TRACERS IN HYDROLOGICAL INVESTIGATIONS

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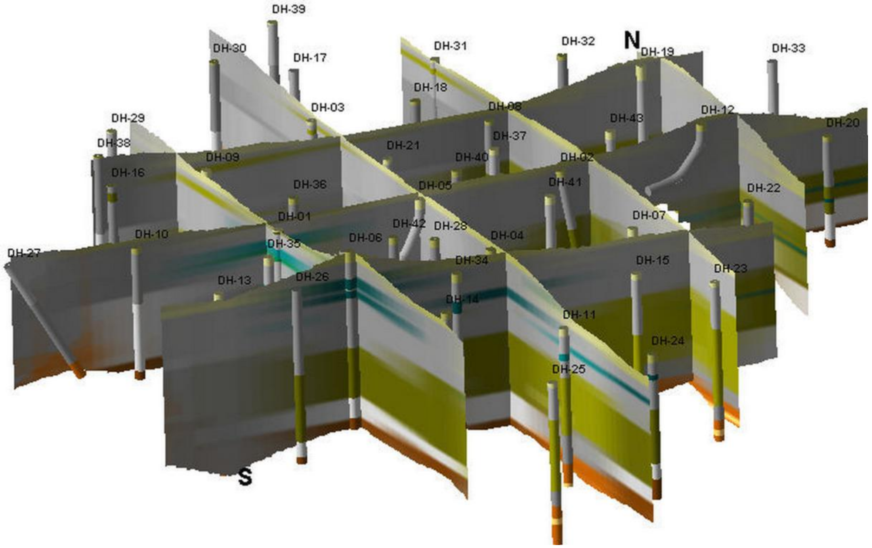
Goal of Groundwater management studies is - betterment of water resources (more water, better quality water and continuous availability)

Conventional investigation techniques:

i) Geological and geophysical surveys to develop aquifer disposition map, identification of recharge areas, GW flow paths, hydraulic interconnection, discharge zones, local, regional and sub-continental flow lines



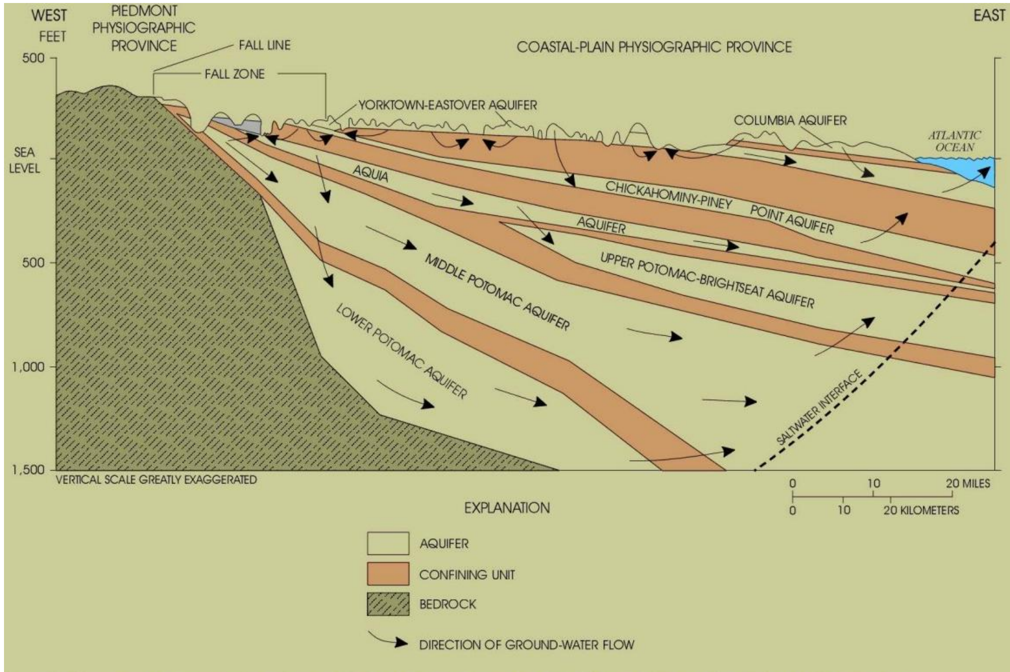
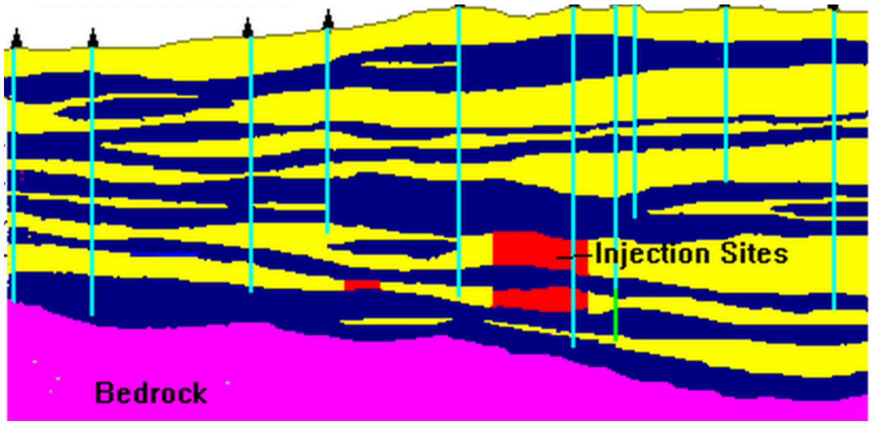
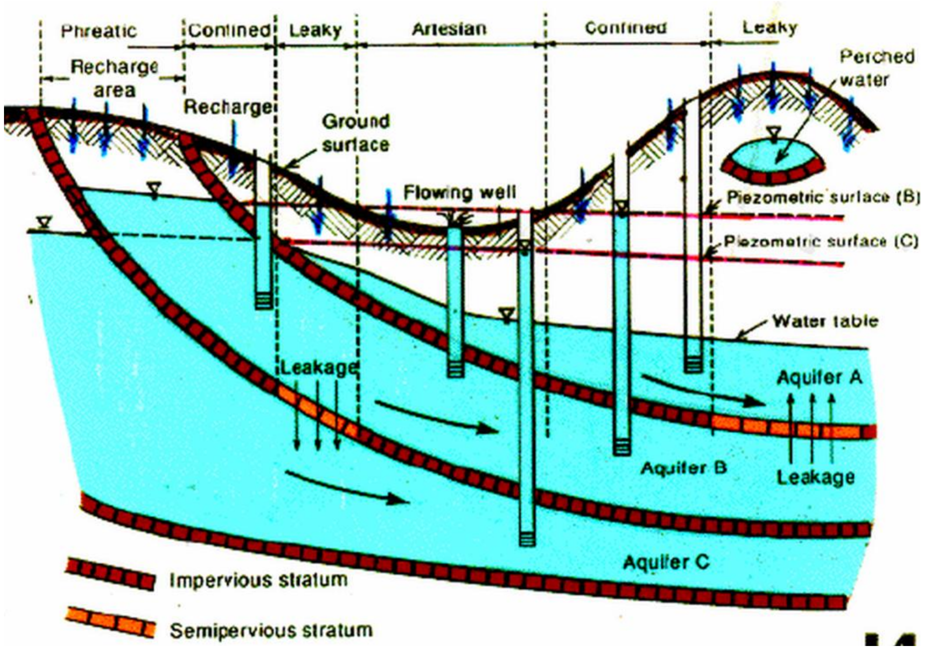


Figure 2. Generalized hydrogeologic section and direction of ground-water flow in the Coastal Plain Province of Virginia. (Modified from

ii) long term water level data, pizometric head data and met-data: to deduce water balance, sustainability of water resource

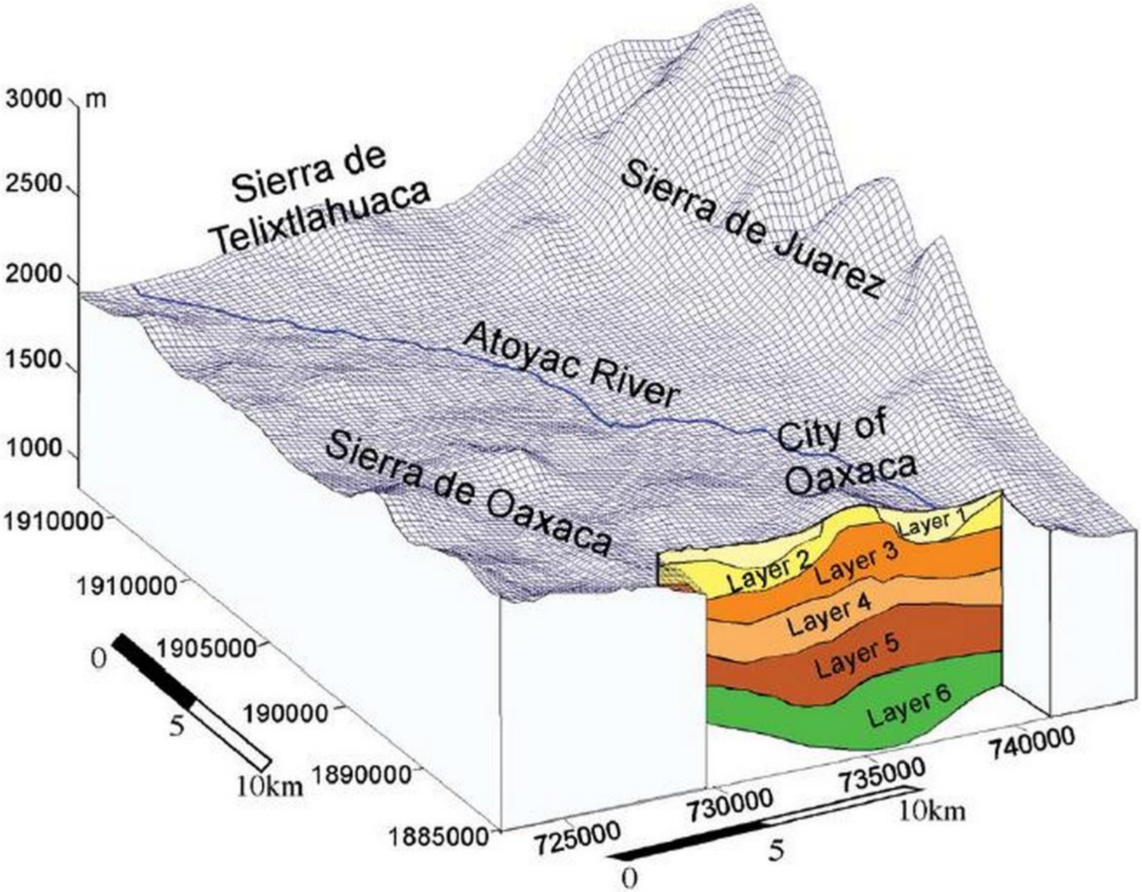


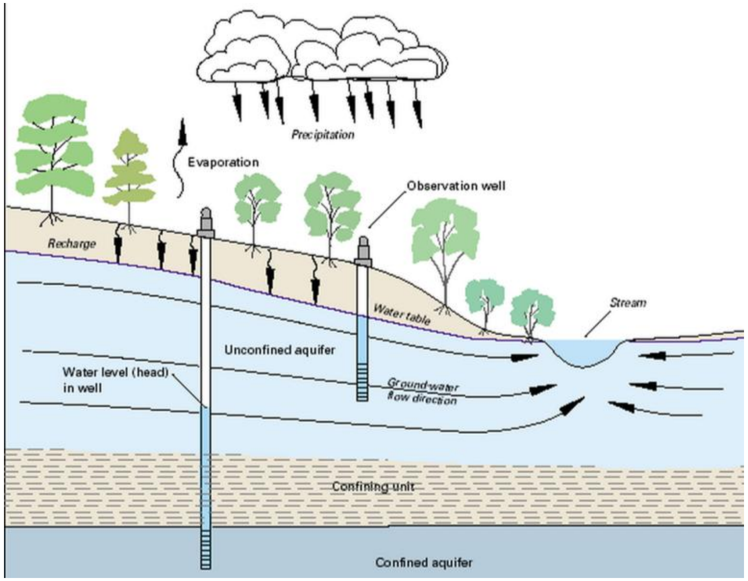
iii) Water quality data: To investigate source and dynamics of pollutants.



Traditional methods (bore hole based litholog details), water level & pizometric head data, water quality data, met-data etc requires high investments, long term monitoring over large spatial coverage and sufficient frequency intervals.

Management Goal: A phenomenological conceptual model and mathematical model helps towards planning, forecasting and implementation of various water related projects.





Tracing flow lines using tracer techniques

Basis: oceans form one end member that contains fairly well mixed tracer composition

Chemical tracers (incorporated during precipitation, during infiltration in ground, water-soil-rock interaction):

Dissolved ions (cations & anions),
Dissolved gases, (N_2, O_2, noble gas, gases of biogenic origin (CO_2, CH_4, H_2S)
Dissolved contaminants : Fertilizers, pesticides, industrial waste
Heavy metals: Arsenic, mercury, lead, copper etc
Radioisotopes (natural or artificial): ^{3}H, ^{14}C, ^{36}Cl
(Age: Young water: replenishing continuously; old water: mining)

Applicability of Stable isotopes as tracers: for evaporation from oceans, cloud formation, precipitation, run-off, evaporation

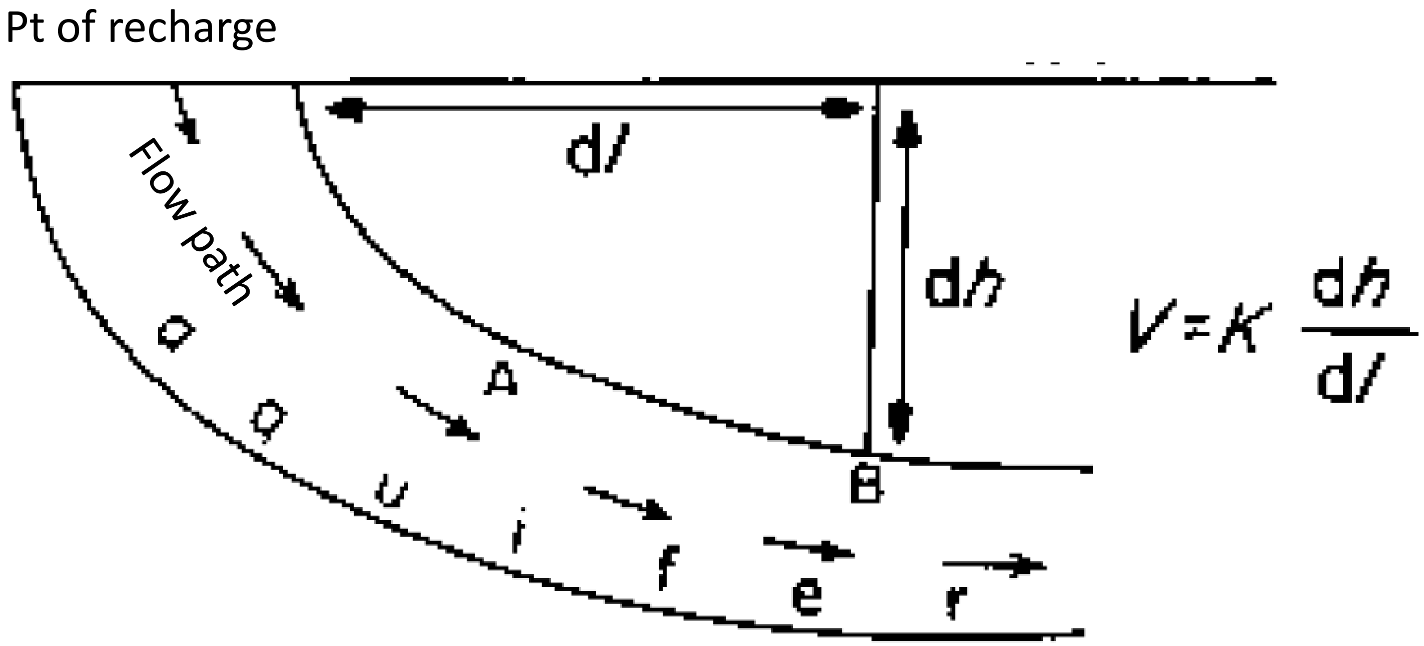
Other tracers like Temperature fluctuation: at time scales at daily, seasonal, annual, intervals source dependent etc

(GW temp =150C, local annual average temp 280C. Interprete ?)

Measurement: Variation in tracer concen., amount along the GW flow path.

Limitation in measurements: Interpretation of water quantity, quality and sustainability details at regional scale using scattered point analysis

Management emphasis: on shorter water resources and poorer water quality regions.



$V = K \frac{dh}{dl}$

Schematic representation of Darcy's law applied to 1-dimensional confined groundwater flow system

Groundwater age $t = \Delta l/V$

Remark: Groundwater has no singular age due to dispersion & mixing along the flow path

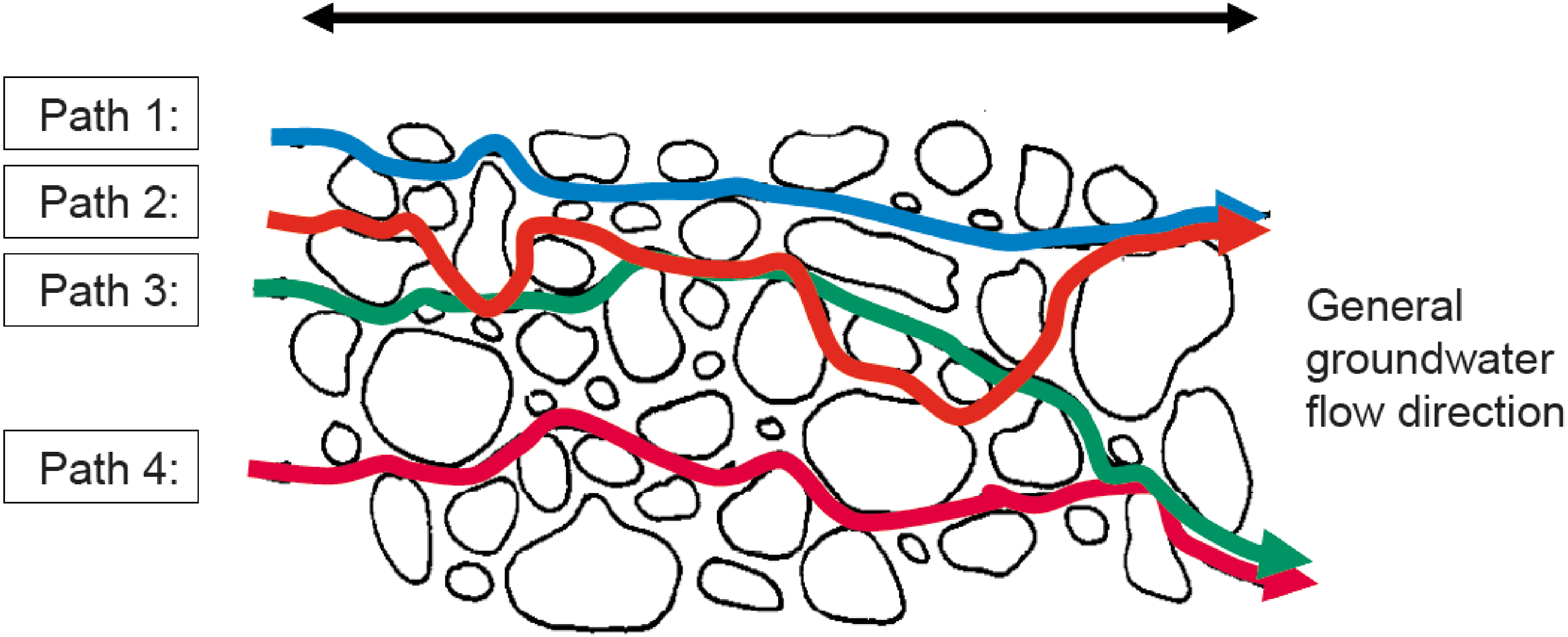
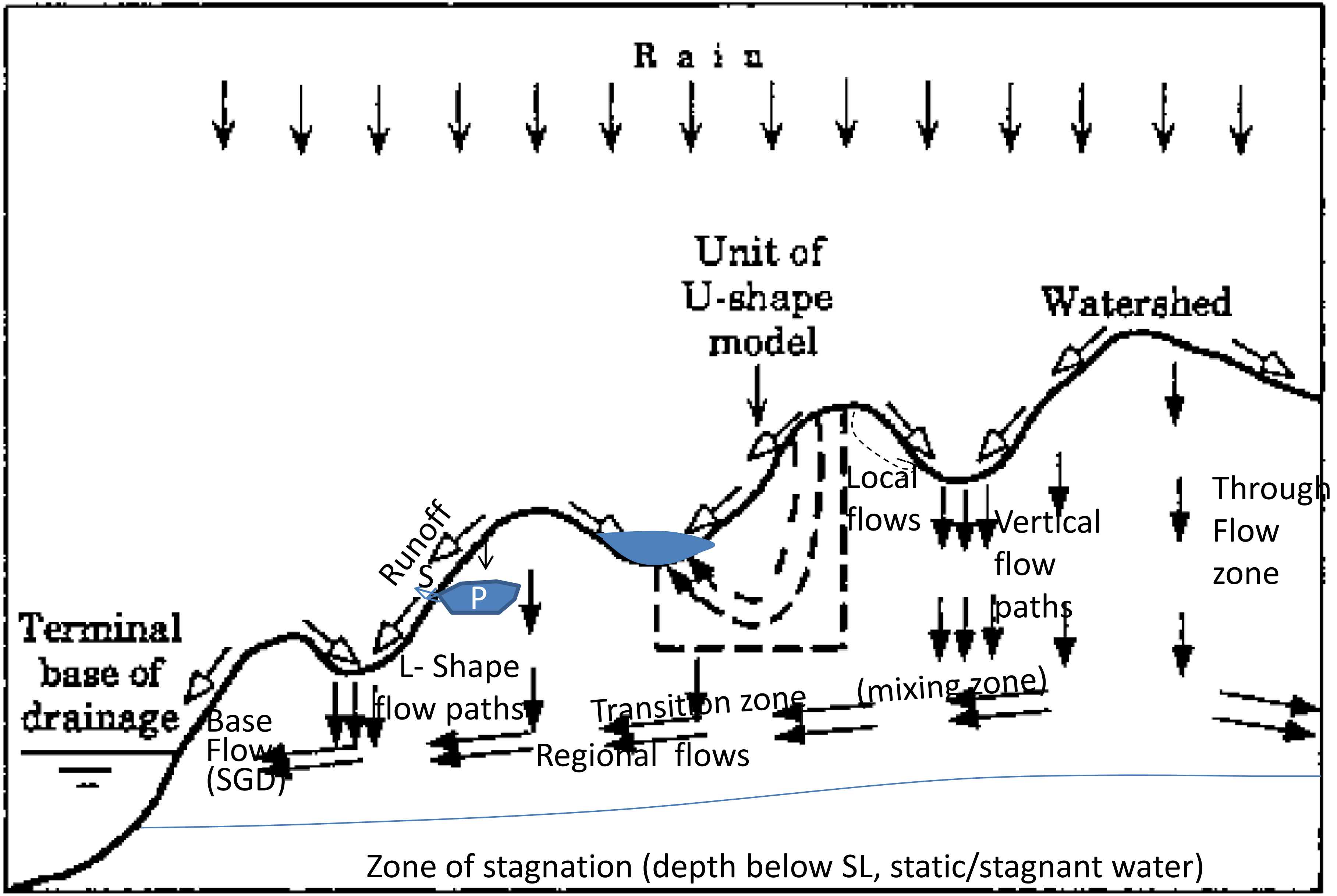
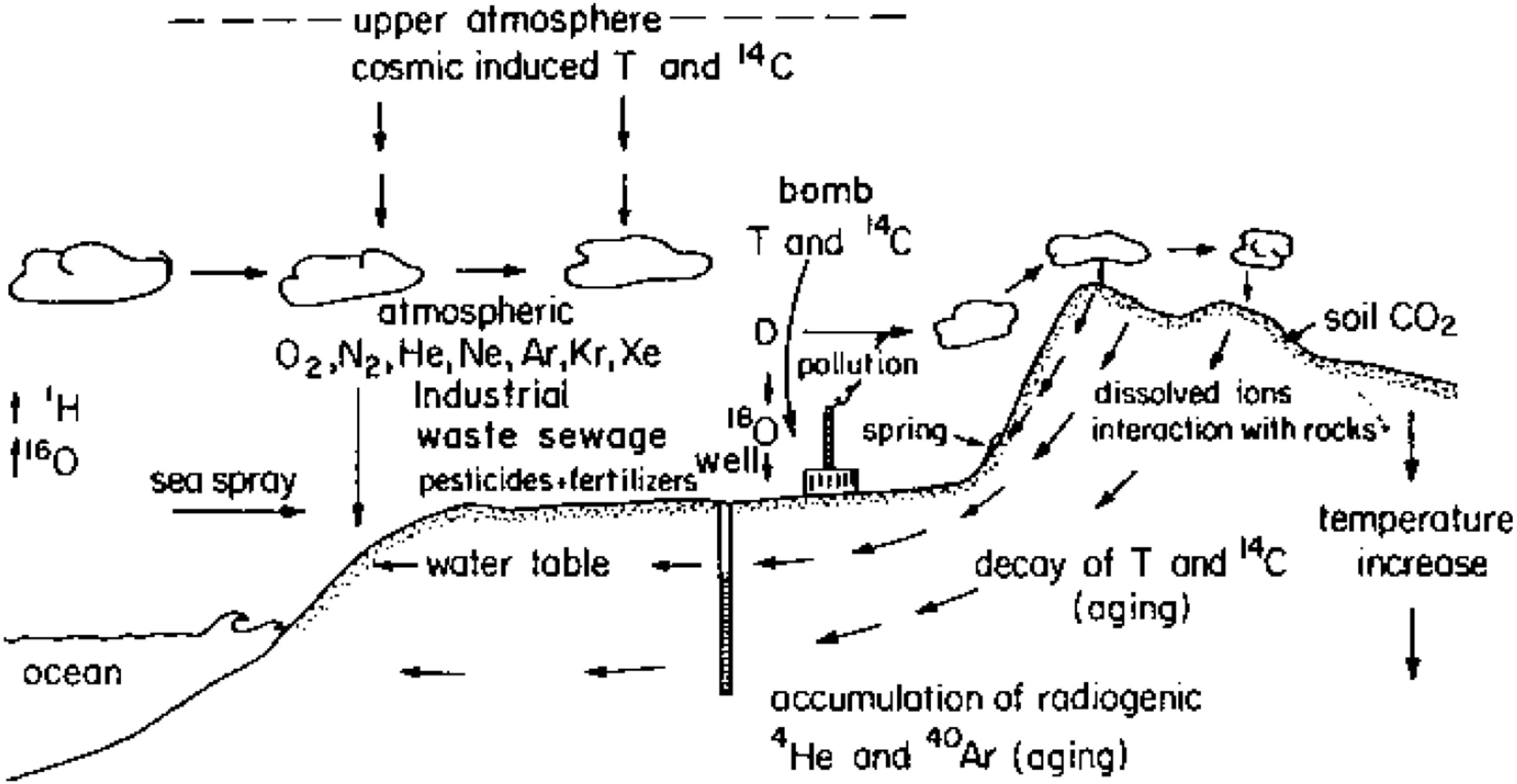


Fig: Dispersion during groundwater flow. Groundwater routes through different paths (paths 1, 2, 3, 4) leading to groundwater age dispersion at a position ∆x at the downstream



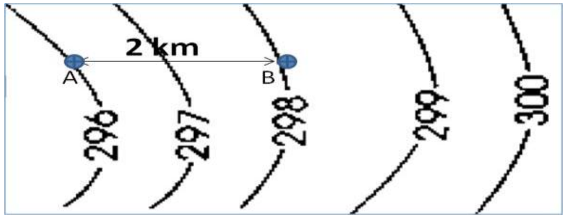
Groundwater flow system: U-shape & L-shape flow paths, groundwater flow system (Local flows, intermediate flows, regional flows), Perched aquifer, (P), springs (S), base flow (modified from Mazor)

1. A well has an upper dry section	Aerated zone
2. A well has a lower part filled with water	Saturated zone
3. The water table often rises seasonally	Recharge
4. The water table often falls seasonally	Discharge
5. The upper soil dries up seasonally	Evaporation
6. Plants depend on rain or irrigation	Transpiration

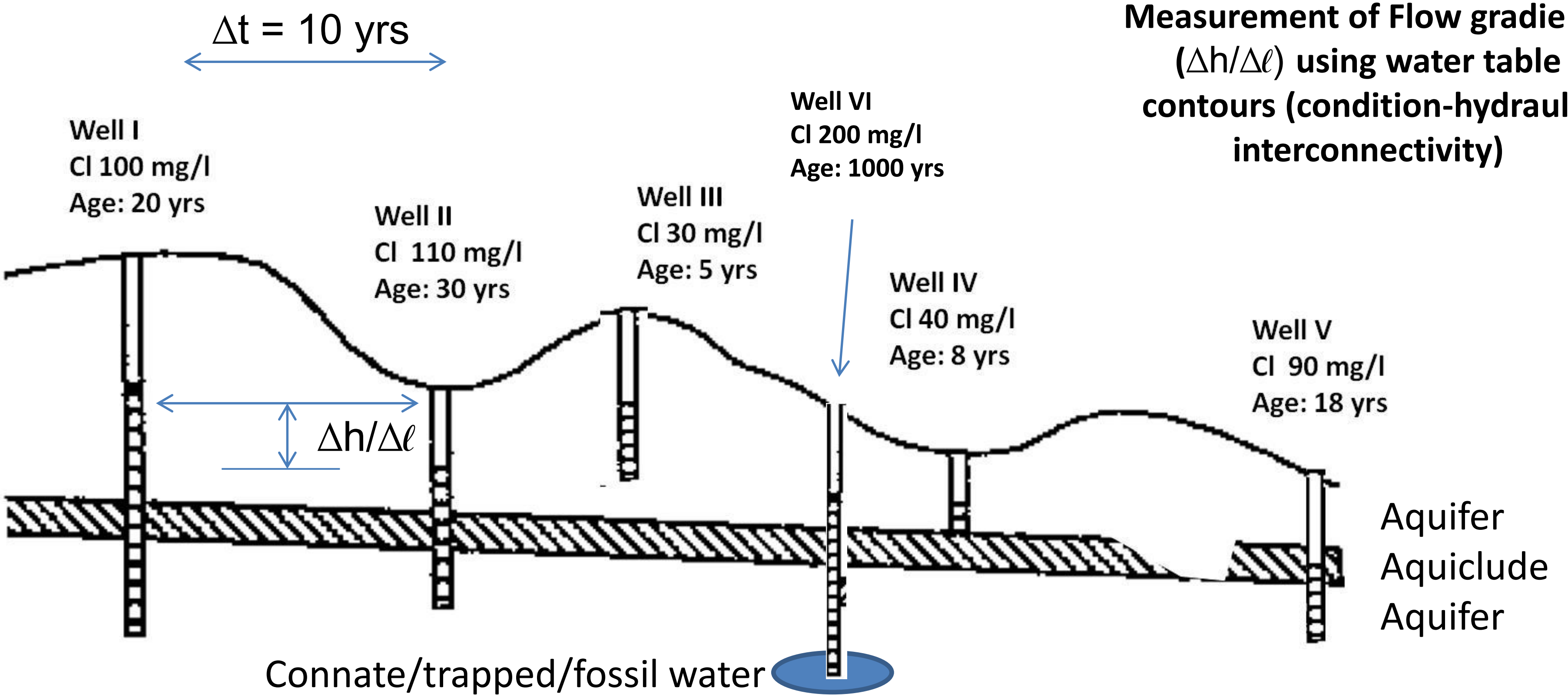


- At which point is all this information erased?
- What kinds of information are inscribed into water underground?

Water in clouds is tagged by an enrichment of H & O isotopes, separated during evaporation. At cloud stage dissolves, ^{3}H, ^{14}C, various gases(O_2, N_2, noble gases (He, Ne, Ar, Kr, and Xe). Gas dissolution is dependent on temperature and altitude (pressure). Isotopes provide continental scale information & rain-out process. During infiltration, pesticides, fertilizers, industrial pollutants, sewage etc In the underground, radiometric age (^{14}C, ^{3}H, ^{4}He ^{40}Ar) clock provides a new tracer. Temperature of deeper water provides tracer for regional circulation.



Measurement of Flow gradients ($\Delta h/\Delta \ell$) using water table contours (condition-hydraulic interconnectivity)



Δt = 10 yrs

Well I
Cl 100 mg/l
Age: 20 yrs

Well II
Cl 110 mg/l
Age: 30 yrs

Well III
Cl 30 mg/l
Age: 5 yrs

Well VI
Cl 200 mg/l
Age: 1000 yrs

Well IV
Cl 40 mg/l
Age: 8 yrs

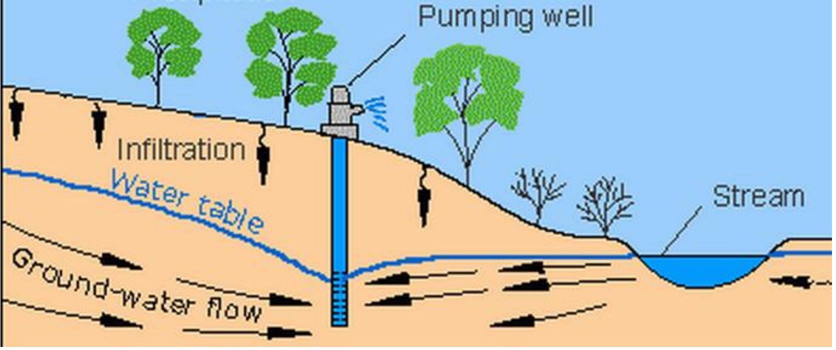
Well V
Cl 90 mg/l
Age: 18 yrs

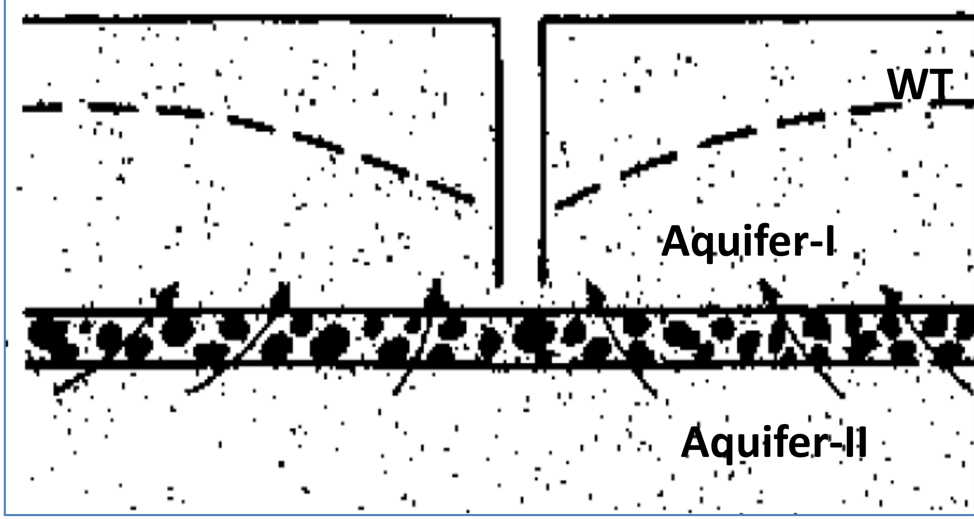
$\Delta h/\Delta \ell$

Aquifer
Aquiclude
Aquifer

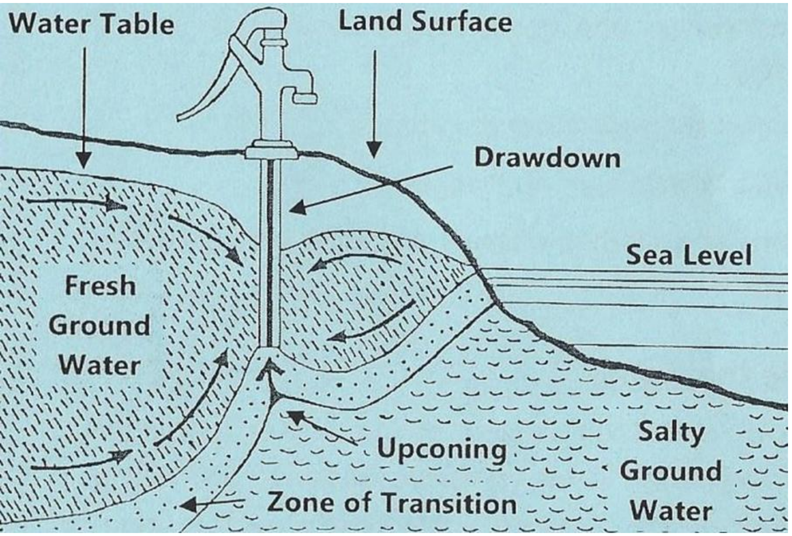
Connate/trapped/fossil water

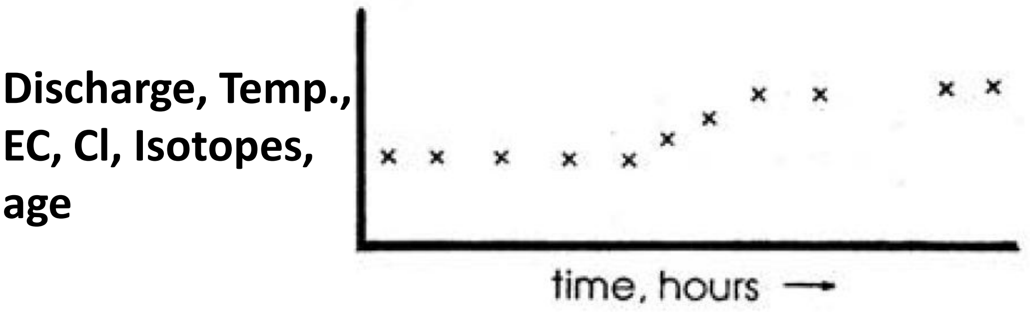
Groundwater age and dissolved ion concentration increases gradually along flow line (piezometric head contours). Low age indicates recharge zone. Groundwater in deeper aquifers are usually older compared to shallow aquifer. A sudden variation in age and dissolved conservative ion concentration indicates tapping of different aquifer or groundwater mixing (hydraulic interconnectivity).



