

Environmental Transport

Principles of Environmental Toxicology
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Learning Objectives

- Understand the spatial and temporal diversity of toxicological and contamination events.
- Describe the linkage between natural forces and chemodynamics of contaminants.
- List important zones of impact and understand the relationships of human activity and potential for chemical release and contamination.

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Learning Objectives, 2

- Understand the relationship of transport and specific chemical processes of contaminants.
- Explore, as an example, the fundamental processes of dissimilatory iron reducing bacteria and their role in contaminant transformation and transport.
- Develop knowledge of groundwater movement and processes related to contamination.

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Learning Objectives, 3

- Understand the interaction of non-aqueous phase liquids with groundwater.
- Gain an introductory understanding of atmospheric transport of contamination using acid rain as an example.

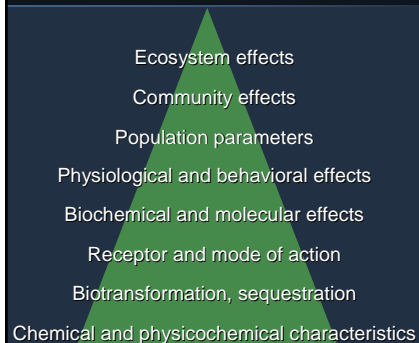
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Transport of Contaminants

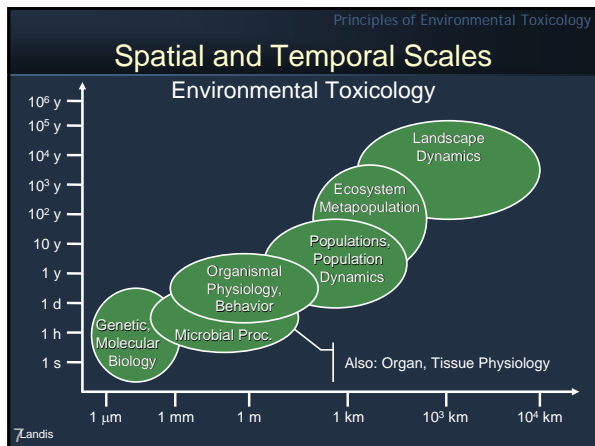
- Spatial and temporal diversity.
 - Impact can be local to global.
 - Timescale of interest can be seconds to millennia (radionuclides).
- Important interactions between molecular events and biological events.
 - Beyond even the population level.
- Important interactions between chemodynamics (e.g., fugacity, volatilization, dissolution) and the forces of nature.
 - Wind (thermal), water (thermal, gravity), biological (movement, e.g., wings, fins).

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Scale of Environmental Toxicology



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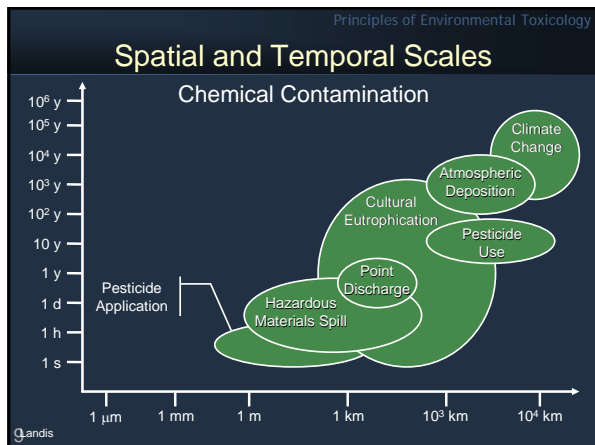


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Scale of Contamination

- Small effects can have global implications.
 - All effects first at the molecular level.
- Chemodynamics and physical properties of the chemical interacting with the forces of nature define scale potential.
 - E.g., ozone depletion.
- Natural processes should not be ignored.
 - Chemical contributions, “evolutionary change”
 - Early earth had a reducing atmosphere until photosynthesis contaminated the atmosphere with “toxic” oxygen.

