of runoff volume and erosion mass
            a. Conservation tillage systems; contouring plowing; closely grown crops; tile drainage
        2. Control of concentration
            a. Timing of application/planting; reduction in rate of application; avoiding direct soil application; use of controlled release formulations; incorporation of chemical to deeper layers of soil profile
        3. Control of edge-of-field to stream losses
            a. Filter strips and grassed waterways; terraces; catchment basins

% of Pesticide Lost

surface runoff

subsurface flow

1000   100   10   1   0.1

K_d

Appropriate BMP

erosion & sediment control

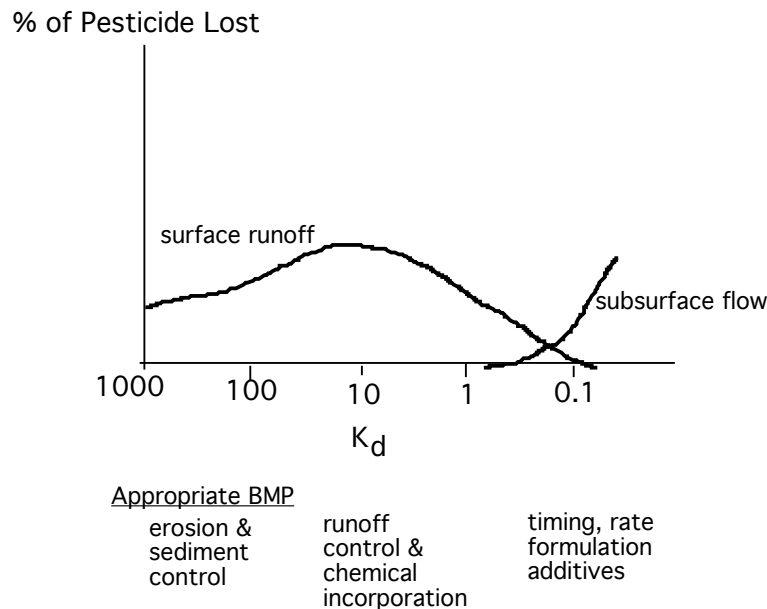runoff control & chemical incorporation

timing, rate formulation additives

Figure 7. The above BMPs are most appropriate to the corresponding Kd shown above in the graph. Note that the percentage of pesticide loss in runoff and/or leaching is related to the K_d of the compound.

XI. Theoretical Aspects of Leaching
    A. Physical Model of Soil (Figure 8)
        1. Structure of soil is determined by packing of grains or particles (schematics of model on following page)

Soil Models for Texture & Moisture Holding Capacity

| Coarse | Fine | Fine |

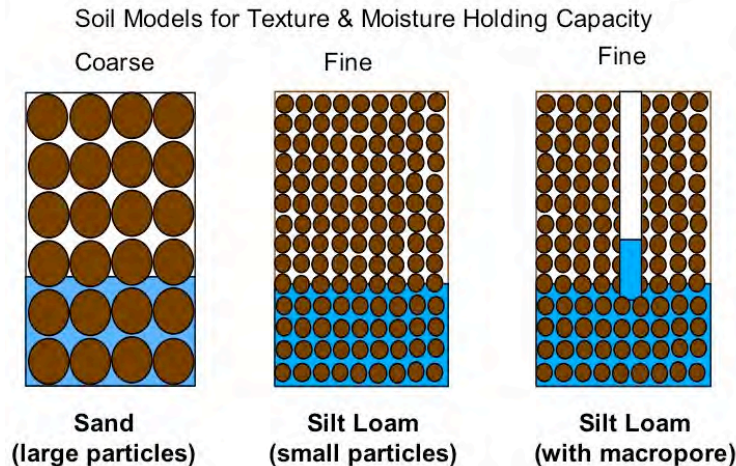| Sand (large particles) | Silt Loam (small particles) | Silt Loam (with macropore) |

Figure 8. Models for packing of soil particles of different textures and a macropore in a silt loam.

