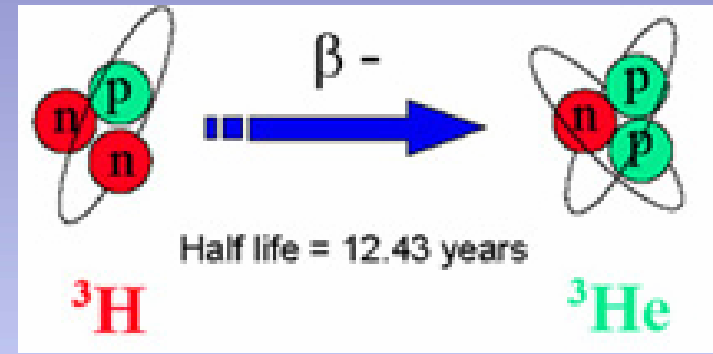


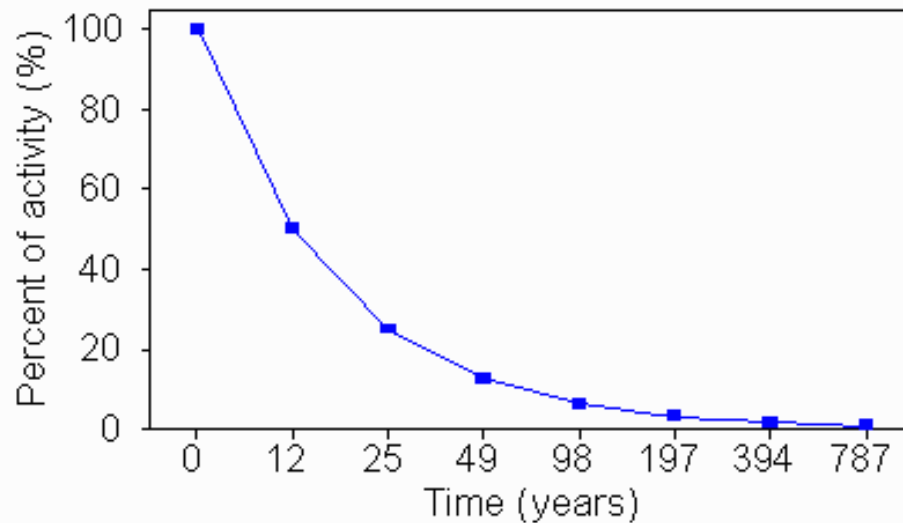
Groundwater age dating

${}^3\text{H} \rightarrow {}^3\text{He}$ A good tracer because ${}^3\text{H}$ is right in the water. HTO instead of H_2O .



Decay Curve for Tritium

Amount of radioactivity vs time



Tritium forms ${}^3\text{He}$ by beta decay with a half-life of about 12.4 years.

$$1\text{ TU} = 1 (\text{T}) / 10^{18}\text{H}$$

${}^3\text{He}/{}^3\text{H} \rightarrow \text{age}$.

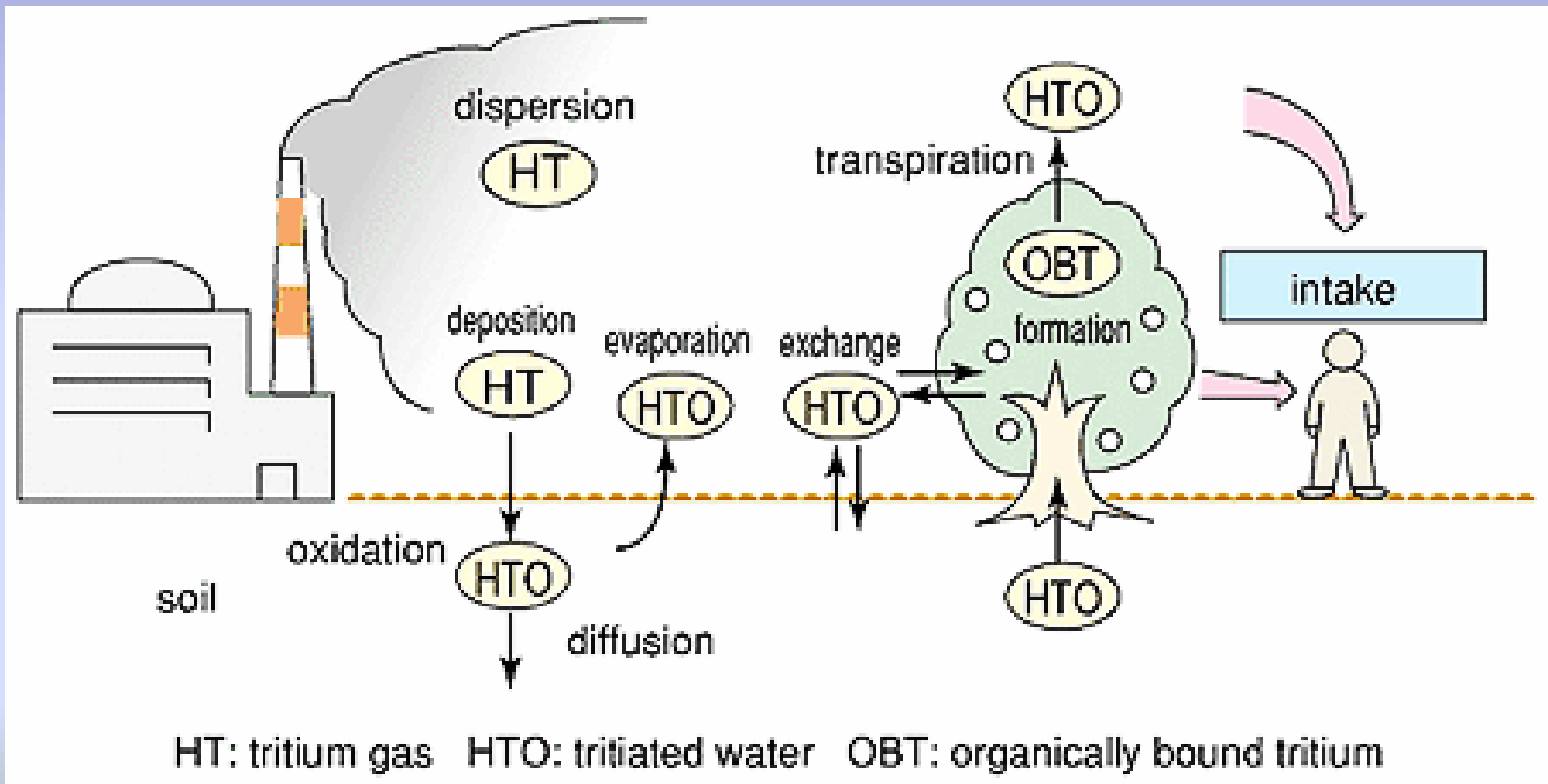
- Tritium has been used for many years (produced by atmospheric nuclear testing). Nobody tried to apply the decay pair in ground water until the late 1980's (although it had been suggested by the oceanographers that were already using it in 1970- hydrologists more concerned about water supply issues related to 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 (tracer) viewpoint can tell a lot about the system.

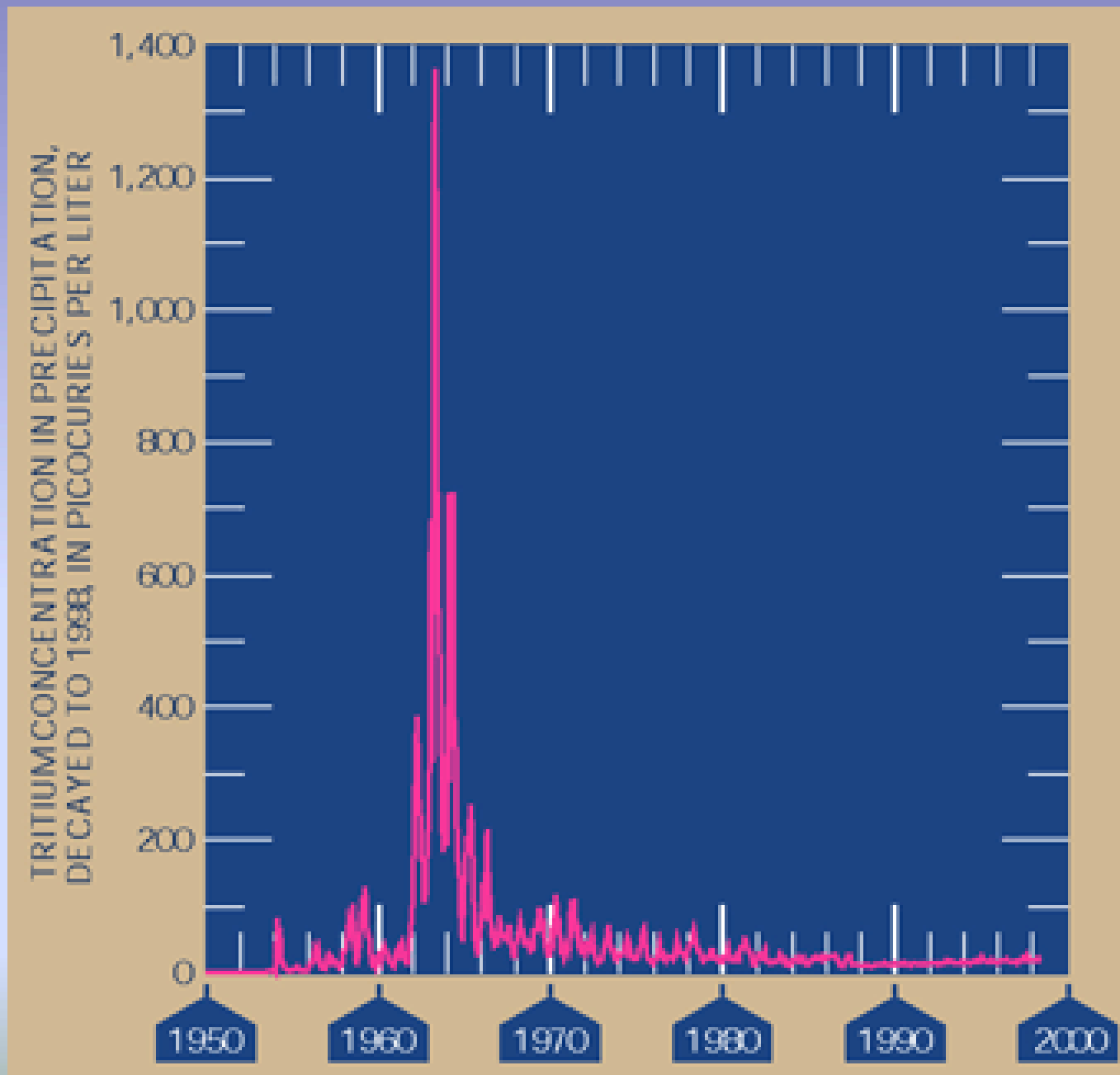
- **Dramatic increase in tritium as the Cold War heated up.** At its peak in 1963, the furious explosions of nuclear weapons prior to the atmospheric test ban-- mostly Russian tests in Kamchatka (USA tests in Pacific Ocean)
- About 25% of tritium in troposphere mixes into the stratosphere each year-- reason for gradual decrease with time.
- **Last 20 years or so-- stabilized at about 20 tritium units in New York.** 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



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



Tritium Concentration in Precipitation, Decayed to 1998



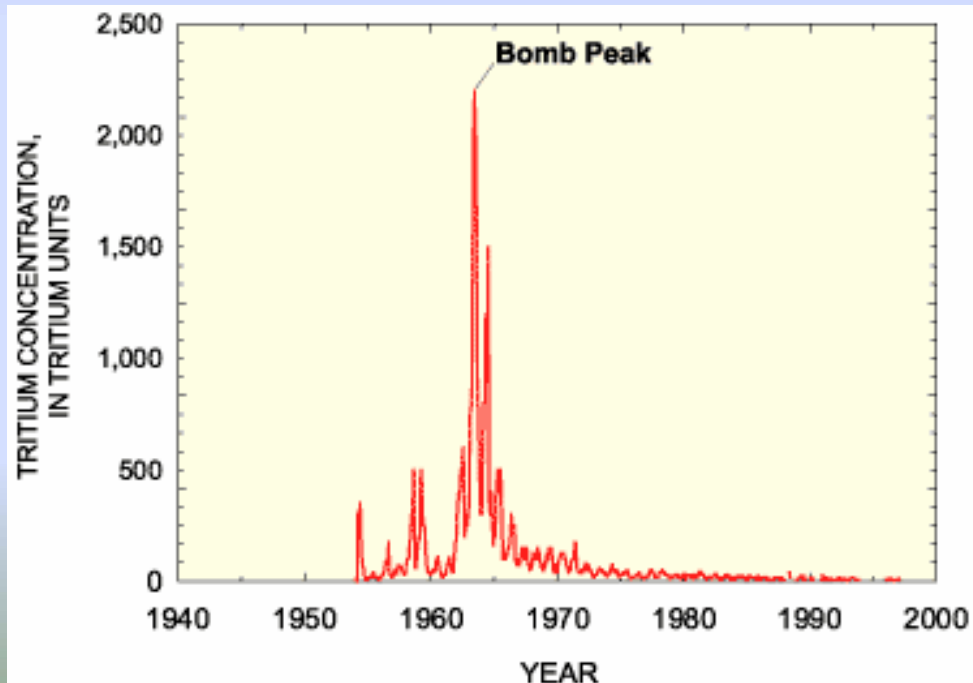
- **Places are affected differently by the tritium** → Places with large marine influence have lower tritium values while places that are dominated by mainly only local precipitation, have higher amounts. e.g. Mexico has only 3-4 tritium units.
- **Latitude:** **50°N → high**
 0° → lower 30°S → lower

→ function of where the input is (land based) 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 → tritium-helium system).

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

http://images.google.com/imgres?imgurl=http://toxics.usgs.gov/photo_gallery/photos/tritium/cab_fig18a.gif&imgrefurl=http://toxics.usgs.gov/definitions/tritium.html&h=325&w=340&sz=21&tbnid=xIJSz6yBEsgJ:&tbnh=109&tbnw=114&start=1&prev=/images%3Fq%3Dtritium%2Batmosphere%26hl%3Den%26lr%3D

Estimated tritium concentration in precipitation for the Tidewater area of Virginia, 1954 to 1997.



Tritium/Helium technique

^3He → 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 68×10^{-12} cc ^3He /kg water or about 1700 million atoms ^3He /kg water.

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

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

$^3\text{He}^* = ^3\text{He}$ from tritium decay

$1/\lambda =$ decay constant

$$N = N_0 e^{-\lambda t} \quad \rightarrow \quad ^3\text{H} = ^3\text{H}_0 e^{-\lambda \tau} \quad \rightarrow \quad ^3\text{H} = (^3\text{H} + ^3\text{He}) e^{-\lambda \tau}$$

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

Things to note:

- This travel time doesn't require you to know the initial tritium value
- $^3\text{He} + ^3\text{H} =$ conservative tracer in ground water.
- $^3\text{He}/^3\text{H}$ '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 estimates from plume release. **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.

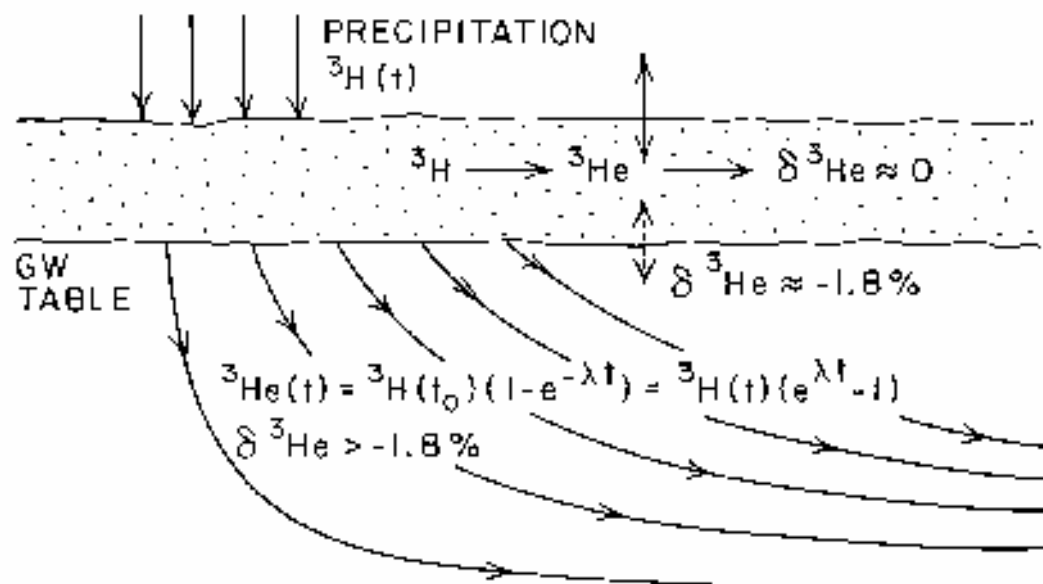
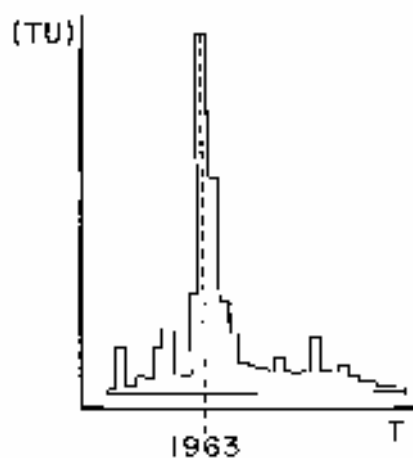
Age gradient ---> a very robust establishment of vertical velocity.

