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Global applications of stable isotopes for identifying nitrate pollution sources in groundwater: a comprehensive review

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As a critical resource for both livelihoods and economic progress, groundwater is increasingly endangered by nitrate contamination stemming from intensive agriculture, landfill leachates, wastewater effluents, soil nitrogen leaching, sewage discharge, and other anthropogenic influences. Stable isotopes ($\delta^{15}\text{N}-\text{NO}_3^-$, $\delta^{18}\text{O}-\text{NO}_3^-$, $\delta^{11}\text{B}$) have emerged as powerful tools to distinguish pollution sources, including synthetic fertilizers, animal manure, domestic wastewater, and atmospheric deposition. In regions with intensive agriculture and urban sprawl, nitrate concentrations frequently exceed safe thresholds, underscoring the need for precise source identification to guide mitigation strategies. While traditional vulnerability mapping elucidates contamination pathways, it often fails to resolve specific sources. The integration of multi-isotope tracers (e.g., $\delta^{11}\text{B}$ with $\delta^{15}\text{N}-\text{NO}_3^-$, $\delta^{18}\text{O}-\text{NO}_3^-$) alongside hydrochemical data has emerged as an effective approach to address this gap, particularly in complex hydrogeological settings. While previous reviews have addressed nitrate contamination and isotope applications, this study adds value through its updated scope (2015–2025), global comparison, emphasis on multi-isotope integration, and the presentation of a unified framework and best practices for source identification. The findings highlight actionable insights for groundwater protection and advocate for the widespread adoption of isotopic tools in sustainable water management worldwide.

KEYWORDS

groundwater pollution, nitrate, contamination, stable isotopes, pollution sources, isotope hydrology

Introduction

Groundwater is a vital resource, sustaining life by supplying drinking water and supporting irrigation systems (Subba Rao et al., 2020; Gugulothu et al., 2022). However, its quality is deteriorating globally, jeopardizing agricultural productivity and human health. Nearly half of the world's population relies on groundwater for daily needs (Mukherjee and Singh, 2018; Adimalla and Qian, 2019), yet this critical resource is increasingly threatened by rapid agricultural expansion, industrial activities, and urbanization (Zhaoshi et al., 2021). The overuse of fertilizers and pesticides, along with untreated sewage and industrial effluents, has severely degraded both surface and subsurface water quality (Suthar et al., 2009). Moreover, dynamic groundwater–surface water exchanges influence the physical, chemical, and biological characteristics of aquatic ecosystems (Valett and Sheibley, 2009). In this context, a thorough

understanding of aquifer geochemistry becomes essential for diagnosing contamination processes and supporting effective groundwater management strategies (Wu et al., 2021; Eid et al., 2023).

In recent decades, groundwater extraction has surged in response to growing agricultural, industrial, and domestic demands, accompanied by rising contamination from organic, inorganic, and emerging pollutants (Sharma et al., 2022). Among these, nitrate (NO_3^-) contamination has emerged as one of the most widespread and persistent challenges affecting groundwater quality. Key anthropogenic sources include atmospheric deposition, chemical fertilizers, animal manure, and untreated urban or industrial waste (Kelepertzis et al., 2023).

To address this growing concern, the concept of groundwater vulnerability—which assesses the susceptibility of aquifers to contamination—has become central to sustainable water resource management (Bera et al., 2021; Paul and Das, 2021). Various assessment techniques, such as DRASTIC, GOD (Arauzo, 2017), SINTACS (Meng et al., 2020), and GALDIT (Boufekane et al., 2022), integrate hydrogeological parameters to delineate areas at risk of contamination. While these models are effective in identifying zones of heightened vulnerability, they often fall short in accurately determining specific nitrate pollution sources, particularly in regions with complex land use and overlapping anthropogenic activities.

To address this limitation, stable isotope techniques have emerged as powerful tools. In particular, nitrogen ($\delta^{15}\text{N}$) and oxygen ($\delta^{18}\text{O}$) isotopes in nitrate can distinguish between pollution from fertilizers, wastewater, and manure (Kendall, 1998; Panno et al., 2001; Bu et al., 2017; Zhou et al., 2022; Li et al., 2025). Boron isotopes ($\delta^{11}\text{B}$) further enhance source discrimination, especially in complex hydrogeological and land-use settings (Komor, 1997; Sankoh et al., 2021).

This review aims to provide a comprehensive synthesis of global applications of stable isotopes in identifying nitrate sources in groundwater. It is structured around six thematic components: (1) methodological approaches for data collection and the spatial distribution of studies; (2) patterns and severity of nitrate contamination at a global scale; (3) environmental and anthropogenic drivers influencing nitrate dynamics; (4) roles and developments of isotopic techniques in groundwater research; (5) specific applications of $\delta^{15}\text{N}$, $\delta^{18}\text{O}$, and $\delta^{11}\text{B}$ in nitrate source discrimination; and (6) implications for groundwater protection and future directions for research and management.

Data collection and geographic distribution of studies

This review employed a systematic approach to collect and analyze global literature on groundwater nitrate contamination and isotopic tracing techniques. An extensive literature search was conducted using academic databases such as Scopus and Web of Science, supplemented by Google Scholar and ResearchGate. To ensure a focus on recent methodological advances, emerging isotope tracers, and updated hydrochemical applications, the review specifically targeted peer-reviewed publications from 2015 to 2025. This period reflects a decade marked by significant growth in multi-isotope integration, the use of $\delta^{11}\text{B}$, and the incorporation of isotopic tools into groundwater management frameworks. Keywords focused on core concepts such as “groundwater nitrate contamination,”

“stable isotopes,” “pollution sources,” and isotopic markers (“ $\delta^{15}\text{N}$ – NO_3^- ,” “ $\delta^{18}\text{O}$ – NO_3^- ,” “ $\delta^{11}\text{B}$ ”), along with related terms like “hydrochemical parameters” and “groundwater vulnerability.” The selection process prioritized articles indexed in Web of Science and Scopus, applying a two-stage screening: initial relevance based on isotope use in source identification, followed by methodological quality control to remove duplicates and redundant studies. Emphasis was placed on research integrating multi-isotope approaches with hydrochemical data for complex contamination scenarios.

The systematic review followed the PRISMA 2020 guidelines (Page et al., 2021), with the study selection process summarized in Figure 1. A total of 634 records were identified through database searches (Scopus = 400, Web of Science = 234). After the removal of 150 duplicate records and 40 flagged by automation tools, 444 articles remained for screening. Of these, 180 were excluded during the title and abstract review. The remaining 264 reports were sought in full text, of which 225 were successfully retrieved and assessed for eligibility. At this stage, 115 reports were excluded due to incomplete isotopic data ($n = 50$), lack of source apportionment analysis ($n = 40$), or absence of a nitrate/isotope focus ($n = 25$). The final 110 studies met all inclusion criteria and were incorporated into the synthesis.

The systematic review reveals a varied global distribution of studies (Figure 2) focusing on nitrate isotopes in groundwater. China leads with the highest number of relevant studies ($n = 24$), followed by the United States ($n = 11$) and India ($n = 9$), reflecting strong research engagement in these regions. Other countries with moderate representation include Ghana ($n = 7$), Greece ($n = 5$), Italy ($n = 4$), and Israel ($n = 2$), as well as several countries with three studies each, such as Algeria, Argentina, South Korea, and Mexico. European countries like France, Germany, Belgium, and Spain contributed one to two studies each. Notably, Morocco appears with 14 studies, which, while not employing stable isotope techniques, were included to illustrate the widespread and persistent nitrate pollution in the region. Their inclusion serves to emphasize the lack of isotopic applications in Moroccan groundwater research and highlights a significant regional research gap. Some countries, such as Indonesia, Kenya, Nigeria, and Pakistan, are represented by only one study. This underscores both the global relevance of nitrate-related issues and the uneven distribution of isotopic research across regions. The temporal and geographical distributions of studies are shown in Figure 3 (by year) and Figure 4 (by continent), respectively.

