Nitrate Contamination in Groundwater of Arid and Semi-Arid Regions, Ecotoxicological Impacts, and Management Strategies

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Contents

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Abstract Groundwater is the primary source of drinking and irrigation in arid and semi-arid regions. In the last few decades, groundwater contamination by nitrate has reached its maximum levels. Several geogenic and anthropogenic sources were found to be responsible for the nitrate contamination. Studies around the globe show that the extensive use of nitrogen-based fertilizers is the principal cause of nitrate contamination in arid and semi-arid aquifers. Nitrate in the drinking water can harm human health by resulting in methemoglobinemia, infectious diseases, thyroid problems, and increased risk of colorectal cancer. Therefore, the growing demand for groundwater, especially in arid and semi-arid regions, necessitates the development of effective nitrate removal strategies. Several existing technologies, such as reverse osmosis, ultrafiltration, chemical and biological denitrification, ion exchange, adsorption, and electrodialysis, can remove nitrate from groundwater. However, their applicability is contingent on several variables, including necessary infrastructure, the cost-effectiveness of the technology, scalability, and its widespread acceptance. Management of nitrate-contaminated groundwater entails source reduction, removal or transformation technologies, groundwater conservation, education, legislation, and guiding principles. Thus, this chapter focuses on nitrate contamination in groundwater, health and environmental impacts, management strategies, and options for safe water supply in arid and semi-arid regions worldwide.

Keywords Arid and semi-arid regions, Groundwater nitrate, Groundwater quality management, Human health effects, Methemoglobinemia, Remediation technologies

1 Introduction

Sustainable development goals created by the UN general assembly require the provision of high-quality drinking water. According to the WHO, one-third of the global population lacks access to clean and safe drinking water. Groundwater is a principal source of fresh water, which provides almost 50% of the world's drinking water and around 43% of irrigation water. This resource is under threat from several factors, including climate change, land use, and rapid population growth [1]. The quality and quantity of many aquifers in arid and semi-arid regions worldwide are degrading, especially where groundwater is the only source of drinking and irrigation. A decline in the water table and deterioration of groundwater, especially with nitrate contamination, is the major problem in arid and semi-arid regions [2]. Several natural and anthropogenic nitrate sources can contaminate groundwater. Some of the primary reasons for an elevated level of nitrate in aquifers of arid and semi-arid regions include mineralization of organic plants, agricultural activities (mainly inorganic fertilizers), industrial activities, human waste disposal (septic and sewage disposal), and nitrification of soil organic nitrogen [2–5]. Agricultural irrigation return flows in arid and semi-arid regions often contain elevated levels of salts, nitrate, and pesticides [6]. Numerous studies have shown that groundwater nitrate is driven majorly by the extensive use of fertilizers or manure in agro-based activities in these regions [7, 8].

The WHO [9] has established 50 mg/L as the safe drinking water level for nitrate, while the Bureau of Indian Standards (BIS) has set this limit to 45 mg/L (IS: 10500-2012). Nitrate levels in drinking water that exceed this limit can impair ecosystems and human health. Blue baby syndrome or methemoglobinemia is one of drinking water's most visible side effects with nitrate concentrations above the WHO-recommended limit [7]. Furthermore, the elevated levels of nitrates can cause infectious diseases, thyroid issues, increased risk of colorectal cancer, methemoglobinemia, congenital disabilities, possibly stomach cancer, and low birth weight [1, 10, 11]. The overgrowth of aquatic plants and algae due to excess nitrates in surface water causes eutrophication [12]. It can cause permanent damage to aquatic ecosystems, even to the point of causing mass fish mortality. Likewise, irrigation with nitrate-polluted groundwater may harm crop production. The Food and Agriculture Organization (FAO) has established a threshold value of 22 mg/L for irrigation water; a level above this may damage sensitive crops like sugar beet or grapes [1].

In arid and semi-arid regions, alternative water supply sources are becoming scarcer while groundwater demand is rising. There is an urgent need to develop technologically and economically sustainable, accessible, and practical solutions for mitigating nitrate pollution [7]. Several existing technologies, such as reverse osmosis, ultrafiltration, chemical and biological denitrification, ion exchange, adsorption, and electrodialysis are capable of removing nitrate from groundwater [7, 13]. However, their applicability depends on several variables, including necessary infrastructure, the cost-effectiveness of the technology, and its widespread acceptance and scalability [11]. It is also imperative to develop and implement nitrate management measures for groundwater. Nitrogen source inventories, basin management plans, and identifying and quantifying primary sources and their loads to groundwater are some strategies for reducing nitrate pollution. The management of nitrate-contaminated groundwater in arid and semi-arid regions should include source reduction measures, removal or transformation technologies, groundwater conservation, educational actions, legislative efforts, and practical guidelines [10, 14–16]. Therefore, this chapter aims to focus on nitrate contamination in groundwater, their health and environmental impacts, management strategies, and options for safe water supply in arid and semi-arid regions globally.

2 Detection and Analysis of Nitrate

Numerous techniques can be utilized to detect and analyze nitrate in groundwater. Before analysis, it is necessary to consider some common factors, such as proper sampling, storage conditions, interference ions, etc. The sample must be filtered through 0.45 μm membranes to remove turbidity and bacteria. Those samples that cannot be analyzed immediately should be refrigerated at 4°C and must not acidify because rapid oxidation of nitrite to nitrate happens at lower pH. Several widely known analytical methods for nitrate determination and their fundamental features are discussed here.

2.1 Ion Chromatography

Ion chromatography is the most extensively used analytical technique for analyzing nitrate in groundwater. This technique is based on ion exchange and conductivity-based detection. It also permits the analysis of additional anions in water samples, such as nitrite, chloride, fluoride, sulfate, and nitrate. Ion chromatography utilizes ion exchange resins to separate atomic or molecule ions based on their interaction with the specific resin. The advantages include being free from ionic interference, high accuracy and precision, a variety of detection modes, high separation efficiency, selectivity, and speed and detection thresholds ranging from 0.01 to 1 mg/L [12, 17–19]. However, a disadvantage of the technique is that organic acids may affect analytical procedures.

2.2 Colorimetry

Many colorimetric methods are available for nitrate analysis in the water samples; they use copper-treated cadmium metal to reduce nitrate to nitrite. Nitrite is then combined with additional regents to produce a highly colored diazonium dye that can be detected at 520 nm. However, cadmium and hydrazine used in these techniques generate toxic by-products; hence waste disposal must be regulated [2]. For nitrate analysis, similar enzymatic approaches may utilize hydrazine or nitrate reductase. The enzymatic approach has the benefit of avoiding the harmful effects of cadmium and hydrazine.

2.3 Ion-selective Electrode

Ion-selective electrodes can detect nitrate in groundwater samples with high precision. Potentiometric measurements of nitrate using ion-selective electrodes allow relatively rapid measurement of NO_3^- -N concentration ranging from 0.14 to 1,400 mg/L. However, this method is susceptible to significant interferences and requires linear calibration and controlled conditions for reliable results [2].

