

ISOTOPE GEOCHEMISTRY AND ITS APPLICATION IN HYDROLOGICAL STUDIES: A REVIEW

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Abstract

Isotopes may be defined as alternative forms of an element produced by variations in the number of neutrons in nucleus (Richard, 2006). Isotopes in hydrology give a direct insight into the movement and distribution processes within the hydrological system. Water in its natural state contains environmental isotopes and conclusions may be drawn from their abundance variations. Isotopes which are naturally produced and incorporated into the hydrological cycle, are often referred to as "Environmental Isotopes" (Yurtsever and Araguas, 1993). Examples are Oxygen isotopes (¹⁶O, ¹⁷O and ¹⁸O), Hydrogen isotopes (¹H, ²H and ³H), Sulphur isotopes (³²S, ³³S and ³⁴S) etc. Included in this group are also isotopes released due to man-made activities, but distributed in the environment at regional or global scale due to natural processes. The isotopes commonly employed in hydrological studies are the heavy stable isotopes of the water molecule, deuterium and oxygen-18 and the radioactive isotopes, tritium and carbon-14. The stable isotopes are excellent indicators of the circulation of water, while the radioactive isotopes are of special value in detecting the residence time, assuming no contamination of the water has occurred. The applications of these characteristics in connection with surface and groundwater resources are discussed briefly with few case histories.

Keywords: Isotopes, Water resources, Hydrological, Geochemistry, Applications.

1. Introduction

Isotope geochemistry is an aspect of geology that is based upon the study of natural variations in the relative abundances of isotopes of various elements. Variations in isotopic abundance are measured by isotope ratio mass spectrometry, and can reveal information about the ages and origins of rock, air or water bodies, or processes of mixing between them (Nada and Dusan, 2006). Isotope hydrology is the study of the Isotope signatures of water (Nwachukwu et al., 2014).

Isotopes are atoms of the same element that have different numbers of neutrons (Richard, 2006). Differences in the number of *neutrons* among the various isotopes of an element mean that the various isotopes have different masses. The superscript number to the left of the element designation is called the *mass number* and is the sum of the number of protons and neutrons in the isotope.

For example, among the hydrogen isotopes, deuterium (denoted as D or ^2H) has one neutron and one proton. This mass number of 2 is approximately equal to twice the mass of protium (^1H), whereas tritium (^3H) has two neutrons and its mass is approximately three times the mass of protium. Isotopes of the same element have the same number of protons. For example, all isotopes of oxygen have 8 protons; however, an oxygen atom with a mass of 18 (denoted ^{18}O) has 2 more neutrons than oxygen with a mass of 16 (^{16}O).

Isotopes which are naturally produced and incorporated into the hydrological cycle, are often referred to as "Environmental Isotopes" (Yurtsever and Araguas, 1993). Examples are Oxygen isotopes (^{16}O , ^{17}O and ^{18}O), Hydrogen isotopes (^1H , ^2H and ^3H), Sulphur isotopes (^{32}S , ^{33}S and ^{34}S) etc. Included in this group are also isotopes released due to man-made activities, but distributed in the environment at regional or global scale due to natural processes.

Variations in the stable isotopes of water, such as ^{18}O and ^2H , are widely used as environmental tracers in studying hydrological processes (Buttle, 1998, Clark, 1997, Calligaris et al., 2018). Short and long-term isotope signals in precipitation are thus transmitted through the whole (Clark, 1997.) Isotopes of particular interest for hydrological studies include the stable isotopes of water (^{18}O catchment, ^2H), which are incorporated within the water molecule (H_2^{18}O , $^1\text{H}_2\text{H}^{16}\text{O}$), and exhibit systematic spatial and temporal variations as a result of isotope fractionations that accompany water-cycle phase changes and diffusion (Clark, 1997).

The developments in isotope geochemistry have lead to significant advances in the ability to undertake source determinations at contaminated sites; unravel commingled plumes of contaminants; and monitor natural attenuation at contaminated sites.

Isotope techniques are effective tools for fulfilling critical hydrological information needs, such as:

- i. The origin of groundwater;
- ii. The determination of its age, velocity, and direction of flow;
- iii. The interrelations between surface waters and groundwaters;
- iv. The possible interconnections between different aquifers; and

- v. Aquifer characteristics such as porosity, transmissivity, and dispersivity.

The cost of such investigations according to Pradeep et al., (2002) is often relatively small in comparison with the cost of classical hydrological techniques, and in addition isotopes provide information that sometimes could not be obtained by other techniques.

“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. Isotopes employed in hydrological studies could either be stable or unstable (radioactive) isotopes.

Environmental isotopes (either radioactive or stable) have the distinct advantage over injected (artificial) tracers that they facilitate the study of various hydrogeological 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 of groundwater systems. The use of artificial tracers generally is effective for site-specific, local applications” (Pradeep et al., 2002).

This review paper provides an overview in the use of naturally occurring stable isotopes including radiogenic isotopes which are important hydrological tracers for hydrological studies. It is a matter of fact that the isotopic systematics of specific ratios or single isotopic abundances are well known, whereas other isotopes are considered not too exhaustively discussed as no many data are still available. Eventually, new isotopic pairs have recently been applied to the context of environmental geochemistry and can be considered as new frontiers in this important discipline.

