Hydrology Measurements

Stefan Uhlenbrook

Introduction to Isotope Hydrology

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Introduction of the Lecturer

- Hydrologist originally from Freiburg, Germany
- MSc, PhD and ‘habilitation’ in Freiburg
- In Delft, the Netherlands, since January 2005: Professor of Hydrology at UNESCO-IHE, Delft
- *Since November 2009: part-time professor for experimental hydrology at TU Delft*
- Working experiences mainly in catchments in Germany, Austria, USA, East Africa, sub-Saharan Africa, Vietnam, Iran and Palestine, and recently some other more humid places (i.e. Thailand and Malaysia)
- “experimentalist” and “modeler”

Sources of course notes and further information

- Books:
  - Kendall and McDonnell (Eds.) 1998: Isotope Tracers in Catchment Hydrology, Elsevier
  - Kaess (Ed.), 1998: Tracing Techniques in Geohydrology, - Rotterdam Balkema
  - Mook, W. G. (2001): Environmental Isotopes in the Hydrological Cycle- Principles and Applications. UNESCO-IAEA, IHP Publications. (free at the web!)
  - Aggarwal P.K., Gat J.R., Foehlich K.F.O., 2005: Isotopes in the water cycle. Springer, 381 p.
  - Clark, I.D. and Fritz, P.:Environmental isotopes in hydrogeology. Lewis Publishers, 1997

- Jeff McDonnell's web page:
- www.cof.orst.edu/cof/fe/watershd/shortcourses.php

- Carol Kendall's web page:
- http://wwwrcamnl.wr.usgs.gov/isoig/res/

- Isotope Hydrology Section:
- http://www-naweb.iaea.org/napc/ih/index.html

- Global Network for Isotopes in Precipitation:
- http://www-naweb.iaea.org/napc/ih/GNIP/IHS_GNIP.html

- Isotope and Geochemistry web page:
- http://www.eeb.cornell.edu/isogeochem/

…. I am sure there is more available!

Acknowledgements for some of the material used in this course

- Prof. Chris Leibundgut, Univ. of Freiburg, Germany (i.e. general, artificial tracers)
- Prof. Jeff McDonnell, Oregon State Univ., Corvallis, USA (i.e. isotope tracers)
- Dr. Jens Lange (i.e. general, artificial tracers, case studies)
- Dr. Doug Burns, USGS, USA (i.e. isotope tracers)
- Dr. Pardeep Agarwall, IAEA, Vienna, Austria (i.e. isotope tracers)
- Dr. Axel Suckow, IAEA, Vienna, Austria (i.e. radioactive tracers)
- Dr. Paul Königer (i.e. artificial tracers)

- *…. many others are not mentioned!*
- *… sorry, but my references are sometimes incomplete!!*

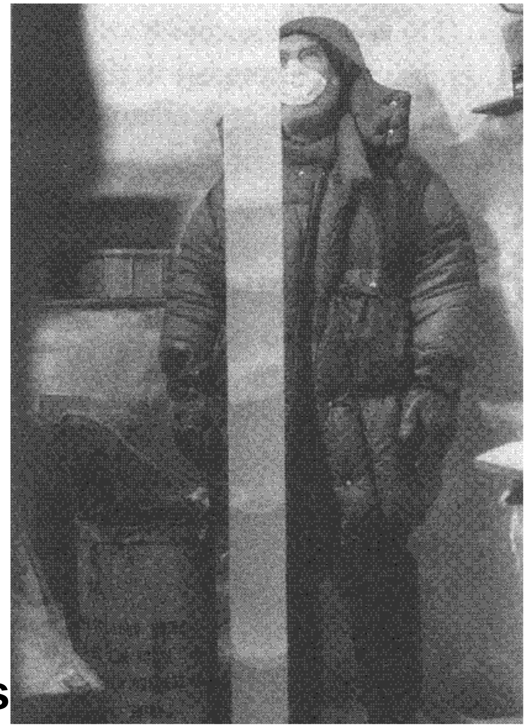
Remember the basic hydrological questions that tracers can help address

- Where does runoff originate in a catchment?
- How long has water resided in different hydrological storages?
- How fast does water move in different hydrological storages?
- How does groundwater and surface water interact?
- What biogeochemical processes affect water chemistry?
- What are the rates of these biogeochemical processes?

Questions relevant for isotope hydrology

Isotope tracers

- Can provide information about climatic conditions (also paleoclimatology)
- Some isotopes (^{18}O, ^{2}H, ^{3}H) behave conservatively during transport as they are part of the water molecule, thus they reflect mixing and transport processes
- Identification of source and movement of water
- Identification of dynamics of hydrologic processes



Isotope contents of ice in Antarctica help to understand previous climates

Definitions

- Atoms of the same element that have a different number of neutrons, and therefore a different mass
- Examples:
  - oxygen ^{16}O, ^{17}O, ^{18}O
  - hydrogen H, ^{2}H (= deuterium, D), ^{3}H (= tritium, T)
- Superscript is the mass number and reflects the sum of protons and neutrons (sometimes written as O-18 or 18-O)
- Stable isotopes do not decay, for example ^{2}H or ^{18}O
- Radioactive (unstable) isotopes decay to more stable forms at a known rate, for example ^{3}H decays to ^{3}He
- General distinction:
  - Isotope Hydrology: ^{18}O, ^{2}H, ^{3}H, components of the water molecule (i.e. age dating, mixing, runoff sources and flow paths, groundwater/surface water interactions, climate indicator, …) **this course!**
  - Isotope Biogeochemistry: ^{15}N, ^{13}C, ^{34}S, etc. (i.e. biogeochemical processes)

Isotope basics

$^{16}_{8}O$

Mass number (= protons + neutrons)

8 protons (positive), 8 electrons (negative),
8 neutrons (neutral)

Atomic number (= protons)

- Protons and neutrons in the nucleus have approximately the same weight
- Electrons (negative charge) are lighter and are located in electron shells

$^{18}_{8}O$

8 protons, 8 electrons, 10 neutrons

- Nuclides with same atomic number (i.e. an element) but different mass number are called isotopes
- 92 natural elements have more than 1000 stable and radioactive isotopes

Some common environmental isotopes

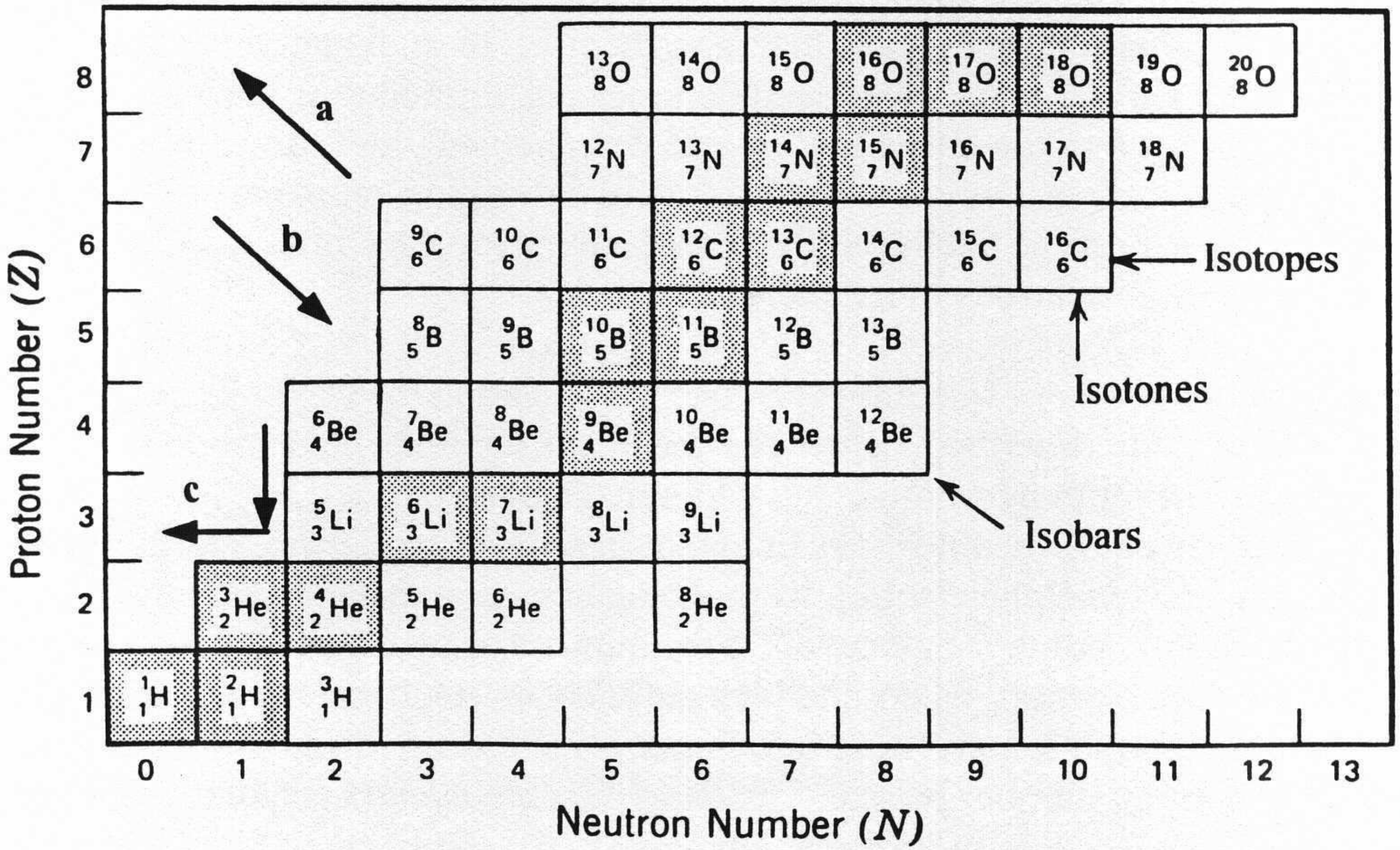


Figure 2.1. Partial chart of the elements. Each square represents a particular nuclide. The shaded squares are stable atoms and the unshaded squares are unstable or radioactive nuclides. Arrows at the left side of the diagram show the shifts in proton and neutron number caused by different decay mechanisms: beta decay (a), positron decay and beta capture (b), and alpha decay (c). Modified from Faure (1986).

Source: Kendall, 1998

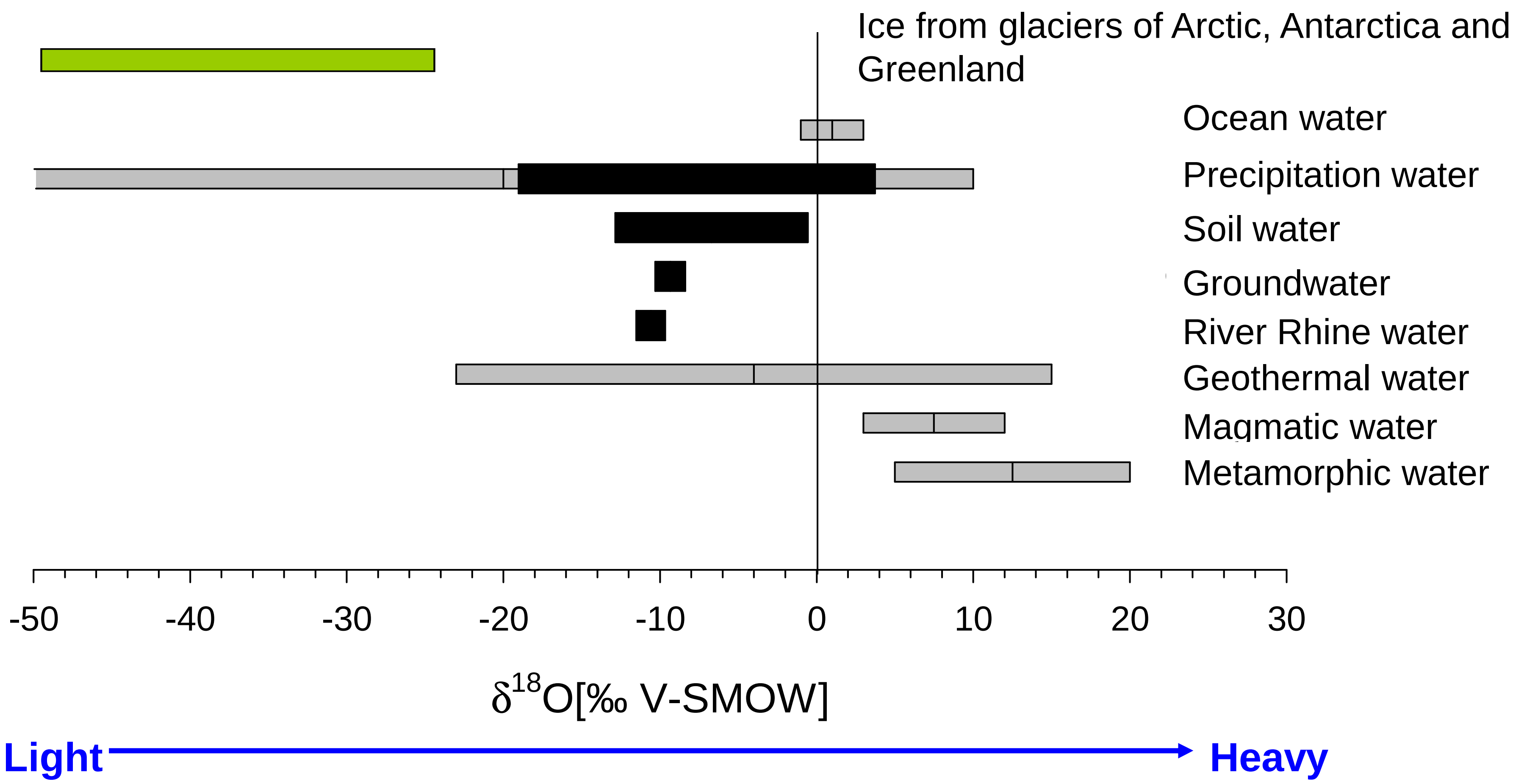
Natural abundance – ratios are very small

