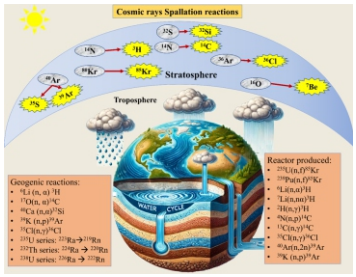
भूजल प्रबंधन के लिए नाभिकीय तकनीक

1

पर्यावरणीय रेडियोआइसोटोप का उपयोग करके भूजल काल-निर्धारण

दीक्षा पंत*, हेमंत मोहोकर एवं के. तिरुमलेश
आइसोटोप जल विज्ञान अनुभाग, आइसोटोप एवं विकिरण अनुप्रयोग प्रभाग, भा.प.अ. केंद्र, ट्रांबे-४०००८५, भारत



विभिन्न न्यूक्लाइडों का उत्पादन

सारांश

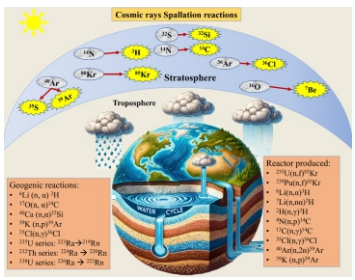
भूजल एक महत्वपूर्ण संसाधन है, और इसके धारणीय प्रबंधन के लिए पुनःभरण दरों, प्रवाह गतिक एवं आवासी काल की उचित समझ की आवश्यकता होती है। पर्यावरणीय रेडियोआइसोटोप महीनों से लेकर लाखों वर्षों तक विभिन्न समयमानों पर भूजल के कालनिर्धारण हेतु शक्तिशाली उपकरणों के रूप में काम करते हैं। यह लेख भूजल आयु निर्धारण में ट्रिशियम (^{3}H), क्रिप्टोन-81/85 ($^{81/85}Kr$), आर्गन-39 (^{39}Ar), सिलिकॉन-32 (^{32}Si), कार्बन-14 (^{14}C), और आयोडीन-129 (^{129}I) सहित प्रमुख रेडियोआइसोटोप के अनुप्रयोग का अन्वेषण करता है। प्रत्येक आइसोटोप भूजल के परिवर्तन में अनूठी अंतर्दृष्टि प्रदान करता है, जो आधुनिक/हाल के (महीनों से वर्षों), पुराने और जीवाश्म भूजल (सदियों से सहस्राब्दियों) के बीच अंतर को सक्षम बनाता है। कई आइसोटोप अनुरेखणों को एकीकृत करके, भूजल प्रणालियों की अधिक व्यापक समझ प्राप्त की जा सकती है, जो जल संसाधन प्रबंधन और संदूषण जोखिम मूल्यांकन में मदद कर सकती है, जो जलवायु परिवर्तन और बढ़ती वैश्विक मांग के सामने भूजल की दीर्घकालिक स्थिरता सुनिश्चित कर सकती है।

Nuclear Techniques for Groundwater Management

1

Groundwater Dating using Environmental Radioisotopes

Diksha Pant*, Hemant Mohokar and K. Tirumalesh
Isotope and Radiation Application Division, Bhabha Atomic Research Centre, Trombay-400085, INDIA



Production of various nuclides

ABSTRACT

Groundwater is a vital resource, and its sustainable management requires a proper understanding of recharge rates, flow dynamics, and residence times. Environmental radioisotopes serve as powerful tools for dating groundwater over various timescales, from months to millions of years. This article explores the application of key radioisotopes, including Tritium (^{3}H), Krypton-81/85 ($^{81/85}Kr$), Argon-39 (^{39}Ar), Silicon-32 (^{32}Si), Carbon-14 (^{14}C), and Iodine-129 (^{129}I) in groundwater age determination. Each isotope provides unique insights into groundwater movement, enabling the differentiation among modern/recent (months to years), old and fossil groundwater (centuries to millennia). By integrating multiple isotopic tracers, a more comprehensive understanding of groundwater systems can be achieved, which can help in water resource management and contamination risk assessment ensuring long-term sustainability of groundwater in the face of climate change and increasing global demand.

