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Pollution source identification methods and remediation technologies of groundwater: A review

Ya-ci Liu[a, b], Yu-hong Fei[a,*], Ya-song Li[a], Xi-lin Bao[a], Peng-wei Zhang[a]

[a] *Fujian Provincial Key Laboratory of Water Cycling and Eco-Geological Processes, Institute of Hydrogeology and Environmental Geology, Chinese Academy of Geological Sciences, Xiamen* 361000, *China*
[b] *Key Laboratory of Water and Soil Resources Conservation and Restoration in the Middle and Lower Reaches of Yellow River Basin, MNR, Zhengzhou* 450016, *China*

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ABSTRACT

Groundwater is an important source of drinking water. Groundwater pollution severely endangers drinking water safety and sustainable social development. In the case of groundwater pollution, the top priority is to identify pollution sources, and accurate information on pollution sources is the premise of efficient remediation. Then, an appropriate pollution remediation scheme should be developed according to information on pollution sources, site conditions, and economic costs. The methods for identifying pollution sources mainly include geophysical exploration, geochemistry, isotopic tracing, and numerical modeling. Among these identification methods, only the numerical modeling can recognize various information on pollution sources, while other methods can only identify a certain aspect of pollution sources. The remediation technologies of groundwater can be divided into *in-situ* and *ex-situ* remediation technologies according to the remediation location. The *in-situ* remediation technologies enjoy low costs and a wide remediation range, but their remediation performance is prone to be affected by environmental conditions and cause secondary pollution. The *ex-situ* remediation technologies boast high remediation efficiency, high processing capacity, and high treatment concentration but suffer high costs. Different methods for pollution source identification and remediation technologies are applicable to different conditions. To achieve the expected identification and remediation results, it is feasible to combine several methods and technologies according to the actual hydrogeological conditions of contaminated sites and the nature of pollutants. Additionally, detailed knowledge about the hydrogeological conditions and stratigraphic structure of the contaminated site is the basis of all work regardless of the adopted identification methods or remediation technologies.

1. Introduction

Groundwater has been widely used in human daily life and economic development due to its high quality and easy extraction. Globally, 25×10^9 people only rely on groundwater to meet their daily demand for drinking water (UNESCO, 2012). Under the influence of population growth, urbanization, and climate change, groundwater has been severely over-exploited in many regions, including northern China, the western United States, Mexico, Iran, parts of India, and North Africa (Qian H et al., 2020). In 2021, the groundwater utilization of China reached 85.38×10^9 m^3, of which 78.72×10^9 m^3 was extracted from northern China. The Beijing-Tianjin-Hebei region, which suffered water shortage, had a total water supply of 18.87×10^9 m^3 (excluding ecological water replenishment from other basins) in 2021, including groundwater utilization of 8.95×10^9 m^3 (Ministry of Water Resources, PRC, 2021). Therefore, groundwater is vital to people's daily life and development. However, frequent groundwater pollution events present severe challenges to groundwater management.

Groundwater pollution is mainly divided into inorganic pollution and organic pollution. Inorganic pollutants mainly include nitrate nitrogen, nitrite nitrogen, and ammonia nitrogen (collectively referred to the three nitrogen compounds), as well as heavy metals As, Cd, Cr (VI), Pb, and Hg. Organic pollutants mainly include aromatic hydrocarbons, halogenated hydrocarbons, and organic

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First author: *E-mail address*: liuyaci11@163.com (Ya-ci Liu).

* Corresponding author: *E-mail address*: yuhong_fei@163.com (Yu-hong Fei).

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pesticides. The groundwater near a smelter in Shanxi Province, China was severely contaminated with heavy metals including Pb, Zn, and Cd, whose concentrations exceeded the standards by a factor of 98.8, 61.4, and 334.1, respectively (Liu Y et al., 2015). The groundwater around a chemical plant in Jiangsu, China was contaminated with complex organic pollutants such as carbon tetrachloride and tetrachloroethylene, with a total detection rate of over 80% (Liu WJ et al., 2018). The list of soil pollution risk control and remediation for the construction land in the Beijing-Tianjin-Hebei region shows that chemical pollution sites accounted for up to 44.1% in 2019, and main pollutants included benzene series, chlorinated hydrocarbons, and petroleum hydrocarbons, which accounted for 68.42%, 57.89%, and 42.10%, respectively (Beijing Municipal Ecology and Environment Bureau, 2019; Department of Ecology and Environment of Hebei Province, 2019; Tianjin Ecology and Environment Bureau, 2019). The investigation and assessment of groundwater pollution have covered an area of 4.4×10^6 km^2 in China, and 3.1×10^4 sets of groundwater samples have been collected. The results show that groundwater pollution is mainly distributed in the form of spots (sites) and include both organic and inorganic pollution (China Geological Survey, 2016).

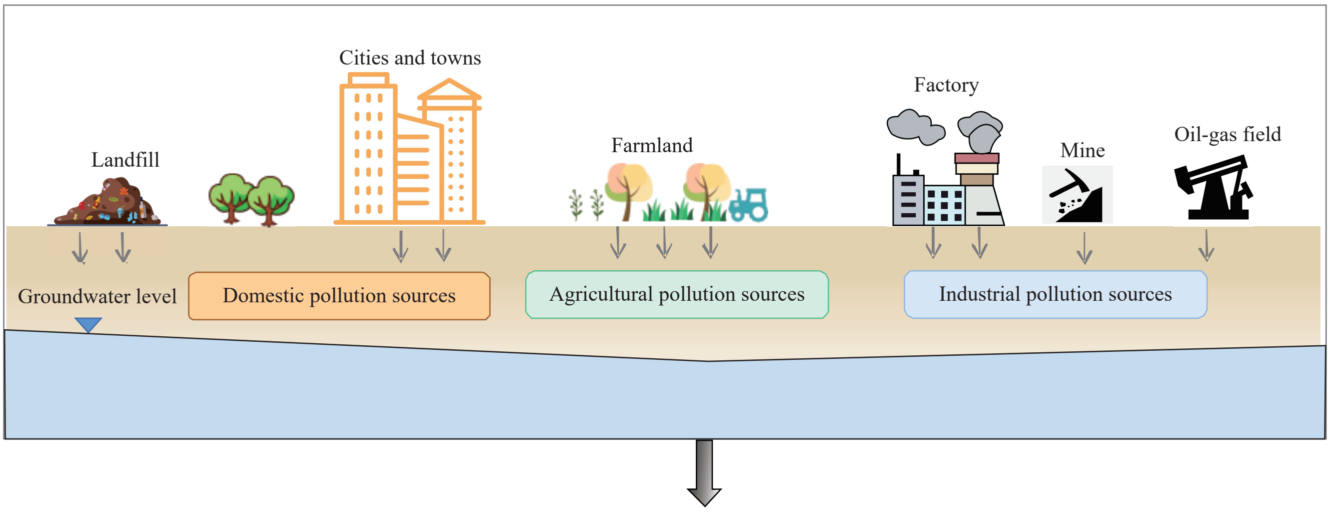
In the case of groundwater pollution, the top priority is to identify the pollution sources, and then feasible and scientific pollution remediation schemes should be developed according to the pollution type and intensity. Apparently, the pollution source identification and remediation of groundwater are equally important for groundwater management. This review detailed the pollution source identification methods and remediation technologies of groundwater.

