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REVIEW

Migration and Transformation Mechanism and Source Analysis of "Three Nitrogen" Pollutants in Groundwater

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ABSTRACT

Contamination of groundwater with the three forms of nitrogen (nitrate N, nitrite N, ammonium N) is a common environmental issue in agricultural, urban, industrial and animal production areas. The nitrogen species are highly mobile, stable, toxic, and redox-sensitive, but are also strongly coupled by biogeochemical reactions. This review systematically summarises the occurrence characteristics, migration behaviour, transformation mechanisms, and source analysis methods for three nitrogen pollutants in groundwater. Nitrate is highly soluble, poorly adsorbed, and the most mobile of the different forms in toxic aquifers. Although nitrite is normally transient, its presence may indicate incomplete nitrification, incomplete denitrification, or a lack of redox stability. Across the levels of ammonium, adsorption, ion exchange, organic nitrogen mineralization, dissimilatory nitrate reduction to ammonium (DNRA), and reducing environments are more strongly affected. The largest nitrogen sources are fertilizer application, manure, sewage leakage, septic systems, livestock wastewater, landfill leachate, industrial discharges, atmospheric deposition, soil organic nitrogen, and geological release of N. But the identification of sources is complicated by the transformation processes as groundwater moves. Thus, a combination of hydrochemical, stable isotopes, microbial functional genes, groundwater flow analysis, laboratory experiments and reactive transport modeling is crucial for the use of integrated approaches. This review emphasizes the importance of moving away from the traditional single-species approach towards a coupled source–migration–transformation approach

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and offers scientific guidance to support groundwater nitrogen pollution tracing, risk assessment, and remediation.
Keywords: Groundwater Contamination; Three Nitrogen Pollutants; Nitrate; Ammonium; Source Apportionment

1. Introduction

Groundwater is considered one of the most valuable strategic freshwater resources for drinking-water, agricultural and domestic irrigation, industrial production, and ecosystem maintenance[1]. Groundwater is typically found to have a slower hydrodynamic exchange, longer residence time, more water–rock interaction, and delayed response to external sources of pollution when compared to surface water[2]. Groundwater is relatively stable for use as a water source, but these characteristics also mean once groundwater becomes contaminated, the contaminants can remain, travel long distances, and pose long-term ecological and human health concerns. In areas of intensive agriculture, rapid urbanization, stock farming, seepage of sewage, landfill leachate and over-fertilising, nitrogen contamination is one of the most prevalent and persistent types of ground water quality degradation[3]. According to the U.S. Environmental Protection Agency, nitrate sources in groundwater sources include fertilizer runoff, septic tanks, sewage, and natural deposits and nitrate levels above 3 mg/L is considered to be a contaminant, and concentrations above 1 mg/L could indicate human activity.

Nitrogen pollutants in groundwater are primarily present as nitrate nitrogen, nitrite nitrogen and ammonium/ammonia nitrogen (also known as the "three nitrogen" pollutants) in environmental studies[4]. They are not independent contaminants, but are interconverted by physical, chemical and microbial processes. The nitrate nitrogen is typically highly soluble and is not strongly adsorbed by the aquifer media, and readily travels with the groundwater flow[5]. Nitrite nitrogen is generally an intermediate species that is relatively unstable in the environment, but is very susceptible to changes in redox and can be produced during incomplete nitrification and denitrification[6]. The effect of cation exchange, mineral adsorption, sediment organic matter and redox driven oxidation is more pronounced to ammonium nitrogen[7]. Thus, the external source loading and internal transformation capacity of the aquifer systems are both considered in the environmental behavior of "three nitrogen" pollutants.

Groundwater N contamination and its health and environmental impacts have been well acknowledged. Excessive exposure to nitrate and nitrite in drinking water can be harmful to infants with methemoglobinemia or "blue-baby syndrome"[8]. EPA's National Primary Drinking Water Regulations establish maximum concentrations of 10 mg/L nitrate (as N) and 1 mg/L nitrite (as N). In addition to the risks of drinking-water safety, nitrogen-rich groundwaters may also flow into rivers and lakes, reservoirs, wetlands, and coastal waters, where they cause eutrophication and changes in the functions of the aquatic ecosystems[9]. Nitrogen contamination in many agricultural and peri-urban aquifers is a multi-source, multi-process issue, and has arisen after a time of accumulation, delayed leaching, hydrogeological connectivity, and coupled biogeochemical transformation.

Existing research has significantly improved the understanding of nitrate contamination in groundwater, particularly regarding the spatial distribution, the agricultural sources of nitrate, isotope tracing and health risk assessment. The use of stable isotope methods, specifically $\delta^{15}N$ and $\delta^{18}O$ of nitrate, have become valuable tools to determine the source of N (either from fertilizer, manure, sewage or soil sources) and $\delta^{11}B$ can assist in source discrimination in complex hydrogeological and land-use situations[10]. Nitrate and ammonium contaminants have also been recently compared in regional groundwater contamination, with nitrate contamination more widespread and more mobile, and ammonium contamination more localised and more associated with shallow sediments, adsorption and reduced conditions. While these studies offer valuable knowledge, most reviews currently available only consider nitrate or, at best, compare nitrate and ammonium[11]. Despite the fact that nitrite is an essential intermediate in the nitrogen transformation, it is often overlooked as an indicator of non-completed redox conversion of nitrogen, imbalance of microbial community or hotspots of transient nitrogen transformation.

Another weakness of the literature is that the source analysis and the analysis of the mechanism of transformation are separated. In reality, all the above factors (and oth-

ers) control nitrate, nitrite and ammonium at the same time in groundwater. For instance, the same nitrate concentration can be from direct fertilizer leaching in an oxic shallow aquifer, from nitrification of the leached ammonium in a sewage affected aquifer, or from the remaining nitrate following partial denitrification in a redox transition zone[12]. In the same way, enrichment of ammonium can occur due to inputs from sewage, mineralization of organic nitrogen, dissimilatory nitrate reduction to ammonium and release from clay minerals and organic-rich sediments[13]. Thus, any assessment of nitrogen sources that fail to account for transformations may result in a skewed source distribution, and any assessment of transformations without restriction on sources may mask source control priorities.

Subsurface nitrogen cycling has also recently been modified due to the development of new groundwater microbiology knowledge[14]. The genes involved in N-cycling can be widespread in aquifer systems and are generally abundant in the metagenomic samples, suggesting that N-cycling can be an important function of these microbial communities. This implies that groundwater aquifers are not passive transport media, but active biogeochemical reactors. The fate of the "three nitrogen" pollutants can be influenced by various processes, which may act synergistically. The coupled processes are particularly relevant for groundwater systems with fluctuating water tables, in river–groundwater exchange areas, agricultural recharge zones, landfills and in redox-stratified groundwater systems.

The novelty of this review is the coupling of the three pollutant (migration – transformation – source) systems of nitrogen as a whole and not as individual nitrogen species. Firstly, the review sets the nitrate, nitrite and ammonium in an integrated network of nitrogen transformations, highlighting their mutual interconversion under various hydrogeological and redox scenarios[15]. Second, it emphasizes the use of nitrite as a diagnostic intermediate to help identify incomplete nitrification, denitrification, DNRA and anammox processes[16]. Thirdly, it combines the use of hydrochemical indicators, stable isotopes, microbial functional genes, numerical simulations and source apportionment techniques to separate external source signals from internal transformation effects[17]. Fourthly, it will tie mechanistic understanding to the use of groundwater, helping to enable more precise tracking of pollution, risk assessment and development of designs for remediation, and control of the nitrogen load[11].

Thus, this review is designed to comprehensively summarize the recent advances in the understanding of the behavior of nitrate nitrogen, nitrite nitrogen, and ammonium nitrogen during migration and transformation in groundwater as well as the methods used to analyze its sources[18]. It will first briefly highlight the occurrence characteristics and hydrogeological controls of 'three nitrogen' pollutants, then consider important microbial and abiotic transformation pathways, and finally discuss both natural and anthropogenic sources and common source apportionment methods critically. Lastly, a multi-depth monitoring, isotope tracing, microbial ecology and reactive transport modeling integrated framework for future research will be proposed. This article introduces the concept of coupled processes, which broadens the science behind groundwater nitrogen pollution and offers a more complete understanding of the processes that can be used to prevent and remediate groundwater pollution from nitrogen[19]. The overall conceptual framework of this review, linking nitrogen sources, migration pathways, transformation mechanisms, and management implications, is illustrated in **Figure 1**.

This review was conducted through a systematic literature search across multiple scientific databases, including Web of Science Core Collection, Scopus, Google Scholar, and PubMed, covering publications from January 2000 to July 2026 to capture both foundational studies and recent advances in groundwater nitrogen research. The search strategy employed combinations of Boolean operators and keywords organized into three thematic categories: primary terms related to nitrogen species ("groundwater" OR "aquifer") AND ("nitrate" OR "nitrite" OR "ammonium" OR "ammonia" OR "three nitrogen"); process-related terms ("migration" OR "transport" OR "transformation" OR "nitrification" OR "denitrification" OR "DNRA" OR "anammox" OR "ammonification"); and source-related terms ("source" OR "source apportionment" OR "source identification" OR "isotope" OR "tracer"). Studies were included if they: (1) addressed groundwater nitrogen contamination with relevance to at least one of the three nitrogen species; (2) reported original data or provided comprehensive reviews; (3) were published in peer-reviewed journals or official technical reports; and (4) were written in English. Studies were excluded if they focused exclusively on surface water or soil nitrogen

without groundwater relevance, were conference abstracts lacking sufficient data, or concentrated solely on nitrogen removal technologies without groundwater context. The initial database searches yielded approximately 1,200 potentially relevant articles, which were reduced to 850 after duplicate removal. These underwent title and abstract screening, resulting in 320 articles for full-text review, with an additional 180 articles identified through reference list screening of included reviews and key studies. The final synthesis incorporated 82 key references that best represented the most relevant and high-quality evidence on groundwater nitrogen migration, transformation mechanisms, and source analysis methods. While this review primarily focused on English-language publications, which may introduce language bias, the comprehensive search strategy and systematic selection process ensure a rigorous and representative synthesis of the current state of knowledge on "three nitrogen" pollutants in groundwater.