Global assessment of nitrate contamination in groundwater systems

Groundwater constitutes the principal water source for drinking and agricultural purposes in arid and semi-arid regions, where surface water availability is severely limited (Zazouli et al., 2024). Over recent years, reliance on groundwater has increased significantly (Zhou et al., 2020; Subba Rao et al., 2020). However, groundwater contamination has emerged as a pressing environmental challenge with significant regional and global implications (Gao et al., 2020; He et al., 2020). This contamination is driven by various factors, including erratic rainfall, rapid urbanization, intensive irrigation, excessive fertilizer use, unregulated industrial activities, population growth,

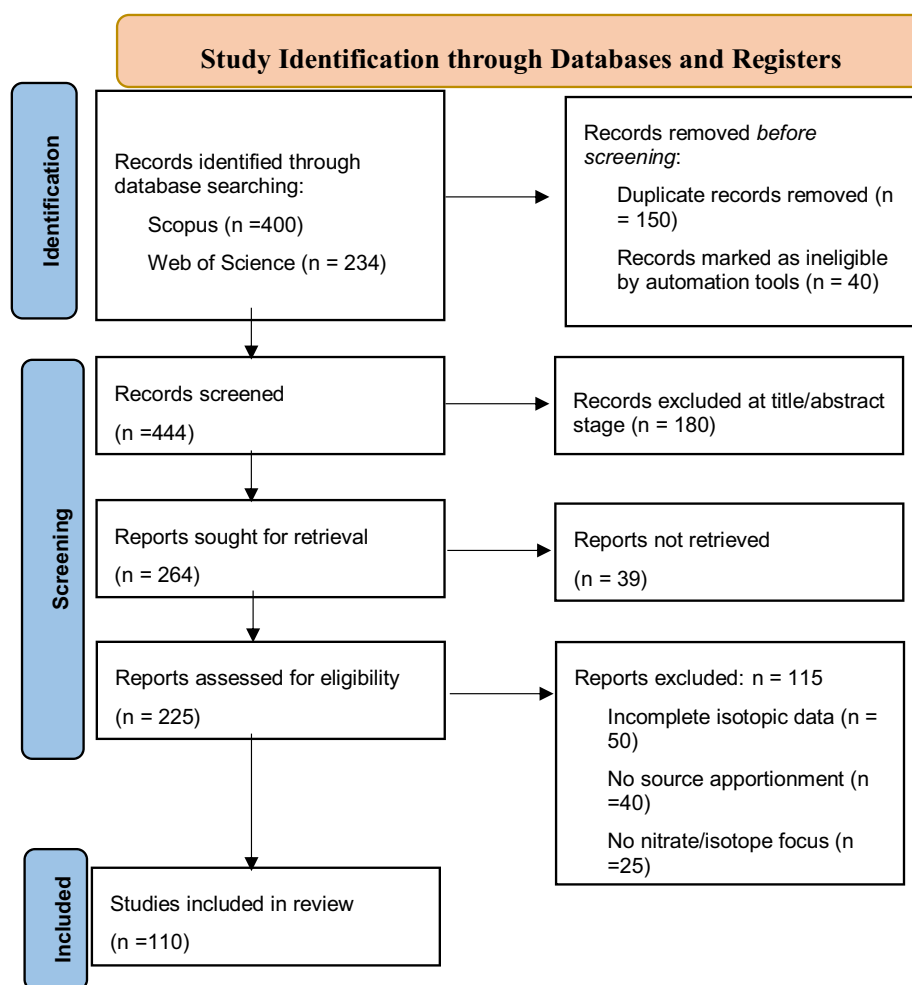


FIGURE 1
PRISMA 2020 Flow Diagram.

and both anthropogenic and geogenic pollution (Gao et al., 2020; Kumar et al., 2021; Subba Rao et al., 2020). Among the most concerning groundwater pollutants is nitrate (NO_3^-), which has become a global issue due to its elevated concentrations. High levels of nitrate in groundwater pose serious risks to human health, particularly through drinking water exposure (Adimalla and Qian, 2021).

Agriculture is the primary source of nitrate pollution, with excessive nitrogen fertilizer use and animal waste contributing significantly. In addition, poorly designed septic systems also lead to nitrate leaching into the water Table. NO_3^- pollution originates from both point sources—such as domestic sewage discharges, cesspools, and dairy lagoons—and non-point sources, including agricultural runoff from synthetic fertilizers and manure, soil nitrogen leaching, and atmospheric nitrogen deposition. These sources vary in spatial and temporal patterns, complicating efforts to trace and manage nitrate contamination in groundwater systems (Gao et al., 2020; He et al., 2020). In intensively farmed regions, groundwater nitrate (NO_3^-) concentrations frequently reach alarming levels, with recorded values exceeding 250 mg/L (Hilal et al., 2024)—five times the World Health Organization's (WHO) recommended limit of 50 mg/L for drinking water. Studies in various agricultural zones have

documented a steady increase in nitrate pollution over recent decades (Nouzha et al., 2016; Aziane et al., 2020; El Khodrani et al., 2020).

In areas with high agricultural activity, particularly those cultivating vegetables and industrial crops, nitrate concentrations in groundwater often exceed safe thresholds (Nouzha et al., 2016). These elevated levels are primarily attributed to livestock waste discharge, excessive chemical fertilizer use, and pesticide infiltration. River basins in agricultural regions frequently experience nitrate pollution due to farming practices, urban expansion, and industrial processes (Kanga et al., 2020).

Inefficient irrigation practices significantly worsen groundwater contamination, contributing to both water resource depletion and environmental degradation through nitrate leaching and eutrophication processes (El Khodrani et al., 2020). Research has shown that nitrate levels are often higher in wells near irrigated farmlands, where excess water application facilitates nitrate transport into the subsurface (Benkaddour et al., 2020).

Additionally, studies have detected agricultural chemicals in a significant proportion of monitored wells, with insecticides and nitrogen-based fertilizers being major contributors (El Bouzaidi et al., 2023). These findings underscore the urgent need for improved agricultural practices, stricter pollution controls, and sustainable groundwater management strategies worldwide.

