

SUMMARY OF ISOTOPES IN CONTAMINANT HYDROGEOLOGY

SEGUN ADELANA
University of Ilorin
Ilorin, Nigeria

INTRODUCTION

The word contaminant is a general term to describe dissolved constituents, nonaqueous phase liquids (NAPLs), or industrial solvents which, when added to water as a result of human activities, impair groundwater quality. To an important extent, the complexity of a groundwater contamination problem can be determined by whether or not NAPLs are present (1). Obviously, contaminants related to anthropogenic activities are one of the major threats facing groundwater resources today. Groundwater contamination can have a significant impact on the present and future use of groundwater resources as a source of drinking water for an increasing population living in cities and rural areas (2).

In the investigation of problems posed by contaminants in the hydrologic environment, the modern approach is to use a combination of tracers. These tracers include radioactive isotopes (such as ^3H , ^{13}C , ^{14}C), stable isotopes (^{18}O , ^2H), and dissolved geochemical constituents (Cl^- , SO_4^{2-} , NO_3^- and some cations). An important facet of contaminant hydrogeology is the movement of liquids that are immiscible with water through the vadose zone as well as below the water table. Such liquids are usually called nonaqueous phase liquids. There are numerous cases of groundwater contamination involving organic liquids that are either insoluble or partially soluble in water. When the densities of these liquids are greater than that of water, they are called dense nonaqueous phase liquids (DNAPLs). Those whose densities are less than that of water are light nonaqueous phase liquids (LNAPLs). They could also be partially soluble in water, such that both dissolved and nonaqueous phases may be present (3–7).

The major groups of contaminants in hydrogeology include radionuclides, trace metals, and nutrients. They could also be classified as inorganic and organic contaminants. These include synthetic organic compounds, hydrocarbons, and pathogens (7). Some types of these contaminants are inorganic chemicals that are either metallic or nonmetallic (1,8). Included in the group of organic contaminants are NAPLs, which naturally subdivide into LNAPLs and DNAPLs (7).

A wide variety of materials have been identified as contaminants found in groundwater. An extensive listing of these compounds is tabulated in (Reference 7, pp. 3–10). Many of these materials will dissolve in water to different degrees. Some of the organic compounds are only slightly soluble and will exist in both dissolved form and as an insoluble phase, which can also migrate through the ground (7). According to (2), the main relevant organic

compounds of the LNAPLs are benzene, toluene, ethylbenzene, and xylenes (BTEx) from spills at gas stations and industrial facilities. The most common compounds of the group found in groundwater are perchloroethene (PCE), trichloroethene (TCE), *cis*-1,2-dichloroethene (*cis*-1,2-DCE), and dichloroethane (DCA) (9). In terms of environmental contamination, the major concern is focused on those organic compounds that are not readily degraded by bacteria, either in the soil zone or in sewage treatment facilities. The presence of these substances in the surface environment is becoming increasingly pervasive (8).

The sources that contribute to groundwater contamination are varied. Among these are land disposal of solid wastes, inorganic substances, metal and nonmetal trace elements. Other sources of groundwater contamination are from introducing of salts on roads to combat ice in winter, the infiltration of leachate from tailings in the mining industry, seepage from industrial water lagoons and septic tanks of urban waste disposal systems, wastewater discharge into rivers and lakes, agricultural wastes and fertilizers, saline or geogenic polluted water attracted by overexploitation of groundwater, and fossil fuels (1,7,8,10,11). Inorganic cations and anions occur in nature and may come from natural as well as anthropogenic sources. Some of the radionuclides are naturally occurring; others are man-made and come from the production and testing of nuclear weapons.

There are three important attributes that distinguish sources of groundwater contamination: (1) their degree of localization, (2) their loading history, and (3) the kinds of contaminants emanating from them (1). From the work of Domenico and Schwartz (1) contaminants are organized by groups according to reaction type and mode of occurrence. Six categories have been tabulated:

- Category 1—Sources designed to discharge substances, for example, subsurface percolation (from septic tanks and cesspools), injection wells (hazardous and nonhazardous wastes), and land application.
- Category 2—Sources designed to store, treat, and/or dispose of substances; discharge through unplanned release, for example, landfills, open dumps (including illegal dumping waste), residential or local disposal wastes, waste tailings, material stockpiles (nonwaste), graveyards, animal burial, surface and underground storage tanks, and containers.
- Category 3—Sources designed to retain substances during transport or transmission, for example, pipelines and materials transport and transfer operations.
- Category 4—Sources discharging substances as a consequence of other planned activities, for example, irrigation practices, pesticide applications, fertilizer applications, animal feeding operations, deicing salt applications, urban runoff, percolation of atmospheric pollutants, and mining and mining drainage.
- Category 5—Sources providing conduits or inducing discharge through altered flow patterns, for

example, production wells (oil/gas wells, geothermal and heat recovery wells, water supply wells), other nonwaste wells (monitoring and exploration wells), and construction excavation.

Category 6—Naturally occurring sources whose discharge is created and/or exacerbated by human activity, for example, groundwater–surface water interactions, natural leaching, saltwater intrusions and brackish water upconing, or intrusion of other poor-quality natural water.

For details of sources and background concentrations of contaminants in groundwater, refer to Forstner and Wittman (10). More information on inorganic contaminants is available in Reference 7 (Chapter 6), Reference 1 (Chapter 17); methods of detecting groundwater contamination are fully discussed in Domenico and Schwartz (1), and the sources and hydrochemical behavior of contaminants are described in Chapter 9 of Reference 8 as well as Chapter 1 of Reference 11. As a general introduction to groundwater contamination and related literature, the following are suggested for further reading: Baetsle (12), Fuhrman and Barton (13), Hall (14), Scalf et al. (15), Miller et al. (16), Summers and Spiegel (17), Cherry et al. (18), Back and Cherry (19), Fried (20), Todd and McNulty (21), Wilson et al. (22), Freeze and Cherry (8), IAEA (23, 24), Pearson et al. (25), Fetter (7), Pankow and Cherry (9), Domenico and Schwartz (1), and Seiler (11).

