Groundwater Contamination and Remediation

Table 12.1 Sources of Groundwater Contamination

Groundwater Quality Problems That Originate on the Land Surface

1. Infiltration of contaminated surface water
2. Land disposal of solid and liquid waste materials
3. Stockpiles, tailings, and spoil
4. Dumps
5. Salt spreading on roads
6. Animal feedlots
7. Fertilizers and pesticides
8. Accidental spills
9. Particulate matter from airborne sources
10. Composting of leaves and other yard wastes

Groundwater Quality Problems That Originate Above the Water Table

1. Septic tanks, cesspools, and privies
2. Surface impoundments
3. Landfills
4. Waste disposal in excavations
5. Leakage from underground storage tanks
6. Leakage from underground pipelines
7. Artificial recharge
8. Sumps and dry wells
9. Graveyards

Groundwater Quality Problems That Originate Below the Water Table

1. Waste disposal in wet excavations
2. Agricultural drainage wells and canals
3. Well disposal of wastes
4. Underground storage
5. Secondary recovery
6. Mines
7. Exploratory wells and test holes
8. Abandoned wells
9. Water-supply wells
10. Groundwater development

Source: Modified from U.S. EPA, 1990, *Ground Water, Volume 1: Ground Water and Contamination.* EPA/625/6-90/016a.

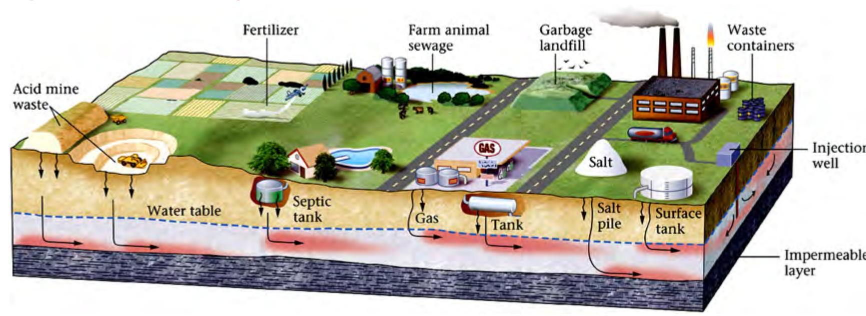
Pollution

Various types of pollutants:

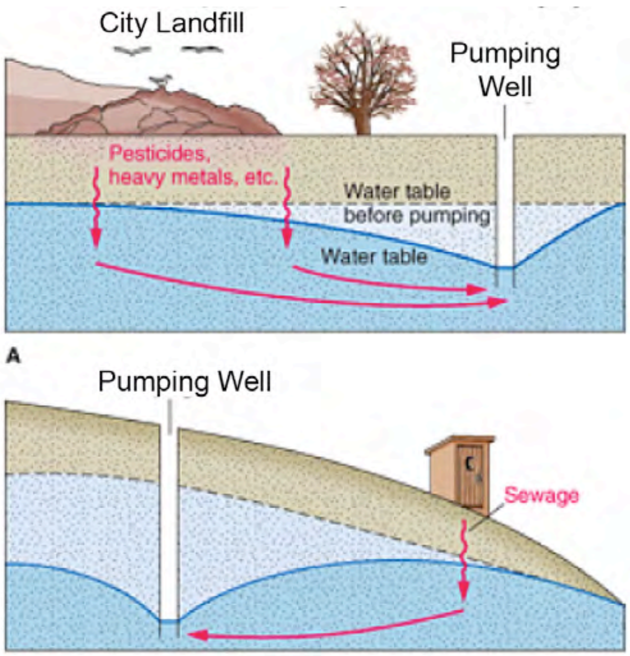
- Pesticides and herbicides (i.e., DDT);
- Fertilizers (nitrate is a big problem);
- Heavy metals (i.e., Pb, Hg, Cu, Cr, Cd, etc.) – can come from mine waste dumps and leached into groundwater;
- Bacteria, viruses, and parasites (sewage and slaughter houses, etc.);
- Industrial waste (i.e., cyanide, PCBs or polychlorinated biphenols);
- Radioactive waste: mainly from arms race and nuclear power. Now have to deal with waste!
- Acid mine drainage: $FeS_2 + 2H_2O + O_2 = 2H_2SO_4 + Fe^{2+}$
- Gasoline/petroleum products (leaky tanks);
- Landfills.

Groundwater Usage Problems

Groundwater Contamination

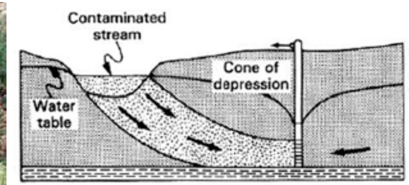


Sources of contaminants: Agriculture (pesticides, herbicides, fertilizer, animal sewage); Industry (dangerous organic and inorganic compounds); effluent from "sanitary" landfills and septic tanks; petroleum products; radioactive wastes (weapons manufacture, hospitals, spent fuel disposal); acid mine drainage.



Land Surface Contamination

- Surface water contamination has been a recognized problem throughout history.
- Remediation of surface drinking water began in mid 19th century and was common in industrialized countries by late 19th century.
- Link between surface water contamination and groundwater contamination was much later.

