Screening methodology of groundwater priority-control pollutants: A case study

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Abstract. As an important source of domestic water and drinking water, the groundwater quality is crucial. Reasonable screening of typical groundwater pollutants is crucial for studying groundwater quality. At present, most research in Linyi focus on the distribution and utilization of water resources, few research focuses on groundwater quality. Therefore, this paper introduces a method of screening priority pollutants, that is, the screening method based on pollution assessment. This method can help to clarify research priorities and make targeted recommendations. In this paper, the study area is a Development Zone of Linyi. Based on groundwater monitoring data of November 2012 and November 2017, a screening method of groundwater priority control pollutants based on pollution assessment is applied to screen out typical pollutants of shallow groundwater quality. It will provide reference for future managements and planning of groundwater in the Development Zone. After pollutants screening and assignment calculation, the results show that the typical pollutants in groundwater are nitrite, anionic surfactant, ammonia nitrogen, fluoride, sodium, nitrate, permanganate index, sulfate, chloride, total hardness, total dissolved solids.

1. Introduction
Groundwater resources have the advantages of being hardly polluted, good water quality, widely distributed, and strong drought resistance. Therefore, it has become an important source of drinking water, industrial and agricultural production water in many countries and regions, especially in arid and semi-arid area [1,2]. With the continuous acceleration of urbanization since the 21st century, man-made factors and natural factors mutually affect the groundwater quality, making the environmental problems of groundwater increasingly serious. It is not only threatening human health, but also affecting economic development and social prosperity [3,4]. As a consequence, the quality of groundwater is particularly important for the sustainable development of society.

Reasonably and objectively, screening groundwater pollutants is the key to study groundwater quality. There are many types of pollutants in groundwater, the existing technology has not reached the level of controlling them one by one. Therefore, those pollutants that are serious to the environment and harmful to human health can be screened out as typical pollutants for research [5]. Currently, the typical methods of screening groundwater pollutants are fuzzy comprehensive evaluation method [6,7], health risk assessment method [8], BP neural network [9], potential hazard index [10] and based on priority pollutants screening risk assessment [11]. Practices show that the above methods have obtained
certain results in the research of typical pollution screening of groundwater. But most of them require more basic information such as the sources of surface pollution, the pollutants characteristics and environmental hazards, and the lithological structure thickness of underground structure to complete the screening work. The work is difficult and the practical application effect is poor. The screening method based on pollution assessment for groundwater priority control pollutants is a screening system specifically applicable to areas with weak basic data. The basis of this system is pollution assessment. Typical pollutants are screened out by comparing different types of pollutants for comparison. It is not only to maximize the use of water quality monitoring data, but also easily reflect the current status of groundwater quality [12].

The research area is a Development Zone, which is located in the southeast of Linyi City. It is dominated by agriculture and supplemented by industrial industry [13,14]. Since the Development Zone establishment in 2003, the economy has developed rapidly. Groundwater is not only the main source of drinking water, but also the main source of water for agricultural irrigation and industrial production [15]. However, the large-scale man-made production activities caused by the rapid development of industry and agriculture have caused groundwater quality to be polluted to a certain extent [16]. Polluted groundwater will affect the sustainable economic development of the Development Zone. At present, most research in Linyi focus on the distribution and utilization of water resources. Few researches focus on groundwater quality. This paper is based on the "National Linyi Economic and Technological Development Zone Planning Environmental Impact Tracking Evaluation Study" project.

According to the collected hydrogeological data and groundwater monitoring data of the Development Zone, the screening method of the groundwater quality priority control pollutants used in the area. The result will provide a reference for groundwater quality evaluation and management in the area.

The rest of the paper is organized as follow: Chapter 2 is consisting of two sections. One section presents the related information about the study area and the data source. Another section introduces methodology of the proposed approach; the application research results and discussions are included in Chapter 3; at last, Chapter 4 is to draw conclusions, analyze the limitations and future works.

2. Materials and methods

The Development Zone is located in the southeast of Linyi, between 118° 23′~118° 32′E longitude and 34° 53′~35° 02′N latitude and 223 km² in area. Its geographical position is shown in Figure 1. The region is in a warm temperate continental monsoon climate zone, with southeast winds prevailing in summer and northeast winds prevailing in winter. The annual average wind speed is 2.6 m/s, and the maximum wind speed is 24 m/s. The annual average temperature is 13.3 °C, the extreme maximum temperature is 37.2 °C, and the extreme minimum temperature is -13.9 °C. The annual average annual precipitation in the area is 862.5 mm, and the average annual runoff depth is 329.9 mm. More than 73% of the annual precipitation in the study area and more than 80% of the annual runoff are concentrated in June to September of each year. Interannual changes in rainfall and runoff are large and unevenly distributed throughout the year.

