Groundwater age dating

³H → ³He A good tracer because ³H is right in the water. HTO instead of H₂O.





Tritium forms ³He by beta decay with a half-life of about 12.4 years.

 $^{1}TU = ^{1}T / 10^{18}H$

3
He/ 3 H = age.

http://wwwchem.csustan.edu/chem3070/images/tritium.gif

•Tritium has been used for many years (produced by atmospheric nuclear testing). Nobody tried to apply the decay pair in ground water until the late 1980's (although it had been suggested by the oceanographers that were already using it 23 years earlier- more concerned about water supply, agriculture).

* This method is not seen in any textbook and therefore hasn't caught on that fast. Many hydrologists approach from physical rather than a chemical viewpoint, but the chemical can tell a lot about the system.

- * Dramatic increase in tritium as the Cold War heated up. At its peak, the furious explosions of nuclear weapons prior to the ban-- mostly Russian tests (others may have gone out over the oceans).
- About 25% of tritium in troposphere mixes into the stratosphere each year-reason for gradual decrease with time.
- Last 20 years or so-- stabilized at about 30 tritium units. The tritium is still in the hydrologic system→ due to weapons, plants, etc?
- The dismantling of nuclear war heads may cause an increase in tritium again. And a lot of tritium is contained in the H-bomb which must be refurbished in tritium about every 18 months due to leakage.

http://canterbury.cyberplace.org.nz/peace/nukenviro.html





Tritium Concentration in Precipitation, Decayed to 1998



http://water.usgs.gov/pubs/circ/circ1213/major_findings2.htm

 Places are affected differently by the tritium → Places with large marine influence have lower tritium values while places that are landlocked with mainly only local precipitation, have high ratios. Mexico has only 3-4 tritium units.

Latitude: 50°N→ high 0°→ lower 30°S→lower

Data derived from estimation technique of Michel (1989). Values not corrected for radioactive decay.

http://images.google.com/imgres?imgurl=http://toxics.usgs.gov/ph oto_gallery/photos/tritium/cab_fig18a.gif&imgrefurl=http://toxics.us gs.gov/definitions/tritium.html&h=325&w=340&sz=21&tbnid=xIJSz6 yBEsgJ:&tbnh=109&tbnw=114&start=1&prev=/images%3Fq%3Dtriti um%2Batmosphere%26hl%3Den%26lr%3D





 \rightarrow function of where the input was and where the stratosphere mixes (more readily at high latitudes).

Idea is to take a known system and to try new idea to see if the results are the same (new idea \rightarrow tritium-helium system).

Tritium/Helium technique

³He \rightarrow normally 7 ppt (parts per trillion) in the atmosphere.

⁴He → normally 5.2 ppm (parts per million) in the atmosphere (i.e.much more common).

When rainwater falls to the earth ---> it is in solubility equilibrium with the atmosphere and therefore some of the ³He and the ⁴He will dissolve into the ground water at about 68 x 10-12 cc³He/kg water or about 1700 million atoms He/kg water.

Therefore, have to subtract atmospheric ³He because it is not produced by decay.

Environmental behavior of tritium after tritium gas was released to the atmosphere



HT: tritium gas HTO: tritiated water OBT: organically bound tritium

http://inisjp.tokai.jaeri.go.jp/ACT96E/04/0408.htm

t(travel time) = $(1/\lambda) \ln(^{3}He^{*} + 1)$ 3H

He* = He from tritium decay

 $1/\lambda$ = decay constant

 $N = N_0 e^{-\lambda t}$ \rightarrow $^{3}H = {}^{3}H_0 e^{-\lambda \tau}$ \rightarrow $^{3}H = ({}^{3}H + {}^{3}He)e^{-\lambda \tau}$

 $[^{3}\text{He}]_{w} = kP_{3\text{He}} \rightarrow (^{3}\text{He} / ^{4}\text{He})_{w} = 0.985(^{3}\text{He} / ^{4}\text{He})_{air}$

Things to note:

- This travel time doesn't require you to know the initial tritium value
- ³He + ³H = conservative tracer in ground water.
- ³He/³H 'clock' is set to zero at water table.
- Why? At water table in contact with the atmosphere- in solubility equilibrium where ${}^{3}\text{He}/{}^{3}\text{H} = 0$.