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Natural Forces

- Natural forces acting upon earth move mobile components of the ecosphere.
- Atmosphere.
 - Gaseous and particulate transport.
- Hydrosphere.
 - Surface water, ground water, atmospheric water.
- Lithosphere.
 - Surface and subsurface soils, dust.
- Biosphere.
 - Nutrient and contaminant cycling.

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Compartments

- Intracompartment and interfacial chemodynamics will affect transport.
- Rate of movement can impact if receptors are exposed and when.
 - Air → fast movement.
 - Can allow for few reactions between source and receptor.
 - Surface water → moderately fast.
 - Site specific considerations important.
 - Groundwater → slow.
 - Can allow for complex abiotic and biotic reaction pathways.

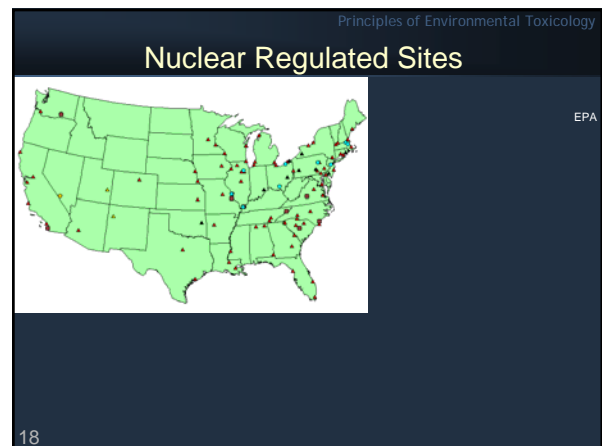
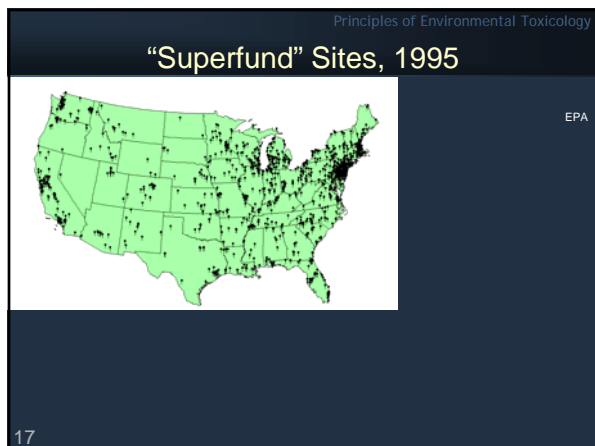
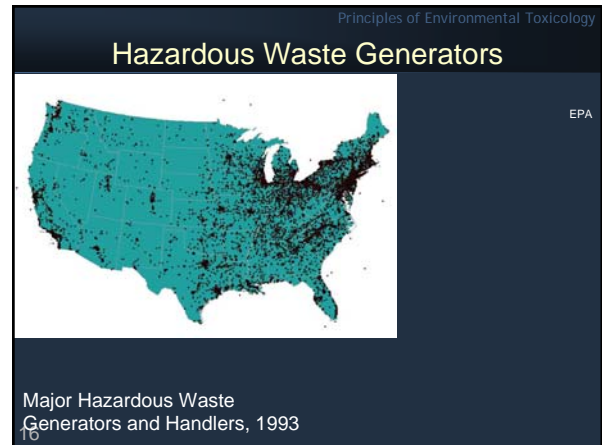
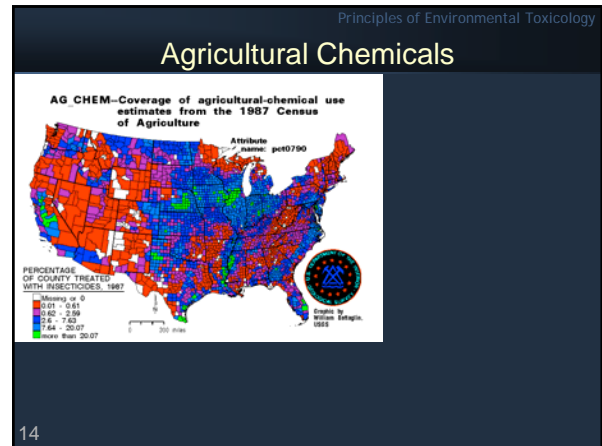
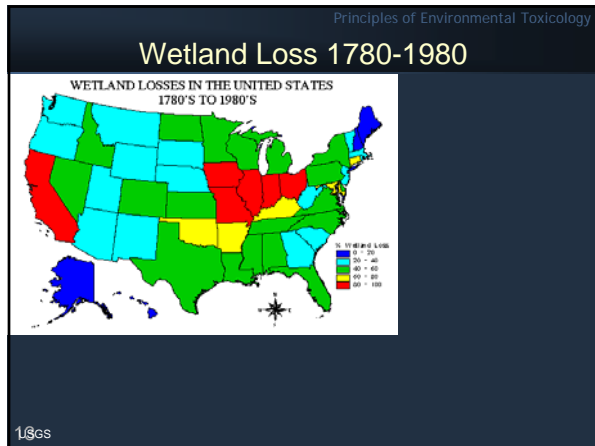
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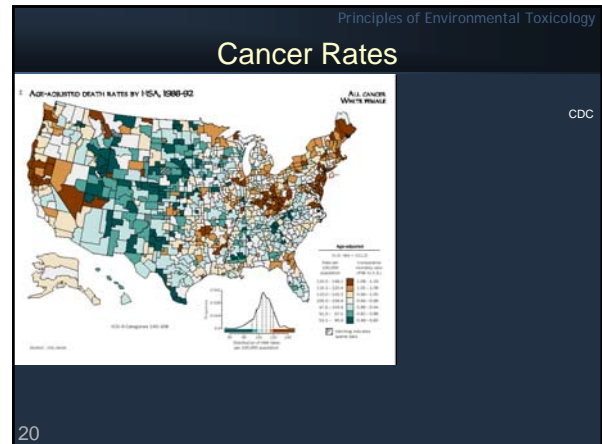
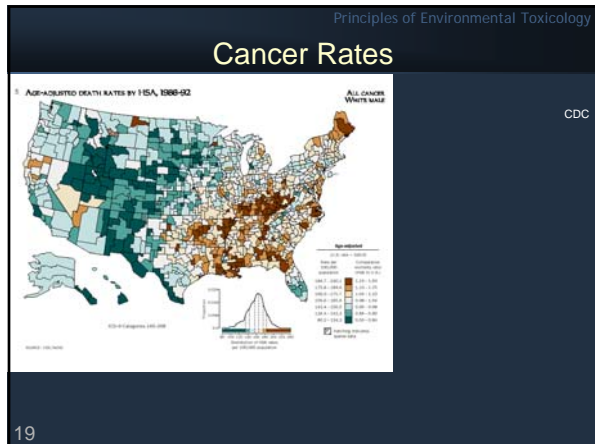
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Important Zones of Impact