KEYWORDS: *Groundwater, Environmental radioisotope*

**Author for Correspondence: Pant Diksha*
E-mail: diksha@barc.gov.in

Background

Water is fundamental to life, supporting ecosystems, biodiversity, and human civilization. However, uneven distribution, population growth, urbanization, and industrial expansion are placing immense pressure on water resources. With global demand expected to exceed supply by 40% by 2030, the risk of water scarcity is rising. Ensuring long-term availability requires sustainable management strategies, particularly in the face of climate change. A deep understanding of aquifer replenishment and residence time is essential for effective policy development. Isotopes play a key role in this process, offering valuable insights into water origins, movement, and recharge while also helping assess climate change impacts.

Radioisotopes are unstable nuclei that decay through alpha, beta, or gamma radiation at a known rate. Once introduced into a system, changes in their concentration provide valuable insights into residence time and environmental processes. Radioisotopes are produced through various natural and artificial processes, including radiogenic decay, geogenic release, cosmogenic interactions, and anthropogenic activities (Table 1). Each process contributes to the presence of radioisotopes in the environment, making them useful for groundwater dating and other scientific applications. Radiogenic produced isotopes are formed by the natural radioactive decay of long-lived parent isotopes (produced at the time of earth's formation) present in the Earth's crust. For example, Helium-4 (^{4}He) is generated from the decay of Uranium-238 (^{238}U) and Thorium-232 (^{232}Th) in rocks, gradually accumulating in groundwater. Radon-222 (^{222}Rn), a decay product of Uranium-238, is released from rocks into groundwater and is commonly used to study water flow. The other way is geogenic production of radioisotopes in the earth crust. These isotopes include Radiocarbon (^{17}O (n, α) ^{14}C), Tritium (^{6}Li (n, α) ^{3}H), Silicon-32 (^{40}Ca (n, α) ^{32}Si), Argon-39 (^{39}K (n, p) ^{39}Ar), and Chlorine-36 (^{35}Cl (n, γ) ^{36}Cl) are naturally in the Earth's crust and are mobilized into groundwater through weathering, leaching, and rock-water interactions (Fig.1). Then, there are cosmogenic produced radionuclides. High-energy cosmic rays interact with atmospheric producing radioisotopes that enter groundwater through precipitation or surface infiltration. Radiocarbon and tritium are dominantly forms in the atmosphere through the interaction of cosmic rays with nitrogen. Other cosmogenic radionuclides include Argon-39, Silicon-32, Chlorine-36, Beryllium-7, Krypton-85 and Sulphur- 35 that are used for dating groundwater on months to millennial timescales (Table 1). The radioisotopes are also added into environment through anthropogenic activities such as nuclear tests, reactor operations, and industrial processes introduce artificial radioisotopes. These include Tritium, Radiocarbon, Chlorine-36, Argon-39 and Krypton-85 (^{85}Kr). All these isotopes provide unique insights into groundwater movement, enabling the differentiation among modern/recent (months to years), old and fossil groundwater (centuries to millennia) (Fig. 2).

The information obtained using isotopic techniques enhance decision-making, improve conservation efforts, and provide a scientific foundation for sustainable water use (IAEA, 2006). Integrating isotopic analysis into hydrological studies enables governments to develop effective policies. Groundwater sustainability depends on understanding residence times to balance extraction with recharge. Determining how long groundwater has been underground helps guide water use, assess contamination risks, and ensure long-term availability.

Isotopes for Very Short Residence Time (days to months)

Understanding groundwater residence time in the range of days to months is crucial for assessing rapid recharge, contamination risks, and groundwater-surface water interactions. It helps detect pollution events, manage drinking water sources, and evaluate aquifer vulnerability. This knowledge supports sustainable water use and protects ecosystems dependent on groundwater flow (Cook & Herczeg, 2000). Radon-222 (^{222}Rn) is a naturally occurring radioactive isotope with a half-life of 3.8 days, produced from uranium-238 decay in rocks and sediments, dissolving into groundwater as it moves through uranium-bearing formations. It is measured using smart radon meter (Fig.3a). Due to its continuous generation and rapid decay, ^{222}Rn is widely used to investigate groundwater-surface water interactions, groundwater flow rates, preferential flow paths and recent recharge events. However, factors such as geological radon sources and degassing influence its effectiveness. Another short-lived isotope used is radium particularly ^{223}Ra (half-life: 11.4 days) and ^{224}Ra (half-life: 3.66 days) for understanding water-rock interactions, transport dynamics, fresh-saline water interactions, residence times, SGD, and mixing processes in aquifers (Moore, 2000). It is measured using radium delayed coincidence counter (Fig. 3b).