The hydrogeological unit of the study area is belonging to the Yishu Fault Zone in the middle and low hills of The Central and South Shandong Province. The thickness of the quaternary system is thin, the thickness of the weathering layer of the lower bedrock is small, and the structural fissures of the deep bedrock are not developed. So, there is no good aquifer, and the groundwater is relatively lack. Relevant data from the local Water Conservancy Bureau shows that the groundwater extraction in the study area is about 7 million m³/a. In recent years, groundwater in the area is severely deficient and pollution has become increasingly serious.

2.1. Monitoring data

As the amount of groundwater fluctuates greatly during the wet and dry periods, groundwater quality is also changeable [17]. Generally, the concentration of most heavy metals and organics in dry periods are higher than those in wet periods, therefore, the overall water quality in the dry periods is worse than that in the wet periods [18]. To some extent, groundwater quality during the dry season can represent
poor water conditions in the region during the year. From the point of this view, this paper uses the monitoring data of shallow groundwater in November 2012 and November 2017. There are 39 monitoring indicators shown in Table 4. There are 18 sampling points in total, and the specific distribution is shown in Figure 1.

![Figure 1. Map of study area with groundwater sampling locations.](image-url)

2.2. Indicators extraction
Based on the pollution assessment, the groundwater priority control pollutant screening method comprehensively uses the natural component pollution assessment, the artificial component pollution assessment and the typical pollutant screening method of index toxicity. According to the requirements of this method, the indicators need to be divided into two categories: natural component and artificial component. By comparing the natural component divided by the apparent background value and the artificial component divided by the detection limit, the pollution degree of each indicator can be identified and quantified. Then, the toxicity corresponding to the pollution degree of each indicator is superimposed by the factor quantization multiplication method. The ranking results of groundwater pollutants are obtained comprehensively, and the typical pollutants affecting groundwater quality are screened according to the scores from high to low.

2.2.1 Classification of groundwater quality indicators. According to the requirements of the screening method and the relevant indicators classification principles [19], combined with the hydrogeological characteristics of the study area and the actual detection of the indicators, the 39 groundwater quality indicators detected are classified. The results are showed in Table 1.
Table 1. The classification of groundwater quality indicators.

| Category                  | Name of indicators                                                                 | Number |
|---------------------------|-------------------------------------------------------------------------------------|--------|
| Natural component         | total hardness, total dissolved solids, permanganate index, sulfate, chloride, sulfide, ammonia nitrogen, volatile phenols, anionic surfactant, iron, manganese, copper, zinc, sodium, nitrate, nitrite, iodide, fluoride, cyanide, mercury, cadmium, arsenic, chromium, lead, nickel. | 25     |
| Artificial component      | hexachlorobenzene, hexachlorohexane (total), DDT (total), carbon tetrachloride, tetrachloroethylene, 1,1-dichloroethylene, trichloromethane, trichloroethylene, 1,2-dichloroethane, benzene, ethylbenzene, xylene, toluene, vinyl chloride. | 14     |

2.2.2 Calculation method of screening indicators. (1) Pollution assessment of natural component

Each indicator in the natural components divided by its corresponding apparent background value, this ratio reflects the severity of the pollution. The calculation formula is as follows:

\[ W_{ik} = \frac{C_{ik}}{B_k} \]  

where \( W_{ik} \) is the pollution degree of \( k \) index at \( i \) sampling point (dimensionless), \( i \) is any groundwater sampling point, \( k \) is any index of natural components, \( C_{ik} \) is the measured concentration of \( k \) index at \( i \) sampling point (mg/L), \( B_k \) is the apparent background value of the \( k \) index (mg/L).

The apparent background value of the natural component is a concentration value, which refers to the concentration of groundwater in the natural state affected by normal human activities [20]. Because the basic information such as groundwater hydrogeological conditions in the study area is not detailed enough, and the number of groundwater sampling points is small. The method used in this paper to obtain the apparent background value comes from the British Geological Survey, the "cumulative frequency curve method" [21, 22]. The concentration corresponding to 90% of the cumulative frequency of each indicator is used as the apparent background value.

