The Abdus Salam
International Centre for Theoretical Physics

2465-2

Joint ICTP-IAEA Workshop on Evaluating Groundwater Pathways and Residence Times as part of Site Investigations and Post-Closure Safety Assessments for Geological Repositories'

17 - 21 June 2013

Shallow Active Systems Analysis and Recent Advances in Isotopic Methods for Residence Time Determinations <50,000y. "DATING GROUNDWATER OF AGES YOUNGER THAN 50,000 YEARS

Takuya MATSUMOTO

Isotope Hydrology Section
Dept. of Nuclear Sciences & Applicatons
IAEA
Austria

Water Resources Programme

Dating groundwater of ages younger than 50,000 years

Takuya Matsumoto
Isotope Hydrology Section
Division of Physical and Chemical Sciences
Department of Nuclear Sciences and Applications
International Atomic Energy Agency
t.matsumoto@iaea.org

Water Resources Programme

Young ground water dating

- Young groundwater is typically found at depths from 0 to 50 meter in unconsolidated sediments and at depths up to 300 meter in fractured-rock systems.
- Shallow groundwater systems are commonly used for drinking water sources and they make up a large part of the baseflow in rivers and lakes.
- Because they are shallow (= recently recharged), they are more susceptible to contamination than deeper groundwaters.
- Groundwater age can be used to determine recharge rates and refine hydrologic models of groundwater systems and thus to predict the contamination potential and estimate the time needed to flush contaminants through a groundwater system.
- The 0- to 50-year time scale is particularly relevant to environmentally sensitive shallow groundwater systems, but before 1980s, there were no reliable means of dating groundwater recharged during this time scale.

Water Resources Programme

Types of dating tools

1. Tracer Dating Technique: time vs. tracer's concentration curve to date groundwater age

   CFC & Tritium

2. Radioactive Decay Dating:

   ^{3}He-T, ^{14}C, Radio-Kryptons (half-life & concentration of daughter (+ parent) isotopes)

3. Linear Accumulation Dating: Using time-dependent input from external source

   ^{4}He & ^{40}Ar (ages from concentrations and known input rates).

Water Resources Programme

Tritium & CFCs

1. During the past 50 years, human activities have released an array of chemical substances to the atmosphere.
2. Tritium (^{3}H) in water vapour from detonation of nuclear bombs in the 1950's and early 60'.
3. CFC (Chloro-Fluoro-Carbons) from refrigeration and other uses from 1950's to 80's, dissolve in precipitation.
4. These atmospheric substances became incorporated in the Earth's hydrologic cycle and can be found in groundwater that has been recharged within the past 50 years.

Water Resources Programme

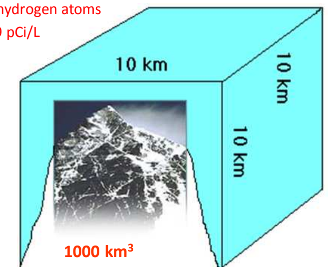
Tritium

- Tritium (Half-life 12 years)
  - Sources
    - Non-Human: Cosmic Ray bombardment on 14N in upper atmosphere (a fast neutron (which must have energy greater than 4.0 MeV) interacts with atmospheric nitrogen). Tritium concentrations due to this natural process is estimated to be between 4 to 25 TU depending on location

1 tritium atom per 1E+18 hydrogen atoms

1 TU = 0.118 Bq/L = 3.19 pCi/L

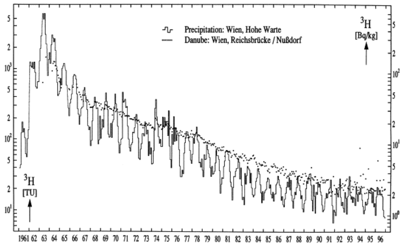
$1\ cm^3$



Water Resources Programme

Tritium

- Tritium (3He, Half-life 12 years)
  - Man-made Tritium: Released during 1950-60s nuclear bomb tests
  - >1000 TU in mid 60s in Northern hemisphere
  - Groundwater recharged after this time period is “labeled” with high Tritium signals.



The decline of tritium is not due only to decay (5.5 % per year), but also due to attenuation by the oceans and groundwaters has reduced levels considerably faster than by decay alone.

Theodorsson, Applied Radiation and Isotopes, 1999

Water Resources Programme

Tritium

Tritium is a useful guide to distinguish between recharge that occurred before atomic weapons testing and more recent recharge:

- High continental latitudes < 4TU
- Low continental latitudes < 1 TU (Fontes, 1979)

Estimating absolute age of young groundwater based on tritium concentration alone is not straight forward. Need assumption for groundwater flow models & mixing with existing groundwater during recharge.

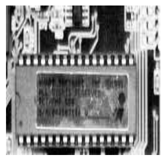
Age commonly can be reliably determined from data on tritium and its decay product (helium-3). The 3H/3He age is based on a calculation that determines the amount of 3He derived from radioactive decay of 3H in the water.

Water Resources Programme

CFC

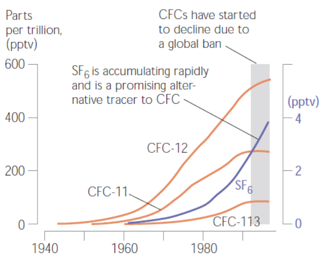
CFC-11	CFC-12	CFC-113
CCl_3F	CCl_2F_2	$C_2Cl_3F_3$
Cleaning Agents, Foam Blowing agents, Propellants in aerosol cans, Refrigeration agents, …		

Production of CFCs ceased in mid 1990s due to their impact on the Ozone Layer depletion. Current estimates of the atmospheric lifetimes of CFC-11, CFC-12 and CFC0113 are about 50 to 100 years.



Water Resources Programme

CFC



CFCs and sulfur hexafluoride (SF_6) concentrations (mixing ratios) for air over North America during the last 50 years.

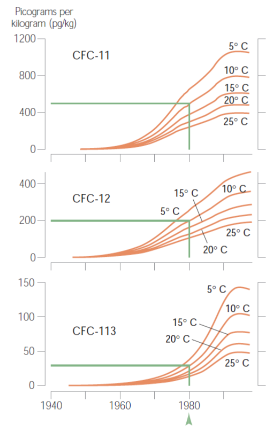
USGS, Fact Sheet 134-99 (1999)

CFC-11	CFC-12	CFC-113
CCl_3F	CCl_2F_2	$C_2Cl_3F_3$
Cleaning Agents, Foam Blowing agents, Proellants in aerosol cans, Refrigeration agents, …		

Production of CFCs ceased in mid 1990s due to their impact on the Ozone Layer depletion. Current estimates of the atmospheric lifetimes of CFC-11, CFC-12 and CFC-113 are about 50 to 100 years.