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

$(V_z)(\text{Porosity}) = 40(.3) = 12 \text{ cm/year} = \text{recharge.}$

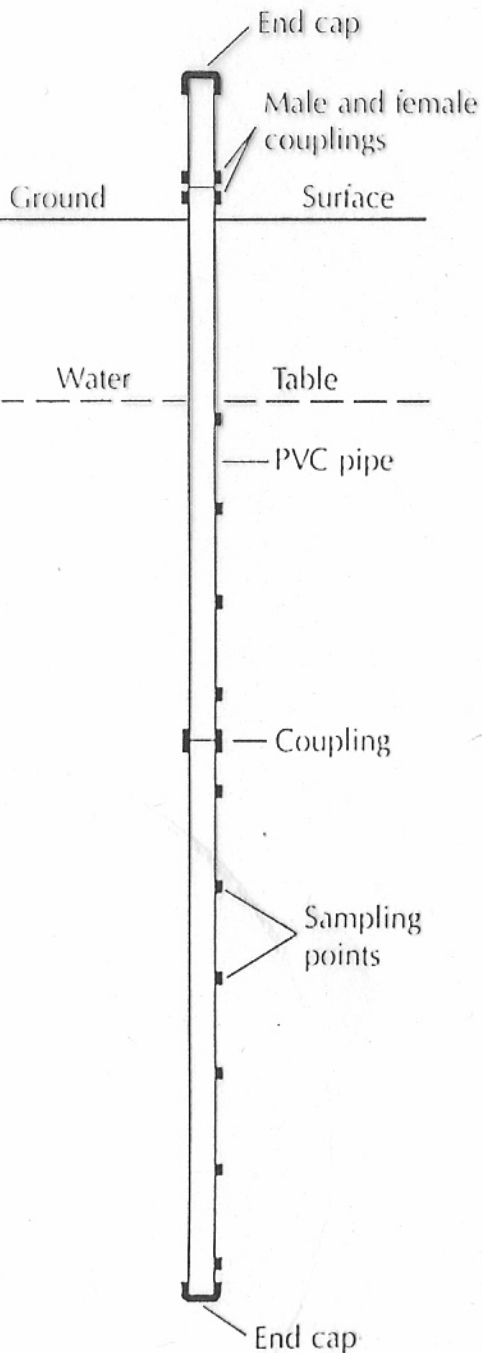
- ^3He and ^3H is a conservative ground water tracer because there is no chemistry involved (He is inert); movement is controlled only by physical mechanisms.
- Helium diffusion is faster than tritium diffusion so is complicated by diffusion effects at peak age.
- When you sample below the water table, 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.

$^3\text{H}/^3\text{He}$ dating

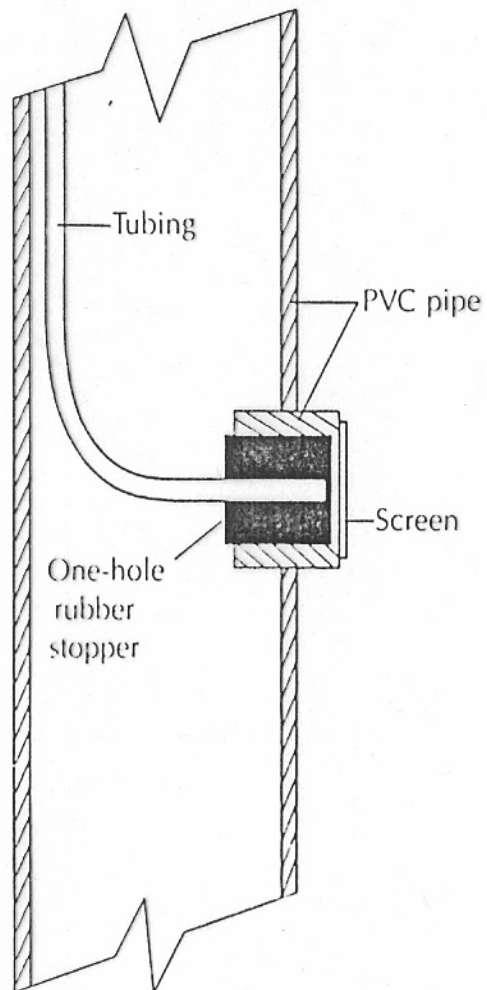


$$\tau = \frac{T_{1/2}}{\ln 2} \cdot \ln \left[1 + \frac{[{}^3\text{He}]}{[{}^3\text{H}]} \right]$$

Field Installation



Cross Section of Sampling Point

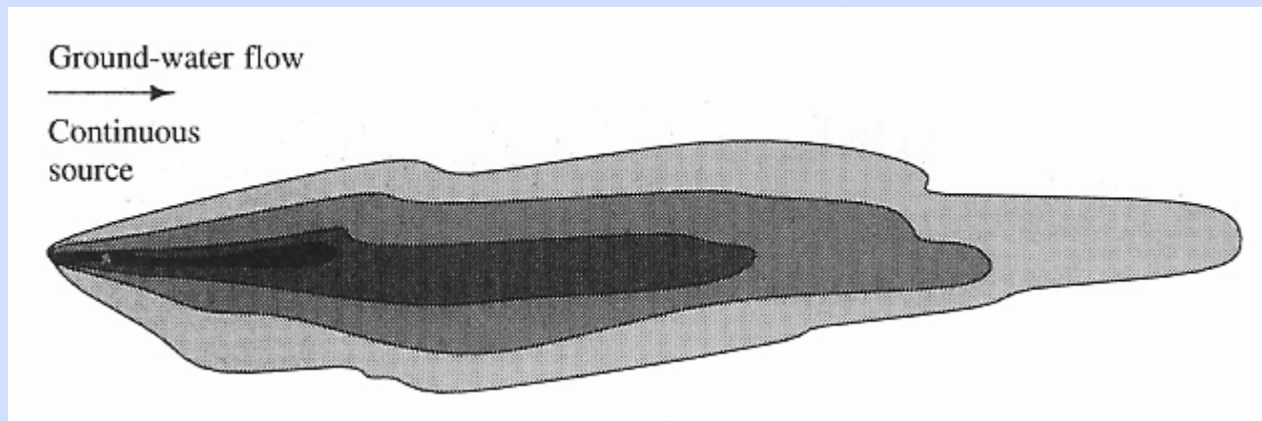


Multilevel groundwater sampling device for use in sandy soil.

Source: J.F. Pickens and others.
Ground Water Monitoring Review,
1, no.1 (1981):48-51.

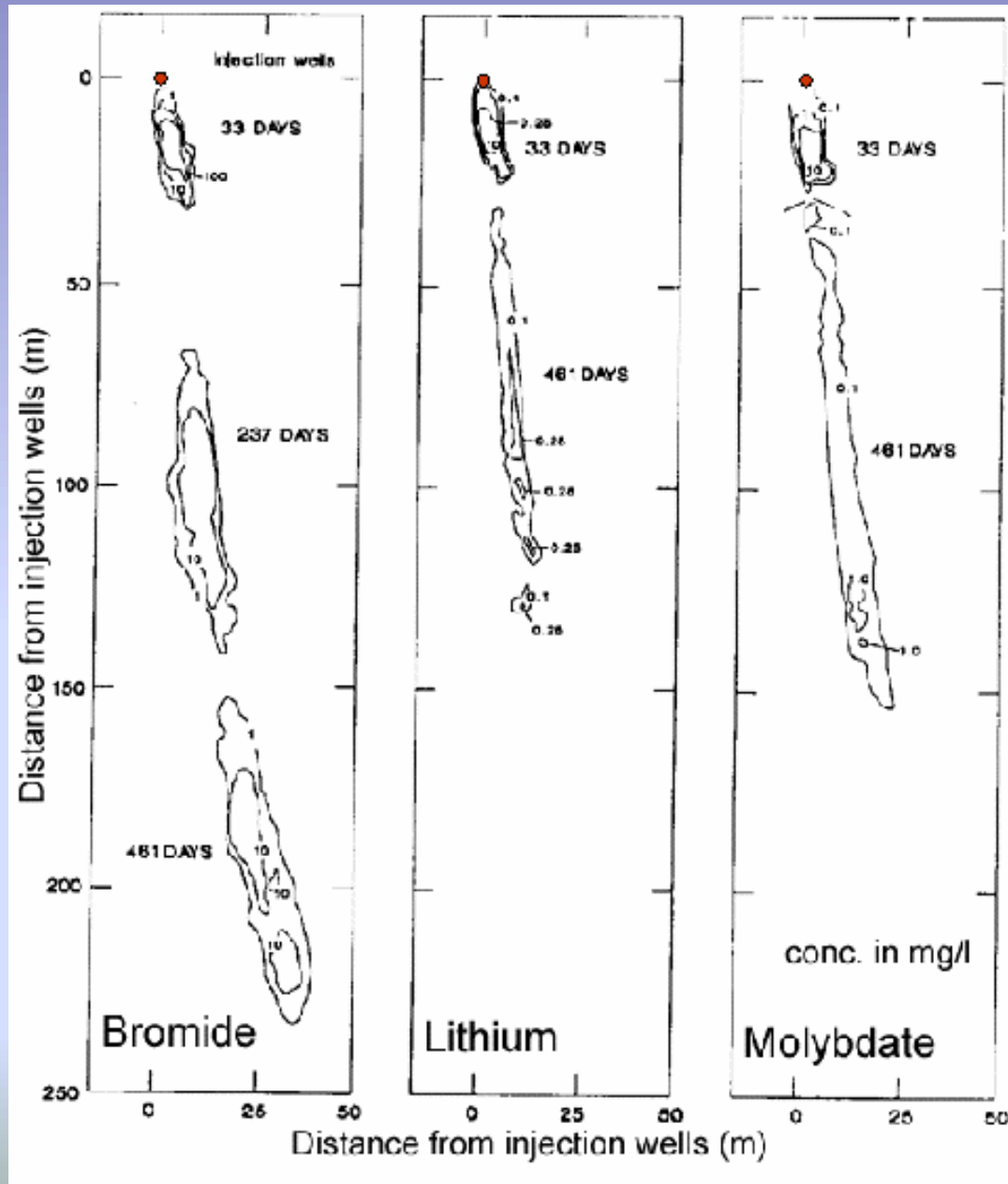
Conservative Groundwater tracers

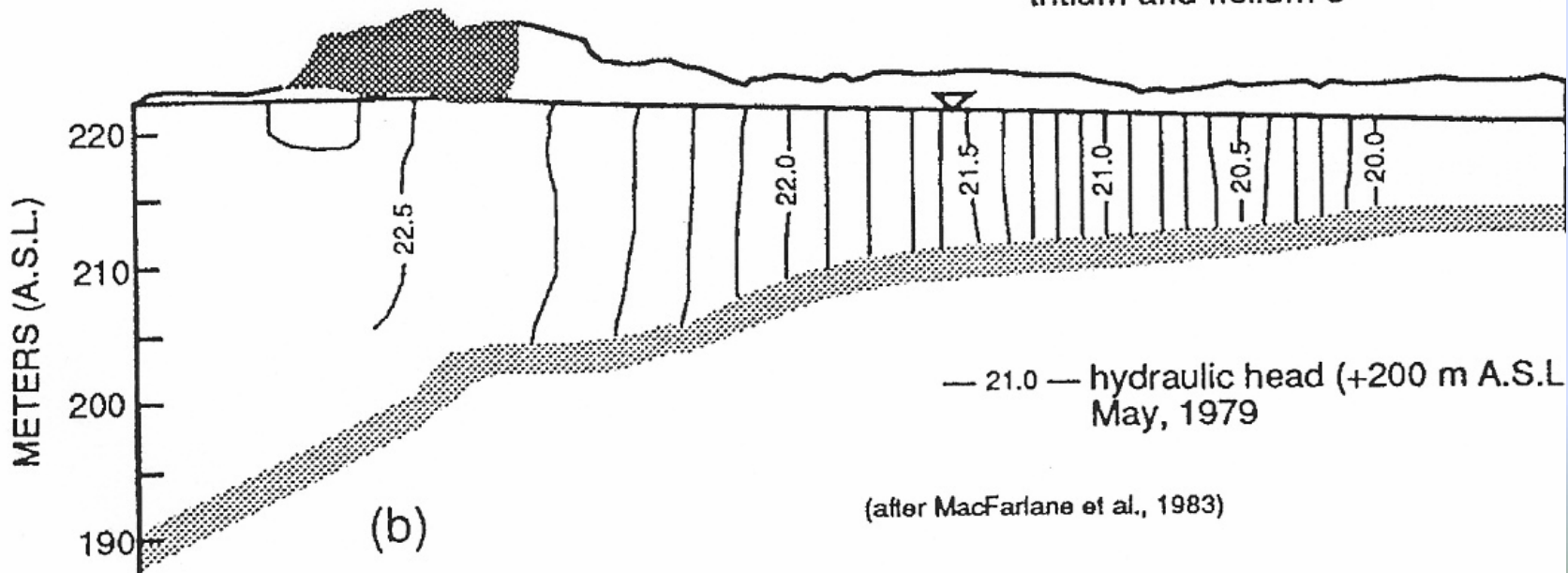
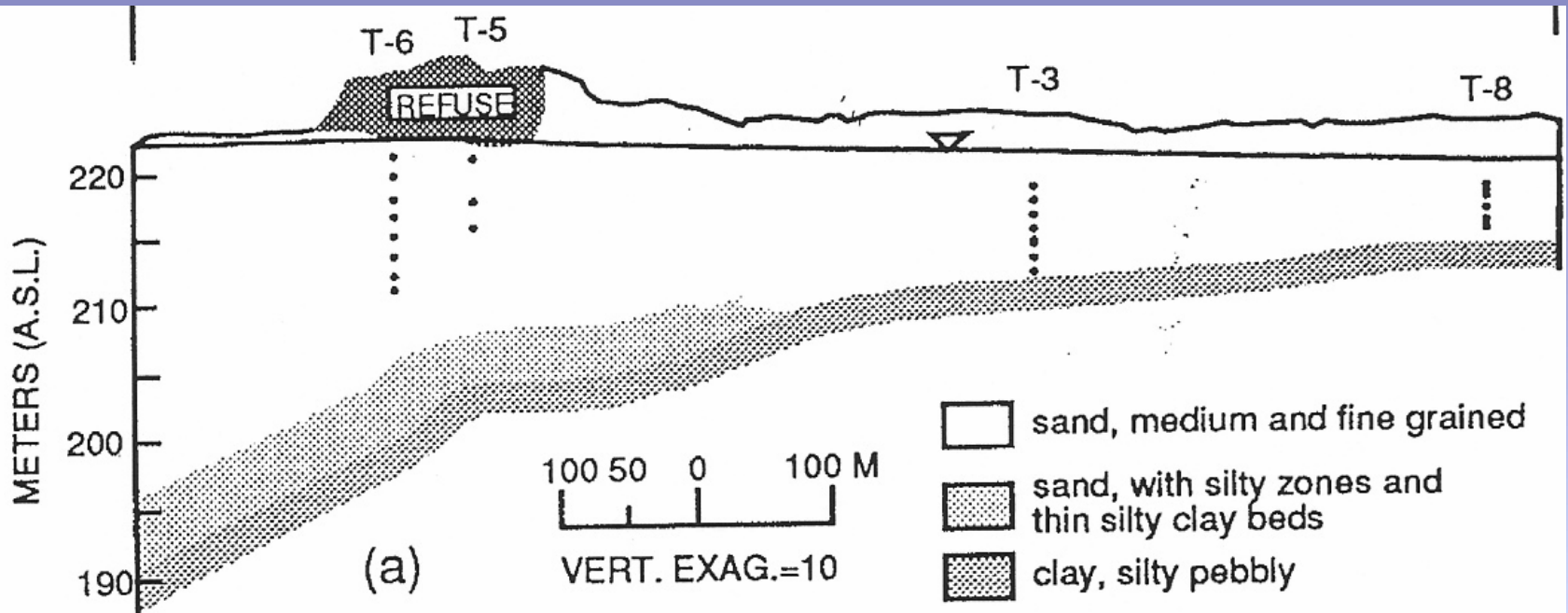
- tracer moves at the same rate as the water
 - not impeded by methods such as chemical reactions or degradation. Influenced only by physical processes such as mixing, diffusion, etc.
- * See page from book: John Cherry, Camp Borden, Ontario.



