ISOTOPE STUDIES FOR IDENTIFICATION OF ORIGIN AND RECHARGE AREAS OF SPRINGS

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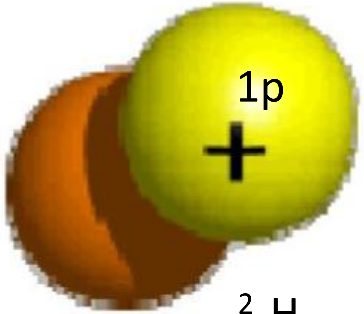
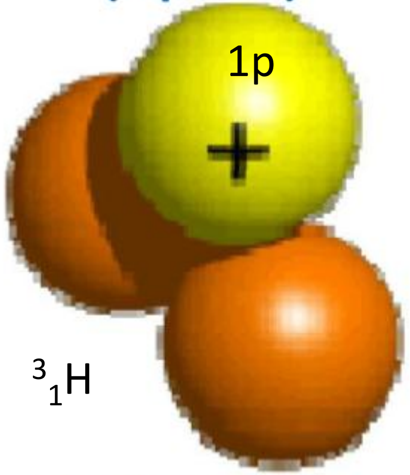
BASICS OF ISOTOPES HYDROLOGY

ISOTOPES OF HYDROGEN

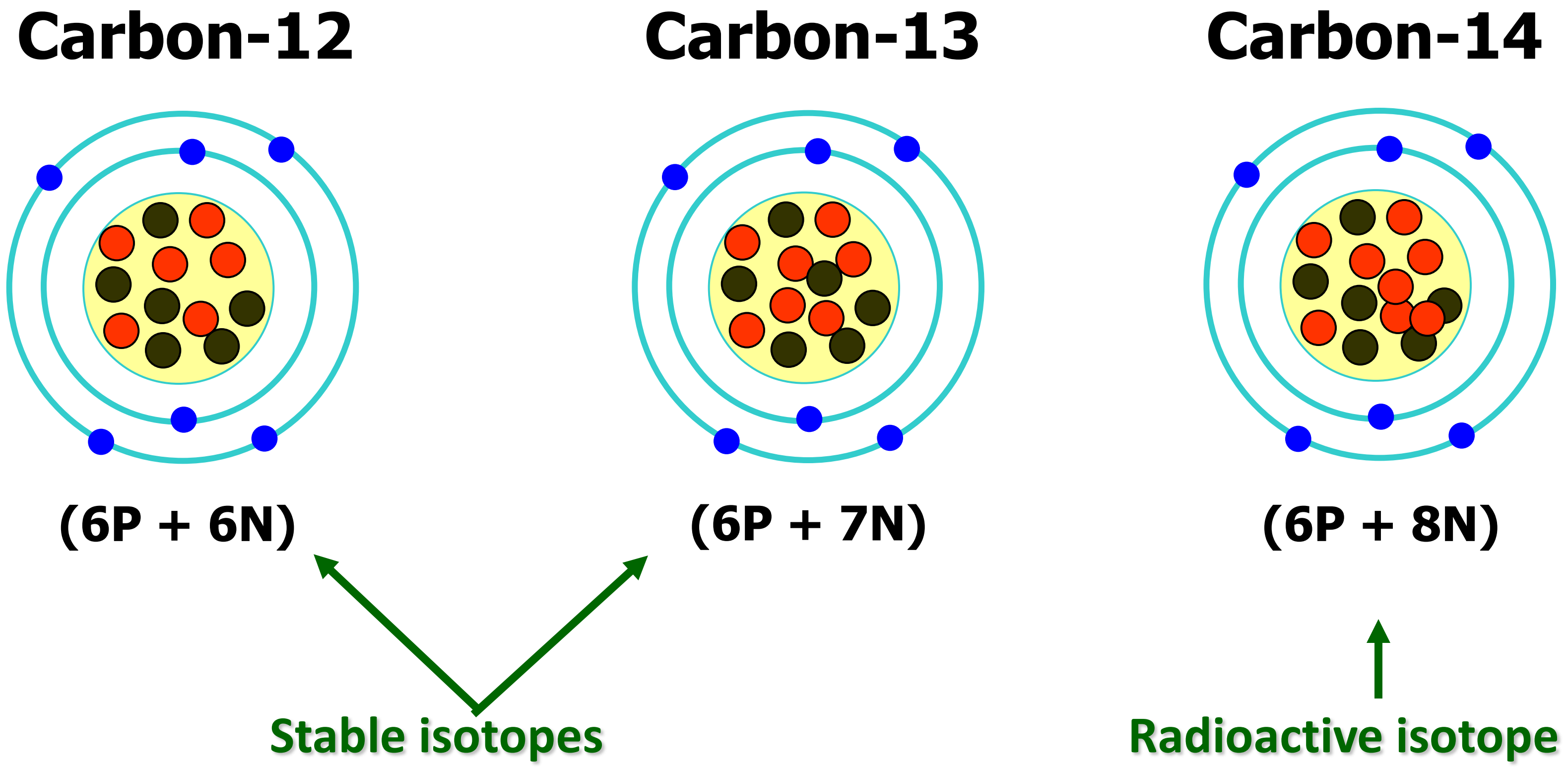
Name : (Nucleus)	Protium (1p)	Deuterium (1p +1n)	Tritium (1 p+ 2n)
Schematic:			
Mass No (N+P) Atomic No(P) Element	$^{1}_{1}H$	$^{2}_{1}H$	$^{3}_{1}H$
Characerstic:	Light (Stable)	Heavy (Stable)	Still Heavy (Radioactive)
Abundance:	99.985%	0.015%	"decays" to 3He

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

Chemical analysis ? Physical estimation ✓

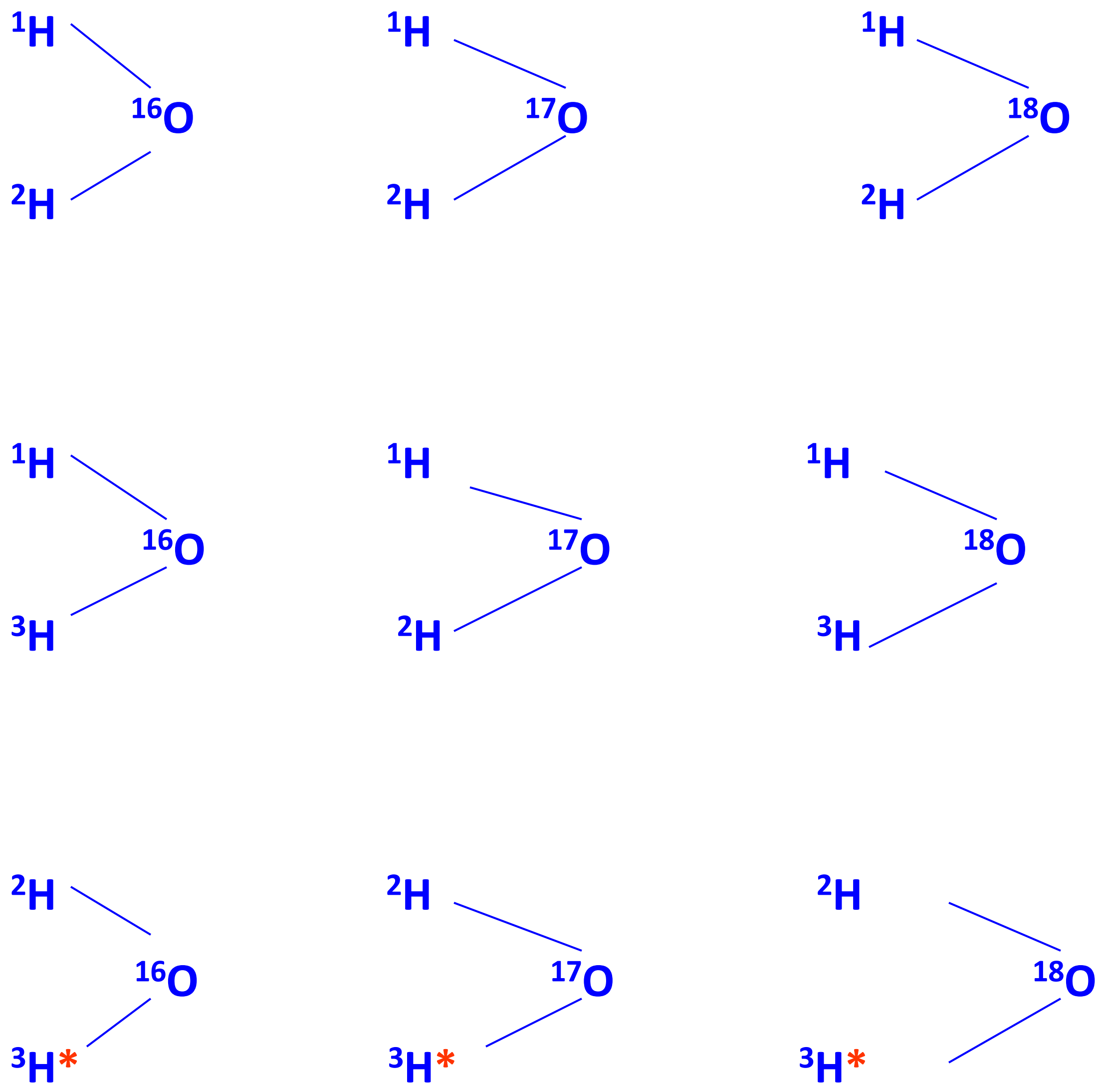
eg., R = $^{18}O/^{16}O$

- **Some isotopes are stable, while others are unstable, or radioactive.**



R. Doucett

ISOTOPICALLY LABELLED DIFFERENT TYPE OF WATER MOLECULES



Isotopes Tracers

Environmental Isotope

Artificial or injected isotopes

Stable isotopes of water and Contaminants

^{2}H, ^{18}O,

^{15}N, ^{34}S, ^{13}C

RA isotopes of water and contaminants

^{3}H (nat./event marker),

^{14}C (nat./event marker),

^{32}Si, ^{222}Rn, ^{36}Cl, ^{81}Kr, ^{85}Kr, ^{132}Cs,

ENVIRONMENTAL ISOTOPES

- Available in the Earth's Atmosphere
- Stable and Unstable
- Neither to buy nor to inject
- Naturally introduced in the hydrological cycle
- Evaporation, condensatation & mixing processes
- Very Sophisticated Instruments are Available
- Not harmful

Environmental Isotopes

Stable Isotopes

Do not decay spontaneously (stable over time)

Examples: ^{18}O, ^{2}H, ^{13}C

Used as Tracers

Radioactive Isotopes

Emit alpha and beta particles and decay over time

Examples: ^{3}H (Tritium), ^{14}C

Used for Dating

Stable Isotope Hydrology

Atoms with:
same number of e^- & p^+, but
different number of n

δ notation

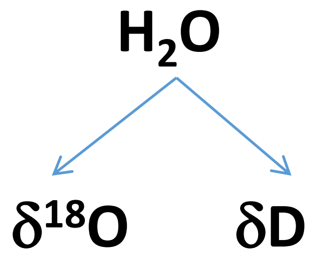
$$\delta_{sample} = \frac{R_{sample} - R_{standard}}{R_{standard}} \times 1000 \ (‰)$$

Say, $(^{18}O/^{16}O)_{Std.}$ = 0.0020052; $(^{18}O/^{16}O)_{Smpl}$ = 0.0020054

[(for every 1 atom of ^{18}O/0.0020052)~ 498.7 atoms of ^{16}O]

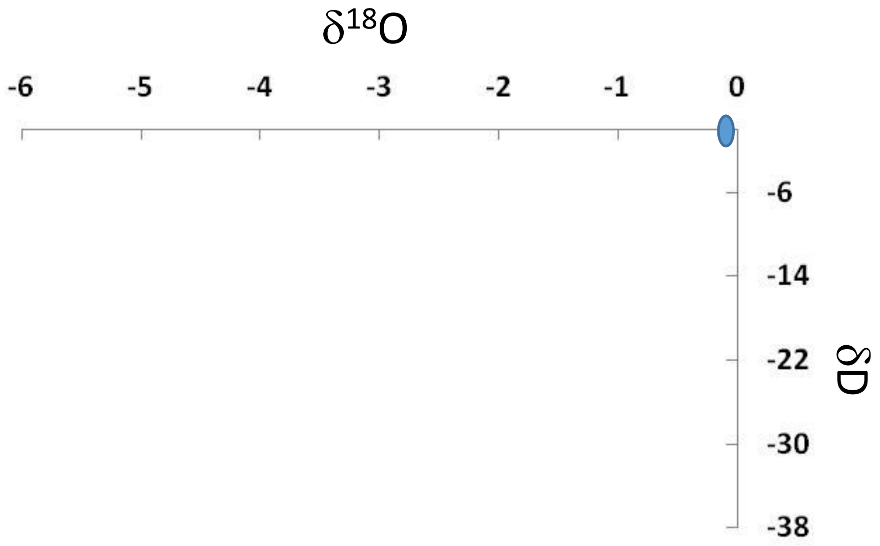
$$\delta^{18}O = \frac{0.0020054 - 0.0020052}{0.0020052} \times 1000 \ (‰)$$

$\delta^{18}O$ ~ +0.1 (‰); Easy to represent, better precision , no need to know absolute ratio.



What is $\delta^{18}O$ of water that contains 1 part ^{18}O per 499 parts of ^{16}O atoms ? (assume in std wtr contains 1 part ^{18}O per 498 parts of ^{16}O atoms)

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



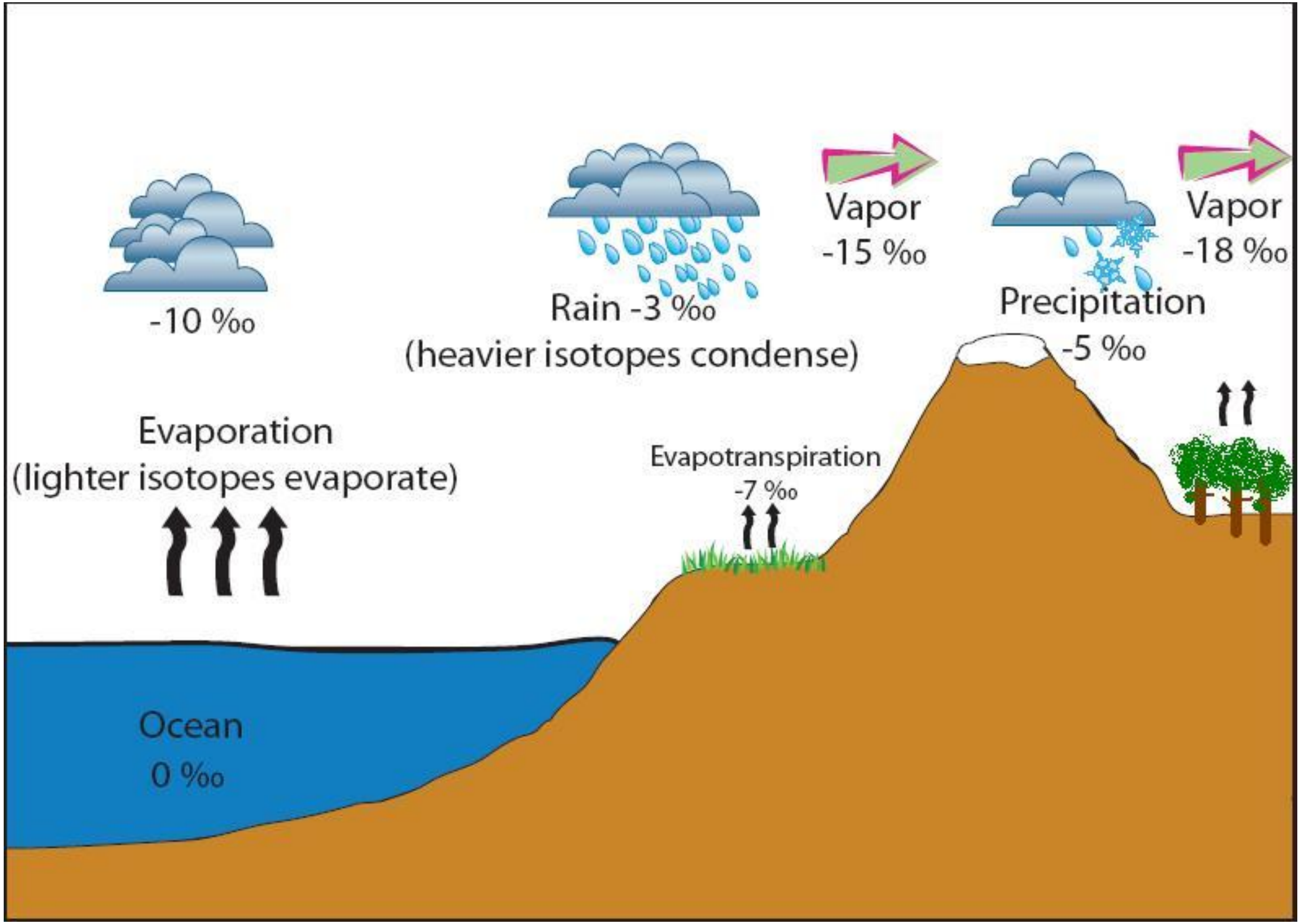
(show) that $\delta D_{std} = 0$

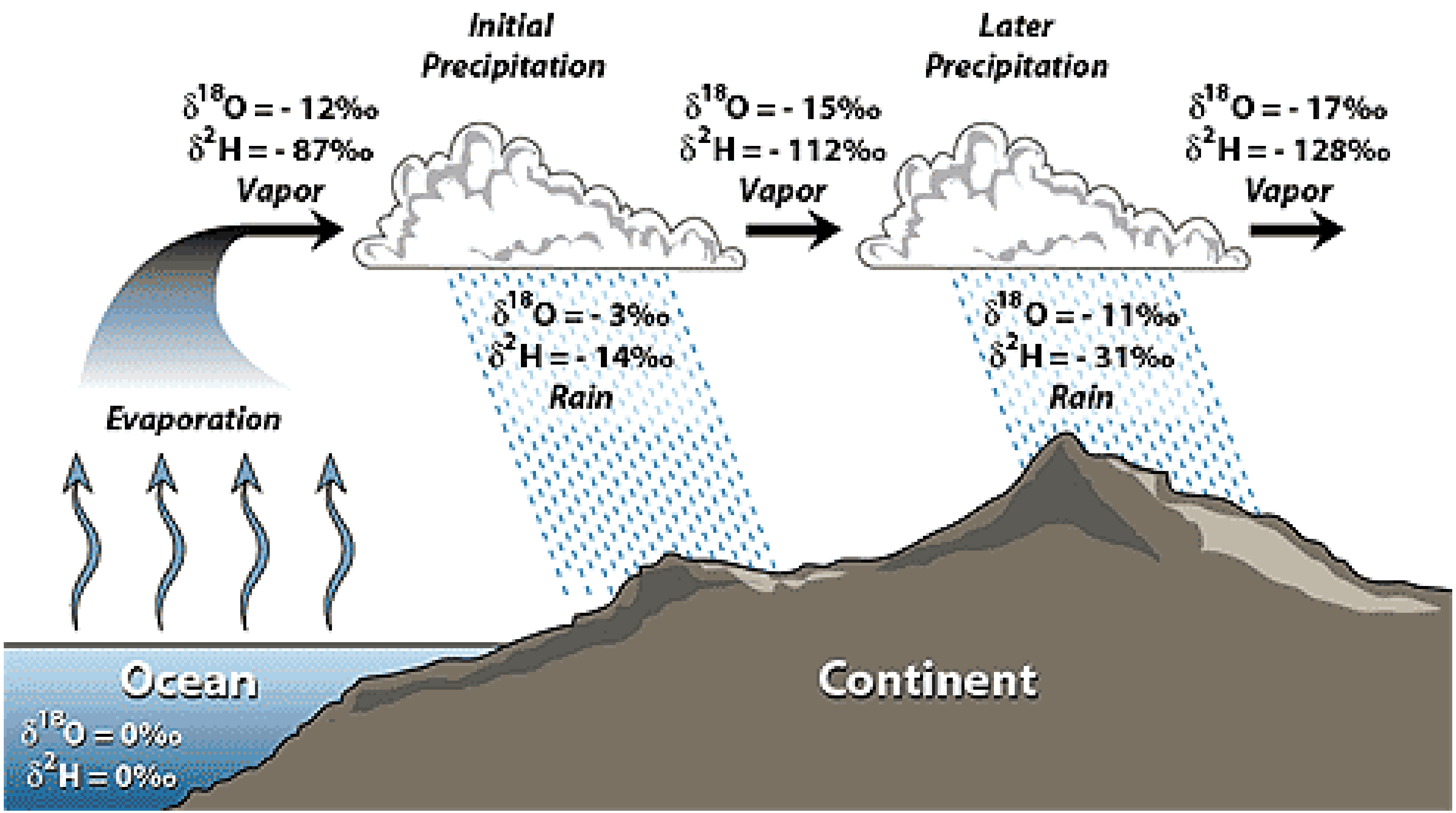

CONTINUOUS FLOW SIRMS
Stable Isotope Ratio Mass Spectrometer

Isotopic Fractionation:

Evaporation: Lighter molecules preferentially evaporates (depletion of vapour)

Condensation: Heavier molecules preferentially condense (enrichment in rain)





Rainout effect

(Coplen et al., 2000)

Meteoric Water Line

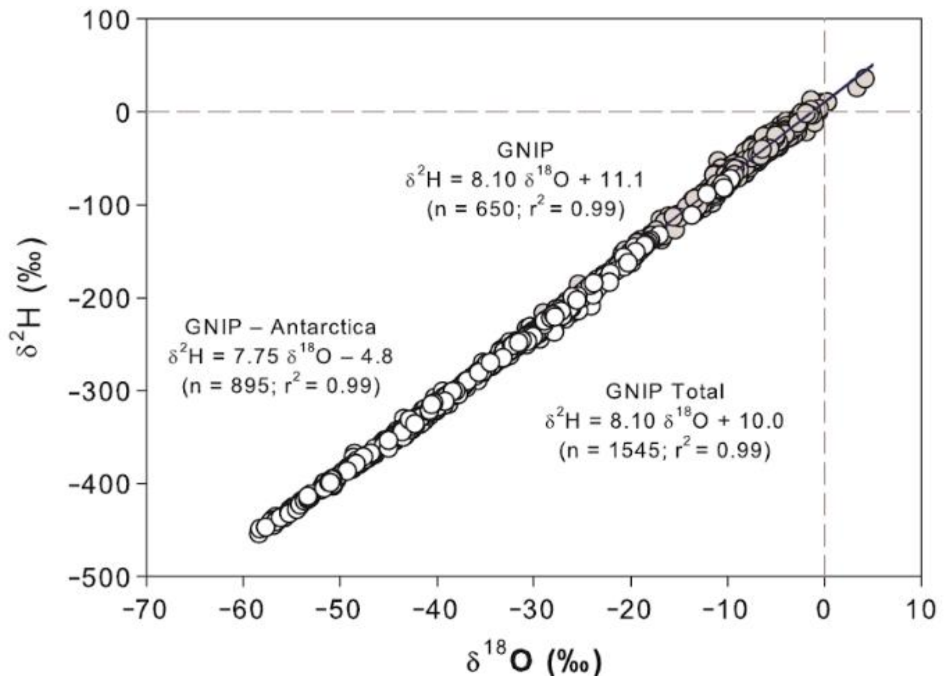


Fig: Relationship between long-term deuterium vs oxygen-18 annual means for GNIP stations collecting precipitation samples on monthly basis and for Antarctic snow