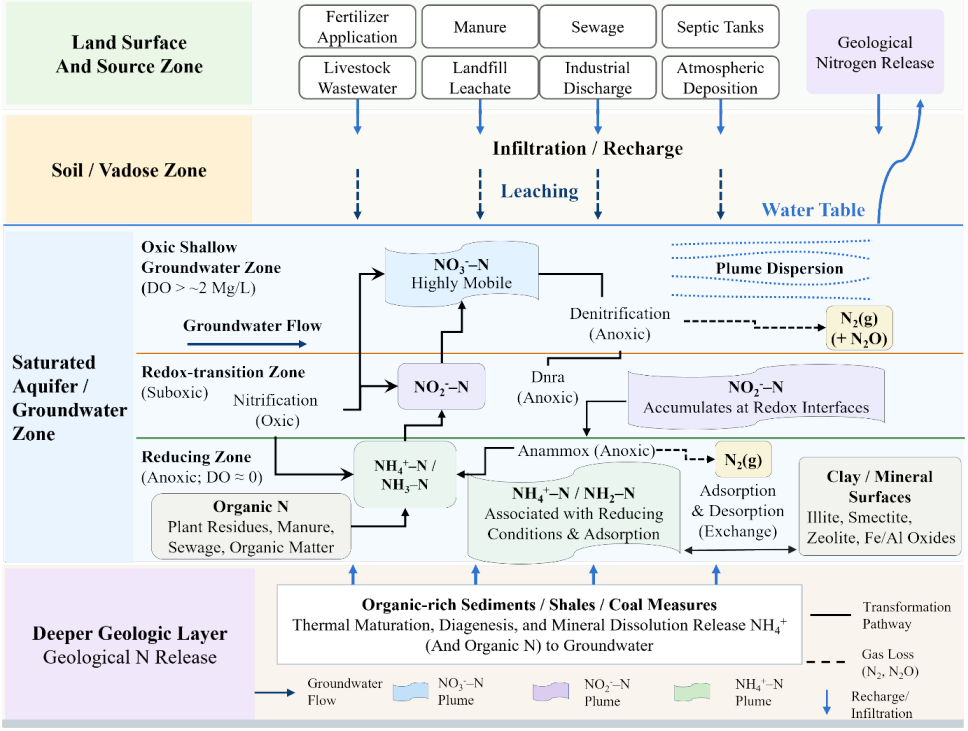

Figure 1. Conceptual framework of source–migration–transformation processes of "three nitrogen" pollutants in groundwater.

2. Occurrence Characteristics and Migration Behavior of "Three Nitrogen" Pollutants in Groundwater

2.1. Occurrence Forms and General Distribution Characteristics

The three nitrogen pollutants as part of the ground water are typically considered the different oxidation states of reactive nitrogen in the subsurface: nitrate nitrogen, nitrite nitrogen, and ammonium nitrogen [4]. Their occurrence is variable, as each of these forms of nitrogen can be converted to the others under appropriate hydrochemical, redox and microbial conditions. Thus, the concentration of any one nitrogen species measured in groundwater is the sum of the external input, migration, retention and transformation in situ. **Table 1** provides a summary of the various forms of nitrogen that occur in the environment, their mode of occurrence, migration characteristics, and controlling factors and environmental implications.

Nitrate N is typically the most common and widespread pollutant found in shallow oxygenated groundwater, of the three forms. This occurs primarily due to the high solubility of nitrate, low affinity of nitrate to most aquifer minerals, and high mobility of nitrate with groundwater flow. After nitrate is leached from soils or the vadose zone into an aquifer, it may travel long distances in a permeable sandy, gravelly, fractured, or karst aquifer. Ammonium nitrogen, however,

tends to be more localised, as it can be absorbed by clay minerals, organic matter and negatively charged minerals. Under reducing conditions, however, ammonia can be stable for an extended period of time, and can even build up in aquifers where there is sewage, landfill leachate, manure wastewater or natural organic nitrogen input [5].

Table 1. Occurrence characteristics and migration behavior of "three nitrogen" pollutants in groundwater.

Nitrogen Species	Dominant Occurrence Conditions	Mobility in Groundwater	Main Controlling Factors	Environmental Implication
Nitrate nitrogen, NO_3^-–N	Oxic shallow aquifers, agricultural recharge zones, irrigation return-flow areas	High	Groundwater flow, hydraulic conductivity, recharge intensity, dissolved oxygen, denitrification potential	Most likely to form large-scale pollution plumes and affect drinking-water safety
Nitrite nitrogen, NO_2^-–N	Redox-transition zones, incomplete nitrification or denitrification zones	Moderate but unstable	Dissolved oxygen, redox potential, microbial imbalance, pH, organic carbon availability	Useful indicator of active or incomplete nitrogen transformation
Ammonium nitrogen, NH_4^+–N	Reducing aquifers, sewage-affected groundwater, landfill plumes, organic-rich sediments	Low to moderate	Cation exchange, adsorption, clay minerals, organic matter, nitrification, DNRA	May persist for long periods and act as a delayed internal nitrogen source
Organic nitrogen	Soil, vadose zone, sediments, manure, sewage, landfill leachate	Variable	Mineralization rate, microbial activity, temperature, organic matter composition	Important precursor of ammonium and nitrate pollution
Dissolved gaseous nitrogen species	Denitrifying and anammox-active zones	Usually not transported as a major dissolved pollutant	Denitrification, anammox, gas exchange, groundwater residence time	Indicates potential permanent removal of reactive nitrogen

Nitrite nitrogen is typically found in low amounts as it is an unstable intermediate product of the nitrification and denitrification processes. It is most common when there is inadequate transformation of nitrogen in the system, and not necessarily due to the build-up of a long-term surplus. Nitrite usually is not regarded as a major factor because it is present in such small concentrations and has such short residence times, but has considerable diagnostic value. High nitrite levels may indicate redox disturbance, inadequate oxygen supply for nitrification, inadequate denitrification, or a rapid change in microbial activity. Nitrite should not be considered as a minor contaminant, however, it can be used as a good indicator of the active nitrogen transformation zones in groundwater systems [6].

2.2. Spatial Distribution Patterns in Aquifer Systems

Groundwater nitrate, nitrite and ammonium concentrations are highly influenced by groundwater spatial distribution, which depends on land-use, aquifer structure, recharge characteristics and redox zonation [20]. Nitrogen fertilizers, manure applications, irrigation return flow and leaching from the soil profile all contribute to nitrate enrichment in shallow groundwater in agricultural areas where excessive nitrogen use is occurring. In urban and peri-urban settings nitrate and ammonium could be linked to septic tanks, sewage leakage, wastewater irrigation, and landfill leachate. All three forms of nitrogen can be present in the same sample from livestock intensive sites but the ratio of the three nitrogen species will vary depending on the degree of organic nitrogen degradation and the amount of oxygen present in the aquifer.

Generally nitrate is the predominant species in shallow oxic aquifers with high recharge rates and adequate dissolved oxygen [21]. Nitrate can be reduced as the water flows into deeper or reducing zones, by either denitrification or dissimilatory nitrate reduction to ammonium. In contrast, ammonium is more likely to be enriched in deeper, poorly oxygenated and organic-rich or clayey aquifers [22]. This is a vertical zonation from oxidizing to reducing environment. But this is not always the case. Ammonium chloride may also be present in shallow aquifers that are highly contaminated with sewage or landfill leachate, near the surface. Likewise, when nitrate contamination in deep aquifers can be traced to agricultural nitrate movement through fractures and/or karst conduits, nitrate could also be present in higher concentrations [23].

The shape of nitrogen pollution plumes is influenced by the direction of groundwater flow, the hydraulic gradient, the permeability of the aquifer, and the distribution of the sources of nitrogen vertically. Nitrate plumes tend to be long, extending down the main groundwater flow path; ammonium

plumes can be shorter and more influenced by local redox conditions and adsorption [11]. Hotspots of nitrite can be found at the interface of oxic and anoxic zones, where nitrification and denitrification are competing processes [24]. The patterns indicate that groundwater nitrogen pollution is not a reflection of surface nitrogen loading and should be treated as a three-dimensional and process-dependent phenomenon.

2.3. Temporal Variation and Delayed Pollution Response

Temporal changes in "three nitrogen" pollutants have strong linkages with rainfall, irrigation, fertilizer use, groundwater level fluctuation, and seasonal changes in microbial activities [25]. Nitrogen, which accumulates in the soil and vadose zone in agricultural areas, is easily leached downward by recharge water, resulting in higher nitrate concentrations after fertilization and/or irrigation. In coarse-textured soils or under preferential flow conditions, nitrate can be quickly carried out of the root zone and into shallow groundwater with high-intensity rainfall. But during periods of intense recharge, dilution can also happen, depending on the amount of water added to the system and the amount of pollutants mobilized.

Changes in the redox conditions resulting from the seasonal variation in groundwater levels can affect the speciation of nitrogen. With a rising water table, the previously unsaturated sediments containing high levels of organic matter and N can be saturated, leading to ammonification, denitrification, or release of ammonium. Once the water table is lowered, oxygen uptake may rise which promotes nitrification and the conversion of ammonium to nitrate. This variation can create alternating areas of nitrate formation and reduction, creating complex temporal dynamics [26].

The issue of groundwater nitrogen pollution is that it has a time lag between where it comes from and when it pollutes the aquifer. Nitrogen added to the land surface can either stay in the soil or the vadose zone and be available for groundwater leaching for many years. This means that current groundwater nitrate levels may be indicative of past fertilizer applications and not present use. The lag effect makes it difficult to control the pollution, since improvements in groundwater quality through reductions in surface nitrogen inputs may be delayed. A temporal analysis should, therefore, account for the legacy nitrogen in soils, sediments and unsaturated zones, as well as recent land-use activities [27].