2.4 Nitrate Test Strip

A sample can be screened for nitrate interferences before analysis using test strips. Test strips are easy and quick but inaccurate in the evaluation process. For example,

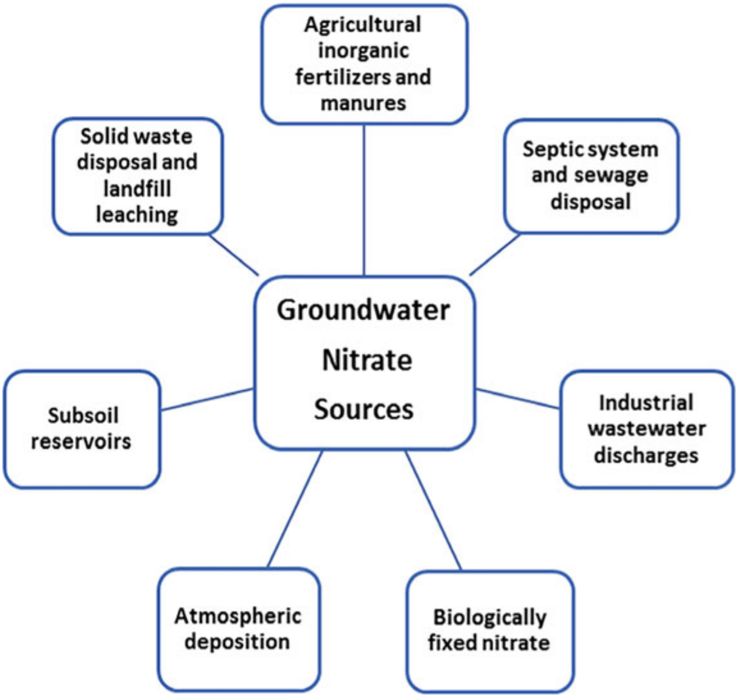

Fig. 1 Possible groundwater nitrate sources in arid and semi-arid regions

Table 1 Sources of nitrate in arid and semi-arid regions

Sources	Descriptions	Examples
Point	Single identifiable source and high concentration at a particular location	Concentrated animal confinement areas, leaky septic tanks, manure storage areas, accidental spills of nitrogen-rich chemicals, and dairy lagoons
Diffuse	Multiple sources dispersed around a region emit pollutants and have long-term impacts on human health and the ecosystem	Nitrogenous fertilizer, manure, and chemicals in agriculture, sewage pipe leaks, inappropriate household waste disposal, mining activities, dissolved nitrogen in precipitation, and return flow after irrigation

(Source: Adopted from [20]; [21])

Hach™ test strips are widely used based on the color change in response to the nitrate concentration and allow rapid evaluation of nitrate [2].

3 Sources of Nitrate Contamination in Groundwater of Arid and Semi-arid Regions

According to available scientific literature, the sources of nitrate in groundwater in arid and semi-arid areas are natural and/or anthropogenic (Fig. 1). As stated in Table 1, these sources can also be categorized as point and diffused sources.

3.1 Natural Sources

Natural sources of nitrate include geogenic (nitrate from natural subsoil reservoirs), atmospheric deposition, biologically fixed nitrogen, and groundwater-immanent input from other aquifers that may be hydraulically connected [2]. Nitrate reservoirs have been discovered in the subsoil of many dry regions of the world, and these reservoirs may be a substantial geogenic source of nitrate in groundwater [12]. Additionally, the fixation of nitrate by plants in arid regions can increase nitrate levels in groundwater [6]. Nitrate can be found naturally in nitrate salt deposits such as sodium nitrate. The continuing interaction between minerals and bacteria located in fissures and crevices in geologic formation leads to nitrate contamination of groundwater [7]. However, the natural background concentration of NO_3^--N in groundwater is far below 10 mg/L due to precipitation infiltration and mineralization of organic plants and animals; if these concentrations rise, it could be due to agricultural, industrial, or human waste disposal [22].

3.2 Anthropogenic Sources

Human actions, directly and indirectly, affect the quality of groundwater. Many anthropogenic factors affect the augmentation of nitrate in groundwater, like excessive use of fertilizers, septic systems, and human-induced wastes [23, 24]. Over-application and unscientific use of nitrogen-based fertilizers is the primary culprit of nitrate pollution in arid and semi-arid aquifers [2, 25]. Ammonium in inorganic fertilizers converts to the more mobile nitrate form in an oxidizing soil environment. Enzyme urease converts urea into nitrate, which is then utilized by plants or leaches into shallow aquifers [22]. Further, irrigated agriculture on heavily fertilized sandy soils is more susceptible to nitrate leaching. A variety of sources, including agriculture (primarily inorganic fertilizers, livestock manure, etc.), industry (untreated and poorly treated industrial wastewater), human waste disposal (septic and sewage disposal), landfill leaching, manure ponds, and polluted river and aquifer interactions, all contribute to nitrate contamination in groundwater [2–6, 8, 26]. Regarding nitrogen-related water quality indicators (nitrate, nitrite, and ammonia), agriculture sector pollution exceeds that of urban and industrial sources [6]. The primary causes

Table 2 Limit of nitrate concentration in drinking water permitted by various agencies

Organizations/ agencies	Conc. as NO_3^- (mg/L)	Con. as NO_3^- -N (mg/L)	References
WHO	50	10	Zendehbad et al. [28], WHO [9]
BIS	45	–	Singh et al. [13]; IS:10500-2012 [29]
US-EPA	45	10	Xin et al. [15], EPA [30]
EDWD	50	–	Xin et al. [15], Agarwal et al. [31]
MEP, China	–	10	Agarwal et al. [31]

MEP Ministry of Environmental Protection, *EDWD* European Drinking Water Directive

of nitrate pollution in developing nations are low living standards, inadequate sanitation, leaking septic tanks, and improper sewage disposal [1]. Similarly, nitrate concentrations are higher in many urban areas due to increasing human and animal waste [23]. Furthermore, stable isotope studies indicate that most nitrate in groundwater of arid and semi-arid regions is due to fertilizers and human waste [12]. A small contribution of nitrate may be from the industrial sectors that use nitric acid, urea, and anhydrous ammonia. In addition, as the forest has a high capacity for nitrogen transfer, deforestation also results in nitrate leaching into groundwater [27].

4 Drinking Water Standards

Primary drinking water regulations are intended to safeguard public health from specific contaminants such as nitrate. High nitrate levels in drinking water can pose several health risks; consequently, various agencies worldwide have established safe nitrate levels in drinking water. Environmental protection agencies set a limit of 10 mg/L for NO_3^- -N in drinking water, below which no adverse effects on human health due to methemoglobinemia were observed [22]. A comparison of the nitrate concentration standards established by various agencies is shown in Table 2.