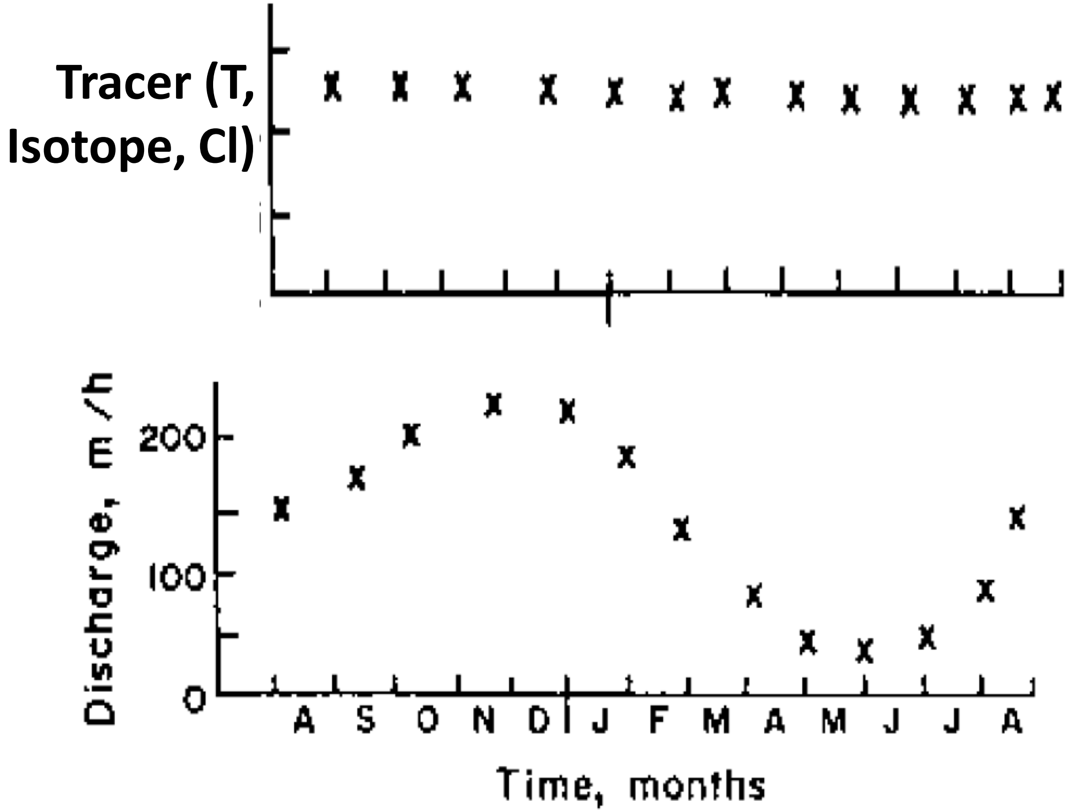


Pumping test assumes tapping of single aquifer. Breaching of aquifer may be identified using tracers

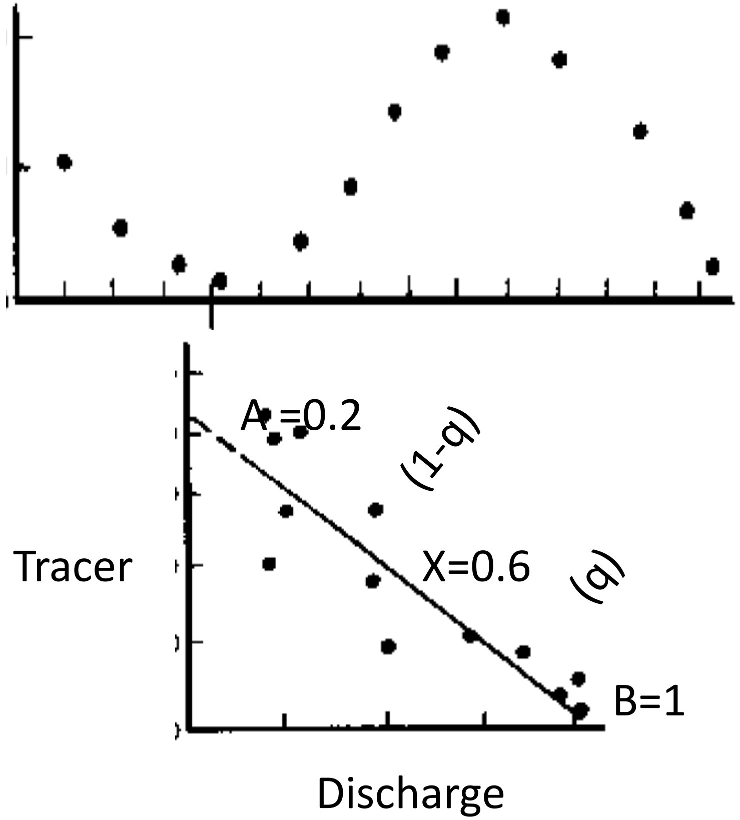




Use of tracer technique to identify multi-aquifer system and in deciding the pumping schedule



Single source involved in the discharge

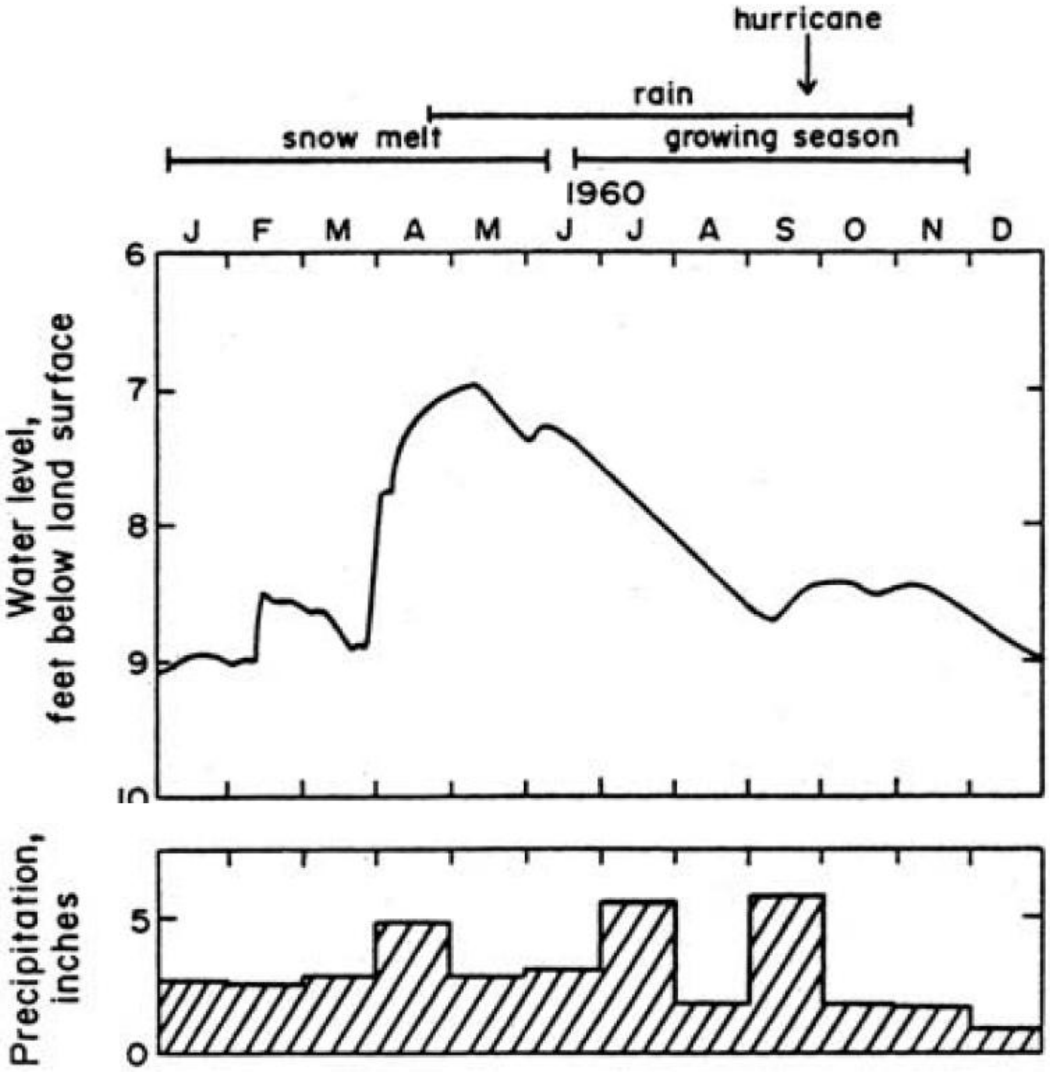


Identifying the end members (sources A & B) in the discharge using tracers

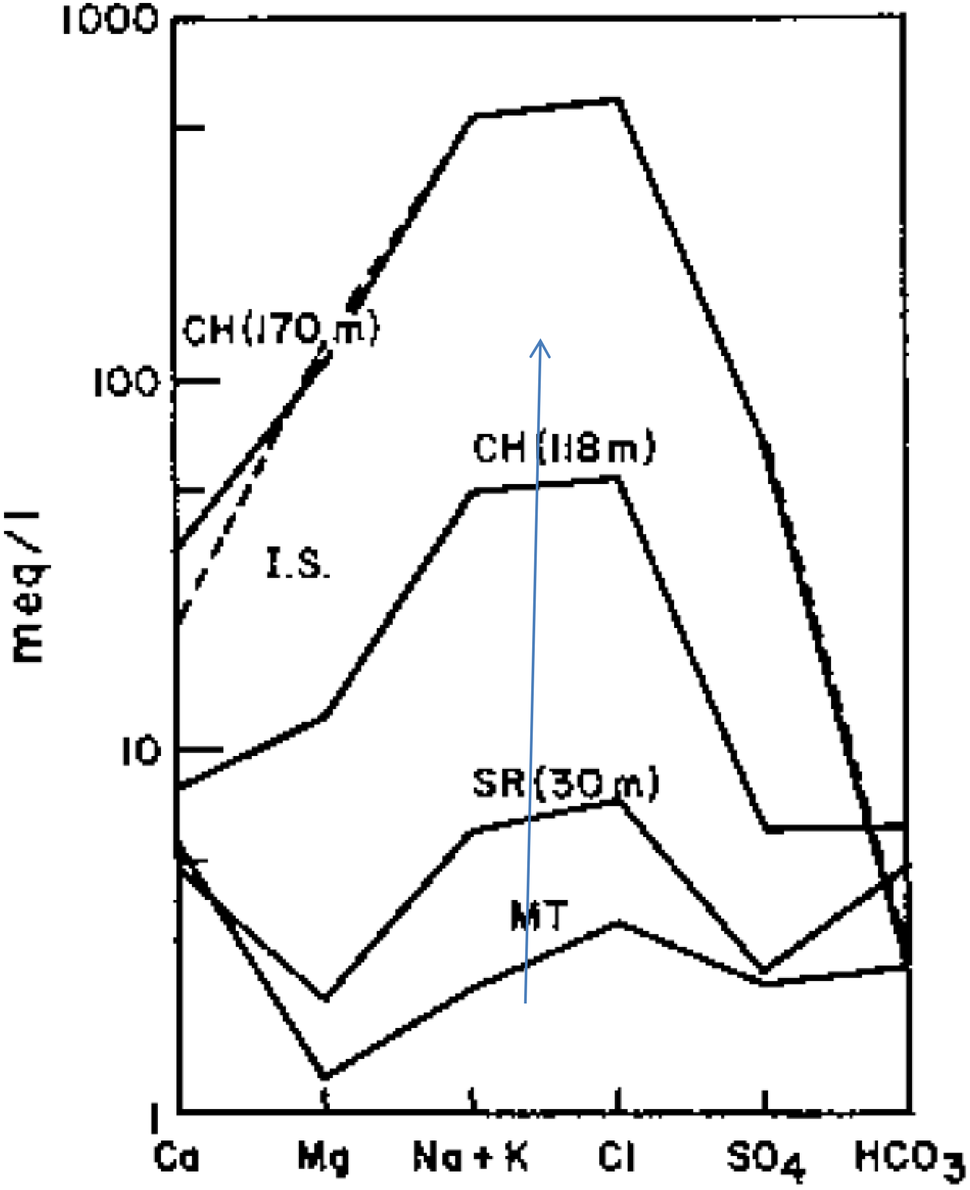
Resolving the contributing sources in the discharge (hydrograph separation)
(Assumption: The two sources have distinct tracer composition)

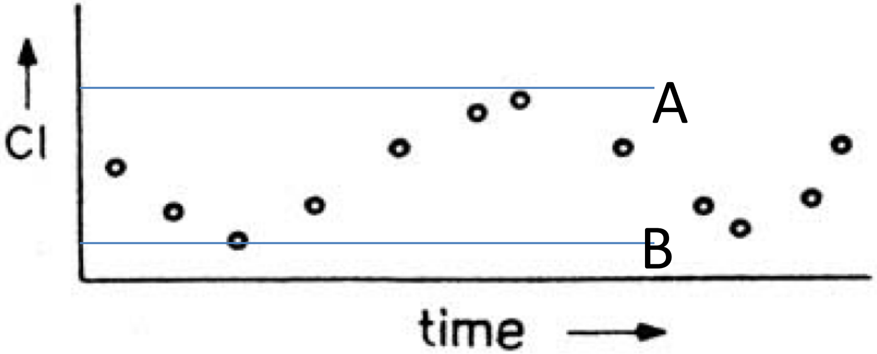
Say, A= 0.2 meq/l; B= 1 meq/l and x=0.6 meq/l
Say fraction of B in x is q
Then; 0.2 (1-q)+1x(q) = 0.6; therefore, q = 0.5 ie, x contains 50 % of A & B sources

[1 meq of SO_4^{2-}= (32+64)/2 = 48g]



Hydrograph of an observation well at the Saratoga National Historic Park, New York (after Winslow et al., 1965), and local precipitation graph.



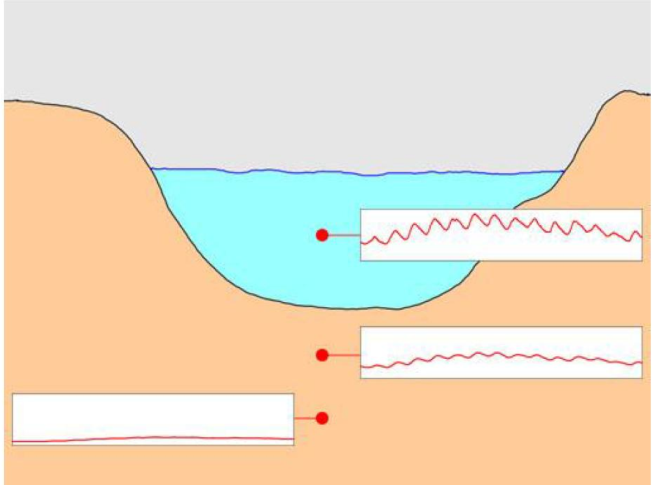


Change in salinity of pumped water due to combination of saline water source (A) and fresh water sources (B).

A case showing increasing salinity concentration with increasing well –depth in coastal area of Ionian sea (Cottechia et al., 1974)

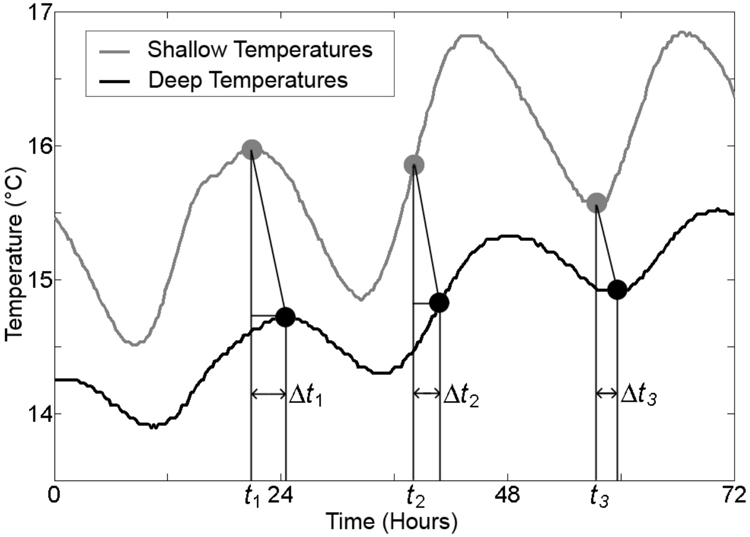
Temperature As Tracer in GW Studies

Temperature provides a good tracer because it can be measured automatically and continuously. The change in temperature at sub-surface may be used to monitor residence time relative to river stage.



Similar to high frequency continuous temperature recorders the conductivity recorders of water may also be used as natural tracers for residence time in subsurface.

Low cost, accurate, multipoint temperature/EC/WL recorders with transmitters provide online monitoring and tracing of hydrologic system



Data displaying Phase Lag

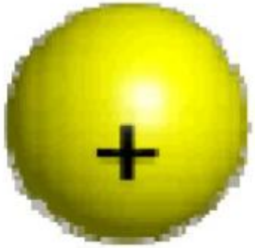
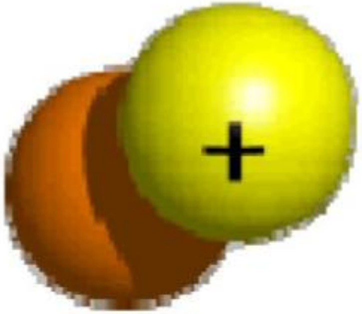
Isotopes

Stable

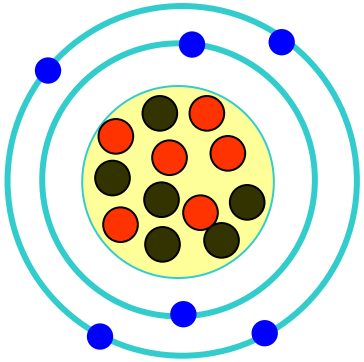
Unstable

Environmental

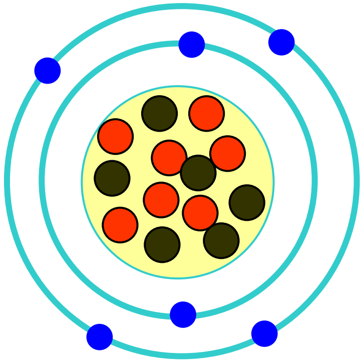
ISOTOPES OF HYDROGEN

Name : (Nucleus)	Protium (1p)	Deuterium (1p +1n)
Schematic:		
Characerstic:	Light (Stable)	Heavy (Stable)
Abundance:	99.985%	0.015%

Carbon-12



Carbon-13



^{18}O, (^{17}O), ^{16}O

Chemical analysis ? Physical estimation ✓

eg., $R = {}^{18}O/{}^{16}O$

δ- NOTATION IN STABLE ISOTOPES

$$\delta D‰ = \frac{(D/H)_{sample} - (D/H)_{SMOW}}{(D/H)_{SMOW}} \times 1000$$

$$\delta^{18}O‰ = \frac{(^{18}O/^{16}O)_{sample} - (^{18}O/^{16}O)_{SMOW}}{(^{18}O/^{16}O)_{SMOW}} \times 1000$$

$\delta D = s\ \delta^{18}O + d$ (d-excess) ---- MWL

Types of water samples	**Use as a tracer to monitor Processess**
Seawater (surface, deep)	Evaporation, circulation, mixing
Atmospheric air-moisture, cloud vapour	Cloud formation, Continental-regional-local moisture circulation, condensation process, cyclone, cloud-burst
Precipitation	Local and Global **MWL**, a reference line for comparison and interpretation of various hydrological processes
Snow, dew	Condensation process, moisture removal process
Glacial core & melt	Paleoclimate record, sublimation process
Soil moisture	Recharge & ET process
SW (river, lake, canal, ponds)	Water balance, hydrograph separation, contamination transport
Groundwater	Recharge (modern/paleo), recharge source, flow dynamics, cont. transport
Moisture in plant & animal products	Hydrological exchange process, tracer to monitor dissolve constituents

Significance of Stable Isotope Tracers

- Best known conservatives as these are parts of water molecules itself
- Spatial/temporal variation of $\delta^{18}O$, δD and d-excess (fractionation proces) in the water cycle is directly used to trace the hydrological processes and also provide check for internal consistency of the results
- LMWL/GMWL, SMOW etc provide standard comparison/end member to examine various hydrological processes
- Established isotopic-effects in meteoric water (Temp/Altitude/lattitude/ continental/seasonal/amount) simplifies the interpretation
- Tritium which is also a part of water molecule can be used to generate time frame in the investigations
- Other chemical tracers can be examined in relation with isotopic tracers
- The data can be incorporated in hydrological modeling software

Isotope Effects Observed in Precipitation (Fractionation)

1. Temperature Effect (δ-T Relationship):

Decreasing δ values with decreasing T

1. Latitude Effect

- Decreasing δ values with increasing Latitude

0.65‰/°Latitude in continental area ; 0.2‰/°Latitude in colder regions

1. Continental Effect

- Decreasing δ values with increasing inland distance: **^{18}O**: ~2.0‰/1000km

2. Amount Effect

- Increasing δ values with decreasing amount of rain

3. Altitude Effect

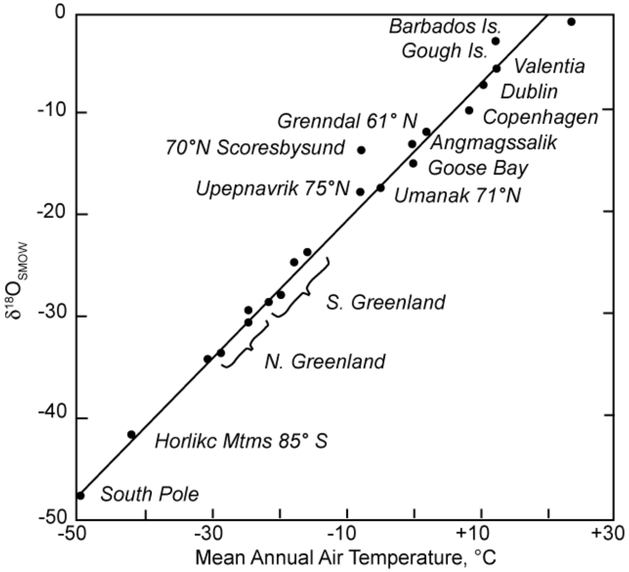
- Decreasing δ values with increasing altitude

O-18: 0.15 to 0.6‰/100m; D: 1.0 to 4.0‰/100m

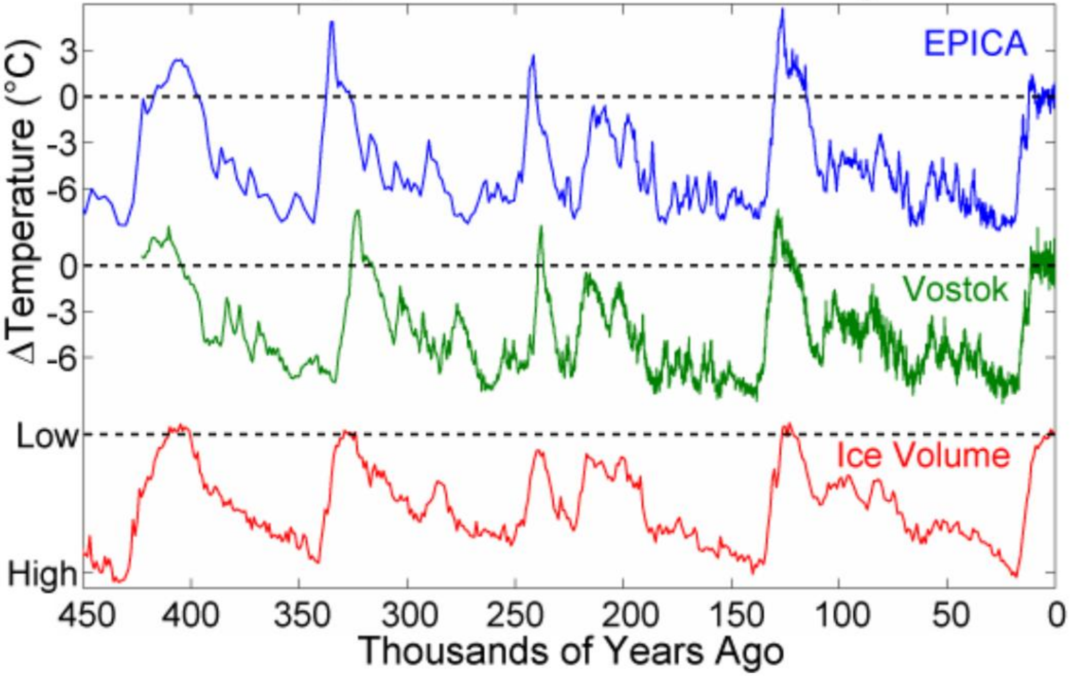
4. Seasonal Effect

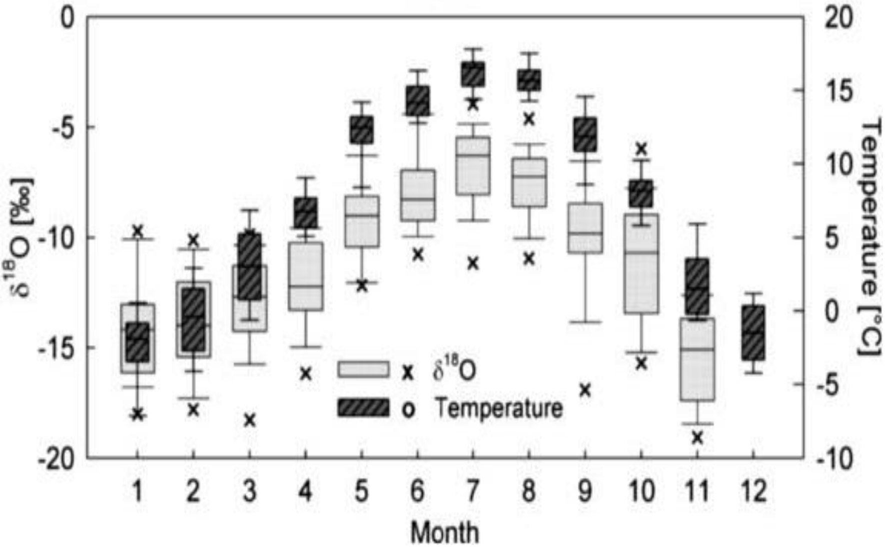
- Greater seasonal extremes in T generate strong seasonal variations

Isotope Effects in Precipitation: Application in paleoclimate studies



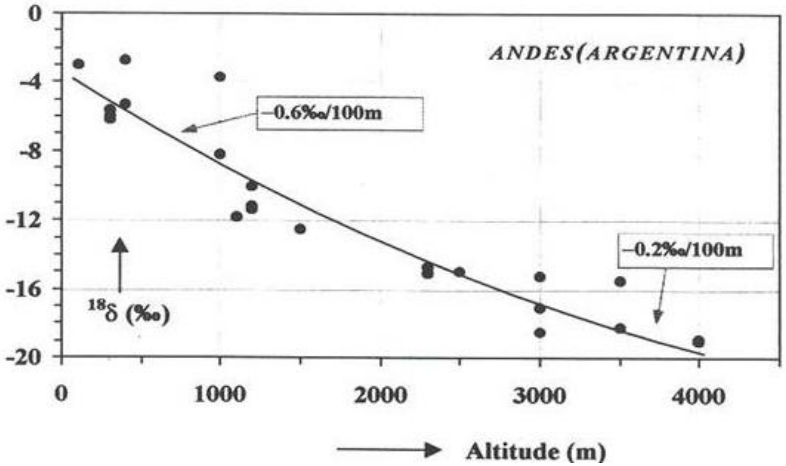
Temperature Effect





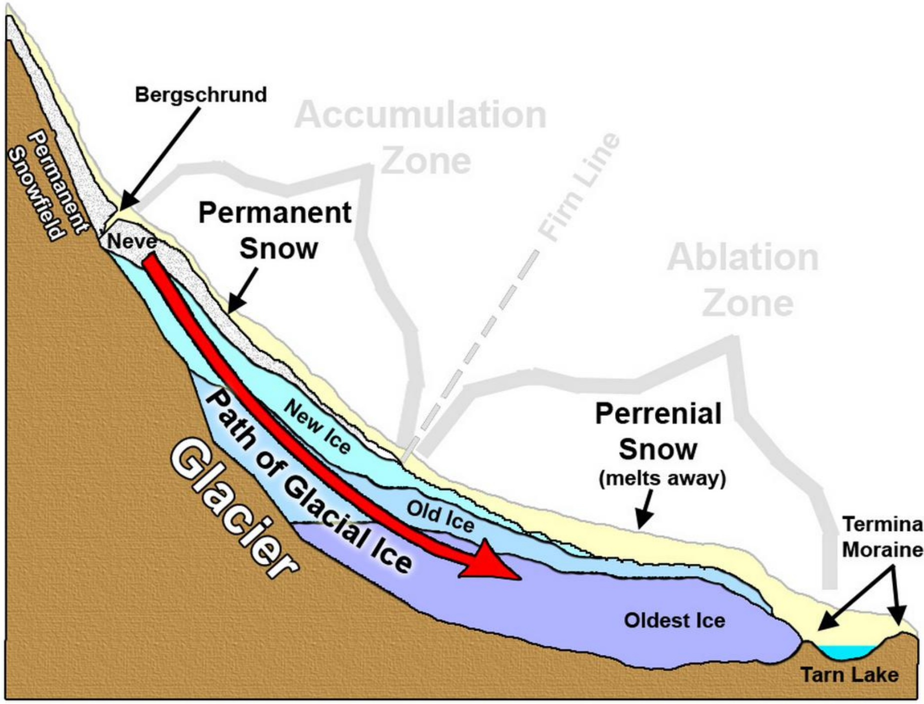
Seasonal effects in isotopes in rainfall in (Data: Garmisch, Germany, 1984–2002).

The blue and green lines depict two different Antarctic ice cores (taken from ice about 350 miles apart) and the variations in oxygen/deuterium isotopes of ice cores are converted into temperature changes. The red line depicts global ice volume reconstructed from $\delta^{18}O$ measurements on benthic foraminifera (Lisiecki and Raymo 2005). The y-axis shows temperature change; today's climate is at zero – the dashed line.

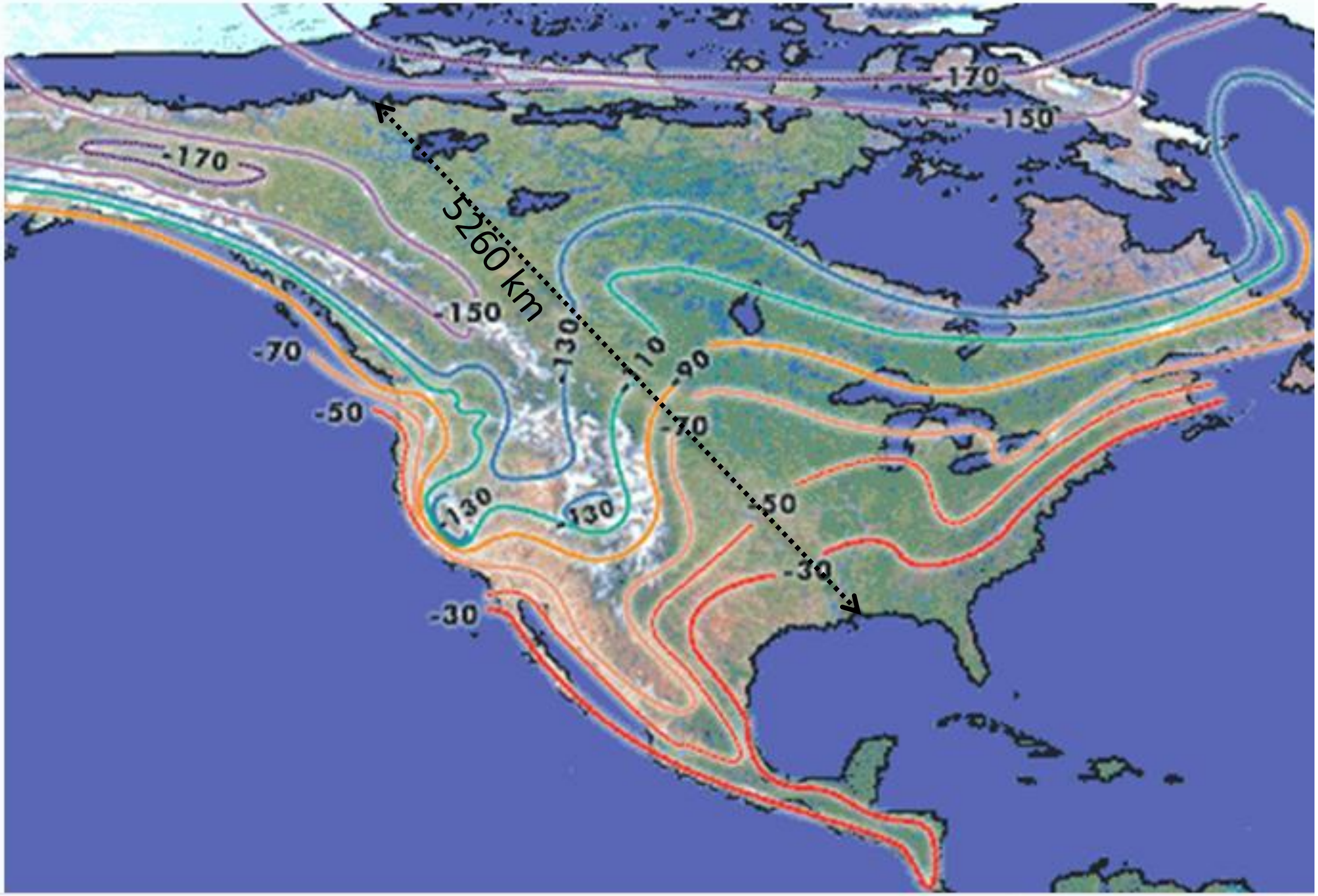


Altitude effect (Vogel et al., 1975)

Altitude Effect and its application to identification of recharge altitude of hydrological flow path (springs, glaciers, groundwater etc)



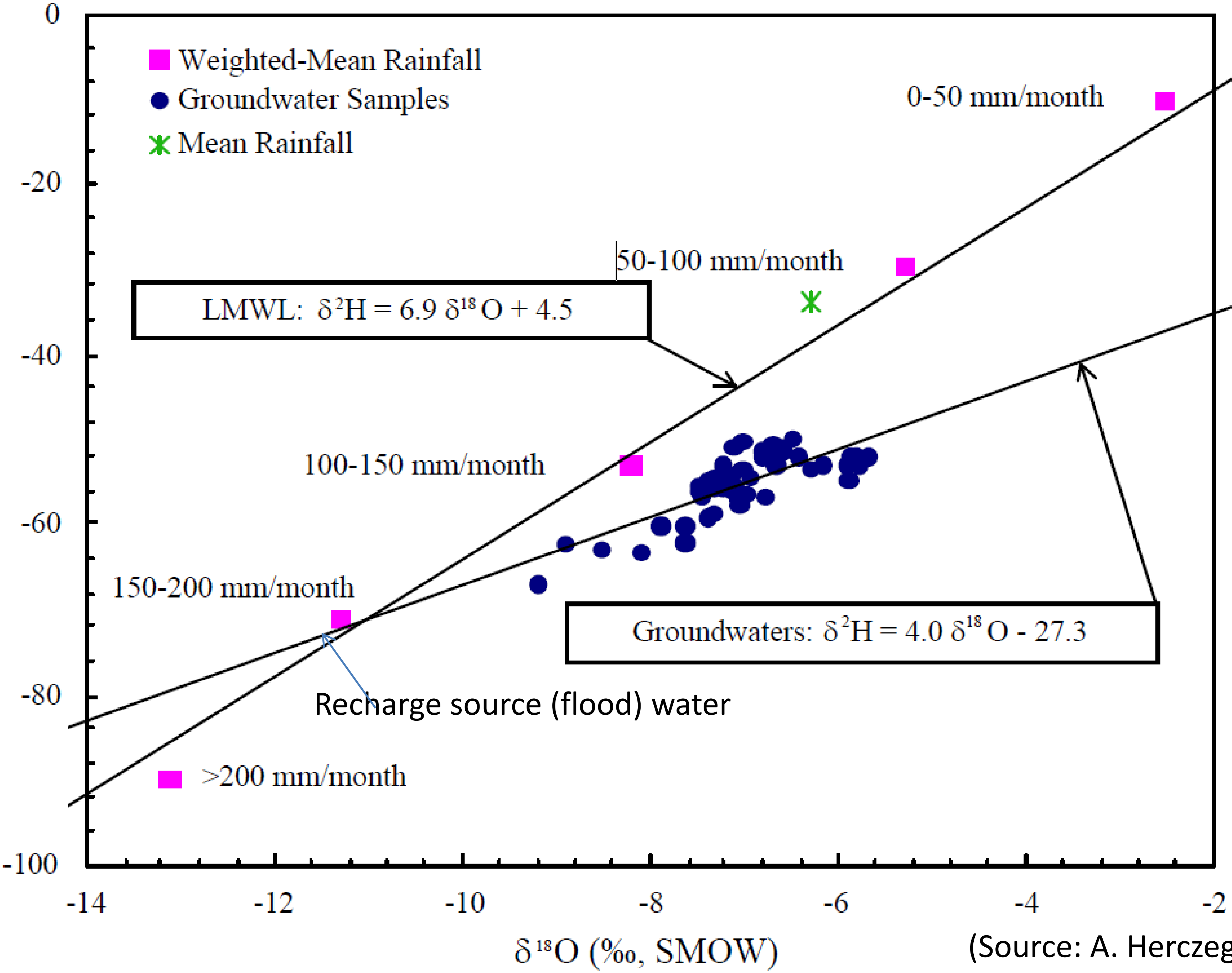
δD of precipitation in North America



The extent of continental effect depends on the prevailing direction of the movement of air masses, rather than simply on distances from the ocean.