- Often interfacial, high population or diverse.
 - Coastal zones/waterfronts.
 - Historically popular place to discharge waste.
 - Estuaries.
 - Chemical changes at the fresh-salt water interface modify solution characteristics and reactivity of contaminants.
 - Riparian areas.
 - Wetlands.
 - Often closed or “confined” oasis populations.
 - Urban areas/nesting areas.
 - High population of receptors.

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- ## Chemical Processes
- Transport is controlled by complex interactions between physical, chemical and biological processes.
 - A mass balance equation to predict contaminant movement must also contain terms to account for chemical and microbiological processes.
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- ## Chemical Reactions
- Inorganic chemical reactions.
 - Solubility.
 - Dissolution.
 - Precipitation.
 - Complexation rxns.
 - Sorption and surface chemistry.
 - Ion exchange rxns.
 - Redox chemistry.
 - Organic chemical reactions.
 - Sorption.
 - Hydrolysis.
 - Co-solvation.
 - Ionization.
 - Volatilization.
 - Dissolution.
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- ## Sorption
- Most important process affecting transport of organic contaminants.
 - For non-polar organics, sorption is considered a partitioning process between the aqueous phase and the porous medium.
 - Can be described by a linear Freundlich isotherm, where the sorbed concentration is a fn of aq concentration and the partition coefficient K_p .
 - Mechanism of organic sorption is hydrophobic bonding between C and om.
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- ## Hydrolysis
- Direct reaction of dissolved contaminant with water molecules.
 - Often forming an alcohol or alkene.
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Co-Solvation and Ionization

- Processes that may decrease sorption and therefore increase transport.
- Co-solvation increases interaction of solute and solvent.
 - Important at the source since only large concentrations are effective.
- Acidic compounds (phenols/organic acids) can lose a proton and become more water soluble.

