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Study on the Determination and Prevention Methods of Groundwater

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Abstract. Excessive discharge of industrial wastewater and abuse of fertilizers have polluted a large amount of groundwater, seriously threatening sustainable development. Therefore, it is urgent to protect groundwater resources, improve the determination of pollution sources, and implement prevention and control measures. This paper describes the current mainstream determination methods of groundwater pollution sources, analyzes the main pollution sources, and comprehensively discusses the advantages and disadvantages of different prevention and control methods. It evaluates the current major large-scale models, combines the existing models with current conditions, prospects, and development potential of its actual production application. It divides the process technology in detail, evaluates the impact of by-products on the environment, economic costs, and human resources investment, and combines these factors with actual implementation. This paper summarizes the current main sources of nitrate pollution through the traceability method currently used in the market, presents different prevention and control methods for different situations, compares the advantages and disadvantages of each method, and makes prospects for future development. A comprehensive discussion presents the best solution for different environmental conditions at present and refines the selectivity of various solutions.

Keywords: nitrate pollution, groundwater, nitrate pollution prevention and control, nitrate pollution determination

1. Introduction

Groundwater, with its vast reserves and high stability, serves as a critical source of water for industrial, agricultural, and domestic use. However, in recent years, neglect toward industrial wastewater and domestic sewage discharge has led to severe nitrate contamination in groundwater across multiple regions. For instance, approximately 39.8% of groundwater near Yantai exceeds the Class III limit specified in China's Quality Standard for Groundwater (GB/T 14848-2017) [1]. In Dalian, the proportion of groundwater exceeding the standard has reached 77.8% [2]. Therefore, scientifically tracing the sources of groundwater nitrate pollution and implementing effective prevention measures are urgently needed.

Currently, researchers have successfully applied integrated techniques such as numerical modeling and isotope tracing to achieve precise source identification of pollution. Meanwhile, researchers have employed various remediation methods—such as microbial remediation, permeable

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reactive barriers (PRBs), and catalytic reduction—to treat contaminated groundwater, followed by further optimization and refinement of these strategies. Hui-Zhen Xu effectively removed nitrate from groundwater using an electrokinetic-permeable reactive barrier (EK-PRB) hybrid technology [3]. Song demonstrated effective nitrate elimination in wastewater via emulsified oil-stimulated microbial denitrification [4].

Through a systematic evaluation of prevailing remediation technologies, this research seeks to advance source identification, pollution tracing, and optimized treatment approaches for nitrate-polluted groundwater, offering actionable recommendations.

2. Groundwater nitrate pollution sources

2.1. Main sources of groundwater nitrate pollution

2.1.1. Agricultural activities

Crops typically exhibit low nitrogen fertilizer utilization efficiency, generally below 40%. Consequently, excessive fertilizer application results in unabsorbed nitrates infiltrating groundwater or entering water bodies via surface runoff, causing widespread contamination.

Song's research in Barcelona, Spain, demonstrated a significant impact of agricultural nitrogen fertilizers on groundwater, with nitrate concentrations increasing by approximately 80% between 1978 and 1984 [5]. In Illinois, USA, between 1949 and 1969, an 11-fold increase in nitrogen fertilizer use led to an approximate threefold rise in nitrate concentrations in nearby rivers [6]. The use of untested water sources for daily irrigation—especially if contaminated—can exacerbate groundwater nitrate pollution. Excessive irrigation can accelerate the leaching of surplus nitrates from soil, while improper manure management in livestock farming also poses contamination risks. The practice of open-air disposal of massive volumes of manure from concentrated animal feeding operations (CAFOs) creates significant nitrate pollution pathways. Rainfall or irrigation water will percolate downward, penetrating the plant root zone and eventually reaching underground aquifers. During heavy rain or snowmelt events, nitrates may enter lakes, reservoirs, and other surface water bodies via runoff, causing more severe contamination. Farmers often apply large quantities of inadequately treated manure wastewater directly to farmland, leading to nitrate levels that exceed both the soil's assimilative capacity and crop nutrient demands, resulting in widespread water contamination.

