Groundwater Contamination Studies by Environmental Isotopes: A review

Barbara Nisi, Brunella Raco, and Elissavet Dotsika

Abstract Water demand for urban, industrial, and agricultural purposes is a major concern in developed and third world countries. A careful evaluation for an appropriate and sustainable use of water resources is a priority. Geochemical processes can lead to measurable variations of the aquatic environment, which can be studied through the analysis of the dissolved solutes. Even if this review is not meant to be exhaustive, it is intended to give a view on the importance of environmental isotopes in the context of groundwater quality assessments. This is done by briefly recalling some basic notions for each described system, followed by relevant applications and reports about some significant case studies. This review includes well-established isotopic systematics, such as those of O and H in water, C in dissolved inorganic carbon (DIC), S and O in sulfates, and N and O in nitrates and those of boron and Sr, which in the last lustrums have found large application in the field of water geochemistry. This chapter ends with some examples related to nontraditional isotopes, i.e., Fe, Cr, and Cu, in order to highlight the potential of the environmental isotopes to trace sources, fate, and behavior of different solutes and metals in surface water and groundwater.

Keywords Environmental isotopes, Groundwater, Isotopic fractionation, Land management, Untraditional isotopes

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Abbreviations

AMD	Acid Mine Drainage
CCS	Carbon Capture and Storage
CDT	Canyon Diablo Troilite
CIMWL	Central Italy Meteoric Water Line
DIC	Dissolved Inorganic Carbon
GMWL	Global Meteoric Water Line
IAEA	International Atomic Energy Agency
IRMM	Institute for Reference Materials and Measurements
MMWL	Mediterranean Meteoric Water Line
NIST	National Institute of Standards and Technology
SLAP	Standard Light Antarctic Precipitation
SMOW	Standard Mean Ocean Water
SRM	Standard Reference Materials
VPDB	Vienna Pee Dee Belemnite
VSMOW	Vienna Standard Mean Ocean Water

1 Introduction

Deterioration of water quality has received considerable attention over the last few decades in response to the increasingly severe contamination of surface water and shallow groundwater by anthropogenic contaminants [1, 2]. Groundwater is an important alternative source of water supply for those cities located in arid to semiarid climates. New awareness of the potential danger to water supplies posed by the use of agricultural chemicals and urban industrial development has also focused attention on the nature of rainfall–runoff and recharge processes and the mobility of various solutes in shallow systems [3]. A proper assessment of ground-water quality requires the quantification of the total recharge and the composition of the various sources involved. These quantitative assessments enable to identify the origin and the fate of chemical compounds and also develop management practices to preserve water quality and devise remediation plans for sites that are already polluted.

Natural waters are complex chemical solutions. They always contain a number of dissolved species, suspended materials, and organic substances. Stable, radio-genic, and radioactive isotopes of elements or compounds present in the aqueous medium are outstanding sources of information on the processes occurring in the hydrosphere [4]. The most widely used isotopes in hydrogeochemistry are the stable isotopes of oxygen, hydrogen, carbon, sulfur, and nitrogen and the cosmo-genic radioisotopes such as tritium and carbon-14. Other investigations on the stable and radioactive isotopes of helium, strontium, and others are also frequently applied. However, in the recent years, nontraditional stable isotopes of metals (e.g., Li, Mg, Fe, Cu, Zn) have been successfully studied in different geological mate-rials, as more precise and powerful instrumentations and improved analytical capabilities have been introduced. Similarly, investigations on mass-independent isotope geochemistry, the use of clumped isotope geochemistry, and measurements of position-specific isotope effects in organic compounds will be providing new insights in the comprehension of the geochemical processes that affect the exoge-nous and endogenous cycles of the elements, opening new frontiers in the field of isotope geochemistry.

Environmental isotope studies of natural waters are concerned with the princi-ples governing the distribution of the stable and radioactive isotopes in the hydro-sphere. Such studies are aimed to estimate the factors that determine these principles and to interpret hydrodynamical and hydrogeochemical processes involved on the basis of the isotope composition of the various elements in solution. Currently, environmental isotopes routinely contribute to such investigations, complementing geochemistry and hydrogeology. For instance, the stable isotopic composition of water is modified by meteoric process, and so the recharge waters in a particular environment will acquire a characteristic isotopic signature. This signature then serves as a natural tracer. Isotope tracers have been extremely useful in providing new insights into hydrologic processes because they integrate small-

Fig. 1 Differences in the chemical properties of the isotopes H, C, N, O, and S

scale variability to give an effective indication of the processes occurring at catchment-scale.

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.

The main purpose of this chapter is to provide an overview of recent advances in the use of naturally occurring stable isotopes including radiogenic isotopes (e.g., Sr), which are important hydrological tracers for recognizing natural and anthropogenic processes in aquifer systems.

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.

The structure of this chapter reflects the composite framework described above. This chapter firstly reviews well-established isotopic applications (oxygen and hydrogen in H_2O, carbon in dissolved inorganic carbon (DIC), nitrogen and oxygen in nitrates, and sulfur and oxygen in sulfates, whose reference isotopes are reported in Fig. 1). Then, some hints about recently applied isotopic ratios ($^{87}Sr/^{86}Sr$ and $^{11}B/^{10}B$) are described. The last part of the chapter deals with new isotopic ratios (iron, chromium, and copper), whose studies are still to be defined as they deserve to be more deeply investigated. For the sake of brevity, radiometric age dating of water with ^{3}H, ^{14}C, ^{81}Kr, and ^{36}Cl has been omitted in this chapter, being rather marginal to the context. The reader may refer to the following papers, which are specifically addressed to the topics related to water dating: e.g., Morgenstern et al. [5] and Stewart et al. [6] (tritium), Schiff et al. [7] and Mayorga et al. [8]

(carbon), Lange and Hebert [9] and Visser et al. [10] (krypton), and Palau et al. [11] and Khaska et al. [12] (chlorine).

2 Hydrogen and Oxygen Stable Isotopes

2.1 Background Principles

Both hydrogen and oxygen consist of a number of isotopes, whose variations in natural waters are the basis for applying the isotope methodology in hydrology. Hydrogen, whose major stable isotope is ^{1}H, occurs in the hydrosphere at a mass abundance of 99.985% and is accompanied by 0.015% of the heavy isotope, ^{2}H or *deuterium*. The chemical element oxygen has three stable isotopes, ^{16}O, ^{17}O, and ^{18}O, with abundances of 99.76, 0.035, and 0.2%, respectively [4]. Stable environmental isotopes are measured as the ratio of the two most abundant isotopes, for instance, ^{2}H/^{1}H or ^{18}O/^{16}O (the rare isotope at numerator and the more abundant at denominator), and are referred to international reference standards by using the typical δ notation defined as follows:

$$\delta = \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \tag{1}$$

where R is the abundance ratio of the isotopic species (i.e., ^{2}H/^{1}H or ^{18}O/^{16}O). Since δ is usually a small number, the "delta" is given in ‰ (per mil, equivalent to 10^3). The δ notation for ^{2}H/^{1}H and ^{18}O/^{16}O can be expressed as ^{2}δ or δ^2H and ^{18}δ or δ^{18}O, respectively. The accepted standard for the isotopes in water is VSMOW (Vienna Standard Mean Ocean Water), which is close to the original standard of SMOW (hypothetical water catalogued by the former National Bureau of Standards), as defined by Craig [13]. Abundance ratios for ^{2}H/^{1}H$_{\text{VSMOW}}$ and ^{18}O/^{16}O$_{\text{VSMOW}}$ are $155.75 \pm 0.05 \times 10^{-6}$ [14–16] and $2{,}005.20 \pm 0.45 \times 10^{-6}$ [17], respectively. These abundances are the values reported for the reference standard VSMOW, defining the value of δ=0‰ on the VSMOW scale. For waters which have depleted δ^2H and δ^{18}O values with respect to that of ocean water, a second water standard was distributed by the International Atomic Energy Agency (IAEA): Standard Light Antarctic Precipitation (SLAP). This value with respect to VSMOW was evaluated on the basis of an interlaboratory comparison by IAEA, defined as δ^2H $= -428.0$‰ VSMOW and δ^{18}O$_{\text{SLAP}} = -55.50$‰ VSMOW [18].