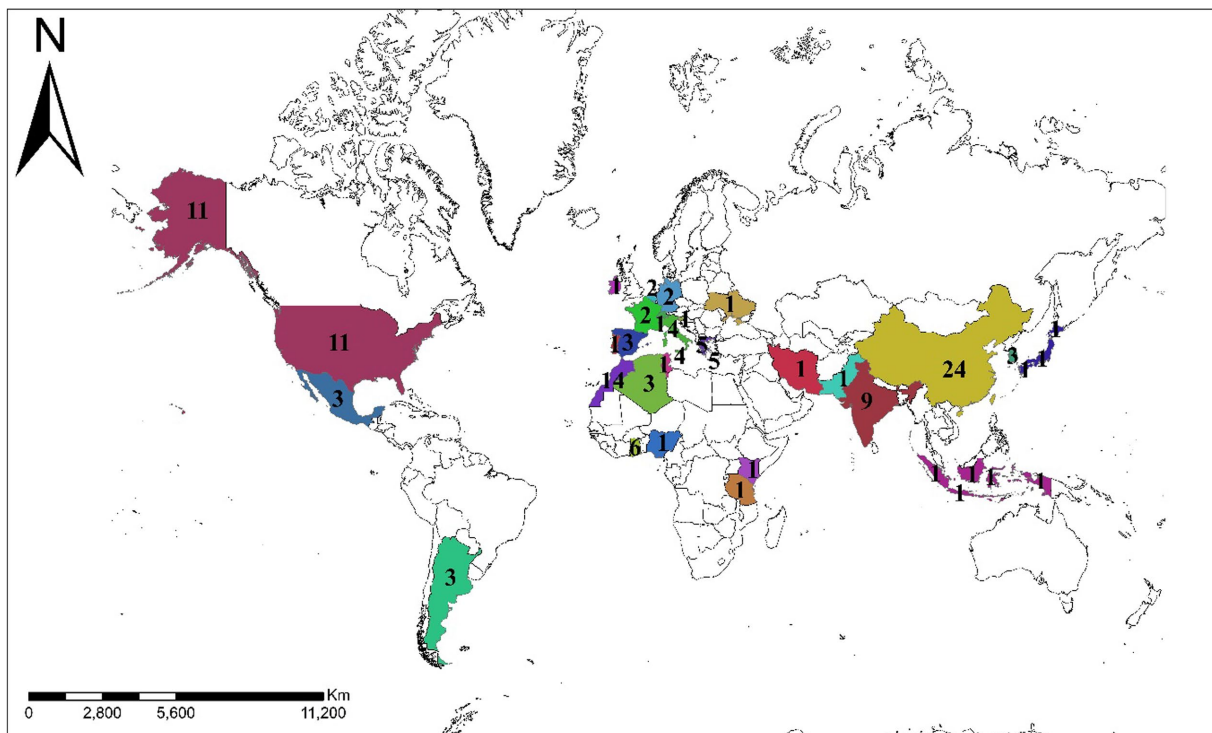


FIGURE 2
Global distribution of studies.

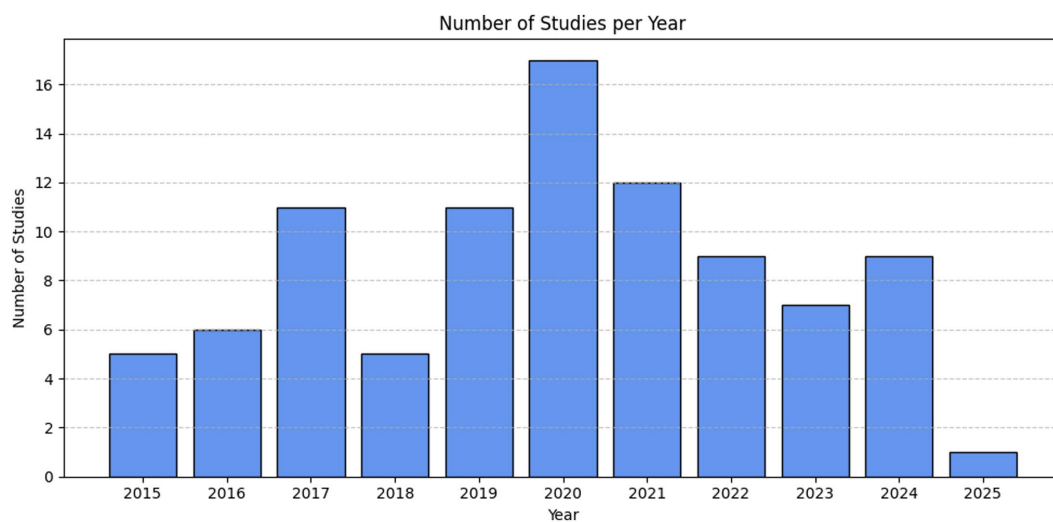
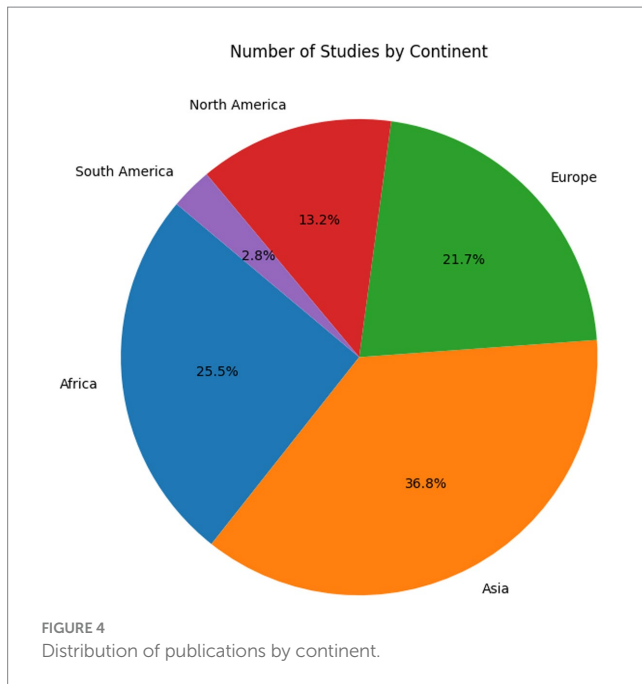


FIGURE 3
Distribution of studies by year.

Factors influencing nitrate contamination in groundwater

Nitrate contamination in groundwater is influenced by a complex interplay of factors, making the relationship between surface nitrogen sources and subsurface nitrate levels highly intricate (Malki et al., 2017). A significant portion of nitrogen from fertilizers can leach into groundwater due to irrigation or precipitation (Van Meter et al.,

2016). Excessive fertilizer application increases soil nitrate levels and organic matter, which stimulates microbial processes such as nitrification and denitrification. These biological activities alter the soil's capacity to retain pesticides by affecting microbial degradation rates and chemical interactions (Oumara and El Youssefi, 2022). When nitrogen inputs surpass crop uptake, soluble nitrate compounds infiltrate groundwater, leading to contamination (El Khodrani et al., 2020).



Studies have shown that reducing fertilizer application does not immediately lower groundwater nitrate levels due to legacy nitrogen in the subsurface (Wang et al., 2015). Key determinants of nitrate contamination include climate conditions, such as rainfall patterns, temperature, and seasonal variability that influence nitrate leaching and microbial processes, as well as fertilizer type, manure management practices, and soil properties (El Khodrani et al., 2020). Aquifer depth also plays a critical role, with shallow aquifers being more vulnerable to nitrate leaching due to their proximity to surface processes, while deeper aquifers often exhibit delayed or reduced contamination (Aziane et al., 2020).

Additional factors influencing nitrate transport include soil texture, permeability, rainfall intensity, recharge rates, water table depth, evapotranspiration, and irrigation efficiency (Barakat et al., 2020). Regions with high precipitation require careful groundwater management to minimize nitrate leaching and associated risks, as increased rainfall can both dilute nitrate concentrations in groundwater and enhance nitrate transport through soil, potentially spreading contamination over a larger area (Wang et al., 2015).

