Week fourteen

I. Water quality

Water quality is defined by the dissolved solids and gases as well as suspended matter.

TDS - total dissolved solids is what would remain should a liter of water be evaporated. Note that this includes suspended solids (e.g., SiO2).

- **Fresh**: 0-1000 mg/l
- **Brackish**: 1000-10,000
- **Saline**: 10,000 - 100,000
- **Brine**: >100,000

Major cations: Ca, Mg, Na, K

Major anions: Cl, SO4, CO3, HCO3

Behind these major constituents are the minor constituents such as iron, manganese, nitrate etc., then there are the trace elements which are important at very small concentrations (arsenic, lead, cadmium) these are measured in micrograms per liter.

Historically water contamination problems were concerned with microorganisms, primarily Giardia, E-coli, and viral agents. Surprisingly enough groundwater has been a bigger culprit than surface water.

In recent years chemical contamination, particularly by organic solvents has come to the forefront.

II. Water quality standards

The EPA sets standards for drinking water based on:
- Ability to detect a material
- Potential for health risk
- Potential for occurrence

MCLG - maximum contaminant level goal,
- 0 for carcinogens
- Acceptable daily intake for others

MCL - maximum contaminant limit (enforced), set to be as close to MCLG as is feasible.
III. Sample collection

before starting:

1. purpose of the sampling program, regional water quality is different than remediation

2. sampling sites (number and location)

3. target species ad quantification limits, need to have a rough idea in order to select analytical method

4. QA paper trail

5. QC
   - spiked samples - use knowns to test accuracy
   - replicates to test precision
   - field blanks to test sampling gear

IV. monitoring wells

the term monitoring well has a legal definition, these are installed for the purpose of determining ground-water quality at a specific location

where do you put the things

most monitoring wells are installed in dirt, using a hollow-stem auger, soil samples may be collected along the stem during advancement

the well itself consists of casing and screen, the materials and size of these are chosen depending on the location

for most purposes, PVC pipe is used for the casing, noting that glue is not used to make connections as that might contaminate the samples

screens are chosen to keep out the surrounding material and are often made of stainless steel, multilevel samplers may be installed in place of a single screen, note that as monitoring wells are designed to sample at a specific location, the screen is generally of a relatively short length

after installation the hole surrounding the monitoring well is backfilled and sealed at the surface, again the methods for this are regulation driven

finally the well is developed to remove any material that may be blocking the screen, for monitoring wells this is usually done by surging the well, after development solid material is bailed out of the well
note that at a contaminated site, all the material removed may be hazardous waste and the drilling equipment may have to go through some sort of decontamination ritual

V. withdrawing samples from wells

well must be purged before sampling

sampling device must
  collect a representative sample
  easily cleaned
  get water to the surface
  capable of purging well
  inert with respect to water
  reliable

possible sampling devices include
  bailers
  bladder pumps
  borehole probes
  syringe sampler
  peristaltic pumps
  Kemmerer sampler

VI. sampling in the vadose zone

can't pump

liquids move downward, vapors in all directions

gas well - this is essential a gravel column with an impermeable seal at the top. the sampling tube passes through the cap and is open in the gravel, gravel will stay drier than surrounding soil

suction lysimeter
  clog
  filter out suspended solids
  limit on the amount of pressure
  real small sampling area

collection lysimeter - pretty much a collection gallery placed under a landfill cover prior to emplacement
VII. mass transport

once a contaminant gets in the GW, it’s movement is modified by

diffusion
    simple molecular scale movement in response to concentration gradients
    in low K materials this process may dominate
    solute can move faster than GW
advection
retardation
chemical reactions
biologic activity

VIII. diffusion

\[ F = -D \frac{dC}{dx} \]

\( F \) = mass flux of solute per unit area per unit time

\( D \) = diffusion coefficient (area/time)

\( C \) = concentration (mass/volume)

what this equation says is that a solute will move from areas of high concentration to low concentration, and that the rate of movement is proportional to the concentration gradient

this is Fick's first law for 1-d diffusion

Fick's second law relates to systems that are varying in time

\[ \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \]