Sulfur-35 (^{35}S) is a short-lived radioactive isotope (half-life: 87 days) effective for dating very young groundwater, typically within weeks to a year. It is produced naturally in the

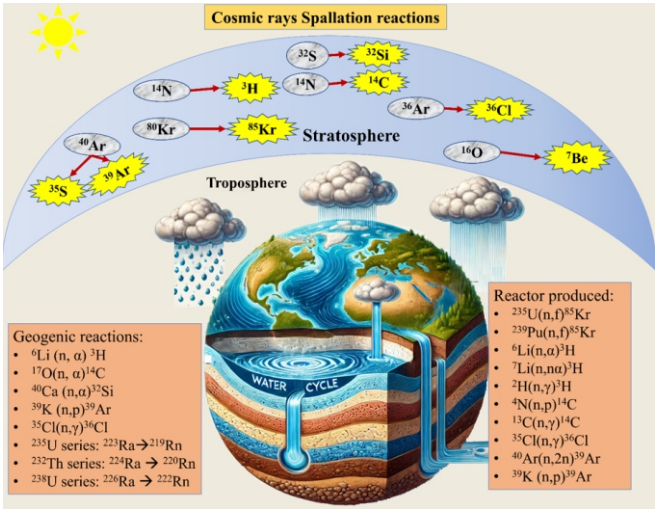


Fig.1: Production of various nuclides.

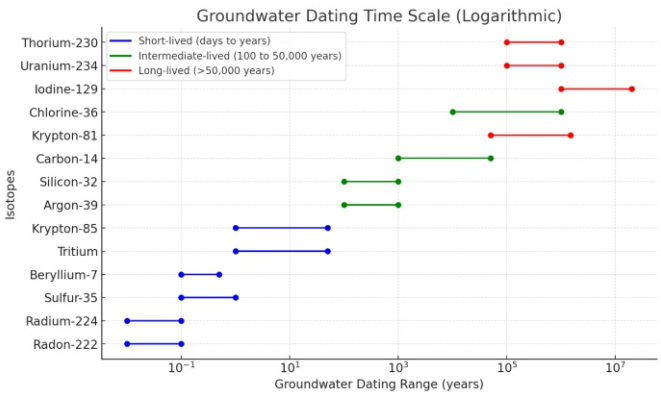


Fig.2: Logarithmic time scale of groundwater dating radionuclides, grouped by short-, intermediate-, and long-lived isotopes.

Table 1: Various radionuclides used for estimation of groundwater residence time.