Water Resources Programme

CFC



USGS, Fact Sheet 134-99 (1999)

GW dating with CFC-11, CFC-12, CFC-113.

(1) Their amounts in the atmosphere over the past 50 years have been reconstructed

(2) Their solubility in water are known, and

(3) Their concentrations in air and young water are high enough that they can be measured.

Concentrations in Water

↓ Henry's law Constants (Temperature dependent)

Atmospheric Concentrations at recharge

↓ Input Function (Site-dependent)

Groundwater Age

Water Resources Programme

Types of dating tools

1. Tracer Dating Technique: time vs. tracer's concentration curve to date groundwater age

   CFC & Tritium

2. Radioactive Decay Dating:

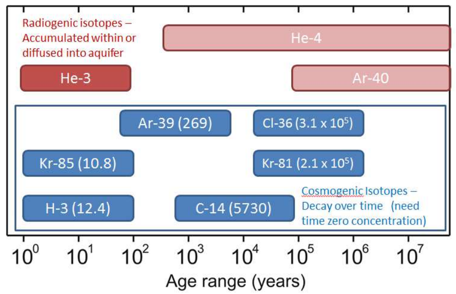
   ^{3}He-T, ^{14}C, Radio-Kryptons (half-life & concentration of daughter (+ parent) isotopes)

3. Linear Accumulation Dating: Using time-dependent input from external source

   ^{4}He & ^{40}Ar (ages from concentrations and known input rates).

Water Resources Programme

Groundwater dating with isotopes



For young groundwater <100 years, He-3, T, Kr-85 have applicable half-lives (the source for ^{85}Kr is reprocessing of nuclear fuel rods). Difficult to collect and analyse, thus is not yet a practical dating tool for groundwater studies.

Water Resources Programme

Radioactive Decay as a clock

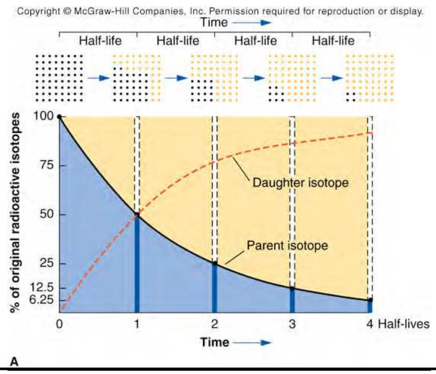
Basic Decay Equations

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

$$D = D_0 + (N_0 - N)$$
$$D = D_0 + N(e^{\lambda t} - 1)$$

D = daughter atoms
N= parent atoms remaining

By assuming/constraining D_0, the age can be obtained by present-day concentration of D and N.



Water Resources Programme

Groundwater Dating with ^{3}H-^{3}He

- Some characteristics of Helium
  - 5.24 ppm by volume in the atmosphere
  - Not heavy enough to be gravitationally captured in the atmosphere – continuously escaped to space.
  - Escape and addition from inside the earth is now in the steady state with helium residence time of 10^6 years.
  - 99.99986% is ^{4}He – natural abundance of ^{3}He is extremely low (Sensitive to addition of ^{3}He produced by decay of equally rare tritium in water).
  - ^{3}He/^{4}He ratios in the air is globally uniform with atmospheric mixing time of a few years. (Quantification for discriminating ^{3}He derived from air and from the tritium decay)

Water Resources Programme

Groundwater Dating with ^{3}H-^{3}He

$$D = D_0 + N(e^{\lambda T} - 1)$$

$$[^3He]_t = [^3He]_0 + [^3T]_t(e^{\lambda T} - 1)$$
$$[^3He]_0 = constrainable$$

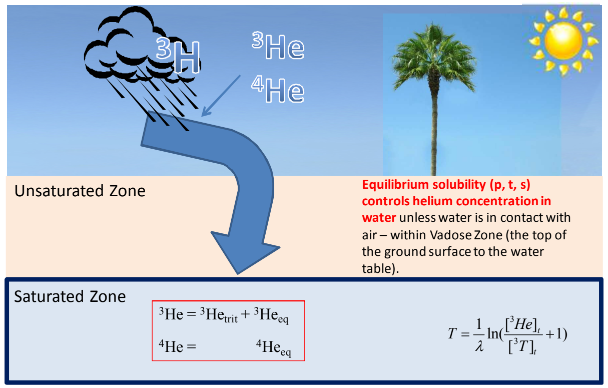
$$T = \frac{1}{\lambda}\ln\left(\frac{[^3He]_t}{[^3T]_t} + 1\right)$$

^{3}He at the time of recharge can be estimated from recharge temperature (air contains small amount of ^{3}He which will be dissolved into the rain water).

Underlying assumption – The groundwater system should be closed in terms of **tritium and its daughter ^{3}He** from its isolation from air to sampling.

Called "tritiugenic helium"

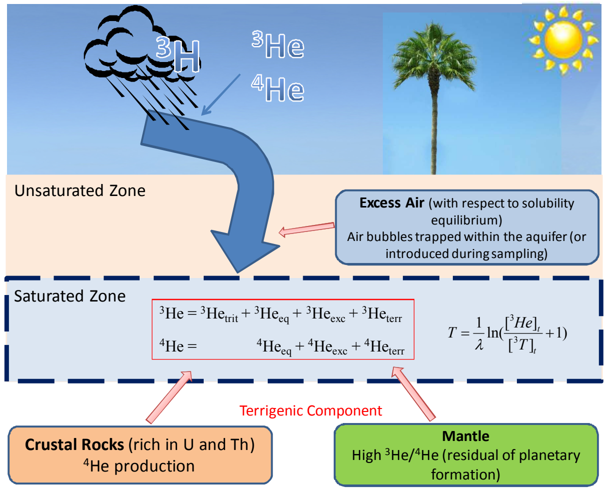
An ideal case in which fulfils the closed system assumption



Saturated zone is a closed system with respect to dissolved gases.

^{3}He concentration will begin to rise. ^{3}H/^{3}He used to determine a time period for which groundwater has been isolated from the atmosphere (e.g., time since recharge)

Helium in groundwater is a mixture of components from different sources.