2. Occurrence and Characteristics of Environmental Isotopes

The environmental isotopes represent one of the most useful tools in geochemistry to investigate groundwater quality, geochemical evolution, recharge processes, rock–water interaction, and the origin of salinity and contaminant processes (Barbara et al. 2014).

“Environmental isotopes, both stable and radioactive, occur in the atmosphere and the hydrosphere in varying concentrations. So far, the most frequently used environmental isotopes include those of the water molecule, hydrogen (^2H or D, and ^3H) and oxygen (^{18}O), as well as carbon (^{13}C and ^{14}C) occurring in water as constituents of dissolved inorganic and organic carbon compounds. ^2H , ^{13}C and ^{18}O are stable isotopes of their respective elements whereas ^3H and ^{14}C are radioactive isotopes. The stable isotopes are usually measured using an isotope ratio mass spectrometer, in terms of the isotope ratios of the less abundant to more abundant isotope, for example, $^2\text{H}/^1\text{H}$ and $^{18}\text{O}/^{16}\text{O}$ (^1H and ^{16}O being the number of atoms of the most abundant isotopes of the respective elements). The radioactive isotopes are measured either by the counting of their radioactive decays (low-level counting, for example, by liquid scintillation counter) or the number of atoms (using accelerator mass spectrometry) in a given sample”(Pradeep et al., 2002).

2.1 Stable Isotopes

Stable isotopes are naturally occurring isotopes of light elements which do not undergo any decay to produce daughter isotopes (Nwachukwu et al., 2014) for example Nitrogen (^{14}N , ^{15}N), Oxygen (^{16}O , ^{18}O), Sulphur (^{32}S , ^{34}S), etc. Stable isotopes of many different elements are used in hydrology; however, the most commonly used are those of oxygen and hydrogen. Variations in stable isotope ratios of natural compounds are governed by chemical reactions and phase changes because of the energy difference between chemical bonds involving different isotopes of an element. Such energy differences are caused by the relative mass difference between isotopes (Pradeep et al., 2002). The stable isotopes of light elements show greater variations because they have larger relative mass differences. For example, the magnitude of variations in $^2\text{H}/^1\text{H}$ is greater than in $^{18}\text{O}/^{16}\text{O}$ because the mass difference between ^2H and ^1H is 2:1 while the same for ^{18}O and ^{16}O is 1.1:1. Stable isotope ratios in hydrology are conventionally reported as per mil (‰) deviation from those of a standard using the δ (delta) notation:

$$\delta\text{‰} = \left(\frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \right) \times 1000 \dots \dots \dots 1$$

where R is isotope concentration ratio ($^2\text{H}/^1\text{H}$, $^{13}\text{C}/^{12}\text{C}$, $^{15}\text{N}/^{14}\text{N}$, $^{18}\text{O}/^{16}\text{O}$, $^{34}\text{S}/^{32}\text{S}$) of a sample or a standard.

Table 1: Environmental Stable Istopes and their Applications.

(After Archana et al., 2014)

Isotope	Ratio	% Natural abundance	Reference (ppm)	Commonly measured phases	Application in hydrology
^2H	$^2\text{H}/^1\text{H}$	0.015	VSMOW (155)	$\text{H}_2\text{O}, \text{CH}_4$	Origin of water
^{13}C	$^{13}\text{C}/^{12}\text{C}$	1.11	VPDB	CO_2 , Carbonates	Carbonates source, Groundwater Dating
^{15}N	$^{15}\text{N}/^{14}\text{N}$	0.366	Air N_2 (3677)	$\text{N}_2, \text{NH}_4\text{NO}_3$	Source of pollution
^{18}O	$^{18}\text{O}/^{16}\text{O}$	0.204	VSMOW (2005)		Origin of water
^{34}S	$^{34}\text{S}/^{32}\text{S}$	4.21	CDT		Origin of salinity, Redox condition of aquifer
^{37}Cl	$^{37}\text{Cl}/^{35}\text{Cl}$	24.23	SMOC (0.324)	Saline waters	Source of pollution
^{87}Sr	$^{87}\text{Sr}/^{86}\text{Sr}$	07.00	USGS Tridacna	Solution	Provenance of water
^{11}B	$^{11}\text{B}/^{10}\text{B}$	80.1	NISTRM 951 – (Sodium borate)	Solution	Source of pollution

Table 2: Stable Isotope in Hydrological Studies and their Applications.
 (After Yurtsever and Araguas, 1993)

Isotope	Potential Application
Oxygen – 18 (¹⁸ O) and Deuterium (² H)	<ul style="list-style-type: none"> - Genesis of water - Source of replenishment to groundwater and process tracing - Component tracing – mixing proportion of different components of flows; hydraulic interconnections - Paleohydrological indicators - Geothermal activity
Carbon – 13 (¹³ C)	<ul style="list-style-type: none"> - Origin of carbon compounds - Correction for 14C age dating
Sulphur – 34 (³⁴ S)	<ul style="list-style-type: none"> - Natural tracer for sulfates in water - Identification of source pollution
Nitrogen – 15 (¹⁵ N)	<ul style="list-style-type: none"> - Origin of nitrates - Identification of sources of pollution

