

Review

Global Perspectives on Groundwater Decontamination: Advances and Challenges of the Role of Permeable Reactive Barriers

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Abstract: Ensuring access to clean water for drinking, agriculture, and recreational activities remains a global challenge. Groundwater, supplying approximately 50% of domestic water and 40% of agricultural irrigation, faces increasing threats from climate change, population growth, and unsustainable agricultural practices. These factors contribute to groundwater contamination, notably nitrate pollution resulting from excessive fertilizer use, which poses risks to water quality and public health. Addressing this issue demands innovative, efficient, and sustainable remediation technologies. Permeable reactive barriers (PRBs) have emerged as promising solutions for in situ groundwater treatment, using reactive media to transform contaminants into less toxic forms. PRBs offer advantages like low energy consumption and minimal maintenance. This study uses bibliometric analysis to explore the scientific production of PRBs for nitrate remediation, revealing research trends, key focus areas, and significant contributions. It included 141 articles published from 1975 to 2023. Early research focused on basic mechanisms and materials like zero-valent iron (ZVI), while recent studies emphasize sustainability and cost-effectiveness using low-cost materials such as agricultural byproducts. The findings highlight a growing focus on the circular economy and the need for more in situ studies to assess PRB performance under varying conditions. PRBs show significant potential for enhancing groundwater management and long-term water quality in agricultural contexts.

Keywords: permeable reactive barrier; groundwater; denitrification; nitrate; agro-industrial waste

1. Introduction

Ensuring access to high-quality water for human consumption, food production, and recreational activities remains a global challenge [1]. Notably, groundwater is the primary



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source of fresh water essential for sustaining life worldwide [2,3]. It is estimated to supply approximately 50% of the water used for domestic purposes and 40% for agricultural irrigation [4]. However, the integrity and availability of groundwater are increasingly threatened by a confluence of factors, including water stress, climate change, rising population, desertification, and the effects of conventional agricultural practices, both geogenic and anthropogenic in origin [1,4–6].

Groundwater contamination has consequently emerged as a significant and widespread global issue, closely linked to climate change, the water–energy–food nexus, public health, sustainable aquifer management, and extraction activities [3,7–10]. Given these challenges, groundwater management is intrinsically connected to the 17 Sustainable Development Goals (SDGs) established by the United Nations in the 2030 Agenda for Sustainable Development, particularly SDG 6 (Clean Water and Sanitation) and SDG 13 (Climate Action) [11]. This context underscores the pressing need for innovative strategies in the agro-industry that ensure efficient water use and protect groundwater quality.

Among the various forms of groundwater contamination, the presence of anionic pollutants, particularly nitrates, has become a pressing concern [12], especially in regions where groundwater is used for human consumption [13]. This issue is mainly driven by the excessive application of fertilizers and nitrogen-based chemicals in agriculture, which frequently leach into both surface and groundwater, appearing as nitrate, nitrite, and ammonium [14]. Studies reveal that only about 30 to 40% of nitrogen fertilizer is used by crops, while 12.5% to 45% of nitrogen ends up leaching into groundwater [15]. Agricultural practices are thus considered the leading global source of this pollutant, representing a diffuse source of contamination that ultimately reaches surface water and groundwater systems [4]. This contrasts with other pollution sources, such as septic tanks, wastewater treatment plants, industrial effluents, and landfills, categorized as point sources of pollution [2,16,17].

The consequences of nitrate contamination in groundwater are extensive, negatively impacting environmental, social, and economic sectors. In some cases, the harmful effects of nitrate pollution can be irreversible. To protect human health, the World Health Organization (WHO) has established a maximum permissible concentration of nitrate in drinking water at 50 mg/L [18], a similar value adopted by the European Union [19], in contrast with other countries such as the United States of America [20] and Canada with a maximum value of 45 mg/L [21,22].

Notably, acute risk exposure has intensified in many Asian countries. In contrast, chronic risk exposure has shifted from primarily affecting high-income regions, such as Europe and North America, to middle-income countries in Asia and Africa [23–25]. These findings underscore the urgent need for robust regulatory frameworks to reduce anthropogenic nitrogen inputs into aquatic ecosystems substantially.

Consequently, these pressing global environmental needs have led to the pursuit of sustainable alternatives for remediating contaminated groundwater. Among these alternatives, permeable reactive barriers (PRBs) have gained significant interest and have been broadly studied for the in situ treatment of groundwater contamination. PRBs offer a viable solution, emerging as a favorable alternative to the conventional pump-and-treat technology. While pump-and-treat methods have been widely applied, they are often criticized for their prolonged treatment duration and high operational costs [12,26–28]. This framework highlights the need for more efficient, cost-effective, and environmentally sustainable remediation techniques to address groundwater contamination challenges. Furthermore, tackling nitrate contamination requires an interdisciplinary approach integrating hydrochemistry, ecohydrology, and water management, among others, reflecting the complex interactions between natural processes and human activities.

PRBs offer an energy-efficient solution for groundwater treatment by utilizing natural water flow driven by gradient pressure, a process inherently linked to subsurface hydrology, thereby minimizing the need for additional energy inputs. This efficiency, low maintenance requirements, and long-term effectiveness make PRBs compelling for groundwater remediation [29–31]. PRB, strategically installed to intersect the contaminated groundwater flow at a perpendicular angle, employs reactive materials to transform harmful contaminants into less toxic forms directly at the treatment site [28]. The dynamics of contaminant movement and their interactions within the PRB are governed by two fundamental principles: Darcy's Law and Fick's Law, both of which are fundamental to hydrology and studies of contaminant transport. Darcy's Law provides insights into fluid flow through porous media, while Fick's Law describes the diffusion process, detailing how contaminants migrate from areas of higher concentration to lower concentration. These scientific principles are instrumental in modeling and predicting how contaminants diffuse through the PRBs' reactive materials, guided by the concentration gradients [12].

Research in this field has predominantly focused on laboratory analyses, state-of-the-art reviews, modeling, and in situ studies. Recently, there has been a notable increase in studies examining the application of in situ PRBs, particularly for treating nitrate contamination. Some innovative approaches have explored the use of solid organic substrates derived from agricultural waste, including wheat straw, rice straw, mulch, luffa, and corn cobs. These materials have shown promise in facilitating denitrification in PRBs for groundwater treatment. However, the initial stages of accelerated carbon release from some reactive materials can pose limitations. Despite these challenges, ongoing research emphasizes the need for more in situ or pilot-scale studies. These studies are crucial for assessing the longevity of PRBs and factors such as environmental, geological, and hydrological conditions at the site, particularly for remediating groundwater contaminated with nitrates [32,33].

Despite the agricultural sector's predominant role in contributing to groundwater contamination, it also holds the potential to be part of the solution. Bridging agricultural sustainability and groundwater hydrology through technologies like PRBs can foster circular economies, thereby mitigating environmental impacts. One way to address this and achieve some level of mitigation is by using agro-industrial waste PRBs for groundwater treatment and enhancing the industry's circularity [25,32,34–39]. These materials have shown promise in facilitating denitrification processes, offering a sustainable approach to addressing nitrate contamination.

An exploratory study employing bibliometric analysis is conducted to examine the scientific literature related to PRBs for the remediation of nitrate-contaminated groundwater. Bibliometric analysis is the study of the evolution of the scientific literature published over a specific period and within a particular research area, summarizing the development, trends, and impact of studies on the topic over time [40]. Various authors have employed bibliometric analysis; for instance, Guleria et al. conducted a bibliometric analysis on contaminant transport modeling. Their keyword co-occurrence analysis revealed a significant relationship between the groundwater node and the nitrate contaminant [40]. This approach has also been applied in fields such as geothermal studies [41], groundwater life cycle assessment [42], wetland ecosystems and climate change [43], sustainable water resource management [44], the food–energy–water nexus [45], and intellectual property [46].

In this context, implementing PRBs has emerged as a promising solution for mitigating nitrate contamination in groundwater, particularly when utilizing low-cost, locally sourced materials. This study examines how PRBs can utilize agricultural residues and industrial byproducts, which are often overlooked despite their significant potential for reuse in sustainable remediation strategies. These materials contribute to reducing envi-

ronmental impact by promoting resource efficiency and aligning with the principles of a circular economy. Although recent studies, such as Vakili et al. [47], have demonstrated a growing interest in using PRBs for groundwater remediation, this work presents a novel contribution by focusing specifically on nitrate removal, the role of agro-industrial waste, and their potential integration into circular and context-appropriate PRB systems. This study identifies key research trends, material performance, and implementation challenges through a comprehensive bibliometric and critical analysis, providing valuable insights for designing more sustainable and site-specific groundwater remediation technologies.

2. Materials and Methods

Literature reviews increasingly play a pivotal role in synthesizing scientific research, leveraging existing knowledge, and providing evidence-based insights that serve as valuable decision-making tools. While several qualitative and quantitative methods exist to understand, organize, and analyze literature, bibliometric analysis stands out for its ability to systematically provide statistical information based on elements such as titles, keywords, author names, and document types, among other pertinent information, allowing for addressing both global and local perspectives. This study employs a bibliometric analysis to address the following research question: how can PRBS for the remediation of nitrate contamination in groundwater provide effective solutions from the agricultural sector's perspective and enhance circularity? To address this target, the methodology of this study is structured into three distinct phases (Figure 1):

- **Data collection:** The Web of Science (WoS) database was used to access scientific articles from peer-reviewed journals. The literature review focused on nitrate, groundwater, and permeable reactive barriers. The search equation nitrate AND groundwater AND PRBs was applied in the topic search category, which includes keywords, titles, and abstracts. The search was conducted on 6 June 2023. The inclusion criteria encompassed publications from 1975 to 2023, resulting in 141 articles.
- **Document filtering:** The inclusion criteria for the type of documents encompassed articles, review articles, conference papers, news articles, and those designated as “early access” in all available languages. Data analysis from WoS indicated that 98.62% of the retrieved documents were in English, 0.69% in Mandarin, and 0.69% in German. Although the search was conducted for publications from 1975 to 2023, the earliest article retrieved in WoS that matched the topic search criteria and was available for full-text access was published in 2001. This indicates that either the terminology became widely adopted in indexed literature from 2001 onwards or that earlier works were not accessible through WoS at the time of the search. As a result, 136 documents were selected for in-depth analysis.
- **Data analysis:** A WoS data analyzer was employed to discern scientific production trends over time and identify key research areas of focus [21]. Graphical representations of bibliometric maps were created using the VOSviewer visualization software, version 1.6.19, developed by Jan Van Eck and Ludo Waltman [48]. VOSviewer is frequently used in bibliometric analyses to visualize bibliometric networks [49–52]. This utility is attributed to its functionality in constructing maps and groupings, either by the density of nodes or the distance between them, which signifies the relationships among the nodes [48]. The *.txt file exported from the Web of Science database was input into VOSviewer to generate these maps.

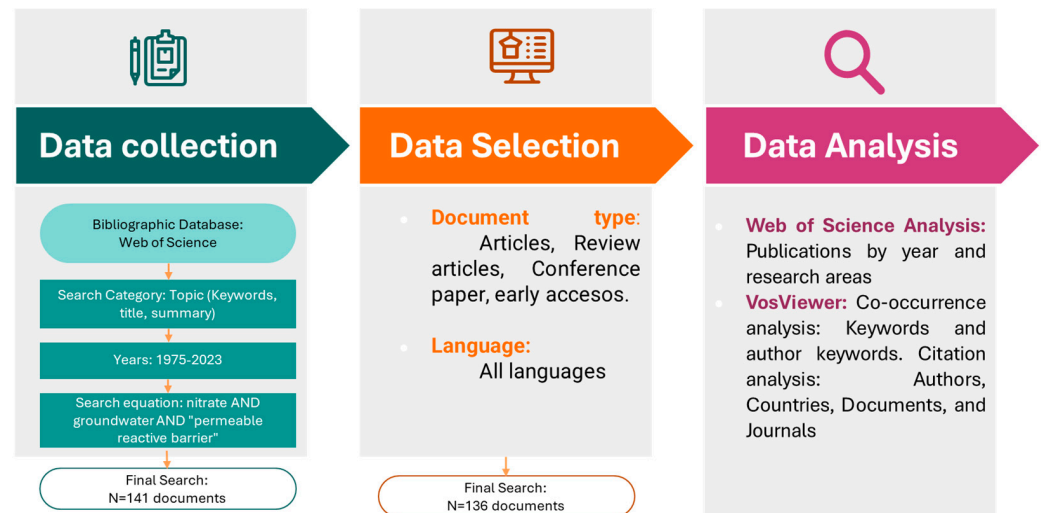


Figure 1. A research framework proposed for the bibliometric analysis of groundwater nitrate contamination remediation using PRBs.

A co-occurrence analysis of both total and author keywords was conducted to elucidate trends and connections within the scientific literature over the selected period [43]. First, the total keyword analysis was performed to examine the keywords used in the articles under review. This method identifies the selected articles' recurring themes, patterns, and connections [53]. Doing so reveals the primary topics and emerging trends in the relevant field of research. On the other hand, the author keyword analysis entails an examination of the frequencies and connections between the specific keywords chosen by each author. Such analysis provides a more detailed insight into the authors' research interests and approaches [54]. In bibliometric maps, the size of the circles increases in proportion to the frequency of a keyword's occurrence in the documents. Connections, indicated by links between keywords, reveal their relationships, with thicker lines denoting stronger relationships.

Additionally, the colors in the map delineate various groups or clusters, which are organized based on the strength of relationships between the keywords. Thus, closely related keywords appear closer to each other on the map. A citation analysis was also employed to assess the contribution of different countries, documents, and journals based on the total number of citations and articles published. Citations hold significant value in research as they are a key measure of the influence and impact of studies within a specific field [55].

Furthermore, a density view and an element label of the nodes were used to depict the results. The density view is instrumental in visualizing the significance of the map's most prominent areas or elements. Here, the color intensity of a map area correlates with the concentration of elements in a node and the relevance of its neighboring elements. The areas of greatest density represent higher importance, denoting a more extensive accumulation of documents or citations and their interconnectedness. Furthermore, in the label view, elements are represented by points or nodes. The size of each node reflects its significance within the overall map. Clusters or groups are formed through the relationships between these nodes, where the thickness of the lines connecting the nodes indicates the strength of their relationship and level of agreement [48].