(2) Pollution assessment of artificial component

Each indicator in the artificial components divided by its corresponding detection limit, this ratio reflects the severity of the pollution. The calculation formula is as follows:

\[ W_{ij} = \frac{C_{ij}}{X_j} \]  

where \( W_{ij} \) is the pollution degree of \( j \) index at \( i \) sampling point (dimensionless), \( i \) is any groundwater sampling point, \( j \) is any index of artificial components, \( C_{ij} \) is the measured concentration of \( j \) index at \( i \) sampling point (mg/L), \( X_j \) is the index detection limit of the \( j \) index (mg/L).

(3) Characterization of indicator toxicity

In order to characterize the harmful properties of natural and artificial components, the toxicity of each index is used as a screening factor. Toxicity is characterized by the reciprocal of the concentration limit of each indicator. The concentration limit of each indicator in the study refers to the Class III water standard of the Groundwater Quality Standard (GB / T 14848-2017) and Groundwater quality standard (DZ/T 0290-2015) Grade-III and Sanitary standards for drinking water (GB5749-2006) requirements for water quality index limits.

(4) Factor quantization multiplication method

In this paper, factor quantization multiplication is used to realize the screening of typical pollutants in groundwater in the study area. The first step is to use the factor quantization multiplication method to quantitatively assign the total pollution degree of each indicator, the median pollution degree and the toxicity. Assignment methods will be introduced in the following content. The second step is to multiply the assigned total value, the assigned median value and the assigned toxicity value, aiming to rank the calculated values in descending order. The larger the calculated value, the greater the harm caused by this indicator. The calculation formulas are as follows:

\[ T_k = \sum_{i=1}^{N} W_{ik} \]  

where \( T_k \) is the total pollution degree of \( k \) index (dimensionless).
\[ S_k = Q_k \times M_k \times C_k \quad (4) \]

where \( T_k \) is the total pollution degree of \( k \) index (dimensionless). \( S_k \) is the quantitative characterization of the pollution caused by the \( k \)-th index to groundwater quality (dimensionless). The value is the comprehensive score of the harmfulness of this pollutant to groundwater. \( Q_k \) is the total value of the pollution degree (dimensionless); \( M_k \) is the median value of the pollution degree at each sampling point of the \( k \)-th index (dimensions); \( C_k \) is the quantitative characterization of the toxicity at each sampling point of the \( k \)-th index (dimensions). Especially, \( Q_k \) and \( M_k \) are different from \( W_{ik} \) in formula (1) and \( W_{ij} \) in formula (2), \( Q_k \), \( M_k \) and \( C_k \) are calculated by the assignment method.

(5) Assignment method

First, rank \( T_k \) in descending order, and assign 1 when the obtained value is 0. If the number of \( T_k \) equal to 0 is \( x \), the remaining values are assigned from \( x + 1 \) to \( x \). Through the above steps, we will obtain \( Q_k \) (the total value of pollution degree). Similarly, \( M_k \) (the median value of the pollution degree) and \( C_k \) (the values that characterize toxicity) can be obtained by the same way. Assign values from 1 to \( n \). In particular, if the values are the same, assign the smaller value.

3. Results and discussion

In this paper, a total of 36 sets of monitoring data from 2012 and 2017 are used as data sources. Cumulative frequency curve method is used to calculate the apparent background values. Taking the total hardness and permanganate index as examples, the cumulative frequency curves are shown in Figure 2. According to this method, the corresponding apparent background values of all indicators can be calculated. The results are shown in Table 2.

By formula (3), the total pollution degree of natural components indicators can be calculated. Similarly, we will obtain the medium of natural components indicators by Microsoft Excel 2013. In order to facilitate comparison, the total and the median of natural components indicators below the detection limit indexes are set to 0. The results are showed in Table 3.