Element	**Isotope**	**Abundance (%)**	**Ratio**
Hydrogen	^{1}H	99.985	
	^{2}H (D)	0.015	150.022 e-6
Carbon	^{12}C	98.892	
	^{13}C	1.108	112.04 e-4
Oxygen	^{16}O	99.759	
	^{17}O	0.037	370.894 e-6
	^{18}O	0.204	2044.928 e-6

Isotope units

- Stable isotope compositions (water sample) of low mass elements such as O, H, C, N, and S are expressed in “delta” units (δ) expressed as the deviation from a standard (std) in parts per thousand ($^{o}/_{oo}$ or per mil)
- Example:
  $\delta^{18}O\ (^{o}/_{oo}) = ([(^{18}O/^{16}O)sample\ /\ (^{18}O/^{16}O)std] - 1) \cdot 1000$
- positive value means sample ratio is greater than std.
- negative value means sample ratio is less than std.

$\delta^{18}O$ values in nature



Source: CLARK & FRITZ (1997); extended with data from Leibundgut (2002)

Additional units

- ^{3}H expressed as Tritium Units (TU), one TU = 1 tritium atom per 10^{18} H atoms
- 1 TU = 0.119 Bq = 7.1 decays per minute in 1 liter water [dpm/l]
- ^{3}H may also be expressed as pCi/L where 1 TU = 3.2 pCi/L
- ^{14}C expressed as percent of modern carbon (pmc)
- Many heavy isotopes are expressed as an absolute ratio, for example $^{87}Sr/^{86}Sr$

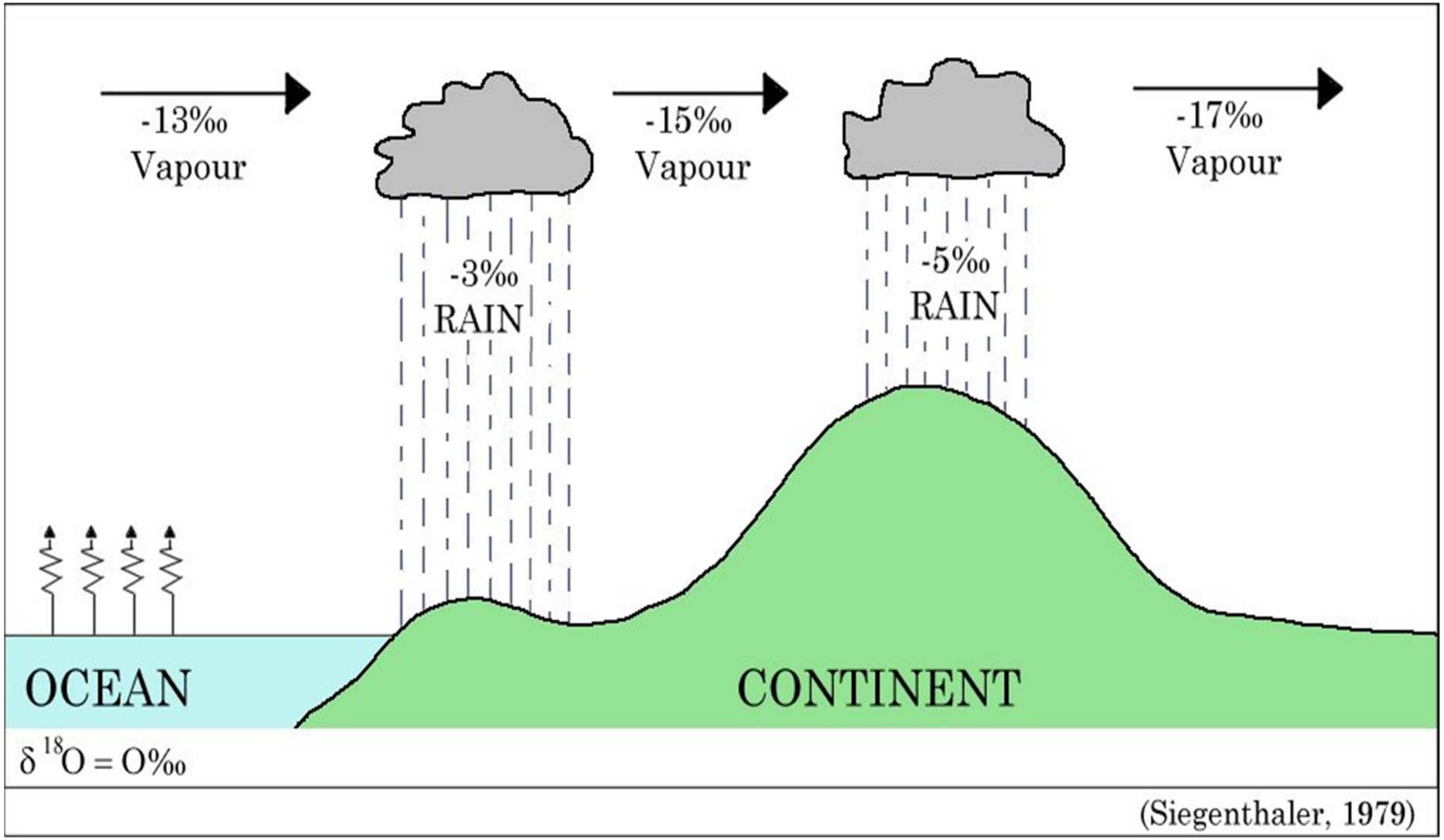
Isotope fractionation

- Phenomenon whereby the isotopic composition of an element in a given compound or ion changes during the transition of the element from one compound or physical state to another
- Proportions of isotopes will change during chemical or biological reactions and phase changes
  - Mass dependent: depend on the mass difference between isotopes
  - Non-mass dependent: depend on the structure of the nucleus
- Fractionation is temperature dependent; stronger fractionation for phase change during low temperatures
- Isotopic composition can shift even if there are no large changes in phase (liquid/gas); for example, soil water in contact with soil gas of a different isotopic composition

Evaporation and condensation (change of phase)

- The condensate becomes enriched in the heavy isotope (^{18}O, ^{2}H) relative to the vapor
- During evaporation/melting the remaining water (water/ice) becomes heavier (enriched in heavy isotopes)
- Rain becomes progressively lighter as storms move inland from the ocean
- Evaporation is strongly affected by humidity – the higher the humidity, the smaller the change in $\delta^{18}O$ and δD during evaporation
- Net effect of evaporation and condensation produces a meteoric water line

Evaporation and condensation effects



Controls of the spatial variation of $\delta^{18}O$ and δD in precipitation

- **Apparent Temperature Effect** – precipitation becomes heavier as temperature increases, $\delta^{18}O$ +0.5 ‰/°C
- **Amount Effect** – rainout creates progressively lighter precipitation during an event
- **Evaporation Effect** – precipitation may evaporate as it falls, especially through dry air, becomes heavier
- **Altitude Effect** – precipitation becomes lighter with increasing elevation on windward side of mountains
  - ^{18}O: -0.15 to –0.5‰/100 meters
  - D: -1.5 to -4‰/100 meters
- **Continental Effect** – precipitation becomes progressively lighter inland from moisture source

Temperature effect

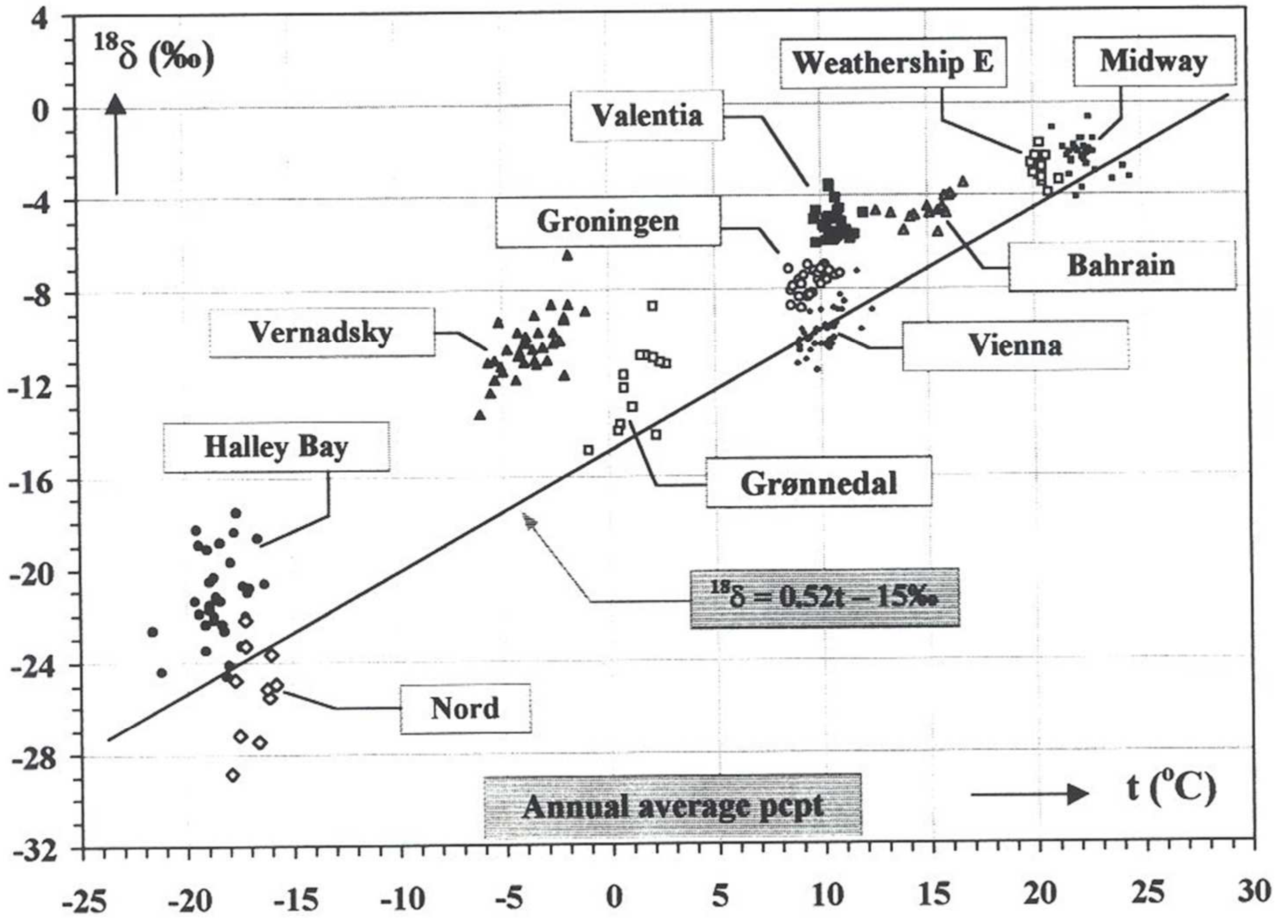


Fig.4.9 Weighted average annual values of $^{18}\delta$ in precipitation (pcpt) vs the mean surface air temperature, showing the variations from year to year (data from the GNIP network).