ENVIRONMENTAL ISOTOPES IN CONTAMINANT HYDROGEOLOGY

Introduction

For many years, environmental isotopes have been used in hydrogeology to address a range of issues such as evaluation of recharge areas, determination of groundwater residence time, and evaluation of surface water–groundwater interactions. Isotope studies applied to a wide spectrum of hydrologic problems related to both surface and groundwater resources as well as environmental studies in hydro-ecological systems are presently an established scientific discipline, called “Isotope Hydrology.” However, it is now becoming increasingly popular to use environmental isotopes as tracers to provide information about sources of contaminants and processes that affect these compounds in the groundwater flow system (2).

In essence, isotope techniques are becoming an integral part of many hydrologic investigations and sometimes a unique tool in studies related to groundwater contamination. Stable and radioactive environmental isotopes have now been used for more than four decades to study hydrologic systems, particularly in determining the hydrodynamics of aquifers, and have proved useful for understanding groundwater systems. The applications of isotopes in hydrogeology 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 the distinct advantage over injected (artificial)

tracers in that they facilitate the study of various hydrologic processes on a much larger temporal and spatial scale through their natural distribution in a hydrologic system. Thus, environmental isotope methodologies are unique in regional studies of water resources to obtain the time and space integrated characteristics of groundwater systems. The use of artificial tracers generally is effective for site-specific, local applications (26,27). Environmental isotopes can now be used to trace the pathways as well as spatial distribution and temporal changes in pollution patterns for assessing pollution migration scenarios and planning for aquifer remediation (27,28).

Recent research and the development of new analytical methods have led to fast expansion of the application of isotopes in hydrogeology. In particular is the introduction of techniques that make it possible to measure isotopic ratios of individual compounds at low concentrations (29). These have opened new and exciting possibilities for using isotopes in organic contaminant studies in groundwater. For example, nitrogen and carbon isotopes can now provide information regarding such attenuation processes as the denitrification and biodegradation of halogenated solvents, respectively (28).

Environmental isotopes have, therefore, become useful tools in differentiating between different sources of organic contaminants or in assessing biotic and abiotic transformation processes associated with natural attenuation or engineered groundwater remediation techniques (30–32). The isotope method used to evaluate the degradation of organic contaminants relies on the frequent occurrence of small differences in the degradation rate between molecules of the same contaminant that contain different isotopes. Usually, the rate is slightly faster for molecules that contain light isotopes (e.g., ^{12}C) compared to those that contain heavy isotopes (e.g., ^{13}C) because bonds between light isotopes are weaker. As a result, degrading contaminants should contain increasingly more of the heavier isotope (^{13}C) as degradation proceeds, and thus the ratio between heavy and light isotopes ($^{13}\text{C}/^{12}\text{C}$) is expected to increase (2). Oxygen-18 in dissolved oxygen also has a significant potential as a tracer to evaluate the fate of oxygen in contaminated plumes.

The sequel to these environmental isotope studies has focused on the light elements and their isotopes: hydrogen (^1H , ^2H , ^3H), carbon (^{12}C , ^{13}C , ^{14}C), nitrogen (^{14}N , ^{15}N), oxygen (^{16}O , ^{18}O), and sulfur (^{32}S , ^{34}S). These are the most important elements in biological systems that occur in relatively great abundance and also participate in most geochemical reactions (33). Other less important and less abundant isotopes (^{17}O , ^{33}S , ^{36}S) are not often employed in environmental studies but have significance in very specific studies. Table 1 lists the isotopes of major elements used in environmental studies and their average abundances in natural compounds.

Uses of Isotopes in Contaminant Hydrogeology

General uses of environmental isotopes in contaminant studies are often based on evaluating the various sources of contaminants in both surface and groundwater. The isotope approach to evaluating these sources relies mostly on the distinct isotope composition, that can characterize

Table 1. Isotopes of Major Elements Used in Environmental Studies^a

Element	Isotopes	Average Terrestrial Abundance, (%)	Comments ^b
Hydrogen	¹ H	99.984	Radioactive, $t_{1/2} = 12.35$ years
	² H	0.015	
	³ H	10^{-14} to 10^{-16}	
Carbon	¹² C	98.89	Radioactive, $t_{1/2} = 5730$ years
	¹³ C	1.11	
	¹⁴ C	$\sim 10^{-10}$	
Oxygen	¹⁶ O	99.76	
	¹⁷ O ^c	0.037	
	¹⁸ O	0.1	
Nitrogen	¹⁴ N	99.34	
	¹⁵ N	0.366	
Sulphur	³² S	95.02	
	³³ S ^c	0.75	
	³⁴ S	4.21	
	³⁶ S ^c	0.02	
Strontium	⁸⁴ Sr ^c	0.56	
	⁸⁶ Sr	9.86	
	⁸⁷ Sr	~ 7.02	
	⁸⁸ Sr ^c	82.56	
Uranium	²³⁴ U	~ 0.0056	Radioactive, $t_{1/2} = 2.47 \times 10^5$ years
	²³⁵ U ^c	0.7205	Radioactive, $t_{1/2} = 7.13 \times 10^8$ years
	²³⁸ U	99.274	Radioactive, $t_{1/2} = 4.51 \times 10^9$ years

^a Reference 33.^b $t_{1/2}$ = half-life.^c These isotopes are not presently used in environmental studies.

the different sources of contaminant (2,34). Environmental isotopes have found good use as tracers both artificially and naturally (26,35–38). For general review of the use of environmental isotopes in contaminant hydrogeology and potential future use of these tracers in vulnerability studies in groundwater, see References 2,27 and 28.

Environmental isotopes have been found widely applicable, especially in identifying the origin of water that is infiltrating an aquifer (28). Obviously, there is a relationship between recharge and the vulnerability of groundwater to contamination because the transport of many contaminants to the saturated zone of the aquifer occurs in the dissolved phase as part of the recharge process (39). Generally, ¹⁸O and ²H, among the various environmental isotopes, are most widely used in defining groundwater recharge areas as well as their origins. Changes in the isotopic relationships between ¹⁸O/¹⁶O and ²H/¹H, during the evaporation and condensation of water allow defining its origin (28).