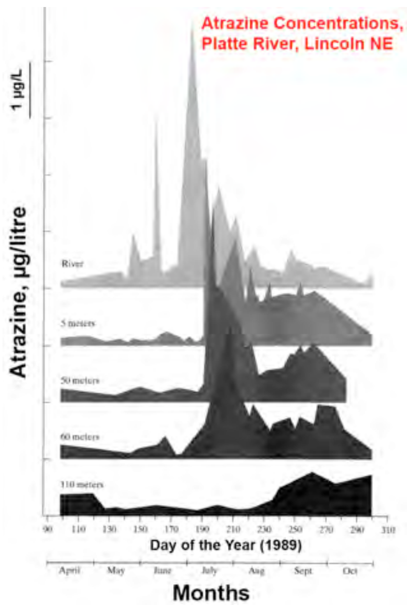


Land Surface Contamination

– A contaminated stream may, during usual conditions, be a discharge point for an aquifer.

– During a drought, or if a well is installed nearby, the lowering of the water table (or creation of 'cone of depression') can cause the stream to change to a recharge point and the contamination from the stream will enter the aquifer.

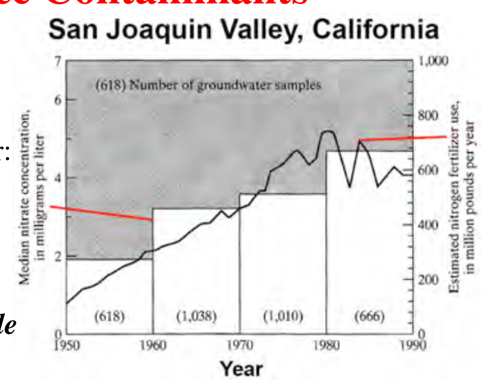
– Platt River atrazine contamination of wells (herbicide for corn; Lincoln, Nebraska).



Land Surface Contaminants

Fertilizer and ***pesticide/ herbicide*** applications

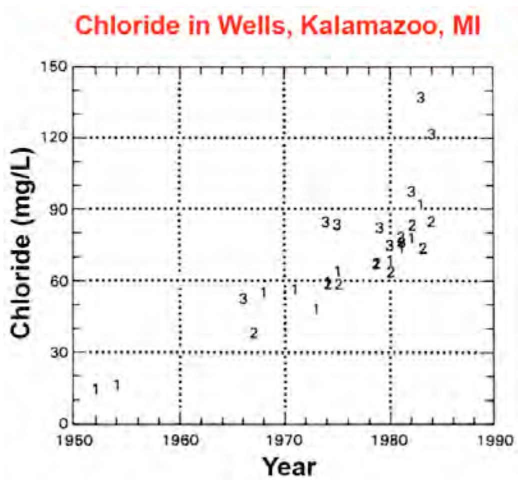
- ***Fertilizers*** usually high in ***nitrate*** - very soluble in water:
  - Many wells in agricultural areas elevated nitrate levels.
  - Can cause heart defects in newborns.
- ***Pesticides*** usually ***less mobile*** but ***more toxic***!
  - Mobility controlled by soil and rock characteristics.
  - Karst regions - high hydraulic conductivity – often high pesticide concentrations in wells.



Increased fertilizer contamination impact on groundwater quality.

Fertilizer (pesticides, road salt) referred to as ***non-point sources*** of contamination since they are applied to large surface areas.

Road salt - Example of water soluble and mobile contaminant!



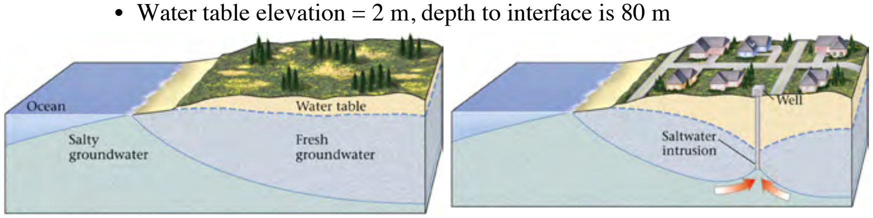
Increased use of road salt – increase in Cl in groundwater

Land Surface Contaminants

- ***Accidental Spills***
  - Oil, gasoline, hazardous waste, chemical spills
  - Can infiltrate aquifers and contaminate groundwater systems
  - Usually small extent - clean-up usually effective if soon after spill
- ***Uncontrolled dumping of wastes***
  - Leaching of contaminants and infiltration to groundwater system
- ***Feedlots***
  - Runoff from exposed feedlots can lead to high NO_3 & PO_4 levels in groundwater

Saltwater Intrusion

- ***Coastal communities***
  - Seawater intrusion is a serious problem in coastal areas
  - Near the shore there is an interface between fresh groundwater and saline groundwater from the ocean
- ***Ghyben-Herzberg relation***
  - Depth below sea level of the interface at any point inland from the shore ***is equal to 40 times*** the elevation of the water table above sea level at that point
    - Water table elevation = 2 m, depth to interface is 80 m



Saltwater Intrusion

- ***Coastal communities***
  - Pumping lowers the water table in the vicinity of the well = rising of the interface between fresh and saline groundwater
    - Pumping lowers the water table 1 m, then the corresponding rise in the interface is 40 m
    - Wells can become contaminated by saline groundwater if overpumped
  - Hard to recover from this type of contamination and many wells need to be abandoned