2.1.2. Domestic sewage and waste pollution

Domestic sewage contains a significant amount of nitrogen-rich organic pollutants, such as urine and kitchen waste. During natural degradation, these compounds are converted into nitrates through microbial processes, involving organic nitrogen mineralization and nitrification.

For example, the degradation of 1 liter of domestic sewage can produce approximately 110 milligrams of nitrate. If untreated sewage is directly discharged and infiltrates groundwater, it causes contamination. Even if sewage enters underground pipelines or septic tanks through standard processes, aging infrastructure or poor sealing may still lead to leaks, allowing nitrates to directly infiltrate groundwater. Urban drainage systems with design flaws or inadequate maintenance can further exacerbate contamination. Even after secondary treatment, effluent from wastewater treatment plants may still contain high concentrations of nitrate nitrogen. Meanwhile, the sludge

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produced during wastewater treatment also contains highly concentrated nitrogen, and improper disposal of either effluent or sludge can lead to groundwater contamination through leaching.

Additionally, open garbage dumps in some areas contain kitchen waste, feces, and discarded pharmaceuticals—all rich in organic nitrogen. Under anaerobic conditions, this organic nitrogen decomposes into ammonia, which later undergoes nitrification and infiltrates groundwater through leaching, leading to excessive nitrate concentrations.

The contamination can spread extensively, potentially affecting areas several kilometers downstream, making it a significant pollution source for local groundwater nitrate levels.

2.1.3. Industrial discharges

Industrial discharges also serve as a significant source of nitrate contamination in groundwater. Many industrial processes generate nitrogen-containing wastewater. The chemical industry, including fertilizer production (such as ammonium nitrate and nitrate-phosphate), generates large amounts of nitrogen-containing wastewater, while nylon and adipic acid manufacturing produce wastewater rich in nitrates and nitrites during the nitric acid oxidation of cyclohexanone. Similarly, high-temperature energy industries like coal-fired power plants, steel mills, and cement factories also contribute significantly to nitrate pollution.

During high-temperature combustion of fossil fuels, atmospheric nitrogen and organic nitrogen in the fuel are converted into nitrates. Pharmaceutical factories frequently use nitrating agents in the synthesis of common drugs such as antibiotics and vitamins, resulting in wastewater containing organic nitro compounds. The aforementioned sources all represent major industrial contributors to nitrate pollution. If industrial wastewater undergoes incomplete treatment or is discharged directly without any treatment, it can contaminate groundwater systems through surface runoff or infiltration into subsurface soils. Some solid waste byproducts, when exposed to rainwater leaching, undergo conversion of nitrogen-containing compounds into nitrates that infiltrate groundwater. Even when properly treated and disposed of in landfills, the nitrate content in leachate remains a direct threat to groundwater systems. This is particularly critical given its rapid leakage potential and high concentration levels, making it an extremely significant pollution source.

2.2. Main methods for tracing groundwater nitrate pollution sources

2.2.1. Isotopic tracing method

This technique identifies pollution sources by analyzing stable isotope ratios of δ¹⁵N and δ¹⁸O in nitrates.

To implement this method, representative sampling points (e.g., groundwater, soil porewater, precipitation) must first be selected based on local hydrogeological conditions. The water samples then undergo pretreatment, including filtration to remove particulates and bacteria, followed by the addition of bactericides or flash-freezing to prevent microbial activity from altering isotopic compositions. Next, nitrate extraction and purification are performed, followed by enrichment using the denitrifying bacterial method, where nitrous oxide gas is collected for mass spectrometric analysis. Finally, dual-isotope plots are generated based on mass spectrometry results, and mixed models are applied to quantify the proportional contributions of different pollution sources.

The isotopic tracing method exhibits strong specificity, demonstrating significant differentiation among various pollution sources while maintaining broad applicability. It can easily identify dominant sources within complex mixed contamination and be integrated with other hydrological

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models for dynamic tracking. In the future, this method holds potential for combined use with: 1. Triple oxygen isotopes (Δ¹⁷O) to precisely quantify atmospheric inputs; Boron isotopes (δ¹¹B) to enhance discrimination between sewage/manure sources; Microbiomics (e.g. denitrifier community structure) to corroborate pollution types, thereby improving accuracy. However, the isotopic tracing method also has limitations: high costs requiring sophisticated instrumentation, and susceptibility to environmental interference (e.g., natural denitrification and ammonia volatilization altering original isotopic signatures). Additionally, spatial and temporal variability may lead to deviations in results, necessitating comprehensive consideration of these factors in practical applications.