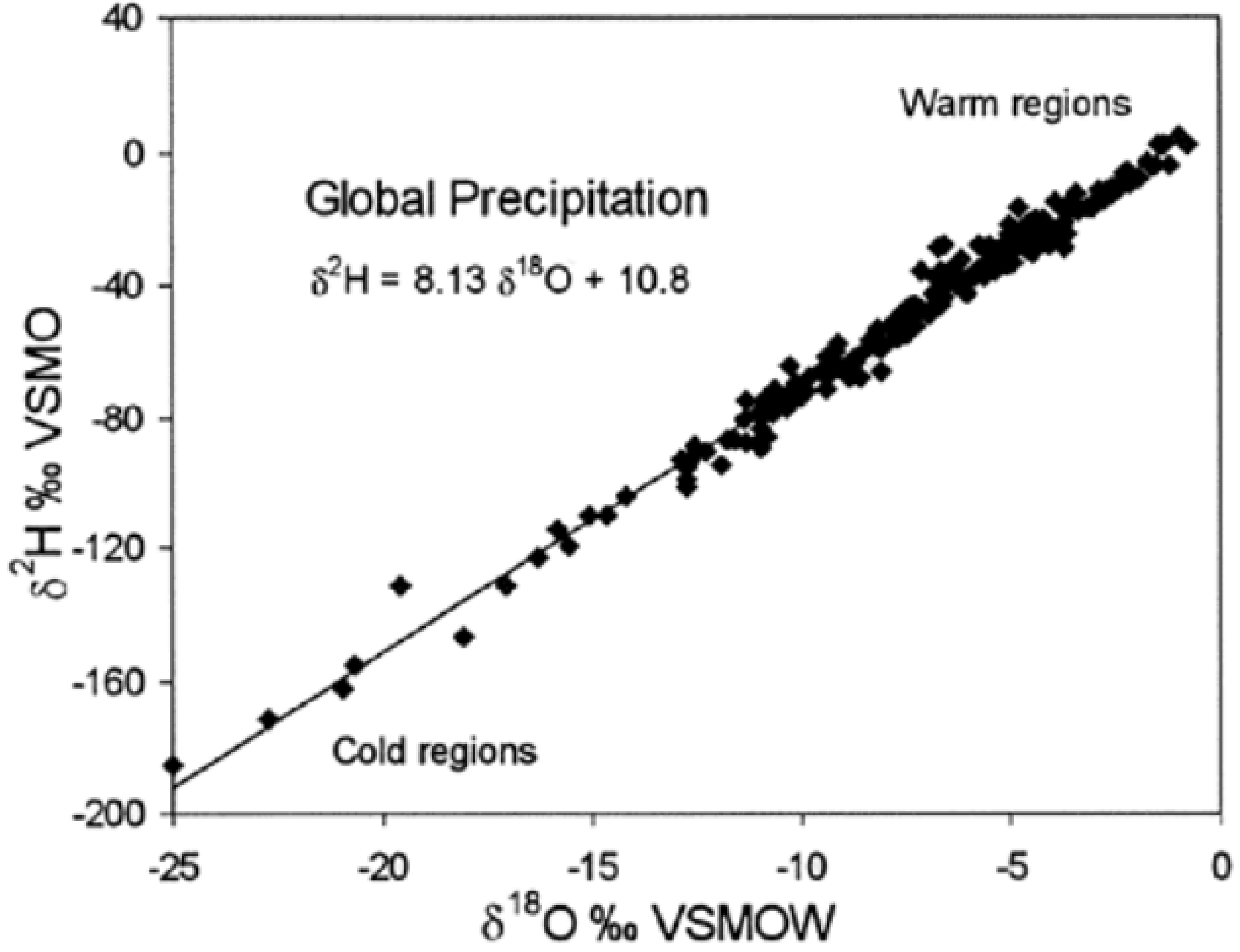
Global Meteoric Water Line (GMWL).

$\delta D = 8\delta^{18}O + 10$ .....(Craig, 1961)
This is a Global relation between ^{18}O & ^{2}H in precipitation)

Further updated as :

$\delta D = 8.20\ (\pm 0.07)\ \delta^{18}O + 11.27$ (±0.07 (in VSMOW scale) …(Rozanski et al., 1993).

The ratio of 2H and 18O in precipitation anywhere in the world will plot close to this line

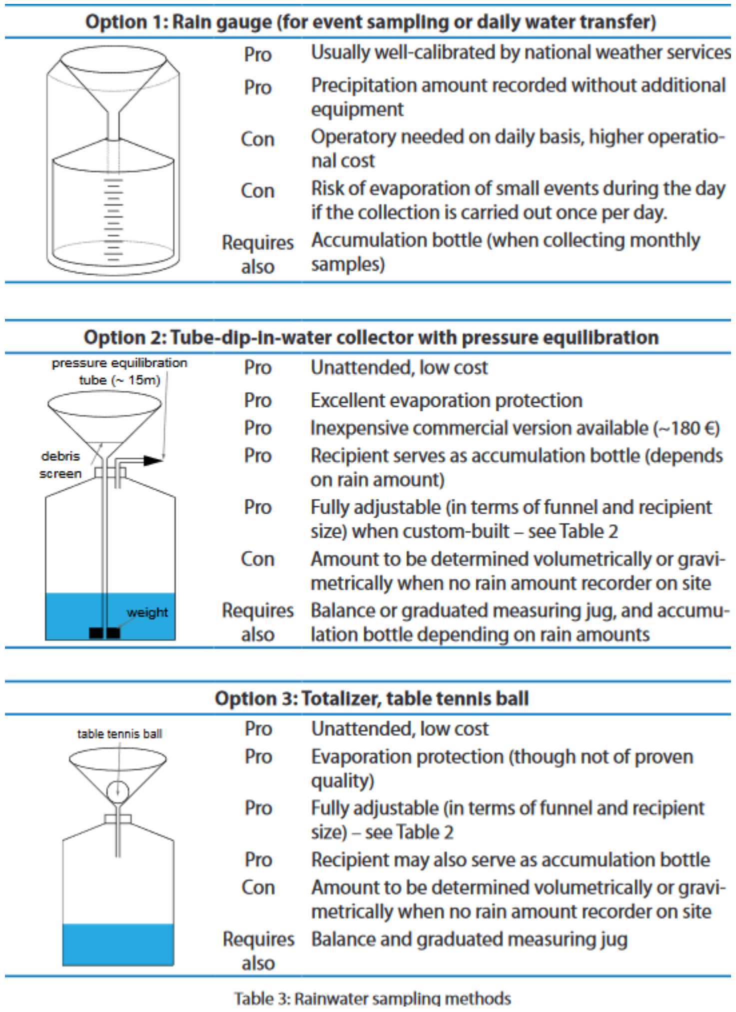


The 'weighted mean' value of precipitation at a given station is calculated as:

$$\overline{\delta}_w = \frac{\sum_{i=1}^{n} P_i \delta_1}{\sum_{i=1}^{n} P_1}$$

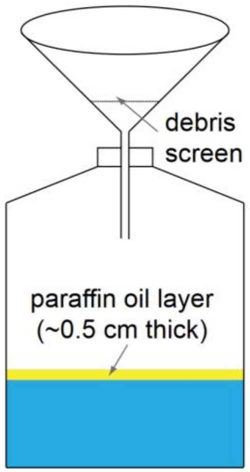
where Pi and δ_i; denote the monthly precipitation and its δ-value.

IAEA/GNIP Precipitationsampling guide



Option 1: Rain gauge (for event sampling or daily water transfer)		
	Pro	Usually well-calibrated by national weather services
	Pro	Precipitation amount recorded without additional equipment
	Con	Operatory needed on daily basis, higher operational cost
	Con	Risk of evaporation of small events during the day if the collection is carried out once per day.
	Requires also	Accumulation bottle (when collecting monthly samples)
Option 2: Tube-dip-in-water collector with pressure equilibration		
pressure equilibration tube (~ 15m); debris screen; weight	Pro	Unattended, low cost
	Pro	Excellent evaporation protection
	Pro	Inexpensive commercial version available (~180 €)
	Pro	Recipient serves as accumulation bottle (depends on rain amount)
	Pro	Fully adjustable (in terms of funnel and recipient size) when custom-built – see Table 2
	Con	Amount to be determined volumetrically or gravimetrically when no rain amount recorder on site
	Requires also	Balance or graduated measuring jug, and accumulation bottle depending on rain amounts
Option 3: Totalizer, table tennis ball		
table tennis ball	Pro	Unattended, low cost
	Pro	Evaporation protection (though not of proven quality)
	Pro	Fully adjustable (in terms of funnel and recipient size) – see Table 2
	Pro	Recipient may also serve as accumulation bottle
	Con	Amount to be determined volumetrically or gravimetrically when no rain amount recorder on site
	Requires also	Balance and graduated measuring jug

Table 3: Rainwater sampling methods

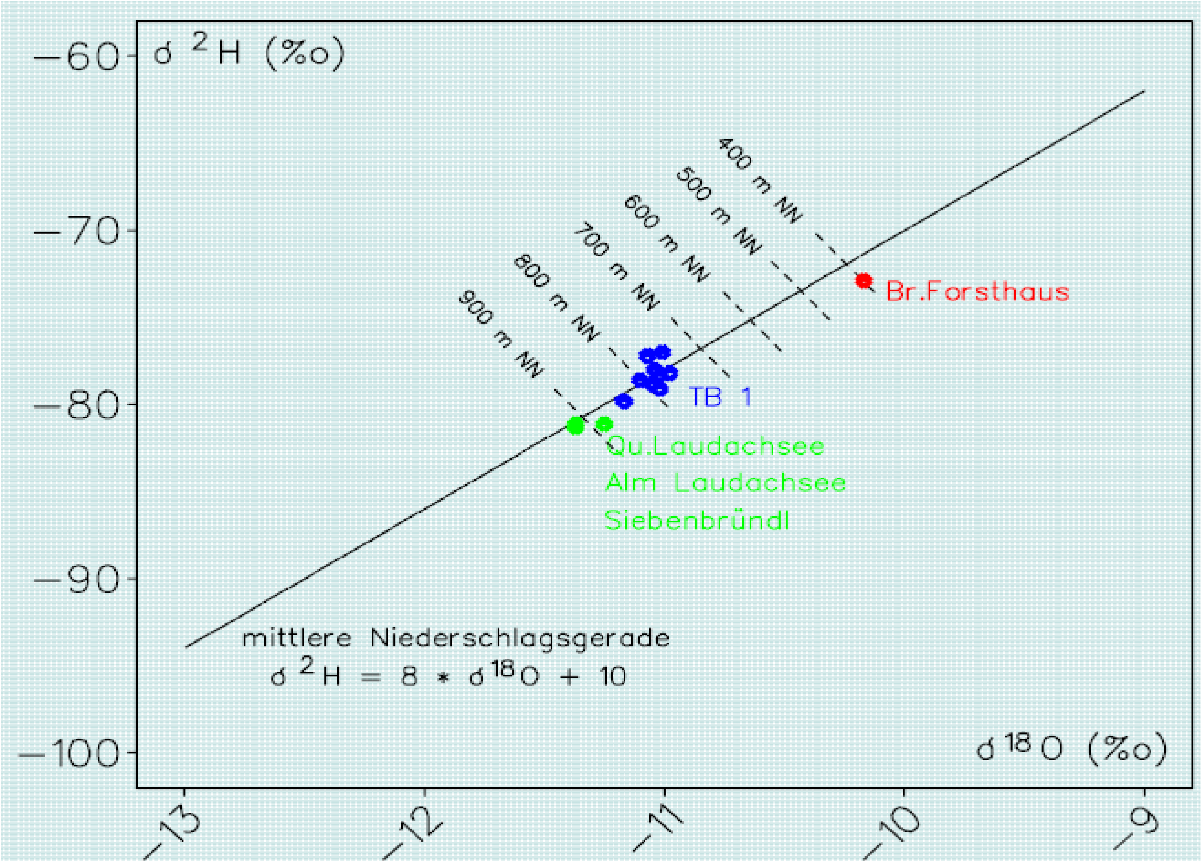


http://www-naweb.iaea.org/napc/ih/documents/other/gnip_manual_v2.02_en_hq.pdf

http://www-naweb.iaea.org/napc/ih/documents/other/GNIP%20station%20operation%20manual_Feb13_EN.pdf

http://www-naweb.iaea.org/napc/ih/documents/userupdate/sampling.pdf

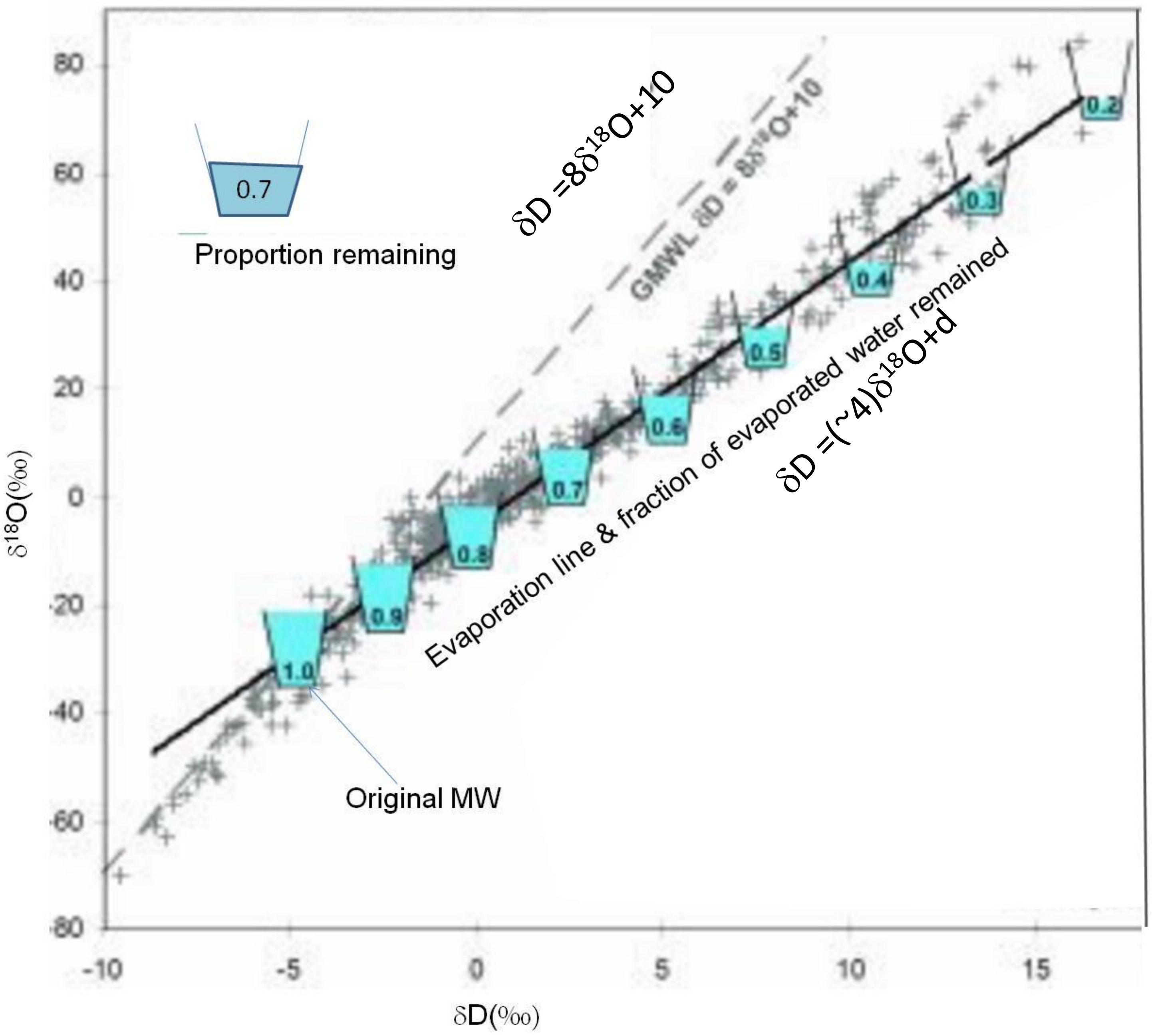
LMWL or RMWL: Deviation (slope & intercept) from GMWL at regional scale due to regional atmospheric vapor circulation, local meterological conditions, large local water bodies etc. The local meteoric water line is a convenient reference line for the understanding and tracing of local groundwater origins and movement (establish if possible).



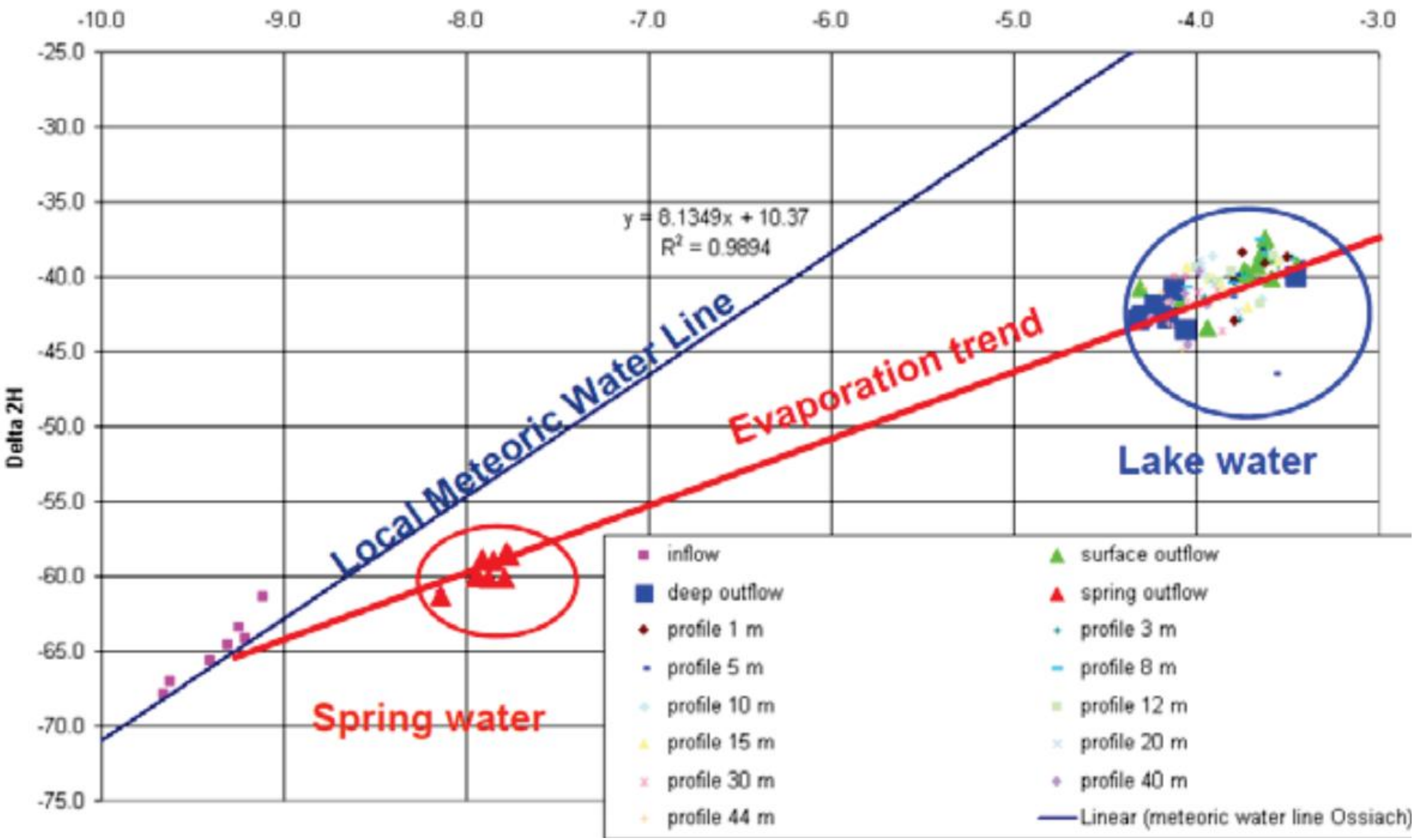
Schematic of LMWL indicating elevation of precipitation at different altitudes (Source: HYDROISOTOPE, GMBH, Germany)

STABLE ISOTOPES OF SURFACE WATER
(Evaporation effect)