2.2 Radioactive (Unstable) Isotopes.

Radioactive (Unstable) Isotopes are nuclides that have unstable nuclei that decays, emitting alpha, beta, and sometimes gamma rays (Nwachukwu et al., 2014). Examples are decay of radioactive ¹⁸F to stable ¹⁸O, ¹⁴C to stable ¹⁴N, etc. Among the environmental radioisotopes, tritium and carbon-14 have found the widest application in groundwater studies. Radioactive isotopes (also called radioisotopes) occurring in groundwater originate from natural and/or artificial nuclear processes. Cosmogenic radioisotopes are produced in nuclear reactions between the nucleonic component of cosmic radiation and the atmosphere. Anthropogenic radioisotopes are produced in nuclear bomb tests and nuclear reactors. The concentrations of all these radioisotopes in groundwater are very low and usually measured by counting their decay rate A in a given sample. The number of atoms N in a sample can be derived from A by the relationship:

$$A = N \cdot \lambda \dots \dots \dots 2$$

where λ , the decay constant, is related to half-life $T_{1/2}$ by the equation $\lambda = \ln 2 / T_{1/2}$. For long-lived radioisotopes such as ³⁶Cl and ¹²⁹I, the decay rate becomes immeasurably small. In these cases the number of atoms has to be measured directly, which is possible by the accelerator mass spectrometry (AMS) technique. The AMS technique is superior to the conventional decay counting for ¹⁴C, since AMS requires a very small sample size (up to 1000 times less than conventional requirement) for analysis.

Table 3: Environmental Radioisotopes and their Applications. (After Archana et al., 2014)

Isotope	Half life (years)	Type	Energy (MeV)	Applications in hydrology
Tritium (^3H)	12.3	β	0.019	Young groundwater dating
Carbon (^{14}C)	5730	β	0.156	Old groundwater dating
Chlorine 36 (^{36}Cl)	3.1×10^5	β	0.714	Very old groundwater dating
*Cesium – 137 (^{137}Cs)	30	β	0.661	Sediment dating

Table 4: Radioactive Isotopes in water resources studies (After Yurtsever and Araguas 1993)

Isotope	Half-life (years)	Source (origin)	Present Limitations
85Kr	10.8	Nuclear reactors	Sampling, counting
3H	12.43	Cosmic rays Thermonuclear Nuclear reactors	
32Si	100	Cosmic rays Thermonuclear Crustal (?)	Initial activity Sample size counting time
39Ar	269	Cosmic rays Crustal	Sample size counting time
14C	5730	Cosmic rays Thermonuclear Crustal	Complex geochemistry Isotope exchange processes
81Kr	210000	Cosmic rays	Analytical
234U	250000	Decay chain interactions	Initial activity
36Cl	306000	Cosmic rays Nuclear tests Crustal (?)	Initial activity (?) Sources and in-situ production (?)

3. Overview of Application of Isotope Geochemistry in Hydrological Studies.

Application of isotopes includes tracing the evolution of a water mass from its origin as precipitation, through its recharge processes, and ending at its appearance in an aquifer. Besides this, isotopes can be used to determine the origin of specific solutes in groundwater. This type of application commonly involves stable isotopes. The other main class of isotope applications was derived from the decay of radioisotopes. Unlike stable isotope applications that shed light on geochemical evolution in aquifers, radioisotopes are primarily used to define the relative or absolute age of water in an aquifer. Methodologies based on the use of isotopes in a full spectrum of hydrological problems encountered in water resource assessment, development, and management activities are already scientifically established and are an integral part of many water resource investigations and environmental studies. The concept of “Tracing” is applied for these methodologies, in which either naturally occurring isotopic species (environmental isotopes) or intentionally introduced tracers are employed. A variety of well-established and field-verified isotopic techniques offer useful tools, with proven technological and economic benefits for water resource assessment, development, and management.

3.1 Groundwater Origin, Recharge, and Mixing Processes (Groundwater movement)

One of the most typical applications in isotope hydrology is the identification of recharge areas of underground aquifers by comparing the isotopic signatures of precipitation and with those of groundwater collected from springs and/or wells.

Spatial variability of the $\delta^2\text{H}$ or $\delta^{18}\text{O}$ values in precipitation reflects the combination of source-region labeling, rainout, and recycling effects that affect air masses bringing vapor to different geographic regions. The isotopic compositions of precipitation have been mapped at several scales: global distribution (Bowen, and Revenaugh, 2003), regional scale (Longinelli, and Selmo, 2003), and detailed scales (Liotta et al, 2013; Minissale and Vaselli, 2011) and references therein proposed an alternative method based on indirect measurements using karst springs as natural pluviometers in Italy. They recalculated the average elevations of their recharge areas by shifting the original altitude values of spring waters along the 0.2 ‰ line, proposed by Longinelli and Selmo, as representative of the mean isotopic altitude gradient ($\Delta\delta^{18}\text{O}$) for the Italian meteoric precipitations.