2. Identification of groundwater pollution sources

Groundwater pollution sources include industrial, agricultural, and domestic pollution sources (Fig. 1). The locations, intensity, and pollutant pathways of pollution sources can be identified through the inversion of investigation data, thus restoring the migration and transformation processes of pollutants in groundwater (Wang JR and Hu LT, 2017; Wu YH et al., 2023; Sun QF et al., 2022). Accurate identification of pollution sources is the premise of efficient pollution treatment and remediation of groundwater. The methods for identifying groundwater pollution sources mainly include geophysical exploration, geochemistry, isotopic tracing, and numerical modeling (Miline E and Perrochet P, 2007).

2.1. Geophysical exploration

Geophysical exploration, which was developed based on



Type	Pollution source	Main contaminants
Domestic pollution sources	Municipal sewage	Nitrate, nitrite, ammonia, COD, pathogenic microorganism, etc.
	Landfill	Heavy metal, nitrate, nitrite, ammonia, COD, organic matter, etc.
Agricultural pollution sources	Fertilizers and pesticides	Nitrogen, phosphorus, organonitrogen, organophosphorus, etc.
	Sewage (or reclaimed water) for irrigation	Nitrate, nitrite, ammonia, COD, etc.
Industrial pollution sources	Mine	Heavy metal, sulfide, nitride, etc.
	Oil-gas field	Petroleum, volatile phenol, COD, acids, bases, etc.
	Tailings pond	Heavy metal, etc.
	Hazardous waste disposal site	Heavy metal,COD, oils, etc.

Fig. 1. Pollution sources and main pollutants of groundwater.

the different physical and chemical properties of pollutants and surrounding media, is used to survey the distribution of physical fields using specialized instruments and equipment to analyze the distribution and migration of pollutants. The commonly used geophysical methods include the resistivity method, the magnetotelluric method, the geological radar method, nuclear magnetic resonance, and seismic exploration (Zhong Q, 2014). Groundwater with inorganic pollution has medium-low dielectric and high electrical conductivity. By contrast, the groundwater with organic pollution, including light non-aqueous phase liquids (LNAPLs) and dense non-aqueous phase liquids (DNAPLs), shows low dielectric and high resistance. The groundwater with mixed pollution generally shows the electrical characteristics of water with inorganic pollution. These electrical characteristics determine the feasibility of geophysical methods. In practical applications, an appropriate geophysical method or a combination of geophysical methods can be selected according to the pollutant type and hydrogeological conditions of contaminated sites.

High-density resistivity method, one of the most widely used and effective methods, has been well applied in pollution scenarios caused by heavy metals, nitrates, and landfill leachate (Yang DQ, 2020; Hu KY, 2021; Maurya PK et al., 2017). Hasan M et al ’s (2020) study shows that electrical resistivity imaging (ERI) combined with vertical electrical sounding (VES) can determine the boundaries of contaminated and brackish aquifers to facilitate groundwater extraction. Satellite remote sensing and surface electrical geophysical techniques have also been widely used to identify groundwater discharge zones and pollutant flow paths. LANDSAT satellite data can be used to identify the locations of groundwater discharge (seepage) in a typical heterogeneous environment (Sass GZ et al., 2014). Surinaidu L et al. (2021) proposed a multidisciplinary approach to identify leakage sources in highly contaminated groundwater environments for the first, which integrates information from satellite-based observations of land surface temperature, ERI, continuous soil conductivity analysis, soil moisture measurement, and groundwater level monitoring.

2.2. Geochemistry

The geochemical method is first used to ascertain the characteristics of groundwater recharge and discharge through hydrogeological surveys and then identify the types and release intensity of pollutants through the statistical analysis and quality assessment of the content and chemical forms of pollutants. This method is mainly used to identify the pollution sources of inorganic pollutants such as heavy metals and the three nitrogen compounds. The commonly used geochemical techniques include conventional hydrochemical analyses (e.g., Piper diagrams, concentration contour maps, Gibbs diagrams, and ion ratio coefficient) and multivariate statistical analyses (e.g., descriptive statistical analysis, correlation analysis, factor analysis, and cluster analysis).

Based on the geochemical method, the pollution status of groundwater in the North China Plain, the plain of Huaihe River Basin, the Yangtze River Delta, and the Pearl River Delta in China has been systematically assessed, and the main sources of the three nitrogen compounds, heavy metals, and organic matter in these regions have been assessed (Zhang ZJ et al., 2012; Wen DG et al., 2012). Shi H et al. (2021) analyzed the spatial distribution patterns of heavy metals using ArcGIS and identified the sources of heavy metals using correlation coefficients and principal component analysis (PCA) based on the exposure characteristics of eight heavy metals in 44 groundwater samples. Qin Z et al. (2019) determined the main factors influencing water quality, identified the pollution sources, and finally revealed the spatial distribution of pollution sources through factor analysis. Furthermore, they determined the contribution rate of each pollution source using absolute principal component scores-multiple linear regression (APCS-MLR). Khous D et al. (2019) evaluated the quality of groundwater in the alluvial aquifers of the Eastern Mitidja Plain and determined the natural and artificial sources of trace metals through PCA.