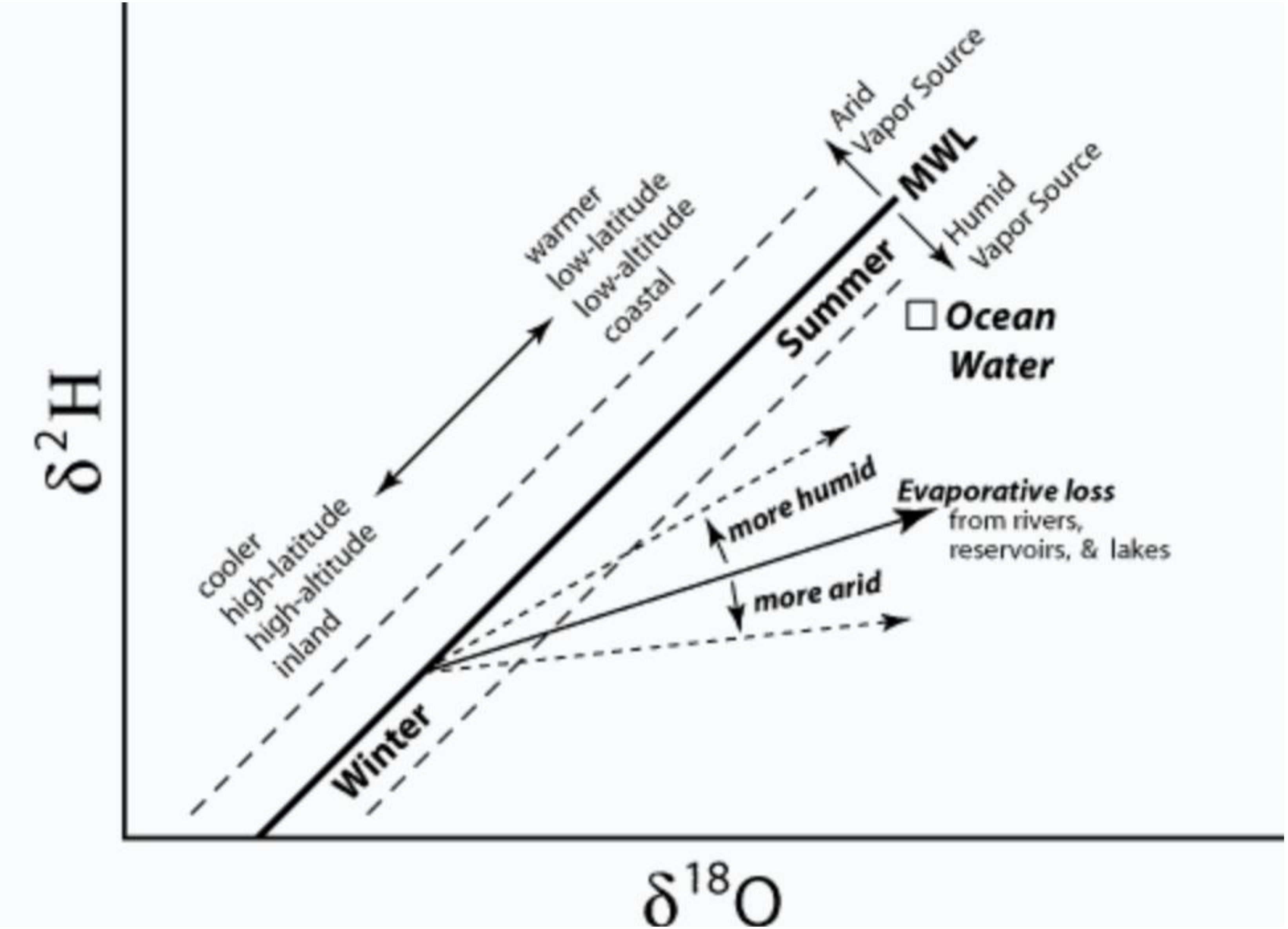
MWL & Evaporation Line



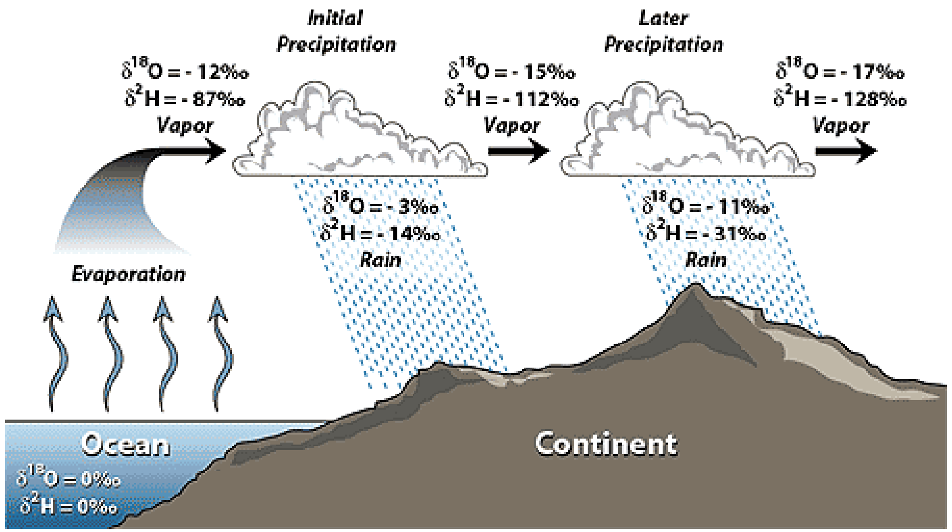
0.7
Proportion remaining
$\delta D = 8\delta^{18}O+10$
GMWL $\delta D = 8\delta^{18}O+10$
Evaporation line & fraction of evaporated water remained
$\delta D = (\sim 4)\delta^{18}O+d$
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
Original MW
$\delta^{18}O$(‰)
δD(‰)
80
60
40
20
0
-20
-40
-60
-80
-10
-5
0
5
10
15

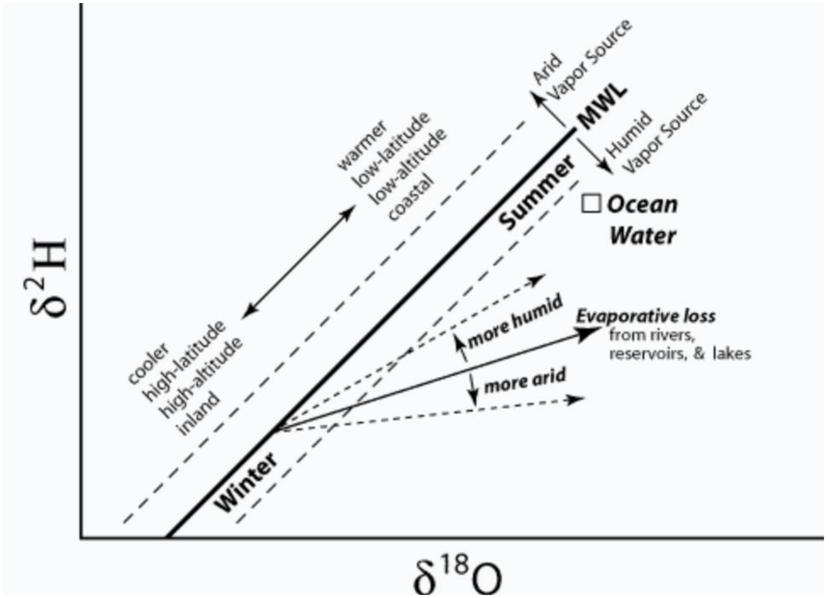


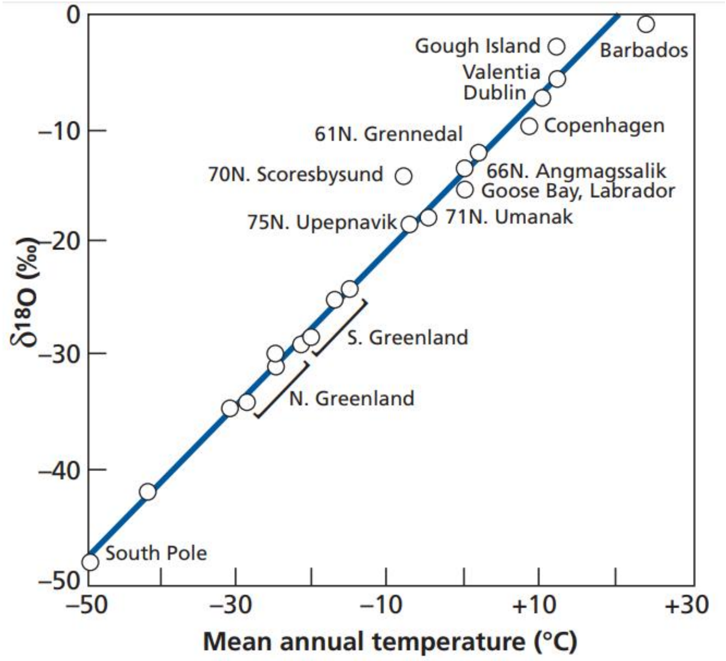
Till Harum et al., 2013; I**nteraction of lakes with local groundwater systems – environmental isotopes as tool for water balance investigations**

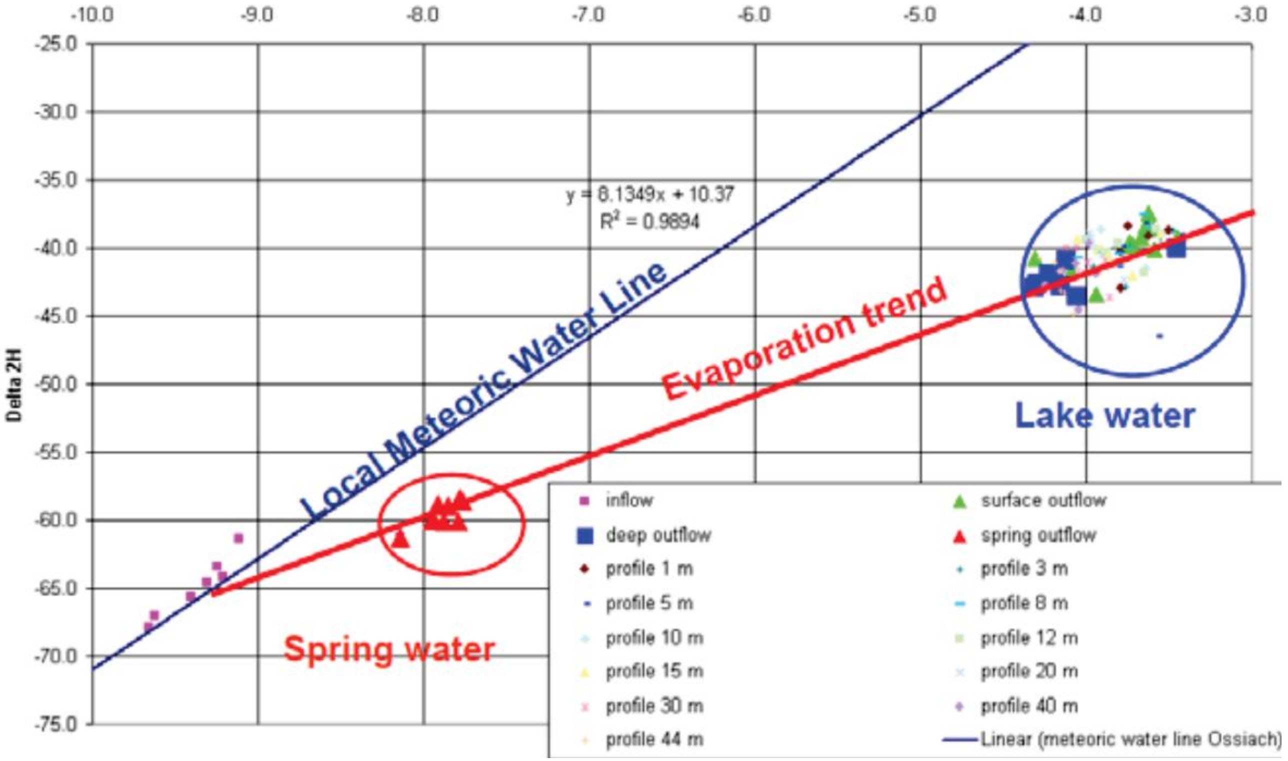


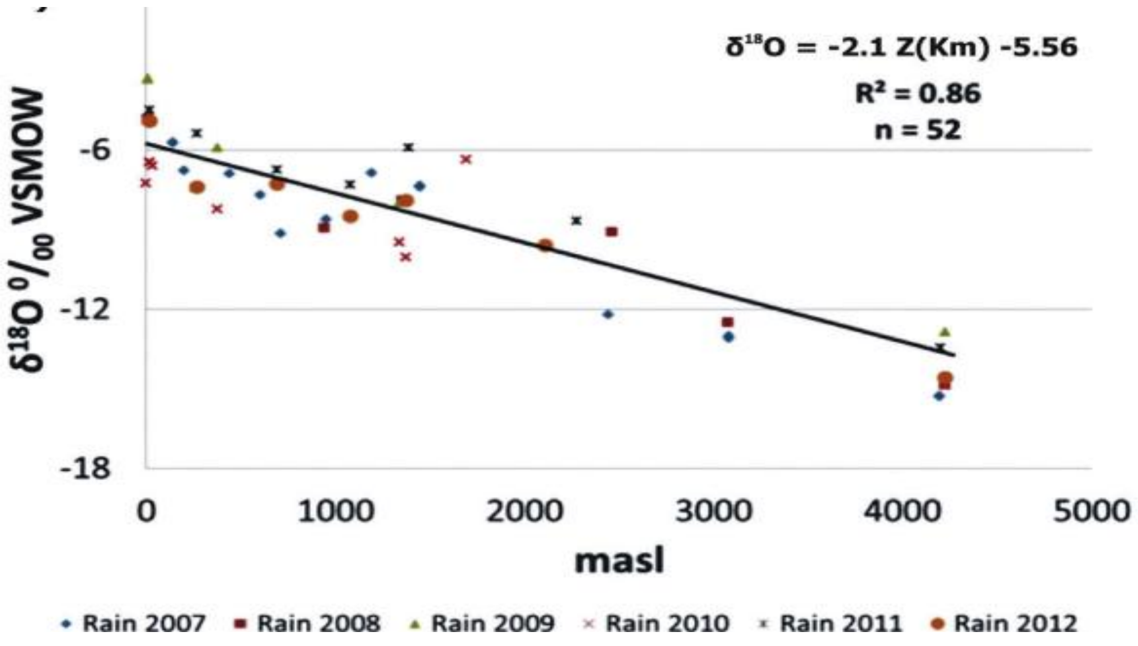
Summary diagram of how hydrologic processes affect Oxy. & Hydr. Composition of water

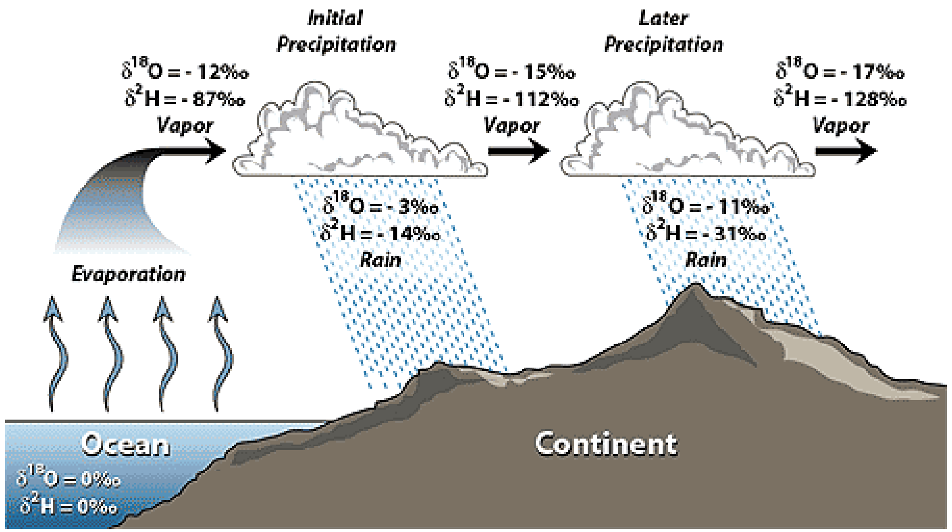

Initial Precipitation
Later Precipitation
δ18O = - 12‰
δ2H = - 87‰
Vapor
δ18O = - 15‰
δ2H = - 112‰
Vapor
δ18O = - 17‰
δ2H = - 128‰
Vapor
δ18O = - 3‰
δ2H = - 14‰
Rain
δ18O = - 11‰
δ2H = - 31‰
Rain
Evaporation
Ocean
δ18O = 0‰
δ2H = 0‰
Continent


δ2H
δ18O
Arid Vapor Source
MWL
Humid Vapor Source
Ocean Water
warmer low-latitude low-altitude coastal
Summer
cooler high-latitude high-altitude inland
Winter
more humid
Evaporative loss from rivers, reservoirs, & lakes
more arid


δ18O (‰)
Mean annual temperature (°C)
0
−10
−20
−30
−40
−50
−50
−30
−10
+10
+30
Gough Island
Barbados
Valentia
Dublin
61N. Grennedal
Copenhagen
70N. Scoresbysund
66N. Angmagssalik
Goose Bay, Labrador
75N. Upepnavik
71N. Umanak
S. Greenland
N. Greenland
South Pole


-10.0
-9.0
-8.0
-7.0
-6.0
-5.0
-4.0
-3.0
-25.0
-30.0
-35.0
-40.0
-45.0
-50.0
-55.0
-60.0
-65.0
-70.0
-75.0
Delta 2H
y = 8.1349x + 10.37
R² = 0.9894
Local Meteoric Water Line
Evaporation trend
Lake water
Spring water
inflow
surface outflow
deep outflow
spring outflow
profile 1 m
profile 3 m
profile 5 m
profile 8 m
profile 10 m
profile 12 m
profile 15 m
profile 20 m
profile 30 m
profile 40 m
profile 44 m
Linear (meteoric water line Ossiach)





ALTITUDE EFECT

Altitude/elevation/orographic effect: -1 to -**4** ‰ per 100 m rise in altitude

Quezadas et al., Geofís.Intl vol.54 no.3 México jul./sep. 2015

Application of Altitude effect: Recharge source of spring water

Isotopes

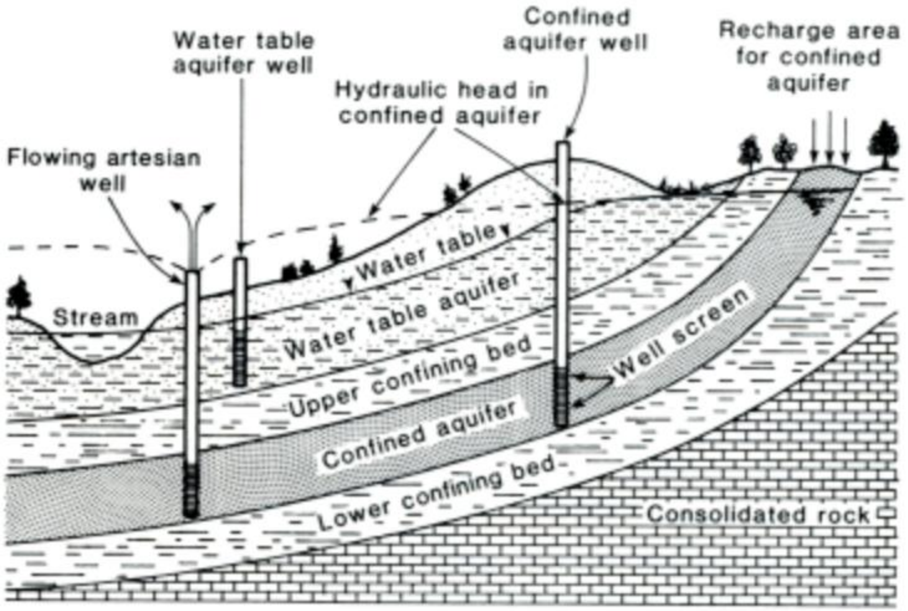
Stable

Unstable

Environmental

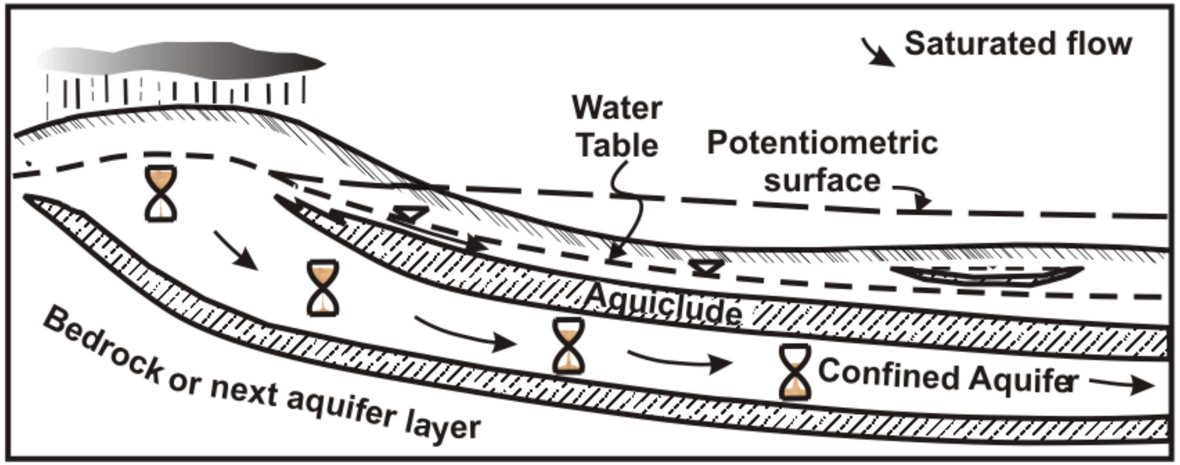
GROUNDWATER DATING

Groundwater age



Environmental Isotopes tracers: Radioactive isotopes

Groundwater system (after Johnson, 1975)



Equation for Radioactive Decay

$$\frac{dN}{dt} = -\lambda N$$

λ: Decay constant: It is the probability that any given nucleus will disintegrate in the interval of time dt.