3. Results

3.1. Evolution of the Scientific Production

The production of articles in the field has exhibited a rising trend in recent years, indicating an increasing interest in this area of research, as shown in Figure 2. A peak in publication volume was observed in 2020, with 15 articles published, representing approximately 9% of the total publications analyzed. Subsequently, there was a consistent output in both 2021 and 2022, with each year seeing the publication of 12 articles. However, a slight decrease is noted in 2023, with six publications recorded as of June 2023, as depicted. Regarding article types, 84.46% were research articles, 7.43% were review articles, and 5.41% were conference papers (Proceeding papers).



Figure 2. Annual scientific production on using PRBs for groundwater nitrate remediation over time.

3.2. Articles by Research Areas

The distribution of articles across various research areas is illustrated in Figure 3. It reveals that most of the articles fall within the thematic area of ecological environmental sciences, accounting for 42% of the total. This is followed by water resources, representing 22% of the articles, and engineering, comprising 21%. Other areas include geology, at 6%; applied microbiology in biotechnology, at 2%; chemistry, at 2%; and materials science and agriculture, which account for 1% of the total articles.

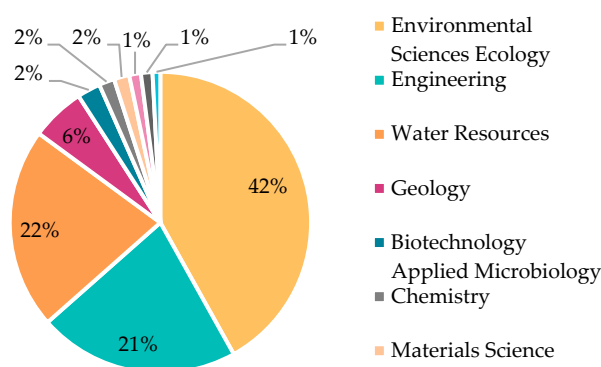


Figure 3. Overview of the field distribution of the final dataset retrieved from the WoS database and used for the bibliometric analysis, in which the environmental sciences ecology is the most prominent development field.

3.3. Bibliographic Mapping

3.3.1. Keyword Co-Occurrence Analysis

The co-occurrence analysis of keywords was key in revealing the research direction and the most significant topics related to PRBs and nitrate contamination over the analyzed period [55]. Drawing from the methodology developed by Salimi et al. [43], this analysis encompassed 136 articles and identified 776 keywords. By applying a minimum keyword occurrence threshold of five, 58 keywords were mapped, resulting in four distinct clusters.

The keyword co-occurrence network map, as depicted in Figure 4, illustrates the primary topics associated with PRBs, groundwater, and nitrate. The nodes' sizes in this map indicate the frequency with which specific keywords appear. Prominent keywords such as “permeable reactive barrier”, “denitrification”, “water”, “Zero valence iron”, and “groundwater” are represented by larger nodes, indicating a higher frequency of occurrence. This pattern suggests that the assessment of PRBs for remediating nitrate-contaminated groundwater has predominantly focused on materials like zero-valent iron (ZVI) and processes such as denitrification.

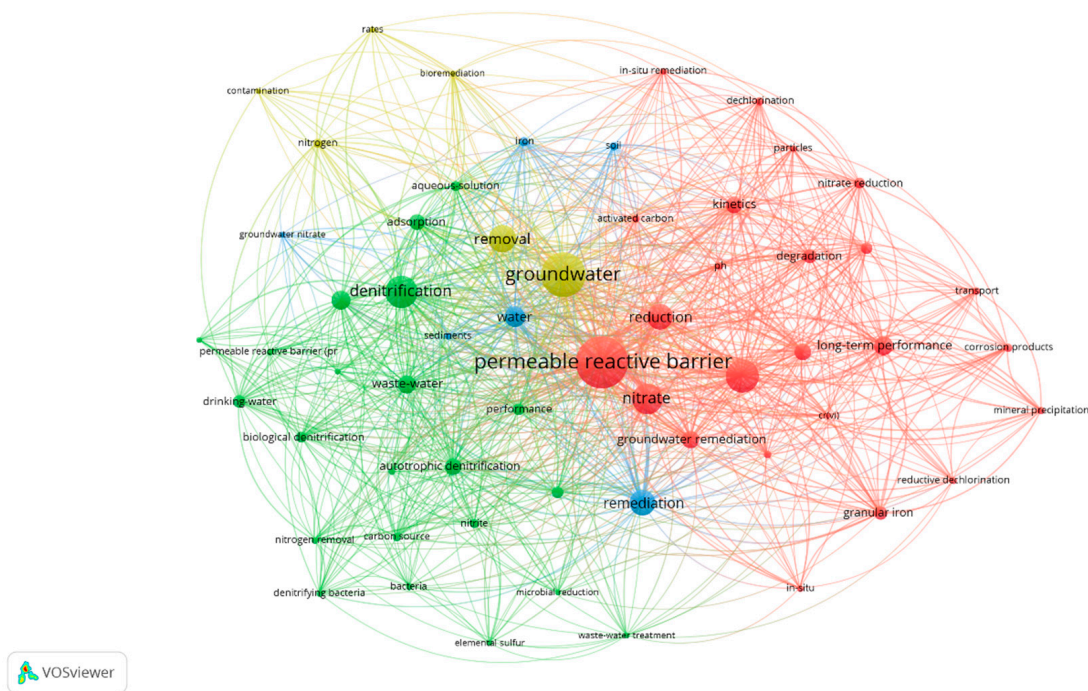


Figure 4. Keyword co-occurrence network map illustrating the most important topics related to permeable reactive barriers, groundwater, and nitrate.

Different clusters in the network map, denoted by various colors, highlight strong relationships among keyword groups:

- **Cluster 1 (red):** This cluster contained the highest number of keywords, totaling 24. The most frequent keywords were “permeable reactive barrier” (81 occurrences), followed by “Zero-valence iron” (45) and “nitrate” (41). Other significant keywords in this cluster included “groundwater remediation” (20 occurrences), “pH” (7), “nitrate reduction” (11), “long-term performance” (22), “in situ remediation” (6), “degradation” (15), “zero-valent iron” (19), and “transport” (7). The strong interconnection between ZVI, groundwater remediation, nitrate, and PRBs suggests that this cluster emphasizes using PRBs for groundwater remediation using ZVI.
- **Cluster 2 (green):** This cluster comprises 22 keywords, with “denitrification” (44 occurrences) as the most frequent, followed by “nitrate removal” (22) and “wastewater” (21). Additional keywords included “biological denitrification” (11), “contaminated groundwater” (12), “drinking water” (13), “denitrifying bacteria” (6), “carbon sources” (8), and “water treatment” (5). This cluster predominantly pertains to biological denitrification for nitrate removal.
- **Cluster 3 (blue):** This group included six keywords, led by “remediation” (33 occurrences) and followed by “water” (25). Other keywords were “sediments” (6), “soil” (8), “iron” (9), and “nitrate in groundwater” (5). This cluster focuses on water remediation for nitrate contamination.

- Cluster 4 (yellow): This group also comprised six keywords, with “groundwater” (66 occurrences) as the most frequent, followed by “removal” (35). Other keywords in this group included “rate” (5), “nitrogen” (9), “groundwater contamination” (12), and “bioremediation” (5). This cluster likely pertains to the bioremediation of nitrate-contaminated groundwater.

A temporal analysis of keyword occurrence from 2012 to 2018 revealed evolving trends, as shown in Figure 5. In 2012, keywords like “bioremediation”, “transportation”, “granulated iron”, “long-term performance”, and “hexavalent chromium” were prominent. Between 2012 and 2014, there was a shift towards keywords like “iron zero valence”, “pH”, “reduction”, and “kinetics”. From 2014 to 2016, there was a noticeable increase in keywords such as “permeable reactive barriers”, “groundwater”, “denitrification”, “bacteria”, “nitrate”, “nitrite”, “remediation”, “water”, and “nitrate reduction”. For the years 2016 to 2018, keywords such as “soil”, “nitrate reduction”, “removal”, “nitrate removal”, and “permeable reactive barriers” (PRBs) became increasingly prevalent. Following 2018, the focus shifted to terms such as “in situ”, “water treatment”, “microbial reduction”, “denitrifying bacteria”, “groundwater remediation”, “nitrogen”, “adsorption”, and “activated carbon”.

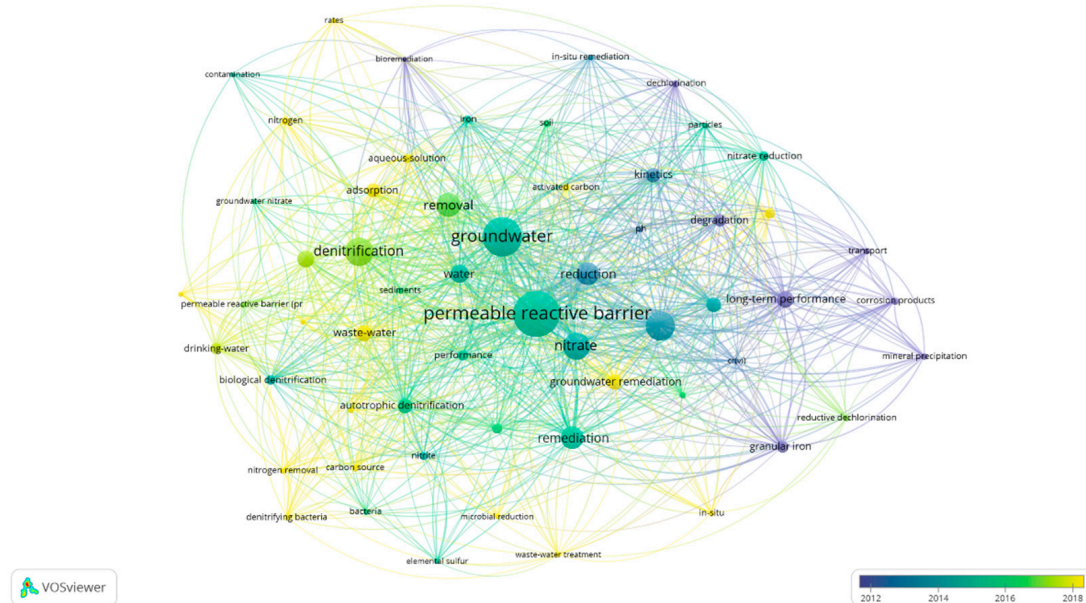


Figure 5. Temporal analysis of the keyword co-occurrence over the analyzed period for permeable reactive barriers, groundwater, and nitrate.

Overall, the shift in keywords over time reflects a movement from more traditional physicochemical remediation approaches to more integrated, often biologically based methods that offer sustainable, long-term solutions to pollution, particularly in groundwater and soil. The increasing complexity of keywords and the introduction of new terms suggest that the field is expanding with the latest technologies and that there is a growing understanding of the interactions between various remedial techniques and the environments in which they are applied. This trend is likely driven by the increasing global urgency to address pollution and sustainability in different sectors, such as agriculture, and the technological advances that enable more precise and effective interventions.

3.3.2. Co-Occurrence Analysis of Author Keywords

The author keywords were analyzed for the 136 articles, each with a minimum occurrence of five. Out of 411 total author keywords, 11 interconnected nodes or keywords were identified. The keyword network map highlights “permeable reactive barrier” as the

most frequent keyword (48 occurrences), followed by “denitrification” (32), “groundwater” (26), “nitrate” (24), and “zero-valent iron” (19). A strong linkage is observed between “permeable reactive barrier” and keywords such as “groundwater”, “nitrate”, “zero-valent iron”, and “denitrification”.

The map resulted in three groups, as observed in Figure 6a:

- Cluster 1 (red): Comprising four keywords, with “denitrification” having the highest frequency (32). Other keywords included “adsorption” (5), “permeable reactive barrier (PRB)” (6), and “remediation” (8).
- Cluster 2 (green): Containing four keywords, where “permeable reactive barrier” was the most frequent (48). It also included “groundwater remediation” (16), “nitrate removal” (9), and “zero-valent iron” (19).
- Cluster 3 (blue): Composed of three keywords, with “groundwater” being the most frequent (26), followed by “nitrate” (24) and “autotrophic denitrification” (7).

The keyword citation analysis is shown in Figure 6. Figure 6b shows that “groundwater”, “zero-valent iron”, and “nitrate removal” have the highest number of citations. At the same time, there is a decrease in citations for “permeable reactive barrier”, “denitrification”, “nitrate”, and “groundwater remediation”. The temporal analysis of the author’s keywords in Figure 6c reveals that up to 2012, the keyword “iron zero valence” was prominent. From 2012 to 2016, “permeable reactive barrier”, “nitrate”, and “groundwater” were key terms. From 2016 onwards, the terms “denitrification” and “groundwater remediation” gained more prevalence. This indicates the evolving focus of research over the past few years.

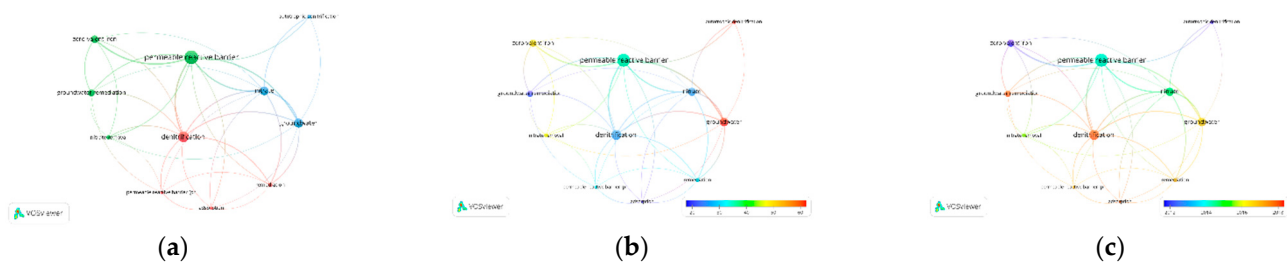


Figure 6. Co-occurrence analysis of authors’ keywords: (a) cluster analysis, (b) keyword citation analysis, and (c) temporal analysis of the authors’ keywords.

3.3.3. Distribution of Publications in Journals

The distribution of publications across journals is depicted in Figure 7, which shows the leading journals where the relevant articles were published. A minimum threshold of five documents per journal was applied, identifying nine journals out of sixty-one. A density visualization highlighted the journals with the highest citation count, with circle sizes proportional to each journal’s citation numbers. Larger circles indicate a higher citation frequency in that journal.