Source: IAEA

Altitude effect

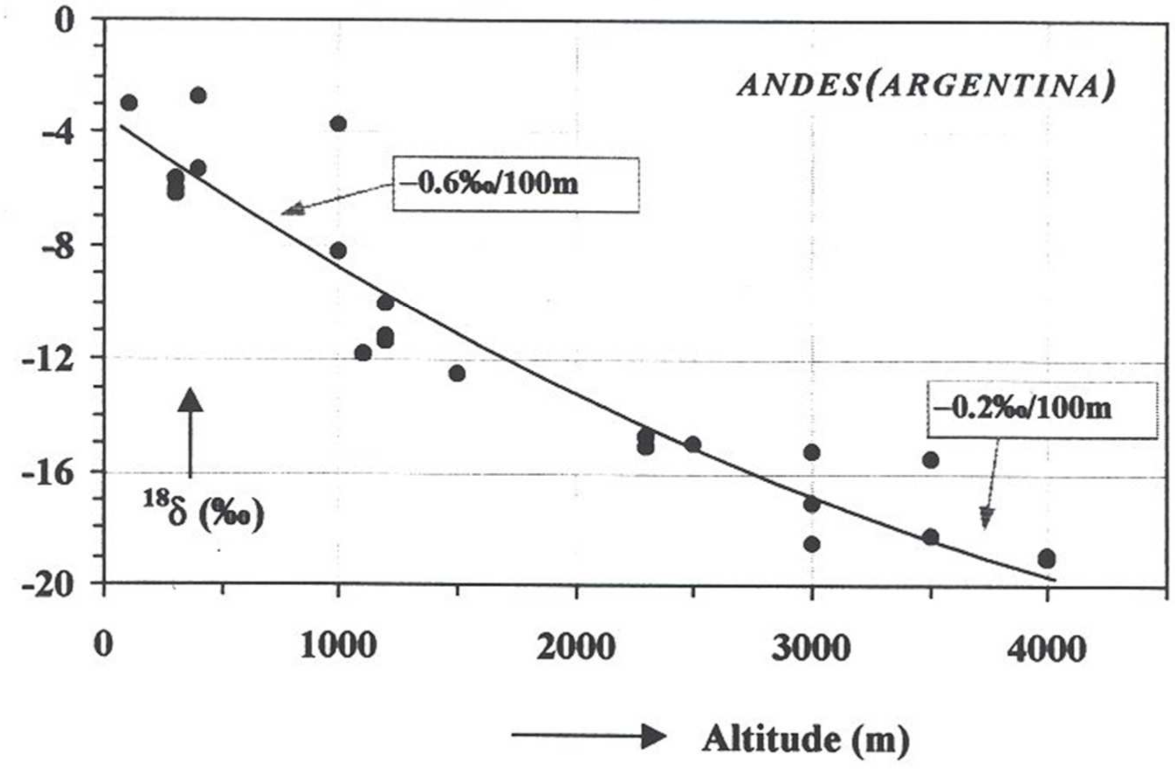
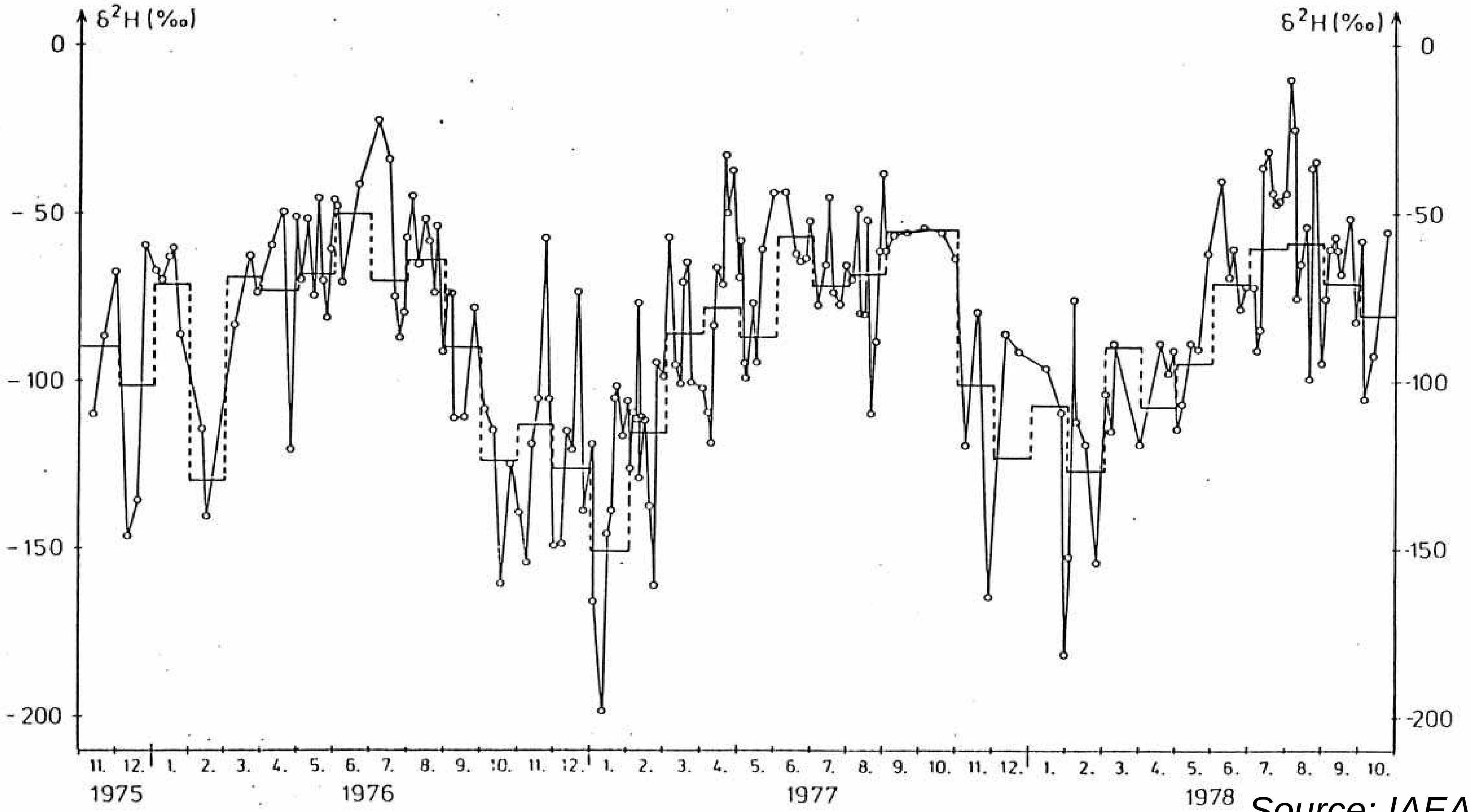


Fig.4.7 Example of the altitude effect on precipitation for the eastern slopes of the Andes mountains, as deduced from samples of undeep groundwater/soilwater, collected from springs. The magnitude of the effect is increasing from –0.2 to –0.6‰/100m (Vogel et al., 1975).

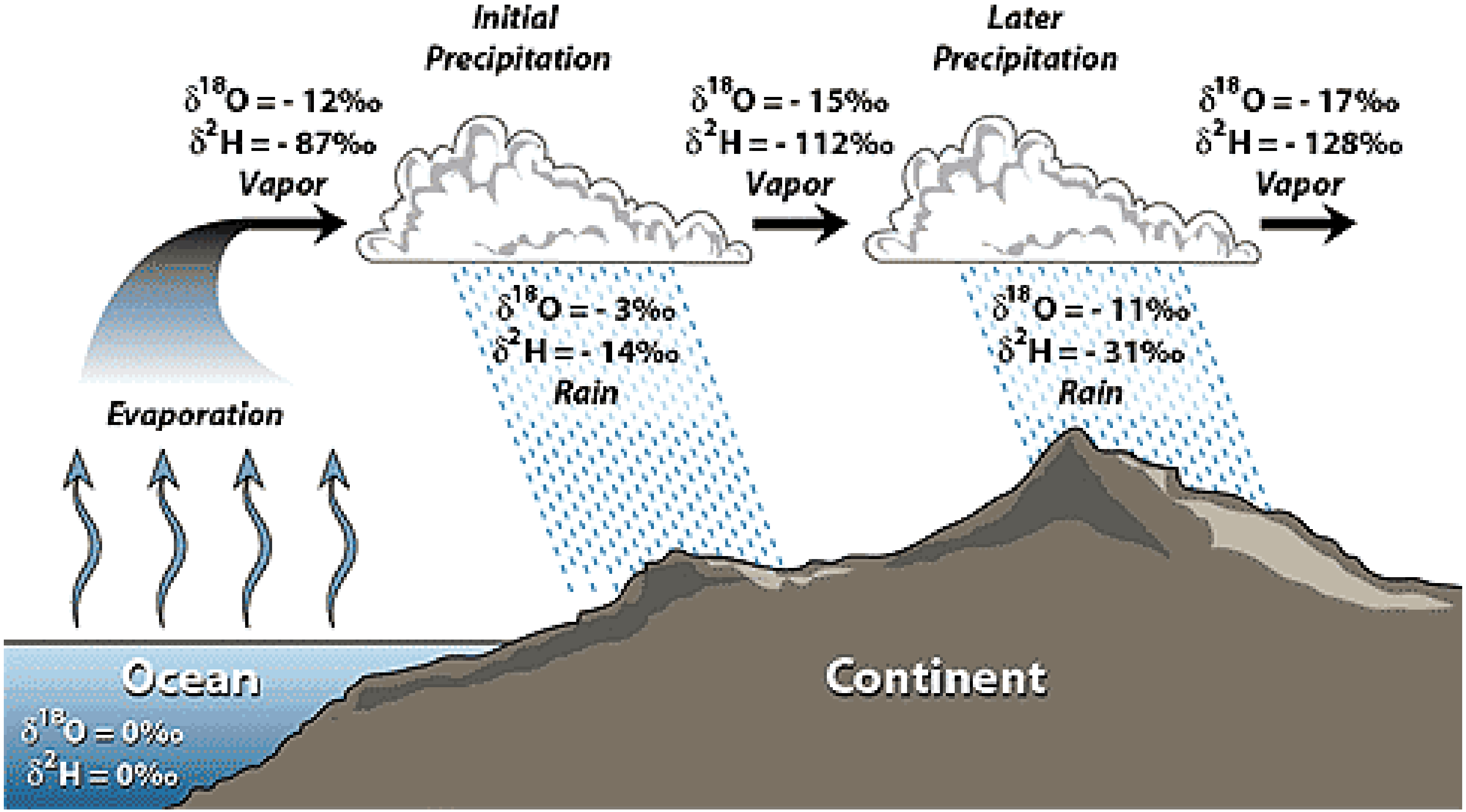
Source: IAEA

Seasonal effects
(southern Germany)



Source: IAEA

Continental effect



http://www.sahra.arizona.edu/programs/isotopes/oxygen.html

Amount effect

(better: intra-storm variability!)