λN : Activity (A)

$$N = N_0 e^{-\lambda t}$$

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

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

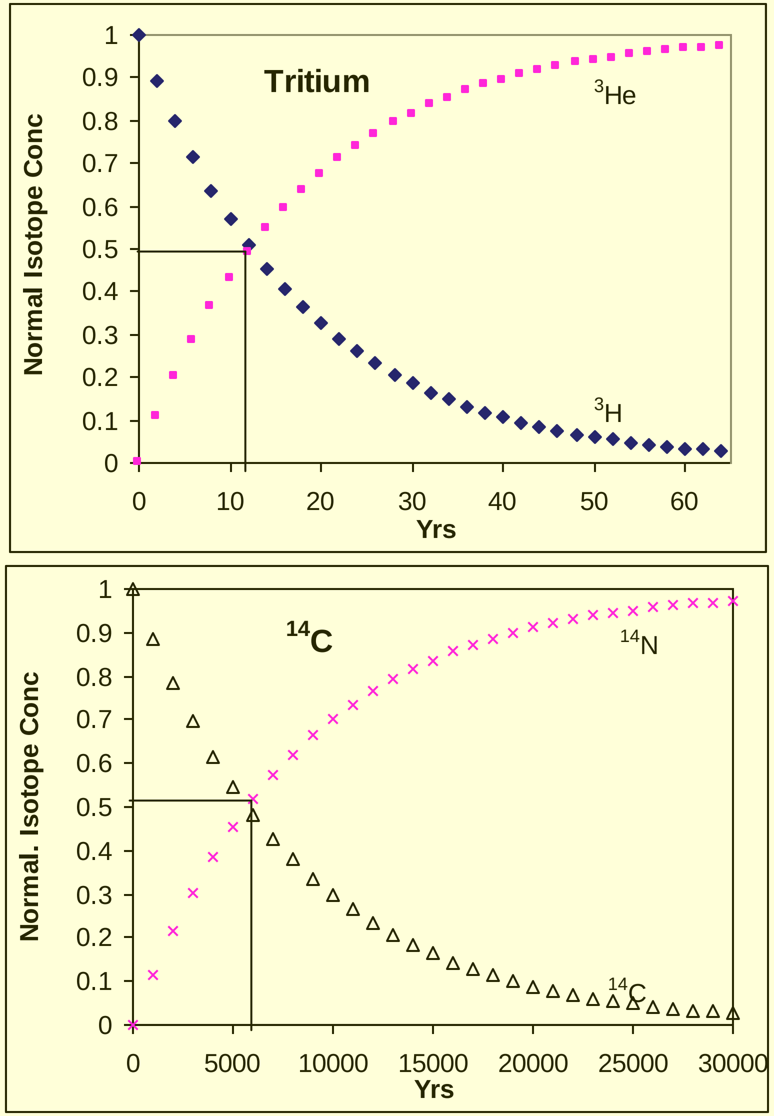
$$\lambda = 0.693/(t_{½})$$

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

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

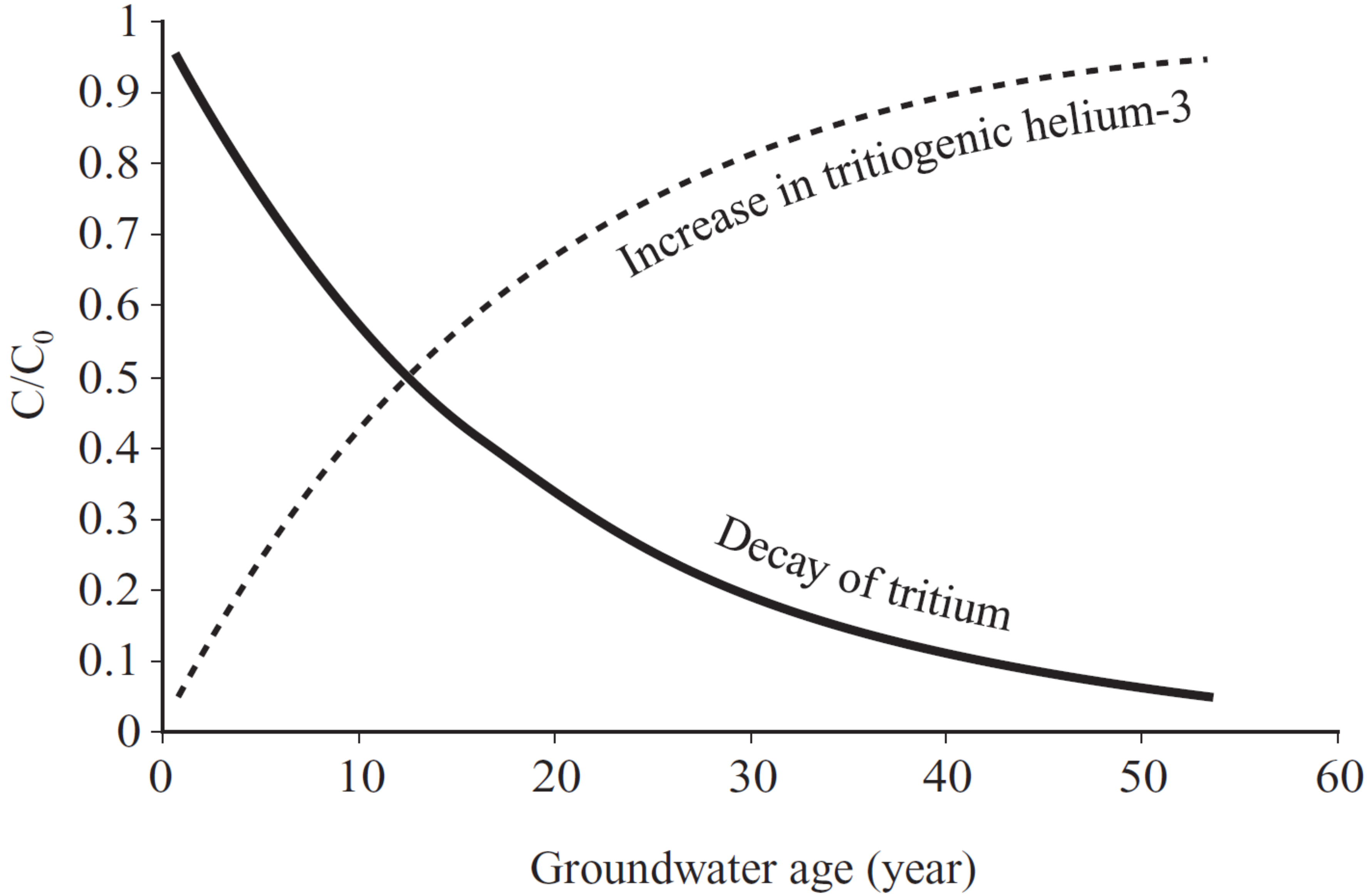
For ^{14}C: $A = A_0 \exp(-0.00012*t)$

For t= 12.32; A= 0.5Ao



Radioactivity Characteristic of tritium and radiocarbon

Dating by $^3H/^3He$ technique



Decay of tritium atoms and increase in ^3He atoms in the GW system.

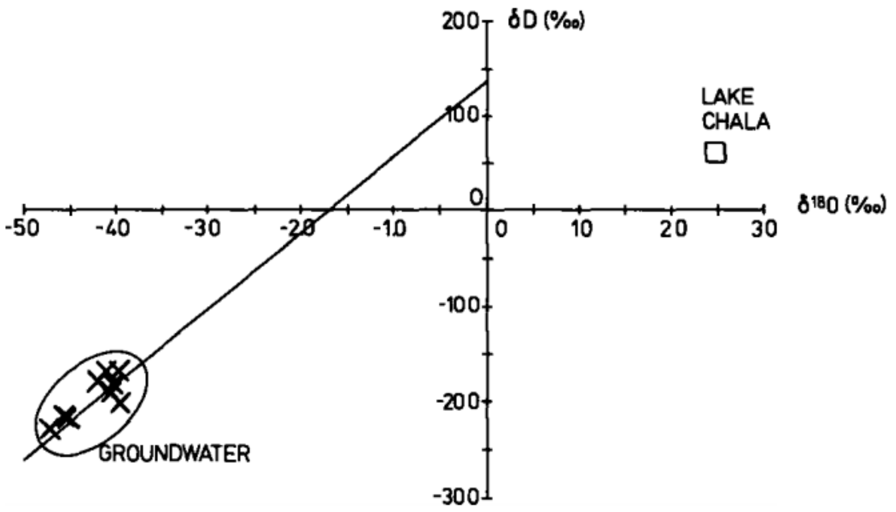

Ultra Low Level Liquid Scintillation Counter
2007/12/26 15:27

CASE STUDIES

INTERACTION OF LAKE CHALA (TANZANIA) WITH LOCAL GW & SPRINGS

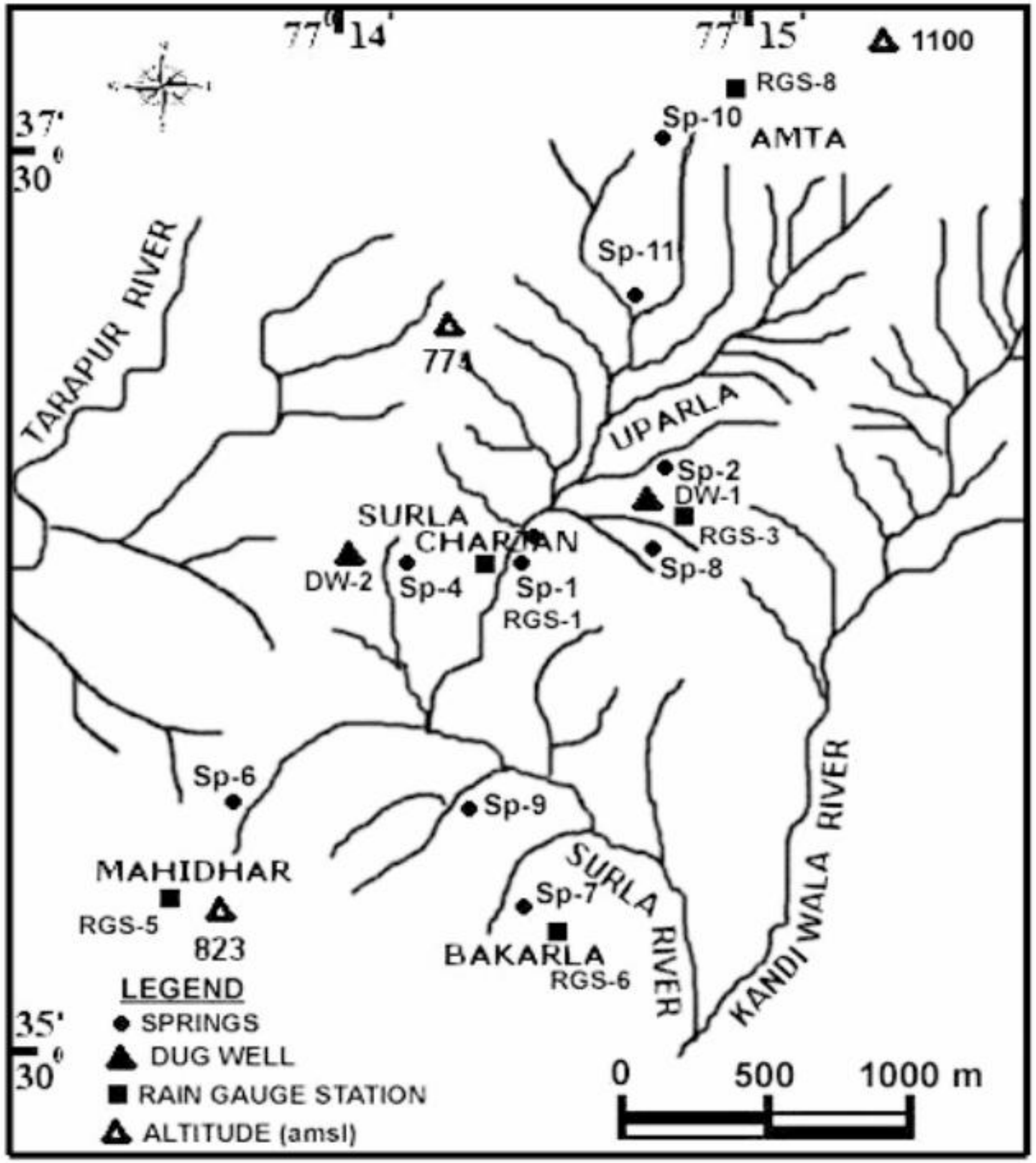
Lake Chala is a volcanic crater lake located at an elevation of 840 m on Mt. Kilimanjaro on the border between Kenya and Tanzania. There are many springs in the region. Examine, whether lake water contributes in the discharge of these springs (Payne, 1970).

	$\delta^{18}O$ (‰)	δD (‰)
Lake Chala, 1967	2.51	7.3
Lake Chala, 1968	2.43	4.9
Homer Spring	−3.96	−20.5
Kileo Spring	−4.72	−23.3
Kitovo Spring	−4.56	−21.9
Lenonya Spring	−4.11	−17.3
Little Lumi Spring	−4.20	−18.3
Magi ya Waleni Spring	−3.97	−17.2
Njoro Kubwa Spring	−4.05	−19.4
Njoro Ndogo Spring	−4.04	−18.6
Latema borehole	−4.53	−22.1

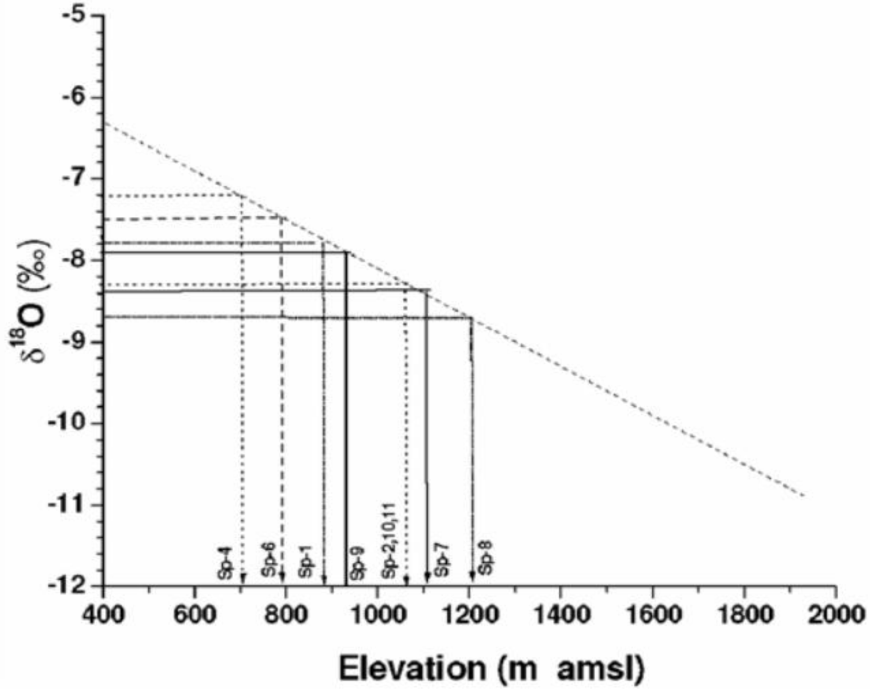


The stable isotope composition of Lake Chala does not vary with time Groundwater fall on MWL
Lake water isotopic composition is markedly different from MWL & GW No Lake water-GW interaction line is observable
Conclusion: No exchange of water between GW-Lake water exist

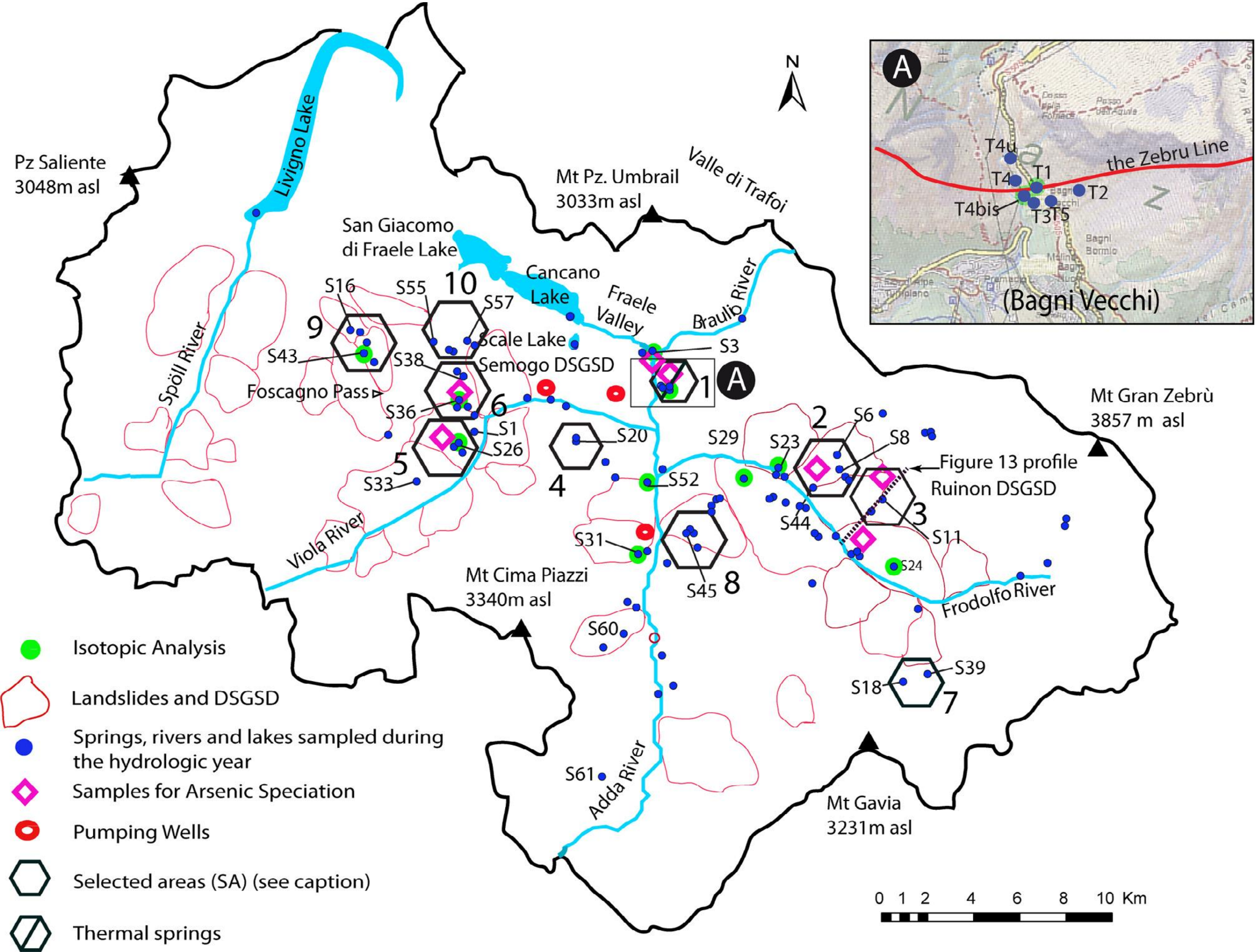
Recharge altitude of springs in Surla Valley, Sirmaur, Himachal Pradesh (U Sarvana Kumar, Curr. Sc. 2012, 87-90)

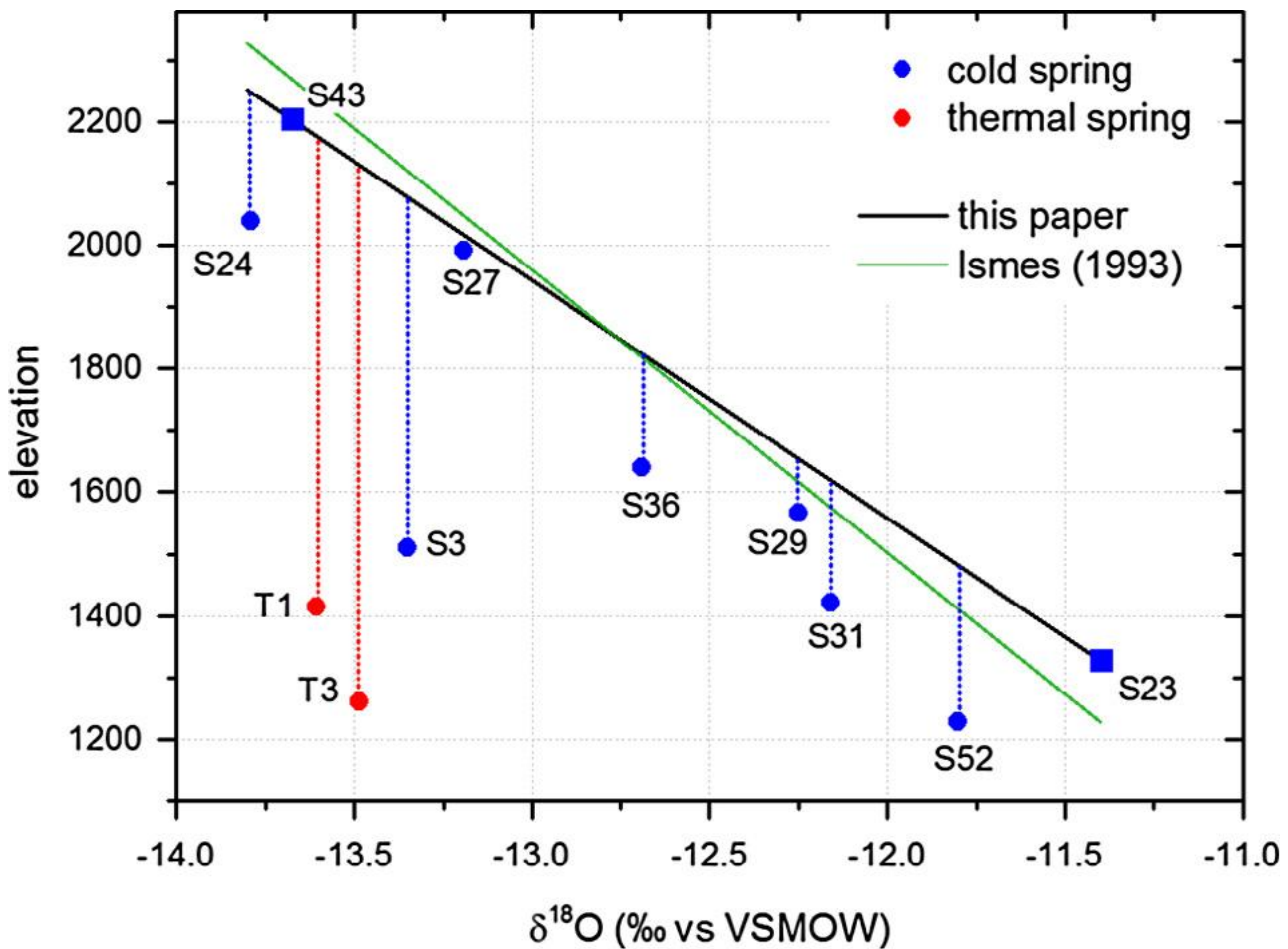


Sample no.	Location	Discharge elevation (m amsl)	Estimated recharge elevation (m amsl)
Sp-1	Surla Amta	627	850
Sp-2	Surla Upparla	645	1050
Sp-4	Surla Charjan	643	700
Sp-6	Mahidhar	718	800
Sp-7	Bakarla	721	1100
Sp-8	Kaharwali	648	1150
Sp-9	Bakarla	633	920
Sp-10	Amta	985	1070
Sp-11	Surla Amta	759	1050