A relationship is observed between *Journal of Hazardous Materials* and *Chemosphere*. At the same time, a distinction is noted between *Water Research* and *Journal of Contaminant Hydrology*, which were found to be related. Table 1 provides detailed information on the number of citations and documents for each journal.

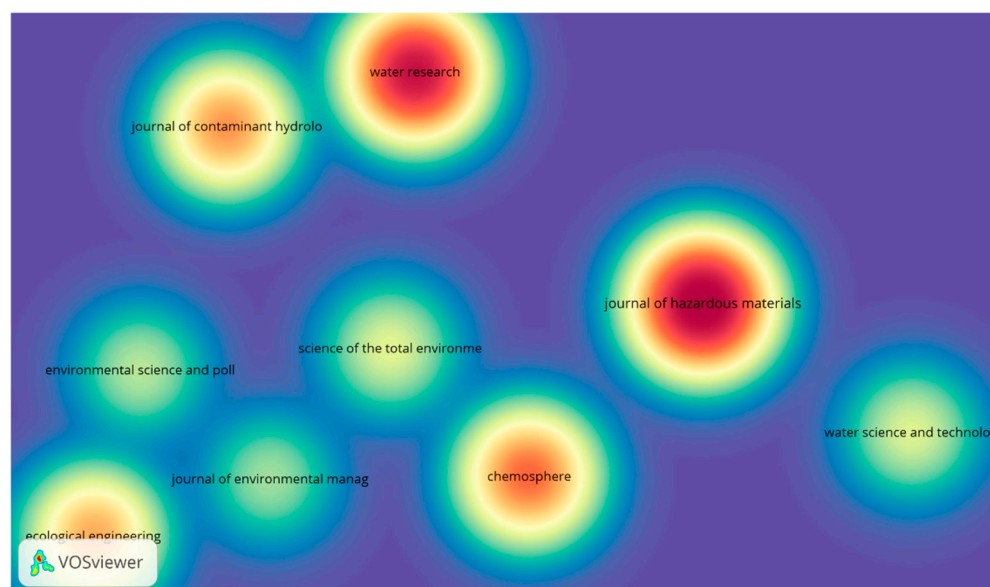


Figure 7. Distribution of publications across journals from the WoS database for PRBs, groundwater, and nitrate.

Table 1. Journals with the highest number of citations and documents.

Journal	Citations	Documents
<i>Journal of Hazardous Materials</i>	1180	5
<i>Water Research</i>	916	8
<i>Chemosphere</i>	469	10
<i>Journal of Contaminant Hydrology</i>	361	8
<i>Ecological Engineering</i>	316	5
<i>Science of the Total Environment</i>	96	6
<i>Water Science and Technology</i>	92	5
<i>Environmental Science and Pollution Research</i>	68	7
<i>Journal of Environmental Management</i>	57	9
Total	3555 citations	63 documents

The journal *Journal of Hazardous Materials* leads in citation counts with 1180 citations, followed by *Water Research* with 916 citations, *Chemosphere* with 469 citations, and *Journal of Contaminant Hydrology* with 361 citations. Notably, *Chemosphere* has the highest number of published documents, totaling ten, whereas *Journal of Environmental Management* has nine publications, and both *Journal of Contaminant Hydrology* and *Water Research* have eight. Of the 61 surveyed, these nine journals account for 46% of the published documents and 51% of the citations, highlighting their significant contribution to this field.

3.3.4. Contributions—Country

A citation analysis was conducted to identify the countries most cited in this research area. A threshold of at least five documents per country was set, including eight countries out of thirty-seven. The density visualization for citations (Figure 8) indicates that the United States has the highest number of citations, totaling 3306, followed closely by China, with 3191. Other notable contributions include Italy with 486 citations, South Korea with 331, Spain and Japan with 207, Canada with 153, and Iran with 95.

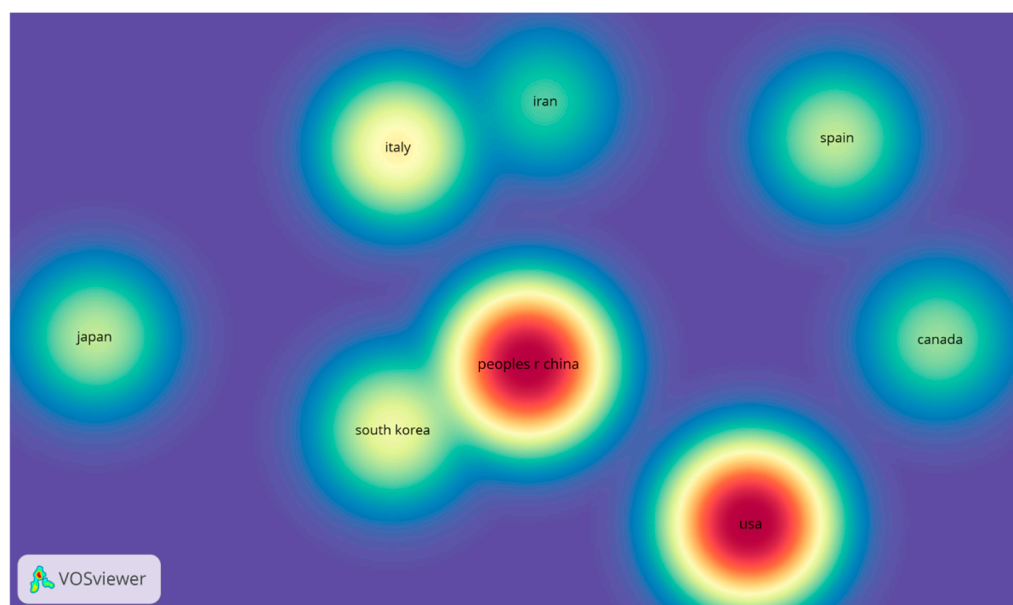


Figure 8. Density visualization of citations by country from the Web of Science (WoS) database for PRBs, groundwater, and nitrate.

Regarding document contributions, China has the highest number of publications, accounting for 50 documents. The United States follows with thirty-three publications, South Korea with twelve, Iran with ten, Spain with eight, Italy with seven, and Canada contributing with six. Most of the document production is concentrated in Asia. However, North American countries, specifically the United States and Canada, contributed significantly, with 38 documents. With two documents, Brazil is highlighted as the sole Latin American country contributing to this field (Figure 9).

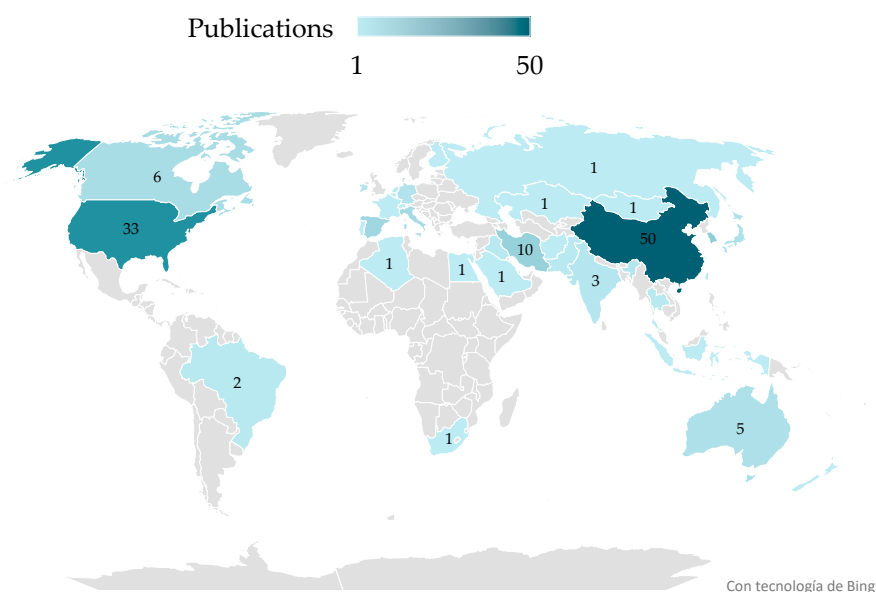


Figure 9. Density visualization of document contributions by country from the WoS database for PRBs, groundwater, and nitrate.

3.3.5. Most Cited Published Documents

An analysis was conducted to identify the most cited documents in the field, setting a minimum criterion of 150 citations per document. This threshold resulted in the selection of nine documents out of one hundred thirty-six. These documents were mapped using

VOSviewer, which eased the analysis of the most relevant and frequently occurring terms within these documents, thus revealing the relationships among them (Figure 10).



Figure 10. Most relevant authors based on a cluster analysis of the number of publications in WoS [14,56–63].

Cluster 1 comprises the most significant number of nodes, with five documents [56–60]. These documents primarily focus on using ZVI in water treatment and as a component in PRBs. ZVI has been extensively studied and applied in the treatment of toxic groundwater contaminants due to its abundance, cost-effectiveness, and reducing capacity for oxidized contaminants, such as hexavalent chromium (Cr (VI)) [60].

For instance, Lai and Lo [58] undertook an evaluation of hexavalent chromium (Cr (VI)) removal using acid-washed ZVI (AW-Fe0) under varied groundwater geochemical conditions using column experiments. This research highlights the potential of ZVI in addressing specific challenges posed by contaminants. Similarly, the study in [59] focused on the kinetics of arsenate As (V) and arsenite As (III) elimination using ZVI in aqueous solutions through batch assays. This study highlighted the efficacy of ZVI as a reactive medium in PRBs, particularly for mixed inorganic contaminants. It also highlighted the necessity of considering the effects of anion competition in designing such barriers for field applications.

Furthermore, Alowitz et al. [56] investigated the influence of various iron metal types, surface area concentration, and pH values (ranging from 5.5 to 9.0) on nitrate, nitrite, and Cr(VI) removal rates. The findings from this study are crucial in determining the parameters for effective PRBs.

In a comprehensive review, Fu et al. [60] discussed the recent advances of ZVI as a reactive material, the range of contaminants it can remove from groundwater and wastewater, its reaction mechanisms, and its efficiency in contaminant removal. This review concluded that while ZVI barriers are effective for in situ groundwater remediation, their long-term performance issues and the potential benefits of combining ZVI with other materials or technologies warrant further exploration.

Additionally, Guan et al. [57] explored the limitations of ZVI technology in a review article, proposing various countermeasures and future research directions. This study highlights the importance of improving ZVI corrosion resistance and enhancing reactant mass transfer to broaden the application scope and increase the efficiency of ZVI-based treatments.

Cluster 2, comprising three significant documents [14,59,60], explores the use of organic carbon sources in denitrification to remove nitrate. This cluster provides valuable insights into the efficacy and dynamics of different organic materials in enhancing the denitrification process. For instance, Gibert et al. [14] focus on assessing the nitrate removal capacity of seven organic substrates through batch experiments. Following these initial tests, one substrate was chosen for further exploration in bench-scale column experiments,

simulating a PRBs. The study found that a softwood organic substrate, comprising branches, bark, and a minor proportion of leaves, exhibited a remarkable nitrate removal efficiency of over 98% through denitrification. This efficiency was significantly higher than other substrates, including hardwood, mulch, conifers, willow wood chips, compost, and freshly fallen leaves. Consequently, softwood was identified as an adequate material for PRBs, offering an alternative to traditional wood usage.

In contrast, Cameron et al. [63] suggest a shift from the conventional use of wood media in PRBs to more labile carbon sources, arguing that these alternatives could achieve higher nitrate removal rates and potentially reduce installation costs. This study comprehensively evaluated the effectiveness of nine diverse organic carbon sources, each with five different particle sizes, to ascertain the impact of particle size on the denitrification process. This study was conducted over a period of 23 months and at varying temperatures. It stands out due to its extended timeframe and the significant volume of carbon media tested, surpassing previous laboratory-scale experiments. Among the materials analyzed, corn cob and hardwood emerged with notable nitrate removal rates, highlighting the potential of varied organic substances in denitrification.

In another study, Wang et al. [62] offer a broad analysis of the solid-phase denitrification process, focusing on diverse types of solid carbon sources used for nitrate removal in water. This review encompasses both natural and synthetic biopolymers, including wood chips, sawdust, straw, cotton, corn cobs, algae, bark, polyhydroxyalkanoates (PHAs), polycaprolactone (PCL), polybutylene succinate (PBS), polylactic acid (PLA), and various other biodegradable polymers. These materials display desired efficiency, cost-effectiveness, and availability. Additionally, the study addresses critical aspects, including the influence of these materials on the microbial community in biofilms, potential adverse effects, and the overall costs associated with the denitrification process.

Cluster 3 comprises a single yet influential study performed by Rocca et al. [61], which, despite its standalone position, is one of the most cited in this field of study. This document presents a comprehensive review article that addresses various technologies for treating nitrate-contaminated waters, primarily focusing on in situ applications. These include chemical reduction, adsorption, and biological denitrification, which can be implemented via PRBs or the direct injection of liquid and gaseous reactive compounds into groundwater. This review proposes an innovative approach that combines heterotrophic and autotrophic denitrification processes, utilizing cotton as a source of organic carbon, a support material, and ZVI to generate cathodic hydrogen gas. This combination enhances autotrophic growth and effectively removes contaminants like nitrate, chlorinated ethane, and chromium (VI) from water bodies.

In addition to the insights provided by individual studies, Table 2 offers a comprehensive overview of the nine most cited articles in the domain. It details the number of citations each article has received and the frequency of these citations. The article [39] leads the list with 1078 citations, followed by Guan et al., 2015 [57] and Alowitz and Scherer, 2002 [56] with 635 and 538 citations, respectively. Notably, Fu et al., 2014 [60] also hold the highest citation frequency, calculated as the total number of citations divided by the number of years since publication, with a score of 119.78. This is followed by Guan et al., 2015 [57] with 79.38 and Wang and Chu, 2016 [62] with 48.57, indicating these works' significant and ongoing impact on the field.

Table 2. The most cited publications analyzed from the WoS database for PRBs, groundwater, and nitrate.