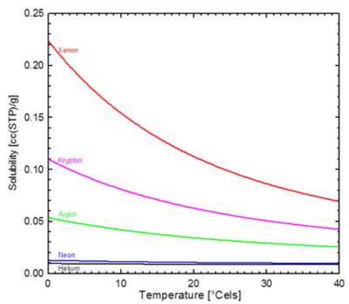
$T\,/\,^3He$ Dating of Groundwater: Separation of Helium Components

$$^3He_{meas} = {}^3He_{trit} + {}^3He_{eq} + {}^3He_{exc} + {}^3He_{terr}$$

$$^4He_{meas} = {}^4He_{eq} + {}^4He_{exc} + {}^4He_{terr}$$

- He_{eq}: Solubility equilibrium, **needs infiltration temperature (noble gases themselves can be a thermometer)**
- He_{exc} Excess air determined via Ne
- He_{terr} separation possible if either crustal He ($^3He/^4He < 10^{-8}$) or mantle He ($^3He/^4He > 10^{-5}$) present, not for both

Noble Gas-(Palaeo) temperatures



Knowledge of concentrations of all noble gases (Ne, Ar, Kr and Xe) is needed to estimate recharge temperature.

$T\,/\,^3He$ Dating of Groundwater: Separation of Helium Components

$$^3He_{meas} = {}^3He_{trit} + {}^3He_{eq} + {}^3He_{exc} + {}^3He_{terr}$$

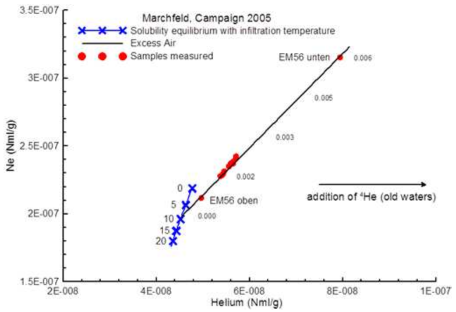
$$^4He_{meas} = {}^4He_{eq} + {}^4He_{exc} + {}^4He_{terr}$$

- He_{eq}: Solubility equilibrium, needs infiltration temperature (based on Ne, Ar, Kr, Xe concentrations)
- He_{exc} Excess air determined via Ne, Ar, Kr and Xe concentrations
- He_{terr} separation possible if either crustal He ($^3He/^4He < 10^{-8}$) or mantle He ($^3He/^4He > 10^{-5}$) present, not for both

Water Resources Programme

IAEA

Mixng of Eq-Air & excess Air



Analytical results cannot be directly used for ^{3}He-T dating.

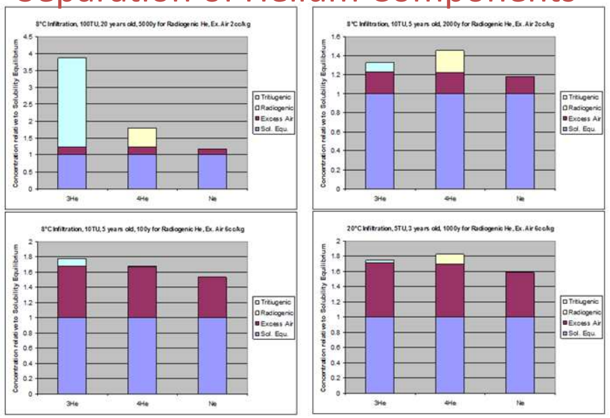
How to estimate Tritiogenic ^{3}He from analytical results?

Measurable			Terrigenic		Excess Air		Solubility Eq.
3He	=	3He Trit. +	3He Ter.	+	3He Excess	+	3He Eq.Sol.
4He			4He Ter.		4He Excess		4He Eq.Sol.
Ne					Ne Excess		Ne Eq.Sol.
Ar					Ar Excess		Ar Eq.Sol.
Kr					Kr Excess		Kr Eq.Sol.
Xe					Xe Excess		Xe Eq.Sol.

Water Resources Programme

IAEA

T / ^{3}He Dating of Groundwater: Separation of Helium Components



Water Resources Programme

IAEA

Principle of T/3He dating - Summary

$$T = \frac{1}{\lambda}\ln\left(\frac{[^3He]_t}{[^3T]_t}+1\right)$$

^{3}H-^{3}He ages are obtained after assessing non-tritiugenic ^{3}He components based on analysis of Ne, Ar, Kr, Xe and on some additional assumptions.

Ages are independent from tritium input function – meritorious as relatively few continuous measurements of ^{3}H were made during the 1960s and 1970s, leading to uncertainties in the spatial and temporal distribution of the 3H input function.

Current analytical methods are sufficient to date ground water ranging from about 0 to 50 years with a typical uncertainty of approximately ±1 years.

It is an apparent age, – Not necessarily the true age of the groundwater (dispersion, mixing, degassing etc…).

Measurement Steps for Noble Gases in Water Samples:

Sampling of water or gas samples in the field

Cu-Tube (water sampling), Diffusion/Contactor Samplers (on-site sampling of dissolved gas)

Gas extraction from water (if Cu-tube is used).

Water Vapour Transport through a Capillary Tube

1 ccSTP in 40g

Separate Reactive Gases (O_2, N_2, CO_2, CH_4...) from Noble Gases

Chemical Getters

Residual: 0.01cc, mainly Argon

Separate Noble Gases (He, Ne, Ar, Kr, Xe)

Cryo techniques down to 10K (-263ºC)

Some amounts: 5e-6cc ^{4}He, 5e-12cc ^{3}He

Measure Each Noble Gas in a dedicated Mass Spectrometer

High resolution magnetic sector field Mass Spectrometers (SMS) for ^{3}He

Simple Quadrupole Mass Spectrometers (QMS) for all others

Water Resources Programme

STEP 1: Sampling

Helium is highly diffusive element – They pass through glass/plastic.

Need to avoid contact with atmosphere during sampling.

Exchange with the atmosphere breaks the closed system principle of the isotope clock.

Not all wells or pumps are suitable for noble gas sampling, because of the requirements of closure against air or other gas phases and of sufficient pressure to prevent degassing.

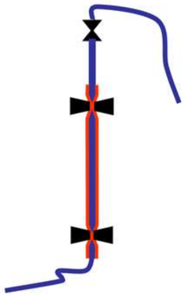
Closed boreholes are highly desirable, open wells or springs are problematic, because they allow gas exchange.

Ideal are artesian wells with sufficient pressure or wells pumped by a submersible pump.

Water Resources Programme

Water Sampling by Cu-tube

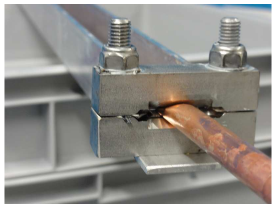
Water is sampled by continuously flowing it (without any bubbles) and by closing two clamps tightly.

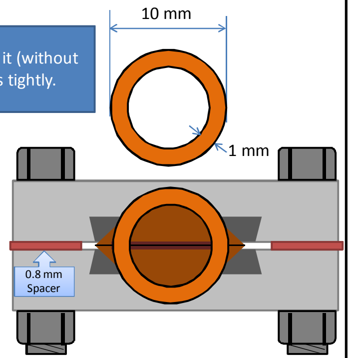


Water Resources Programme

Water Sampling by Cu-tube

Water is sampled by continuously flowing it (without any bubbles) and by closing two clamps tightly.