Contamination in the Unsaturated Zone

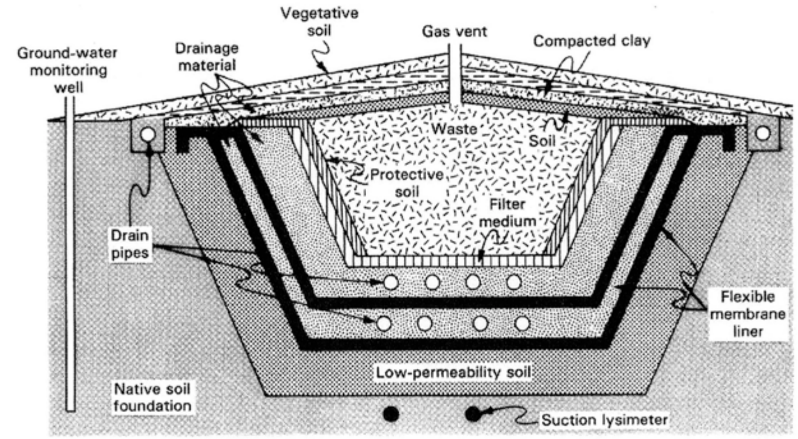
- Pre-1970 most common method of waste disposal
  - SHALLOW BURIAL
  - Leaching from unsaturated zone to saturated zone extremely common in buried waste areas
- Post-1970 regulations for disposal of wastes
  - Waste now separated into more or less inert materials, municipal and household wastes and hazardous wastes
  - Disposal of each type requires different precautions
  - ***Landfills*** are the predominant type of unsaturated zone waste disposal

Landfills

- 2 types:
  - ***Secured Landfill***
  - ***Sanitary Landfill***

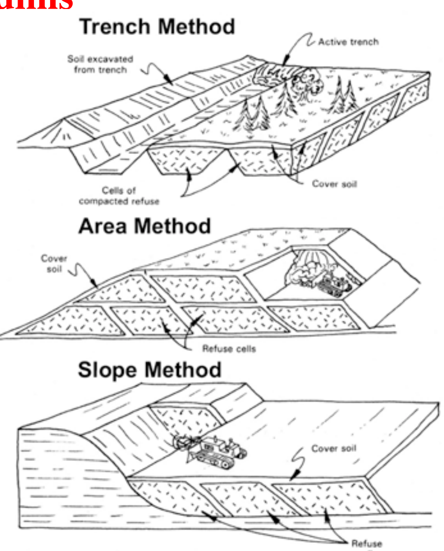
Secured Landfill

- Used for disposal of hazardous wastes;
- Requires engineered leachate barriers;
- Regular monitoring of unsaturated and saturated zones.



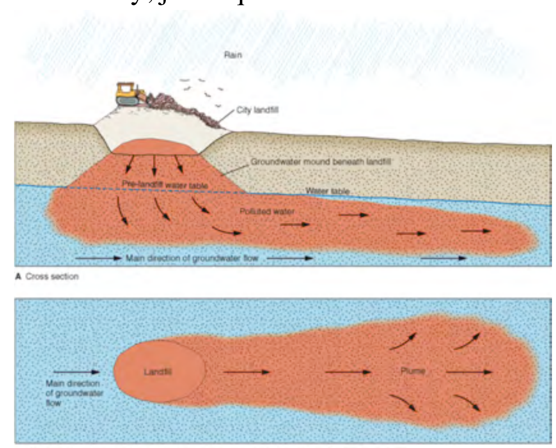
Landfills

- ***Sanitary Landfill***
  - Used for disposal of less hazardous wastes;
  - Modern design tends to try to isolate the waste into "cells" within the overall landfill.



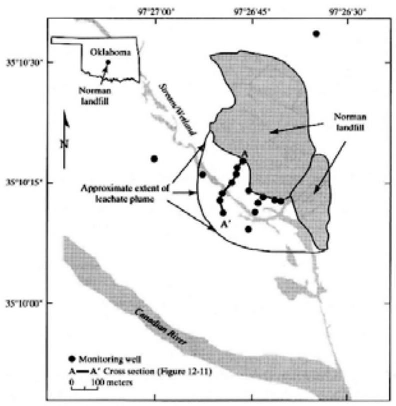
Landfills

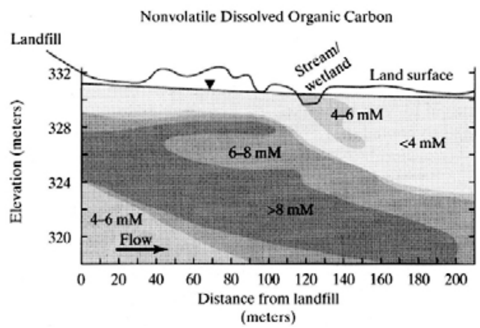
- ***Problem*** - non sustainable over long periods of time:
  - All landfills will leak eventually, just a question of time.
- US ~100,000 active and inactive landfills:
  - Virtually all built prior to 1970 – ***NOT*** designed with stringent contamination prevention measures;
  - Rain percolation cause leaching – ***leachate*** will enter groundwater;



- Contaminants/leachates define a "***leachate plume***" in groundwater.