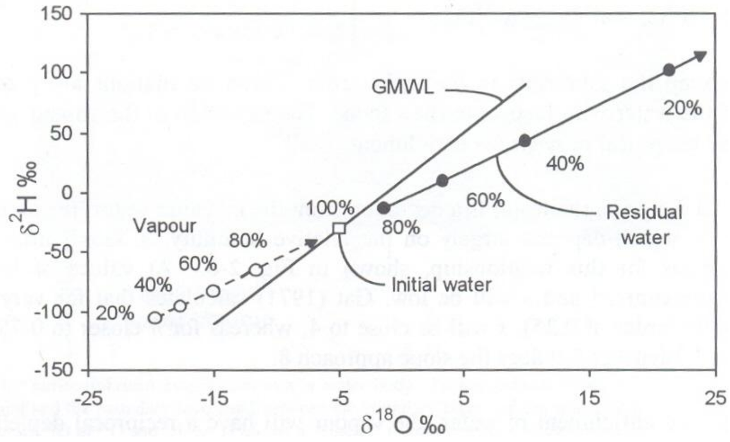
(Continental effect: ^{18}O: ~2.0‰/1000km)

Application of Amount Effect to identify the event recharge: A case from Ti-Tree basin, central Australia

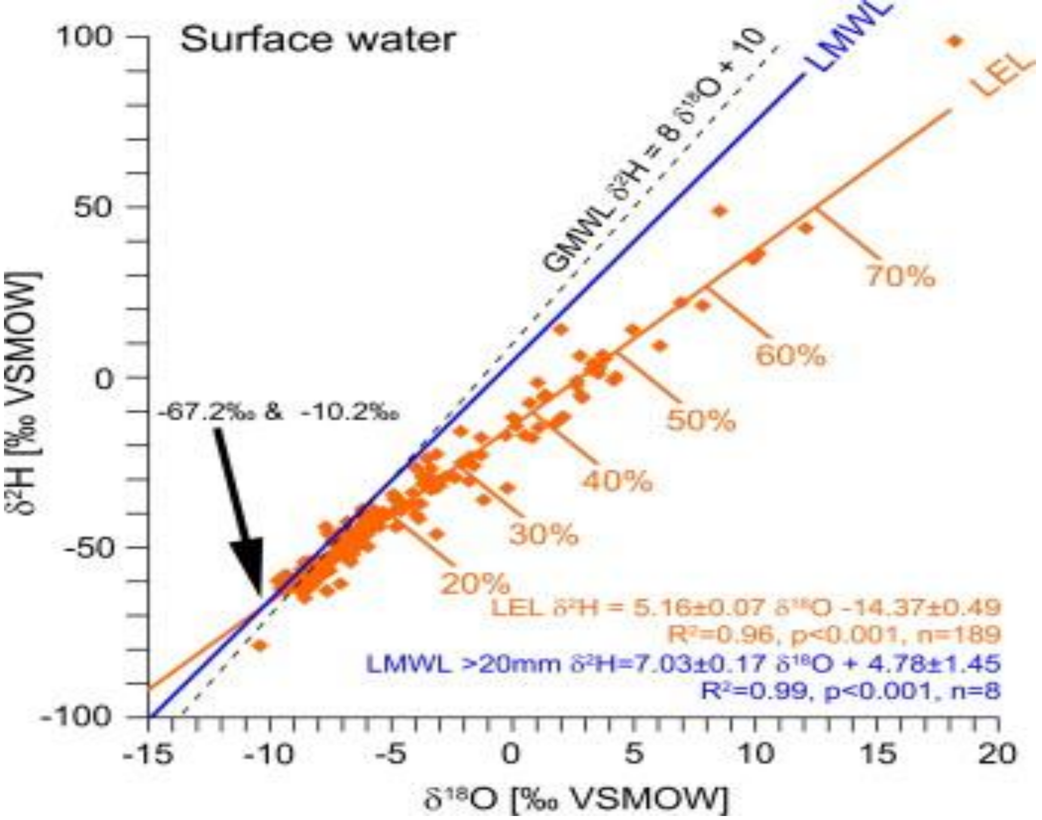


Recharge source (flood) water

(Source: A. Herczeg



Evaporative enrichment of water in closed basin lakes.

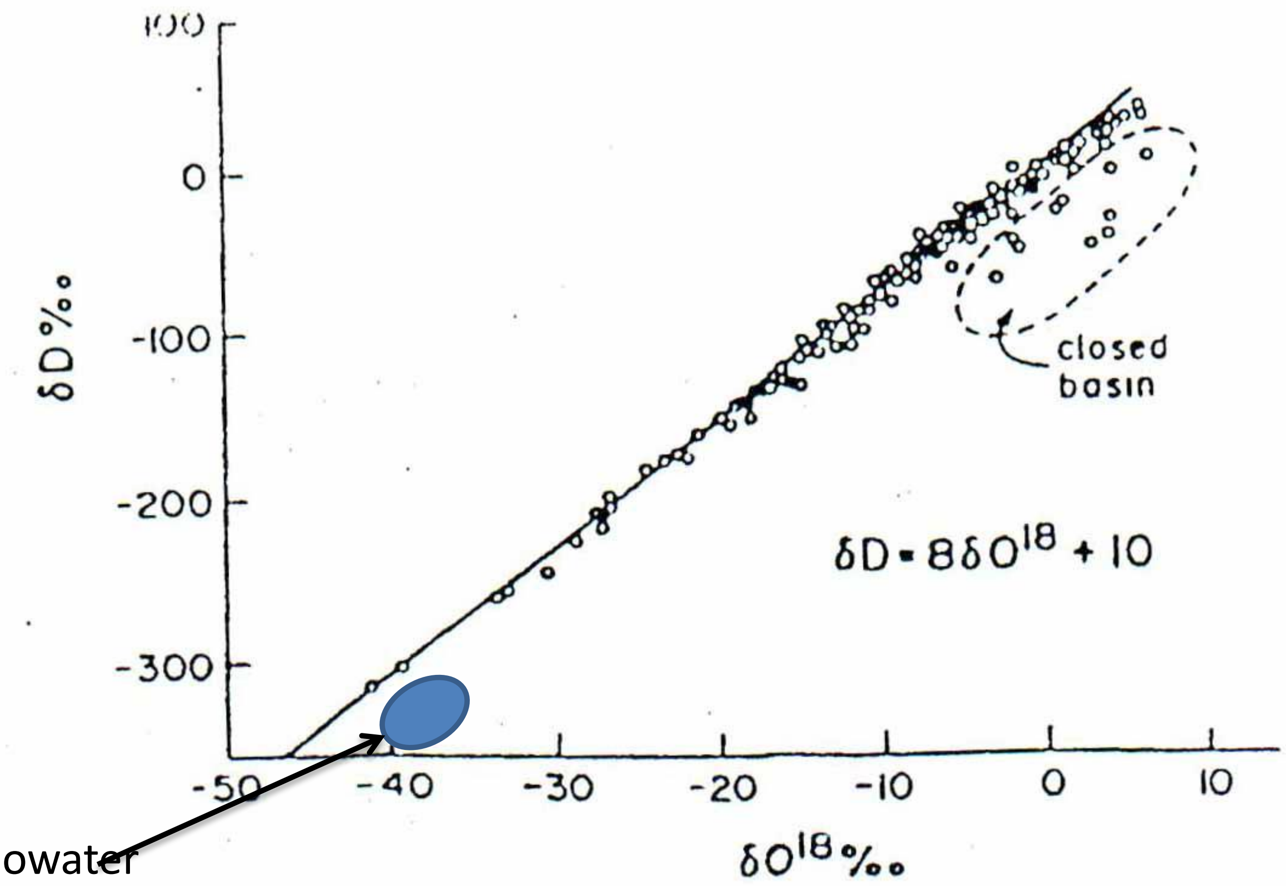


Local Evaporation Line (LEL) for the Hamersley Basin, Pilbara, calculated based on 189 surface water samples. The LEL and LMWL allows calculation of the initial stable isotope composition of water supplying surface pools (−67.2‰ for δ^2H and −10‰ for δ^{18}O). Approximate evaporation loss was calculated based on long term average air temperature (24 °C) and relative humidity (31%) observed in the Newman station from 1994 through 2010 (http://www.bom.gov.au) after Fellman et al. (2011). Journal of Hydrology Volume 475 2012 281 - 293

GMWL

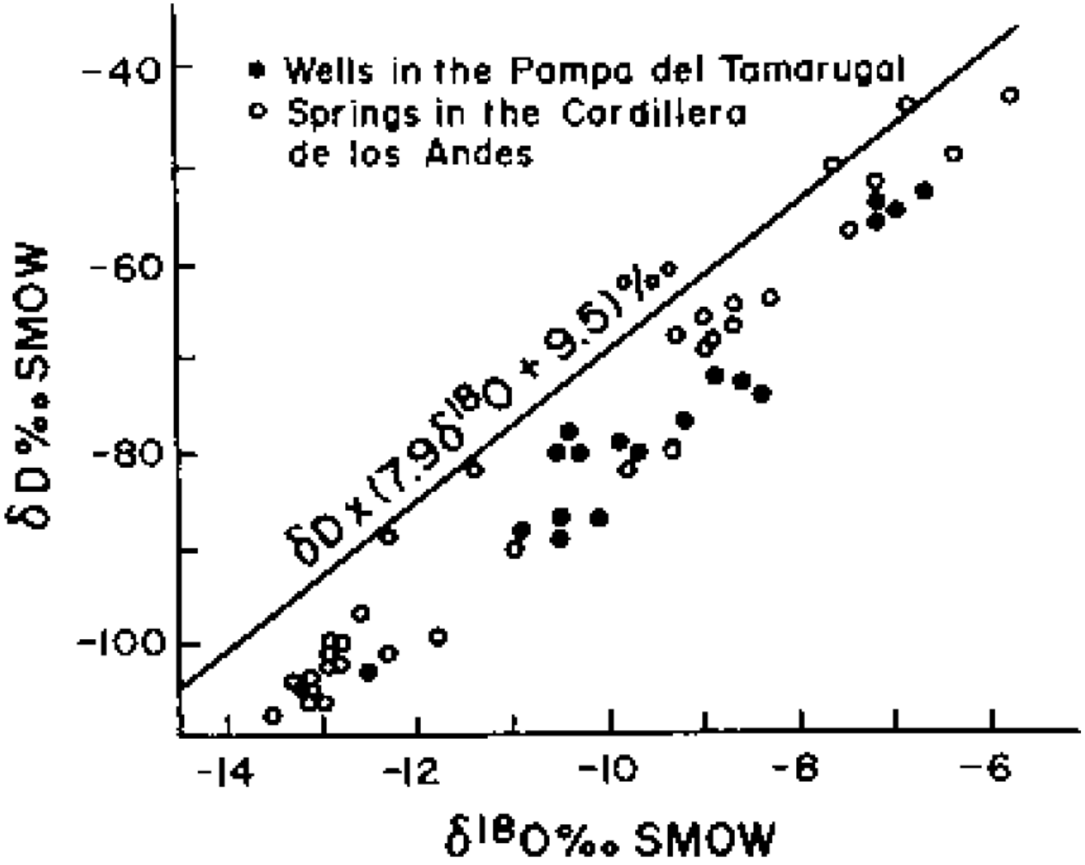
Points along GMWL vary based on temperature and latitude

Some points fall off line owing to extensive evaporation



Paleowater

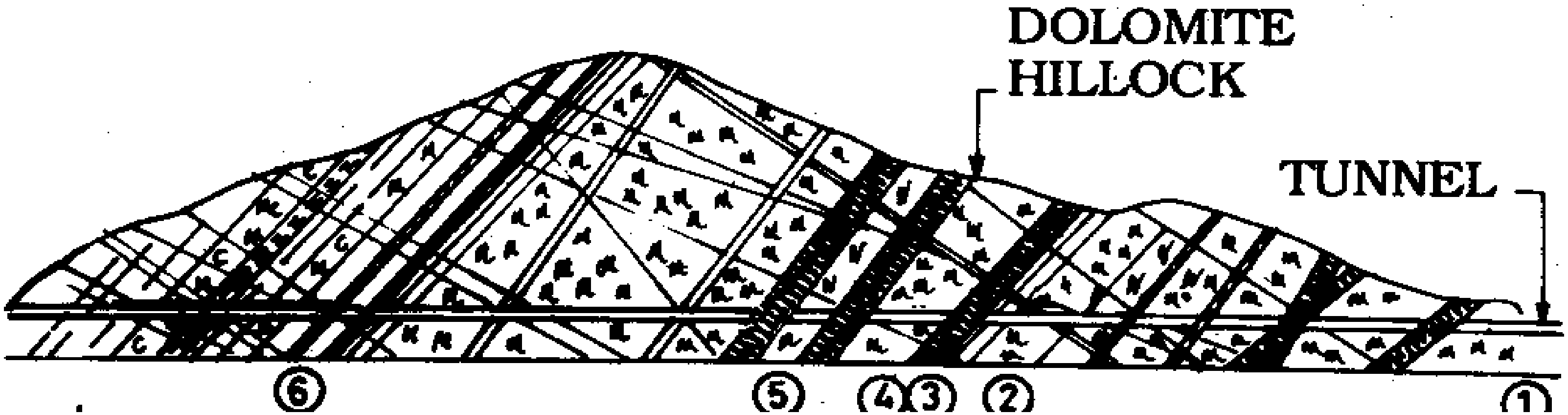
Fig. Isotopic data of about 400 samples of rivers, lakes and precipitation from various parts of the world. The best-fit line was termed the *meteoric line*. Its equation, as found by Craig (1961a), is $\delta D = 8\delta^{18}O + 10$. The data in the encircled zone of 'closed basins' is for East African lakes with intensive evaporation.



Isotopic composition of groundwaters of northern Chile. The values lie below the meteoric line of local precipitation, explained by the investigators (Fritz, et al., 1979) as reflecting secondary fractionation by evaporation prior to infiltration, or the presence of ancient waters that originated in a different climatic regime.

ENVIRONMENTAL ISOTOPIC INVESTIGATION ON SEEPAGE DURING TUNNELING FOR A HYDROELECTRIC PROJECT

- **PROBLEM:** During construction of Tail Race Tunnel for the SALAL HYDROELECTRIC PROJECT in JAMMU several seepages encountered.



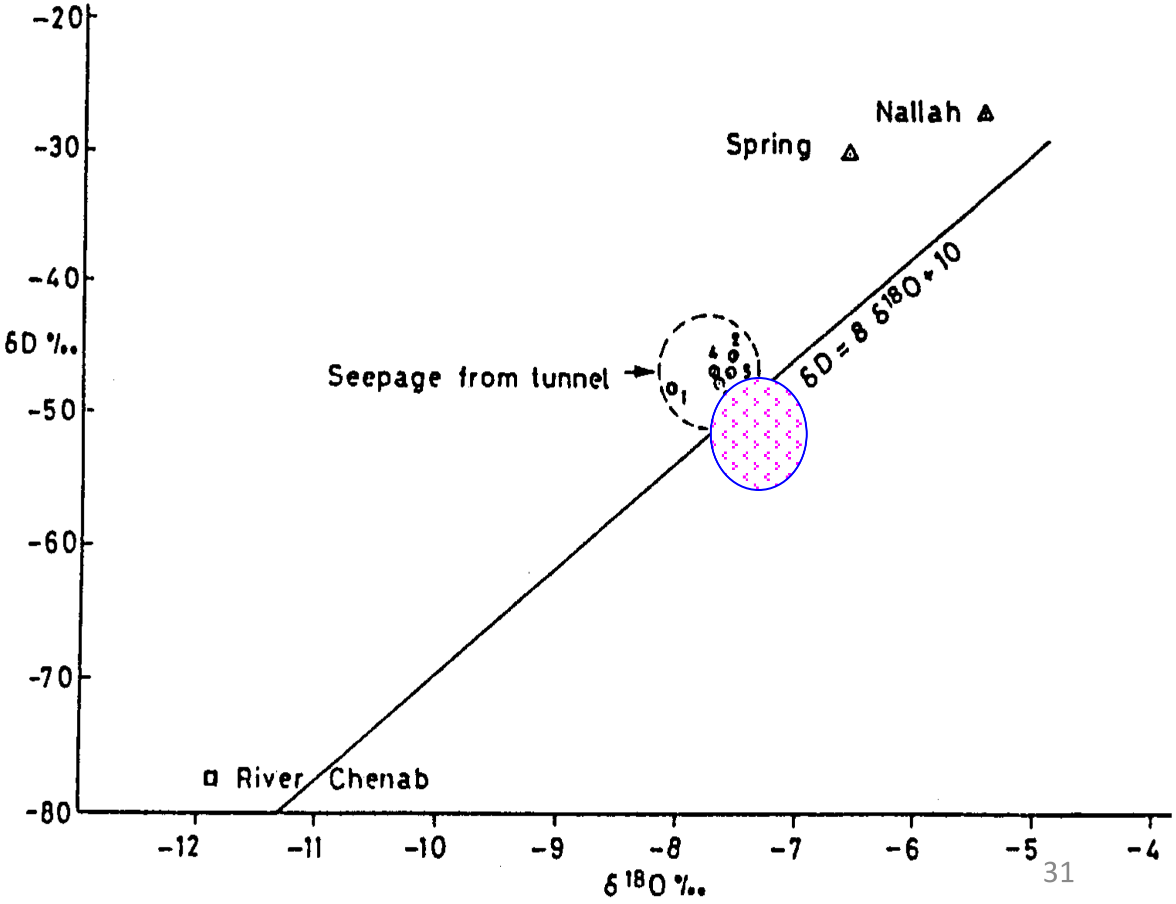
- Tunneling was through a DOLOMITIC ROCK, highly jointed and often crumbly and sheared [Tunnel: 2.4 km long & 11 m dia, to carry the tail waters from the power house and put them back into the river (CHENAB).

Possible sources of seepage

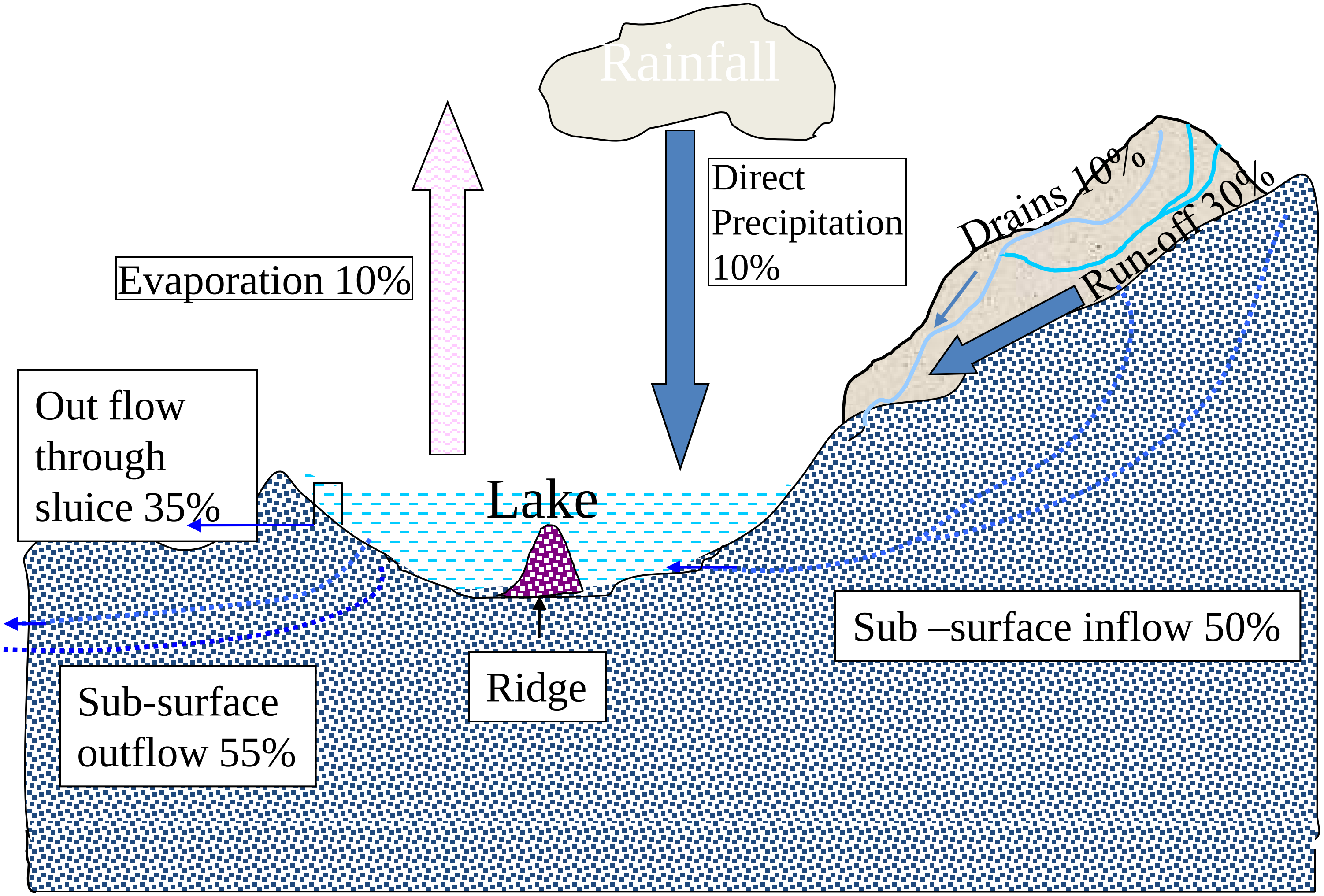
- **Chenab river,** which hugs the hill and/or
- **Perched water bodies,** in the rock mass above the tunnel

INFERENCES

- · δD & $\delta^{18}O$ of seepages from the tunnel is different from the River CHENAB and other surface waters
  - Local waters not the source
- River CHENAB has depleted isotopic composition as it originates from higher altitudes of Himalayas



WATER BALANCE COMPONETS OF LAKE NAINITAL



Rainfall

Evaporation 10%

Direct Precipitation 10%

Drains 10%

Run-off 30%

Out flow through sluice 35%

Lake

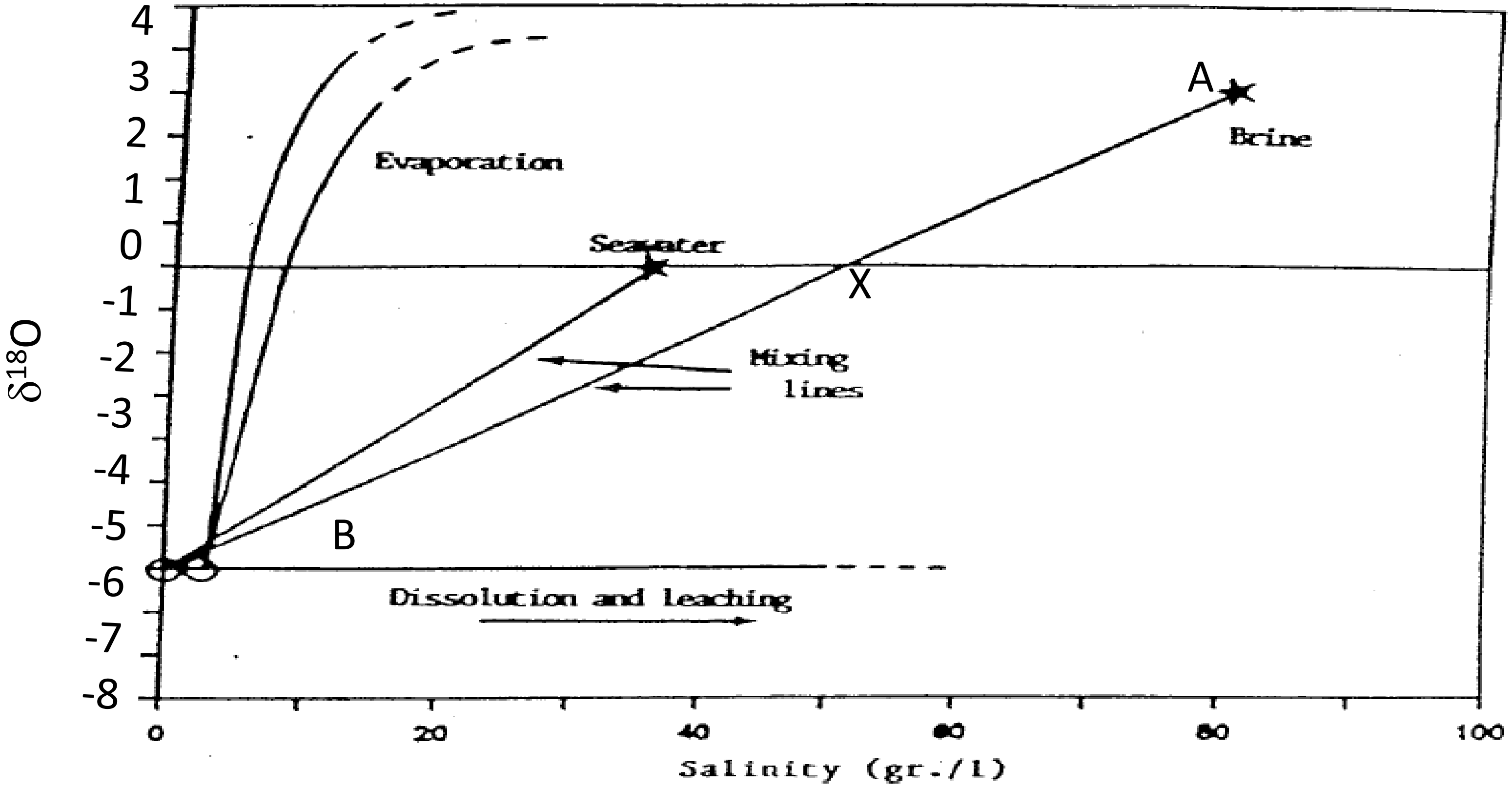
Ridge

Sub –surface inflow 50%

Sub-surface outflow 55%

% expressed with respect to the total inflow (4.45 Mm^3) and outflow (4.68 Mm^3).

RELATION BETWEEN SALT CONTENT AND STABLE ISOTOPES FOR DIFFERENT SALINIZATION MECHANISMS

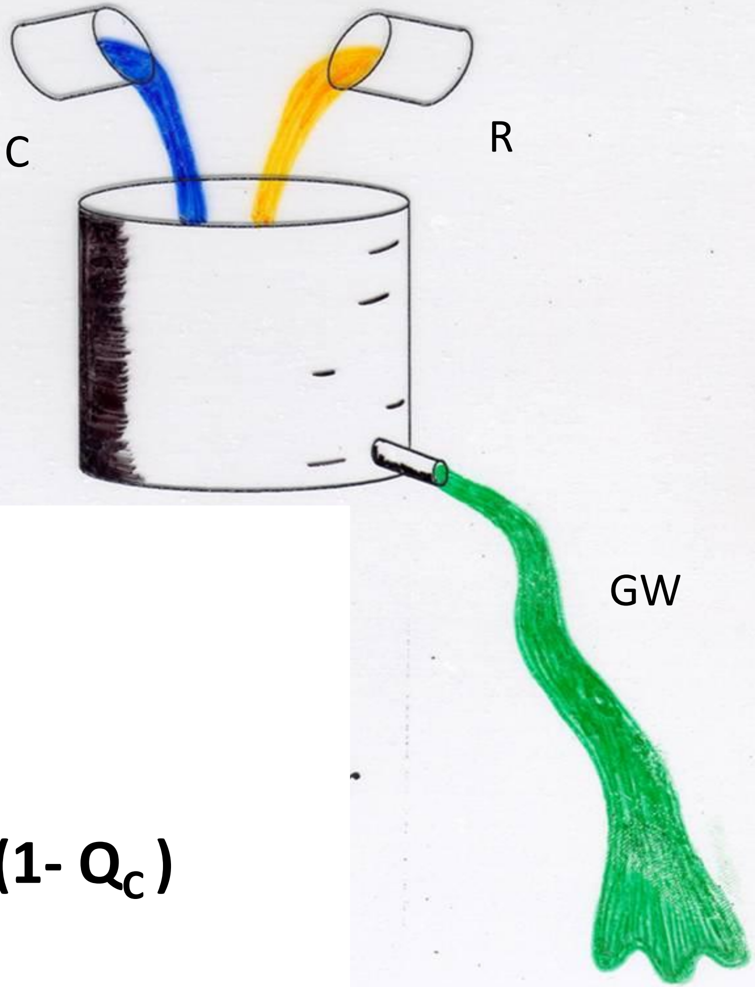


Evaporation: Enriches δ^{18} O and δD; not much increase in salinity

Leaching of salts: Increase in salinity, marginal enrichment in δ^{18} O and δD

Mixing with saline water: Enrichment in δ^{18} O, δD and salinity

Two End Member Mixing Model

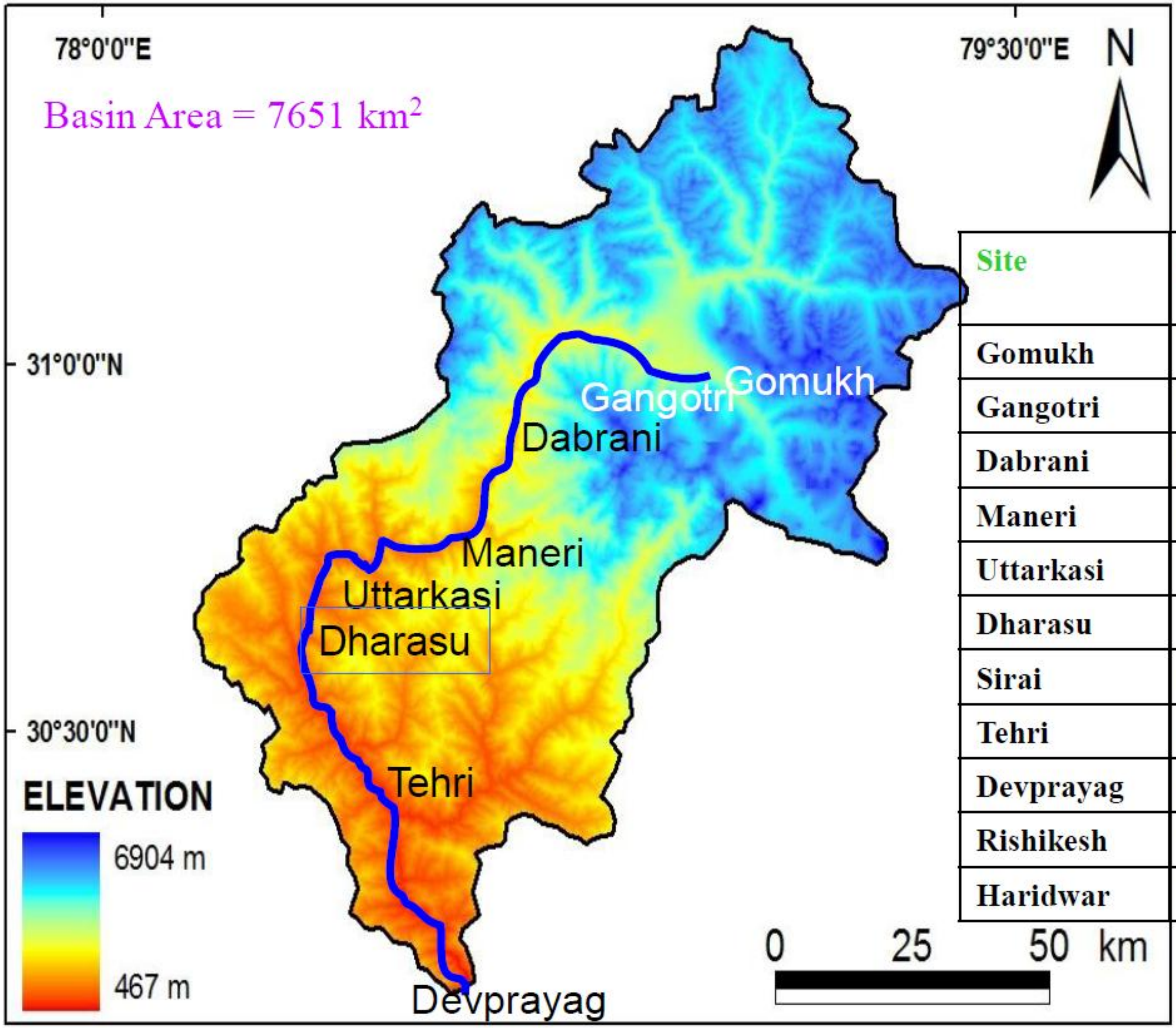


$$Q_{GW} = Q_C + Q_R$$

$$1 = Q_C + (1 - Q_C)$$

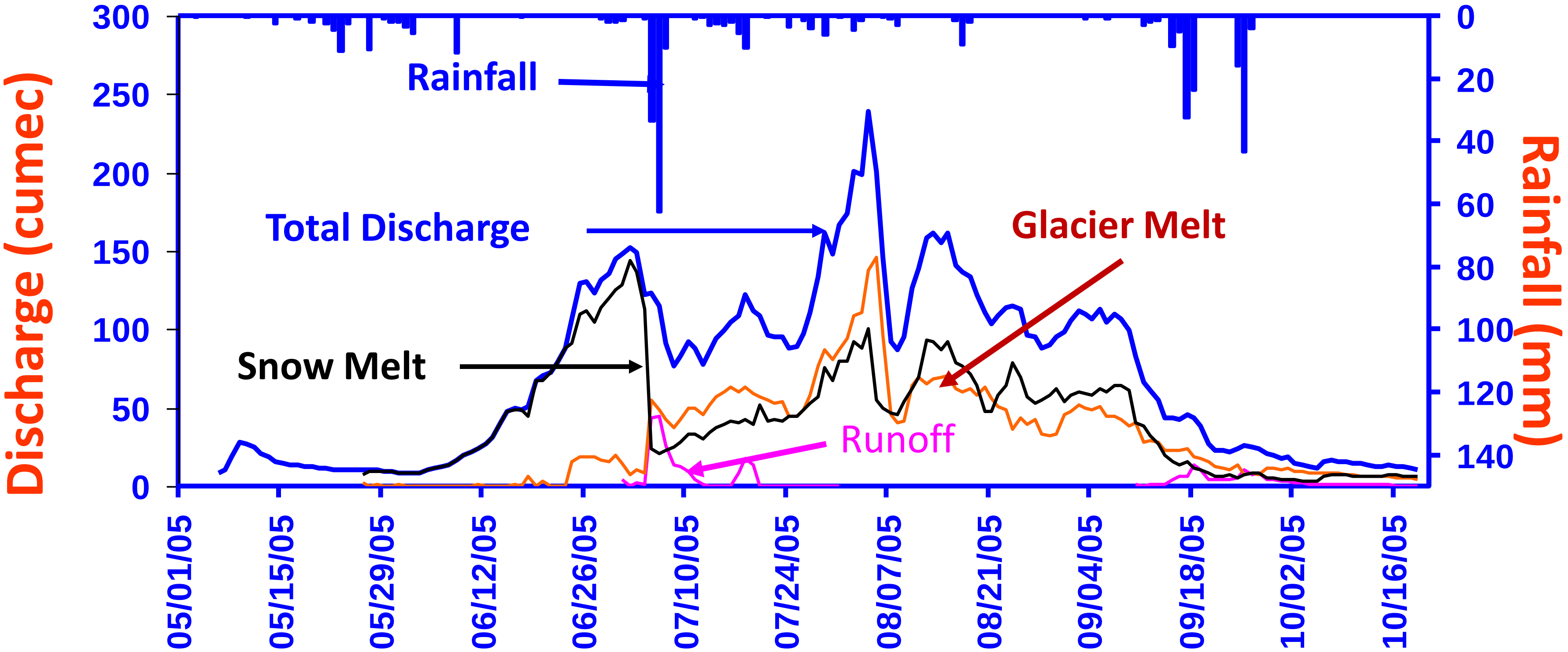
$$\delta_{GW} = \delta_C Q_C + \delta_R (1 - Q_C)$$

$\therefore Q_C$ can be estimated
$\therefore$ Q_R and Q_{GW} also can be estimated.