Cu-tube is sealed by “cold-welding” of metal to metal interface.

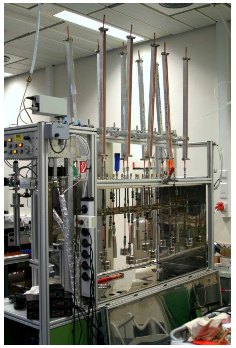
IAEA Water Resources Programme

STEP 2: Gas Extraction

Cu-tubes are brought back in the lab and subjected for gas extraction

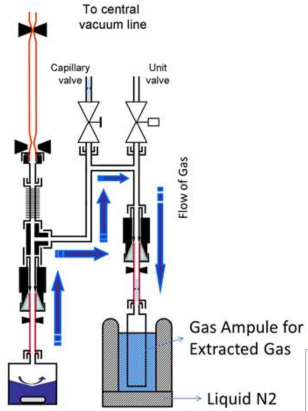
	cm^3STP	mole
^{3}He	3E-12	1E-16
^{4}He	2E-06	8E-11
^{20}Ne	7E-06	3E-10
^{40}Ar	1E-02	6E-07
^{84}Kr	2E-06	7E-11
^{132}Xe	1E-07	4E-12

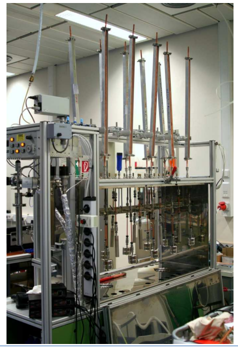
+ Majar Gases, such as N2, O2, CO2, CH4 etc….



IAEA Water Resources Programme

STEP 2: Gas Extraction



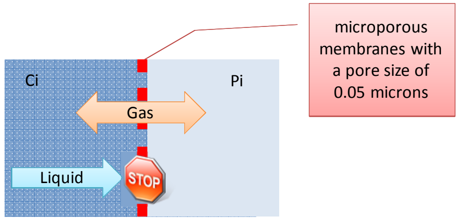


- Quantitative transfer of extracted gases to a dedicated gas storage ampoule using a water vapour stream through a capillary.
- 10 parallel units, 3 cycles of extraction per week (> 100 samples par month).

IAEA Water Resources Programme

Gas Sampling with membrane

Direct gas sampling is possible in the field by using a membrane technology



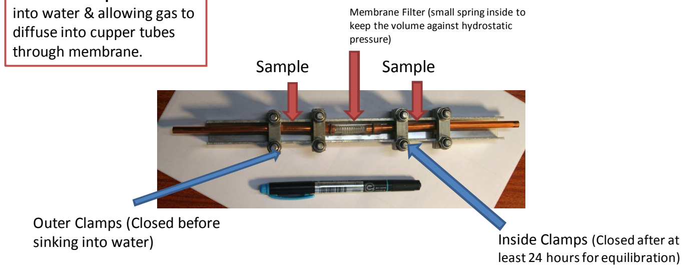
Ci = k × Pi (Henry's law)

Ci: Concentration of given gas species = important unknown to obtain
K: Henry's constant = known (**water temperature** needed)
Pi: Partial Pressure of given gas species = will be known parameters by analysis
(Molar fraction of noble gas can be determined by mass spectrometer, **Total Pressure of Dissolved Gas needs to be measured in water at sampling**)

IAEA Water Resources Programme

Gas Sampling with membrane

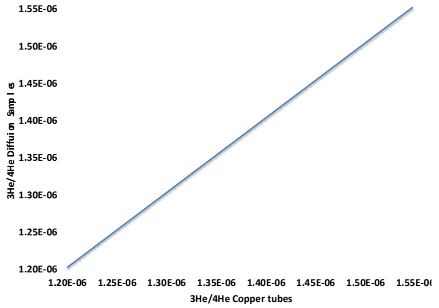
Diffusion Sampler: Sunk into water & allowing gas to diffuse into cupper tubes through membrane.



Pros: Light & Small (easy handling), multiple sampling
Cons: Time consuming (>24 hrs of waiting)
Need probes for water temperature & Total Dissolved Gas Pressure (TDGP)
Time integration over sampling period if water composition changes with time

Water Resources Programme

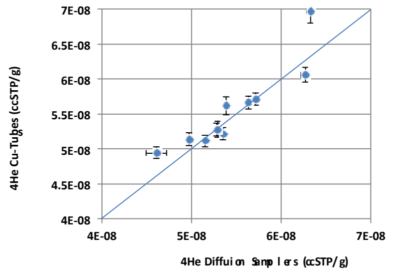
$^3H/^4He$: Copper Tubes Vs Diffusion Samplers



From IAEA's Coordinated Research Projects (2012)

Water Resources Programme

^4He: Copper Tubes Vs Diffusion Samplers



From IAEA's Coordinated Research Projects (2012)

Gas Sampling with membrane

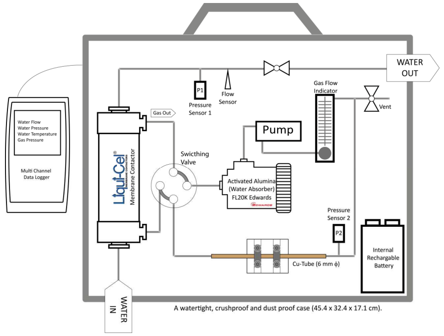
Contactor Sampler: A compact device that can extract gas from continuous flow of sample water

Shorter extraction time than diffusion samplers.
No external probes required
Weights 10 kg – still lighter than a full box of Cu-tubes.

Water Resources Programme

Gas Sampling with membrane

Contactor Sampler: A compact device that can extract gas from continuous flow of sample water



Water temperature & total Pressure of sampler can be directly measured by a built-in censors (No temperature & TDGP probes required)

Measurement Steps for Noble Gases in Water Samples:

Sampling of water or gas samples in the field

Cu-Tube (water sampling), Diffusion/Contactor Samplers (on-site sampling of dissolved gas)

Gas extraction from water (if Cu-tube is used).

