

Groundwater dating: a comprehensive approach to discovering hidden pathways

Florent BARBECOT
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AIH Montpellier - 2016





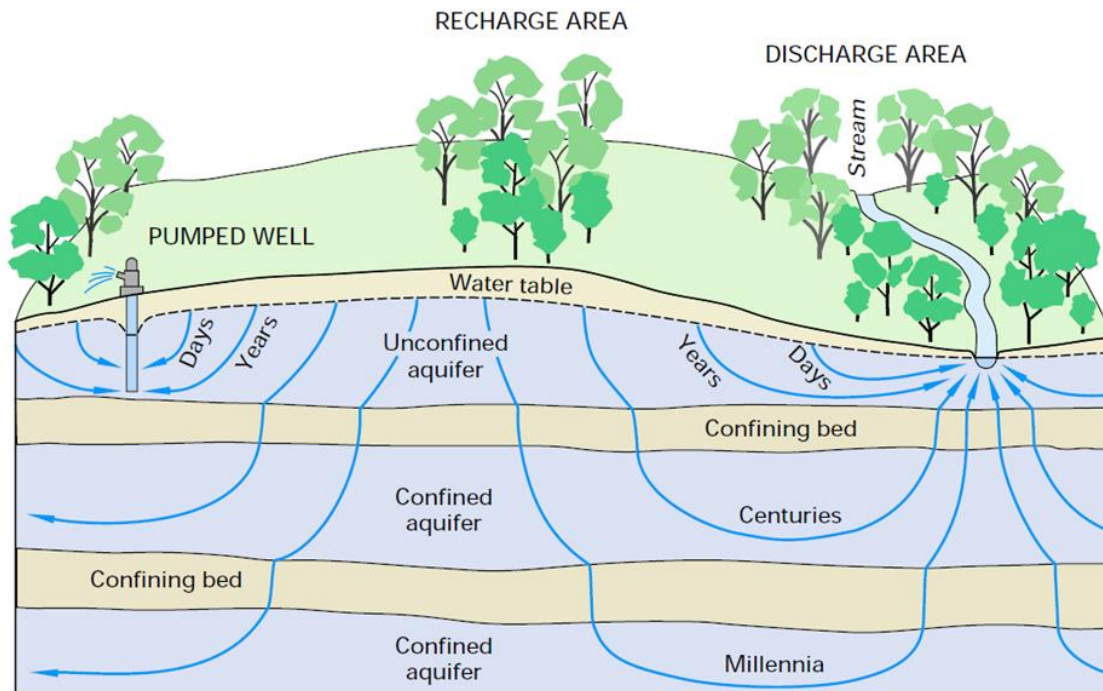
**A third of global river discharge derives from groundwater that was recharged by precipitation less than a few months earlier
(Jasechko et al. 2016)**





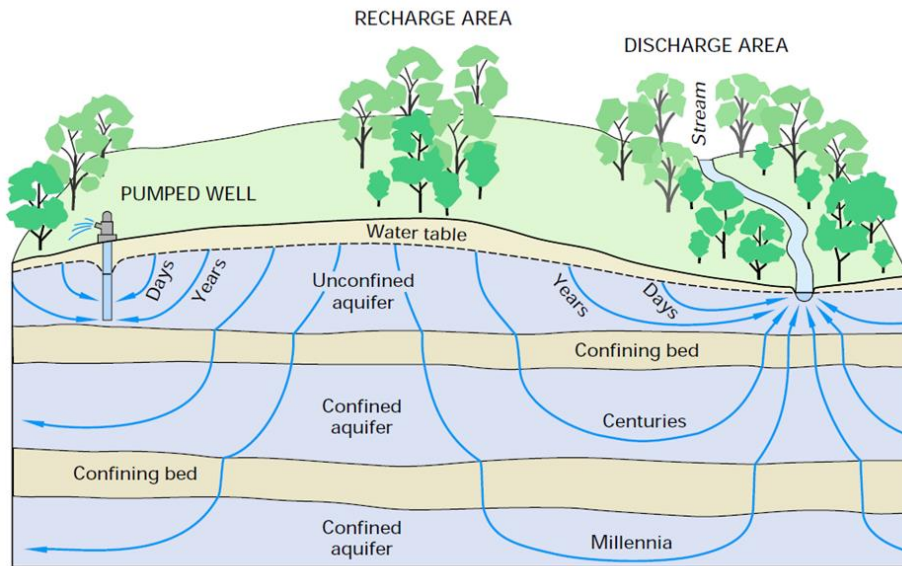
**A third of global river discharge derives from groundwater that was recharged by precipitation less than a few months earlier
(Jasechko et al. 2016)**

**Less than 6% of the total global groundwater store was recharged less than 50 years ago
(Gleeson et al. 2016)**



(Fan, 2016)

Very young age suggests that the groundwater comes from recent and local precipitation

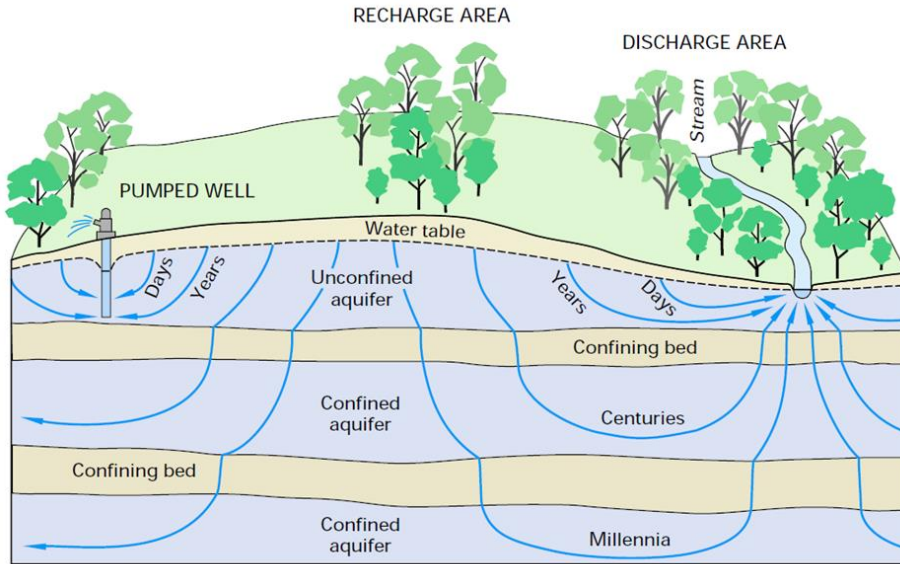


(Fan, 2016)



Norilsk City
Credit: darkroastedblend.com

Very young age suggests that groundwater comes from recent and local precipitation



(Fan, 2016)



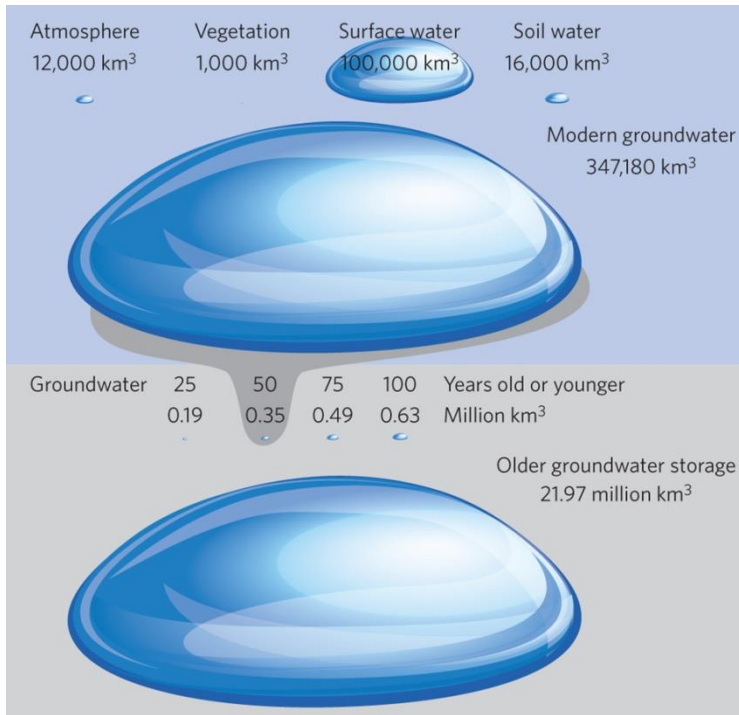
Norilsk City darkroastedblend.com

Very old age suggests that groundwater was recharged long ago



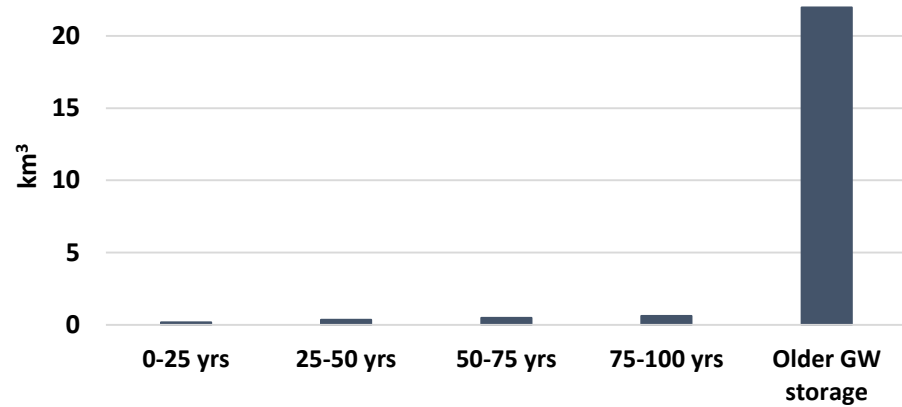
Le forage d'Aïn Galaka, Tchad. panoramio.com

How much and how old?

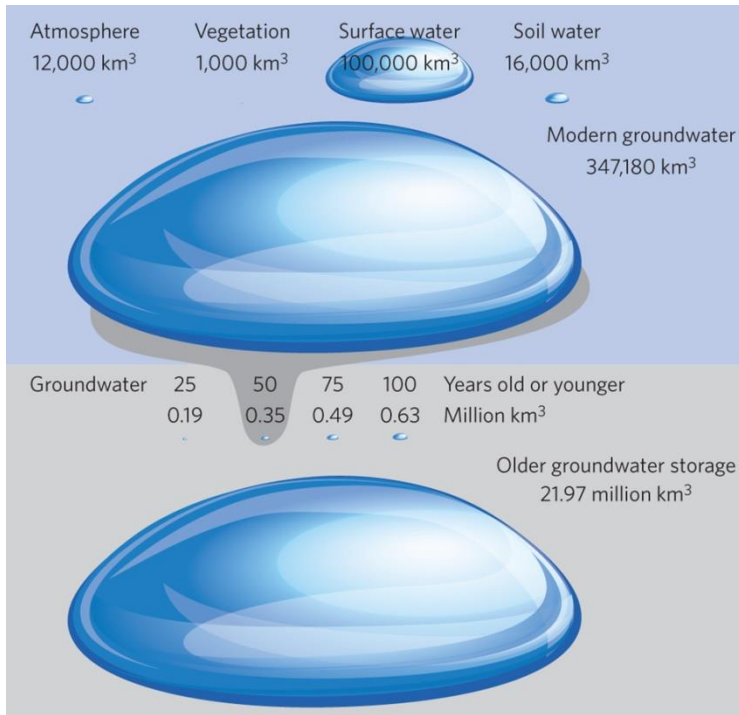


(Gleeson et al. 2016)

Volumes of groundwater stored in the global water cycle

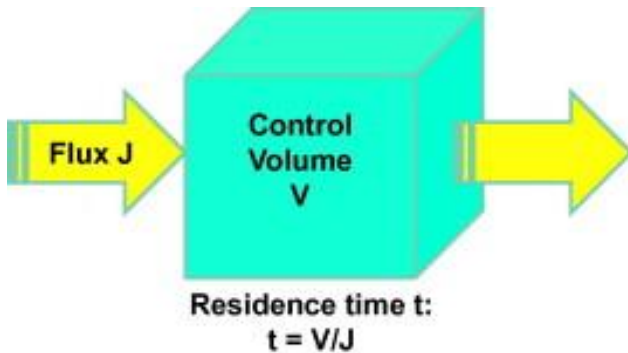
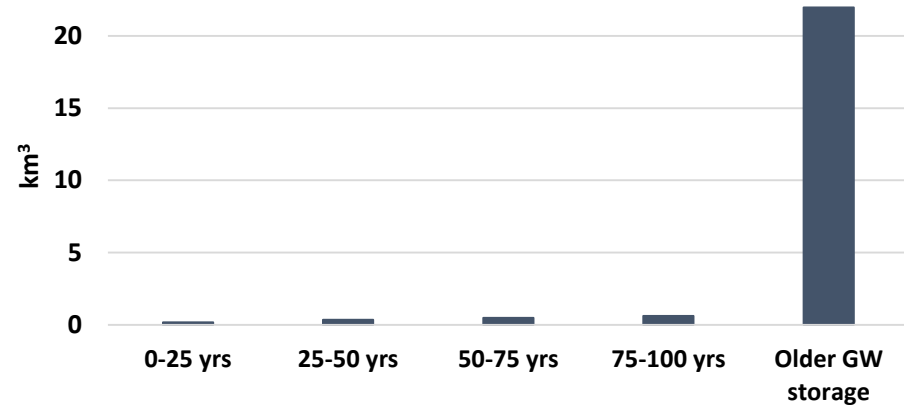


How much and how old?

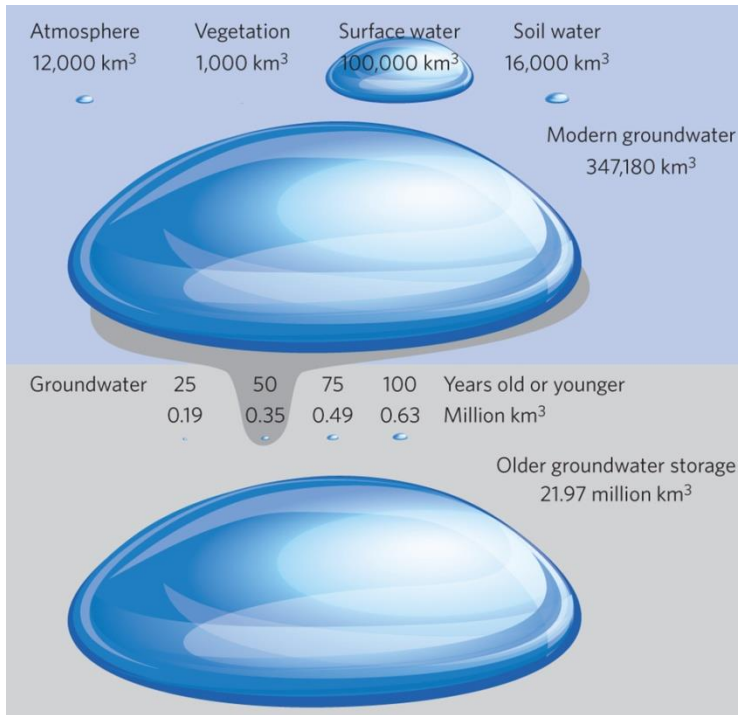


(Gleeson et al. 2016)

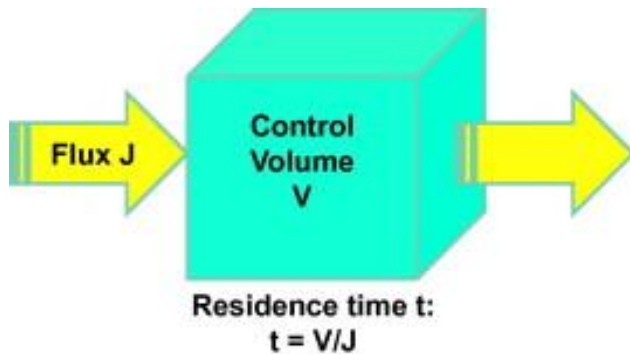
Volumes of groundwater stored in the global water cycle



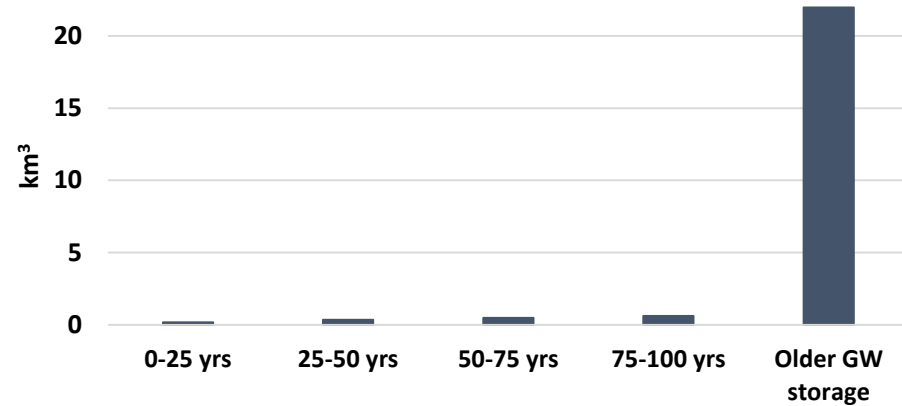
How much and how old?