The isotopes of hydrogen and oxygen, being components of water molecules, are indicators of all the processes of natural water movement, which have occurred during the history of existence of the Earth. According to Rozanski et al. [4] in the hydrologic cycle, the variability ranges of ^{2}H/^{1}H and ^{18}O/^{16}O are between -450 and $+100$‰ and from -50 to $+50$‰, respectively. In general, the ^{2}H/^{1}H or ^{18}O/^{16}O ratios mainly vary due to phase changes from vapor to liquid or ice and vice versa.
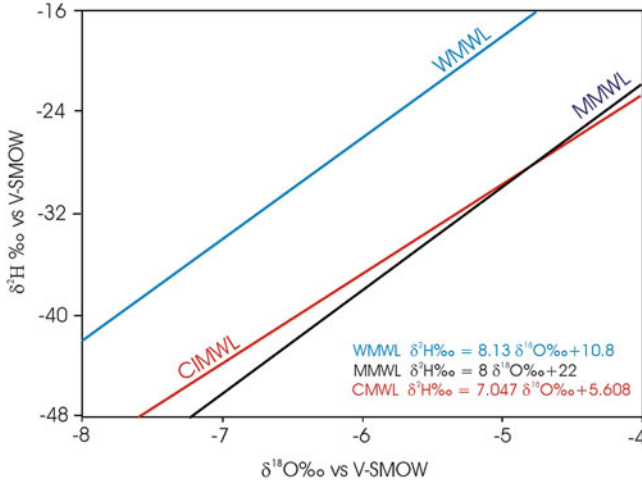
Fig. 2 Binary diagram of the isotopic ratios of hydrogen vs. oxygen. Mediterranean Meteoric Water Line (MMWL) [20], World Meteoric Water Line (WMWL) [21], and Central Italy Meteoric Water Line (CIMWL) [22]. From Sappa et al. [23], modified

The ratios of hydrogen and oxygen isotopes are linearly correlated, and the trend of variations characterizes the Global Meteoric Water Line (GMWL) where $\delta^2H = 8\delta^{18}O + 10$ [19]. Later on, Gat and Carmi [20] suggested for the Mediterranean Meteoric Water Line (MMWL) the relationship $\delta^2H = 8\delta^{18}O + 15$ between δ^2H and $\delta^{18}O$. In the classical δ^2H vs. $\delta^{18}O$ binary diagram, the reference meteoric lines, e.g., GMWL and MMWL, are commonly drawn with those of local and/or regional interest (Fig. 2). For the most part, the positive intercept in this regression originates from the difference in isotopic fractionation effects of water-vapor equilibrium and of vapor diffusion in air (e.g., review of [24]). Deviations from a line with slope of 8 and zero intercept indicate an excess (or depletion) of deuterium defined by Dansgaard [25] as d-excess $= \delta^2H - 8\delta^{18}O$. It has mainly been correlated with the environmental conditions existing in the source area of the water vapor [20, 26]. The degree of excess (or depletion) is phenomenologically related to geographic parameters such as latitude, altitude, and distance from the coast and to the fraction precipitated from a vapor mass content (e.g., [27–31]) (Fig. 3).

2.2 Groundwater Origin, Recharge, and Mixing Processes

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 groundwaters collected from springs and/or wells.

Spatial variability of the δ^2H or $\delta^{18}O$ values in precipitation reflects the combination of source-region labeling, rainout, and recycling effects that affect air masses
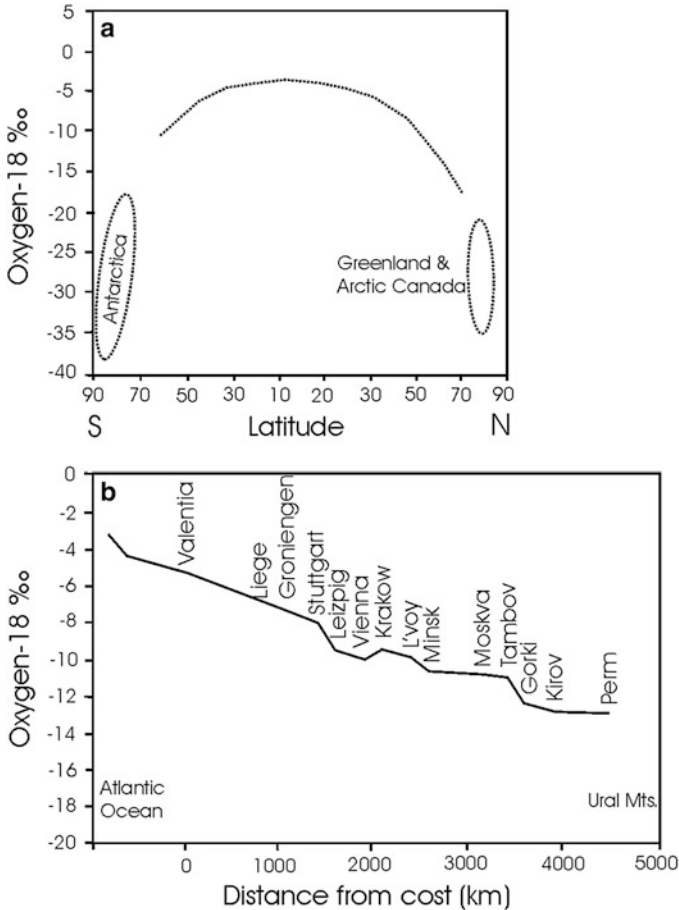
Fig. 3 Distribution of $\delta^{18}O$ values correlated with latitude (**a**) and distance from the cost (**b**)

bringing vapor to different geographic regions. The isotopic compositions of precipitation have been mapped at several scales: global distribution (e.g., [32]), regional scale (e.g., [22]), and detailed scales (e.g., [33]). Minissale and Vaselli [34] 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 δ‰ m^{-1} line, proposed by Longinelli and Selmo [22], as representative of the mean isotopic altitude gradient ($\Delta\delta^{18}O$) 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 [35, 36]. The development of tracer techniques using stable isotopes enables approaches to groundwater movement in many regions [37–45]. The case

study of the Souss Basin, which is one of the most important basins in Southern High Atlas Mountains (Morocco), describes the typical problem of water in arid areas. According to Bouragba et al. [46], hydrogen and oxygen isotopic signatures reveal a rapid infiltration before evaporation of meteoric waters. The depletion in groundwater stable isotopes shows a recharge under different conditions. During wet periods, the precipitation altitude was indeed higher than that observed in different meteorological conditions [46].

The δ^{18}O and δ^2H values from shallow groundwater systems reflect those of the local average precipitation although they can be modified at some extent by selective recharge and fractionation processes, which may alter the pristine δ^{18}O and δ^2H values before the water reaches the saturated zone. The recent study by Liu and Yamanaka [47] has dealt with the quantitative contribution of different sources feeding the groundwater recharge applying an isotopic (δ^{18}O and δD) and hydrochemical approach to facilitate an integrated management of ground and surface water resources. This investigation was carried out in the area of Ashikaga (central Japan) that hosts the largest plain of Japan, which is traversed by the Watarase River. Sampling included meteoric waters, which were collected monthly for one year, 12 groundwaters from domestic wells, and 4 river samples. The isotopic signatures allowed to distinguish the different origins of the waters. The isotopic composition of pluvial water varied temporally in response to several factors (temperature effect and amount effect), with remarkably differences between the warm (April to September) and the cool (October to March) periods. It is considered that precipitation in the warm period is a more effective recharge source than that in the cool period. The 1-year observation of the isotopic signature of precipitation was not however assumed as representative of the local precipitation. On the contrary, river water and groundwater samples clearly showed weak variation, and their δ values were significantly distinct with respect to those of precipitation, suggesting considerably long residence times (at least >1 year). In addition, the close relationship observed between the mean δ values of river water and the mean elevation of the catchment reflected the altitude effect. In more detail, the low δ values of the river water corresponded to high elevation of its recharge zone. The isotopic composition of the groundwater samples ranked them between pluvial and river waters. This was also indicating (i) evaporation from shallow wells, (ii) contribution of the aquifer to the river recharge, and (iii) mixing processes of waters with different origins, e.g., direct infiltration, river seepage, and mountain block recharge.

Salinization of water resources is one of the most widespread processes that deteriorates water quality. Salinization is due to the inflow of saline dense water during heavy withdrawals of freshwater from coastal aquifers and/or mobilization of saline formation waters by overexploitation of inland aquifer systems. The combined use of oxygen and hydrogen isotopes is presently able to identify different salinization pathways. For instance, recently by a temporal monitoring of superficial waters, Petrini et al. [48] have examined the issues related to salinization and water quality in the drainage system of Ravenna coastal plain that extends for about 1,500 km^2 bordered to the east by the northern Adriatic Sea

coastline (Italy). In this study, the combined use of oxygen and hydrogen demonstrated to be a useful tool in the management of water resources, allowing the water sources, recharge processes, and the risk of saltwater intrusion or pollution to be investigated. In particular, the oxygen and hydrogen isotopic composition of rainwater was used to construct a local meteoric water line defining a correlation given by $\delta^2H = (7.00 \pm 0.17) \times \delta^{18}O$ (5.80 ± 1.3). In addition, they showed that waters from the coastal system range in composition from -8.53 to -0.69‰ and from -60.10 to -5.44‰ for $\delta^{18}O$ and δ^2H, respectively, reflecting the variable contribution of a marine component.