New isotope applications are being developed in organic contaminant studies of groundwater. These studies have shown that carbon isotopes allow very sensitive evaluation of the fate of precursors and by-products of the biodegradation of chlorinated compounds, which are the most common organic contaminants found in groundwater. Potentially new applications include ¹⁸O to evaluate the fate of oxygen in contaminant plumes and ¹¹B in salinization and nitrate studies of groundwater (2). Table 2 shows the potential/common applications of isotopes in groundwater pollution studies.

Boron-11, a stable isotope of boron, has also been used to differentiate nitrate from sewage and fertilizers as well as to trace the sources of salinity in groundwater. This

approach was used to differentiate isotopic composition of injected treated wastewater and irrigation-affected water ($\delta^{11}\text{B} > 40\text{‰}$) distinctly and to trace the effect of injection into an alluvial aquifer near El Paso, Texas (40).

It has also been possible to approach the tracing of various organic pollutants (chlorinated hydrocarbons) in groundwater by using a combination of the isotopes ¹³C/¹²C, ²H/¹H, and ³⁷Cl/³⁵Cl. For example, the isotopic ratios ³⁷Cl/³⁵Cl and ¹⁰B/¹¹B have been used recently in pollution studies of groundwater (41,42). The strontium isotopic ratio (⁸⁷Sr/⁸⁶Sr) is also a valuable tracer for studies related to the mixing and origin of mineralized groundwater. It is a tracer for the origin of salinity, groundwater movement, and water–rock interactions (43,44). In the past, a combination of stable and radioactive isotopes that has dissolved geochemical constituents has been used in tracing the migration of contaminants in groundwater (45–47).

According to Hirata and Varnier (28), isotope techniques are useful in determining groundwater pollution vulnerability, to the extent that they allow for better understanding of the degree of access provided for penetration of contaminants and the attenuative capacity offered by the geologic medium (Table 3).

The most frequently used environmental isotopes in contaminant hydrogeology include nitrogen isotopes (¹⁴N/¹⁵N), chlorine - 37, the sulphur isotope (³⁴S), carbon isotopes (¹³C, ¹⁴C), and the boron isotope (¹¹B). Those of the water molecules (¹⁸O, ²H) are also sometimes used with some of these isotopes in groundwater contamination studies. Following are brief descriptions of the isotopes commonly employed in contaminant hydrogeologic studies.

Table 2. Common/Potential Isotopes Used in Groundwater Pollution Studies^a

Isotope(s)	Potential/Common Applications
¹³ C in HCO ₃ ⁻ and CH ₄	Identifying of methane sources Monitoring CO ₂ and CH ₄ production in biodegradation studies
³⁴ S and ¹⁸ O in SO ₄ ²⁻	Identifying of sources of pollution Acidification and acid mine drainage
¹⁵ N and ¹⁸ O in NO ₃ ⁻ , NH ₄ ⁻ , N ₂	Origin of nitrates Sources of pollution Microbial denitrification processes
¹¹ B in B(OH) ₄ ⁻ and B(OH) ₃ ⁻	Identifying of pollution sources Characteristics of brines, source of salinity
Chlorine-37 (³⁷ Cl)	Identifying pollution sources Characteristics of brines, sources of salinity
Tritium (³ H)	Indicators of recent pollution/recharge Water transport in the unsaturated zone
Strontium isotope ratio (⁸⁷ Sr/ ⁸⁶ Sr)	Tracer for the origin of salinity, mixing, and origin of mineralized groundwater, groundwater movement, and water–rock interactions.
Uranium isotopes (²³⁴ U, ²³⁸ U)	Sensitive indicators of radioactive pollution in natural waters, Rock–water interaction, dating of old groundwater

^a Modified from Reference 27.**Table 3. The Use of the Isotope Technique for Groundwater Pollution Vulnerability Characterization^a**

Component of Aquifer Pollution Vulnerability	Information Related to	Isotope Technique
Hydraulic accessibility of the saturated aquifer to penetration of pollutants	Identification of recharge/discharge areas	¹⁸ O in H ₂ O ² H in H ₂ O
	Degree of aquifer confinement	⁸⁵ Kr flow through fissured rock
	Definition of period of recharge	³ H in H ₂ O (environmental and applied tracer)
	Identification of paleowaters	⁵¹ Cr, ⁵⁸ Co, ⁶⁰ Co, ¹³¹ I (applied tracers)
	Interconnection of surface and groundwater	
Attenuative capacity of strata overlying the saturated zone, resulting from the physicochemical retention or reaction of pollutants	Determination of transit time of water through the saturated and unsaturated zones (advective flow)	Dating young water ³ H ³ He
		Dating midage water ³⁹ Ar
		¹⁴ C, correction with ¹³ C in HCO ₃ ⁻
		⁸¹ Kr
		Dating old water ⁸¹ Kr ²³⁴ U
	Identification of physico chemical reactions of pollutants (degradation)	¹⁵ N and ¹⁸ O in NO ₃ ⁻ , NH ₄ ⁺ , N ₂ , microbial denitrification processes
		¹³ C, biodegradation of synthetic solvents and fuel
		³⁴ S, oxidation/reduction of sulfur
<i>Pollution hazard factors</i>	<i>Information related to</i>	<i>Isotope technique</i>
Definition of pollutant origin	Identification of source of pollution	³⁴ S and ¹⁸ O in SO ₄ ²⁻ , acidification and acid mine drainage ³⁷ Cl, ¹¹ B, in B(OH) ₄ ⁻ and B(OH) ₃ ⁻ characteristics of brines; sources of salinity ¹⁵ N and ¹⁸ O in NO ₃ ⁻ , NH ₄ ⁺ , N ₂ ¹⁸ O, ² H in H ₂ O, salinization mechanisms, recycling of irrigation water ¹⁴ C and ¹³ C for origin of sources of organic compounds

^a After Reference 28.