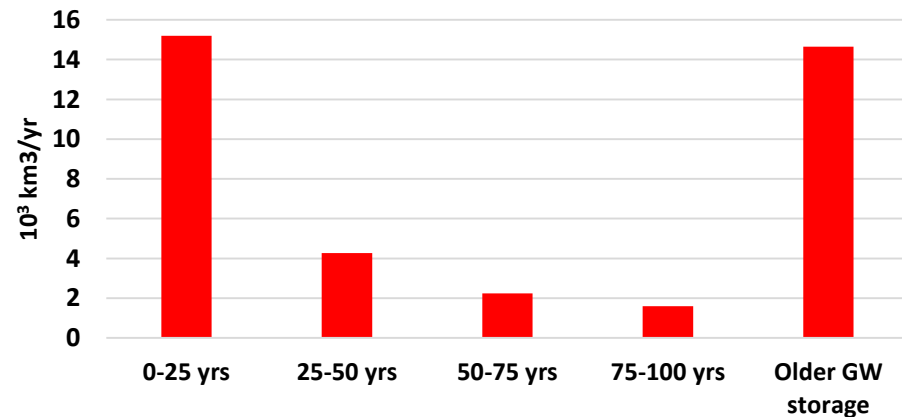
(Gleeson et al. 2016)



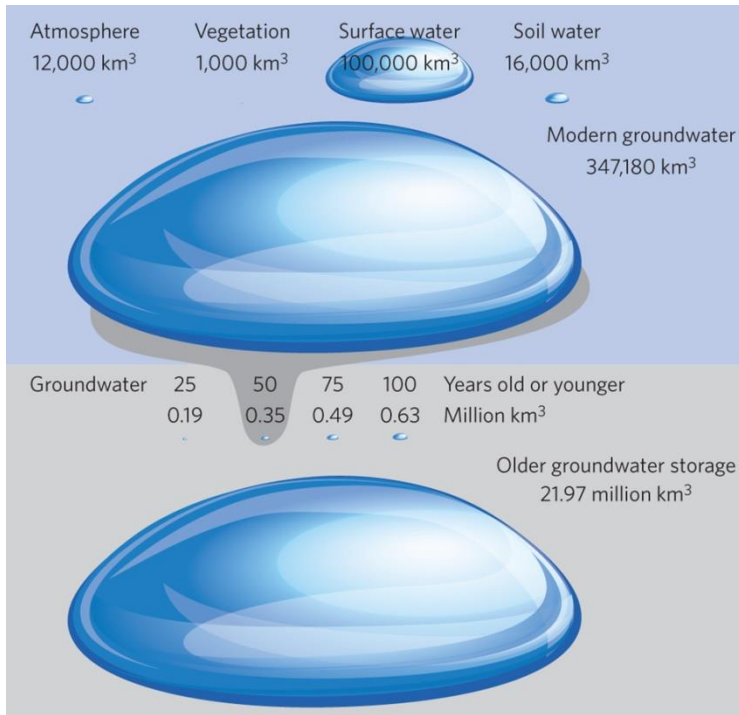
Volumes of groundwater stored in the global water cycle



Fluxes of groundwater stored in the global water cycle

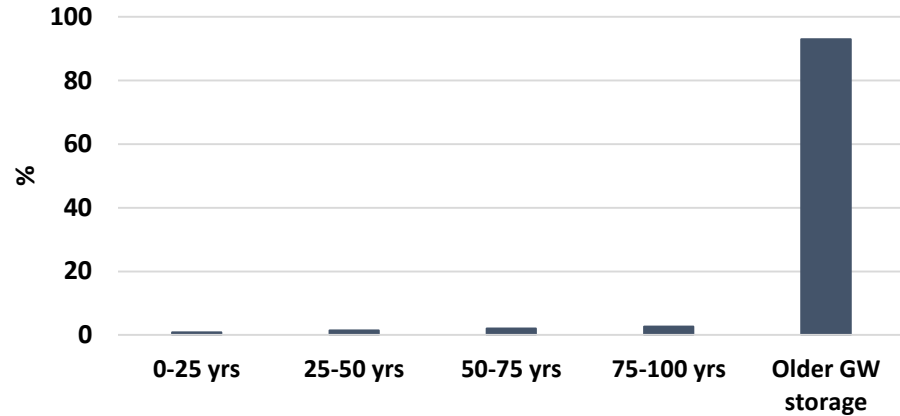


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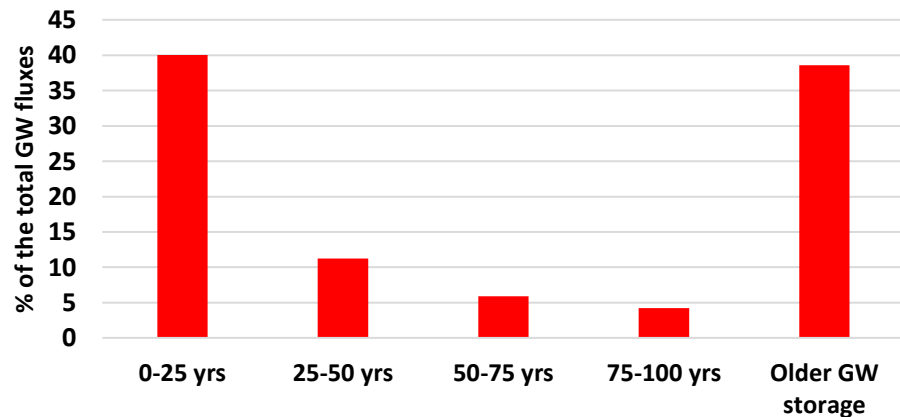


(Gleeson et al. 2016)

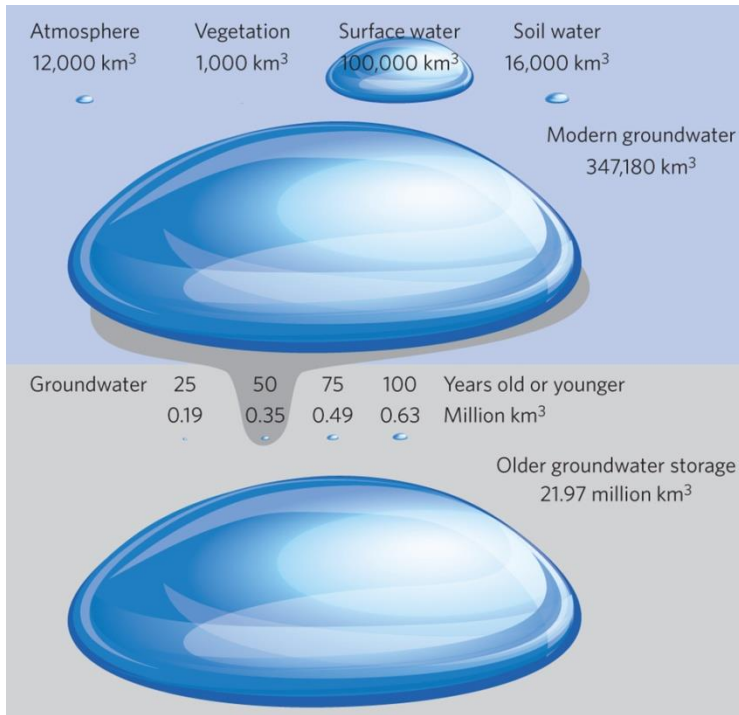
% Volumes of groundwater stored in the global water cycle



Fluxes of groundwater stored in the global water cycle

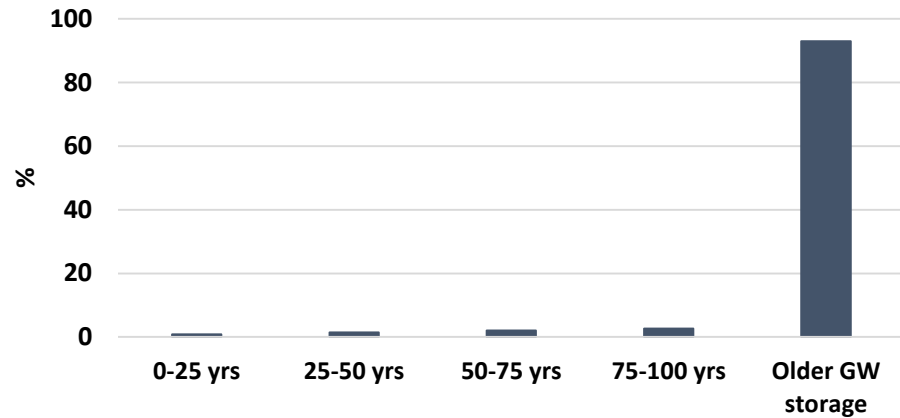


How much and how old?

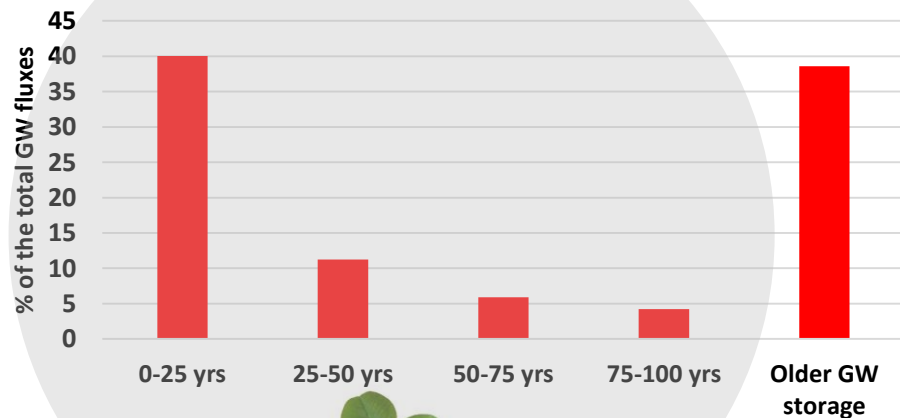


(Gleeson et al. 2016)

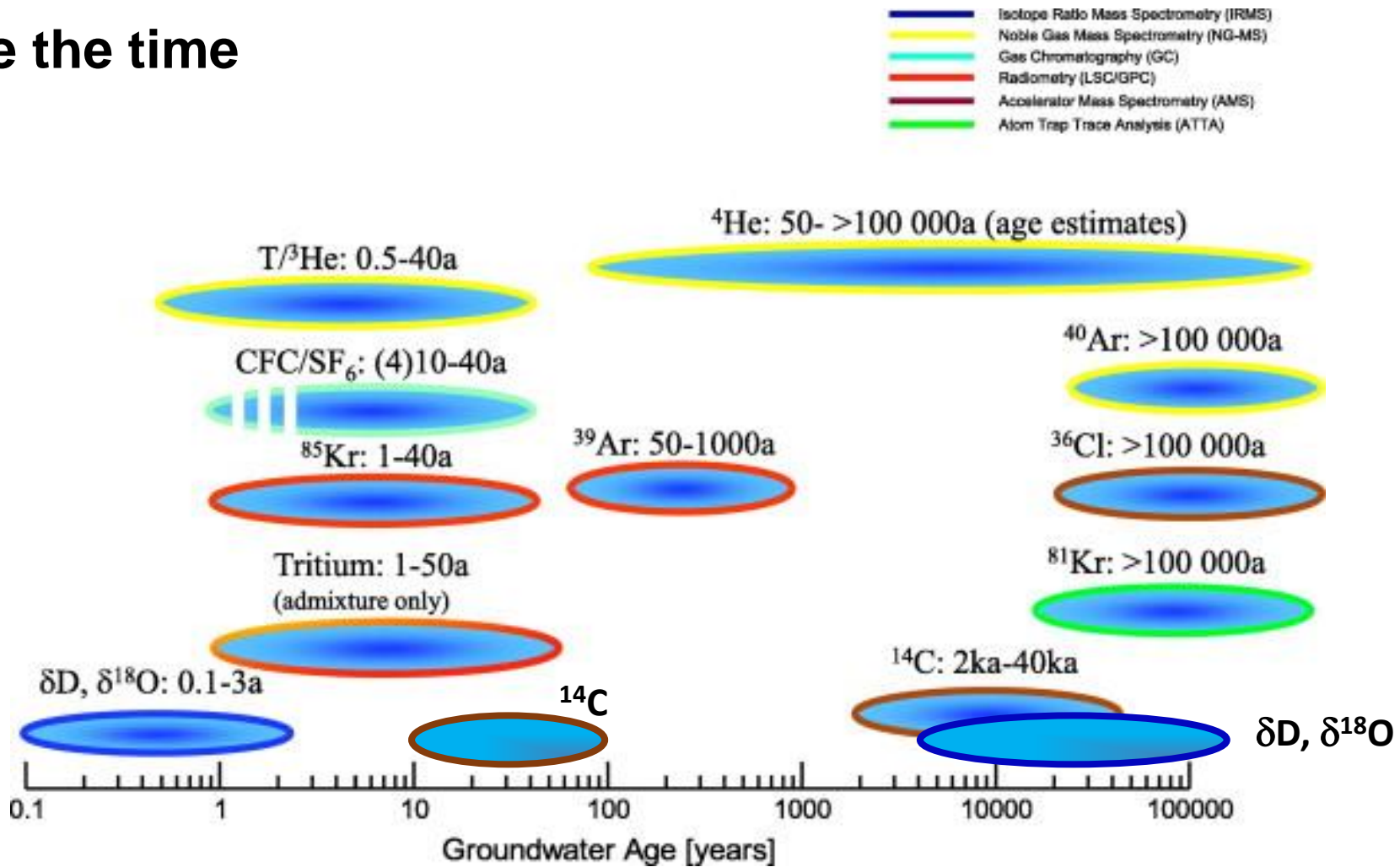
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Fluxes of groundwater stored in the global water cycle

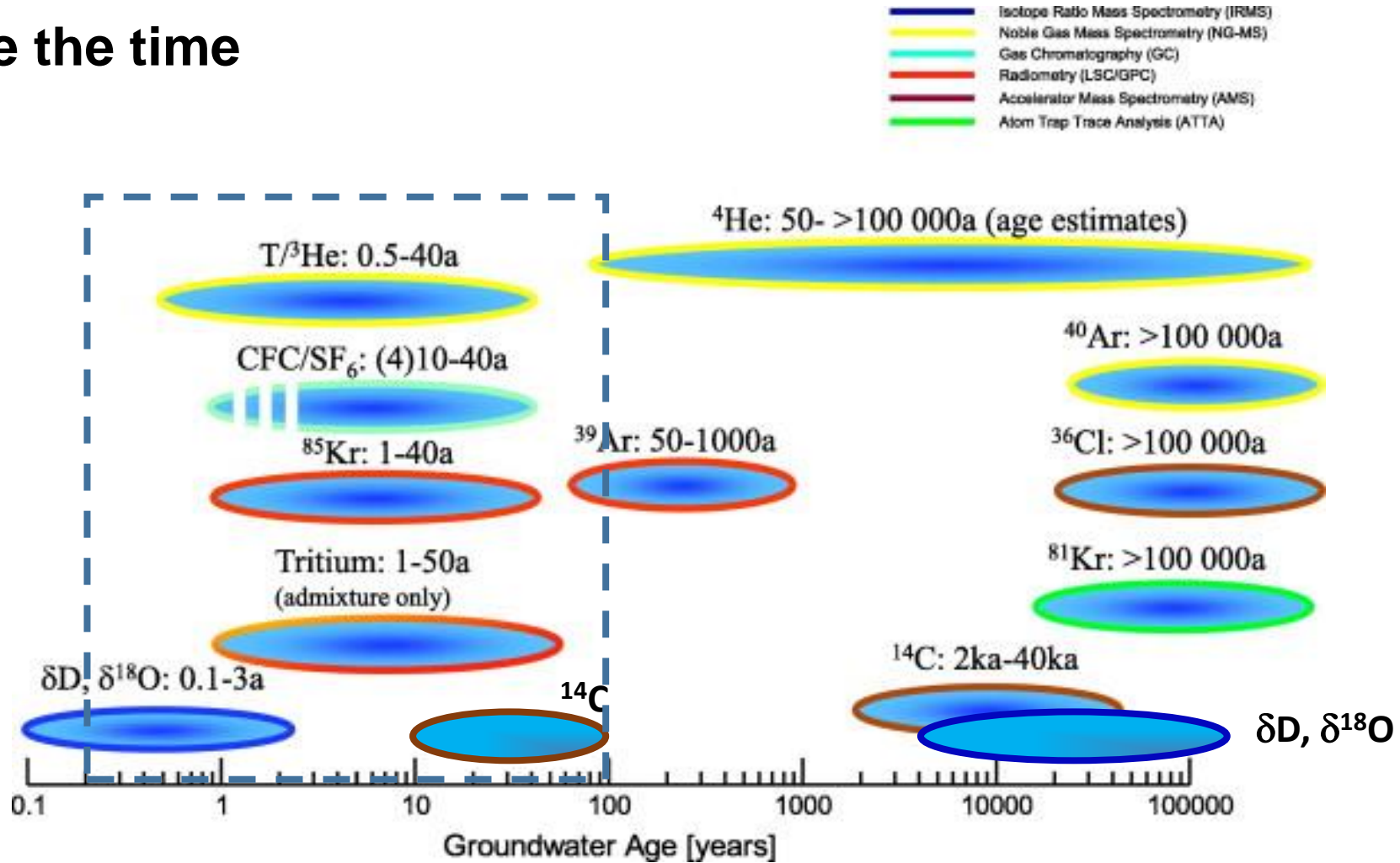


Trace the time



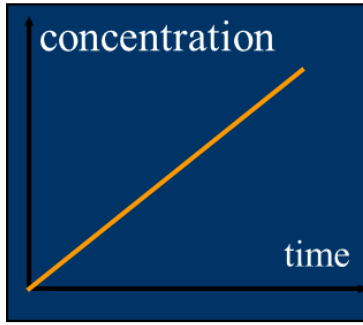
(Modified from Suckow 2014, Baudron 2014, Bartyzel & Rozanski 2016)

Trace the time

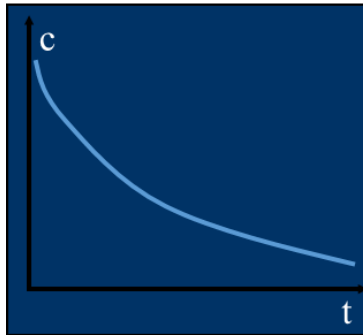


- Basics on few tracers
- Examples

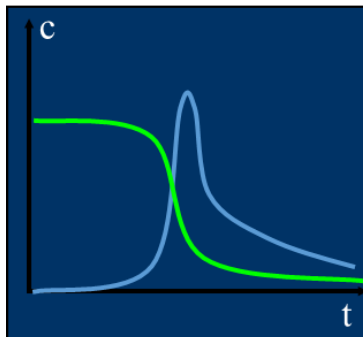
Trace the time



- **Accumulation:** decay of radioactive elements within the aquifer ^4He , ^{40}Ar ,....