Norman Landfill, Oklahoma



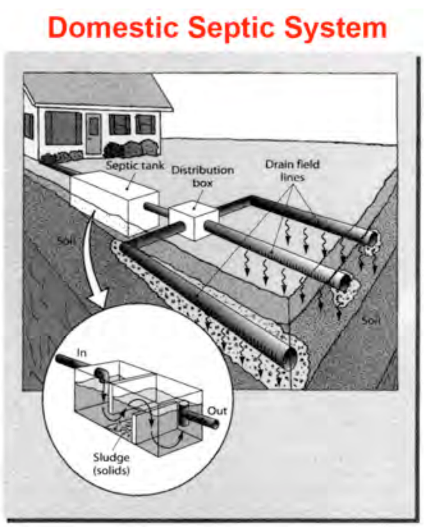


Disposal of Liquid Wastes

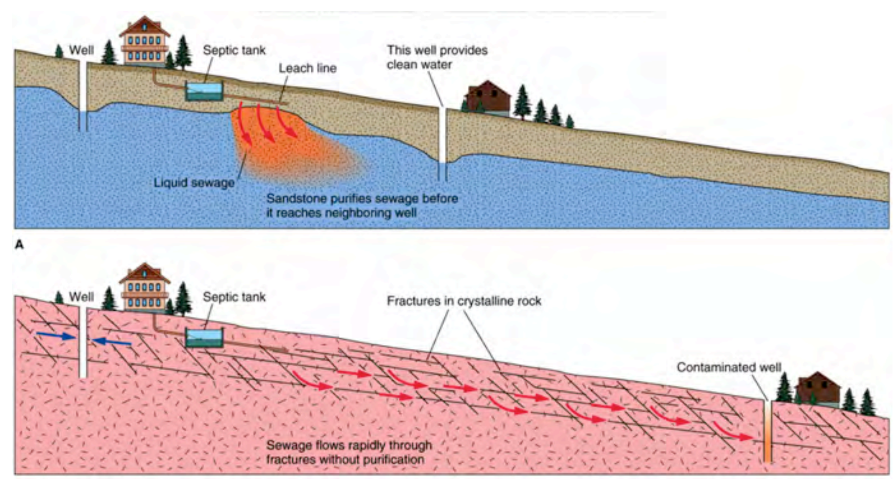
- **Main types**
  - Septic tanks and septic systems
  - Surface impoundments (tanks to hold waste)
  - Underground petroleum storage tanks
  - Underground hazardous waste storage tanks
  - Underground pipes

Liquid Wastes

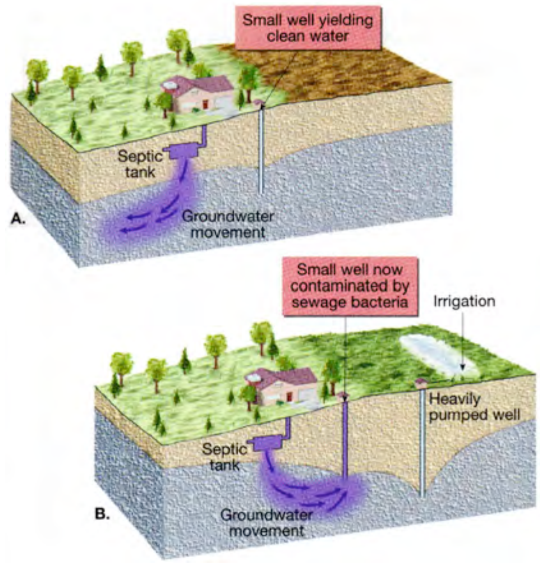
- ***Septic systems*** common in rural areas and non-sewered suburban locations.
- Septic tank retains solid material while liquid waste is discharged through 'drain field lines':
  - Idea - soil purifies waste prior to reaching groundwater.
  - Wells - NEVER build downflow of drain field lines…..
  - Sometimes purification occurs, sometimes it doesn't.



Septic Systems

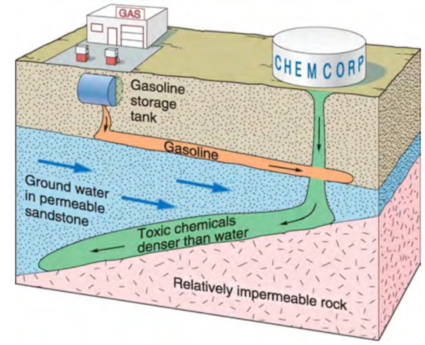


Septic Systems



Liquid Wastes

- ***Petroleum/hazardous waste tanks***
  - US ~680,000 underground storage tanks according to EPA (Environmental Protection Agency);
  - Old tanks made of steel - corrosion and leakage common;
  - New tanks made of fiberglass-reinforced plastic;
  - 2003: ~440,000 documented cases of contaminant release; ~300,000 cleanups completed.
- ***Graveyards***
  - Biological and chemical contaminants;
  - 1800's to early 1900's - High levels of arsenic, used as embalming fluid.



Saturated Zone Contamination

- Practices involving soley saturated zone – ***direct contamination of groundwater*** without passage through unsaturated zone.
- **Example** - use of abandoned excavations associated with mines and gravel production for waste disposal.
- ***Excavations and mines as waste dumps***
  - Old excavation or mine may be dry (or partially) soon after being abandoned
  - Local towns/industries use this as waste dump
  - Water table rises over time up to excavation or mine site
  - Waste now in direct contact with groundwater flow system
- ***Old mines***
  - Sulfide minerals oxidize to produce sulfuric acid
  - Acid mine drainage
  - Very low pH, helps mobilize metals

Berkeley Pit, Butte, Montana

- Open pit copper mine - filled with water after abandonment
- Water **pH=2.5**, high concentrations of cadmium, arsenic, zinc, sulfuric acid
- 1995 - flock of geese land in the pit, promptly die

  ARCO says pit safe
- Water is being "mined" due to high metal concentrations (e.g. Cu 187 ppm!)