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Volatilization and Dissolution

- Important for volatile compounds.
- Volatilization determined by
 - Area (grain size, water content).
 - Vapor pressure.
- Rate of diffusion.
 - Solubility driven.

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Inorganic Chemicals

- Total concentration is less important because of speciation.
 - Not descriptive enough to determine properties.
- Knowledge of the speciation of a metal is required to predict transport.
 - Free ions.
 - Insoluble species.
 - Metal/ligand complexes.
 - Adsorbed species.
 - Immobilized by ion exchange.
 - Differing oxidation state.

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Solubility, Dissolution, Precipitation

- Mineral dissolution and weathering determine the natural composition of water.
 - Source of most of the inorganic ions.
 - Common ion effect.
- Natural weathering can modify pH.
- Leachate is a dissolution process.
- Precipitation happens when a solubility limit is reached.

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Complexation Reactions

- A metal ion reacts with an anion that functions as a ligand.
 - New soluble species called a complex.
- Transition metals form strong complexes
 - $\text{Fe(III)} > \text{Hg} > \text{Cu} > \text{Pb} > \text{Ni} > \text{Zn} > \text{Cd} > \text{Fe(II)} > \text{Mn} > \text{Ca} > \text{Mg}$
 - Ligands: OH^- , Cl^- , SO_4^{2-} , CO_3^{2-} , S^{2-} , F^- , NH_3 , PO_4^{3-} , CN^-
- Ligands usually in excess.
- Organic ligands: amines, phenols, humic materials.

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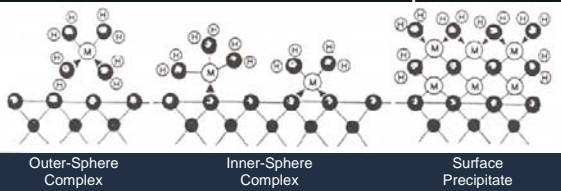
Ion Exchange Reactions

- "Sorption" to a three dimensional porous matrix containing fixed charges.
- Ions held by electrostatic forces rather than by coordination bonding.
- Anion binding to clays.

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Metal Oxide Surface Complexes



Outer-Sphere Complex Inner-Sphere Complex Surface Precipitate

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Redox Chemistry

- Change of oxidation state.
- Important determinant for transport.
 - Cr (VI), toxic, mobile.
 - Cr(III), immobile, insoluble.
 - Se(VI), mobile, less toxic.
 - Se(IV), less mobile, more toxic.
- Redox state of an aquifer is closely related to microbial activity.
- Redox reactions that occur depend on the dominant electron potential.
 - The primary redox active species; e.g. $\text{Fe}^{2+}/\text{Fe}^{3+}$.

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Factors Affecting Mobility


- Amount and form of the metal.
- Soil properties affecting metal retention.
 - Bulk density, surface area, particle size distribution, pH, redox status, ion exchange capacity, organic matter, metal oxides present, type and amount of clay minerals.
- Soil organic matter is one of the primary immobilizing processes for trace and toxic metals (subsoils lend greater mobility).
- Properties of the leachate phase.
 - Complexation w/ anions; Pb w/ HCO_3 .

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Focus: Sedimentary Iron

- Percent levels of iron oxides in soils and sediments can be a controlling factor in several abiotic and biotic pathways for fate and transport of organic and inorganic contaminants.



Understanding the abiotic and biotic reaction pathways of environmental iron is currently regarded as a key component in the developing knowledge base of environmental systems and their response to contamination.