2.2.2. Numerical modeling approach

The primary numerical models currently in use include the MODFLOW and FEFLOW models. The MODFLOW model employs the finite difference method to construct a 3D groundwater flow model, integrating hydrological data to simulate flow direction and velocity, while backtracking virtual particles to identify contamination sources. The FEFLOW model utilizes unstructured grids, incorporates advection-dispersion-reaction equations, and employs forward/inverse algorithms with reverse particle tracking to trace contamination sources. It can integrate with IoT and real-time monitoring systems. The numerical modeling approach is efficient, cost-effective, and suitable for large-scale screening, offering accurate source identification for both agricultural/industrial pollution and point-source localization. However, high-resolution models require heavy computational loads, relying on parallel computing or GPU acceleration, and are highly dependent on hydrological data accuracy, often necessitating physical surveys, which increase costs. Over-simplification of parameters (e.g., denitrification rates affected by seasonal temperature variations) may compromise tracing precision.

3. Groundwater nitrate pollution prevention and control methods & key applications

3.1. Microbial Remediation

Microbial Remediation employs denitrifying bacteria (e.g., Pseudomonas, Bacillus) and autotrophic microbes to reduce nitrates stepwise to nitrogen gas (N₂) via natural anaerobic denitrification, thereby eliminating nitrate contamination. In practice, engineered strains are introduced, leveraging the rapid reproduction rates of bacteria and fungi. By optimizing reaction conditions such as dissolved oxygen levels, denitrification can be selectively enhanced to minimize secondary pollution and ensure controllable byproducts. It avoids secondary environmental harm caused by chemical agents or physical methods, reduces residual chemical reagents, and offers high ecological compatibility, strong environmental adaptability, and low cost by relying on natural microbial metabolism. Its sustainability stands out as the most prominent among the available solutions. However, this method also has drawbacks, such as causing local nitrogen accumulation despite achieving significant removal rates, necessitating additional steps like artificial oxidation.

3.2. Catalytic Reduction

Catalytic Reduction involves the use of catalysts under controlled conditions (e.g., catalyst type, pH, temperature) to selectively convert nitrates into targeted products such as nitrogen gas (N₂) or ammonium (NH_4^+), facilitating subsequent treatment. Currently, the primary methods include chemical catalytic reduction and electrocatalytic

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reduction. Their advantage lies in rapid reaction rates—tasks requiring hours or even days for microbial denitrification can be completed by catalytic reduction within minutes. It is particularly suitable for large-scale rapid treatment in agricultural and industrial wastewater, offering superior controllability and selectivity (>80% efficiency) compared to microbial remediation. By controlling reaction conditions, it can suppress the generation of harmful byproducts, reducing the risk of secondary pollution.

Catalytic reduction remediation also has certain limitations. For example, common wastewater components like sulfides and organic compounds may cover the catalyst's active sites, leading to catalyst poisoning and deactivation. This significantly shortens the catalyst's service life, while the regeneration process for some catalysts requires high energy input and may risk damaging their structural integrity. Improper control of reaction conditions—such as incompatible pH levels or incorrect hydrogen flow rates—may result in nitrates being reduced to nitrites, necessitating additional treatment steps. Additionally, while catalytic reduction is environmentally friendly, it requires hydrogen as a reducing agent, leading to high transportation costs, averaging a staggering $4 to $6 per kilogram. Moreover, hydrogen poses explosion risks during transport, increasing system complexity and operational hazards. To address these challenges, current research focuses on developing low-cost non-precious metal catalysts and coupled green hydrogen source technologies.