Site	Distance (km)	Altitude (m)
Gomukh	0	3800
Gangotri	18	3050
Dabrani	68	2050
Maneri	110	1300
Uttarkasi	138	1140
Dharasu	168	839
Sirai	183	630
Tehri	198	640
Devprayag	233	481
Rishikesh	293	356
Haridwar	320	274

Hydrograph Separation Using Isotopic Technique at Gomukh

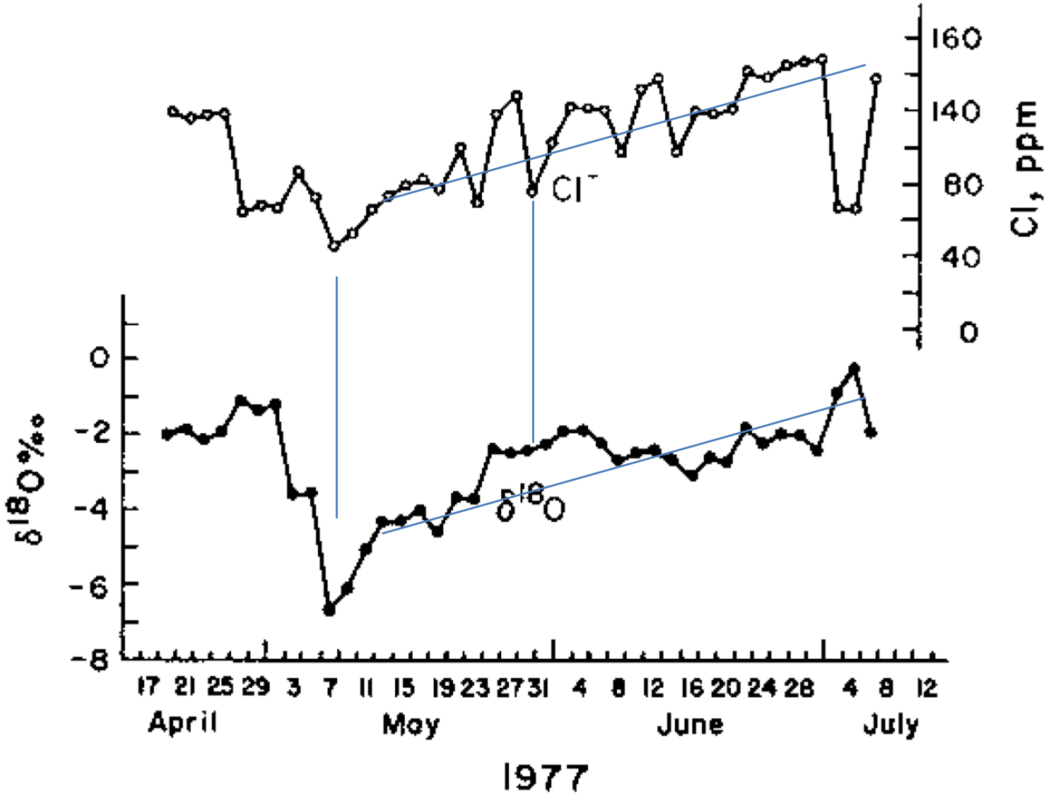


<u>Out of Total Discharge</u>

Snow Melt water = 56%

Glacier Melt water = 41%

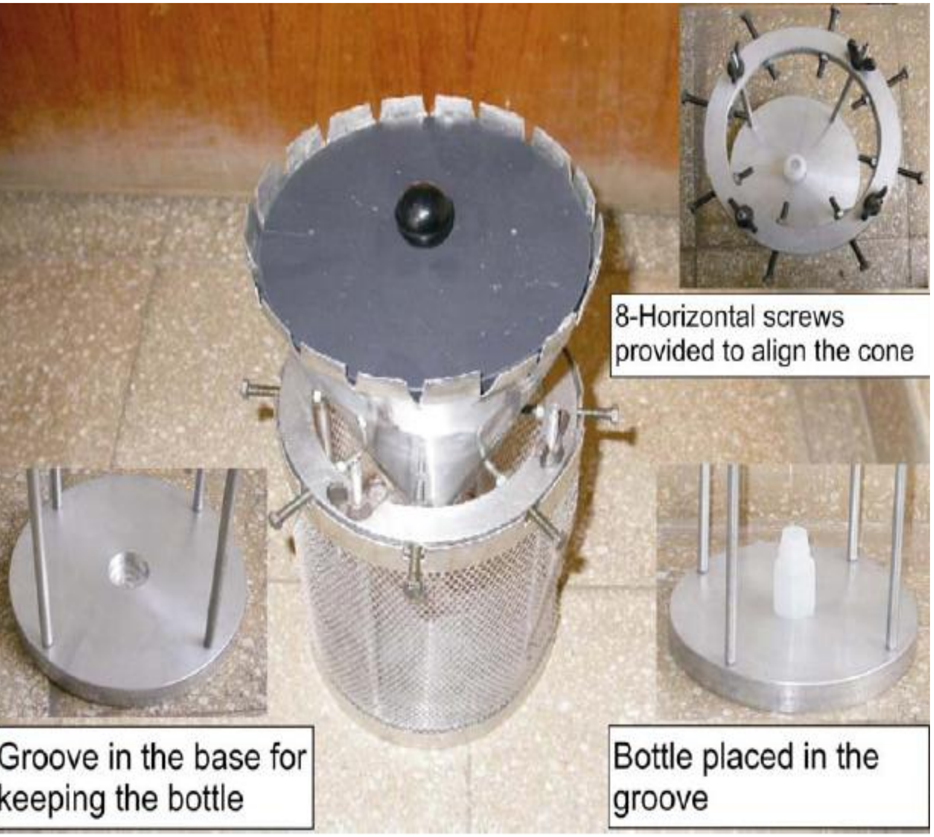
Rainfall Contribution = 3%



Chemical (Cl) and Isotope (δ^{18}O) correlation: -

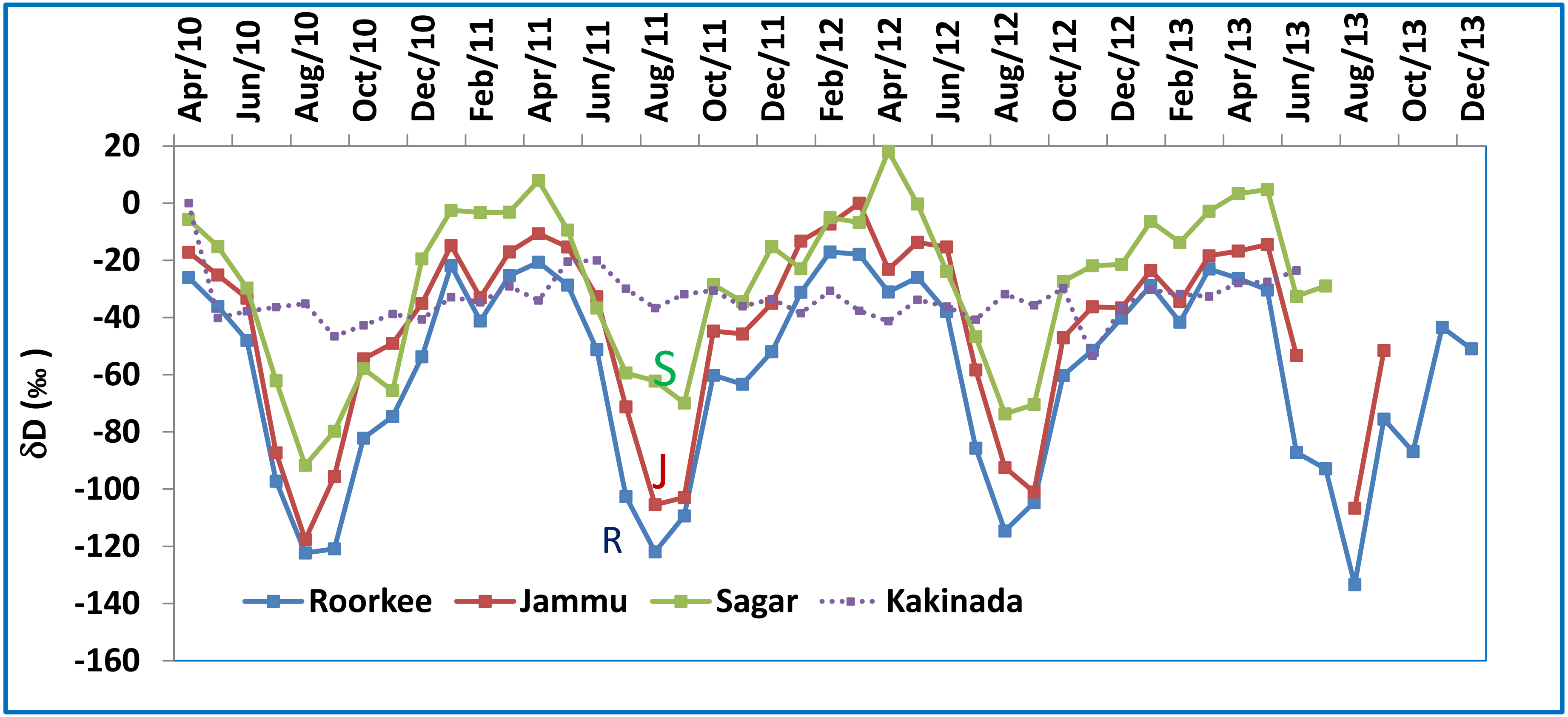
Chloride and δ^{18}O values in repeatedly collected samples of the Pajeu River, northeastern Brazil. A general correlation is seen, revealing the role of evaporation, most important during July (rise in ambient temperatures and low river flow). (From Salati et al., 1980.)

CONDENSATION METHOD



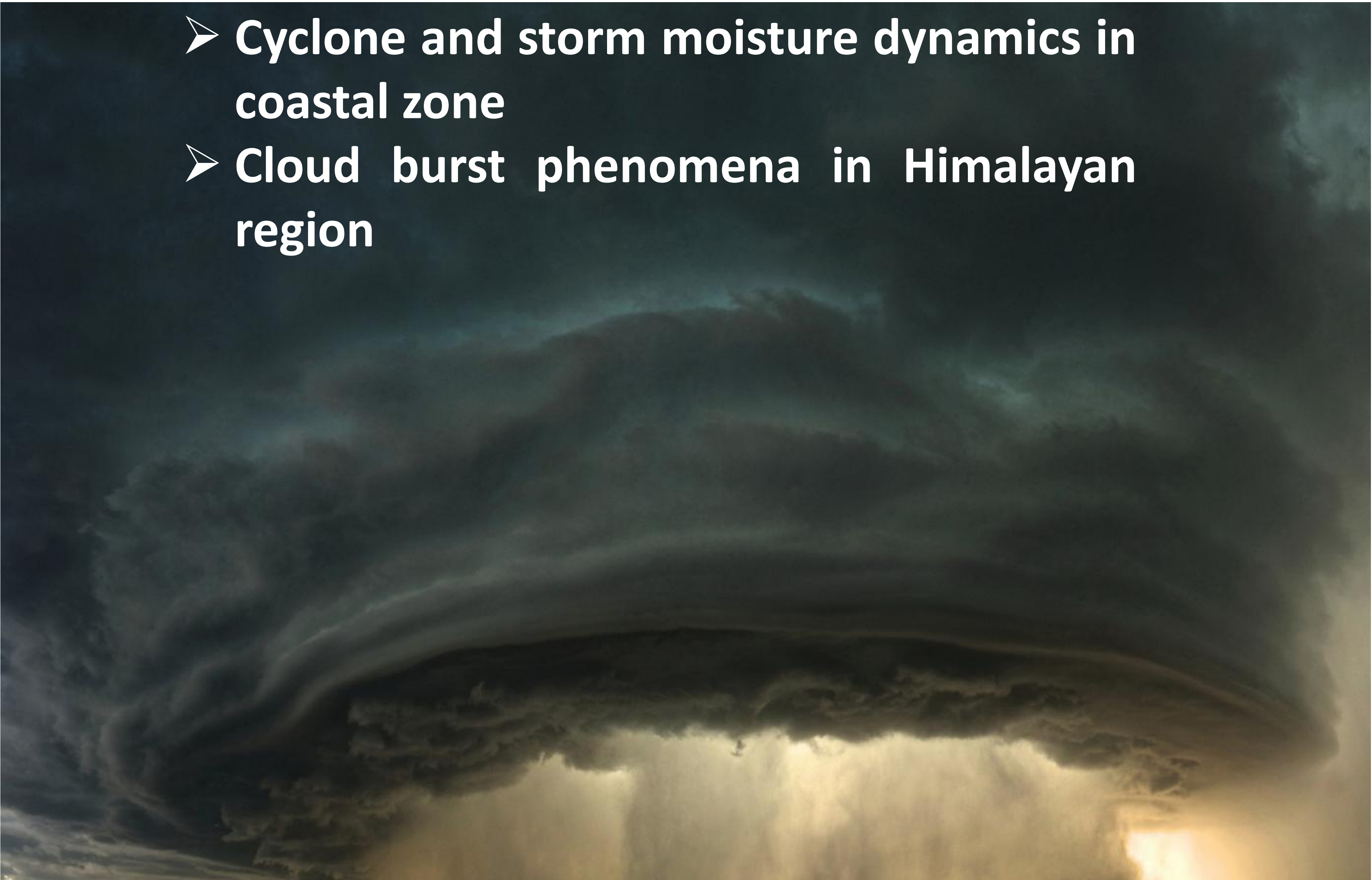
No-LN_2

VARIATION OF ISOTOPIC COMPOSITION OF GLV(LIQUID CONDENSATION METHOD)



New Avenues:

- **Vapour dynamics in arid regions**
- **Cyclone and storm moisture dynamics in coastal zone**
- **Cloud burst phenomena in Himalayan region**



Isotopes

Stable

Unstable

Environmental

Equation for Radioactive Decay

$$A_t = A_0 \exp^{(-\lambda t)}$$

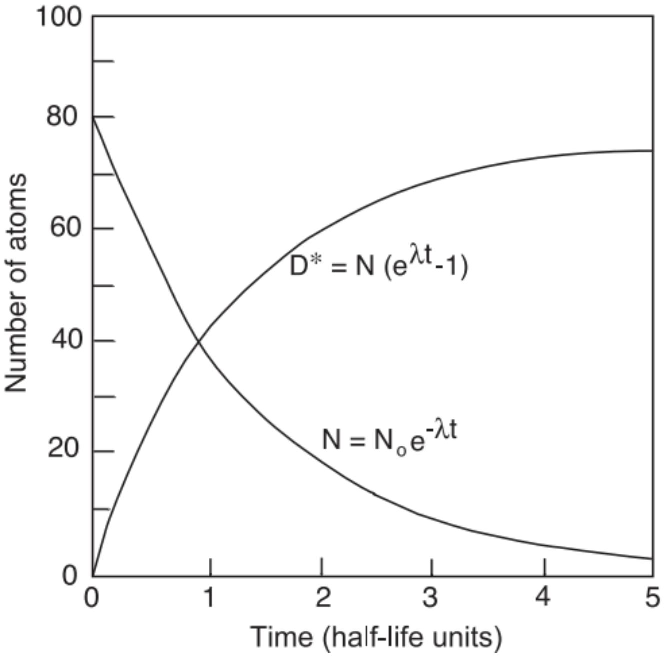
$\lambda = 0.693/(t_{½})$

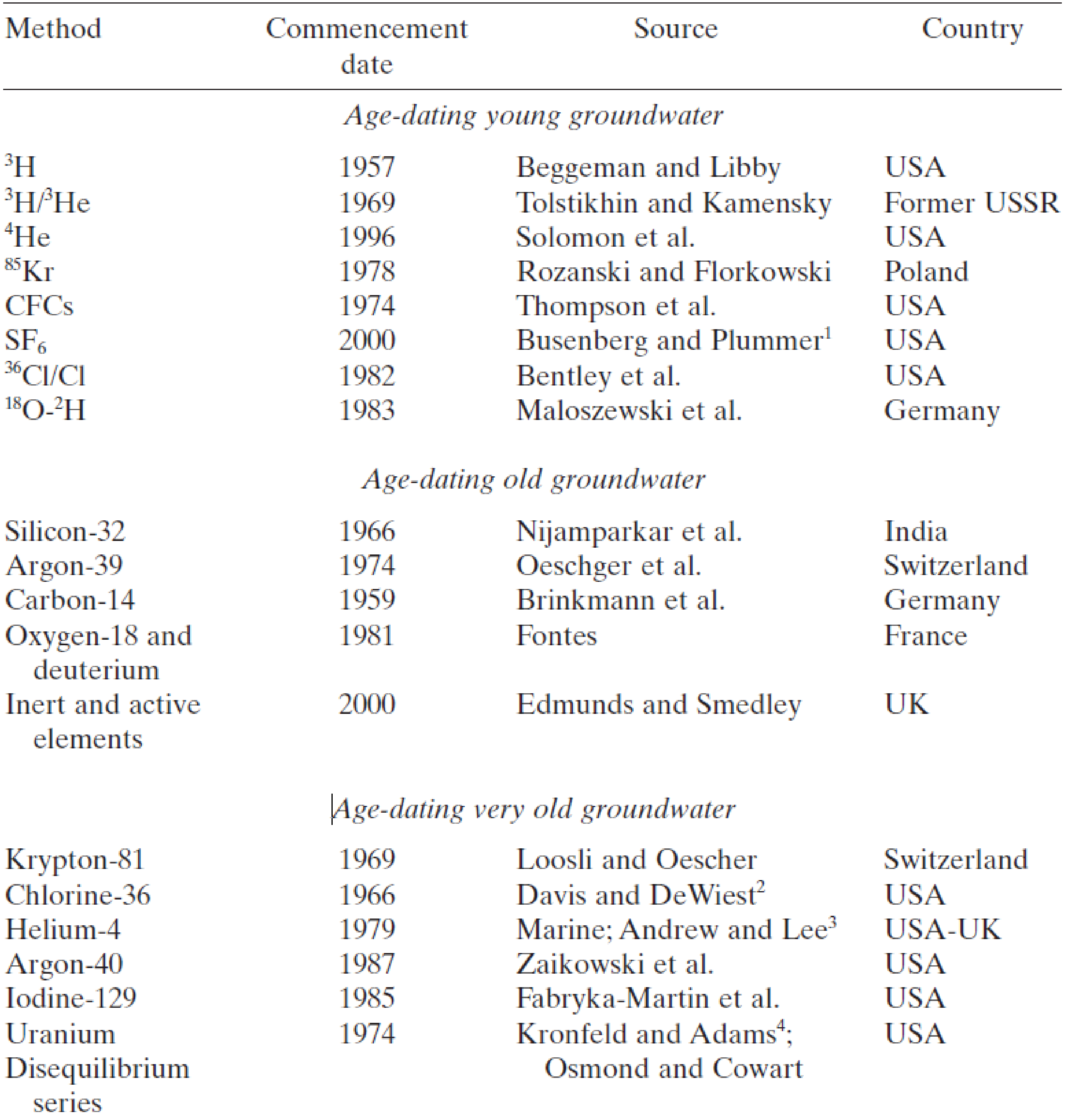
The decay of parent atoms N at any time t is given by : $N = N_0 x e^{-\lambda t}$

D^* is the amount of daughter isotope produced during time t; $D^* = N_0 - N$

If D_0 is those present initially then the total daughter isotope 'D' after time t is

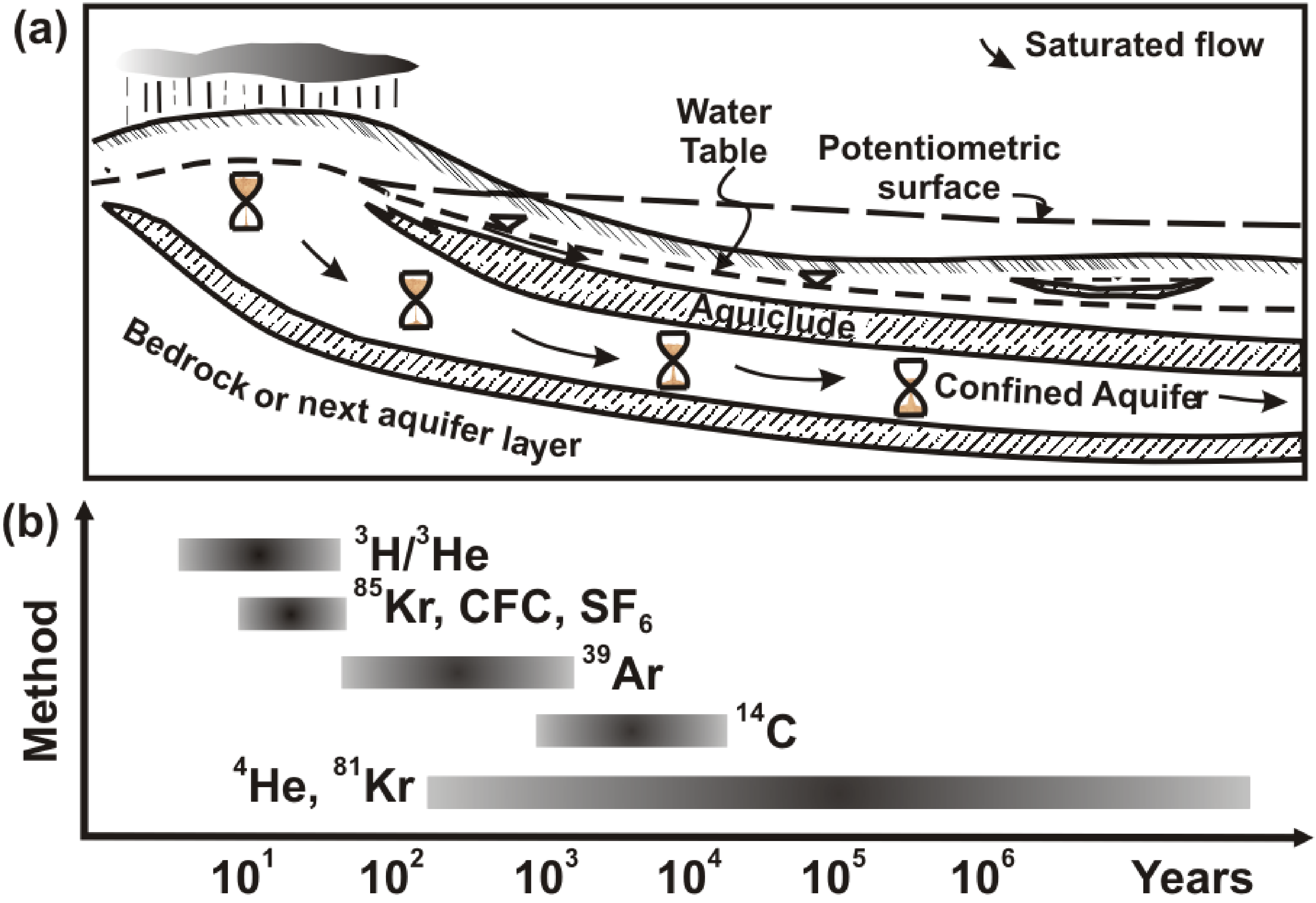
$$D = D_o + N(e^{\lambda t} - 1)$$





Method	Commencement date	Source	Country
Age-dating young groundwater			
^{3}H	1957	Beggeman and Libby	USA
$^{3}H/^{3}He$	1969	Tolstikhin and Kamensky	Former USSR
^{4}He	1996	Solomon et al.	USA
^{85}Kr	1978	Rozanski and Florkowski	Poland
CFCs	1974	Thompson et al.	USA
SF_6	2000	Busenberg and Plummer[1]	USA
$^{36}Cl/Cl$	1982	Bentley et al.	USA
^{18}O-^{2}H	1983	Maloszewski et al.	Germany
Age-dating old groundwater			
Silicon-32	1966	Nijamparkar et al.	India
Argon-39	1974	Oeschger et al.	Switzerland
Carbon-14	1959	Brinkmann et al.	Germany
Oxygen-18 and deuterium	1981	Fontes	France
Inert and active elements	2000	Edmunds and Smedley	UK
Age-dating very old groundwater			
Krypton-81	1969	Loosli and Oescher	Switzerland
Chlorine-36	1966	Davis and DeWiest[2]	USA
Helium-4	1979	Marine; Andrew and Lee[3]	USA-UK
Argon-40	1987	Zaikowski et al.	USA
Iodine-129	1985	Fabryka-Martin et al.	USA
Uranium Disequilibrium series	1974	Kronfeld and Adams[4]; Osmond and Cowart	USA

Age dating methods, the commencement dates, the pioneering scientists, and the country of origin


(a)
Saturated flow
Water Table
Potentiometric surface
Aquiclude
Confined Aquifer
Bedrock or next aquifer layer
(b)
Method
$^3H/^3He$
^{85}Kr, CFC, SF_6
^{39}Ar
^{14}C
^4He, ^{81}Kr
10^1
10^2
10^3
10^4
10^5
10^6
Years

- *Groundwater age is defined as the amount of time that has elapsed since a particular water molecule of interest was recharged into the subsurface environment system until this molecule reaches a specific location in the system where it is either sampled physically or studied theoretically for age-dating.*

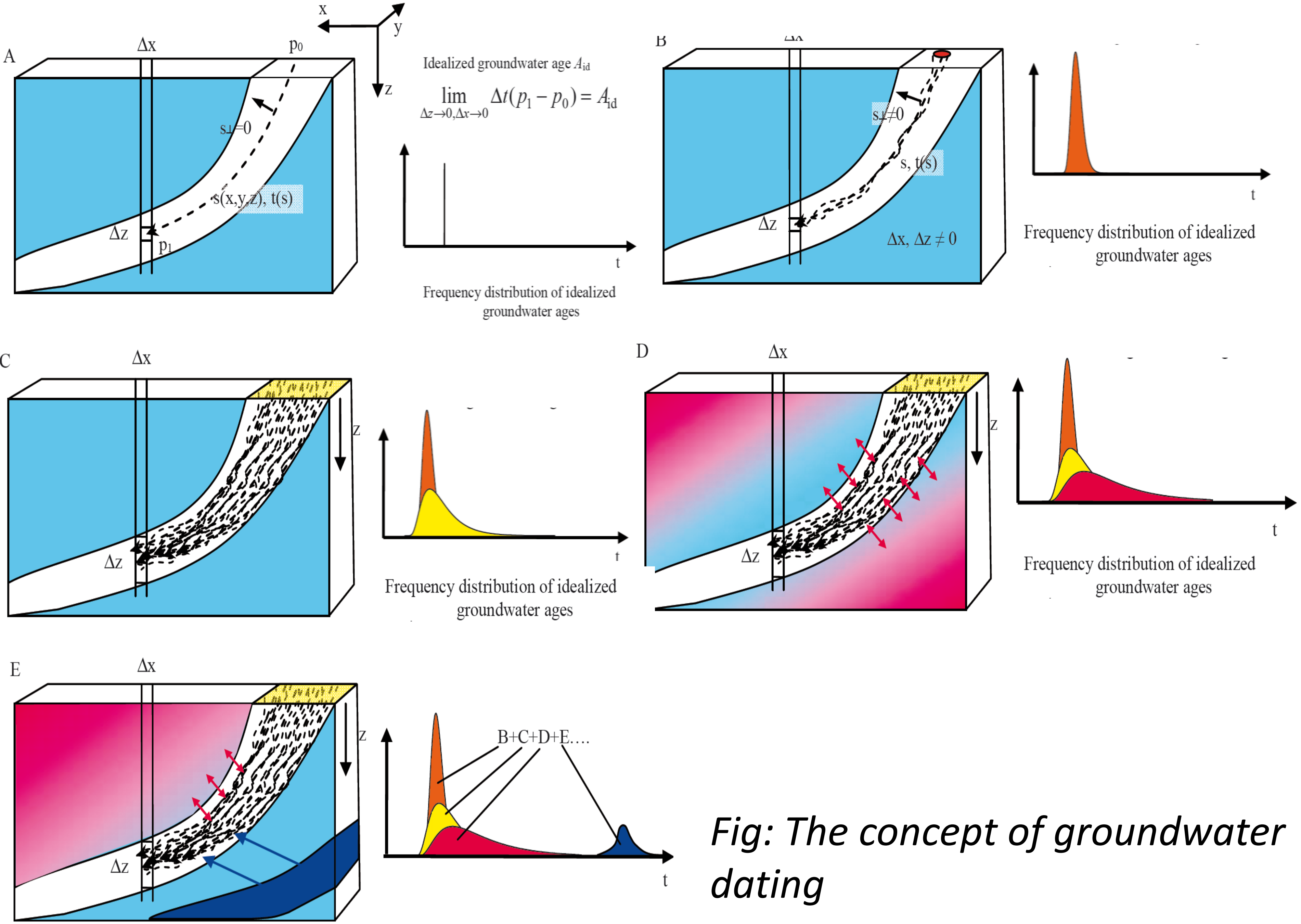
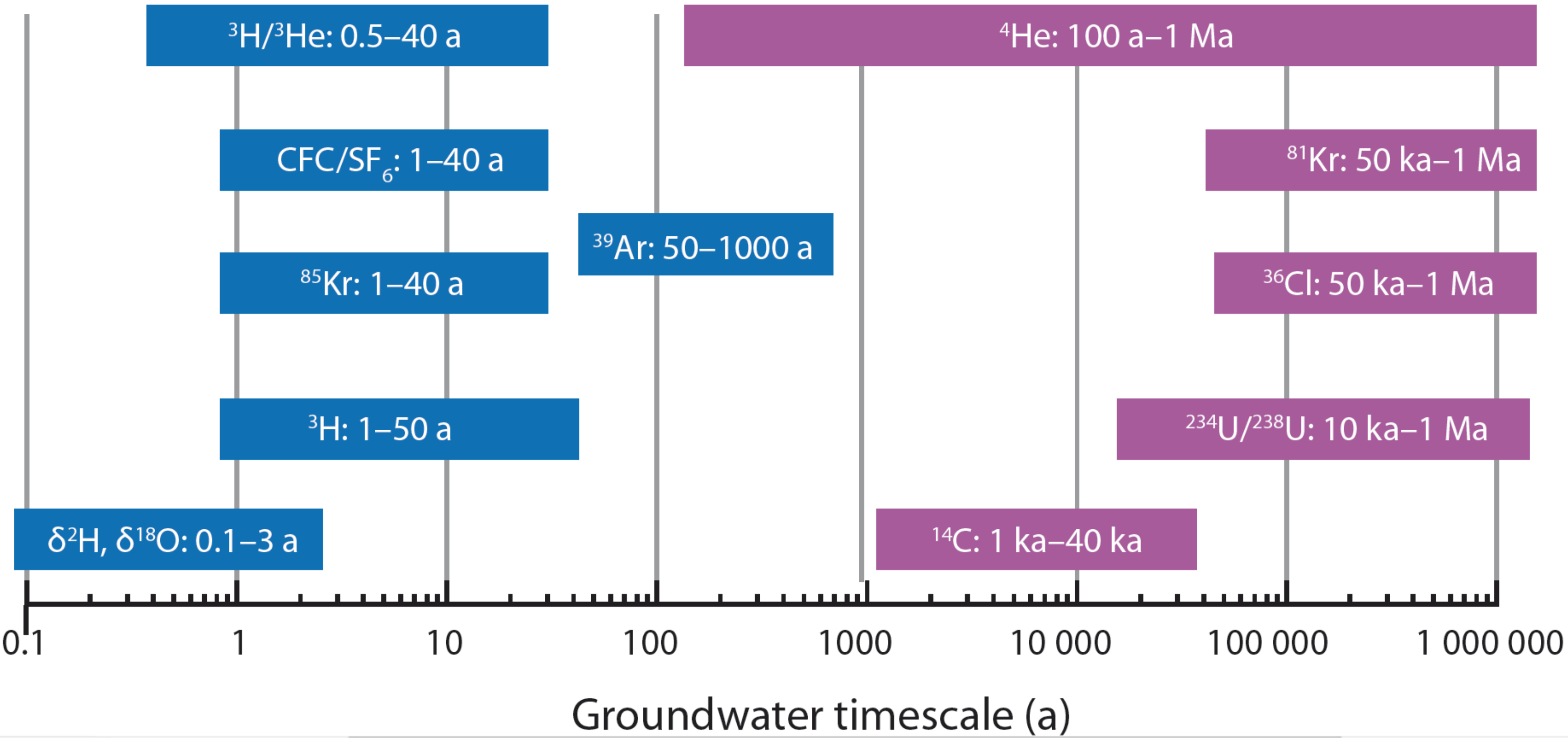
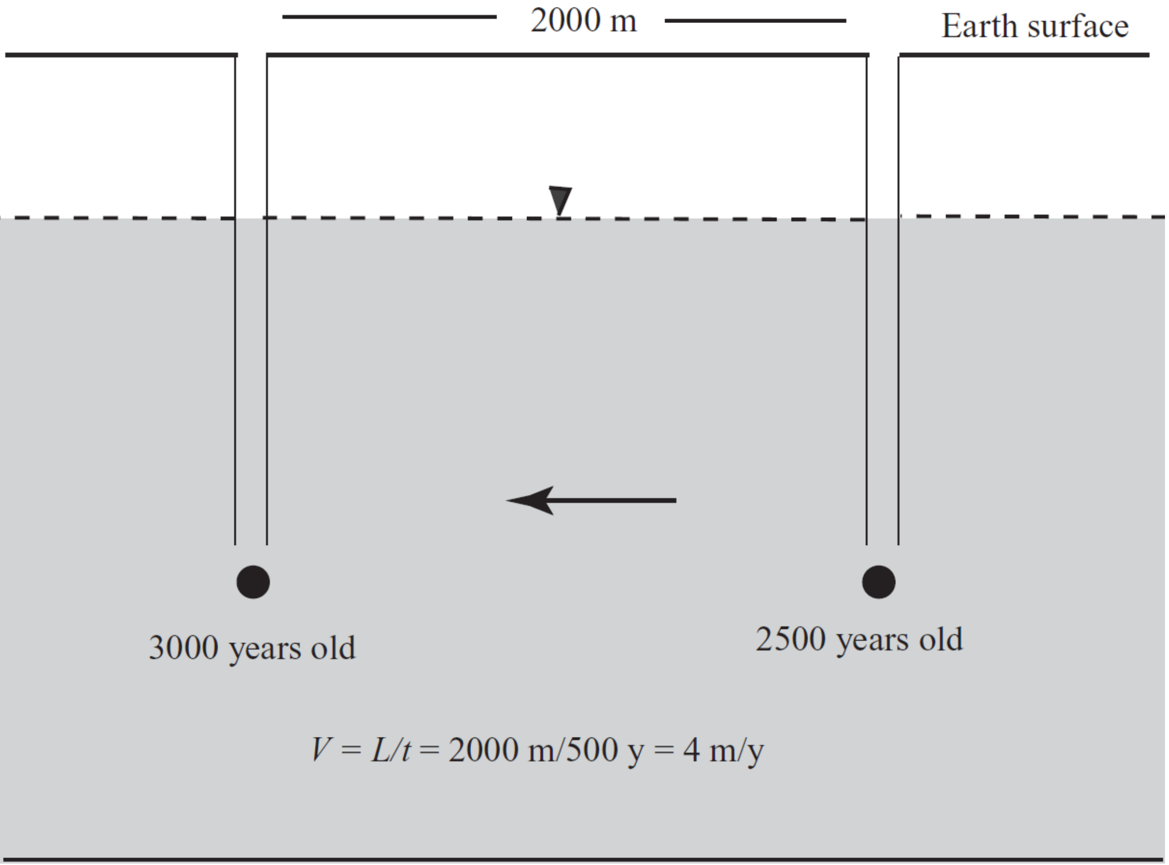


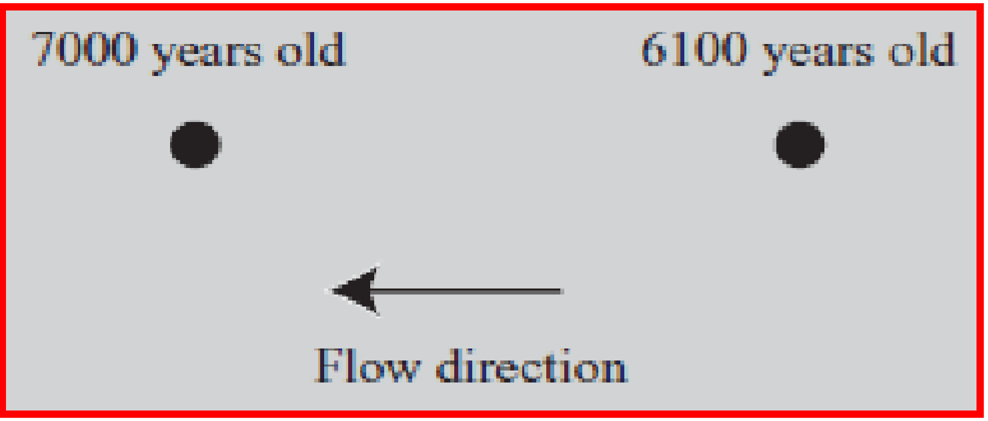
Fig: The concept of groundwater dating



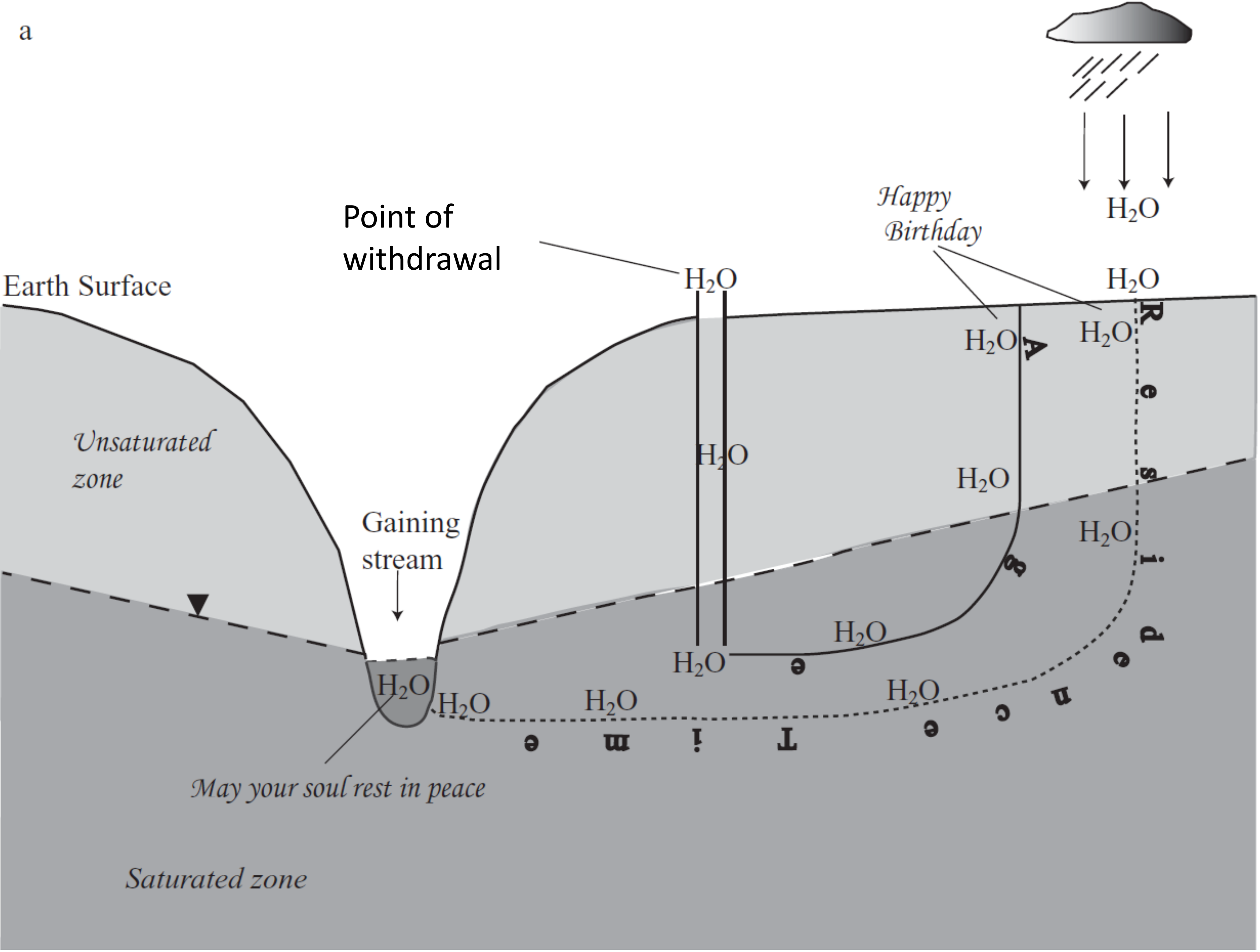
³H/³He: 0.5–40 a
⁴He: 100 a–1 Ma
CFC/SF₆: 1–40 a
⁸¹Kr: 50 ka–1 Ma
³⁹Ar: 50–1000 a
⁸⁵Kr: 1–40 a
³⁶Cl: 50 ka–1 Ma
³H: 1–50 a
²³⁴U/²³⁸U: 10 ka–1 Ma
δ²H, δ¹⁸O: 0.1–3 a
¹⁴C: 1 ka–40 ka
0.1
1
10
100
1000
10 000
100 000
1 000 000
Groundwater timescale (a)



Groundwater flow rate analysis require distance between piezometers and age of groundwater in each piezometer.