2.4. Hydrogeological Controls on Migration

Aquifer systems have a transport capacity and attenuation potential, which is determined by hydrogeological conditions. One of the primary controls is aquifer lithology [28]. High permeability in sandy and gravel aquifers leads to rapid nitrate migration and decreases the amount of time for nitrate to interact with reactive minerals and organic matter. This limits natural attenuation and the potential for widespread nitrate contamination. Clayey or silty aquifers tend to have lower hydraulic conductivity, however, and also high adsorption properties, that could help to slow down the migration of ammonium and to increase nitrogen retention. Low permeability may also lead to reduction conditions that promote the persistence of ammonium, however.

Karst and fractured-rock types are especially susceptible to nitrogen contamination because contaminants may not be filtered by the soil matrix and can quickly enter into the groundwater through fractures, conduits, sinkholes and preferential flow paths. Nitrogen can move rapidly in these systems without undergoing significant filtration or biogeochemical modification. Nitrogen pollution in karst groundwater is frequently poorly known, depending on the irregular connection of conduits and fractures. This is more challenging than for porous media aquifers to monitor and identify sources [29].

The behavior of nitrogen is also affected by groundwater flow velocity and residence time. The shorter the residence time the more conservative the transport of the nitrate will be, while longer residence time will allow for more extensive denitrification, adsorption, or microbial transformation. Long residence time does not always mean low pollution risks, however. Ammonium can remain stable for extended periods of time when reducing aquifers and nitrate may remain stable when aquifers have an inadequate supply of organic carbon and flow rates are slow. Thus, the influences of residence time should be assessed in combination with the redox condition, availability of electron donor, and microbial activity [30].

2.5. Physicochemical Factors Regulating Mobility

Migration of "three nitrogen" pollutants is closely related to physicochemical conditions such as pH, dissolved oxygen, oxidation–reduction potential, temperature, organic

carbon, salinity, and mineral composition. The most significant, in particular, is the dissolved oxygen as it controls the most important nitrogen transformation pathway. Nitrification can be expected under oxic conditions, which will increase the mobility of nitrate. Nitrate can be converted to ammonium under anoxic or anaerobic conditions either by denitrification or dissimilatory nitrate reduction to ammonium [21].

The pH has an influence on the speciation of ammonium and on adsorption and microbial activities. In normal pH groundwater, it is not free ammonia but rather ammonium. Ammonium is a positively charged ion, and is therefore held on to by the cation exchange action of clay minerals and organic matter. This retention will lower its apparent migration rate but can also result in a secondary pollution reservoir. Ammonium can be released back into the groundwater, extending the contamination period even after the external sources of ammonium have been reduced, if the hydrochemical conditions change [31].

Organic carbon has a dual role. It has the potential to stimulate denitrification as an electron donor, thus enhancing nitrate attenuation. But overloading with organic matter (such as sewage, manure or landfill leachate) can use up the oxygen and create reducing conditions that can cause ammonium to build up. Therefore, besides the reduction of nitrogen pollution, the organic carbon alters the speciation and the pathways of nitrogen transformation. This is why, in sections of an area that is impacted by organic wastewater, the nitrate may be low and ammonium may be high [32].

2.6. Migration Differences among Nitrate, Nitrite, and Ammonium

The three species of nitrogen exhibit distinct migration behaviours depending on the differences in charge, stability and reactivity. Nitrate generally is the most easily leached form since it is negatively charged and is not strongly bound to most aquifer media. Advection, dispersion, dilution and biological reduction are the major processes controlling its migration. Nitrate contamination, therefore, is a good indicator of strong hydraulic connectivity between surface sources and groundwater [33].

Nitrite has intermediate behavior and is highly reactive. Its concentration is not so dependent on physical transport, rather it relies on transformation balance. When the amount of nitrite produced is greater than the amount of nitrite consumed then there is temporary accumulation. This renders the use of nitrite as a useful indicator of activity and not a conservative indicator of pollution sources [34].

Ammonium less mobile than nitrate due to adsorption and ion exchange and can be stable under reducing conditions. It is often retarded compared with groundwater flow during migration, but this retardation may also lead to a greater persistence over time. Ammonium can be released as a delayed internal source, if the aquifer has a high adsorption potential and the sediments contain ammonium .

2.7. Critical Insights

Concentration data is not enough to explain the occurrence and migration of “three nitrogen” pollutants. A high nitrate concentration may be associated with high leaching and oxic transport but a low nitrate concentration is not necessarily a low source of nitrogen pollution as nitrate can be converted into N_2 or NH_4 through changes. Likewise, high ammonium could be from direct contamination, or from reduction in situ processes. Although the concentration of nitrite is low, it can show important transformation boundaries [34].

Going forward, future studies must do more than the assessment of individual species and use nitrate, nitrite, and ammonium as a connected pattern of groundwater N-cycling indicators [35]. Understanding their migration must be based on a reliable understanding of their hydrogeological, redox chemical, microbial transformation, and source loading characteristics. This multifaceted approach is necessary to ensure a proper understanding of the difference between pollutant transport and pollutant transformation and to develop effective groundwater nitrogen management strategies.

3. Transformation Mechanisms of “Three Nitrogen” Pollutants in Groundwater

3.1. Microbial Nitrogen Cycling Pathways in Groundwater

Groundwater is a dynamic, biogeochemical environment where nitrate, nitrite, and ammonium continually transform as a result of microbial metabolism, redox conditions, electron donors, and mineral surfaces [36]. The processes of transformation of “three nitrogen” pollutants are primar-

ily controlled by nitrification, denitrification, dissimilatory nitrate reduction to ammonium, anaerobic ammonium oxidation, ammonification and microbial assimilation. These processes can either result in retention of the reactive nitrogen, its conversion to another form of dissolved nitrogen, or permanent loss from the aquifer as gas nitrogen.

The favored pathway of transformation is highly redox sensitive. Ammonium can be easily oxidized to nitrate by nitrification in oxic groundwater and this results in higher mobility of N. Nitrate in anoxic groundwater can be converted to nitrogen gas via denitrification or to ammonium via dissimilatory nitrate reduction to ammonium, or it can be subject of anaerobic ammonium oxidation [7]. Thus, the same aquifer could have multiple N transformation zones through the groundwater flow path. Recharge areas tend to be more oxic and suitable for nitrification and nitrate reduction may be favored in deeper or downgradient zones with increased organic carbon and decreased dissolved oxygen.

An important finding is that several processes are usually involved in the transformation of nitrogen in ground water. Rather, several routes can exist simultaneously and compete with each other. For instance, nitrification may lead to the production of nitrate which can then be denitrified, and partial denitrification can result in nitrite production which can promote anammox [37]. Under carbon-rich and strongly reducing conditions, DNRA can be a competitor of denitrification for nitrate. This pathway competition is one reason for complex and non-linear distribution of nitrogen species in groundwater.

3.2. Nitrification and Nitrite Accumulation

Nitrification is an aerobic (or micro-aerobic) microbial process in which ammonium is first converted into nitrite and then into nitrate. It can be broken down into two stages: ammonia oxidation and nitrite oxidation. Ammonium is oxidized to nitrite by ammonia oxidizing bacteria and archaea, and nitrite to nitrate is oxidized by nitrite-oxidizing bacteria [24]. Nitrification is especially significant in shallow groundwater, recharge zones, river bank filtration, wastewater-influenced aquifers and where oxygen is introduced due to water-table fluctuations.

Nitrification has a displeasing effect on the environment. On the other hand it lowers the concentrations of ammonium, which can help in improving the groundwater quality when ammonium is the main pollutant [12]. On the contrary, it transforms relatively immobile ammonium to highly mobile nitrate, which poses the risk of long-distance movement. The conversion is particularly relevant in aquifers where sewage, manure or landfill leachate is added, such that oxygen becoming available in such water can result in the release of nitrate as a secondary source.

Accumulation of nitrite is generally not a problem during nitrification because under stable oxic conditions, nitrite is rapidly oxidized to nitrate. But if ammonia oxidation is greater than nitrite oxidation then nitrite can build up. This imbalance may be due to inadequate dissolved oxygen levels, low temperatures, pH stress, toxic chemicals, salinity fluctuations or a lack of nitrite-oxidizing microorganisms. If there is alternating oxic and anoxic conditions in an aquifer, then nitrite may also be temporarily trapped at oxic/anoxic interfaces [38].

The significance of the accumulation of nitrite in the environment is that nitrite is more reactive and toxic than nitrate. More significantly, it is a sensitive marker for the lack of complete nitrogen transformation. Higher nitrate concentrations are not only considered a concentration anomaly in the context of groundwater monitoring. It can show these active transformation zones that are characterized by oxygen supply and microbial activity, and by an unstable redox state. Hence, nitrite can be a valuable mechanistic tool for the understanding of dynamic transformation of nitrogen pollutants [34].

3.3. Denitrification and Nitrate Attenuation

Denitrification is a natural attenuation process that is among the most significant for nitrate contaminated groundwater [12]. These are the step-wise reductions of nitrate to nitrite, nitric oxide, nitrous oxide and finally nitrogen gas in anoxic (low oxygen) conditions. Dissolved nitrate may be removed from groundwater through this pathway, rather than just being converted into another form of dissolved N. Therefore, denitrification is considered to be one of the important self-purification processes in the aquifer.

Dissolved oxygen, oxidation–reduction potential, available organic carbon, electron donors, nitrate concentration, microbial community structure, and groundwater residence time are all factors that affect the occurrence and efficiency of denitrification. Low dissolved oxygen is a prerequisite as oxygen is the first electron acceptor. The electron donor

is usually organic carbon but reduced inorganic compounds like pyrite, ferrous iron and sulfide can also facilitate autotrophic denitrification. Wherever organic rich sediment, riparian aquifers, wetlands, and sewage contaminated ground water systems exist, denitrification may significantly deplete nitrate levels [32].