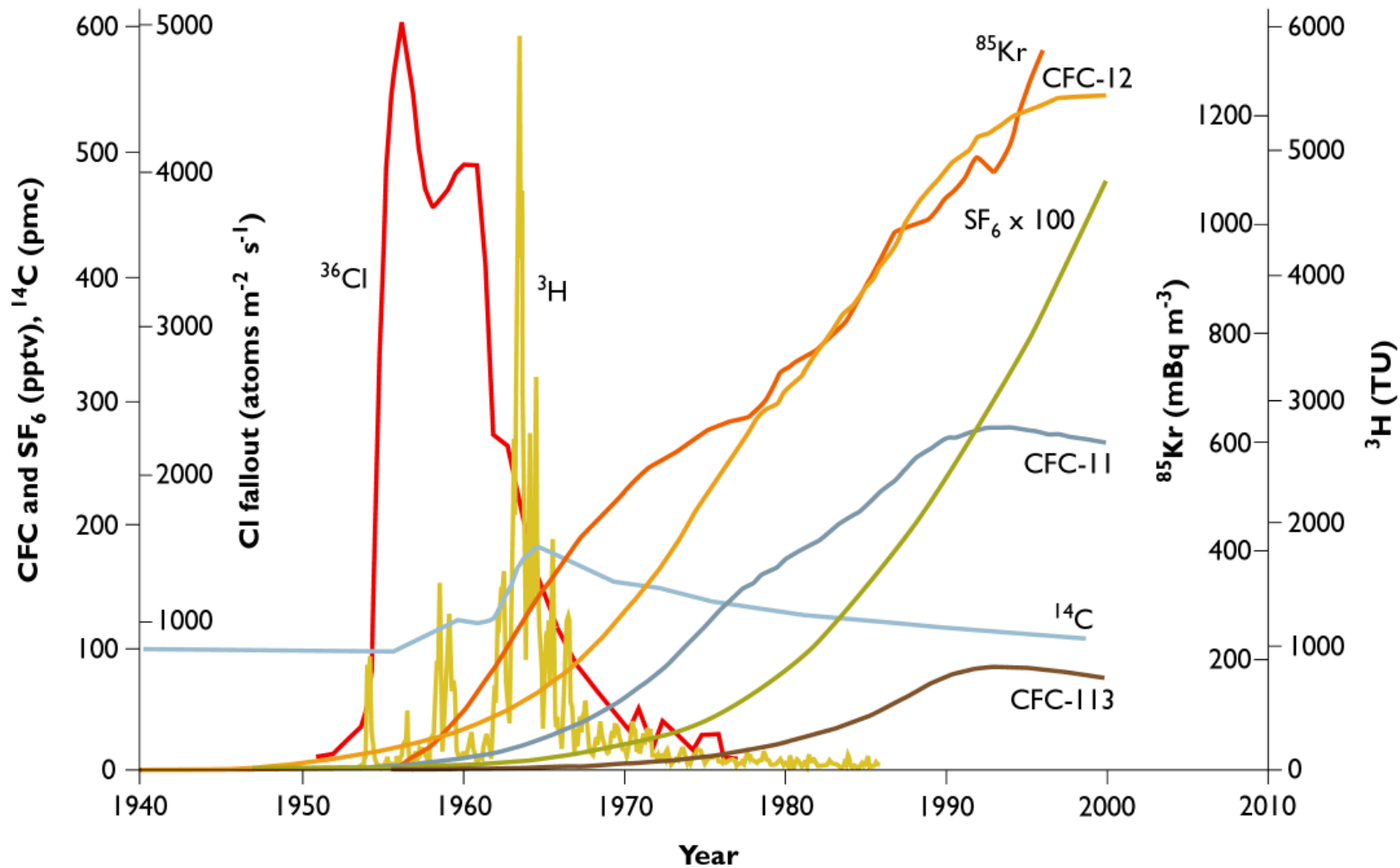


- **Radioactive tracers:** decay of a initial activity ^3H , ^{85}Kr , ^{39}Ar , ^{14}C , ^{81}Kr

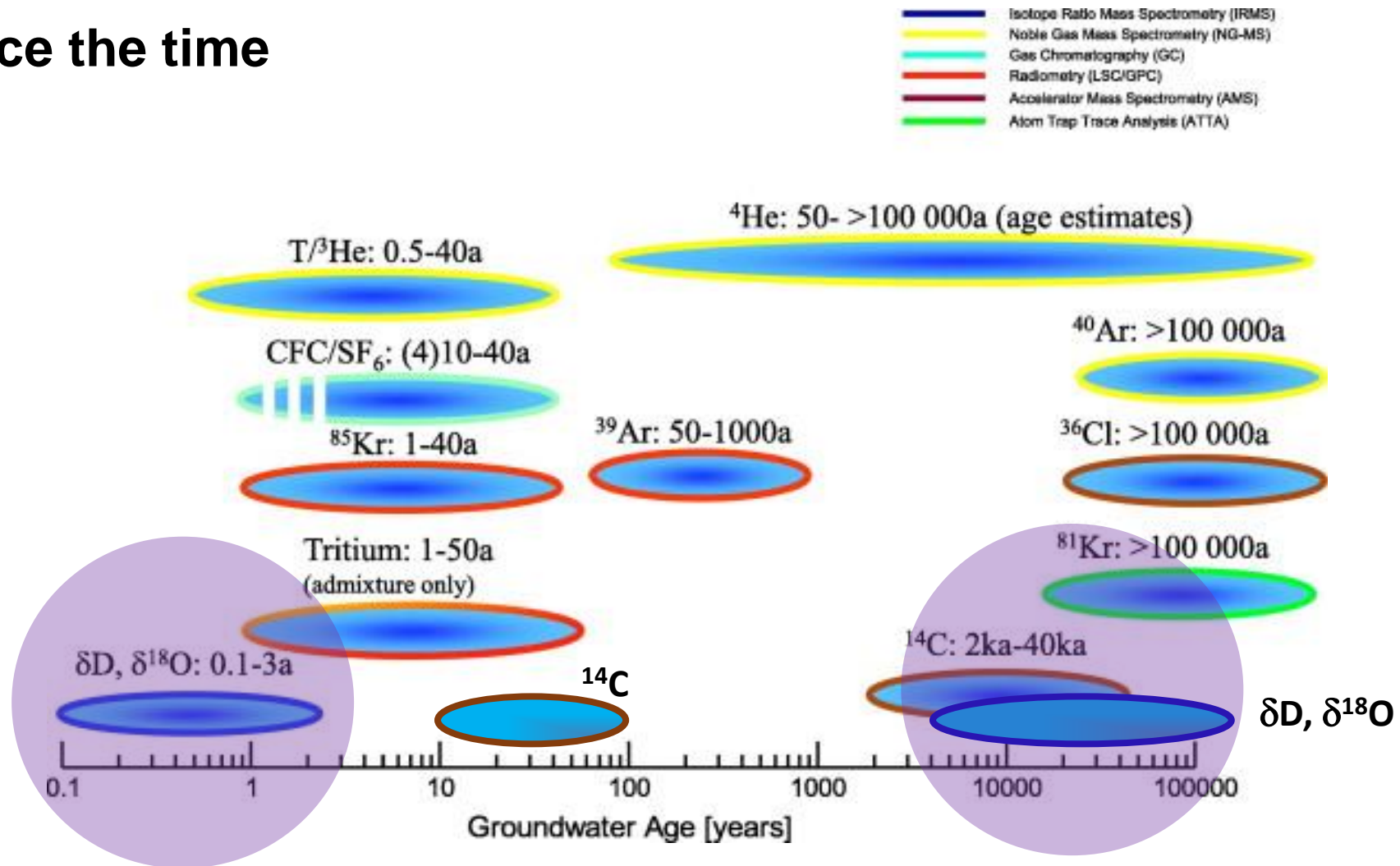


- **Transient tracers :** variable input, related to human activities (^3H), (^{14}C), CFC, SF_6 , ^2H - ^{18}O

Trace the time

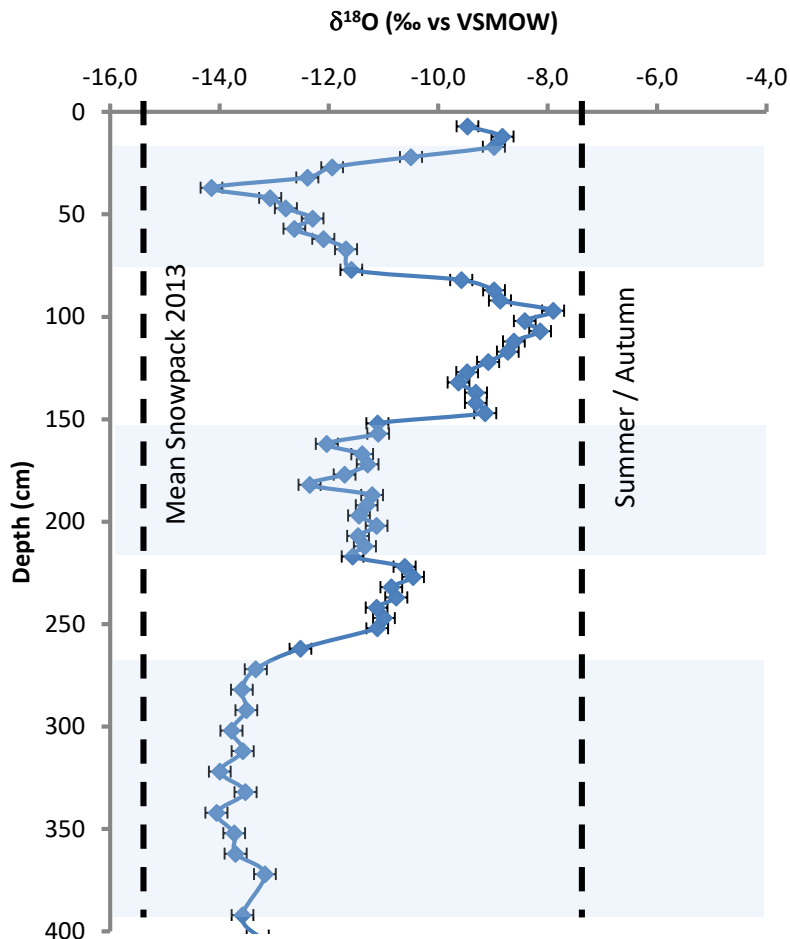


Trace the time



(Modified from Suckow 2014, Baudron 2014, Bartyzel & Rozanski 2016)

Trace the time using stable isotopes



Snowpack melting

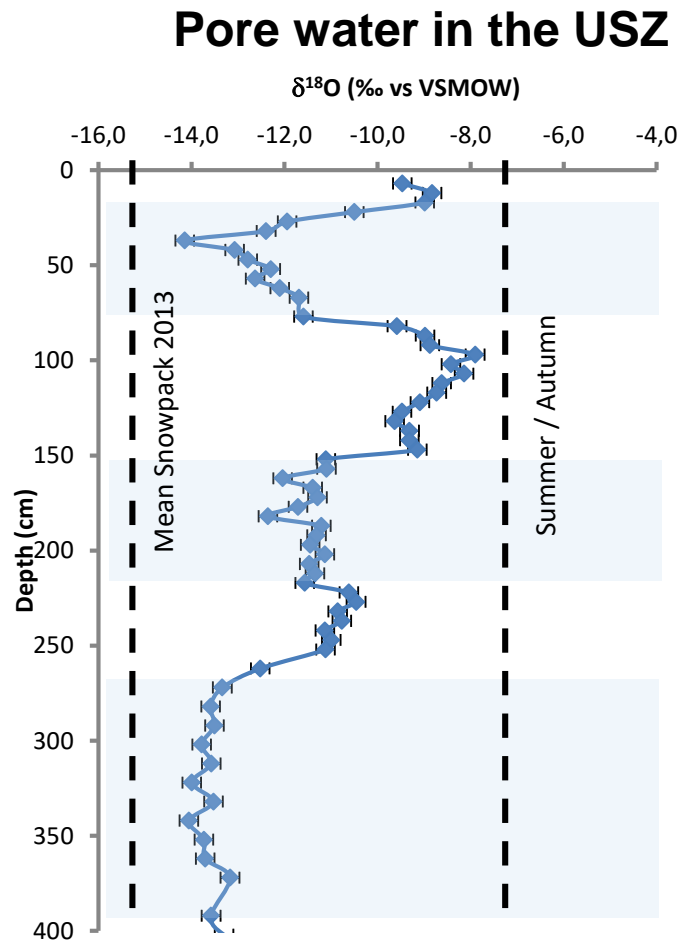
(Barbecot et al, 2014)



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IRRES : Infrastructure de Recherche sur la Recharge des Eaux Souterraines
Research facility on Groundwater recharge (IRRES)

Trace the time using stable isotopes



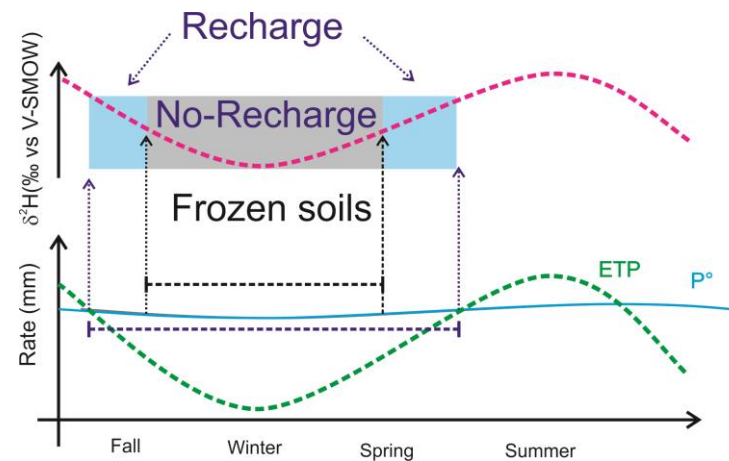
Snowpack melting

(Barbecot et al, 2014)

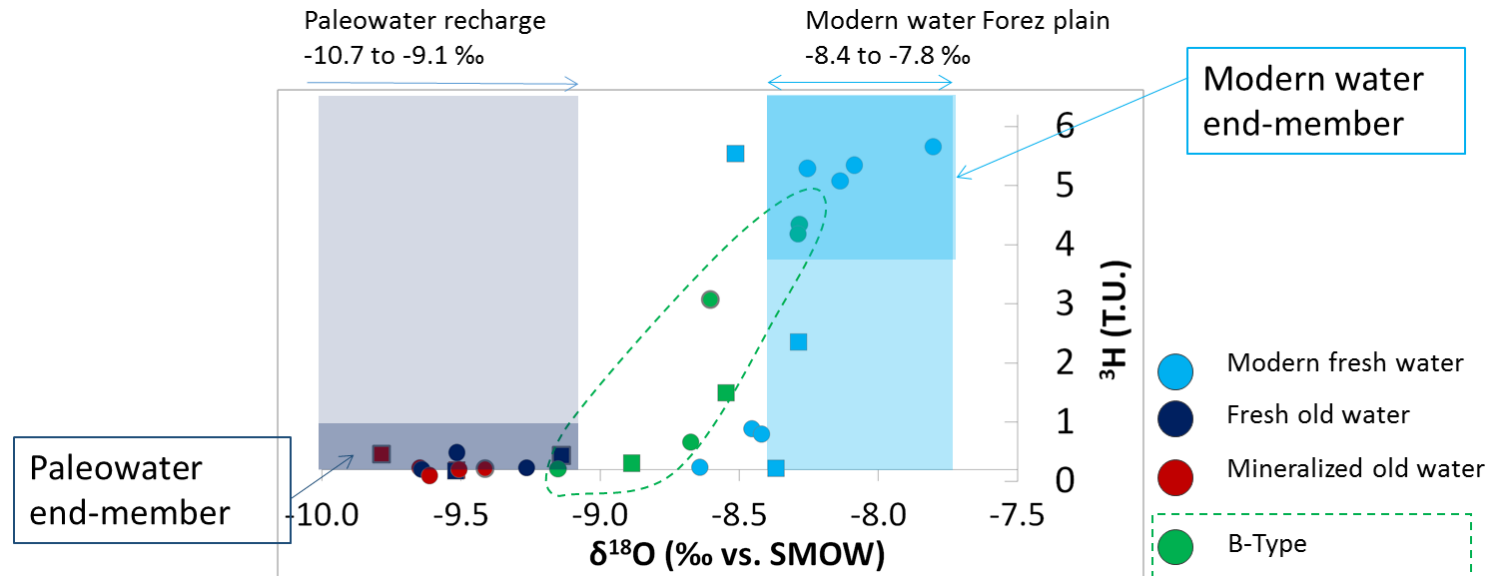


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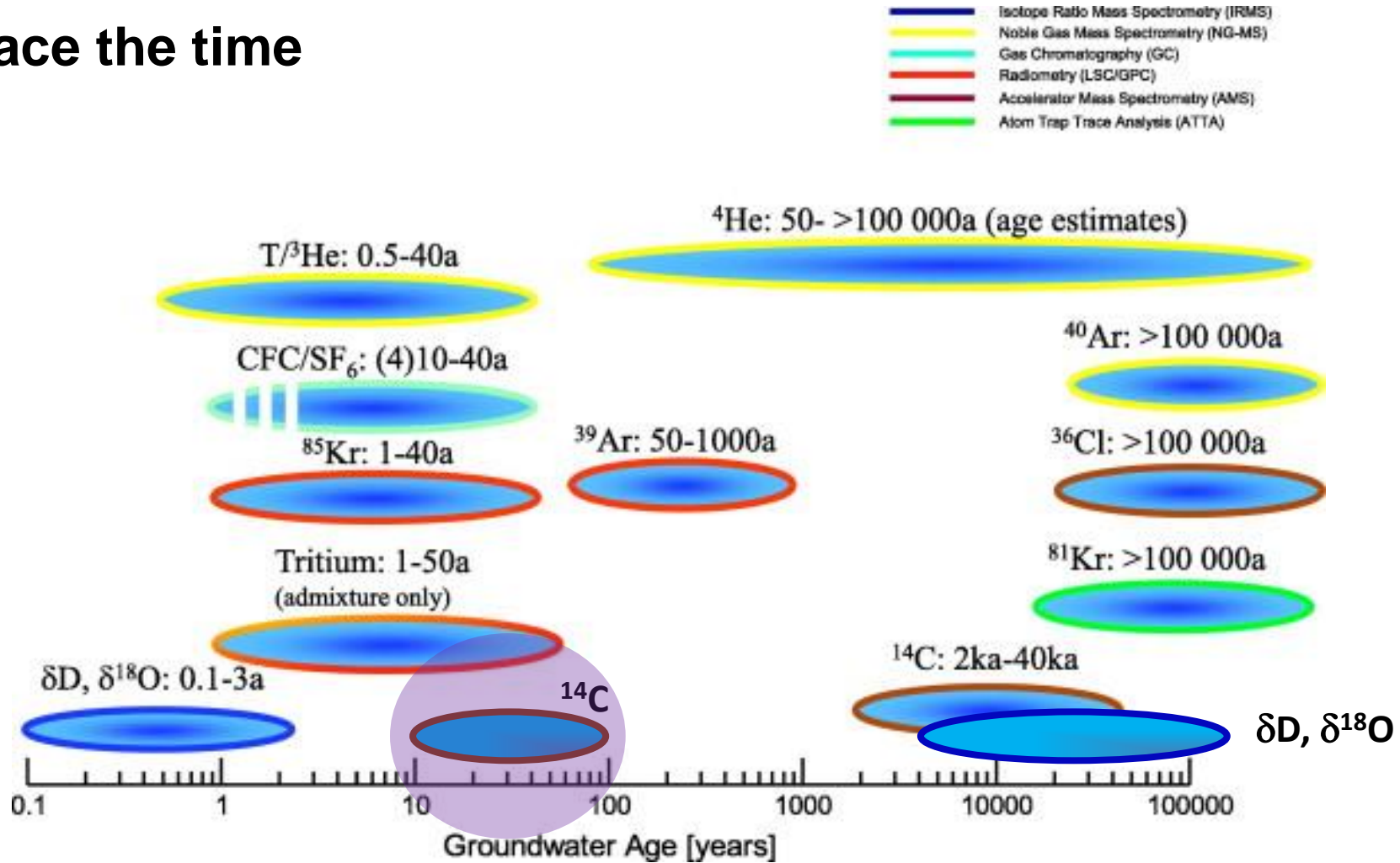