Nitrogen Isotopes (¹⁴N/¹⁵N). The most common contaminant identified in groundwater is dissolved nitrogen in the form of nitrate (NO₃⁻). Other forms of inorganic nitrogen are nitrite (NO₂⁻), nitrogen gas (N₂), ammonia (NH₄⁺), and cyanide (CN⁻). Nitrogen is also a major constituent

of organic matter as amino acids (7). These contaminants are becoming widespread due to increased agricultural activities worldwide and disposal of sewage on or beneath the land surface.

Nitrogen occurs as two isotopes in nature: ^{14}N ($\approx 99.6\%$) and ^{15}N ($\approx 0.36\%$). ^{14}N is more abundant in the atmosphere than ^{15}N . Hence, the $^{15}\text{N}/^{14}\text{N}$ ratio in nitrate can be used to distinguish the origin of nitrates either from animal/human wastes or from the application of chemical fertilizers (48,49). The origin of contamination by nitrates can be determined through the relationship between $^{15}\text{N}/^{14}\text{N}$ and standard values ($\delta^{15}\text{N}$). Combined isotope analyses of nitrogen and oxygen in NO_3^- leave fingerprints on natural and anthropogenic sources of nitrate; on microbial denitrification, nitrification and biological fixation processes; and on the nitrogen budget in groundwater (50–53).

Therefore, the $\delta^{15}\text{N}$ values of dissolved nitrates, ammonium, and organic nitrogen in soil water are well distinguished from one region to another. The $\delta^{15}\text{N}$ of animal waste is between $+5$ to 15‰ , and fertilizers have a $\delta^{15}\text{N}$ of about 0‰ . However, for nitrogenous fertilizers, these values lie between -4‰ and $+4\text{‰}$ (50,54).

For more information and related nitrogenous inputs in groundwater, refer to Foster and Crease (55), Kreitler and Jones (56), Létolle (57), Kreitler and Browning (58), White (59), Flipse et al. (60), Heaton (60), Mariotti (61), Flipse and Bonner (62), Tessendorff (63), Hübner (64), Mariotti (65), Böttcher et al. (51), Exner and Spalding (66), Aravena et al. (52), Buzek (67), Révész et al. (68), Pauwels et al. (69), Tore et al. (70), and Anwar and Ghosh (71).

Chlorine-37. Naturally, chlorine exists with two common stable isotopes: ^{35}Cl ($\approx 75.7\%$) and ^{37}Cl ($\approx 24.2\%$). Chloride ions are generally not reactive and as such, do not participate in redox reactions, are not sorbed onto mineral or organic surfaces, and do not form insoluble precipitates. As a result, ^{37}Cl is sometimes used as a conservative tracer in groundwater studies. Data are expressed as $\delta^{37}\text{Cl}$ with respect to the standard mean oceanic chloride (SMOC). The ratio $^{37}\text{Cl}/^{35}\text{Cl}$ is measured by isotope ratio mass spectrometry (IRMS). Precision must be better than $\pm 0.1\text{‰}$ (72). $\delta^{37}\text{Cl}$ values contain information on the origin of chloride ions in fresh and polluted groundwater as well as in subsurface brines (30,41,42).

In geochemical studies generally, chlorine isotopes are not highly fractionated, but research has shown that measurable fractionations can be used to distinguish sources of groundwater mixing (73). The ^{37}Cl content of chloro contaminants in groundwater can fingerprint the sources of contaminants and salinity. It is therefore a potential tool in contaminant hydrogeology (27,43).

Sulphur Isotope (^{34}S). Sulphur has four stable isotopes: ^{32}S (95.02%), ^{33}S (0.75%), ^{34}S (4.21%), and ^{36}S (0.02%). The abundance ratio of ^{34}S and ^{32}S is generally given as a $\delta^{34}\text{S}$ value. Iron sulfide from the troilite phase of the Diablo Canyon iron meteorite (DCT) (that has a $^{32}\text{S}/^{34}\text{S}$ ratio of 22.220) is conventionally used as a standard (72). ^{34}S is one of the distinct isotopes that can be used to characterize different sources of sulfate contamination. For example, high sulfate in aquifers in areas close to mine tailings could be associated with the oxidation of sulfide minerals in the tailings. However, other sources of sulfate in aquifers such as gypsum of marine origin, input from

volcanic sources, or sulfate from recirculated water from agriculture have been identified (2). Generally, sulfate produced from sulfide minerals is much more depleted in ^{34}S and ^{18}O than marine sulfate (74,75).

Moreover, owing to isotope fractionation during sulfate reduction, ^{34}S and ^{18}O in sulfate can also be used to evaluate the fate of sulfate in groundwater flow systems (76). The isotopic composition of sulfate can also be an indicator of anthropogenic pollution of groundwater (75).

Carbon Isotopes (^{13}C , ^{14}C). Carbon has three isotopes in nature: ^{12}C , ^{13}C , and ^{14}C . The heavy carbon isotope, ^{14}C , is unstable and decays radioactively into ^{14}N . The stable isotopes of carbon, ^{13}C and ^{12}C , have an average ratio of about 1:100 (72). The isotopic composition of carbon in the dissolved carbon constituents of groundwater is very variable. The sources of carbon dissolved in groundwater are soil CO_2 , CO_2 of geogenic origin or from magmatic CO_2 (from deep crustal or mantle sources) or in fluid inclusions, living and dead organic matter in soils and rocks, methane, and carbonate minerals (53). Each of these sources has a different carbon isotopic composition and contributes to total dissolved carbon in various proportions. Therefore, the isotopic composition of dissolved inorganic carbon compounds in groundwater has a wide range of $\delta^{13}\text{C}$ values.