The determination of the origin of groundwater as well as the manner and the rate of recharge and discharge is of major importance for its management especially in waterless areas (Chen et al., 2012 and Yin et al, 2010). The development of tracer techniques using stable isotopes enables approaches to groundwater movement in many regions (Lorenzen, et al., 2011).

3.2 Groundwater Salinization (Water Quality)

Groundwater salinization in coastal regions is frequently observed in confined aquifers as well as in unconfined aquifers. In the case of unconfined aquifers close to coastal regions, water

salinization is, as previously mentioned, usually induced by seawater intrusion relative to a decline in the piezometric level, which is commonly associated with excessive pumping (overexploitation) of groundwater. In the case of coastal confined aquifers, the groundwater system is generally isolated from seawater by confining bed of clay-rich sediments, which were mostly deposited in the latest transgressions. Yamanaka and Kumagai (2006) used a combination of $\delta^{34}\text{S}_{\text{SO}_4}$ values (ranging from +1.2 to +79.5‰) and chemical compositions of brackish groundwater to examine the provenance of salinity in a confined aquifer system in the SW Nobi Plain (central Japan). They highlighted that water chemistry was explained by sulfate reduction in combination with the mixing of two types of seawater: (i) present seawater and (ii) SO_4 -free seawater, with the fresh recharge water. In particular, the $\delta^{34}\text{S}_{\text{SO}_4}$ values showed that present and fossil seawaters were responsible at most of 10.7 and 9.4% of the brackish groundwater volume, respectively. Deterioration of the quality of groundwater in urban areas has become a major environmental concern worldwide. In this respect, researchers have applied $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ since they have a distinctive isotopic composition to identify pollution sources. Cortecchi et al. (2002) investigated the $\delta^{34}\text{S}_{\text{SO}_4}$ isotopic signature of the Arno river (northern Tuscany, Italy) and its main tributaries in order to constrain the areal distribution of the anthropogenic contribution across a heavily industrialized and densely urbanized territory, where the human load increases downwards from the Apennine ridge to the Tyrrhenian sea coast. These authors observed that the $\delta^{34}\text{S}_{\text{SO}_4}$ values from natural inputs were ranging approximately between 15 and +4‰, likely related to the oxidation of pyrite disseminated in bedrocks, and $\delta^{34}\text{S}_{\text{SO}_4}$ values between +15 and +23‰, as a result of dissolution processes of evaporitic rocks. Conversely, the sulfur isotopic signature associated with anthropogenic sources (possibly in the chemical forms of Na_2SO_4 and FeSO_4) was characterized by $\delta^{34}\text{S}_{\text{SO}_4}$ values varying between 1 and 8‰.

Urban groundwater contamination problems are becoming increasingly recognized in all Asian megacities (Hosono, T., et al. 2011). In the Taipei (Taiwan) urban area, one of the most densely populated areas in the world, the investigation of the hydrogeochemical groundwater characteristics and the causes of pollution are subjects of prime importance for water resource preservation in the Pacific island. Hosono et al., explored the $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ isotope variability with the aim of understanding the subsurface nature and environmental status of such area. Importantly, they isotopically recognized possible sources, which were affecting the Taipei groundwater system. Within the analyzed data, the sulfate isotopic compositions of waters reacted with chemical fertilizers showed that the $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ values were ranging from 5.0 to +14.4‰ and from +13.1 to +25.7‰, respectively.

3.3 Tritium (^3H) and Carbon-14 (^{14}C) (Water Quality and Pollution).

The environmental radioisotopes of ^3H and ^{14}C have transient concentrations in the hydrological system due to both their radioactive decay properties (which is a function of time) and also variable input - concentrations. This facilitates the study of water movement dynamics in the "time" domain. In general, the basic information to be obtained from these isotopes refers to "travel time" of water within a given system and/or to its distribution. In the case of tritium, it can be readily used for qualitative (or semi-quantitative) assessment of the presence

of recent recharge to groundwater systems, since the history of the tritium concentrations in the precipitation is fairly well defined. Groundwater containing measurable tritium concentrations provides clear evidence of recharge occurring into the system during the last three to four decades. The case of absence of tritium, however, could be indicative of either recharge being not significant during the above cited period, or the travel times involved in the system being longer than the time required for the decay of the isotope during its transport. One of the most important contributions of environmental tritium has been the study of moisture movement in the unsaturated zone as a means of estimating the amount of direct rainfall recharge to unconfined aquifers. The basic principle underlying this application is to detect the 1963 tritium peak in the vertical moisture profile in the unsaturated zone so that the moisture stored above the location of the peak would be direct measure of the replenishment rate. One of the earlier applications of the method was in a sand dune area at Dahna, Saudi Arabia (Dinçer, 1974). The radioactive isotope ^{14}C , is also naturally produced in the atmosphere by cosmic radiation. It is readily oxidized to carbon dioxide and enters into the carbon cycle. Its natural production is rather constant and its input to hydrological systems can be assumed to be steady-state for practical purposes. The concentration of C is expressed as "percent of the ^{14}C of Modern Carbon" (pmc). It has a half-life of 5730 years. Unlike tritium, ^{14}C is not a conservative tracer providing direct indication of the travel time, due to complex chemical reactions involved during the transport process. The concentration of this isotope in water is often measured as the ^{14}C activity in the Dissolved Inorganic Carbon (DIC), which is altered due to interactions of water with the aquifer matrix. Various chemical and isotopic models have been suggested to account for these chemical reactions as to arrive at true travel time estimates of the water, rather than the apparent value (Fontes, 1983). One of the simplest approaches is based on the use of ^{14}C content of the DIC, so that the chemical dilution of C activity due to water-matrix interaction is accounted for, and the initial ^{14}C activity (C_0) is estimated (Salem et al, 1980). Furthermore, physical retardation processes which may possibly occur due to diffusion into aquitard porous matrix in such slow moving systems, may also add uncertainty to the estimates of groundwater travel times based on ^{14}C isotope (Sudicky and Frind, 1981). Most of the other environmental radioactive isotopes are of potential use in determination of the groundwater travel times over different time scales, but their routine applications are presently hindered due to either analytical efforts required or to lack of understanding of their natural production rates in different hydrogeological conditions.