Radionuclide	Natural Production & Reactions	Reactor Production & Reactions	Half-life	Decay Type	Energy (keV)	Groundwater Dating Range
Radon-222 (^{222}Rn)	Decay of Uranium -238	N/A	3.8 days	Alpha decay	5,590	Days to weeks
Radium-223 (^{223}Ra)	Decay of Uranium -235	Neutron activation: ^{222}Rn(n,γ)^{223}Ra	11.4 days	Alpha decay	5,780	Days to weeks
Radium-224 (^{224}Ra)	Decay of Thorium -232	Neutron activation: ^{223}Ra(n,γ)^{224}Ra	3.66 days	Alpha decay	5,790	Days to weeks
Sulfur-35 (^{35}S)	Cosmic-ray spallation ^{40}Ar(n,α)^{35}S	Neutron activation of Sulfur-34: ^{34}S(n,γ)^{35}S	87 days	Beta decay	167	Weeks to a year
Beryllium -7 (^{7}Be)	Cosmic-ray spallation ^{16}O (p,X)^{7} Be	Proton irradiation of Lithium: ^{7}Li(p,n)^{7}Be	53.3 days	Electron capture	477.6	Weeks to months
Tritium (^{3}H)	Cosmic-ray interaction ^{14}N(n,p)^{3}H	Fission in nuclear reactors, bomb testing	12.3 years	Beta decay	18.6	Years to 50 years
Krypton-85 (^{85}Kr)	N/A	Fission of Uranium-235/Plutonium -239	10.76 years	Beta decay	687	1 to 50 years
Argon-39 (^{39}Ar)	Cosmic-ray interaction ^{40}K(n,2n)^{39}Ar	Neutron activation of Argon-38: ^{38}Ar(n,γ)^{39}Ar	269 years	Beta decay	565	100 to 1,000 years
Silicon-32 (^{32}Si)	Cosmic-ray spallation ^{40}Ar(p,8n)^{32}Si	N/A	172 years	Beta decay	225	100 to 1,000 years
Carbon-14 (^{14}C)	Cosmic-ray interaction ^{14}N(n,p)^{14}C	Neutron activation of Nitrogen-14 in reactors	5,730 years	Beta decay	156	1,000 to 50,000 years
Krypton-81 (^{81}Kr)	Cosmic-ray spallation ^{84}Kr(n,4n) ^{81}Kr	N/A	229,000 years	Beta decay	129	50,000 to 1.5 million years
Chlorine-36 (^{36} Cl)	Cosmic-ray interaction with Argon-40 and neutron activation of Calcium-40: ^{35}Cl(n,γ)^{36} Cl, ^{40}Ca(n,α)^{36}Cl	Neutron irradiation of Chlorine-35: ^{35}Cl(n,γ)^{36}Cl	301,000 years	Beta decay	714	10,000 to 1 million years
Iodine-129 (^{129}I)	Cosmic-ray spallation of Xenon-128: ^{128}Xe(n,γ)^{129}Xe → β^{-} → ^{129}I	Neutron activation of Iodine-128 in reactors	15.7 million years	Beta decay	194	1 million+ years
Uranium-234 (^{234}U)	Decay of Uranium -238	N/A	245,500 years	Alpha decay	4,770	100,000 to 1 million years
Thorium-230 (^{230}Th)	Decay of Uranium -234	N/A	75,380 years	Alpha decay	4,686	100,000 to 1 million years

atmosphere by cosmic ray interactions and enters groundwater primarily through precipitation. It's measured after separation of dissolved sulphur followed by counting in liquid scintillation counter (Fig.3c). Because of its short half-life, ^{35}S is ideal for studying recent recharge, infiltration rates, and rapid groundwater flow in shallow aquifers (IAEA, 2013). A key application of ^{35}S is identifying seasonal recharge patterns. By measuring its concentration in groundwater, one can determine whether water has infiltrated within the past few months, helping assess aquifer replenishment and water sustainability. It is also useful for tracing contaminant movement, identifying sources and timescales of pollution transport in groundwater systems. Beryllium-7 (Be-7) is also applied in short-term groundwater dating due to its 53.3-day half-life. It is produced by cosmic-ray spallation in the atmosphere and attaches to aerosols before depositing via precipitation. Be-7 is particularly valuable in monitoring stormwater infiltration, runoff contributions, sediment transport, and erosion rates, providing insights into hydrological and environmental changes.

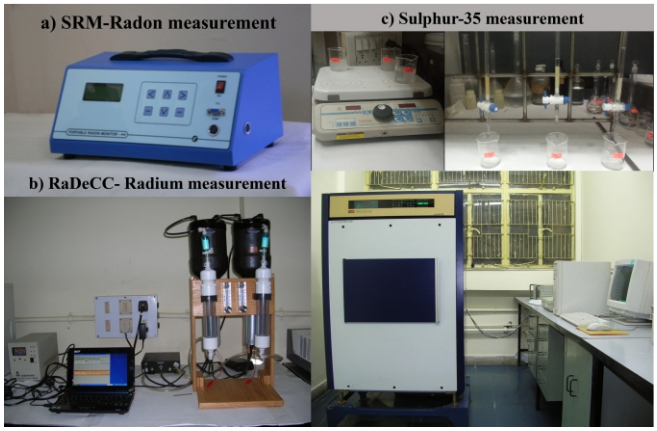


Fig.3: Measurement of isotopes for very short residence time.

