

Application of Nuclear Techniques in Water Quality Assessment

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The total amount of water on this earth is virtually constant but its distribution over time and space varies to a great extent. Wherever people live, they must have a clean and continuous water supply as a primary requirement to the human beings. The assessment of quality, supply, and renewal of resources of water is a well known problem, but it is becoming critical with increasing demand of fresh water due to alarming growth of population and rapid industrialization.

In the past few decades, sophisticated nuclear-hydrological instruments have been developed to measure accurately both radioactive as well as stable isotopes and accordingly various nuclear methods have been evolved. It is therefore, now very easy to solve many hydrological problems related to planning of water resources, agriculture, industry, and habitation using isotope techniques which were very difficult, sometimes impossible to tackle in the past.

Isotopes – Basic

Isotopes are the atoms of an element having same atomic number (Z) but different atomic weight (A). In other words, the atoms of an element having different number of neutrons (N) but same number of protons or electrons are called isotopes. For example, hydrogen has three isotopes having the same atomic number of 1 but different atomic masses or weights of 1, 2 and 3 respectively i.e.,

1_1H_0 - only one proton in nucleus and one electron revolving around the nucleus in an orbit.

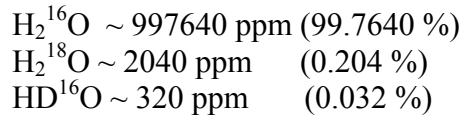
2_1H_1 - one neutron added to the nucleus of 1_1H_0 atom.

3_2H_2 - one more neutron added to the nucleus of 2_1H_1 .

Similarly oxygen has eleven isotopes, ${}^{12}O$, ${}^{13}O$, ${}^{14}O$, ${}^{15}O$, ${}^{16}O$, ${}^{17}O$, ${}^{18}O$, ${}^{19}O$, ${}^{20}O$, ${}^{21}O$ and ${}^{22}O$, but except ${}^{16}O$, ${}^{17}O$, and ${}^{18}O$ all other isotopes are radioactive and their existence in nature is very small. The carbon also has three isotopes ${}^{12}C$, ${}^{13}C$ and ${}^{14}C$.

Over 2000 isotopes of 92 naturally occurring elements have been identified out of which several hundred are stable isotopes. But for hydrological investigations, we talk much about hydrogen and oxygen stable isotopes. As we know water molecule is made up of two hydrogen atoms and one oxygen atom therefore, many combinations (18) are possible out of which ${}^1H^1H^{16}O$, ${}^1H^1H^{17}O$, ${}^1H^2H^{16}O$, ${}^1H^2H^{17}O$, ${}^1H^2H^{18}O$, ${}^1H^3H^{16}O$ and ${}^1H^3H^{17}O$ are

important. The natural occurrence of few very important types of water molecules is given below:



Measurements of stable isotopes are done in terms of abundance ratios i.e. atomic mass of heavy atom to the atomic mass of light atom. For example heavy water $^2\text{H}_2^{16}\text{O}(\text{D}_2^{16}\text{O})$ has a mass of 20 compared to normal water $^1\text{H}_2^{16}\text{O}$ which has a mass of 18. Similarly heavier stable molecule of water D_2^{18}O has a mass 22. This is because of the variation in the number of neutrons.

Isotopic Composition in Precipitation: The isotopic composition of atmospheric moisture and consequently precipitation, exhibits a broad spectrum of spatial and temporal variation. Based on the IAEA/WMO Global Network for Isotopes in Precipitation (GNIP) database on monthly composite samples of precipitation, the following characteristics were identified.

Latitude effect: The heavier isotopic content decreases with increasing latitude. The poleward transport of this vapour results in the rain-out process and consequent depletion in the isotopic ratio of precipitated water.

Continental effect: The heavier isotope ratio decreases inland from the coast (approximately 2‰ per 1000 km). Basically, the rain-out process is responsible for this effect, implying that oceans are the major sources of vapour that precipitates over the continents.

Seasonal effect: Winter precipitations are depleted in ^{18}O and D relative to the summer precipitations. This effect is more pronounced in mid and high latitude regions, due to seasonal variation in total precipitation water, seasonally modulated evapotranspiration over continental regions and seasonally changing source areas of the vapour and different storm trajectories.

Amount effect: An apparent relationship between the amount of rainfall and its isotopic ratio exists, i.e. for greater amount of rainfall; the isotopic ratios are more depleted. This effect is more pronounced during periods of low precipitation, because of the evaporative enrichment of raindrops as a consequence of lower humidity. Conversely, high intensity and heavy rainfall tend to modify the isotopic ratio of the surrounding atmospheric water vapour beneath the cloud base through exchange processes, thereby preserving the in-cloud isotopic signatures.