1) Evaluating the pollution of gw
2) GW flow velocity
3) Resource assessment: Mapping of old gw
4) GW freshening by mixing with modern recharge
5) Mapping of waste disposal sites, recharge sites etc.



Point of withdrawal

Absolute Age,
Relative Age,

GW residence time = GW age + GW life expectancy

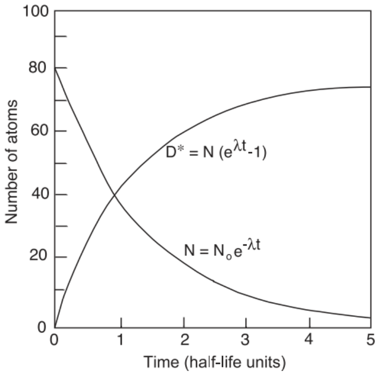
Groundwater age may be derived by various means:

Decay of Radioisotope

From decreases in concentration of radioactivity with time due to decay of radioactive decay using the equation: $A=A_0\exp(-\lambda t)$

Eg: ^{3}H, ^{14}C, ^{32}Si, ^{35}S, ^{36}Cl, ^{39}Ar and ^{81}Kr

Combined parent and daughter product: ^{3}H-^{3}He dating



Accumulation of daughter isotope: Example: ^{4}He accumulating from radioactive decay of U and Th; ^{40}Ar from decay of K

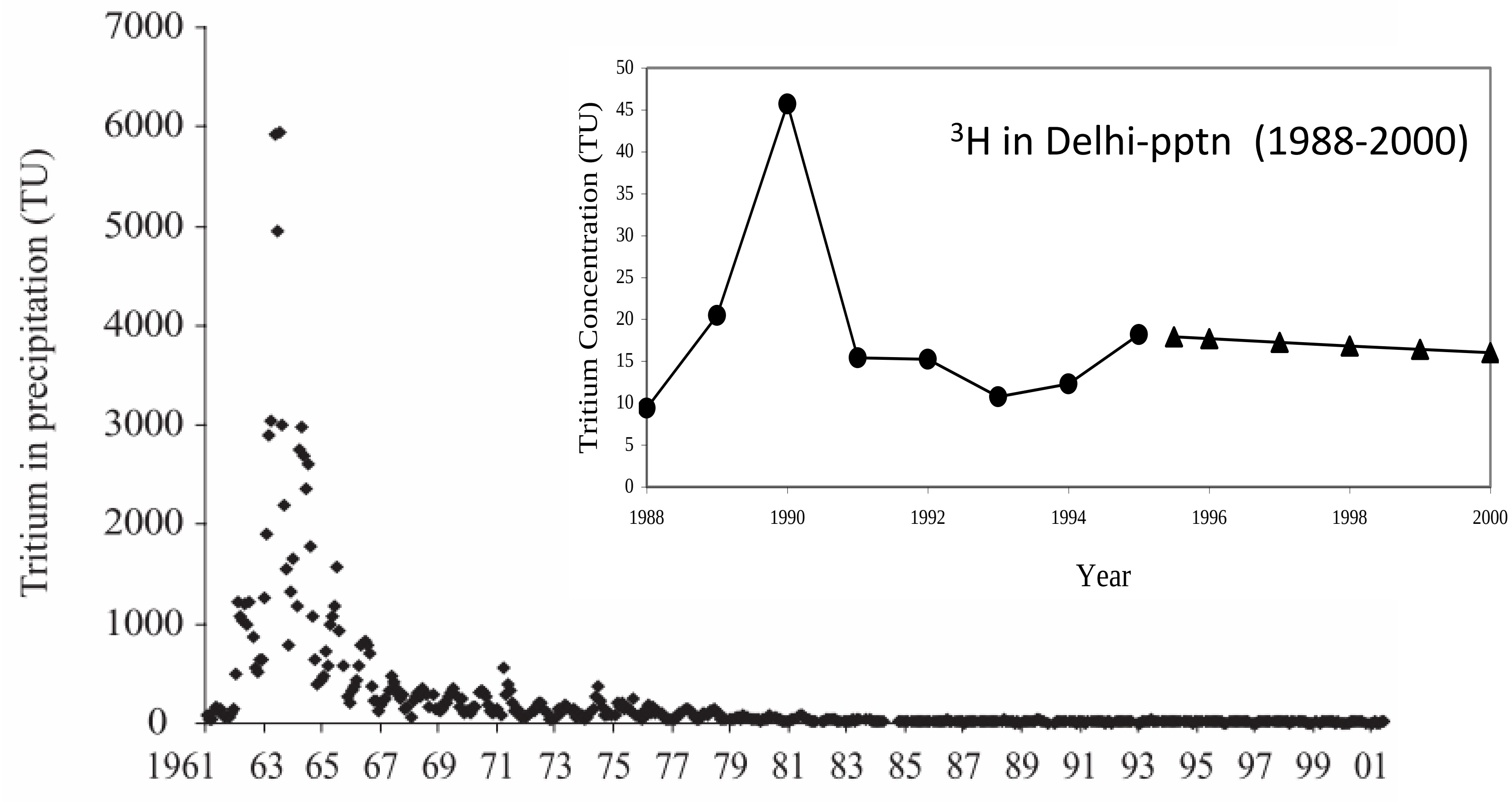
Event markers : ^{3}H, ^{85}Kr, CFC and SF_6 etc. Change in concentration with time has fixed behaviour . The method works over the period during which input concentrations have changed and when they have been measured or can be modelled reliably. Since most of these markers are anthropogenic, they provide age for young waters.

DATING YOUNG GROUNDWATERS

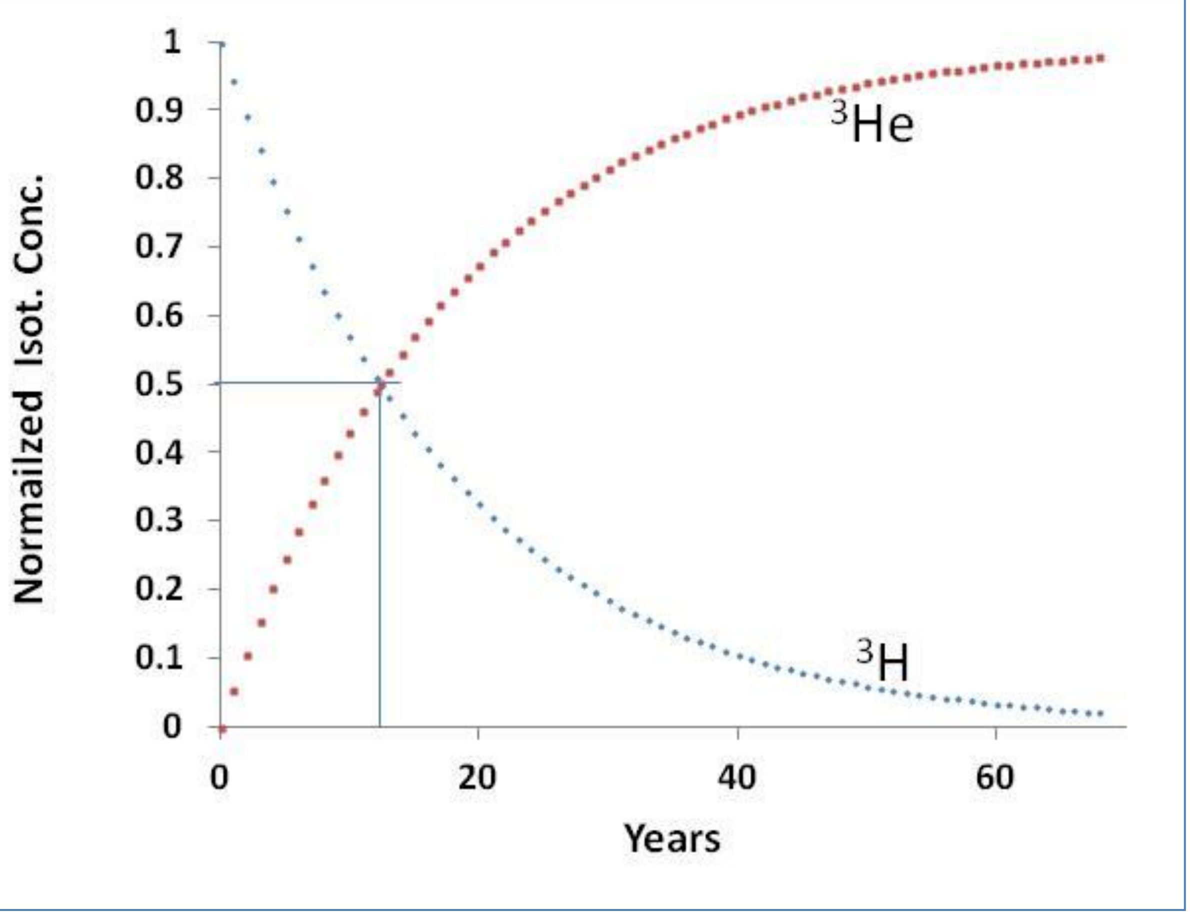
^{3}H dating

Atmospheric production of tritium: By cosmic-ray bombardment of fast neutrons (>4MeV) and atmospheric nitrogen (Young and Foster, 1972):

$$^{14}_{7}N + n \rightarrow {}^{12}_{6}C + {}^{3}_{1}H$$



Tritium in the atmospheric precipitation at Vienna,



Tritium Dating
Half life: 12.33 yrs

$^3_1$H → $^3_2$He + β^- (E_{max} = 18 KeV)

$$t = -17.77 \ln \frac{^3\mathrm{H}_t}{^3H_o}$$

1) ^{3}H: Easy to measure; difficult to assess exact initial concentration.
2) ^{3}H-^{3}He: Expensive technique, very few labs in the worldwide operating, contamination from other ^{3}He sources.

1 TU = 1 mg THO/10^9 tones H_2O

= 6.686×10^{10} tritium atoms/kg of water

= 1(^{3}H)/10^{18}(^{1}H) = 0.1181 Bq/kg

= 3.193 pCi/kg = 7.1 dpm/l of water.

1Bq/L =8.47 TU

Calculate ^{3}H activity of 1TU water:

No. of H atoms in 1 L of H_2O: 6.023×10^{23}x2 (H atoms)x(1000/18 molecular wt) = 66.92×10^{24}

TU is defined as 1 atom of ^{3}H in 10^{18} atoms of H.

If the above water is 1TU then it contains $66.92\times10^{24}/10^{18}$ no of ^{3}H atoms= 66.92×10^6 no. of ^{3}H atoms in 1 liter of water.

Sp. Activity = $N\lambda$ = 66.92 $\times10^6$x (0.693/12.33 years) = 0.119 counts/sec/liter of water

=0.119Bq/kg

1TU =0.119 Bq/L therefore, 1Bq/L = 8.4TU

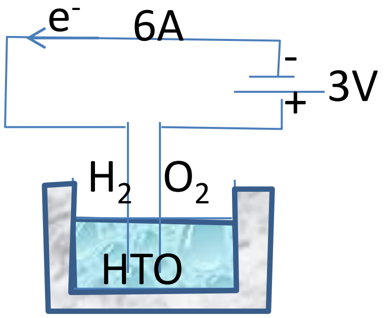
Tritium Measurement in Groundwater

Sample Collection : 600 ml

Primary Distillation: To remove salts (to avoid corrosion)

Enrichment of tritium (Electrolytic enrichment):

$$\begin{array}{l} H_2O, HTO \\ (500\ ml) \end{array} \xrightarrow[Na_2O_2]{DC\ Current,\ T\sim0^0C} 20ml\ Enriched\ water$$



Post Distillation: with $PbCl_2$ to remove Na, to recover H_2

Beta Counting : Sample +Cocktail

Step 1. Enrichment: STD, Sample -> k times activity

Step 2: Beta counting: $(\text{Counts})_{STD}$ for known $[\text{TU (activity)}]_{STD}$

Step 3: Estimation of Instrument calibration factor: TU/count

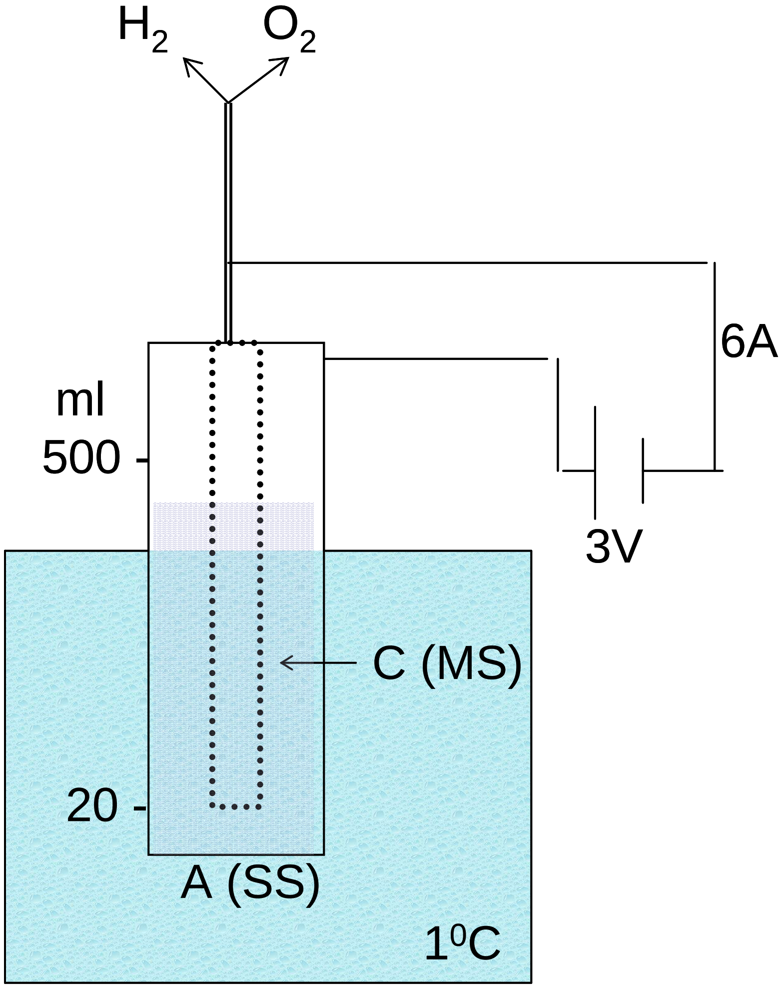
Step 4: Sample activity (beta count is measured)

Step 5: $(\text{Count})_{Sample}$ x Inst. Calib. Factor = TU of sample

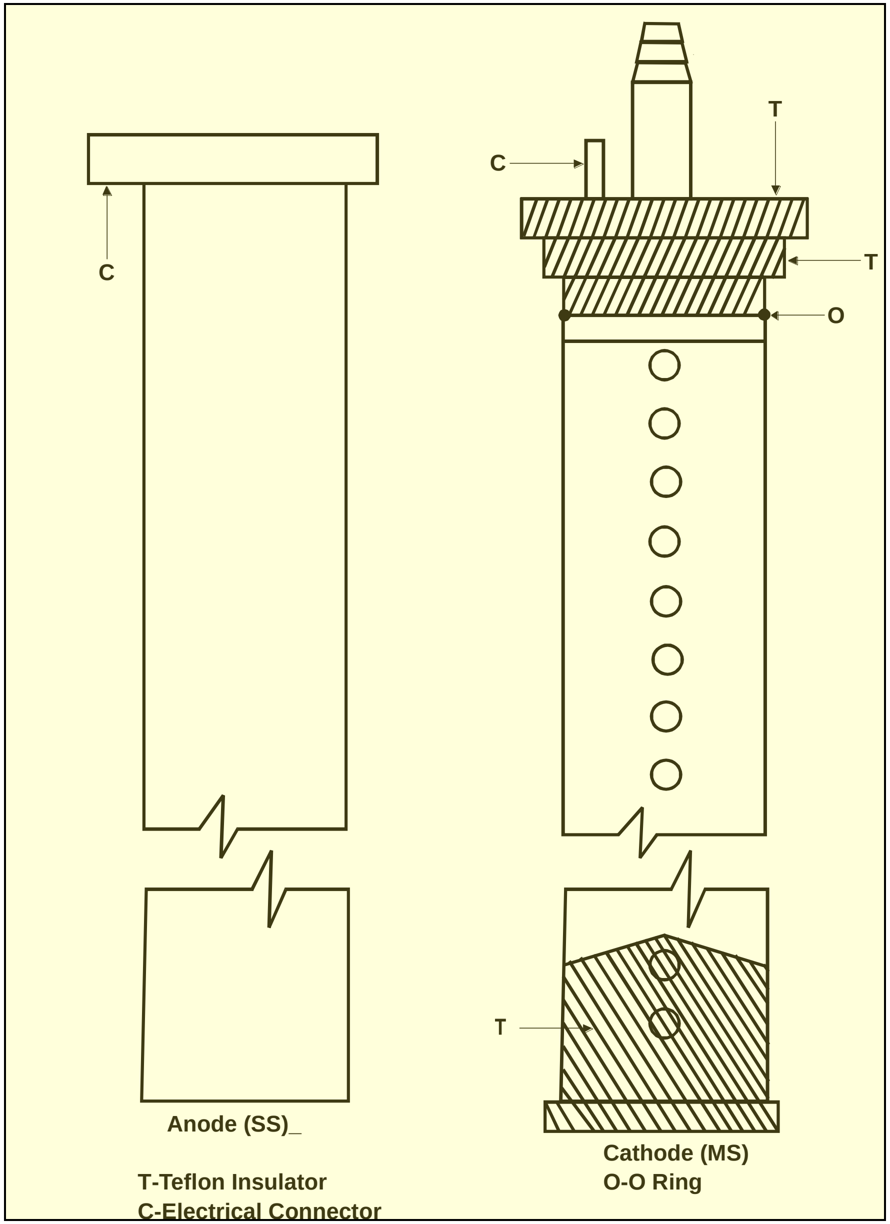
Instruments For Groundwater Dating

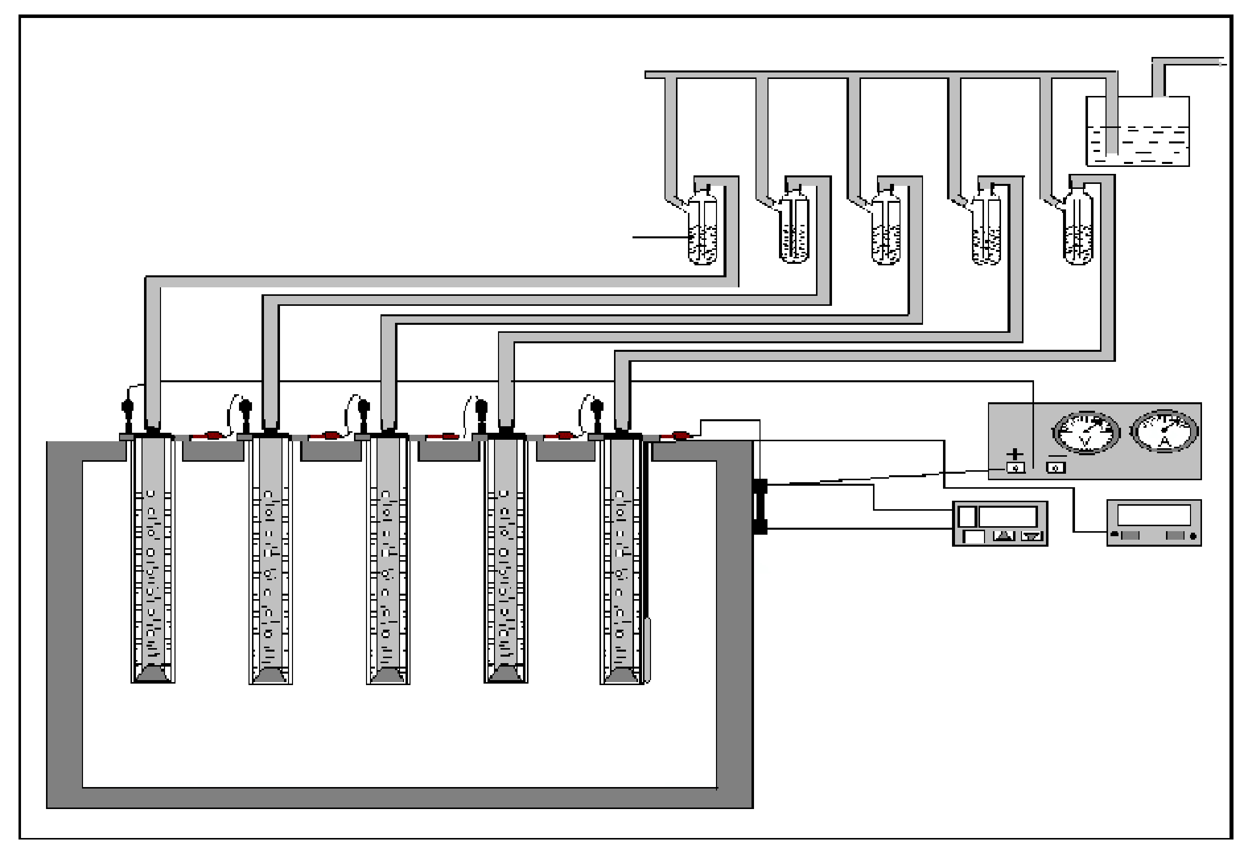
BENZINE SYNTHESISER

Ultra Low Level Liquid Scintillation Counter



Tritium Enrichment (Schematic)





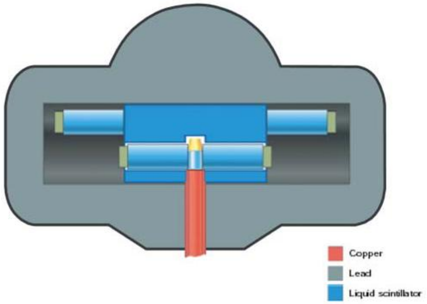
Tritium Enrichment Unit

Post Distillation

$Na_2O_2 + 2H_2O \rightarrow 4NaOH + O_2$

$PbCl_2 + 2NaOH \rightarrow Pb(OH)_2 + 2NaCl$

$Pb(OH)_2 \rightarrow PbO + H2O$



Passive shielding

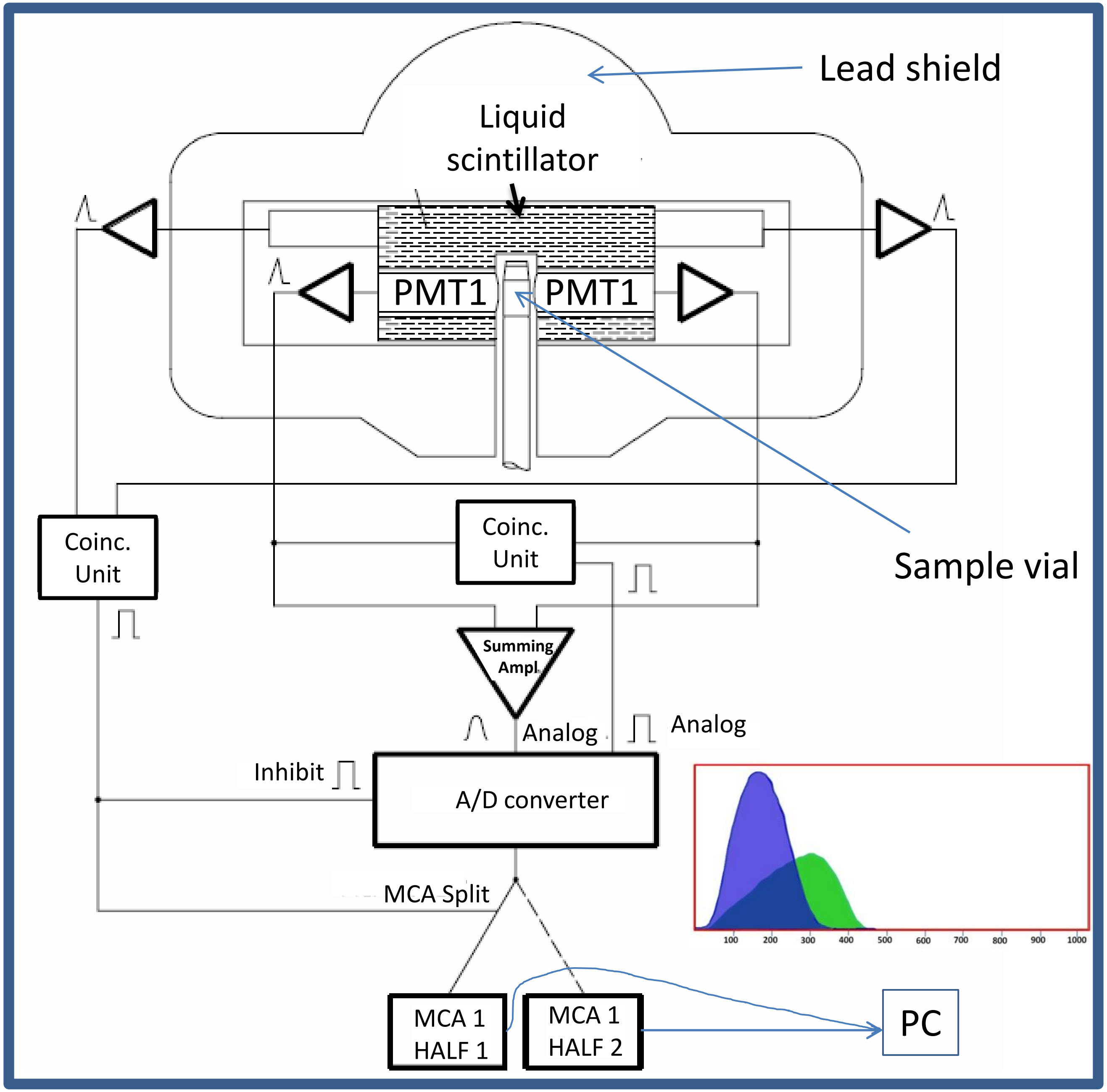


Fig : Ultra Low Level Liquid Scintillation Spectrometer (Front view, internal structure and typical ^{3}H & ^{14}C spectrum)

- <0.8 TU indicates submodern water (prior to 1950s)
- 0.8 to 4 TU indicates a mix of submodern and modern water
- 5 to 15 TU indicates modern water (<5 to 10 years)
- 15 to 30 TU indicates some bomb tritium
- >30 TU: recharge occurred in the 1960s to 1970s

The cost of analysis is about USD 300

Advantages and Disadvantages

Advantages

1. Tritium is a well-established and a well-known method with plenty of references.
2. Laboratory facilities are worldwide and the cost of analysis is relatively small.
3. Tritium can still be regarded as a supplementary dating method.
4. It is the only tracer that is part of the water molecule.

Disadvantages

1. The method is approaching its expiry date.
2. Due to the strong latitudinal variation, it would be difficult to precisely determine the initial value even if the bomb-peak tritium effects on the environment are completely vanished.

Tritium –Helium Dating

Groundwater Age (in years) = $-17.8 \mathit{ln} \, (1+ {}^3He_{trit}/{}^3H)$

Example: The concentration of tritium and tritiogenic helium in a groundwater sample are 53TU and 24.6TU, respectively. What is the age of this sample?

$$t = 17.85 \ln (1+ 24.6/53) = 6.8 \text{ years}$$

Cost of analysis (for $^3H/^3He$ dating) : ~ USD 700

Noble gas	Abundance in air (% by volume)
He	5.2×10^{-4}
Ne	1.8×10^{-3}
Ar	0.934
Kr	1.0×10^{-4}
Xe	9×10^{-6}

Advantages

1. In average situations (medium-thickness unsaturated zone, limited sources of helium, etc.), the resolution of this method is high.
2. Data collected can be used for both $^3H/^3He$ and tritium methods.
3. This method will be applicable for a long time, i.e., its effectiveness is not reduced in the future as is the case with some methods like CFCs, tritium, etc.
4. This method does not need the initial value, a parameter that is fundamental and problematic for many of the dating methods.

Disadvantages

1. Sampling and analysis are expensive and laboratory facilities are not available worldwide.
2. It is a difficult exercise to separate tritiogenic helium from the other heliums.

