Evaluation of Groundwater Quality in a Chemical Plant Considering Leaching Tests

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Abstract. The investigation and evaluation of groundwater pollution in chemical contaminated sites is an important part of site pollution investigation and remediation. This paper takes a chemical contaminated site in Jingzhou City as the research object, through carrying out sample collection and soil column leaching experiments, adopting single index evaluation method and comprehensive pollution index method to evaluate the site pollution, and exploring the spatial distribution characteristics of pollutants. The results showed that: the groundwater and soil of the site were seriously polluted and the comprehensive pollution evaluation was extremely heavy pollution; the spatial distribution of pollutants was large, and the shallow soil pollution was more serious than that of the deep layer; and the soil backfilled after remediation treatment was subject to secondary pollution. The study provides a reference for the investigation and evaluation of groundwater pollution at the site, and provides a scientific basis for the pollution prevention and control of chemical production sites and the reuse of land after demolition and relocation.

Keywords: groundwater quality evaluation; groundwater pollution; soil column leaching test; quality evaluation

1 Introduction

Human activities that pollute groundwater significantly damage the natural environment and ecosystems. These activities pose a threat to groundwater sources and create risks for surface water sources [1]. Studies have shown that groundwater quality is determined not only by natural processes such as recharge water quality, groundwater flow rate, lithology of aquifers, and interactions with other types of aquifers, but also by anthropogenic activities such as industry, agriculture, and pollution discharge that alter the water cycle [2, 3]. Chemical industrial parks are industrial zones primarily focused on the development of the chemical industry. Groundwater pollution in these areas is typically characterized by multiple sources and a concealed nature [4]. In recent years, environmental problems have received the attention of the government and the widespread concern of the nation, and many provinces and cities have upgraded their industrial structure or fully implemented the "Retreat to Three" in the built-up areas of

H. Bilgin et al. (eds.), *Proceedings of the 2024 6th International Conference on Civil Engineering, Environment Resources and Energy Materials (CCESEM 2024)*, Advances in Engineering Research 253,
https://doi.org/10.2991/978-94-6463-606-2_39

the cities, and a large number of chemical enterprises have been shut down or relocated [5-7]. Lu et al. [8], Liu et al. [9], and Zhao et al. [10] conducted relevant studies on groundwater monitoring during site environmental investigations. Their research revealed that industrial production processes generate large quantities of wastewater and waste residues containing toxic substances. If the residues are not treated and are directly deposited on the soil surface, groundwater may be seriously contaminated when the toxic substances on the soil surface leak into the aquifer [11]. Once groundwater is contaminated, it is difficult to restore water quality and requires a long recovery cycle [12].

The chemical plant site is located on the first level of Han River terrace with flat and open terrain. The terrace consists of Quaternary Holocene (Q4) clay, powdery fine sand and gravelly medium-coarse sand. The site covers a total area of about 6.94 × 104 m2. The chemical plant was established in the 1950s, and during the production period it mainly produced pharmaceutical raw materials, intermediates, pharmaceutical preparations and their derivatives until 2015, when the production was stopped and relocated, and the site has now been dismantled and levelled, and the soil contamination remediation is currently underway (Fig.1).

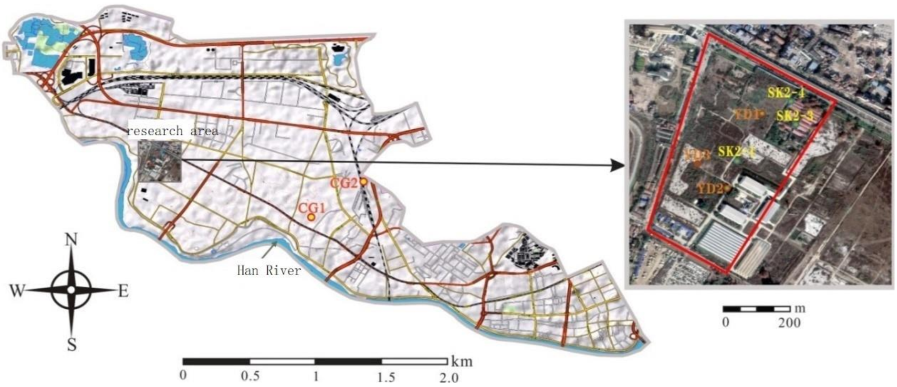

Fig. 1. Location of the site and plan view of the sampling points.