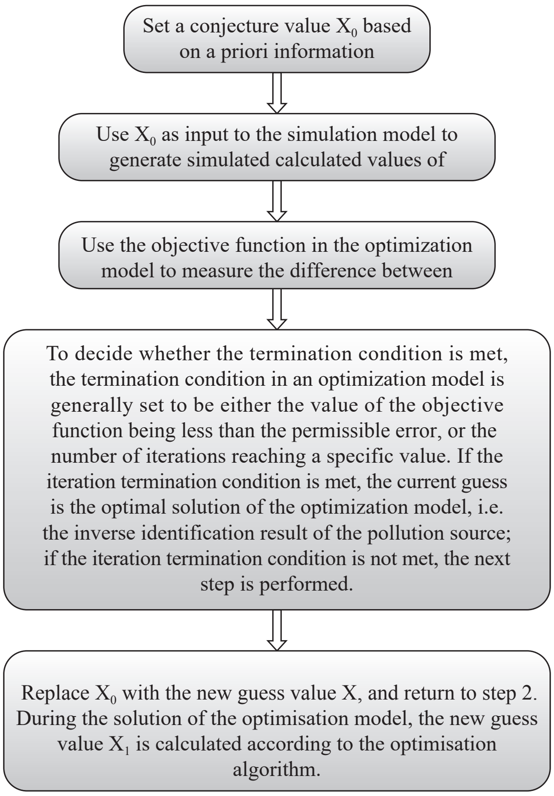
2.3. Isotopic tracing

Isotopic tracing is to identify the sources and formation process of pollutants based on the isotopic ratios of elements in environmental materials. The most widely used hydrogeochemical isotopes include the stable isotopes of O, H, C, S, and N and the radioactive isotopes including ^{3}H, and C^{14} (Nisi B et al., 2016). This method has been widely used in the arbitration, source analysis, and tracing of environmental pollutants. Presently, stable isotope tracing is frequently used to analyze the sources of nitrate nitrogen, organic carbon, and nitrogen. To further improve the tracing accuracy, increasingly more researchers have adopted the multi-isotope technique or the combination of isotopes and other techniques to trace the sources of pollutants. For instance, hydrochemical analysis, stable isotopes of water (δ^{18}O, δ^{2}H), and stable isotopes of nitrate (δ^{15}N, δ^{18}O) were combined to study the sources of nitrate (Ma WJ et al., 2020). Ascertaining the hydrogeological and hydrogeochemical conditions of a groundwater system is a prerequisite for isotope tracing and helps explain the sources of groundwater pollution more rationally.

Ren K et al. (2021) revealed that multiple isotopes (C, N, and O) and hydrochemistry could be used to analyze the sources and transformation process of nitrate (NO_3^-) in water bodies of underground river basins and that the SIAU model could be used to quantitatively calculate the contribution ratios of NO_3^- from different inputs. Li SL et al. (2010) showed that the combination of nitrate isotopes and chemical composition could identify the main pollution sources of karst groundwater systems and characterize the processes affecting nitrate. Cortecci G et al. (2001) studied the δ^{34}S-SO$_4$ isotopic signatures of the Arno River (Northern Tuscany, Italy) and its tributaries, delineating the geographical distribution of anthropogenic contributions in a highly industrialized and urbanized region. They pointed out that the human load increased gradually from the Apennine Ridge to the Tyrrhenian Sea coast. In addition to conventional isotopes, non-conventional stable isotopes (Fe, Cr, and Cu) also have potential for tracing the sources and behavior of metals. Fe has four natural stable isotopes, namely ^{54}Fe (5.84%), ^{56}Fe (91.76%), ^{57}Fe (2.12%), and ^{58}Fe (0.28%), Cr has four stable isotopes, namely ^{50}Cr (4.35%), ^{52}Cr (83.79%), ^{53}Cr (9.50%), and ^{54}Cr (2.36%), and Cu has two stable isotopes, namely ^{63}Cu (69.1%) and ^{65}Cu (30.9%) (Rosman JR and Taylor PD, 1998). In the study of Fe isotopes of suspended particulate matter in the Pearl River of southwestern China, the analysis of the enrichment factors and the weak correlation between δ^{56}Fe and δ^{66}Zn indicated quite limited Fe input from human activities (Han GL and Zeng J, 2021). Cr isotopes were used to analyze the source composition of Cr in sediments from different reaches of the heavily contaminated Xiaoqing River in Shandong Province, indicating that δ^{53}Cr near the pollution sources was the most affected by anthropogenic Cr (VI) emissions (He X et al., 2020). As indicated by the Cu isotope ratio and the material balance equation, the contribution rates of rock weathering, municipal sludge, and smelting tailings to particulate matter Cu in the Pearl River were 76.4%, 15.4%, and 8.2%, respectively (Zeng J and Han GL. 2020).

2.4. Numerical modeling

The inversion of groundwater numerical models is used to invert the governing equation (the model structure and parameters), boundary conditions, or initial conditions of a water environmental system based on the known spatial-temporal distribution of pollutants (Liu XD et al., 2009). Targeting different problems, the groundwater numerical models can be used to identify parameters, source and sink, boundary conditions, and initial conditions individually and determine two or more of these aspects simultaneously (Wang JR and Hu LT, 2017). The methods for solving inverse problems can be divided into direct and indirect methods. Direct methods mainly include backtracking and regularization-based methods. Indirect methods mainly include the simulation optimization algorithm and probabilistic method. The simulation optimization algorithm is the main method for solving the inverse problem of the pollution source identification of groundwater (Fig. 2). At present, the most widely used model for solute transport in saturated groundwater is the MT3DMS, which covers convection, dispersion/diffusion, source/sink mixing, and chemical reactions and can be coupled with MODFLOW to simulate the transport and transformation of multiple pollutants (Zheng C and Wang PP, 1999).



Set a conjecture value X_0 based on a priori information

Use X_0 as input to the simulation model to generate simulated calculated values of

Use the objective function in the optimization model to measure the difference between

To decide whether the termination condition is met, the termination condition in an optimization model is generally set to be either the value of the objective function being less than the permissible error, or the number of iterations reaching a specific value. If the iteration termination condition is met, the current guess is the optimal solution of the optimization model, i.e. the inverse identification result of the pollution source; if the iteration termination condition is not met, the next step is performed.

Replace X_0 with the new guess value X, and return to step 2. During the solution of the optimisation model, the new guess value X_1 is calculated according to the optimisation algorithm.

Fig. 2. Flow chart of the simulation optimization method (after Hou ZY, 2018).