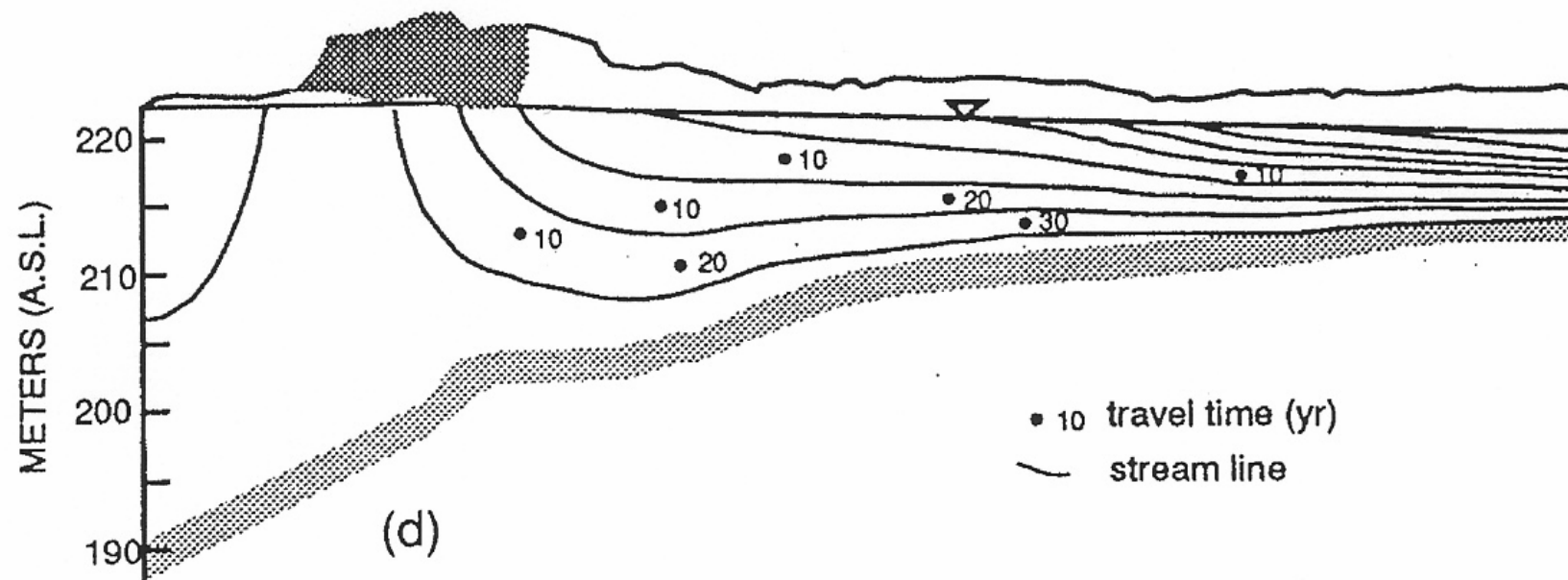
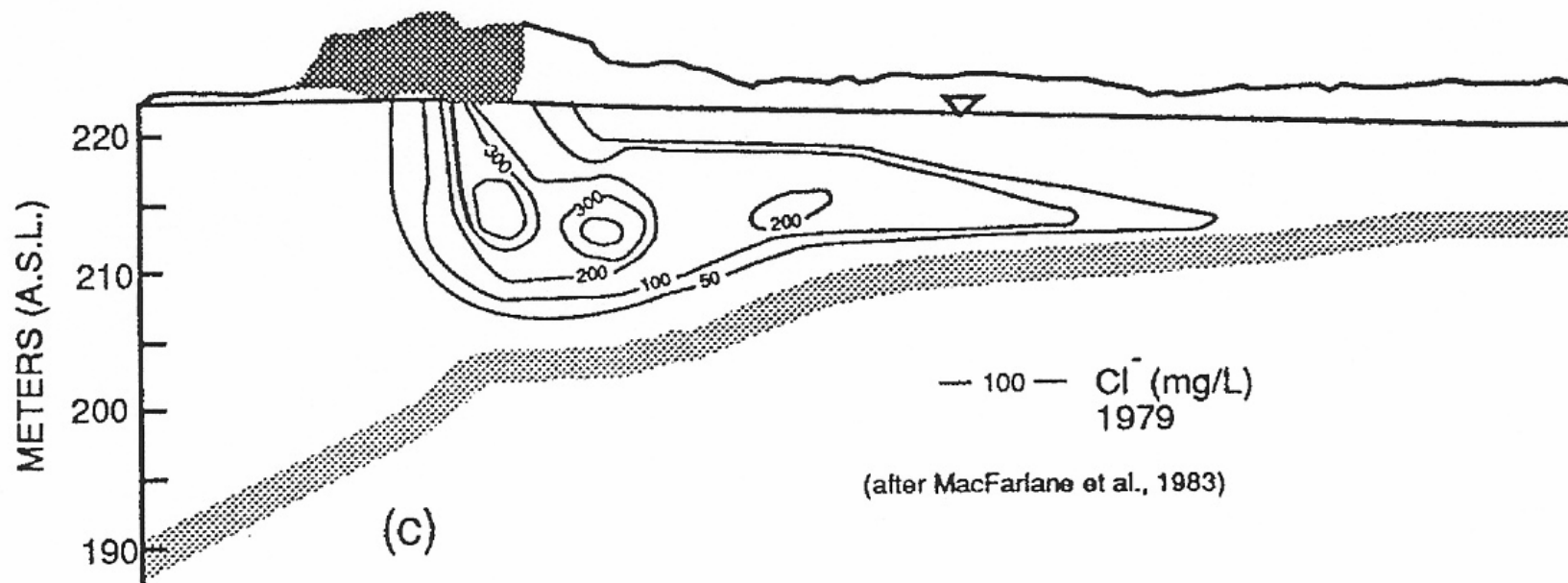
Plume resulting from the continuous injection of a tracer into a two-dimensional flow field.

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



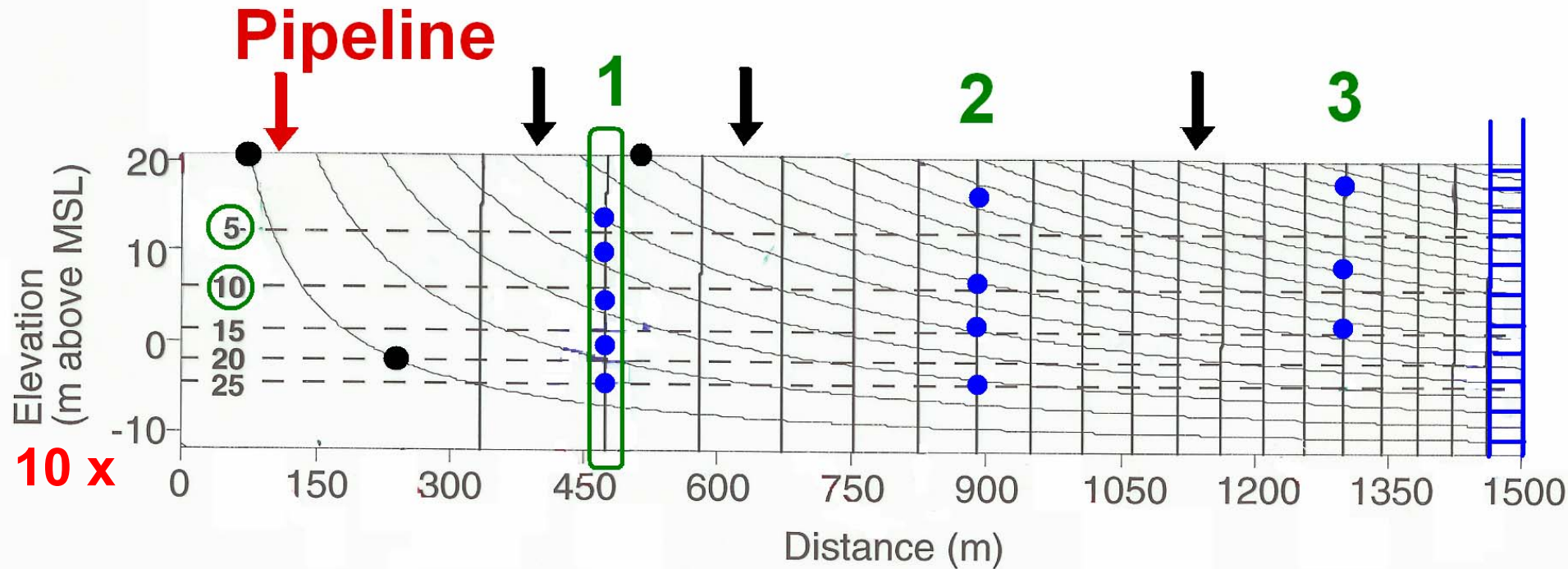


(after MacFarlane et al., 1983)



Model Simulation

Uniform Recharge – 60 cm/yr



High degree of vertical stratification

Vertical age gradient tells you how much recharge is coming through into the system → 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?

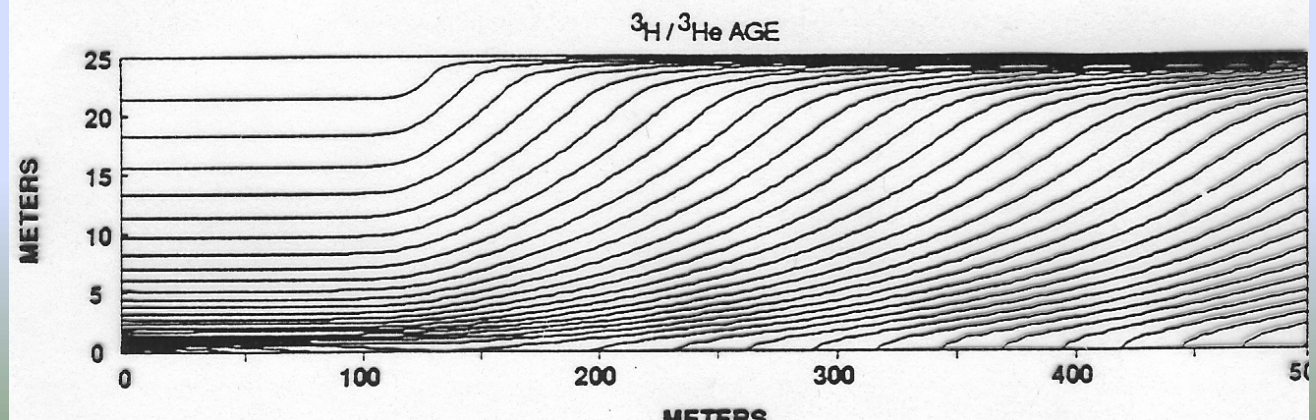
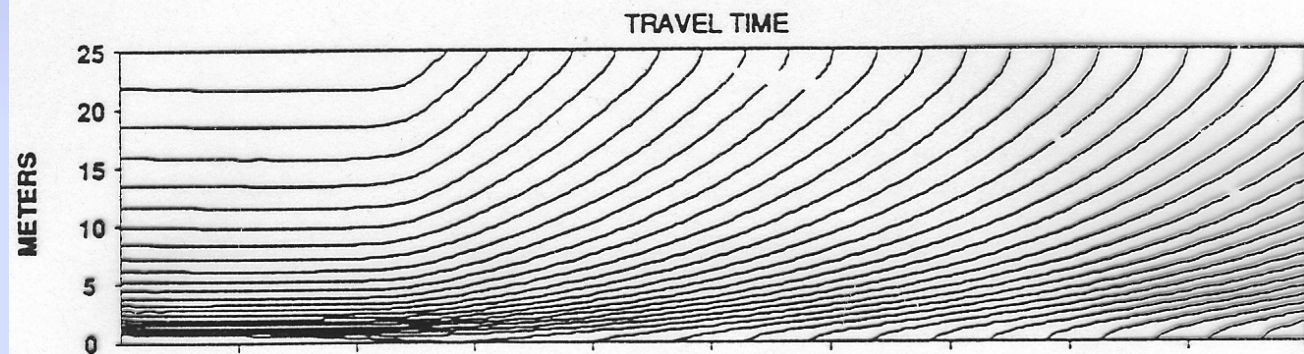
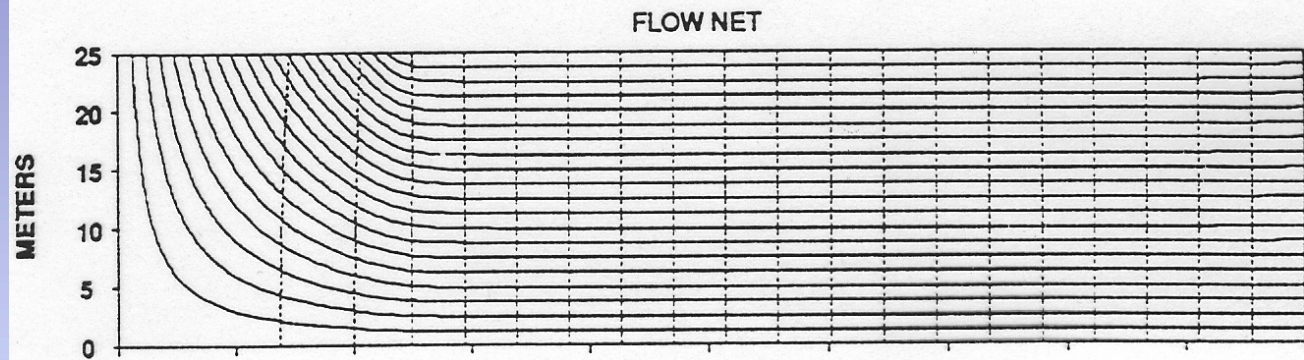
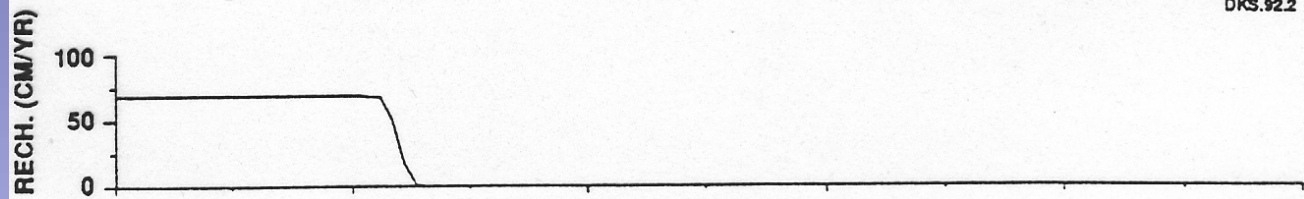
- Might want to know how quickly a contaminant will migrate off sight
- Well is screened over entire interval to get the most information in the radial sense.

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

- Don't know exactly where the water is coming from.