Low nitrate concentrations, however, should not be a substitute for denitrification. Nitrate reductions can occur if the water is diluted, mixed with low nitrate water, absorbed by plants in shallow systems, subjected to DNRA, or input is not provided [39]. Supporting evidence (such as a reduction in nitrate along a flow path, an enriched nitrate isotopic signature, decreased dissolved oxygen, increased bicarbonate, excess nitrogen gas, and/or detection of denitrification functional genes) is typically required to reliably identify denitrification.

There are environmental trade-offs to denitrification too. If denitrification is incomplete, it may result in nitrite or nitrous oxide, which are environmentally important compounds. Nitrite may be a sign of incomplete reduction and N_2O is a potent greenhouse gas. Thus, it is important to assess nitrate attenuation by denitrification, not only based on nitrate removal efficiency, but also on the completeness of the reduction pathway [40].

3.4. Dissimilatory Nitrate Reduction to Ammonium

The dissimilatory nitrate reduction to ammonium (DNRA) is a microbial process whereby nitrate is converted to nitrite and then to NH_4^+ [41]. While denitrification releases N as gas from the ground-water, DNRA retains N in the ground-water as ammonium. This separation is important for groundwater pollution control because DNRA can result in both a decrease in nitrate and an increase in ammonium levels.

The conditions where DNRA is favored are strongly reducing, high organic C availability, high C/N ratios, and low nitrate availability [42]. It can be found in aquifers contaminated with sewage, manure, landfill leachate, organic-rich sediments or ground water that is stagnant. In such environments, microorganisms can accept nitrate as an electron acceptor and turn it to ammonium. This leaves the resulting ammonium behind in the aquifer or it can be absorbed by the sediments in the aquifer.

Denitrification and DNRA are competing processes that are key controls on the fate of nitrogen. Nitrogen gas generation can occur naturally and attenuate nitrate pollution when denitrification is the dominant process. If DNRA dominates, nitrate can be consumed from the groundwater, but reactive nitrogen is not removed, it is converted to ammonium. If only nitrate is monitored, this can result in misinterpretation. Reduced ground water nitrate could be interpreted as low nitrate and high ammonium level, and be associated with a change in nitrate to ammonium [43].

DNRA also affects the long-term response of nitrogen pollution. Ammonium-generating by DNRA can be sorbed onto mineral surfaces and then desorbed or oxidized to nitrate when the redox conditions become more favorable for nitrification. Therefore, DNRA can generate an internal nitrogen source which could lead to a lagged contamination even if the external nitrate contribution is reduced [39].

3.5. Anaerobic Ammonium Oxidation and Coupled Pathways

Anammox or anaerobic ammonium oxidation involves oxidation of ammonium under anoxic conditions by nitrite to generate N gas [44]. This pathway is significant because of its role in removing ammonium without the need for oxygen. In groundwater, anammox is likely to take place in redox-transition zones where ammonium and nitrite are in the same environment. These can occur at the oxic–anoxic groundwater boundary, river–groundwater interfaces, landfills, wastewater contaminated aquifers, or sediments with significant vertical redox gradients.

Anammox's importance is that it links the transformation of ammonium and nitrite to the permanent removal of nitrogen. However, anammox requires the presence of nitrite, which is often generated by partial denitrification, partial nitrification and nitrate reduction. Thus, anammox is rarely found to occur alone. It is generally linked with other processes of the nitrogen transformation. For instance, nitrification can generate nitrite from ammonium in micro-oxic zones while denitrification can provide nitrite from nitrate in anoxic zones. Alternatively, DNRA can combine with anammox to yield ammonium which can then be anaerobically oxidized [16].

The coupled pathways generate complicated transformation networks of N in the aquifer. Partial nitrification, denitrification, DNRA and anammox can occur on a single

redox interface. The relative contribution of each pathway varies as a function of oxygen, organic carbon, nitrate loading, pH, temperature, and the microbial community composition. This is the reason why nitrogen species may change rapidly over short distances, in particular where pollution plumes and geochemical transition zones are located [37].

Anammox is a process of great theoretical value for nitrogen removal, but is challenging to assess at the field scale in groundwater. This is because anammox rates are often low, spatially variable and concentration-based data alone is not sufficient to distinguish anammox from denitrification. To assess its actual contribution to nitrogen attenuation, therefore, isotope tracing, molecular biological methods and reactive transport modeling are required [10].

3.6. Ammonification and Organic Nitrogen Mineralization

Organic N is being converted to ammonium by microbes, this is called ammonification. It is a significant link between the organic nitrogen inputs and inorganic "three nitrogen" pollutants. Large inputs of organic nitrogen can be added to the subsurface in aquifers that are impacted by manure, sewage, landfill leachate, wastewater irrigation, or organic-rich sediments. This organic nitrogen can be broken down by the microorganisms to ammonium, which can raise the level of ammonium in ground water [45].

Ammonification is an important process that is frequently overlooked in groundwater studies due to the fact that it is often only the inorganic nitrogen species that are looked at. Soils, sediments and the vadose zone may, however, serve as a long-term pool of organic nitrogen. Organic nitrogen can be mineralized to ammonium and release it into groundwater long after external loads of nitrogen have ceased. This ammonium can be subsequently nitrified to nitrate under oxic conditions, and remain or increase under reducing conditions [16].

Temperature, pH, composition of organic matter, microbial activity and moisture are major factors affecting ammonification [46]. It tends to be more active in shallow aquifers where there is lots of biodegradable organic matter available. Mineralization can be significant in deep aquifers over longer residence times, albeit slower. Thus, organic N transformation must be added to groundwater N budgets, particularly where historical wastewater discharges or heavy livestock use have occurred.

3.7. Abiotic Transformation and Retention Mechanisms

While in many groundwater systems microbial processes control nitrogen transformation, abiotic processes also have significant roles in controlling mobility and persistence of "three nitrogen" pollutants. Ammonium is particularly affected by adsorption and ion exchange. The positive charges of ammonium allow it to be absorbed by the negative charges of clay minerals, organic matter and cation exchange sites. This will reduce the rate at which the ammonium moves compared to groundwater flow and may temporarily decrease the dissolved ammonium concentration [7].

Adsorption of ammonium is however reversible. Adsorptions of ammonium may be released from groundwater by changes in pH, ionic strength, competing cation concentrations and groundwater chemistry. For instance, a high concentration of sodium, potassium, calcium or magnesium can be present which may compete for exchange sites with ammonium. This implies aquifer sediments are a sink as well as a secondary source of ammonium [47].

Redox process could also be mediated by minerals and affect nitrate and nitrite transformation. The reduction of nitrate can be abiotic or microbially mediated, and reduced iron, manganese minerals, and organic matter can undergo this process. Pyrite oxidation and nitrate reduction could lead to autotrophic denitrification in some aquifers whereas Fe/Mn cycling could influence nitrite stability and attenuation of nitrate. These reactions are related to the overall geochemistry of groundwater and the cycling of nitrogen [48].

In most situations, abiotic processes are not responsible for all of the nitrogen transformation system but they do drive the direction and rate of microbial processes. Thus, it is important to understand the interaction between microbial metabolism and geochemical reactions driven by minerals when studying nitrogen transformations [49].

3.8. Critical Insights on Transformation Mechanisms

The concept of coupled transformation of nitrate, nitrite and ammonium in groundwater is preferred over the idea of sequential individual transformations. Nitrification increases

the mobility of nitrate, denitrification removes nitrate, DNRA retains nitrogen as ammonium, anammox removes ammonium and nitrite and ammonification continuously supplies ammonium from organic nitrogen [41]. Under local hydrogeochemical conditions these pathways could reinforce, compete or inhibit each other. A comparison of the dominant transformation pathways, environmental factors, controlling factors, and pollution implications is presented in **Table 2**.

Table 2. Major transformation pathways of "three nitrogen" pollutants in groundwater.

Transformation Pathway	Main Reaction Direction	Dominant Environmental Condition	Controlling Factors	Effect on Groundwater Nitrogen Pollution
Ammonification	Organic N → NH_4^+	Organic-rich aquifers, sewage- or manure-affected zones	Organic matter availability, microbial activity, temperature, pH	Produces ammonium and may provide a long-term internal nitrogen source
Nitrification	$NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$	Oxic or micro-oxic groundwater	Dissolved oxygen, ammonia-oxidizing microorganisms, pH, temperature	Reduces ammonium but increases mobile nitrate pollution
Nitrite oxidation	$NO_2^- \rightarrow NO_3^-$	Oxic groundwater	Oxygen, nitrite-oxidizing bacteria, redox stability	Prevents nitrite accumulation but enhances nitrate formation
Denitrification	$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$	Anoxic groundwater with electron donors	Organic carbon, nitrate concentration, low dissolved oxygen, denitrifying bacteria	Removes nitrate, but incomplete denitrification may produce nitrite or N_2O
DNRA	$NO_3^- \rightarrow NO_2^- \rightarrow NH_4^+$	Strongly reducing, carbon-rich environments	High C/NO_3^- ratio, limited nitrate, low redox potential	Decreases nitrate but retains reactive nitrogen as ammonium
Anammox	$NH_4^+ + NO_2^- \rightarrow N_2$	Anoxic redox-transition zones	Coexistence of ammonium and nitrite, anammox bacteria, low oxygen	Removes ammonium and nitrite as nitrogen gas
Adsorption/ desorption	Dissolved $NH_4^+ \rightleftharpoons$ adsorbed NH_4^+	Clay-rich or organic-rich aquifers	Cation exchange capacity, pH, competing ions, salinity	Retards ammonium migration but may create secondary release risk
Mineral-mediated nitrate reduction	NO_3^-/NO_2^- reduction coupled with Fe, Mn, or S cycling	Reducing aquifers with reactive minerals	Fe^{2+}, Mn^{2+}, pyrite, organic matter, microbial mediation	May contribute to nitrate attenuation and alter groundwater geochemistry

One important implication is that the concentration of any one nitrogen species does not provide information on the level of pollution or direction of transformation. Low nitrate can be a sign of successful denitrification, but can also be a sign of DNRA generating ammonium. High ammonia can be due to direct sewage input, organic nitrogen mineralization, or nitrate reduction. Nitrite, typically found in small amounts, serves as a good indicator of incomplete transformation and redox instability [50].