Carbon isotopes (^{13}C , ^{14}C) can be used to evaluate the origin of methane in landfills (2). The origin of methane is a common problem in landfills located in old quarries. Methane in this type of environment can be thermocatalytic in origin, associated with gases present in the bedrock or/and originating in the landfill itself (2). According to Schoell (77), gases of thermocatalytic origin are generally more enriched in carbon-13 ($\delta^{13}\text{C} > -50\text{‰}$) than methane of biogenic origin ($\delta^{13}\text{C} < -50\text{‰}$). In addition, Hackley et al. (78) proved that catalytic gases are devoid of carbon-14, whereas methane in landfills has a ^{14}C content higher than 100% modern carbon (pmc). Obviously, due to carbon-14 from thermonuclear explosions, any carbon in domestic waste that was deposited in a landfill after 1950 is usually characterized by a ^{14}C content higher than 100 pmc (2). Furthermore, carbon isotopes have also been employed in monitoring CO_2 and CH_4 production in biodegradation studies in unsaturated areas impacted by organic contamination (79,80).

Boron Isotope (^{11}B). Natural boron has two stable isotopes, ^{11}B ($\approx 80\%$) and ^{10}B ($\approx 20\%$). The variation in the ratio of these two isotopes is expressed in $\delta^{11}\text{B}$ (‰) with respect to SRM-951 NBS standard (81). Generally, boron is present in groundwater mainly as trigonal undissociated boric acid, $\text{B}(\text{OH})_3^0$, and its conjugate base, tetrahedral borate, $\text{B}(\text{OH})_4^-$. Tetrahedrally coordinated boron is more isotopically depleted (i.e., lower in $\delta^{11}\text{B}$) relative to trigonally coordinated boron; thus the $\delta^{11}\text{B}$ of dissolved boron in groundwater is usually higher than that in aquifer rocks (81).

Boron is used as tracer in groundwater because of its high solubility in aqueous solution, natural abundance in all waters, and the lack of effects from evaporation,

volatilization, and oxidation–reduction reactions. The concentrations of boron in pristine groundwaters are generally low (<0.05 mg/L), and contaminant sources are usually enriched in boron (e.g., sea water: 4.6 mg/L; domestic wastewater: 1 mg/L; flyash leachate: 14 mg/L; landfill leachate: 6 mg/L), so the $\delta^{11}\text{B}$ of groundwater is highly sensitive to the impact of contamination (81). The large isotopic variation of the potential sources can be used to trace the origin of contamination. Vengosh (81) reported that coastal aquifers affected by seawater intrusion and marine-derived fossil brines are characterized by high $\delta^{11}\text{B}$ values (up to 60‰). In contrast, domestic wastewater that has relatively high boron concentrations and a high B/Cl ratio has $\delta^{11}\text{B}$ values of 0‰ to 12.9‰. Boron stable isotope ratios have a potential to play a role in pollution studies (82). They also have applications in the characterization of brines and geothermal waters (83).

It will suffice at this point to say that some of these environmental isotopes are in themselves a source of groundwater contamination, especially radioactive isotopes. Radioactive isotopes, also known as radionuclides, are therefore discussed in the following section in relation to groundwater contamination.

Radioactive Contaminants

It is now well known that numerous human activities have created nuclear isotopes by detonating nuclear weapons and constructing nuclear reactors. A number of radionuclides are produced in the earth's atmosphere by nuclear reactions caused by cosmic rays. Cationic radionuclides may be subjected to ion exchange and other processes that sorb the radionuclides onto mineral organic surfaces in the soil (7). Examples of transition metals that have large distribution coefficients and hence low mobilities in waters are listed in References 7 and 84. ^{90}Sr , ^{137}Cs , and ^{226}Ra are involved in cation exchange similar to other exchangeable cations, for example, Ca^{2+} and Mg^{2+} (84).

Many of these radionuclides are frequently produced as fission products from the decay of ^{235}U and ^{239}Pu and from neutron activation of stable isotopes. These processes result in the production of more than 75 radionuclides such as ^{137}Cs , ^{134}Cs , ^{58}Co , ^{51}Cr , ^{54}Mn , ^{55}Fe , ^3H , and ^{131}I (1). Table 4 lists the various sources of environmentally important radioactive isotopes. These are elements that undergo spontaneous decay resulting in the release of energy as well as energetic particles and consequent formation of different isotopes. They occur either naturally or are created by bombardment of the

earth by cosmic radiation (7) and undergo spontaneous decay resulting in the release of energy as well as energetic particles and consequent formation of different isotopes.

The nuclear industry has been the main generator of radioactive contaminants. However, potential sources occur throughout the nuclear fuel cycle, which involves mining and milling uranium, uranium enrichment and fuel fabrication, power plant operation, fuel reprocessing, and waste disposal (1). In the examples presented by Domenico and Schwartz, the United States, Japan, France, and Germany have large numbers of light-water reactors that use enriched uranium (^{235}U) as the predominant fuel source and possibly ^{239}Pu and ^{238}U . The process of enrichment and fuel fabrication is also accompanied by generation of the following radionuclides: ^{238}U , ^{235}U , ^{137}Cs , and ^{90}Sr , which are common contaminants.

Furthermore, there are potential radionuclide contaminants that result from the processing of raw uranium ore (during mining operation) alongside other nonradioactive pollutants, which include ^{238}U , ^{230}Th , ^{226}Ra , and ^{222}Rn . Examples of locations where this type of contamination occurs are Colorado, New Mexico, Texas, Utah, Wyoming, northern Saskatchewan, and Ontario (1).

PRACTICAL APPLICATIONS OF ENVIRONMENTAL ISOTOPES IN SOLVING GROUNDWATER CONTAMINATION PROBLEMS

Many examples exist in the literature on the use of environmental isotopes in solving groundwater contamination problems. There are also case studies in publications, which have addressed the applications of isotopes in contaminant hydrogeology. In this section, the results of the application of isotopes in groundwater contamination studies, particularly in solving specific problems are summarized. The case studies cut across continents and varied hydrogeologic settings. Some of these applications are based on single isotopes, and others combine several isotopes, particularly oxygen with nitrogen and sulfur to understand the origin and migration of contaminants in groundwater. However, some case studies applied an integrated approach (using isotope techniques and conventional hydrochemistry) to interpret contaminant sources and pathways. This is not an exhaustive listing but rather selected to demonstrate the applications of environmental isotopes in solving specific hydrogeologic problems. For more information and examples, refer to the IAEA TECDOC series and other edited specialist volumes.