Research in agricultural areas has documented widespread nitrate exceedances of the World Health Organization's recommended limits, particularly in regions with sandy soils and shallow water tables (Marouane et al., 2015). Seasonal variations further affect nitrate dynamics, with spring rainfall promoting pollutant transport to deeper layers and summer conditions accelerating nitrification, leading to seasonal nitrate peaks (Aziane et al., 2020).

Heavy rainfall events often lead to a rapid increase in nitrate concentrations in groundwater due to accelerated infiltration of nitrate-rich surface water and soil solutions into the aquifer (Wang et al., 2015). This initial spike is typically followed by a gradual decline as hydrological conditions stabilize and dilution occurs. Several interrelated factors influence these dynamics, including soil texture and permeability, which control water movement; land use and fertilizer application timing; and microbial processes such as nitrification and denitrification that modify nitrate concentrations

within the subsurface. Additionally, climate variables like precipitation intensity, frequency, and seasonal distribution play a critical role in modulating nitrate transport and transformation. Understanding these complex interactions is essential for developing adaptive land-use practices and targeted mitigation strategies, such as controlled fertilizer application schedules, buffer zones, and improved manure management, to effectively reduce nitrate pollution in vulnerable aquifers and optimize groundwater resource management.

Overview of isotope applications in groundwater research

Nisi et al. (2016) emphasize that effective groundwater quality management depends on accurately identifying pollution sources. In many countries, traditional groundwater assessments have predominantly used hydrochemical analysis, geophysical techniques, and evaluation indices to measure pollutant levels in water samples and leachates. Although these approaches offer important data on contamination extent and aquifer vulnerability, they frequently fall short in pinpointing specific pollution origins. The advent and application of isotope techniques have revolutionized groundwater studies by enabling researchers to trace pollution sources and gain a clearer understanding of the origin of surface and groundwater recharge (Jia et al., 2020). Stable isotopes have broad applications in hydrological investigations. From their use, we gain crucial insights into aquifer–aquifer interconnections, groundwater age, and sources of contamination, among other important aspects (Oteng Mensah et al., 2014; Yidana et al., 2015). These techniques, some of which operate on the principle of tracer analysis, track the transport and transformation of key contaminants, such as nitrates, chlorinated compounds, and other anthropogenic pollutants, within aquatic systems. Isotopic composition is quantified using delta (δ) notation, representing the ratio of isotope abundances relative to a standard reference (Xu et al., 2016; Sankoh et al., 2021), as shown in Equation (1).

$$\delta = \left(\frac{R_{\text{Standard}}}{R_{\text{Sample}}} - 1 \right) \times 10^3 \quad (1)$$

where: R_{Sample} are the heavy (rare) to light (abundant) isotope ratios of the sample; R_{Standard} are the heavy (rare) to light (abundant) ratios of the standard. Oxygen (O), hydrogen (H), carbon (C), sulfur (S), and nitrogen (N) are among the most widely used isotopes in environmental studies (Sankoh et al., 2021). For over eight decades, environmental isotopes (Table 1) have been extensively applied in water bodies and other materials to enhance our understanding of hydrogeological and environmental processes.

Tracing nitrate pollution sources using dual isotopes ($\delta^{15}\text{N}$, $\delta^{18}\text{O}$) and $\delta^{11}\text{B}$

Groundwater contamination arises from both natural sources, such as soil nitrogen and atmospheric deposition, and anthropogenic sources, including synthetic fertilizers, manure, sewage, industrial waste, excessive fertilizer leaching, uncontrolled landfill disposal,

TABLE 1 Environmental isotopes used for various groundwater studies.

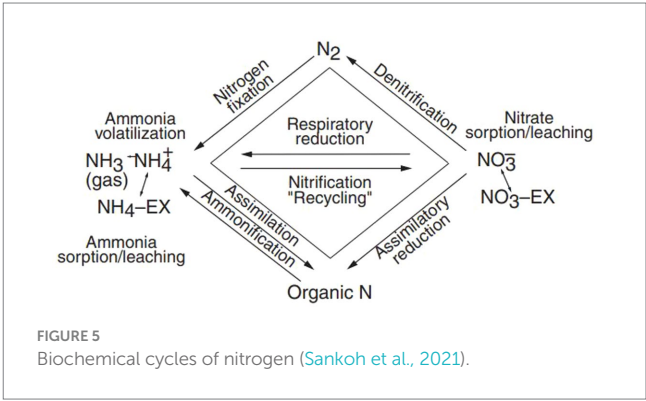
Element	Isotope notation	Isotopic ratio	Natural abundance (%)	Application	Ref.
H	$\delta^2\text{H}$	$^2\text{H}/^1\text{H}$	0.015	Water origin	Adomako et al. (2010)
H	^3H	-	1×10^{-18}	Landfill leachate	Pujiindiyati and Sidauruk (2015)
N	$\delta^{15}\text{N}$	$^{15}\text{N}/^{14}\text{N}$	0.366	Pollution sources	Chen et al. (2019)
Cl	$\delta^{37}\text{Cl}$	$^{37}\text{Cl}/^{35}\text{Cl}$	24.23	Transformation of chlorinated compounds	Zimmermann et al. (2020)
B	$\delta^{11}\text{B}$	$^{11}\text{B}/^{10}\text{B}$	80.1	Pollution source (anthropogenic/geogenic)	Nigro et al. (2017)
O	$\delta^{18}\text{O}$	$^{18}\text{O}/^{16}\text{O}$	0.204	Water origin	Adomako et al. (2010)
S	$\delta^{34}\text{S}$	$^{34}\text{S}/^{32}\text{S}$	4.21	Sulfate sources (landfill, AMD)	Nisi et al. (2016)

sewage infiltration, and seawater intrusion. Except for seawater intrusion, which primarily introduces saline water rather than nitrate contaminants, these sources contribute nitrates with distinct isotopic signatures. This variability in isotopic fingerprints makes stable isotope analysis a powerful tool for identifying the origins and pathways of nitrate pollution in groundwater (Sankoh et al., 2021). Nitrogen, a key tracer for nitrate sources, has two stable isotopes: $\delta^{14}\text{N}$ (99.63% abundance) and $\delta^{15}\text{N}$ (0.37% abundance). Since different nitrate (NO_3^-) sources exhibit unique isotopic signatures, $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ analysis helps pinpoint contamination pathways (Sankoh et al., 2021).

When tracing nitrate sources in freshwater, understanding the processes affecting $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ is critical. Major nitrate contributors include agricultural runoff and industrial discharges, with microbial processes, such as ammonia volatilization, denitrification, and nitrification that play a pivotal role in nitrogen cycling (Figure 5). Notably, ammonia volatilization and denitrification can significantly enrich $\delta^{15}\text{N}$ in residual groundwater nitrate (Sankoh et al., 2021).