Trace the time using stable isotopes



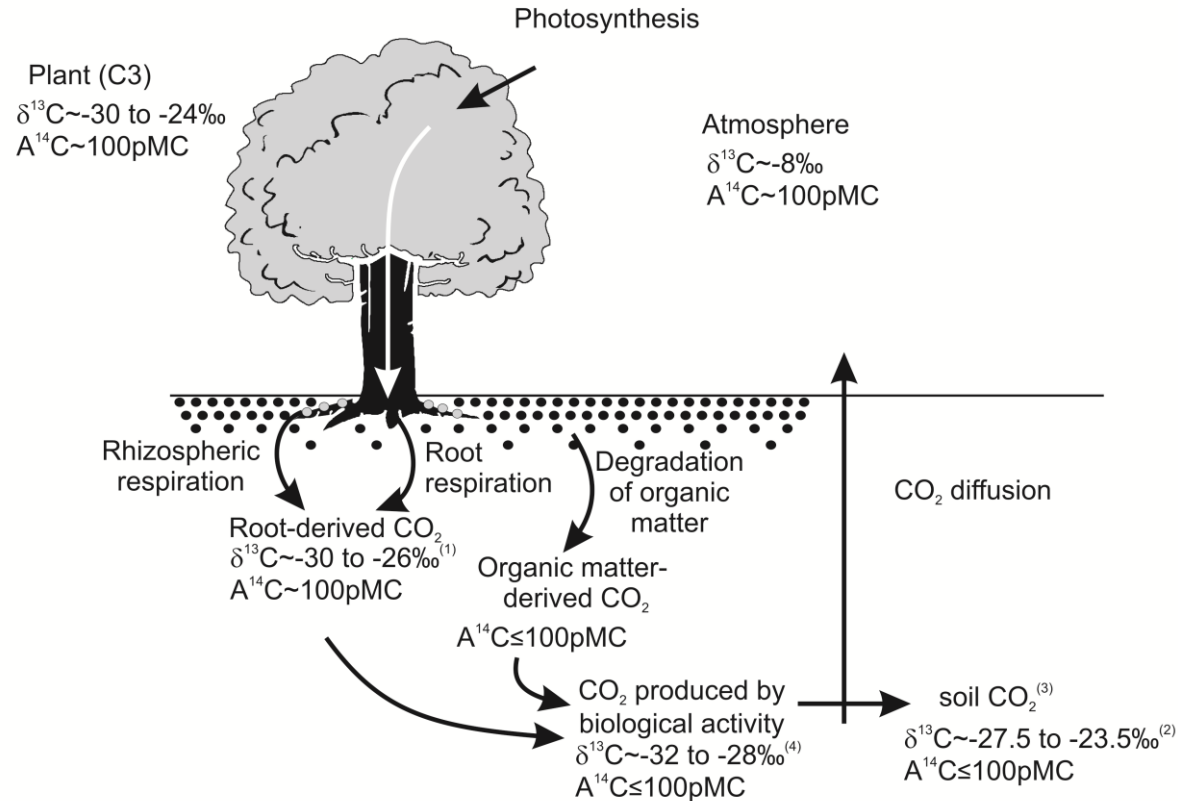
M. Alazard et al (session 8.04, #2037) Origin of groundwater and CO_2 in the crystalline environment of Saint Galmier, France

Trace the time



(Modified from Suckow 2014, Baudron 2014, Bartyzel & Rozanski 2016)

A deep understanding of tracer transfer within the USZ



(1) from literature (Lichtfouse et al., 1995; Lin et al., 1999; Krull et al., 2002; Badeck et al., 2005; Chemidlin Prévost-Bouré et al., 2009; Marron et al., 2009),

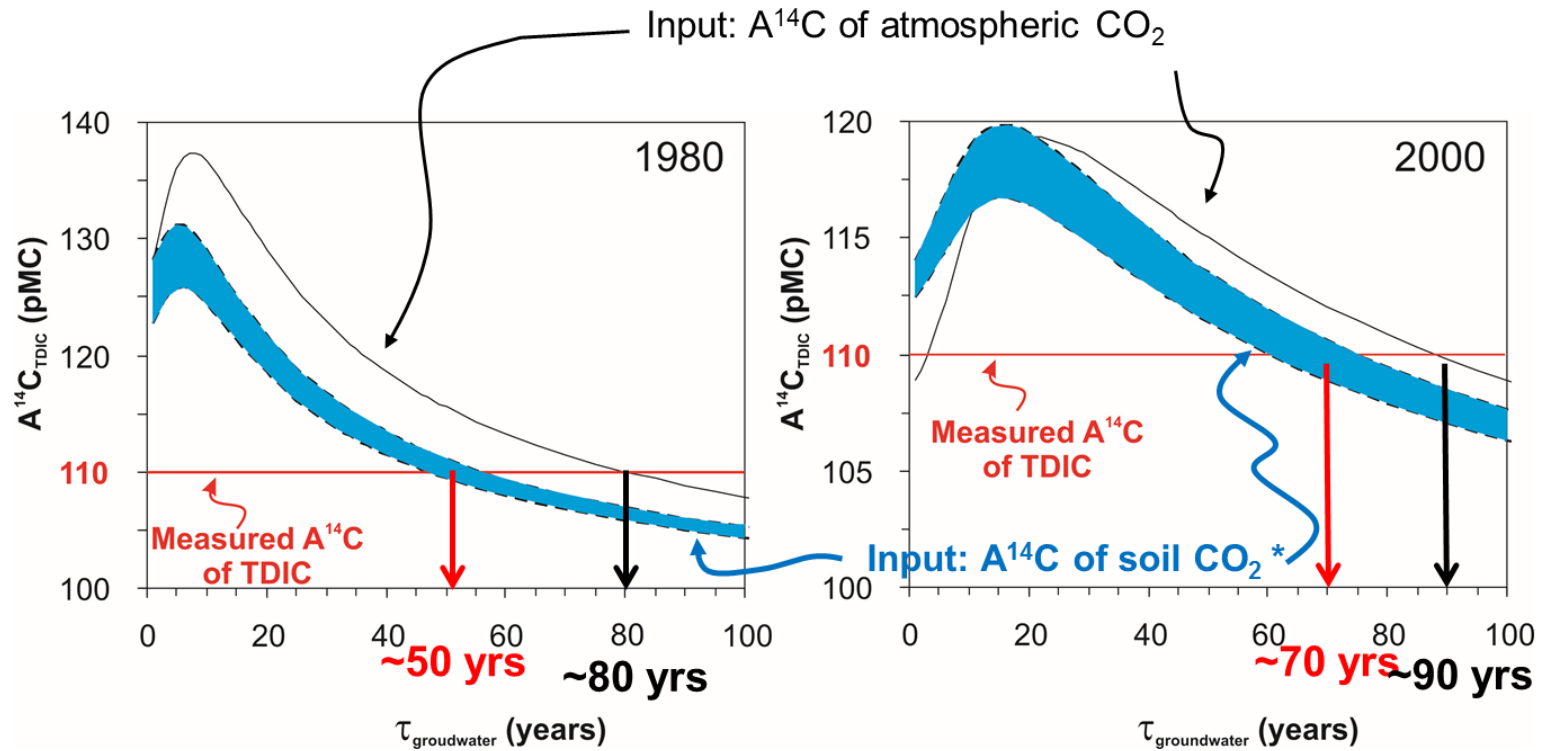
(2) from soil CO_2 data in Fontainebleau sands site,

(3) The diffusion of CO_2 from soil to atmosphere leads to a ^{13}C enrichment of +4.4‰ between soil CO_2 and the CO_2 produced by biological activity (Cerling et al., 1991; Davidson, 1995)

(4) from soil CO_2 data and the enrichment factor associated to diffusion

(Gillon et al., 2012)

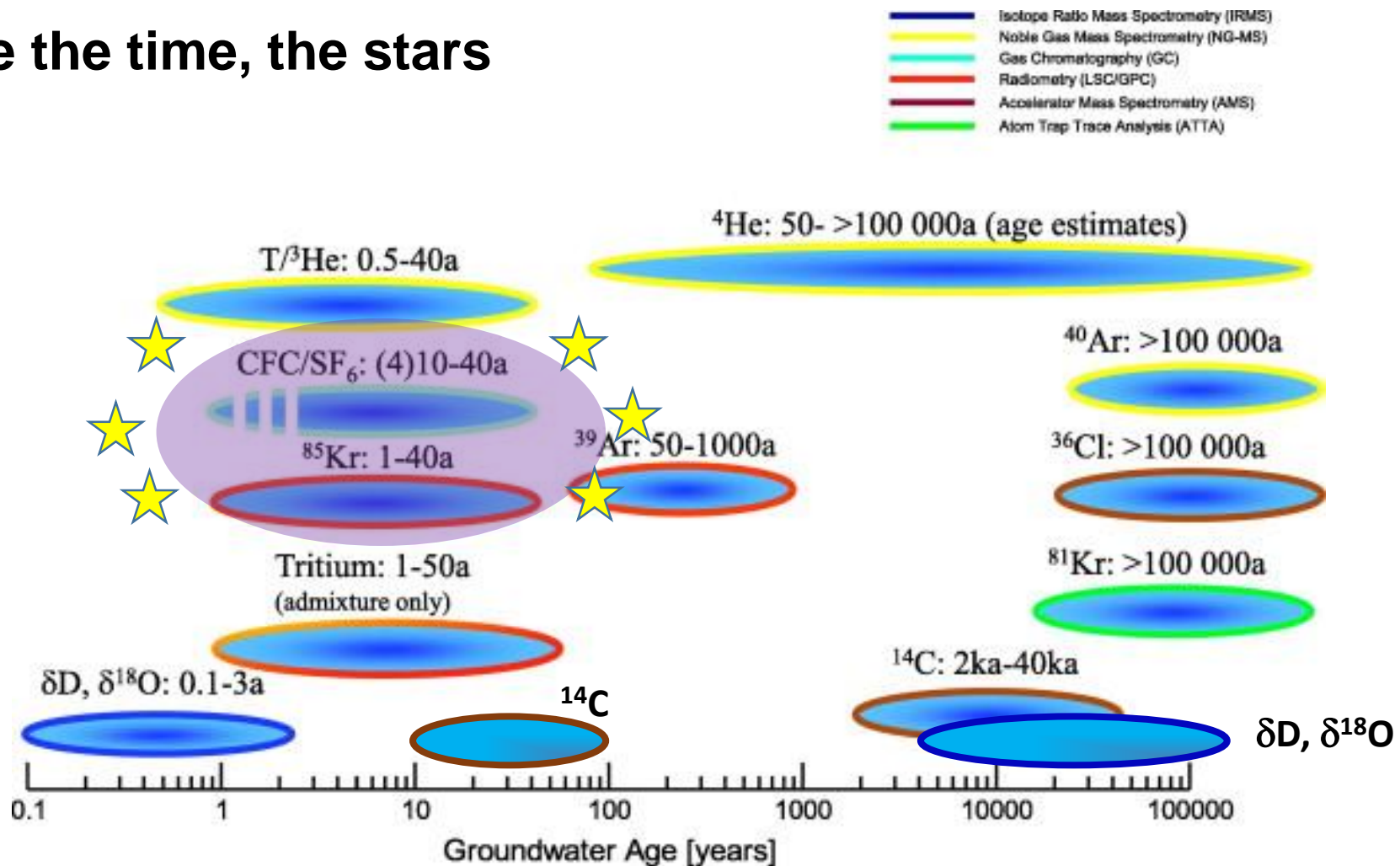
Radiocarbon in modern water



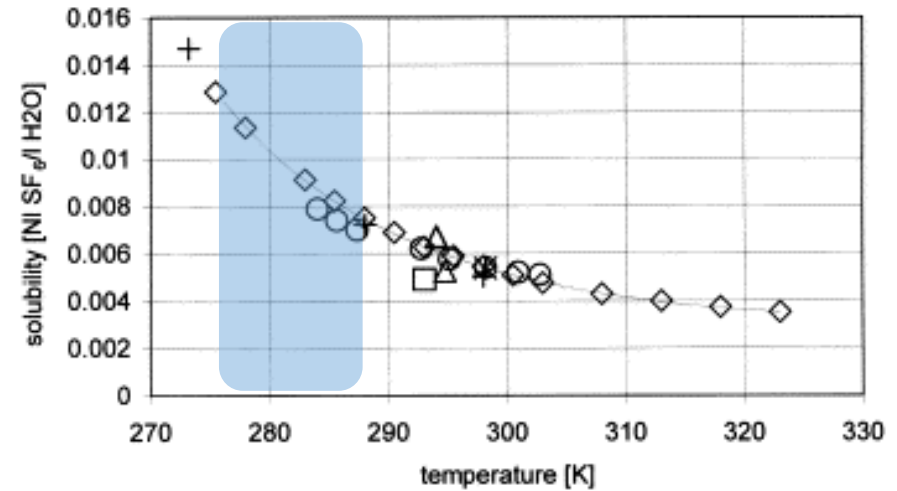
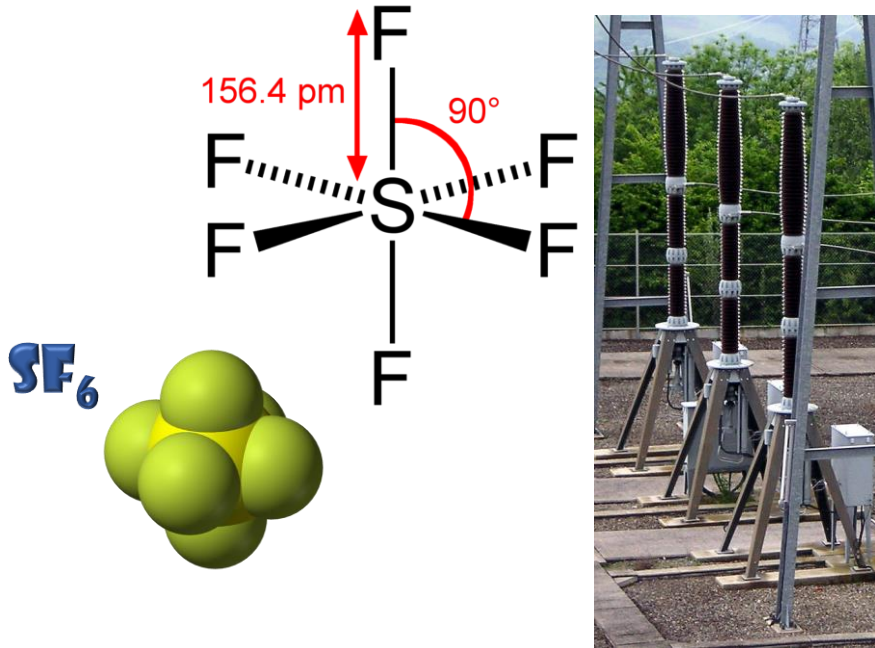
(Gillon et al, 2012)

~ 20 yrs uncertainty on the starting blocks ..

Trace the time, the stars



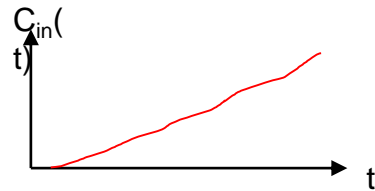
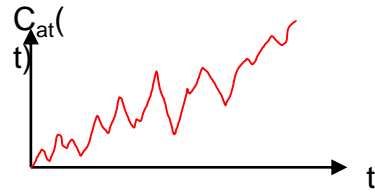
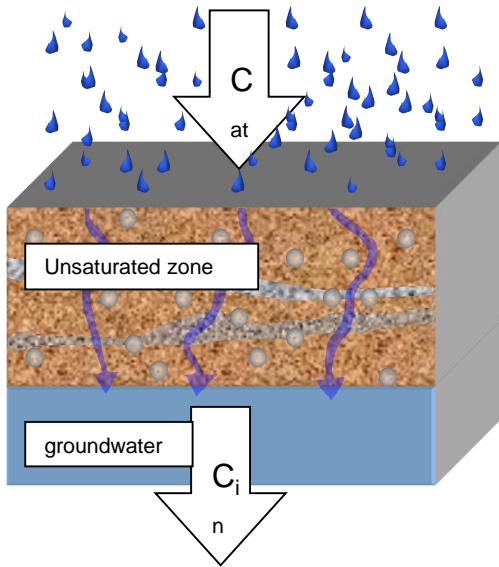
(Modified from Suckow 2014, Baudron 2014, Bartyzel & Rozanski 2016)



+ Friedman, 1954	○ Morrison and Johnstone, 1955
◇ Ashton et al. 1968	✱ Gerrard, 1980
□ Watson and Liddicoat, 1985	△ Wanninkhoff et al. 1991
— Wilhelm et al., 1977	

(Klump, 2007)

- inorganic, colorless, odorless, non-flammable, **extremely potent greenhouse gas**
- excellent electrical insulator.
- High atmospheric residence time : up to 3200 yrs (*Ravishankara et al., 1993*)
- Low solubility + T dependence



- USZ buffer the atmospheric variability ([SF₆] and T)

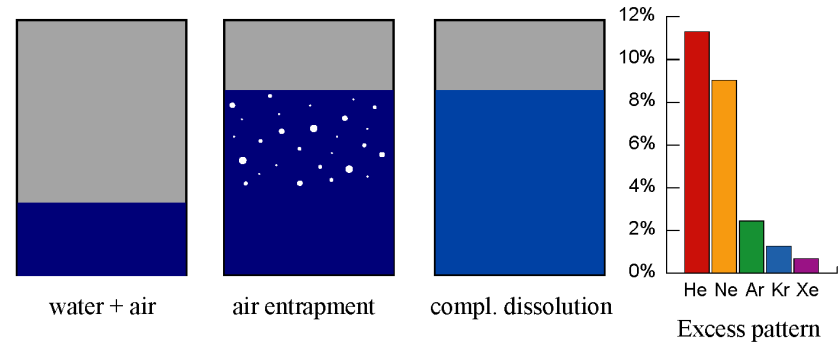
(Klump et al, 2008; Corcho et al, 2007; Goody et al 2006)



Sampling the USZ in the Paris Basin

Origin and composition of excess air

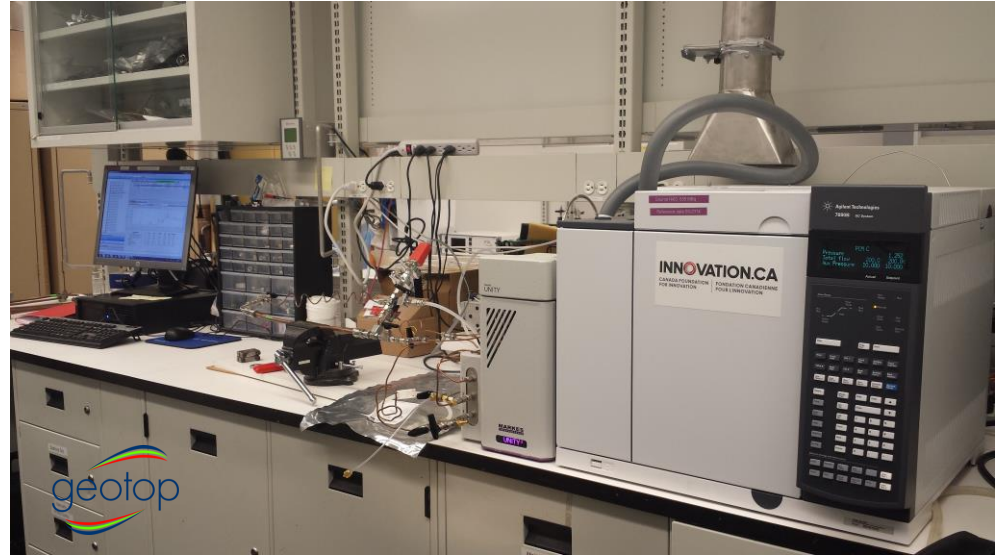
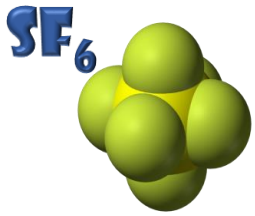
Classical model: Complete dissolution of entrapped air bubbles
 ⇒ composition of excess air = composition of atmospheric air