Altitude effect: When saturated air moves upward, it cools, resulting in condensation and consequent release of heat, which in turn counteracts the cooling. The fractionation of stable isotope taking place due to this adiabatic lapse rate is about $0.6^\circ\text{C}/100\text{m}$. For $\delta^{18}\text{O}$, the temperature dependence during adiabatic cooling is about $0.5\text{‰}/^\circ\text{C}$. This means that

there may be about 0.3‰ variation in $\delta^{18}\text{O}$ per 100 metres variation in altitude. The altitude gradient (per 100 metres) varies between -0.1 ‰ and -0.5 ‰ for $\delta^{18}\text{O}$ and -2.5 ‰ and -4 ‰ for δD .

$\delta^{18}\text{O}$ - δD relationships: The relationship between $\delta^{18}\text{O}$ and δD in freshwaters was noted by Craig as early as in 1953. A best fit line was proposed (Craig's line) for the $\delta^{18}\text{O}$ and δD data of samples collected from different parts of the world:

$$\delta\text{D} = 8 \delta^{18}\text{O} + 10$$

Currently, the equation of the Global Meteoric Water Line (GMWL) developed using the long-term weighted mean hydrogen and oxygen isotopic ratios collected under GNIP database is:

$$\delta\text{D} = 8.2 \delta^{18}\text{O} + 11.27$$

Radioisotopes

The unstable isotopes are the atoms of an element which do not satisfy with the present arrangement of atomic particles and disintegrate by giving out alpha (α), beta (β) particles and/or gamma (γ) radiation etc. and transform into another type of atom. This process continued till the stable nuclide (element) is formed. Because of disintegration or the property of giving out radiation, the unstable isotopes are also called radioactive isotopes.

In early days, the use of radioisotopes was in vogue. Mostly, the radioisotopes, artificially produced in reactor/laboratory, were used as tracers. The radioisotope of hydrogen (tritium) in the form of water molecule ($^3\text{H}_2\text{O}$) and denoted by symbol ^3H or T is still widely used for various hydrological studies. There are other varieties of artificially produced radioisotopes like ^{60}Co , ^{82}Br , ^{131}I , ^{137}Cs , ^{198}Au , ^{226}Ra / ^{241}Am etc. that are used for various hydrological investigations.

However, with the introduction of sophisticated instrumentation, the radioisotopes that occur in traces in the environment and past and parcel of hydrological cycle are used. This has reduced the use of artificial radioisotopes tremendously which may have an unwanted impact of health hazards in the mind of users as well as in the public.

Applications of Isotopes in Hydrology and Water Resources

Applications of isotopes in hydrology are based on the general concept of "tracing", in which either intentionally introduced isotopes or naturally occurring (environmental) isotopes are employed. Environmental isotopes (either radioactive or stable) have a distinct advantage over injected (artificial) tracers is that these facilitate the study of various hydrological processes on a much larger temporal and spatial scale through their natural distribution in a hydrological system. Thus, environmental isotope methodologies are unique in regional studies of water resources to obtain time and space integrated

characteristics whereas the artificial tracers generally are effective for site-specific, local applications. Generally, isotope tracers are not used as an independent tool but to supplement hydrogeological, geophysical and geochemical information for a better understanding of the processes taking place in a hydrological system. Therefore, in hydrological investigations, isotope techniques should be used routinely along with hydrochemical and hydrogeological techniques. As all isotopic, hydrogeological, hydrochemical and hydrodynamic interpretations are space and time related, it is imperative that one should consider all the related aspects of water sampling and prevailing hydrogeological conditions in a study area. A large variety of environmental stable and radioactive isotopes are employed for hydrological studies (e.g., ^2H , ^3H , ^3He , ^4He , ^6Li , ^{11}B , ^{13}C , ^{14}C , ^{15}N , ^{18}O , ^{34}S , ^{36}Cl , ^{37}Cl , ^{81}Br , ^{81}Kr , ^{87}Sr , ^{129}I , ^{137}Cs , ^{210}Pb etc.). However, the stable isotopes have the distinct advantage over injected (artificial) tracers (^3H , ^{46}Sc , ^{60}Co , ^{82}Br , ^{131}I , ^{198}Au , etc.) in that they facilitate the study of various hydrological processes on a much larger temporal and spatial scale through their natural distribution in a system. Earlier-, artificially produced radioactive isotopes were being used with a very limited scope of their use as tracers only, but now environmental isotopes both radioactive and stable isotopes are widely used for a variety of applications with no fear of health hazards. Environmental isotopes are freely available in the atmosphere and automatically injected in to the hydrologic cycle. Therefore, the users have neither to purchase these isotopes nor to inject them in the hydrological system.