5 Nitrate as a Global Groundwater Pollutant in Arid and Semi-Arid Regions

Nitrate is a tasteless, odorless form of nitrogen and is naturally produced in the soil and other mediums, such as groundwater. It is an essential component of the nitrogen cycle and is used by most plants as a macronutrient. Nitrate can leach easily into the aquifers from the unsaturated soil zone because of high solubility and mobility in water [21]. Due to its significant solubility, it is known as the most prevalent pollutant in groundwater. Nitrate may be represented in drinking water as nitrate and nitrate-nitrogen [15]. The aridity index classifies arid lands into a desert (i.e., hyper-arid and arid) and semi-desert (i.e., semi-arid). These regions are characterized by fluctuating precipitation, high evaporation rates, and an annual wet and dry season [32]. About one-third of the world's population resides in drylands, which account for about 41% of the planet's surface area [33]. Most people in these regions rely on the groundwater supply for daily requirements. Additionally, a considerable proportion of the population relies on agricultural activities for survival. Over the past several decades, unsustainable agrarian practices have increased the potential of groundwater pollution with nitrates [14]. Agricultural irrigation return flows contain high salts and nitrate concentrations, eventually leaching and contaminating groundwater [6]. In addition, urbanization, industrialization, and waste disposal can contribute significantly to groundwater nitrate contamination worldwide [2]. These anthropogenic activities demonstrate that nitrate is the most prevalent pollutant in the groundwater of arid and semi-arid regions.

Studies have shown that nitrate is the most prevalent pollutant in the aquifers of arid and semi-arid regions worldwide. Alsabti et al. [34] found that 68% of groundwater samples of Kuwait Bay had nitrate concentrations above WHO standards, ranging from 22.7 to 803.9 mg/L due to anthropogenic factors such as fertilizer use and urbanization. From 1991 to 2003, a total of 5,101 groundwater wells were sampled in 51 research studies across the United States; more than 4% of the sampled wells had nitrate levels above the EPA [30] limit of NO_3^--N [35]. Shukla and Saxena [27] pointed out that San Joaquin Valley (United States) is the nitrate's epicenter and affects over 275,000 people. Rahmati et al. [36] reported that 12.9% of samples from the Ghorveh-Dehgelan aquifer in Kurdistan (Iran) surpassed the maximum permissible level set by WHO [9]. Antiguedad et al. [37] observed the presence of nitrate concentrations in many alluvial floodplains in Europe. According to Beutel et al. [38], nitrate concentrations exceeding 10 mg/L as NO_3^--N are most common in the eastern alluvial fans subregion Central Valley of California. Nawale et al. [39] point out that the Wardha sub-basin (India) has a high health risk of non-carcinogenic disease due to drinking nitrate-contaminated groundwater. Adimalla [40] demonstrates that the aquifers of Telangana (India) have a concentration of nitrate (NO_3^-) ranging from 17 to 120 mg/L, and around 57% of samples were above the BIS permissible limits for drinking water. Zendehbad et al. [28] found that the urban aquifer of Mashhad (Iran) has excessive nitrate in 110 wells out of 261 wells due to sewage contamination. Jandu et al. [41] found that 86% of samples had nitrate content higher than the WHO maximum safe limit and found to be in the range of 10.2 to 519.6 mg/L in Jhunjhunu, Rajasthan (India). Ahadal and Suthar [42] studied the Malwa region of Punjab (India) and found that over 92% of sites have higher nitrate than the WHO recommendation. Waste dump sites, animal waste, nitrogen-based fertilizers, and industrial effluents are the foremost reasons for contamination. Further, Table 3 demonstrates the groundwater nitrate, possible sources, and sample percentages exceeding various drinking water standards worldwide in arid and semi-arid regions. In addition, Fig. 2 depicts sampling locations/regions of reported nitrate in arid and semi-arid regions of the world and Fig. 3 gives

Table 3 Regions/locations demonstrating groundwater nitrate concentration along with possible sources and sample percentages exceeding various drinking water standards in arid and semi-arid regions worldwide

Location/ region no.	Region/location	Climate	Reported value as NO_3^- (mg/L)	Percentage of sample > DWS (mg/L as NO_3^-)	Possible nitrate sources	References
1	Churu Rajasthan, India	Arid and Semi-arid	Min = 0.8 Max = 498.7 Mean = 44.7	NS = 515 28.54% > BIS	Anthropogenic activities	Tanwer et al. [43]
2	South Kuwait's Bay, Kuwait	Arid	Min = 22.7 Max = 803.9 Mean = 143.8	NS = 19 68.42% > WHO	Agricultural fertilizers, sewage disposal and landfills	Alsabti et al. [34]
3	Cuddapah, South A.P, India	Semi-arid	Min = 23.2 Max = 110.8	NS = 30 86% > BIS	Anthropogenic activities	Sunitha et al. [44]
4	Maadher central parts, Hodna, Algeria	Semi-arid	Min = 12 Max = 407 Mean = 173	NS = 33 67.64% > WHO	Agricultural activities and dumping sites	Selmane et al. [45]
5	Djelfa region, Algeria	Semi-arid	Min = 3 Max = 336	NS = 19 58% > WHO	Agricultural fertilizers and livestock waste	Ali Rahmani and Chibane [46]
6	Coastal parts, Southern Saudi Arabia	Arid	Min = 7 Max = 124 Mean = 48	NS = 80 45% > WHO	–	Masoud et al. [47]
7	North-eastern, Iran	Semi-arid	–	NS = 82 48% > HWC	Agricultural fertilizers and sewage effluents	Atabati et al. [48]
8	Nile Valley, Qena City, Egypt	Arid	Min = 0.1 Max = 257 Mean = 53	NS = 41 30% > WHO	Chemical fertilizers and manure	Mohammed et al. [49]
9	Shekhawati region, Northern India	Semi-arid	Min = 2 Max = 1803	NS = 163 65% > BIS	–	Singhal et al. [50]
10	Tiruppur region, Southern India	Semi-arid	Min = 10 Max = 290 Mean = 83.45	NS = 40 58% > WHO	Agricultural fertilizers, manure and septic tanks	Karunanidhi et al. [51]

(continued)

Table 3 (continued)

Location/ region no.	Region/location	Climate	Reported value as NO_3^- (mg/L)	Percentage of sample > DWS (mg/L as NO_3^-)	Possible nitrate sources	References
11	Telangana, India	Semi-arid	Min = 12 Max = 212 Mean = 69	NS = 105 71% > BIS	–	Adimalla et al. [52]
12	Kano plains, Kisumu city, Kenya	Arid and Semi-arid	Min < 0.04 Max = 90.6	NS = 62 63% > WHO	Sewage and manure application	Nyilitya et al. [53]
13	Telangana, India	Semi-arid	Min = 17 Max = 120 Mean = 58.74	NS = 35 57% > WHO	Agricultural fertilizers, human and livestock waste	Adimalla and Li [23]
14	Telangana, India	Semi-arid	Min = 4 Max = 440 Mean = 73	NS = 194 52% > WHO	Agricultural activities	Adimalla and Wu [10]
15	Yamuna sub-basin Pani-pat, Haryana, India	Semi-arid	Min = 0.5 Max = 69 Mean = 12.8	NS = 74 6.6% > WHO	–	Kaur et al. [54]
16	Guanzhong basin, China	Semi-arid	Min = 0 Max = 90 Mean = 18.26	NS = 191 24.61% > WHO	Agricultural fertilizers, manures, septic tanks and organic effluent	Zhang et al. [55]
17	Bardaskan, Southeast Iran	Arid	Min = 0 Max = 77.37 Mean = 17.57	NS = 30 6.6% > WHO	–	Radfarda et al. [56]
18	Sylhet, Bangladesh	Semi-arid	Min = 0 Max = 25.86 Mean = 5.70	NS = 23 -	–	Ahmed et al. [57]
19	Varamin aquifer, Tehran, Iran	Semi-arid	Min = 0.22 Max = 74.14	NS = 70 11.42% > WHO	Agricultural fertilizers, domestic waste and sewage	Nejatijahromi et al. [58]