Application of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ isotopic signatures for tracing nitrate contamination sources

The use of nitrogen isotopes, specifically $\delta^{15}\text{N}$, has been explored in several recent studies (Bu et al., 2017; Peters et al., 2019; Ren et al., 2014) to trace the sources of nitrate (NO_3^-) pollution. Despite its effectiveness in distinguishing between various nitrate sources, the $\delta^{15}\text{N}$ method faces challenges. Specifically, it struggles to differentiate between atmospheric nitrate, soil nitrate, inorganic fertilizers, manure, and landfill waste, as the multiple nitrogen transformations involved cause overlapping $\delta^{15}\text{N}$ values. To address this uncertainty, researchers have turned to the use of oxygen isotopes ($\delta^{18}\text{O}-\text{NO}_3^-$), which can complement $\delta^{15}\text{N}$ data. However, the application of $\delta^{18}\text{O}-\text{NO}_3^-$ also presents difficulties, as its values tend to overlap for sources such as ammonium fertilizers, soil nitrogen, and manure, complicating the identification of nitrate sources (Minet et al., 2012). In response to these challenges, the combination of $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$, forming a dual isotope approach, has been applied by (Lasagna et Luca; 2019) to improve the accuracy of identifying nitrate sources. This dual isotope technique has become a widely adopted method to trace and



characterize nitrate pollution in different environments by analyzing the distinct $\delta^{18}\text{O}-\text{NO}_3^-$ and $\delta^{15}\text{N}-\text{NO}_3^-$ signatures (Jiang et al., 2016; Puig et al., 2017; Wen et al., 2018; Fernandes et al., 2019; Nyilitya et al., 2020; Weitzman et al., 2021; Ju et al., 2023).

Isotopic fingerprints of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ in nitrate from manure and septic waste

Septic tanks, landfills, animal manure, sewage, and sludge are significant contributors of nitrate pollution in aquatic systems. These waste sources typically contain organic nitrogen compounds, such as urea and organic nitrate, which undergo microbial transformations, primarily ammonification, nitrification, and denitrification leading to enriched $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ isotopic signatures.

Between 2015 and 2025, a wide range of studies conducted across Asia, Africa, Europe, and the Americas utilized stable isotope techniques to trace nitrate contamination sources. In groundwater systems, $\delta^{15}\text{N}$ values from 0 to +9‰ and $\delta^{18}\text{O}$ values from +2.5 to +7.5‰ were linked to inputs from fertilizers, soil organic matter, excreta, and wastewater (Deng et al., 2024). Seasonal variations were also observed in river systems, with higher $\delta^{18}\text{O}$ values in summer and lower $\delta^{15}\text{N}$ in winter, reflecting shifts in nitrate sources throughout the year (Wang et al., 2024).

In the Liao River Basin, isotopic signatures ($\delta^{15}\text{N}-\text{NO}_3^-$: +7.7‰ to +14.6‰; $\delta^{18}\text{O}-\text{NO}_3^-$: +0.6‰ to +11.2‰) were attributed to domestic, industrial, and agricultural effluents (Zhang et al., 2024). Downstream increases in $\delta^{15}\text{N}-\text{NO}_3^-$, averaging $+13.1 \pm 2.2$ ‰, in industrialized areas of Greece also indicated intensified organic pollution (Kyritidou et al., 2024). Wastewater samples tended to display lower and more variable isotope values, as seen in $\delta^{15}\text{N}-\text{NO}_3^-$ values of +4.7‰ to +12.6‰ and $\delta^{18}\text{O}-\text{NO}_3^-$ of +1.7‰ to +5.7‰, consistent with mixed inputs from soils and manure (Quinodoz et al., 2024). In Tunisia, $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ ranged from +0.9‰ to +23.8‰ and +5.3‰ to +21.5‰ respectively, again pointing to wastewater and manure as dominant sources (Boumaiza et al., 2022). High $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values in aquifers adjacent to streams in South Korea (up to +28.0‰ and +23.0‰, respectively) suggested strong inputs from animal waste and sewage (Ju et al., 2023). Similarly, seasonal changes in isotopic values ($\delta^{15}\text{N}$: +1.05‰ to +15.47‰; $\delta^{18}\text{O}$: -7.92‰ to +22.94‰) were consistent with variable contributions from manure, sewage, and fertilizers (Wang et al., 2023). Evidence of mixed anthropogenic sources is further supported by isotope ranges of $\delta^{15}\text{N}$: +2.0‰ to +14.5‰ and $\delta^{18}\text{O}$: +0.3‰ to +11.0‰ (Kelepertzis et al., 2023). Sewage sludge, in particular, has shown highly enriched isotopic values, with $\delta^{15}\text{N}$ reaching +33.8‰ and $\delta^{18}\text{O}$ up to +57.5‰ due to processes like nitrification and partial denitrification (Lorette et al., 2022).

In Mexico, nitrate in groundwater showed $\delta^{15}\text{N}-\text{NO}_3^-$ values between +8.86‰ and +39.67‰, and $\delta^{18}\text{O}-\text{NO}_3^-$ values up to +14.89‰, indicating a strong influence from domestic wastewater and manure (Torres-Martínez et al., 2021). Comparable findings were noted in Argentina, where $\delta^{15}\text{N}$ values above +12.8‰ were attributed to septic tank seepage (Blarasin et al., 2021). In Ghana, Lartsey et al. (2024) investigated nitrate contamination sources in groundwater and surface water of the north-western Volta River Basin using hydrochemical and multi-isotopic approaches, showing that the dominant sources of nitrate are manure and sewage, with a smaller contribution from soil nitrogen. Isotopic analysis ($\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of NO_3^-) and mixing models revealed that manure accounts for an average of 74% of nitrate in groundwater, while soil nitrogen contributes about 10%. Recharge primarily originates from rainfall, with some influence from the Black Volta River, and biological processes such as nitrification and denitrification affect nitrate concentrations. Although about 80% of samples were classified as pollution-free based on the Nitrate Pollution Index, anthropogenic inputs were evident near discharge zones, highlighting the significant role of agricultural and domestic waste in groundwater nitrate contamination in the region. Similarly, groundwater in northern Ghana displayed $\delta^{15}\text{N}$ values of +5.8‰ to +7.0‰ and $\delta^{18}\text{O}$ values near +17‰, indicative of contamination from domestic and animal waste (Gibrilla et al., 2020), while seasonal variations in Greece also revealed $\delta^{15}\text{N}$ values between +4.6‰ and +17.7‰, again pointing to inputs from soil and organic waste (Kazakis et al., 2020).

In Kenyan urban centers, $\delta^{15}\text{N}$ values soared to +51.8‰ during the dry season, clearly implicating sewage and manure (Nyilitya et al., 2020). Multi-source river systems displayed extremely variable nitrate isotope signatures, with $\delta^{15}\text{N}$ from -23.5‰ to +32.0‰ and $\delta^{18}\text{O}$ from -12.7‰ to +39.2‰, depending on pollution sources and hydrological conditions (Peters et al., 2019). Urban groundwater studies in Eastern Europe revealed $\delta^{15}\text{N}$ values between +12.6‰ and +18.0‰, and $\delta^{18}\text{O}$ from -0.1‰ to +8.7‰,

both consistent with anthropogenic waste inputs (Vystavna et al., 2017). In the White Volta River in Ghana, $\delta^{15}\text{N}$ values up to +22.1‰ were also linked to sewage and animal waste (Anornu et al., 2017). Similarly, values up to +32.5‰ for $\delta^{15}\text{N}-\text{NO}_3^-$ and +18.1‰ for $\delta^{18}\text{O}$ were recorded in Spanish waters, pointing to manure and wastewater under denitrifying conditions (Puig et al., 2017).

In northern China, groundwater showed isotope values ranging from -0.6‰ to +31‰ for $\delta^{15}\text{N}-\text{NO}_3^-$ and from +16.3‰ to +37.4‰ for $\delta^{18}\text{O}-\text{NO}_3^-$, suggesting diverse sources including manure and volatilized ammonia (Jiang et al., 2016). Foundational data by Li et al. (2007) established that $\delta^{15}\text{N}$ values from +10‰ to +25‰ are typical of animal manure and ammonia volatilization. The primary sources of nitrate pollution identified in these studies include animal manure, sewage, ammonia volatilization from urea, agricultural activities, farming, and denitrification processes influenced by precipitation.