Article	Year	Citations	Document Type	Citation Frequency	Reference
The use of ZVI for groundwater remediation and wastewater treatment: A review	2014	1078	Review	119.78	[60]
The limitations of applying ZVI technology in contaminants sequestration and the corresponding countermeasures: The development of ZVI technology in the last two decades (1994–2014)	2015	635	Review	79.38	[57]
Kinetics of Nitrate, Nitrite, and Cr (VI) Reduction by Iron Metal	2002	538	Article	25.62	[56]
Arsenate and arsenite removal by ZVI: Effects of phosphate, silicate, carbonate, borate, sulfate, chromate, molybdate, and nitrate, relative to chloride	2001	397	Article	18.05	[59]
Biological nitrate removal from water and wastewater by solid-phase denitrification process	2016	340	Review	48.57	[62]
Nitrate removal and hydraulic performance of organic carbon for use in denitrification beds	2010	213	Article	16.38	[63]
Overview of In-Situ Applicable Nitrate Removal Processes	2007	205	Review	12.81	[61]
Removal of chromium (VI) by acid-washed ZVI under various groundwater geochemistry conditions	2008	184	Article	12.27	[58]
Selection of organic substrates as potential reactive materials for use in a denitrification PRB.	2008	174	Article	11.60	[14]

4. Discussion

Global research on nitrate pollution, groundwater quality, and PRBs highlights a dynamic interest in developing innovative and sustainable methods for treating contaminated groundwater. These studies primarily focus on utilizing PRBs to remove pollutants, thereby enriching the field of environmental sciences, with a particular emphasis on water resource management. The comprehensive literature review portrays research directions in ecological and environmental sciences, water resources, and engineering, highlighting emerging trends and challenges of groundwater remediation. The focus on PRBs highlights their significance in purifying nitrate-contaminated water, with a targeted investigation into ZVI groundwater remediation and nitrate removal. The review identifies diverse research strategies, underscoring significant advancements and ongoing challenges in groundwater decontamination. The analysis reveals a comprehensive integration of concepts, with PRBs emerging as a pivotal technology for treating nitrate-contaminated water. The prevalent use of ZVI in PRBs for nitrate removal and groundwater remediation reflects a concentrated scholarly interest in these materials and methods, mapping a clear trajectory for future research in these vital areas.

4.1. Permeable Reactive Barriers: Global Perspective

An analysis of 141 publications from 1975 to 2023, primarily conducted by China, the United States, and South Korea, reveals these countries as leaders in environmental research, largely due to their rapid industrialization and deteriorating water quality. The alignment of this work with the United Nations' Sustainable Development Goals (SDGs) reflects its international influence. Despite the limitations of English-focused analysis, broader reviews employing bibliometric analysis offer insights into the hydrological, chemical, geological, and microbiological challenges. Abiotic removal of arsenic and other contaminants is a promising water quality technology, with denitrifying bacteria also improving the hydraulic flow.

However, challenges such as carbonate accumulation and material selection must be addressed to improve the effectiveness of PRBs in water pollution control. Long-term field testing and research on microbial interactions are essential for continuously improving PRBs for sustainable groundwater remediation. Overcoming ion competition, biofouling, and economic profitability is crucial for advancing PRB technology.

These implications underscore the importance of ongoing research, in situ validation, and multidisciplinary approaches to ensure the effectiveness, sustainability, and practical applicability of proposed groundwater remediation technologies. Future research opportunities in groundwater remediation include exploring global trends, analyzing country-specific contributions, and fostering interdisciplinary collaboration among ecological, environmental, water resources, and engineering sciences. Aligning research with the United Nations' Sustainable Development Goals (SDGs), particularly SDG 6, which focuses on clean water and sanitation, is crucial for addressing challenges and enhancing remediation technologies.

In addition, implementing PRBs must align with national and international regulatory frameworks to ensure safe and practical application in groundwater protection. In the United Kingdom, the Environment Agency developed a regulatory approach combined with best practice guidance to support the deployment of PRBs for various contaminants, including mixed plumes [64]. This regulatory support has facilitated the transition from pilot to full-scale PRB applications, particularly for controlling diffuse groundwater pollution, aligning with the EU Water Framework Directive.

Similarly, PRB systems have been tested in Belgium under laboratory conditions to treat landfill leachate, successfully reducing contaminants to levels below regulatory discharge limits [65]. In China, the development of multimedia PRBs (M-PRBs) has also demonstrated compliance with regulatory thresholds for ammonium and nitrate levels in groundwater [66]. These examples highlight how PRBs can be engineered to meet specific legal and environmental standards.

At the international level, the United Nations Sustainable Development Goal 6 (Clean Water and Sanitation) emphasizes improving water quality by reducing pollution and minimizing the release of hazardous chemicals and materials. PRBs, especially those utilizing low-cost and sustainable media, provide an effective tool to help achieve these goals by supporting the safe reuse of groundwater resources for both agricultural and domestic use.

Despite these advances, global policy integration remains uneven. More efforts are needed to harmonize technical guidelines, performance monitoring, and post-installation assessments of PRBs. Future research should evaluate the integration of PRBs into national water policies, considering regional priorities, environmental standards, and long-term sustainability.

4.2. Exploring Opportunities: Challenges in Research Outcomes

Challenges in hydrological, chemical, geological, and microbiological aspects encourage the development of integrated analyses that consider the interplay between these elements and their collective impact on the effectiveness of groundwater remediation strategies [7]. A thorough analysis of the effects of competing anions, such as phosphates, silicates, carbonates, borate, sulfates, chromate, molybdate, and nitrates, on the removal of arsenic species using iron oxide as a PRB is crucial in the studies reviewed [59,67–71]. Additionally, some research significantly focuses on understanding microbial dynamics [72–74] for the in situ implementation of PRBs [69,75–82], with particular emphasis on removing diverse pollutants like uranium, technetium, and nitrate, highlighting the importance of biological processes in the effectiveness of these barriers [7,24,34,38,61,71,78,83–96].

The reviewed studies emphasize the critical role of hydrological conditions, including flow dynamics, permeability variations, and residence time, in determining nitrate attenuation efficiency [16,81,97]. Groundwater flow variability, influenced by fractured bedrock, dual flow systems, and dilution from river sources, can create preferential pathways that reduce the uniformity of contaminant capture and nitrate reduction efficiency [81,97,98].

Chemical interactions, including pH fluctuations and the corrosion of reactive metals, further influence the performance of PRBs by affecting both permeability and reactivity. Corrosion products, such as iron oxides and carbonates, can precipitate and reduce the permeability of reactive media over time, hindering nitrate removal. The presence of competing anions, including phosphates, sulfates, and carbonates, can also interfere with nitrate reduction capacity by altering the reactivity of the PRB media and limiting the available reactive surface area [50,81,97,99]. As highlighted in the reviewed papers, effective modeling and scenario analysis require the simultaneous consideration of these chemical processes alongside hydrological complexity to ensure accurate predictions of long-term remediation performance [50,97,99].

Geological heterogeneity introduces another layer of complexity, as variations in aquifer structure and substrate composition impact the transport and dilution of contaminants. Variations in soil composition and low-permeability zones can either promote localized treatment efficiency or lead to contaminant bypassing, depending on the distribution of reactive media and the hydrogeological setting. For example, while PRBs succeeded in nitrate attenuation in some regions, areas with lower permeability and complex flow patterns exhibited lower treatment efficiency, emphasizing the importance of site-specific assessments for optimized performance [16,97,98].

Microbiological factors, such as the activity of denitrifying bacteria, also play a critical role in nitrate removal within PRBs [16]. The interaction between microbial communities, hydrological residence time, and the availability of carbon sources can significantly affect the denitrification rate and overall PRB efficiency [16,43]. However, microbial activity can also contribute to biofouling and clogging over time, thereby reducing the permeability and long-term sustainability of the remediation system. Furthermore, temperature changes and nutrient availability influence microbial activity and reactive media stability, underscoring the need for balanced biological activity with long-term operational stability [43,97].

The evaluation of the impact of chemical processes on the hydraulic performance of PRBs through experiments with FeO provides valuable insight into this scientific dialogue [100]. Moreover, the discussion extends to metallurgical processes in PRB applications, addressing the associated operational challenges and the relevance of heterotrophic–autotrophic denitrification coupling [101,102]. From exploring alternative carbon sources to reducing nitrates with zero-valent nanoparticles and assessing the long-term performance of denitrification walls, these studies offer practical and economically viable solutions for environmental remediation [72,90,103,104]. Understanding the complexities of chem-

ical and biological processes is crucial for designing effective strategies in groundwater contaminant remediation, significantly contributing to advancing knowledge in this multidisciplinary field.

Considering these interconnected hydrological, chemical, geological, and microbiological processes, the reviewed studies emphasize the need for integrated assessment frameworks in designing and evaluating PRBs for groundwater nitrate remediation. The dynamic interaction between these factors improves the reliability of treatment strategies and underscores the importance of site-specific variability in remediation performance [16,43,50,81,97–99].

Furthermore, while numerous studies highlight the potential and success of PRBs in nitrate and heavy metal remediation, it is equally important to examine real-world limitations and operational failures that have emerged in field applications. For instance, Liang et al. [105] found that nitrate removal efficiency decreased over time due to biomass overgrowth and carbonate precipitation, which reduced permeability and limited contaminant contact with reactive zones. Similarly, Grau-Martínez et al. [106] documented the failure to fully intercept the contaminated plume, which was caused by hydrogeological heterogeneity and insufficient pre-installation site characterization, leading to preferential flow and bypassing. In Zhang et al. [33], the Cr(VI) removal efficiency declined as ZVI particles became passivated, and seasonal hydraulic changes led to plume diversion, indicating the importance of adaptive design strategies. Gibert et al. [107] reported unexpected dilution from lateral water inputs due to heavy rainfall, which affected the interpretation of nitrate removal performance, highlighting the need for continuous hydrological monitoring. In the studies performed by Wen et al. [36], early operation of a PRB filled with raw agricultural straw led to secondary pollution from nitrogen compounds and high chromaticity, prompting the development of engineered composite materials (e.g., SCCMs) to regulate carbon release and enhance microbial activity. Lastly, Liu et al. [108] showed that loess-based barriers lost performance as the adsorption capacity for heavy metals reached saturation and contaminant sources expanded beyond the PRB's effective range. These real-world cases underline that PRB failure often results from inadequate site assessment, media degradation, and unanticipated external factors. This reinforces the need for modular, resilient, and site-specific PRB systems supported by long-term monitoring. These findings emphasize that beyond laboratory efficacy, the field performance of PRBs relies heavily on adaptable design, material stability, and continuous environmental assessment to prevent long-term system degradation.

4.3. Comparison of PRB with Other Technologies for Groundwater Nitrate Remediation

Given their established role in groundwater remediation, PRBs, particularly those using ZVI or enhanced with nanoscale materials, are often used as a benchmark against which alternative or complementary technologies are evaluated. Recent studies have explored integrated systems, innovative configurations, and competing approaches, including electrokinetic regeneration, constructed wetlands, and non-pumping reactive wells, providing insights into each technique's comparative advantages, limitations, and suitability. Nanoscale zero-valent iron (nZVI) has further enhanced these barriers' reactivity and surface area, improving nitrate reduction rates in many laboratory and pilot-scale studies [109,110]. However, these applications are not without challenges. Issues such as long-term clogging, limited permeability, agglomeration of nanoparticles, and potential environmental toxicity, especially from nZVI, necessitate exploring complementary or alternative approaches.

Several studies have sought to integrate or compare PRBs with other technologies to enhance performance or overcome limitations. Ghaeminia and Mokhtarani [88] inves-

tigated an integrated PRB–electrokinetic (PRB-EK) system, which regenerates saturated activated carbon in situ and prolongs the media’s lifespan by promoting nitrate migration via electromigration and electroosmosis. This combination effectively extended treatment longevity from 59 to 111 h, indicating that electrokinetics can complement PRBs by rejuvenating reactive media and enhancing nitrate mobility within the barrier. Similarly, Alyani et al. [111] demonstrated that coupling electrokinetics with granular activated carbon in a PRB system can significantly enhance nitrate removal efficiency, achieving reductions of over 90% depending on the applied voltage. Their findings underscore the relevance of optimizing electrical parameters and system configuration. They demonstrate that electrokinetic-assisted PRBs can outperform conventional systems, particularly in terms of treatment duration and adaptability to variable flow conditions. Furthermore, the study highlighted the importance of pH control and current intensity in maintaining high removal rates without compromising water quality.

Maharjan et al. examined constructed wetlands (CWs), particularly those with tidal flow and zeolite substrates [112]. Unlike PRBs, CWs integrate plants and microbial processes as a passive, low-cost alternative and are particularly well suited to small rural settings. Although CWs do not achieve the same reaction rates as chemically driven PRBs, their sustainability and biological regeneration potential, especially for ammonium nitrogen, make them attractive under certain conditions. These systems function as a contrast rather than a complement to PRBs, offering different operational and ecological advantages.

Non-pumping reactive wells (NPRWs) filled with mixtures of nZVI and carbon substrates present another promising alternative, particularly for deep aquifers where traditional PRBs are impractical [104]. NPRWs serve as a functional substitute for PRBs, enabling modular deployment at greater depths and mitigating the risks associated with direct nanoparticle injection. Integrating chemical and biological denitrification processes in NPRWs enhances their robustness and adaptability to varying groundwater conditions.

Pulse injections of nZVI in well-based denitrification systems (WDBs) represent a dynamic variation of in situ treatment. Gibert et al. [107] demonstrated that combining biostimulation (with acetate) and nZVI-assisted abiotic chemical nitrate reduction (ACNR) resulted in greater than 99% nitrate removal, significantly outperforming either method alone. This synergistic approach addresses the limitations of PRBs, such as reactivity loss or microbial inhibition, and can be applied in scenarios that require rapid intervention without the need for permanent subsurface structures.

A similar enhancement strategy was explored by Khalil et al. [113], who developed a continuous-flow system incorporating nZVI and bimetallic nZVI-Cu. Their findings highlighted the role of operational parameters (e.g., recirculation and Cu doping) in mitigating the influence of interfering substances in natural waters, showcasing potential improvements applicable to PRBs as well.

Systematic reviews by Araújo et al. [110] and Eljamal et al. [109] underscore both the promise and the uncertainty surrounding nZVI-based PRBs. While laboratory and pilot-scale studies confirm their efficacy, long-term environmental and health risks, including particle agglomeration and mobility, remain areas of concern. These reviews suggest that the success of nZVI-PRBs hinges on factors such as stabilization methods, delivery techniques, and site-specific hydrogeology.

More complex systems, such as sequential multi-barriers combining oxygen-releasing compounds (ORCs), clinoptilolite, and spongy iron, offer an advanced form of PRB with distinct functional zones for nitrification, ion exchange, and denitrification [114]. This multibarrier design reflects a trend toward hybrid PRBs that integrate multiple removal mechanisms, aiming to address the limitations of simpler systems. While performance was

promising, with up to 90% ammonium nitrogen removal, challenges such as diminished capacity over time and the need for design optimization remain.