2 Materials and Methods

2.1 Sample Collection and Testing Items

2.1.1 Sampling Points.

This site contamination investigation in accordance with the principle of production area distribution to determine the groundwater and soil sampling points. According to the analysis of pollution sources and the distribution of the original factories within the site combined with the guideline layout requirements to determine the sampling points (100cm, 100~200cm, 200~300cm); the sample volume of soil samples is 6 in total, and the sample volume of groundwater is 7. The planimetric distribution map and point information of each sampling point are shown in Fig.1 and Table 1.

Table 1. Site groundwater and soil sampling site information.

Point Number	Point Description
Water sample points	
SK2-1	Chemical plant production area, there is a sludge pond next to this point, the sludge pond emits odour.
SK2-3	Non-chemical plant production area.
SK2-4	Non-chemical plant production area.
CG1	CG1 long view hole is located on the north bank of Han River.
CG2	CG2 long view hole is located on the north bank of Han River and north of CG1 long view hole.
Soil sample points	
YD1	Soil located in the centre of the chemical plant in the study area, used to study the characteristics of pollutant distribution in the vertical direction.
YD2	Located outside the chemical plant in the study area, surface soil was taken for parallel comparison of contamination inside and outside the site.
YD3	Soil from the site that has been remediated and returned to its original position to test the effectiveness of remediation of contaminated soil.

2.1.2 Testing Items.

(1) The full analytical test items of the water samples of the three monitoring wells taken from the study area in 2018 were 46 items, including: color, smell and taste, turbidity, visible to the naked eye, pH, total hardness, total dissolved solids, sulphate, chloride, iron, manganese, copper, zinc, cyanide and fluoride.

(2) Soil column leaching experiment leachate analysis test items are 27 items, including: aluminium, boron, barium, beryllium, bismuth, cadmium, cobalt, chromium (hexavalent), copper, iron, lithium, magnesium, pH and so on. Sample testing was carried out according to relevant national standards.

2.2 Soil Column Leaching Test

2.2.1 Experimental Device.

Experimental materials taken from the inner diameter of 5cm, a height of 30cm of plexiglass column, soil column inlet connected to the Mars bottle and peristaltic pump as a water supply device, can be achieved by replenishment of the flow rate control, in order to form a stable flow field, the bottom of the soil column has a diameter of 5mm holes, holes connected to the silicone tube used to receive the filtration solution.

2.2.2 Experimental Steps.

(1) Before the beginning of the experiment, the six groups of soil samples collected were loaded into the soil column and gently compacted. In order to prevent the distilled

water from infiltrating unevenly and the soil from blocking the water outlet, the water inlet and outlet were filled with quartz sand of 5cm thickness. Between the quartz sand and soil layers, a nylon net with aperture of 1mm is used to ensure smooth water seepage and uniform infiltration of leachate.

(2) After the soil sample filling is completed, distilled water is used to enter from the bottom of the soil column filtration tube, exhaust the air in the soil column, so that all soil columns are saturated with soil immersed in water, and after a certain period of time, the upper part of the soil column tube is filtrated by the water supply device, and the filtrate is picked up from the bottom of the soil column tube by the water sampling bottle. The leaching experiment was carried out continuously day and night with distilled water, and the experiment was stopped when the measured conductivity value of the leachate was nearly stable.

(3) Each time from the filtrate extracted 50mL, determination of pH and conductivity, followed by the filtrate sent to the test, to obtain the detection value, statistical indicators of contamination, the calculation of the mass of each group analyzed, and plotting the concentration and precipitation mass change curve with time.

2.3 Water Quality Classification and Evaluation Methods

2.3.1 Quality Classification.

Based on the "Groundwater Quality Standard (GB/T14848-2017)", with reference to the quality requirements for drinking water, industry, agriculture and other water, it is classified into five categories according to the high and low content of each component. Namely, I, II, III, IV and V categories, of which V category is the worst.

2.3.2 Evaluation Methods.

(1) Single-indicator evaluation method: Determine the groundwater quality category according to the indicator limit interval in which the indicator value is located; when the indicator limit value of different groundwater quality categories is the same, it will be from the best rather than the worst; when determining the evaluation results, it will be from the worst rather than the best, and use the level of the worst indicator in the evaluation grade of each indicator as the evaluation result of the whole groundwater sample, and point out the indicator of the worst category.