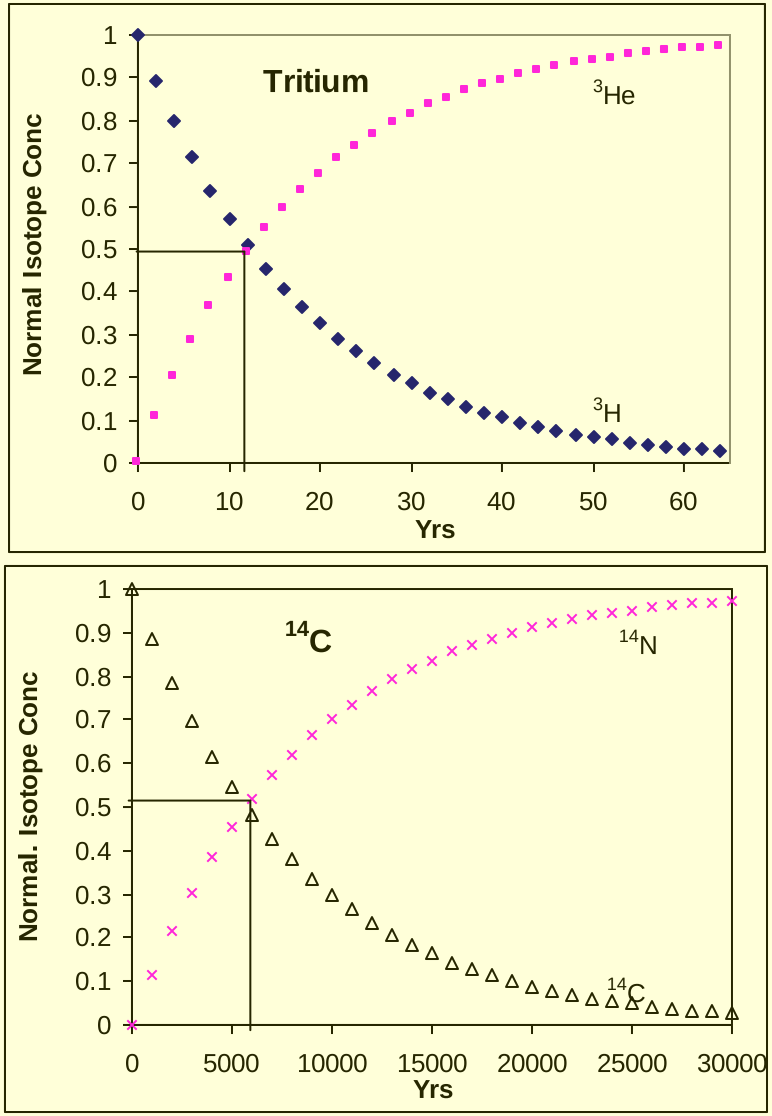
$$\lambda = 0.693/(t_{½})$$

$t_{½}$ for ^{3}H= 12.32 years, for ^{14}C =5730 years

For tritium: $A= A_0 \exp(-0.05621*t)$

For ^{14}C: $A= A_0 \exp(-0.00012*t)$

RADIOCARBON DATING OF DISSOLVED INORGANIC CARBON IN GROUNDWATER



Radioactivity Characteristic of tritium and radiocarbon

RADIOCARBON

Production in atmosphere:

$$^{14}{}_{7}N + {}^{1}{}_{0}n \rightarrow {}^{14}{}_{6}C + {}^{1}{}_{1}H$$

$$^{14}{}_{6}C + O_2 \rightarrow {}^{14}{}_{6}CO_2$$

β^- -Decay :

$$^{14}{}_{6}C \rightarrow {}^{14}{}_{7}N + {}^{o}{}_{-1}e \ (E_{max} = 156 \text{ keV})$$

Half life: 5730 yrs

Activity of 100% Modern Carbon (100pMC) = 13.6 dpm/g of carbon

Incorporation of CO_2 in water cycle

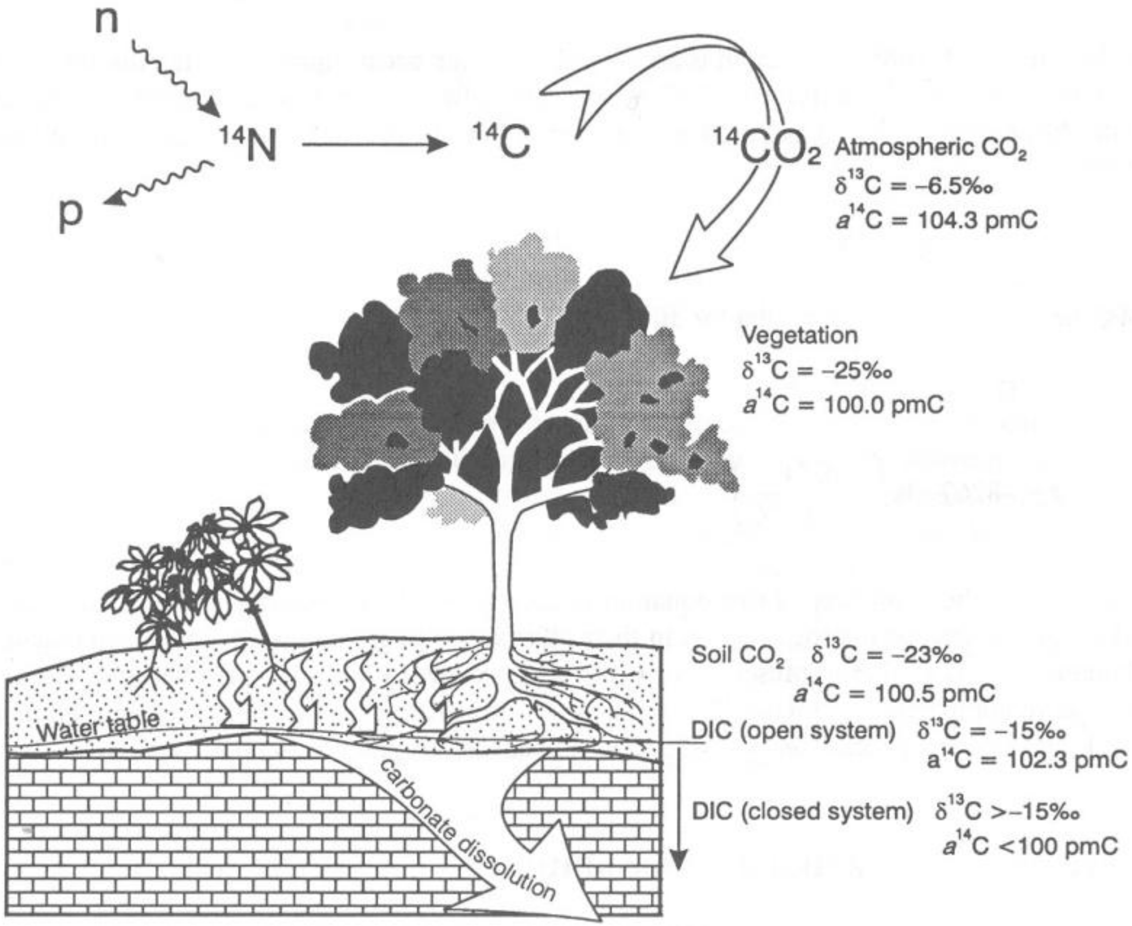
1 Chemical Process:

$CO_2(gas) \leftrightarrow CO_2(aqueous) \leftrightarrow H_2CO_3 \leftrightarrow HCO_3^- + H^+ \leftrightarrow CO_3^{--} + H^+$

$CO_3^{--} + Me^{++} \leftrightarrow MeCO_3$

Where Me^{++} is generally Ca^{2+} but can include Mg^{2+}, Ca^{2+} and 2 Na^+ in highly saline aquifers.

2. Biogenic pathways:



SAMPLE COLLECTION FOR RADIOCARBON DATING

$$\boxed{\text{Water (200-300 lit) containing DIC}} \xrightarrow[\text{Enhance pH >10}]{\text{NaOH to}} \boxed{+ BaCl_2} \xrightarrow[\text{For rapid precipitation}]{\text{+ Praestol}} BaCO_3$$

Sample Pre-treatment (Chemical Enrichment)

$$\boxed{3BaCO_3 + 2H_3PO_4} \longrightarrow \boxed{Ba_3(PO_4)_2 + 3H_2O + 3CO_2}$$

1) CO_2 absorption technique : CO_2+ Carbosorb -> Carbamate (a dense liquid) -> Counting

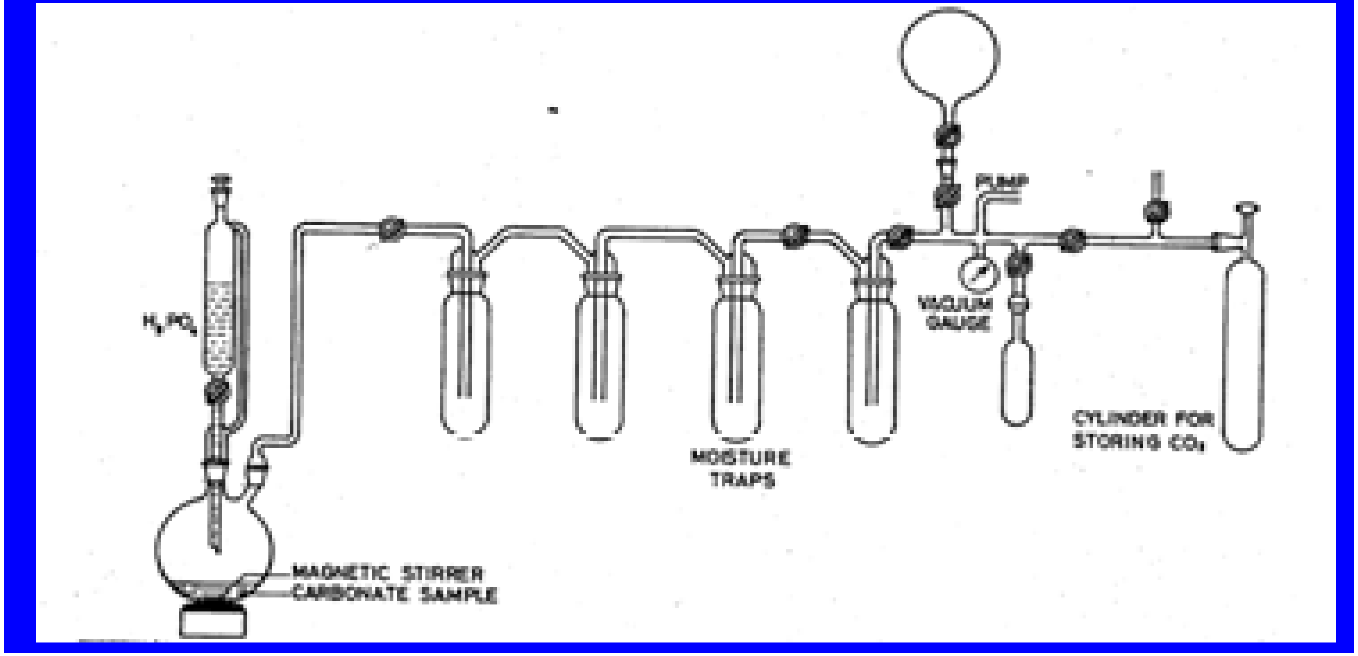
2) Benzene synthesis:

$$\boxed{CO_2 + Li_2C_2} \xrightarrow{\sim 800^0C} \boxed{Li_2C_2} \xrightarrow[\text{(Hydrolysis)}]{+H_2O} C_2H_2$$

$$\boxed{3C_2H_2} \xrightarrow[\text{Pt-chrome Or Al-chrome}]{\sim 100^0C} C_6H_6 \longrightarrow \boxed{\text{Beta-Counting}}$$

2. Carbon dioxide preparation from the precipitate

Barium carbonate is reacted with orthophosphoric acid to give carbon dioxide (CO_2) using vacuum line

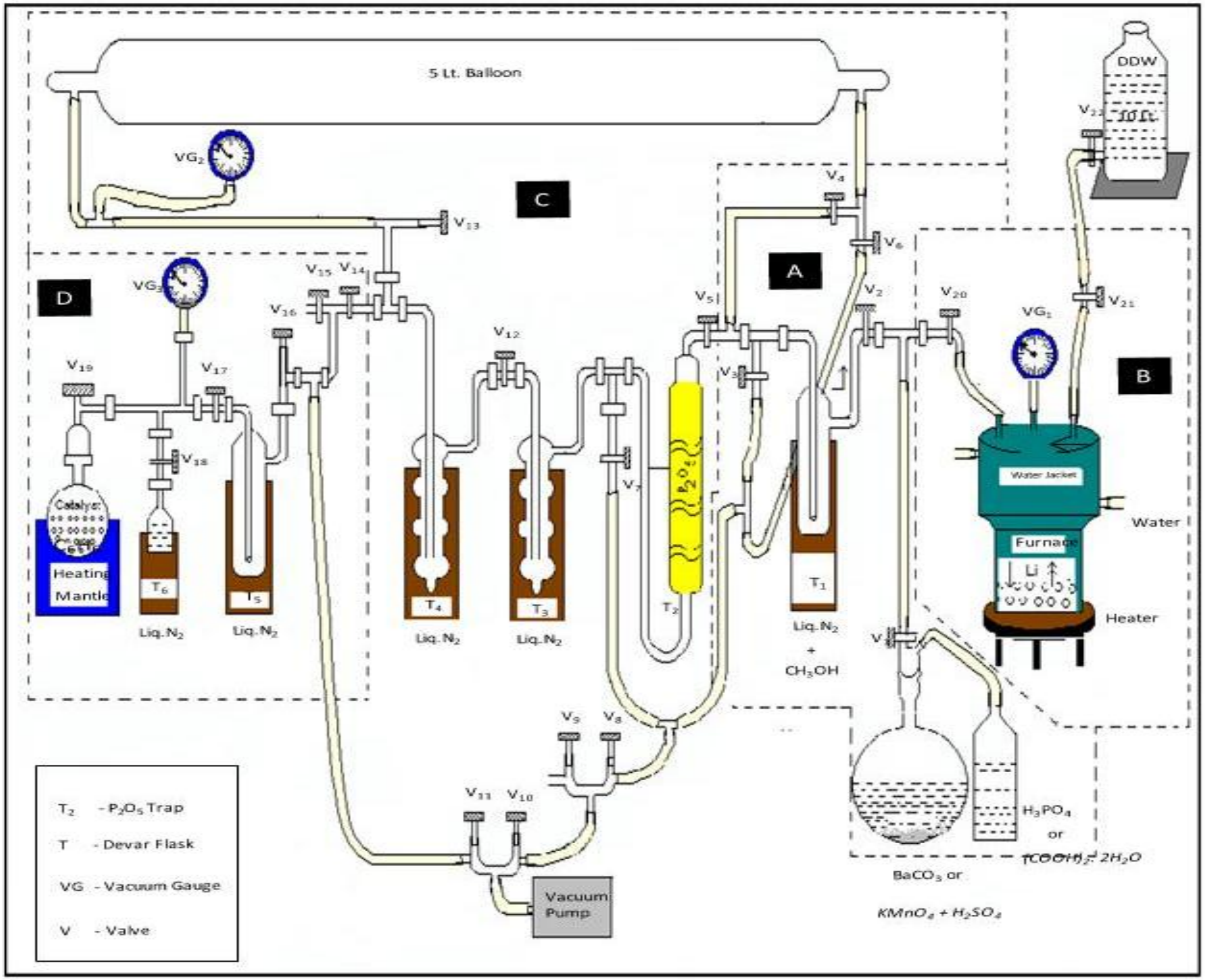


CO_2 Preparation

$$CaCO_3/BaCO_3 + H_3PO_4 \xrightarrow{27\,^{o}C} CO_2 + H_2O + CaHPO_4/BaHPO_4$$

19.5/38.7 gm	19.2 gm/ 11 ml	8.6 gm/ 4.5 lit.	3.5 gm	26.6/45.8 gm

$$3BaCO_3 + 2H_3PO_4 \text{ ----------}\rightarrow Ba_3(PO_4)_2 + 3CO_2 + 3H_2O$$

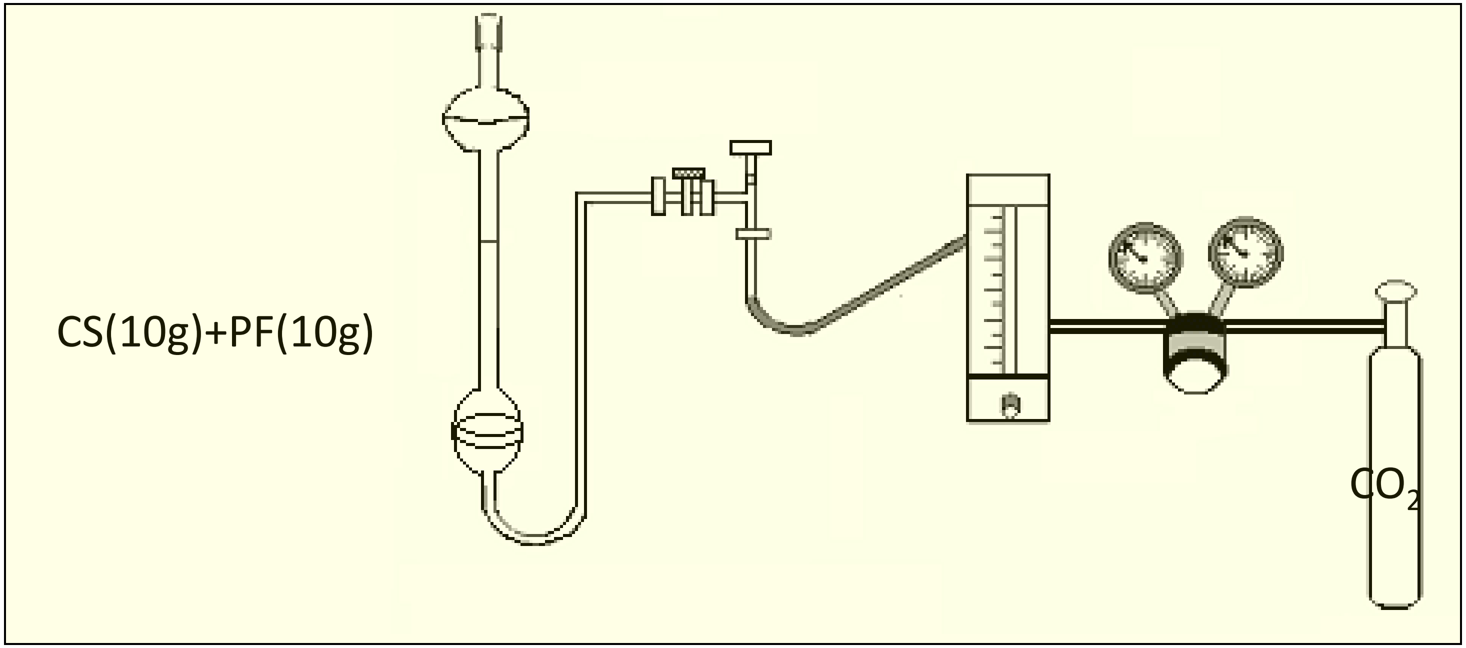


$$BaCO_3 \xrightarrow{H_3PO_4} CO_2 \xrightarrow{Li(800^0C)} 2C \xrightarrow{H_2O} C_2H_2 \xrightarrow{Vanadium/Al\text{-}Chrome} C_6H_6$$

CO_2 and Benzene preparation line

BENZINE SYNTHESISER

Carbosorb



CO_2 absorption line

CO_2 absorption is carried out 20 days after its preparation to allow for ^{222}Rn decay to occur
$T_{1/2}$ of ^{222}Rn = 4.6 days

Requirement 3.5g of CO_2 absorbed
= ~[3.5x13.56dpm/44 mole wt]x50% Counting efficiency = 0.54dpm

CALCULATION

- Half-life of ^{14}C is 5730 a (years).
- Decay equation: $A_t = A_0 \times e^{-\lambda t}$

A_0 and A_t are ^{14}C initial activity, and activity after time ‘t’, λ is decay constant.

$$t = -8267 \times \ln(A_t/A_0) \qquad [\text{year}]$$

- A_t and A_0 are expressed (normalized w.r.t. 100 pMC) in pMC (pre industrial C is taken as 100 pMC: 13.56 dpm/g of C)
- $t = -8267 \times \ln(A_{tN}/A_{0N}) \quad [\text{year}]$
- If A_0 is diluted by a factor q then A_{oN} becomes qA_{0N}
- $t = -8267 \times \ln(A_{tN}/(qA_{0N})) \qquad [\text{year}]$

Dilution factor

- Detection limit 0.8 pMC
- BKG is subtracted in sample and std counts

Dilution Factor q:

- Calcite (limestone) dissolution, beginning in the recharge area
- Dolomite dissolution
- Exchange with the aquifer matrix
- Oxidation with old organics found within the aquifer and other biochemical reactions
- Diffusion of ^{14}C into the aquifer matrix

q is estimated using suitable modeling technique

Models for Estimation of dilution factor ‘q’

1) Statistical Model

A number of characteristic **q** values have been reported in the literature (Vogel 1970)

0.65 – 0.75 for karst systems

0.75 – 0.90 for sediments with fine grained carbonate, loess soil

0.90 – 1.00 for crystalline rocks

- Range of q: Pure lime stone ~ 0 to pure crystalline quartzitic-1

2) Alkalinity correction model: For calcite dissolution in closed system condition

$$q = \frac{\text{mDIC}_{rech} \qquad \text{DIC during recharge}}{\text{mDIC}_{fin} \qquad \text{DIC at the time of sampling}}$$

where mDIC_{rech} is the 14C active DIC gained by dissolution of soil CO2 during recharge, and mDIC_{fin} is the total carbonate content at the time of sampling. This approach does not account for open system carbonate dissolution during recharge. This is applicable for geochemically simple systems.

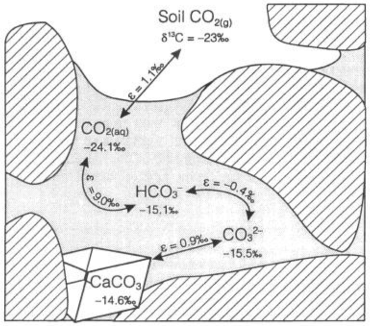
3) Pearson’s Model (δ^{13}C mixing model)

The principal of this model is similar to that of chemical mixing model, except for end members of the mixing which are ^{13}C contents of the recharging waters and solid carbonate. The q factor is as follows

$$q = \frac{\delta^{13}C_{DIC} - \delta^{13}C_{carb}}{\delta^{13}C_{rec} - \delta^{13}C_{carb}}$$

Meas .in GW - Dissolved carb.

Recharging water – Dissolved Carb



Where

$\delta^{13}C_{DIC}$ = measured ^{13}C in groundwater
$\delta^{13}C_{rec}$ = ^{13}C of DIC in the recharging waters ~23 ‰
$\delta^{13}C_{carb}$ = ^{13}C of the calcite being dissolved = 0 ‰

4) Chemical mass-balance

- Calculation by chemical data

$$m\mathrm{DIC}_{\mathrm{final}} = m\mathrm{DIC}_{\mathrm{recharge}} + [m\mathrm{Ca}^{2+} + m\mathrm{Mg}^{2+} - m\mathrm{SO}_4^{2-} + \tfrac{1}{2}(m\mathrm{Na}^{+} + m\mathrm{K}^{+} - m\mathrm{Cl}^{-})]$$

m = concentration in moles/liter

5) Fontes-Garnier model

- Open and closed system dissolution are considered
- $mDIC_{carb}$ = mCa + mMG –mSO4 + ½(mNa + mK –mCl)

- This DIC consists of two parts:
    - dissolved in open system: C-14 exchange with soil CO2
    - dissolved in closed system (C-14 dead)

Additional complications to ^{14}C dating

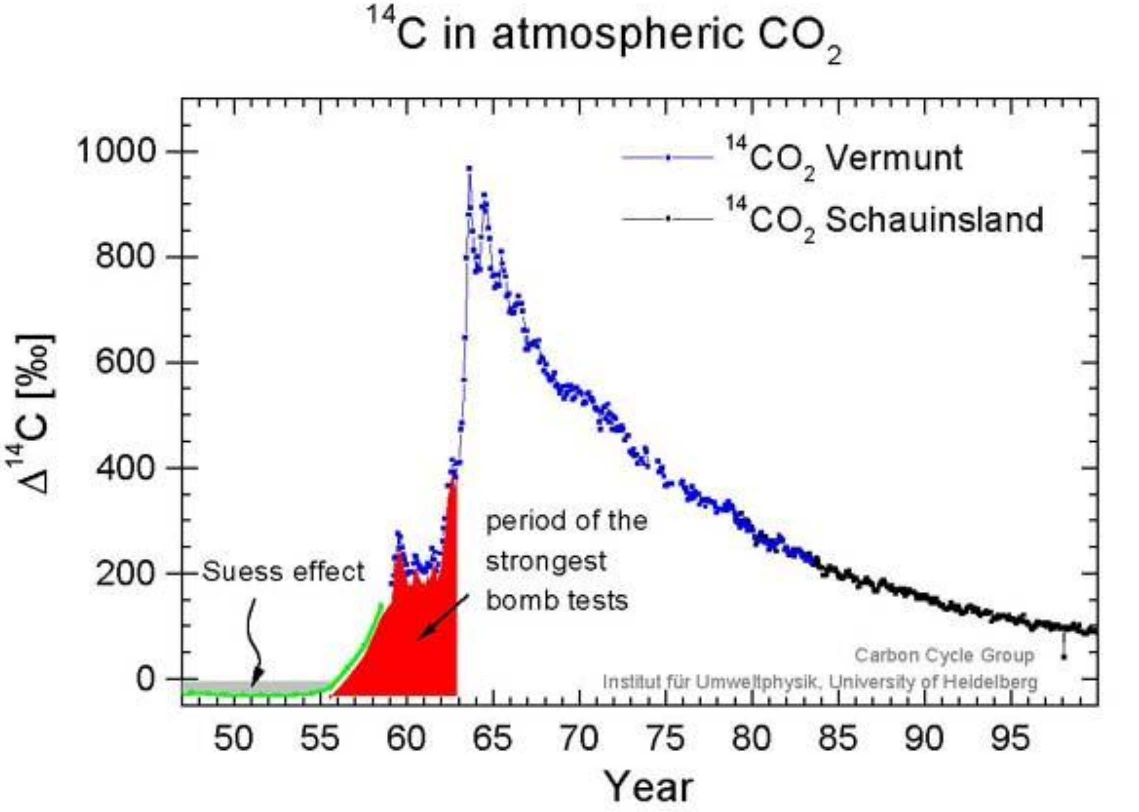
The ^{14}C acquired from the soil, diluted by carbonate dissolution and exchange may have further dilution which may need correction. Addition reactions which may take place are as follows:

- Matrix diffusion
- Sulphate reduction
- Incorporation of geogenic CO_2
- Methanogenesis

Change in Atmospheric ^{14}C activity:

Bomb produced ^{14}C & ^{14}C free CO_2 release

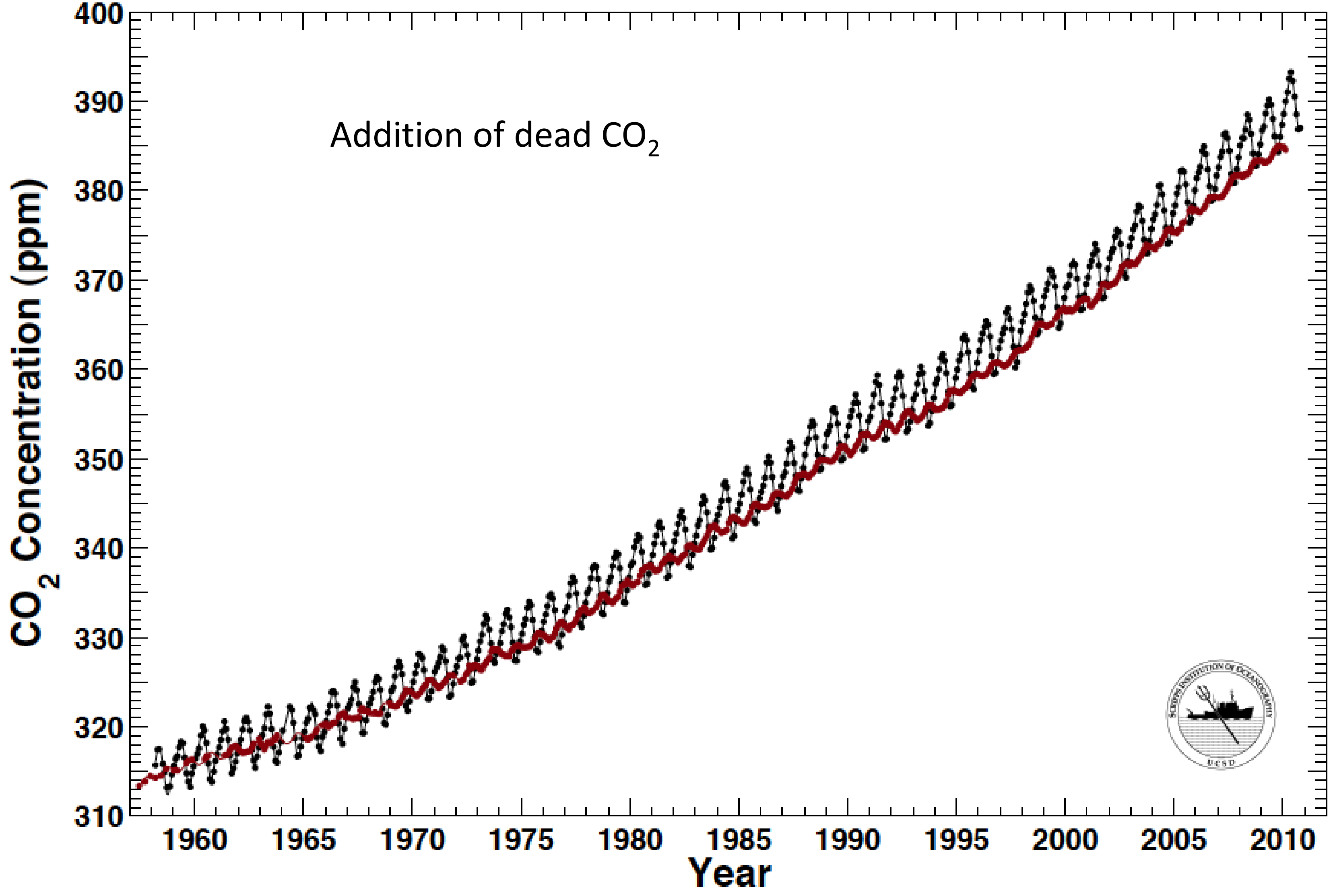
1) Bomb produced ^{14}C



http://www.iup.uni-heidelberg.de/institut/forschung/groups/kk/14co2.ht

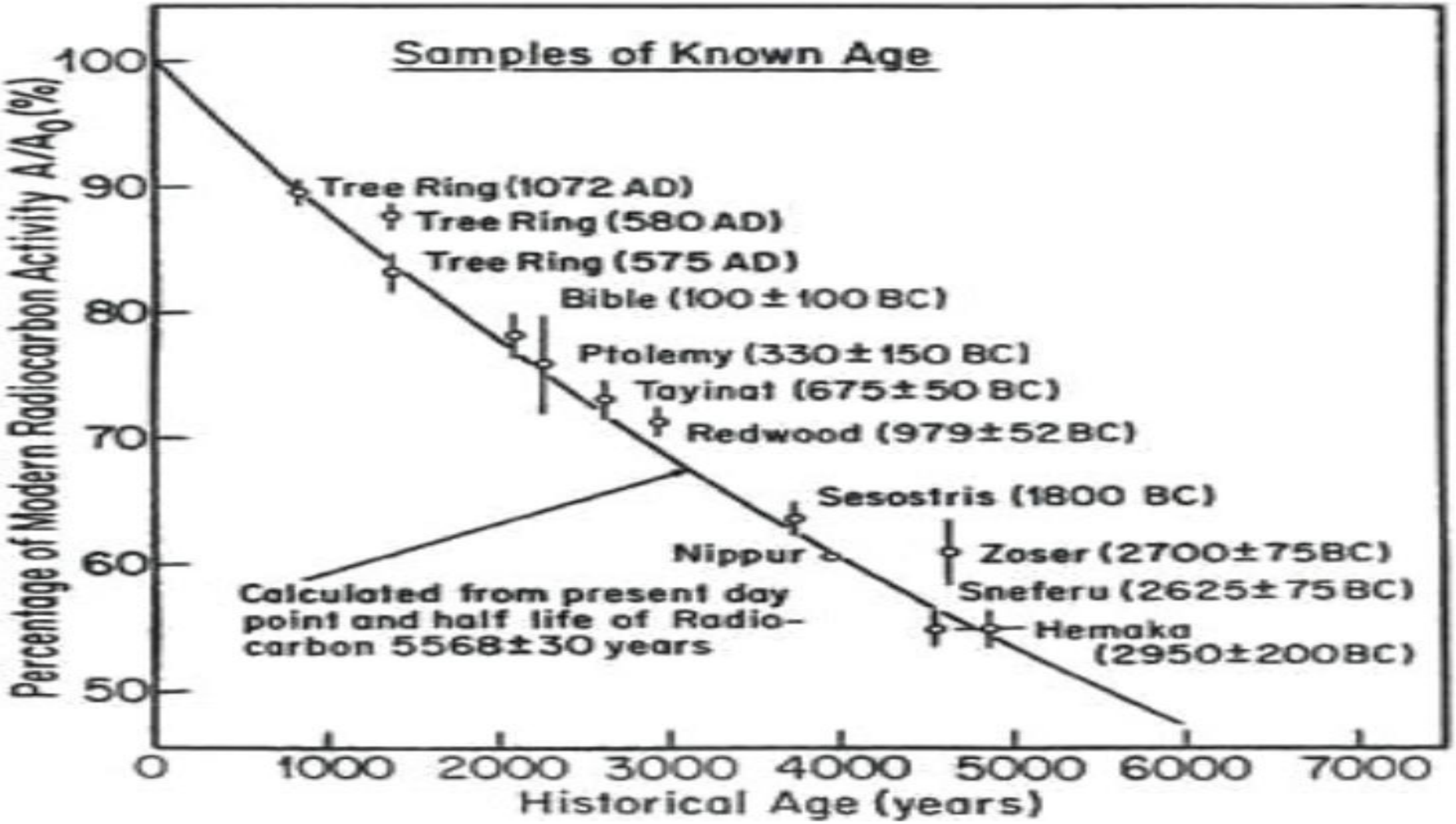
Mauna Loa Observatory, Hawaii and South Pole, Antarctica
Monthly Average Carbon Dioxide Concentration

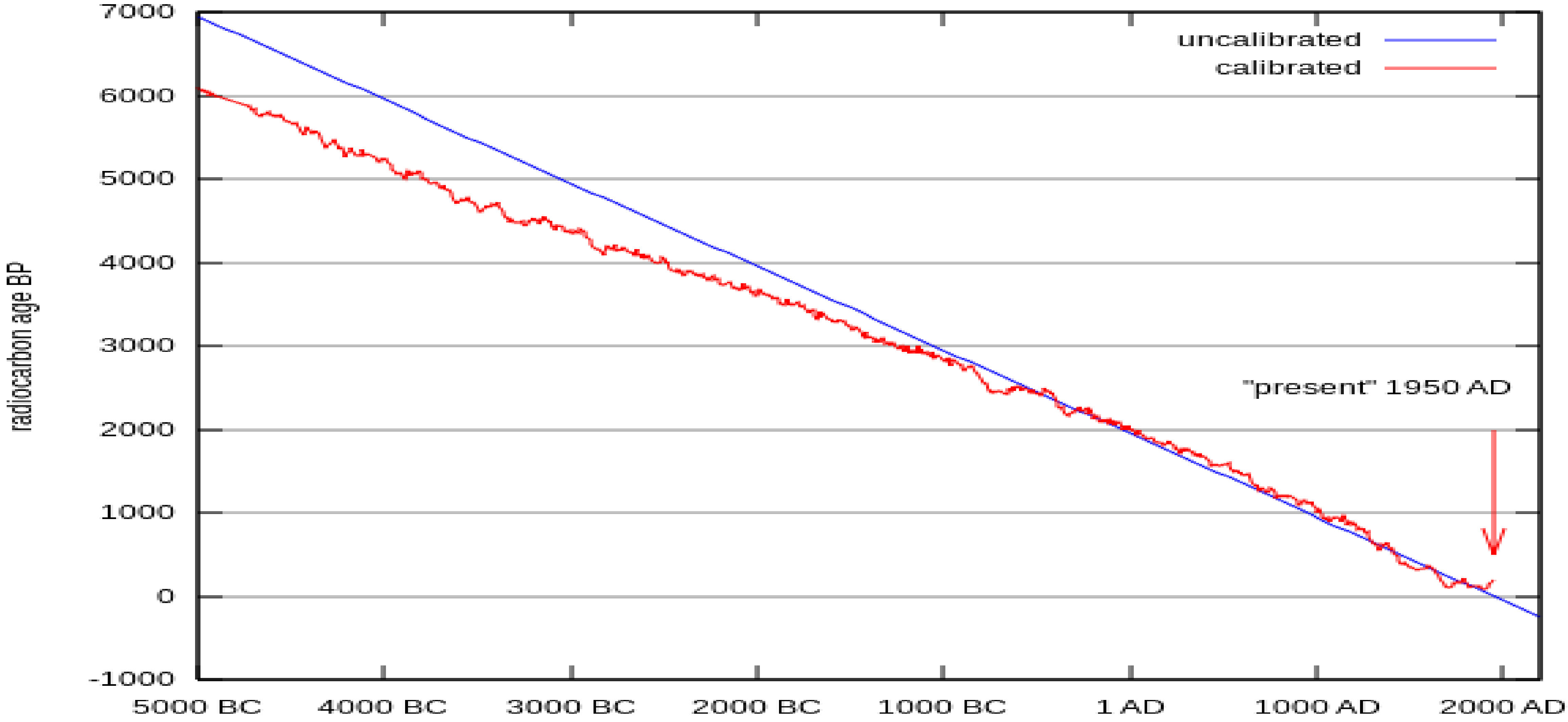
Data from Scripps CO_2 Program Last updated October 2010



Addition of dead CO_2

1st ^{14}C dating inter-comparison with historical ages




radiocarbon age BP
7000
6000
5000
4000
3000
2000
1000
0
-1000
5000 BC
4000 BC
3000 BC
2000 BC
1000 BC
1 AD
1000 AD
2000 AD
uncalibrated
calibrated
"present" 1950 AD

Advantages and Disadvantages

Advantages

- It is an old and well-established method that has been proved and developed by considerable research during the last half-century. It is applicable to a variety of materials and processes.
- Sampling and analysis for this method are now routine and cheaper than the majority of the dating methods.
- It is, in one sense, the only method available to date old groundwaters and to fill the dating range between young and very old groundwaters.
- The deficiencies, the principles, and the positive points of the methods are all well known.