Water Vapour Transport through a Capillary Tube

1 ccSTP in 40g

Separate Reactive Gases (O_2, N_2, CO_2, CH_4...) from Noble Gases

Chemical Getters

Residual: 0.01cc, mainly Argon

Separate Noble Gases (He, Ne, Ar, Kr, Xe)

Cryo techniques down to 10K (-263ºC)

Some amounts: 5e-6cc ^{4}He, 5e-12cc ^{3}He

Measure Each Noble Gas in a dedicated Mass Spectrometer

High resolution magnetic sector field Mass Spectrometers (SMS) for ^{3}He

Simple Quadrupole Mass Spectrometers (QMS) for all others

IAEA Water Resources Programme

Noble Gas Measurement

Noble Gas System @ the IHL, IAEA

VG5400 + 3 QMS + Dedicated Gas Handling System

Will be updated to new generation mass spec (Thermo Helix SFT)

IAEA Water Resources Programme

Noble Gas Measurement

Amount of Noble Gases in 1 sample

	cm^{3}STP	mole
^{3}He	3E-12	1E-16
^{4}He	2E-06	8E-11
^{20}Ne	7E-06	3E-10
^{40}Ar	1E-02	6E-07
^{84}Kr	2E-06	7E-11
^{132}Xe	1E-07	4E-12

We only have a limited amount of noble gases so that the process needs to be done under very clean static vacuum (10^{-7} ~10^{-8} mbar)

Separate Reactive Gases (O_2, N_2, CO_2, CH_4...) from Noble Gases

Chemical Getters

Residual: 0.01cc, mainly Argon

Separate Noble Gases (He, Ne, Ar, Kr, Xe)

Cryo techniques down to 10K (-263ºC)

Some amounts: 5e-6cc ^{4}He, 5e-12cc ^{3}He

Measure Each Noble Gas in a dedicated Mass Spectrometer

High resolution magnetic sector field Mass Spectrometers (SMS) for ^{3}He

Simple Quadrupole Mass Spectrometers (QMS) for all others

IAEA Water Resources Programme

Noble Gas Measurement

Sector-type Mass Spectrometer

High Mass Resolution

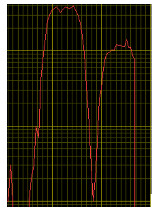
necessary to separate ^{3}He and HD^{+} peaks)

High Senstivity

1 cps = 1 x 10^{-14} cm^{3}STP of ^{3}He

Dedicated to helium analysis only

$^{3}He^{+}$ HD^{+}



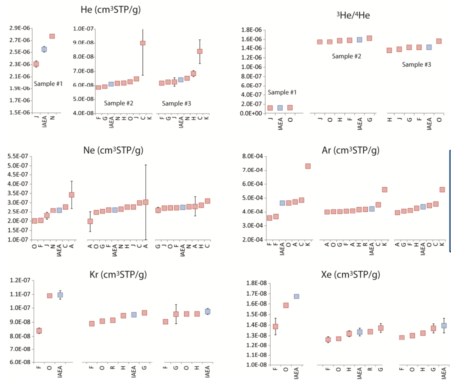
Measure Each Noble Gas in a dedicated Mass Spectrometer

High resolution magnetic sector field Mass Spectrometers (SMS) for ^{3}He

Simple Quadrupole Mass Spectrometers (QMS) for all others

Water Resources Programme

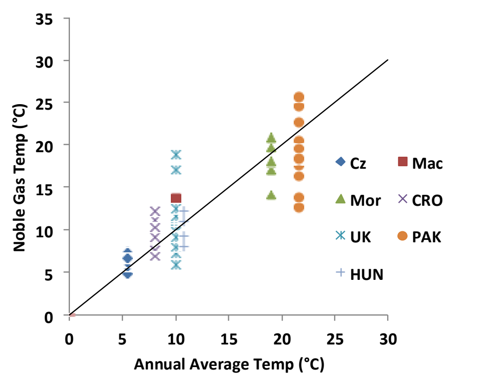
IAEA's noble gas: Performance



T-³He apparent ages
Sample #2: 10.0 ± 0.4 Years
Sample #3: 7.2 ± 0.3 Years
Noble Gas Temperature
Sample #1: 4.2 ± 0.8 °C
Sample #2: 9.1 ± 0.4 °C
Sample #3: 8.4 ± 0.8 °C

Water Resources Programme

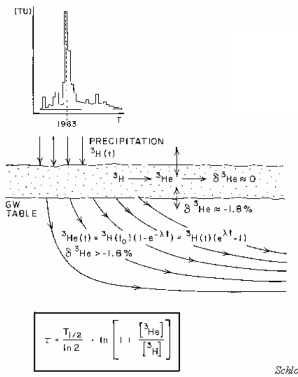
Noble Gas Temperature Vs Mean Annual Temperature



From IAEA's Coordinated Research Projects (2012)

Water Resources Programme

Applications of T-³He age



Schlosser et al., In: Isotope techniques in the study of Environmental Change, IAEA, 1998

Vertical T-³He profiles allowed determination of ground-water recharge rates (e.g., Schlosser et al., 1988; Solomon et al., 1993).

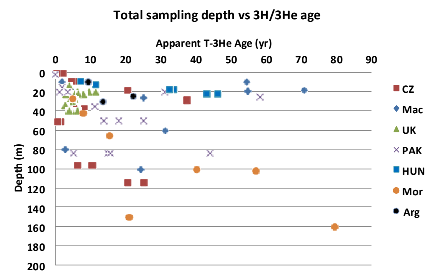
Horizontal transects of T-³He ages with increasing distance from recharge gives groundwater flow rates.

Paleo-temperature (T-³He ages combined with noble gas temperature)

Insights into mixing of waters with different ages

Water Resources Programme

Vertical Profile to Recharge Rate

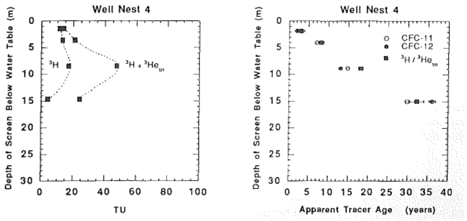


From IAEA's Coordinated Research Projects (2012)

- A systematic increase in age with depth.
- Slope of a depth – age trend provides insights into a vertical component of groundwater flow velocity, which then converted to recharge rate with a knowledge of porosity of the aquifer.

IAEA Water Resources Programme

Vertical Profile to Recharge Rate



Ekwurzel et al., 1994, Water Resource Res, 30, 1693-1708

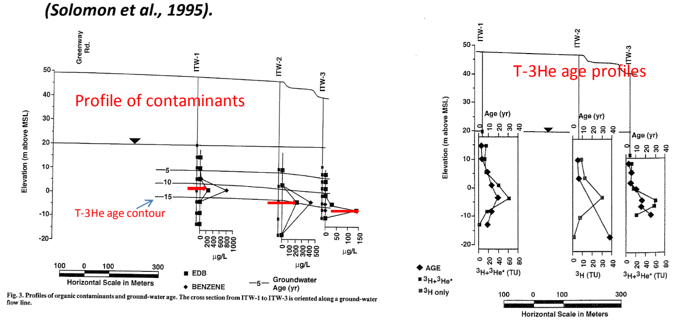
Groundwater ages are vertically stratified.