(2) Comprehensive Pollution Index Method: The evaluation of groundwater pollution reflects the degree of pollution of groundwater affected by human activities, and the pollution index method is the most commonly used evaluation method in the current evaluation of groundwater pollution, which is commonly used in the evaluation of soil, air and water pollution:

$$P_{ki} = \frac{C_{ki} - C_0}{C_{III}} \tag{1}$$

Where, P_{ki} denotes the pollution index of the i -th indicator of k water samples; C_{ki} denotes the actual test value of the i -th indicator of k water samples; C_0 denotes the background value of the i -th indicator of k water samples; in this paper, there is no background value, so take the limit value of the Class III indicator of the Groundwater Quality Standard (GB/T14848-2017) as a reference value; C_{III} denotes the limit value of the i -th indicator of k water samples in the Groundwater Quality Standard; and C_{III} denotes the limit value of the i -th indicator of k water samples in the Groundwater Quality Standard (GB/T14848-2017). According to the pollution index grading standard, the pollution level of each water sample is divided into levels (Table 2), and after the evaluation of the pollution of individual indicators is completed and the levels are divided sequentially, the pollution level of individual indicators of each water sample is compared, and the result of the level with the highest pollution level is taken as the result of the comprehensive evaluation of the pollution of the groundwater of the water sample.

Table 2. Pollution Index Classification Criteria.

Pollution category	Unpolluted	Lightly polluted	Moderately polluted	Heavily polluted	Severely polluted	Extremely polluted
Pollution classification	I	II	III	IV	V	VI
Index range	$P_{ki} \leq 0.2$	$0 < P_{ki} \leq 0.2$	$0.2 < P_{ki} \leq 0.6$	$0.6 < P_{ki} \leq 1.0$	$1.0 < P_{ki} \leq 1.5$	$P_{ki} > 1.5$

3 Migration Law of Inorganic Components in Leaching Experiment

The permeability of soil is generally expressed by the permeability coefficient, which can characterize the impermeability of soil. Its calculation formula is as follows:

$$K = QL / Aht \tag{2}$$

Where, K is the permeability coefficient, cm/s; Q is the total volume of water passing through the soil sample at a fixed time, mL; L is the height of the soil column, cm; A is the cross-sectional area of the soil column, cm^2; h is the water head acting on the soil column, cm; and t is the test time, s.

The interval values of average flow rate and permeability coefficient of soil column were calculated to be 1.56~169.99 mL/d and 0.06~13.84 cm/d, respectively. Comparing the average flow rate and permeability coefficient of six groups of drenching experiments, it can be seen that the average flow rate and permeability coefficient of YD2 were the largest, and it had the fastest drenching rate, YD3 was the second fastest, and YD1 had the slowest drenching rate, and the permeability coefficients were about 3 times of those of YD3, respectively, 72~230 times under different layers of YD1, and the permeability coefficient of each soil column varied greatly, which was mainly related to the nature of the soil, and the results preliminarily indicated that the seepage control performance of YD1 was the best, and the seepage control performance of YD2 was the poorest.

The inorganic components of the leachate all showed the process of higher concentration at the initial stage and gradual attenuation at the later stage, especially the concentration of the initial leachate was the highest (Fig. 2). Most of the inorganic components were detected at the highest concentration in the initial leachate, indicating that the dry soil had the highest degree of precipitation during the saturation process of water infiltration, and that the precipitation efficiency of the components gradually decreased as the saturation infiltration process continued. This also indicates that in the study site, the initial stage of the sub rainfall event will precipitate relatively high concentrations of pollutants, and with piston infiltration, the later recharge rainfall will delay the pollutants precipitated from the earlier rainfall leachate downward, and the surface pollutants will gradually affect the lower soil and groundwater.