Isotopes for Short Residence Time (months to few years)

Tritium (^{3}H) is a radioactive isotope of hydrogen with a half-life of approximately 12.3 years, making it a key tracer in hydrogeological studies (Cartwright & Morgenstern, 2016) for dating young groundwater within a range of years to five decades. It is naturally produced in the upper atmosphere through cosmic ray interactions and enters the hydrological cycle via precipitation. Tritium in groundwater may also be from

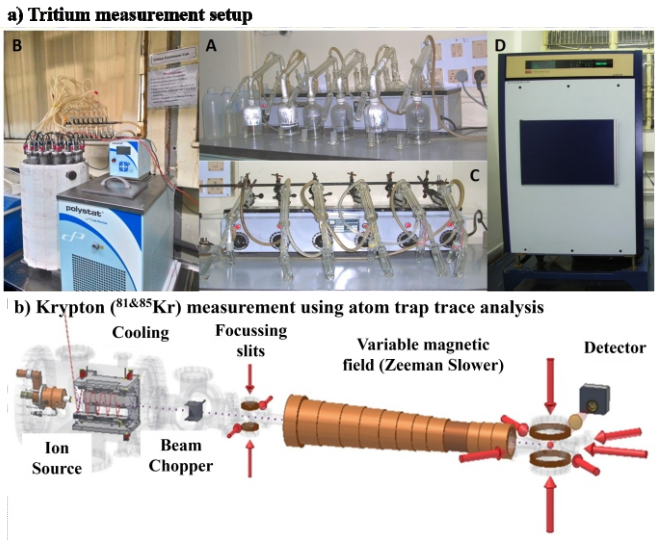


Fig.4: Measurement of isotopes for short residence time.

nuclear weapons testing and anthropogenic activities such as paint industries, nuclear reactors, and atmospheric releases. Tritium concentration in precipitation varies with latitude, geography, and time, with higher levels in the Northern Hemisphere due to more natural production at the poles. Continental precipitation generally has higher tritium concentrations than marine precipitation due to proximity to atmospheric sources and reduced dilution. Due to low natural concentrations, tritium is electrolytically enriched before measurement using a liquid scintillation counter (Fig.4a).

Tritium is particularly useful for estimating recharge rates by tracing precipitation infiltration into aquifers. It also helps track groundwater movement and mixing, providing crucial information about flow dynamics and residence times. This is especially important in aquifers where old and young waters mix due to natural hydrological processes or human activities such as pumping. Tritium enables both qualitative and quantitative groundwater dating, distinguishing modern from older water and estimating recharge times based on tritium decay, aiding hydrological and environmental studies. Models like piston flow, exponential mixing and dispersion models are used for estimating groundwater age using tritium. The piston flow model assumes groundwater moves as a discrete unit through the aquifer without mixing while exponential mixing model applies to unconfined or well-mixed systems, where older and younger water blend, resulting in a distribution of groundwater ages rather than a single value. The dispersion model accounts for flow variations, considering the effects of diffusion and mixing along the flow path. Additionally, the tritium-helium ($^{3}H/^{3}He$) method refines age estimates by measuring helium-3 produced from tritium decay, significantly improving groundwater dating accuracy (Schlosser et al., 1988).

Krypton-85 (^{85}Kr) is an inert radioactive isotope with a half-life of 10.76 years, making it a valuable tracer for dating young groundwater in the range of 1 to 50 years (Ekwurzel et al., 1994). It is an anthropogenic isotope primarily released into the atmosphere from nuclear fuel reprocessing with well-documented atmospheric concentration since the 1950s. However, measuring ^{85}Kr requires specialized noble gas mass spectrometry (Fig. 4b), making it more complex and costly.

Apart from radioisotopes, certain gases are used for residence time estimation in correlation with radioisotopes. These gases, including chlorofluorocarbons (CFCs) and sulphur hexafluoride (Sf6), serve as valuable tracers for young groundwater dating, typically within 10 to 70 years (Solomon & Cook, 2000) their atmospheric histories are well documented.

Isotopes for Intermediate Residence Time (centuries to ten thousand years)

Groundwater residence times of centuries to tens of thousands of years reveal paleoclimate conditions, recharge history, long-term flow patterns, solute transport, and water-rock interactions. They help assess fossil groundwater sustainability and natural geochemical evolution. The most suitable tracers in intermediate time range are Argon-39 (^{39}Ar), Silicon-32 (^{32}Si), and Carbon-14 (^{14}C) (Table 1). Among them, Carbon-14 is the most widely used due to its extensive applicability, well-documented production mechanisms, and established correction models for accurate age determination.