![Figure 2. Cumulative frequency curve chart (a–b).](image)

| Name of indicators          | Background value | Name of indicators          | Background value |
|-----------------------------|------------------|-----------------------------|------------------|
| total hardness              | 777              | nitrate                     | 45.5             |
| permanganate index          | 1.49             | nitrite                     | 0.012            |
| total dissolved solids      | 515              | fluoride                    | 1.34             |
| anionic surfactant          | 0.07             | chloride                    | 212              |
| sulfate                     | 223              | sodium                      | 65               |
| ammonia nitrogen            | 0.22             |                             |                  |
Table 3. The total and median of natural components (2012 and 2017).

| Name of indicators       | Total 2012 | Total 2017 | Median 2012 | Median 2017 |
|--------------------------|------------|------------|-------------|-------------|
| total hardness           | 15.66      | 11.60      | 0.90        | 0.60        |
| total dissolved solids   | 16.16      | 16.17      | 0.91        | 0.90        |
| permanganate index       | 16.06      | 8.14       | 0.92        | 0.42        |
| sulfate                  | 14.42      | 12.38      | 0.66        | 0.67        |
| chloride                 | 14.15      | 10.69      | 0.43        | 0.55        |
| sulfide                  | 0          | 0          | 0           | 0           |
| ammonia nitrogen         | 6.32       | 14.36      | 0.28        | 0.18        |
| volatile phenols         | 14.86      | 9.71       | 0.86        | 0.5         |
| anionic surfactant       | 0          | 14.41      | 0           | 0           |
| iron                     | 0          | 0          | 0           | 0           |
| manganese                | 0          | 0          | 0           | 0           |
| copper                   | 0          | 0          | 0           | 0           |
| zinc                     | 0          | 0          | 0           | 0           |
| sodium                   | 14.51      | 14.41      | 0.70        | 0.69        |
| nitrate                  | 11.00      | 10.53      | 0.59        | 0.62        |
| nitrite                  | 11.67      | 5.17       | 0.46        | 0.17        |
| iodide                   | 0          | 0          | 0           | 0           |
| fluoride                 | 8.75       | 14.04      | 0.44        | 0.57        |
| cyanide                  | 0          | 0          | 0           | 0           |
| mercury                  | 0          | 0          | 0           | 0           |
| cadmium                  | 0          | 0          | 0           | 0           |
| arsenic                  | 0          | 0          | 0           | 0           |
| chromium                 | 0          | 0          | 0           | 0           |
| lead                     | 0          | 0          | 0           | 0           |
| nickel                   | 0          | 0          | 0           | 0           |

The detection limit requirements of artificial component come from the "Regulations for the Investigation and Evaluation of Regional Groundwater Pollution" (DZ / T0288-2015). According to the monitoring result of artificial components, it can be known that the monitoring value of each indicator in 2012 and 2017 are not detected, so the total and the median of each indicator is set to a value of 0.

Combining pollution assessment of natural component, pollution assessment of artificial component and the toxicity characterization results, the calculation is performed using the factor quantified multiplication. The results of screened groundwater indicators in 2012 and 2017 were obtained. The results are showed in Table 4.

It can be seen from Table 4 that the typical pollutants affecting the shallow groundwater quality in the dry periods in 2012 and 2017 are the same in the types, and the main difference is that the indicators have slightly different levels of groundwater pollution. The typical pollutants of shallow groundwater quality in the dry period of 2012 are ranked in descending order of anionic surfactant, nitrite, ammonia nitrogen, permanganate index, fluoride, nitrate, sodium, sulfide, chloride, total hardness, soluble total solids; while in 2017 it are nitrite, anionic surfactant, ammonia nitrogen, fluoride, sodium, nitrate, permanganate index, sulfate, chloride, total hardness, solubility, total solids. It can be seen that the groundwater pollutant screening results obtained by the factor quantization multiplication method are mainly based on the salt index of natural components, which may be related to the lithological characteristics, hydrological conditions, and long-term agricultural activities of the study area. The scores with a low order of magnitude are mainly heavy metal indicators and organic indicators in natural and artificial component that are below the detection limit or not detected. This phenomenon indicates that the impact...
of the above pollutants on the composition of the research area is extremely small. It can be concluded that the study area has put in place measures to control the emissions of heavy metals and organics.

Table 4. The calculation results of the factor quantization multiplication method for groundwater indicators (2012 and 2017).