Overall, PRBs remain a core technology in groundwater remediation; however, their integration with electrokinetic, NPRWs, CWs, and pulse-injection systems reveals a broader toolkit for tailored, site-specific solutions. The continued evolution of PRB design, primarily through nanoscale materials and multi-zone configurations, suggests a future in which hybrid and adaptive systems will play an increasingly central role.

4.4. Addressing Economic and Viability Challenges Associated with the Use of Reduced Metals in Remediation Methods

The generation of metallic ions and pH changes present an opportunity to optimize the PRBs employed. Detailed studies of bacterial release and iron as byproducts of nitrate removal and assessing effects from impurities derived from limestone and other minerals present in decontamination procedures significantly enhance their effectiveness [28,92,115] and mitigate environmental safety implications [87,116–118].

Regarding the challenges inherent to hydrochemical, microbiological, and geochemical processes in developing practical and sustainable strategies, environmental factors such as temperature, fluid dynamics in aquifers, and the effectiveness of carbon sources against the raw materials used for the PRB are noteworthy. For barriers using biological raw materials, the variability in effectiveness depends on the contaminants, which affect water quality and influence salinity indices [70,119–122]. Likewise, the residence time of contaminants within the barrier depends on the raw materials [24,25,34,36,123] of the barrier and its design [65,109,116], as well as the temperature and permeability of the barrier [85,124–126]. One factor that influences in situ measurement results is the barrier's response to the hydrogeological and chemical environment, as it limits contaminant capture and can yield results that differ significantly from those of laboratory tests. Addressing these limitations could improve the effectiveness and sustainability of PRBs in groundwater remediation.

4.5. Agricultural Industry as a Source of Materials and a Pathway for Sustainability and Circularity

Agricultural activities are a significant source of groundwater contamination, introducing pollutants primarily through fertilizers and pesticides to maximize global crop yields. These practices have significantly increased food production by tripling it over the past fifty years, largely due to the extensive use of nitrogen fertilizers [36,38,127]. Besides this, agricultural activities and their byproducts and waste can generate material that, if not disposed of properly, can pose substantial health and environmental risks [122,128,129], increasing the sources of pollution and problems associated with agricultural activity and agricultural engineering.

As widely reported in the literature, denitrification, a primary process for nitrate reduction in the vadose zone and groundwater, often faces limitations due to the scarcity of organic carbon. However, available research has indicated that adding an organic layer under the topsoil at point sources, like septic tank drainage fields and composting sites, enhances nitrate removal, recognizing the effectiveness and potential use of some agricultural residues such as pine bark, distillers' grains, woodchips, and corncob, that exhibits high C/N ratios and permeability [34,36,39,62,66,102,130–132]. These materials not only offer a sustainable alternative but also exhibit high denitrification performance, which can be further enhanced through alkaline treatment to increase the digestibility of carbohydrates like cellulose and hemicellulose [74,131,133]. This treatment has effectively exposed biodegradable components to bacteria, increased lignin removal efficiency, and facilitated the breakdown of complex organic materials [132].

The use of agro-industrial waste for biological denitrification presents a promising method for mitigating the environmental impacts of agriculture. This strategy promotes sustainability and circularity by repurposing agro-industrial waste as raw materials for PRBs [25,115]. It demonstrates that these materials can release more carbon than other natural resources, such as woodchips, underscoring their potential in sustainable groundwater remediation practices.

Finally, as depicted in Figure 11, the evolution of PRB research has demonstrated significant advancements from its inception in the 1990s to the present day. Early developments focused on the fundamental concepts and mechanisms using ZVI to address chlorinated solvents and heavy metals. As the research progressed into the mid-2000s, the scope broadened to include diverse materials, such as iron sulfides and zeolites, and the integration of biological processes, including heterotrophic–autotrophic denitrification, to tackle a more comprehensive array of contaminants. The late 2000s brought attention to practical challenges, emphasizing hydraulic conductivity, mineral precipitation, biofouling, and efforts to optimize PRB design for real-world applications. The early 2010s witnessed the introduction of advanced materials, particularly nano zero-valent iron (nZVI), which enhanced initial reactivity and highlighted the need for stability and mass transfer solutions. Recent developments since the mid-2010s have shifted towards sustainability and cost-effectiveness, incorporating low-cost materials like agricultural byproducts and combining various reactive media to enhance efficiency and longevity.

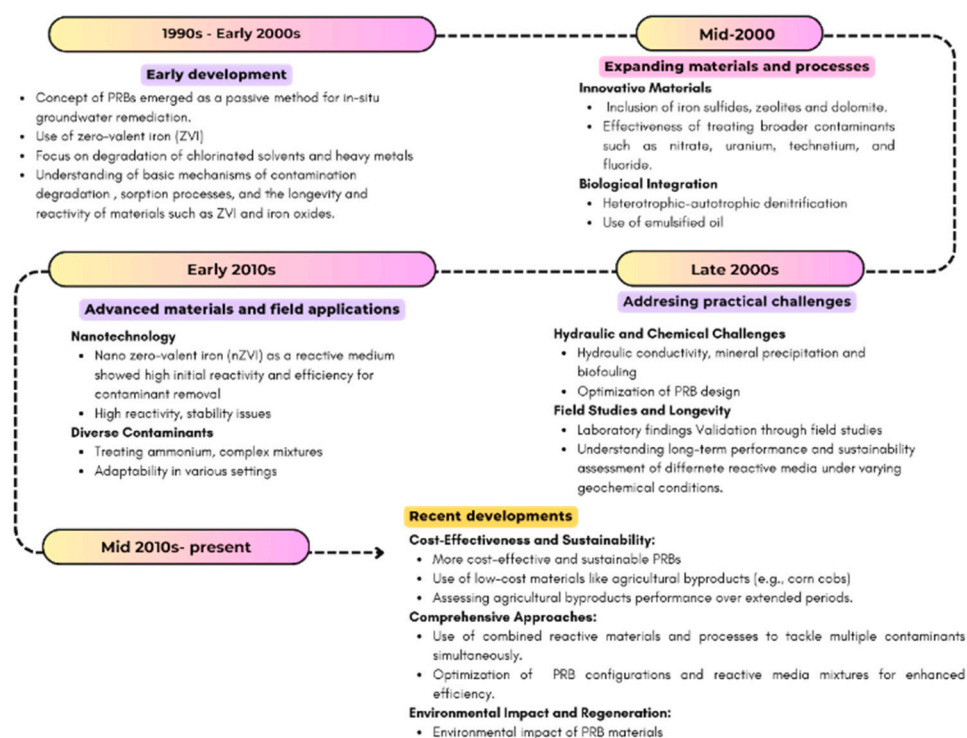


Figure 11. The overall development timeline of PRBs for groundwater denitrification.

To critically assess the diversity and performance of materials explored in the recent literature, including agricultural byproducts, biodegradable polymers, and various iron-based media, a comparative synthesis is presented in Table 3. This table highlights key operating conditions, nitrate removal efficiencies, byproduct formation, and notable observations from selected studies. Including PRB-implemented systems and potential candidates under simulated conditions allows a broader understanding of current advances and practical challenges in designing and optimizing reactive barriers for nitrate remediation.

Table 3. Comparative analysis of materials for nitrate removal in PRB and related systems.

Active Material	Operating Conditions	Nitrate Removal (%)	Byproducts	Key Observations	PRB Implemented	References
ZVI granular	Lab column, 1.2 m depth, 25 °C	>95%	NH ₄ ⁺ , trace NO ₂ [−]	Effective long-term nitrate removal with gradual passivation	Yes	[59]
Agricultural waste + ZVI (sawdust + corn stalks + zeolite)	Column, 30 °C, 65 mg/L NO ₃ [−]	>90%	NH ₄ ⁺ (0.02–0.12 mg/L), NO ₂ [−] (0.7–2.5 mg/L)	Sawdust + corn stalks + zeolite show stable removal	Yes	[87]
Corncob + zeolite	Lab column, 16 °C, HRT 2.5–24 h	85.9–98.9%	NO ₂ [−] , NH ₄ ⁺ transient	Corncob shows efficient removal at different NO ₃ [−] levels	Yes	[34]
Sequential PRB (biozone + ZVI)	Column setup	>95%	NO ₂ [−] , NH ₄ ⁺	Biozone enhances nitrate reduction prior to ZVI	Yes	[104]
nZVI + xanthan + mulch	Column setup, 10 days	5.7% ↑ vs. bare nZVI	Not specified	Stabilization improves longevity and performance	Yes	[129]
mZVI + AC in alginate	Batch tests, pH 7	2.46× vs. mZVI	None reported	Encapsulation prevents aggregation and improves reactivity	Potential (not PRB tested)	[134]
Organic mix + ZVI wire	Batch tests, pH ~7	Up to 93.3%	None reported	ZVI + rice husk/straw improves denitrification	Potential (not PRB tested)	[128]
PHA, PLA, PBS, etc.	Various (drinking water, aquaculture, effluent)	60–100%	None reported	Solid-phase denitrification using biodegradable materials	Potential (not PRB tested)	[62]
Alkali-treated corncob, straw	Unsaturated soil incubation, 28 days	Complete in 14–28 days	CO ₂ , trace NO ₂ [−] ; low N ₂ O	Improved DOC and lower N ₂ O with treated materials	Potential (not PRB tested)	[132]
ZVI with cation/anion-enhanced soil	Batch tests, alkaline soil	Up to 96–99%	NH ₄ ⁺ primary product, some NO ₂ [−]	Cations (Fe ³⁺ , Cu ²⁺) and citrate enhance performance	Potential (not PRB tested)	[135]
Mixed carbon (sawdust + cornstalk)	Column, ambient temp., 15 days	>90%	NO ₂ [−] , NH ₄ ⁺	Stable removal with nitrite/ammonia accumulation	Yes	[136]
Biochar + ZVI + reactive media	Pilot PRB, 1.2 m depth	~95%	Not reported	Enhanced adsorption and reduction via biochar synergy	Yes	[81]

The compiled studies reveal a diverse range of materials tested for nitrate removal, either as part of implemented PRBs systems or under conditions that simulate potential PRB operation. Granular and microscale ZVI remain the most widely studied and reliable materials, demonstrating high nitrate removal efficiencies (>95%) in column setups [59,104], though passivation and ammonia production are recurring issues. Encapsulated ZVI systems using calcium alginate or stabilizing agents like xanthan gum have shown improved iron utilization and reduced aggregation [129,134], indicating strong potential for field deployment despite requiring further validation in real PRB contexts.

Organic-based carbon substrates, such as sawdust, corncob, and straw, are effective low-cost alternatives that support solid-phase denitrification. When combined with ZVI (e.g., Liu et al. [34]; Kijjanapanich and Yaowakun [128]), they enhance electron availability and nitrate reduction, though nitrite and ammonium byproducts are often reported. Alkaline-treated residues further boost performance by increasing bioavailable carbon and reducing N₂O emissions, positioning them as promising materials for both nitrate mitigation and greenhouse gas control [132].

Biodegradable polymers such as PHA, PLA, PBS, and PCL [62] also offer stable denitrification performance across various water types, with minimal byproducts and high removal efficiency. However, high costs and slower startup phases may limit their scalability. Meanwhile, materials like zeolite, when used in combination [83], help support microbial attachment and control effluent quality. Guan et al. [136] and Tang et al. [135] underscore the importance of evaluating co-contaminants and soil chemistry. They show that factors such as ion interference and green rust formation can significantly influence PRB longevity and nitrate conversion pathways.

While ZVI remains a cornerstone for PRB systems, its combination with biodegradable substrates or stabilization strategies offers a pathway toward more resilient, cost-effective, and environmentally sustainable nitrate remediation technologies.

This comprehensive overview highlights the dynamic progression and ongoing innovation in PRB technology, which aims to provide practical and sustainable solutions for groundwater remediation, particularly in the context of agricultural impacts. By addressing the scientific and practical aspects of PRB implementation, this research lays the groundwork for future, more resilient and environmentally friendly remediation strategies, particularly in addressing and overcoming the challenges related to achieving sustainability and circularity in the agricultural sector.

5. Conclusions

This study presents a comprehensive bibliometric and critical analysis of the global research landscape on PRBs for groundwater remediation, focusing on nitrate removal. Over nearly three decades, from 1995 to 2023, PRBs have undergone significant evolution in design, materials, and applications. The analysis of 141 articles highlights the increasing integration of sustainable materials, such as agricultural residues and industrial byproducts, into PRB systems, aligning with broader goals of resource efficiency and environmental sustainability.

Mapping by specific themes and keyword co-occurrence analysis revealed that while traditional materials like ZVI remain central, research has progressively incorporated bio-based materials and hybrid systems to enhance performance, reduce costs, and address site-specific constraints. Moreover, using low-cost organic materials from agricultural activities has gained prominence. Experimental studies have shown high denitrification rates and improved carbon release profiles, which may contribute to potential greenhouse gas mitigation, especially when materials are pre-treated to enhance biodegradability.

The bibliometric trends indicated a noticeable decline in publication output between 2020 and 2023. However, this decline should not be interpreted as a reduced interest in the topic. The search scope in this study was limited to documents indexed up to 2023. The preliminary data from 2024 and 2025 suggest a resurgence in research activity. Thus, this temporary decline was likely influenced by global disruptions related to the COVID-19 pandemic, which may have affected laboratory work, field in situ applications, and international collaboration. The current upward trend depicts the relevance of PRBs in addressing water quality challenges.

Future research should further explore the long-term performance and field validation of PRBs incorporating agro-industrial waste, assess the ecotoxicological impact of degradation byproducts, and consider context-specific factors such as climate, soil type, and contaminant load. In addition, strengthening interdisciplinary collaboration and integrating life cycle and techno-economic assessments will also be essential for scaling PRB technologies as viable solutions for nitrate-contaminated groundwater.

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writing—review and editing, G.C.S.H., J.Á.-B., E.D. and M.D.L.A.O.D.R.; financing acquisition, E.D., M.D.L.A.O.D.R. and G.C.S.H. All authors have read and agreed to the published version of the manuscript.