        2. The larger the particles (for example, sand would predominantly have particles or grains 50 μm - 2 mm in diameter) then the looser the packing, the larger the voids, but overall the less volume taken up by the pores
            a. Pore volume--in a given volume of soil, the volume taken up by the pores, whether filled with water or air, is the pore volume
        3. The smaller the particles (for example, clays, and soils with equal amounts of clay and silt [loams]) then the tighter the packing, but the greater the number of pores and thus the pore volume
        4. Rate of infiltration will be controlled by the soil structure; for ex., soils with many pores that are generally very small (i.e., fine textured soils) or fewer pores but comparatively large (coarse textured soils)
            a. The latter situation (i.e., coarse texture) will result in faster infiltration into soil but a lower soil moisture holding capacity
            b. The former situation (i.e., fine texture) will results in slower infiltration into soil, but a higher moisture holding capacity
            c. Note that the moisture is held in the pores by capillary forces
            d. Water moves into the pores under gravitational pressure;
                1. After a rainfall, the pores near the surface of the soil become full of water (saturated); a "head" or hydraulic pressure is created relative to the unsaturated volume under the surface
                2. Water then "pushes" into the lower parts of the profile under gravity;

a. When the pressure of the "push" is balanced with the pressure from the pores filled with water below, then the water stops flowing

5. Macropores
   a. Pores or channels created by old root and earthworm channels or cracks and fissures (for ex. in clays);
      1. Usually greater than 75μm in diameter although size can vary
   b. Too wide for capillary forces
   c. Water will start to flow into macropores only after micropores fill up (these will fill up first because of capillary tension) or if the upper interior surfaces of the macropore are already wet

B. "Physical Model of Chemical": Chemical mass can be partitioned among different phases
   1. Gaseous (soil air)
   2. Dissolved (soil water)
   3. Adsorbed (stored mass, organic matter and/or clay sorbed)

C. Two transport mechanisms for dissolved phase
   1. Convection (advection)--transport by bulk movement of water in the pores
      a. In an analogous sense to eddy diffusion, there are small-scale convective fluctuations; this type of movement is called hydrodynamic dispersion
      b. Preferential flow model (owing to presence of macropores)
         1. Soil is full of local pathways like structural voids created from old biological channels (for ex., old root channels) that can carry water at velocities much greater than those of the surrounding matrix even when the entire field surface is uniformly watered.
   2. Diffusion
      a. Must consider the tortuosity of movement in the dissolved phase by diffusion (also applies to vapor phase movement);
         1. Distribution of pores is chaotic; thus, tortuous movement increases the path length that a molecule must travel in soil.

XII. **Measuring Leaching in Soil**
   A. Techniques
      1. Soil thin layer chromatography
         a. Measure an Rf, the movement of the chemical relative to the water front
      2. Soil columns
         a. Packed
            1. Soil aggregation structure destroyed
            2. Possibility of wall effects
         b. Intact
            1. Soil aggregation structure preserved
            2. Cores taken from field without disrupting soil profile
      3. Lysimeters
         a. Laboratory and field scale
         b. Intact monoliths of soil although people also pack columns and call them lysimeters

        c.   Mass balancing of water
        d.   Subsampling possible
        e.   Usually of larger diameter
        f.   Term also applied to soil water samplers
    4. Ground water monitoring field studies
        a.   Wells
        b.   Profile sampling
  B. The Break-Through Curve (BTC) (Figure 9)
    1. The volume of the pore space in the column is known or can be measured
    2. Water with chemical is added to the top of the column or lysimeter
    3. When the water first exits, this is called the break-through; ditto for when the chemical first exits
        a.   Breakthrough of the chemical should lag behind the water (remember the chemical is retarded by sorption in the soil)
    4. A curve of chemical concentration (or tritiated water as a marker for the water flow) can be plotted relative to pore volumes flowing through the soil
        a.   Pore volumes would thus be the volume of water held in the pores of the soil
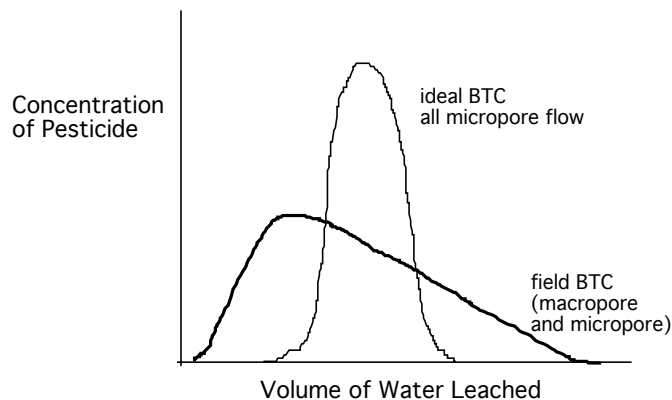