20	Nirmal Province, Telangana, India	Semi-arid	Min = 0.8 Max = 80 Mean = 36.91	NS = 34 26% > BIS	Agricultural fertilizers, sewage disposal and septic system	Adimalla et al. [59, 60]
21	Malwa region, Punjab, India	Semi-arid	Min = 38.45 Max = 198.05 Mean = 33.45	NS = 76 92% > BIS	Agricultural fertilizers	Ahada and Suthar [42]
22	Scopia basin, Central Greece	Semi-arid	Min = 6.2 Max = 134.6	NS = 41 29% > WHO	Geogenic, fertilizers and wastewater	Charizopoulos et al. [61]
23	Halayieb, Egypt	Arid	Min = 11.7 Max = 131.27	NS = 11 54.54% > WHO	–	Zaki et al. [62]
24	Bou-Areg, Nador region, Morocco	Semi-arid	Min = 16 Max = 300	NS = 94 50% > WHO	Agricultural activities	Re and Sacchi [63]
25	Zhongning, Ningxia, Northwest China	Arid	Min = 59.6 Max = 103 Mean = 17.9	NS = 50 60% > WHO (NO_3^--N; 10 mg/L)	Agricultural fertilizers and wastewater	Chen et al. [64]
26	Lar area, Southern Iran	Arid	Min = 1.5 Max = 70.7	NS = 34 5.9% > WHO	Agricultural activities	Rezaei et al. [65]
27	Kharkiv City, East Ukraine	Semi-arid	Mean = 31.8 –	NS = 25 30% > WHO	Sewage disposal	Vystavna et al. [66]
28	Bahira plain aquifer, Central Morocco	Arid	Min = 0.5 Max = 584	NS = 62 18% > WHO	Agricultural activities	Karroum et al. [67]
29	Ghorveh Dehgelan aquifers, Western Iran	Semi-arid	Min = 12.4 Max = 111.6 Mean = 32.15	NS = 93 12.9% > WHO	Agricultural fertilizers	Rahmati et al. [36]
30	Basin of Seversky Donets River, Russia/Ukraine	Semi-arid	Min = 37.2 Max = 189.9	NS = 39 7.69% > WHO	Natural and anthropogenic	Vystavna et al. [68]
31	Southeast, Granada, Peninsula	Semi-arid	Min = 4 Max = 561 Mean = 74.5	NS = 175 -	–	Rodriguez-Galiano et al. [69]

(continued)

Table 3 (continued)

Location/ region no.	Region/location	Climate	Reported value as NO_3^- (mg/L)	Percentage of sample > DWS (mg/L as NO_3^-)	Possible nitrate sources	References
32	Southern Hodna, Algeria	Arid	Min = 6 Max = 158 Mean = 76.28	NS = 18 61% > WHO	Agricultural fertilizers	Abdesselam et al. [25]
33	Basin and ranges of USA	Semi-arid	Min = 0.1 Max = 130	NS = 3,539 8% > WHO	Agricultural fertilizers or urban waste	Anning et al. [70]
34	Toyserkan, western Iran	Semi-arid	Min = 1 Max = 162 Mean = 30	NS = 95 9.5% > WHO	Manure and inorganic fertilizers	Jalali [71]
35	Castilla-La Mancha, Southeast Spain	Semi-arid	Min = 0.4 Max = 125	NS = 684 –	Agricultural activities	Moratalla et al. [72]
36	Tumkur Taluk, Karna-taka, India	Semi-arid	Min = 0.44 Max = 261 Mean = 54.3	NS = 269 48.5% > BIS	–	Ramakrishnaiah et al. [73]
37	Badain Jaran desert, Northwest China	Arid	Min = 0.1 Max = 113	NS = 52 32%, > WHO	Agricultural activities nitrification, subsistence farming and grazing	Gates et al. [74]
38	Serowe, Botswana	Semi-arid	Min = 0 Max = 219 Mean = 22.8	NS = 51 –	Agricultural fertilizers, manures, septic tanks and precipitation	Stadler et al. [75]
39	Livermore, USA	Semi-arid	Min = 5.2 Max = 60.2	NS = 35 17% > WHO	Agricultural fertilizers and livestock waste	Moore et al. [76]

No. of Samples (NS); Drinking Water Standards (DWS): (BIS, 45 mg/L; WHO, 50 mg/L; HWC, NO_3^--N; max., 10 mg/L)

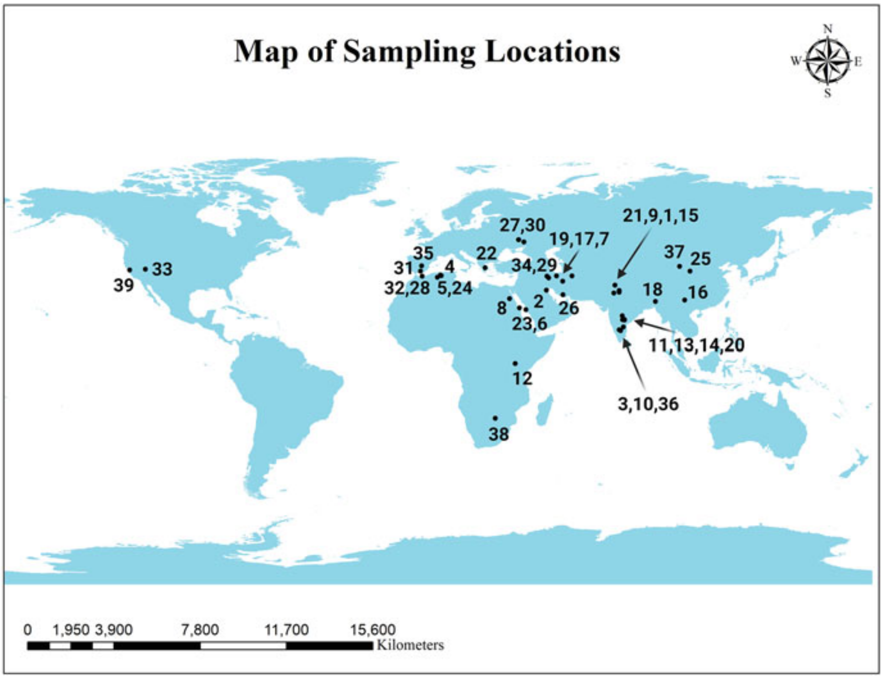

Fig. 2 Sampling locations/regions of reported nitrate in groundwater of arid and semi-arid regions

a visual representation of sampling locations together with the percentage of samples exceeding various nitrate drinking water guidelines.