3.4 Organic Contaminants (Water Quality)

Groundwater contaminations with organic pollutants have become a global environmental problem, especially in industrialized countries. Organic compounds are released into the subsurface in various ways (e.g. accidental spills, improper disposal methods, leaking underground storage tanks). The fate and behaviour of these compounds in the soil and groundwater media depends on a number of physicochemical and biological processes. Each process defines an independent set of compositional and isotopic changes. The fact that stable carbon and chlorine isotope compositions of organic chemicals vary depending on the manufacturer and time-frame that they were produced (factors include the conditions and the pathways used to synthesize the compound) allows to identify sources of a chemical or to trace the time of contaminant release in the environment. This has been found for polycyclic

aromatic hydrocarbons (PAHs) (O'Malley et al, 1996), polychlorinated biphenyls (PCBs) (Drenzek et al, 2001) methyl tert-butyl ether (MTBE) (Smallwood et al, 2001), chlorinated ethenes (Jendrzewski et al, 2001) and BTEX (Benzene, Toluene, Ethyl-benzene, Xylenes) compounds (Dempster *et al.*, 1997). In order to reliably determine that two field samples are isotopically distinct, differences in isotopic values of not less than 1.0 ‰ (or ± 0.5 ‰ precision on each $\delta^{13}\text{C}$) are required. Isotopic composition of a contaminant fractionated during (bio)chemical transformation has been used to assess in situ biodegradation of organic contaminants in groundwater, since the isotopic enrichment of the residual pollutant is the best evidence to demonstrate (bio)degradation of these compounds. Isotope data are usually evaluated using the Rayleigh equation to estimate the extent of contaminant biodegradation or the first-order rate constants, assuming that the change in the average isotopic signature is subject to very robust fractionation. However, the Rayleigh equation is developed for homogeneous systems while in the subsurface, contaminants can migrate at different velocities due to physical heterogeneity. This approach leads to a systematic underestimation of the actual value due to the fact that it does not accommodate for the subsurface physical heterogeneity of field sites. A substantial systematic effect occurs especially for the quantification of the first-order rate constants (up to 50 % underestimation of actual rate), while it is relatively small for the quantification of biodegradation (<5 % underestimation of actual degree of biodegradation) (Abe and Hunkeler 2006). Further implications for practical application of isotope studies in contaminated aquifers are the processes of natural attenuation that involve small isotope fractionation, such as mixing, sorption (Slater et al., 2000) or evaporation (Harrington *et al.*, 1999), and may confound quantification of a fractionating degradation processes using a simple streamline-Rayleigh approach (Kopinke *et al.*, 2005). Although measured isotope ratios may, under special circumstances, overestimate the extent of degradation, they will not overestimate the extent of net removal from the aquifer. Thus, isotopic analysis can offer definitive demonstration of the degradation.

3.5 Water Quality and Pollution.

Pollutants in surface water and groundwater come from various sources such as agriculture, industry, or human waste or may be present naturally due to geochemical processes taking place in aquifers. Agriculture, industry and households each produce different kinds of pollutants. By studying the chemical and isotopic composition of a pollutant, scientists can determine its origins (Laura Gil/IAEA). For example, nitrate ion (NO_3^-), which is made up of nitrogen and oxygen, is a common pollutant. Nitrogen has two stable isotopes of different weight. This difference in weight is not the same in human waste and in fertilizers. Fertilizers use nitrogen from the air, whereas humans and animals go through a biological process that changes nitrogen into different forms. As a result, pollutants derived from various sources can be identified based on these isotopic weight differences (Laura Gil/IAEA).

3.6 Origin and Transport of Water in the Water Cycle

Every water molecule (H₂O) is made of two hydrogen (H) atoms and one oxygen (O) atom, but these are not all the same: some atoms' isotopes are lighter and some are heavier. Scientists use precise analytical equipment to measure these tiny weight differences in water samples.