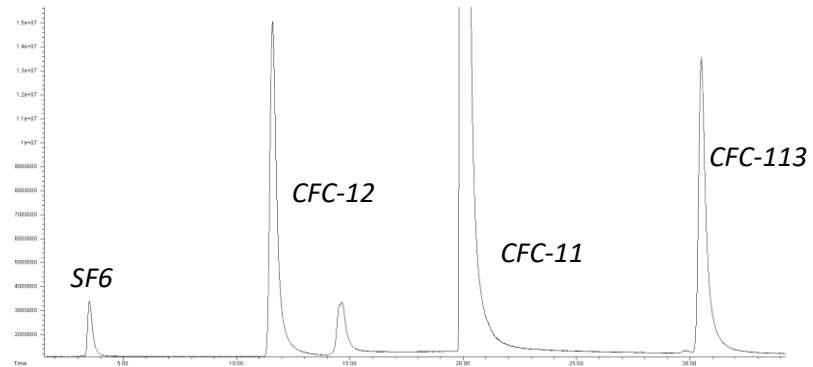
$$C_i = C_i^{eq}(T, S, P) + Az_i$$

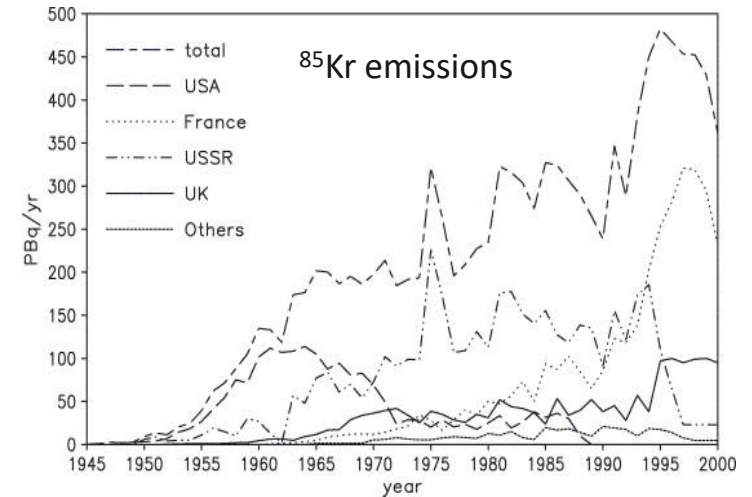
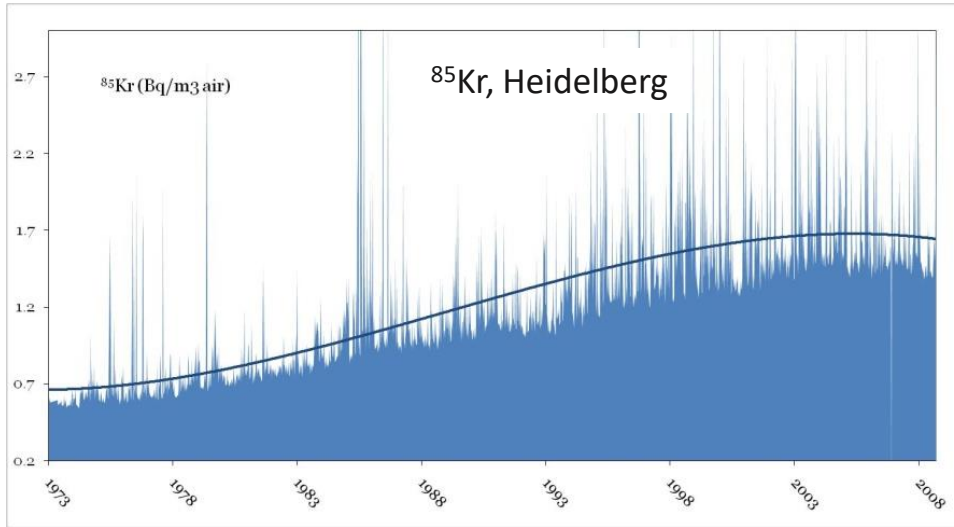
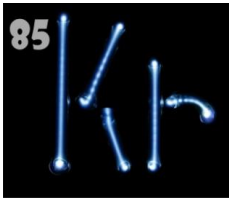
A: Concentration of excess air

From W. Aeschbach-Hertig



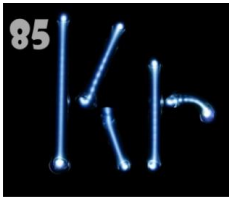
- Head space + chromatographic separation
- GC + ECD
- ~ 0,5 L of water



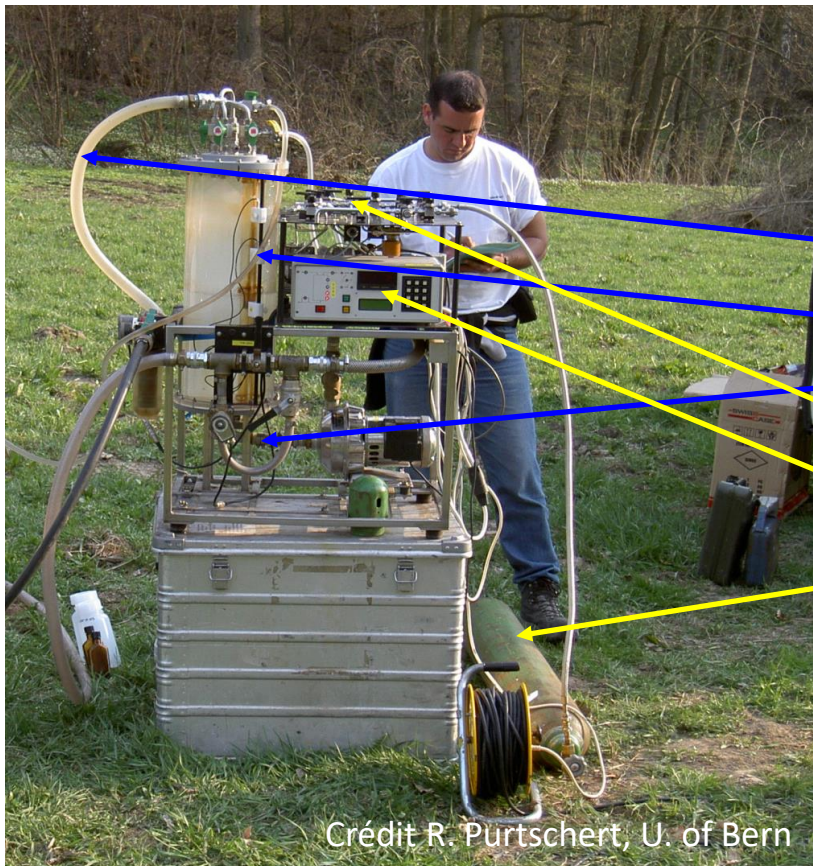


(Winger et al, 2005)

- Noble Gas
- 6 IS + ~10 IR
- ^{85}Kr radioactif, $T_{1/2} = 10.76$ yrs
- From U & Pu fission
- Reprocessing nuclear fuel
- Well documented
- 1 to 2 Bq / m³ air

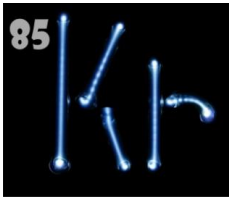


- ^{85}Kr activity normalized to stable Kr content : don't care about solubility or excess air
- Low contents
- Need of $\sim 300\text{ L}$ (Kr)
- Degazed on field

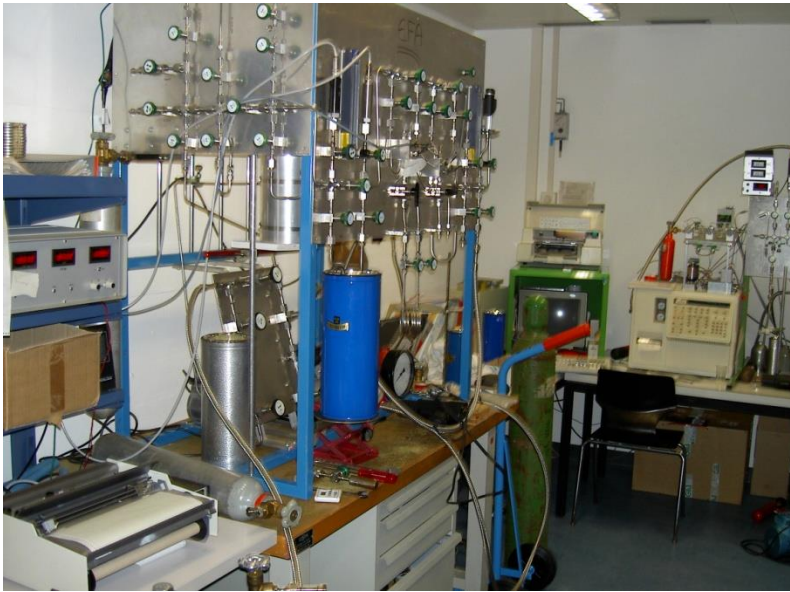


- Water inlet
- Extraction cylinder
- Water outlet
- Pumps, Compressor
- Electronic controller
- Sample tank

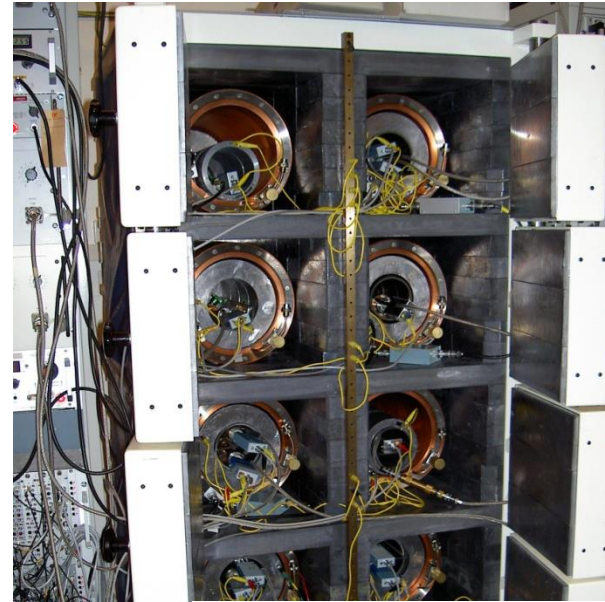
Crédit R. Purtschert, U. of Bern



- Separation of Kr
- Low level β^- counting



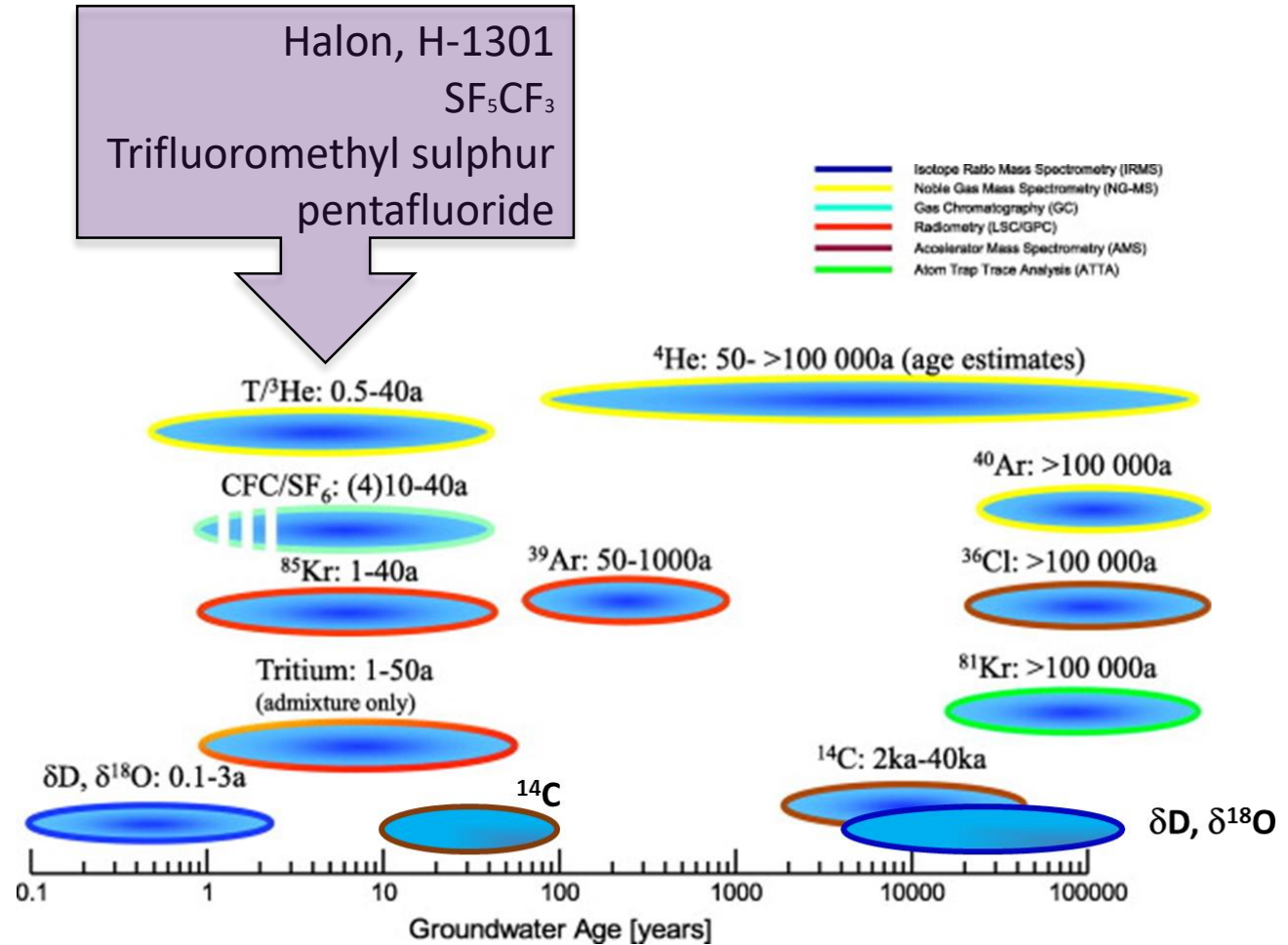
(Loosli et al 1999)



Climate and Environmental Physics

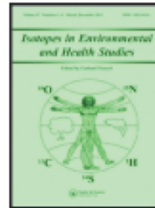
Roland Purtschert,
Climate and Environmental Physics
Physics Institute
University of Bern
email: purtschert@climate.unibe.ch

Trace the time with other tracers



(Modified from Suckow 2014, Baudron 2014, Busenberg and Plummer 2008, Bartyzel & Rozanski 2016)

Trace the time with other tracers



Isotopes in Environmental and Health Studies



ISSN: 1025-6016 (Print) 1477-2639 (Online) Journal homepage: <http://www.tandfonline.com/loi/gieh20>

Dating of young groundwater using four anthropogenic trace gases (SF_6 , SF_5CF_3 , CFC-12 and Halon-1301): methodology and first results

Jakub Bartyzel & Kazimierz Rozanski

Halon, H-1301
 SF_5CF_3



Geochemistry
Geophysics
Geosystems

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Published by AGU and the Geochemical Society

Article

Volume 11, Number 11

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Q11001, doi:10.1029/2010GC003312

ISSN: 1525-2027

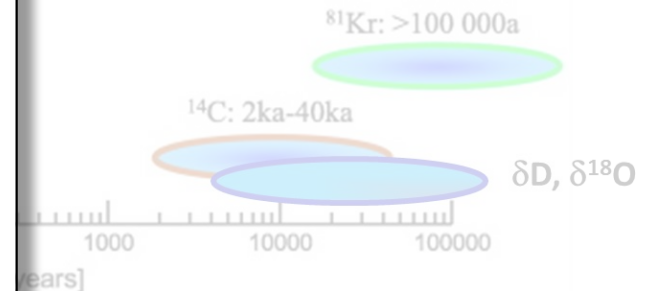
A rapid method for the measurement of sulfur hexafluoride (SF_6), trifluoromethyl sulfur pentafluoride (SF_5CF_3), and Halon 1211 (CF_2ClBr) in hydrologic tracer studies

Eurybiades Busenberg and L. Niel Plummer

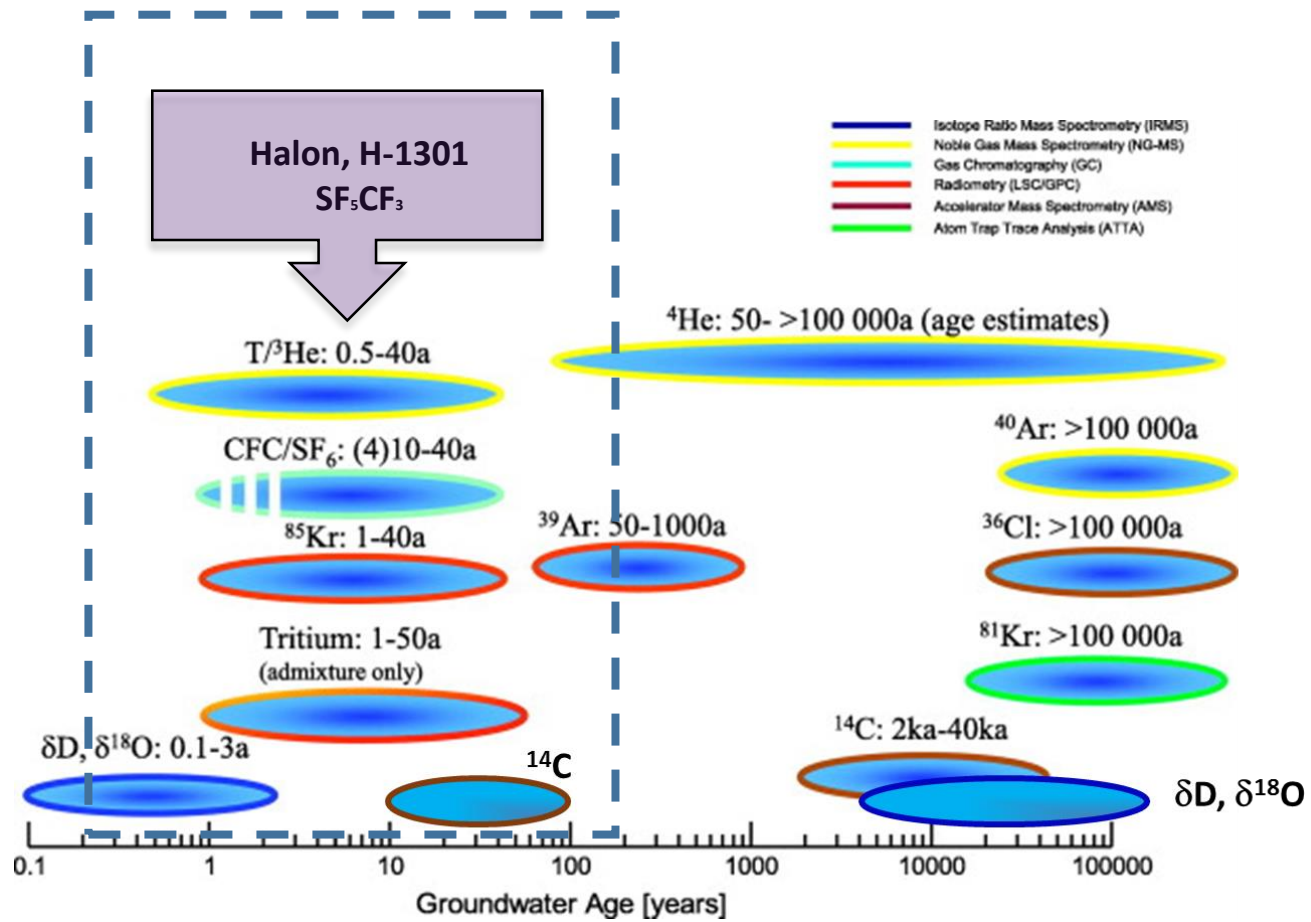
U.S. Geological Survey, Mail Stop 423, Reston, Virginia 20192, USA (ebusenbe@usgs.gov; nplummer@usgs.gov)

[1] A rapid headspace method for the simultaneous laboratory determination of intentionally introduced hydrologic tracers, sulfur hexafluoride (SF_6), trifluoromethyl sulfur pentafluoride (SF_5CF_3), Halon 1211 (CF_2ClBr), and other halocarbons in water and gases is described. The high sensitivity of the procedure allows for introduction of minimal tracer mass (a few grams) into hydrologic systems with a large dynamic range of analytical detection (dilutions to $1:10^8$). Analysis times by gas chromatography with electron capture detector are less than 1 min for SF_6 ; about 2 min for SF_6 and SF_5CF_3 ; and 4 min for SF_6 , SF_5CF_3 , and Halon 1211. Many samples can be rapidly collected, preserved in stoppered septum bottles, and analyzed at a later time in the laboratory. Examples are provided showing the effectiveness of the gas tracer test studies in varied hydrogeological settings.