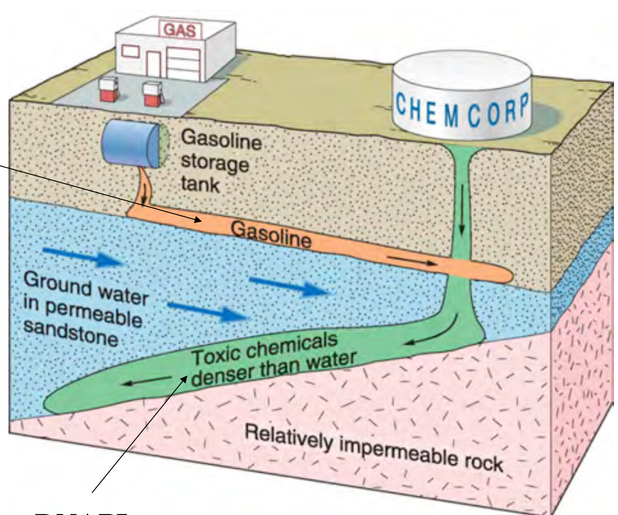
Environmental Regulations

- Environmental regulations and laws administered by USEPA – US Environmental Protection Agency
- ***Clean Water Act (CWA)*** – 1972 (amended 1977)
  Regulates treatment of wastewater discharged to environment
- ***Safe Drinking Water Act (SDWA)*** – 1974 (amended 1986)
  Establishment of drinking water standards for public supplies

Transport of Contaminants in Groundwater Systems

- ***Mass transport*** - movement of contaminants through the subsurface
- An important distinction:
  - Is the contaminant an ***aqueous-phase liquid***?
    - Contaminant is dissolved in water
  - Or is the contaminant ***non-aqueous phase liquid*** (***NAPL***)?
    - Contaminant is ***immiscible*** *(does not mix)* in water
    - ***Petroleum products*** are the most common NAPL contaminant
    - Other organic fluids are often NAPLs
    - ***DNAPL*** - dense non-aqueous phase liquid
      - Denser than water
    - ***LNAPL*** - light non-aqueous phase liquid
      - Less dense than water

LNAPL



DNAPL

Aqueous Phase Mass Transport

- Aqueous solutions containing a low concentration of contaminants move in essentially the same way as pure groundwater
- At higher concentrations of contaminants, ***density*** changes may become important and can factor in groundwater flow
- How much of the contaminant will dissolve in the groundwater?
  - For metals (inorganic compounds), highly dependent upon the geochemical conditions of the leaching solution – pH and oxidation state of the soil/rock

Aqueous Phase Mass Transport

When dealing with ***organic contaminants:***

- solubilities are highly variable (see Table).

Octanol-water partition coefficient:

$$K_{ow} = C_{oc}/C_w$$

- C_{oc} is the eqm. concentration of the phase in octanol and C_w is the eqm. concentration of the phase in water;
- The higher the value of K_{ow} (usually expressed as a log value), the more likely the phase will be non-aqueous (***hydrophobic***).

Henry's Constant:

- High values of Henry's Constant indicate that the organic compound dissolved in water is likely to volatilize and enter into a vapor phase;
- Implications for flow in the unsaturated zone, gaseous component may separate from liquid, and hence type of remedial action used for a contamination site.

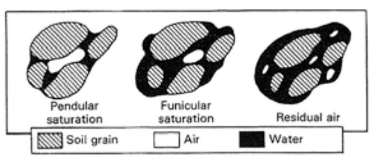
Table 12.3 Properties of Common Groundwater Subsurface Contaminants

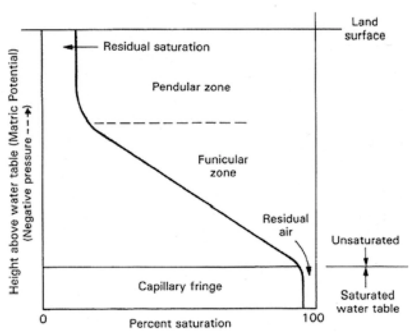
		Property[a]		
Compound	Density, g/mL	Solubility, mg/L	Henry's[b] Constant, atm	$Log_{10}K_{ow}$
Trichloroethene	1.4	1,100	550	2.29
Tetrachloroethene	1.63	200	1,100	2.88
Chloroform	1.49	8,200	170	1.95
Benzene	0.876	1,808	240	2.01
Toluene	0.876	535	308	2.69
1,2-Dichlorobenzene	1.305	145	90	3.38
Phenol	1.07	93,000[c]	0.04	1.49
1,1-Dichloroethene	1.013	250	1,400	0.73
1,1,1-Trichloroethane	1.435	480	860	2.49
Vinyl chloride	gas	1,100	35,500	0.60
Methyl ethyl ketone	0.805	260,000	1.5	0.26
Acetone	0.79	1,000,000	1.0	−0.24
Ethylene dibromide	2.18	3,400	26	1.80

Source: E. Bouwer, J. Mercer, M. Kavanaugh, and F. Digano, 1988, Coping with groundwater contamination, *Journal of the Water Pollution Control Federation*, 60:1415–1423.
[a]Values for temperature of 20° to 25° C.
[b]Values should be considered representative of literature data; wide ranges in values are common.
[c]Depends on pH.

Unsaturated Zone Transport of Contaminants

- Surface and above water table contaminations have to progress through the unsaturated zone in order to reach the groundwater system
- Remember that……
  – In the unsaturated zone, fluid pressure is less than atmospheric pressure;
  – Basically, forces such as suction or surface tension (on water) act against gravity;
  – ***Matric potential*** is a 'lump term' used to describe these (countering) effects.
- Distribution of the Matric potential (or height above water table) *versus* percent saturation.