6 Identification of Various Nitrate Sources in Groundwater

Although there are several approaches for identifying nitrate sources in groundwater, the stable dual isotopes (nitrogen and oxygen) approach is extensively used and widely accepted to identify agricultural fertilizers, manure, human waste, and other sources. Many scientific studies globally successfully used $\delta^{15}N$ and $\delta^{18}O$ isotope composition of NO_3^- to identify different sources, fate, and their related contributions to nitrate in aquifers [24, 28, 77]. The numerous sources (e.g., atmospheric, agriculture fertilizer and sewage, or manure) have distinct compositions of nitrogen ($^{15}N/^{14}N$) and oxygen ($^{18}O/^{16}O$) isotopes, which are widely used for source identification of Nitrate [77, 78]. However, a homogeneous signal of dual isotopes in aquifers reveals naturally occurring nitrate [75]. Nitrate derived from fertilizers and sewage has a distinct range of ^{15}N- NO_3^-, whereas soil microbial and atmospheric source has a different range of ^{18}O- NO_3^- [78]. When numerous nitrate sources are

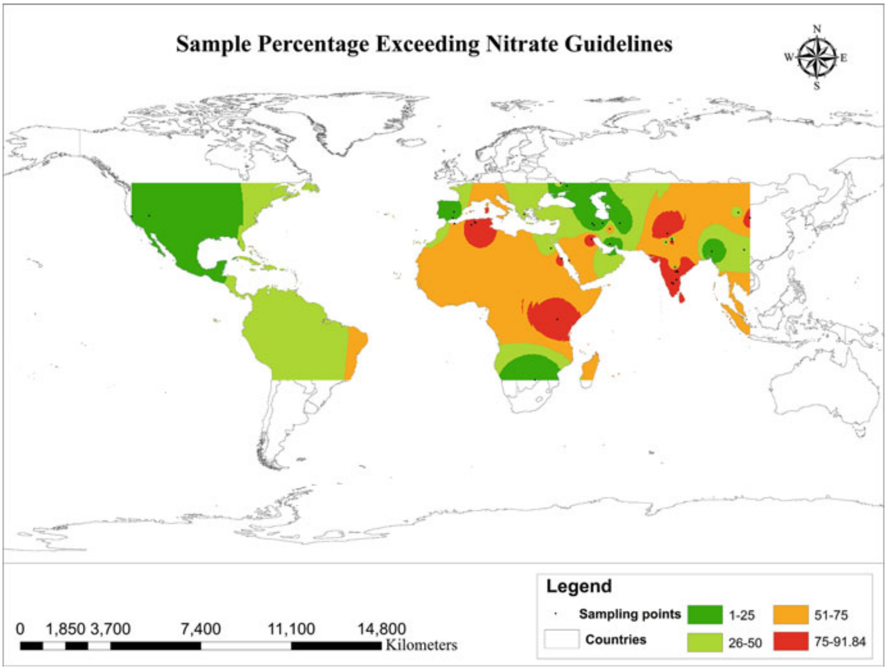

Fig. 3 Locations along with the percentage of samples exceeding various nitrate drinking water guidelines

present, isotopic quantification is also accompanied by evaluation uncertainty and lacking [77].

7 Nitrogen Transformation Processes

Nitrogen is accessible to plants through ammonium and nitrate via nitrification or nitrogen fixation activities within the root zone. Some bacterial species, including those that interact with the roots of higher plants and those that are free-living, can assimilate atmospheric nitrogen. Some fungi and blue-green algae species can also assimilate atmospheric nitrogen. Under aerobic conditions, Nitrosomonas species convert organic nitrogen, ammonium ion (NH_4^+), or ammonia to NO_2^- (nitrite), which is then converted into nitrate by nitrite-oxidizing bacteria such as Nitrobacter species [2]. Nitrate is created when soil-dwelling aerobic and anaerobic bacteria decompose dead plants and other organic remains into ammonium ions, which are then changed into nitrate. The soil biota quickly converts ammonium to nitrate in soils under aerated or oxidizing conditions. Globally, around 193 million tons of biological nitrogen fixation (land and seas) and 94 million non-biological (atmospheric lightning and industrial) fixations occur [27, 79]. There are many ways to reduce nitrate levels, such as plant absorption, mineralization-immobilization

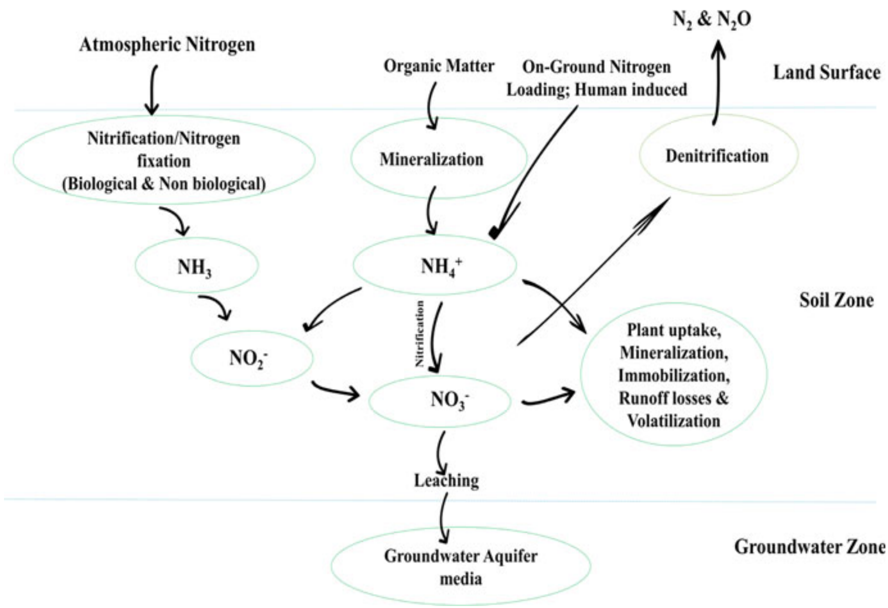

Fig. 4 Subsurface nitrogen transformation processes and nitrate leaching

processes, volatilization, runoff losses, and denitrification. These processes limit the nitrate flux into groundwater either individually or in combination.

However, nitrate ions are weakly bound to soil particles (negatively charged) and may percolate into the aquifer. When oxygen is scarce in soil for microbial respiration, microbial denitrification is frequently observed with greater than 60% pore saturation. Nitrate or nitrite is employed as the terminal electron acceptor in the respiratory process of microbial reduction of nitrate ions when oxygen is scarce. As a result, high energy molecule adenosine tri-phosphate is produced. The electron transfer during this phase provides energy to the denitrifying bacteria to stimulate new cell biomass [7]. Autotrophic and heterotrophic denitrification is essential for converting nitrate into nitrogen gas to reduce nitrate leaching in groundwater. Several factors influence nitrate leaching, including land use patterns, on-ground nitrogen loading, groundwater recharge, soil nitrogen dynamics, soil properties, and groundwater level [21]. Different ecosystems have varying capacities for nitrogen accumulation and transmission, which can be used to estimate the probability of nitrate contamination. An ecosystem's ability to accumulate nitrate is referred to as the accumulation potential, whereas the ability to transfer nitrate to another ecosystem is referred to as the transfer potential. The atmosphere and agricultural systems have substantial transmission potential, increasing groundwater pollution likelihood [27]. Figure 4 demonstrates the subsurface nitrogen transformation processes and nitrate leaching into groundwater.