The simulation optimization model based on an artificial neural network (ANN) can effectively determine the pollution source locations of aquifers. For large-scale aquifers, the pollutant concentration can be predicted using neural network models, each of which was established for an observation location (Leichombam S and Bhattacharjya RK, 2016). The pollutant leakage amount from a groundwater pollution source can be obtained accurately using the simulation optimization model based on the genetic algorithm (Xiao CL et al., 2015). In addition, the simulation optimization method based on radial basis functions has high accuracy, is time-saving, and can be used to calculate the leakage amount from a pollution source (Xiao CN et al., 2016). Skaggs and Kabala reversed the pollutant release process from a pollution source using Tikhonov regularization (TR) based on the one-dimensional homogeneous steady flow model assuming that the pollution source location was known. Their results proved that the accuracy of plume concentration depends on the description accuracy and dispersal extent of the current plumes (Skaggs TH and Kabala ZJ, 1994). Li L et al. (2020) proposed a Bayesian model-based pollution-probability estimation method to determine groundwater risk sources. Moreover, with the event of anomalous Cr^{6+} and $CHCl_3$ contents in an agricultural irrigation well in the lower reaches of an industrial agglomeration area as a case study, they calculated the probability that the index anomalies originated from eight risk sources. This method can quickly locate groundwater pollution sources before a detailed investigation.

2.5. Comparison of methods for pollution source identification

Among the identification methods, only the numerical modeling can recognize various information on groundwater pollution sources, while other methods can only identify a certain aspect of pollution sources (Table 1). After nearly 30 years of development, the numerical modeling of groundwater has been improved with the achievement of the water quality inverse. However, the solute transport of groundwater is controlled by many factors, such as geological conditions, parameter properties, and hydrogeochemical reactions. The aquifer parameters influence the identification results of pollution sources. Inaccurate aquifer parameters will lead to inaccurate identification results of pollution sources. Therefore, inaccurate reverse simulation is still the greatest obstacle to the applications of the numerical modeling method. It is an important development direction for the inversion method of pollution source numerical models to describe the water flow and quality model more accurately, introduce more efficient calculation methods, and convert the theoretical research of the models into practical applications.

The identification system can be established by comprehensively applying various methods in surveys of groundwater pollution sources. The identification results obtained using various methods can be compared and verified to improve the reliability and accuracy of the identification results. For example, the geophysical exploration method tends to yield multiple solutions in anomaly interpretation, and the anomaly interpretation can be combined with environmental geological and geochemical surveys to conform with the actual situation more accurately. Zhang T (2021) identified the nitrate pollution sources of groundwater based on conventional hydrochemical analysis, nitrogen and oxygen isotopes, and numerical modeling, obtaining accurate identification results. It is noteworthy that a detailed study of the hydrogeological conditions and stratigraphic structure of contaminated sites is the basis of pollution source identification regardless of the adopted methods.

3. Groundwater remediation technologies

The remediation of contaminated groundwater began in the late 1970s. The establishment of the US EPA’s Superfund program in 1980 elevated the contaminated site remediation by making it be subject to national law, and Superfund has contributed greatly to the development of the methods and techniques for contaminated site remediation. Appropriate remediation technologies are developed based on hydrogeological conditions, lithological characteristics, data on pollution sources, and economic costs. The remediation of contaminated groundwater can be classified differently based on remediation locations and methods. The remediation technologies can be divided into *in-situ* and *ex-situ* remediation technologies according to remediation locations (Zhao YS, 2007), and the remediation methods include physical, chemical, microbiological, and natural attenuation methods (Fei YH et al., 2022). Specifically, the physical method uses hydrodynamic fields to control pollutant transport and reduce pollutant dispersion; the chemical method uses chemicals to oxidize or reduce pollutants; the microbial method uses indigenous or cultivated microfloras to degrade pollutants into non-toxic or less toxic substances, and the natural attenuation method uses natural processes to decompose and alter organic pollutants leaking into the soil or groundwater (Zhao YS, 2007).

3.1. In-situ remediation technologies

3.1.1. In-situ injection

The *in-situ* injection uses chemical methods to convert pollutants into harmless substances on the principle of *in-situ* oxidation or reduction. The reagents injected *in-situ* mainly consist of chemical reagents (oxidizing or reducing agents) and microbial agents (Fig. 3).

Oxidizing agents are injected into contaminated groundwater to increase the dissolved oxygen content and promote the oxidation and decomposition of organic substances. The commonly used oxidants include chlorine

Table 1. Comparison of the method identification for pollution sources.

Identification method	Advantages	Disadvantages	Main application scenario
Geophysics	Rapid, low-cost, no damage *in-situ*, continuous information, real-time dynamic monitoring of pollution trend	It is only suitable for pollution detection with large physical difference from rock strata and depth less than 30 m. With the higher accuracy requirements, the shallower the detection range. There are multiple solutions to the interpretation of abnormal results	Heavy metal or nitrate pollution, landfill, tailings leachate, oil leakage, etc.
Geochemistry	The mixed pollution type and concentration can be identified, and the actual pollution situation can be truly reflected.	Large sampling range, small number of samples, low precision, low work efficiency, regional continuous monitoring data can not be quickly obtained	Heavy metal, “three nitrogen”, and other inorganic matter
Isotope tracing	Pollutants can be quantitatively studied, the contribution rate of different pollution sources can be calculated, and the specific emission enterprises of pollutants can be accurately identified.	It is necessary to ensure that there are identifiable differences in isotope values among the pollution sources. The greater the difference, the higher the recognition and the easier it is to distinguish. Isotopes do not fractionate in the environment, or their fractionation can be recognized	Nitrate, sulfate, organic carbon, organic nitrogen, Fe, Cr, Cu, etc.
Numerical modeling	Low-cost, large area, and the various information of groundwater pollution sources (such as the location of pollution sources, leakage history, etc.) can be identified simultaneously.	Groundwater solute transport is controlled by many factors such as stratum conditions, parameter and hydrogeochemical reactions, which makes it difficult for reverse simulation to reflect the actual situation objectively	Petrochemical plant, landfill and other point pollution sources

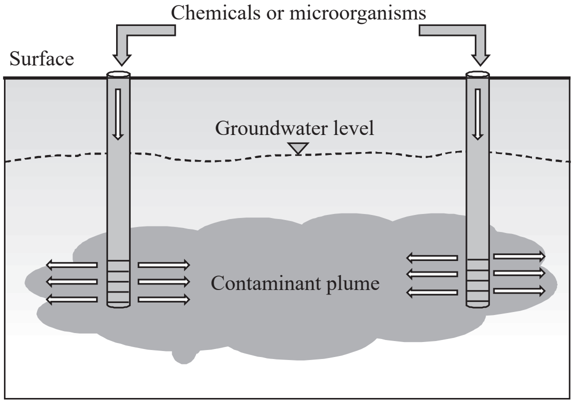


Fig. 3. Schematic diagram of *in-situ* injection.

dioxide, Fenton's reagent, hydrogen peroxide, hypochlorite, potassium permanganate, ozone, and calcium peroxide. Among them, calcium peroxide can control the H_2O_2 and O_2 release rates to meet the requirements of pollutant oxidation and degradation, saving raw materials and balancing oxygen levels (Pu SY et al., 2020).