Figure 9. Breakthrough curves (BTCs) for a pesticide added to a soil column and then leached with water. Note in the ideal BTC, the pesticide (or any contaminant) would move with the water front flowing through the micropores. When all the micropores are filled, water would start leaching out of the bottom of the column and the pesticide would move with it, all coming out in a pulse with a normal distribution. When there is a macropore, some of the water "short-circuits" the micropores, and flows down the macropore. The chemical leaching through a macropore would breakthrough the column faster than the chemical leaching only through a micropore (think of the micropore as having a diameter small enough for capillary forces; the macropore would be wider than the diameter where capillary forces are active). The rest of the chemical is "hung up" in the micropore, so it lags behind and comes out over a much longer period of time

XIII.   Factors Affecting Movement

A.   (Factors Affecting Movement of Chemicals to Groundwater--can be characterized generally as field factors and chemical factors; when all of the factors (or most of them) appear in combination, than the potential for GW contamination is high).

B.   Field Factors
1.   Recharge--total precipitation and irrigation recharge greater than about 25 cm/yr. Soil drainage ability can be influential; soils with low moisture holding capacity will have a high recharge rate
2.   Nitrates--high levels may be indicative of contamination potential, but this has not been substantially validated
3.   Aquifer--unconfined; porous soil lying above an unconfined aquifer (i.e., an aquifer not overlain by an impermeable layer, usually composed of clay)
4.   Soil with pH or other factors that provide stability to the chemical residues

C.   Chemical Factors
1.   Mobility
   a. $C_W > \sim 30$ ppm
   b. $K_d < 5$, and usually < 1 or 2 (soil-water distribution coeff.)
   c. $K_{oc} < 300\text{-}400$
   d. $K_H < 10^{-2}$ atm-m^3/mol
   e.   speciation: negatively charged or with partial neg. charge at ambient pH
2.   Persistence
   a.   Hydrolysis $t_{1/2} > \sim 25$ wks
   b.   Photolysis $t_{1/2} > \sim 1$ wk
   c.   Soil $t_{1/2} > 2\text{-}3$ wks

D.   Prediction of Leaching Potential--the Gustafson Nomograph
1.   Developed for pesticides--develop a ground water ubiquity score (GUS) which is related to the potential for leaching in a column of soil; this is best used as a screening procedure

$$ GUS \;=\; \log_{10} T_{\frac{1}{2}} x\,(\,4 \;-\; \log_{10} K_{oc}\,) $$

2.   Utility:
   a.   To determine priorities for a multi-chemical monitoring program
   b.   To enable chemical companies to determine the need for monitoring and modeling prior to submission of a new pesticide data package to a regulatory agency
   c.   To enable regulatory officials to determine the need for additional modeling or monitoring of a pesticide prior to making regulatory decisions
   d.   To enable user groups to determine whether use of certain pesticides should be continued after careful consideration of the toxicology profile and the site-specific hydrology

E.   The Role of Recharge Factors and Depth of Aquifer Recharge itself can be further subdivided into:
1.   Soil properties, for ex., coarse textured soils transmit water more easily; thus convective flow (or advection) is much faster than in highly structured soils

with minimal macropores; macropore flow however can promote rapid leaching

2. Timing of rainfall--rainfall soon after chemical "hits" the ground promotes leaching because of higher concentration and less time for sorption and degradation
   a. Some pesticide studies show there is a seasonality to detection of pesticides in shallow ground water (Figure 10)
   b. Ambient soil moisture prior to first heavy rainfall after chemical lands on soil is important to leaching; generally the higher the ambient moisture, the more likely the chemical will leach with the first saturating rainfall
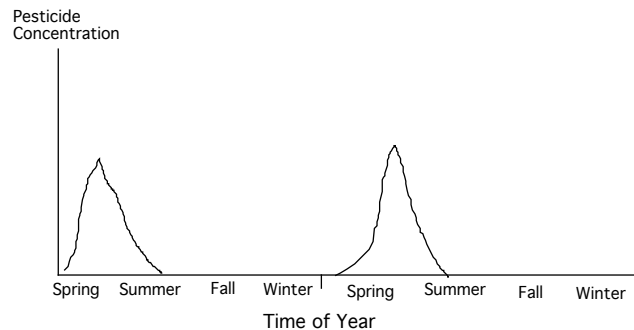

Figure 10. Seasonality of leaching is related to both pesticide application periods and occurrence of rainfall.