Time here also has a nice progression from surface to deep layers and parallels the travel time based on Cl. **Why is it offset?** Because the clock was set to zero at about 70-80 cm below the water table (about 1 year's travel time). This is because the water travels in pulses and usually mostly in the springtime.

Age gradient ---> a very robust establishment of vertical velocity.

2 m/5 years = Vz = 40 cm/year.

 (V_z) (Porosity) = 40(.3) = 12 cm/year = recharge.

Vertical age gradient tells you how much recharge is coming through into the system \rightarrow how fast things are moving

What determines the flow, is what you put in at the top.

• With rainfall = 80-100 cm/year, the recharge at the source is about 60 cm/year.

- but 1 km away, recharge is only 12 cm/year. Why? Because the source, as a dump is relatively devoid of any life, whereas the trees 1 km away extract 80-90% of the water.

- How do you get horizontal and vertical velocities?
 - Might want to know how quickly a contaminant will migrate off sight
 - Well is screened over entire interval to get the most information in the radial sense.

→A lot of information is lost about the aquifer by sampling over entire interval.

- Don't know exactly where the water is coming from.
- \rightarrow should only sample about 10 centimeters instead of 1-2 meters.

If trying to find contaminant and it is moving at a narrow level, it will enter the well and be diluted by relatively pure water. "Water table aquifer"

³H - ³He dating of ground water Cape Cod, MA

Purpose:

1. Demonstrated the usefulness of this technique in establishing rates of ground water flow.

2. Assists in establishing rates of plume migration.

•Tritium (³H) input from thermonuclear weapons tests (peak in 1963); no longer a sustained input.

•Age doesn't require knowledge of tritium input function.

•Amount of tritium in 1 nuclear warhead = amount in the earth's atmosphere.



Munitions uncovered in a burial site at the J-1 Range during IAGWSP investigations.



http://www.ldeo.columbia.edu/~martins/plumeflow/ppt/ppt2_1_00/sld023.htm

³H ----(beta decay β^-) \rightarrow ³He (trace isotope of He) Half life : t_{1/2} = 12.4 years

Assume all 4He in atmosphere, correct for 3He. ³He less soluble in water then 4He, so any excess ³He is from tritium (³He*) [Solubilities: ³He - about 7 ppt ; 4He - about 5.2 ppm]

Travel time $t = (1/\lambda) \ln [(^{3}He/^{3}H) + 1]$

We want to measure the excess over solubility. Assume ⁴He in atmosphere, assume ³He/⁴He in air is constant = $1.4 \times 10-6$.

Cape Cod - ³*H*/³*He dating*



Dunkle-Shapiro et al. (1999) Groundwater, 37, 861

The ³He/³H clock is set to zero at the water table because vadose zone exchange with atmosphere through change in temperature (air exchange) -- solubility equilibrium.

Vertical Age Gradient = recharge rate (combine recharge rate and hydraulic head)

FS-12 Field Site with Water Level Contours, the location of multilevel wells, and the extent of a benzene plume determined in the 1991 study.



Fig. 1. FS-12 field site with water level contours, the location of multilevel monitoring wells, and the extent of a benzene plume determined in the 1991 study.

Solomon et al., 1995

- ³He and ³H is a conservative ground water tracer because there is no chemistry involved (He is inert); movement is controlled only by physical mechanisms.
- Helium diffusion is faster than tritium diffusion so is complicated by diffusion effects at peak age.
- When you sample below the water table, have to screen over a very small interval (<15cm).
 - Ages are vertically stratified.
 - But, most regulations make you screen over 5 feet!
 - EPA says well should be > 2 feet.
 - Bad because there's a large interval, then remove a lot of water from the system to clean the well.
 - Must remove 3 well volumes until you can be sure that your water is really up into the aquifer.
 - Also- screening over a large interval means getting several ages at once.
 - To sample only over a discrete interval, place small wells in the hole at different depths.

Cape Cod is a terminal moraine with outwash plain (mostly sand).

Snake Pond is a surface expression of the water table, as are most lakes.

Spill components at this base

- 1. Aviation fuel.
- 2. JP4 (jet fuel; more like kerosene).