The reduction method uses reducing agents to transform or degrade pollutants in groundwater. It has been found that chlorinated hydrocarbon pollutants can be dechlorinated when contacting metal catalysts, thus, achieving remediation purposes (Lowry GV and Reinhard M, 1999). Gillham RW and O'Hannesin SF (1994) first proposed using zero-valent iron to remediate groundwater suffering chlorinated organic pollution. A recent study shows that zero-valent iron nanoparticles can reduce and remove many pollutants from groundwater, such as halogenated hydrocarbons and heavy metals Cr, Pb, and As. This method has the advantages of low costs, simple construction, low disturbance, and desired remediation effects. However, its tendency to agglomeration, precipitation, and passivation leads to reduced remediation performance (Zhang W et al., 2012).

Wang D et al. (2018) established an *in-situ* (nano-zero-valent iron agents) injection restoration system for a Cr(VI)-contaminated groundwater site in the production workshop of an electroplating plant in Beijing, and the long-term monitoring results showed that the reduction rate of Cr(VI) reached 99%. *In-situ* and *ex-situ* chemical oxidation methods were used to remediate the karst water pollution in fissures of Ordovician limestones below coal seams in closed pit coal mines in Shandong Province. Firstly, curtain grouting was conducted to block the pollutants. Secondly, the contaminated water was pumped out to be treated with the advanced Fenton oxidation progress. Thirdly, oxidizing agents were injected *in-situ* to remove residual pollutants through a pumping cycle. The results showed that the COD concentration reached 2–340 mg/L and chloromethane reduced from 137–410 μg/L to 13–262 μg/L (Han Y et al., 2019).

In-situ addition of microbial agents generally involves screening suitable strains and adding agents to alter environmental conditions to improve the activity of the flora. This technology includes aerobic and anaerobic microbial remediation (Mani TS and Chaurasia S, 2018). Microbial remediation is characterized by low costs and low secondary pollution and is suitable for the treatment of large contaminated areas (Zhang S et al., 2016, 2017). Researchers have isolated strains that aerobically degrade volatile organochlorine pollutants from a petrochemical wastewater treatment plant (Li MT et al., 2008). Anaerobic microbial degradation presents a higher proportion than aerobic microbial degradation (Wang P et al., 2021). Reductive dechlorination by anaerobic microorganisms played a major role in the *in-situ* remediation of chlorinated hydrocarbon pollution in an automotive part plant in Shanghai (Meng L et al., 2014). The organic pollutant 1, 2, 4-trichlorobenzene in groundwater from an industrial contaminated site in Nanjing was completely degraded under *in-situ* anaerobic conditions (Qiao W et al., 2018).

3.1.2. Permeable reaction barriers

The currently popular permeable reactive barrier (PRB) involves installing a permeable barrier filled with active reactive materials. When contaminated groundwater flows through the barrier, pollutants are removed through adsorption, precipitation, redox, and microbial degradation caused by the reactive materials. This barrier can be combined with various remediation methods and is widely used to treat various types of pollution (Fig. 4).

Common PRB structures include continuous reactive walls and funnel-and-gate systems (Faisal AAH et al., 2018; Chen ZR et al., 2012). A continuous reactive wall is generally used for slight groundwater pollution. By contrast, a funnel-and-gate system is generally used for severe groundwater pollution in a large contaminated area. Both structures are suitable for shallow groundwater, while a perfusion treatment belt PRB can be used for sites with deep groundwater (Song QW et al., 2019). In addition, the active reaction materials should be resistant to corrosion and have long-lasting activity, including zero-valent iron, activated carbon, ion exchange resins, chelating agents, and microorganisms.

As the most typical application in engineering as a reaction medium of a PRB, zero-valent iron was used for the remediation of Cr(VI)- and TCE-contaminated groundwater in a metal plating plant in Elizabeth City, North Carolina, USA in the early 1990s. Three years of monitoring results showed that the Cr(VI) concentration was reduced from 3 mg/L to almost zero and the maximum TCE concentration

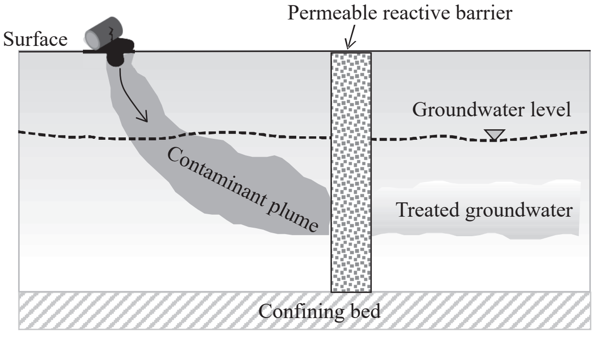


Fig. 4. Schematic diagram of a permeable reactive barrier.

was reduced from 114 μg/L to 2.9 μg/L. After 22 years of operation, the TCE removal rate was still up to 98% (Torres E et al., 2017). In a military base in Ontario, Canada, a mixture of 22% granulated iron and 78% sand was used to form a permeable wall, removing 90% of trichloroethylene and 86% of tetra vinyl chloride (O'Hannesin SFUO and Gillham RW, 1998). The iron-modified manganese ore, which has been found to be the most effective in removing arsenic, was applied to the PRB technique at the As-contaminated site in Suxian District, Chenzhou City (Huang YB, 2018). Two PRB demonstration projects in Shenyang and Jiaozuo were completed by the China University of Geosciences (Beijing), and the monitoring results showed that the zeolite permeable reactive barrier could effectively remediate ammonia nitrogen pollution *in situ* (Hou GH et al., 2014; Li SP et al., 2014). Schwarz A et al. (2021) evaluated the long-term operating performance of a PRB utilizing sulfide diffusion exchange that was employed to treat mine acid wastewater using a small reactor indoors. The evaluation results showed that 87% of iron and 79% of zinc were removed.

3.1.3. Air sparging

Air sparging (AS) uses shafts to establish an air injection-extraction system to inject air below the water table. In this way, pollutants transition from the liquid phase into the gas phase, and pollutant-laden gases rise to the vadose zone under buoyancy. Then, the gases are pumped out using an air extraction system for surface treatment, thus achieving groundwater remediation (Fig. 5).