3 Carbon Stable Isotopes

3.1 Background Principles

The chemical element carbon has two stable isotopes, ^{12}C and ^{13}C, and their abundances are of about 98.9 and 1.1%, respectively. Ratios of these isotopes are reported in ‰ relative to the Vienna Pee Dee Belemnite (VPDB) standard. The $^{13}C/^{12}C$ ratio of the VPDB standard is 0.011796 [49] and is expressed as $\delta^{13}C$, similarly to Eq. (1) for hydrogen and oxygen isotopes.

Carbon isotope analyses are useful when studying aquatic and hydrogeological systems in contact with CO_2. Examples of such applications include investigations in carbon cycle and flux (e.g., [50–53]), chemical weathering (e.g., [54]), degassing from thermal and cold springs (e.g., [55, 56]), volcanic–hydrothermal systems (e.g., [57, 58]), and, as a relatively new field, geochemical trapping in CO_2 injection (carbon capture and storage (CCS)) projects (e.g., [59–61]).

Measurements of concentration and $\delta^{13}C$ values of DIC, which is referred to the following equation [62]:

$$\delta^{13}C_{DIC} = \delta^{13}C_{\left(CO_{2(aq)} + HCO_3^- + CO_3^{2-}\right)} \tag{2}$$

are routinely used in studies of carbon geochemistry and biogeochemistry of natural waters. Part of the carbon cycle is shown in Fig. 4. The primary reactions that generate DIC are weathering of carbonate and silicate minerals produced from (i) acid rain or other strong acids, (ii) carbonic acid formed by the dissolution of biogenic soil CO_2 as rainwater infiltrates, and (iii) dissolution of deep CO_2 (typically in active tectonic areas). The DIC pool can be influenced by contributions from groundwater, tributary streams, biogenic uptake and release of CO_2, and CO_2 invasion from or evasion to the atmosphere. These processes influence both DIC concentrations and $\delta^{13}C_{DIC}$ values. Changes in the carbon isotopic ratios result from isotope fractionation processes accompanying the transformation of carbon or from mixing of carbon from different sources. The $\delta^{13}C_{DIC}$ values in catchment waters are generally in the range of -5 to -25‰ [63]. $\delta^{13}C$ values together with
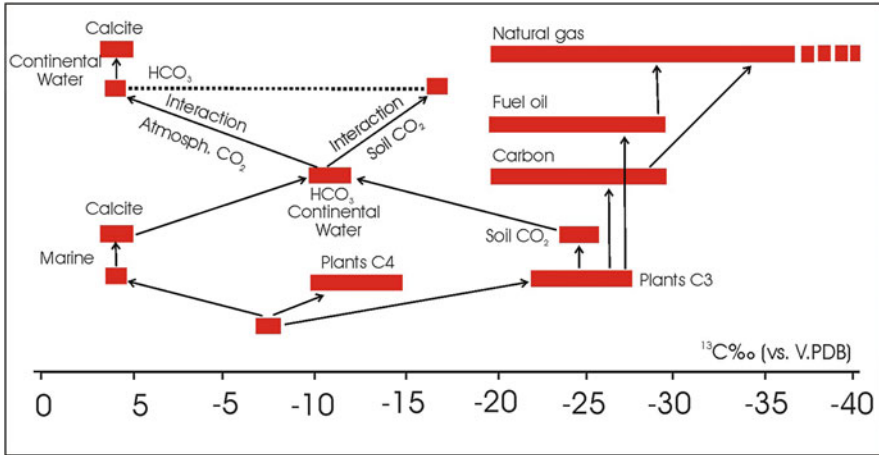
Fig. 4 Conceptual model showing the main processes that control the sources of dissolved inorganic carbon (DIC)

major ion chemistry and/or other isotope tracers (e.g., $\delta^{34}S$, $^{87}Sr/^{86}Sr$) can be used to evaluate proportions of DIC [64] and to estimate sources, sinks, and fluxes of carbon (e.g., [65, 66]).

3.2 Applications to Environmental Geochemistry Studies

Numerous authors have analyzed and used carbon isotopes as indicators of biogeochemical reactions taking places within catchment and river basins (e.g., [54, 67, 68]). Large rivers play an important role in controlling the $\delta^{13}C_{DIC}$ values by biological recycling of carbon and equilibration with atmospheric CO_2. These studies have shown that upstream reaches and tributaries are cause for the primary pool of DIC supplied to the main stem of large rivers controlling the carbon isotope compositions further downstream (e.g., [69, 70]). Several attempts were made to evaluate the effects of these processes. Atekwana and Krishnamurthy [67] studied the seasonal concentrations and $\delta^{13}C$ of DIC in the river–tributary system in Kalamazoo, southwest Michigan (USA). They reported that the riverine DIC concentrations decreased (from 48.9 to 45.9 and from 60.4 to 48.6 mg C/L for river and tributaries, respectively), while $\delta^{13}C_{DIC}$ values increased (from −9.9 to −8.7 and from −11.4 to −9.7‰ for river and tributaries, respectively) in summertime due to photosynthesis. On the other hand, DIC concentrations incremented (from 51.9 to 53.4 and from 52.2 to 66.8 mg C/L for river and tributaries, respectively) and $\delta^{13}C_{DIC}$ values decreased (from −9.9 to −10.2 and from −9.3 to −12.8‰ for rivers and tributaries, respectively) during the late fall as photosynthesis declined and in-stream decay and respiration increased. These authors suggested that the difference in absolute values of concentrations and those of

$\delta^{13}C_{DIC}$ between the main river and its tributaries was derivable by shorter residence times of water in the tributaries when compared to those of the main course.

DIC concentrations and $\delta^{13}C_{DIC}$ values are also useful tracers of the DIC sources and the evolutionary history of DIC in contaminated streams. Atekwana and Fonyuy [71] and Ali and Atekwana [72] measured the $\delta^{13}C_{DIC}$ values to assess the extent of H^+ production from acid mine drainage (AMD) pollution of stream waters on inorganic carbon processing and $\delta^{13}C_{DIC}$ over spatial and temporal scales. Ali and Atekwana [72] investigated at the Federal Tailings Pile in the St. Joe State Park in southeastern Missouri (USA) the acidification and neutralization effects on the carbonate evolution in a shallow aquifer affected by a metal sulfide-rich and carbonate-rich tailing pile. Their isotopic modeling suggested that in the vadose zone, HCO_3^- dehydration produced degassing of $CO_{2(g)}$ from pore water and groundwater with $\delta^{13}C_{DIC}$ of -3.1 to -6.8‰.

Changes in the pH values resulting from AMD pollution and the chemical evolution of AMD in streams affect the speciation of DIC. Most importantly, the decrease in stream of pH due to AMD-produced H^+ drove DIC speciation to carbonic acid (H_2CO_3), which subsequently dissociated to $CO_2(aq)$. The degassing of CO_2 from streams should be accompanied by enrichment in $\delta^{13}C_{DIC}$ due to preferential loss of ^{12}C with respect to ^{13}C [73]. Atekwana and Fonyuy [71] demonstrated that $\delta^{13}C_{DIC}$ enriched by <3.0‰ when CO_2 loss was proton enhanced and isotopic fractionation was mostly controlled by diffusion. The $\delta^{13}C_{DIC}$ value enriched by >3.0‰ when CO_2 loss was neutralization induced and CO_2 loss was accompanied by partial exchange of carbon between DIC and atmospheric CO_2. Atekwana and Fonyuy [71] concluded that DIC loss and $\delta^{13}C_{DIC}$ enrichment in AMD-contaminated streams were depending on (i) the amount and rate of production of proton formed by metal hydrolysis, (ii) mechanism of CO_2 loss, and (iii) buffering capacity of the streams.