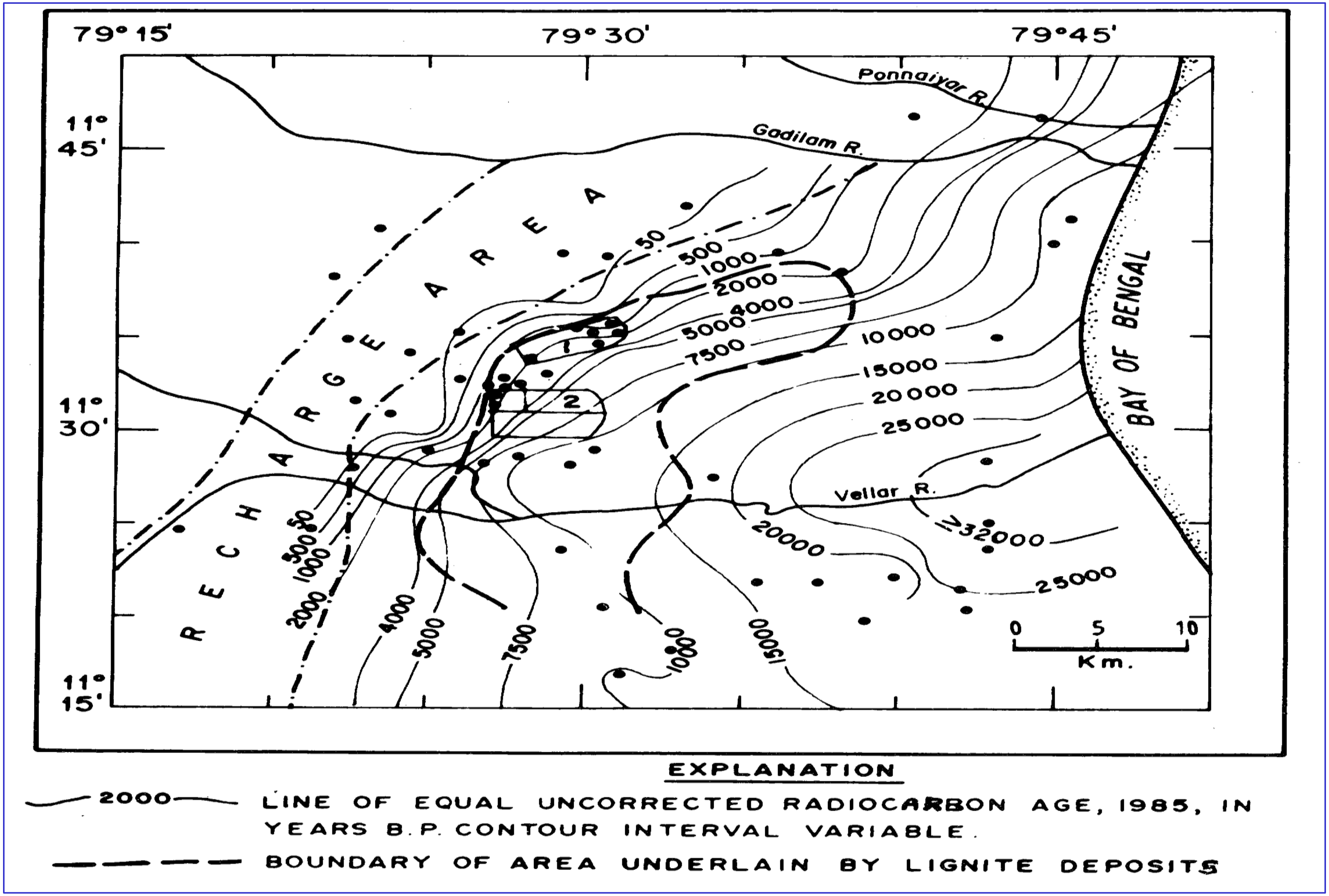
Disadvantages

- It is an extremely difficult task to determine the correct initial value due to the various processes that modify ^{14}C signature of the percolating rainwater.
- A large number of geochemical reactions modify the concentration of ^{14}C in the groundwater. It has been tried to alleviate this problem by taking into account a large number of processes, but an appreciable amount of uncertainty surrounds the validity of this approach and the results obtained.
- Having pointed out the above two major obstacles, it is safe to conclude that the ^{14}C method is often a semi quantitative technique.

Natural Radioactivity (^{14}C & ^{3}H) in waters

Process	^{3}H	^{14}C
Production (Due to C.Rays)	${}^{14}_{7}N + {}^{1}_{o}n \rightarrow {}^{3}_{1}H + {}^{12}_{6}C$ ${}^{3}H + {}^{1}H + (O) \rightarrow {}^{1}H^{3}HO$	${}^{14}_{7}N + {}^{1}_{0}n \rightarrow {}^{14}_{6}C + {}^{1}_{1}H$ ${}^{14}_{6}C + O_2 \rightarrow {}^{14}_{6}CO_2$
Decay	${}^{3}_{1}H \rightarrow {}^{3}_{2}He + \beta$ (E_{max} = 18 KeV)	${}^{14}_{6}C \rightarrow {}^{14}_{7}N + {}^{o}_{-1}e$ (E_{max} = 156 keV)
Half Life	12.328 yrs	5730 yrs
Atm. Activity	~10TU, 1.19Bq/kg water	100pmc: 13.56dpm/g of C
Age equation	$t_{yrs} = -17.7866 \ln (A/A_o)$ A0 need to be correctoed for bomb produced $_{3}H$ activity	$t_{Yrs} = - 8266.6 \ln (A/qxA_o)$ A_0 – (^{14}C activity changed in atmos.)+ dilutes due to dissolution of mineral carbon during infiltration
Sample amount	500 ml water	100 lit (assuming 300mg/l HCO_3 & 75% extraction eff.) ⇒ 4.4g carbon
Enrichment	Elec.Enr. (~25 times)	C_6H_6 or carbosorb (CS) (10^3 times)
Counting	Beta counting	Beta counting

Case Studies of ^{14}C & ^{3}H dating in India

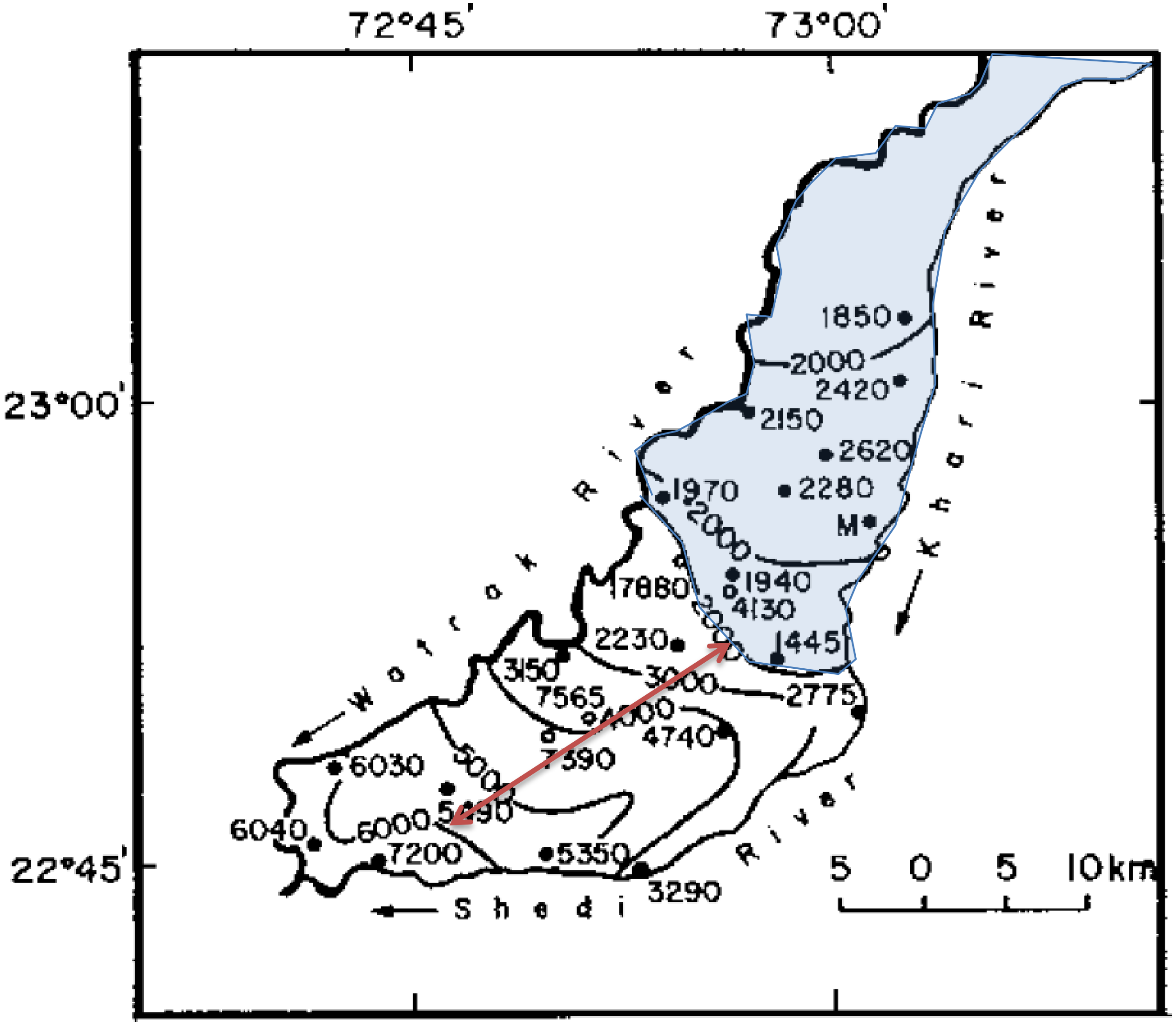


EXPLANATION

—2000— LINE OF EQUAL UNCORRECTED RADIOCARBON AGE, 1985, IN YEARS B.P. CONTOUR INTERVAL VARIABLE.

— — — — BOUNDARY OF AREA UNDERLAIN BY LIGNITE DEPOSITS

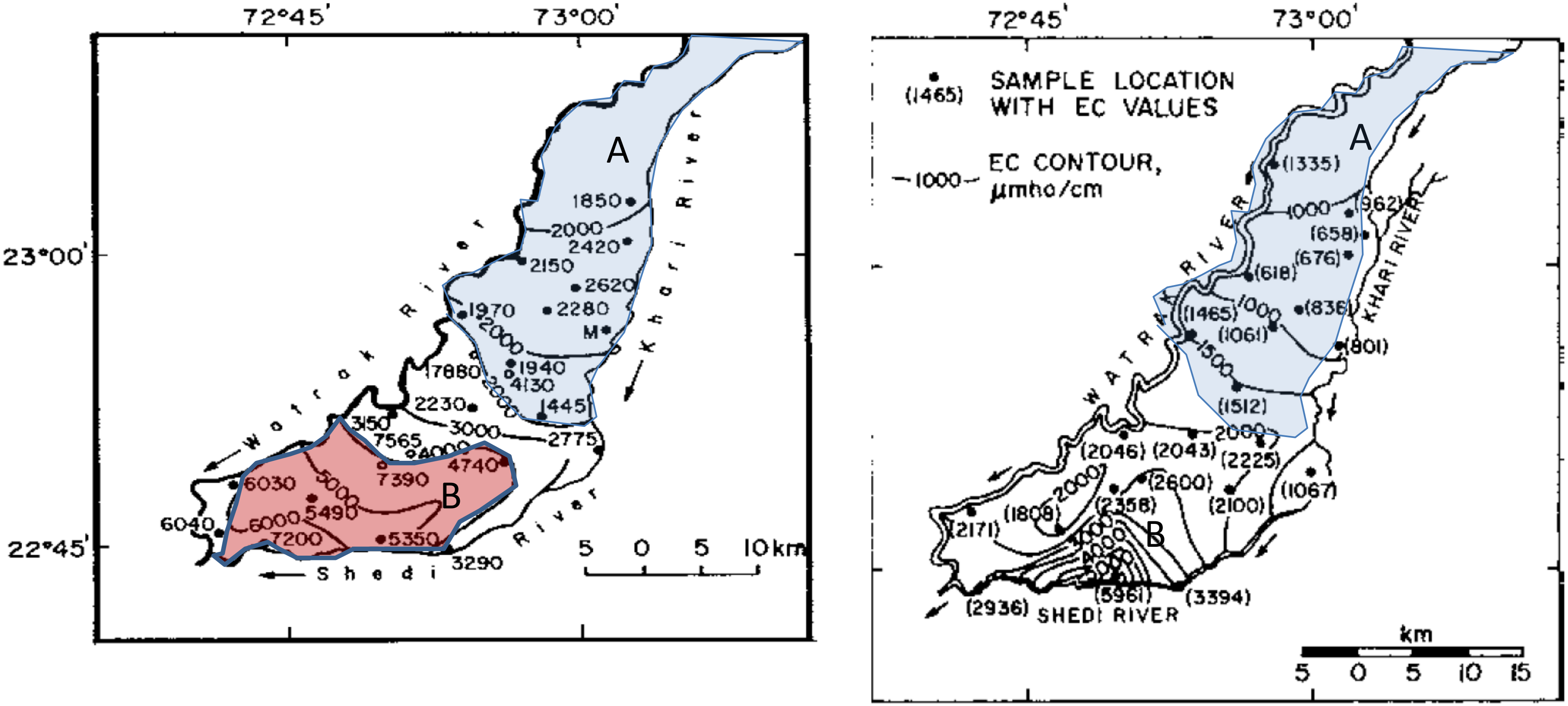
Nayveli open cast mine 200 km south of Chennai; aquifer depressurization, induced recharge; Correlation exist between potentiometric head and groundwater age.(Sukhija et al., Hydrogeol. 1996)



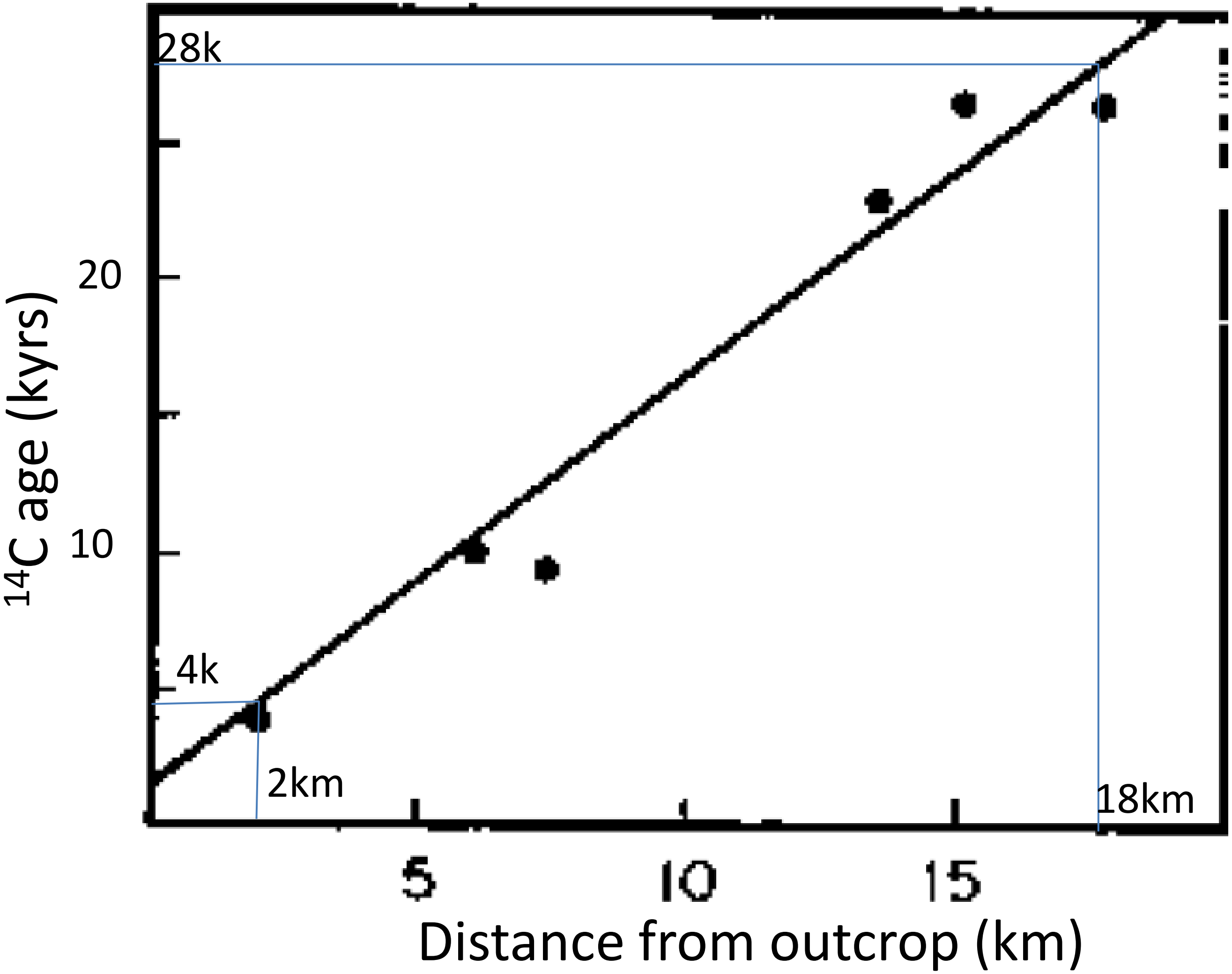
Recharge area – 85pmc = 2kyrs

^{14}C dating of GW of
Watrek Shedi Basin
(Borole et al, 1979)

Contour distance (6kyr-2kyr) is 24 km
=24km/4kyrs = 6m/yr is the average GW flow velocity



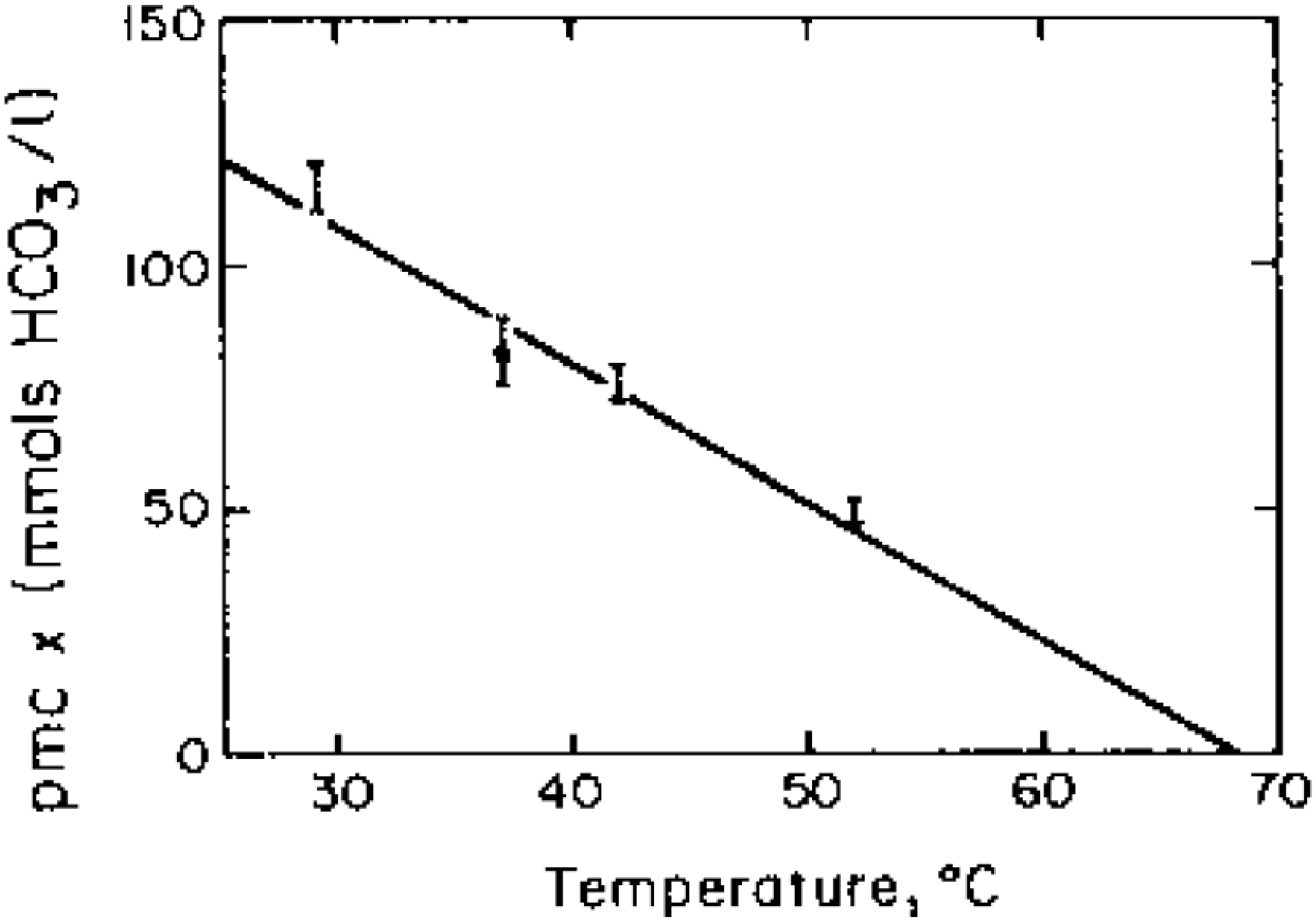
Age & EC contour relation: The recharge area reveals fresh water values around 1000-1500 mmho/cm, whereas gradual salinization is observed down-gradient in the confined section (shaded as region in B). (From Borole et al., 1979.)



V= (18-2)km/(28-4)ky

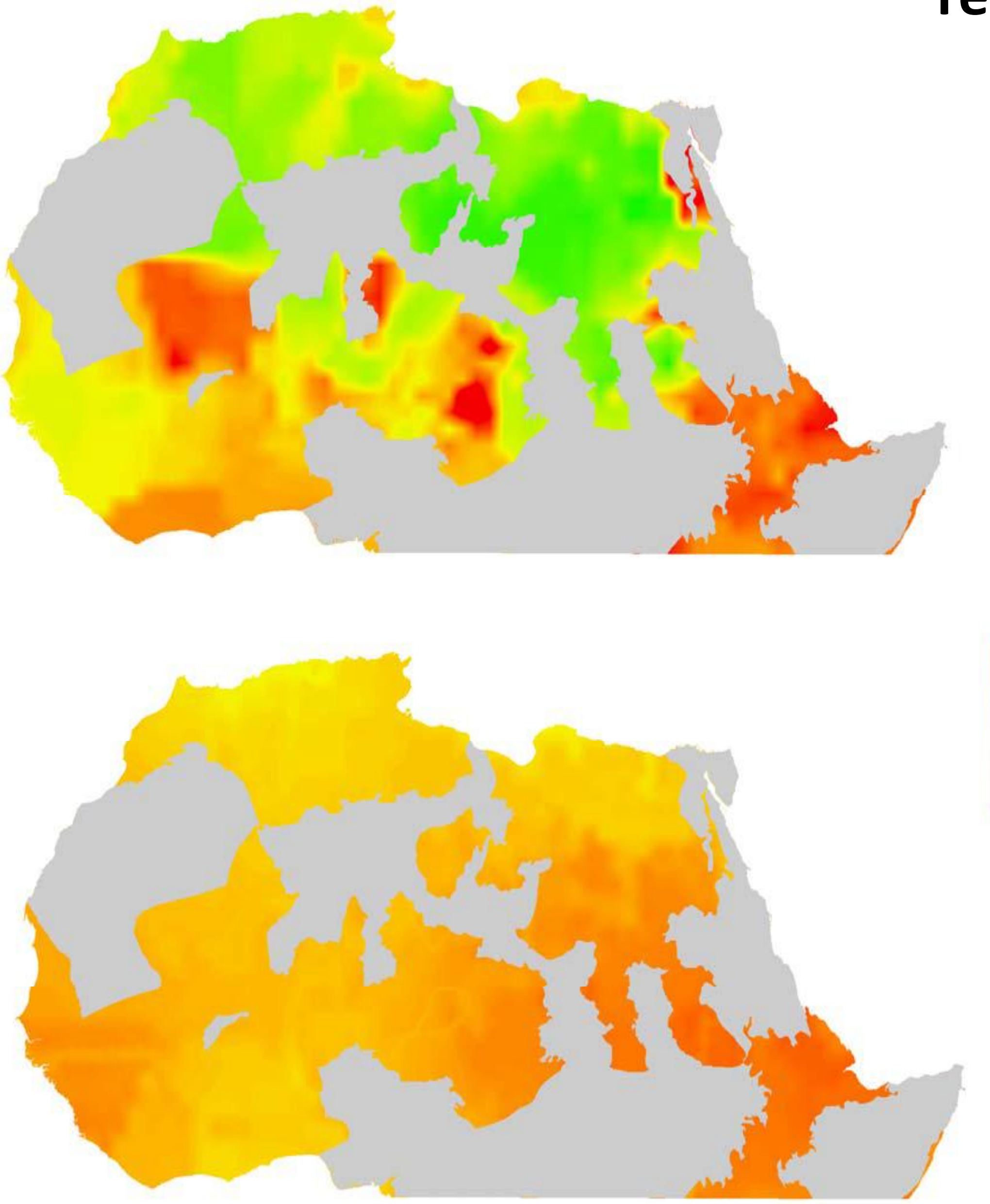
= 0.66m/yr

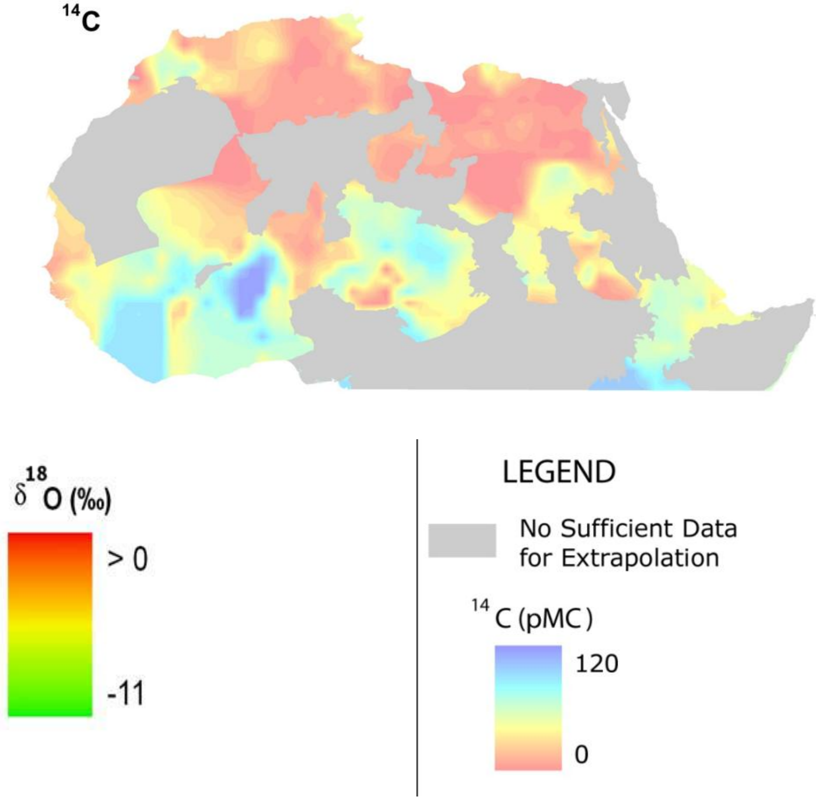
Groundwater age of artesian wells near the south coast of South Africa as a function of the distance from the outcrop of water-bearing strata. (From Vogel, 1970.)



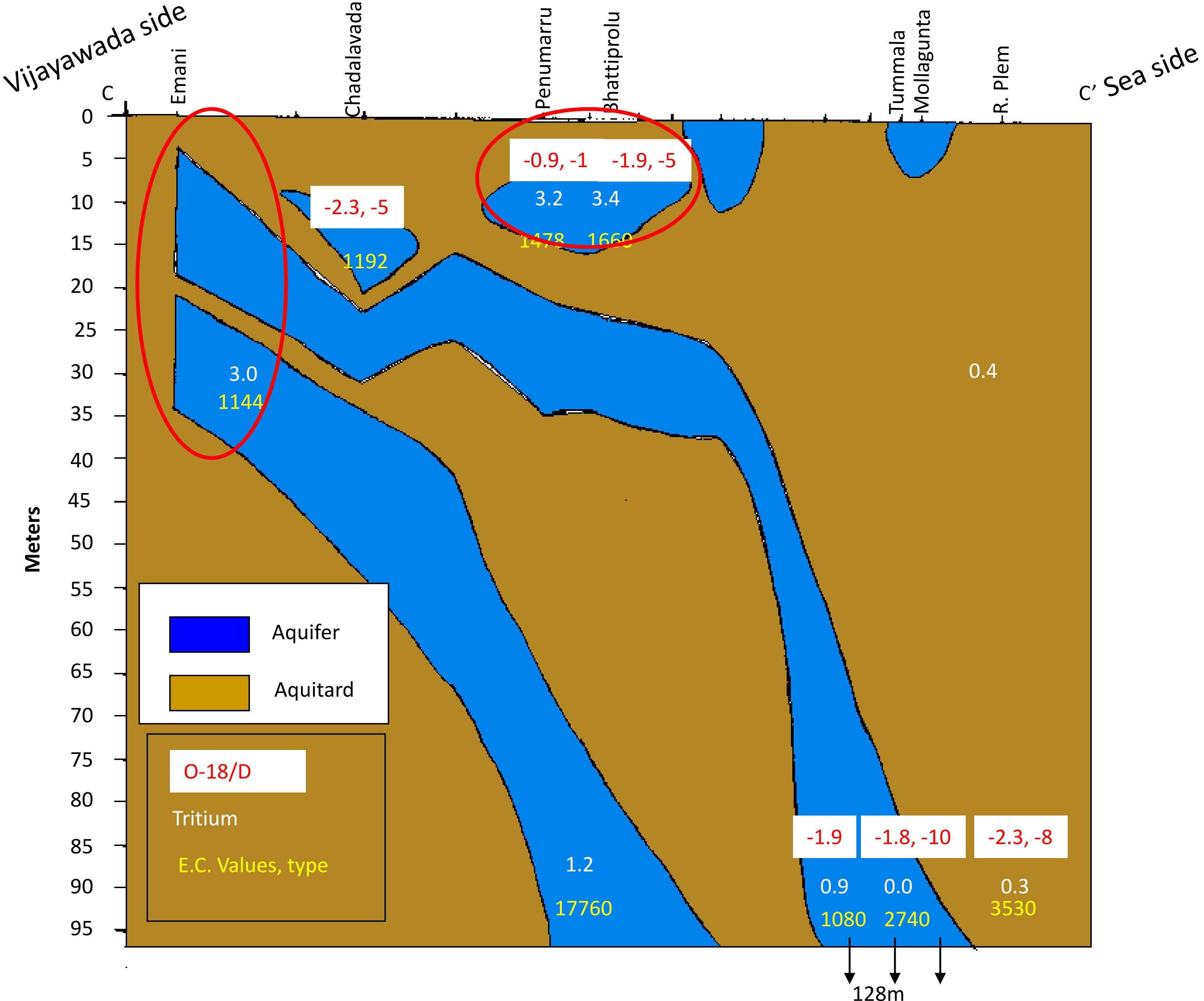
^{14}C versus temperature in the (hot water) spring complex of Hammat Gader. The negative correlation extrapolated to 0 pmc, obtains a value of 69^0C. The hottest end member observed (spring) has temperature 52^0C. (From Mazor et al., 1973.)

Isotopic contrast between paleowaters and recent recharge

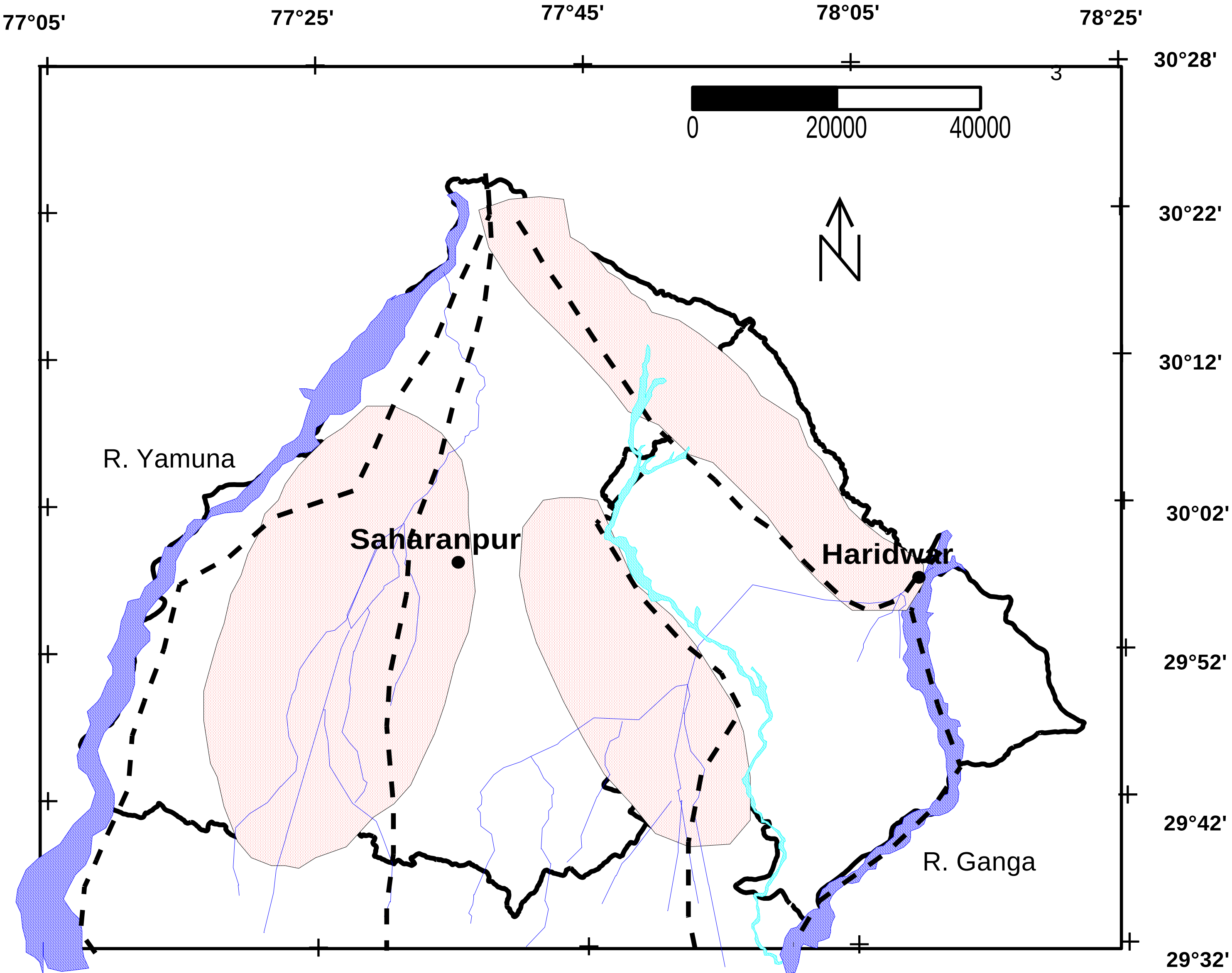




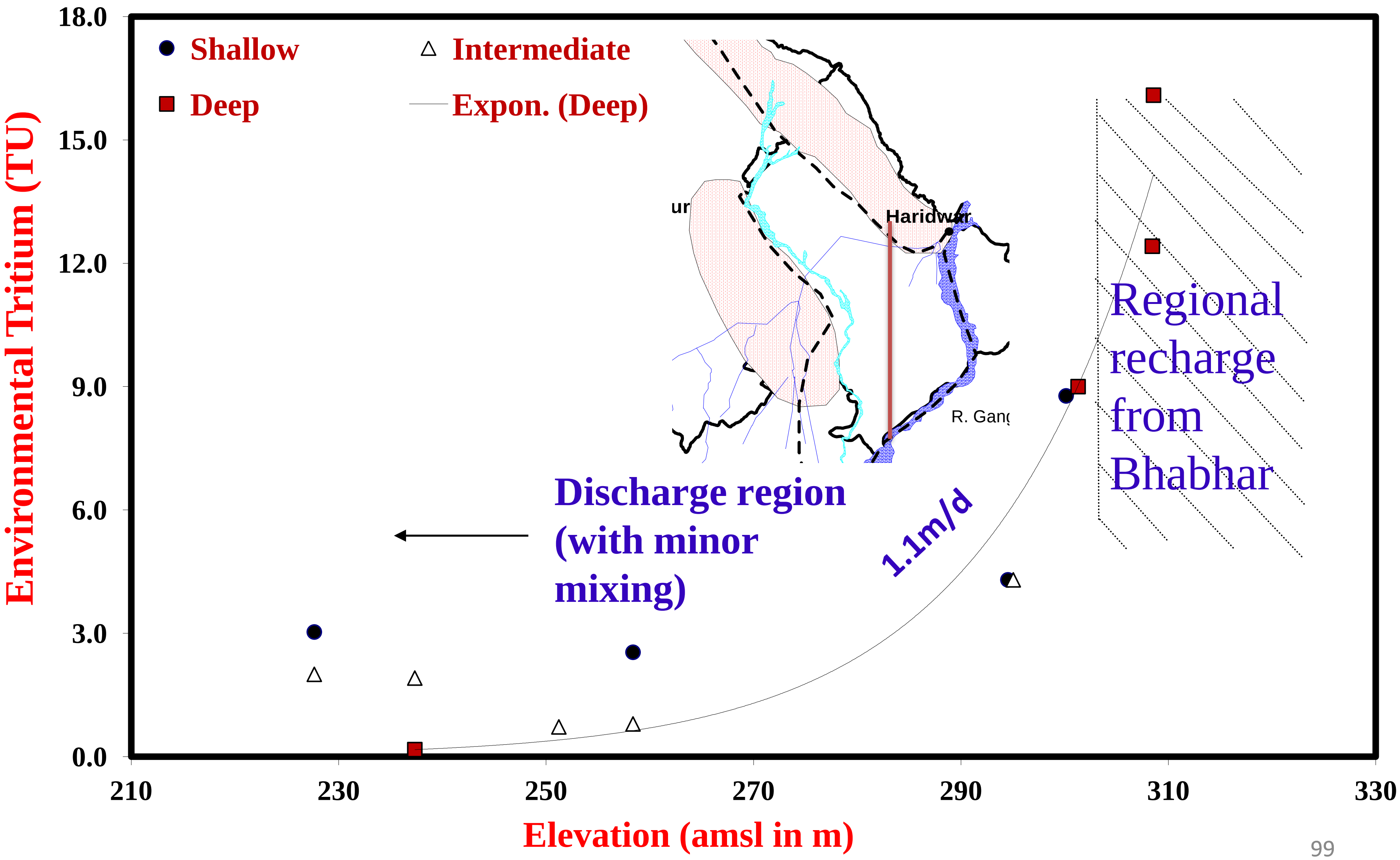
Isotope contents in “deep” groundwaters – Northern Africa
→mapping fossil gw