Table 4. Various Sources of Environmentally Important Radioactive Isotopes^a

Source	Radionuclides
Naturally occurring	^{40}K , ^{222}Rn , ^{226}Ra , $^{230,232}\text{Th}$, $^{235,238}\text{U}$
Cosmic irradiation	^3H , ^7Be , ^{14}C , ^{22}Na
Nuclear weapon tests	^3H , ^{90}Sr , ^{137}Cs , $^{239,240}\text{Pu}$
Mining wastes—uranium, phosphate, coal	^{222}Rn , ^{226}Ra , $^{230,232}\text{Th}$, $^{235,238}\text{U}$
Industrial wastes—nuclear power plants, weapons manufacturing, research and medical waste	$^{59,63}\text{Ni}$, ^{60}Co , ^{90}Sr , $^{93,99}\text{Zr}$, ^{99}Tc , ^{107}Pd , ^{129}I , ^{137}Cs , ^{144}Ce , ^{151}Sm , $^{152,154}\text{Eu}$, ^{237}Np , $^{239,240,242}\text{Pu}$, $^{241,243}\text{Am}$

^aReference 7.

Fritz et al. (45) studied the possible movement of leachate from a sanitary landfill in Frankfurt am Main, Germany. Interpretation of results of both isotopic and chemical data in the pollution monitoring showed that $\delta^2\text{H}$ and $\delta^{18}\text{O}$ are most useful in tracing the leachate and mapping the pollution plume. Three groups were identified from $\delta^{18}\text{O}$ data: The first group (-8.6‰ to -8.0‰) is of uncontaminated groundwater; the second group (-6.7‰ to -6.3‰) is polluted groundwater, and the third group (-3.0‰ to -2.0‰) reflects recharge from lake water. The same $\delta^{18}\text{O}$ data have also been used (by these researchers) to calculate the percentage of leachate water in each well, and this was helpful in producing a map of the pollution plume at the landfill site.

Mazor et al. (85) conducted a study of groundwater contamination by a slaughterhouse at Lobatse, Botswana. The results of this study revealed that tritium and chloride were the most conservative tracers in this case. The slaughterhouse used water from a dam, and this water (when sampled and analyzed) had tritium concentrations that were significantly higher than those in the local groundwater. High tritium concentrations/contamination were observed in wells near the slaughterhouse and along the Peleng riverbed into which the effluent was released. Other wells (according to the researchers) showed low tritium and chlorine values, indicating that they were not contaminated.

Egboka (46), in the investigation of problems posed by contaminants in the hydrologic environment, used a combination of tracers: radioisotopes, such as bomb tritium, stable isotopes (^{18}O and ^2H), and dissolved geochemical constituents (Cl , SO_4 , NO_3 and some major cations). These isotopes, in combination with the dissolved geochemical constituents, have been used to delineate the aerial extent of spread of leachate plumes in landfills and spillage zones and around sewage lagoons. He presented two case studies where this multitechnique approach was used successfully to investigate environmental pollution and contamination. These include using bomb tritium, ^{18}O , ^2H , Cl^- , and SO_4^{2-} to investigate the leachate migration in an aquifer beneath an abandoned landfill at CFB Borden, Ontario (Canada) and the Lake Chad drainage basin (NE Nigeria), where ^3H , ^{18}O , ^2H , ^{14}C , and ^{13}C were extensively analyzed.

Song et al. (86) used ^{34}S in 66 water samples and 30 rock (anhydrite) samples to determine the origin of sulfate in the stable isotopic composition and geochemistry of fresh water and brine in Sichuan Basin, China. The results indicate that $\delta^{34}\text{S}$ values of saline waters are similar to those in the samples collected from different sections of the same sequence and differ from different strata. These authors considered that the evaporate of the early Triassic was formed in an enclosed and reductive beach and the facies belongs to the beach salt-lake in the environment of a supratidal zone and that of the middle Triassic belongs to lagoon-salt-lakes in the intertidal environment. The consistency of $\delta^{34}\text{S}$ in water and rock implies that they have a common source of sulphur.

Wassenaar (87) carried out a representative study in Abbotsford aquifer (a regional aquifer in Canada characterized by nitrate concentrations between 80 and

160 mg/L) using the isotopes of ^{15}N and ^{18}O . In this case, it was well documented that the main sources of nitrate were manure produced in the poultry industry and inorganic fertilizers used in cultivated fields. Based on the ^{15}N data, it was shown that most of the nitrate in the contaminated groundwater has $\delta^{15}\text{N}$ values greater than $+8\text{‰}$. Wassenaar (87) demonstrated that the main source of this nitrate was the manure piles that were deposited on top of the aquifer.

Similarly, a nitrate study carried out by Auge and Nagy (88) in the city of La Plata (Argentina) illustrates one of the applications of nitrogen isotopes in Latin America. The isotope study, which was part of a comprehensive hydrogeologic study of this aquifer, aimed to provide information about the sources of high nitrate observed in production wells in the city of La Plata. According to these researchers, the main potential sources of nitrate in this area are fertilizers and manure from agricultural and pasture areas located upgradient of the city of La Plata and leakage from the sewage system and possibly landfills located downgradient of the center of the city. A regional nitrate study showed a plume that had high nitrate concentration below the city. From the result, the nitrogen isotope pattern showed a clear trend toward enriched $\delta^{15}\text{N}$ values correlated with an increase in nitrate concentration. The high nitrate concentration (80–120 mg/L as nitrate) and enriched $\delta^{15}\text{N}$ values (14–15‰) correspond to groundwater located below the city. The low nitrate concentration (15–40 mg/L) and depleted $\delta^{15}\text{N}$ values (7–11‰) correspond to groundwater representing the agricultural areas and wells located upgradient on the high nitrate concentration plume. The enriched $\delta^{15}\text{N}$ values indicated input of nitrate from an enriched ^{15}N source associated with domestic wastes.