Snake Pond





http://www.mmr.org/IRP/genprog/factshts/images/snake.pdf

Looked at xylene, benzene, EDB (= ethelyne dibromide, volatile, in Pb gasoline, keeps Pb from Pb oxide).

- xylene, benzene only sparingly soluble in ground water and are large molecules (→ move slowly)
- EDB small molecules, moves at about the rate of ground water.
- ***vertical stratification in ground water.
- The major spill of aviation gas in 1974, which sank quickly to the water table even though less dense than water.
 - * a peak of all 3 in 1976.



Fig. 2. Profiles of ${}^{3}H/{}^{3}He$ age and ${}^{3}H + {}^{3}He^{*}$. The cross section from ITW-1 to ITW-3 is oriented along a ground-water flow line. Note that for ITW-2, only ${}^{3}H$ is plotted because a complete profile of ${}^{3}He^{*}$ was not obtained. Where duplicate samples were obtained, the plotted values are averages with outliers removed.



Fig. 3. Profiles of organic contaminants and ground-water age. The cross section from ITW-1 to ITW-3 is oriented along a ground-water flow line. Solomon et al., 1995



Profiles of Observed and Simulated Ground-Water Age

Fig. 4. Profiles of observed and simulated ground-water age. The simulated profiles were obtained by optimizing the fit between the observed and simulated age by adjusting the vertical velocity at the water table.

Solomon et al., 1995

Simulated stream function, hydraulic potentials, and the configuration of the water table

Solomon et al., 1995



Fig. 5. Simulated stream functions, hydraulic potentials, and the configuration of the water table (note expanded scale). Also shown is the simulated location of water recharged in 1975 beneath Greenway Road at various points in time along the flow system. The shaded region highlights a flow line and does not represent a simulated contaminant plume.

Cape Cod (Le Blanc et al. (1991))



http://www.ldeo.columbia.edu/~martins/plumeflow/ppt/ppt2_1_00/sld024.htm



Schlosser et al., In: Isotope techniques in the study of Environmental Change, IAEA, 1998

Wetting Fluid - fluid that coats grain surfaces due to surface tension.

- aviation gas not soluble in water and therefore is excluded from water.
- moves through pore spaces to water table where it floats, sits and slowly dissolves.
- EDB is conservative, is right there with bomb peak when xylene and benzene at 0 (they're already gone).

* As go deeper, flow speeds up in horizontal away from flow divide.
* close to flow divide, longer time spurt in vertical as a result of the hydraulic potentials.

Hydraulic conductivity K

- Can look at it in terms of V_{horizontal} or K_h.
- the vertical component of the flow really shows how the system is behaving.



Figure 6.6 Fetter, Applied Hydrogeology 4th Edition



The relationship between moisture potential, Ψ , and volumetric water content, θ_v , for clay soil.

> Figure 6.7 Fetter, Applied Hydrogeology 4th Edition



▲ FIGURE 6.8

Idealized curves showing relationships of volumetric water content, θ_v , hydraulic conductivity, K, and soil-moisture tension head, ψ . The effect is included for wetting and drying cycles.

Fetter, Applied Hydrogeology 4th Edition

Hydraulic conductivity K

Vogel Model:

K_V **= 0.1 K**_H K=hydraulic conductivity $V_z = \underline{B} * \ln(B/(B-Z))$ t

 $V_x = (V_z * x) / B$

B=aquifer thickness

x=distance from flow divide

t=travel time

Z=depth below water table



Fig. 6. Geometry of an unconfined aquifer used in the Vogel model.

Determination of hydraulic gradients from piezometer installations.



Freeze and Cherry, Figure 2.6

Steady flow through an unconfined aquifer resting on a horizontal impervious surface

Steady flow through a confined aquifer of uniform thickness



Figure 4.17. Fetter, Applied Hydrogeology 4th Edition

Figure 4.16. Fetter, Applied Hydrogeology 4th Edition

 \rightarrow Equation that governs fluid flows are fairly straight forward. Only rigorous in interpretation and when in 3 dimensions.

 \rightarrow Essentially, the velocity will depend on the hydraulic conductivity; therefore need to establish the hydraulic conductivity of the medium.



