

Lecture 13, Retardation of Chemical Movement in Aquifers and Biodegradation of Chemicals in Aquifers and the Unsaturated Zone

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Dispersion –

- **Mixing that occurs as a result of the winding torturous path that water travels through a porous medium. This is Fickian transport by dispersion. Fickian mass transport is driven by the concentration gradient and is described by Ficks First Law.**
- Here: $D = \alpha * v$, where D is the mechanical dispersion coefficient in $[L^2/T]$, α is the dispersivity of the aquifer (the median grain diameter of the aquifer $[L]$) and v is the seepage velocity in L/T
- So this can be inserted into $J = -D(dC/dx)$ to determine flux density knowing the change in chemical concentration per distance change.

Retardation of Chemical Movement by Sorbtion

- The slowing of movement or transport of chemicals relative to water in an aquifer.
- Sorption on to grains of aquifers or**
- Sorption on to Iron Oxyhydroxide or Organic Coatings on aquifer grains.**
- **Adsorption** – Chemical sticks to the two-dimensional surface of a solid.
- **Absorption** - Chemical diffuses into the three-dimensional solid.
- Sorbates-Solids capable of sorbing chemicals-clays, metal oxides, carbon and even plastics
- Refer back to the Freundlich Constant and Figure 1-10 on page 50-51 of text.

Descriptors of Retarded or Slowed Chemical Movement

- $K(p)$ - partition coefficient, describes the solid-water partition coefficient or the mass of chemical absorbed to soil to the amount dissolved in water.
- R =retardation factor in $[M/L^3 / M/L^3]$ =
[Mobile chemical] + [sorbed chemical] / [Mobile chemical]
= 1 + sorbed concentration/mobile concentration
- So the rate at which the center of mass of a sorbing chemical moves through the aquifer is equal to;
- v/R where v is the seepage velocity
- The significance of this is that if a chemical has a retardation factor of 10 then it will move only 1/10th as fast as a packet of water in the aquifer.
- Refer to figure 3-28 on page 250.

Chemical Sorption by Organic Carbon

- Many organic pollutants are hydrophobic or lipophylic and are thus easily sorbed into fats, oils and organic carbon in the soil.
- So to predict their movement in soil we need to introduce the **Koc or the Organic Carbon – Water Partition Coefficient.**
- Koc = chemical concentration sorbed to organic carbon/chemical concentration in water
= mg/g /mg/ml
- So the partitioning between water and bulk soil can be determined by-
 $K_d = f_{oc} K_{oc}$ where f_{oc} is the fraction of soil that is organic carbon.
- Table 3-5, page 251 shows the relationships to calculate Koc from Kow

Sorption by Ion Exchange

- Many inorganic pollutants may exist as positively charged cations and negatively charged anions. These pollutants can sorb into aquifer solids **by ion exchange** and thus be retarded.
- A common ion exchanger in an aquifer is clay, which can have an excess of negative charge. The clay takes up counterions (in this case cations like Cu^{+2} or Ca^{+2}).
- Clay can have a cation exchange capacity of up to 2 meq/gram of clay (Remember 1mmol Ca^{+2} is 2meq while 2mmole of Na^{+1} is needed for 2 meq).—So the ion exchange occurs to electroneutrality when there is equilibrium.
- Ion exchange can also be used as a means to clean water of pollutants.
- Distribution coefficients for ionic contaminants are usually determined experimentally. This is done in a **batch test** in which the ionic concentration on a fixed volume of aquifer solids is the numerator and the denominator is the ionic concentration in the pore water.
- **The background chemistry must be the same to compare $K(d)$ because the concentration of other ionic compounds will affect ion exchange distribution.**

Surface Complexation-

- A process by which an ionic chemical forms both electrostatic and chemical bonds with the metal or oxygen atoms of a metal Oxyhydroxide surface. An example is $\text{Fe}(\text{OH})_3$.
- Electroneutrality is assumed but can include layers of ions laying within a few nm of the surface.
- This is a pH dependent process because H^+ ions compete with metal ions for surface sites.

Nonideality in Retardation

- A single $K(d)$ for sorption is justified for locations where equilibrium between phases occurs rapidly. But often this isn't the case-
 1. At high concentrations, sorption is inherently non-linear.
 2. Background pore water chemistry changes often-so there is a great effect on ion exchange.
 3. Slow kinetics results in long equilibrium times.
- These conditions all lead to tailing as described again on page 250, figure 3-28.