Thus, future research is needed that incorporates nitrogen species measurements with other information including dissolved oxygen, redox potential, organic carbon, major ions, isotopes, and groundwater flow data, together with information on functional genes [51]. The only way that these researchers can determine source input from in situ transformation and assess whether aquifers serve as a nitrogen transport pathway, temporary storage region, or a true removal reactor is through this integrated approach.

An important consequence of this is that the amount of one nitrogen species does not necessarily indicate the level or direction of pollution. A low nitrate concentration could be a sign of successful denitrification, which also can be a result of ammonium production by DNRA. High ammonia concentrations can be the result of direct sewage contamination, organic nitrogen mineralization or nitrate reduction. Nitrite is a useful indicator of incomplete transformation and redox instability, and while it is typically found in small amounts, it is an excellent indicator [50].

Future studies are hence required to integrate monitoring of nitrogen species with measurements of dissolved oxygen, redox potential, organic carbon, major ions, isotopes, and groundwater flow data as well as functional genes [51]. Researchers can only be able to differentiate the source input from in situ transformation and assess whether aquifers are a nitrogen transport pathway, a temporary storage reservoir, or a true removal reactor with this integrated approach.

4. Source Analysis of "Three Nitrogen" Pollutants in Groundwater

4.1. Natural Sources of Groundwater Nitrogen

The most important natural sources of nitrogen in groundwater include soil organic nitrogen mineralization, atmospheric deposition, biological nitrogen fixation and nitrogen containing geologic materials [52]. These are generally associated with low concentrations of nitrogen, typically in the natural hydrochemical background, in undisturbed aquifer systems. In some hydrogeological and geochemical circumstances, however, natural N is a significant source of nitrate, nitrite or ammonia enrichment.

Soil organic nitrogen is a very common natural source of nitrogen in groundwater. In soil and sediments, ammonium can be released from organic matter through mineralization, which works through a process of microorganisms decomposing the organic matter. This ammonium can be further oxidized to nitrate under oxic conditions via nitrification, and then moved downward with recharge water. Naturally mineralized nitrate may enter shallow groundwater in humid regions with good infiltration and nitrate may build up in the vadose zone in arid/semi-arid regions and be flushed into aquifers during high rainfall or irrigation events [52].

Nitrogen deposition is another source of nitrogen to groundwater, especially where it is affected by industrial emissions, vehicle exhaust, biomass burning and agricultural volatilization of ammonia [53]. Nitrogen input from the atmosphere is typically smaller than input from fertilizer or sewage, but can be important in recharge areas with thin soils, high precipitation and/or sensitive aquifer systems. Difficult to distinguish from anthropogenic sources as atmospheric deposition may be increased by anthropogenic sources.

Geological sources are particularly important for groundwater with a high amount of ammonium [22]. Buried organic nitrogen or exchangeable ammonium can be present in significant amounts in sediments containing organic matter, peat beds, marine sediments, coal-bearing beds, and clay-rich aquitards. In the course of long-term water–rock interaction, ammonia can be added to groundwater by mineralization, desorption, or ion exchange. This natural release of ammonium will be retained under aquifer reduction, as a result of the limited oxygen supply in the aquifer, nitrification will be limited. It is thus not always safe to conclude that high NH_4 concentrations are solely due to modern pollution. In deep or confined aquifer, it is crucial to distinguish between geogenic ammonium and anthropogenic ammonium.

4.2. Agricultural Sources

Groundwater nitrogen contamination is one of the largest anthropogenic sources of nitrogen pollution, including agriculture [54]. Large amounts of reactive nitrogen are introduced into the soil–groundwater system by excessive or inefficient use of synthetic nitrogen fertilizer, manure, irrigation water and soil amendments. Under heavily cultivated areas, nitrate contamination is more likely to occur because nitrate is easily leached from most soils and aquifer materials.

Nitrogen transformation in agriculture starts from the root zone. Nitrogen in the form of urea, ammonium or nitrate can be utilized by plants, lost to soil organic matter, volatilized, denitrified or leached to the bottom of the soil [55]. Excess nitrogen in the soil and vadose zone occurs when the amount of fertilizer supplied to the crop is not required. This nitrogen may get translocated into shallow ground water during the rainfall or irrigation. The vadose zone can be the primary source of legacy nitrogen, and can continue to release nitrate to groundwater for many years after the reduced fertilizer application, especially in areas with multiple time applications for several years.

The complexity is increased by the organic nitrogen, ammonium, nitrate and dissolved organic carbon present in manure and livestock waste [56]. Organic nitrogen can be converted to ammonium and ammonium can be converted to nitrate when soil is oxic (after manure application). Thus, under redox conditions and travel time, manure nitrogen can be present as either nitrate or ammonium in the groundwater. Nitrate frequently co-occurs with chloride, potassium, dissolved organic carbon, and/or microbial indicators, indicating that this source is possibly manure or wastewater.

Irrigation in agricultural areas may also favor migration of nitrogen through the soils, either by increasing recharge or by dissolving already stored nitrate from the unsaturated zone. Irrigation return flow is one of the biggest sources of nitrate leaching in arid and semi-arid areas. Concurrently, over-irrigating can cause an increase in groundwater levels and redox potential which could influence nitrification, denitrification and ammonium release. This means that there

are risks of agricultural nitrogen pollution not only related to irrigation management but also to the properties of the soil, its ability to absorb nitrogen, and to hydrogeological vulnerability [57].

4.3. Domestic Sewage and Septic Sources

Nitrogen contamination in urban, peri-urban and rural residential areas is a significant issue due to domestic sewage, septic tanks, leaking sewer systems, and rural sanitation systems [58]. Nitrogen released from sewage is generally in excess of ammonium and organic nitrogen. Ammonium can be adsorbed, be oxidized to nitrate or be trapped under reduced conditions as it flows through soil and aquifer materials. Therefore, the concentration of nitrogen species found in groundwater may change greatly from one point to another from the source.

In shallow aquifers with good oxygenation, sewage ammonium may be oxidized to nitrate, forming nitrate plumes that can be downgradient from septic systems or leaking pipelines. However, under anaerobic conditions (low oxygen concentrations) or high organic loading, the predominant form of nitrogen in the aquifer may be ammonium. This distinction is significant because nitrate plumes tend to be more mobile, whereas ammonium plumes can be more localised but can persist [11].

Septic systems play a significant role in rural and suburban communities without any centralized wastewater treatment. In areas where septic tanks are densely concentrated or the septic tanks are poorly designed and in a highly permeable soil, nitrogen may quickly enter the groundwater. This risk is increased if water tables are shallow, or if drinking-water wells are near zones of wastewater infiltration. Groundwater in those situations may be enriched in nitrate, ammonium, chloride, bicarbonate, sodium, boron and dissolved organic matter [59].

One of the most important challenges in locating the origin of the sewage is that the N isotopic signature of manure can also overlap with that of sewage [10]. They can both exhibit enriched N15 values as a result of ammonia volatilisation and microbial transformation. So nitrate isotopes are not a sole basis to identify the sewage source. Should include hydrochemical data, land use data, artificial sweeteners, pharmaceuticals, microbial markers and groundwater flow analysis if available.

4.4. Livestock, Landfill, and Industrial Sources

Nitrogen can be released from livestock breeding areas in great quantities through manure storage, discharge of waste water, feed lot runoff and land application of animal wastes [56]. The sources usually contain elevated levels of ammonium, organic N, DOC, chloride, potassium and phosphorus. Waste management, if poor, can cause nitrogen to percolate into shallow groundwater and be mineralised, nitrified, denitrified or DNRA depending on the aquifer conditions.

Nitrogen pollution can often be spatially heterogeneous around livestock facilities. Often, ammonium and organic nitrogen are predominant in the vicinity of waste lagoons or manure piles because of direct inputs and the lack of oxygen. Nitrification of ammonium can result in nitrate increasing a little further downgradient. In very reducing plumes nitrate can be consumed and ammonium can be present. So, the lack of nitrate at livestock facilities does not necessarily mean low nitrogen impact; it could also mean that reducing conditions and nitrogen is converted to ammonium [55].

Another source is landfill leachate, particularly for water with high concentrations of ammonia. Ammonium, dissolved organic matter, chloride, alkalinity, iron, manganese and organic contaminants are common constituents of leachate with high levels of concentration. Ammonium can be very resistant to oxidation in the strongly reducing conditions that are typically found in landfills, and can persist for long periods and travel with landfill leachate-damaged groundwater. Nitrate can be present at the edges of landfill plumes, where oxygen is present, and nitrification can take place, or may be absent from the core of a landfill where oxygen is not available [60].

The industrial sources are diverse and depend on the type of production. Nitrogen can be added to groundwater as a result of fertilizer production, food processing, chemical production, coking, explosives production, or wastewater discharge. In the case of industrial nitrogen pollution, there are typically co-contaminants, including sulfate, heavy metals, organic compounds, salinity, and abnormal pH. In industrial areas, source analysis is thus highly demanding and must take a combined approach to nitrogen species and site-specific chemical fingerprints [61].

Table 3 provides an overview of the groundwater 'three nitrogen' pollution sources (both natural and anthropogenic), and their diagnostic indicators.

Table 3. Main sources and diagnostic indicators of groundwater "three nitrogen" pollution.