The isotope techniques have potential to trace the complete hydrological cycle and processes that take place during the exchange and transition of water from one phase to another phase. Eventually, Isotope Hydrology has developed into a multidisciplinary field. With the development of sophisticated and automated instrumentation for very precise isotopic measurements, new approaches are being developed and new applications and tools are being added to the isotope toolbox. Now Isotope techniques can effectively be used in carrying out various hydrological studies. Specifically, the Isotope can be used for tracing the source, movement, and pollution of ground water. List of application of isotopes in various fields of hydrology and water resources is given below:

- Estimation of age of ground water using ^3H and ^{14}C Dating.
- Estimation of sedimentation rates in water bodies using ^{137}Cs and ^{210}Pb dating techniques.
- Dating of waters and sediments using ^{222}Rn , ^{226}Ra & ^{238}U .
- Estimation of soil erosion in watersheds/ catchments using ^{137}Cs and ^{210}Pb radiometric dating of sediment.
- Estimation of groundwater flow velocity and direction.
- Study of irrigation return flow and recharge to groundwater due to precipitation using artificial tritium.
- Discharge measurement of mountainous rivers using radiotracers like ^3H , ^{82}Br and ^{131}I .
- Seepage/leakage from water bodies using radiotracers like ^3H , ^{82}Br , ^{131}I and ^{198}Au .
- Measurement of soil moisture and density variation, and movement through

unsaturated zone and recharge to groundwater.

- Isotopic variation in space and time in precipitation and other waters- Basic data generation.
- Identification of recharge sources and zones for deeper aquifers.
- Sources of salinity and sea water intrusion.
- Water balance of water bodies.
- Artificial recharge studies.
- Groundwater pollution sources.
- Hydrograph separation into snowmelt, surface runoff and groundwater components.
- Leakage from Dams and Reservoirs.
- Recharge zones of springs in mountainous region.
- Interconnections and interactions of Water bodies (LakeSprings-Aquifers-Rivers).
- Snow and Glacier studies.
- Forest and Ecological studies.
- Watershed management.
- Climate change
- Boron isotopes can be used to identify traces of sewage pollution in groundwater.
- Chlorine isotopes can help in ascertaining the origin of the salinity and velocity of slow moving groundwater systems.
- Methods are now further refined for the measurement of isotopes like ^{85}Kr and ^3He for determining the age of young water and the origins of fluids.

Application of Isotopes in Water Quality Studies

The quality of groundwater is diminished by both organic and inorganic contaminants. Environmental isotopes have much to offer where the contamination of groundwater is of concern. Their analysis can provide information on the origin of contaminants, geochemical reactions and microbiological processes in the subsurface. They are also important in evaluating the sensitivity of groundwater to contamination from surface water, or determining the integrity of aquitard barriers.

Agricultural Watersheds

The application of both fertilizers and pesticides/herbicides threatens the quality of groundwater and surface water in agricultural watersheds. The reliance by farming families and rural communities on potable groundwater supplies compounds the risk. The predominance of septic systems and municipal waste dumps in such watersheds adds a further complication to understanding sources and pathways of groundwater contaminants.

Recharge origin and mixing in groundwater

- Monitoring ^{18}O and ^2H is a fundamental tool to determine the recharge origin and mixing of groundwater in water-supply aquifers.
- The ^{13}C in DIC and DOC distinguishes between sources of carbon, monitors solute pathways, and identifies recharge through cultivated fields. This approach benefits from the difference between C_3 and C_4 type vegetation, and differences in recharge conditions.
- ^{14}C is a less routinely employed isotope in contaminant studies, but offers potential in distinguishing carbon sources in groundwater.
- In this area of investigation, the usefulness of time-series data spanning at least one to several years provides a wealth of information on the dynamics of recharge.

Nitrate and ammonium from fertilizers, feedlots and manure stockpiles

- ^{15}N and ^{18}O in NO_3 and nitrogen compounds to determine sources (fertilizers vs. septic effluent), and to document whether denitrification may be occurring.
- DIC and DOC participate in the denitrification process. Monitoring these species is of primary interest.

Chlorocarbon pesticides

- The use of ^{13}C and ^{37}Cl has yet to be proven, but may help determine the fate of pesticides after application. Distinguishing biodegradation, volatilization and export with foliage are future possibilities.