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References

1. Fernández-López, J.A.; Alacid, M.; Obón, J.M.; Martínez-Vives, R.; Angosto, J.M. Nitrate-Polluted Waterbodies Remediation: Global Insights into Treatments for Compliance. *Appl. Sci.* **2023**, *13*, 4154. [CrossRef]
2. United Nations. *Informe Mundial De Las Naciones Unidas Sobre El Desarrollo De Los Recursos Hídricos 2023: Alianzas y Cooperación Por El Agua*; UNESCO: Paris, France; United Nations: Paris, France, 2023; ISBN 978-92-3-300212-8.
3. Davamani, V.; John, J.E.; Poornachandhra, C.; Gopalakrishnan, B.; Arulmani, S.; Parameswari, E.; Santhosh, A.; Srinivasulu, A.; Lal, A.; Naidu, R. A Critical Review of Climate Change Impacts on Groundwater Resources: A Focus on the Current Status, Future Possibilities, and Role of Simulation Models. *Atmosphere* **2024**, *15*, 122. [CrossRef]
4. Abascal, E.; Gómez-Coma, L.; Ortiz, I.; Ortiz, A. Global Diagnosis of Nitrate Pollution in Groundwater and Review of Removal Technologies. *Sci. Total Environ.* **2022**, *810*, 152233. [CrossRef]
5. Saleem, S.; Levison, J.; Parker, B.; Martin, R.; Persaud, E. Impacts of Climate Change and Different Crop Rotation Scenarios on Groundwater Nitrate Concentrations in a Sandy Aquifer. *Sustainability* **2020**, *12*, 1153. [CrossRef]
6. Banerjee, A.; Creedon, L.; Jones, N.; Gill, L.; Gharbia, S. Dynamic Groundwater Contamination Vulnerability Assessment Techniques: A Systematic Review. *Hydrology* **2023**, *10*, 182. [CrossRef]
7. Huno, S.K.M.; Rene, E.R.; van Hullebusch, E.D.; Annachatre, A.P. Nitrate Removal from Groundwater: A Review of Natural and Engineered Processes. *J. Water Supply Res. Technol. AQUA* **2018**, *67*, 885–902. [CrossRef]
8. Xin, J.; Wang, Y.; Shen, Z.; Liu, Y.; Wang, H.; Zheng, X. Critical Review of Measures and Decision Support Tools for Groundwater Nitrate Management: A Surface-to-Groundwater Profile Perspective. *J. Hydrol.* **2021**, *598*, 126386. [CrossRef]
9. Gani, A.; Hussain, A.; Pathak, S.; Omar, P.J. Analysing Heavy Metal Contamination in Groundwater in the Vicinity of Mumbai’s Landfill Sites: An In-Depth Study. *Top. Catal.* **2024**, *67*, 1009–1023. [CrossRef]
10. Singh, V. Water Pollution. In *Textbook of Environment and Ecology*; Singh, V., Ed.; Springer: Singapore, 2024; pp. 253–266. ISBN 978-981-99-8846-4.
11. ONU. Objetivos y Metas de Desarrollo Sostenible—Desarrollo Sostenible. Available online: <https://www.un.org/sustainabledevelopment/es/objetivos-de-desarrollo-sostenible/> (accessed on 24 June 2021).
12. Budania, R.; Dangayach, S. A Comprehensive Review on Permeable Reactive Barrier for the Remediation of Groundwater Contamination. *J. Environ. Manag.* **2023**, *332*, 117343. [CrossRef]
13. Siarkos, I.; Mallios, Z.; Latinopoulos, P. An Integrated Framework to Assess the Environmental and Economic Impact of Fertilizer Restrictions in a Nitrate-Contaminated Aquifer. *Hydrology* **2024**, *11*, 8. [CrossRef]
14. Gibert, O.; Pomierny, S.; Rowe, I.; Kalin, R.M. Selection of Organic Substrates as Potential Reactive Materials for Use in a Denitrification Permeable Reactive Barrier (PRB). *Bioresour. Technol.* **2008**, *99*, 7587–7596. [CrossRef] [PubMed]

15. Zhao, Q.; Li, F.; Zhu, A.; Zhang, X.; Chen, H.; Sun, T. Risk Assessment of Nitrate Pollution in the Shallow Groundwater of the Mihe Alluvial–Diluvial Fan Based on a DEA Model. *Water* **2022**, *14*, 1360. [\[CrossRef\]](#)
16. Karlović, I.; Posavec, K.; Larva, O.; Marković, T. Numerical Groundwater Flow and Nitrate Transport Assessment in Alluvial Aquifer of Varaždin Region, NW Croatia. *J. Hydrol. Reg. Stud.* **2022**, *41*, 101084. [\[CrossRef\]](#)
17. Gutiérrez, M.; Biagioni, R.N.; Alarcón-Herrera, M.T.; Rivas-Lucero, B.A. An Overview of Nitrate Sources and Operating Processes in Arid and Semiarid Aquifer Systems. *Sci. Total Environ.* **2018**, *624*, 1513–1522. [\[CrossRef\]](#)
18. World Health Organization. *Nitrate and Nitrite in Drinking-Water*; World Health Organization: Geneva, Switzerland, 2016.
19. Directiva (UE) 2020/2184 del Parlamento Europeo y del Consejo de 16 de diciembre de 2020 Relativa a la Calidad de las Aguas Destinadas al Consumo Humano (Versión Refundida) (Texto Pertinente a Efectos del EEE). *Off. J. Eur. Union* **2020**, *435*, 1–62. Available online: <https://eur-lex.europa.eu/legal-content/ES/ALL/?uri=CELEX:32020L2184> (accessed on 24 March 2025).
20. United States Environmental Protection Agency. Estándares Del Reglamento Nacional Primario de Agua Potable. In *Agua Potable En Español*; US EPA: Washington, DC, USA, 2000.
21. Health Canada. *Guidelines for Canadian Drinking Water Quality: Guideline Technical Document—Nitrate and Nitrite*; Health Canada: Ottawa, ON, Canada, 2013; ISBN 978-1-100-22999-7.
22. Bryan, N.S.; van Grinsven, H. Chapter Three—The Role of Nitrate in Human Health. In *Advances in Agronomy*; Sparks, D.L., Ed.; Advances in Agronomy; Academic Press: New York, NY, USA, 2013; Volume 119, pp. 153–182.
23. Mahaqi, A.; Mehiqi, M.; Moheghy, M.A.; Moheghi, M.M.; Hussainzadeh, J. Nitrate Pollution in Kabul Water Supplies, Afghanistan; Sources and Chemical Reactions: A review. *Int. J. Environ. Sci. Technol.* **2022**, *19*, 6925–6934. [\[CrossRef\]](#)
24. Li, S.; Wu, Y.; Nie, F.; Tu, W.; Li, X.; Luo, X.; Luo, Y.; Fan, H.; Song, T. Remediation of Nitrate Contaminated Groundwater Using a Simulated PRB System with an La-CTAC-Modified Biochar Filler. *Front. Environ. Sci.* **2022**, *10*, 986866. [\[CrossRef\]](#)
25. Ozkaraova, E.B.; Kalin, R.M.; Gkiouzepas, S.; Knapp, C.W. Industrial and Agricultural Wastes as a Potential Biofilter Media for Groundwater Nitrate Remediation. *Desalination Water Treat.* **2019**, *172*, 330–343. [\[CrossRef\]](#)
26. Richa, A.; Touil, S.; Fizir, M. Recent Advances in the Source Identification and Remediation Techniques of Nitrate Contaminated Groundwater: A review. *J. Environ. Manag.* **2022**, *316*, 115265. [\[CrossRef\]](#)
27. Ye, J.; Chen, X.; Chen, C.; Bate, B. Emerging Sustainable Technologies for Remediation of Soils and Groundwater in a Municipal Solid Waste Landfill Site—A Review. *Chemosphere* **2019**, *227*, 681–702. [\[CrossRef\]](#)
28. Zhang, W.; Bai, Y.; Ruan, X.; Yin, L. The Biological Denitrification Coupled with Chemical Reduction for Groundwater Nitrate Remediation via Using SCCMs as Carbon Source. *Chemosphere* **2019**, *234*, 89–97. [\[CrossRef\]](#)
29. Al-Hashimi, O.; Hashim, K.; Loffill, E.; Marolt Čebašek, T.; Nakouti, I.; Faisal, A.A.H.; Al-Ansari, N. A Comprehensive Review for Groundwater Contamination and Remediation: Occurrence, Migration and Adsorption Modelling. *Molecules* **2021**, *26*, 5913. [\[CrossRef\]](#) [\[PubMed\]](#)
30. Faisal, A.A.H.; Sulaymon, A.H.; Khaliefa, Q.M. A Review of Permeable Reactive Barrier as Passive Sustainable Technology for Groundwater Remediation. *Int. J. Environ. Sci. Technol.* **2018**, *15*, 1123–1138. [\[CrossRef\]](#)
31. Singh, R.; Chakma, S.; Birke, V. Performance of Field-Scale Permeable Reactive Barriers: An Overview on Potentials and Possible Implications for In Situ Groundwater Remediation Applications. *Sci. Total Environ.* **2023**, *858*, 158838. [\[CrossRef\]](#) [\[PubMed\]](#)
32. Sanchez Hidalgo, G.C.; Deago, E.; Ortega Del Rosario, M.D.L.A. Permeable Reactive Barriers for In Situ Remediation of Nitrate-Contaminated Groundwater: A Review. In Proceedings of the 2022 8th International Engineering, Sciences and Technology Conference, IESTEC, Panama City, Panama, 19–21 October 2022; pp. 469–476.
33. Zhang, W.; Zhu, Y.; Gu, R.; Liang, Z.; Xu, W.; Jat Baloch, M.Y. Health Risk Assessment during In Situ Remediation of Cr(VI)-Contaminated Groundwater by Permeable Reactive Barriers: A Field-Scale Study. *Int. J. Environ. Res. Public Health* **2022**, *19*, 13079. [\[CrossRef\]](#)
34. Liu, Y.; Liu, Y.; Ma, L.; Gong, Y.; Qian, J. Corncob PRB for On-Site Nitrate Removal in Groundwater. *Arab. J. Geosci.* **2020**, *13*, 1084. [\[CrossRef\]](#)
35. Al-Mansoria, N.J.; Al-Baidhani, J.H.; Al-Bakric, M.J. Seeds-Based Activated Carbon for Copper Removal from Groundwater. *J. Eng. Sci. Technol.* **2020**, *15*, 1622–1638.
36. Wen, Z.; Nan, S.; Ying, B.; Lin, Y. The Innovative Application of Agriculture Straw in In Situ Field Permeable Reactive Barrier for Remediating Nitrate-Contaminated Groundwater in Grain-Production Areas. *Biochem. Eng. J.* **2020**, *164*, 107755. [\[CrossRef\]](#)
37. Sánchez Hidalgo, G.C.; Ortega, M.D.L.Á.; Deago, E. Enhanced Biological Nitrate Removal from Groundwater in Humid Tropical Regions Using Corn Cob-Based Permeable Reactive Barriers: A Case Study from Panama. *Water* **2024**, *16*, 1668. [\[CrossRef\]](#)
38. Zhao, B.; Sun, Z.; Liu, Y. An Overview of In-Situ Remediation for Nitrate in Groundwater. *Sci. Total Environ.* **2022**, *804*, 149981. [\[CrossRef\]](#)
39. Li, J.; Zhang, B. Woodchip-Sulfur Packed Biological Permeable Reactive Barrier for Mixotrophic Vanadium (V) Detoxification in Groundwater. *Sci. China Technol. Sci.* **2020**, *63*, 2283–2291. [\[CrossRef\]](#)
40. Guleria, A.; Chakma, S. A Bibliometric and Visual Analysis of Contaminant Transport Modeling in the Groundwater System: Current Trends, Hotspots, and Future Directions. *Environ. Sci. Pollut. Res.* **2023**, *30*, 32032–32051. [\[CrossRef\]](#) [\[PubMed\]](#)