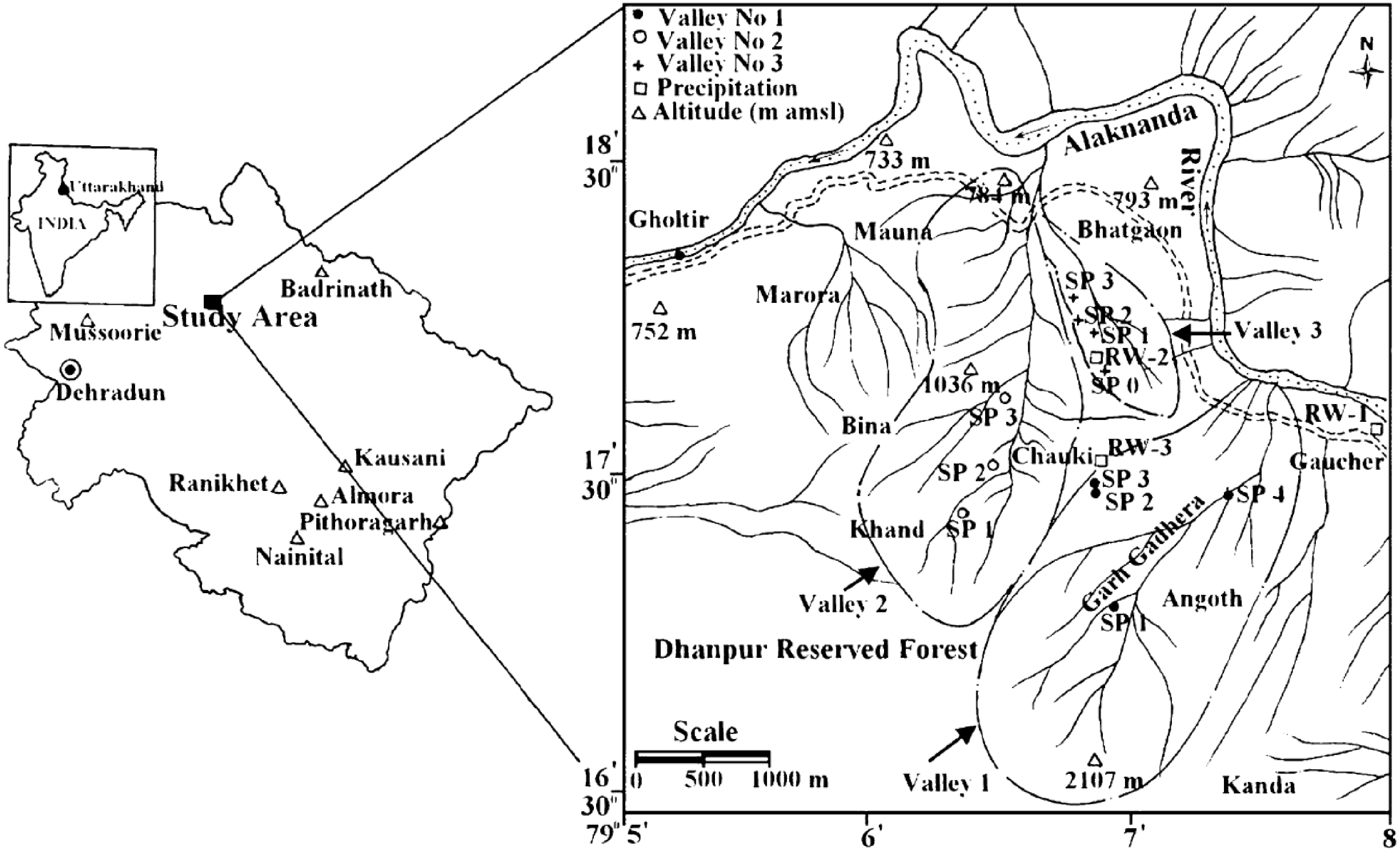
Recharge altitude of Italian Alps (Arsenic contaminated spring water) [Reyes et al., J Hydrol, 2015]



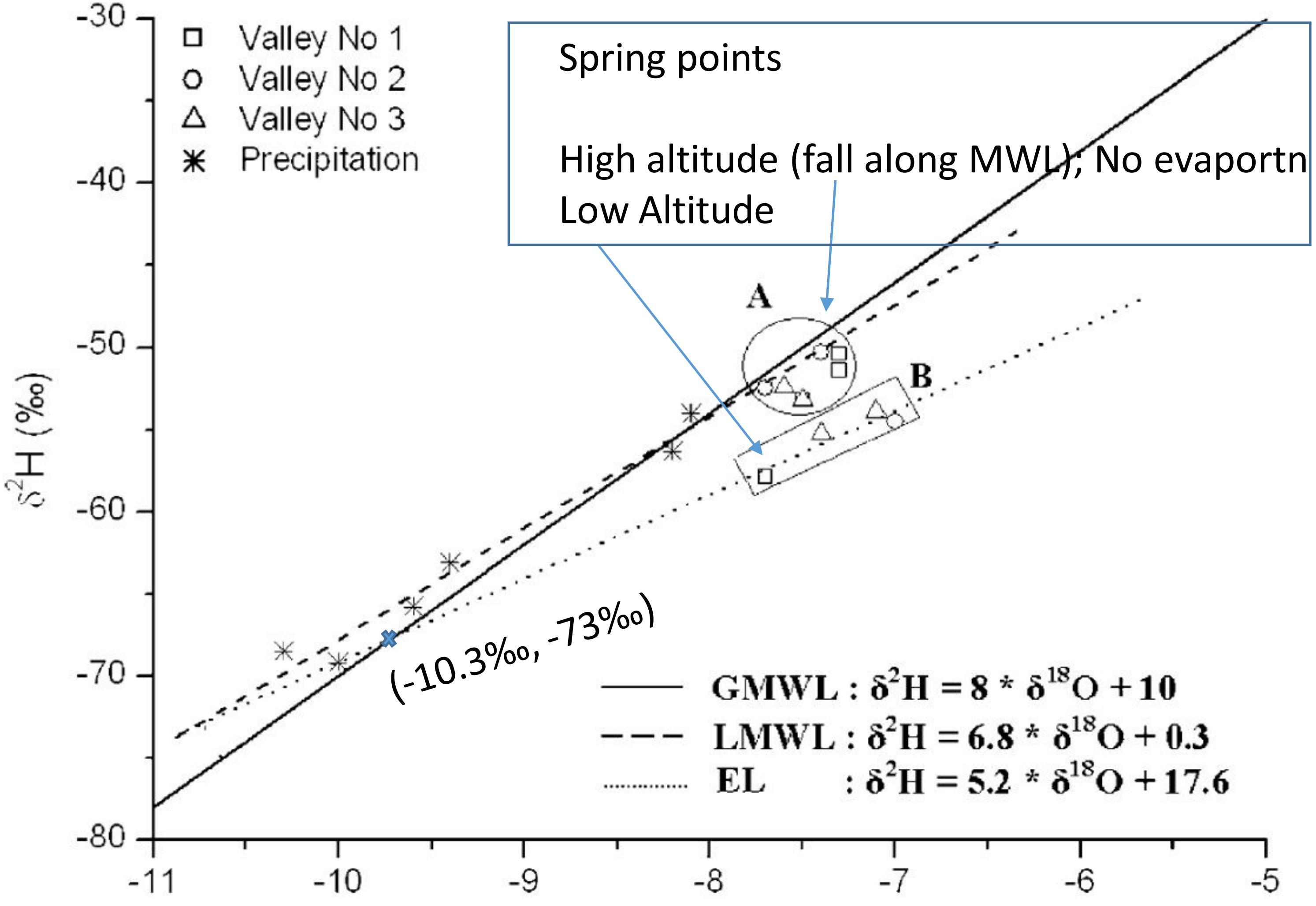


GW age: ~ 10yrs in the case of hot water springs and ~ 2 years for cold springs

Recharge zones of springs in Gauchar, Chamoli, Uttarakhand



Curr. Sc., Shivanna et al., 2008



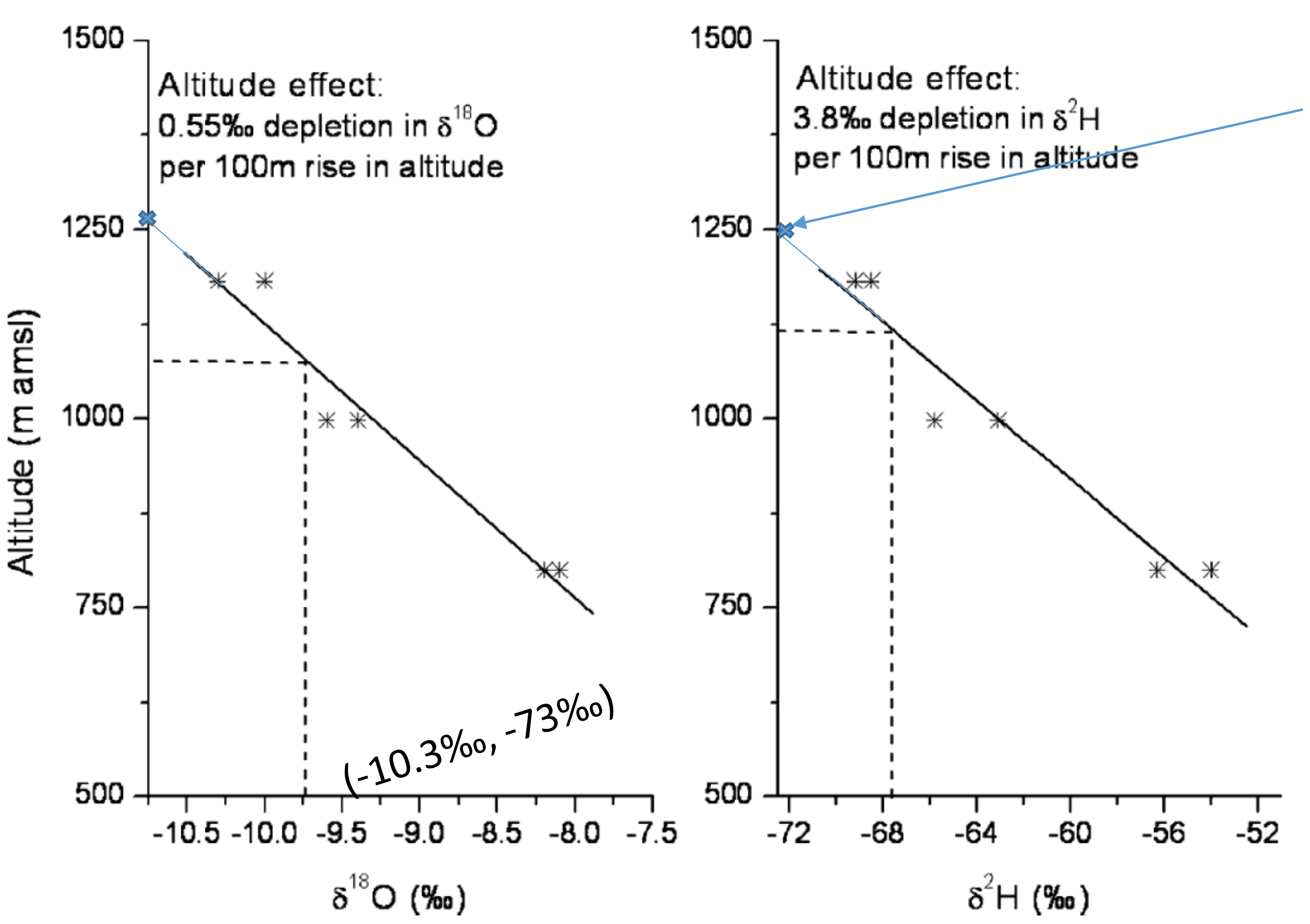
High altitude springs dry-up during summer ➔ mainly pptn as recharge source; Tritium = 11.5 TU

The high altitude spring water is more enriched than low altitude spring water

Reason: Observed isotope data is of specific month's rain when the rain was enriched in isotopic composition. Therefore, recharge area estimate using altitude effect and observed isotopic composition may not result true recharge altitude.

Low alt springs continue with reduce discharge in summer => pptn+GW; Tritium = 9.5 TU => Longer residence time

Isotope line extrapolated back provides initial isotopic value of spring = (-10.3‰, -73‰) for $\delta^{18}O$, δD respct.



Recharge alt of low alt springs as per the corrected isotopic data is = 1250m msl

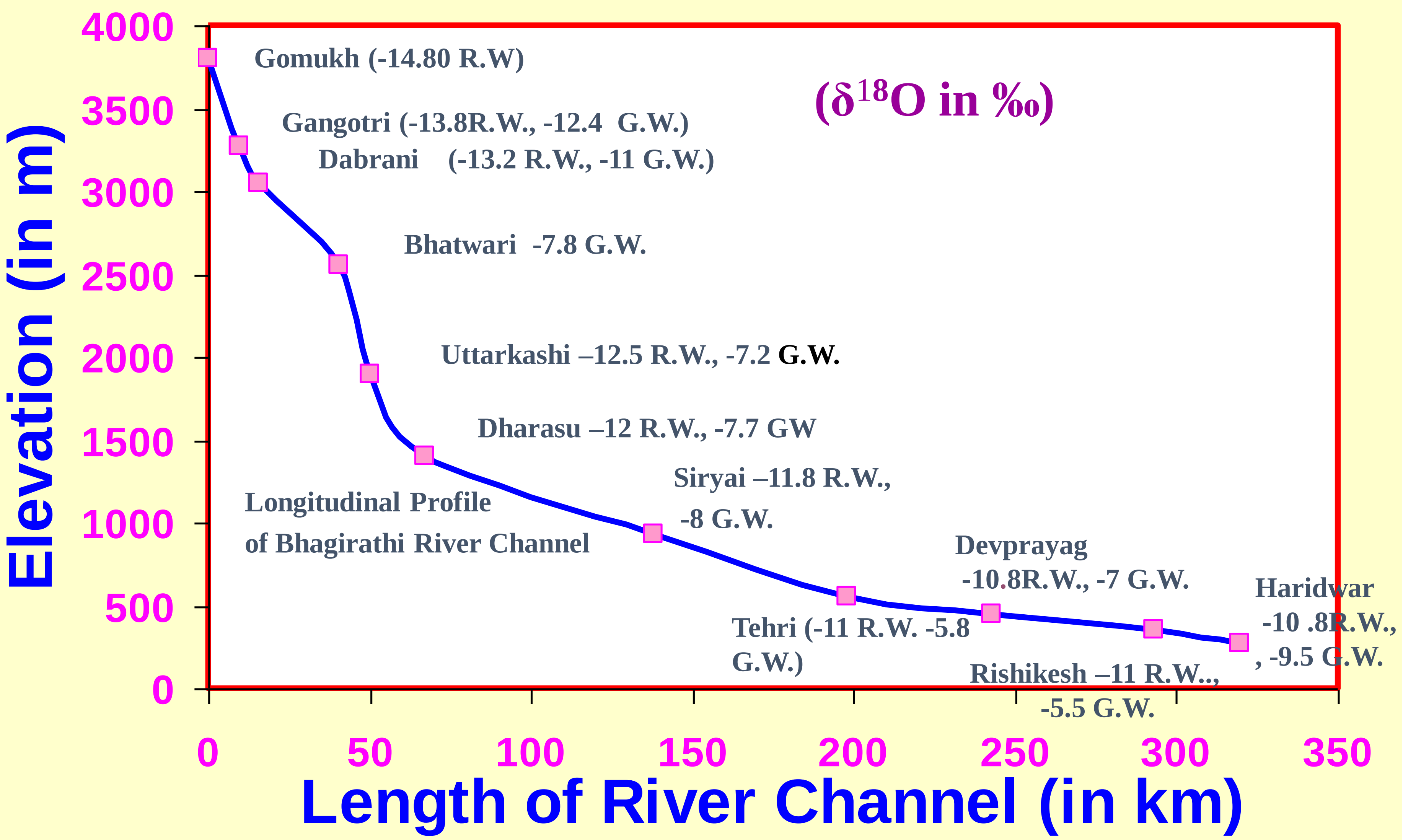
Based on physical survey (geology, geomorphology) and isotopic data, recharge zones at 3 locations were mapped around 1250 msl. Based on survey, 3 locations at 1020 msl, 1270 msl and 1330 msl were identified

At the identified 3 sites the recharge structures like sub-surface dykes, (5 nos), check bunds (2 nos) and few trenches were constructed.

Dotted line: Recharge alt of low altitude springs (for un-corrected data)
Corrected recharge altitude for the low alt. isotopic springs for isotopic value (-10.3‰, -73‰) for $\delta^{18}O$, δD respctively is 1250 msl

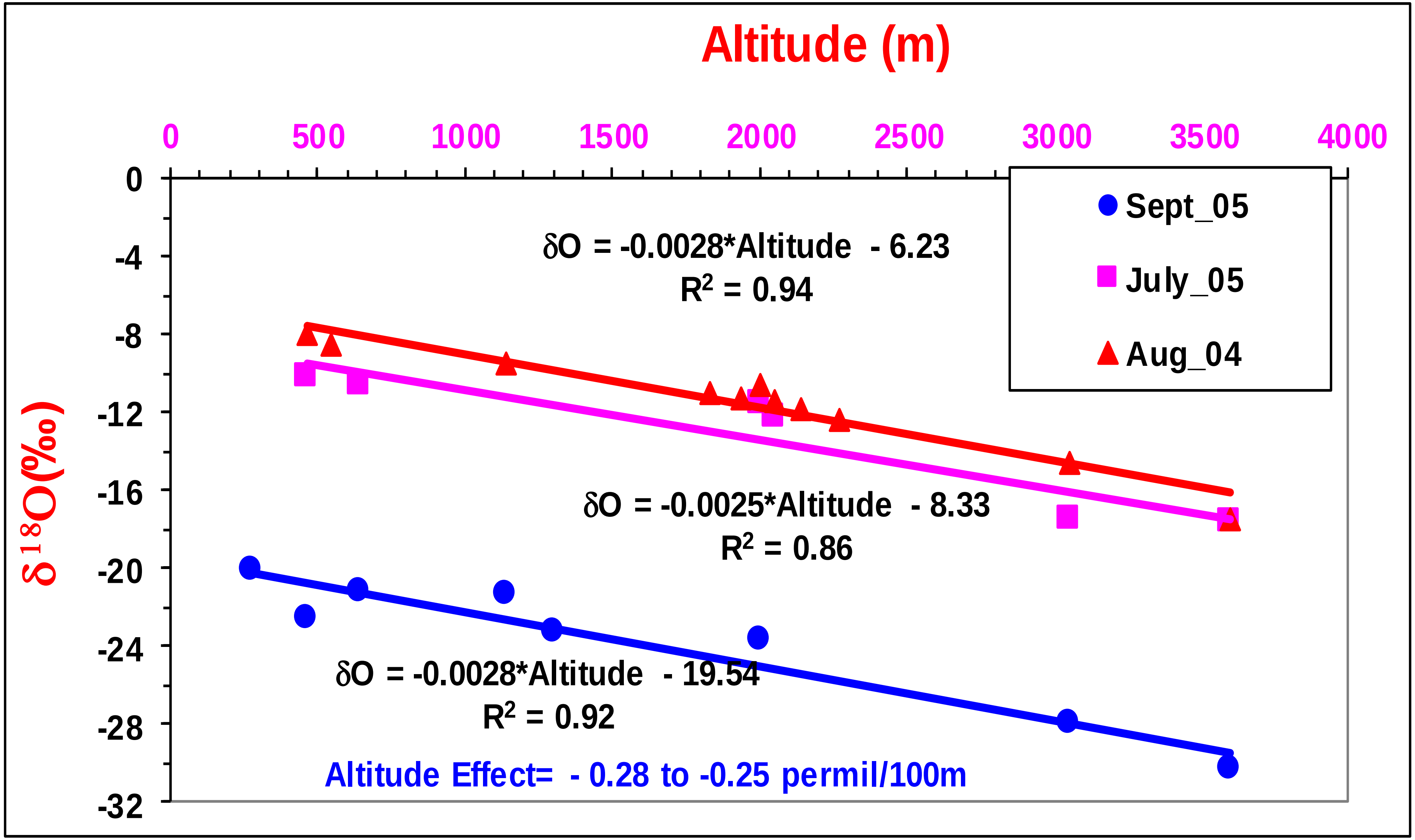
Initial cumulative discharge of springs = 375.4 l/min
After recharge measures, cum discharge of springs = 708.1 l/min