Source Type	Main Nitrogen Forms Released	Typical Co-Indicators	Dominant Affected Groundwater Environment	Diagnostic Challenge
Synthetic fertilizer	NO_3^-, NH_4^+, urea-derived N	Elevated NO_3^-, sometimes SO_4^{2-}, Ca^{2+}, Mg^{2+}, crop-land association	Agricultural shallow aquifers	Fertilizer nitrate may overlap with soil nitrogen after nitrification
Manure application	Organic N, NH_4^+, NO_3^-	Cl^-, K^+, DOC, phosphate, microbial indicators	Agricultural and livestock areas	Isotope signatures may overlap with sewage sources
Domestic sewage and septic systems	Organic N, NH_4^+, NO_3^- after nitrification	Cl^-, Na^+, HCO_3^-, boron, pharmaceuticals, artificial sweeteners	Urban, peri-urban, and rural residential aquifers	Nitrogen species change strongly with distance and redox condition
Livestock wastewater	Organic N, NH_4^+, NO_3^-	High DOC, Cl^-, K^+, phosphate, microbial contamination	Feedlots, manure lagoons, breeding facilities	Strong redox gradients may mask nitrate contamination
Landfill leachate	NH_4^+, organic N	High Cl^-, alkalinity, DOC, Fe, Mn, conductivity	Landfill-affected reducing aquifers	Ammonium may persist even where nitrate is absent
Industrial wastewater	NO_3^-, NH_4^+, organic N, process-specific N	Abnormal pH, salinity, SO_4^{2-}, heavy metals, organic compounds	Industrial parks and contaminated sites	Highly site-specific chemical fingerprints
Atmospheric deposition	NO_3^-, NH_4^+	Rainfall chemistry, low to moderate N input	Recharge areas, thin soils, vulnerable aquifers	Often difficult to separate from diffuse anthropogenic inputs
Geological nitrogen release	NH_4^+, organic N-derived NH_4^+	Reducing conditions, high HCO_3^-, Fe, Mn, methane, clay or organic-rich sediments	Deep, confined, or organic-rich aquifers	Must be distinguished from sewage, landfill, or manure input

4.5. Hydrochemical Indicators for Source Identification

Hydrochemical indicators are very useful for source tracing and understanding the processes of transformation. Major ions, nutrient ratios, trace elements, dissolved organic carbon and redox sensitive species can be used to differentiate between agricultural, sewage, livestock, landfill, industrial and natural sources [62]. But the application of hydrochemical evidence needs to be interpreted with care as original source signatures can be altered by mixing and transformation.

Agricultural fertilizer-associated nitrate is frequently accompanied by high levels of calcium, magnesium, sulfate, or bicarbonate, depending on the type of soil amendments and fertilizer used [63]. Chloride, sodium, potassium, bicarbonate, dissolved organic carbon, and in some cases phosphate concentrations are often high in manure and sewage sources. Ammonium, chloride, alkalinity, iron, manganese, and organic matter are common contaminants found in landfill leachate. Geological ammonium may be present in reducing groundwater where the concentrations of bicarbonate, methane, iron, or manganese are high, but where there are no obvious signs of recent surface contamination.

Other ratios, such as nitrate/chloride, ammonium/chloride, nitrate/bicarbonate, and nitrogen/phosphorus, can further indicate the source type and degree of transformation [34]. Chloride is commonly used as a conservative tracer because it is less reactive than nitrogen. High nitrate to chloride ratios could be due to fertilizer leaching, and high chloride and ammonium or nitrate could mean that sewage, manure, or landfill influence is present. But chloride can come from various sources such as road salt, evaporite dissolution, seawater intrusion, and industrial wastewater. Hence, ratio-based interpretation should include land-use and hydrogeological evidence.

Nitrogen species are especially redox sensitive, and this is in part why redox indicators are so important. Loss of nitrate can be attributed to denitrification, dilution, or a lack of a source, and can be determined using dissolved oxygen, oxidation–reduction potential, iron, manganese, sulfate, sulfide, methane, and dissolved organic carbon. If the redox information is not provided, the source analysis can be misleading. For instance, if a reducing aquifer has low nitrate levels, it is not necessarily due to low N loading, but rather to active nitrate reduction [26].

4.6. Stable Isotope Tracing

One of the most powerful tools for groundwater nitrogen source apportionment is stable isotope analysis. Both nitrate isotopes, $\delta^{15}N–NO_3^-$ and $\delta^{18}O–NO_3^-$, are widely used to identify nitrate from synthetic fertilizers, soil nitrogen, manure, sewage, atmospheric deposition, and nitrification.

Generally speaking, the range of isotopes is distinct for a particular source of the element; however, there is some overlap in the ranges. One of the prime drawbacks of isotope-based source identification is this overlap[10].

Nitrate isotope analysis can be used not only for source discrimination but also for process interpretation. The remaining nitrate is usually found to be isotopically heavier during the denitrification process due to preferential reduction of lighter nitrate isotopes. Hence, it is possible to use isotope enrichment to identify nitrate attenuation even if concentrations are not. Therefore, the use of isotope enrichment can identify nitrate attenuation in cases where concentration data is not available[64]. This same fractionation of photon energy can make the original source signature (spectrum) difficult to see. Under conditions of strong denitrification, the isotope values of nitrate can move away from their source values in such a way that, if it is not taken into account, the source assignment may be incorrect.

Other isotopic systems may provide better source identification. Boron isotopes can be beneficial in some cases for separating sewage and manure from synthetic fertilizers. Isotopes of ammonium can also be used to trace the source of ammonium and the processes by which it is transformed, but are used less frequently than the nitrate isotopes. Water isotopes can help answer questions about recharge sources, evaporation effects, and groundwater flow paths. The isotopes of nitrate together give a more powerful interpretation than any of the isotopes individually[65,66].

However, there are some uncertainties associated with isotope tracing. Source isotope values vary across the region, and local end-member data is sometimes unavailable. Isotopic signatures can be altered due to mixing, nitrification, denitrification, DNRA, volatilization, and assimilation[67]. Hence, isotope analysis should be used as part of a more comprehensive hydrogeochemical and hydrogeological interpretation rather than as a 'stand-alone' source-identification tool.

4.7. Quantitative Source Apportionment Models

Increasingly, quantitative models are employed to estimate the contributions of various N sources to groundwater contamination[11]. These are usually end-member mixing models, isotope mixing models, Bayesian models, multivariate statistical analysis, receptor models, or machine-learning models. These models have the potential to convert qualitative source information into quantitative estimates that are useful for pollution management and policy design.

The advantage of Bayesian isotope mixing models is that they can account for uncertainty in input isotope values and generate probability distributions for the source contributions. Bayesian methods are more appropriate than simple linear mixing models for complex groundwater systems with multiple sources. The end member selection, prior assumptions, and isotope fractionation corrections, however, have a significant impact on model results[68].

Multivariate statistical techniques can help identify patterns in hydrochemical variables and group samples with similar source characteristics, including principal component analysis, cluster analysis, factor analysis, and positive matrix factorization. These approaches can be helpful for large datasets, but they do not necessarily provide insights into causal mechanisms. Incorporating land-use, hydrogeological, and monitoring data, machine-learning models can help enhance pattern recognition and prediction. Therefore, models based solely on data can be prone to overfitting and may not be interpretable without constraints informed by nitrogen transformation mechanisms[69].

A good source apportionment model should integrate results from isotope analysis, hydrochemistry, spatial analysis, groundwater flow direction, land use, and transformation-process correction. The quantitative results should be considered limiting values rather than actual values, particularly in aquifers where redox transformation is high and multiple pollution sources are present[11].

4.8. Uncertainty and Critical Insights in Source Analysis

The source analysis of "three nitrogen" pollutants is uncertain due to the reactivity, mobility, and transformability of nitrogen species[66]. Unlike conservative contaminants, nitrate, nitrite, and ammonium can transform migration. Consequently, the nitrogen species found in the monitoring well may differ markedly from those emitted by the pollution source. This transformation makes it harder to attribute the source of the pollution.

One big question is what happens when source signatures overlap. Under certain conditions, nitrate concentrations

or isotope ratios can be created by fertilizer use, soil nitrogen, manure, sewage, and atmospheric deposition [70]. Another uncertainty is the spatial heterogeneity. Samples of groundwater taken from one well can be mixtures of water from various depths, flow paths, and recharge periods. The additional complicating factors of temporal variability include changes over time in fertilizer application, rainfall, irrigation, wastewater leakage, and fluctuations in the water table.

The most salient lesson learned is the need to connect source analysis with transformation analysis. A high nitrate concentration can be a sign of fertilizer leaching, but it can also result from the nitrification of ammonium from sewage. High ammonium can be attributed to direct sewage input, landfill leachate, DNRA, organic nitrogen mineralization, and geological release. Being low does not necessarily mean being weak: Nitrite can be quickly consumed. Thus, it is essential to consider the source input, migration pathway, residence time, redox condition, and microbial transformation together for reliable source identification [7].

Source analysis needs to shift from a single-index approach to a multi-evidence approach in the future. Using hydrochemistry, isotopes, microbial indicators, land-use mapping, groundwater ages, and reactive transport modeling will reduce uncertainty and enhance the reliability of source apportionment [20]. This holistic approach is critical for differentiating the external pollution load from internal nitrogen cycling and for developing specific groundwater protection measures.

5. Integrated Methodological Framework and Future Research Directions

5.1. Integrated Monitoring Framework for Groundwater Nitrogen Pollution

A comprehensive monitoring program is necessary to obtain a reliable understanding of the migration, transformation, and source contributions of "three nitrogen" pollutants, rather than relying on individual concentration measurements [71]. Nitrogen has traditionally been studied in groundwater, with particular emphasis on nitrate concentration, since nitrate is readily transported and often exceeds drinking-water standards. But this may not account for the diagnostic value of nitrite and ammonium, particularly in aquifers where redox reactions are frequent, or in aquifers with sewage inputs, landfill leachate, organic-rich sediments, or high microbial activity. Hence, it is necessary to obtain data on nitrate N, nitrite N, and ammonium N simultaneously to follow the entire transformation pathway of groundwater N.

Monitoring networks are especially important for spatial design. Monitoring wells should be located along groundwater flow paths from recharge areas to discharge areas, as well as from potential pollution sources to receiving groundwater environments downgradient. Nitrogen species may exhibit high vertical variation, and so multi-depth sampling is required. Nitrate can be the dominant groundwater constituent in oxic recharge conditions, and ammonium can be the dominant constituent in reducing groundwater conditions. If vertical resolution is unavailable, samples from long-screened wells can mask actual transformation zones by mixing waters from different depths [7].