41. Wan, X.; Zhang, H.; Shen, C. Visualization Analysis on the Current Status and Development Trend of Geothermal Research: Insights Into the Database of Web of Science. *Front. Energy Res.* **2022**, *10*, 853439. [\[CrossRef\]](#)
42. Herrera-Franco, G.; Carrión-Mero, P.; Montalván-Burbano, N.; Mora-Frank, C.; Berrezueta, E. Bibliometric Analysis of Groundwater's Life Cycle Assessment Research. *Water* **2022**, *14*, 1082. [\[CrossRef\]](#)
43. Salimi, S.; Almuktar, S.A.; Scholz, M. Impact of Climate Change on Wetland Ecosystems: A Critical Review of Experimental Wetlands. *J. Environ. Manag.* **2021**, *286*, 112160. [\[CrossRef\]](#)
44. Durán-Sánchez, A.; Álvarez-García, J.; Del Río-Rama, M.D.I.C. Sustainable Water Resources Management: A Bibliometric Overview. *Water* **2018**, *10*, 1191. [\[CrossRef\]](#)
45. Zhu, J.; Kang, S.; Zhao, W.; Li, Q.; Xie, X.; Hu, X. A Bibliometric Analysis of Food–Energy–Water Nexus: Progress and Prospects. *Land* **2020**, *9*, 504. [\[CrossRef\]](#)
46. Aristodemou, L.; Tietze, F. The State-of-the-Art on Intellectual Property Analytics (IPA): A Literature Review on Artificial Intelligence, Machine Learning and Deep Learning Methods for Analysing Intellectual Property (IP) Data. *World Pat. Inf.* **2018**, *55*, 37–51. [\[CrossRef\]](#)
47. Vakili, M.; Ebadi, T.; Hajbabaie, M. A Systematic Analysis of Research Trends on the Permeable Reactive Barrier in Groundwater Remediation. *Int. J. Environ. Sci. Technol.* **2025**, *22*, 503–520. [\[CrossRef\]](#)
48. van Eck, N.J.; Waltman, L. Software Survey: VOSviewer, a Computer Program for Bibliometric Mapping. *Scientometrics* **2010**, *84*, 523–538. [\[CrossRef\]](#)
49. Zhang, H.; Liu, X.; Yi, J.; Yang, X.; Wu, T.; He, Y.; Duan, H.; Liu, M.; Tian, P. Bibliometric Analysis of Research on Soil Water from 1934 to 2019. *Water* **2020**, *12*, 1631. [\[CrossRef\]](#)
50. Herrera-Franco, G.; Montalván-Burbano, N.; Carrión-Mero, P.; Bravo-Montero, L. Worldwide Research on Socio-Hydrology: A Bibliometric Analysis. *Water* **2021**, *13*, 1283. [\[CrossRef\]](#)
51. Renzi, M.; Pauna, V.H.; Provenza, F.; Munari, C.; Mistri, M. Marine Litter in Transitional Water Ecosystems: State of The Art Review Based on a Bibliometric Analysis. *Water* **2020**, *12*, 612. [\[CrossRef\]](#)
52. Velasco-Muñoz, J.F.; Aznar-Sánchez, J.A.; Belmonte-Ureña, L.J.; López-Serrano, M.J. Advances in Water Use Efficiency in Agriculture: A Bibliometric Analysis. *Water* **2018**, *10*, 377. [\[CrossRef\]](#)
53. Abdelwahab, S.I.; Taha, M.M.E.; Moni, S.S.; Alsayegh, A.A. Bibliometric Mapping of Solid Lipid Nanoparticles Research (2012–2022) Using VOSviewer. *Med. Nov. Technol. Devices* **2023**, *17*, 100217. [\[CrossRef\]](#)
54. Dash, S.; Kalamdhad, A.S. Science Mapping Approach to Critical Reviewing of Published Literature on Water Quality Indexing. *Ecol. Indic.* **2021**, *128*, 107862. [\[CrossRef\]](#)
55. Karimidastenaie, Z.; Avellán, T.; Sadegh, M.; Kløve, B.; Haghighi, A.T. Unconventional Water Resources: Global Opportunities and Challenges. *Sci. Total Environ.* **2022**, *827*, 154429. [\[CrossRef\]](#)
56. Alowitz, M.J.; Scherer, M.M. Kinetics of Nitrate, Nitrite, and Cr(VI) Reduction by Iron Metal. *Environ. Sci. Technol.* **2002**, *36*, 299–306. [\[CrossRef\]](#)
57. Guan, X.; Sun, Y.; Qin, H.; Li, J.; Lo, I.M.C.; He, D.; Dong, H. The Limitations of Applying Zero-Valent Iron Technology in Contaminants Sequestration and the Corresponding Countermeasures: The Development in Zero-Valent Iron Technology in the Last Two Decades (1994–2014). *Water Res.* **2015**, *75*, 224–248. [\[CrossRef\]](#)
58. Lai, K.C.K.; Lo, I.M.C. Removal of Chromium (VI) by Acid-Washed Zero-Valent Iron under Various Groundwater Geochemistry Conditions. *Environ. Sci. Technol.* **2008**, *42*, 1238–1244. [\[CrossRef\]](#)
59. Su, C.M.; Puls, R.W. Arsenate and Arsenite Removal by Zerovalent Iron: Effects of Phosphate, Silicate, Carbonate, Borate, Sulfate, Chromate, Molybdate, and Nitrate, Relative to Chloride. *Environ. Sci. Technol.* **2001**, *35*, 4562–4568. [\[CrossRef\]](#)
60. Fu, F.; Dionysiou, D.D.; Liu, H. The Use of Zero-Valent Iron for Groundwater Remediation and Wastewater Treatment: A Review. *J. Hazard. Mater.* **2014**, *267*, 194–205. [\[CrossRef\]](#) [\[PubMed\]](#)
61. Cameron, S.G.; Schipper, L.A. Nitrate Removal and Hydraulic Performance of Organic Carbon for Use in Denitrification Beds. *Ecol. Eng.* **2010**, *36*, 1588–1595. [\[CrossRef\]](#)
62. Wang, J.; Chu, L. Biological Nitrate Removal from Water and Wastewater by Solid-Phase Denitrification Process. *Biotechnol. Adv.* **2016**, *34*, 1103–1112. [\[CrossRef\]](#) [\[PubMed\]](#)
63. Rocca, C.D.; Belgiorno, V.; Meric, S. Overview of In Situ Applicable Nitrate Removal Processes. *Desalination* **2007**, *204*, 46–62. [\[CrossRef\]](#)
64. Bone, B.D.; Harris, R.C.; Smith, J.W.N.; Boshoff, G.A.; Kalin, R.M.; Thurgood, R.; Morgan, P. The Development and Use of Permeable Reactive Barrier Technologies and Potential Future Applications in the UK. In *Permeable Reactive Barriers*; Boshoff, G.A., Bone, B.D., Eds.; 2005; Volume 298, pp. 52–59.
65. Nooten, T.V.; Diels, L.; Bastiaens, L. Design of a Multifunctional Permeable Reactive Barrier for the Treatment of Landfill Leachate Contamination: Laboratory Column Evaluation. *Environ. Sci. Technol.* **2008**, *42*, 8890–8895. [\[CrossRef\]](#)
66. Kong, X.; Bi, E.; Liu, F.; Huang, G.; Ma, J. Laboratory Column Study for Evaluating a Multimedia Permeable Reactive Barrier for the Remediation of Ammonium Contaminated Groundwater. *Environ. Technol.* **2015**, *36*, 1433–1440. [\[CrossRef\]](#)

67. Wang, X.; Xin, J.; Yuan, M.; Zhao, F. Electron Competition and Electron Selectivity in Abiotic, Biotic, and Coupled Systems for Dechlorinating Chlorinated Aliphatic Hydrocarbons in Groundwater: A Review. *Water Res.* **2020**, *183*, 116060. [\[CrossRef\]](#)
68. Ruhl, A.S.; Jekel, M. Influence of Hydronium, Sulfate, Chloride and Other Non-Carbonate Ions on Hydrogen Generation by Anaerobic Corrosion of Granular Cast Iron. *Water Res.* **2013**, *47*, 6044–6051. [\[CrossRef\]](#)
69. Gu, B.H.; Watson, D.B.; Wu, L.Y.; Phillips, D.H.; White, D.C.; Zhou, J.Z. Microbiological Characteristics in a Zero-Valent Iron Reactive Barrier. *Environ. Monit. Assess.* **2002**, *77*, 293–309. [\[CrossRef\]](#)
70. Sun, Y.; Chen, S.S.; Tsang, D.C.W.; Graham, N.J.D.; Ok, Y.S.; Feng, Y.; Li, X.-D. Zero-Valent Iron for the Abatement of Arsenate and Selenate from Flowback Water of Hydraulic Fracturing. *Chemosphere* **2017**, *167*, 163–170. [\[CrossRef\]](#)
71. Vishnyakova, A.; Popova, N.; Artemiev, G.; Botchkova, E.; Litt, Y.; Safonov, A. Effect of Mineral Carriers on Biofilm Formation and Nitrogen Removal Activity by an Indigenous Anammox Community from Cold Groundwater Ecosystem Alone and Bioaugmented with Biomass from a “Warm” Anammox Reactor. *Biology* **2022**, *11*, 1421. [\[CrossRef\]](#) [\[PubMed\]](#)
72. Pensky, J.; Fisher, A.T.; Gorski, G.; Schrad, N.; Bautista, V.; Saltikov, C. Linking Nitrate Removal, Carbon Cycling, and Mobilization of Geogenic Trace Metals during Infiltration for Managed Recharge. *Water Res.* **2023**, *239*, 120045. [\[CrossRef\]](#) [\[PubMed\]](#)
73. Liu, C.; Chen, X.; Banwart, S.A.; Du, W.; Yin, Y.; Guo, H. A Novel Permeable Reactive Biobarrier for *Ortho*-Nitrochlorobenzene Pollution Control in Groundwater: Experimental Evaluation and Kinetic Modelling. *J. Hazard. Mater.* **2021**, *420*, 126563. [\[CrossRef\]](#) [\[PubMed\]](#)
74. Xie, Y.; Zhang, D.; Lou, S.; He, F.; Yin, L. Slowly Released Carbon Source from Composite Materials System for Removing Nitrate Pollution in Groundwater. *RSC Adv.* **2017**, *7*, 10215–10220. [\[CrossRef\]](#)
75. Doherty, R.; McPolin, B.; Kulesa, B.; Frau, A.; Kulakova, A.; Allen, C.C.R.; Larkin, M.J. Microbial Ecology and Geoelectric Responses across a Groundwater Plume. *Interpret. J. Subsurf. Charact.* **2015**, *3*, SAB9–SAB21. [\[CrossRef\]](#)
76. Li, S.; Zhang, Y.; Yin, S.; Wang, X.; Liu, T.; Deng, Z. Analysis of Microbial Community Structure and Degradation of Ammonia Nitrogen in Groundwater in Cold Regions. *Environ. Sci. Pollut. Res.* **2020**, *27*, 44137–44147. [\[CrossRef\]](#)
77. Gorski, G.; Dailey, H.; Fisher, A.T.; Schrad, N.; Saltikov, C. Denitrification during Infiltration for Managed Aquifer Recharge: Infiltration Rate Controls and Microbial Response. *Sci. Total Environ.* **2020**, *727*, 138642. [\[CrossRef\]](#)
78. Hiller-Bittrolff, K.; Foreman, K.; Bulseco-McKim, A.N.; Benoit, J.; Bowen, J.L. Effects of Mercury Addition on Microbial Community Composition and Nitrate Removal Inside Permeable Reactive Barriers. *Environ. Pollut.* **2018**, *242*, 797–806. [\[CrossRef\]](#)
79. Gandhi, S.; Oh, B.T.; Schnoor, J.L.; Alvarez, P.J.J. Degradation of TCE, Cr(VI), Sulfate, and Nitrate Mixtures by Granular Iron in Flow-through Columns under Different Microbial Conditions. *Water Res.* **2002**, *36*, 1973–1982. [\[CrossRef\]](#)
80. Liu, S.; Gao, B.; Xiong, X.; Chen, N.; Xuan, K.; Ma, W.; Song, Y.; Yu, Y. Treatment of Nitrate-Contaminated Groundwater Using Microbially Enhanced Permeable Reactive Barrier Technology. *Environ. Sci. Water Res. Technol.* **2023**, *9*, 1610–1619. [\[CrossRef\]](#)
81. Beganskas, S.; Gorski, G.; Weathers, T.; Fisher, A.T.; Schmidt, C.; Saltikov, C.; Redford, K.; Stoneburner, B.; Harmon, R.; Weir, W. A Horizontal Permeable Reactive Barrier Stimulates Nitrate Removal and Shifts Microbial Ecology During Rapid Infiltration for Managed Recharge. *Water Res.* **2018**, *144*, 274–284. [\[CrossRef\]](#) [\[PubMed\]](#)
82. Li, S.; Huang, G.; Kong, X.; Yang, Y.; Liu, F.; Hou, G.; Chen, H. Ammonium Removal from Groundwater Using a Zeolite Permeable Reactive Barrier: A Pilot-Scale Demonstration. *Water Sci. Technol.* **2014**, *70*, 1540–1547. [\[CrossRef\]](#) [\[PubMed\]](#)
83. Zhang, L.; Zheng, L.; Xiao, J.; Zhang, L.; Liu, H.; Wang, L. Experimental Study on Removal of Nitrate in Groundwater PRB. In Proceedings of the International Conference on Water Resource and Environmental Protection WREP 2014, Antalya, Turkey, 13–15 May 2014; pp. 206–210.
84. Rodriguez-Maroto, J.M.; Garcia-Herruzo, F.; Garcia-Rubio, A.; Gomez-Lahoz, C.; Vereda-Alonso, C. Kinetics of the Chemical Reduction of Nitrate by Zero-Valent Iron. *Chemosphere* **2009**, *74*, 804–809. [\[CrossRef\]](#) [\[PubMed\]](#)
85. Yang, W.; Shi, S.; Sun, B. Removal Effect of the Immobilized Biological Medium of PRB on Groundwater Nitrate. In Proceedings of the Conference on Environmental Pollution and Public Health, Wuhan, China, 10–11 September 2010; Volume 1–2, p. 1114.
86. Lu, Q.; Jeon, S.-W.; Gui, L.; Gillham, R.W. Nitrate Reduction and Its Effects on Trichloroethylene Degradation by Granular Iron. *Water Res.* **2017**, *112*, 48–57. [\[CrossRef\]](#)
87. Zhou, W.; Sun, Y.; Wu, B.; Zhang, Y.; Min, H.; Miyahara, T.; Zhang, Z. Autotrophic Denitrification for Nitrate and Nitrite Removal Using Sulfur-Limestone. *J. Environ. Sci.* **2011**, *23*, 1761–1769. [\[CrossRef\]](#)
88. Ghaemina, M.; Mokhtarani, N. Remediation of Nitrate-Contaminated Groundwater by PRB-Electrokinetic Integrated Process. *J. Environ. Manag.* **2018**, *222*, 234–241. [\[CrossRef\]](#)
89. Rao, S.M.; Malini, R. Use of Permeable Reactive Barrier to Mitigate Groundwater Nitrate Contamination from On-Site Sanitation. *J. Water Sanit. Hyg. Dev.* **2015**, *5*, 336–340. [\[CrossRef\]](#)
90. Hosseini, S.M.; Ataie-Ashtiani, B.; Kholghi, M. Bench-Scaled Nano-Fe⁰ Permeable Reactive Barrier for Nitrate Removal. *Ground Water Monit. Remediat.* **2011**, *31*, 82–94. [\[CrossRef\]](#)
91. Liu, S.; Gao, B.; Xuan, K.; Ma, W.; Nan, M.; Jia, C. Denitrification Performance and Mechanism of Permeable Reactive Barrier Technology with a Sulfur Autotrophic Denitrification Composite Filler in Rare Earth Mine Engineering Applications. *Water Air Soil Pollut.* **2023**, *234*, 76. [\[CrossRef\]](#)