F. Deeper wells tend to be "cleaner" on average than shallow wells (following graph illustrates the results from a US Geological Survey Study; Figure 11)
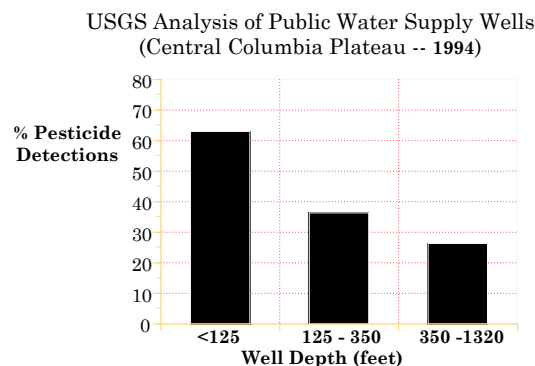

Figure 11. Percentage of pesticide detections in wells decreases with depth of well. (Redrawn based on Williamson et al. 1998)

G. Facilitated Transport of hydrophobic compounds by association with dissolved organic matter
   1. Partitioning of neutral organic compounds into dissolved humic materials can enhance the apparent solubility of contaminants and reduce the apparent partition coefficient to the soil
   2. Implications: cause contaminant spreading in ground water, or can help aquifer clean up (pump and treat technology)

H. Adding organic carbon to soil can decrease leaching--either by increasing sorption or stimulating degradation (Figure 12)
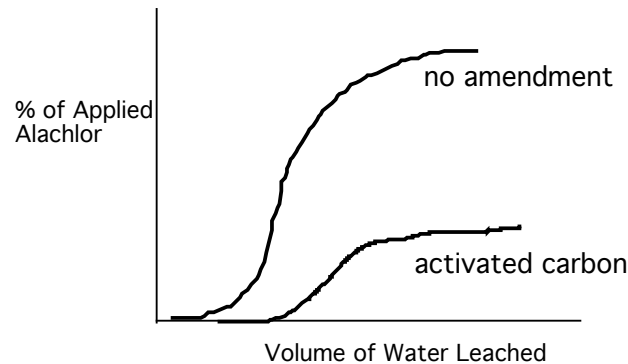

Figure 12. In a soil column experiment, addition of activated carbon to the top of the soil retarded the movement of the herbicide alachlor through the column despite saturating amounts of water added. (Based on Guo et al. 1993)

I. Role of Chemical Concentration & Degradation Potential
    1. Tendency to leach proportionally greater at higher concentrations than the same chemicals at lower concentrations;
        a. The breakthrough curves tend to be shifted to the left at higher concentrations; the reason is nonlinear adsorption isotherms and lack of equilibrium
            1. A nonlinear isotherm (i.e., n from Freundlich isotherm would be <1) would imply decreasing sorption with increasing concentration
                a. Amount of pesticide sorbed continues to increase but a decreasing rate with each increase in solution concentration
            2. Chemicals at high concentrations, which are characteristic of spills and wastes tend to be more persistent; (Figure 13)
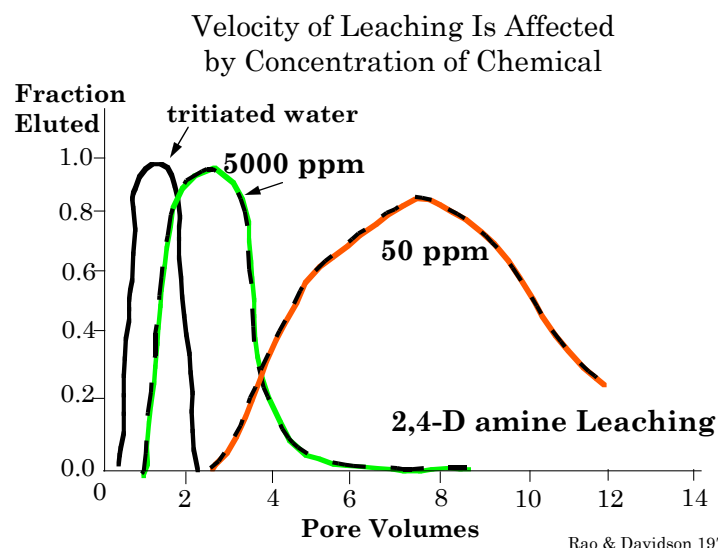