| No. | Name                        | Total assignment | Median assignment | Toxicity assignment | Score 2012 | Score 2017 |
|-----|-----------------------------|------------------|-------------------|--------------------|------------|------------|
| 1   | anionic surfactant          | 36 31            | 36 32             | 15 15              | 19440 14880 |
| 2   | nitrite                     | 32 29            | 32 29             | 18 18              | 18432 15138 |
| 3   | ammonia nitrogen            | 29 37            | 29 30             | 13 13              | 10933 14430 |
| 4   | permanganate index          | 38 30            | 39 31             | 7 7                | 10374 6510 |
| 5   | fluoride                    | 30 36            | 31 34             | 8 8                | 7440 9792 |
| 6   | nitrate                     | 31 32            | 33 36             | 6 6                | 6138 6912 |
| 7   | sodium                      | 35 38            | 35 38             | 5 5                | 6125 7220 |
| 8   | sulfate                     | 34 35            | 34 37             | 3 3                | 3468 3885 |
| 9   | chloride                    | 33 33            | 30 33             | 3 3                | 2970 3267 |
| 10  | total hardness              | 37 34            | 37 35             | 2 2                | 2738 2380 |
| 11  | total dissolved solids      | 39 39            | 38 39             | 1 1                | 1482 1521 |
| 12  | mercury                     | 1 1              | 1 1               | 37 37              | 37 37     |
| 13  | hexachlorobenzene           | 1 1              | 1 1               | 37 37              | 37 37     |
| 14  | DDT (total)                 | 1 1              | 1 1               | 37 37              | 37 37     |
| 15  | volatile phenols            | 1 1              | 1 1               | 35 35              | 35 35     |
| 16  | carbon tetrachloride        | 1 1              | 1 1               | 35 35              | 35 35     |
| 17  | cadmium                     | 1 1              | 1 1               | 32 32              | 32 32     |
| 18  | vinyl chloride              | 1 1              | 1 1               | 32 32              | 32 32     |
| 19  | hexachlorocyclohexane (total) | 1 1              | 1 1               | 32 32              | 32 32     |
| 20  | arsenic                     | 1 1              | 1 1               | 29 29              | 29 29     |
| 21  | lead                        | 1 1              | 1 1               | 29 29              | 29 29     |
| 22  | benzene                     | 1 1              | 1 1               | 29 29              | 29 29     |
| 23  | sulfide                     | 1 1              | 1 1               | 27 27              | 27 27     |
| 24  | nickel                      | 1 1              | 1 1               | 27 27              | 27 27     |
| 25  | 1,2-dichloroethane          | 1 1              | 1 1               | 25 25              | 25 25     |
| 26  | 1,1-dichloroethylene        | 1 1              | 1 1               | 25 25              | 25 25     |
| 27  | tetrachloroethylene         | 1 1              | 1 1               | 24 24              | 24 24     |
| 28  | cyanide                     | 1 1              | 1 1               | 22 22              | 22 22     |
| 29  | chromium                    | 1 1              | 1 1               | 22 22              | 22 22     |
| 30  | trichloromethane            | 1 1              | 1 1               | 21 21              | 21 21     |
| 31  | trichloroethylene           | 1 1              | 1 1               | 20 20              | 20 20     |
| 32  | iodide                      | 1 1              | 1 1               | 19 19              | 19 19     |
| 33  | manganese                   | 1 1              | 1 1               | 18 18              | 18 18     |
| 34  | iron                        | 1 1              | 1 1               | 15 15              | 15 15     |
| 35  | ethylbenzene                | 1 1              | 1 1               | 15 15              | 15 15     |
| 36  | xylene                      | 1 1              | 1 1               | 13 13              | 13 13     |
| 37  | toluene                     | 1 1              | 1 1               | 12 12              | 12 12     |
| 38  | copper                      | 1 1              | 1 1               | 8 8                | 8 8       |
| 39  | zinc                        | 1 1              | 1 1               | 8 8                | 8 8       |
4. Conclusion

This paper presented a typical pollutants screening method based on pollution assessment and applied to a Development Zone of Linyi with groundwater monitoring data. Under the circumstances that the basic data such as groundwater hydrogeological conditions in the study area are weak and not detailed enough, and the groundwater monitoring data are not abundant, the screening method of groundwater priority control pollutants based on pollution assessment has good results. In this paper, the typical pollutants that affect the shallow groundwater quality of the study area during the dry periods in 2012 and 2017 are nitrite, anionic surfactant, ammonia nitrogen, fluoride, sodium, nitrate, permanganate index, sulfate, chloride, total hardness, total dissolved solids. The research results provide a basis for scientific management and planning of groundwater resources in the study area.

There were still limitations in this study. In the process of screening priority control pollutants, this paper directly calculated the product of indicators by factor quantization multiplication method, while ignored the correlation between the indicators. In the future, we will continue to analyze the correlation among indicators. We will also combine with new technologies, such as deep learning methods, to make the screening results more convincing.

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