Monitoring stable carbon isotopes and subsequent determination of isotope mass balance is a method to evaluate the fate of CO_2 and distribution of DIC in deep aquifers. Recently, this approach was applied to several studies related to the subsurface storage of CO_2 (CCS), e.g., geochemical trapping in CO_2 injection projects (e.g., [59, 60]). Nisi et al. [61] investigated the isotopic carbon of dissolved CO_2 and DIC related to surface and spring waters and dissolved gases in the area of Hontomín–Huermeces (Burgos, Spain) to verify whether CO_2 leakages, induced by the injection of CO_2, might have been able to affect the quality of the waters in the local shallow hydrological circuits. In fact, the isotopic and chemical equilibrium of the C-bearing inorganic species can be used to trace CO_2 leakage if the injected CO_2 would have an isotopic carbon ratio that differs with respect to that already present [74]. Industrial CO_2 to be injected in a pilot site is indeed usually derived by refinery gas processing, and the $\delta^{13}C_{CO2}$ values are rather negative, e.g., from -36 [61] to -28‰ VPDB as that used in the Ketzin pilot site [75]. Nisi et al. [61] reported that the baseline of $\delta^{13}C_{DIC}$ of the Hontomín–Huermeces shallow aquifer had a value -10‰ VPDB and that the $\delta^{13}C_{CO2}$ values measured in the Hontomín–Huermeces waters are clustering around -20‰ VPDB, i.e., more positive than those of the injected CO_2 at Ketzin and likely similar to that expected to be injected

in the Spanish site. Nisi et al. [61] applied a theoretical model representing the DIC and $\delta^{13}C_{DIC}$ evolution of infiltrating water through carbonate terrains where a CO_2 source was active, according to two different ways: (i) addition of soil CO_2 deriving from oxidation of organic matter and root respiration (biogenic) and (ii) addition of deeply derived CO_2 and in equilibrium with calcite. This model predicted that the injection of CO_2 with a carbon isotopic value of $-30‰$ VPDB should decrease $\delta^{13}C_{DIC}$ to more negative values than those measured. By simulating the addition of 100 steps of 0.01 mol of CO_2 ($\delta^{13}C_{CO2} = -30‰$ VPDB and $\delta^{13}C_{DIC} = -10‰$ VPDB) and considering the maximum (0.008 mol/kg), minimum (0.0033 mol/kg), and mean (0.0052 mol/kg) DIC values of the Hontomín–Huermeces waters, the resulting $\delta^{13}C_{DIC}$ and DIC values would indeed be $-28.6‰$ and 0.12 mol/kg, $-29.4‰$ and 0.11 mol/kg, and $-29.1‰$ and 0.11 mol/kg, respectively.

4 Sulfur Stable Isotopes

4.1 Background Principles

Sulfur has four stable isotopes: ^{32}S (95.02%), ^{33}S (0.75%), ^{34}S (4.21%), and ^{36}S (0.02%) [76]. Like ^{18}O, ^{2}H, and ^{13}C, sulfur isotopes are expressed with the delta notation defined by Eq. (1). Stable isotope compositions are reported as $\delta^{34}S$, ratios of $^{34}S/^{32}S$ in ‰ relative to the standard CDT (FeS phase of the Canyon Diablo Troilite meteorite) for which the value 0.0450 was assigned. Figure 5 shows the ranges of $\delta^{34}S$ values found in nature for a number of different forms of sulfur.

Sulfur species can be sampled from water as sulfate (SO_4^{2-}) or sulfide (H_2S or HS^-) for measuring $\delta^{34}S$ and, for sulfate, $\delta^{18}O$. Oxygen-18 in sulfate is referred to the VSMOW reference standard. Bacterial reduction of SO_4 is one of primary sources to explain the sulfur isotopic variability observed in natural aquatic systems. Sulfate-reducing bacteria utilize dissolved sulfate as an electron acceptor during the oxidation of organic matter, producing H_2S gas that has a $\delta^{34}S$ value of $-25‰$, i.e., lower than that of the sulfate source [64]. On the other hand, not significantly fractionation of sulfur isotopes is expected for the following processes, such as (i) isotopic exchange between SO_4^{2-} and HS^- or H_2S in low-temperature environments, (ii) weathering of sulfate minerals and sulfide, and (iii) adsorption–desorption interactions with organic matter [78, 79].

The main use of sulfur isotopes has been aimed to understand the formation of polymetallic sulfide ore deposits, which can be originated in either sedimentary or igneous environments. $\delta^{34}S$ values exceeding $+20‰$ are found in association with evaporitic rocks and limestone deposits [63]. Sulfur associated with diagenetic environments generally reflects the composition of biogenic sulfide produced by bacterial reduction of marine sulfate and generally shows negative $\delta^{34}S$ values (from -30 to $+5‰$, [80, 81]). On the other hand, sulfur associated with crystalline rocks derived from the mantle is isotopically similar to that of the reference
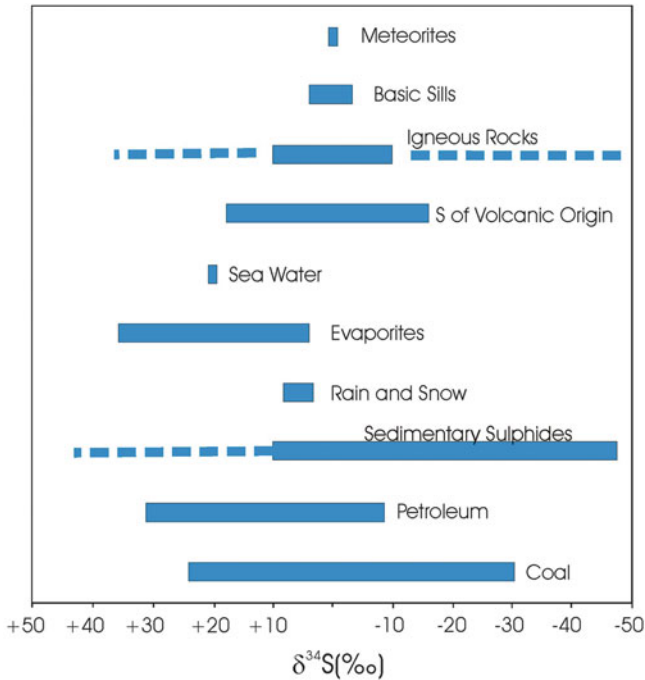
Fig. 5 Sulfur isotope distribution in nature. From Thode [77], modified

standard, whose $\delta^{34}S$ values are from 0 to +5‰. Nevertheless, volcanic rocks are occasionally characterized by $\delta^{34}S$ values up to +20‰, suggesting recycling processes of oceanic sulfate at subduction zones.

In environmental geochemistry studies, the evaluation of sulfate sources and cycling has been coupled with the analysis of the oxygen isotopic composition of sulfate. Sulfur and oxygen isotopic compositions of dissolved sulfate ($\delta^{34}S\text{-}_{SO4}$ and $\delta^{18}O\text{-}_{SO4}$, respectively) have been used to clarify sources and transformation processes of sulfur in aquatic systems associated with anthropogenic activities. These isotopes can provide meaningful information about various potential sources of sulfate in the watershed (e.g., dissolution of sulfate-bearing evaporitic minerals, such as gypsum and anhydrite, mineralization of organic matter, oxidation of sulfide minerals, infiltration from anthropogenic sources, atmospheric deposition) (e.g., [82, 83]). In recent years, the use of stable sulfur isotopes has been expanded to address diverse surface water and groundwater issues, e.g., cycling of sulfur in agricultural watersheds, origin of salinity in costal aquifers, groundwater contamination by landfill leachate plumes, and acid main drainage (e.g., [84–87]).

4.2 Application Studies to Groundwater and Surface Waters

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 [88] used a combination of $\delta^{34}S\text{-}_{SO_4}$ 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 $\delta^{34}S\text{-}_{SO_4}$ 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 $\delta^{34}S\text{-}_{SO_4}$ and $\delta^{18}O\text{-}_{SO_4}$ since they have a distinctive isotopic composition to identify pollution sources. Cortecci et al. [89] investigated the $\delta^{34}S\text{-}_{SO_4}$ 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 $\delta^{34}S\text{-}_{SO_4}$ values from natural inputs were ranging approximately between -15 and +4‰, likely related to the oxidation of pyrite disseminated in bedrocks, and $\delta^{34}S\text{-}_{SO_4}$ 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 $\delta^{34}S\text{-}_{SO_4}$ values varying between 1 and 8‰.

Urban groundwater contamination problems are becoming increasingly recognized in all Asian megacities ([90] and reference therein). 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. [90] explored the $\delta^{34}S\text{-}_{SO_4}$ and $\delta^{18}O\text{-}_{SO_4}$ 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 $\delta^{34}S\text{-}_{SO_4}$ and $\delta^{18}O\text{-}_{SO_4}$ values were ranging from -5.0 to +14.4‰ and from +13.1 to +25.7‰, respectively. Dissolved sulfate derived by chemical detergents had

δ^{34}S-$_{SO_4}$ and δ^{18}O-$_{SO_4}$ values from -3.7 to $+24.4$‰ and from $+11.6$ to $+20.6$‰, respectively. Eventually, the isotopic compositions of industrially processed high concentration sulfuric acid were characterized by δ^{34}S-$_{SO_4} = 1.2$‰ and δ^{18}O-$_{SO_4} = 9.5$.