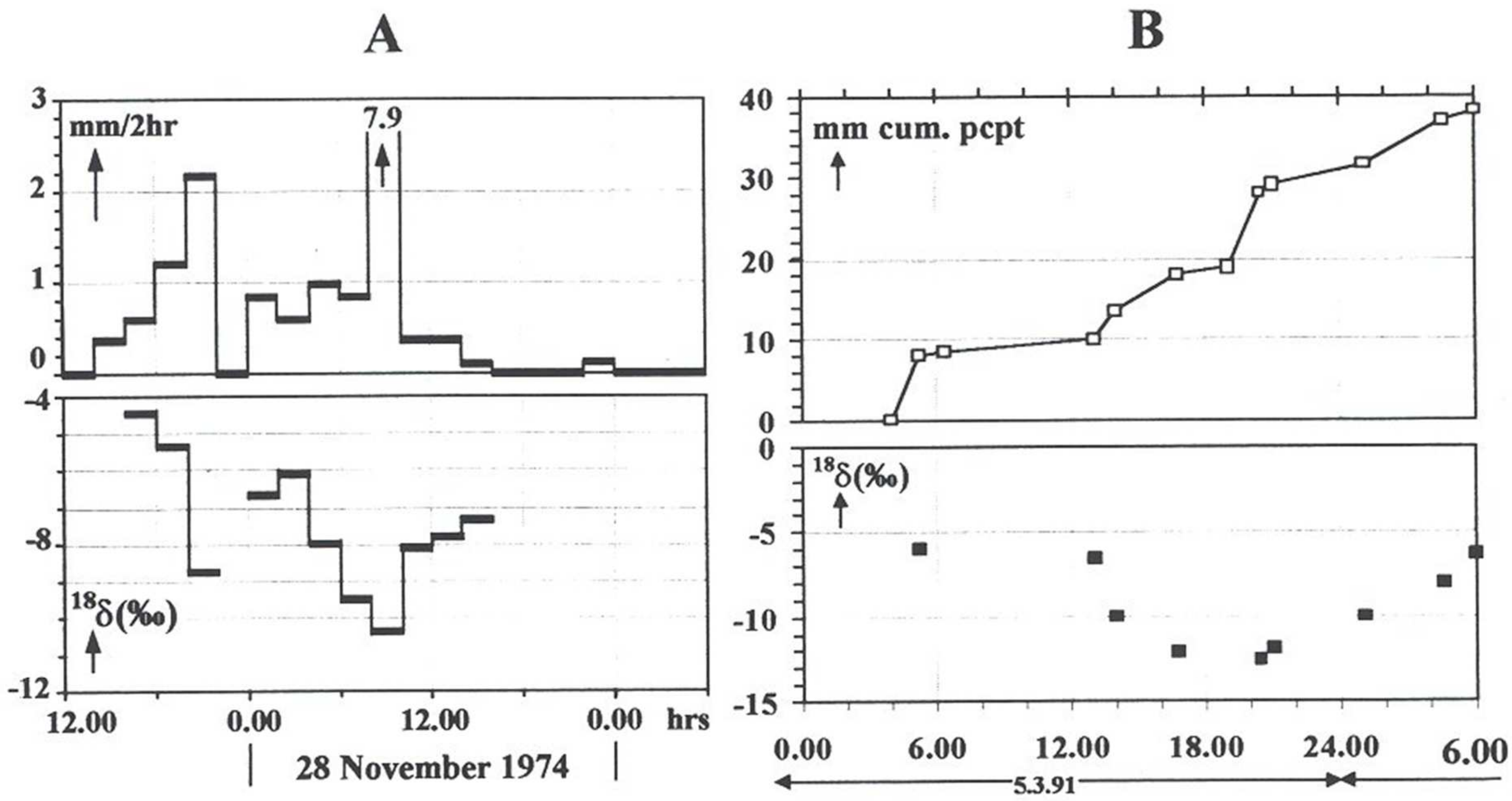
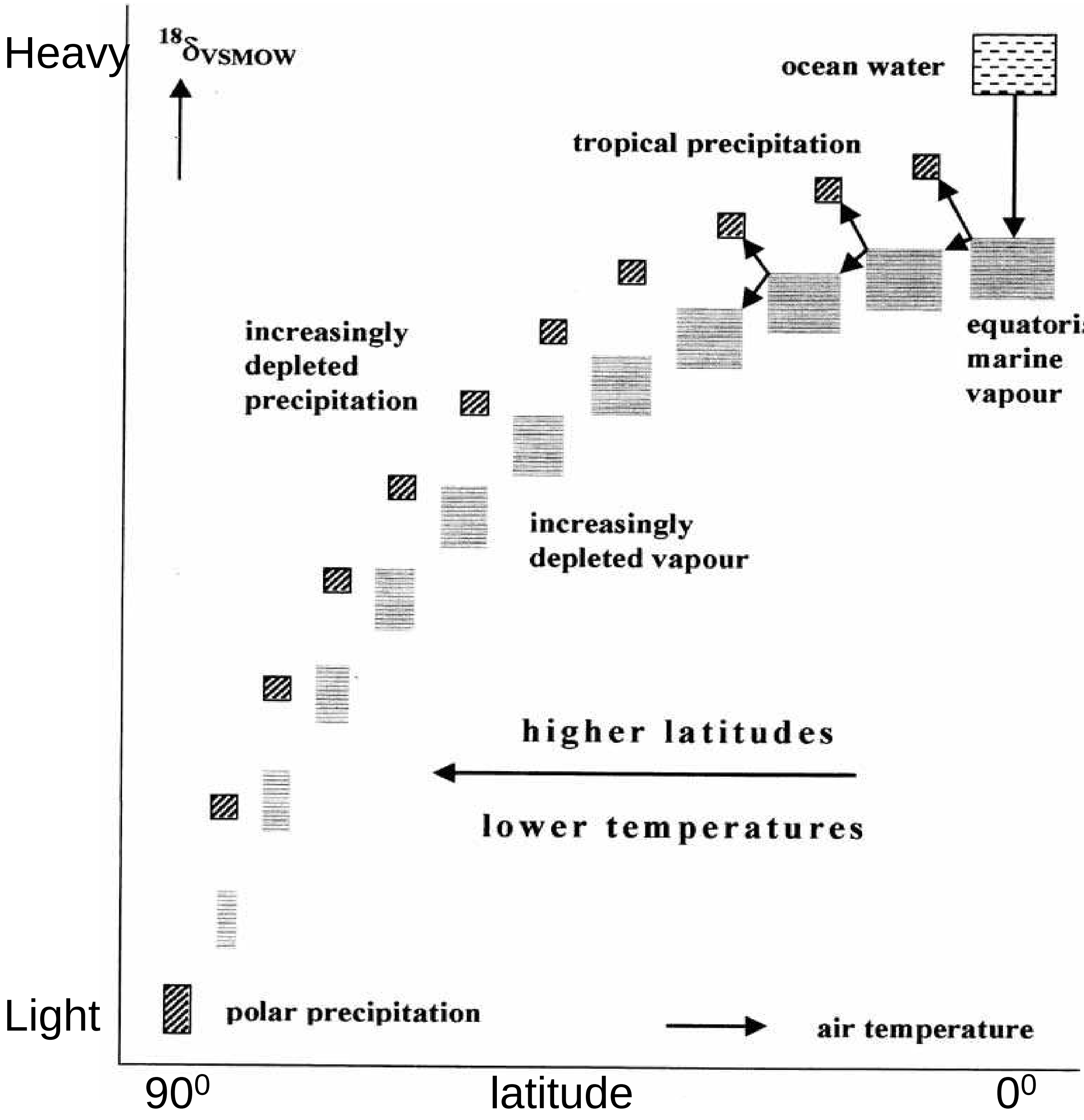


Fig.4.8 Time sequence of the isotopic composition of precipitation during showers; examples are shown for two cases of convective storms: **A)** rain intensity in mm/2 hours (Mook et al., 1974); **B)** cumulative rain over variable periods.

Source: IAEA

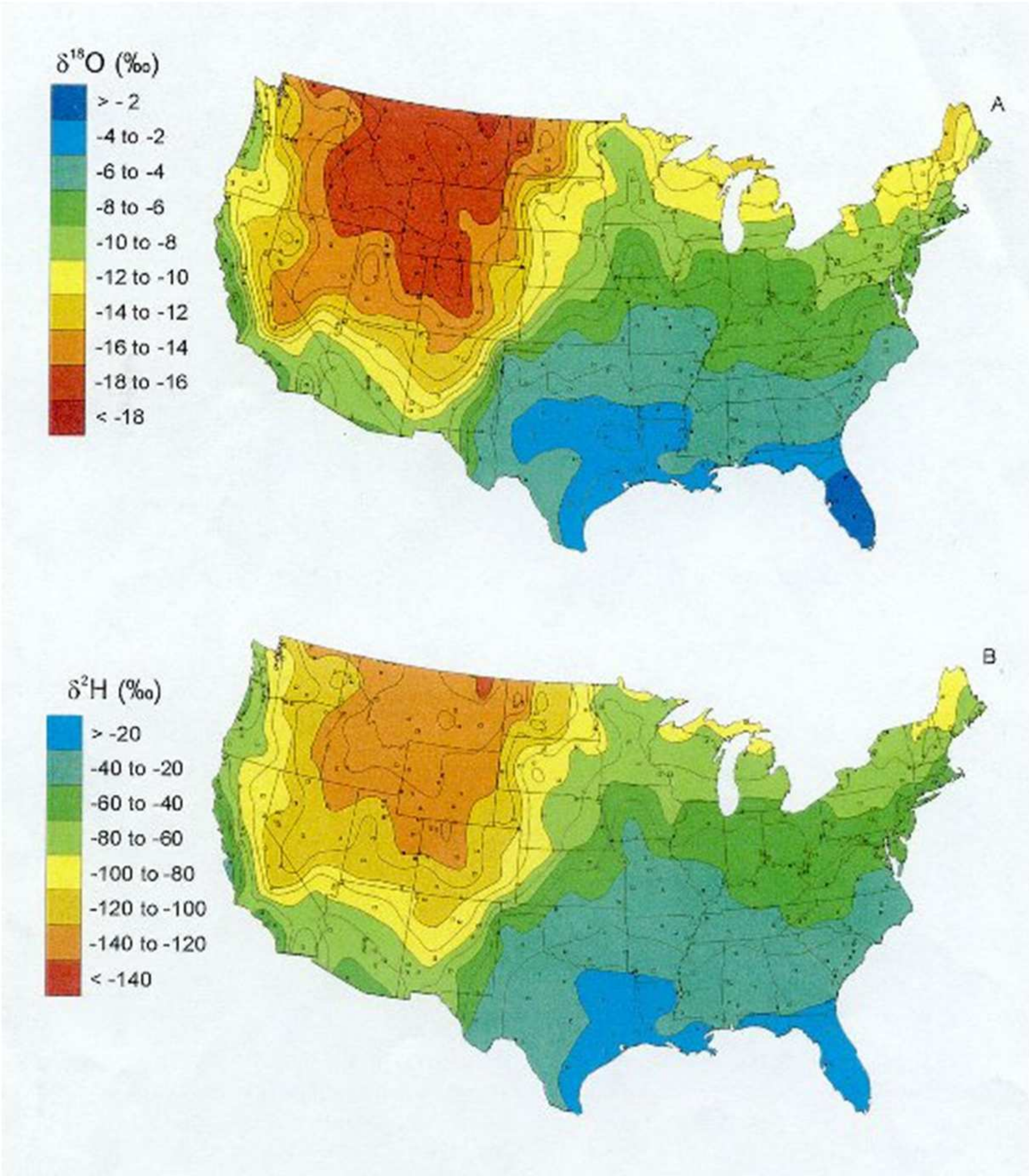


Latitudinal effect

Source: IAEA

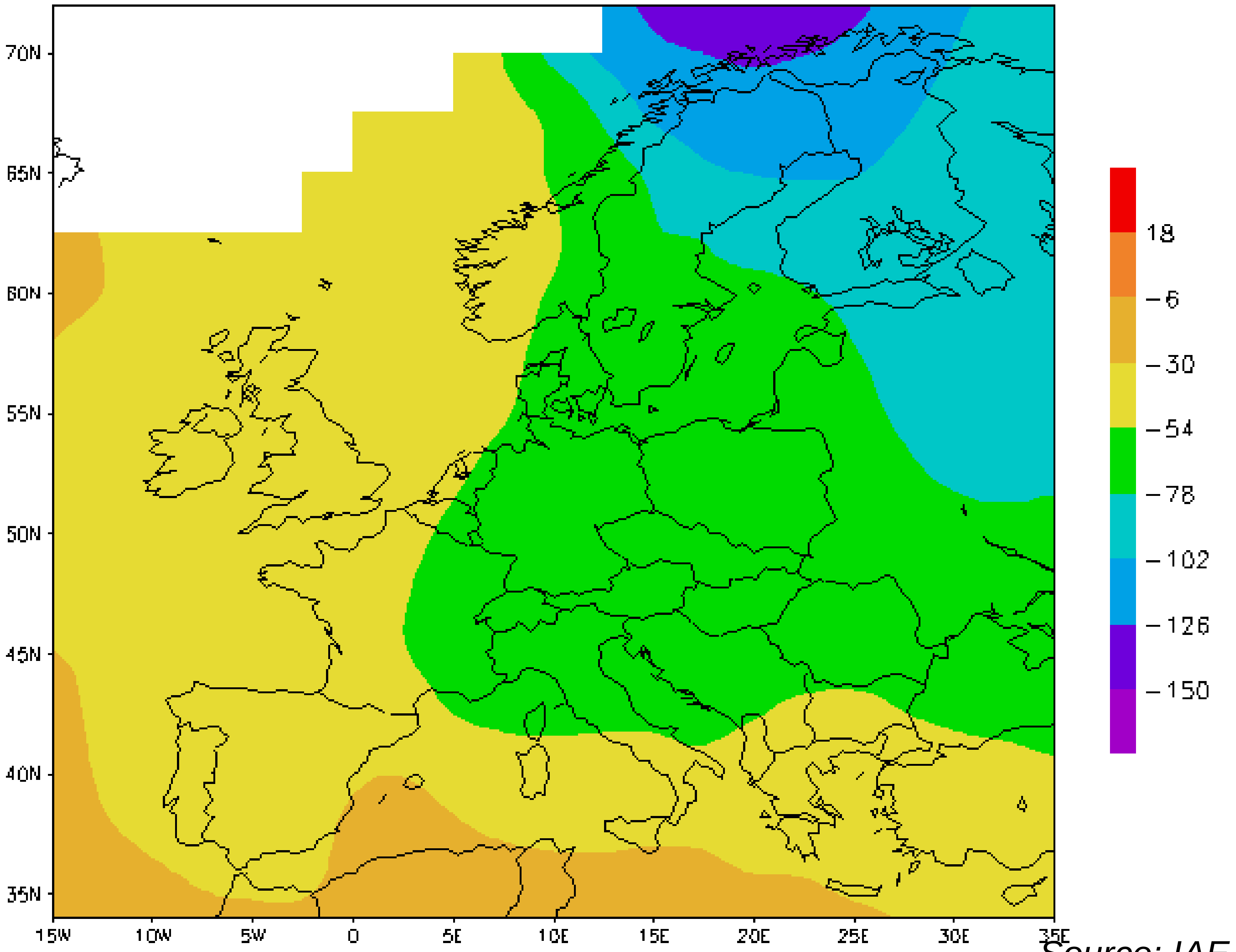
Spatial variations in the USA

Why are patterns of $\delta^{18}O$ and δD so similar?