Septic effluent

- Septic systems are potential sources of DOC, NO_3 , and fecal coliform bacteria in well water. Distinguishing between domestic and agricultural sources relies on the conjunctive use of ^{15}N and ^{18}O in NO_3 . They also are used to show denitrification.
- ^{13}C in DOC and DIC can be important to trace carbon sources.
- Cl^- and potentially ^{37}Cl can signal septic effluent in agricultural watersheds.

Soil deterioration

- Soil salinization and water logging are problems in irrigated fields. Soil acidification by oxidation of high S soils is also a problem for arable lands recovered from coastal areas.
- ^{18}O and ^2H in shallow groundwaters and soil moisture columns can be used to quantify evaporative losses and water budgets.
- ^{34}S and ^{18}O in SO_4^{2-} bring insights into sources of salinity and oxidation processes.
- Carbon cycling and distinguishing active (labile) vs. refractory C in soils is traced with ^{13}C and ^{14}C in DIC and DOC.

Groundwater resources

- In arid regions, as well as temperate zones, groundwater resources are important for irrigation and potable water supply. Over exploitation and supply are at issue.
- ^{18}O and ^2H are important in groundwater provenance studies.
- ^3H , ^{14}C and other dating methods are necessary to assure the long-term viability of exploitation schemes. This is particularly so in and regions where fossil groundwaters are generally used.

Sanitary landfills

In the past, municipal garbage dumps (sanitary landfills are only a recent technology) were unlined and sited with little regard to the local hydrogeology. The consequence is that leachate and gas migration is now threatening groundwater resources. Licensing modern sanitary landfills requires monitoring programs in the event of a failure in the liner or leachate collection systems. Environmental isotopes in conjunction with geochemistry play a role in identifying leachate migration from older, non-engineered sites or modern landfills.

Identification of leachate contamination

- Methane production from DOC is an indication of the strongly reducing conditions in landfill leachate. Both ^{13}C and ^2H in CH_4 are indicators of biogenic methane and can be used to identify the source.
- The strong enrichment in ^{13}C of DIC generated through methanogenesis in landfills is characteristic of leachates. This would contrast with the low values for uncontaminated groundwaters.
- The $\delta^2\text{H}$ content of leachate water can be enriched by extensive methanogenesis, and offers additional evidence of that process.
- $\delta^{15}\text{N}$, $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ can be used to identify the origin of N- and S-species in groundwater where landfill leachate or other sources may occur.
- $\delta^{37}\text{Cl}$ and other isotopes in conjunction with chemistry may prove useful in identifying leachate contamination of groundwater.

Siting of new facilities

- Site evaluations and baseline monitoring are now universally required for licensing new sanitary and other landfill facilities, to demonstrate the security of groundwaters from contamination. The application of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ is necessary to determine groundwater origin.
- Where aquitards are present, ^{18}O , ^2H , ^3H and possibly ^{37}Cl can be used to determine rates of diffusive transport and whether rapid movement from surface through fractures and discontinuities may take place.

Fuel and solvent contaminated sites

Remediation of soils and aquifers contaminated with organic liquids can be achieved through methods such as biodegradation and reductive dehalogenation. Volatilization is discouraged because of restrictions on emissions to the air. Attenuation through sorption is also less desirable since the contaminant is not removed from the aquifer. Isotopes can be useful in monitoring the mechanism, γ -pathway and effectiveness of contaminant loss. They may also help fingerprint the contaminant and establish "ownership" for clean-up.

- Low ^{13}C contents of fuels and solvents produced from fossil fuel contrast with that of DIC in most natural groundwater. The $\delta^{13}\text{C}$ of DIC and DOC can then help identify products of degradation. An approach using carbon mass-balance equations is available to quantify contaminant degradation.
- The build-up of soil CO_2 can often provide evidence for biodegradation. The addition of $\delta^{13}\text{C}$ measurements can help determine the substrate and efficiency of biodegradation.
- Cl^- and ^{37}Cl in degradation products down gradient of treatment walls may prove to be a useful monitoring tool.

Siting hazardous waste facilities

Site characterization for toxic chemical and radioactive waste storage and disposal facilities requires a rigorous evaluation of transport in the geosphere/hydrosphere. Environmental isotopes have been used extensively to characterize groundwater movement and reactions with the far-field geological environment (e.g. IAEA, 1983; Pearson et. al. 1991). The range of applications embraces the entire subject of environmental isotope hydrogeology, including the tracing of groundwater origin and movement, diffusion, age, and solute-specific transport and reaction.

Conclusion

Traditional and recently developed isotopic techniques based on the use of stable isotopes, fallout radionuclides of caesium (Cs), lead (Pb) and beryllium (Be), and compound specific isotope analyses assist in determining agricultural activities that threaten water quality and in identifying hot spots of land degradation in agricultural landscapes.