- Meaning that, if sampled from wells with screens over a large interval, you sampled a mixture of groundwaters with several ages at once.
- Ideally, wells with a very small screen interval (<15 cm) would be ideal to ensure that your sample represents groundwater of single generation.
- At least, sampling would better be done on wells with well-documented depth and screen geometry.

IAEA Water Resources Programme

Use of ^{3}H-^{3}He data to determine the origin and spreading rate of pollutants

Fuel-related organic contaminants in a shallow aquifer of Cap Cod, Massachusetts (Solomon et al., 1995).

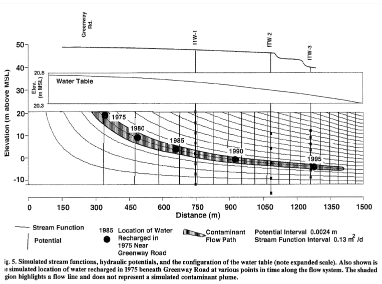


Contaminants flow along a specific horizontal path.
With T-^{3}He ages of same samples, horizontal flow velocity was determined (90 m/year).

IAEA Water Resources Programme

Use of ^{3}H-^{3}He data to determine the origin and spreading rate of pollutants

Fuel-related organic contaminants in a shallow aquifer of Cap Cod, Massachusetts (Solomon et al., 1995).



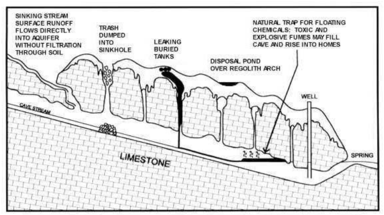
Horizontal Flow Velocity is converted into Hydraulic Conductivity and utilized to refine groundwater flow model.

IAEA Water Resources Programme

Multi Age Tracer Approach to Karst aquifer: Insights into groundwater mixing

Area: Gacka Area, Croatia
Samples: Spring Water (2011 Wet Season and 2012 Dry Season)
Age Tracers: CFC, Tritium & 3He

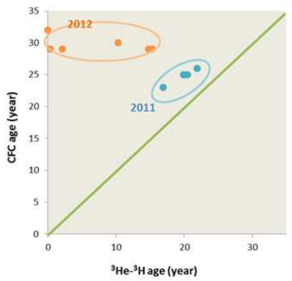
Carried out as a part of IAEA's Coordinated Research Project to test usability of the T-^{3}He method for different hydrologic settings.
Collaborators: Z. Roller-Lutz (Faculty of Medicine, University of Rijeka)



Profile view of karst aquifer showing sources of groundwater contamination

Water Resources Programme

Multi Age Tracer Approach to Karst aquifer: Insights into groundwater mixing



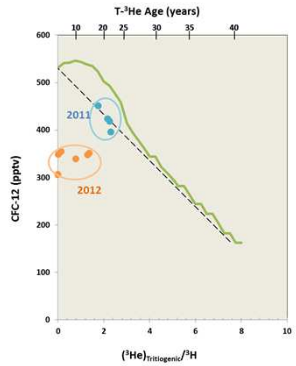
CFC & T-^{3}He ages showed discrepancy – T-^{3}He ages tend to be more variable and younger than CFC ages.

Some wells yielded T-^{3}He ages = 0 years in 2012 (No tritiogenic ^{3}He with helium concentration = air-equilibrated water). (loss of groundwater helium signal)

Between 2011 to 2012, helium seems to be (partially) equilibrated with atmospheric helium. Year 2011 -12 was very dry (less precipitations).

Water Resources Programme

Multi Age Tracer Approach to Karst aquifer: Insights into groundwater mixing



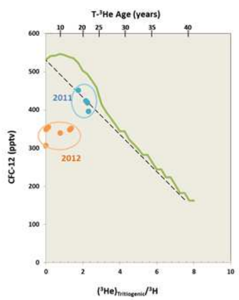
Apparently, Gacka groundwater system cannot be approximated by the "Piston Flow" model (green curve), as expected for karst aquifer.

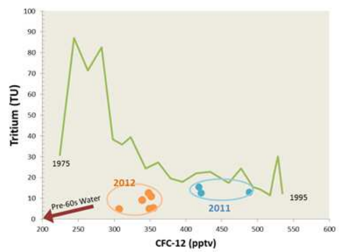
In 2011 (before the dry season), Gacka groundwater is a mixture of young and older (CFC-free) components.

In 2012, partial equilibration of helium with air introduces an additional disturbance in age tracers.

Water Resources Programme

Multi Age Tracer Approach to Karst aquifer: Insights into groundwater mixing





Both CFC and T-3He ages should be regarded as the apparent mean residence time of the karst waters.

Multip-age tracers allowed us to recognize the presence of two water components in this Karst system.

Water Resources Programme

Types of dating tools

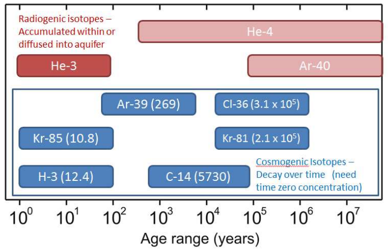
1. Tracer Dating Technique: time vs. tracer's concentration curve to date groundwater age
   - CFC & Tritium
2. Radioactive Decay Dating:
   - ^{3}He-T, ^{14}C, Radio-Kryptons (half-life & concentration of daughter (+ parent) isotopes)
3. Linear Accumulation Dating: Using time-dependent input from external source
   - ^{4}He & ^{40}Ar (ages from concentrations and known input rates).

Water Resources Programme

Linear Accumulation Method

Use age tracers consists of stable nuclides that are produced in the subsurface and accumulate in flowing groundwater.

The isotopes are produced by decay of naturally occurring nuclides with very long half-lives (i.e., decay is slow enough that the parents' abundance, and hence the rate they produce daughter products, is nearly constants).



4He: U & Th decay

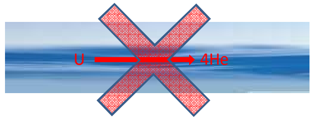
About 10^9 years of $T_{1/2}$

Water Resources Programme

Linear Accumulation Method

Use age tracers consists of stable nuclides that are produced in the subsurface and accumulate in flowing groundwater.

The isotopes are produced by decay of naturally occurring nuclides with very long half-lives (i.e., decay is slow enough that the parents' abundance, and hence the rate they produce daughter products, is nearly constants).



This method is not using parents in water (they are too small to be significant).