Aravena and Robertson (38) used multiple isotope tracers to evaluate denitrification in groundwater and documented that septic systems are point sources of nitrate in groundwater, which was documented in a nitrate plume generated in a large communal septic system operating at a campsite. As a result of oxygen consumption by the oxidation of pyrite and organic carbon in the unsaturated zone, the groundwater became anaerobic in the shallow part of the flow system. A steady decrease in nitrate concentrations from values around 80 mg N/L at the water table to nondetectable was observed versus depth along the groundwater system. A trend toward enriched $\delta^{15}\text{N}$ values accompanied these concentration changes, reaching values as high as $+58\text{‰}$, demonstrated that nitrate attenuation was controlled by denitrification. A linear correlation between $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values in nitrate also supported denitrification as the mechanism for nitrate attenuation in the aquifer.

Tandia et al. (89), in the investigation of the origin, process, and migration of nitrate compounds in the aquifers of the Dakar region, Senegal, used environmental isotopes (^{18}O , ^2H , ^3H , ^{13}C , ^{14}C) along with major inorganic constituents and fecal coliform on yearly water samples. The samples were taken from piezometers, hand-pumped wells, and dug wells in different areas of the Peninsula from 1987 to 1997. Results showed that only a limited area is affected by nitrate pollution in the confined

layer. Stable isotopes, tritium and ^{14}C , gave a better understanding of nitrate contamination of groundwater in this region; tritium in groundwater indicates that nitrate concentration is recent. This has been confirmed by the presence of high activities of ^{14}C (80‰), in good agreement with recent analyses of recharge groundwater.

The distribution of the values of ^{18}O and ^2H (89) around the World Meteoric Water Line indicate that the recharge of the Dakar aquifer system originates from the monsoon rainfall after it has been exposed to evaporation. However, the cluster of points relating to ^{18}O and ^2H were also interpreted as contributions of nitrate contamination along the flow path from east to west.

Buzek et al. (67) investigated the nitrate pollution of a karstic groundwater system in Svaty Jan Pod Skalou in the Czech Republic using $\delta^{18}\text{O}$ in water and $\delta^{15}\text{N}$ in nitrate. Increasing agricultural activity in the republic after the 1960s resulted in contaminating both shallow and deep-water resources. Therefore, to identify the sources of nitrate contamination and evaluate the parameters of the karstic system, the stable isotopes $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ were used together with monitoring of the flow dynamics, water chemistry, and soil composition. The results of the isotopic investigation revealed the sources of nitrate contamination from $\delta^{15}\text{N}$ in soil solutes at sites that had different agronomic records (sequential use of organic and inorganic fertilizers). They further showed that spring-discharge nitrate is formed from an atmospheric source (an average nitrate content of 8 mg/L and $\delta^{15}\text{N}$ of -6‰) and two groundwater components that had nitrate content of 50 to 60 mg/L and $\delta^{15}\text{N}$ values from 2 to 7‰. However, the contribution of groundwater components varied in time more frequently than can be described by the model developed for flow dynamics and ^{18}O . From this case study, data from the flow dynamics, ^{18}O , and tritium gave sufficient information to estimate the volume of the karstic system and the residence times of the three contributions (direct infiltration, fast, and old components) to spring discharge. The estimated turnover time of the old component (about 22 years) could be used for calculating the spring nitrate content in the future.

Aggarwal et al. (90) initiated a study using a suite of different isotopes to fingerprint and determine the source of contaminants in groundwater systems in New Zealand. Four different isotope systems were examined: boron isotopes, oxygen and nitrogen isotopes in nitrates, oxygen isotopes in sulfates, and oxygen and sulfur isotopes in sulfates. In a case study of the semirural Manakau area as well as the South and North Islands (all in New Zealand) conducted to investigate the possibility of using nitrate isotopes to detect the source of nitrate contamination, results showed nitrogen isotope ($+4$ to $+12\text{‰}$) coupled with oxygen isotope measurements ($+5$ to $+9\text{‰}$) and demonstrated that nitrogen is not sourced from fertilizers but from some combination of septic and animal waste. However, for the case study of sulfate isotope used, sulfur and oxygen isotopic compositions of sulfate in river and lake water from seven major catchments of the North and South Islands of New Zealand were determined. The results of the isotope analyses allowed distinguishing between natural (geologic, geothermal, and volcanic) and

anthropogenic (fertilizer) sulfur sources. Boron (B) isotope measurements were also carried out in the Bartholomew (Manawatu) and Petone waters in New Zealand. Results showed that the Cl/B ratio and the $\delta^{11}\text{B}$ of the water from Bartholomew may be interpreted as a consequence of mixing between saline water and freshwater. Seawater (included for comparison) showed a distinctly heavy B isotopic composition, relatively high B concentrations, and a high Cl/B ratio, whereas these two freshwaters contain a variable B isotope ratio that has a low B concentration and a much lower Cl/B ratio than that in the seawater.

Groundwater contamination in coastal aquifers of Israel, Italy, and the United States was determined by boron isotope systematics (81). This work reports isotopic results of contaminated groundwater from the coastal aquifers of the Mediterranean in Israel, the Cornia River in northwestern Italy, and the Salinas Valley in California. The interpretation of the results revealed different contamination sources; underlying saline water of a marine origin in saline plumes in the Mediterranean coastal aquifer of Israel ($\delta^{11}\text{B} = 31.7$ to 49.9‰ ; B/Cl ratio $\sim 1.5 \times 10^{-3}$), mixing of fresh and sea water ($\delta^{11}\text{B} = 25$ to 38‰ ; B/Cl ratio 7×10^{-3}) in saline water associated with a saltwater intrusion into the Salinas Valley, California, and a hydrothermal contribution (high B/Cl of ~ 0.03 ; $\delta^{11}\text{B} = 2.4$ to 9.3‰) in groundwater from the Cornia River, Italy. Vengosh et al. (81) observed that the boron concentrations in pristine groundwaters are generally low (<0.05 mg/L), whereas contaminant sources (e.g., domestic wastewater) are enriched in boron; hence, boron isotopes can be used to evaluate the impact of anthropogenic boron on the environment. Moreover, the isotopic composition of contaminated groundwater has revealed the sources of pollution because different sources are characterized by distinguishable isotopic ratios. For example, seawater ($\delta^{11}\text{B} = 39\text{‰}$), saltwater intrusion, and marine-derived brines (40 to 60‰) sharply differ from hydrothermal fluids ($\delta^{11}\text{B} = -10\text{‰}$ to 10‰) and anthropogenic sources (sewage effluent: $\delta^{11}\text{B} = 0\text{‰}$ to 10‰ ; boron-fertilizer: $\delta^{11}\text{B} = -15\text{‰}$ to 7‰). This research further showed that some differences (up to 15‰) might exist between domestic wastewater and boron fertilizer.