As water evaporates from the sea, the molecules with lighter isotopes tend to preferentially rise, forming clouds with specific isotopic signatures. These clouds have a mix of water molecules that fall in the form of rain. The water molecules with heavier isotopes fall first. Then, as the clouds lose these heavy isotopes and move further inland, lighter isotopes fall in a greater proportion. As water falls to the earth, it fills lakes, rivers and aquifers. By measuring the ratio between heavy and light isotopes in these water bodies, scientists can decipher the origin and movement of water.

3.6 Groundwater Age.

Isotopes are the most direct and powerful tools available to estimate the age, vulnerability and sustainability of water resources. When the groundwater in an aquifer is 'old', this means that the water flow is slow and that the aquifer can take a long time to replenish. When young, groundwater is easily and quickly renewed by rainwater, but can also be easily affected by pollution and changing climatic conditions. In hydrology, some naturally occurring radioactive isotopes present in Water, such as tritium (³H), carbon-14 and (¹⁴C) noble gas radioisotopes, are used to estimate groundwater age. Because these isotopes decay over time, their abundance decreases as the years go by. Higher values mean 'younger' water, while lower values mean 'older' water. For example, groundwater with a detectable amount of tritium may be up to around 60 years old, whereas groundwater with no tritium must be older. Carbon-14 is used for water up to 40 000 years of age and krypton-81 for water that can be up to a million years old.

4.0 Case Histories

4.1 Case History 1

A study on use of environmental isotopes to understand groundwater recharge in Abuja, Nigeria, Dan-Hassan et al., (2016) found that the water in the acquired are of recent and similar recharge conditions. The area studied covers an area of about 5,000Km² in the central part of the Federal Capital Territory, Abuja, Nigeria, stretching along a NE-SW axis, cutting across geological, geomorphological and geopolitical boundaries of the territory. The aquifer systems in the study area are formed by weathered and fractured basement except in the southwestern part, which is formed by the sandstones of the Bida Basin. Eleven groundwater and one rain water samples were collected and analyzed for stable isotopes of deuterium (²H) and Oxygen-18 (¹⁸O) and radioactive isotope of tritium (³H), according to standard methods.

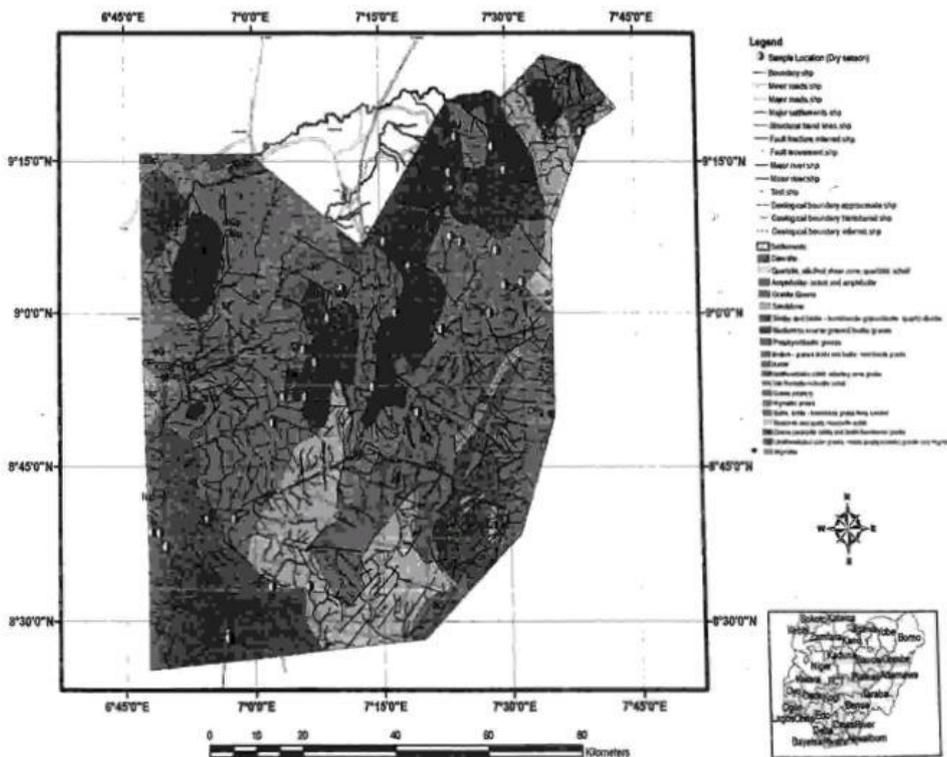


Fig. 1: Geological map of FCT, Abuja (Geological map modified after NGSA, 2004).