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Ferric and Ferrous Iron



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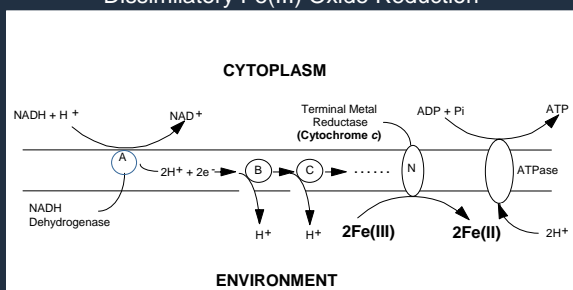
Environmental Fe Reduction

$\text{Fe(III)} \longrightarrow \text{Fe(II)}$

- Abiotic reduction by organics (e.g. reduced quinones, sulfhydryl groups).
- Abiotic reduction by inorganics (e.g. H_2S).
- **Direct enzymatic activity of dissimilatory Fe(III)-reducing bacteria (FeRB).**
 - Dissimilatory: not linked to uptake/assimilation.
 - Assimilatory: linked to uptake/assimilation.

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Coupled to Electron Transport Dissimilatory Fe(III) Oxide Reduction



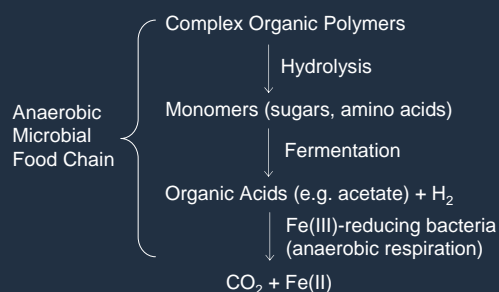
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Dissimilatory Fe(III) Reduction

- Fe(III) present as in natural highly insoluble oxide minerals at circumneutral pH.
- Fe(III) = solid-phase electron acceptor.
- Fe(III) oxide reduction requires direct contact between FeRB and oxide minerals.

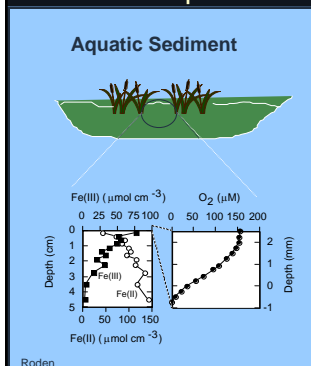
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Coupled to Organic Matter Oxidation



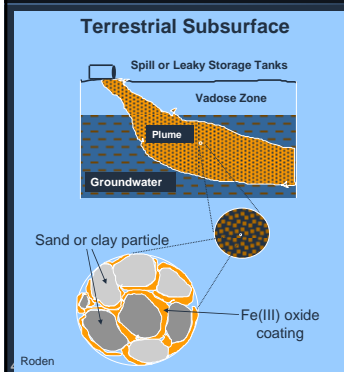
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Aquatic Sediment Iron



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Subsurface Iron



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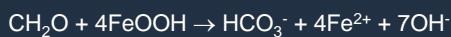
Iron Oxides

- Distinct banding caused by precipitation of iron-oxides as a result of rise and falls in groundwater.
- Bands are highly reactive toward many contaminants and contain microorganisms whose ecology and function is linked to iron geochemistry.

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Significance of DIOR

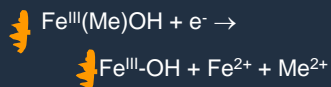
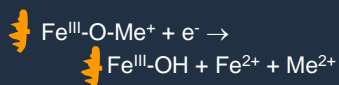


- Oxidation of natural organic matter.
- Suppression of other anaerobic respiratory processes (e.g. sulfate reduction, methanogenesis).
- Generation of high-iron groundwater.
- Alteration of pH/Alkalinity conditions.
- Generation of carbonate (siderite) and magnetic minerals (magnetite).

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Significance of DIOR, 2

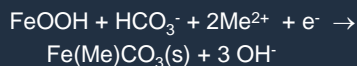
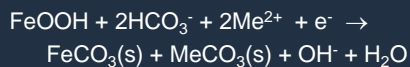
- Release of sorbed and/or coprecipitated trace/toxic metals & radionuclides during reductive oxide dissolution.