Argon-39 (^{39}Ar) is an inert radioactive isotope with a half-life of 269 years, making it particularly useful for dating groundwater within the range of 100 to 1,000 years (Loosli, 1983a). It is produced in the atmosphere through cosmic ray interactions, subsequently enters the hydrological cycle through gas exchange with the atmosphere. ^{39}Ar is present in extremely low concentrations, making its detection challenging, but the development of Atom Trap Trace Analysis (ATTA) (Fig.5a) has significantly improved detection sensitivity (Jiang et al., 2012). However, due to the technical complexity and high costs of measurement, its application in groundwater studies remains limited. Silicon-32 (^{32}Si) is a lesser-known isotope used for groundwater residence time within the 100 to 1,000-year range (Palcsu et al., 2018). It is produced in the atmosphere by cosmic ray spallation and is incorporated into the hydrological cycle via dissolved silicate minerals in precipitation. However, due to its low abundance and (Fig. 5b) difficulties, its application in groundwater studies is still in its early stages.

Carbon-14 (^{14}C) is the most widely used isotope for dating groundwater with residence times ranging from 1,000 to 50,000 years. It has a half-life of 5,730 years, making it suitable for studying long-term groundwater movement, paleoclimate conditions, and aquifer recharge dynamics (Clark & Fritz, 1997). The isotope is produced in the upper atmosphere through cosmic ray interactions forming radioactive carbon dioxide ($^{14}CO_2$), which then integrates into the biosphere and hydrological cycle through atmospheric exchange and biological activity. ^{14}C in groundwater is measured using Liquid Scintillation Counting (LSC) or Accelerator Mass Spectrometry (AMS). Measurements using LSC involves converting dissolved inorganic carbon into benzene or absorbing carbon dioxide into organic compound (Fig.5c) and detecting beta emissions, requiring large sample volumes and having lower sensitivity. AMS, in contrast, directly counts ^{14}C atoms relative to stable carbon isotopes, allowing for smaller sample sizes and higher precision. However, global variations in atmospheric ^{14}C concentration have occurred due to factors such as solar activity, geomagnetic field fluctuations, and anthropogenic influences, including fossil fuel combustion, geochemical interactions and nuclear testing. When water infiltrates the ground, it can dissolve carbonate minerals, introducing dead carbon into solution, thereby diluting the original ^{14}C activity and leading to age overestimation (Vogel, 1970). There are several correction models that address the issues like the Pearson model, Vogel model, Fontes & Garnier model etc. Additionally, mixing of old and young groundwater complicates dating, as the measured ^{14}C activity represents a composite age rather than a discrete recharge event.