The AS technique is suitable for the blow-off of soluble organic matter. This technique promotes the volatilization of residual and adsorbed organic matter (e.g., petroleum and chlorinated hydrocarbon solvents) present below the water table and on the capillary margin, and the oxygen transport facilitates aerobic degradation (Chao HP et al., 2018; Johnson RL et al., 1993). This technique was widely recognized and applied in the late 1980s and the early 1990s, revealing that the performance of this technique was affected by the air injection mode, site conditions, and pollutant characteristics (Neriah AB et al., 2019; Yang X et al., 2005), such as the horizontal extension of gas injection well in the aquifer, the injection of different gases (e.g., hydrogen, propane, and oxygen), and pulsed air injection or the injection of heated air. The factors affecting gas flow patterns were analyzed using a three-dimensional simulation tank, obtaining the following conclusions: There was a positive correlation between the AS pressure and flow; the maximum saturation of gas in the AS remediation was 49%–76%, and the theoretical AS pressure generally did not exceed 60 kPa, otherwise the influence area changed very little (Song XL, 2015; Zhang Y, 2004; Wang HF et al., 2014). As shown by the summary and analysis of a number of AS cases in the USA, lithology and pollutant type significantly affected the AS remediation effect; different injection modes did not yield significantly different remediation effects; the AS using chlorinated solvent produced performed well, and petroleum contaminated sites were prone to rebound after remediation (Bass DH et al., 2000).

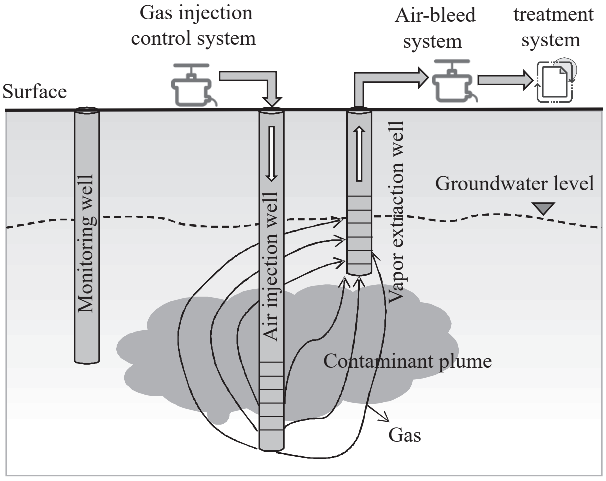


Fig. 5. Schematic diagram of air sparging.

As a type of AS technique, AS using recirculation wells works as follows. A pipe for gas injection and extraction is placed in a closed shaft, which is connected to the groundwater. Then, the gas is injected into the pipe to form a three-dimensional circulation pattern, allowing pollutants to be separated from the water and collected for disposal. This technique is not suitable for large-scale groundwater remediation and low-permeability aquifers. It was once used to remediate groundwater around an effluent discharge pipeline of a chemical plant (Qu Z et al., 2016). Specifically, four recirculation wells and nine monitoring wells were deployed, and the recirculation wells were continuously aerated for 24 hours under a pressure of 200 kPa using air compressors. The highest chlorobenzene concentration near the recirculation wells reached 153.14 mg/L before treatment and dropped to 3.94 mg/L after 28 days of operation. Despite a removal rate of over 95%, the national standard limit of 1.0 mg/L for chlorobenzene was not satisfied, and the subsequent remediation was slow.

3.1.4. Thermal treatment

In-situ thermal treatment is an improvement in air sparging technique. The injection and extraction processes of AS are slow to remove pollutants, particularly those adsorbed in aquifers, and their removal rate is limited by diffusion. Thermal treatment is to heat contaminated groundwater to induce the conversion of pollutants and groundwater into vapor, which is then extracted for surface treatment. The heating methods include the direct injection of hot gas, resistance heating, heat conduction, and radio-frequency heating (Hicknell BN et al., 2018). The surface treatment involves steam-water separation, absorption, chemical oxidation, activated carbon adsorption, or condensation.

The thermal treatment worked well for the removal of DNAPL from low-permeability formations (Baker RS et al., 2016). USEPA has applied resistive heating to remediate several contaminated sites (USEPA, 2004). Zhao YS et al.

(2019) conducted an experiment on the migration pattern of steam in porous media for the remediation of chlorobenzene. They found that with the injection of steam at a rate of 0.3 kg/h, the remediation of chlorobenzene in fine sands by hot steam reached 98.0% after 3.5 h, of which 88.4% was removed by volatilization, 9.6% migrated out with the steam condensation front, and only 2.0% remained in the porous media. Subsurface warming was applied to the remediation of petroleum-contaminated sites in northeastern China (Chu T et al., 2018), achieving a temperature transfer radius of 2–4 m and a pollutant removal radius using the aeration field of up to 10 m. Moreover, the pollutant removal range was increased by 3–5 m and the removal rate was effectively increased by 40%–50% compared with non-warming-enhanced conditions.

3.2. Ex-situ remediation technologies

3.2.1. Pump-and-treat technique

The pump-and-treat (P&T) technique is an early and widely-used groundwater remediation technique. Depending on the pollution characteristics, a certain number of pumping wells are placed to pump the contaminated groundwater to the surface to be remediated by physical, chemical, and microbiological methods using above-ground treatment equipment. Afterward, the treated groundwater is recharged underground or discharged into the pipe network (Fig. 6).

The recovery rate of pumped-out treated pollutants may not always reach 100%. For pumping-irrigation double wells, the stable groundwater flow field under well disturbance can be divided into an internal circulation zone, an external circulation zone, and a non-circulation zone. The recovery rate depends on the direction and relative intensity of lateral groundwater runoff and increases with an increase in the pumping flow (Zhang S et al., 2020).

The P&T technique was applied to the groundwater remediation of a relocated chemical plant in Shanghai, where the groundwater was contaminated by arsenic, benzene, ethylbenzene, carbon tetrachloride, and chloroform, with a contaminated area of 1189 m^2. For this plant, 4475 m^3 of contaminated groundwater was remediated as follows. A total of 33 pumping wells were placed, with a pumping rate of 150–200 m^3/d. After pumping, the groundwater was treated using the process of “primary sedimentation + advanced oxidation + coagulation and sedimentation” (Wang JL, 2019). Chen S (2020) remediated groundwater contaminated by a diesel spill in an electroplating industry enterprise by combining the surface drenching with the P&T technique. Specifically, the heavily contaminated soil was excavated first, and then nine nozzles were set up at the leak point to sprinkle water at a rate of 1.3 m^3/h for 2 h per day. Besides, five nozzles were set up at the greenbelt to the west of the leak point to sprinkle water at a rate of 0.7 m^3/h for 9 h per day. The drenching water into the groundwater was pumped to be treated. After nine months of remediation, the petroleum concentration in the groundwater was reduced to less than 0.3 mg/L, meeting the standard limit.