Diffusion coefficient is a property of the ionic species and is on the order of \( 10^{-9} \) m\(^2\)/s

even though individual species are assigned rates, the solution must remain electrically neutral

in porous media diffusion does not occur at the same rate as it does in an open beaker because the media gets in the way and inhibits communication, the effect of this tortuosity can only be determined by measuring \( D^* \) in the media itself (\( D^* \))

it is assumed that \( D^* = D \) times a constant, but that is not necessarily so

in places where groundwater movement is slow (clay) diffusion may be the dominant mechanism of transport
IX. mechanical dispersion

non-reactive solutes will flow with the water, mean fluid velocity is

\[ v_x = -\frac{K}{n} \frac{dh}{dx} \]

however, the specific velocity will differ due to

1) faster flow through large pores
2) faster flow in pore centers
3) different flow paths

these three effects introduce both longitudinal (\(\alpha_l\)) and lateral dispersion

for practical applications, dispersion and diffusion are grouped into coefficients of hydrodynamic dispersion, we will only consider longitudinal behavior

\[
\frac{\partial C}{\partial t} = D_L \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x}
\]

where

\[ D_L = a_L v_x + D^* \]

note that this collapses to Ficks second law for zero velocity, also note that some of the solute will diffuse ahead of the water carrying it

these equations are not easy to solve, the 1D solution for a pulse under steady flow conditions is:

\[
C = \frac{C_0}{2} \left[ \text{erfc} \left( \frac{L - v_x t}{2\sqrt{D_L t}} \right) + \exp \left( \frac{v_x L}{D_L} \right) \text{erfc} \left( \frac{L + v_x t}{2\sqrt{D_L t}} \right) \right]
\]

what this equation says is that the center of the solute pulse is moving at the same rate as the mean groundwater velocity and is normally distributed about that

a continuous point source will lead to the formation of a plume that grows in the downstream direction

a slug will increase in size and decrease in concentration as it moves down gradient
heterogeneity really screws this up, and DL becomes scale dependent

X. retardation

conservative solutes do not react with the soil/water

clay adsorption - clay minerals tend to have negative charges on the outside of the plates so that cations, particularly divalent ones will stick

it is commonly assumed that the effect of this adsorption is simply to slow the rate of the advancing plume with no change in shape of the RTD

\[ v_c = \frac{v_s}{1 + \rho_b K_d \theta} \]

where \( \rho \) is bulk density, \( \theta \) is moisture content

\( K_d \) is defined as the rate of change in solute adsorbed with respect to solute concentration, and is commonly assumed to be linear

organic molecules can also stick to organic molecules in the soil or degrade through either biotic or abiotic activity

XI. degradation

pH
temperature
state of oxidation/reduction
critters
other chemicals present

XII. types of contamination

septic tanks and cesspools - anaerobic decay performs tertiary treatment, effluent contains bacteria and viruses (typhoid, dysentery) problems occur in

thin soils
high GW (most aerobic decay occurs in vadose zone)
high density
high K soils (rapid transport)

landfills liquid draining (or flowing) through is called leachate
natural attenuation landfill - uses vadose zone to destroy leachate
lined landfill - leachate collection system

cap is critical to landfill performance

LNAPL
  floats on the water table
  partitions (dissolves) into the GW
  leaves residual in the vadose zone

DNAPL does the same but sinks

mining - pyrite releases sulfuric acid, uranium etc.

what else
  oil brines, salt piles, fertilizer, evap ponds, salt water intrusion, leakage from
  sewers and storm drains

XIII. restoration

source control
  excavate whole thing
  install cap to minimize infiltration
  minimize through flow
    slurry wall
    grout curtain (through the waste package)
    gradient control well - lower WT so it doesn’t pass through waste

treatment
  no action - natural flushing (dilution is the solution to pollution)
  in situ treatment
    critters
    chemical
      spread limestone on ground (or fill a trench) for pH

extraction - pump and treat
  plume stabilization wells reverse the gradient
    inside plume
    outside plume would expand contaminated area
  initially you get a lot out, but effectiveness decreases exponentially
fractured rock with DNAPLS is unlikely for extraction

capture zone is defined as the up-gradient and down-gradient regions that contribute flow to a well