In Israel, Shalev et al. (2015) report that nitrate contamination of groundwater in the Central Arava Valley is primarily linked to agricultural sources, with isotopic and chemical analyses indicating that all applied fertilizers (synthetic nitrate, synthetic ammonium, and manure) contribute to contamination, generally in proportion to their use in local fertilization schemes, alongside occasional inputs from leaking sewage reservoirs. Similarly, in the Gaza Strip, Shomar et al. (2008) found that groundwater is mainly impacted by manure and, to a lesser extent, by septic effluents and sludge, while synthetic fertilizers play only a minor role. Isotopic signatures ($\delta^{15}\text{N}$ and $\delta^{18}\text{O}$) confirm these patterns: manure and sludge exhibit enriched $\delta^{15}\text{N}$ values (+4.6 to +11.9‰), whereas synthetic fertilizers are near 0‰, corresponding to the ranges observed in groundwater (+3.2 to +12.8‰). No significant denitrification was detected in Gaza, and in both regions, irrigation practices and recharge dynamics strongly influence nitrate leaching. These findings underscore the utility of isotope-based approaches for distinguishing contamination sources and guiding sustainable groundwater management.

Isotopic fingerprints of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ in ammonia from fertilizers and precipitation

The intensive and often poorly regulated use of nitrogen-based fertilizers in agriculture has significantly elevated nitrate (NO_3^-) concentrations in groundwater systems. Synthetic fertilizers such as urea, potassium nitrate (KNO_3), and ammonium nitrate (NH_4NO_3), derived from industrial nitrogen fixation, typically exhibit $\delta^{15}\text{N}$ values between -4‰ and +4‰, reflecting their atmospheric nitrogen origin. In the Erhai Basin, nitrate isotopic compositions revealed $\delta^{15}\text{N}-\text{NO}_3^-$ values ranging from -0.64‰ to +17.67‰ (mean: +6.89‰) and $\delta^{18}\text{O}-\text{NO}_3^-$ from -1.87‰ to +24.43‰ (mean: +7.88‰), with microbial nitrification dominating approximately 60% of samples particularly in oxygen-rich upstream and littoral zones while denitrification was identified in only 13.56% of cases (She et al., 2024).

Seasonal isotopic shifts further illustrate the dynamic nature of nitrate inputs. During the dry season, $\delta^{18}\text{O}-\text{NO}_3^-$ values ranged from -5‰ to +16.85‰ (mean: +2.68‰), and $\delta^{15}\text{N}-\text{NO}_3^-$ from -1.17‰ to +8.40‰ (mean: +2.28‰). Conversely, the wet season displayed $\delta^{18}\text{O}-\text{NO}_3^-$ values from -4.78‰ to +11.59‰ (mean: -0.52‰) and $\delta^{15}\text{N}-\text{NO}_3^-$ from -0.63‰ to +27.06‰ (mean: +1.83‰), suggesting additional inputs from organic fertilizers and domestic effluents (Su et al., 2024).

Isotopic compositions typical of synthetic fertilizers were also documented elsewhere. For example, $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of approximately +0.5‰ and +7‰, respectively, were reported in a wastewater-influenced context (Quinodoz et al., 2024). In agricultural areas, Kim et al. (2023) recorded broader $\delta^{15}\text{N}$ - NO_3^- values (+3.0‰ to +27.5‰) and $\delta^{18}\text{O}$ - NO_3^- values (−2.4‰ to +7.7‰), indicating a mixture of sources, including livestock waste, synthetic fertilizers, and soil-derived nitrogen. In riverine systems, dominant nitrification processes were inferred from $\delta^{15}\text{N}$ - NO_3^- values around +5‰ and $\delta^{18}\text{O}$ - NO_3^- around +4‰, with over 70% of $\delta^{18}\text{O}$ - NO_3^- values aligning with microbial nitrate production (Zhou et al., 2022).

Despite their typically low $\delta^{15}\text{N}$ signatures (−8‰ to +7‰), synthetic nitrate fertilizers can exhibit enriched $\delta^{15}\text{N}$ - NO_3^- values following post-application transformations such as nitrification (Piatek et al., 2005). The $\delta^{18}\text{O}$ of nitrate formed via nitrification reflects a combination of oxygen from atmospheric O_2 ($\approx +23.9$ ‰) and water (≈ -25 ‰ to +4‰), producing $\delta^{18}\text{O}$ - NO_3^- values that generally lie between −10‰ and +10‰ (Kendall, 1998; Kendall and Aravena, 2000; Mayer et al., 2001; Veale et al., 2019). This trend was evident in the observations by Weitzman et al. (2021), who reported $\delta^{18}\text{O}$ - NO_3^- values ranging from −3.2‰ to +17.4‰, and by Wen et al. (2018), who found $\delta^{18}\text{O}$ - NO_3^- between +0.07‰ and +1.77‰ both consistent with agricultural inputs.

In regions of Nebraska, groundwater nitrate concentrations ranged from 6.5 to 53 mg/L, with $\delta^{15}\text{N}$ - NO_3^- values between −0.3‰ and +7.8‰, and $\delta^{18}\text{O}$ - NO_3^- values from −1.4‰ to +7.8‰, reflecting predominant inputs from ammonium nitrification and soil organic nitrogen (Spalding et al., 2019). Although synthetic nitrate fertilizers are characterized by higher $\delta^{18}\text{O}$ - NO_3^- values due to their exclusive reliance on atmospheric oxygen (typically +17‰ to +25‰), such values are rarely observed in field settings (Mayer et al., 2001; Veale et al., 2019). For example, $\delta^{18}\text{O}$ - NO_3^- values reported in boreholes, wells, and surface waters across Ghana ranged from +5.1‰ to +8.83‰ (Anornu et al., 2017), well below the levels typical of atmospheric nitrate deposition ($\approx +60$ ‰ to +70‰) or synthetic fertilizers. Similarly, groundwater nitrate in Mexico showed $\delta^{18}\text{O}$ - NO_3^- values between +3.84‰ and +10.96‰ (Pastén-Zapata et al., 2014). These findings, supported by Kendall (1998) and Mayer et al. (2001), further underscore that nitrification can elevate $\delta^{18}\text{O}$ - NO_3^- values by up to 5‰ above theoretical estimates, reinforcing the role of microbial activity in shaping isotopic profiles.

Isotopic fingerprints of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ in atmospheric deposition

Atmospheric nitrate originates from nitrogen oxides (NO_x), which are primarily produced through fossil fuel combustion in power plants, vehicles, and industrial processes. These NO_x compounds undergo various atmospheric transformations, including nitrification, denitrification, and ammonia volatilization, depending on whether nitrogen is present as ammonium (NH_4^+) or nitrate (NO_3^-), and on the nature of anthropogenic inputs in precipitation. As a result, atmospheric nitrate exhibits highly variable $\delta^{15}\text{N}$ values, typically ranging from −0.6‰ to +31‰ (Jiang et al., 2016).

However, $\delta^{15}\text{N}$ alone may not reliably distinguish atmospheric nitrate from other anthropogenic sources due to overlaps in isotopic

signatures. In contrast, $\delta^{18}\text{O}$ - NO_3^- provides a more definitive tracer. Atmospheric deposition of nitrate is generally characterized by highly enriched $\delta^{18}\text{O}$ values, typically ranging from +60‰ to +70‰ (Kendall et al., 2007). This contrasts with biologically derived nitrate in soils and water, which usually exhibits $\delta^{18}\text{O}$ values between 0.8‰ and 5.8‰ (Chen et al., 2019) or between −15‰ and +15‰ (Shi et al., 2014).