3.3. Permeable Reactive Barrier (PRB)

Permeable Reactive Barrier (PRB) Method refers to an in-situ groundwater nitrate remediation technology that fills the treatment zone with reactive materials, such as solid carbon sources, composite biological materials, and metal-based substrates. The system transforms nitrate contaminants in groundwater passing through the barrier into less harmful substances via processes such as biodegradation, chemical precipitation, redox reactions, adsorption, and leaching, retaining them within the barrier to achieve remediation of the contaminated flow. The core mechanism is biological denitrification, where heterotrophic denitrification supplies electrons (via carbon sources) to reduce nitrates to nitrogen gas (N₂) under anaerobic conditions, mediated by denitrifying bacteria. Materials like corn straw and loofah slowly release dissolved organic matter to drive these reactions. Simultaneously, autotrophic denitrification occurs, using zero-valent iron or hydrogen as electron donors, combined with adsorbents (e.g., zeolite) for removal. The internal structure adopts a multi-unit zoning design integrated with continuous barriers to prevent secondary contamination. Typically installed within underground aquifers, it is positioned perpendicular to the direction of groundwater flow. Recent studies have explored combining Permeable Reactive Barriers (PRBs) with electrokinetics by filling them with zero-valent iron media. Experiments demonstrated that nearly all nitrate nitrogen was converted into low-toxicity nitrogen gas or ammonium within 100 hours. This method offers higher cost-effectiveness, enhanced efficiency, and environmental sustainability, exhibiting greater development potential and room for improvement. For example, when coupled with Pd-biofilm reactors or iron micro-battery technology, the former enhances metal ion removal efficiency without being inhibited by nitrate concentrations. The latter utilizes biologically slow-released carbon and iron to create a micro-electric field, accelerating electron transfer. In the future, this method holds potential for integration with other solutions to develop tailored approaches better suited to local environmental conditions. However, the method also has significant drawbacks. On the technical level, excessive biofilm thickness requires regular flushing.

The passivation of iron materials also necessitates periodic reactivation through ultrasonication or electrochemical methods to restore their activity. These measures increase both labor and material costs. Additionally, they fail to fully resolve secondary contamination issues, such as ammonium

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accumulation in zeolite walls or organic matter leakage at the effluent outlet. Moreover, operation requires inoculation with local denitrifying bacteria to enhance regional adaptability, along with additional labor costs to maintain stable anaerobic conditions for optimal reaction efficiency.

4. Future prospects for groundwater nitrate pollution control

In recent years, rapid climate change and combined anthropogenic-natural effects have significantly accelerated nitrogen migration. For instance, Zhang's research revealed that excess nitrogen in the Qinhuangdao Yinma River area primarily originates from atmospheric deposition, while the Gutun region's surplus nitrogen is mainly attributed to local hydrological cycling [7,8]. Therefore, national authorities should actively promote the integrated application of numerical modeling and isotopic tracing tools, leveraging these technologies across multiple scales and with high precision. Additionally, by incorporating IoT, big data, and AI-driven real-time monitoring systems, dynamic pollution early-warning and source-tracking capabilities can be achieved, while simulating groundwater solute transport to optimize remediation strategies. For remediation technologies—such as microbial remediation, catalytic reduction, and permeable reactive barriers—a comprehensive, adaptive integration should be employed. Tailored adjustments based on regional specifics and pollution source characteristics will enhance precision and effectiveness. Meanwhile, the nation should actively engage in coupled global hydrological cycle research, analyzing groundwater flow directions from a climate change perspective to prevent cross-regional contamination. Particular attention must be paid to the rising groundwater levels in North China, which exacerbate nitrate infiltration. This necessitates integrated control technologies, refined management, region-specific strategies, and globalized governance. Smart technologies should be leveraged to enhance prevention, while prioritized remediation efforts target already contaminated water sources [9-11].

5. Conclusion

This paper examines the primary sources of nitrate pollution in groundwater and evaluates the strengths and weaknesses of various traceability methods. This study comprehensively summarizes the advantages and limitations of essential human-intervention methods for remediating existing nitrate contamination in groundwater. The paper discusses context-specific efficient response strategies, practical implementation challenges of various methods, and a screening framework for locally optimal solutions, integrating economic conditions, labor costs, and material expenses. In the future, China should focus on optimizing nitrate quantification and remediation methods, reducing large-scale costs, and enhancing monitoring and prevention efficiency to facilitate practical deployment and global scalability.

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