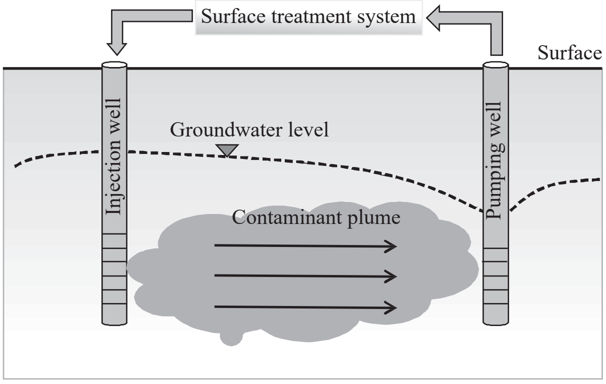


Fig. 6. Schematic diagram of the P&T technique.

3.2.2. Multi-phase extraction

Multi-phase extraction (MPE) is used to remove gaseous contaminants from groundwater and the vadose zone by pumping using a high vacuum system, in which contaminants can be simultaneously extracted from soil gas and groundwater to the surface for multi-phase separation and treatment. The extraction systems are divided into single- or double-pump structures, and their operation mode is as follows. The liquid-phase extraction decreases the water level. As a result, the capillary edge of the vadose zone is exposed, and the pollutants in this zone are removed through gas-phase extraction.

The performance of the MPE technique is influenced by many factors such as the gas-phase mass transfer coefficient, soil water content, organic matter content, soil structure, and the biodegradability of contaminants. The numerical simulation of multi-phase flow can be used in the MPE technique to guide the multi-phase extraction, thus optimizing the MPE operation. The remediation performance of the MPE technique can be improved by accurately capturing parameters such as pump position, flow rate, LNAPL gas-phase mass transfer coefficient, and soil-water characteristics (Edwards DA et al., 2002; Qi S et al., 2020).

In China, the MPE technique has been applied in conjunction with the *in-situ* oxidation method at many sites. For example, the MPE and the *in-situ* chemical oxidation were combined to remediate the benzene-contaminated groundwater at a contaminated site of a chemical plant. The removal rate of chlorobenzene, 1,2-dichlorobenzene, and 1,4-dichlorobenzene reached 99% after 25 days of contamination (Wang JH et al., 2017). In the remediation of groundwater contaminated with petroleum hydrocarbons, benzenes, and PAHs in an electronic machinery factory, the MPE technique was used to intensively remove LNAPLs from groundwater, and then the *in-situ* chemical oxidation was applied, achieving the remediation goal in 45 days (Wang L et al., 2014). Zhang J et al. (2016) used sodium persulfate as an oxidant and achieve degradation rates of petroleum hydrocarbons, benzene, and PAHs of 99.8%, 94.4%, and 92.2%, respectively.

3.3. Comparison of groundwater remediation technologies

Among the common remediation technologies, the PRB technique is the most widely used currently due to its wide applicability and encouraging treatment results. However, its disadvantages of easy blockage and difficult maintenance should not be overlooked (Table 2). Dozens of groundwater remediation technologies have emerged, and they have different application conditions. Therefore, it is necessary to select one or several technologies in combination to achieve the desired remediation performance according to the actual situation (including hydrogeological conditions and the nature of pollutants) of the contaminated site. For example, given that the P&T technique has the disadvantages of trailing and rebounding, the activator can be injected *in situ* to improve the treatment effect and reduce remediation costs. The AS technique can form an enhanced aerobic microbial decomposition zone when the oxygen content rises near the circulation well. Therefore, this technique can be combined with several other techniques such as microbial remediation and gas-phase extraction to improve efficiency.

In view of the complexity and spatial variability of groundwater pollution and the spatial heterogeneity of hydrogeological conditions, it is feasible to adopt zoned and graded remediation strategies for areas with different pollution levels and risks. For highly contaminated areas caused by nonaqueous phase liquids, high-intensity remediation can be adopted to rapidly reduce the total amount of pollutants. For moderately contaminated areas, long-term remediation with relatively low intensity can be adopted to reduce remediation costs and secondary pollution. For low-risk lightly-contaminated areas, risk management measures can be applied. Depending on the contamination characteristics, the multi-technology and multi-method coupling approach can be adopted to produce a complementary effect (Song YN et al., 2020).

Each contaminated site has unique characteristics and it is impractical to form its remediation scheme by copying remediation projects of other sites. A groundwater remediation scheme should be determined and implemented in three steps, namely indoor experimental trial, site pilot, and formal implementation in sequence. Moreover, groundwater dynamic models and corresponding virtual simulation software should be adopted to determine the optimal remediation technology/technology combination and engineering parameters.

4. Discussion and suggestions

(i) Accurate identification of pollution sources is a prerequisite for efficient groundwater remediation. Ascertaining the migration and transformation processes of

Table 2. Comparison of groundwater remediation technologies.