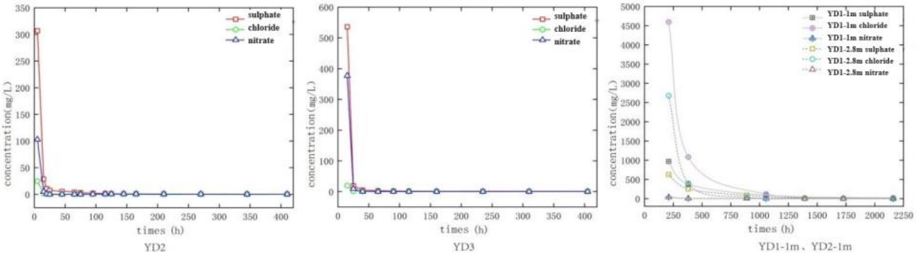

Fig. 2. Variation curves of sulphate, nitrate and chloride concentration with time in leaching experiment.

According to the results of the hydro chemical testing of the leachate samples, the precipitation capacity of sulphate, nitrate and chloride, which have high ionic concentrations in the initial received leachate, was compared, and the precipitation mass curves of different components in different soil columns could be derived by calculating the sum of the products of the concentrations of inorganic components and the corresponding volume of leachate at different time periods (Fig. 2).This curve characterizes the magnitude of the precipitation capacity of the soils at different sampling points by comparing:

(1) Under the same test conditions, sulphate, nitrate and chloride were the first to be precipitated from YD2 soil column, followed by YD3 soil column, while YD1 was the slowest to be precipitated; the difference between the precipitation rate and the precipitation mass was large, as well as the difference in the precipitation capacity of different components in the same soil column (Fig. 3).

(2) Chloride: According to the precipitation mass curve of chloride, it can be seen that the precipitation mass curves of YD2m and YD3 soil columns basically overlap (Fig. 3a), indicating that the difference in the precipitation capacity of chloride between the two is relatively small. At the same time, the chloride precipitation mass curves of soil column YD1 were significantly higher than those of YD2m and YD3, indicating that the chloride concentration in the soil at this point was high and its precipitation

capacity was also strong. The spatial size of chloride precipitation capacity is: YD1>YD2≈YD3; and vertically to the YD1 point: 2m> 1m> 2.8m>0m.

(3) Nitrate: under different sampling depths, the precipitation quality curves of YD1-1m, YD1-2m and YD1-2.8m soil columns basically coincide (Figure 3b), indicating that the differences in the precipitation capacity of the three are small. The highest precipitation mass was found in YD1-0m, while YD3 was the second highest. The spatial chloride precipitation capacity is YD1>YD3>YD2, and the vertical upward YD1 point is 0m with the strongest precipitation capacity, and 1, 2, and 2.8m with small differences in precipitation capacity.

(4) Sulphate: the final precipitation quality of YD1-0m is obviously larger than that of other points, and the spatial precipitation capacity is as follows: YD1>YD2≈YD3; vertically upward at point YD1: 0m> 1m> 2.8m>2m.

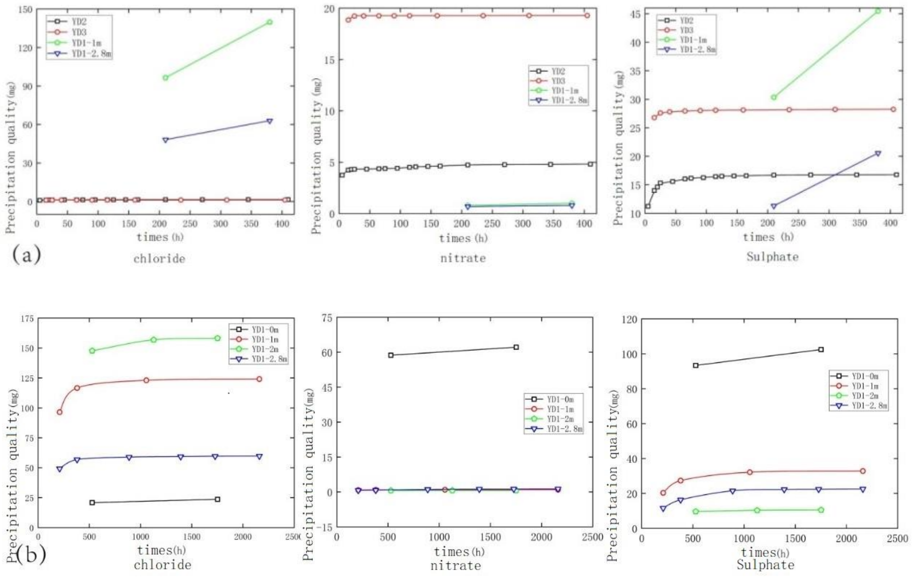

Fig. 3. Variation curves of precipitated mass of sulphate, nitrate and chloride as a function of time in leaching experiments.