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Significance of DIOR, 3

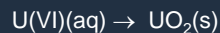
- Immobilization of trace/toxic metals, radionuclides during carbonate mineral precipitation (e.g., Sr).



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Significance of DIOR, 4

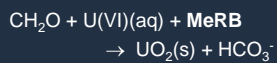
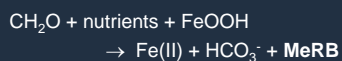
- Fe(II) (surface-bound) as a reductant for abiotic contaminant transformations.



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Significance of DIOR, 5

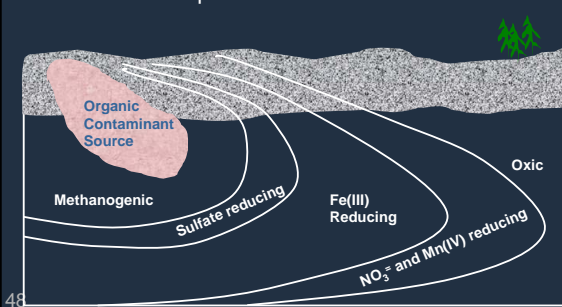
- Production & maintenance of metal-reducing bacterial (MeRB) populations capable of reducing mobile toxic metals (e.g. Cr(VI), Co(III), U(VI)) to less mobile forms.



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Significance of DIOR, 5

- Oxidation of aromatic hydrocarbons in petroleum-contaminated aquifers. Lovley



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Groundwater

- Half of US population use GW for drinking water.
- GW provides 1/5 of the fresh-water supply.
 - >30 trillion gallons of GW.
- Ground water can become surface water.
- Also serves as a sink for wastes (gravity!).
 - Accidental spills, fertilizer runoff, ag chemical leaching, leaky sewers, septic tank discharge, urban storm water runoff, industrial lagoons, waste injection wells.

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Understanding Transport

- Prediction of time of arrival and concentration at a receptor monitoring well, water supply, surface water.
- Design of cost effective and safe waste management facilities.
- Installation of effective monitoring systems.
- Development of efficient and cost-effective strategies for remediation.

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Contaminant Movement

- Contaminants in GW will move primarily in the horizontal direction that is determined by the hydraulic gradient.
- Contaminants will decrease in concentration because of dispersion (molecular and hydraulic), filtration, sorption, chemical processes and microbial degradation.
 - Some of these processes, such as dispersion, will treat all contaminants equally.
 - Prediction of movement is difficult because of the complexity of the subsurface.

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Advection-Dispersion Theory

- Study of Advection/Dispersion is useful for predicting when an action limit will be reached.
 - Advection: transport of a non-reactive tracer at groundwater velocity.
 - Dispersion: molecular diffusion, hydrodynamic mixing; causes decrease in concentration with increase in length of flow.
- Need to understand A/D for risk assessment and remediation.

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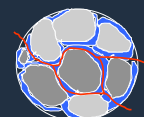
NAPL

- Non aqueous phase liquids.
- Non-soluble to slightly soluble.
- Description based on density of bulk contaminant relative to water.
- LNAPL.
 - Light non-aqueous phase liquids.
 - Floaters: petroleum hydrocarbons.
- DNAPL.
 - Dense non-aqueous phase liquids.
 - Sinkers: Chlorinated solvents; TCE.

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Transport, Dissolution of NAPLS

- As NAPLs move through a soil column, they displace water and air.
- Water is the wetting agent so it tends to cover sand grains and line the pores.
 - NAPL goes around or through center pore.
- Since the phases are both active, the permeability of the geologic media changes.
 - Reduction in permeability depends on medium.
- Surfaces are "wetted" by H₂O.



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Relative Permeability Example

- Cubic meter of soil with a 35% porosity and containing TCE at 20% residual saturation.
- Implies that there is 0.07 cubic meters of TCE (103 kg) within the soil.
- If the solubility of TCE is 1,100 mg/L and if groundwater flows through the soil at 1.7 cm/day, removal by dissolution will take 15.4 yrs!