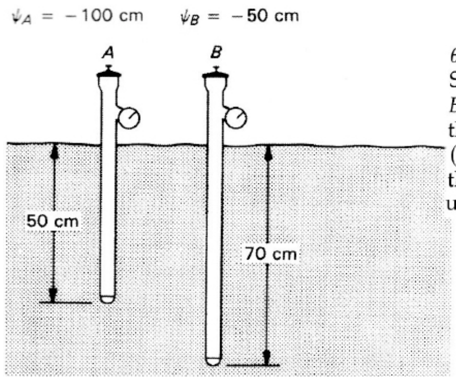




Unsaturated Zone Transport

- ***At water table***: fluid pressure = atmospheric pressure
  – Matric potential = 0 (void space is saturated with water)
- ***In capillary fringe***: fluid pressure < atmospheric pressure and pores are saturated
  – Matric potential < 0
- ***Funicular zone***: fluid pressure < atmospheric pressure and pores are only partially saturated, but water dominates pore space
  – Matric potential << 0
- ***Pendular zone***: fluid pressure << atmospheric pressure and pores only slightly saturated, air dominates pore space, no more reduction in saturation level
  – Matric potential << 0, results in thin films and narrow capillaries filled with water

Unsaturated Zone Transport



$\theta = -50 + (-70) = -120$ cm. Since the head at tensiometer B (-120 cm) is larger than the head at tensiometer A (-150 cm), the flow is in the direction of B to A, or upward.

- Matric potential is measured with a ***tensiometer***
  - Tube with a porous cup on the end
  - Tube is totally filled with water and connected to a vacuum gauge at the top
  - Water is drawn out through the porous cup into the soil, creating a vacuum in the tube, which is measured by the gauge

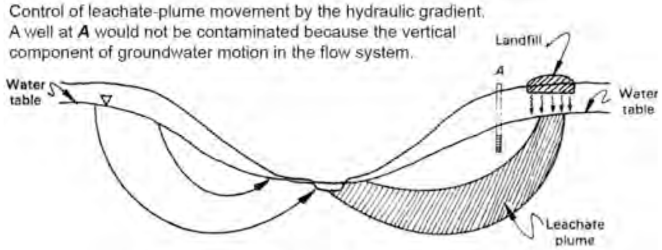
Unsaturated Zone Transport

- Effect of Matric potential
  - Low matric potential (i.e. large negative values) tends to keep water from moving downwards in the unsaturated zone
  - Total head = elevation head + matric potential
    - Lower (more negative) matric potential = lower head
    - Water always flows from regions of high total head to regions of low total head
- So what happens when it rains?
  - Water infiltrates the surface and increases the % saturation
  - Lowers the matric potential
  - Water flows downwards in a wetting front
    - Can be homogeneous OR preferential
    - Preferential more common where water follows crack, macropores, root casts, burrows, etc

Saturated Zone Transport

- Once contaminants reach the water table…
  - They will move in the direction of groundwater flow
  - ***Contaminant density*** is an important control
    - If contaminant density > groundwater - contaminant plume will move in direction of groundwater flow but have a significant downward component to it;
    - If about the same as groundwater - will basically follow the hydraulic gradient;
    - If lower than groundwater - will stay near the water table.

Control of leachate-plume movement by the hydraulic gradient. A well at ***A*** would not be contaminated because the vertical component of groundwater motion in the flow system.



Saturated Zone Transport

- How do contaminants move within the saturated zone?
  - 2 physical mechanisms:
    - ***Advection***
    - ***Hydrodynamic dispersion***
- ***Advection***
  - Transport of contaminants by the bulk movement of flowing water in response to the hydraulic gradient
  - Rate of movement estimated by ***average linear velocity***
    - Why average? Nature of flow in porous media – i.e. very variable – dependent on path taken by H_2O molecules (variation in size of microscopic flow channels)

Avg. linear velocity (v) = K·I/n

K = hydraulic conductivity

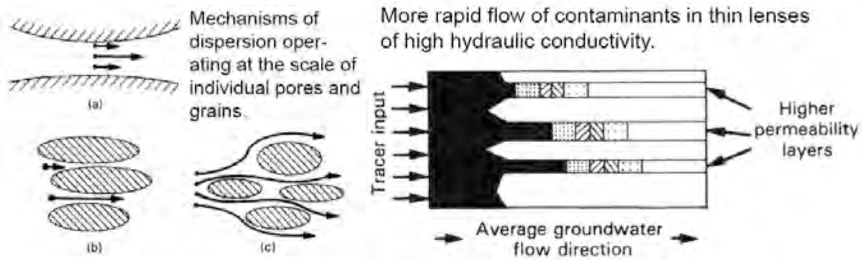
I = hydraulic gradient

n = porosity

Saturated Zone Transport

Hydrodynamic dispersion

- Results in spreading of the contaminated zone along the flow path due to:
  - Higher flow rates in the center of the plume than the margins
  - More rapid flow through larger pores
  - Lateral expansion of the contaminant due to having to water flow around aquifer grains
- Results in the fixed mass of contaminants being spread over larger area = reduction in concentration



Saturated Zone Transport – Aqueous Phase

- ***Attenuation Mechanisms***
  - Attenuation = dying out of the contaminant plume

  - Hydrodynamic dispersion
  - ***Adsorption***
  - Acid-base reactions
  - Solution-precipitation reactions
  - Redox reactions
  - ***Microbial synthesis***
  - Radioactive decay
  - Biodegradation