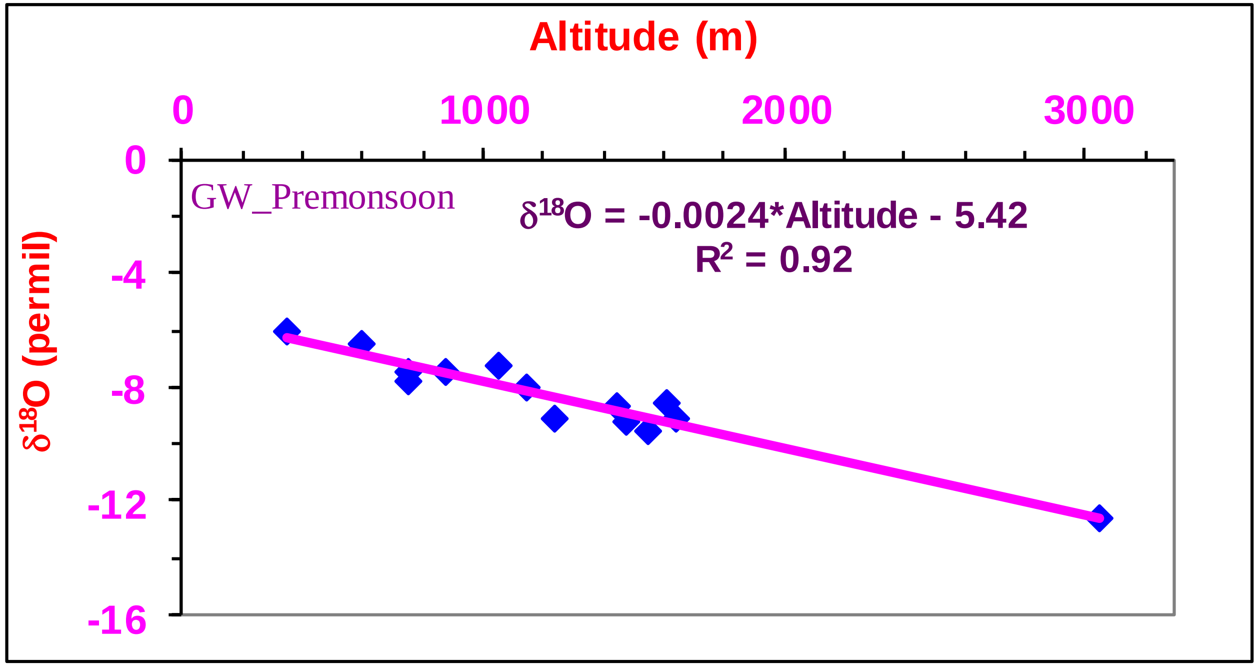
SPATIAL VARIATION IN ISOTOPIC VALUE

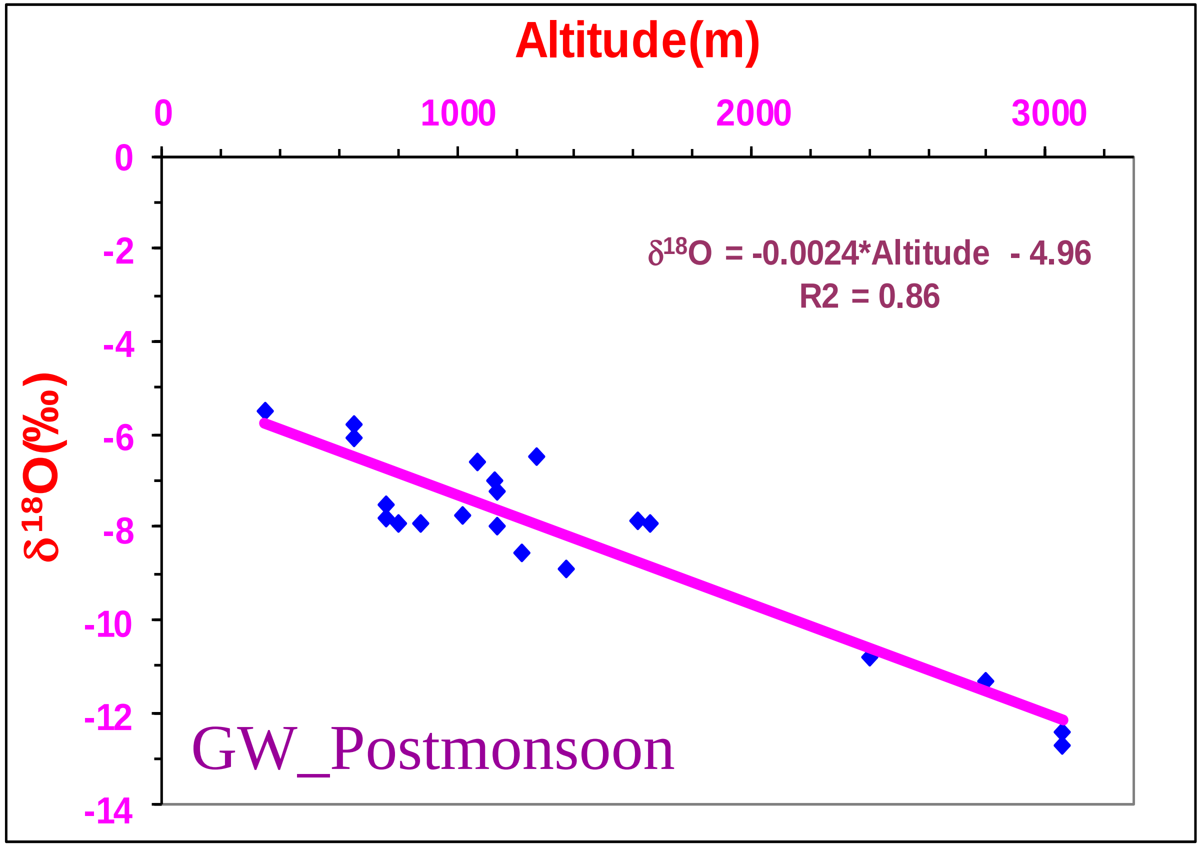


NIH Study

Precipitation




Altitude (m)
0
1000
2000
3000
0
-4
-8
-12
-16
δ18O (permil)
GW_Premonsoon
δ18O = -0.0024*Altitude - 5.42
R2 = 0.92


Altitude(m)
0
1000
2000
3000
0
-2
-4
-6
-8
-10
-12
-14
δ18O(‰)
δ18O = -0.0024*Altitude - 4.96
R2 = 0.86
GW_Postmonsoon

Altitude of recharge zones of springs

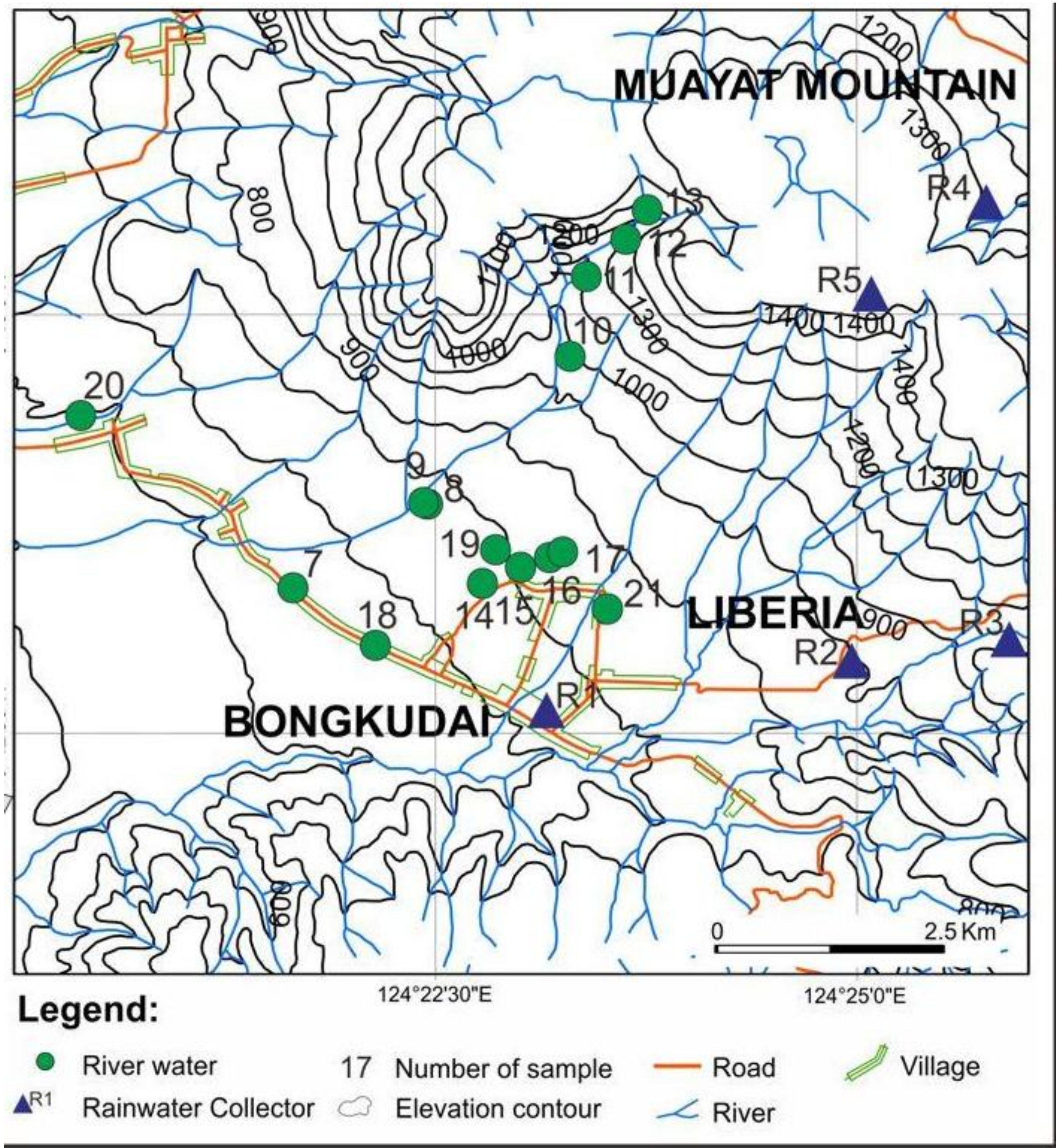
Spring name, (msl)	$\delta^{18}O$ (‰)		Estimated recharge altitude
	Spring	Precipitation	
Siyansu (752)	-7.76	-4.76	1515
Bhinu (1256)	-7.1	-6.78	1350
Koti (1450)	-8.6	-7.55	1725
Tehri (640)	-9.3	-4.3	1900
Sirai (658)	-9.2	-4.4	1875
Maldewal (755)	-8.6	-4.8	1725

Spring points fall on LMWL (Siyansu, Bhinu, Koti)

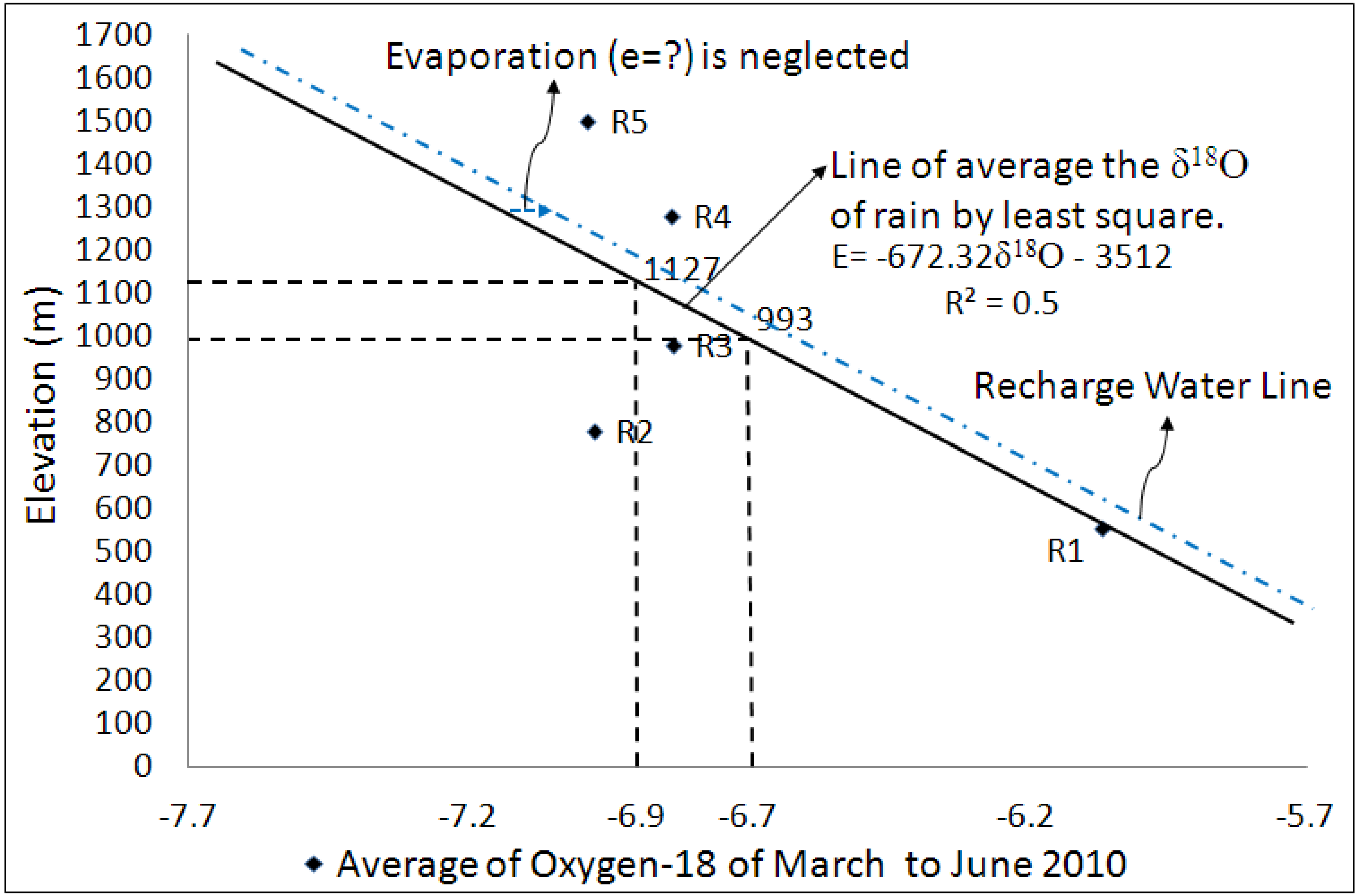
Fall on Evp line (Evp 1,2 & 3) (Tehri, Sirai, Maldewal)

$\delta\ ^{18}O$ = -0.26 per mill/100 m

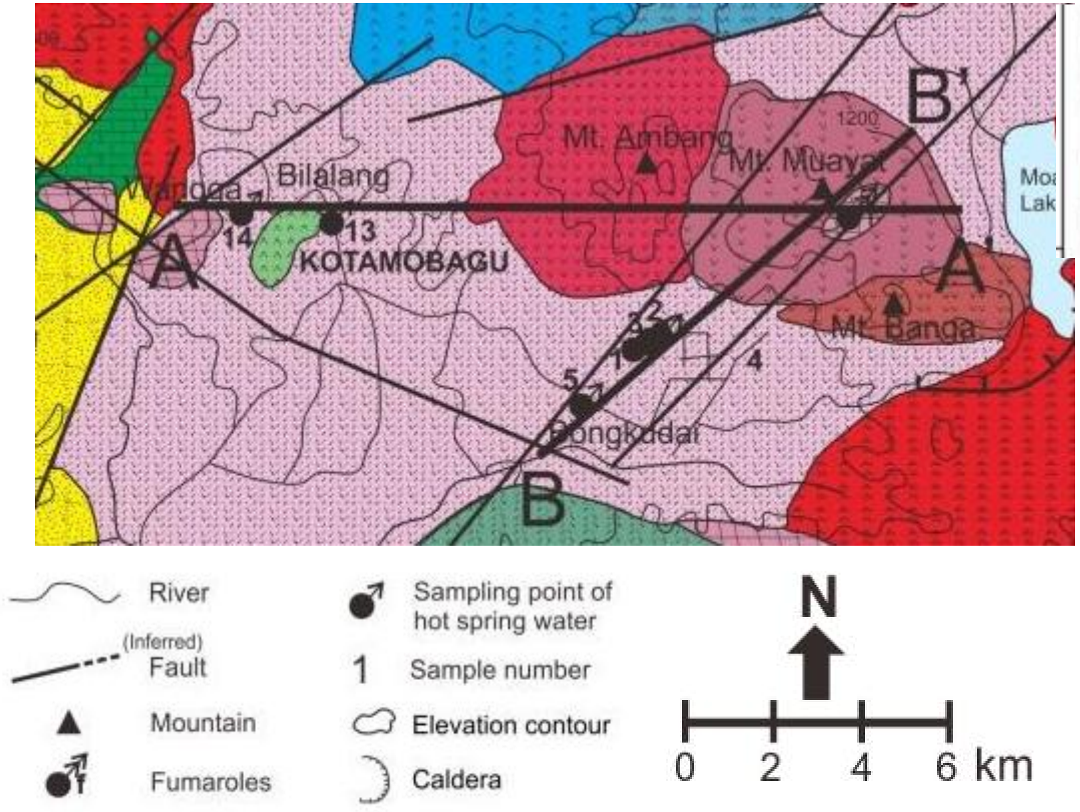
Recharge elevation of hot springs in the Mt Muayat, N. Sulawesi, Indonesia (Hendra et al., 2012)

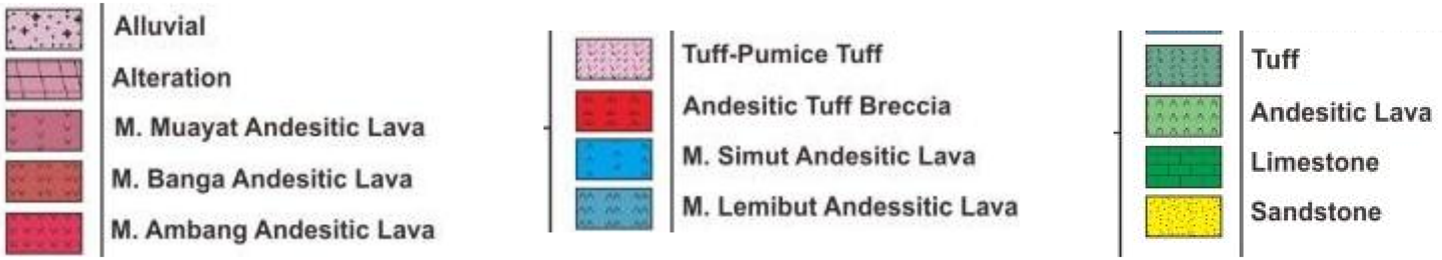


https://pangea.stanford.edu/ERE/pdf/IGAstandard/SGW/2012/Riogilang.pdf

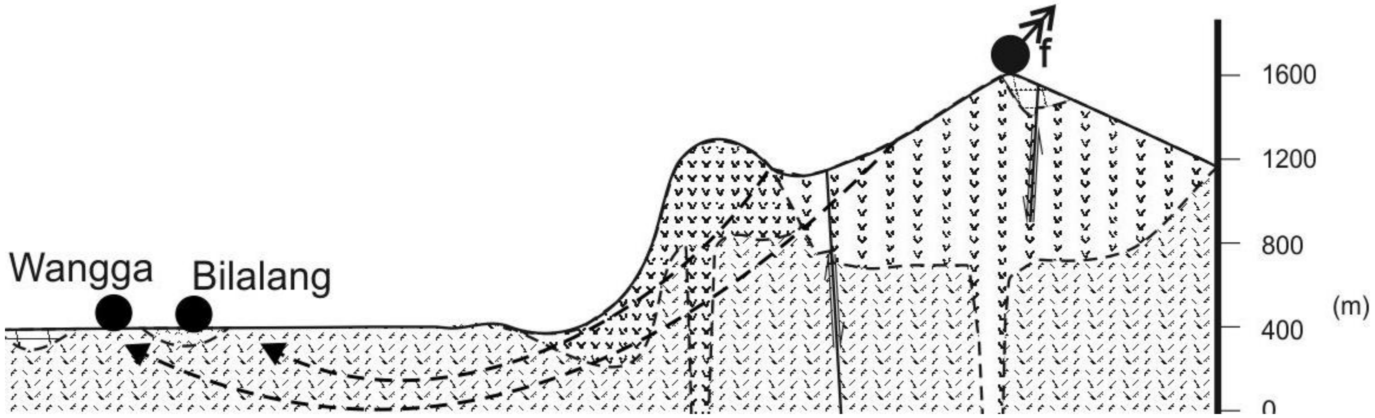


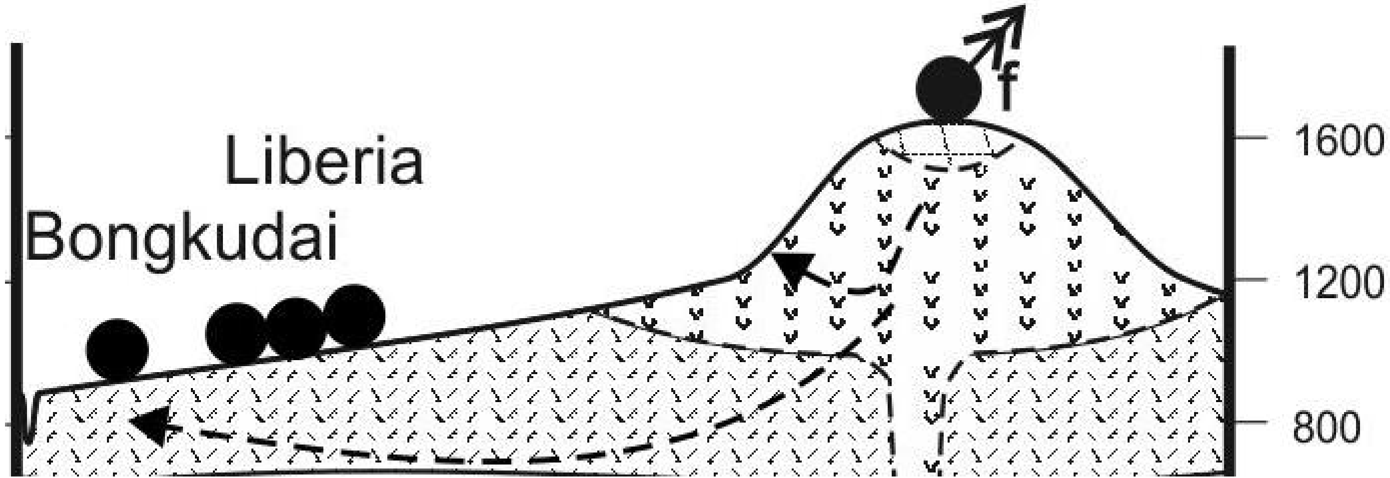
0.15‰ per increasing
100m





Symbols & lithology





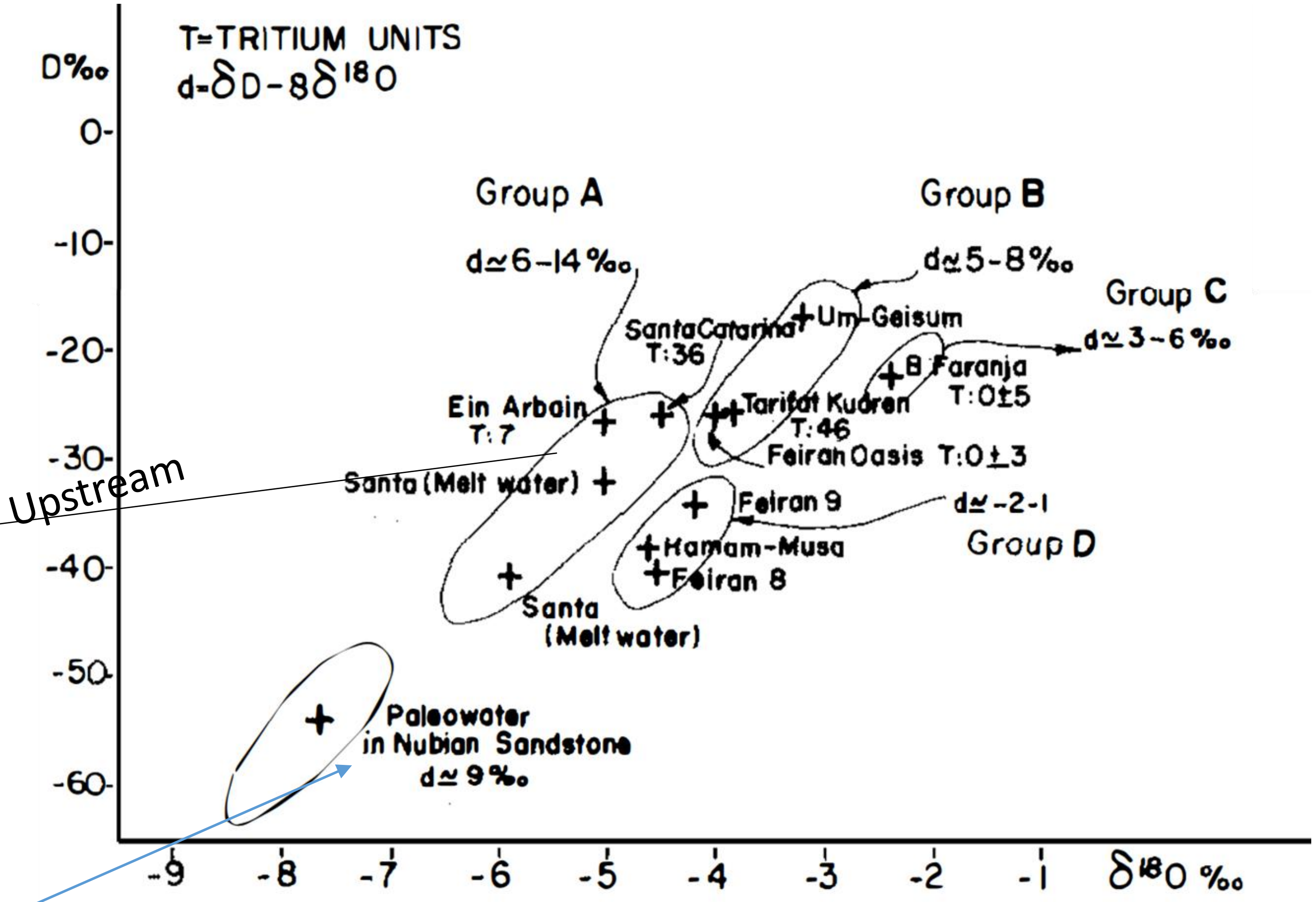
Recharge elevation of hot springs in Indonesia