4 Water Quality Evaluation and Pollutant Spatial Distribution Characteristics

4.1 Water Quality Evaluation of Monitoring Wells

Three groups of water samples taken from the site in 2018 were tested for 46 indicators, and the indicators were evaluated based on the single-indicator evaluation method. The level of the worst indicator was adopted as the evaluation result of the whole groundwater samples, and the groundwater in SK2-1, SK2-3, and SK2-4 were all class V. Among them, the water samples of SK2-1 showed that 26.1% of the indicators reached the standard of class V water, which accounted for a ratio of about 4 times and 12 times of that of SK2-3 and SK2-4; and the indicators of SK2-1, SK2-3, and SK2-4 that reached class III and class III and above were 30.5 per cent, 21.7 per cent and 13.0 per cent, respectively; and the largest proportion of Class I and II water quality indicators was in SK2-4, at 86.9 percent.

In addition, the pollution index P_{ki} of the six inorganic components (pH, sulfate, chloride, nitrate, total hardness, total dissolved solids) in the water samples taken from SK2-1 and the two blank control sites CG1 and CG2 at different time periods were calculated respectively by using Eq. (1).Comparison of the pollution indices of the individual indexes of the inorganic components showed that (Table 3), the chloride, total hardness, and total dissolved solids pollution indices of water samples taken from SK2-1 in 2018 , total hardness, and total dissolved solids pollution indices are all greater than 1.5, and the pollution categories are all extremely heavy pollution, i.e., the comprehensive evaluation result of groundwater pollution in SK2-1 is extremely heavy pollution; the pollution indices of the six inorganic components in CG1 are all less than 0.2, and the pollution categories are all uncontaminated, and the comprehensive evaluation result is uncontaminated; there are five pollution indices of the five inorganic components in CG2 that are less than 0.2, and the pollution indices of total hardness between 0.2 and 0.6, and the comprehensive evaluation result is medium pollution. Continuing to compare the pollution indices of the six inorganic components of the SK2-1 monitoring wells in July 2018, May and October 2019, the degree of pollution in 2018 was significantly more severe than that in 2019, and the integrated pollution category in 2019 showed a rebound, changing from medium pollution to heavier pollution.

Table 3. Comparison of detected values of individual indicators and pollution indices of inorganic components of groundwater.

Sampling point	Sampling time	pH	Sulphate	Nitrate	Chloride	Total hardness	TDS	Comprehensive evaluation results
SK2-1	2018.07	7.39(I)	142.0(I)	0.14(I)	1930(VI)	1880(VI)	5410(VI)	extremely heavy pollution
SK2-1	2019.05	7.71(I)	192.2(I)	2.87(I)	82.36(I)	544(III)	993(I)	mesopollution
SK2-1	2019.10	7.61(I)	159.0(I)	3.81(I)	206.0(I)	736(IV)	1335(III)	heavier pollution
CG1	2018.07	7.57(I)	11.02(I)	ND(I)	23.83(I)	431(I)	512(I)	uncontaminated
CG2	2018.07	7.36(I)	16.49(I)	ND(I)	26.85(I)	579(III)	649(I)	mesopollution

4.2 Evaluation of Leachate Water Quality

The maximum concentration of each inorganic component in the leachate was statistically analyzed, and the 16 inorganic indicators (aluminium, boron, barium, beryllium, cobalt, chromium, copper, iron, manganese, zinc, fluoride, chloride, nitrite, nitrate, sulphate, pH) with evaluation grades in the "Groundwater Quality Standard (GB/T14848-2017)" among the 27 test indicators were selected for evaluation according to the single-indicator evaluation and the comprehensive pollution index method. Evaluation by single-indicator and comprehensive pollution index method.

(1) The results of single-indicator evaluation show that: the leachate of YD2 and YD3 have 2 indicators reaching the standard of Class V water; the leachate of YD1-0m, 1m and 2.8 have 4, 3 and 2 indicators reaching the standard of Class V water; the leachate of YD1-2m has no indicator reaching the standard of Class V, and its worst water quality type is Class IV. According to the number of polluted indicators, it can be seen that the leachate of YD1-0m is most seriously polluted.