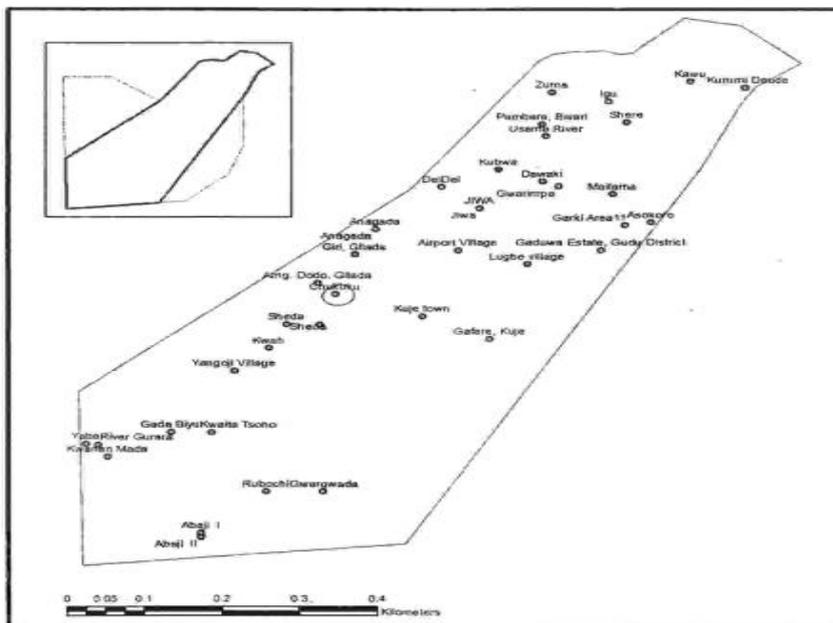


Fig.2: Map of the study area within the FCT showing sampling locations (Dan-Hassan et al., 2016).

Results of the isotope analyses revealed that the measured $\delta^2\text{H}$ values of the groundwater samples range from -17.1 to -14.3‰ while that of $\delta^{18}\text{O}$ range from -3.53 to -2.59‰. The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ diagram shows that the water types originated from precipitation as the samples

plot around the Global Meteoric Water Line (GMWL) with a deuterium excess in the range of 10 ± 2.7 . This indicates similar recharge conditions and an isotopic enrichment by evaporation. Tritium (^3H) concentration for the groundwater samples varies from 2.3 to 5.0 TU with a mean of 3.56 TU while that of the only rainwater sample was 4.85 TU. Applying qualitative age categorization, the study concluded that the range of tritium values depicts active recharge and recent groundwater.

4.2 Case History 2

In another related study by Oteze (1989) on the environmental isotope hydrology of the main Rima Aquifer waters of the Sokoto basin, Nigeria has shown the Rima aquifer is not of modern recharge. During the study water samples were collected from the main Taloka aquifer from six sample locations for Tritium, Deuterium and Oxygen-18 analyses. While four samples were obtained for ^{13}C and ^{14}C analyses. The locations chosen were Jega, Tambawel, Marnona, Wurno, Goronyo, and Chiadawa. The isotopic studies carried out (^{14}C , ^{13}C , ^{18}O , ^2H , and ^3H) on the water samples from the six locations show that waters in the Taloka aquifer were recharged more than 40,000 years ago.

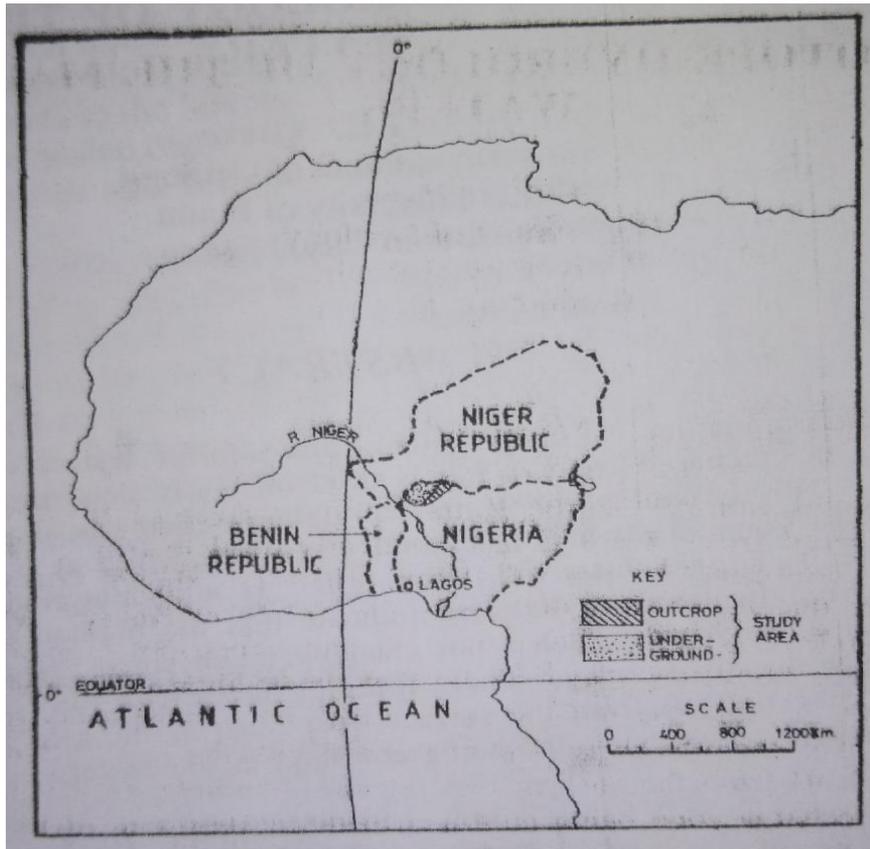


Fig. 3: Location map of the Rima Group Formations (Oteze, 1988).