Source: Kendall and Coplen, 2001

Weighted Annual δ²H (GNIP – IAEA)



Source: IAEA

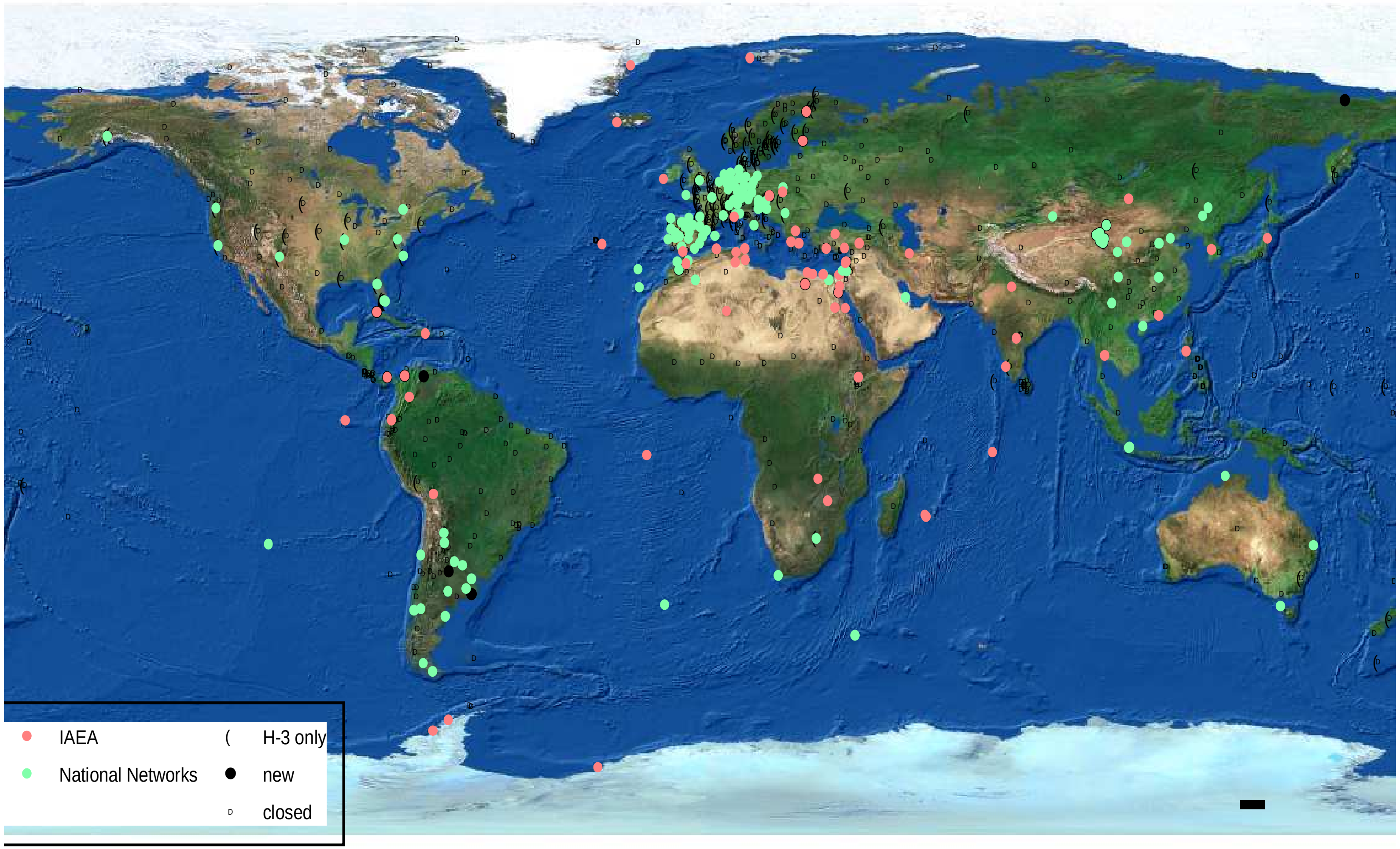
Taking water samples for isotope analysis (^{18}O, D and ^{3}H)

- No evaporation from the sample bottle
- No evaporation from precipitation sampler

danger of fractionation!

- dry bottles, no mixing with old water
- pumping of fresh groundwater from wells
- samples volumes depend on the device,
  - usually 100 ml are enough for ^{18}O and D
  - up to one liter for ^{3}H

Global Network of Isotopes in Precipitation (GNIP)



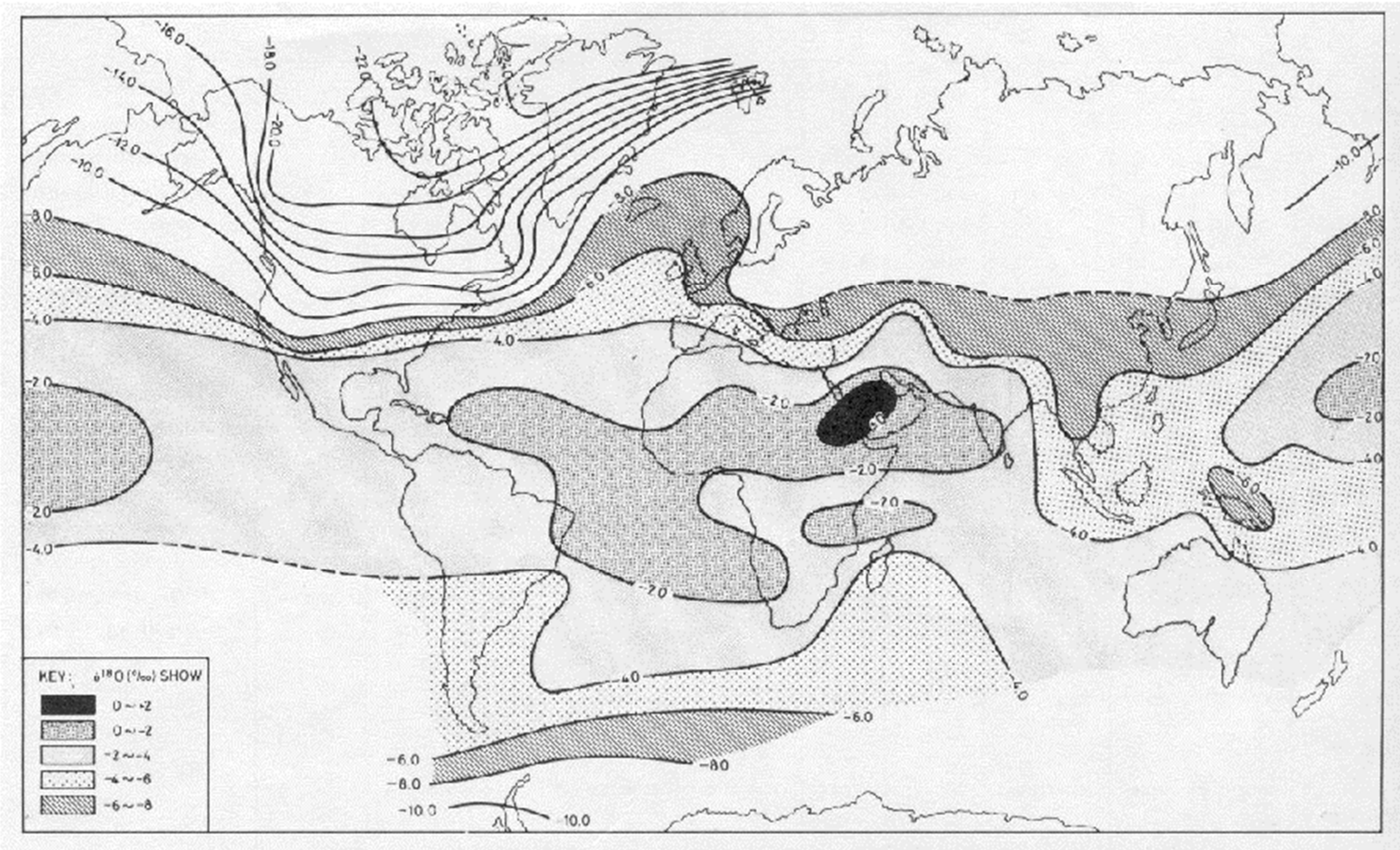
Precipitation sampler

Source: IAEA

Information available at the GNIP database

- 183 active stations in 53 countries
- The Isotope Hydrology Laboratory of IAEA is currently performing isotope analyses of about 30 % of the collected precipitation samples; 33 other labs are involved
- Available are isotope data (H-2, O-18, H-3), basic meteorological variables (type and amount of precipitation, surface air temperature and vapour pressure)
- 88,000 records from 700 stations located in 101 countries
- First data of tritium was collected in 1953
- First data of stable isotopes were collected in 1960

Global isotopic composition of precipitation



Source: IAEA

Generalization
Isotopic composition of precipitation

- Consistent <u>average</u> compositions over time and space
- <u>Annual</u> cycle of compositional changes — *heavy* in summer and *light* in winter; becomes muted towards equator
- Large variation <u>among</u> storms
- Often considerable <u>variability</u> within storms
- Snow often plots along lines of higher d-excess than rain
- Storms derived from different storms tracks may have consistently different meteoric water lines

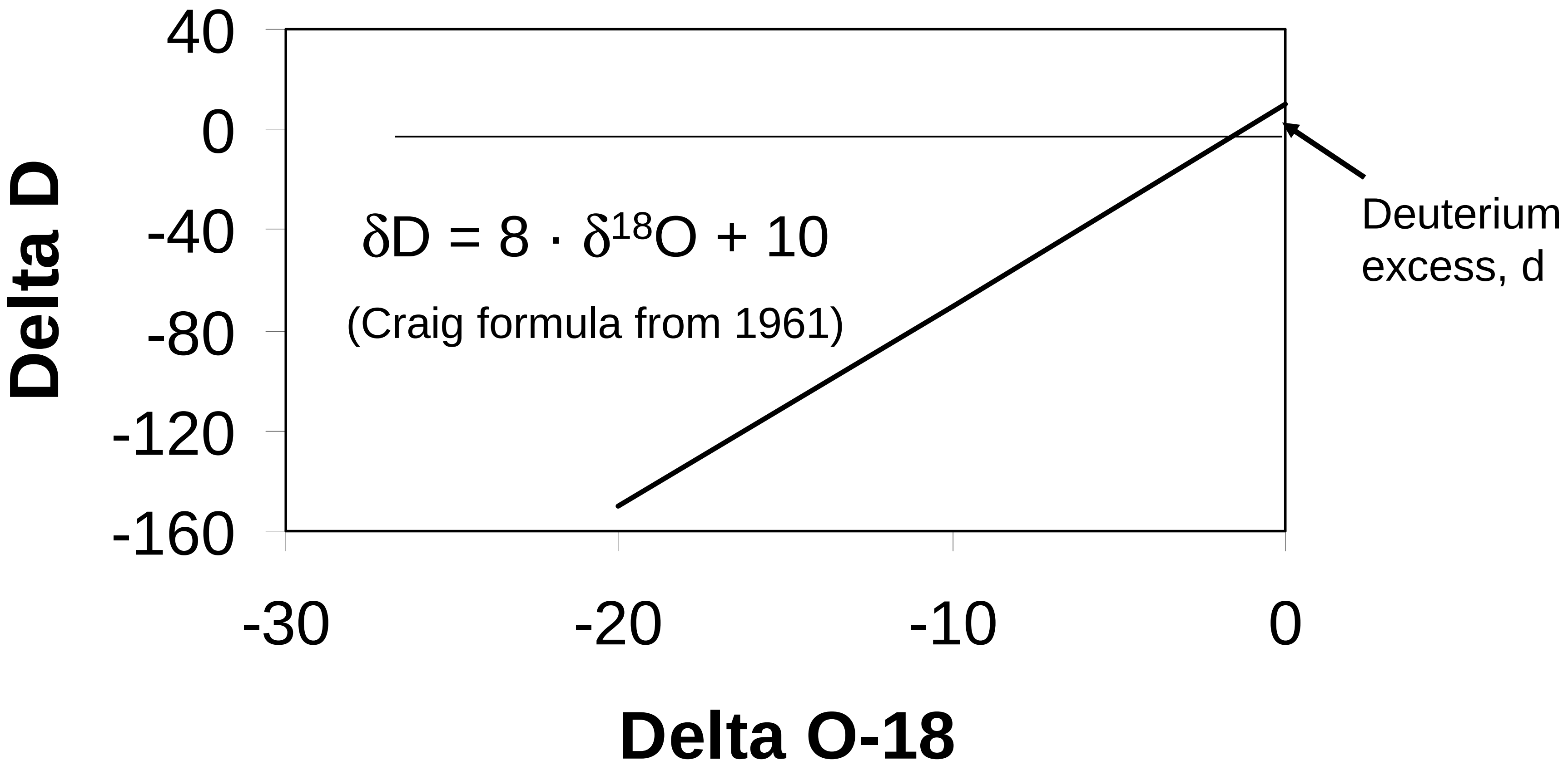
Global Meteoric Water Line (GMWL)