For instance, Jiang et al. (2016) reported $\delta^{18}\text{O}$ - NO_3^- values exceeding +30‰ in atmospheric nitrate. Similarly, Ogrinc et al. (2019) recorded $\delta^{18}\text{O}$ - NO_3^- values as high as +34.6‰ in groundwater from the Sava River aquifer, implicating atmospheric deposition as the dominant nitrate source. These findings are consistent with observations in areas lacking significant land-based anthropogenic pollution. Moreover, Shi et al. (2014) noted that rainfall nitrate can initially present $\delta^{18}\text{O}$ values between +65‰ and +70‰, but these values rapidly decline to 2–5‰ after biological processing in the soil.

The elevated $\delta^{18}\text{O}$ values in atmospheric nitrate are attributed to photochemical reactions and incomplete fossil fuel combustion (Kendall et al., 2007). During these reactions, atmospheric molecular oxygen naturally enriched in $\delta^{18}\text{O}$ is incorporated into nitrate molecules, leading to pronounced isotopic enrichment. As Ogrinc et al. (2019) explain, photochemical processes driven by sunlight enhance the $\delta^{18}\text{O}$ content of atmospheric compounds, thereby producing nitrate with distinctive $\delta^{18}\text{O}$ signatures.

Combining $\delta^{11}\text{B}$ and $\delta^{15}\text{N}$ isotopic analysis to identify groundwater contamination sources

The non-conservative behavior of nitrogen can interfere with isotopic fractionation, making it challenging to accurately identify the sources of NO_3^- in groundwater (Widory et al., 2005). This challenge can be addressed by combining $\delta^{15}\text{N}$ and $\delta^{11}\text{B}$ isotopic analyses, as suggested by Bronders et al. (2012) and Saccon et al. (2013).

Boron exists in nature as two isotopes, ^{10}B and ^{11}B , which exhibit significant mass differences. This mass disparity leads to a broad natural variability in $\delta^{11}\text{B}$ values, enabling the differentiation of various boron sources in groundwater.

In industrial applications, boron compounds such as boric acid and borate minerals are extensively used in manufacturing glass, porcelain, carpets, leather, photographic chemicals, cosmetics, fertilizers, and metals (Vengosh et al., 1998). Sodium perborate, commonly found in household cleaning products as a bleaching agent, also contributes to boron accumulation in wastewater. When these products are released into the environment, boron-containing effluents can infiltrate water resources (Vengosh et al., 1998).

Conventional wastewater treatment processes are ineffective at removing elemental boron, making $\delta^{11}\text{B}$ a reliable and conservative tracer for identifying wastewater contamination (Saccon et al., 2013). Due to its stability, widespread use in agriculture and industry (Saccon et al., 2013), and natural occurrence in saline waters, $\delta^{11}\text{B}$ is a valuable tool for pinpointing pollution sources. These sources include fertilizers, septic system effluents, wastewater discharges, animal manure, and seawater intrusion.

Boron isotope variations ($\delta^{11}\text{B}$) in natural and anthropogenic sources

Boron isotope ratios ($\delta^{11}\text{B}$) reliably trace both natural and anthropogenic water contamination sources, from seawater intrusion to agricultural impacts (Reed and Duranceau, 2016). Initial applications by Komor (1997) introduced $\delta^{11}\text{B}$ as a co-tracer for nitrate pollution, complementing its prior use in hydrogeochemical assessments (Vengosh et al., 1998; Bassett, 1990).

Natural waters such as pristine groundwater are typically characterized by enriched $\delta^{11}\text{B}$ values ($\sim 30\text{‰}$) and low boron concentrations (0.01–0.13 mg/L) (Vengosh et al., 1998; Widory et al., 2005). Seawater shows even higher $\delta^{11}\text{B}$ values ($+33\text{‰}$ to $+60\text{‰}$) with boron concentrations averaging 1.9 mg/L and reaching up to 5.04 mg/L (Vengosh et al., 1998; Tirez et al., 2010).

Animal manure exhibits source-specific $\delta^{11}\text{B}$ signatures. Hog manure ranges from 7.2‰ to 42.4‰ with boron concentrations as high as 8.12 mg/L, while cattle manure shows $\delta^{11}\text{B}$ values between 6.2‰ and 24‰ but with lower boron concentrations (0.05–0.41 mg/L) (Komor, 1997; Widory et al., 2005; Tirez et al., 2010). Interestingly, groundwater impacted by pig manure retains similar $\delta^{11}\text{B}$ values to the manure itself, while cattle manure-impacted groundwater becomes more enriched (32.5–38.6‰), possibly due to isotopic fractionation (Komor, 1997).

Sewage and detergents contribute significantly to anthropogenic boron in water bodies, largely due to sodium borate (NaBO_3) used in cleaning products. Sewage effluents generally display $\delta^{11}\text{B}$ values from -2.8‰ to $+12.9\text{‰}$ and boron concentrations ranging from 0.13 to 4.1 mg/L (Vengosh et al., 1998; Widory et al., 2005; Tirez et al., 2010). The overlap in $\delta^{11}\text{B}$ values between sewage and natural borate minerals (e.g., sodium perborate) highlights the difficulty in distinguishing some anthropogenic inputs. Furthermore, municipal solid waste leachates show $\delta^{11}\text{B}$ values of $+3\text{‰}$ to $+10\text{‰}$, similar to sewage sources (Nigro et al., 2017), suggesting overlapping contamination signatures.

Inorganic fertilizers display variable $\delta^{11}\text{B}$ compositions. Komor (1997) reported $\delta^{11}\text{B}$ values of $\sim 0.7\text{‰}$ for NH_4NO_3 , $\sim 0.4\text{‰}$ for urea, and $\sim 14.8\text{‰}$ for phosphate fertilizers, with boron concentrations ranging from 0.46 to 13.3 mg/L. In contrast, Tirez et al. (2010) observed different $\delta^{11}\text{B}$ values for urea (20.6‰) and NPK fertilizers (0.2–7.2‰), highlighting formulation-dependent variability.

Postigo et al. (2021) integrated $\delta^{11}\text{B}$ with $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ isotopes to trace nitrate sources in the Llobregat Basin. Elevated $\delta^{15}\text{N}\text{--NO}_3^-$ values (up to $+13.2\text{‰}$) and $\delta^{11}\text{B}$ signatures pointed to dominant inputs from wastewater and manure, while chemical fertilizers contributed to select samples.

Overall, $\delta^{11}\text{B}$ values help differentiate between natural sources, pig and cattle manure, sewage, and fertilizers. However, overlaps—particularly between sewage and landfill leachates—limit $\delta^{11}\text{B}$'s discriminative power in some cases. In such contexts, additional tracers like tritium isotopes are recommended to confirm the origin of nitrate pollution.

$\delta^{11}\text{B}$ as a tracer for pollution source identification

Research conducted across several European countries—including Spain, Portugal, and Italy—has shown that the integrated

use of $\delta^{15}\text{N}\text{--NO}_3^-$, $\delta^{18}\text{O}\text{--NO}_3^-$, and $\delta^{11}\text{B}$ isotopes provides an effective means of identifying nitrate pollution sources, such as organic and inorganic fertilizers, animal manure, and domestic and septic waste (Sankoh et al., 2021).