Other parameters of interest for monitoring include dissolved oxygen, oxidation–reduction potential, pH, temperature, electrical conductivity, dissolved organic carbon, major ions, Fe, Mn, sulfate, methane, and alkalinity [46]. These indicators are useful for determining whether nitrogen species are transported conservatively or whether nitrification, denitrification, DNRA, ammonification, or anammox processes are present. In this regard, a comprehensive monitoring system should consider nitrogen species, redox conditions, and groundwater flow conditions as an integrated dataset.

It is also crucial to monitor them temporarily. Seasonal sampling can show the effects of rain, irrigation, fertilizer application, water-table fluctuations, and microbial activity. Legacy N effects and delayed groundwater responses to pollution control measures are revealed by long-term monitoring. This is particularly relevant to agricultural aquifers, where nitrogen stored in the vadose zone could leach into groundwater over the next few years or decades, even if fertilizer inputs have been reduced [25].

5.2. Coupling Field Observation, Laboratory Experiments, and Modeling

Field observations directly capture actual groundwater conditions but may not fully distinguish among source input, transport, dilution, and transformation. This can be overcome through laboratory experiments that examine specific

mechanisms under controlled conditions. Column experiments, batch adsorption tests, and microcosm incubations can be used to measure ammonium adsorption, nitrate reduction, nitrite formation, organic nitrogen mineralization, and microbial transformations [72]. Laboratory experiments can provide mechanistic parameters when conducted with real aquifer sediments and groundwater, thereby enhancing field interpretation.

But laboratory studies also have drawbacks. Laboratory conditions may not fully mimic field-scale heterogeneity, groundwater flow complexity, redox gradients, microbial community structure, and long groundwater residence times [73]. Thus, a laboratory test should not be applied directly until it is field-tested. Field monitoring and numerical modeling ought to be used to test whether the identified mechanisms and reaction rates are relevant. At the same time, the most effective approach is first to identify potential mechanisms and reaction rates through laboratory experiments.

Reactive transport modeling is a tool capable of connecting observation to mechanism. It can model advection, dispersion, adsorption, ion exchange, nitrification, denitrification, DNRA, and other nitrogen transformation reactions under realistic hydrogeological conditions [74]. These models are particularly useful for assessing the evolution of an existing nitrogen plume, predicting future groundwater quality, and evaluating remediation scenarios. But the model's reliability is critically dependent on reliable hydrogeologic characterization, reaction-rate estimates, source-term definitions, and calibration data.

An integrated field–laboratory–modeling approach can minimize uncertainties in groundwater nitrogen studies [75]. Field data indicate where and when nitrogen pollution happens, laboratory experiments elucidate the transformations, and models capture the interactions of transformations across space and time. This combination yields a stronger effect than either method alone and should be used routinely in future research.

5.3. Application of Isotopes and Molecular Biological Techniques

The use of stable isotopes is fundamental to the study of groundwater nitrogen today, as they can be used to investigate both nitrogen sources and transformations [10]. There are two isotopes of nitrate, $N_{14}O_3^-$ and $N_{15}O_3^-$, and the ratios of the heavy isotopes ($\delta^{15}N - NO_3^-$ and $\delta^{18}O - NO_3^-$) are commonly used to help determine nitrogen sources and detect denitrification. In complex aquifer systems, additional isotopic tracers such as $\delta^{11}B$, $\delta^{2}H$, and $\delta^{18}O$ of water, $\delta^{15}N$–NH_4^+, and dissolved-gas isotopes can enhance interpretation. Isotope data should, however, be used with caution, as transformation processes may alter source signatures.

Multi-isotope coupling and process correction are areas of interest for future development of isotope-based methods. For instance, nitrate isotopes can help determine source categories, and water isotopes can help elucidate recharge pathways and the effects of evaporation. The use of boron isotopes may help identify the origin of sewage and manure in certain environments. The use of ammonium isotopes may provide the origin, adsorption, and nitrification of ammonium. Completing the source apportionment using isotope, hydrochemical, and microbial data makes it more robust [66].

Another important direction is the molecular biological techniques. Nitrification, denitrification, DNRA, and anammox-related microbial communities and functional genes can be identified by quantitative polymerase chain reaction, high-throughput sequencing, metagenomics, and metatranscriptomics [76]. These methods can be used to determine the feasibility of certain transformation pathways in a particular aquifer. For instance, the presence of ammonia-oxidation genes could support nitrification potential, and denitrification genes could support nitrate-reduction capacity.

However, the presence of functional genes does not imply active transformation. The abundance of genes does not necessarily indicate high process rates, as environmental conditions, substrate availability, and microbial activity also influence process rates. Thus, molecular biological evidence should be utilized alongside concentration profiles, isotope fractionation, incubation experiments, and geochemical indicators [10]. Future research should progress beyond community detection to measuring process rates and the roles of microbial function and field-scale nitrogen responses. The key methods used for source identification and mechanism analysis, along with their strengths and weaknesses, are highlighted in **Table 4**.

Table 4. Methods for source analysis and mechanism identification of "three nitrogen" pollutants in groundwater.

Method Category	Application	Advantages	Limitations	Recommended Use in This Review Framework
Conventional hydrochemistry	Identifying nitrogen species, redox conditions, and co-contaminants	Low cost, widely available, suitable for long-term monitoring	Cannot independently distinguish source from transformation	Basic dataset for all groundwater nitrogen studies
Major-ion ratio analysis	Differentiating fertilizer, sewage, manure, landfill, and geological influence	Useful for source screening and plume characterization	Conservative tracers such as Cl^- may have multiple sources	Combine with land use and groundwater flow analysis
Stable nitrate isotopes, $\delta^{15}N–NO_3^-$ and $\delta^{18}O–NO_3^-$	Identifying nitrate sources and denitrification	Strong process and source information	Source ranges overlap; denitrification modifies isotope signals	Use with hydrochemical and redox correction
Additional isotopes, such as $\delta^{11}B$, $\delta^{15}N–NH_4^+$, $\delta^2H–H_2O$, $\delta^{18}O–H_2O$	Distinguishing sewage/manure, ammonium origin, and recharge pathways	Improves interpretation in complex aquifers	Higher analytical cost and need for local end-member data	Apply in mixed-source or transformation-intensive systems
Microbial functional gene analysis	Detecting nitrification, denitrification, DNRA, and anammox potential	Reveals the biological mechanism and pathway potential	Gene presence does not always indicate an active reaction	Combine with isotope tracing and incubation experiments
Laboratory incubation and column experiments	Quantifying transformation rates and adsorption behavior	Mechanistic and controllable	May not fully represent field heterogeneity	Use to parameterize reactive transport models
Groundwater age and flow-path analysis	Linking nitrogen pollution to recharge time and migration history	Helps distinguish recent and legacy pollution	Requires tracer data and hydrogeological interpretation	Important for agricultural and regional aquifer systems
Reactive transport modeling	Simulating migration, transformation, and remediation scenarios	Integrates transport and reaction processes	Sensitive to parameter uncertainty and model assumptions	Use for prediction and management decision-making
Machine learning and geospatial modeling	Predicting pollution vulnerability and identifying high-risk areas	Handles large datasets and complex nonlinear patterns	May lack a mechanistic explanation	Best used as a screening tool combined with process-based models

5.4. Multi-Scale Migration–Transformation Modeling

Groundwater nitrogen pollution is a multi-scale issue. Microbial microhabitats, mineral surfaces, and local redox gradients affect the nitrogen transformation at the pore scale. Hydraulic conductivity, groundwater flow direction, recharge rate, and sediment heterogeneity are important at the aquifer scale. Nitrogen loading occurs at the watershed or regional level and depends on land use, agriculture, urbanization, climate, water management, and surface water–groundwater interaction. Therefore, future research is needed to develop multiscale models that link nitrogen processes across these scales [77].

More focus needs to be placed on the vadose zone in these types of models. The vadose zone can contain significant quantities of legacy nitrate and organic nitrogen in many areas. This retained nitrogen can be a late source to groundwater when it rains, when it is irrigated, or when the water table rises [78]. Pollution-control models that do not account for the vadose zone can underestimate future pollutant loading and overestimate the effectiveness of short-term pollution-control measures. Agricultural and urban recharge areas, however, require coupled soil–vadose zone–groundwater models.

Another frontier of modeling is surface water–groundwater interaction. Nitrogen-polluted groundwater may flow into rivers, lakes, wetlands, reservoirs, and drainage canals, or aquifers may be recharged with surface water containing nitrogen. Nitrification, denitrification, and anammox processes can form hotspots near these interfaces due to redox gradients. So, riparian and hyporheic areas cannot be used solely as boundaries but must be modeled as zones of transformation in nitrogen cycles [27].

The residence time and age of the groundwater should also be considered in migration–transformation analysis [30]. New water from the ground can contain legacy nitrogen or can contain geogenic ammonium. Groundwater age tracers can be used in conjunction with nitrogen species and isotopes to distinguish recent contamination from delayed historical loading better. This is very important to assess the effectiveness of management interventions.

5.5. Emerging Data-Driven and Interdisciplinary Approaches

Data science is rapidly developing, providing new opportunities for groundwater nitrogen research. Machine learning, geostatistics, remote sensing, and geographic information systems can help better predict nitrogen pollution vulnerability and pinpoint high-risk areas [79]. Data-driven models can illustrate spatial patterns that are not apparent with traditional methods alone, when combined with land use, fertilizer application, soil type, topography, aquifer properties, climate, and monitoring data.

Data-driven approaches should be used with caution, though. Machine-learning models can make good predictions, but offer limited mechanistic explanations. Predictions may be unreliable outside the sample area if the training data are biased or incomplete. Thus, there is a need to develop hybrid models that combine data-driven prediction and process-based understanding in the future. In addition, machine learning can be used to recognize pollution hotspots, and reactive transport models can be used to understand the mechanisms of migration and transformation [80].