Recently, the isotopic signature of dissolved sulfate was used to provide valuable information about the nature of water inputs to the sewage flow. The dynamics of various hydrologic processes that commonly occur within the sewer system, such as groundwater infiltration, rainwater percolation, or release from retention basins, can readily be described by using water isotope ratios. Houhou et al. [86] applied a combined water and sulfate dual isotope approach (δ^{34}S-$_{SO_4}$ and δ^{18}O-$_{SO_4}$) to examine the contribution of different water sources to flow within an urban sewer system. Houhou et al. [86] found that sulfate originating from urine was also detected as a tracer of human waste impacts, since δ^{18}O-$_{SO_4}$ of urine is isotopically distinct from other sulfate sources (values around 4.5‰ for δ^{34}S-$_{SO_4}$ and between 5.9 and 7.5‰ for δ^{18}O-$_{SO_4}$). Inorganic sulfate indeed represents the main end product of sulfur metabolism in the human body, although other forms such as ester sulfate represent a 9–15% fraction of the urinary sulfate ([86] and references therein). In the last years, intensive investigations of the stable isotopic composition of sulfate from groundwater, surface waters, and acidic mine drainage were performed due to the dominant role of sulfur as a component of AMD. Isotopic (δ^{34}S-$_{SO_4}$ and δ^{18}O-$_{SO_4}$) compositions can be used to clarify sources and transformation processes of sulfur in aquatic systems associated with coal mining ([87] and references therein). It is well assessed that the exposure of pyrite and other metal sulfides to weathering under atmospheric conditions produces sulfuric acid, with subsequent mobilization of other toxic substances (metals, metalloids) into groundwater and surface water (e.g., [91] and references therein). The Great Falls–Lewistown Coal Field in central Montana contains over 400 abandoned underground coal mines, many of which are discharging acidic waters with serious environmental consequences [84]. In this respect, Gammons et al. [84] examined the spatial and temporal changes in the chemistry of the mine waters and used the stable isotopes to address the sources of water and dissolved sulfate in the abandoned coal mines, as well as the surrounding sedimentary aquifers. They reported that most sulfates in these waters were derived by oxidation of pyrite in the coal with δ^{34}S-$_{SO_4}$ and δ^{18}O-$_{SO_4}$ values ranging from -16.1 to -9.3‰ and from -12.5 to -9.1‰, respectively, while pyrite samples in coal from drill cuttings produced δ^{34}S values from -27.2 to -19.6‰. Bacterial sulfate reduction is known to cause extreme fractionation of S isotopes ([84] and references therein). The fact that the mine waters and pyrite samples in this study are strongly depleted in ^{34}S suggests that bacterial sulfate reduction played an important role in the formation of the high-S coals. Gammons et al. [84] concluded that sulfate in the AMD waters was isotopically distinct from that in the underlying aquifer, and that mine drainage may have leaked into the aquifer.

5 Nitrogen Stable Isotopes

5.1 Background Principles

There are two naturally occurring stable isotopes of nitrogen, ^{14}N and ^{15}N. The majority of N in the atmosphere is consisting of ^{14}N (99.6337%), whereas the remainder is ^{15}N (0.3663%) [92]. Stable isotope ratios are expressed with the delta notation defined by Eq. (1) as δ^{15}N: ^{15}N/^{14}N ratios in ‰ relative to the atmospheric air (AIR-NBS). The dominant source of nitrogen in most natural ecosystems is the atmosphere (δ^{15}N = 0‰). Most terrestrial materials have δ^{15}N values between -20 and +30‰. As a consequence, plants fixing N_2 from the atmosphere have δ^{15}N values of about -5 to +2‰ [93]. Typical available soil N has δ^{15}N values from 0 to +8‰, although the δ^{15}N interval for refractory soil N may be larger [94–96]. Rock sources of N are generally considered negligible contributors to groundwater and surface water, but they can be important in some environments [97]. The use of isotopes to trace nitrogen reactions in hydrology gained further attention when it became possible to routinely measure the ^{18}O contents of nitrate [98]. The combination of δ^{15}N and δ^{18}O (whose values are reported relative to VSMOW) now provides a tool that enables us to distinguish between nitrates of different origins, to recognize denitrification processes, and to discuss the N-budget in the soil–water system (e.g., [94, 96, 99–107]). δ^{15}N values of NO_3 from various sources and sinks are reported in Fig. 6. Nitrate (NO_3) concentrations in public water supplies have risen above acceptable levels in many areas of the world, largely as a result of overuse of fertilizers and contamination by human and animal waste. Identifying
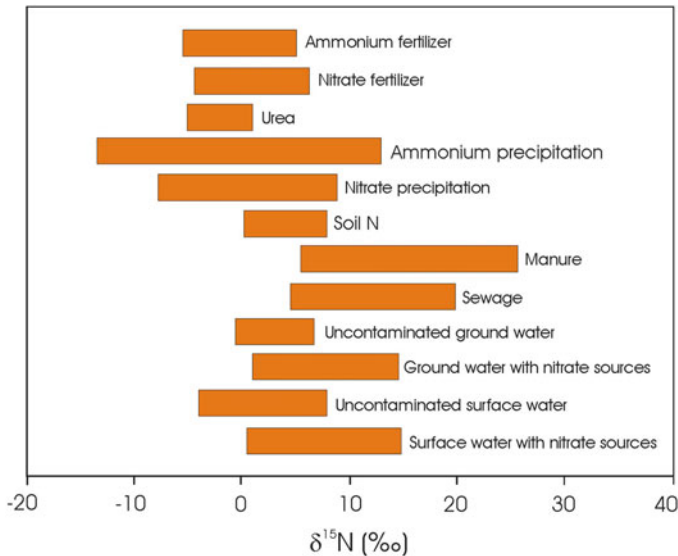

Fig. 6 δ^{15}N values of NO_3 from various sources and sinks. Fields are from Xue et al. [96]

the dominant source or sources of nitrate and other solutes to surface water and groundwater systems is critical for making effective contaminant management decisions. Overuse of fertilizers results in high concentrations of nitrates, able to modify the isotopic composition of $N-NO_3$ in superficial water and groundwater. Nitrates from synthetic fertilizers have $\delta^{15}N$ values varying from -6 to $+6‰$ AIR [94, 96]), while those of $\delta^{18}O$ are $22\pm3‰$ VSMOW [98], because they are produced from atmospheric nitrogen ($\delta^{15}N = 0‰$) and oxygen ($\delta^{18}O = 23.5‰$). Nitrate derived from manure and sewage is isotopically distinct from that of fertilizers in both $\delta^{15}N$ (from $+5$ to $25‰$, [64, 94, 96]) and $\delta^{18}O$ ($<15‰$, [94]). Nitrate from wet and dry atmospheric deposition has a wide range of $\delta^{15}N$ values of approximately -10 to $+15‰$ and can also be originated from human activities, such as agriculture, vehicle exhaust, and power plant emissions [108]. In general, biologically mediated reactions (e.g., assimilation, nitrification, and denitrification) strongly control nitrogen dynamics in the soil and can influence and/or affect nitrogen dynamics in water. For instance, in the stepwise conversion of NO_3^- to N_2, nitrogen isotopes are fractionated: the lighter isotope (^{14}N) is preferentially partitioned in the products, while the heavier one (^{15}N) becomes concentrated in the residual reactants [109]. Several studies have employed both $\delta^{15}N$ and $\delta^{18}O$ of nitrate in the estimation of denitrification in the water system. They reported that a linear relationship, indicating an enrichment of ^{15}N relative to ^{18}O by a factor between 1.3:1, 1.5:1, and 2.1:1, gives strong clues for denitrification processes [110–113].

5.2   Applications to Groundwater and Surface Water Studies

Nitrate contamination of surface water and groundwater is an environmental problem in many regions of the world. High nitrate concentrations in drinking water are also believed to be a health hazard. At global scale, groundwater is a critical resource for both drinking water and other applications, such as agricultural irrigation. A prerequisite for controlling and managing nitrate pollution is to identify sources of nitrate. Contamination of aquifers from nitrate and other solutes is a significant concern, and therefore, the use of nitrate isotopes to understand contaminant sources and nitrate cycling in groundwater has become much more common. Karst aquifers are particularly vulnerable to nitrate contamination from anthropogenic sources due to the rapid movement of water in their conduit networks. Many studies have shown that stable isotope techniques are useful for evaluating sources of nitrogen because certain sources of nitrate have characteristic or distinctive isotopic compositions (e.g., [96] and references therein). Li et al. [114] used nitrate isotopes combined with chemical compositions to identify the primary sources of contamination and characterize the processes affecting nitrate in the karstic groundwater system of the Zunyi area (SW China) during summer and winter. The wide range of $\delta^{15}N_{-NO_3}$ values (from -1.8 to $+22.7‰$) and the intercorrelations between NO_3 and K observed in this study suggested that there

were at least three major sources contributing to the nitrate pollution of the groundwater in Zunyi, which included organic manure and synthetic fertilizer, and urban sewage effluents, while there was no direct evidence to show that denitrification occurred in the aquifer evaluated. However, Einsiedl and Mayer [115] reported that denitrification could have occurred in the porous rock matrix of a karst aquifer in southern Germany.