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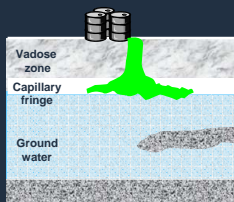
LNAPLs

- As a spilled LNAPL enters the unsaturated zone, it flows through the central portion of the unsaturated pores.
- If the amount of product spilled is small, product flows until residual saturation is reached.
- A three phase system consisting of water, product, and air is formed.
- Partitioning can occur
 - Air, infiltrating H_2O .

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LNAPLs - Large Volumes

- Product flows through the pore space to the top of the capillary fringe.
- Dissolved front and the LNAPL change the phase chemo and physical dynamics.
- Since it is lighter than water it tends to float on the capillary fringe → plume.
- Changes in the water table will effect the depth of the plume.
 - Remember residual saturation.
 - Can be "immobile" to H_2O once saturated.



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DNAPLs

- Can have great mobility in the subsurface as a result of their relatively low solubility, high density and low viscosity.
- Do not readily mix with H_2O and therefore remain as separate phases.
- High density can drive DNAPLs deep into aquifers.
 - When a high density, low viscosity fluid meets a low density (relative), high viscosity fluid the flow is "unstable" and viscous fingering occurs.

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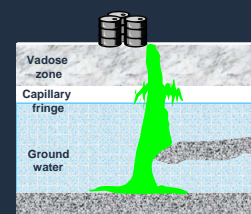
DNAPL Dynamics

- In a spill, a DNAPL flows through the unsaturated zone by gravity towards WT.
- If only a small amount of DNAPL is spilled, it flows until reaching residual saturation in the vadose zone.
 - If there is water in the unsaturated zone, then DNAPL exhibits viscous fingering.
 - Without water, occasionally the DNAPL vapors can sink to the capillary fringe and contaminate the groundwater.

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DNAPLS - Large Volumes

- DNAPL flows until it reaches the capillary fringe and begins to penetrate the aquifer.
- To do this the DNAPL must overcome the capillary forces between the water and the porous soil - critical height calculation.
 - E.g., perchloroethylene calculated critical heights can range from a few centimeters in coarse grains to tens of meters for clays.
- Unfractured clays can be effective DNAPL barriers.



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Atmospheric Transport

- Local and distant impacts possible.
- Natural process contribute.
- Requires:
 - Volatile chemical.
 - Dissolution in water vapor.
 - “Toxic fog”
 - Air buoyancy of particulates.

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Example: Acid Rain

- Precipitation that is more acidic than “background” precipitation. ACS
 - Scandanavia, Canada, US (1st observed in 1800's).
- Can deposit via wet deposition (e.g., rain, snow) or dry deposition (e.g., turbulent exchange, gravity).
 - Dry deposition is usually near an emission source.
- Wet deposition is spatially more distributed ($\geq 10^2$ km)
- Caused by S and N oxides.

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pH of Rain

- Atmospheric carbon dioxide forms carbonic acid naturally in rainwater (pH = 5.6).
- “Normal” background considered to be pH 5-7.
- Ocean bacteria can produce sulfur dioxide and precipitation pH of 4.5.

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Reaction of S, N Oxides

- A portion of S and N oxides released into the atmosphere are converted into sulfuric acid and nitric acid.
- More complex atmospheric reactions can occur (UV, ozone, hydroxyl radical).

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Acid Rain Impacts

- Acid deposition impact is controlled by acidity of the precipitation, meteorological conditions, and buffering capacity of the receptor ecosystem.
- Aquatic systems.
 - Lake acidification in NE, fish loss due to low pH, high Al ion concentration, and low Ca.
- Forests.
 - Acidic cloud water is responsible for high elevation loss in some areas, as well as soil changes.

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Acid Rain Impacts

- Agriculture.
 - Local deposition effects, but no known major spatially distributed impacts.
- Materials.
 - Steel corrosion; carbonate stone dissolution.
- Visibility.
 - Reduced visibility in eastern US due to sulfate aerosols.
- Human health.
 - Exposed populations = adverse health effects(?).

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