There is also a need for interdisciplinary integration. Nitrogen pollution of groundwater is an issue not only in hydrogeochemistry but also in agriculture, ecology, engineering, public health, and management [81]. Successful control of nitrogen will depend on the interplay among hydrogeologists, microbiologists, soil scientists, agronomists, environmental chemists, modelers, and policymakers. This interdisciplinary approach can help develop more realistic pollution prevention strategies, including optimizing fertilizer application, improving wastewater infrastructure, protecting recharge areas, controlling irrigation, and enhancing natural attenuation zones.

5.6. Implications for Pollution Control and Remediation

Understanding the migration and transformation processes of the "three nitrogen" pollutants has direct implications for the management of groundwater pollution. The most basic strategy remains source control. Excessive fertilizer application, use of high-NUE crops, slow-release fertilizers, optimizing irrigation, and adjusting fertilizer application to match crop uptake are strategies to minimize nitrate leaching in agricultural areas. In residential and urban environments, maintaining effective sewage collection systems, septic systems, and preventing sewer leakage are critical. Good management of waste storage, leachate collection, and impermeable barriers around livestock facilities and landfills will minimize the amount of ammonium and organic nitrogen released into the environment [53].

The selection of the remediation strategies should depend on the predominant nitrogen species and aquifer conditions. Increased denitrification through the addition of organic carbon or mineral reduction may be effective for nitrate-contaminated oxic aquifers. Still, there is a risk of nitrite formation, greenhouse gas emissions, and secondary degradation of water quality. For aquifer types with ammonium, approaches can be oxygenation, bio-stimulation of nitrification and denitrification, or controlled reactive barriers. Remediation that alters redox may result in the mobilization of metals or the transformation of one nitrogen species into another; therefore, remediation design will need to account for broader geochemical consequences [11].

Care should be taken to evaluate natural attenuation. Under certain conditions, denitrification or Anammox potential can be very high in some aquifers, whereas in others nitrate is predominantly removed by DNRA [41]. The implications for management differ across these outcomes. True N removal occurs when reactive N is converted to N gas, whereas retention or transformation of reductive N can only delay pollution. Thus, management decisions should be made to differentiate between attenuation, transformation, and temporary storage.

5.7. Future Research Priorities

There are many important points to be addressed in future studies. First, there should be a greater focus on nitrite as a process indicator [34]. Nitrite is normally present at very low concentrations but can indicate incomplete denitrification, incomplete nitrification, breakdown of redox gradients, and active transformation interfaces. Second, ammonium needs to be investigated not only as a direct contaminant but also as an intermediate of the mineralization of organic nitrogen, DNRA, geological release, and sediment desorption [13].

Thirdly, source analysis and transformation correction analysis should be used [20]. Nitrification, denitrification, DNRA, adsorption, and mixing should be explicitly con-

sidered as sources for isotopes and hydrochemical source apportionment. Fourth, field-scale measurements should be used to quantify microbial processes, not just to infer them from laboratory experiments or gene abundance [73]. Fifth, greater research is required on the legacy nitrogen stored in the vadose zone and aquifer sediments, as this internal reservoir may delay groundwater recovery [78].

Lastly, predictive models should be developed that connect pollution sources to aquifer vulnerability, transformation potential, and health or ecological consequences [82]. These can assist with targeted approaches to nitrogen management, rather than a blanket approach to control. A new paradigm for groundwater nitrogen research is emerging through the integration of monitoring, isotopes, microbiology, modeling, and data science, which will help shift the focus from descriptive assessment of groundwater pollution to mechanism-based prediction and sustainable management. Based on the above synthesis, a roadmap for future research on mechanism-based groundwater nitrogen management is presented in **Figure 2**.

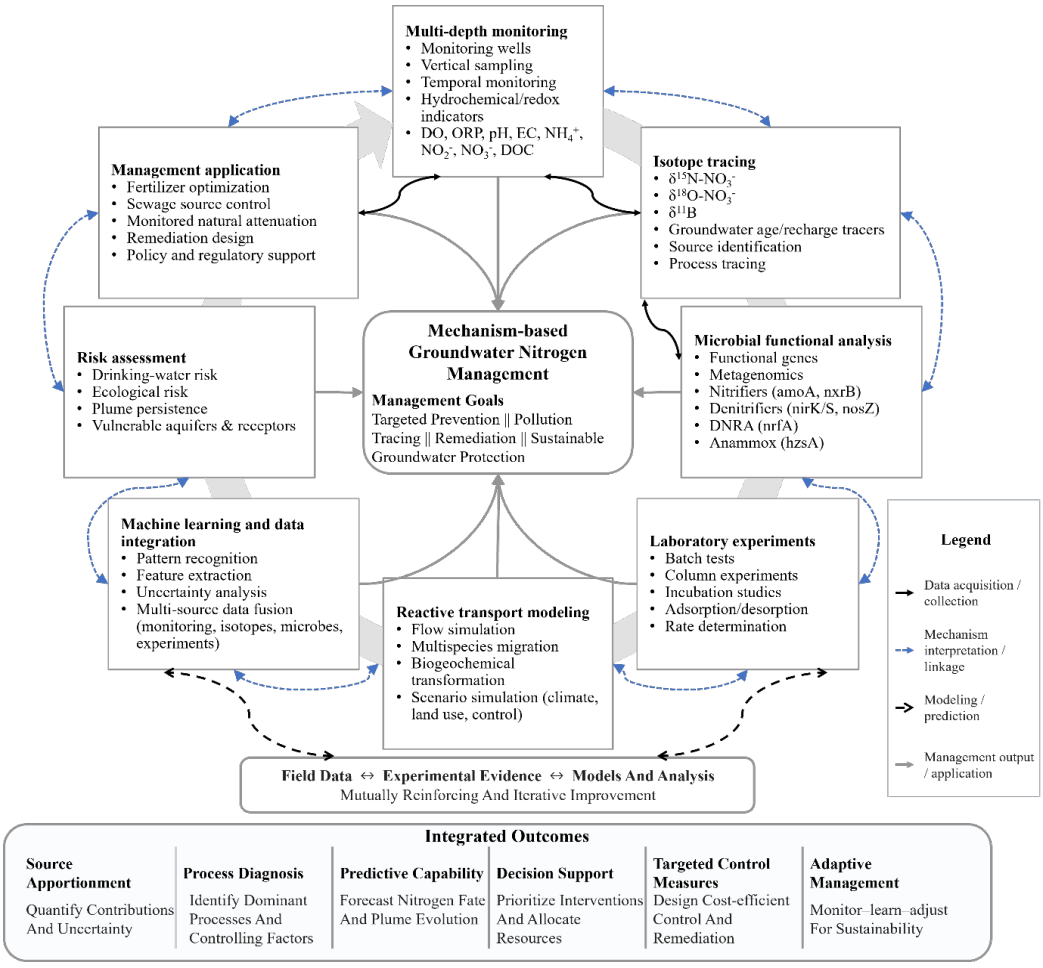

Figure 2. Future research roadmap for mechanism-based groundwater nitrogen management.

6. Conclusions

The contamination of groundwater with three nitrogen constituents (nitrate nitrogen, nitrite nitrogen, and ammonium nitrogen) is a complex environmental issue influenced by source inputs, hydrogeological transport, redox evolution, microbial activity, and water–rock interactions. These three forms of nitrogen are not separate pollutants but are dynamically linked and interconverted via nitrification, denitrification, dissimilative reduction of nitrate to ammonium, anaerobic oxidation of ammonium, ammonification, adsorption/desorption, and mineral-mediated reactions. Thus, the presence of one form of N in groundwater may result from both external contamination and internal transformation processes.

Nitrogen in the form of nitrate is generally the most mobile and widely distributed form, particularly in oxic shallow aquifers where agricultural fertilizer, manure application, irrigation return flow, and sewage leakage are likely to influence nitrogen concentrations. It is also poorly absorbed by soils and highly soluble, which means it can travel far in groundwater. Nitrite nitrogen, though typically seen at low levels, is still very important as it is an unstable intermediate in nitrogen transformations and is diagnostic. This build-up can be caused by incomplete nitrification, incomplete denitrification, redox fluctuation, and/or disruption of the normal microbial balance. The mobility of ammonium nitrogen is less than that of nitrate due to the cation exchange and adsorption processes. Still, it may result from geological release, DNRA, organic nitrogen mineralization, manure, landfill leachate, or sewage.

Groundwater source analysis of N pollution remains a challenge due to the potential for species transformation during transport. Nitrogen loads to the groundwater can include agricultural activities, domestic sewage, septic systems, livestock wastewater, landfill leachate, industrial discharge, atmospheric deposition, soil organic nitrogen, and geological materials. The forms of nitrogen measured in a monitoring well, however, may differ from those originally released from the source. The oxidation of ammonium to nitrate can occur, for instance, from fertilizer or sewage, and nitrate can be reduced to N gas via denitrification or to N gas via DNRA. Therefore, the use of concentration data alone can lead to false identification of the sources.

"The three nitrogen" pollution cannot be well understood unless an integrated analysis of hydrochemical indicators, stable isotopes, microbial functional genes, groundwater flow analysis, laboratory experiments, and reactive transport modeling is combined. Use of dual nitrate isotopes can help interpret sources and identify denitrification. In contrast, other tracers, including boron isotopes, ammonium isotopes, groundwater age indicators, and molecular biological tools, can be used in complex aquifer systems to enhance interpretation. Concurrently, laboratory experiments and mathematical modeling need to be carried out to measure the rate of transformation, the source contributions, and long-term pollution trends, based on field observations.

Future studies need to shift from single species assessment to coupled source–migration–transformation assessment. Special emphasis should be placed on nitrite as a sensitive indicator of transformation interfaces, on ammonium as a pollutant or product of reduction or mineralization, and on legacy nitrogen in soils, vadose zones, and aquifer sediments. Managing the release of external nitrogen in the watershed is only part of the picture for effective groundwater protection; understanding internal nitrogen cycling and delayed release is also important for management. Combining the various aspects of source apportionment and predictive modeling with mechanistic analysis can help create more targeted strategies for preventing groundwater nitrogen pollution, controlling risks, and remediating contaminated sites.

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