Hendra et al., 2012

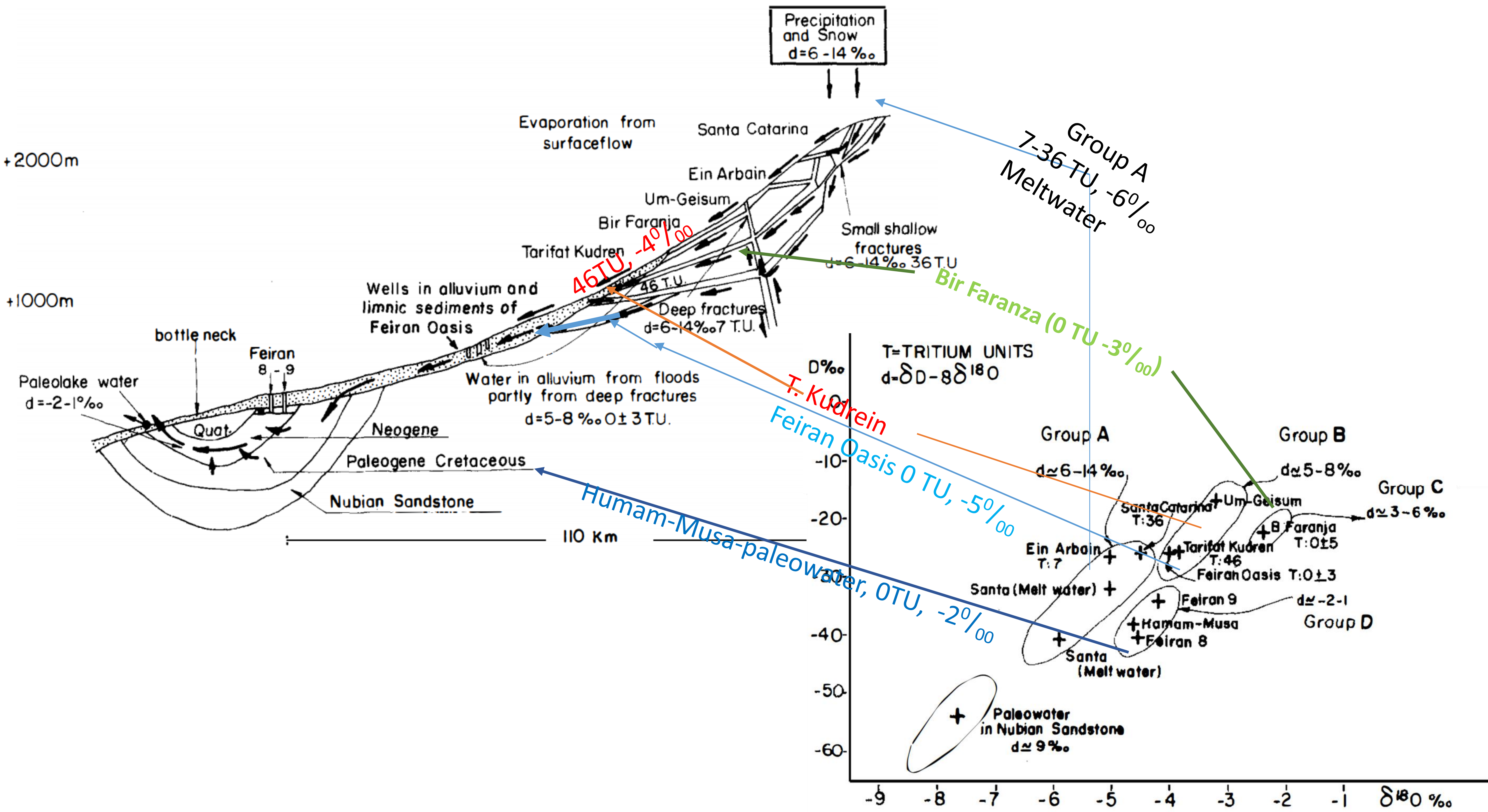
https://pangea.stanford.edu/ERE/pdf/IGAstandard/SGW/2012/Riogilang.pdf

Origin of oasis and paleolake water in arid basin of Israel

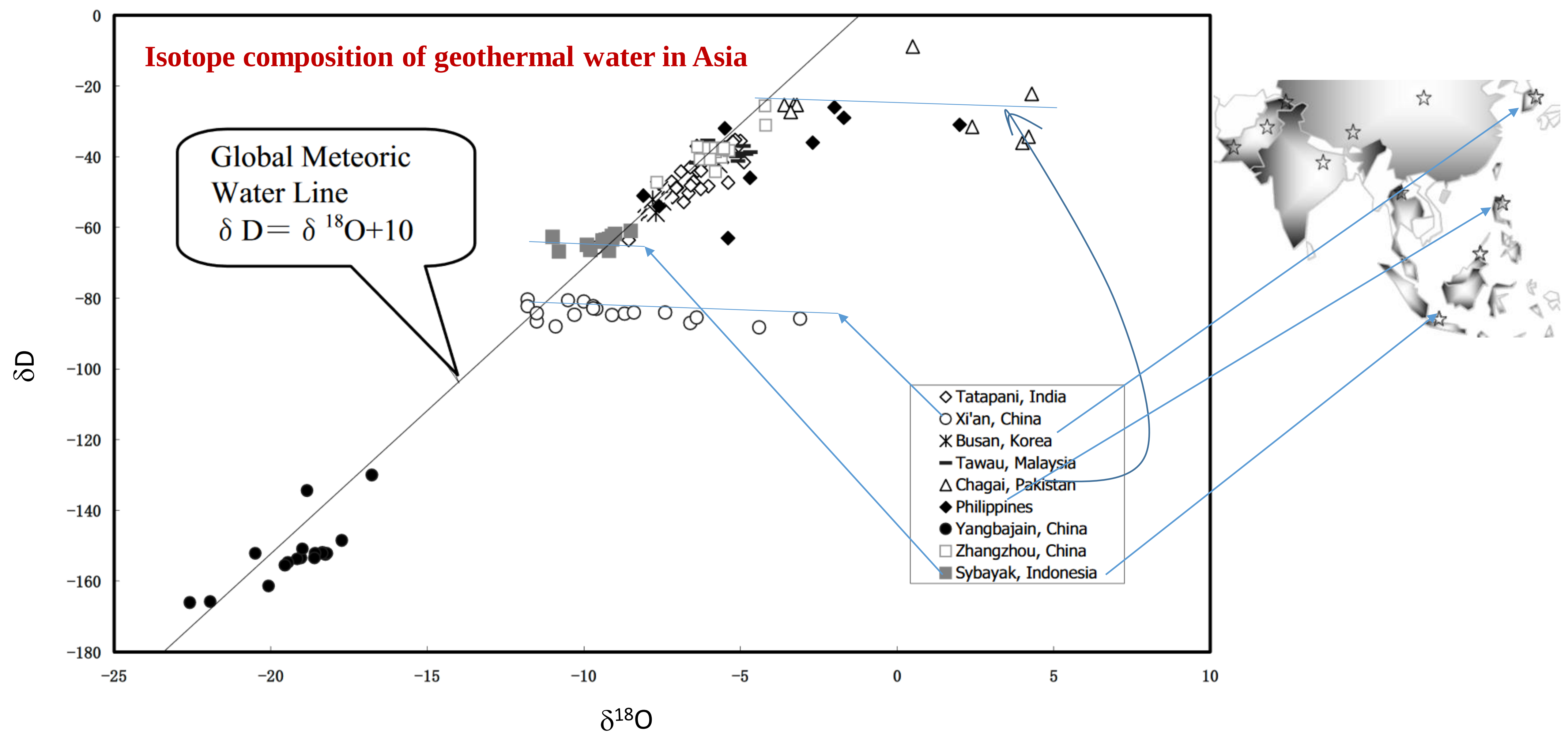
Issar and Gat , 1981; GW



Sinai Basin: Average annual RF: 80mm in upper reaches and 15 mm at lower reaches
In the mountainous region many springs and shallow wells are found in the fractured crystalline rocks and gravel bed. The region also has a paleolake in downstream in the Nubian sandstone formation.

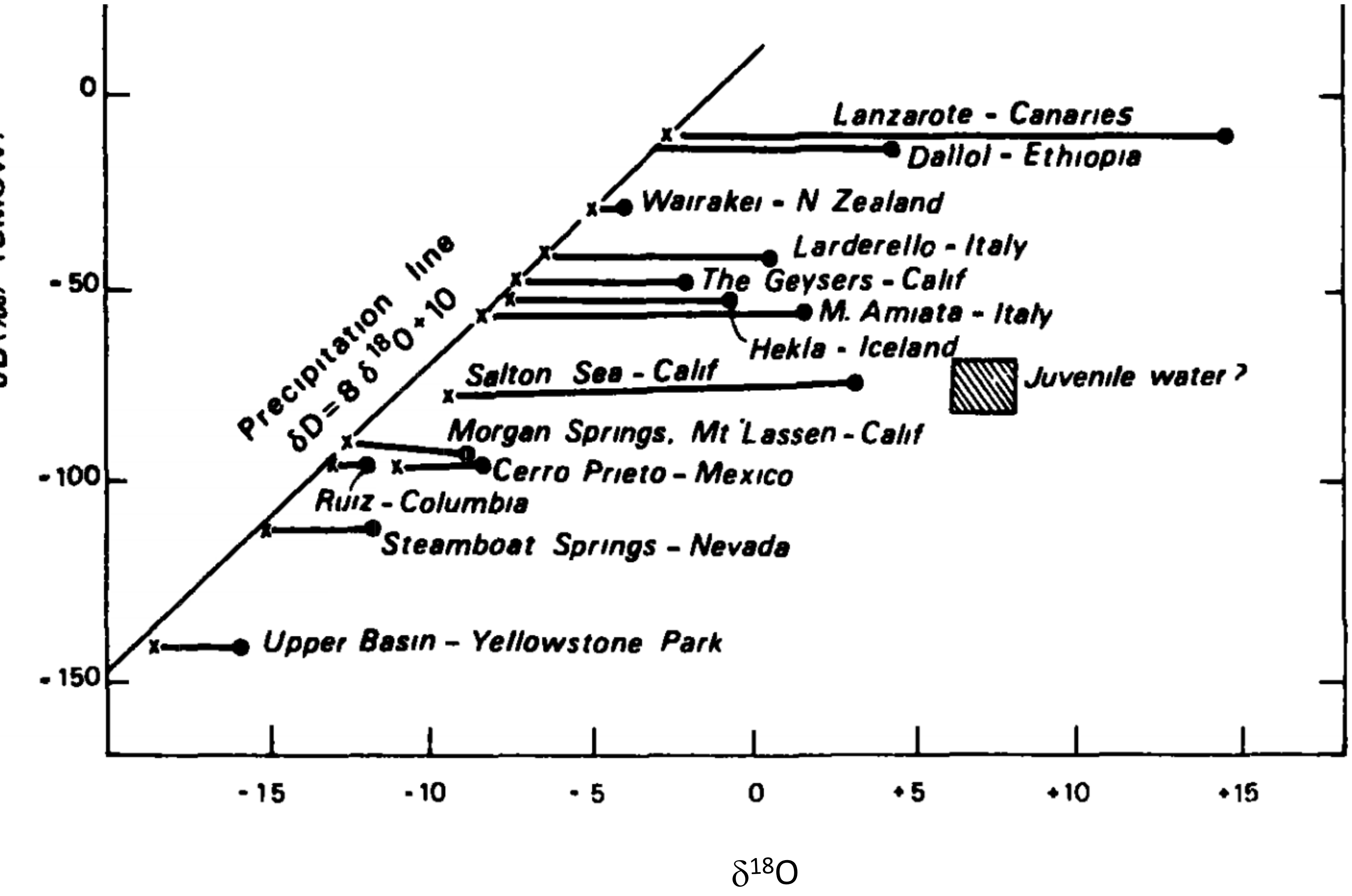


Precipitation and Snow d=6 -14 ‰
Evaporation from surfaceflow
Santa Catarina
Ein Arbain
Um-Geisum
Bir Faranja
Tarifat Kudren
Small shallow fractures d=6-14‰ 36 T.U
46 T.U.
Deep fractures d=6-14‰ 7 T.U.
Wells in alluvium and limnic sediments of Feiran Oasis
Water in alluvium from floods partly from deep fractures d=5-8 ‰ 0± 3 T.U.
bottle neck
Feiran 8 - 9
Paleolake water d=-2-1‰
Quat.
Neogene
Paleogene Cretaceous
Nubian Sandstone
110 Km
+2000m
+1000m
Group A 7-36 TU, -6‰ Meltwater
Bir Faranza (0 TU -3‰)
46TU, -4‰
T. Kudrein
Feiran Oasis 0 TU, -5‰
Humam-Musa-paleowater, 0TU, -2‰
T=TRITIUM UNITS
d=δD-8δ18O
D‰
0
-10
-20
-30
-40
-50
-60
Group A d≃6-14‰
Group B d≃5-8‰
Group C d≃3-6‰
Group D d≃-2-1
Santa Catarina T:36
Um-Geisum
B Faranja T:0±5
Tarifat Kudren T:46
Feiran Oasis T:0±3
Ein Arbain T:7
Santa (Melt water)
Feiran 9
Hamam-Musa
Feiran 8
Santa (Melt water)
Paleowater in Nubian Sandstone d≃9‰
-9 -8 -7 -6 -5 -4 -3 -2 -1
δ18O ‰



Geothermal waters: GW formed from meteoric water undergone through deep circulation may cause significant O-18 shift due to exchange with O-18 of rocks. The exchange is low in case of hydrogen. The equilibrium value depends on the temperature over which exchange occurs

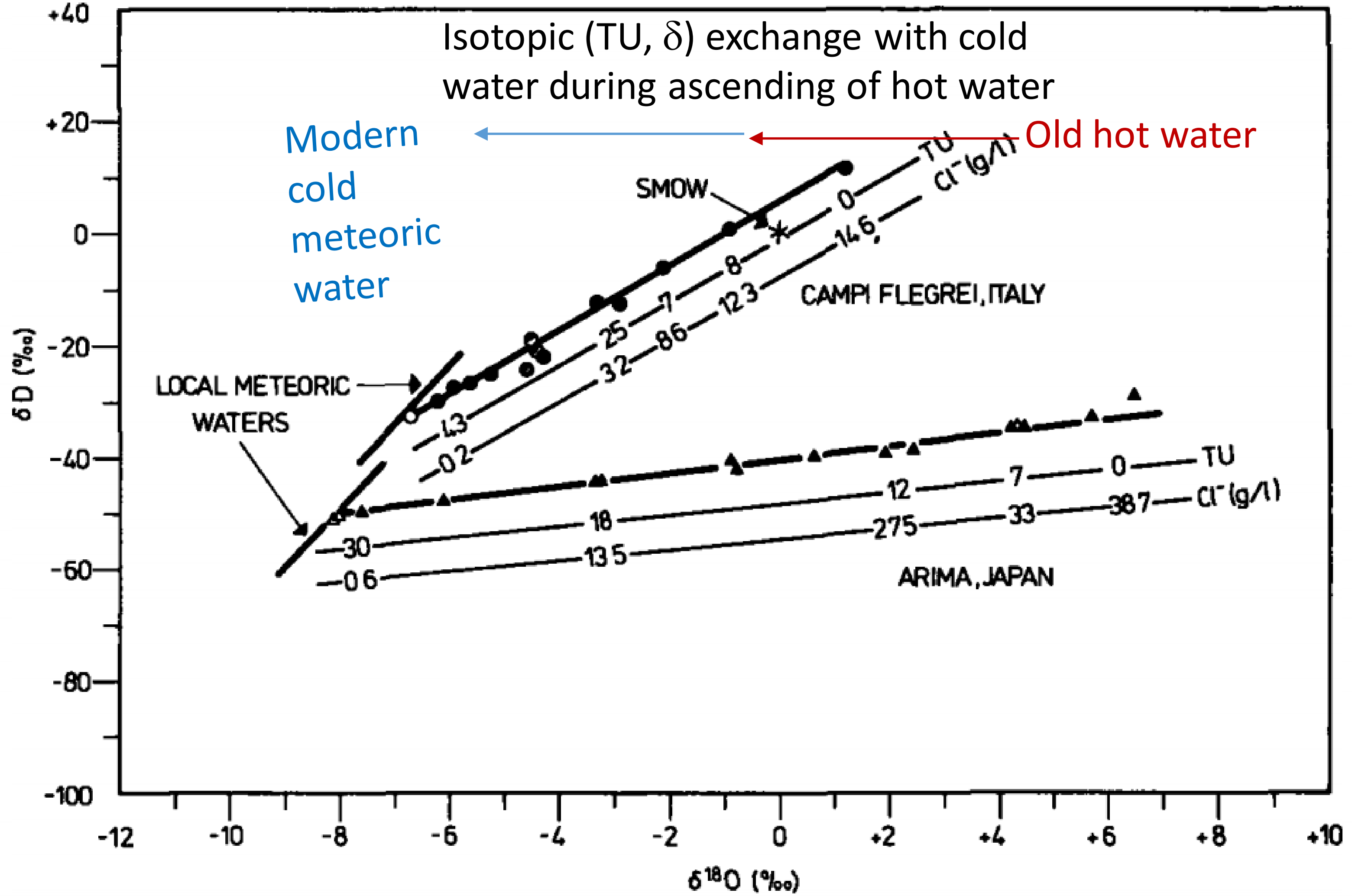
Pang et al., Procd of the 7th Asian Geothermal Symposium, July 25-26, 2006



Along the underground flow in a geothermal field, the $^{18}0$ content increases in the water as a consequence o f a progressive isotopic exchange with rock isotopic composition

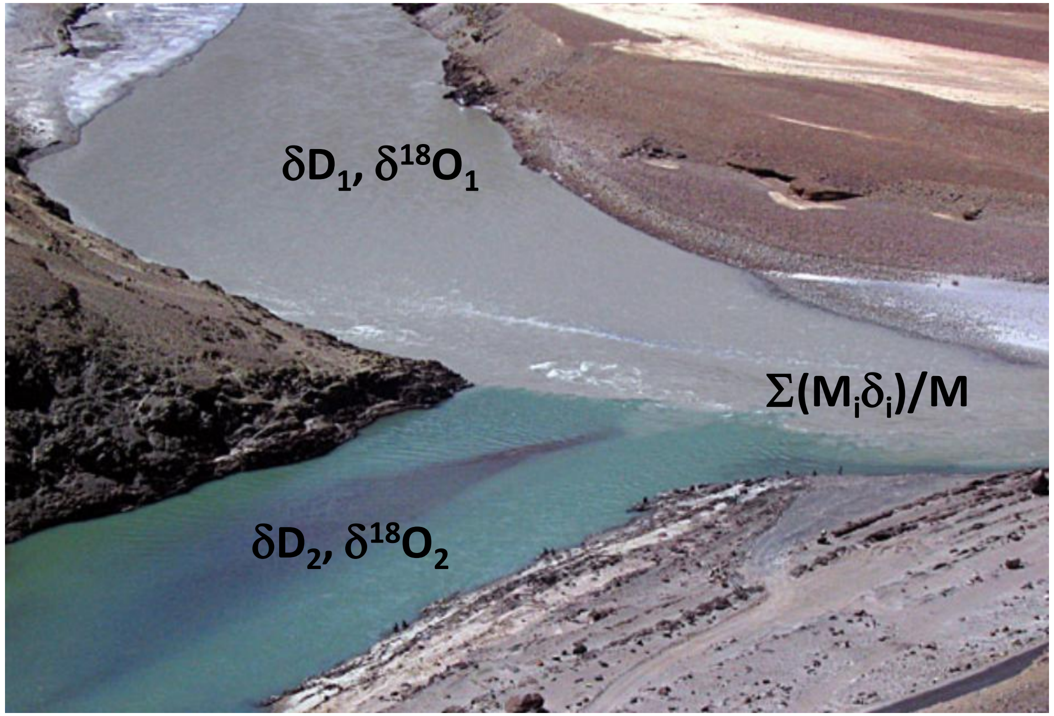
Isotopic composition o f water and steam from some o f the major geothermal systems.

IAEA Tecdoc 1981



$\delta^{18}0$ - δD relationship in geothermal waters from Campi Flegrei, Italy, and Arima, Japan, indicating mixing o f deep brines with recent fresh groundwaters of meteoric origin. The tritium and chloride contents of selected samples are also indicated.