Kazimierz Rozanski (2016): Dating of young anthropogenic trace gases (SF_6 , SF_5CF_3 , CFC-12 and Halon-1301): methodology and first results in *Isotopes in Environmental and Health Studies*, DOI: 10.1080/10256016.2016.1191111



Busenberg and Plummer 2008, Bartyzel & Rozanski 2016

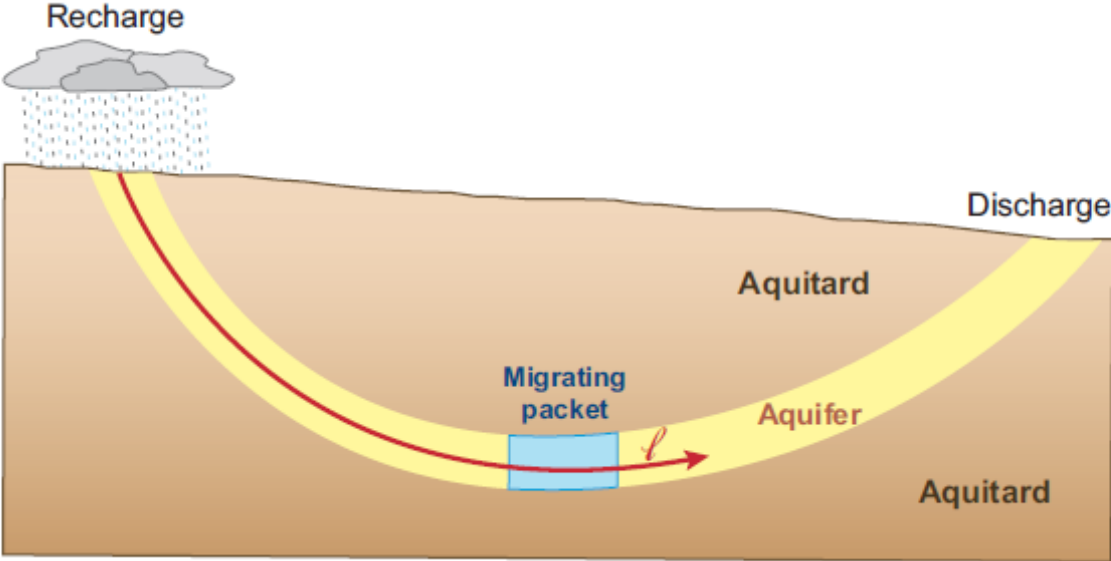


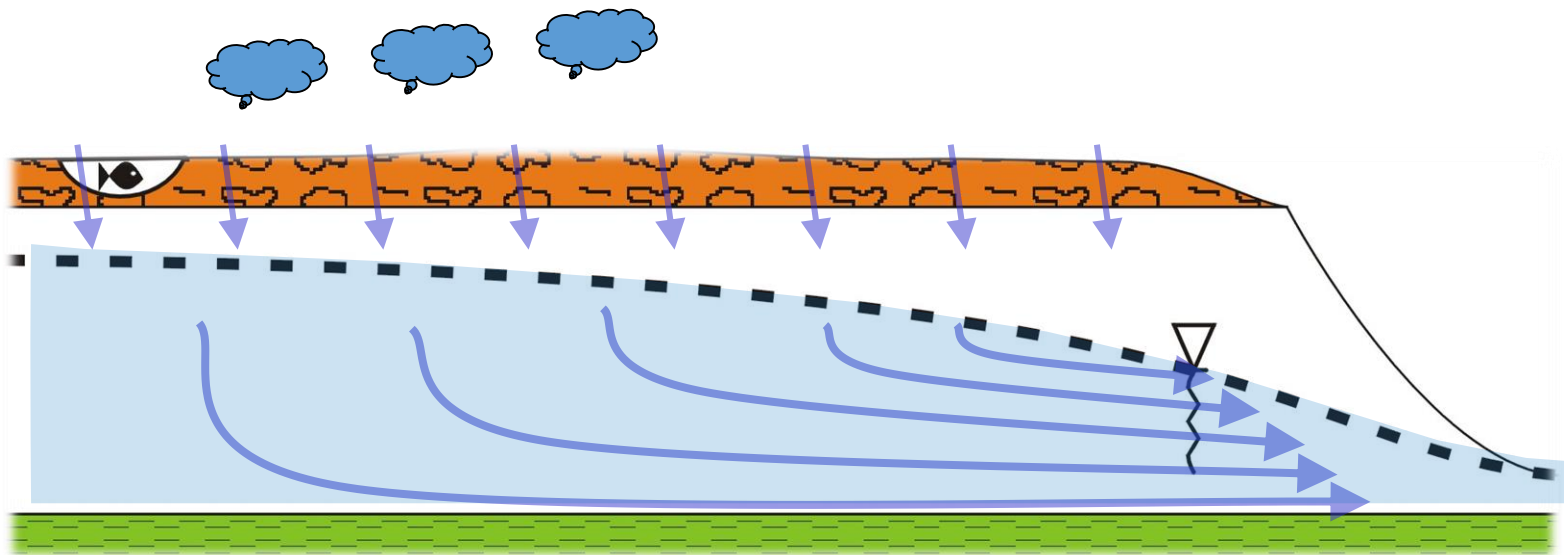
(Modified from Suckow 2014, Baudron 2014, Busenberg and Plummer 2008, Bartyzel & Rozanski 2016)

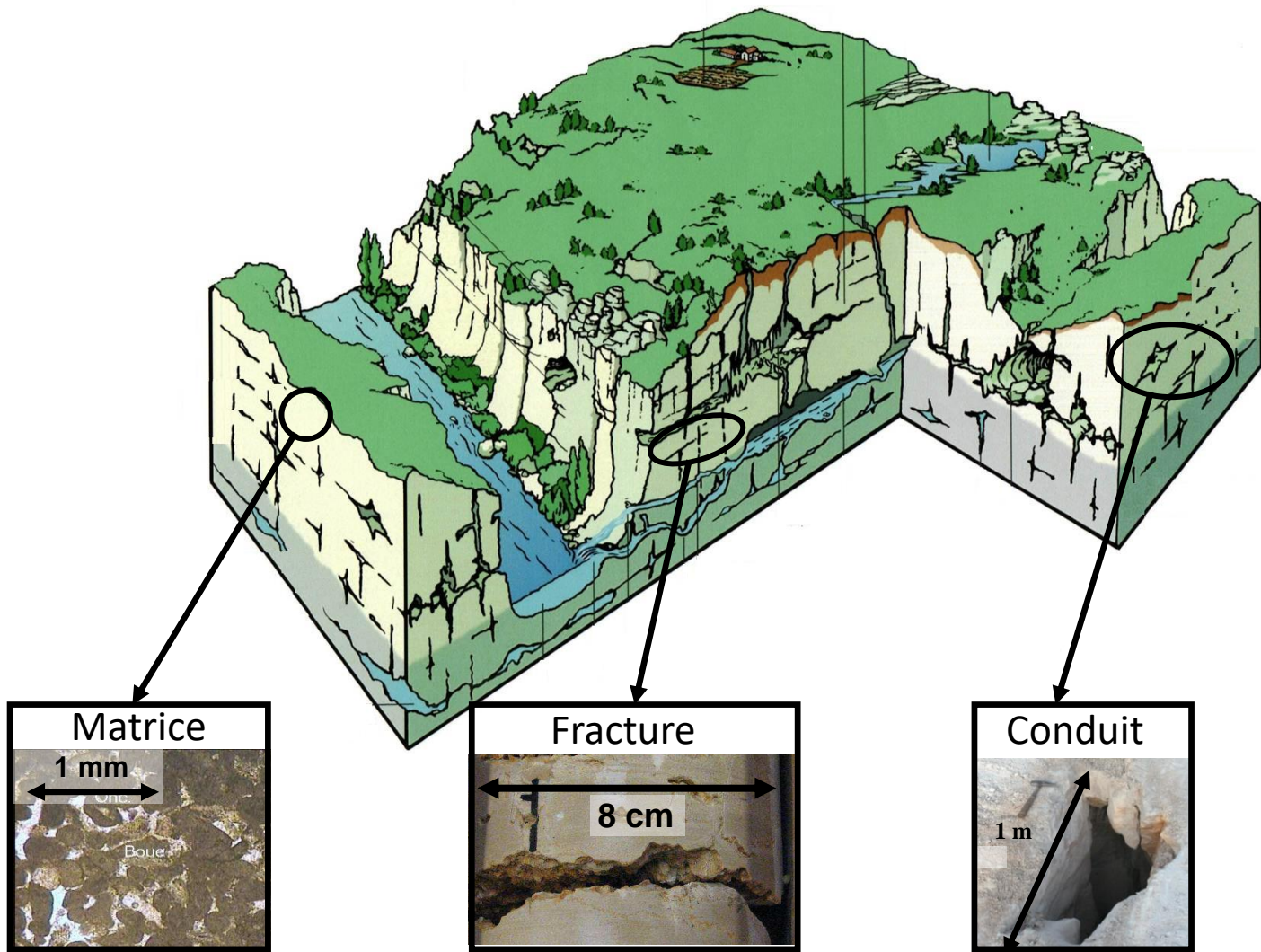
In a nutshell, Hydrogeochemists transform the dark side of human activity into tools for environmental management !



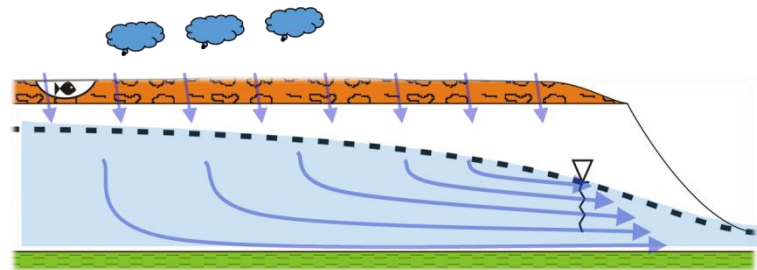
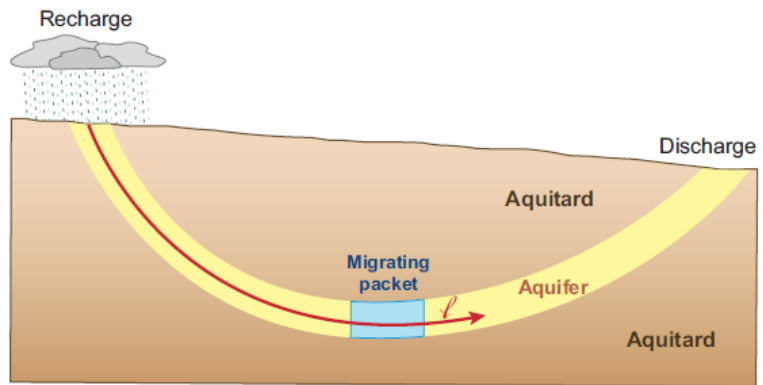
Trace the time, not the age !

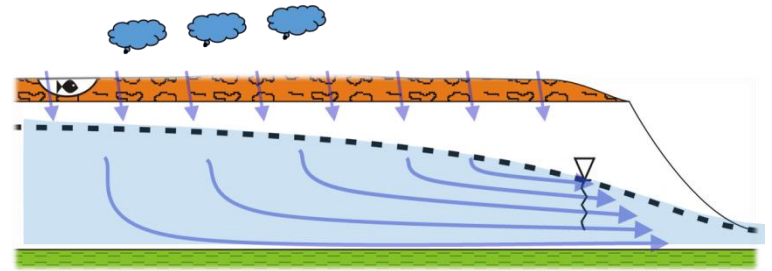
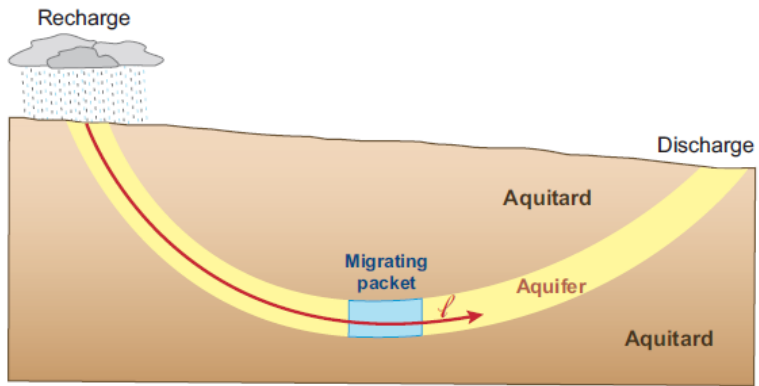






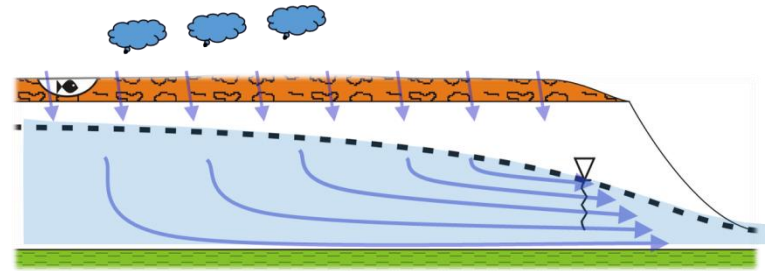
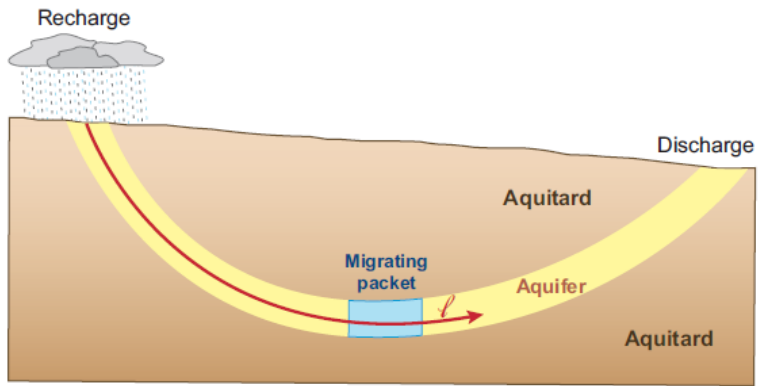
(Modified from Bakalowicz, 2003 in Delbart 2013)



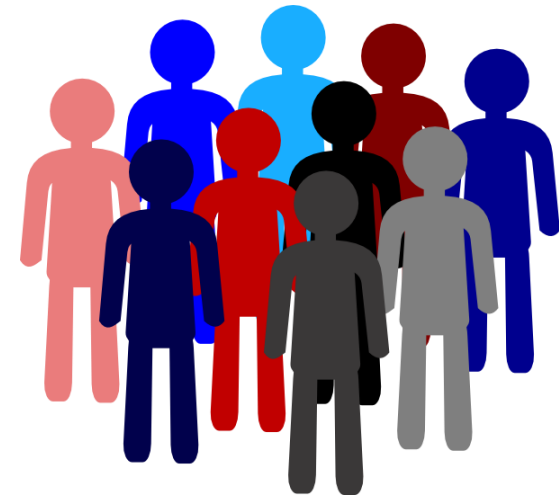


My age is 400 kdays ± 1





My age is 400 kdays ± 1



The IAH assembly “age” is a nonsense

Recharge

Applied Geochemistry 50 (2014) 222–230



ELSEVIER

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Review

The age of groundwater – Definitions, models and why we do not need this term



Axel Suckow*

CSIRO Land & Water, Gate 5 Waite Road, Urrbrae, SA 5064, Australia
National Centre for Groundwater Research and Training (NCGRT), Flinders University, School of the Environment, Adelaide, Australia

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ABSTRACT

The use of environmental tracers to characterise time scales when investigating groundwater is a technology that has been in use for half a century. Its usefulness is beyond controversy. However, the use of the word “age” for groundwater connected with these techniques is misleading due to its inherent connection to the general understanding of human age. “Age” as in the understanding of human age cannot be

My

The AIH assembly “age” is a nonsense

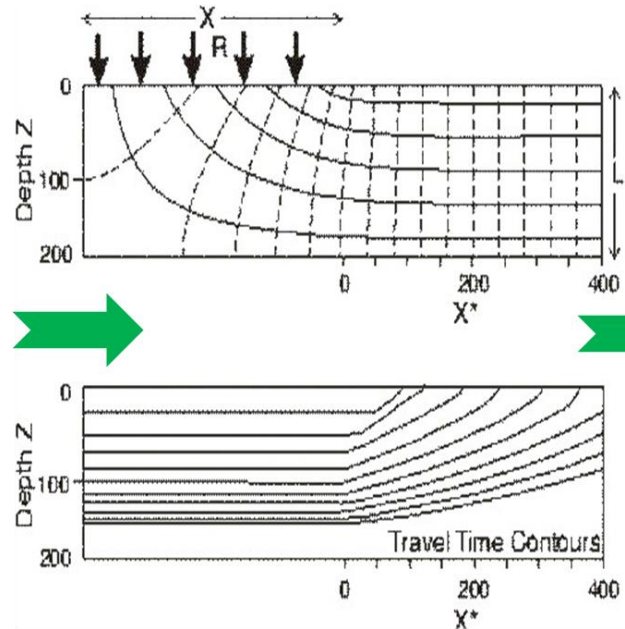
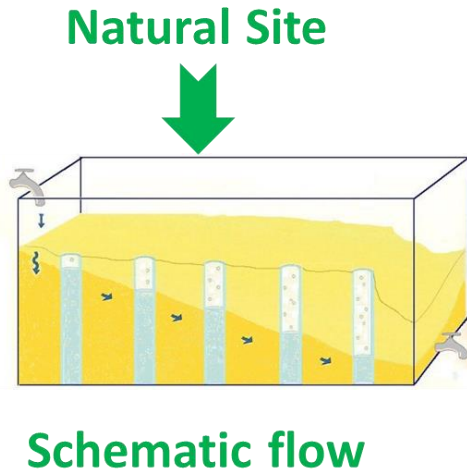


... the “age” of a groundwater sample corresponds generally to a time distribution of many elementary flows. Thus, except in the theoretical case of a pure piston flow system, or of stationary waters entrapped in a geological formation, the concept of groundwater age has little significance.