Attenuation Mechanisms

- ***Adsorption*** - attraction of a contaminant ion to surface of a solid
  - Form of cation exchange: as a contaminant ion is adsorbed, another ion must be released to maintain electrical neutrality
  - ***Clays*** tend to be very good absorbers of contaminants
  - ***Zeolites***
  - ***pH tends to control this process***
  - Nonpolar organic contaminants are strongly attracted to other organic material present in the aquifer

Attenuation Mechanisms

- ***Biodegradation, microbial synthesis***
  - Breakdown of contaminants by microorganisms
  - Chemical environment important, oxidizing conditions often necessary (although some chlorinated contaminants break down under reducing conditions)

- **Non-aqueous phase (NAPL) mass transport through the unsaturated zone**
  - Complex 3 phase system (or more)
    - NAPL (and perhaps a NAPL gas phase)
    - Water
    - Air
  - Flow of a NAPL follows same basic principles as water flow
    - A NAPL will have a certain ***residual saturation*** level
      - Depends upon soil properties
      - Depends upon adhesion of the NAPL
    - In order for a NAPL to move through the subsurface, it must exceed the residual saturation level:
      - After the main NAPL body has passed through a packet of soil, a small amount will remain, filling the pores at the residual saturation level

Table 12.5 Oil Retention Capacities for Kerosene in Unsaturated Soils

Soil Type	Oil Retention Capacity (R) L/m^3	Oil Retention Capacity (R) g/yd^3
Stone, coarse sand	5	1
Gravel, coarse sand	8	2
Coarse sand, medium sand	15	3
Medium sand, fine sand	25	5
Fine sand, silt	40	8

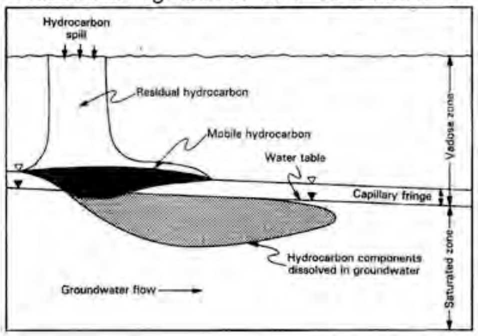
Source: CONCAWE, 1979, *Protection of Groundwater from Oil Pollution*, NTIS PB82-174608.

Unsaturated Zone NAPL Transport

- ***Movement of NAPL through unsaturated zone***
  - Crude oil body begins to move downwards and infiltrate the unsaturated zone under the influence of gravity
  - As it flows downwards, capillary action and the matric potential of the crude resists the downward flow
  - Existing pore fluids must be displaced prior to advancement (water and air)
    - In the near surface unsaturated zone, this is easy as the primary fluid is air
    - Closer to water table, it becomes more difficult as water is the primary pore fluid
    - ***Rate at which the NAPL move*** mostly controlled by ***viscosity*** and ***grain size***
      - High viscosity = slow movement
      - Small grain size = slow movement (due to high residual saturation)

Unsaturated Zone NAPL Transport

- Example continued…
  - Gasoline NAPL reaches the capillary fringe.
    - ***Gasoline = LNAPL.***
    - Begins to pool at the top of the capillary fringe in a layer termed the "***free product***".
    - Will migrate along the top of the capillary fringe in the direction of the slope in the water table.
    - Top of the free product forms the "***oil layer***".
    - Soluble components of the gasoline will dissolve and form a groundwater contaminant plume that moves down-gradient (longer distance than the '***free product***').

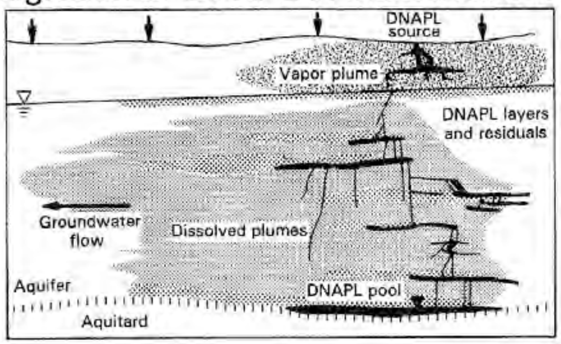


Subsurface Migration of LNAPL Contaminants

Saturated Zone DNAPL Transport

- **Only DNAPLs will be transported through the saturated zone**
  - Movement of DNAPLs through unsaturated zone similar to movement of LNAPLs through unsaturated zone.
  - The DNAPL must overcome the residual saturation level for the contaminant and must move pore fluids in order to progress.
  - Once the DNAPL reaches the top of the saturated zone, instead of ponding, it penetrates the water table and begins to sink.

Migration of DNAPL in the subsurface



Saturated Zone DNAPL Transport

- Will continue to descend until it reaches the first impermeable layer and then will form the ***free product*** layer
- Travels in direction of the slope of the impermeable layer
- Can be in the opposite direction of groundwater flow
- Remnants of the DNAPL will be retained as residual saturation in the descent column and any soluble compounds can be dissolved in the groundwater and will move with groundwater flow
- Locating the free product layer can be difficult because you HAVE to know the geology of the area - can't just follow the hydraulic gradient

Remediation

- **Techniques**
  - Source control
  - Containment
  - Pump and Treat
  - Bioremediation

Remediation Techniques

1. Source Control:

- Procedure - find source and remove it.