Generally speaking, elevated concentrations by nitrate in groundwater and surface water were most often measured in regions of intensive agriculture and principally attributed to the impacts of organic and chemical fertilizer inputs. In this respect, Savard et al. [116] analyzed the isotope ratios of the potential nitrate sources and measured the isotope and concentrations of nitrate in groundwater and surface water samples collected during eight campaigns distributed over the 2003–2004 and 2004–2005 seasonal cycles to constrain a conceptual apportionment model quantifying the relative seasonal N contributions in an area of intense potato production in the Wilmot River basin (PEI, Canada). In the Wilton region, the potential sources of nitrogen included urea fertilizer (H_2NCONH_2), whose $\delta^{15}N$ values were ranging from -1.9 to $+1.1$‰, whereas the wet atmospheric load varied between -11.8 and $+11.4$‰ and $+22.8$ and $+83.2$‰ for $\delta^{15}N$ and $\delta^{18}O$ values, respectively [116]. According to Savard et al. [116], elevated nitrate levels were coupled with agricultural activities and appeared to be most closely associated with extensive use of fertilizers for row crop production, rather than with other potential sources such as atmospheric load.

In agricultural regions, fertilizers and irrigation are the primary factors that contribute to increase world crop production. The use of fertilizers accounts for approximately 50% of the yield increase and greater irrigation for another substantial part [117]. In this respect, China is the world's greatest producer and consumer of fertilizers using about 31% of the total amount of fertilizers used worldwide [118]. Zhang et al. [119], by using a dual isotopic analysis of NO_3, conducted a study in the North China Plain with the aim to identify nitrate pollution in both surface water and groundwater in irrigated agricultural regions. Zhang et al. [119] showed that the main sources of nitrate were nitrification of fertilizer and sewage in surface water, whereas groundwater sources during the dry season were mineralization of soil organic N and sewage. When fertilizers were applied, nitrate was transported by precipitation through the soil layers to the groundwater in the wet season. Savard et al. [116] and Zhang et al. [119] concluded that strategies to attenuate contamination by nitrate in waters of temperate climate row-cropping regions must consider nitrogen cycling by soil organic matter including the crucial role of crop residues throughout both the growing and nongrowing seasons. In particular, they suggested that plowing and its associated stimulation of mineralization and nitrification and the application of manures and its nitrogen loading should be timed to optimize crop uptake and minimize leaching losses.

Identification of nitrate sources is important in preserving water quality and achieving sustainability of the water resources. However, the occurrence of multiple inputs and/or the presence of overlapping point and nonpoint sources makes this task complicated. For instance, sewage and manure end members have overlapping

δ^{15}N-$_{NO_3}$ and δ^{18}O-$_{NO_3}$ values, and their differentiation on this basis is critical. In a recent review, Fenech et al. [103] showed that chemical markers (such as pharmaceuticals and food additives) with nitrate isotopes are suitable to differentiate sewage and manure sources of nitrate contamination. It is worthwhile to mention that a number of potential chemical markers are consumed by both humans and livestock, e.g., antimicrobial agents such as some tetracyclines and sulfonamides ([103] and references therein). Some examples of pharmaceuticals, which are used for the treatment of humans, animals, or both, are given in Fenech et al. [103], indicating these substances as suitable indicators of human and animal sources.
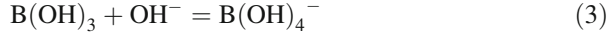
6 Boron and Strontium Isotopes

6.1 Background Principles

Boron is a ubiquitous minor or trace constituent in all natural surface and subsurface aquatic systems. It is mainly derived from the interaction of fluids with the crust (~10–13 mg kg^{-1} B) [120] and/or mixing between fluids from different reservoirs and weathering of rocks and soils characterized by B-bearing minerals, whose the highest concentrations are recorded in waters leaching B-bearing salt deposits [121]. In coastal areas, rain containing sea salt from ocean spray provides another natural B source, but such inputs decline with distance from the coast [122]. The boron budget of surface and subsurface aquatic systems can considerably be affected by discharge of anthropogenic boron-laden waters. Elevated B levels in surface waters most commonly occur in industrial and urban areas. Among the many possible sources of anthropogenic B, domestic and some industrial wastewater effluents, herbicides and insecticides, glass manufacturing wastes, antifreeze, landfill and coal mine leachates, fly ash, petroleum products, slag, sewage sludge, manure, and compost ([123] and references therein) are those which mainly affect the natural waters. In hydrological investigations, the B isotope ratios often provide the fingerprint needed to identify the origin of B dissolved in natural waters, because it enables distinguishing B from natural sources from that due to anthropogenic sources ([124, 125] and references therein).

Boron has two naturally occurring stable isotopes, ^{11}B and ^{10}B. The isotopic composition of boron is expressed as a ratio of the two naturally occurring stable isotopes ^{11}B (80.1%) and ^{10}B (19.9%). The delta notation is similar to that expressed in Eq. (1), i.e., $\delta^{11}B = [(^{11}B/^{10}B)_{sample}/(^{11}B/^{10}B)_{standard} - 1] \times 1,000$, where the standard is the NBS boric acid 951, whose ^{11}B/^{10}B is 4.04362 ± 0.00137 [126].

Boron isotope fractionations are almost entirely controlled by the partitioning between the two dominant dissolved species B(OH)$_3$, trigonal and planar, and B(OH)$_4$$^-$, tetrahedral, through the reaction:

$$B(OH)_3 + OH^- = B(OH)_4^- \tag{3}$$

The relative abundances of the boron-dissolved species are pH dependent.

The large relative mass difference between the two stable boron isotopes leads to a wide range of isotope variations in nature with diagnostic signatures of crustal, meteoric, and marine B sources. The $\delta^{11}B$ approximate ranges of the main B reservoirs are +4 to +58‰ for marine B, −31 to +26‰ for nonmarine B, −17 to −2‰ for igneous B, and −34 to +22‰ for metamorphic B ([127] and references therein). Natural waters (such as seawater, river water, rainwater, groundwater, saline formation water, brines, and geothermal fluids) encompass a range in $\delta^{11}B$ from −16 to +60‰ ([128] and references therein).

Strontium is classified as a trace element, and in aquatic environment, it occurs as a divalent cation that readily substitutes for Ca^{2+} in carbonates, sulfates, feldspars, and other Ca-bearing rock-forming minerals (e.g., plagioclase, apatite, calcium carbonate, especially aragonite). These include the primary mineralogy of the sediments, secondary weathering products, and cement. Strontium has four naturally occurring isotopes, ^{88}Sr, ^{87}Sr, ^{86}Sr, and ^{84}Sr, all of which are stable. The isotopic abundances of strontium isotopes are variable because of the formation of radiogenic ^{87}Sr by the decay of naturally occurring ^{87}Rb. For the Rb–Sr isotope system, the mechanism of interest for the decay is represented by the following equation:

$$^{87}Rb \rightarrow {}^{87}Sr + \beta^- \tag{4}$$

Over time, the amount of the daughter (radiogenic) isotope in a system increases and the amount of the parent (radioactive) isotope decreases as it decays away. If the rate of radioactive decay is known, we can use the increase in the amount of radiogenic isotopes to measure time. In practice, this is commonly done by measuring the concentration of the radiogenic isotope relative to a non-radiogenic isotope of the same element, e.g., ^{87}Sr is referenced to ^{86}Sr and the $^{87}Sr/^{86}Sr$ ratio (e.g., [129]) is measured. Although the minerals in igneous and metamorphic rocks may have identical Sr isotope ratios at the time of formation, the decay of ^{87}Rb (which has a half-life of 4.88×10^{10}, [129]) to ^{87}Sr leads, over time, to differences in $^{87}Sr/^{86}Sr$.