→ Mean Residence Time (MRT)

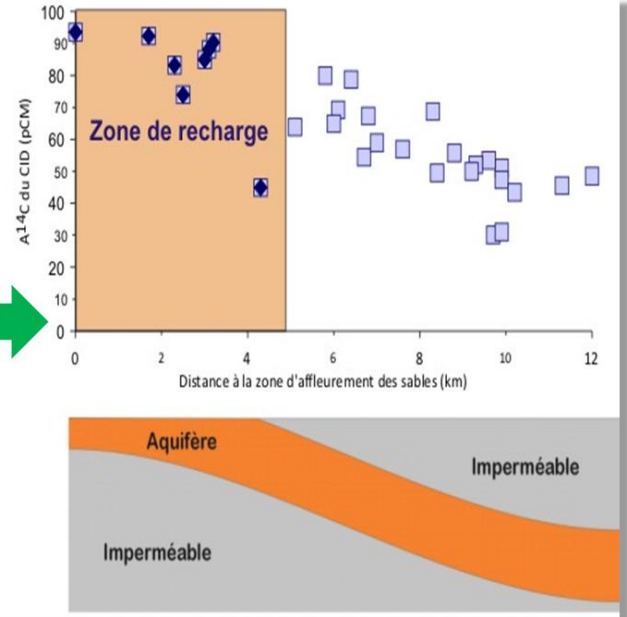
J.-Ch. Fontes (1983) in Guidebook on Nuclear Techniques in Hydrology, IAEA

Hunting the MRT



(Cook & Herczeg, 1999)

Age distribution



(C. Chabault, 2006)

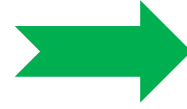
Adapted sampling

We only find what we look for

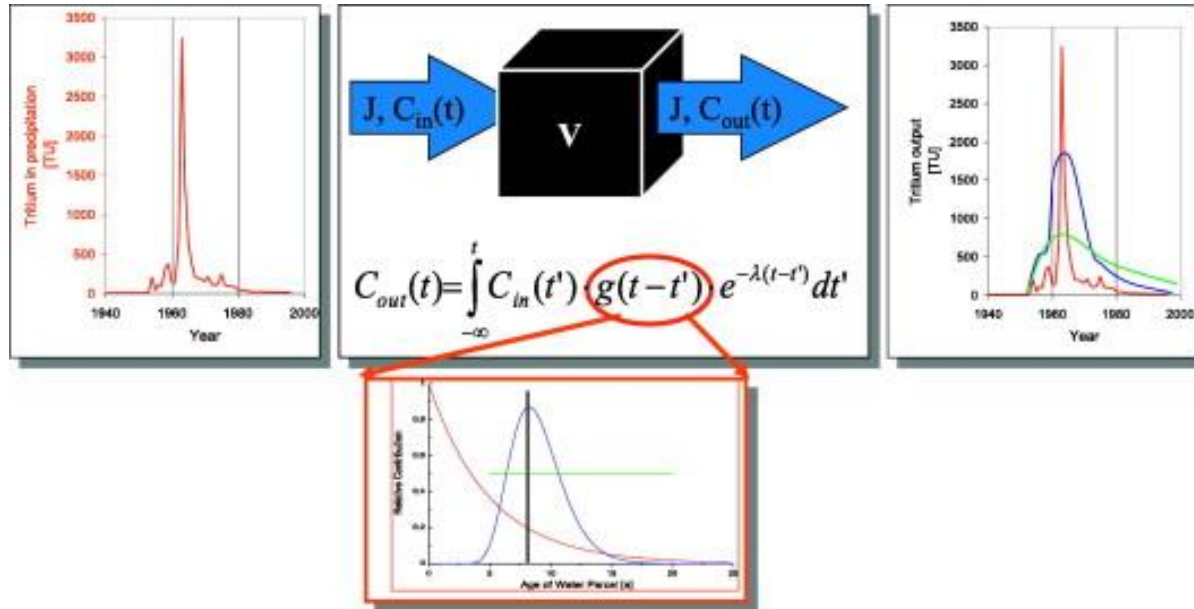
Lumped parameter models

Standard procedure (Forward Modeling)

Tracer
concentration

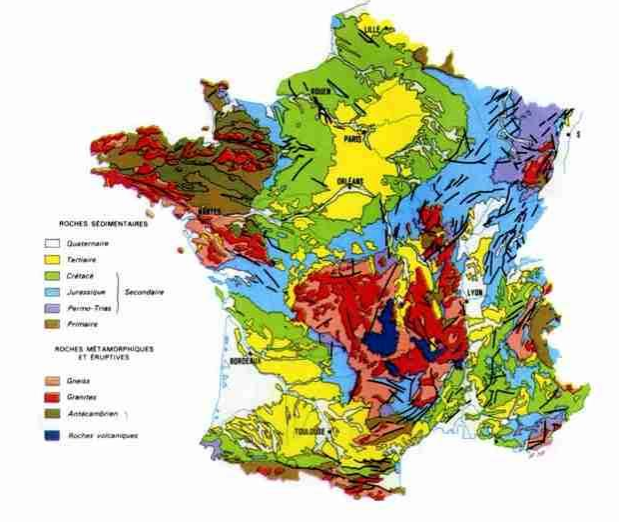


MRT



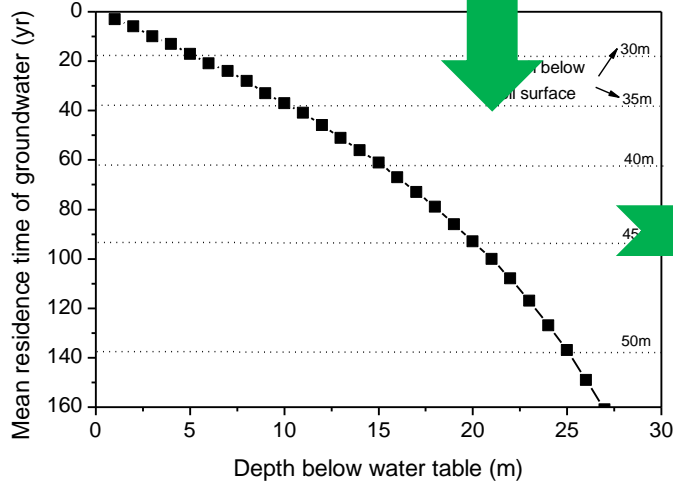
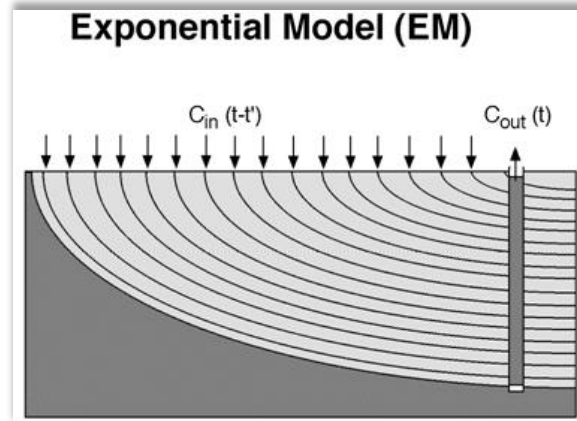
age-dependent weight function

Finding the right sample

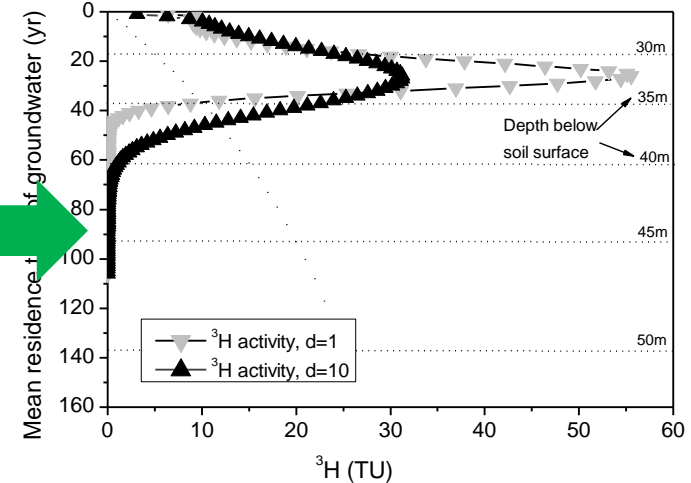


Anticipate age stratification

Flow distribution

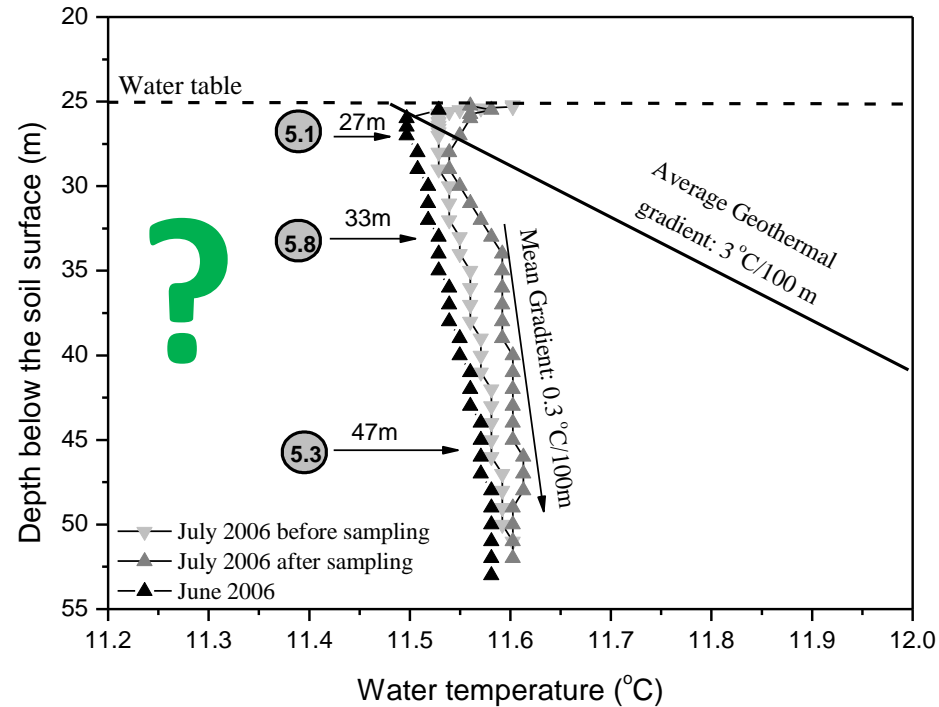
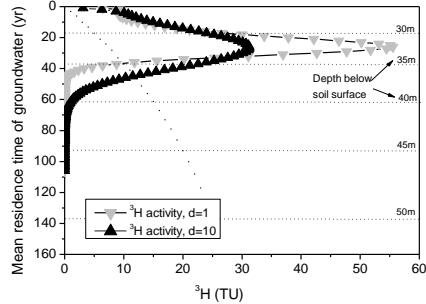
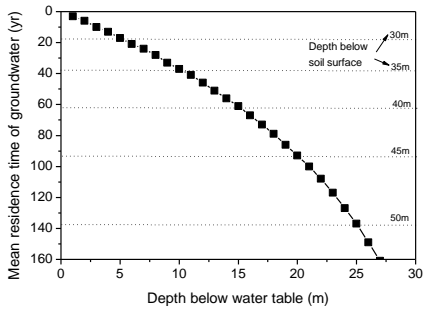


MRT distribution



Tracer distribution

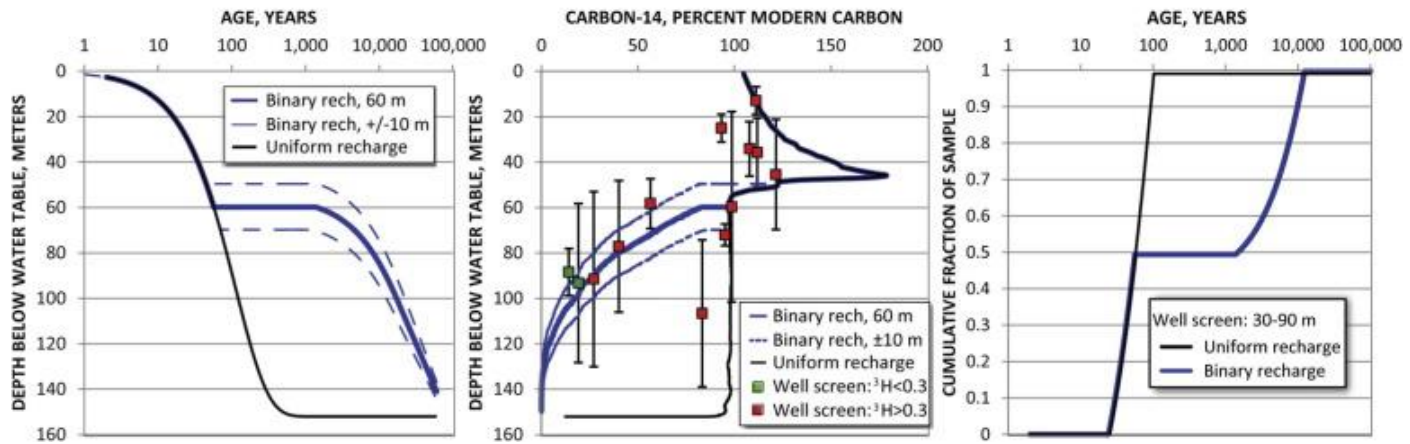
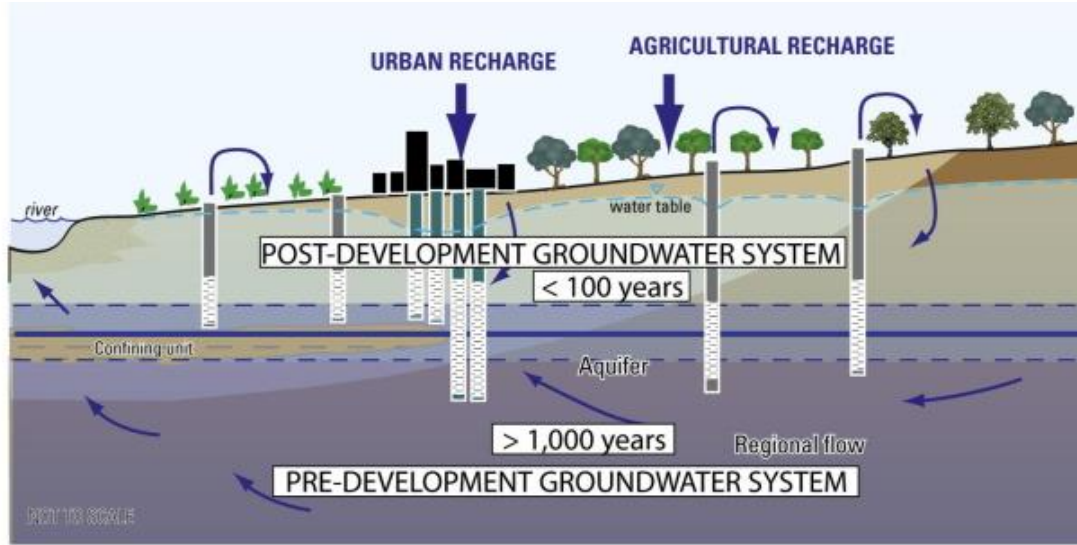
Anticipate age stratification



(Corcho, 2009)

Piezometers are not geochemists best friends....
First discrepancy between model and flow

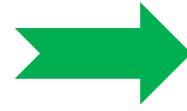
Anticipate age stratification



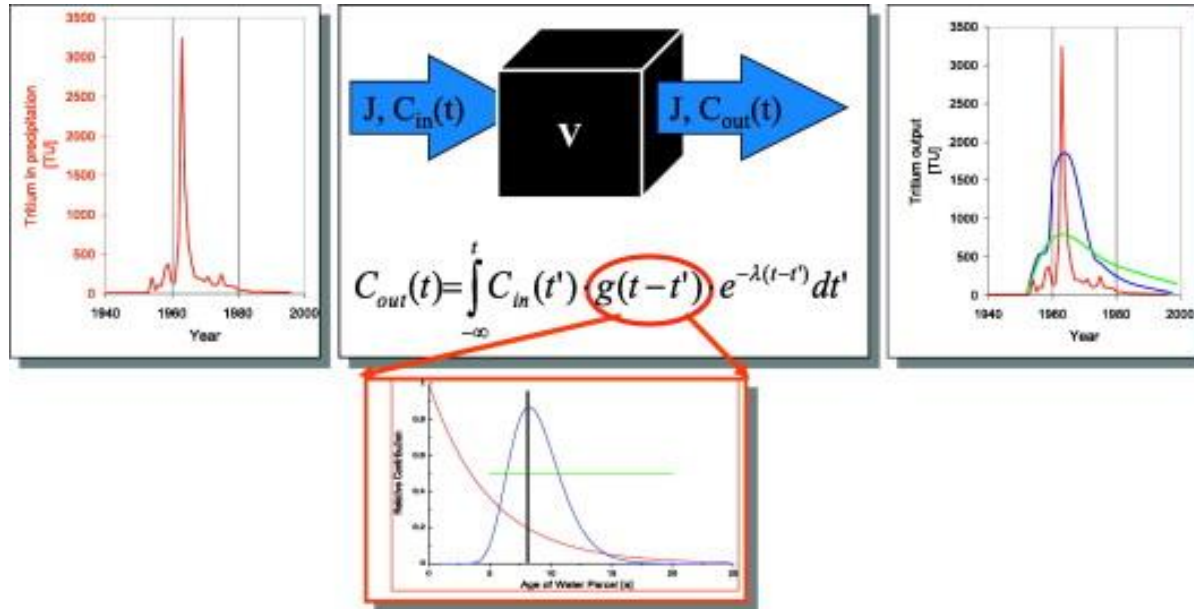
Lumped parameter models / Multi tracers

Standard procedure (Forward Modeling)