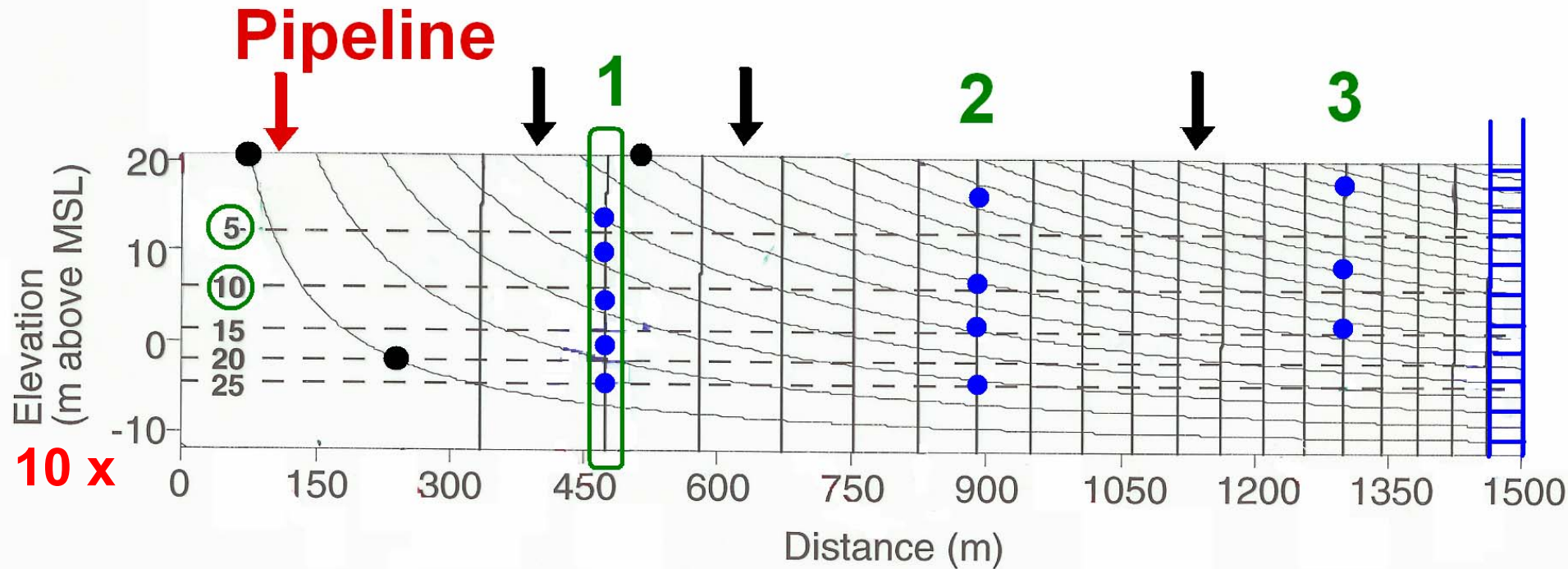
→ should only sample about 10 centimeters instead of 1-2 meters.

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"



Model Simulation

Uniform Recharge – 60 cm/yr



-5- Travel Time (year)
Stream Function
Potential

Potential Interval 0.0028 m
Stream Function Interval 0.12 m² /d

High degree of vertical stratification

^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 than ^4He , so any excess ^3He is from tritium ($^3\text{He}^*$) [Solubilities: ^3He - about 7 ppt ; ^4He - about 5.2 ppm]

– i.e. $^3\text{He}_{\text{total}} = ^3\text{He}_{\text{sol}} + ^3\text{He}^*_{\text{trit}}$

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

We want to measure the excess over solubility.

Assume ^4He in atmosphere, assume $^3\text{He}/^4\text{He}$ in air is constant = 1.4×10^{-6} .

^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.

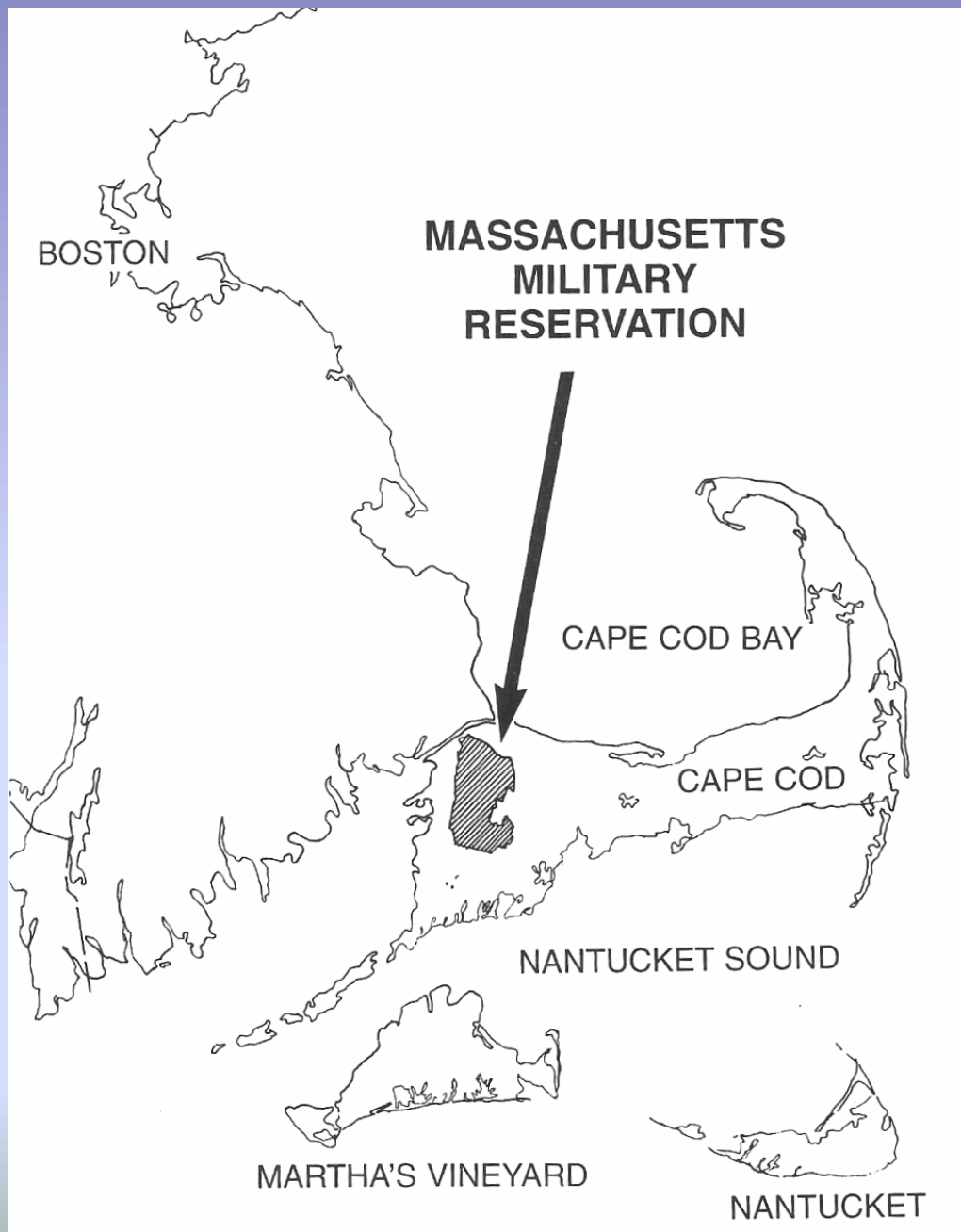
- Tritium (^3H) input from thermonuclear weapons tests (peak in 1963); no longer a sustained input.

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

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

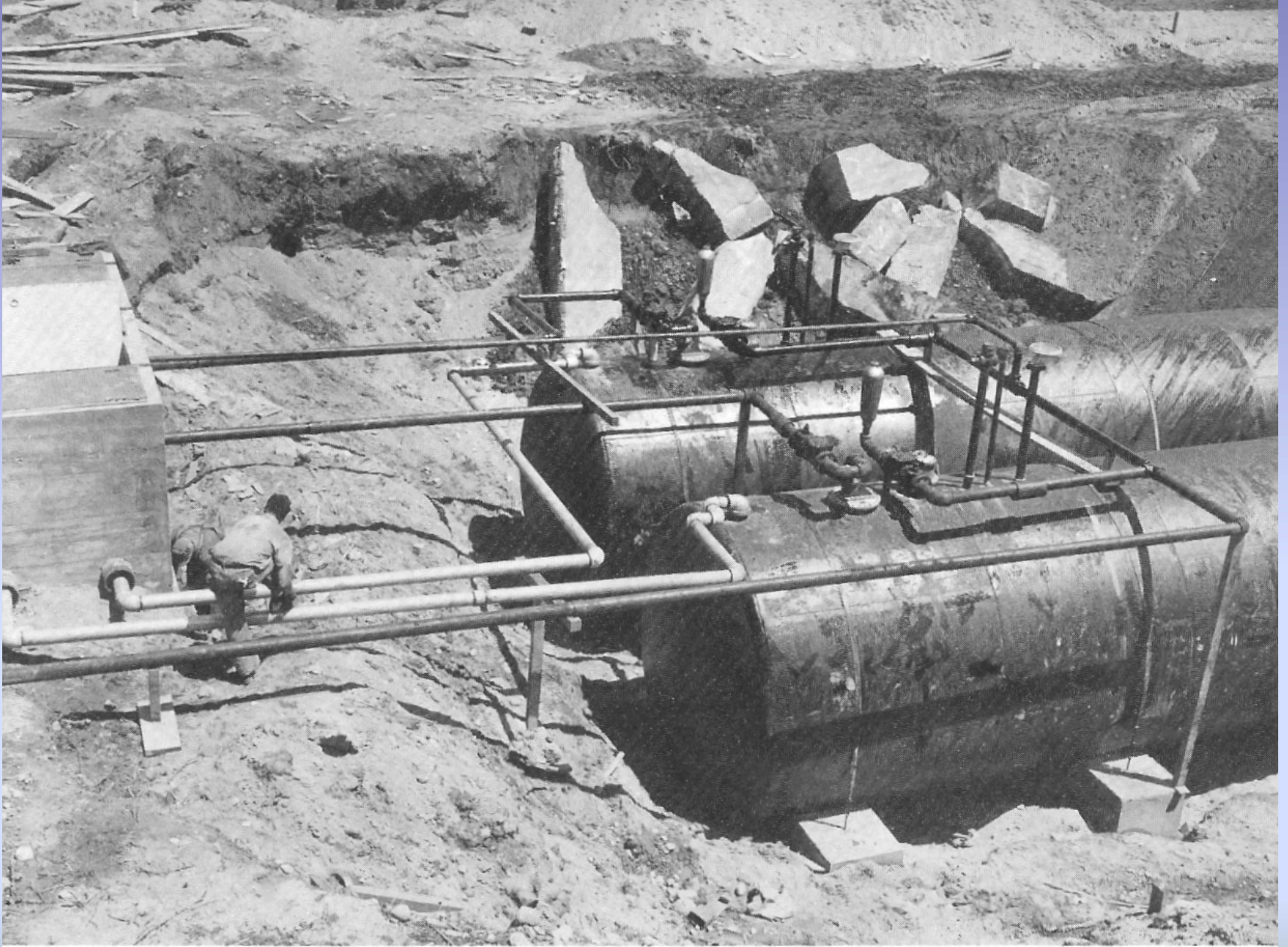


Munitions uncovered in a burial site at the J-1 Range during IAGWSP investigations.



Site Location Map of Massachusetts Military Reservation

*From The Enemy Within:
The Struggle to Clean Up
Cape Cod's Military
Superfund Site*



Underground fuel storage: out of sight, out of mind. June, 1941.

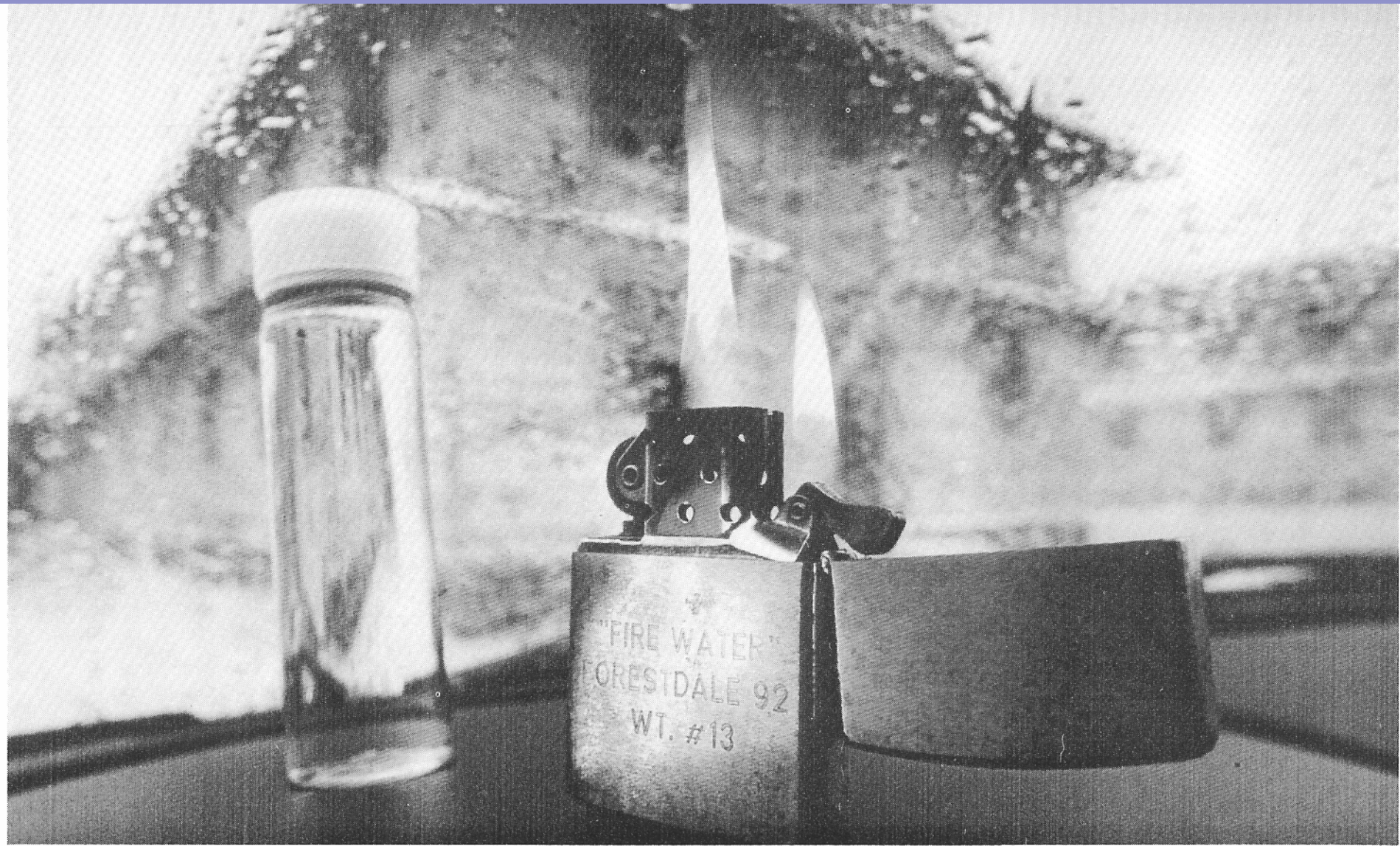


**A toxic stew of
waste chemicals,
dumped on the
ground...**

**Ignited for live
training, 1964.**

Rolbein, 1995



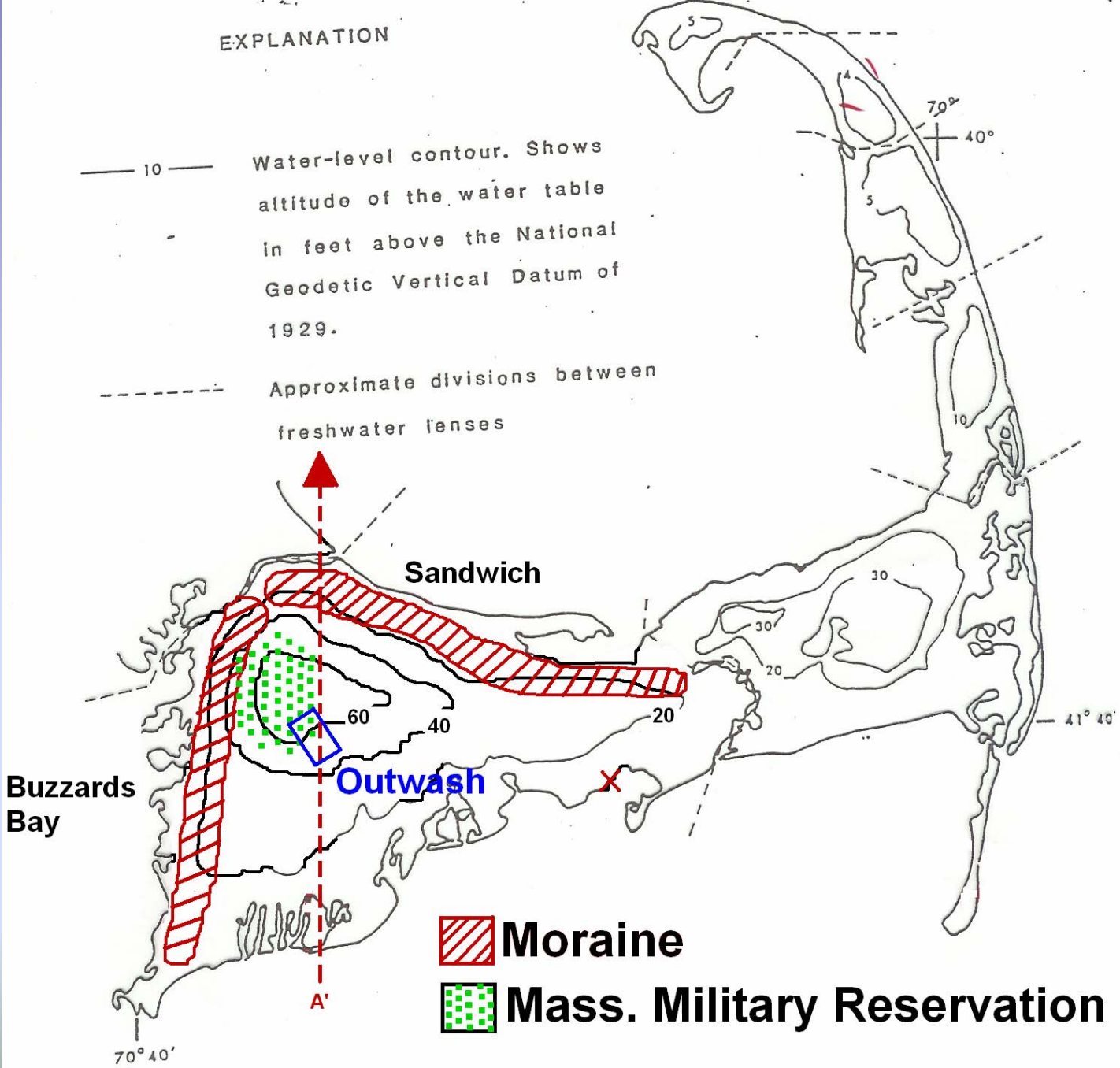


Firewater: A groundwater sample, taken from the area of the Sandwich pipeline, contained enough jet fuel to burn.