Typical soil-moisture-potential –hydraulic conductivity curves for a sandy soil showing the crossover effect for increasing moisture potential (decrease in water content.)

Figure 6.10. Fetter, Applied Hydrogeology 4th Edition

Measurement of hydraulic conductivity: (3 ways)

1. * Apply a hydraulic head and watch how the water flows through the sediments in the lab. One has a continuous supply of water and the other one drains in.

* Large range of potentials (log K). Ie. 2 orders of magnitude with peak at 10-5. This is a log normal distribution-- Where graph peaks equals the average conductivity.



Characteristic curves relating hydraulic conductivity and moisture content to pressure head for a naturally occurring sand soil (after Liakopoulos, 1965a)



Freeze and Cherry, Figure 2.13

Measurement of hydraulic conductivity: (3 ways)

2) Pump testing: Water is pumped out and watched to find the rate at which it fills up. If the sediment is a clay, it will slowly return to equilibrium; if it is sand, it will return more quickly to equilibrium.



Fully penetrating well pumping from a confined aquifer.

Fetter, Applied Hydrogeology 4th Edition



Figure 5.4 Plots of log of dimensionless drawdown as a function of log time for aquifer with various types of overlying confining layer.

- I No leakage
- II Leakage without storage in a finite semipervious layer
- III Leakage with storage in an infinite semipervious layer
- IV Leakage with storage in a finite semipervious layer

Fetter, Applied Hydrogeology 4th Edition

Measurement of hydraulic conductivity: (3 ways)

3. Slug test:



http://www.theshop.net/xibits/litigation/diagrams5.htm

Hvorslov constructed an algorithm:

 $K= \frac{r^2 ln(L/R)}{2Lto}$ r = well radius

L = length

•Can calculate standard K for a medium.

•Can also use a slug test where you drop a slug in to raise the surface of the water and watch the time it takes for the water to sink back down.

Fetter, Applied Hydrogeology 4th Edition



Figure 5.21. Piezometer geometry for Hvorslev method. Note that for a piezometer installed in a lowpermeability unit the value R is the radius of the highest permeable zone that includes the gravel pack zone and L is the length of the gravel pack zone.



→ All of these methods measure the horizontal conductivity → how fast it comes from the sides to recover.

- vertical conductivity is often quite different; hard to get at by the way these pump tests are done.
- Vertical is different because of anisotropy → related to layering which can impede flow vertically but less so horizontally.

Kv= 1/10 (Kh) generally. (h = horizontal).

Other Conservative Groundwater tracers

- \rightarrow tracer moves at the same rate as the water
- → not impeded by methods such as chemical reactions or degradation. Influenced only by physical processes such as mixing, diffusion, etc.
- * See page from book: John Cherry, Camp Bordon, Ontario.



Plume resulting from the continuous injection of a tracer into a twodimensional flow field.

Figure 2.11. Fetter, Contaminant Hydrogeology 3rd Edition

Injection of a slug tracer into a two-dimensional flow field shown at 3 time increments.



Figure 2.12. Fetter, Contaminant Hydrogeology 3rd Edition

- This was an old air force base turned into a hydraulic experimental station in Canada (this would never have been allowed in the US).
- The camp was established around 1940. A place was found to place the trash from the compound-- established a landfill in a relatively out-of-the-way place (without the strong safeguards of today).
- As the rain came down, it would leach out the components which would flow into the ground.

• Appears that the plume flowed from the landfill and moved from south to north (left of the flow in the picture is the ground water divide).

Distance/Time = Rate of Migration of the Plume.

- \rightarrow How things spread by diffusion.
- \rightarrow Important tracer and allowed understanding of system.
- \rightarrow Could compare gradient to hydraulic conductivities.

- Have been able to introduce other tracers into the systemstry to use benign tracers, organic solvents (build barriers to try to stop organic solvents).
- \rightarrow This provided a good tracer:
 - 1. Know when it started (1940's).
 - 2. Produced a relatively benign set of contaminants,
 - mostly CI-, which was simple and easy to analyze.

:. Can trace K movement.



L = 30 ft T = 6 ft

FIGURE 2.14 The effect of changing dispersivity ratio on the spread of a contaminant plume from a continuous source. Source: Robert L. Stollar.