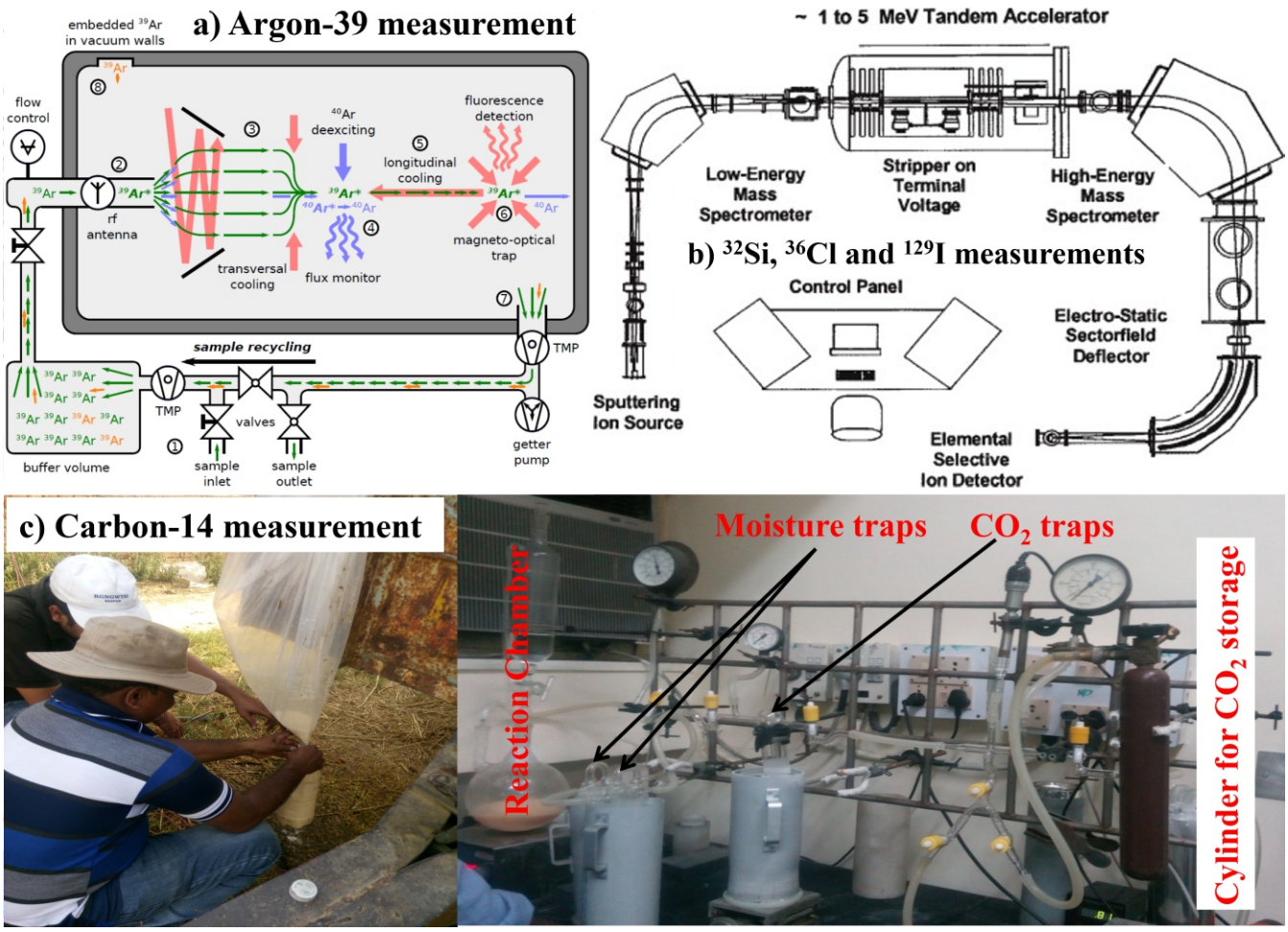


Fig.5: Measurement of isotopes for intermediate residence time.

Isotopes for Long Residence Time (ten-thousand years to million's years)

Groundwater with residence times from tens of thousands to millions of years provides insights into deep crustal fluid evolution, tectonic & geothermal processes, and long-term geochemical & aquifer stability. It supports studies of fossil water reserves and ancient water-rock interactions. Isotopes such as krypton-81 (^{81}Kr), chlorine-36 (^{36}Cl), iodine-129 (^{129}I), and uranium-series isotopes (^{234}U/^{238}U, ^{230}Th/^{234}U, ^{222}Rn) are widely used. ^{81}Kr is an inert noble gas isotope produced by cosmic ray spallation, with a half-life of 229,000 years, making it ideal for dating groundwater between 50,000 and 1.5 million years (Loosli, 1983b). However, measuring ^{81}Kr is complex, requiring Atom Trap Trace Analysis (ATTA), a highly sensitive laser-based technique capable of detecting ultra-low concentrations in groundwater samples (Jiang et al., 2022; Fig.4b). Due to its low natural abundance, large sample volumes of several hundred litres are often needed, which can be challenging. Chlorine-36 (^{36}Cl), with a half-life of 301,000 years, is used to date water between 10,000 and 1 million years. Accelerator Mass Spectrometry (AMS) is the primary method for ^{36}Cl measurement, allowing detection at extremely low concentrations (Fig.5b). However, ^{36}Cl dating is complicated by subsurface production and potential mixing with younger water, leading to age uncertainties. Iodine-129 (^{129}I), with a half-life of 15.7 million years, is another useful isotope for groundwater dating beyond 1 million years, measured using AMS and is particularly valuable in systems with iodine-rich brines. However, anthropogenic sources from nuclear reprocessing and bomb testing have increased ^{129}I concentrations limiting its application for old groundwater dating. Uranium-series isotopes, including ^{234}U/^{238}U and ^{230}Th/^{234}U, are used for dating water up to 1 million years (Osmond & Cowart, 1992). Their use relies on the decay of uranium and thorium isotopes in groundwater, measured using ICP-MS or alpha spectrometry. However, uranium-series dating is affected by chemical interactions with aquifer materials, which can alter isotopic ratios and introduce uncertainty in age estimates. Despite their limitations, these isotopes collectively provide crucial information for understanding long-term groundwater movement, recharge history, and the stability of deep aquifers over geological timescales. The combination of noble gas isotopes, halogens, and uranium-series isotopes enhances the accuracy of groundwater age determinations, supporting sustainable water resource management in arid and fossil aquifer systems.