Biodegradation in groundwater-

- Biodegradation of organic pollutants in groundwater is carried out by bacteria and fungi that are attached to grains of aquifer material as biofilms.
- Uptake rates though are different in biofilms than in batch or continuous cultures because the cell walls are separated from the water containing the pollutant by slime. A concentration gradient than exists in the slime and the thicker the slime the longer it takes for diffusion to occur.

Natural and Enhanced Biodegradation –

- Biodegradation is an important tool for the clean-up of contaminants in groundwater. If we let natural process remove or degrade contaminants this is called **natural attenuation**.
- In-situ bioremediation is the process of enhancing the natural rate of degradation of contaminants in an aquifer.
- Important because pump and treat contaminant reduction is costly and
- Excavating is costly and
- Both result in potential exposure of clean-up workers (risk balancing).

Michaelis-Menten Enzyme Kinetics

- $V = V_{max} \frac{C}{C + K_s}$ Where V is the rate of chemical uptake per cell in mass per cell-Time, V_{max} is the maximum chemical uptake per cell. C is the concentration of the contaminant in water in mass per cubic Liter, and K_s is the half saturation constant also in mass per cubic Liter (Go to page 148, figure 2-26.).

So we can increase the degradation rate by;

- Increasing V_{max} or decreasing K_s –by making conditions in the aquifer more likeable to the species (changing pH, injecting mineral nutrients like phosphate).
- Increasing cell density X .

In-Situ Bioremediation Techniques

- **V_{max} or K is changed by introducing different bacteria or again changing ecological conditions-like pH but also adding oxygen by;**
 - Sparging** – Introduction of oxygen to counteract the rate limiting effect of low oxygen levels in the aquifer. Can introduce either pure O₂ or air or hydrogen peroxide or nitrate.
 - Vacuum extraction**- can have the effect of increasing oxygen levels as a secondary benefit.
- Can also add plasmids to bacteria making them genetically capable of mineralizing specific substances.

The Unsaturated Zone – also called the Vadose zone.

- Soil –soil formation is called diagenesis and the layers of soil are called horizons.
- This region of the subsurface environment is above the saturated zone and it consists of:
 - 0 horizon –organic material
 - A horizon – high humus, partially leached of minerals.
 - B horizon - Zone of illuviation, deposition of minerals
 - C horizon – Parent material.
- This is a critical region for the transport and fate of contaminants because they must go through the unsaturated zone to get to the saturated zone. (and recharge of contaminants can be stopped here before aquifer contamination).
- Water movement (**conductivity**) depends on moisture content between the pores (**percent saturation**).
- In the unsaturated zone the pressure of pore water is less than atmospheric pressure

Pressure Head in the Unsaturated Zone

- Use $\Psi = p/\rho g$ where Ψ is the pressure head, p is the pressure of the pore water, ρ is the density of water and g is acceleration due to gravity.
- Ψ is often called the soil suction – this occurs because of the interaction of the water and soil grains and is greatest in fine media because the menisci between the pore water and soil gas have their smallest radii thus producing the greatest pressure differential.
- **This phenomena is no different than water raising the highest in glass capillary tubes of the smallest diameter.**
- **Flow in the unsaturated zone generally moves downward in response to gravity---but in arid areas the pressure term overwhelms the elevation term in the Darcy equation and water moves according to the spatial variability in the porous material.**

Flow of Non-Aqueous Phase Liquids (NAPL) –

- This is a third fluid phase introduced such as in a leaking underground storage incident or a spill of TCE on soil. This phase moves and behaves differently than both the air and water phases.
- This flow is complicated because
 1. Each have different viscosities.
 2. Different interfacial tensions with each other and
 3. Different capillary interactions with soil grains.
- **Residual Saturation**- This is the amount of a contaminant NAPL present in the porous media when flow stops because of discontinuous NAPL. As the NAPL spreads out it can become discontinuous this prevents the NAPL to flow from one area to another.-----This is the problem of recovery of oil.
- NAPL can be recovered if the vapor pressure is high enough by removal of air – this is known as **vacuum extraction**.
- NAPL can also be removed if large quantities of water are inserted into the vadose zone in one place and removed in another. This is known as **dissolution**.

Flow of Non-Aqueous Phase Liquids (NAPL) –

- If contaminant NAPL gets to the saturated zone and the NAPL is less dense than water it floats and is called a bolus. It can be removed by installation of a well below the spread out film and pumping to form a cone of depression under the bolus so that it is taken into the well.
- **For dense NAPL (DNAPL) the process of recovery may be difficult and may lead to further disturbance of a pool. If a pool of DNAPL can be found under the surface of an aquifer a well can be placed in the zone of the saturated media to remove it. This is a big problem for chlorinated materials such as PCB's which are not very soluble and small quantities can contaminate an aquifer for a long period**