In freshwater systems, the residence times of waters are sufficiently short (days to 10^{2-3} years) compared to the half-life of ^{87}Rb; thus, the radioactive decay of ^{87}Rb can be considered negligible. The application of Sr isotope ratios as a natural tracer in water–rock interaction studies and in assessing mixing relationships is now well established (e.g., [130–133]). $^{87}Sr/^{86}Sr$ ratio is diagnostic of Sr sources and, by analogy, Ca sources. The Sr isotopic signature can usefully be utilized as hydrology tracer since Sr derived from any mineral through weathering reactions maintains in solution the same $^{87}Sr/^{86}Sr$ ratio of the original mineral, i.e., no fractionation processes take place, differently to the stable isotopic systematics previously described. Strontium isotopic fractionation is negligible even when this element

is removed from water by either mineral precipitation or cation exchange process (e.g., [134]). A prerequisite for the use of Sr isotopes as tracer for groundwater pollution is a sufficient variability in the signature of the ^{87}Sr/^{86}Sr ratios among the different end members. Such variations have been observed between natural groundwater and human inputs (e.g., [135–137]).

6.2 Isotope Applications in Hydrology

As previously stated, seawater intrusion has for long been recognized as a serious threat to the groundwater quality in coastal aquifers. The increasing use of groundwater has in many places, especially in arid and semiarid regions, caused kilometer-scale intrusions resulting in severe groundwater quality problems (e.g., [138] and references therein). In this respect, traditional tracers such as chloride yield limited information on hydrochemical evolutionary trends because evapo-concentration effects can mask the indicators of groundwater flow paths. It is in these hydrogeological settings that trace element isotopes become particularly useful. Boron isotopes become much more powerful tools when combined with other isotope systematics such as Sr (e.g., [127, 139, 140]). Recently, Meredith et al. [141] have applied B and Sr concentrations and their isotopic compositions to the alluvial Darling River (a catchment about 650,000 km^2) groundwater system (water samples were collected from 19 wells), which is located in inland Australia in order to provide (i) information on the hydrology of the system, (ii) evaluation of the groundwater recharge, and, finally, (iii) identification of water–sediment interaction processes leading to the hydrochemical evolution of saline groundwaters in the catchment. In this study, the trace element isotopes have showed a complex hydrogeochemical process in the same aquifer system. The δ^{11}B values were all higher than seawater and close to some of the highest δ^{11}B values ever reported in the literature for a groundwater system (from +44.4 to +53.9‰), while the ^{87}Sr/^{86}Sr ratios ranged from 0.708 to 0.713. The measurement of the trace element isotopes permitted to delineate the groundwater end members that included (i) shallow dilute waters from wells proximal to the channel (Darling River), (ii) saline groundwaters from wells located far away from the channel (Darling River), and (iii) deep saline groundwaters. By interpreting the geochemical and isotopic data, it was found that groundwaters influenced by river recharge were controlled by water–sediment reactions that varied substantially within the unsaturated zone. Groundwater–surface water exchange from fresh bank storage formed dilute groundwaters where B and Sr were related to clay mineral reactions.

Several studies have demonstrated the use of ^{87}Sr/^{86}Sr ratio and B isotopes in tracing anthropogenic inputs in groundwater and originated from industrial and household effluents, wastewater, and fertilizers [123, 133, 142–144]. For instance, Petelet-Giraud et al. [145] conducted a study in the Dommel catchment (1,800 km^2 large), which is a riverine system located in northern Belgium (380 km^2) and in the southern part of the Netherlands, with the aim to investigate Sr and B isotopes as

potential tracers to discriminate the natural versus anthropogenic sources of the dissolved load and to identify various pollution sources such as agriculture, industrial activity, and wastewater treatment plants. Hasenmueller and Criss [123] showed that municipal drinking water used for lawn irrigation contributes substantial nonpoint loads of B and other chemicals (S species, Li, and Cu) to surface water and shallow groundwater in the St. Louis (Missouri, USA) area.

Jiang [146] investigated the effects of human activities (agriculture and sewage effluents) on the Sr isotope geochemistry in the Nandong Underground River System, which is located in a typical karst area dominated by agriculture in SE Yunnan Province (China). This study showed that agricultural fertilizers and sewage effluents significantly modified the natural $^{87}Sr/^{86}Sr$ ratio signature of groundwater that was otherwise dominated by water–rock interaction. Three major sources of Sr were distinguished on the basis of $^{87}Sr/^{86}Sr$ ratios and Sr concentrations. Two sources of Sr were the Triassic calcite- and dolomite-rich aquifers, where waters were characterized by low Sr concentrations (0.1–0.2 mg/L) and low $^{87}Sr/^{86}Sr$ ratios (0.7075–0.7080 and 0.7080–0.7100, respectively); the third input was anthropogenic and related to Sr sourced by agricultural fertilizers and sewage effluents with waters affecting the $^{87}Sr/^{86}Sr$ ratios (0.7080–0.8352 for agricultural fertilizers and 0.7080–0.7200 for sewage effluents, respectively), with higher Sr concentrations (0.24–0.51 mg/L).

7 Untraditional Isotopes: The Metal (Fe, Cr, and Cu) Stable Isotopes

The differences in the relative, mass-dependent abundances of stable isotopes have the potential to elucidate sources and fate of contaminants in the biosphere. In this section, the potential uses of nontraditional stable isotope systems to trace sources, fate, and behavior of metals in the environment are presented. In particular, a basic review of isotopic fractionation mechanisms as well as summaries for three contaminants (Fe, Cr, and Cu) and their isotope systematics, fractionation processes, and environmental applications is here provided.

7.1 Iron Isotopes

Iron is an essential nutrient and is the third most abundant element that participates in a wide range of biotically and abiotically controlled redox processes in different geochemical environments. Iron solubility is highly dependent on its redox state. In oxygenated aquatic systems, concentrations of dissolved Fe are generally low due to the low solubility of its oxidized forms, which tend to form nanoparticle aggregates and colloids of oxy-hydroxides, thus precipitating [147, 148]. Iron has

Fig. 7 Iron isotope
distribution in nature. Fields
are from Hoefs [151]
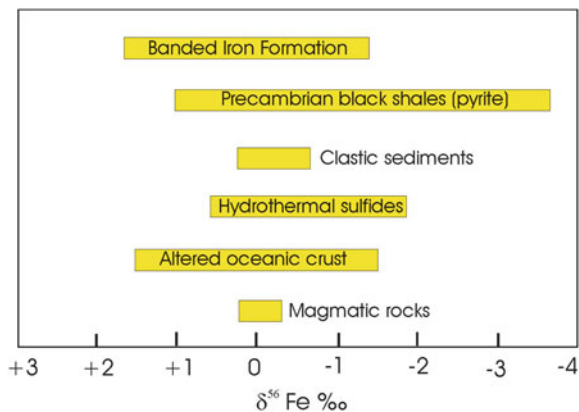
four naturally occurring stable isotopes, ^{54}Fe (5.84%), ^{56}Fe (91.76%), ^{57}Fe (2.12%),
and ^{58}Fe (0.28%), and the natural, mass-dependent isotope variations of Fe in rocks
record a span in the range of ~4‰ for the $^{56}Fe/^{54}Fe$ ratio [149]. Iron isotope data in
the literature have been reported with the standard δ notation, and the $δ^{56}Fe$
($^{56}Fe/^{54}Fe$) and $δ^{57}Fe$ ($^{57}Fe/^{54}Fe$) values are most commonly used as defined by
Eq. (1). The choice of the reference reservoir for calculating δ values is quite
variable among different laboratories. Most authors are used to report the Fe isotope
data as relative to terrestrial igneous rocks or to the IRMM-014 (Institute for
Reference Materials and Measurements) standard [149]. Therefore, interlaboratory
comparisons are obtained by normalizing the Fe isotope ratios to IRMM-014, this
standard rapidly becoming the most accepted interlaboratory standard. According
to Dauphas and Rouxel [150], Fe isotopic systematics can be considered a valuable
tool to study the Fe biogeochemical cycle and can potentially be used to trace its
transport in aqueous systems. Figure 7 shows the ranges of $δ^{56}Fe$ values found in
nature for a number of different forms of iron.