- When precipitation samples from all around the world are plotted in δD *vs*. $\delta^{18}O$ space, they form an approximate line (really a band or narrow oval of data). Harmon Craig (1961):

$$\delta^2H = 8 * \delta^{18}O + 10 ‰$$

- Slope of 8 – close to the ratio of equilibrium fractionation factors of H and O isotopes at 25–30 ^{o}C, and that produced by Rayleigh condensation of rain at 100% humidity
- Y-intercept is 10 due to kinetic enrichment of D in evaporating ocean water – called deuterium excess d

Global Meteoric Water Line



New, more precise formula from IAEA 2004 (based on GNIP data):

$\delta\, ^2H = 8.17\ (\pm 0.07)\ \delta^{18}O + 11.27(\pm 0.65)$ ‰ VSMOW

Deuterium Excess, d

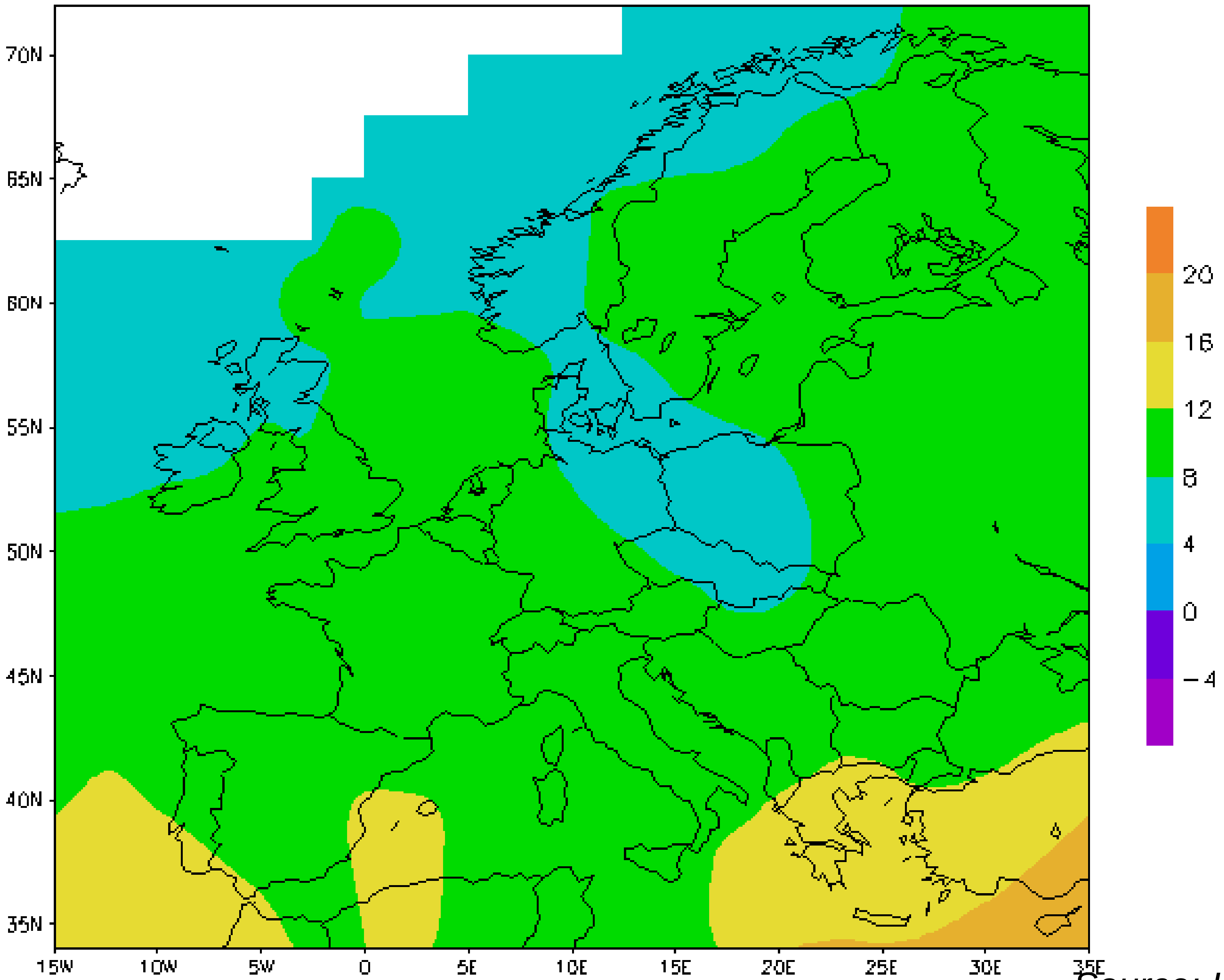
- Value changes with climate – cooler, more humid areas have smaller d values
- Examples: Global mean = +10‰

  North America = +6‰

  Mediterranean = +22‰

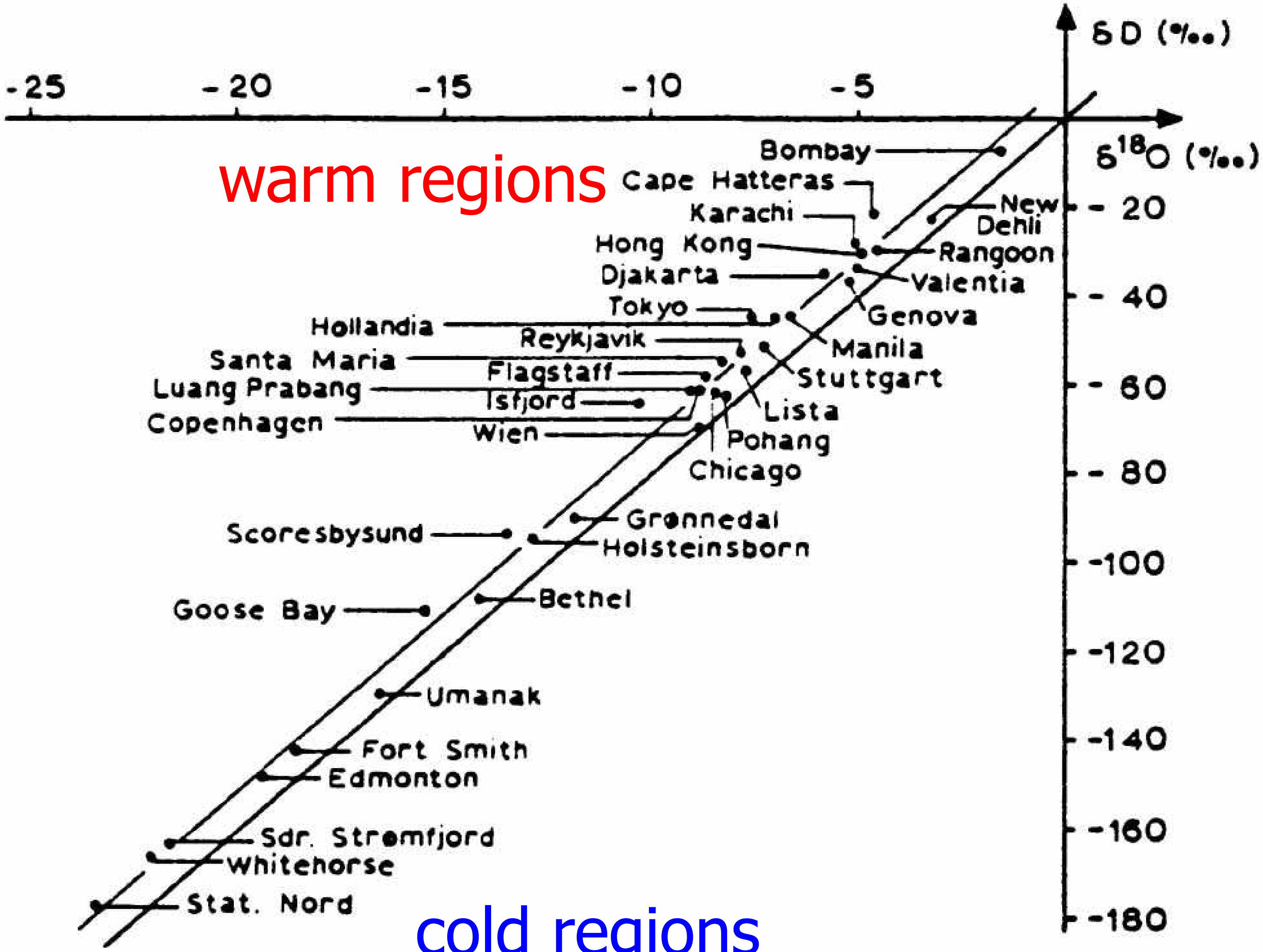
  New Zealand = -0.3‰
- Deuterium excess can sometimes be used to identify water that was recharged during a different climatic regime