Hydrograph separation of a river discharge using stable isotopes



Requirement: River map
Multiple location river water sampling according to the river map (gaining stream/confluence of river/change in river water quality)
At least one year discharge data during sampling time

Required water sample: 15 ml; **δD, $\delta^{18}O$**

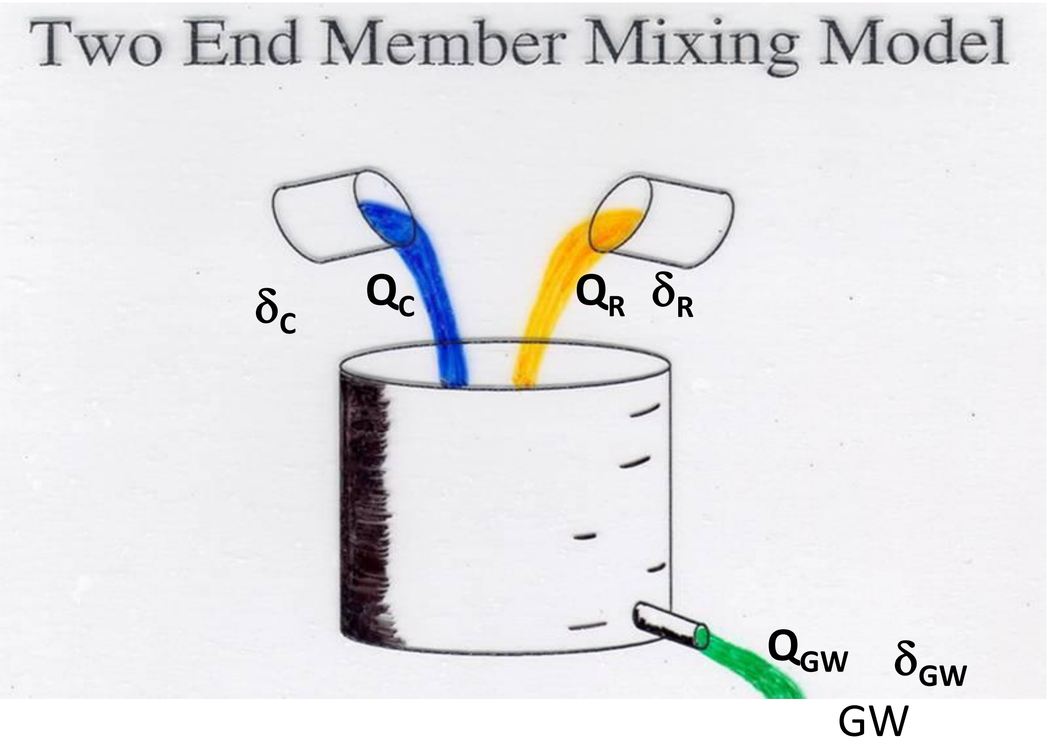
$$Q_{GW} = Q_C + Q_R$$

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

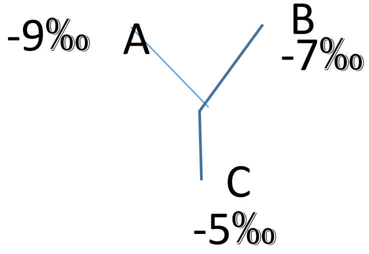
$$\delta_{GW} = \delta_C Q_C + \delta_R (1 - Q_C)$$

∴ Q_C can be estimated

∴ Q_R and Q_{GW} also can be estimated.



At a particular location two rivers A & B join to form the river C . Samples collected from A, B and C yielded isotopic values -9,‰ -5‰ and -7‰ respectively. Using the isotopic data assess the relative contribution of A & B in C. isotopic values of tributaries A & B joins to and become a main river



$$\delta_C = \delta_A Q_A + \delta_B (1 - Q_A)$$

$$-5 = -9Q_A + (-7)(1 - Q_A)$$

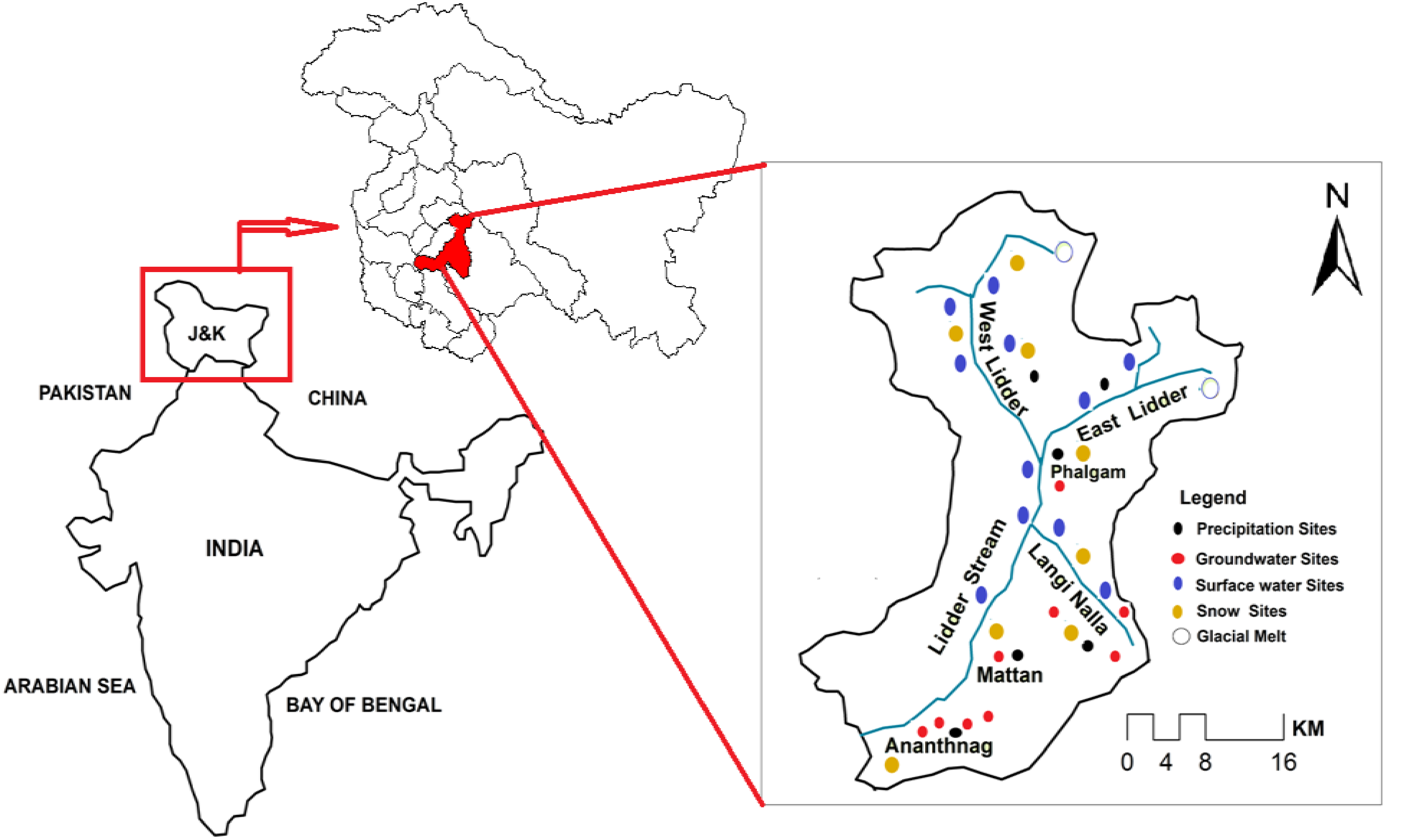


Fig.1: Location and sampling site map of the study area

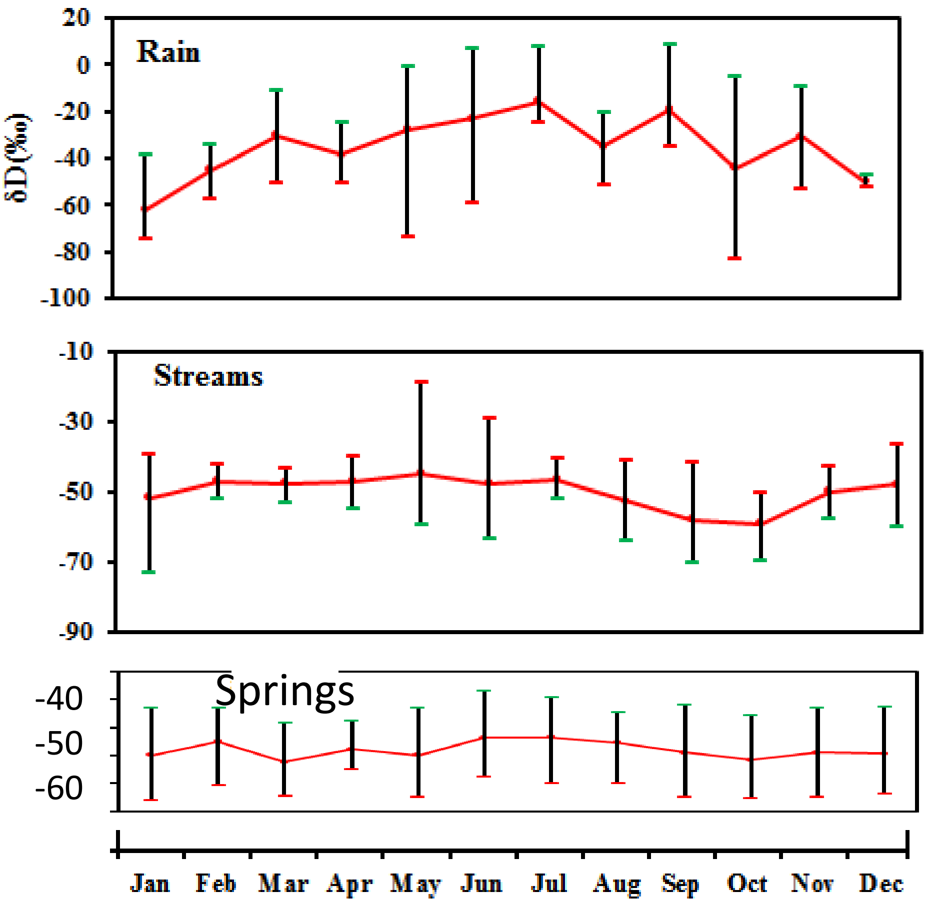
Isotopic composition in streams & springs depends on

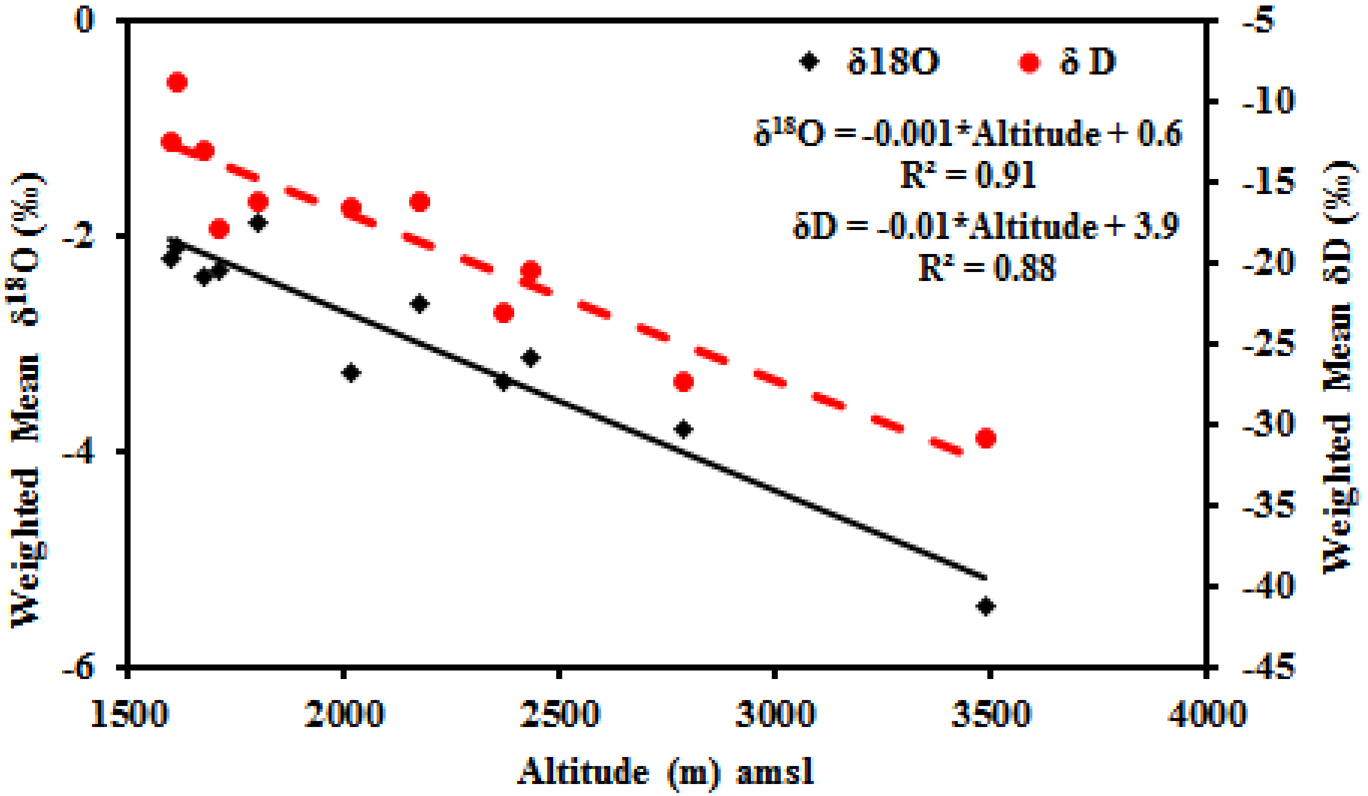
Recharge source: Ptpn (enriched values), snow melt (depleted) : Seasonal isotopic effect discharge components

Catchment effect: Depleted values in upper parts of stream compered to lower part of streams

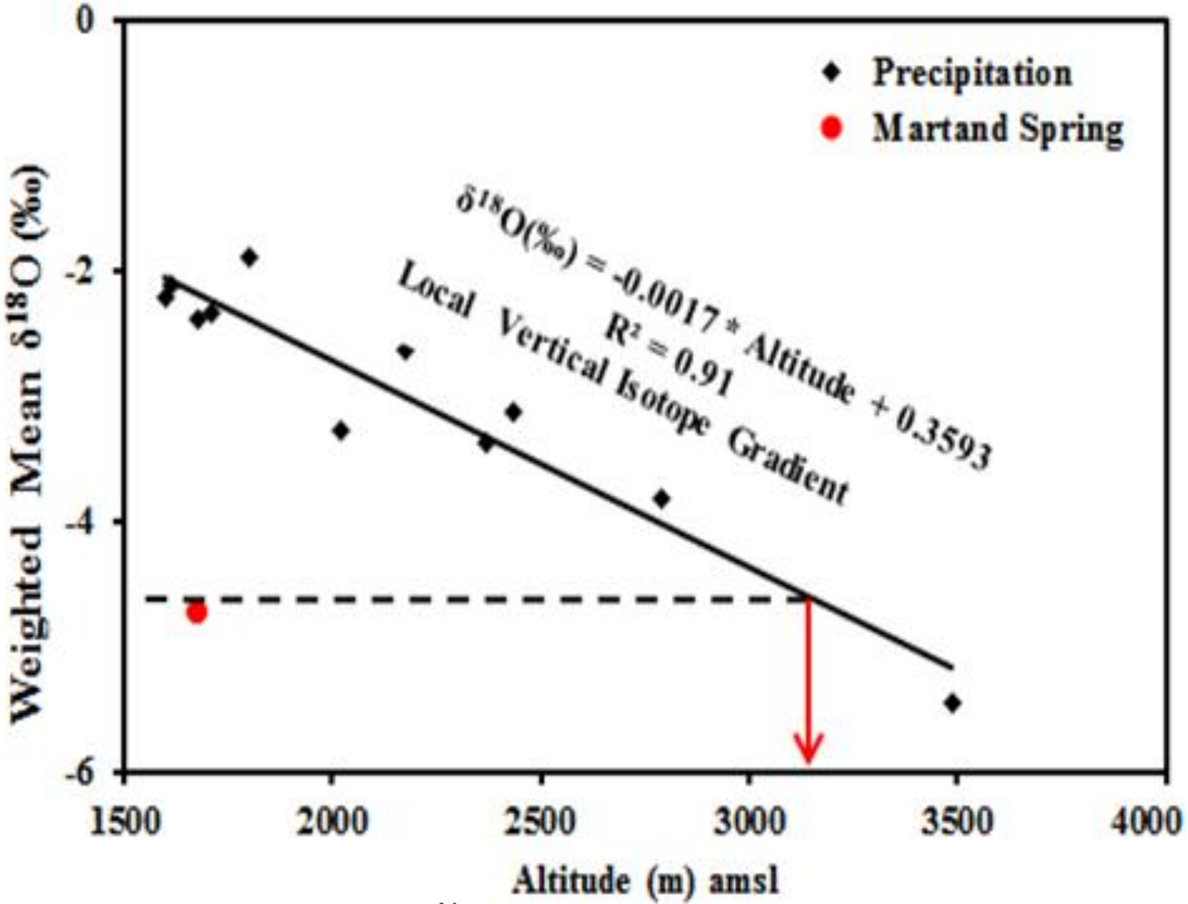
Fast discharge components: Preferential flow paths in GW

Slow discharge components: Baseflow in streams ~ spring water

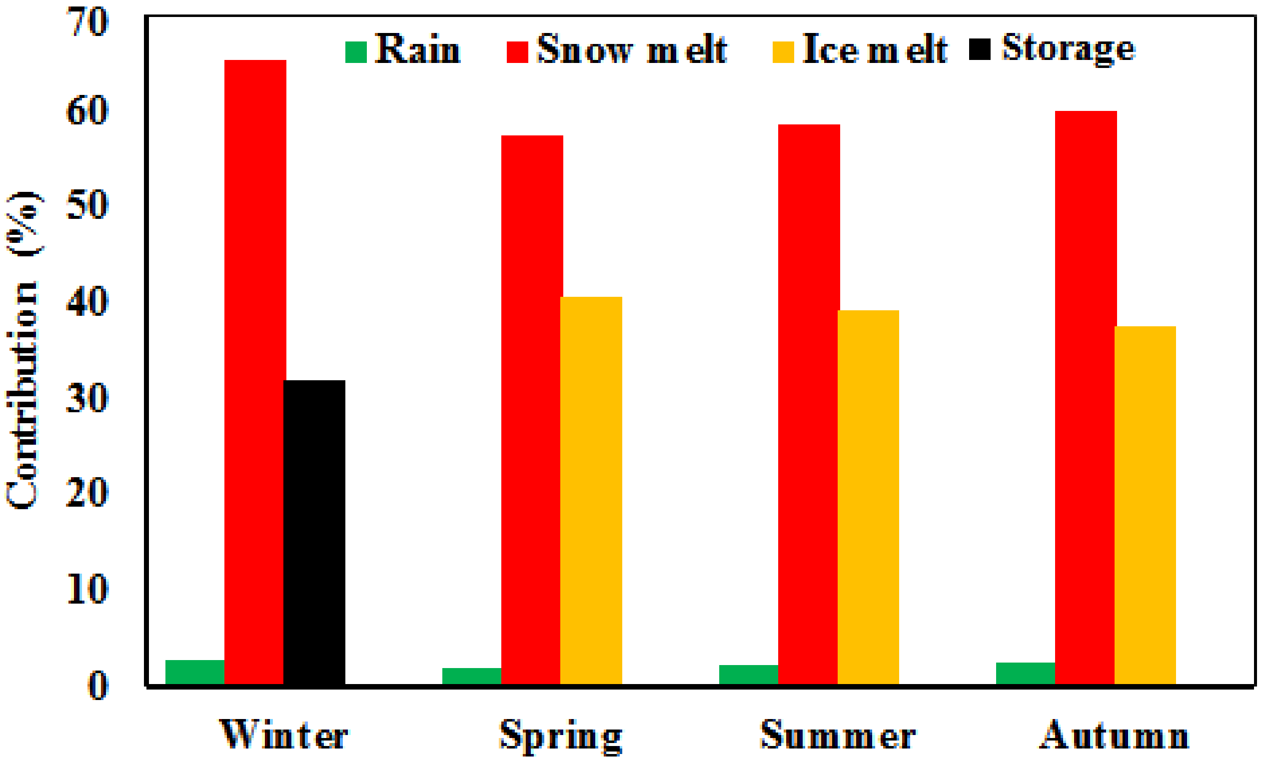


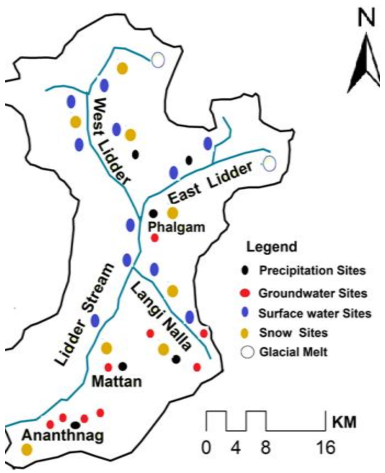


Alt Effect in ppt water: 0.15‰ ($\delta^{18}O$) and 1.16‰ (δD) per 100m change in elevation



Recharge alt of Martnad spring= 3200m





Seasonal contribution of rain, snow and glaciers to Martand karst spring

Isotopes helps to identify whether springs discharge a mixture of waters originating from different recharge areas.

Care should be exercised when estimating the altitude effect solely from precipitation data (GW data may also be used). Estimates based on data of limited duration may differ appreciably from long-term values.

It must be ascertained that the recharge area is unique or made up of different recharge areas (elevations) or different recharge source or the combination of the both.

The isotope data provide a mean altitude of recharge which may be the result of mixing of waters from two or even more areas, each differing in extent and elevation. The interpretation therefore demands a very close co-operation with the hydrogeologist who can define the different possibilities.

If spring water is evaporation affected then use evaporation line to find st. iso. composition of spring water before start of evaporation

Tritium age of spring water can be used to identify mean residential time

Using isotopic mass balance equation relative contribution of multiple recharge sources in the observed spring water can be estimated

This further can be resolved by sampling spring water during multiple seasons

Increase in O-18 composition with no significant change in δD composition indicates geothermal effect in the spring water

THANKS