EXPLANATION

— 10 — Water-level contour. Shows altitude of the water table in feet above the National Geodetic Vertical Datum of 1929.

- - - - - Approximate divisions between freshwater lenses

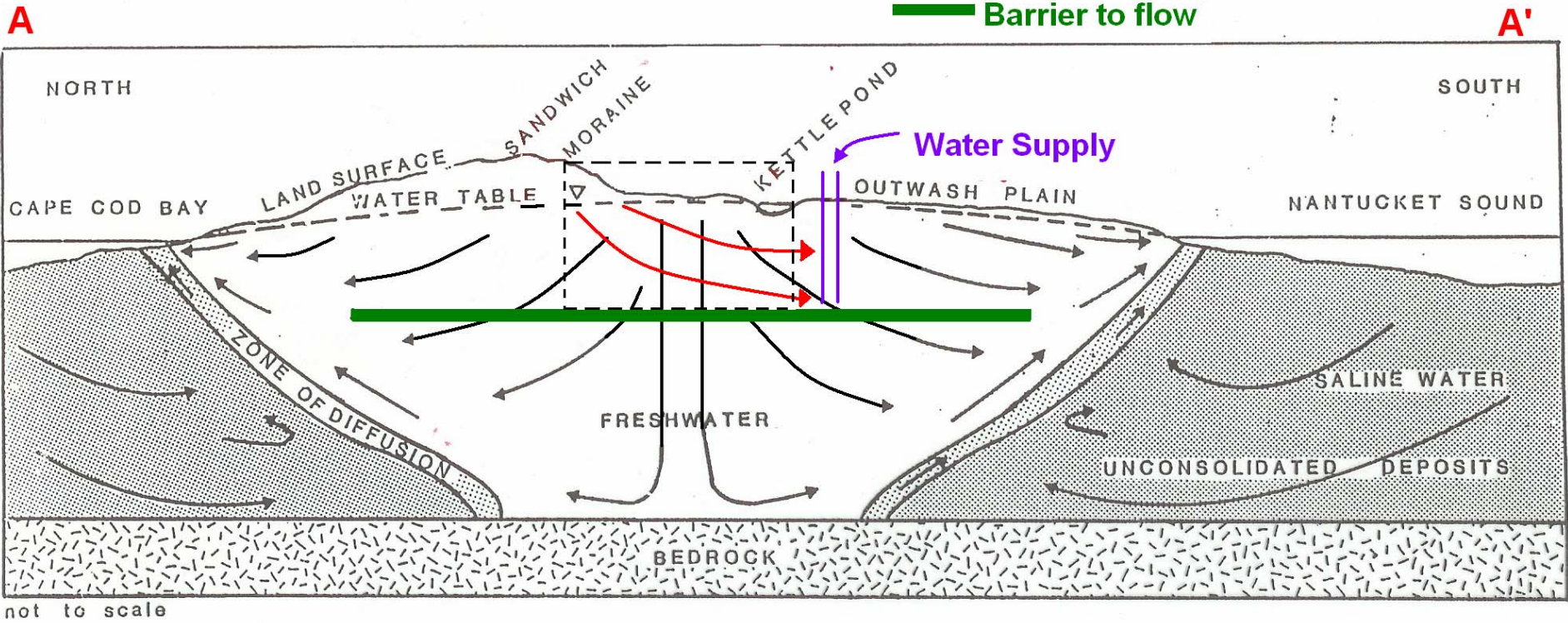


 **Moraine**

 **Mass. Military Reservation**

Idealized north-south section of Cape Cod aquifer showing freshwater lens truncated by bedrock

Lacustrian clay
Barrier to flow



^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 than ^4He , so any excess ^3He is from tritium ($^3\text{He}^*$) [Solubilities: ^3He - about 7 ppt ; ^4He - about 5.2 ppm]

$$\text{-- i.e. } ^3\text{He}_{\text{total}} = ^3\text{He}_{\text{sol}} + ^3\text{He}^*_{\text{trit}}$$

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

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

The $^3\text{He}/^3\text{H}$ 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.

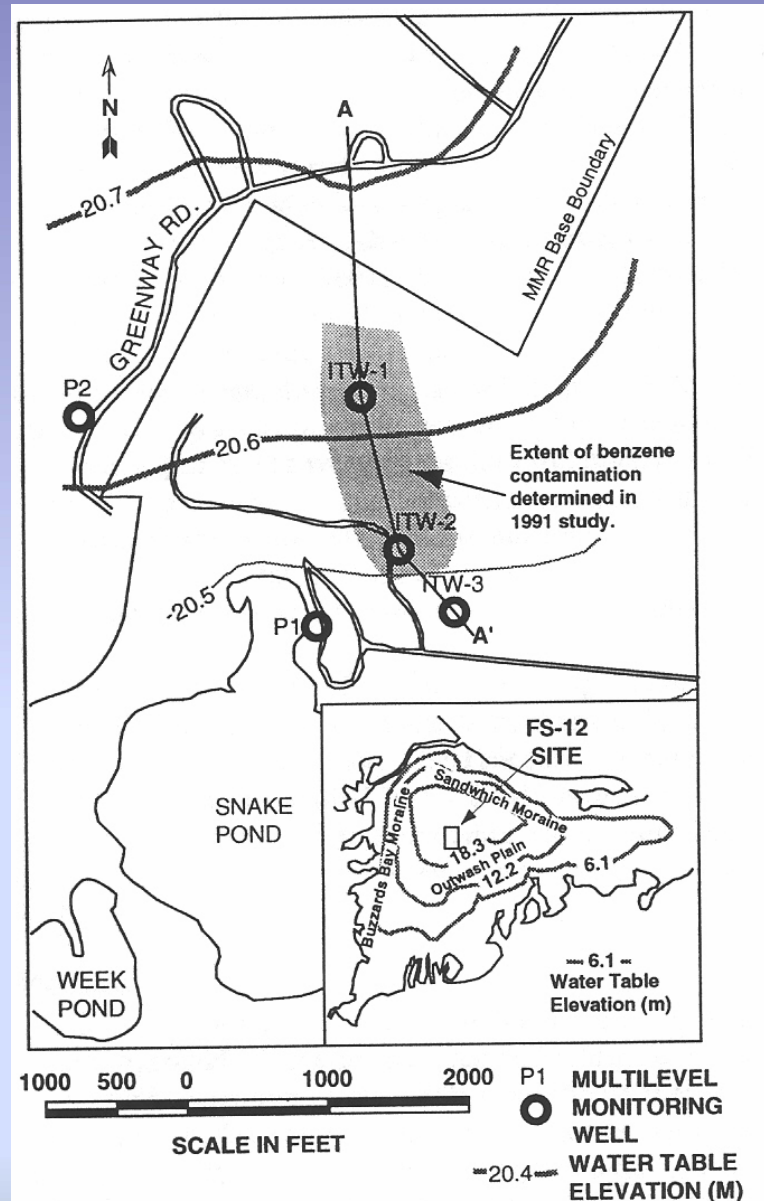


Fig. 1. FS-12 field site with water level contours, the location of multilevel monitoring wells, and the extent of a benzene plume determined in the 1991 study.

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.

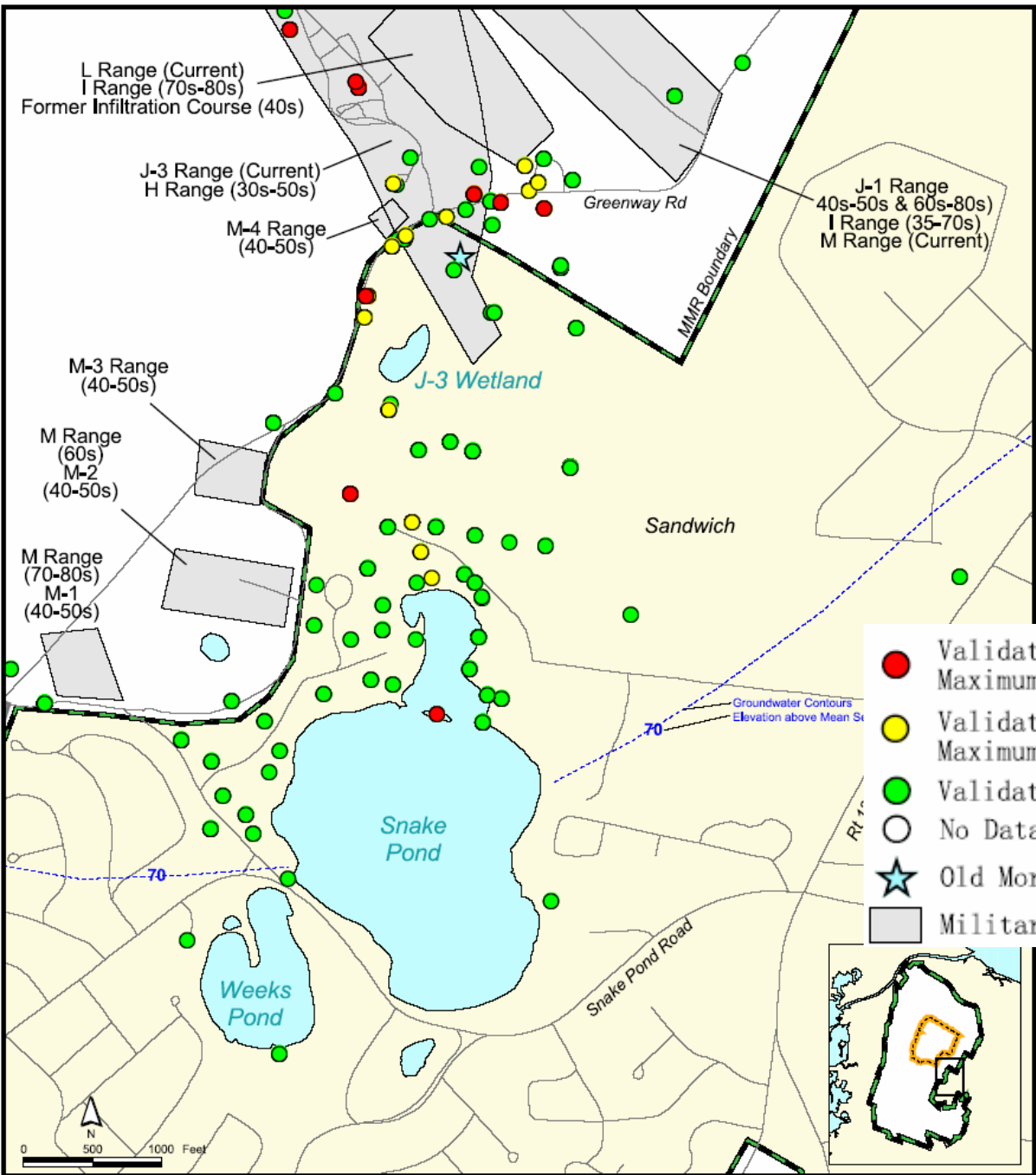
Snake Pond

Spill components at this base

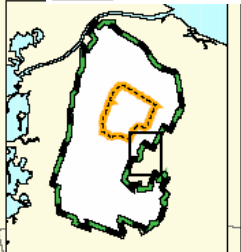
1. Aviation fuel.
2. JP4 (jet fuel; more like kerosene).



IAGWST Explosives and Perchlorate in Groundwater Compared to Maximum Contaminant Level/Advisories



- Validated Detection Greater Than or Equal to Maximum Contaminant Level/Health Advisories
- Validated Detection Less Than Maximum Contaminant Level/Health Advisories
- Validated Non-detect
- No Data Available
- ★ Old Mortar Position
- Military Ranges



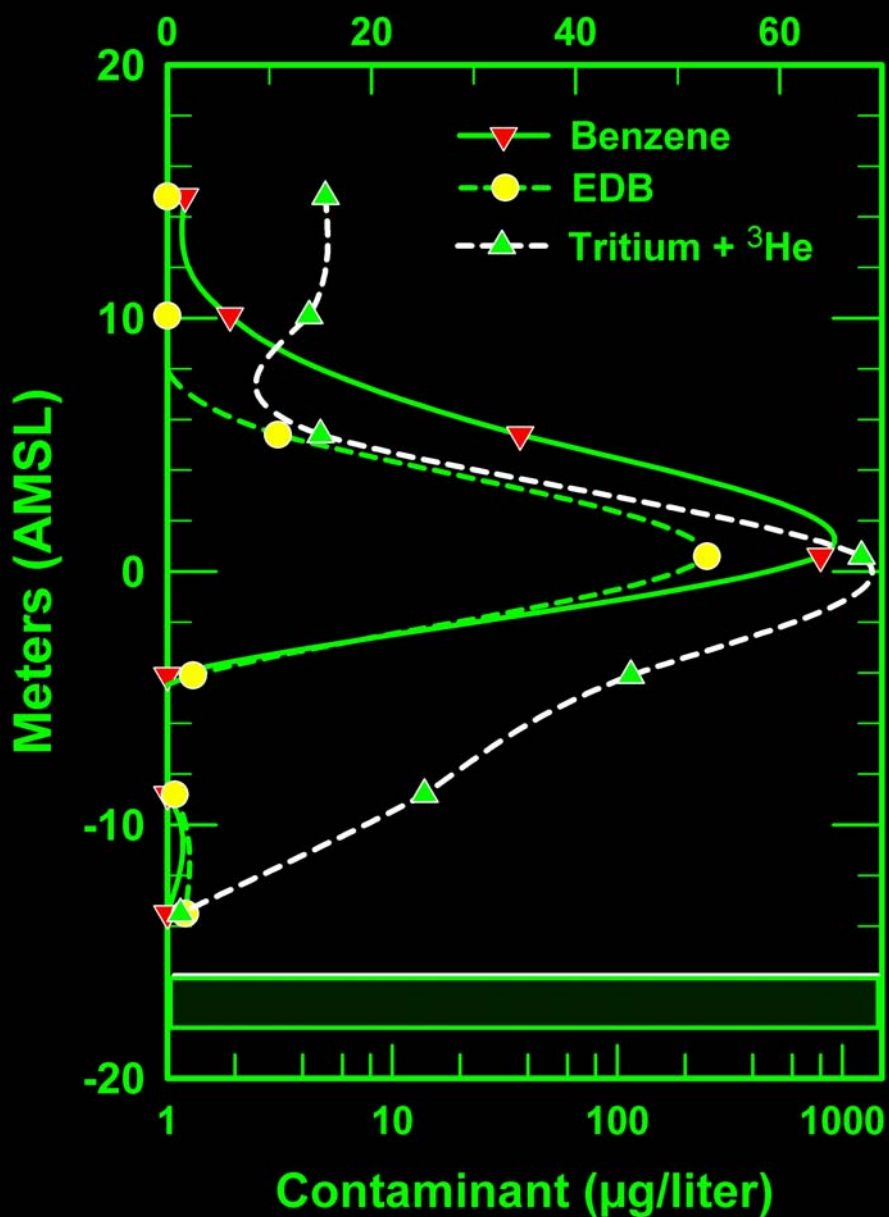
Validated Data as of 02/14/02

Looked at xylene, benzene, EDB (= ethylene dibromide, volatile, in leaded 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.