4He: U & Th decay

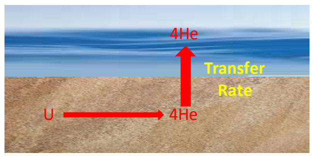
About 10^9 years of $T_{1/2}$

Water Resources Programme

Linear Accumulation Method

Use age tracers consists of stable nuclides that are produced in the subsurface and accumulate in flowing groundwater.

The isotopes are produced by decay of naturally occurring nuclides with very long half-lives (i.e., decay is slow enough that the parents' abundance, and hence the rate they produce daughter products, is nearly constants).

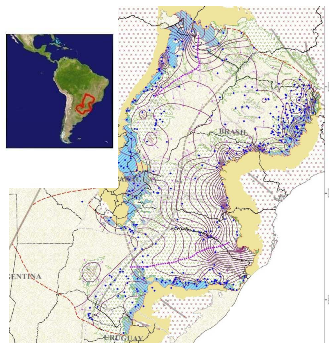


$$Age = \frac{4He\ concentration\ in\ water}{Transfer\ Rate}$$

<u>Fundamentally, different from T-^{3}He dating method</u>

Water Resources Programme

Case Study – Guarani Aquifer



Areal Extent: 1,100,000 Km² (~3000 km N-S) (Argentina, Brazil, Paraguay, Uruguay)

One of the world-largest aquifer holding 37000 km3 of fresh water

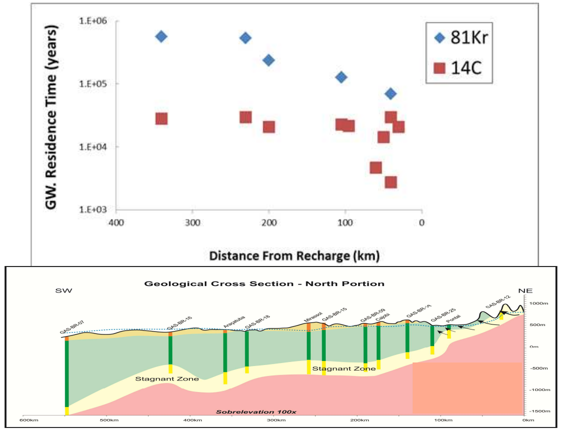
Sufficient supply freshwater to world population for 200 to 2000 years??

Distribution, recharge areas, flow dynamics are not well understood.

Becoming politicized in recent years & control of the resource becomes more controversial.

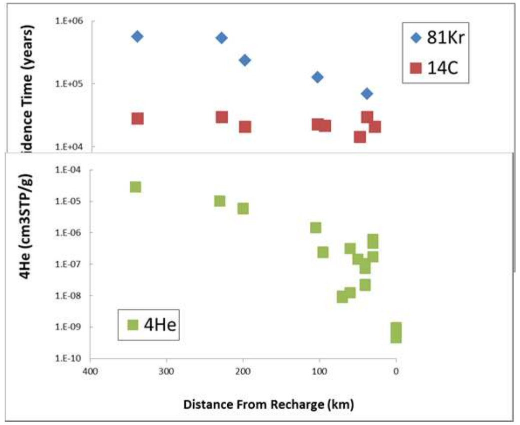
Water Resources Programme

Increasing 81Kr ages along flowpath to the West



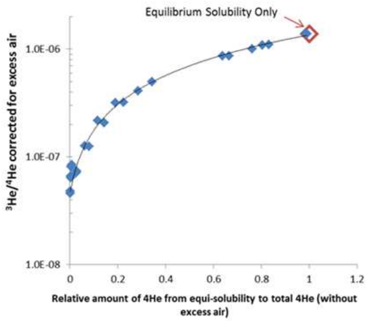
Water Resources Programme

Increasing 81Kr ages along flowpath to the West



Water Resources Programme

^{3}He/^{4}He ratios point to crustal He



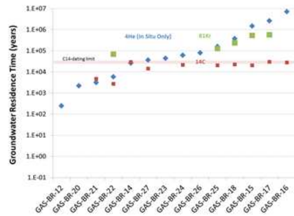
Water Resources Programme

Groundwater Dating by ^{4}He

$$\text{Groundwater Residence Time} = \frac{^4He\ concentration\left(cm^3STP/gram\right)}{^4He\ transfer\ \ rate\ \left(cm^3STP/gram\cdot year\right)}$$

$^4He\ transfer\ rate\ \left(cm^3STP/gram\cdot year\right)$:

- in situ component (U + Th decay within aquifer)
  ~10^{-12} cm^3STP/g/year, significantly overestimated age vs. ^{81}Kr ages



Additional ^{4}He flux is required.

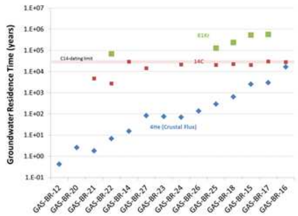
Water Resources Programme

Groundwater Dating by ^{4}He

$$Groundwater\ Residence\ Time = \frac{^{4}He\ concentration\left(cm^{3}STP/gram\right)}{^{4}He\ transfer\ rate\ \left(cm^{3}STP/gram\cdot year\right)}$$

$^{4}He\ transfer\ rate\ \left(cm^{3}STP/gram\cdot year\right)$:

- Crustal Flux (radiogenic ^{4}He produced in crustal basement rocks)
  ~10^{-9} cm^{3}STP/g/year, significantly underestimated age vs. ^{81}Kr



Water Resources Programme

Groundwater Dating by ^{4}He

$$Groundwater\ Residence\ Time = \frac{^{4}He\ concentration\left(cm^{3}STP/gram\right)}{^{4}He\ transfer\ rate\ \left(cm^{3}STP/gram\cdot year\right)}$$

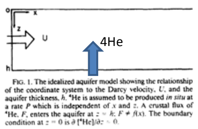
$^{4}He\ transfer\ rate\ \left(cm^{3}STP/gram\cdot year\right)$:

- in situ component (U + Th decay within aquifer)
  ~10^{-12} cm^{3}STP/g/year, significantly overestimated age vs. ^{81}Kr ages
- Crustal Flux (radiogenic ^{4}He produced in crustal basement rocks)
  ~10^{-9} cm^{3}STP/g/year, significantly underestimated age vs. ^{81}Kr

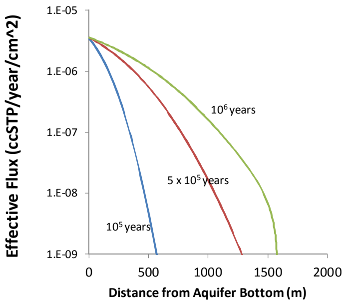
Knowledge on Helium flux specific to study area is a key for dating by ^{4}He.