Remediation technologies		Advantages	Disadvantages	Main remediated contaminants	Suitable site conditions
In-situ remediation technology	*In-situ* injection	Low-cost, simple construction, fast treatment, small ground disturbance	Possible secondary contamination, the remediation effect is easily influenced by the environment, the release of gases or heat from the reaction process affects the distribution of contaminants	Nitrates, heavy metals, chlorinated hydrocarbons, benzenes, petroleum hydrocarbons	Well-permeable aquifers, suitable for sites deeper than 30 m
	PRB	Continuous *in-situ* treatment of a wide variety of contaminants, no need for above-ground water storage units, no media contamination	Easy to clog and difficult to maintain	Wide range of applicable pollutants	Saturated aquifers with hydraulic gradients and weakly permeable layer at the lower interface, where the unconfined aquifer with aquifer depth less than 10 m is the best.
	AS	Low-cost, small number of equipment, easy to install, simple to operate, small ground disturbance	Small restoration area, not suitable for the low permeability aquifers	Soluble volatile organic compounds, chlorinated hydrocarbons, petroleum hydrocarbons	Well permeable, saturated, open aquifers
	In-situ thermal treatment	Can be used in low permeability formations with high remediation efficiency	High energy consumption, not suitable for aquifers with high water volumes	NAPL	Aquifers with low water content, also applicable to low permeability formations
Ex-situ remediation technology	P&T	The principle and equipment are simple to operate. High treatment capacity, and high remediation efficiency	Easily trailing and rebounding of pollutants in the later stages. Great disturbance to groundwater flow and water environment. Little effect on non-aqueous phase liquids (NAPLs). High-cost.	Heavy metals, nitrates, highly soluble organisms	Homogeneous aquifers with high pollutant concentrations, good solubility, and deep burial
	MPE	Environmentally friendly, high remediation efficiency, low ground disturbance, suitable for high concentration contaminated sites, especially for VOCs and petroleum hydrocarbon pollutants.	The gas and liquid phase should be treated separately. Complex process equipment. High-cost, and limited application depth.	VOCs and petroleum hydrocarbons	Permeability coefficients of 0.1 μm/s to 10 μm/s, water content of 40% to 60%. A homogeneous aquifer consisting of sand to clay

pollutants in groundwater (including the location of pollution sources, the start and end time of pollution, and the pollutant emission intensity) can help delineate the groundwater pollution site and establish the groundwater monitoring network for targeted and fine-scale groundwater remediation.

For example, a highly industrialized area in southern India suffered long-standing contaminated groundwater seepage, which severely threatened ecosystems in the lower reaches. However, the leakage source was not identified in the past 30 years, posing a great challenge to regulators. In this case, the groundwater leakage sources in the highly contaminated groundwater environment were successively identified using a multidisciplinary approach that integrated satellite remote sensing, electrical resistivity tomography, and saturated and unsaturated zone monitoring. Based on the identification results of pollution sources, an impermeable wall/slab pile was placed in the groundwater flow direction, and the contaminated groundwater leakage in the dry season was reduced by 79.2%, significantly reducing treatment costs and improving ecosystems in the lower reaches (Surinaidu L et al., 2021).

(ii) Understanding the pollution characteristics is the basis for the pollution prevention and remediation of groundwater. After entering the aquifer, groundwater undergoes pollutant sorption and desorption by rocks and soil, and the pollution level is influenced by water-bearing media and hydrodynamic conditions. Some pollutants are adsorbed by low-permeability soils and are released again under the action of water flow. Therefore, detailed hydrogeological investigations and the assessment of contamination risks and levels are quite necessary for the pollution prevention and remediation of groundwater at contaminated sites.

Groundwater seepage drives pollutant diffusion and is influenced by the heterogeneity of water-bearing media, which results in the uneven distribution of the permeability coefficient. A high permeability coefficient leads to rapid pollutant diffusion, forming dominant pathways and making it difficult to accurately determine the distribution of contaminated groundwater as well as the delivery way and dosage of pollution remediation agents. When pollutants encounter low-permeability strata, their migration is blocked and they are adsorbed by soil. The captured pollutants become new pollution sources, which release pollutants to high-permeability areas, leading to secondary pollution, trailing, and rebounding.

(iii) The investigation and evaluation of contaminated sites facilitate pollution source identification and remediation of groundwater and should be carried out throughout according to the following steps. First, the background information about the contaminated site should be collected, including the geological and hydrogeological conditions, and the current and historical situation, to make a primary identification of pollution. After determining the environmental conditions, pollution type, and potential occurrence, a sampling plan and data evaluation should be conducted to determine the type, concentration (level), and spatial distribution of pollutants. Finally, the site characteristic parameters and the human exposure parameters should be investigated to guide groundwater remediation.

(iv) Future research priorities are to continuously promote technology combination and develop emerging technologies to address complex pollution problems. Owing to the complex types of pollutants and the greatly varying pollution levels in groundwater, it is difficult to achieve the remediation goal using a single technology for pollution source identification and remediation. Furthermore, the reconstruction of multi-point pollution sources is more challenging than that of single-point pollution sources. Therefore, the multi-technology combination is the way forward for the remediation of contaminated groundwater. With technological development and innovation, introducing advanced technologies is also an important development direction in the future. For example, the currently more advanced machine and deep learning methods can be introduced to accurately identify pollution sources.

In addition, it is necessary to further develop environment-friendly remediation technologies, such as microorganism remediation. Owing to the diversity and complex compositions of wastewater, naturally evolving microorganisms generally have limited enzymatic activity to degrade pollutants. Genetic engineering technology can be used to genetically modify these strains to improve their fecundity and degradation activity, thus achieving convenient and effective pollution treatment.

Previous studies mainly focus on the remediation of conventional pollutants but scarcely concern the remediation of emerging pollutants. For example, although microplastics, PFAS, and PPCPs (pharmaceuticals and personal care products) have been frequently detected in groundwater, little research has been conducted on targeted and mature remediation techniques for these pollutants. Therefore, the remediation of emerging pollutants is a research direction that needs urgent attention.

5. Conclusions

(i) The methods for identifying groundwater pollution sources mainly include geophysical exploration, geochemistry, isotopic tracing, and numerical modeling. Among these identification methods, only numerical modeling can recognize various information on groundwater pollution sources, while other methods can only identify a certain aspect of pollution sources. In actual investigations, the identification results obtained using multiple methods can be used for mutual verification to improve the accuracy of pollution source identification.

(ii) Groundwater remediation technologies are divided into *in-situ* and *ex-situ* remediation technologies, and the remediation methods include physical, chemical, biological, and natural attenuation methods. Among the remediation technologies, the PRB technique enjoys wide applicability and encouraging treatment effects and is widely used presently. However, its limitations cannot be ignored. Since different technologies have different application conditions, it is feasible to combine several technologies to achieve the desired remediation performance according to the actual conditions of the contaminated sites.

(iii) Pollution source identification is the basis of groundwater remediation, which in turn is the purpose of pollution source identification. Besides, detailed knowledge about the hydrogeological conditions and stratigraphic structure of contaminated sites is the basis for all work, regardless of the adopted identification methods or remediation technologies.

CRediT authorship contribution statement

Ya-Ci Liu and Yu-Hong Fei conceived of the presented idea and wrote the manuscript. Ya-Song Li supervised the project. Xi-Lin Bao and Peng-Wei Zhang conceived the original idea. All authors discussed and contributed to the final manuscript.

Declaration of competing interest

The authors declare no conflicts of interest.

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