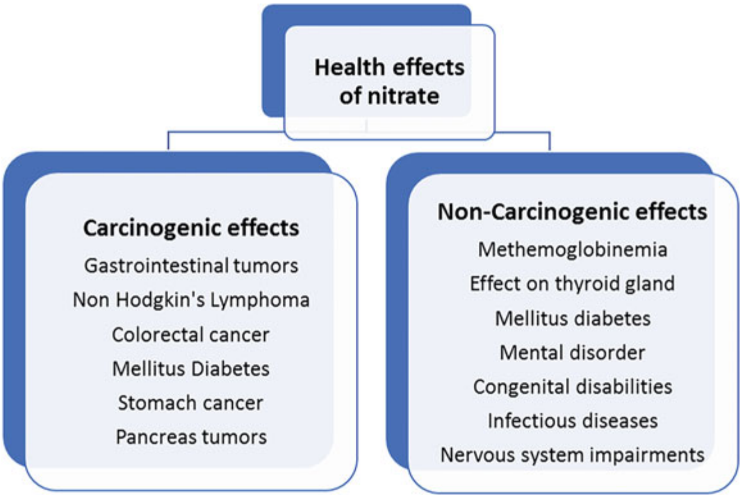

Fig. 5 The major health effects of nitrate in drinking water

8 Effects of Nitrate on Human Health and Environment

Nitrate, a prevalent groundwater pollutant in arid and semi-arid regions, can harm ecosystems and human health. The major effects of nitrate in drinking water are depicted in Fig. 5.

8.1 *Effects on Human Health*

Nitrate in drinking water has adverse health effects if consumed excessively for an extended time period. Humans usually consume nitrate through the consumption of drinking water and food beverages. Still, when the maximum contamination level in drinking water is exceeded, it can account for up to 50% of human nitrate consumption [27]. It can enter the bloodstream from the stomach and upper intestines via drinking water [20]. Most of the nitrite absorption into the bloodstream appears in the intestines. Blue baby syndrome, or methemoglobinemia, is one of the prominent health effects of drinking water with nitrate concentrations greater than the upper safe limit of WHO [9] for an extended period in infants under 6 months of age [7]. Bacteria in the infant gastrointestinal tract convert nitrate to nitrite. Nitrite oxidizes the iron of hemoglobin to generate methemoglobinemia, decreasing the blood's oxygen-carrying capacity. The babies have an unusual blue-grey skin tone associated with 10% or higher methemoglobin levels. If the illness is not diagnosed and treated promptly, it might result in shortness of breath, a heart attack, and mortality [17]. According to the USEPA, the Hazard Quotient (HQ) value for non-carcinogenic human health risks associated with nitrate in drinking groundwater is unity, with a value greater than unity reflecting an individual's susceptibility to non-carcinogenic health risk [54]. Studies also reported that consuming elevated levels of nitrates can cause weakness, vomiting, mental disorder, abdominal disorder, hypertension, dizziness, infectious diseases, nervous system impairments, thyroid issues, gastrointestinal tumors, non-Hodgkin's lymphoma, mellitus diabetes, stomach cancer, pancreas tumors, increased risk of colorectal cancer, congenital disabilities, possible stomach cancer (adults), and low birth weight in humans [1, 5, 10, 11, 24, 80, 81]. Nitrate has been identified as a potential human carcinogen that can produce N-nitroso compounds through endogenous nitrosation [82]. Nitrate has also been associated with chronic digestive diseases and an increased risk of digestive cancer [6].

8.2 Environmental Health Effects

Many streams and rivers rely on groundwater for base flow, and increased nitrate concentrations in groundwater can pollute these resources. When there is an abundance of nitrate in surface water, aquatic plants and algae grow more quickly, causing eutrophication [12]. Eutrophication is commonly associated with anthropogenic nitrate sources. When numerous algae die and decompose, the decomposers consume a substantial amount of oxygen, altering the aquatic ecosystem. The adverse effects of eutrophication include reduced light penetration, decreased plant productivity in deeper waters, and decreased oxygen content in the water body [20]. It can considerably contribute to the eutrophication of coastal and marine environments [2, 83]. Nitrates can cause permanent damage to aquatic ecosystems, even to the point of causing mass fish mortality. Nitrate contamination harms humans by lowering environmental quality, increasing health risks, and increasing environmental management costs. Irrigating with nitrate-contaminated groundwater may damage sensitive crops like sugar-beet or grapes. As a result, the FAO established a 22 mg/L threshold value for irrigation water for sensitive crops [1]. The nitrate-nitrogen concentration in water between 100 and 200 mg/L reduces livestock appetite [84].

9 Technologies for Nitrate Remediation from Groundwater

Technological and economically viable, accessible, and practical solutions are required to mitigate nitrate pollution. The increasing demand for groundwater necessarily involves the development of efficient nitrate removal strategies. Various technologies efficiently removed nitrate from groundwater worldwide depending on infrastructure, affordability, and acceptability. Furthermore, energy and cost-efficient nitrate removal technologies are required to achieve global sustainable development goals and quality standards. Researchers for removing nitrate from groundwater have proposed a wide range of in-situ and ex-situ technologies. The in-situ treatment method involves nitrate treatment at the site, while the ex-situ option primarily involves the pump and treatment method away from the site. However, the ex-situ method is most effective when the contaminant plume is well-defined. The limitations of this method include co-contaminant availability, operation and maintenance, and scale of operation for water treatment. The treatment technologies may be categorized into nitrate reduction and removal methods. Some globally accepted techniques for nitrate removal are ion exchange, reverse osmosis, adsorption, electrodialysis, chemical denitrification using zerovalent iron, and biological denitrification [1, 7, 13, 85–87]. Some of these techniques can be combined for increased effectiveness and offset other technologies' drawbacks. A few conventional nitrate removal techniques are summarized in Table 4.

10 Management Strategies for Safe Water Supply in Arid and Semi-arid Regions

In arid and semi-arid regions, groundwater must be managed sustainably because it is an essential resource for irrigation and drinking water. Developing and implementing management strategies is necessary to reduce the elevated nitrate concentration in aquifers. Also, technological and policy reforms are required to mitigate its effects on humans and the environment. An effective management system should include a well-abandonment strategy and source reduction measures. However, source reduction activities like best agriculture management practices, domestic wastewater treatment, municipal solid waste management, etc., improve groundwater quality over the years to decades, so in-situ remediation may also be considered for hotspot sites with short-term objectives. The management comprises non-structural measures in addition to structural measures like physical activities and construction projects. The non-structural measures include laws, regulations, funding, education, and policies.