Shivanna et al. (91) used environmental isotopes (^{18}O , ^2H , ^3H , ^{14}C , and ^{34}S) along with hydrogeology and hydrochemistry to investigate (1) the source of salinity and the origin of sulfate in the groundwater of coastal Orissa, Orissa state (India) and (2) to study the source of salinity in deep and saline groundwaters of charnockite terrain at Kokkilimedu, south of Chennai, India. The results of the first case indicate that the shallow groundwater (depth <50 m) is fresh and modern. Groundwater salinity in the intermediate aquifer (50–100 m) is due to the Flandrian transgression during the Holocene period. The saline groundwater found below the fresh deep aquifer has marine water entrapped during the late Pleistocene. The source of high sulfate in the groundwater (as identified by the researchers) is of marine origin. In most of the deep aquifers, saline samples showed enriched $\delta^{34}\text{S}$ values ($+20.8\text{‰}$ to $+43.8\text{‰}$) compared with the seawater value, and radiocarbon ages are in the range of 12, 000 to 24, 000 years BP with negligible tritium.

However, in the second case, the results of isotope investigation showed that there are two different sources of salinity in this area: one, the salinity attributed to infiltration of seawater together with the contribution of solute from pseudotachylites observed along the fractures and shear zones in the host rock; second, salinity attributed to solutes mostly from sheared and fractured charnockite rock. The high tritium content observed in this case was interpreted as due mainly to effluent from the nuclear power plant located 0.5 km west of the site and partly due to mixing of surface water with groundwater.

Halas and Trembaczowski (92) applied stable isotopic analysis of oxygen and sulfur in sulfate to trace the sources of groundwater pollutants in the industrial area of Belchatow, central Poland, where a large brown coal deposit is exploited and the coal is burned in an electric power plant. The interpretation of isotope ratios allowed recognizing three groups of sulfates:

- (1) from the leaching of a Permian salt dome,
- (2) produced by the leaching of soluble sulfates from an ash pool, and
- (3) produced by the oxidation of natural sulfides in water-bearing rocks.

It was obvious from the data presented in this work that the oxygen and sulfur isotopic ratios of the dissolved sulfates are informative of their origin.

Liu et al. (93) carried out an investigation of groundwater contamination due to uranium deposits in the Zhoujiashan district of the Xiangshan uranium ore field, China. Samples of groundwater collected from five completed exploration boreholes in the area revealed the pollution source. It was traced and analyzed by using isotope as well as radiohydrochemical techniques. The researchers experimentally proved that the uranium concentration and uranium isotope ratio $^{234}\text{U}/^{238}\text{U}$ in natural waters are two sensitive indicators of radioactive pollution in natural waters. It was concluded that, under present conditions, exploration of uranium deposits might not cause serious groundwater contamination by radioactive elements (U, Ra, Rn, and Tn). Activity ratios $^{226}\text{Ra}/^{228}\text{Ra}$ and $^{230}\text{Th}/^{232}\text{Th}$ in water can be used only as supplementary indicators.

Qureshi et al. (94) used stable carbon isotope ratios as water quality indicators in the coastal areas of Karachi, Pakistan. Stable carbon isotope ratios ($\delta^{13}\text{C}$) of total dissolved inorganic carbon (TDIC), total organic and inorganic carbon in bottom sediments, as well as sea plants in polluted water sources, nonpolluted Karachi seawater, and pollution recipients were used to elaborate the pollution scenario of the shallow marine environment (off the Karachi coast). Groundwater pollution in the coastal areas of Karachi is also reflected in the stable isotope composition of carbon ($\delta^{13}\text{C}$) in the TDIC pool of organic carbon in bottom sediments, mangrove leaves, and seaweed. These results were supplemented with stable isotope analysis of nitrogen ($\delta^{15}\text{N}$) in seaweed and mangroves. Isotopic data revealed that the mangrove ecosystem and its tidal fluctuations play a key role in controlling contamination inventories in the shallow

seawater off the Karachi coast, specifically the Manora Channel. The Karachi harbor zone was reportedly the most heavily polluted marine site in Manora Channel during high as well as low tide.

De Vito et al. (95) carried out a study in a 200 meter long wetland located between agricultural fields and the Boyne River in southern Ontario (Canada) using ^{15}N and ^{18}O (in nitrate) to evaluate the role of denitrification as an attenuative mechanism in nitrate. Results showed that nitrate levels of 30 and 40 mg N/L characterize the groundwater impacting the wetland. A significant change in nitrate concentration was observed by the researchers along the groundwater flow system that reached values as low as 1 mg N/L in areas close to the river. This pattern is accompanied by an isotope trend toward enriched ^{15}N and ^{18}O . The isotopic data and the dissolved organic carbon that increases along the groundwater flow system were interpreted as demonstrating that denitrification is the main process responsible for nitrate attenuation in the area.

According to Aravena (2), applications of isotopes in organic contaminants have focused on evaluating carbon and hydrogen isotope fractionation in biological and physical processes that can affect organic contaminant concentration in groundwater. The results of these studies have shown that very little isotopic fractionation occurred during physical processes (96,97). However, recent analytical developments in stable isotope research have shown that carbon isotopes are very sensitive tracers for evaluating the biodegradation of chlorinated compounds in groundwater (31,32). However, they are not sensitive enough to document biodegradation of petroleum hydrocarbons in groundwater (98,99).

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