9 10 11

Figure 2.12. Fetter, Contaminant Hydrogeology 3rd Edition

Other tracers give time information

- ⁸⁵Kr → made from the reprocessing of nuclear fuel, power plants, high since 1950. But have to process about 200 liters of water, which is a substantial amount.
- CFC's → not conservative, consumed by organisms, adsorbed unto particles, but easy to measure.

⁸⁵Kr: radioactive form of krypton.

- formed during U and Pu fission.
- 52 dpm (0.9 Bq)/cc Kr.
- 1.58 x 10 -11 85Kr/Kr in atmosphere.
- when at water table level, water amount of 85Kr becomes equal to the atmospheric level- don't have to worry about solubility, only have to know the ratio 85Kr/Kr.
 - but need about 100L of water to count ratio, which can bias your results.
- man-made tracer

CFC'S: CFC-11 \rightarrow 220 ppt (today). CFC-12 \rightarrow 400 ppt (today).

- increasing at about 4%/year

Hundreds	Tens	Ones
#C - 1	#H +1	#F

Ex. CFC-11 \rightarrow 1C, 0H, 1F = CCI3F CFC-12 \rightarrow 1C, 0H, 2F = CCI2F2

- have a long residence time of greater than about 100 years.
- brings CI into the atmosphere.

CFC-22 \rightarrow 1C, 1H, 2F = CHCIF2

- short residence time- not as much CI brought into the atmosphereso strive to produce this instead!
- F-11 \rightarrow 5.5 pmol/kg in atmosphere.
- F-12 \rightarrow 2.3 pmol/kg in atmosphere.

Problems:

- temperature dependence : cold- dissolve more gas; warm dissolve less gas.
- anthropogenic sources (landfills).
- organic solvents dissolve large amounts of F-xxx in the air ---> to ground water.
- non-conservative in its behavior because it is organic- can be eaten or absorbed (only F-11 is eaten).
- F-113 behaves similarly to "nasty" molecules but has F instead of H.

Travel time? "Conundrum of Solomon"

- In reality are lines that are almost totally horizontal (paralleled by tritiumhelium age).
- ** Very important for plume hydrology.
- (Keep in mind that no flow is coming out of the bottom of the box).

The vertical velocity is not constant, higher at the beginning and lower further away, a function of z.

[This is happening at Cape Cod, didn't realize how fast the water was moving until it got into the water supply wells].

Behaviors of contaminants

I. Movement:

- the release (plume) will not spread at a constant rate because there are different paths that it could take- it moves with the water- will take short or long paths around grains.

II. Two ways organics migrate

1) **Dissolved**: solubility is proportional to mobility (high solubility, then high mobility).

2) NAPL: non-aqueous phase liquid

NAPL: non-aqueous phase liquid

A) * L-NAPL's: less dense than water.

-ex. Gasoline - forms a pocket which floats on the water table

-soluble material such as *benzene, toluene, xylene* (all organics) dissolves in the water

 \rightarrow the gas just evaporates.

Organic liquids such as gasoline, which are only slightly soluble in water and are less dense than water, tend to float on the water table when a spill

OCCUIS. Figure 10.19. Fetter, Applied Hydrogeology 4th Edition



NAPL: non-aqueous phase liquidB) * D-NAPL's: denser than water.

-ex. *methylene chloride* - when its spilled, it is gone an not seen again.

-trichloroethylene - breaks down to worse things.



FIGURE 6-7 General distribution of a DNAPL in the subsurface following a spill. CONTAMINANT HYDRO-GEOLOGY by Fetter, C. W., ©1993. Reprinted by permission of Prentice-Hall, Inc., Upper Saddle River, NJ.

III. Two types of contaminants (Very broad classes)

A. DNAPL (Dense Non-Aqueous Phase Liquid)
 * TCE (density = 1.46) Solubility in water: 1180ppm
 * TCA (density = 1.33) 1180ppm
 * PERC (percholoethylene, density = 1.6)
 * Methylene Choride (density = 1.33) 1300ppm (highly soluble)

 \rightarrow These are extremely dense.