In Spain, Puig et al. (2017) investigated the Baix Ter Aquifer to trace the origins of nitrate contamination and the geochemical processes influencing its distribution. Their analysis revealed $\delta^{15}\text{N}\text{--NO}_3^-$ values ranging from $+5.0$ to $+32\text{‰}$ and $\delta^{18}\text{O}\text{--NO}_3^-$ values from $+8.9$ to $+18.1\text{‰}$, suggesting significant contributions from sewage, animal manure, and leachates from dumpsites. Similarly, Fernandes et al. (2019) reported elevated $\delta^{15}\text{N}\text{--NO}_3^-$ and $\delta^{18}\text{O}\text{--NO}_3^-$ values in Portugal, pointing to contamination primarily from animal waste and sewage.

Both studies also utilized $\delta^{11}\text{B}$ isotopes to further refine the identification of pollution sources. For example, Puig et al. (2017) found $\delta^{11}\text{B}$ values between $+1.4$ and $+9.0\text{‰}$ in two samples, indicating sewage input, while 10 samples showed values from $+23.5$ to $+34.5\text{‰}$, consistent with pig manure signatures. Likewise, Fernandes et al. (2019) observed $\delta^{11}\text{B}$ values ranging from $+28.5$ to $+44\text{‰}$, supporting the identification of pig manure as a dominant source.

In Italy, Lasagna and De Luca (2019) conducted a study in the Turin-Cuneo plain using $\delta^{15}\text{N}\text{--NO}_3^-$ and $\delta^{18}\text{O}\text{--NO}_3^-$ isotopes to distinguish between synthetic and organic pollution sources. They also applied $\delta^{11}\text{B}$ isotopic analysis to trace anthropogenic inputs, reporting values from $+8.37$ to $+18.05\text{‰}$. These isotopic signatures suggested sewage contamination at the lower end and potential overlap of cattle and pig manure at the higher end. When boron concentrations were considered (0.06–0.09 mg/L), the results aligned more closely with cattle manure, as earlier studies (Widory et al., 2005; Vengosh et al., 1998; Komor, 1997) indicated higher boron levels (1.43–8.12 mg/L) in pig manure and lower levels (0.05–0.41 mg/L) in cow manure.

Overall, the combined application of $\delta^{15}\text{N}\text{--NO}_3^-$, $\delta^{18}\text{O}\text{--NO}_3^-$, and $\delta^{11}\text{B}$ isotopes proves to be a valuable and reliable tool for accurately tracing nitrate sources in complex hydrogeological settings.

Rapid guide to identifying pollution sources through isotope analysis

Tracing groundwater pollution sources using isotopic techniques is essential for effective water quality management. However, interpreting and applying these methods can be complex for researchers, policymakers, and environmental professionals. To facilitate this process, (Table 2) presents a structured overview of key isotopic parameters, their characteristics, and corresponding ranges. This multi-isotope approach, incorporating $\delta^{15}\text{N}$, $\delta^{18}\text{O}$, and $\delta^{11}\text{B}$, enhances pollution source identification by distinguishing between nitrate from precipitation, fertilizers, manure, and sewage contamination. By providing a clear reference, this guide supports informed decision-making and the implementation of targeted pollution mitigation strategies.

Conclusions and perspectives for future groundwater management

Groundwater nitrate contamination continues to pose a significant global challenge, exacerbated by agricultural intensification, urban

TABLE 2 Rapid guide to identifying pollution sources.

Isotope parameter	Source	Characteristic range (‰ or mg/L)	Ref.
$\delta^{15}\text{N}$, $\delta^{18}\text{O}$	Precipitation	$\delta^{15}\text{N}$: -0.6 to $+31$ ‰; $\delta^{18}\text{O}$: $+30$ to $+70$ ‰	Jiang et al. (2016), Kendall et al. (2007), Kendall and Aravena (2000), Veale et al. (2019), and Mayer et al. (2001)
	Soil Nitrogen	$\delta^{15}\text{N}$: $+3$ to $+8$ ‰; $\delta^{18}\text{O}$: -8 to $+12$ ‰	Sigman et al. (2001) and Wang et al. (2024)
	NH_4^+ Fertilizer	$\delta^{15}\text{N}$: -8 to $+7$ ‰; $\delta^{18}\text{O}$: -8 to $+12$ ‰	Wang et al. (2024) and Kelepertzis et al. (2023)
	NO_3^- Fertilizer	$\delta^{15}\text{N}$: -5 to $+8$ ‰; $\delta^{18}\text{O}$: $+17$ to $+25$ ‰	Kelepertzis et al. (2023) and Wang et al. (2024)
	Manure/Sewage	$\delta^{15}\text{N}$: $+5$ to $+25$ ‰; $\delta^{18}\text{O}$: -8 to $+12$ ‰	Lorette et al. (2022), Deng et al. (2024), Quinodoz et al. (2024), Kyritidou et al. (2024), Torres-Martínez et al. (2021), and Blarasin et al. (2021)
$\delta^{11}\text{B}$	Uncontaminated GW	$\delta^{11}\text{B}$: $+23.8$ to $+38.5$ ‰; B: 0.015 – 0.15 mg/L	Dotsika et al. (2010)
	Synthetic Fertilizer	$\delta^{11}\text{B}$: -6 to $+5$ ‰; B: 0.05 – 0.41 mg/L	
	Hog Manure	$\delta^{11}\text{B}$: $+7.2$ to $+42.5$ ‰; B: 1.43 – 8.12 mg/L	
	Cattle Manure	$\delta^{11}\text{B}$: $+22.3$ to $+24$ ‰; B: 0.05 – 0.41 mg/L	
	Sewage/Landfill	$\delta^{11}\text{B}$: $+5$ to $+25$ ‰; B: 0.13 – 4.1 mg/L	

expansion, and inadequate wastewater treatment practices. This review underscores the growing relevance of stable isotope techniques—particularly $\delta^{15}\text{N}$ – NO_3^- , $\delta^{18}\text{O}$ – NO_3^- , and $\delta^{11}\text{B}$ —in accurately identifying the sources of nitrate pollution. While traditional methods such as vulnerability mapping and hydrochemical analyses provide valuable information on contamination pathways, they often fall short in resolving specific pollution origins, especially in complex hydrogeological settings.

The combined use of multi-isotope approaches and hydrochemical data has proven to be a powerful tool for nitrate source apportionment. The inclusion of $\delta^{11}\text{B}$ enhances the reliability of isotopic analysis by addressing key limitations related to denitrification and the overlapping signatures of different nitrogen sources. This integrative approach allows for more accurate assessments of groundwater quality and supports the development of targeted mitigation strategies.

Looking toward the future, the adoption of advanced isotopic techniques should be prioritized in groundwater monitoring and management efforts worldwide. Expanding global and regional datasets, refining analytical methodologies, and fostering collaboration among scientists, water managers, and policymakers will be essential for advancing these tools from research to practical application. Incorporating isotope-based methods into water governance frameworks can significantly improve the precision and effectiveness of pollution control measures, especially in areas facing high nitrate loads.

Ultimately, stable isotope techniques offer a promising pathway toward more informed, science-based groundwater management. Their broader implementation will be crucial to protecting water resources, preserving public health, and ensuring long-term groundwater sustainability in an increasingly vulnerable global environment.

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