(2) The evaluation results of the integrated pollution index method show (Table 4): among the 16 evaluation indicators, the maximum pollution level of the leachate of each soil column is VI, etc., and the integrated evaluation result is extremely heavy pollution, and the most seriously polluted indicators are mainly nitrate and sulphate. While YD1-0m has 5 indicators to reach the maximum pollution level VI, the maximum pollution index P_{ki} is 62.15, and the indicator type is nitrate, indicating that YD1-0m is the most seriously polluted, followed by YD1-1m, which is consistent with the results of single-indicator evaluation.

Table 4. Statistics on the number of contamination classifications of the 16 tested items in different soil columns.

Sampling point/layer	I	II	III	IV	V	VI	Indicator (maximum P_{ki})	Comprehensive evaluation results
YD2	13		1			2	Nitrate (4.15)	extremely heavy pollution
YD3	13		1		1	1	Nitrate (17.85)	extremely heavy pollution
YD1-0m	10			1		5	Nitrate (62.15)	extremely heavy pollution
YD1-1m	10			2		4	chloride(17.38)	extremely heavy pollution
YD1-2m	15					1	Chloride (8.79)	extremely heavy pollution
YD1-2.8m	14					2	Chloride (9.71)	extremely heavy pollution

4.3 Characteristics of Pollutant Spatial Distribution

Combined with the determination of water quality types and pollutants in the previous section, the spatial distribution characteristics of pollutants in the study area can be obtained by spatially comparing and analyzing the pollutants in each sample:

(1) As a whole, the groundwater in monitoring wells SK2-1, SK2-3 and SK2-4 within the site is contaminated to varying degrees, with the groundwater in SK2-1 having the most contaminated indicators and being the most seriously contaminated. Further analysis shows that since monitoring well SK2-1 is located in the production centre area of the chemical plant, it also has the greatest possibility of being contaminated, while SK2-3 and SK2-4 are a certain distance away from the production area of the chemical plant, and the degree of groundwater contamination within the study area is spatially expressed as SK2-1 > SK2-3 > SK2-4.

(2) Statistical analysis of the maximum concentration of each inorganic component in the leachate, as well as comparison of sulfate, nitrate, and chloride with higher concentrations, can lead to the effect of the soil after remediation treatment as well as the characteristics of the contaminants' vertical and spatial distribution. In the spatial distribution and vertical upward concentration data seem to site shallow soil pollution is generally more serious.

(3) The concentration of pollutants in YD3 is higher than that in YD2, which indicates that the soil backfilled after remediation treatment is also subjected to different degrees of secondary pollution, so the soil backfilled after remediation treatment should be protected from pollution appropriately during remediation treatment.

5 Conclusions

This paper takes a chemical pollution site as the research object, and through carrying out sample collection and soil column leaching experiments, evaluates the site pollution by using the single index evaluation method and the comprehensive pollution index method, and explores the characteristics of the spatial distribution of pollutants. The results show that:

(1) From the experimental results, the permeability coefficient of different soil columns varies greatly, and the difference of the same set of analysed capacity of soil at different points is also large, the average flow rate and permeability coefficient of YD2 are the largest, and its leaching speed is the fastest, followed by YD3, and the leaching speed of YD1 is the slowest. That is, YD1 has the best seepage control performance and YD2 has the worst seepage control performance.

(2) The groundwater and soil of the research site are seriously polluted, and the pollution degree is obviously higher than the periphery of the production area. The results of the evaluation of the water quality of the groundwater and the leachate are all inferior V water, and the results of the comprehensive pollution evaluation are extremely heavy pollution, and the most seriously polluted indexes of the leachate are mainly nitrate, sulphate and chloride.

(3) Soil pollution presents the spatial distribution characteristics that the pollution of point YD1 is more serious than that of YD2 and YD3, and the spatial distribution of pollutants within the site varies greatly; the shallow soil pollution of the site is generally more serious than that of the deeper layer; and the soil backfilled after the remediation treatment is subjected to secondary pollution, and it is recommended that the soil backfilled after the remediation process should be protected against appropriate pollution.

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