Examples

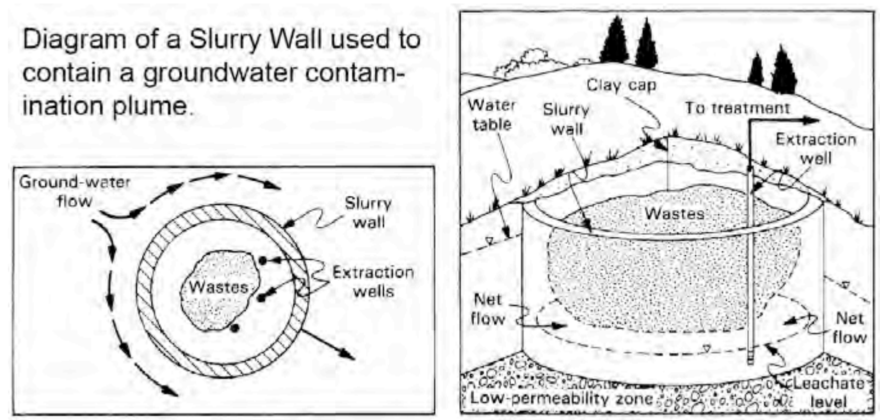
- Leaking underground gas tank:
  - Remove bad tank, possible excavate soil below if gas saturated.
- Poorly constructed landfill
  - Waste can be move to more secure site;
  - Liquid wastes can be funneled to collection point and treated.
- Accidental spills:
  - Area affected by spill can be excavated, removed and treated.
- Only useful if contamination of small extent.
- Important to stop contaminants before they reach water table and migrate!

Remediation Techniques

2. Containment

- If contaminant has reached water table and began to migrate.
- Need to control movement of contaminant within aquifer.
- ***Slurry Wall:***
  - Dig trench around contaminant plume, fill it with impermeable slurry (viscous liquid);
  - Install monitoring wells; contaminated water can be removed and treated.
- Only useful in certain geologic circumstances and during early stages of contaminant migration.

Slurry Wall



Remediation Techniques

3. Pump and Treat

Methods:

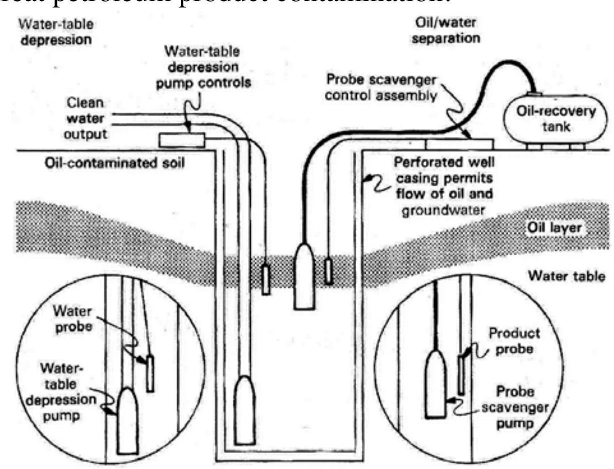
- Use pumping from one or more wells to alter or reverse hydraulic gradient (hence control plume dispersal) – ***'cone of depression' effect.***

If *Light Non-Aqueous Phase Liquids LNAPL present* (less dense than water, e.g. gas or other petroleum products):

- Dual Pump Method:
  - 1st pump creates zone of depression; causes migration of LNAPL layer towards well;
  - 2nd pump placed up at water table; removes LNAPL layer as it reaches pump.

Pump & Treat - Dual Pump System

Used to treat petroleum product contamination.



Deeper pump creates cone of depression causing flow of free product to well. Upper pump removes free product.

Remediation Techniques

3. Pump and Treat - Treatment Methods

- ***Carbon Adsorption*:**
  - Contaminated water passed through carbon filter;
  - Many hazardous contaminants (e.g. chlorinated solvents) will tend to adsorb to this medium.
- ***Air and Steam Stripping*:**
  - Pass air or steam through contaminated water to volatilize contaminants; can then be collected or released into atmosphere.

Remediation Techniques

4. Bioremediation

- Hot topic - lots of active research in this field (including at Notre Dame).
- **Main idea - let the organisms do the work for you:**
  - Many microorganisms can take contaminants and break them down into non-harmful chemical species.
- **Implementation:**
  - Pump and treat - use microorganisms as the treatment method;
  - In-situ - introduce microorganisms to subsurface to remediate OR use natural microbial community.

Summary

Varieties of Pollution and Groundwater Contamination.
Land Surface Contamination: Platt River, San Joaquin Valley; Road Salt.
Land Surface Contaminants: Accidental Spills, Dumping, Feedlots.
Saltwater Intrusion: Coastal Communities; Ghyben-Herzberg Relation.
Contamination in the Unsaturated Zone: Landfills (Secured & Sanitary).
Disposal of Liquid Wastes: Septic Systems, Petroleum Storage Tanks, Graveyards.
Saturated Zone Contamination: Mines & Waste Dumps.
Environmental Regulations: Clean Water Act; Safe Drinking Water Act.
Transport of Contaminants: Mass Transport (DNAPL, LNAPL)

Summary

Unsaturated Zone Transport of Contaminants: Matric Potential, Funicular Zone, Pendular Zone, Tensiometer.
Saturated Zone Transport: Contaminant Density, Advection, Hydrodynamic Dispersion, Attenuation Mechanisms.
Unsaturated Zone NAPL Transport.
Saturated Zone DNAPL Transport.
Remediation: Source Control, Containment (Slurry Wall), Pump and Treat, Bioremediation.