Figure 13. Effect of concentration on leaching of 2,4-D amine through a soil column. Note the breakthrough curve for the pesticide at 5000 ppm was shifted to the left, close to the

BTC for tritiated water, which would not be expected to be sorbed in the soil to any appreciable extent. (redrawn based on Rao and Davidson 1979)

J. Once in ground water, chemicals can be very persistent because there is a tendency for microbial populations to be low; but this situation may exist because of lack of nutrients.
   1. When nutrients are supplied to ground water, the potential for metabolism and degradation of contaminants increases; for example, methane addition can stimulate degradation of TCE, but time frame is relatively long
   2. However, under some conditions, certain nutrients can be inhibitory; for example, sulfate addition can inhibit degradation of TCE
K. Aging Effects
   1. BTC becomes prolonged over a much longer period of time and has a lower peak concentration eluted when "aged" chemicals are compared to freshly injected chemicals (see graph below; native atrazine is the aged pesticide) (Figure 14)
      a. Hypothesis: two compartments, a "fast" compartment in which chemical is sorbed but in rapid exchange with water, and a slow compartment where chemical is sorbed but exchanges with water by radial diffusion. The slow compartment is believed to be microparticles. The organic matter rather than the clay seems to be the sorbent in the slow compartment.
      b. Implications of aging: the pool of slow desorbing chemical may be a source of pulse inputs to groundwater by a desorption-flushing cycle.
      c. Note, however, that aging, while slowing leaching or at least reducing its potential may be a two edge sword. Bioavailability for biodegradation could be reduced. Also, the chemical could be "stored" and slowly "leak" to solution for long times after an initial pesticide application or contaminant spill and subsequent clean up (clean up is never 100%).

Effect of Aging on Leaching of Atrazine From Soil
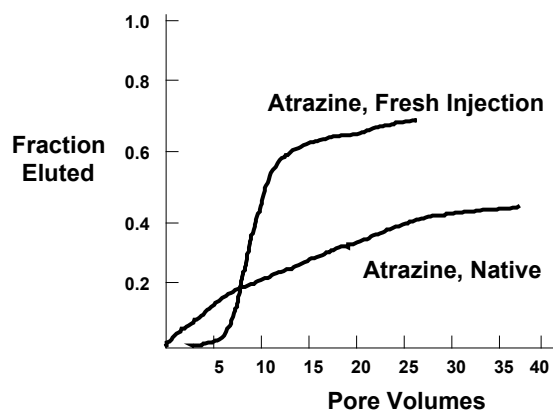
Redrawn from Pignatello et al. (1993)

Figure 14. Leaching of atrazine from aged soil (atrazine residues had persisted at low levels after many years of herbicide) in comparison to leaching of "freshly added" atrazine. (Redrawn from Pignatello et al. 1993)

XIV. Modeling Environmental Behavior of Contaminants
   A. One goal of risk assessment is to estimate (or predict) the likelihood of adverse effects of contaminants to organisms given a set of conditions under which the contaminant is released or is already present in the environment.
      1. Modeling has been used by regulatory agencies, especially by the EPA, to estimate exposure
         a. For pesticide regulation, the model PRZM (Pesticide Root Zone Model) in combination with EXAMS (Exposure Analysis Modeling System) have been intensively used for ecological risk assessment.
         b. PRZM has been used to predict leaching and runoff, while EXAMS has been used to predict the concentrations of pesticide in surface waters
            1. Once PRZM has estimated the runoff into a pond (note that a stagnant body of water is used as the receptor system), then EXAMS takes the runoff concentration and estimates the magnitude of residues at different times following the runoff event (for pesticides, the runoff is assumed to occur shortly after application)
   B. Other models, for example, the various Fugacity models developed by D. Mackay (1979, 1996) have been used to predict the phase distribution of contaminants following their environmental release.
   C. The specific details and mechanics of these models are beyond the scope of this class. However, for your further reference, recently published papers and abstracts about the use and validation of PRZM are shown in the references (Jones and Mangels 2002; Russel and Jones 2002; Singh and Jones 2002). You can obtain these from me if you are interested in modeling pesticide behavior.

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