Vijayawada side
C
Emani
Chadalavada
Penumarru
Bhattiprolu
Tummala
Mollagunta
R. Plem
C′ Sea side
Meters
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
-2.3, -5
1192
-0.9, -1
-1.9, -5
3.2
3.4
1478
1660
3.0
1144
0.4
Aquifer
Aquitard
O-18/D
Tritium
E.C. Values, type
1.2
17760
-1.9
-1.8, -10
-2.3, -8
0.9
0.0
0.3
1080
2740
3530
128m

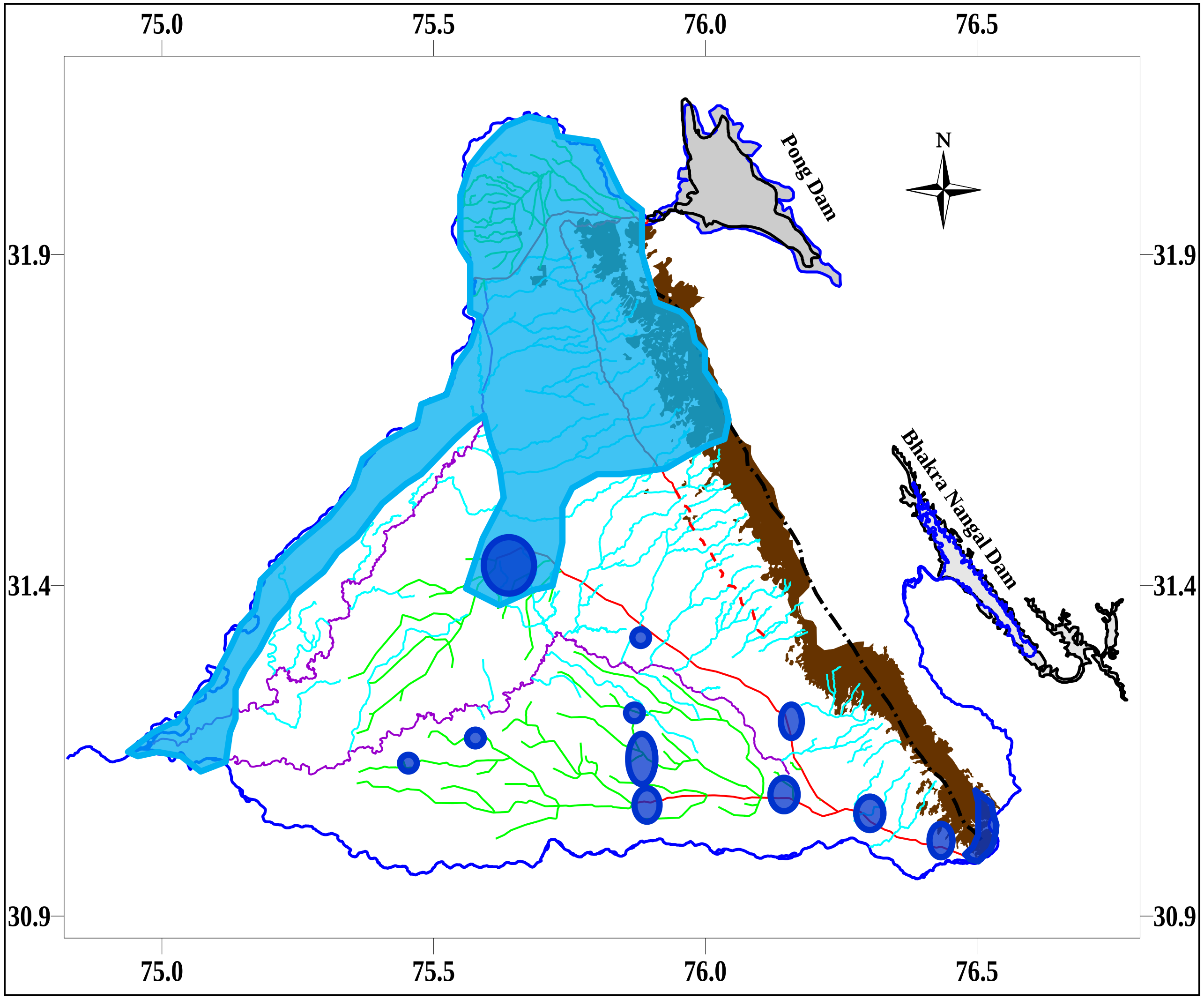
IDENTIFICATION OF GROUNDWATER RECHARGE ZONES



GROUNDWATER FLOW VELOCITY



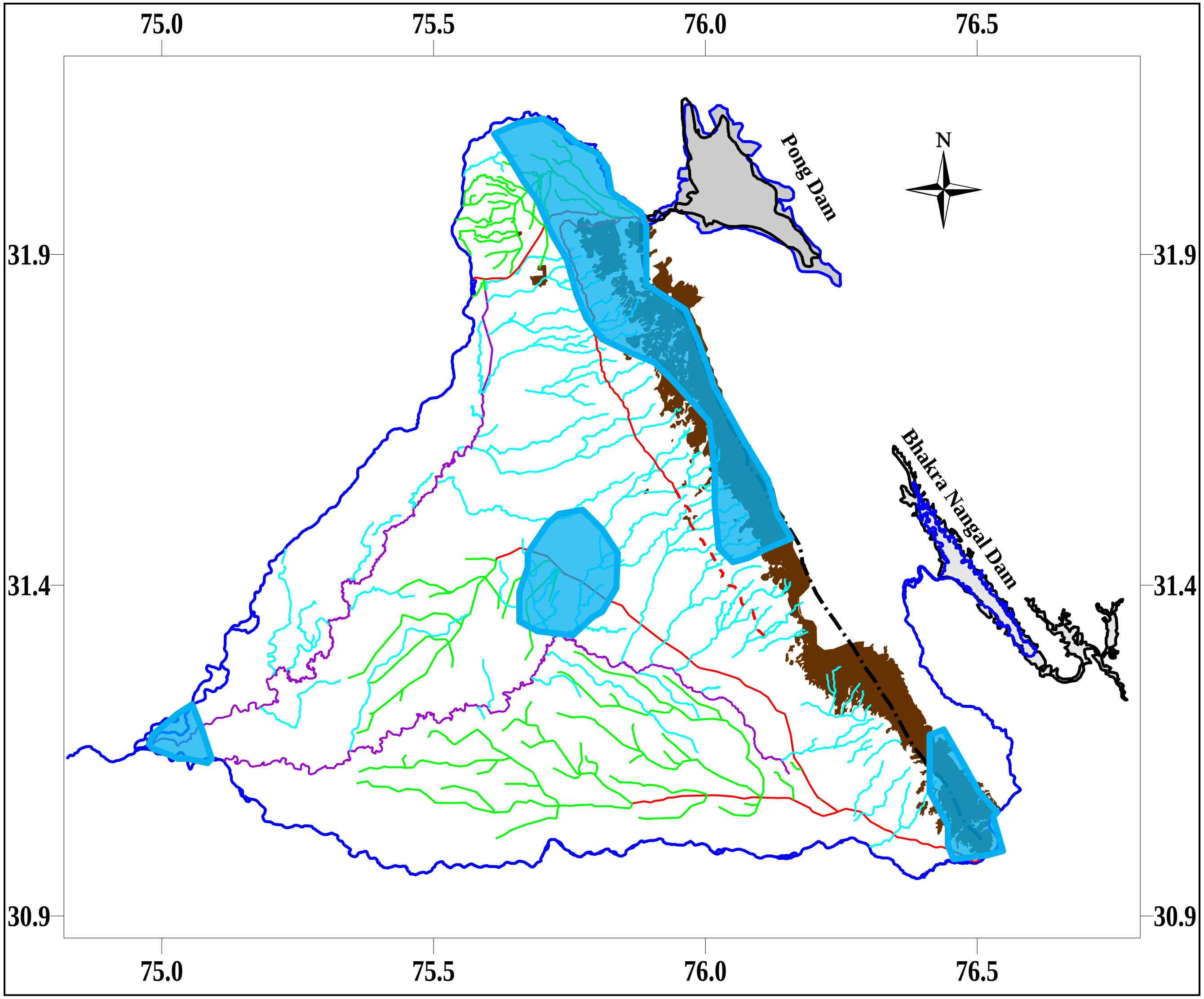
RECHARGE ZONES IN SHALLOW GROUNDWATER



Groundwater age:

- Younger than 12years in Kali Bein Catchment
- 16-12 years in Bist-Doab Canal
- River Bank infiltration: Approx. 1km along Beas River bank, Satluj show no/ negligible amount of infiltration.
- Recharge from Kandi region (including Northern part) 1/3rd area i.e. 3000km^2 Approx.
- Bist- Doab Canal: 100km (i.e. 1%) Approx.

RECHARGE ZONES IN DEEP GROUNDWATER



Groundwater age:

- Younger than 30 years in Kali Bein Catchment
- Recharge from Kandi region: ~5% (500km^2) Approx.
- Shallow- Deep groundwater interaction: at central part: less than 0.5%

DATING BY DISSOLVED GASES

Krypton-85

Half life: 10.76 yrs

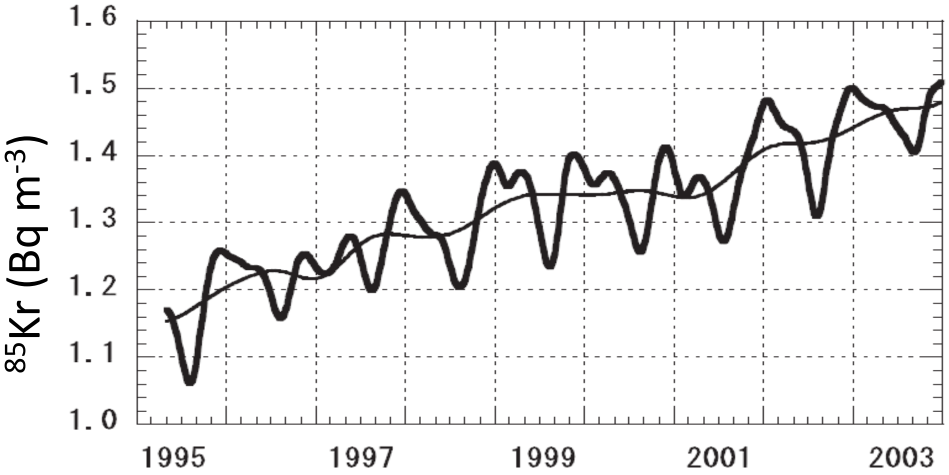
Natural production (Takes place in small amount compared to modern anthropogenic increase in ^{85}Kr concentration)

$^{84}_{36}\mathrm{Kr} + n \rightarrow {}^{85}_{36}\mathrm{Kr} + \gamma$

Manmade ^{85}Kr: Nuclear weapon testing & nuclear reactors (used for commercial energy production and weapons plutonium production).

^{85}Kr in the atmosphere: 1Bq/m^3 and is doubling every 20 years

Temporal variation of ^{85}Kr in Tsukuba



…..Krypton-85

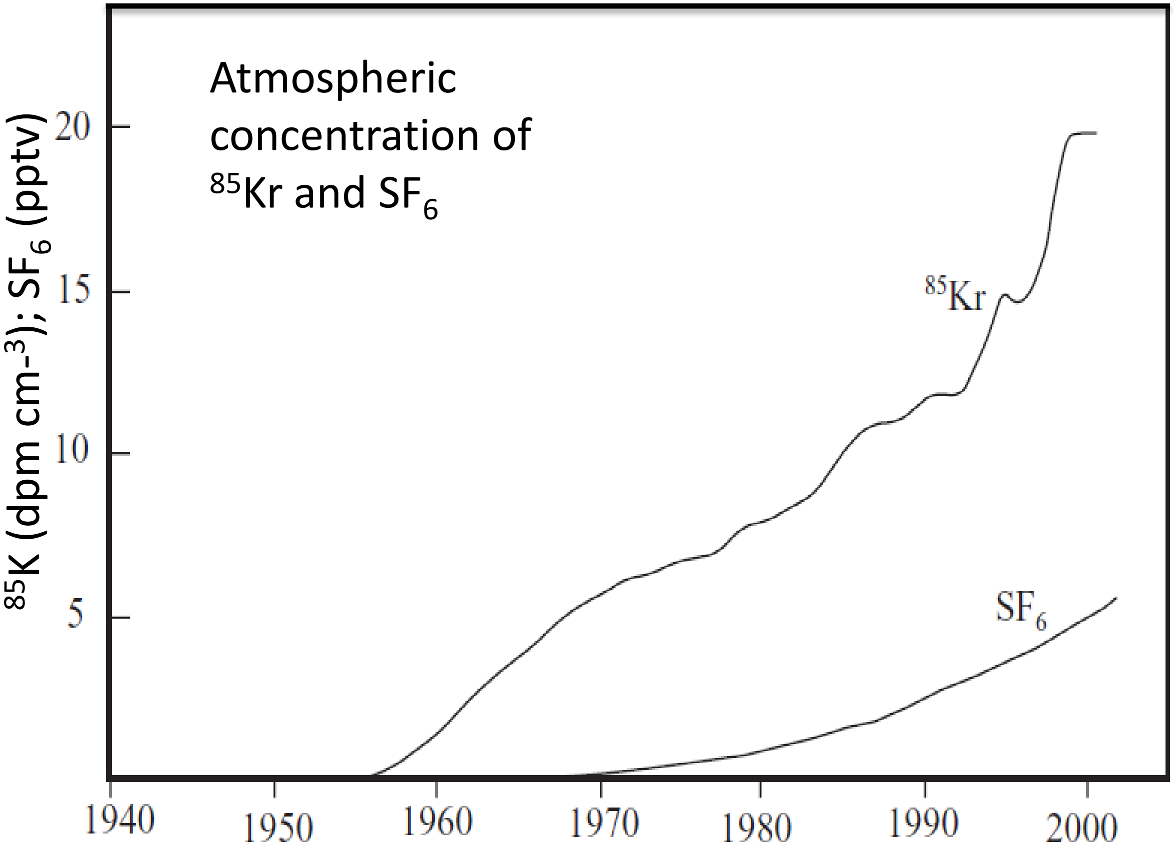
^{85}Kr decay:

$^{85}_{36}\mathrm{Kr} \rightarrow {}^{85}_{37}\mathrm{Rb} + \beta^{-}$

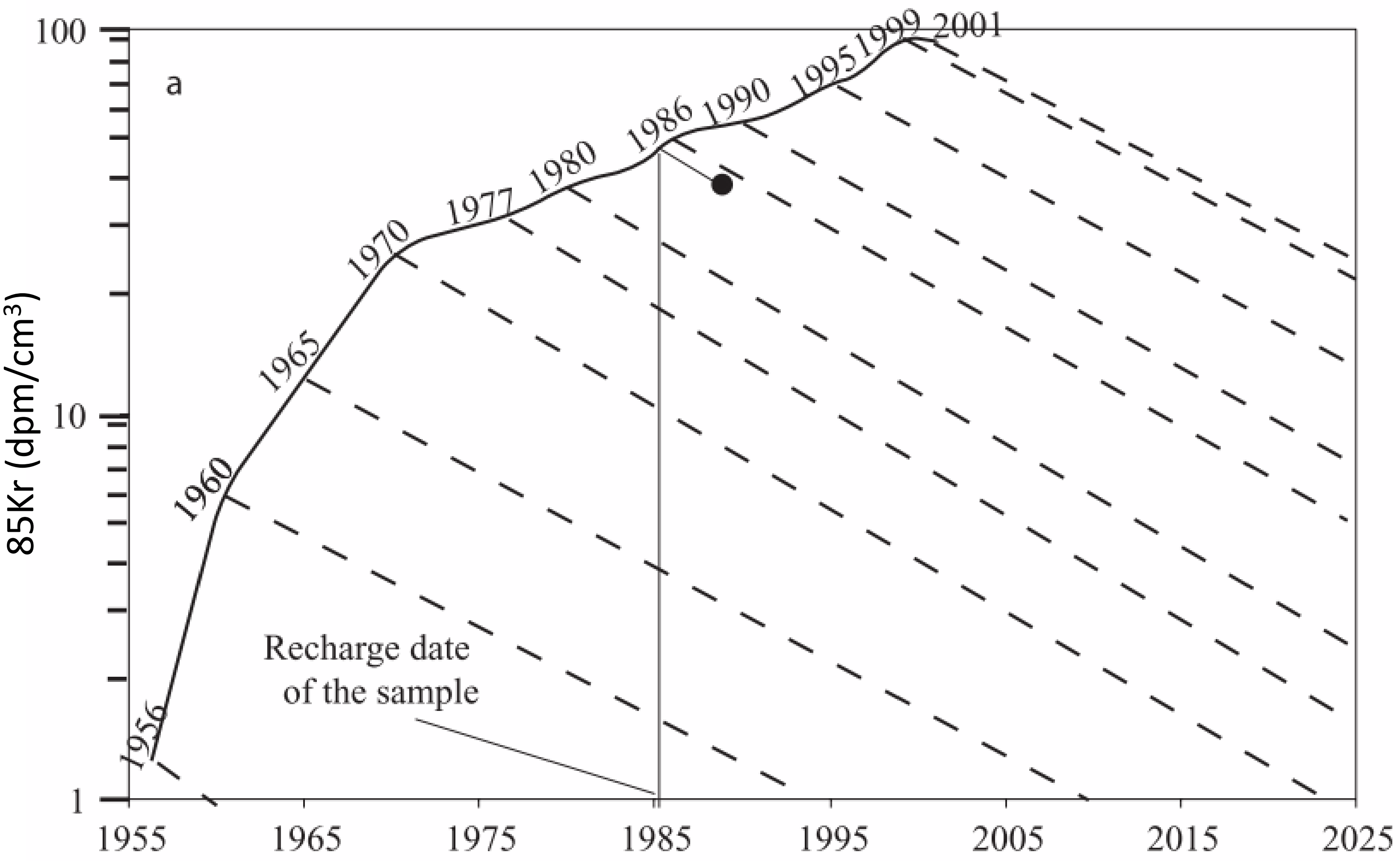
Half life: 10.76 yrs

^{85}Kr dissolves in rain and enters into GW system.

No ^{85}Kr means 1950 water



^{85}Kr measurements are from Freiberg, Germany, and SF_6 data are average values for various coastal sites in the Northern Hemisphere. (Corcho Alvardo et al., 2005)



Dating with ^{85}Kr: Y axis represents log conc of ^{85}Kr; diagonal lines represent the radioactive decay of ^{85}Kr upon entering the groundwater system. On diagonally extending the sample position to reach the krypton concentration curve, the recharge date of the sample can be identified. In the above example, the recharge date of sample represented by black circle 1985.5

Advantages

1. It is an inert gas and therefore less affected to contamination and chemical reactions

2. Since 85Kr is still on the rise the method's applicability continues.

Disadvantages

1. The main disadvantage in using ^{85}Kr is the **large sample-size** requirements and **high costs** due to the specialized measurement methods. There are only a few laboratory facilities worldwide.

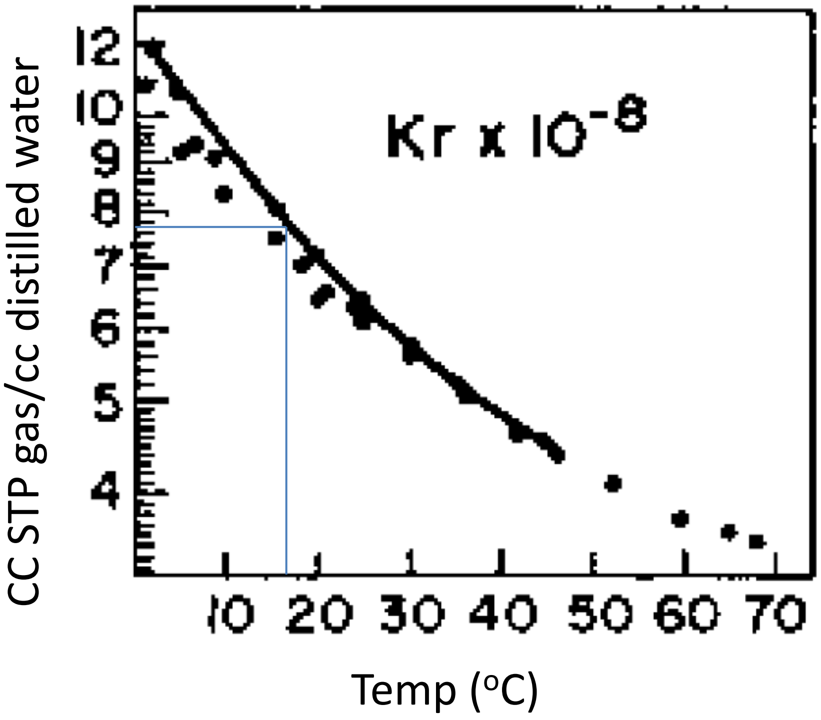
2. In **uranium-rich rocks aquifers**, some proportion of ^{85}Kr is from the in situ production (Lehmann et al., 1993). This may mask the atmospheric component of ^{85}Kr or make it difficult to be distinguished.

THE NOBLE GASES

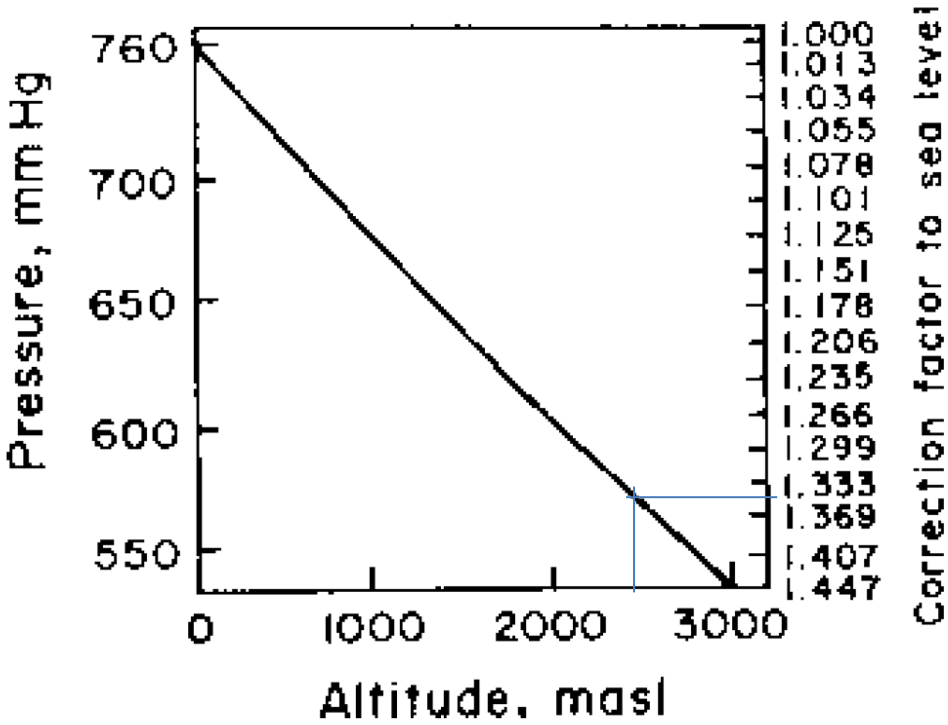
Helium, neon, argon, krypton, and xenon

- **They are not involved in any chemical or biological activity.**
- **They enter groundwater from two distinct major sources: by equilibration with air during infiltration or from deep-seated origins, which include flushing of radiogenic products from aquifer rocks and from mantle-derived gases. The origin of these different sources is identifiable by the isotopic composition.**
- **The initial concentrations of atmospheric noble gases in recharge water can be predicted from the ambient annual temperature and altitude of the suggested recharge area.**
- **The fact that there are five noble gases provides valuable redundancy.**

The higher the altitude, the less noble gases dissolve in water.

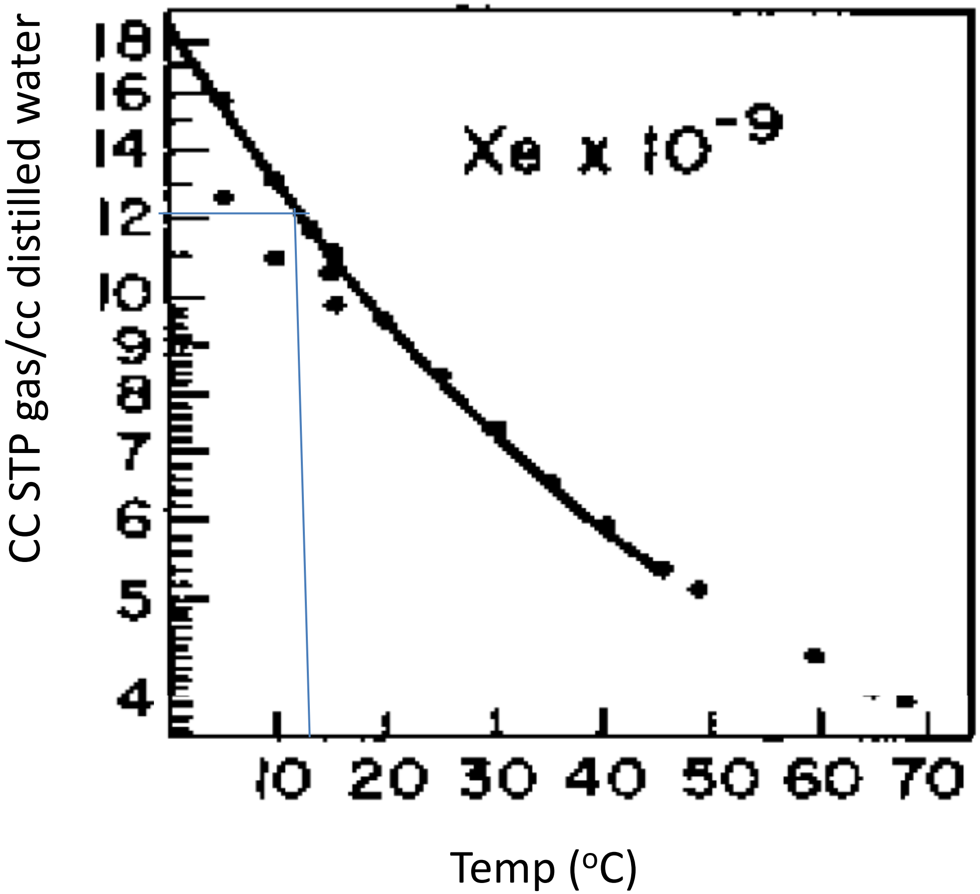


Solubility of Kr in fresh water at sea level (1 atm) as a function of ambient temperature



Atmospheric pressure variations as a function of altitude. Correction factors provide factor to covert noble gas solubility at sea level from desired altitude

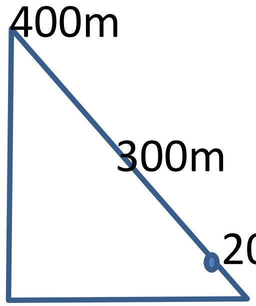
What is solubility of Kr at 18^0C at sea level
Ans: $7.5\text{x}10^{-8}$ cc STP/cc water
What is the solubility of Kr at 18^0C at 2500 masl
Ans: Altitude correction factor= 1.35
Therefore, solubility of Kr at 2.5km alt at 18^0C is
$(7.5\text{x}10^{-8})/1.35 = 5.5 \times 10^{-8}$ cc STP/cc water



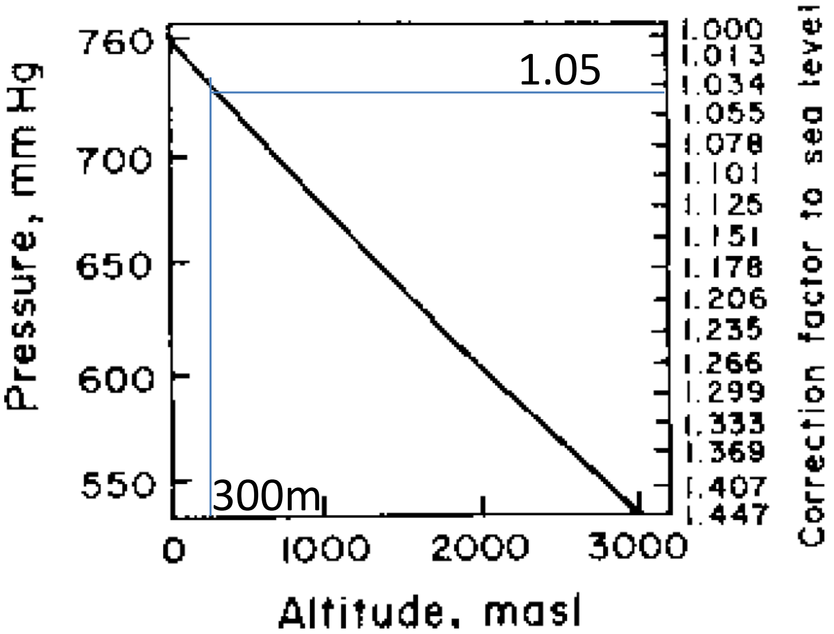
A coastal spring was found to contain 12x10^{-9} cc STP Xe/cc water. What was the ambient temperature at the point of recharge?

Solubility of Xe of value 12x10^{-9} cc STP Xe/cc water is at 12 ^{0}C. Hence, if recharge were at sea level, the ambient temperature would have been 12 ^{0}C.

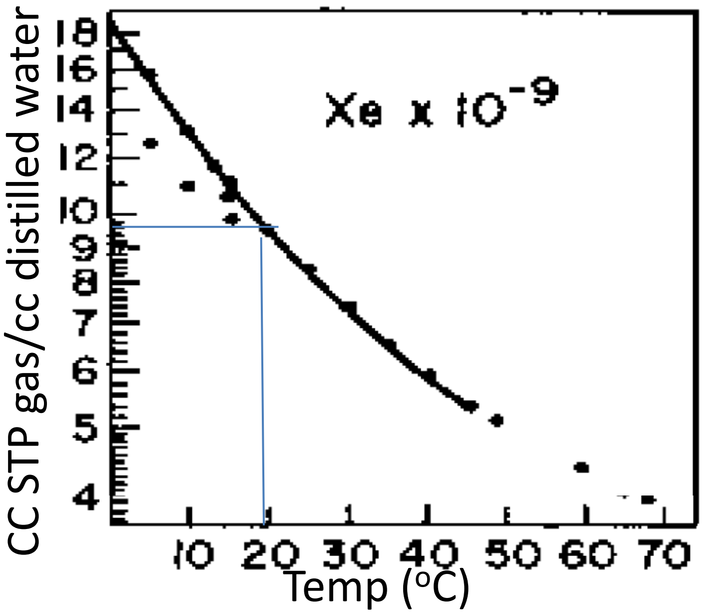
A spring emerges at an altitude of 200 masl. The highest point in the potential recharge area is 400 masl, and the average altitude of the recharge area is (400+200)/2 =300 m. In a water sample of this spring 10x10^{-9} cc STP Xe/cc water were found. What is the recharge temperature?



10x10^{-9} cc STP Xe/cc



The altitude correction factor for 300m is 1.05. Therefore, equivalent Xe concectration at sea level = (10x10^{-9})x1.05 = 9.5 x10^{-9}



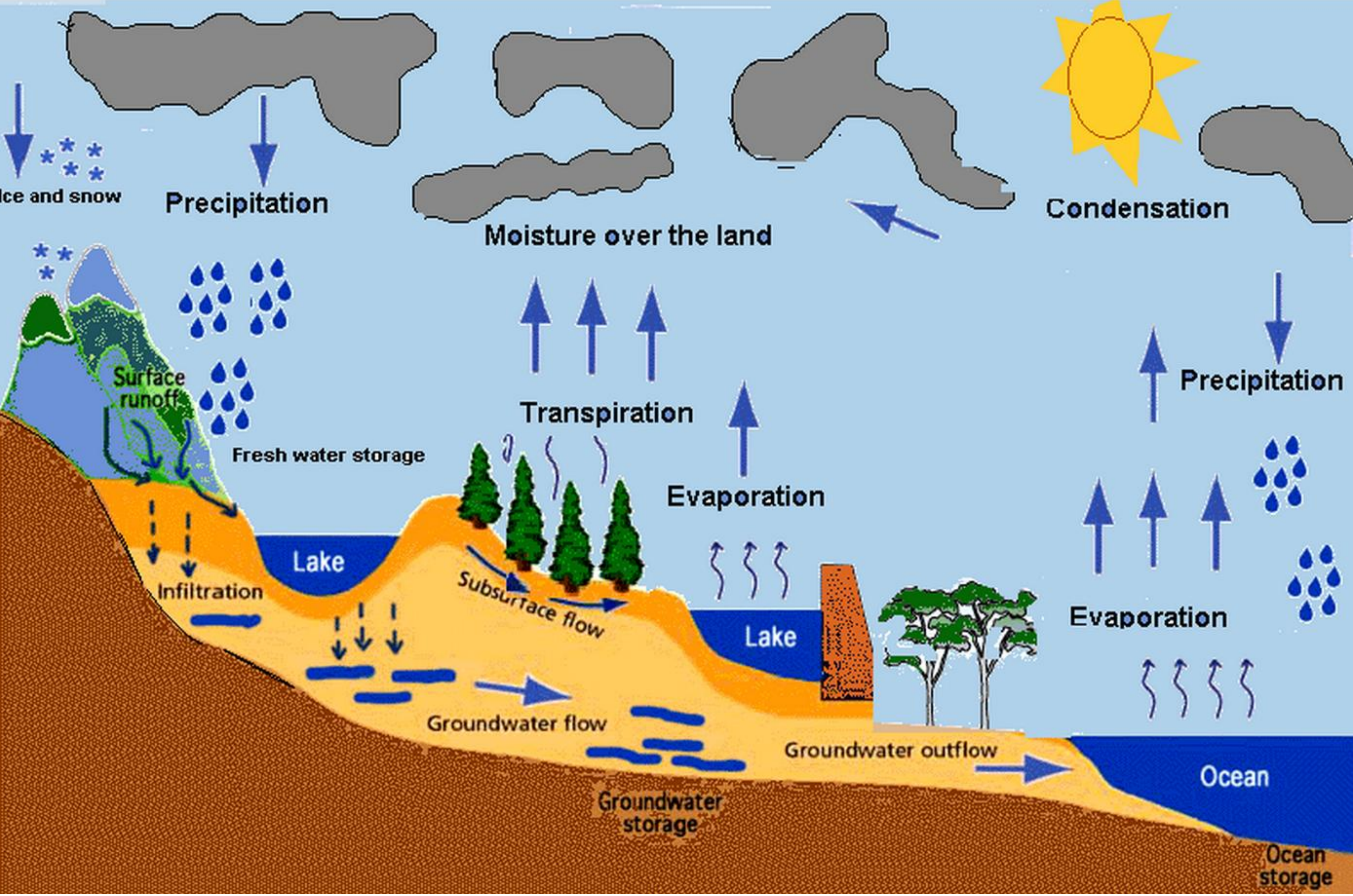
The recharge temperature at 9.5x10^{-9} is ~20^{0}C

By combining groundwater age and nobel gas technique paleo-groundwater recharge temperature can be calculated

Conclusions

- Hydrological cycle is very complex
- Conventional techniques are tedious, time consuming, expensive to conduct and requires large data to generate for developing a phenomenological hydrological model
- Isotopes, noble gases, etc provide new range of tracers in addition to the conventional chemical & temp tracers
- Stable isotopes help in investigating multiaquifer system, interconnectivity in groundwater flow, identification of recharge locations, flow velocity, hydrograph separation, paloe-recharge & old groundwater system etc
- Isotopes in glaciology provide proxy temperature record

- Isotope are useful in water balancing of hydrological system as, it can analyze surface, sub-surface, recharge and ET components
- In atmospheric moisture studies isotopes are useful in investigating moisture circulation pattern
- Variety of dating technique exist to date hydrological system from months to million years. Of these ^{3}H, ^{14}C are most popular ones while the new techniques include Kr, ^{3}H-^{4}He etc
- Dating of waters in conjunction with water quality is useful in investigating water quality evolution for water system of recent origin to paleo system (Watrak example)
- Noble gas provides easy way to examine the recharge water temperature which in conjunction with groundwater dating help in analyzing paleo-recharge conditions


Ice and snow
Precipitation
Moisture over the land
Condensation
Surface runoff
Fresh water storage
Transpiration
Evaporation
Precipitation
Lake
Infiltration
Subsurface flow
Lake
Evaporation
Groundwater flow
Groundwater outflow
Ocean
Groundwater storage
Ocean storage

THANKS

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