10.1 Effective Framework for the Management of Groundwater

Groundwater management involves collecting and analyzing data to identify nitrate-contaminated areas and quantify the scope of the problem. The essential management consideration is the fate and transport of nitrate in unsaturated and saturated zones. The potential sources of contamination are identified to establish available management options that reduce nitrate levels below the established standards. Then, examine the environmental and economic aspects of the available options. Soil and

Table 4 Various conventional nitrate removal techniques, along with their description, benefits, and drawbacks

Techniques	Descriptions	Benefits	Drawbacks	References
Reverse osmosis	In reverse osmosis, groundwater is forced through a cell membrane at a pressure of 300 to 1,500 psi, leaving contaminants on one side and water on another	Continuous operation, used for nitrate-affected saline groundwater, can separate 0.1 to 1 nm pollutants size, post-treatments are not required	High costs of operation, membrane fouling and deterioration, maintenance of membrane and issues of brine effluent disposal	Singh et al. [13], Huno et al. [7]
Ion-exchange	A strong base anion exchange resin is used for NO_3^- exchange with Cl^- and CO_3^{2-} from groundwater.	Regeneration and reuse of exhausted resin, effectiveness, simple to operate, economical method, especially trimethylamine used for nitrate exchange	SO_4^{2-} ions reduce resin's nitrate removal ability, brine disposal, and pretreatment required	Singh et al. [13], Tokazhanov et al. [8]
Electrodialysis	In this technique, ions are transferred from a less concentrated to a more concentrated solution using direct electric voltage and membranes	May simultaneously remove contaminants and desalinate, with greater precision and simple operation	Alkaline conditions reduced the efficiency of nitrate separation, more energy demand and pretreatment required	Abascal et al. [1], Sharma and Bhattacharya [85]
Adsorption	It is a surface phenomenon in which various natural and synthesized sorbents, agri-waste by-products, and industrial wastes are used for pollutant remediation	Convenience, cost-effective, lower energy demands, used for removal of both organic and inorganic pollutants	Removal depends upon initial nitrate concentrations, a dose of adsorbent, reaction time, pH, and operating temperature	Singh et al. [13], Huno et al. [7], Chander et al. [87], Yadav et al. [88]
Biological denitrification	Biological denitrification involves the reduction of nitrate under anaerobic conditions by using bacterial species	Environment-friendly, cost-effective, used for in-situ and ex-situ remediation	Higher levels of nitrate are challenging to eliminate, long time required, need optimum carbon-to-nitrogen ratio, bacterial sludge, high monitoring needs, sensitivity to environmental conditions, risk of	Huno et al. [7]

(continued)

Table 4 (continued)

Techniques	Descriptions	Benefits	Drawbacks	References
			nitrite formation, and post-treatment required	
Chemical denitrification	In this method, chemicals like zerovalent iron, elemental sulfur, zinc, and aluminum are used to reduce nitrate from water	Complete nitrate ion reduction may be achieved using zerovalent iron under controlled acidic conditions	Condition-dependent, ammonia stripping and post-treatment are necessary	Singh et al. [13], Huno et al. [7]
Catalytical reduction	This method removes nitrite and nitrate from water using catalysts such as lead, copper $A1_2O_3$, palladium-alumina, etc.	Complete nitrate removal may be possible	Cost-effectiveness and ammonia formation issue	Tokazhanov et al. [8]
Photo-catalytical method	The method is based on the acceleration of photodegradation of organic pollutants, pathogens, and other pollutants in the presence of a catalyst	High selectivity for a particular pollutant	Formation of nitrite and ammonium, Reusability of the catalyst as it is unchanged during the process	Sharma and Bhattacharya [85], Zhang et al. [89]

groundwater models may be analyzed before decision implementation [21]. Figure 6 depicts the management framework for groundwater resources.

10.2 Nitrate Contamination Management Strategies

Globally, legislative measures are crucial requirements for the management of groundwater resources. Maintaining groundwater quality and preventing future nitrate pollution requires understanding the variables and processes influencing nitrate occurrence, transport, and fate. Nitrogen source inventories and basin management plans are essential for reducing nitrate from aquifers [20]. Preventive measures should be taken to avoid nitrate contamination. Land use planners, decision-makers, and environmental regulators must identify areas with high nitrate loads to implement preventative measures like manure storage in concrete pits to reduce leaching [90]. Furthermore, continuous seasonal groundwater quality monitoring is essential for implementing these measures. Numerous researchers such as

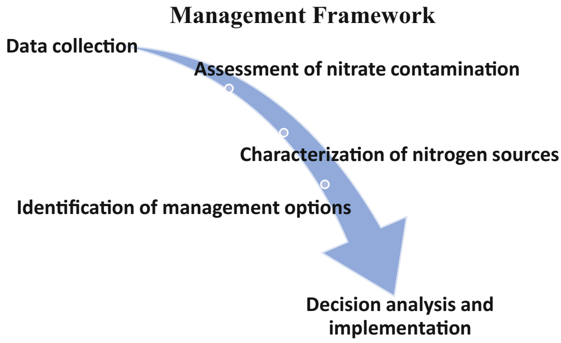

Fig. 6 Management framework for the groundwater resources (Permission from [21])

Singh et al. [13], Rahman et al. [14], Zhang et al. [16], Adimalla and Wu [10], Bastani and Harter [90], Li et al. [91], Han et al. [6], and Almasri [21] proposed nitrate management solutions such as source reduction, removal or transformation technologies, groundwater conservation, educational actions, legislative efforts, and guidelines, among others.

10.2.1 Agricultural Source Management

In agricultural areas, multiple sources may control the dynamics and occurrence of nitrate in groundwater. Here, management should be based on applying fertilizer and manure, cultivation techniques, and irrigation methods. Increasing fertilizer use efficiency, application quantity, and time and implementing integrated nutrient management will help farmers save money on fertilizer application and prevent long-term nitrate contaminations [92, 93]. To reduce reliance on fertilizers and the risk of fertilizer, new strains of nitrogen-fixing microorganisms (like Rhizobium and blue-green algae) with increased nitrogen-fixing capacity should be developed. Furthermore, long-term field research must be conducted to compile an up-to-date list of the best management techniques and application guidelines for fertilizers.

Additionally, various optimization models should be utilized to determine the optimal irrigation and groundwater storage options. Furthermore, each country must enact legislation for agricultural groundwater management, similar to the European Union's nitrates directive for reducing nitrate sources (EC 1991). Online resources for agricultural advice should be made available to decrease nitrate pollution. In 2010, the Chinese Ministry of Agriculture and Rural Affairs issued "Guidance for Scientific Fertilization of Major Crops", which included detailed irrigation and fertilization recommendations [94]. Suitable denitrification models should be developed for groundwater management; these models will reduce nitrate leaching. Implementing and maintaining artificial recharge schemes must involve non-governmental organizations and local governments. Society should be educated on groundwater quality and its proper management through seminars, short films, etc. Several mitigation tactics, such as balanced fertilization, crop rotation, adopting improved irrigation techniques, and implementing environmental legislation, can avert nitrate problems.

10.2.2 Domestic Wastewater Management

Expanding the sewerage network and centralizing the wastewater treatment system will mitigate the detrimental effects of improperly treated domestic wastewater discharge. However, providing complete sewer coverage to all rural and semi-urban areas in arid and semi-arid regions is not feasible due to economic constraints. Domestic wastewater in rural and semi-urban areas is a source of nitrate in groundwater; this issue can be resolved by implementing a decentralized or on-site wastewater treatment system. The wastewater must be collected, treated, and disposed of or reused close to the point of generation in a decentralized treatment system [15]. This technique typically settles solids in a septic tank, followed by treatment in secondary treatment facilities, such as anaerobic lagoons or constructed wetlands.

10.2.3 Solid Waste Management

The top priority of municipal solid waste management should establish a legal framework for regulating landfills and eliminating illegal dumpsites. These regulations typically address location restrictions, liner requirements, leachate collection and removal, and groundwater monitoring requirements from the standpoint of groundwater management. If waste is collected in properly designed, built, and maintained landfills, there is a low chance that contaminants will seep into the groundwater.