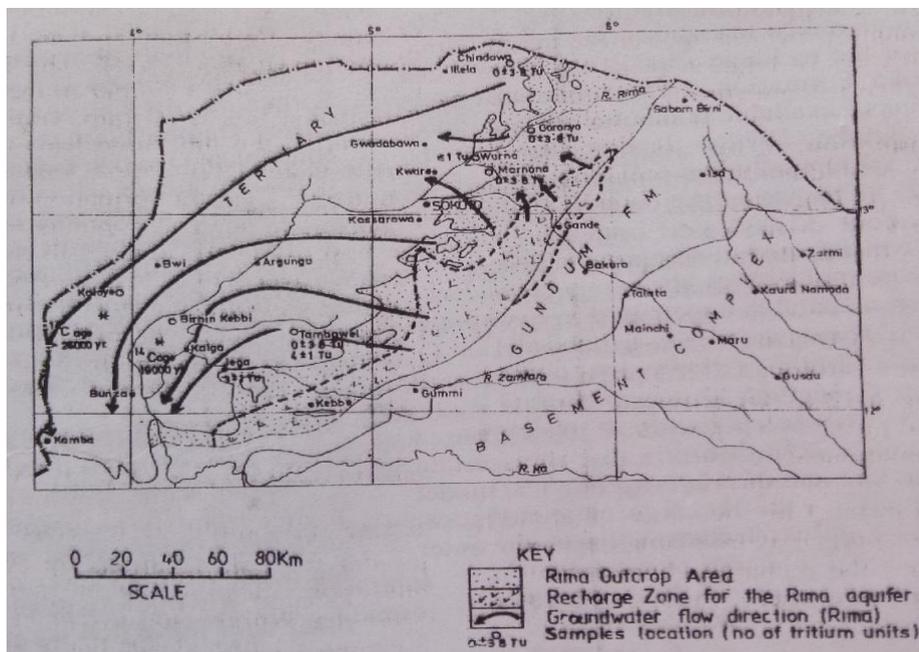


Fig. 4: Hydrogeologic map of the Rima Aquifer (Oteze 1989)

4.3 Case History 3

Archana, S.D. et al, (2014) in another Groundwater pollution studies: Isotope hydrochemical investigations on pollution of groundwater by fly ash dumped in coal open cast mines at Talcher thermal Power Station of NTPC, Odisha, India. Water samples from mine, groundwater, surface water and rain water were analysed for environmental stable isotopes (δD and $\delta^{18}\text{O}$), Tritium, trace elements and major cation and anion. Isotope data suggest that hand pumps in the area are getting recharge from both rain water and the mine water. Tritium values of a few hand pump samples are 2 – 4 TU and local rain water is 4 TU. Hence some wells are mixture of both modern water (shallow aquifer) and older water (deep aquifer). Isotopic data suggest that groundwater in the southern and S-SE part of area near a quarry in the area is influenced by quarry water. The drainage pattern of the area also substantiates this finding. A bore well, which is nearby an old abandoned fly ash pond, measured comparably higher concentrations of Mn and Zn which is above maximum permissible limit (MPL) of drinking water, may be getting recharge from the old abandoned fly ash pond along with rain water. The fly ash leachates in these mines are getting well diluted due to continuous fresh water input from a river (River Brahmini), and hence don't pose any threat to groundwater in downstream. The study concluded that periodical (annual) chemical analysis of groundwater samples are to be carried out in the area to ensure that the chemical toxicity don't exceed MPL for drinking water. To bring down the higher concentrations of toxic ions in the well, the old abandoned fly ash pond needs to be fed with continuous supply of fresh water.

5. Conclusions

An increasing threat to groundwater supplies and surface water quality requires that the origin of specific compounds is determined and the flow of effluents traced in the natural environment. The use of stable and (subordinately) radiogenic isotopes in water quality studies is playing an important role to address water resource sustainability issues worldwide. The possibility to evaluate and quantify effects and modalities of isotopic fractionation affecting the light elements such as oxygen, hydrogen, carbon, sulfur, nitrogen, and boron provides outstanding opportunities to identify sources and to trace transformation processes. Stable isotope applications are nowadays well established approaches in hydrogeochemistry, and some of them are routinely analyzed to contribute to the understanding of the hydrological circuits as well as the presence of anthropogenic contamination/pollution. Environmental isotope geochemistry is a fast-growing discipline as new additional isotopic systems are set up and applied to different geological and urban, industrial, and agricultural areas. In this work have some examples of their application have been provided to highlight the potential of traditional and nontraditional stable isotope systems to trace sources, fate, and behavior of different solutes and metals in surface water and groundwater. Stable isotopes have demonstrated to be a powerful tool in order to analyze situations that cannot be faced with conventional techniques. However, at a large scale, the isotopic signatures can significantly change and often not enough data are provided to determine the original source, as their determination is time-consuming and costly. On the other hand, new techniques, particularly for what regards oxygen and hydrogen isotopes, are presently able to provide a large number of determinations in a short time.

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