Weighted Annual *d*-excess **(GNIP – IAEA)**



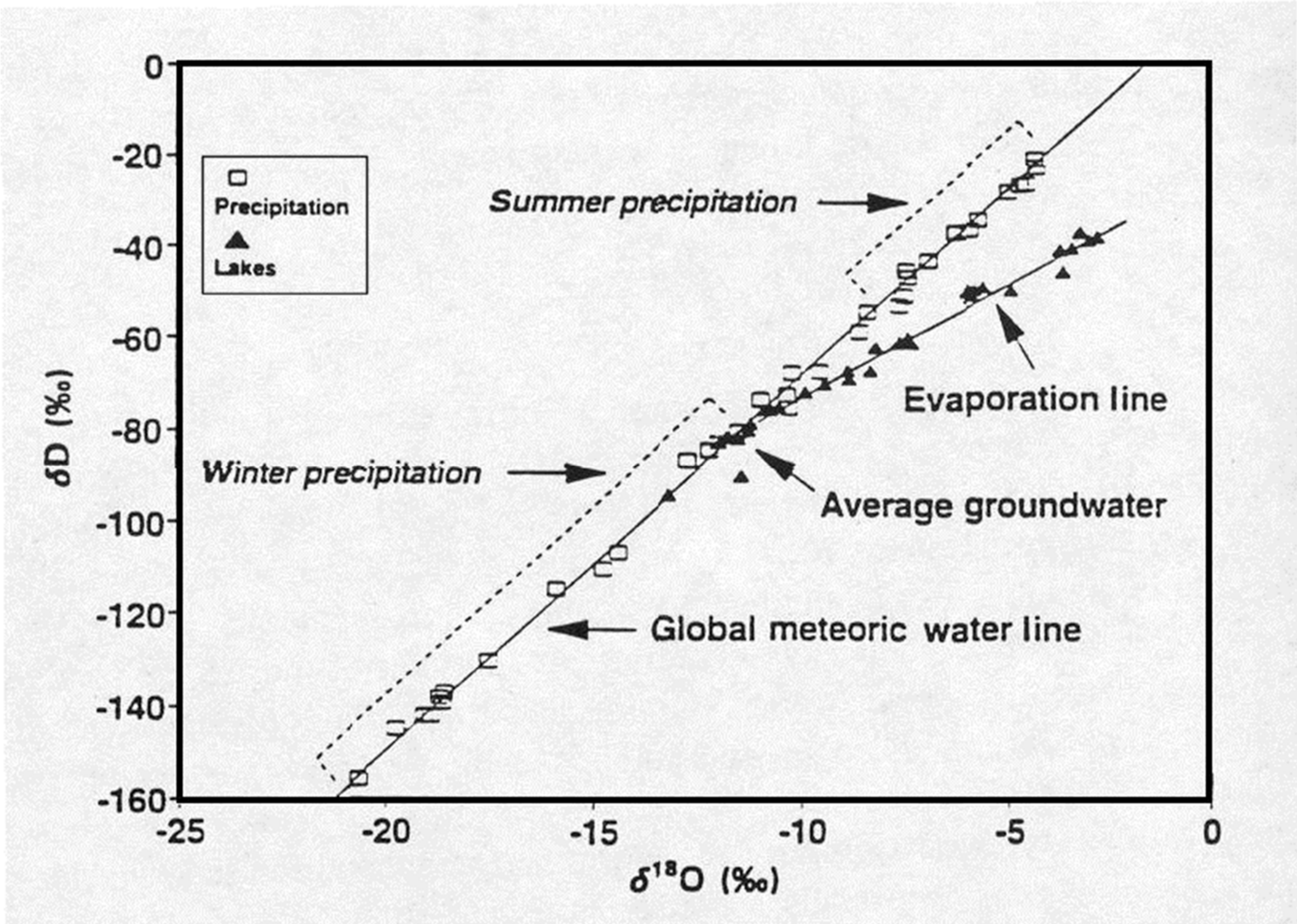
Source: IAEA

Mean values of precipitation water and its position at the meteoric water line



Source: IAEA

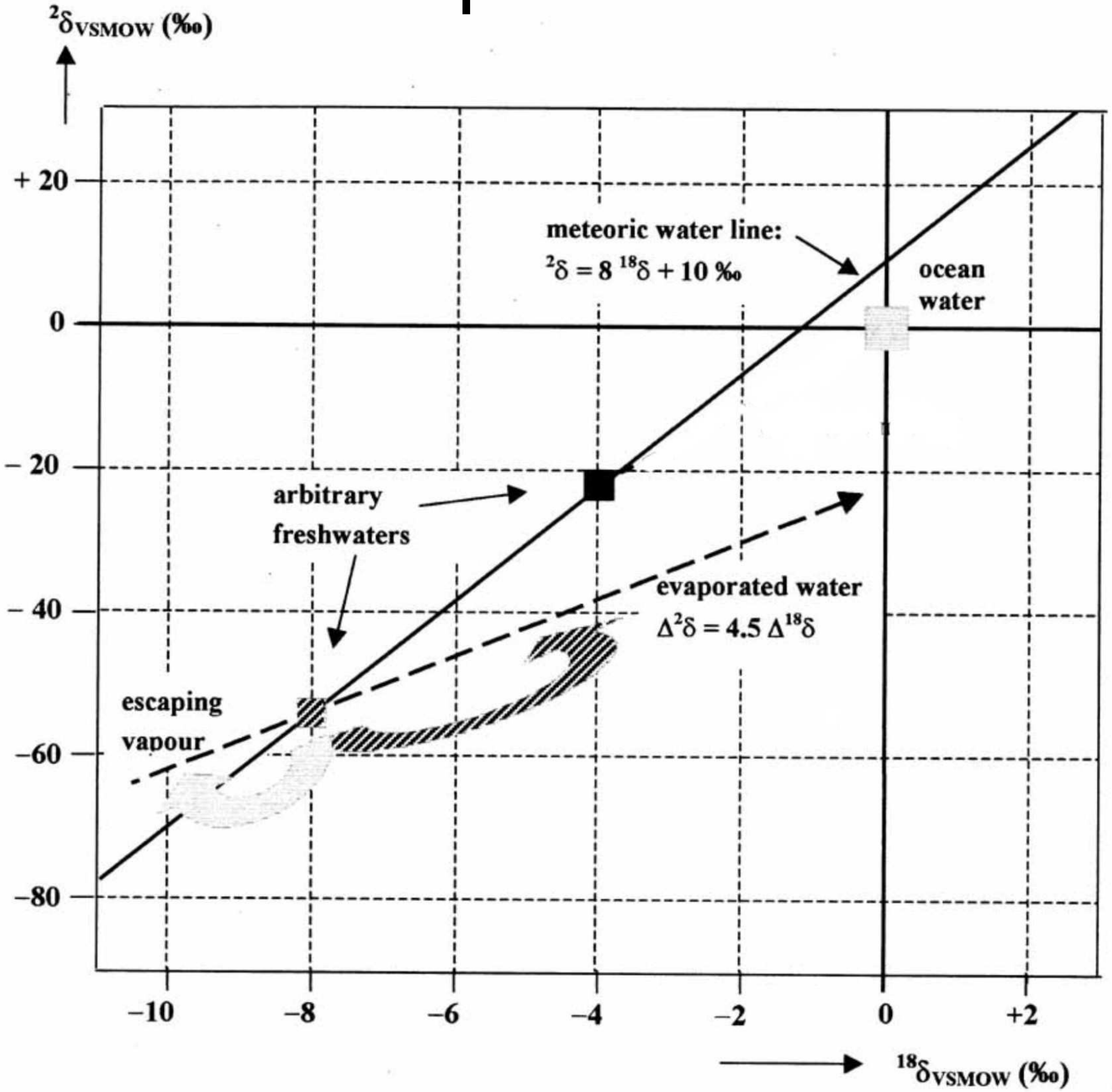
Meteoric water line contains much information