10.2.4 Treatment of Drinking Water

Groundwater is the principal source of domestic drinking water in arid and semi-arid regions of the world. It is expensive and time-consuming to treat highly nitrate-contaminated groundwater, so it is recommended to use alternate drinking water sources if they are available. Nitrate treatment technology should be deployed at drinking water treatment plants to improve the quality of nitrate-contaminated groundwater in regions without alternative water sources [9]. The polluted groundwater can be reused using water treatment technologies. Every country, mainly the developing world must set drinking water standards and provide water within these limits. Several conventional nitrate removal techniques and methods are outlined in Table 4, and they can be implemented in treatment plants based on the requirements.

10.2.5 Other Measures

Groundwater management and its use in conjunction with surface water are essential in arid and semi-arid regions. Recharging aquifers during abundant rainfall is one method of promoting this conjunctive use. Indigenous water management techniques may be used due to their local adaptability compared to more sophisticated and advanced techniques. The nitrate concentration of a particular region must be depicted on several regional or local maps and these maps should be digitized to effectively manage nitrate pollution in groundwater aquifers. Further, GIS should be used to assess the effectiveness of various management strategies because it significantly improves data collection and processing, evaluation of the nitrate leaching risk index, identification of diverse vulnerability zones, model development, and scenario planning for management options. The only appropriate nitrate standard has been set for groundwater; managers should handle these within the scope of the profile from the surface to groundwater. Furthermore, mathematical models of nitrogen transport must be developed to quantify the outcomes of management options before their actual implementations at various spatial and temporal scales. Water experts should increase their research on water quantity and quality to aid government decision-making and achieve sustainable development of the world's water resources. Water specialists and scholars should conduct more research on water quantity and quality to help governments make decisions and accomplish the long-term development of the world's water resources.

10.3 Options for Safe Drinking Water Supply

The drinking water in arid and semi-arid regions is already in poor condition; based on global scientific research data, the following solutions are suggested for safe water supply:

(a) For safe drinking water in arid and semi-arid regions, collecting rainwater and taking precautions against contaminants in rainwater storage tanks is necessary. Local governments should implement rainwater harvesting practices to ensure a safe water supply in the short and long term.
(b) To provide potable water to residential areas of these regions, protected water supply schemes and treatment plants to remove contaminants should be implemented. Furthermore, nitrate pollution must be addressed by installing distillation plants or implementing appropriate removal techniques.
(c) The local government should take immediate action to reduce groundwater nitrate pollution and ensure the availability of potable water from alternate sources (i.e., rivers and canals) in arid and semi-arid regions.
(d) Promote cost-effective, sustainable seawater desalination and ensure a source-to-tap approach to water supply management.
(e) Promoting organic manure over nitrogen-based fertilizers in arid and semi-arid regions.

(f) The use of groundwater in conjunctive with surface water is another option for a safe drinking water supply in arid and semi-arid regions. Mixing contaminated water with clean water decreases nitrate concentration; however, this method is unsafe for infants but safe for animals and adults.

11 Summary and Future Perspective

Nitrate is one of the principal pollutants found in the groundwater globally; excessive levels have adversely damaged ecosystems and human health. Therefore, technological and economically viable, accessible, and practical solutions will be required to mitigate nitrate pollution. Also, policy reforms are needed to minimize its effects on humans and the environment. Nitrogen source inventories, basin management plans, and identifying and quantifying primary sources and their loads to groundwater are some strategies for reducing nitrate pollution. Furthermore, various technologies like reverse osmosis, ultrafiltration, chemical and biological denitrification, ion exchange, adsorption, and electrodialysis have been widely used to eliminate nitrate from groundwater. However, the by-products of these technologies have significant limits; therefore, hybrid methods will be required in the future to combat the nitrate threat. Improved and ongoing communication between scientists, water managers, and water consumers is essential for achieving the sustainability of groundwater resources. The management of nitrate-contaminated groundwater in arid and semi-arid regions should include source reduction measures, removal or transformation technologies, groundwater conservation, educational actions, legislative efforts, and guidelines. Likewise, we can choose appropriate management alternatives with the help of the multicriteria decision analysis approach. In addition to structural measures like physical activities and construction projects, the management includes non-structural measures such as policies, guidance, and funding. Regional actions will be strengthened in the short term to decrease nitrate contamination. However, future research must develop enhanced ways to eliminate nitrate from the environment efficiently.

12 Conclusion

This chapter compiles information on the quality of groundwater aquifers, ecotoxicological impacts, and management options for arid and semi-arid regions worldwide. It has been determined that agricultural fertilizers and septic systems are the principal contributors to nitrate in most arid and semi-arid locations. The existence of nitrate concentrations that exceed WHO standards necessitates an immediate management strategy in order to prevent ecotoxicological effects. Therefore, the region's groundwater requires "Treatment" before consumption and must be safeguarded against additional contamination. The present removal and transformation approaches do not have a distinct impact because they all have advantages and disadvantages. Reverse osmosis, biological denitrification, catalytical reduction, and ion- exchange are the principal treatment techniques; however, they cannot fully remediate nitrates at greater concentrations. Further, management entails source reduction, removal or transformation technologies, groundwater conservation, education, legislation, and guiding principles. The proposed options for safe drinking water must be implemented in arid and semi-arid regions. The findings are anticipated to assist managers in enhancing water quality for environmental protection and human health risk reduction. Considering the present research trends, it is possible to conclude that the surface-to-groundwater profile perspective may encourage the development of additional integrated nitrogen management.

13 Recommendations

Groundwater nitrate management in arid and semi-arid areas necessitates a holistic approach that combines scientific understanding, stakeholder engagement, regulations/laws, and policies. A successful nitrate management plan must include the establishment of sophisticated hydrogeological models capable of modeling groundwater movement and understanding the fate of nitrate. Models' implementation at the national or regional level will facilitate decision-making and management strategy evaluation in arid and semi-arid regions. In addition, the development of a comprehensive database and geographic information systems can help in data analysis and decision-making regarding the best nitrate management plan. Also, the involvement of local communities, farmers, industry leaders, and environmental organizations in the development of inclusive efforts for nitrate groundwater control will be beneficial. Governments should provide financial incentives, technical support, and capacity-building programs in arid and semi-arid regions to encourage farmers and households to adopt sustainable nitrate management practices. Collaboration should be pursued with agricultural communities/departments to promote the implementation of best management practices that reduce nitrate runoff, such as precision agriculture, cover cropping, and controlled drainage. To enforce groundwater protection in nitrate-vulnerable regions in arid and semiarid locations, governments must enact laws and regulations for groundwater protection and land use planning. Regulations or laws at each national or regional level would promote the sustainable use of groundwater, such as permits for well drilling, restrictions on groundwater abstraction, and pollution control measures. The sharing of resources, information, and data between government agencies, research institutions, non-governmental organizations, and local communities should always be taken as a priority for the formulation and implementation of more effective groundwater nitrate management policies. Every nation should invest in preventive measures for nitrate pollution and nitrate remediation technologies research and development programs. Governments should also utilize feedback loops to update policies and plans in arid and semi-arid regions.

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