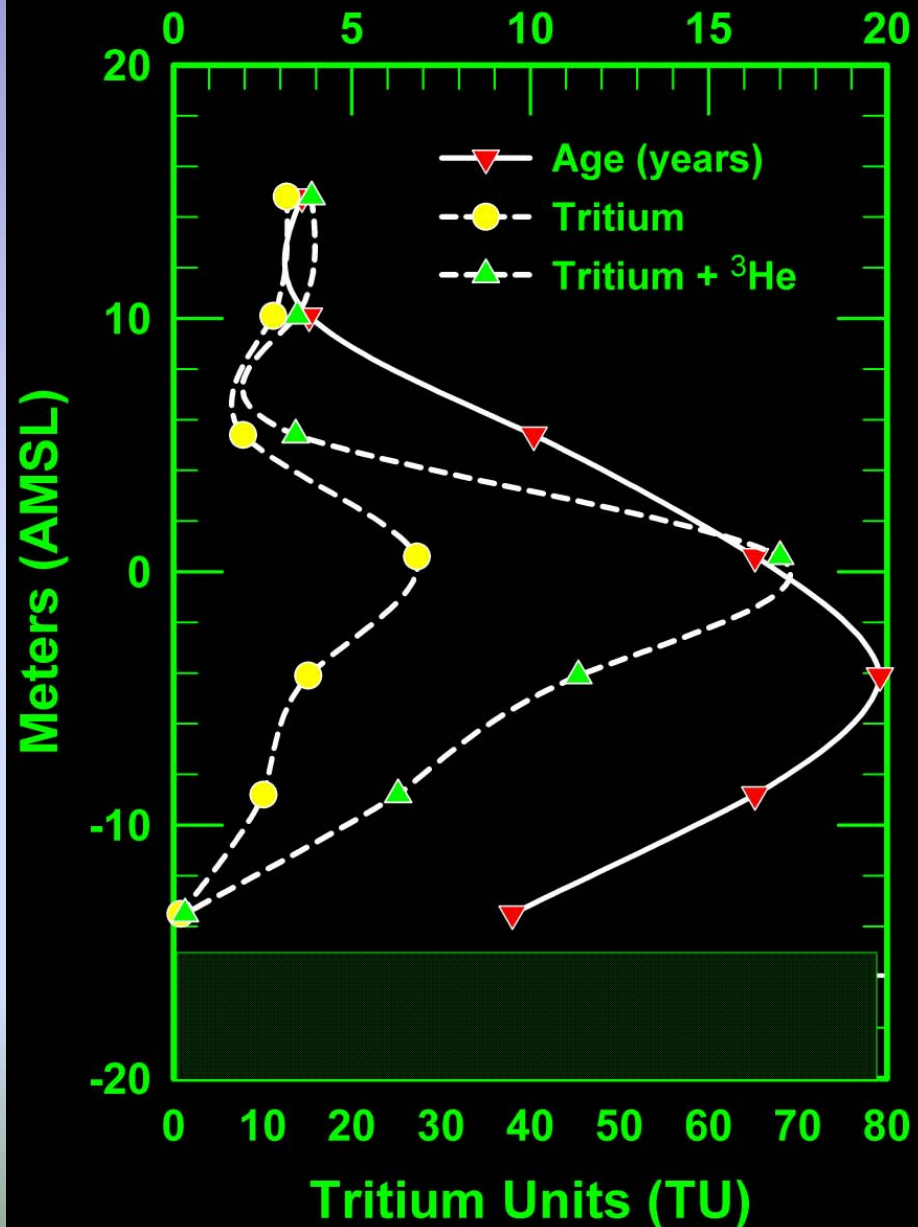
Cape Cod ITW-1

Tritium Units



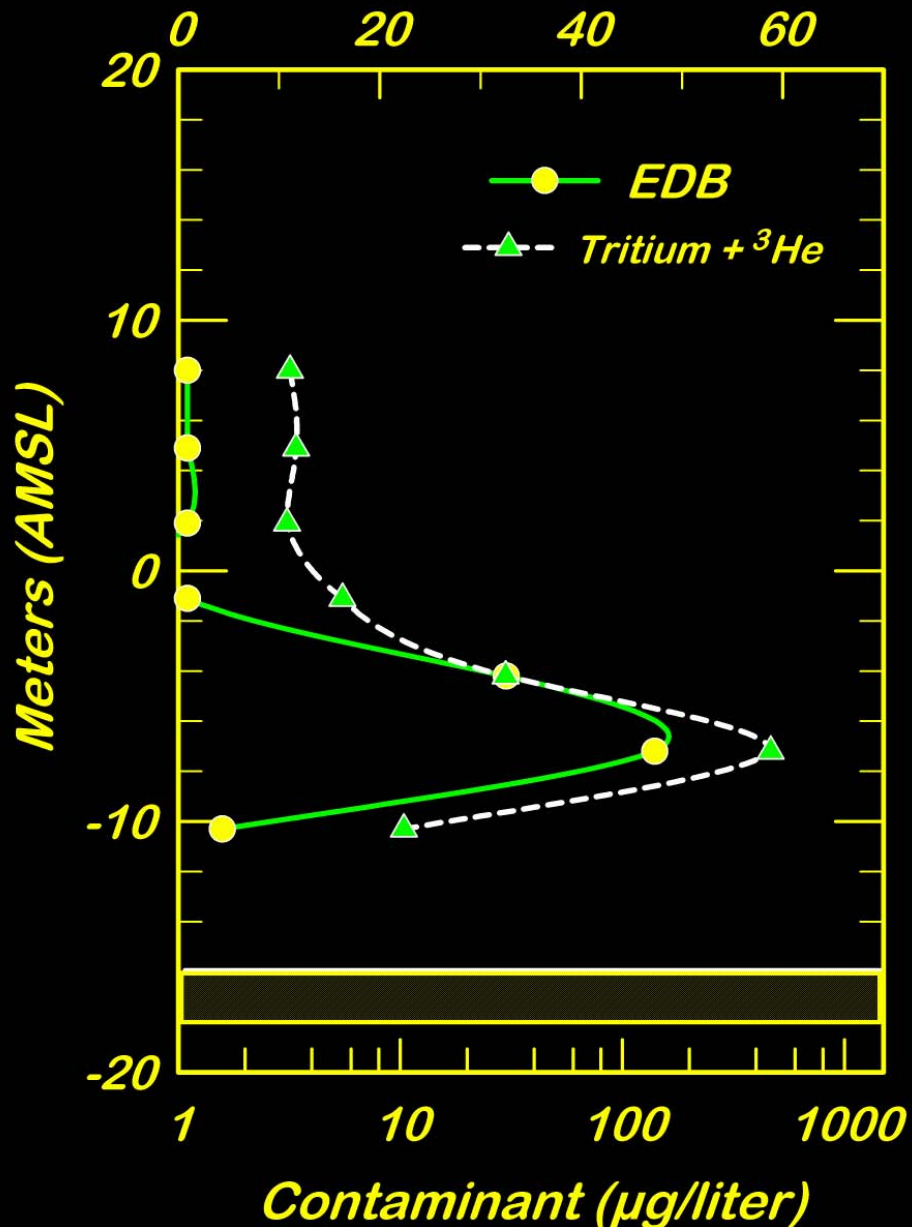
Cape Cod ITW-1

Age (years)



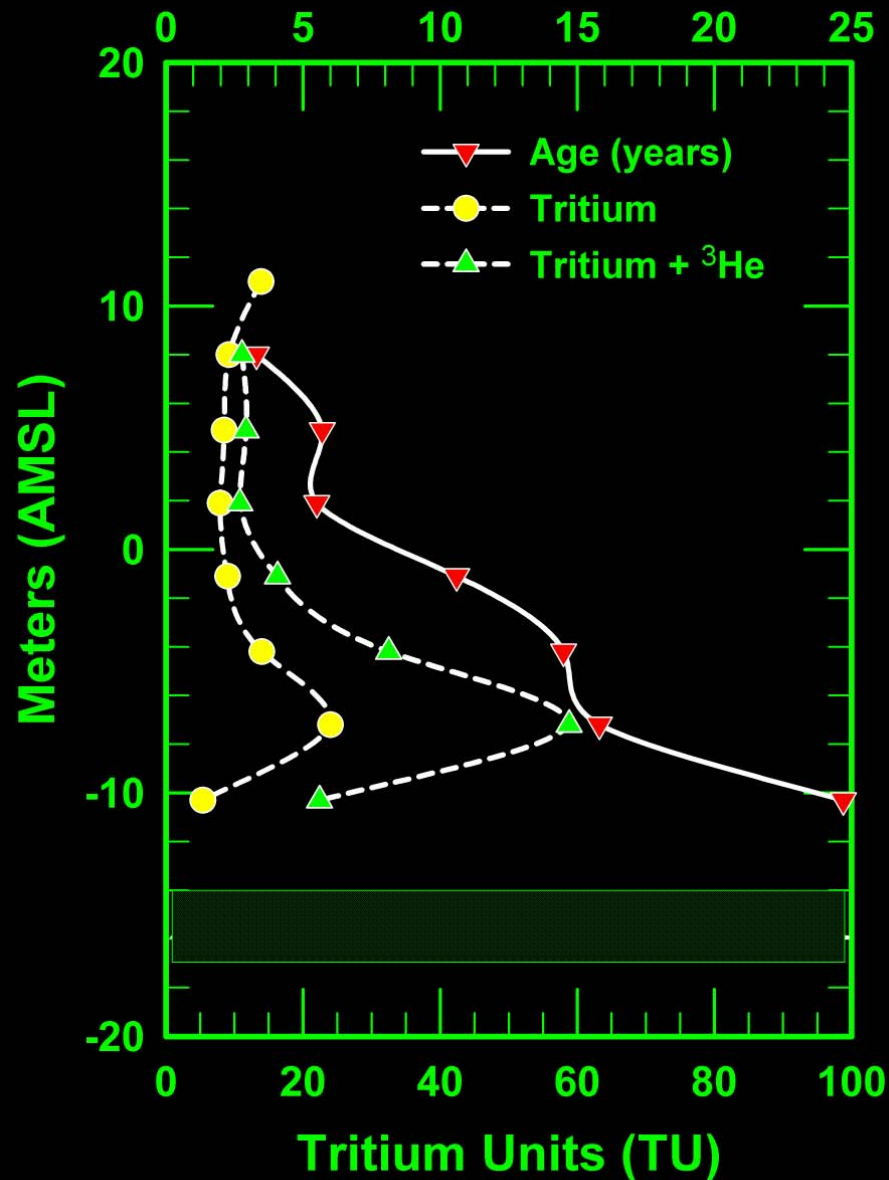
Cape Cod ITW-3

Tritium Units

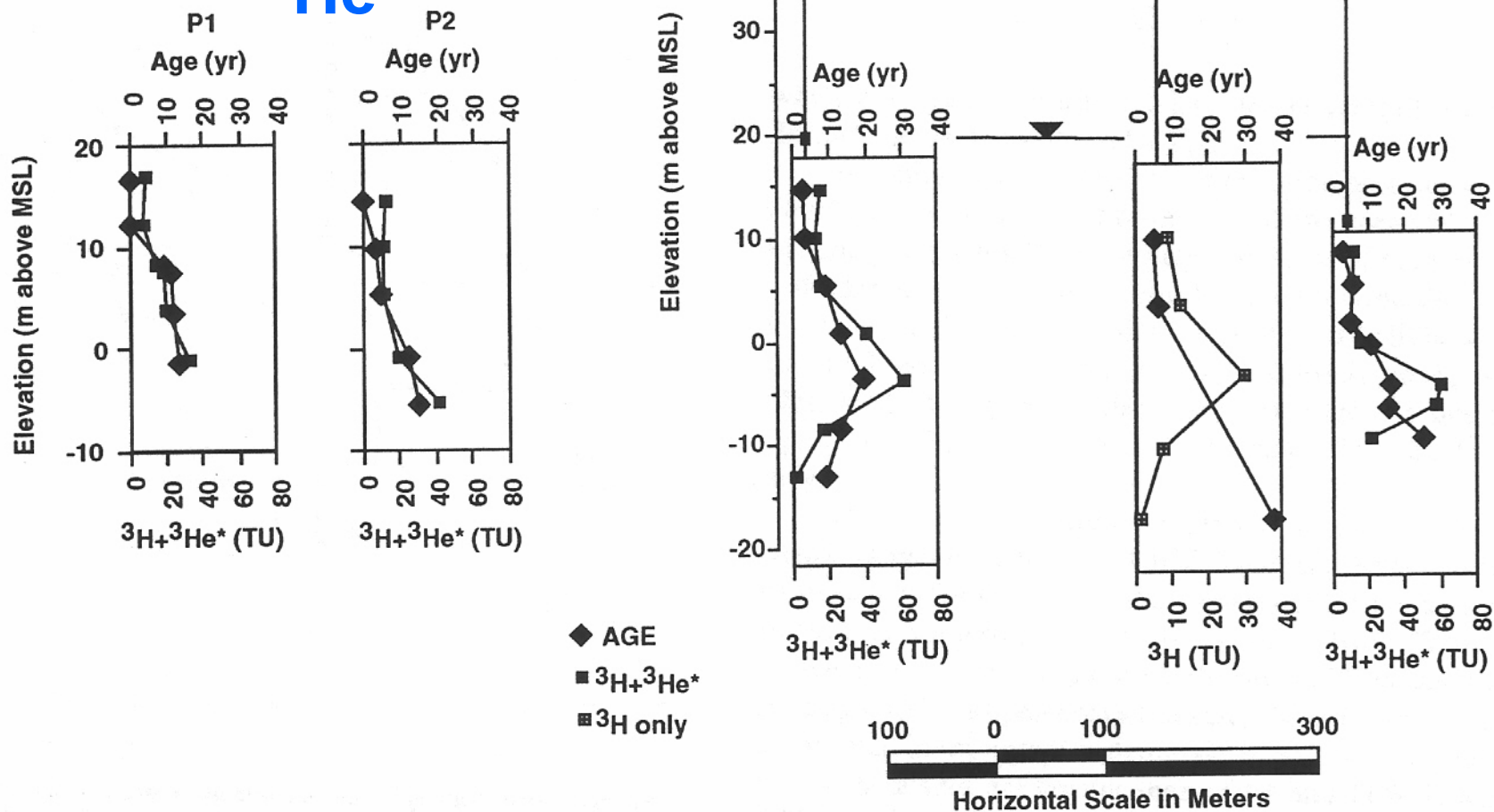


Cape Cod ITW-3

Age (years)