Conclusion

As water scarcity and contamination become global challenges, the integration of isotope hydrology into water resource management will be essential for ensuring long-term groundwater availability and ecosystem protection. Estimating groundwater residence time helps assess recharge rates, manage water resources, and prevent overextraction. It aids in contamination risk evaluation, differentiates modern from fossil water, and informs climate change impact studies. Accurate dating supports sustainable groundwater management, ensuring long-term water availability for agriculture, industry, and human consumption. This article provides an overview on all the possible isotopes, their production, measurements, their application for dating different time ranges and limitations.

References

[1] IAEA (2006). Isotopes in Water Resources Management: Proceedings of a Symposium. International Atomic Energy Agency, Vienna.

[2] Cook, P.G., & Herczeg, A.L. (2000). Environmental Tracers in Subsurface Hydrology Springer.

[3] Moore, W.S. (2000). Ages of continental shelf waters determined from ^{223}Ra and ^{224}Ra. Journal of Geophysical Research, 105(C9), 22117-22122.

[4] IAEA (2013). Isotope Methods for Dating Old Groundwater. International Atomic Energy Agency, Vienna.

[5] Cartwright, I., & Morgenstern, U. (2016). Using tritium to document changing recharge conditions in the Melbourne region, Australia. Hydrological Processes, 30(24), 4358-4372.

[6] Schlosser, P., Stute, M., Dörr, H., Sonntag, C., & Münnich, K.O. (1988). Tritium/3He dating of shallow groundwater. Earth and Planetary Science Letters, 89(3-4), 353-362.

[7] Ekwurzel, B., Schlosser, P., Smethie, W.M., Plummer, L.N., Busenberg, E., Michel, R.L., & Weppernig, R. (1994). Dating of shallow groundwater: Comparison of the transient tracers 3H/3He, chlorofluorocarbons, and 85Kr. Water Resources Research, 30(6), 1693-1708.

[8] Loosli, H.H. (1983a). A dating method with 39Ar. Earth and Planetary Science Letters, 63(1), 51-62.

[9] Loosli, H.H. (1983b). Krypton-81 dating of old groundwater. Earth and Planetary Science Letters, 63(1), 51-62.

[10] Jiang, W., Ashok, S., Yu, L., et al. (2012). Atom-trap trace analysis of 39Ar for groundwater dating. Physical Review Letters, 106(10), 103001.

[11] Jiang, W., Sturchio, N.C., Lu, Z.T., et al. (2022). Advances in 81Kr dating for groundwater. Geochimica et Cosmochimica Acta, 310, 1-18.

[12] Clark, I.D., & Fritz, P. (1997). Environmental Isotopes in Hydrogeology. CRC Press.

[13] Palcsu, L., Major, Z., Papp, L., & Molnár, M. (2018). Determination of groundwater mean residence time using 32Si dating. Applied Geochemistry, 97, 221-227.

[14] Vogel, J.C. (1970). Carbon-14 dating of groundwater. In Isotope Hydrology 1970 (pp. 225-239). International Atomic Energy Agency, Vienna.

[15] Osmond, J.K., & Cowart, J.B. (1992). Uranium-series isotopes in groundwater. Uranium-series Disequilibrium: Applications to Earth, Marine, and Environmental Sciences, 2nd ed., Oxford University Press.

[16] Solomon, D.K., & Cook, P.G. (2000). 3H and 3He. In Cook, P.G., & Herczeg, A.L. (Eds.), Environmental Tracers in Subsurface Hydrology (pp. 397-424). Springer.