Water Resources Programme

^{4}He Flux within Aquifer: Model Prediction



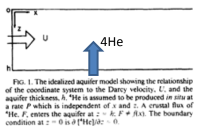
(Torgersen and Ivey, 1985)



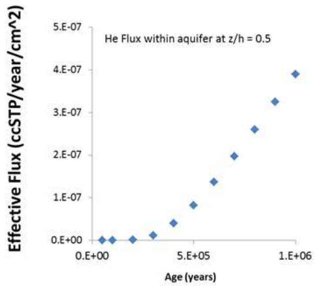
- He-flux within aquifer is depth dependent (Max at the bottom)

Water Resources Programme

^{4}He Flux within Aquifer: Model Prediction



(Torgersen and Ivey, 1985)



- He-flux within aquifer is depth dependent (Max at the bottom)
- He-flux depends also on the age
  - Smaller flux in a rear closer to the recharge area (Younger water).

Water Resources Programme

Groundwater Dating by ^{4}He

$$\text{Groundwater Residence Time} = \frac{^{4}He\ concentration\left(^{cm^3STP}/_{gram}\right)}{^{4}He\ transfer\ \ rate\ \left(^{cm^3STP}/_{gram\cdot year}\right)}$$

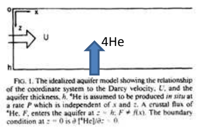
$^{4}He\ transfer\ rate\ \left(^{cm^3STP}/_{gram\cdot year}\right)$:

- in situ component (U + Th decay within aquifer)
  ~10^{-12} cm^3STP/g/year, significantly overestimated age vs. ^{81}Kr ages
- Crustal Flux (radiogenic ^{4}He produced in crustal basement rocks)
  ~10^{-9} cm^3STP/g/year, significantly underestimated age vs. ^{81}Kr

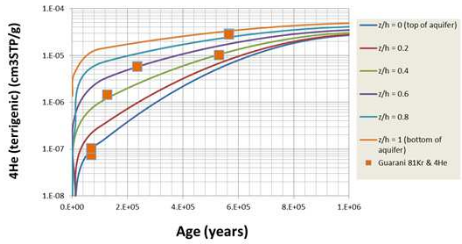
Difficulty in obtaining appropriate helium flux is the major obstacle in ^{4}He dating.

Water Resources Programme

Comparison with GW flow model



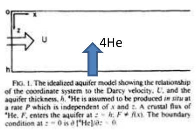
[Torgersen and Ivey, 1985]



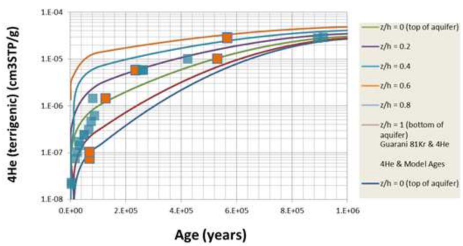
- Observed 4He concentrations and 81Kr age agreed well with groundwater flow model with 4He flux from the aquifer base.
- Might be possible to directly estimate groundwater residence time from 4He concentration without having a difficulty in parameterizing 4He flux distribution (that depends on age and depth).

Water Resources Programme

Comparison with GW flow model



[Torgersen and Ivey, 1985]



- Observed 4He concentrations and 81Kr age agreed well with groundwater flow model with 4He flux from the aquifer base.
- Might be possible to directly estimate groundwater residence time from ^{4}He concentration without having a difficulty in parameterizing ^{4}He flux distribution (that depends on age and depth).
- Further works are in progress in the IAEA.

Water Resources Programme

Types of dating tools

1. Tracer Dating Technique: time vs. tracer's concentration curve to date groundwater age
   CFC & Tritium
2. Radioactive Decay Dating:
   ^{3}He-T, ^{14}C, Radio-Kryptons (half-life & concentration of daughter (+ parent) isotopes)
3. Linear Accumulation Dating: Using time-dependent input from external source
   ^{4}He & ^{40}Ar (ages from concentrations and known input rates).

Water Resources Programme

Concluding Remarks

Each dating technique has advantages and limitations – Important to realize these before using outcomes of analysis as “groundwater ages”. Water is mobile, and tracers are not 100 % conservative – Isotope ages are always considered to be model age and/or apparent age.

Combination of information from multiple isotope methods is desirable.
- If agreed, more confidence
- If not, discrepancy itself can be valuable information to identify processes within aquifers.

In any case, selection of appropriate sampling sites and wells, as well as proper sampling is an important first step for groundwater dating.

Water Resources Programme

IAEA | Water Resources Programme

Activities

Research and development →
- **Coordinated Research Projects (CRP)**
- **Development/adaptation of field and laboratory methods**

Technology transfer → Technical Cooperation Projects

Isotope Hydrology Lab.

Operation of Global Isotope networks and isotope data dissemination

Analytical services/support to labs in Member States
Quality Control of isotope analysis – Intercomparison Exercises
Education and training

Information exchange (Symposia, workshops, sci. meet.)

Partnerships with other UN-Agencies (UN-Water) and other organizations

Water Resources Programme

IAEA | Isotope Hydrology Lab (IHL)

Facility:
- Noble Gas Mass Spectrometry
  - VG5400
  - Helix SFT (will be installed in 2013)
- Stable Isotope-Ratio Mass Spectrometry
  - Delta Plus
- Laser Absorption Spectroscopy Analyzer
  - Picarro L1102 x 1 & LGR DLT 100 x 4
- Liquid Scintillation Counters (Tritium)
- CFC’s and Radon-222
- Radioisotopes (81Kr, in progress)

Water Resources Programme

IAEA | Isotope Hydrology Lab (IHL)

ACTIVITIES:

Capacity Building of Member States
- WR programme is setting up labs in member states
- Training Courses (1-2/year on laser Absorption Analyzer)
- Lecturing courses held in member states
- Day to day supports on external labs

Water Resources Programme

IAEA | Isotope Hydrology Lab (IHL)

ACTIVITIES:

Education/Training Materials, Software

- Training Courses (2/year on laser Absorption Analyzer)
- E-learning
- Day to day supports on external labs

LIMS for Lasers

The IAEA Isotope Hydrology Laboratory (IHL) has partnered with the U.S. Geological Survey to develop a new Laboratory Information Management System (LIMS) for water oxygen and hydrogen isotopes analyses for users of laser absorption spectrographs. *LIMS for Lasers* is a user-friendly MS Access–based instrument and laboratory data management system for all off-axis (OA-ICOS) or cavity ring-down (CRDS) laser absorption spectrographs (LAS) used for δ^2H and $\delta^{18}O$ assays of water. This open-source database software will assist new and current users of LAS instruments to improve their laboratory productivity and QA/QC outcomes, and is available cost-free for all laboratories.