Iron stable isotope fractionations during aqueous and biological processes
include redox reactions [152, 153], adsorption and mineral dissolution [154, 155],
precipitation [156, 157], and dissimilatory Fe reduction, where Fe(III) oxides act as
electron acceptors for anaerobic respiration [158–160]. Beard and Johnson [149]
and references therein reported that in general microbiological reduction of Fe^{3+}
forms a much larger quantity of iron with distinct $δ^{56}Fe$ values than those produced
by abiological processes. The bulk continental crust has $δ^{56}Fe$ values close to zero
[149]. Hydrothermal fluids at mid-ocean ridges and river waters have $δ^{56}Fe$ values
between 0 and −1‰ [161–163]. In modern aqueous environments, such as the
oceans, dissolved Fe contents are low (upper oceans <1 nM, [164]) and their
isotopic compositions are sensitive indicators of Fe sources and pathways. Johnson
and Beard [165] indicated that iron isotopes are exceptional indicators of Fe redox
cycling, particularly in low-temperature environments where isotopic fraction-
ations are relatively large and where significant pools of Fe^{2+} and Fe^{3+} may coexist.
In a recent study, Castorina et al. [166] observed significant variations for the Fe

isotopes measured in Fe-rich groundwaters in aquifers from the Low Friuli Plain coastland (northern Adriatic Sea, Italy), an area impacted by strong industrialization, including past and present metallurgic activities and steel production related to manufacturing of low-alloyed steel. In this study, Fe contents ranged from 0.48 to 9.99 mg/L and from 2.50 to 43.8 mg/L in low-salinity and brackish waters, respectively. The δ^{56}Fe value was varying over a wide range: from -5.29 to $+0.87$‰ in low-salinity waters and between -2.34 and $+2.15$‰ in brackish waters. The isotopically lighter compositions were interpreted as reflecting isotopic fractionation during repeated cycling of Fe precipitation. Castorina et al. [166] concluded that the positive δ^{56}Fe values might be indicative of either a higher solubility of oxy-hydroxides, which during diagenesis preferentially incorporated the isotopically heavier fraction of Fe, or leaching processes of the foundry landfill disposal, which characterizes the site. Recent in-depth reviews on Fe isotope geochemistry may be found in Johnson and Beard [165] and Bullen [167].

7.2 Chromium Isotopes

Chromium is a trace element abundantly occurring in ultramafic and mafic rock minerals and represents an important contaminant in surface water and groundwater although its mobility and environmental impact are strongly depending on its valence state and redox transformations. Chromium is present in two oxidation states, Cr(III), as cation Cr^{3+}, and Cr(VI), as oxyanion (CrO_4^{2-}, $HCrO_4^{-}$, and $HCr_2O_7^{-}$), which have different chemical behaviors: Cr^{3+} is the dominant form in most minerals and in water under reducing conditions, whereas Cr(VI) is stable under oxidizing conditions and highly toxic leading to health problems such as lung cancer and dermatitis (e.g., [168]). Chromium is a common anthropogenic contaminant in surface waters and the potential toxicity of Cr(VI), and its fairly common occurrence as a point-source contaminant has spurred research into the ability of Cr stable isotopes to provide information on Cr sources, transport mechanisms, and fates in the environment. Chromium has four stable isotopes with the following abundances: ^{50}Cr (4.35%), ^{52}Cr (83.79%), ^{53}Cr (9.50%), and ^{54}Cr (2.36%) [169]. Variations of the isotope ratios are expressed using the delta notation according to Eq. (1), the δ^{53}Cr value being relative to the ^{53}Cr/^{52}Cr ratio referred to that of the NIST SRM 797 (National Institute of Standards and Technology Standard Reference Materials) standard. The measured range of ^{53}Cr/^{52}Cr in natural materials is presently -6‰, essentially reflecting the range measured for naturally occurring Cr(VI) in groundwater [170]. Equilibrium fractionations between Cr (VI) and Cr (III) were estimated by Schauble [171], who predicted Cr isotope fractionations of >1‰ between Cr species with different oxidation states. Ellis et al. [172], Sikora et al. [173], Berna et al. [174], Zink et al. [175], Dossing et al. [176], Basu and Johnson [177], Han et al. [178], Jamieson-Hanes et al. [179], and Kitchen et al. [180] studied the fractionation of Cr isotopes in a series of Cr(VI) reduction experiments. The results showed a general trend of

accumulating heavier Cr isotopes in the unreacted Cr(VI) species and an accumulation of the lighter ones in the produced Cr(III), whereas Cr(III) did not undergo rapid isotopic exchange during Cr(III) oxidation runs [175]. These properties make Cr isotope investigations suitable to detect and quantify redox changes in different geochemical reservoirs. In this respect, the tracking of Cr(VI) reduction is especially powerful when dealing with subsoil Cr(VI) contamination and related remediation actions. Recent in-depth reviews on Cr isotope geochemistry may be found in Villalobos-Aragón et al. [181], Bonnand et al. [182], Wanner and Sonnenthal [183], and Frei et al. [184].

7.3 Copper Isotopes

Copper is present in the Earth's crust at mg kg^{-1} level [185] and enters natural water and soil reservoirs from rock weathering and anthropogenic contamination sources. The major Cu-bearing minerals are sulfides (e.g., chalcopyrite, bornite, chalcocite), and, under oxidizing conditions, secondary copper minerals in the form of oxides and carbonates host this chalcophile element. Copper is a nutrient element, although toxic for all aquatic photosynthetic microorganisms when elevated concentrations occur (e.g., [186, 187]), due to its ability to either readily accept or donate single electrons as it changes oxidation states. Copper occurs in two oxidation states, Cu^+ and Cu^{2+}, and rarely in the form of native copper. Copper may form a great variety of complexes with very different coordination numbers such as square, trigonal, and tetragonal complexes. These properties are ideal prerequisites for relatively large isotope fractionations. Copper has two stable isotopes ^{63}Cu (69.1%) and ^{65}Cu (30.9%). As with light stable isotope systems, variations in transition-metal isotope ratios can be described using the δ notation in ‰. The $\delta^{65}Cu$ values are calculated as reported in Eq. (1) and the reference $^{65}Cu/^{63}Cu$ ratio is the NIST SRM 976 (0.4456, [188]). Figure 8 shows the ranges of $\delta^{65}Cu$ values found in nature for a number of different forms of copper.

Experimental investigations have demonstrated that redox reactions between Cu (I) and Cu(II) species are the principal process that fractionates Cu isotopes in natural systems [189]. As a consequence, copper isotope ratios may be used to interpret useful details of natural redox processes. The measured range of $^{65}Cu/^{63}Cu$ in natural materials is approximately 9‰ for solid samples ($\delta^{65}Cu = -3.0$ to +5.7‰) and 3‰ for water samples ($\delta^{65}Cu = -0.7$ to +1.4‰) ([167] and references therein). Recent studies, related to the Cu isotope variations in a variety of stream waters draining historical mining districts located in the USA and Europe, have shown that the $\delta^{65}Cu$ values were varying from −0.7 to +1.4‰, pointing out that Cu mineral weathering did not deliver a single averaged isotope composition to drainage water [190]. At large scale, Cu isotopes can provide important insights about the nature of the parameters which control the fractionation processes. In this respect, Vance et al. [191] studied the $^{65}Cu/^{63}Cu$ ratios in estuarine waters and particulates, riverine, and open ocean waters. They reported that in estuarine samples the $\delta^{65}Cu$ values of dissolved Cu were between 0.8 and

Fig. 8 Copper isotope distribution in nature. Fields are from Ehrlich et al. [189]
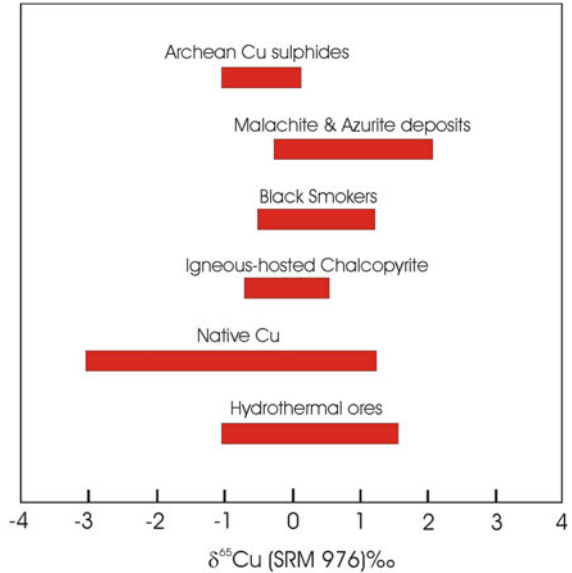
1.5‰, i.e., greater than that of Cu associated with particulate material. Moreover, dissolved Cu in rivers had δ^{65}Cu values ranging from 0.02 to 1.45‰, most of them being heavier than those measured in crustal rocks (+0.16‰). Vance et al. [191] concluded that the isotopic contrast reflects the different partitioning of the weathered pool of Cu between an isotopically light fraction adsorbed onto suspended particles and an isotopically heavy dissolved fraction dominated by Cu bound to strong organic complexes.

8 Conclusions

The use of stable and (subordinately) radiogenic isotopes in hydrologic systems 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 review, we have provided some examples of their application 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. In these studies, 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. Nevertheless, we acknowledge that the best approach in environmental studies is to combine as many tracers as possible, which should include and integrate chemical and isotopic data. This combination constitutes an important requisite for hydrogeochemical researches in general, and for the main focus of this book in particular, regarding study of the main threats to the quality of groundwater.

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