B. LNAPL (Light Non-Aqueous Phase Liquid)

- * Benzene 1800ppm
- * Toluene 500ppm
- * Vinylchloride (density less than water and highly volatile)
- ***NOTE: solubilities given by weight (1 ppm = mg/L).
- → The drinking water standard for these contaminants is at 5 ppb (parts per BILLION)

C. Characteristics:

1. Densities of NAPL's range from .8x water to 1.6x water

- 2. Density is a function of the chloride.
- 3. Higher density contaminants will move quickly down a water table aquifer.
- 4. Porous vs Fractured Systems exhibit very different behavior.
- 5. Pure phase vs. dissolved phase \rightarrow different problems associated with each.

IV. Example: Spill of trichloroethylene (density = 1.33 g/cc).

- not that soluble.
- →What happens: migrates down to bedrock and pools there & slowly dissolves as water flows past.

-- OR --

- if there are lenses of clay, it will pool on them.
- distributed over a wide area, it is impossible to find it and get it out!
- try to pump it out → only end up dissolving it because the water flow over organics increases.
- if spill is 100,000 L at a concentration of 5 ppm, then you have to pump 2 x 109 L of water.
- concentration decrease due to less water-- when the pumping stops, the water flow returns to normal and the concentration goes up.



Organic liquids such as trichloroethylene, which are only slightly soluble in water and are more dense than water, may sink to the bottom of an aquifer when a spill

OCCUIS. Figure 10.20. Fetter, *Applied Hvdrogeology* 4th *Edition*

→ Is there really the possibility of remediating organically contaminated systems or are funds better spent elsewhere?

A. Questions:

1. size of the spill in terms of 1000's of liters of pure contaminant - need to remediate to a few ppb or less??

2. mobility. How fast will this move?

3. degradation \rightarrow rate at which organic material will degrade is dependent on the medium through which it travels. i.e. Small amounts of organic carbon is enough to slow this down.

B. Problems:

Volume calculations:

10,000 liters of contaminant dissolves to affect 6,0
15,000 liters of contaminant dissolves to affect 40
(This takes less than a tanker to contaminate this much!)

How much pure product is there and how can we get to it?

-This ends up causing a lot of problems especially since water wells are close.

How hard will it be to remove ie 5 billion liters of water? EXTREMELY hard! 6,000,000,000 liters of plume!! 40,000,000,000 liters of plume! h!)



http://www.inletkeeper.org/new%20pipelines%20page/Kenai%20National%20Wildlife%20Refuge%20Oil%20Spill.jpg

C. Remediation by the Pump and Treat Scenario

• Process relies on removing large volumes of water. This is not an equilibrium process. Natural flow may be 50 m/year and the flow with the pump may be 500 m/year.

• Find that after the water seems cleans and the pumps are stopped, that the concentration of the contaminant will rise again.

• In a past situation with extensive contamination, 1 million liters were drawn out of the well and treated.

 $1 \text{mg/L} \rightarrow \text{trivial} 1 \text{ kg.}$

The consultant even got out 30 kg. But the spill contaminated on the order of 30 million kgs!!

** This method seems to be the accepted way to clean spills, although it is not necessarily efficient.



The oil spill response team sets up a boom during a recent exercise held in Thames

http://www.ew.govt.nz/regionalservices/civil/spill.htm

D. Why won't it work?

* No aquifer is perfectly homogenous -- Even the simplest aquifer is heterogeneous (ie grain size).

* Conductivity varies by at least an order of magnitude ie about 1 log unit.

- What does this do to the system?
- →Small lenses form whose conductivity is 1 or 2 orders of magnitude less than the rest of the system. The NAPL will congregate on the low permeability area. Therefore it doesn't fall neatly straight down, but will cascade down and form a complex distribution.

D. Why won't it work?

 Water will not be seeing NAPL and therefore may take a long or infinite amount of time to pump out. More time is needed for higher heterogeneity → These stringers of low conductivities hold NAPL and don't allow solubility and movement of it → never attack the material in fine-grained, low conductivity sediments.

* L NAPL is easier to extract by vapor extraction if not too much is dissolved in the plume.



FIGURE 10.27 Use of extraction wells to remove contaminated ground water. Source: U.S. Environmental Protection Agency.

Use of Extraction Wells to Remove Contaminated Ground Waters

Freeze and Cherry, Figure 10.27