Profiles of $^3\text{H}/^3\text{He}$ and $^3\text{H} + ^3\text{He}$



Solomon et al., 1995

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

Profiles of organic contaminants and ground-water age

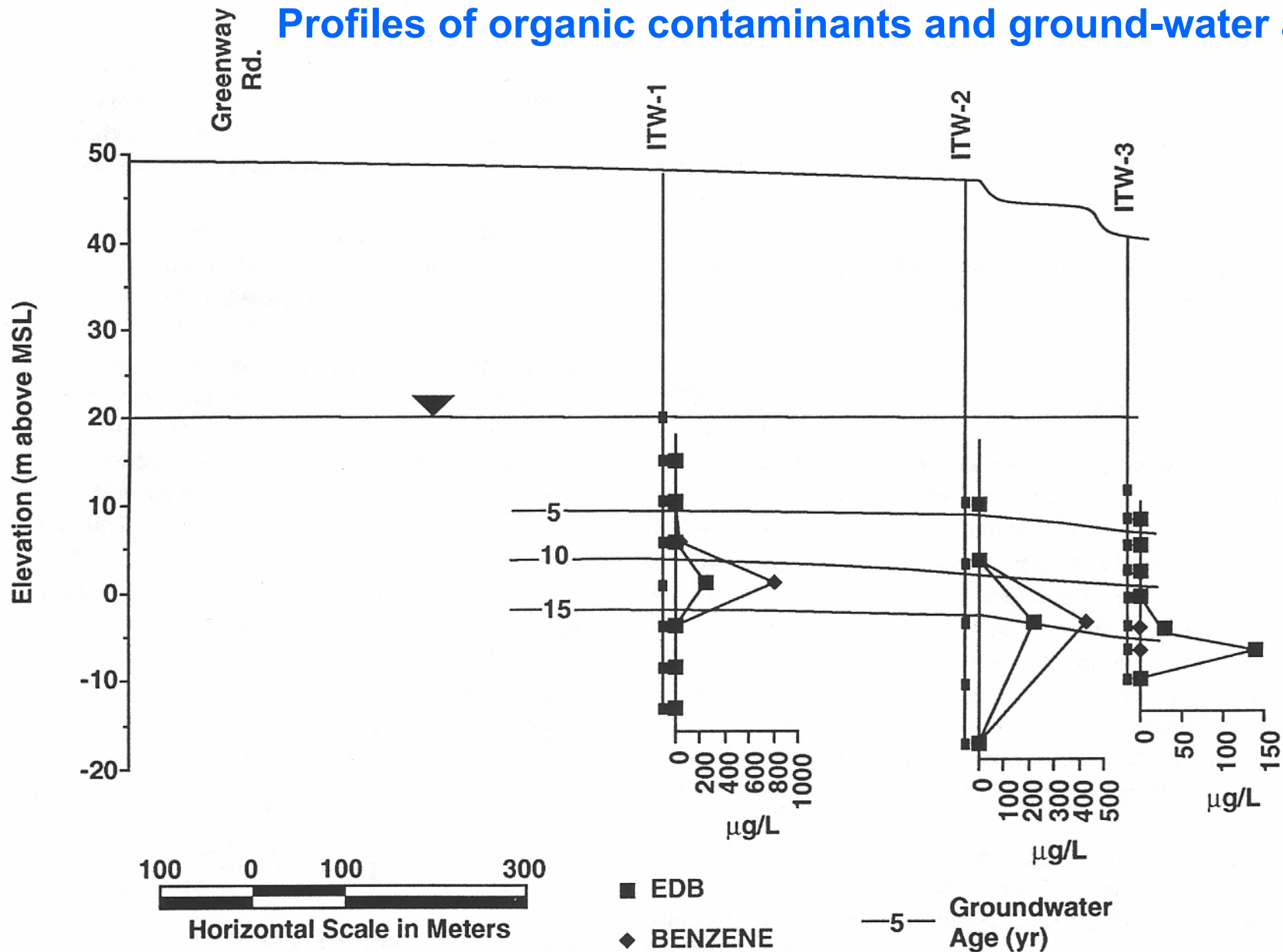


Fig. 3. Profiles of organic contaminants and ground-water age. The cross section from ITW-1 to ITW-3 is oriented along a ground-water flow line. Solomon et al., 1995

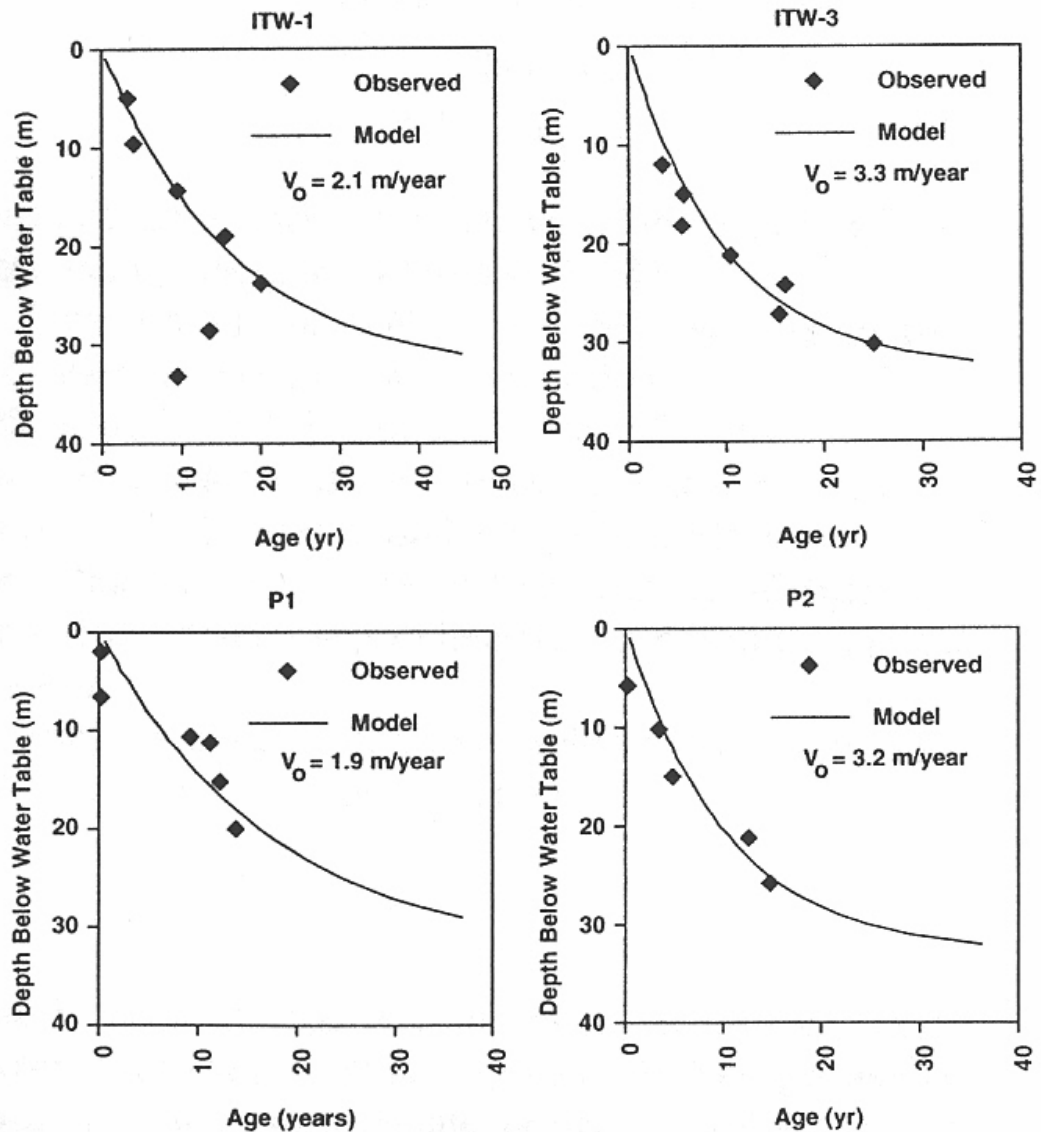


Fig. 4. Profiles of observed and simulated ground-water age. The simulated profiles were obtained by optimizing the fit between the observed and simulated age by adjusting the vertical velocity at the water table.

Profiles of Observed and Simulated Ground-Water Age

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

Solomon et al., 1995

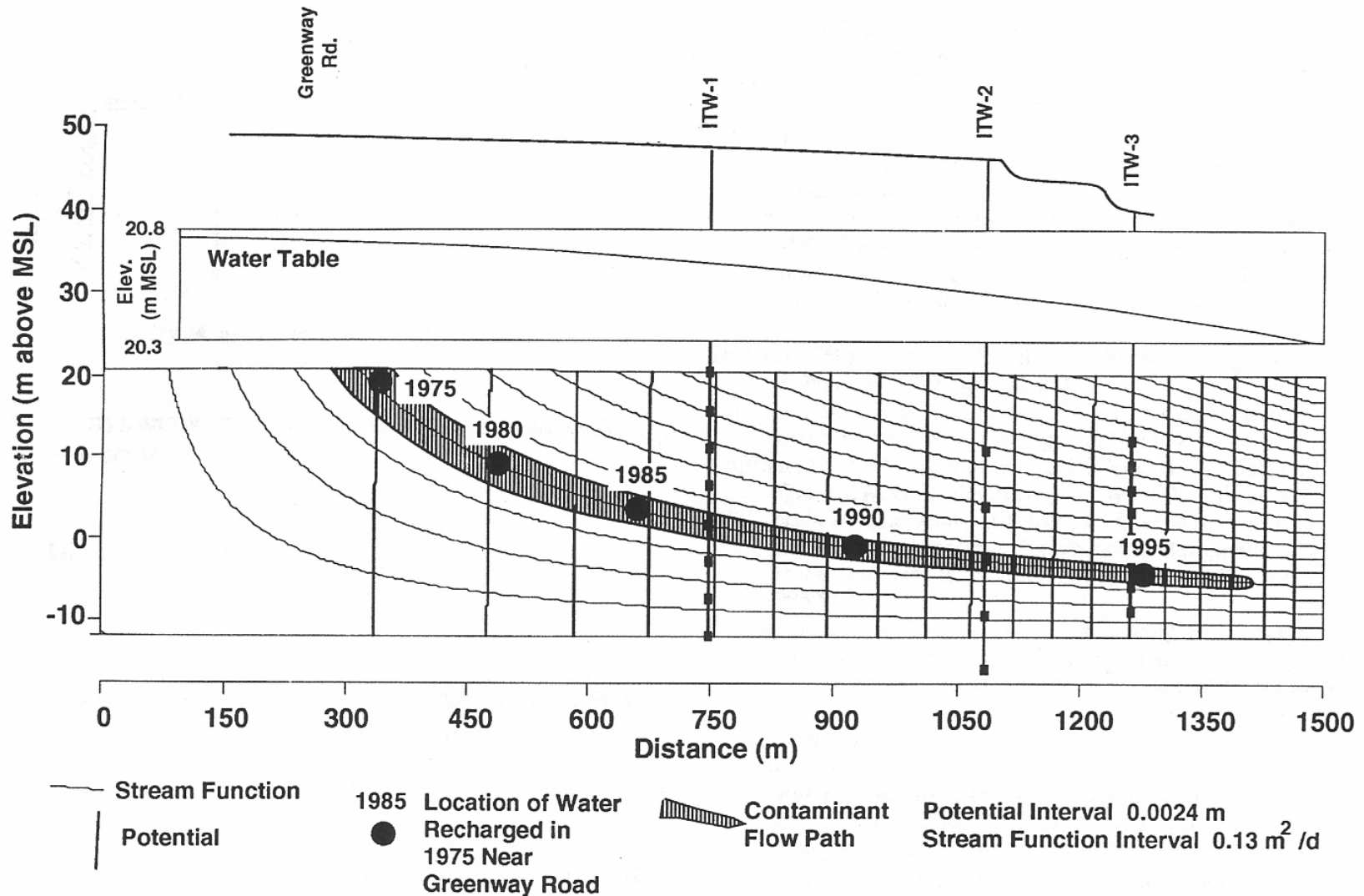
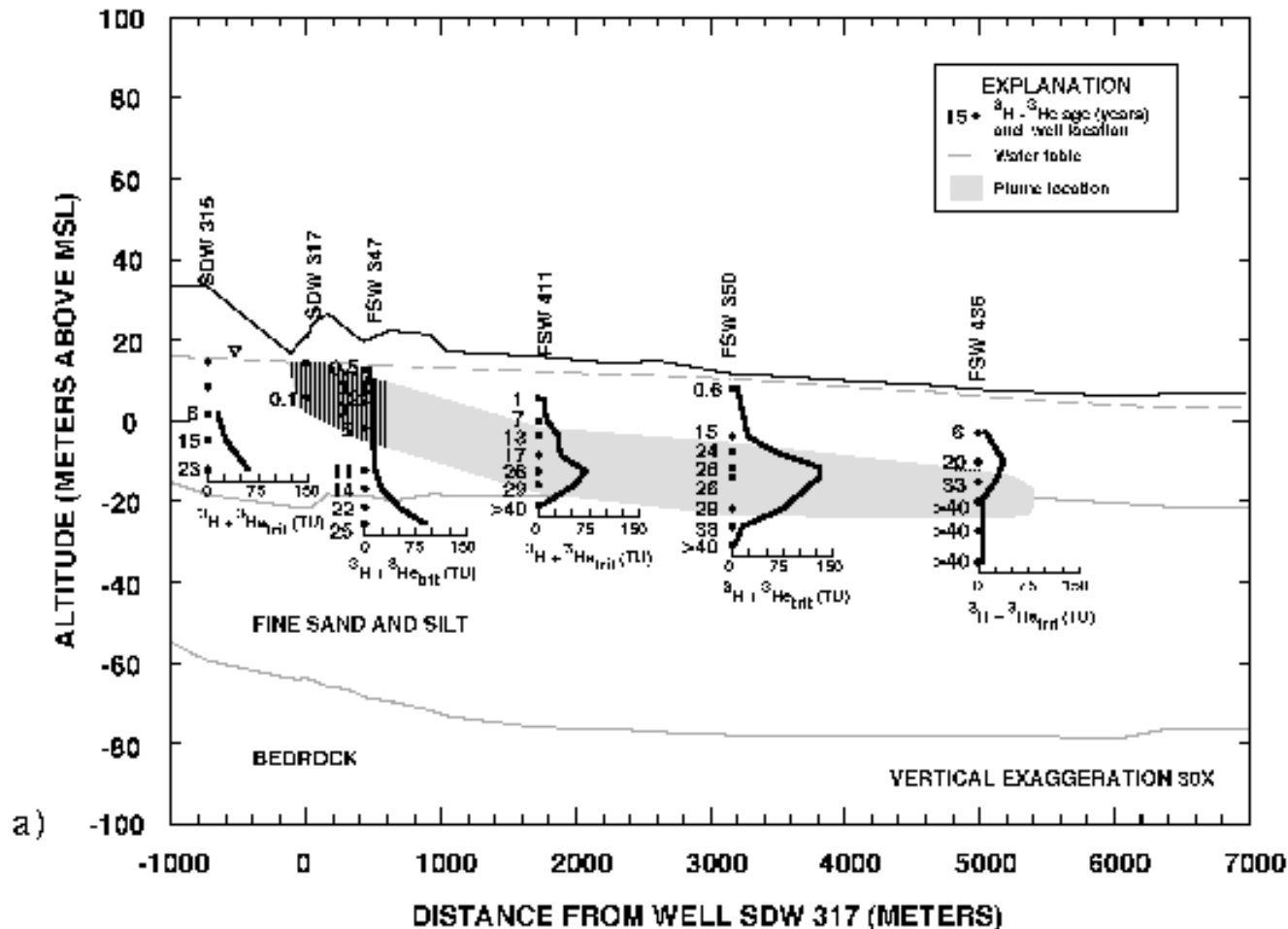


Fig. 5. Simulated stream functions, hydraulic potentials, and the configuration of the water table (note expanded scale). Also shown is the simulated location of water recharged in 1975 beneath Greenway Road at various points in time along the flow system. The shaded region highlights a flow line and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

Cape Cod - $^3\text{H}/^3\text{He}$ dating



b)

Travel time? "Conundrum of Solomon"

– In reality are lines that are almost totally horizontal (paralleled by tritium-helium 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 down, a function of z . Horizontal velocity doubles about every 10 years as one moves down-gradient.