Tracers
concentrations



MRT

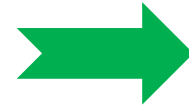


age-dependent weight function

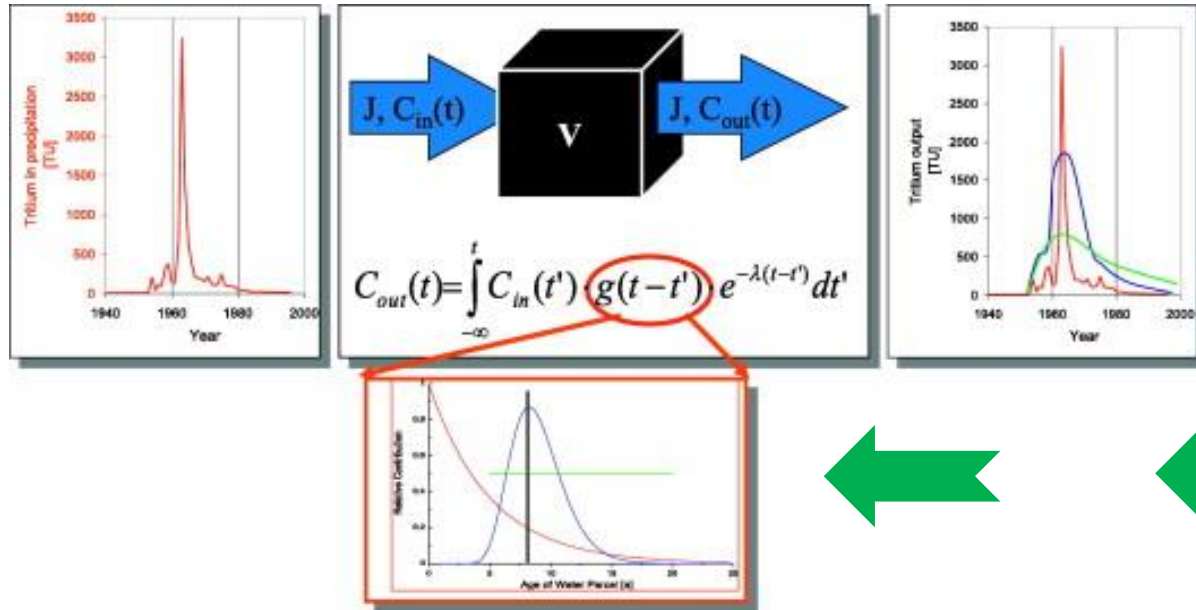
Lumped parameter models / Multi tracers

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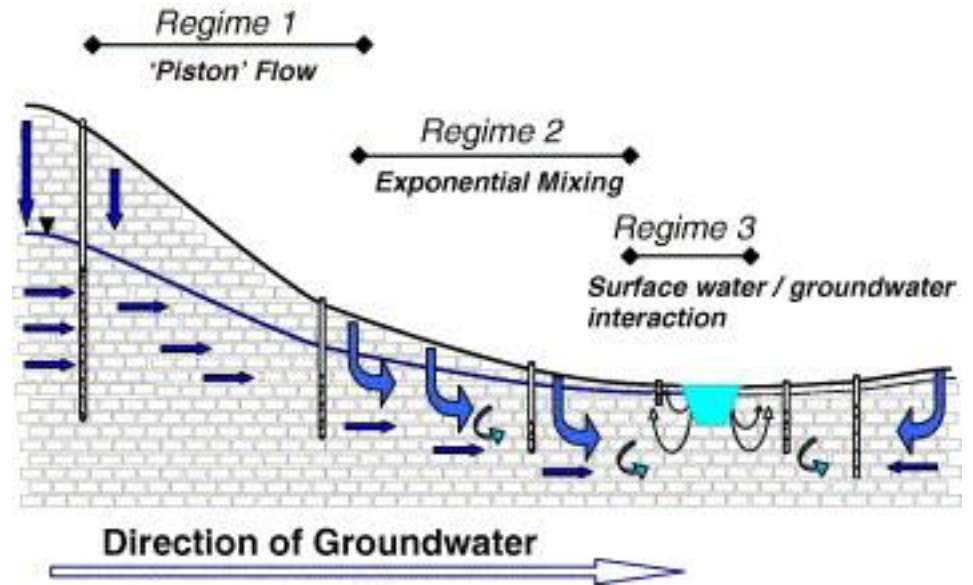
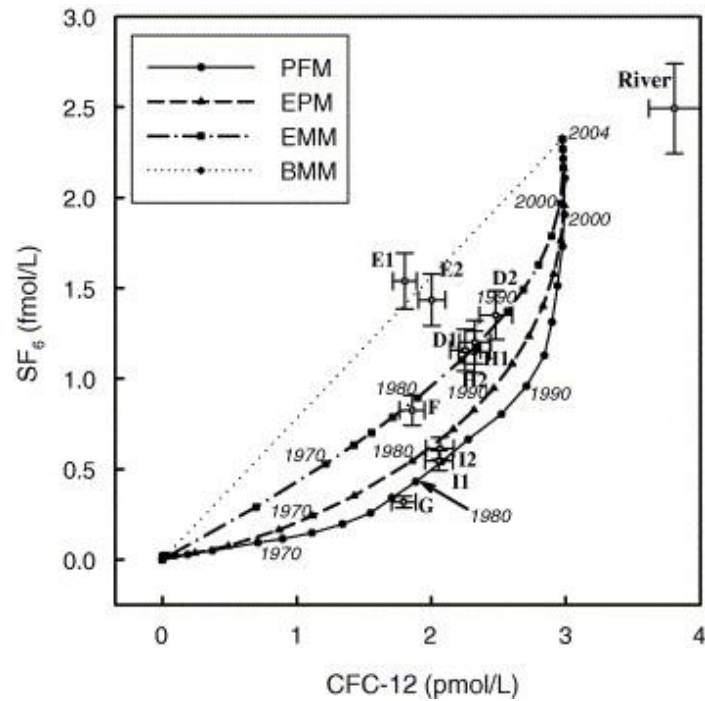
MRT



age-dependent weight function

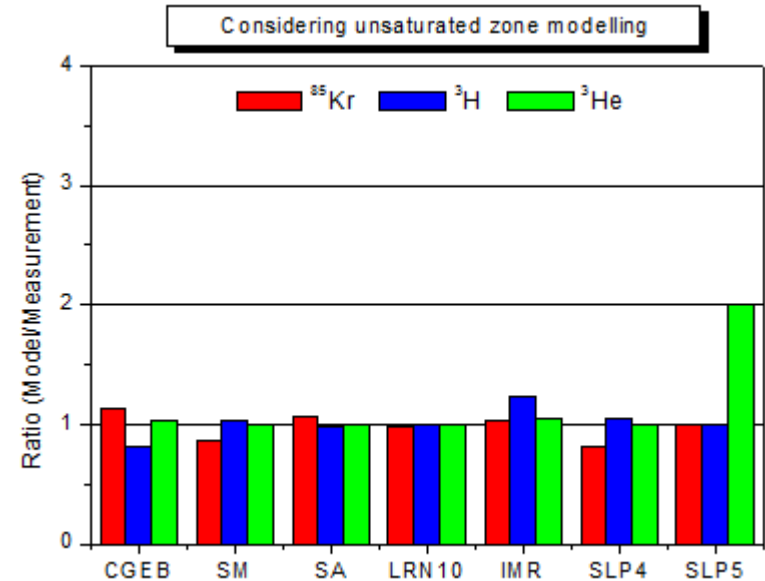
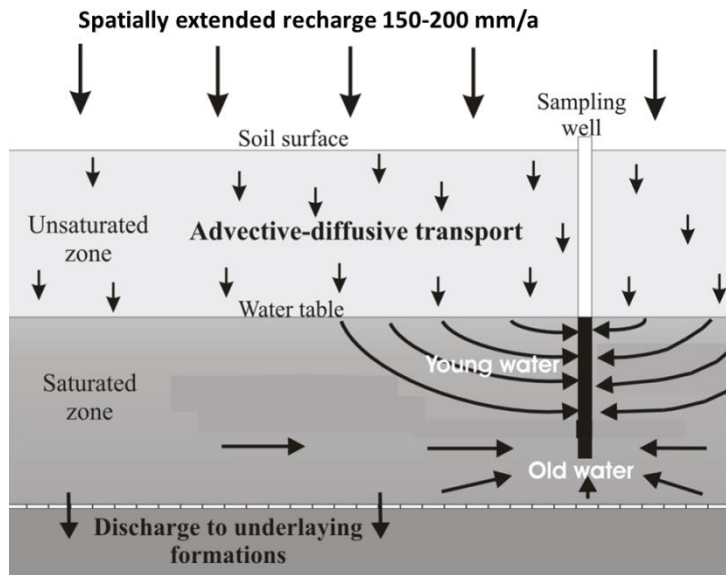
Chalk catchment in southern England

2 tracers, 10 samples



Fontainebleau sands aquifer

4 tracers, 7 samples



Need to solve all the equations in a single model :

$$c_{out}^{85Kr}(T, T_m, m) = \int_0^{\infty} c_{in}^{85Kr}(T-t) \cdot \exp(-\lambda_{85Kr} t) \cdot h(t, T_m, m) \cdot dt$$

$$c_{out}^{3H}(T, T_m, m) = \int_0^{\infty} c_{in}^{3H}(T-t) \cdot \exp(-\lambda_{3H} t) \cdot h(t, T_m, m) \cdot dt$$

$$c_{out}^{3He}(T, T_m, m) = \int_0^{\infty} c_{in}^{3He}(T-t) \cdot (1 - \exp(-\lambda_{3H} t)) \cdot h(t, T_m, m) \cdot dt$$

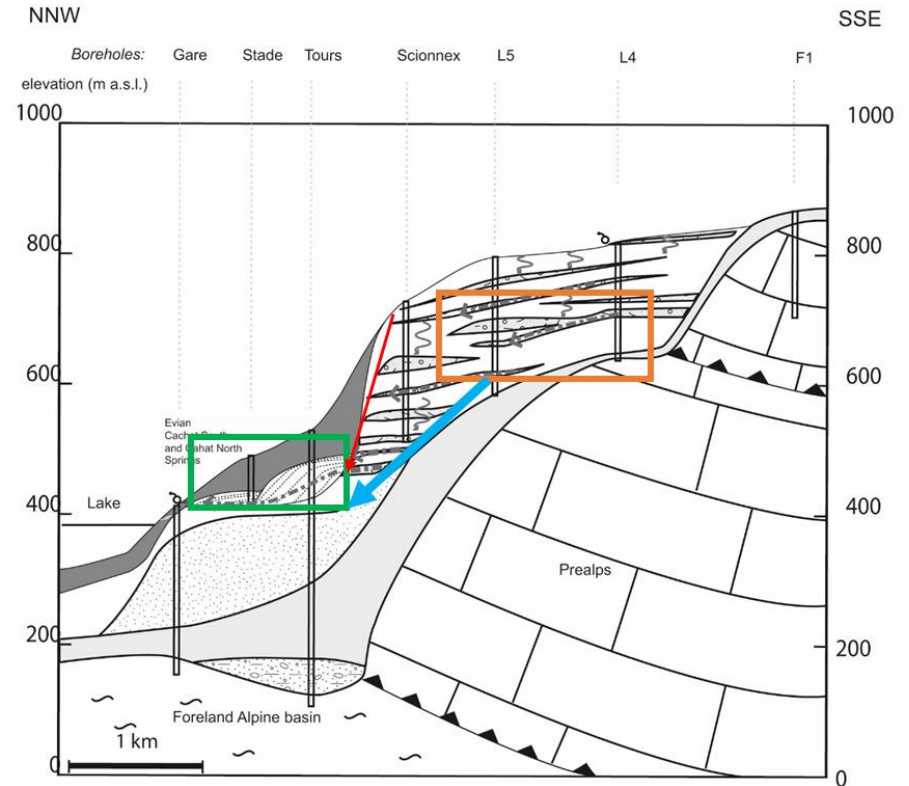
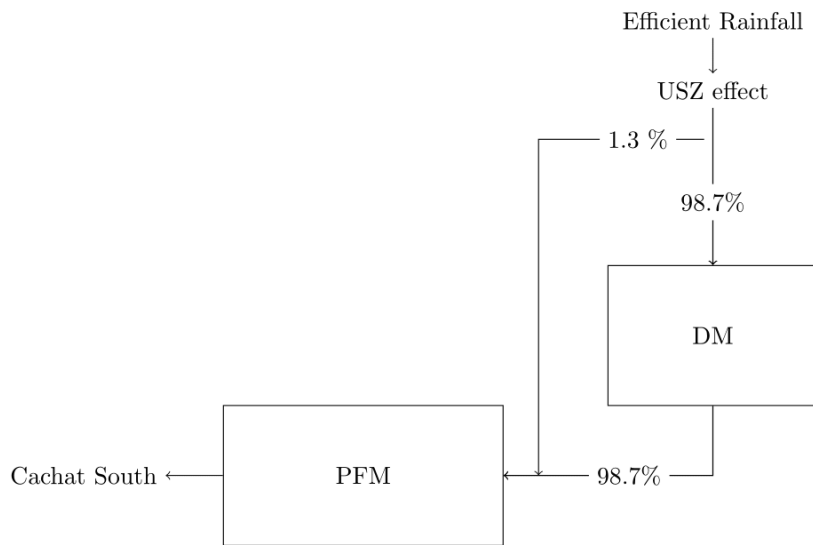
➔ Minimize χ^2 function

Inferring groundwater ages in complex aquifers using gas tracers and tritium

50-years' time series of a water-bound tracer (^3H)

+ a set of ^{85}Kr , ^{39}Ar , CFCs, SF_6 sampled at a single date

A. Henriot et al
(session 8.04, #1919)

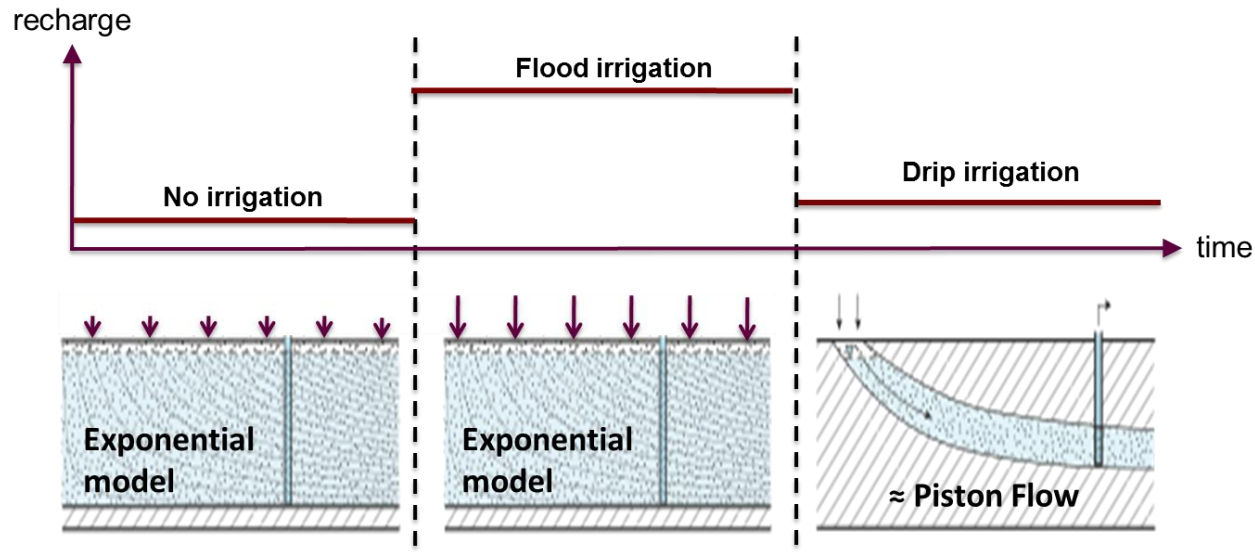
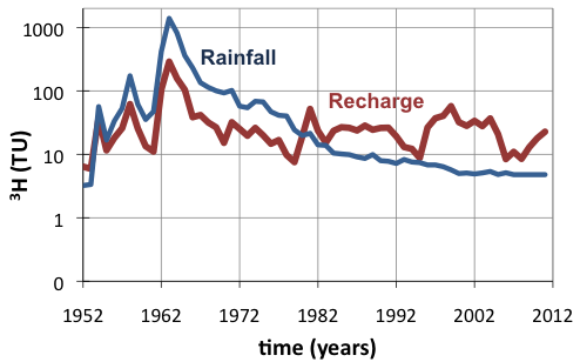


Modern groundwater residence time in a highly anthropized watershed

2 tracers

+ Variable recharge rates

+ Variable tracers input



(P. Baudron et al, 2013)

6 examples, 0 value of MRT

MRT of 25 yrs, ..50 yrs..

6 examples, 0 value of MRT

MRT of 25 yrs, ..50 yrs..

**Significant only if :
MRT + a distribution (age structure)**

As same MRT may lead to different issue

6 examples, 0 value of MRT

MRT of 25 yrs, ..50 yrs..

Significant only if :
MRT + a distribution (age structure)

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+



~



2

6 examples, 0 value of MRT

MRT of 25 yrs, ..50 yrs..

Significant only if :
MRT + a distribution (age structure)

As same MRT may lead to different issue



+

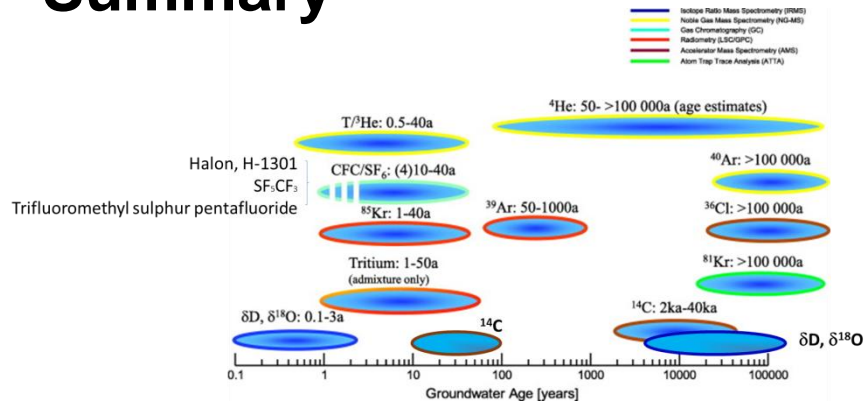


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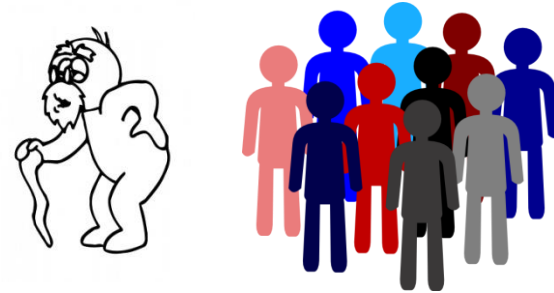
2

Summary

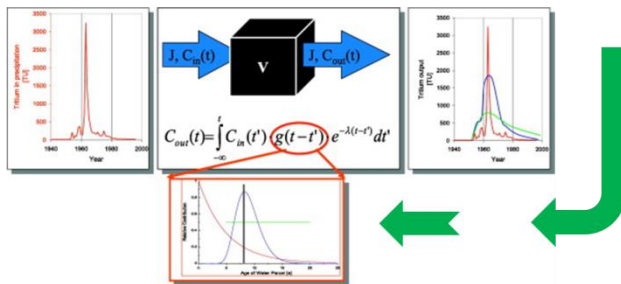


A complete set of tracers in the perfect range of MRT

**Avoid “ages” for GW
Use “Mean Residence Time”**



Tracers concentrations → → → MRT



Evidence, characterize hidden pathways

Never dissociate MRT and age structure