Northern Wisconsin, USA

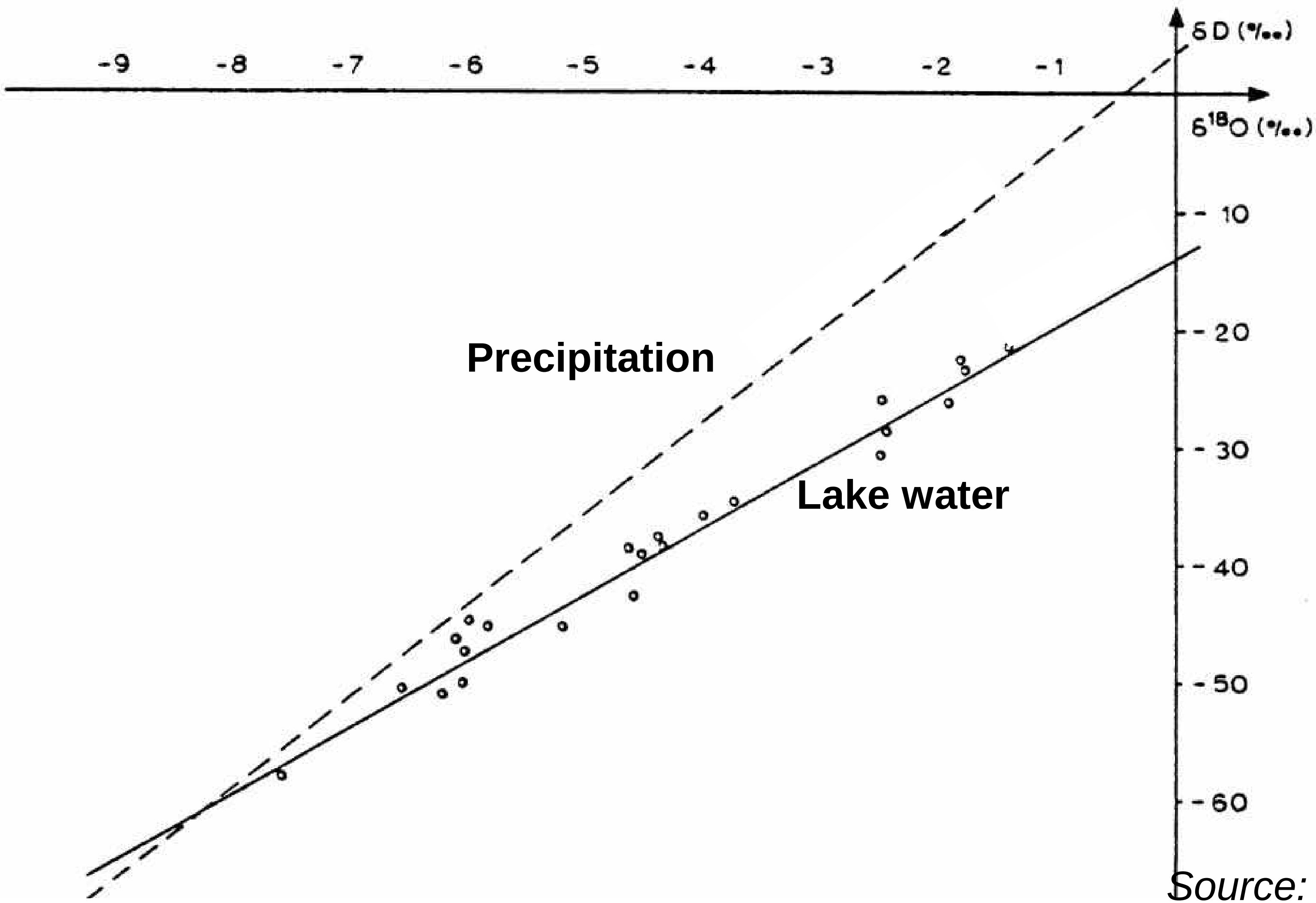
Source: Kendall, 2001

Evaporation lines



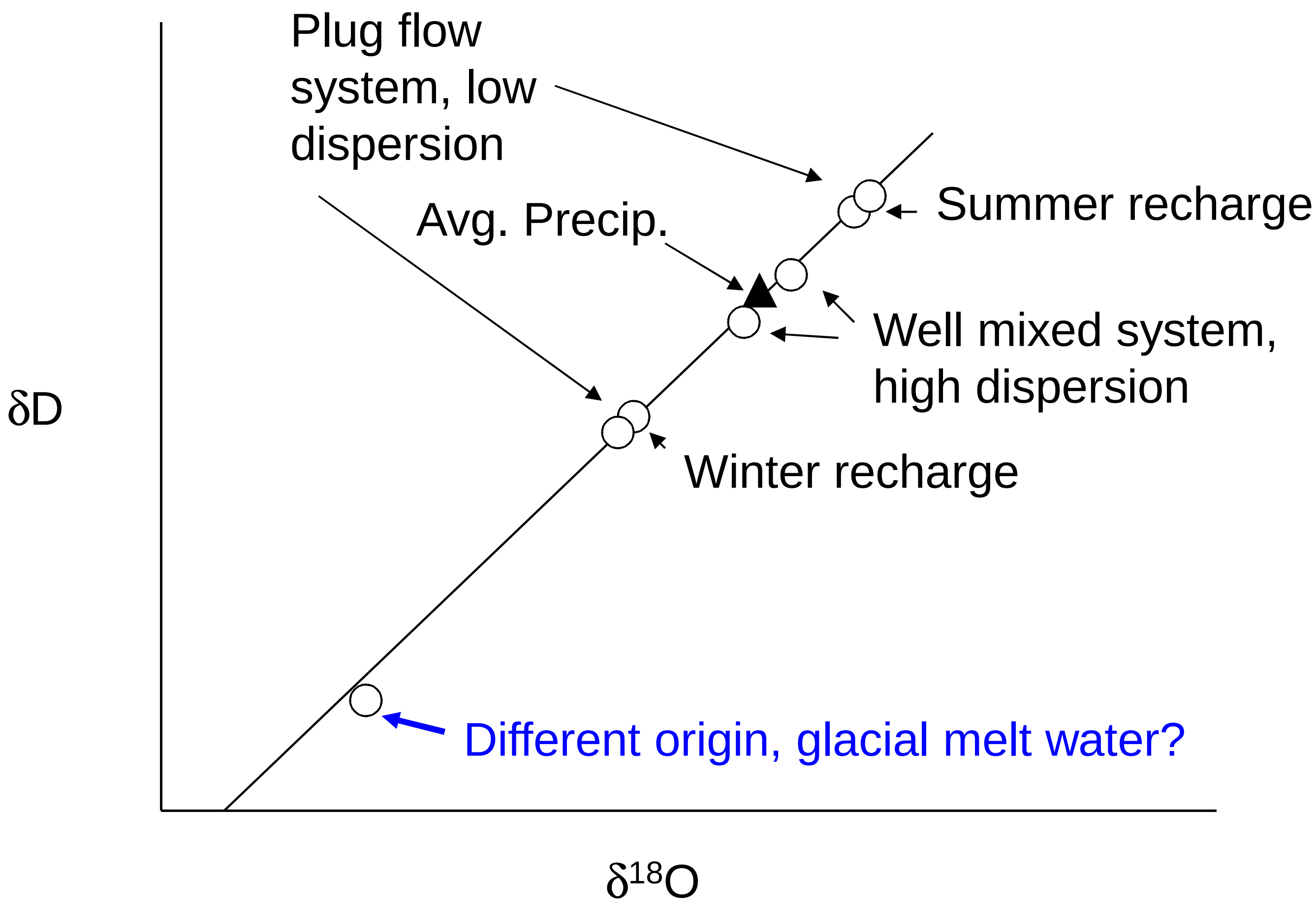
Source: IAEA

D/^{18}O-relation at the lake of Neusiedel, Switzerland

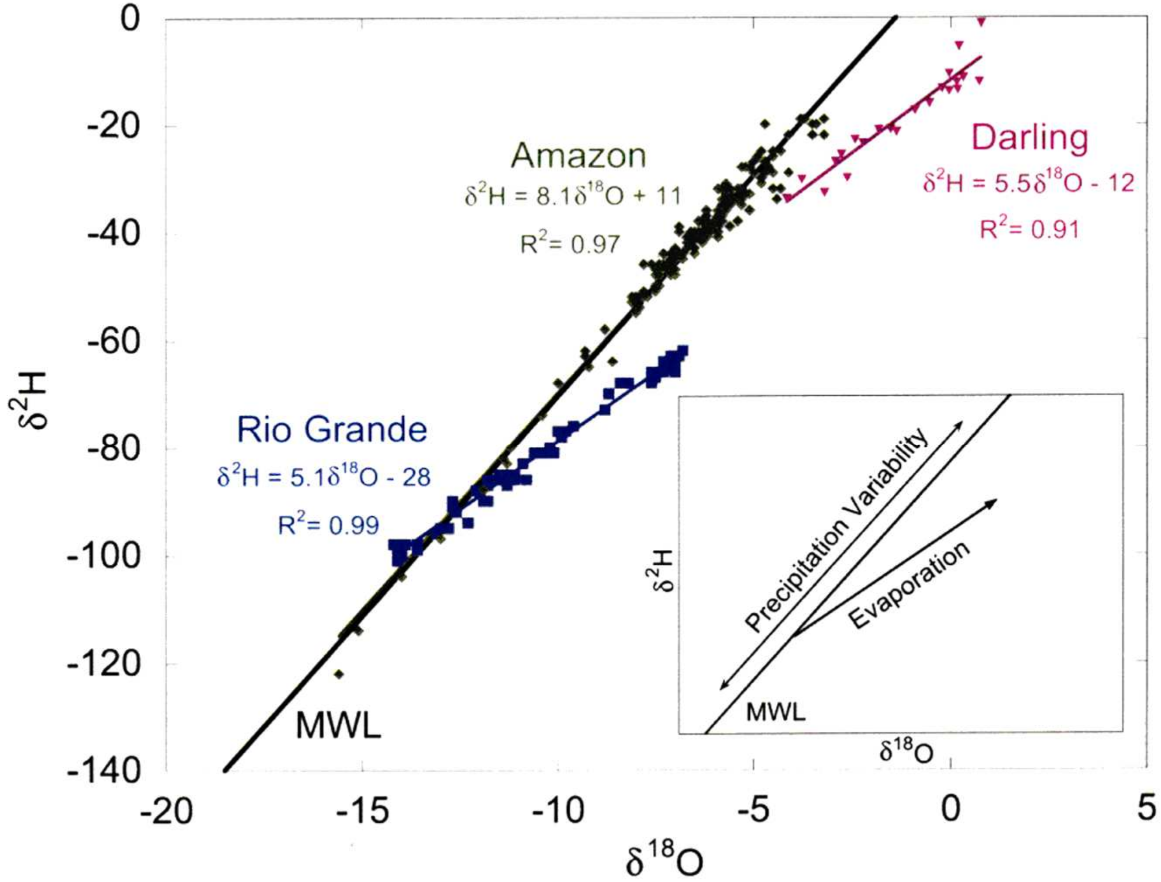


Source: IAEA

Interpretation of MWL: Groundwater isotopic composition



Use LMWL in large rivers



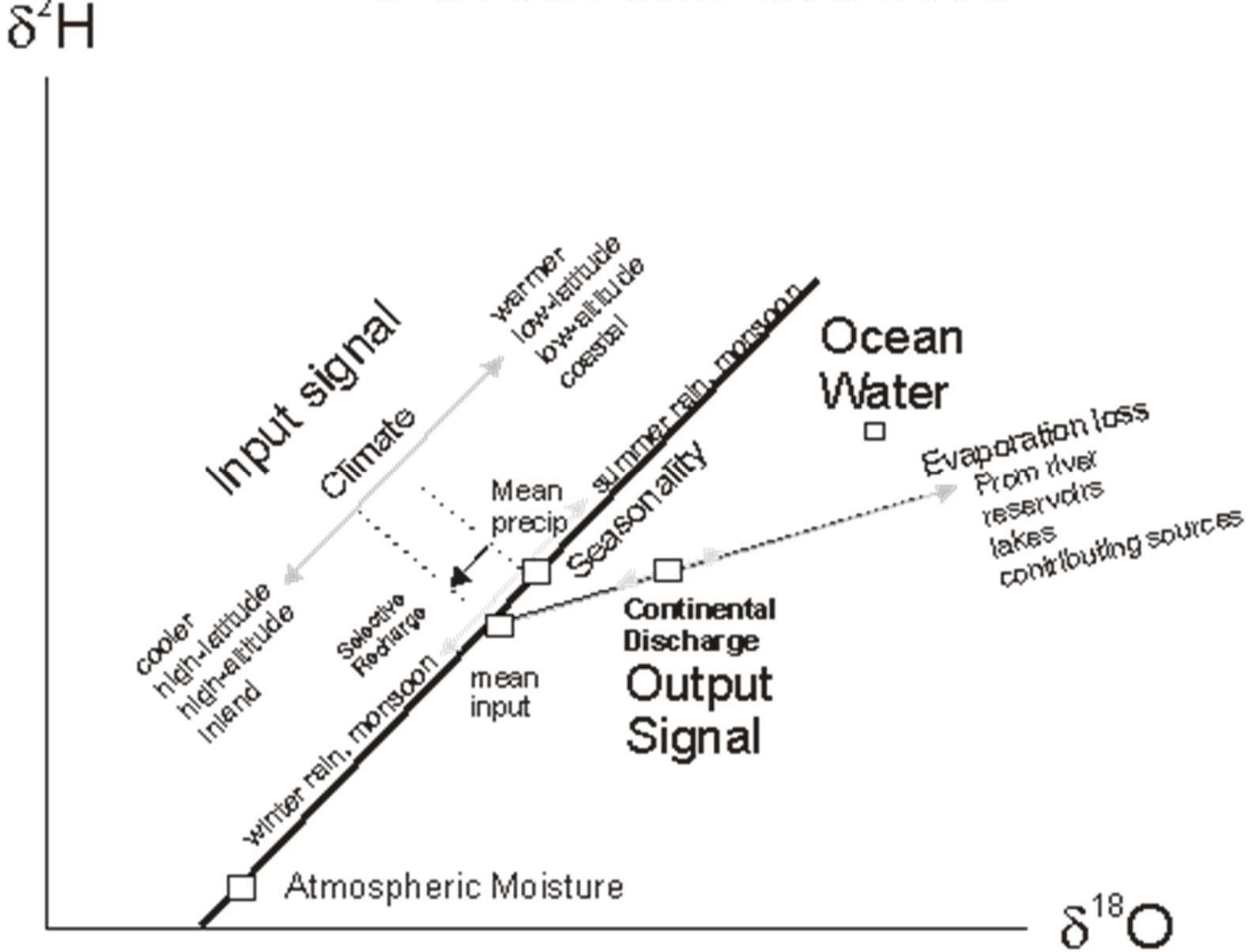
Agarwaal et al., 2002

Overview of some LMWLs

From: E. Mazor (1997) Chemical and isotopic groundwater hydrology. M. Dekker, New York, 413pp; and Clark & Fritz, 1997, 6.

Region	**Meteoric line (‰)**
'Global' (meteoric line)	$\delta^{2}H = 8\delta^{18}O + 10$
Northern hemisphere (continental)	$\delta^{2}H = (8.1 \pm 1)\delta^{18}O + (11 \pm 1)$
Mediterranean (or Middle East)	$\delta^{2}H = 8\delta^{18}O + 22$
Maritime Alps (April 1976)	$\delta^{2}H = (8.0 \pm 0.1)\delta^{18}O + (12.1 \pm 1.3)$
Maritime Alps (October 1976)	$\delta^{2}H = (7.9 \pm 0.2)\delta^{18}O + (13.4 \pm 2.6)$
Northeastern Brazil	$\delta^{2}H = 6.4\delta^{18}O + 5.5$
Northern Chile	$\delta^{2}H = 7.9\delta^{18}O + 9.5$
Tropical Islands	$\delta^{2}H = (4.6 \pm 0.4)\delta^{18}O + (0.1 \pm 1.6)$

Meteoric Water Line (MWL): Generalizations



Source: IAEA

Developing your own LMWL – Good rules of thumb

1. Each site has its own LMWL
2. Need to collect all precipitation for at least 2-3 years at a site to get a good average value for recharge
3. Do not interpolate LMWL or averages from the data for the closest IAEA or other station (but compare with IAEA data)
4. There is lots of spatial and temporal variation in the isotopic composition of precipitation
5. The GMWL or LMWL is not a tight line – they are many lines that fit through an ellipse of data points (uncertainty)

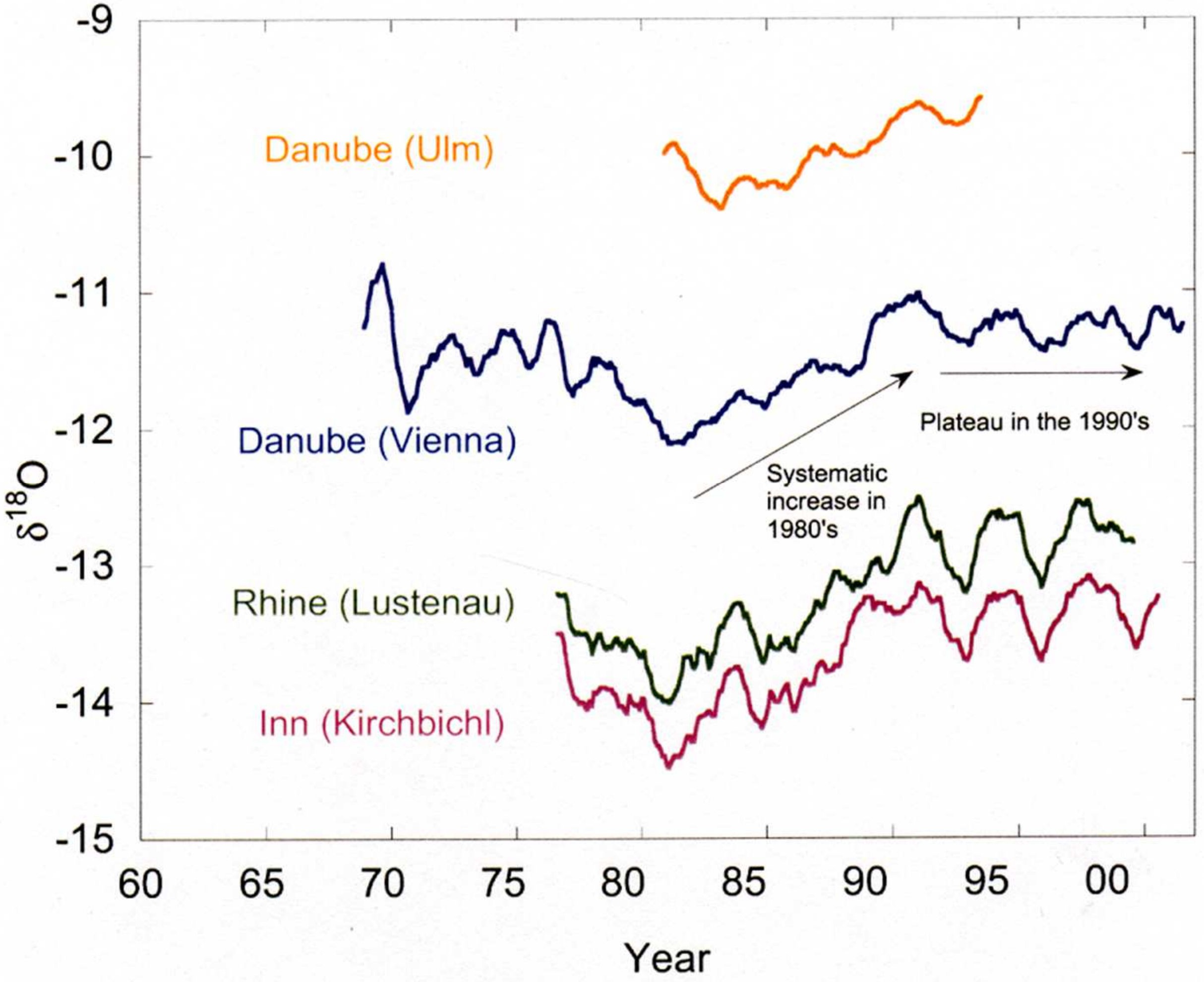
Developing your own LMWL – Good rules of thumb

6. Evaporation causes samples to plot below the MWL
7. Recharge water can be very different from average rainfall
8. Samples easily fractionate in poor quality bottles; use ones with good caps. Wrap in tape or dip in paraffin for long-term storage
9. Samples archive well; collect more samples than you need, and analyze them in groups

Why do waters differ from isotopic composition of precipitation?

- Evaporation of surface waters, interception
- Seasonal recharge (unequal distribution over the year)
- Time lag, waters might reflect past precipitation
- Precipitation sampling site may not be representative of basin (elevation, temp., etc.)
- Mixing of different water components (different groundwater, soil water etc.)
- Damping of the seasonal fluctuations due to dispersion in the system

Data from European rivers –
The Danube is a mixture of many other rivers



Agarwaal et al., 2002

Take home messages

- Stable and unstable (radioactive) isotopes (^{2}H, ^{18}O and ^{3}H, respectively) of water molecule are natural inputs into the hydrological cycle and behave conservatively
- Isotope fractionation due to phase changes or biogeochemical processes
- All precipitation data can be summarized to MWL (^{2}H vs. ^{18}O diagram), but LMWL can vary from this
- Samples at the MWL can be interpreted as summer-winter precipitation, evaporation effects etc.
- There are temperature-, altitude-, amount-, seasonal-, latitudinal-, and continental effects
- Need of a specialized laboratory (but number is increasing; incl. TU Delft, UNESCO-IHE)
- Much data is available at the IAEA (GNIP, GNIR etc)

http://bit.ly/PJiPpA