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

Hydraulic conductivity K

Vogel Model:

$$V_0 = B/t * \ln(B/(B-Z))$$

K=hydraulic conductivity

$$V_x = (V_z * x) / B$$

B=aquifer thickness

x=distance from
flow divide

t=travel time

Z=depth below
water table

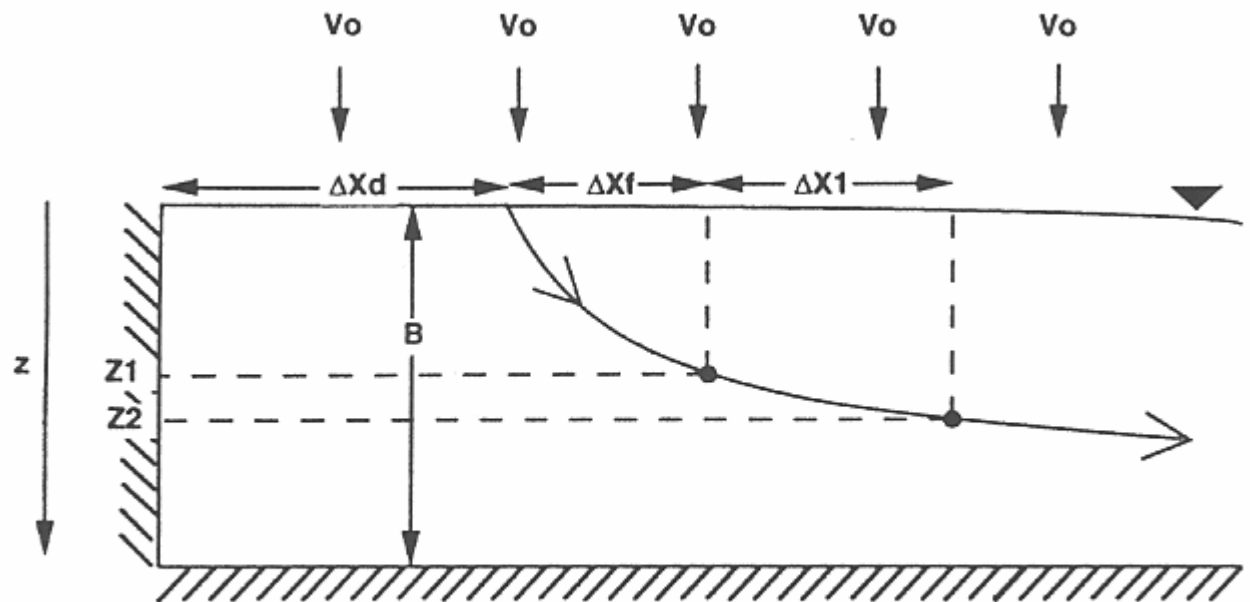


Fig. 6. Geometry of an unconfined aquifer used in the Vogel model.

Hydraulic conductivity K

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

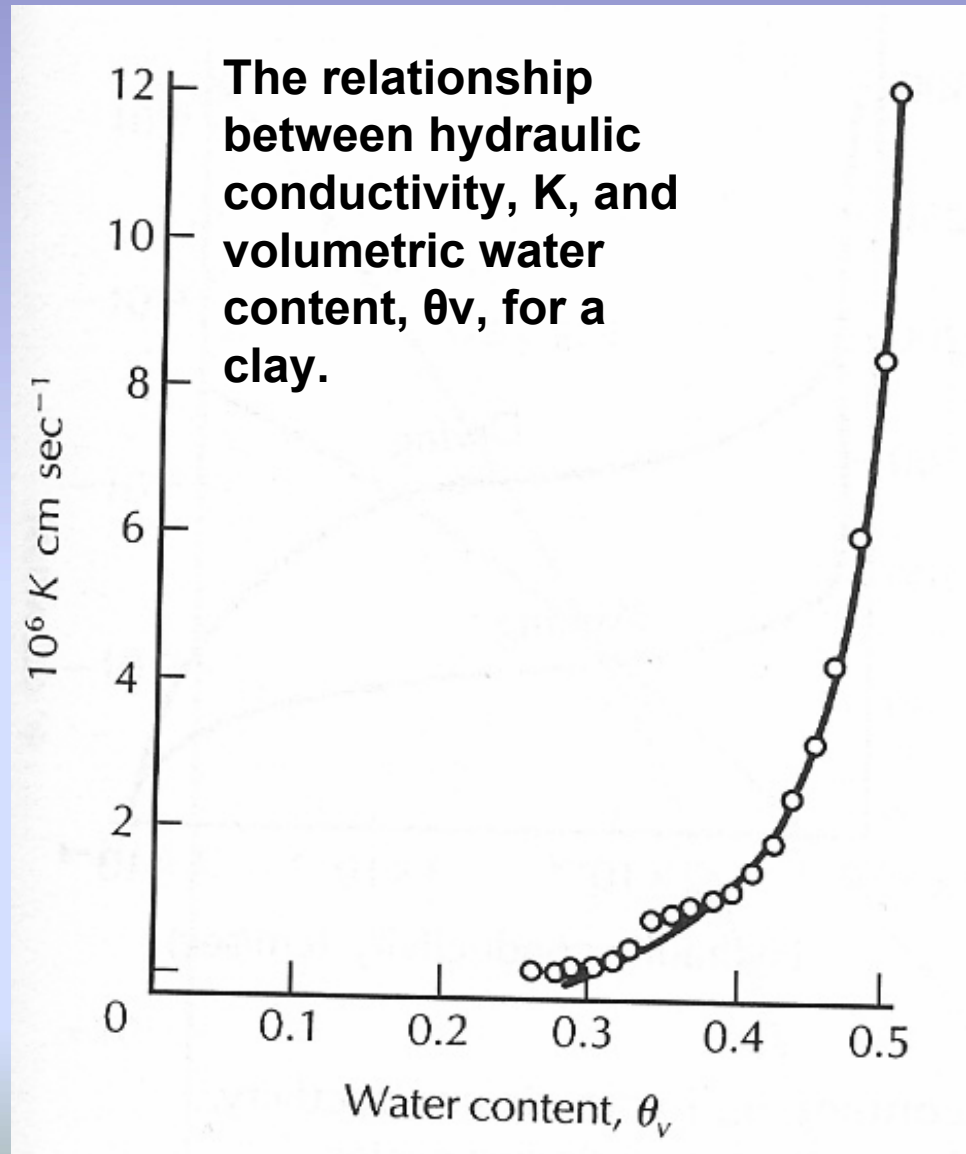
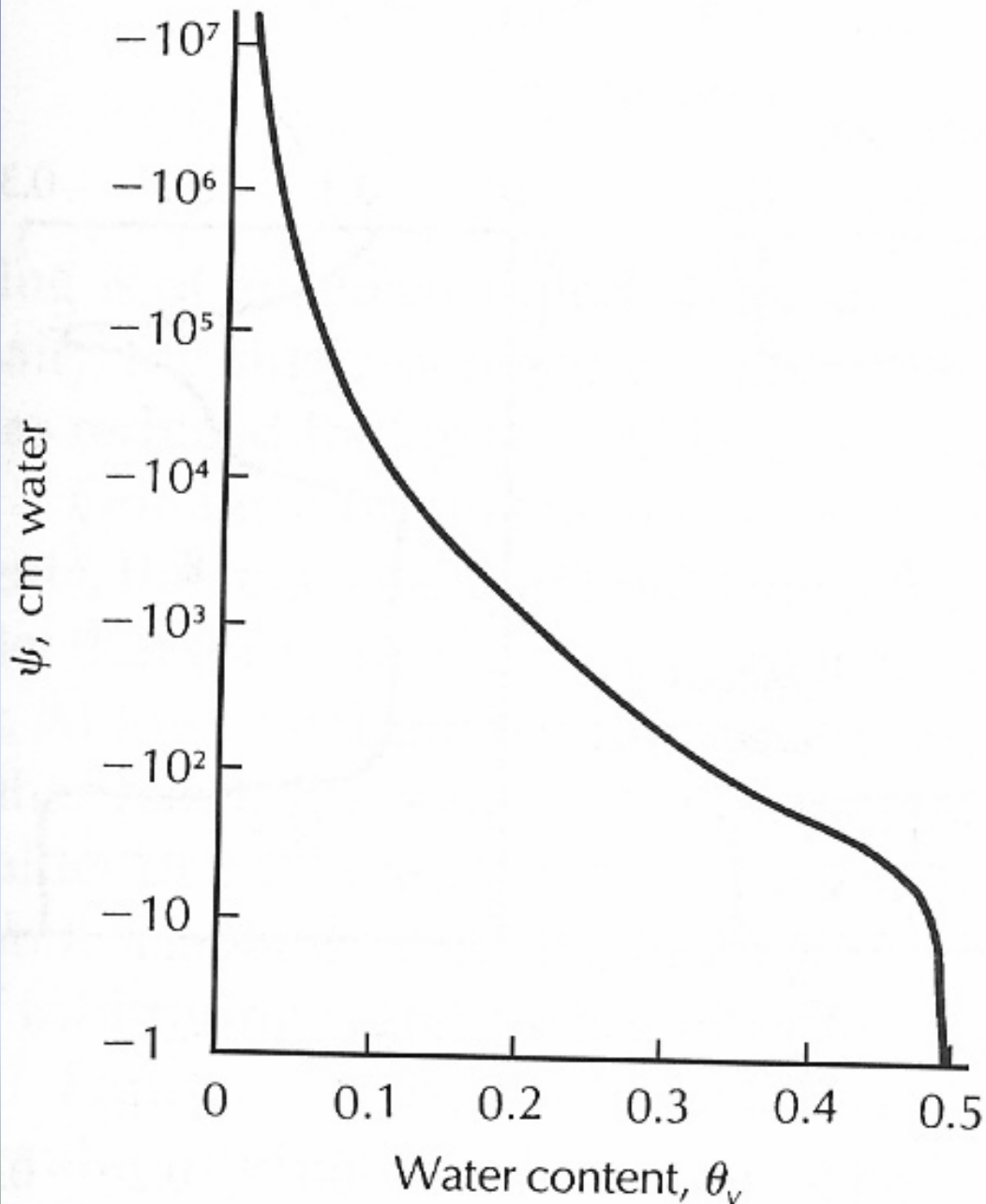
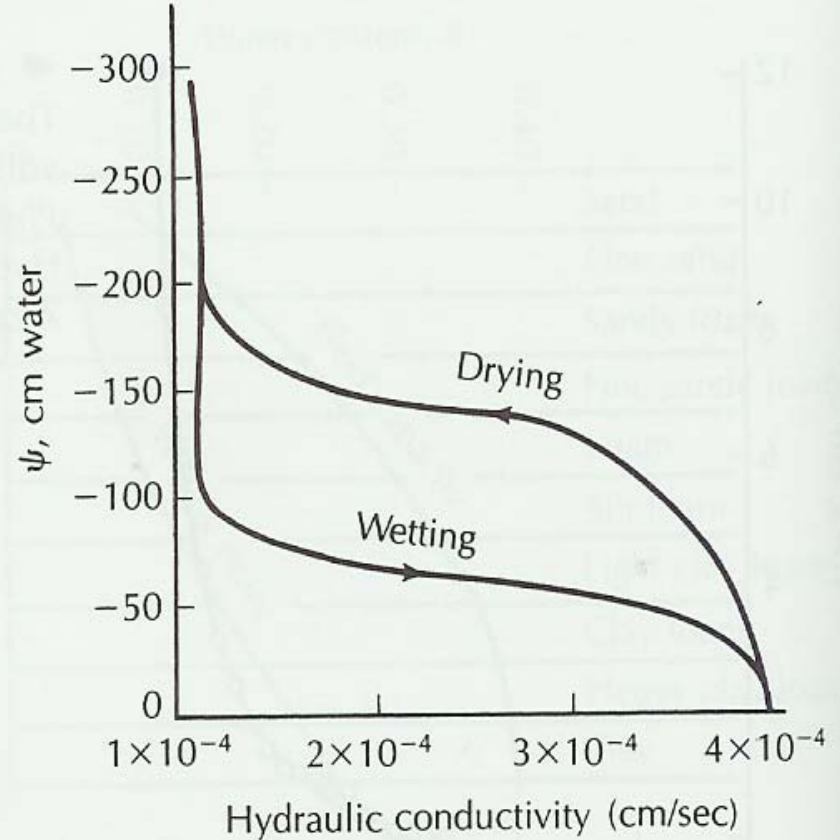
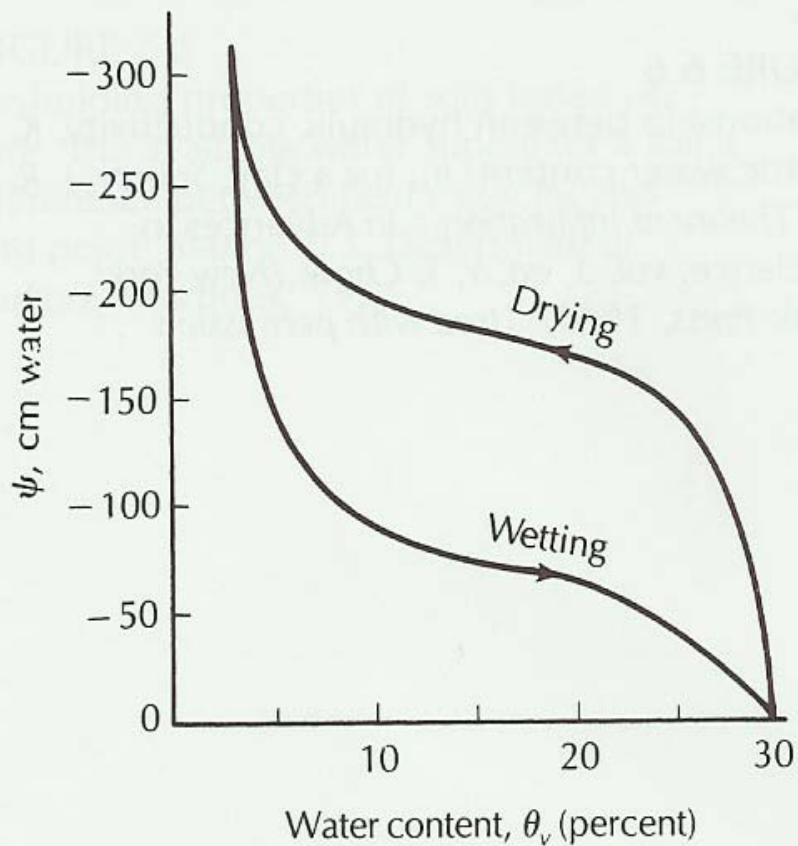


Figure 6.6 Fetter, *Applied Hydrogeology 4th Edition*



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.

Hydraulic conductivity K

Vogel Model:

$$K_V = 0.1 K_H$$

K=hydraulic conductivity

$$V_0 = \underline{B/t} * \ln(B/(B-Z))$$

$$V_x = (V_z * x) / B$$

B=aquifer thickness

x=distance from
flow divide

t=travel time

Z=depth below
water table

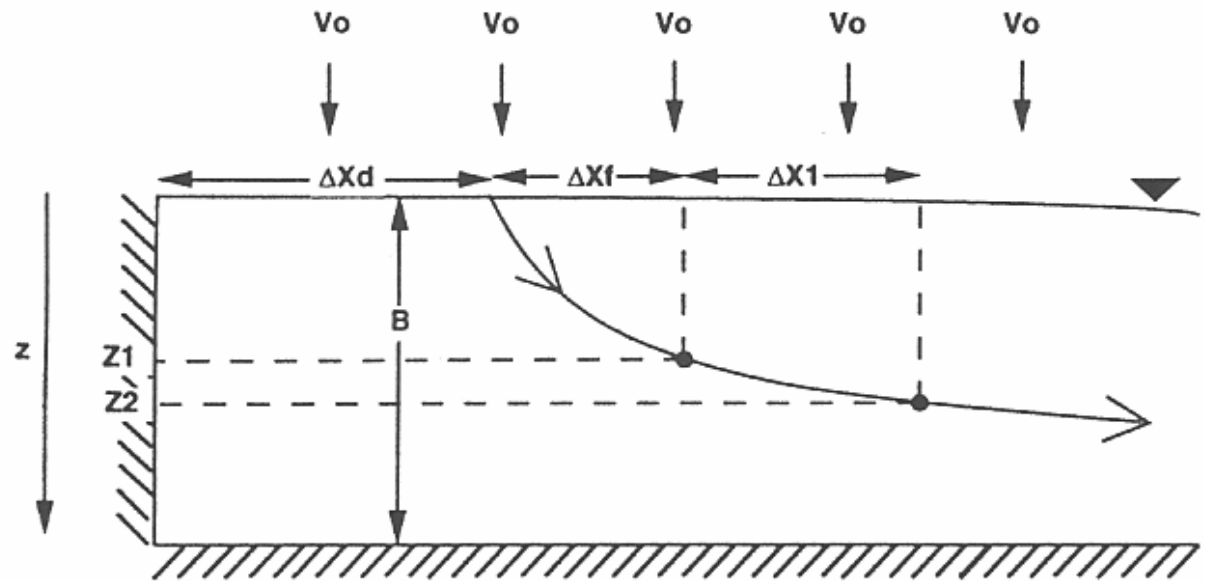


Fig. 6. Geometry of an unconfined aquifer used in the Vogel model.