92. Buyanjargal, A.; Kang, J.; Sleep, B.E.; Jeon, S.-W. Sequential Treatment of Nitrate and Phosphate in Groundwater Using a Permeable Reactive Barrier System. *J. Environ. Manag.* **2021**, *300*, 113699. [\[CrossRef\]](#)
93. Liu, S.-J.; Zhao, Z.-Y.; Li, J.; Wang, J.; Qi, Y. An Anaerobic Two-Layer Permeable Reactive Biobarrier for the Remediation of Nitrate-Contaminated Groundwater. *Water Res.* **2013**, *47*, 5977–5985. [\[CrossRef\]](#) [\[PubMed\]](#)
94. Skinner, S.J.W.; Schutte, C.F. The Feasibility of a Permeable Reactive Barrier to Treat Acidic Sulphate- and Nitrate-Contaminated Groundwater. *Water SA* **2006**, *32*, 129–135. [\[CrossRef\]](#)
95. Wu, Q.; Zheng, C.; Zhang, J.; Zhang, F. Nitrate Removal by a Permeable Reactive Barrier of Fe⁰: A Model-Based Evaluation. *J. Earth Sci.* **2017**, *28*, 447–456. [\[CrossRef\]](#)
96. Lin, K.-S.; Chang, N.-B.; Chuang, T.-D. Decontamination of Nitrates and Nitrites in Wastewater by Zero-Valent Iron Nanoparticles. *NANO* **2008**, *3*, 291–295. [\[CrossRef\]](#)
97. Liang, L.Y.; Moline, G.R.; Kamolpornwijit, W.; West, O.R. Influence of Hydrogeochemical Processes on Zero-Valent Iron Reactive Barrier Performance: A Field Investigation. *J. Contam. Hydrol.* **2005**, *80*, 71–91. [\[CrossRef\]](#)
98. Kamolpornwijit, W.; Liang, L.; West, O.R.; Moline, G.R.; Sullivan, A.B. Preferential Flow Path Development and Its Influence on Long-Term PRB Performance: Column Study. *J. Contam. Hydrol.* **2003**, *66*, 161–178. [\[CrossRef\]](#)
99. Li, L.; Benson, C.H.; Lawson, E.M. Modeling Porosity Reductions Caused by Mineral Fouling in Continuous-Wall Permeable Reactive Barriers. *J. Contam. Hydrol.* **2006**, *83*, 89–121. [\[CrossRef\]](#)
100. Luo, X.; Liu, H.; Huang, G.; Li, Y.; Yan, Z.; Li, X. Remediation of Arsenic-Contaminated Groundwater Using Media-Injected Permeable Reactive Barriers with a Modified Montmorillonite: Sand Tank Studies. *Environ. Sci. Pollut. Res.* **2016**, *23*, 870–877. [\[CrossRef\]](#)
101. Hu, S.; Wu, Y.; Zhang, Y.; Zhou, B.; Xu, X. Nitrate Removal from Groundwater by Heterotrophic/Autotrophic Denitrification Using Easily Degradable Organics and Nano-Zero Valent Iron as Co-Electron Donors. *Water Air Soil Pollut.* **2018**, *229*, 56. [\[CrossRef\]](#)
102. Huang, G.; Huang, Y.; Hu, H.; Liu, F.; Zhang, Y.; Deng, R. Remediation of Nitrate-Nitrogen Contaminated Groundwater Using a Pilot-Scale Two-Layer Heterotrophic-Autotrophic Denitrification Permeable Reactive Barrier with Spongy Iron/Pine Bark. *Chemosphere* **2015**, *130*, 8–16. [\[CrossRef\]](#)
103. Li, T.; Li, W.; Feng, C.; Hu, W. In-Situ Biological Denitrification Using Pretreated Maize Stalks as Carbon Source for Nitrate-Contaminated Groundwater Remediation. *Water Sci. Technol. Water Supply* **2017**, *17*, 1–9. [\[CrossRef\]](#)
104. Hosseini, S.M.; Tosco, T. Integrating NZVI and Carbon Substrates in a Non-Pumping Reactive Wells Array for the Remediation of a Nitrate Contaminated Aquifer. *J. Contam. Hydrol.* **2015**, *179*, 182–195. [\[CrossRef\]](#) [\[PubMed\]](#)
105. Liang, L.; Moline, G.R.; Kamolpornwijit, W.; West, O.R. Influence of Hydrogeochemical Processes on Zero-Valent Iron Reactive Barrier Performance: A Field Investigation. *J. Contam. Hydrol.* **2005**, *78*, 291–312. [\[CrossRef\]](#) [\[PubMed\]](#)
106. Grau-Martinez, A.; Torrento, C.; Carrey, R.; Soler, A.; Otero, N. Isotopic Evidence of Nitrate Degradation by a Zero-Valent Iron Permeable Reactive Barrier: Batch Experiments and a Field Scale Study. *J. Hydrol.* **2019**, *570*, 69–79. [\[CrossRef\]](#)
107. Gibert, O.; Assal, A.; Devlin, H.; Elliot, T.; Kalinc, R.M. Performance of a Field-Scale Biological Permeable Reactive Barrier for In-Situ Remediation of Nitrate-Contaminated Groundwater. *Sci. Total Environ.* **2019**, *659*, 211–220. [\[CrossRef\]](#)
108. Liu, B.; Tang, Z.; Dong, S.; Wang, L.; Liu, D. Vegetation Recovery and Groundwater Pollution Control of Coal Gangue Field in a Semi-Arid Area for a Field Application. *Int. Biodeterior. Biodegrad.* **2018**, *128*, 134–140. [\[CrossRef\]](#)
109. Eljamal, O.; Thompson, I.P.; Maamoun, I.; Shubair, T.; Eljamal, K.; Lueangwattanapong, K.; Sugihara, Y. Investigating the Design Parameters for a Permeable Reactive Barrier Consisting of Nanoscale Zero-Valent Iron and Bimetallic Iron/Copper for Phosphate Removal. *J. Mol. Liq.* **2020**, *299*, 112144. [\[CrossRef\]](#)
110. Araujo, R.; Castro, A.C.M.; Baptista, J.S.; Fiuza, A. Nanosized Iron Based Permeable Reactive Barriers for Nitrate Removal—Systematic Review. *Phys. Chem. Earth* **2016**, *94*, 29–34. [\[CrossRef\]](#)
111. Alyani, S.H.M.; Talebbeydokhti, N.; Ardejani, F.D.; Jashni, A.K.; Rakhshandehroo, R. Optimizing Operational Parameters of Electrokinetic Technique Assisted by a Permeable Reactive Barrier for Remediation of Nitrate-Contaminated Soil. *Iran. J. Sci. Technol. Trans. Civ. Eng.* **2022**, *46*, 2425–2438. [\[CrossRef\]](#)
112. Maharjan, A.K.; Mori, K.; Toyama, T. Nitrogen Removal Ability and Characteristics of the Laboratory-Scale Tidal Flow Constructed Wetlands for Treating Ammonium-Nitrogen Contaminated Groundwater. *Water* **2020**, *12*, 1326. [\[CrossRef\]](#)
113. Khalil, A.M.E.; Eljamal, O.; Saha, B.B.; Matsunaga, N. Performance of Nanoscale Zero-Valent Iron in Nitrate Reduction from Water Using a Laboratory-Scale Continuous-Flow System. *Chemosphere* **2018**, *197*, 502–512. [\[CrossRef\]](#) [\[PubMed\]](#)
114. Huang, G.; Liu, F.; Yang, Y.; Kong, X.; Li, S.; Zhang, Y.; Cao, D. Ammonium-Nitrogen-Contaminated Groundwater Remediation by a Sequential Three-Zone Permeable Reactive Barrier (Multibarrier) with Oxygen-Releasing Compound (ORC)/Clinoptilolite/Spongy Iron: Column Studies. *Environ. Sci. Pollut. Res.* **2015**, *22*, 3705–3714. [\[CrossRef\]](#) [\[PubMed\]](#)
115. Margalef-Martí, R.; Carrey, R.; Soler, A.; Otero, N. Evaluating the Potential Use of a Dairy Industry Residue to Induce Denitrification in Polluted Water Bodies: A Flow-through Experiment. *J. Environ. Manag.* **2019**, *245*, 86–94. [\[CrossRef\]](#) [\[PubMed\]](#)

116. Lee, G.; Rho, S.; Jahng, D. Design Considerations for Groundwater Remediation Using Reduced Metals. *Korean J. Chem. Eng.* **2004**, *21*, 621–628. [\[CrossRef\]](#)
117. Lv, X.; Song, J.; Li, J.; Wu, F. Tertiary Denitrification by Sulfur/Limestone Packed Biofilter. *Environ. Eng. Sci.* **2017**, *34*, 103–109. [\[CrossRef\]](#)
118. Lee, S.; Tase, N. In-Situ Denitrification of Nitrate-Nitrogen Contaminated Groundwater by a Permeable Reactive Barrier Using Sulfur-Limestone. *J. Geogr. Chigaku Zasshi* **2023**, *132*, 231–246. [\[CrossRef\]](#)
119. Pensky, J.; Fisher, A.T.; Gorski, G.; Schrad, N.; Dailey, H.; Beganskas, S.; Saltikov, C. Enhanced Cycling of Nitrogen and Metals during Rapid Infiltration: Implications for Managed Recharge. *Sci. Total Environ.* **2022**, *838*, 156439. [\[CrossRef\]](#)
120. Schrad, N.; Pensky, J.; Gorski, G.; Beganskas, S.; Fisher, A.T.; Saltikov, C. Soil Characteristics and Redox Properties of Infiltrating Water Are Determinants of Microbial Communities at Managed Aquifer Recharge Sites. *FEMS Microbiol. Ecol.* **2022**, *98*, fiac130. [\[CrossRef\]](#)
121. Abu, A.; Carrey, R.; Valhondo, C.; Cristina, D.; Soler, A.; Martinez-Landa, L.; Diaz-Cruz, S.; Carrera, J.; Otero, N. Pathways and Efficiency of Nitrogen Attenuation in Wastewater Effluent through Soil Aquifer Treatment. *J. Environ. Manag.* **2022**, *321*, 115927. [\[CrossRef\]](#)
122. Graffam, M.; Paulsen, R.; Volkenborn, N. Hydro-Biogeochemical Processes and Nitrogen Removal Potential of a Tidally Influenced Permeable Reactive Barrier behind a Perforated Marine Bulkhead. *Ecol. Eng.* **2020**, *155*, 105933. [\[CrossRef\]](#)
123. Guo, C.; Qi, L.; Bai, Y.; Yin, L.; Li, L.; Zhang, W. Geochemical Stability of Zero-Valent Iron Modified Raw Wheat Straw Innovatively Applied to In Situ Permeable Reactive Barrier: N₂ Selectivity and Long-Term Denitrification. *Ecotoxicol. Environ. Saf.* **2021**, *224*, 112649. [\[CrossRef\]](#) [\[PubMed\]](#)
124. Xu, B.; Shi, L.; Zhong, H.; Wang, K. The Performance of Pyrite-Based Autotrophic Denitrification Column for Permeable Reactive Barrier under Natural Environment. *Bioresour. Technol.* **2019**, *290*, 121763. [\[CrossRef\]](#) [\[PubMed\]](#)
125. Robertson, W.D.; Vogan, J.L.; Lombardo, P.S. Nitrate Removal Rates in a 15-Year-Old Permeable Reactive Barrier Treating Septic System Nitrate. *Ground Water Monit. Remediat.* **2008**, *28*, 65–72. [\[CrossRef\]](#)
126. Mittal, A.; Singh, R.; Chakma, S.; Goel, G. Permeable Reactive Barrier Technology for the Remediation of Groundwater Contaminated with Nitrate and Phosphate Resulted from Pit-Toilet Leachate. *J. Water Process Eng.* **2020**, *37*, 101471. [\[CrossRef\]](#)
127. Ismanto, A.; Hadibarata, T.; Widada, S.; Indrayanti, E.; Ismunarti, D.H.; Safinatunnajah, N.; Kusumastuti, W.; Dwiningsih, Y. Groundwater Contamination Status in Malaysia: Level of Heavy Metal, Source, Health Impact, and Remediation Technologies. *Bioprocess Biosyst. Eng.* **2023**, *46*, 467–482. [\[CrossRef\]](#)
128. Kijjanapanich, P.; Yaowakun, Y. Enhancement of Nitrate-Removal Efficiency Using a Combination of Organic Substrates and Zero-Valent Iron as Electron Donors. *J. Environ. Eng.* **2019**, *145*, 04019006. [\[CrossRef\]](#)
129. Naghikhani, A.; Karbassi, A.; Sarang, A.; Baghdadi, M. Investigating the Sustainable Performance of a Nanoscale Zerovalent Iron Permeable Reactive Barrier for Removal of Nitrate, Sulfide, and Arsenic. *AQUA Water Infrastruct. Ecosyst. Soc.* **2023**, *72*, 540–556. [\[CrossRef\]](#)
130. Buyanjargal, A.; Kang, J.; Lee, J.-H.; Jeon, S.-W. Nitrate Removal Rates, Isotopic Fractionation, and Denitrifying Bacteria in a Woodchip-Based Permeable Reactive Barrier System: A Long-Term Column Experiment. *Environ. Sci. Pollut. Res.* **2023**, *30*, 36364–36376. [\[CrossRef\]](#)
131. Fei, Y.; Chen, S.; Wang, Z.; Chen, T.; Zhang, B. Woodchip-Sulfur Based Mixotrophic Biotechnology for Hexavalent Chromium Detoxification in the Groundwater. *J. Environ. Manag.* **2022**, *324*, 116298. [\[CrossRef\]](#)
132. Sun, Z.; Zheng, T.; Xin, J.; Zheng, X.; Hu, R.; Subhan, F.; Shao, H. Effects of Alkali-Treated Agricultural Residues on Nitrate Removal and N₂O Reduction of Denitrification in Unsaturated Soil. *J. Environ. Manag.* **2018**, *214*, 276–282. [\[CrossRef\]](#)
133. Rocca, C.D.; Belgiorno, V.; Meric, S. Heterotrophic/Autotrophic Denitrification (HAD) of Drinking Water: Prospective Use for Permeable Reactive Barrier. *Desalination* **2007**, *210*, 194–204. [\[CrossRef\]](#)
134. Meng, F.; Li, M.; Wang, H.; Xin, L.; Xiaona, W.; Liu, X. Encapsulating Microscale Zero Valent Iron-Activated Carbon into Porous Calcium Alginate for the Improvement on the Nitrate Removal Rate and Fe⁰ Utilization Factor. *Microporous Mesoporous Mater.* **2020**, *307*, 110522. [\[CrossRef\]](#)
135. Tang, C.; Zhang, Z.; Sun, X. Effect of Common Ions on Nitrate Removal by Zero-Valent Iron from Alkaline Soil. *J. Hazard. Mater.* **2012**, *231*, 114–119. [\[CrossRef\]](#) [\[PubMed\]](#)
136. Guan, Q.; Li, F.; Chen, X.; Tian, C.; Liu, C.; Liu, D. Assessment of the Use of a Zero-Valent Iron Permeable Reactive Barrier for Nitrate Removal from Groundwater in the Alluvial Plain of the Dagou River, China. *Environ. Earth Sci.* **2019**, *78*, 244. [\[CrossRef\]](#)

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