

Article

Identification of Priority Pollutants in Groundwater: A Case Study in Xiong'an New Region, China

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Abstract: The pollution of man-made groundwater has become a major global problem that threatens human health and affects the aquatic environment. The establishment of an effective screening system for water pollution assessment is of great importance for maintaining the ecological health of groundwater. In this study, the concentrations of natural and non-natural pollutants in the groundwater of Xiong'an New Area were measured, and the degree of pollution degree and toxicity index of pollutants were used to construct a novel screening method. The result shows that it was more suitable to use the weighted summation method with weights of 0.5, 0.25, and 0.25 for toxicity, total pollution degree, and median pollution degree, respectively. According to the proposed screening method, Benzo[a]pyrene, Hexachlorobenzene, As, Se, Atrazine, Benzo[b]fluoranthene, Ni, Mo, Ti, and naphthalene were identified as the dominant pollutants in the study area and their levels should be strictly monitored.

Keywords: index classification; toxicity quantification; natural and unnatural components; baseline value; pollution degree



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1. Introduction

Groundwater is an essential resource for humans around the world. It provides almost half of the drinking water worldwide, accounts for about 30% of global freshwater resources, and is about 100 times more abundant than surface water resources [1]. However, groundwater is becoming increasingly threatened by chemical pollution. Many organic chemicals, such as pharmaceuticals and personal care products (PPCPs) [2–4], volatile organic compounds (VOCs) [5], and polycyclic aromatic hydrocarbons (PAHs) [6], have been detected in groundwater as a result of human activities. In some areas, the concentration of common pollutants, such as nitrates, fluorides, and heavy metals, exceed the acceptable limit for drinking [7–9]. In comparison with surface water, groundwater pollution is concealed and has a high cost of remediation [10]. Therefore, identification and control of priority pollutants is important for managing groundwater pollution [11].

Screening for priority pollutants to achieve pollutant control is the process of identifying and removing harmful pollutants that exhibit a high probability of occurrence and can cause great harm to the surrounding environment and human health [12]. Many countries and organizations have carried out screening studies for priority pollutants and proposed lists of priority pollutants [13,14]. In 1997, 129 substances were selected by the EPA as priority pollutants on the basis of their toxic effect and frequency of detection in the environment including soil, air, and water [15,16]. The EU ranked pollutants by their exposure and toxic effects and proposed a list of priority pollutants in bodies of water [17–19]. In China, 68 priority pollutants were identified in bodies of water based on a large amount of monitoring data and investigation into pollutant emission and the toxicity of the pollutants [20,21]. There is currently no specific list of priority pollutants for

groundwater with there being only a few reports published on the screening of priority pollutants in groundwater resources.

In addition to pollution by human activities, the natural geological environment can also cause deterioration of groundwater quality [22,23]. For example, saline CO₂-rich waters from deep underground sources can dissolve a variety of minerals during their migration towards the surface, which both causes instability in the aquifer and increases the occurrence of risks, such as karst development [24]. For the evaluation of groundwater pollution, it is important to differentiate natural pollution from anthropogenic pollution [25]. Due to the difficulties in obtaining statistical data, the natural baseline quality of groundwater has always been ignored in the evaluation of groundwater pollution. The current method for evaluating pollution often includes natural pollution of geological origins, which is not effectively distinguished from contamination caused by human activity. As a result, the degree of groundwater pollution is often exaggerated. Therefore, the baseline quality of groundwater should be fully considered during the screening process for priority pollutants, and the pollutants caused by human activities should be specifically identified.

Xiong'an New Region was established by the State Council of China on 1 April 2017, and is of great strategic and practical significance for the coordinated development of the Beijing-Tianjin-Hebei region [26]. The water for agricultural, industrial manufacturing, and living activities in the Xiong'an New Region is mainly derived from groundwater. It is critical to monitor the priority pollutants in the groundwater in Xiong'an New Region to maintain groundwater quality during urban construction. The main objectives of our study were to investigate the quality of groundwater in the Xiong'an New Region and to establish a screening method for controlling pollutants in groundwater based on pollution assessment.

2. Materials and Methods

2.1. Method Development

There are two commonly used screening methods: the risk-based screening method and the scoring method [27]. The exposure and toxicity levels of pollutants are the two main factors taken into account by these two methods, but they differ in how they are represented [28]. The risk-based screening method is easy to use. It calculates a specific ratio of exposure concentration to hazard level, such as a risk score, risk quotient, hazard quotient, exposure activity ratio, or concern index [29]. Ranking with multiple indicators is more preferred and is a popular way to use the arithmetic sum of indicator scores [30]. In practice, a pollutant is identified mainly because its concentration is significantly higher than the local baseline level. This method is called the environmental baseline (EB) method [31]. However, evaluating pollutant concentration alone is clearly insufficient because the pollutant toxicity should be considered when assessing risk towards human health [32]. Liu et al. screened the priority pollutants in drinking water by considering the effluent concentration, accumulation index, ease of purification, and carcinogenic risk [33]. The screening methods of priority pollutants carried out in the US and other countries are summarized in Table S1 [34–41].

The screening of the priority pollutants in groundwater requires the effective assessment of water quality monitoring data. The detected level, environmental hydrological condition, and substance toxicity should be fully considered in the assessment process. The indices should be divided into two categories: natural and unnatural components according to the source of the pollutants. Unnatural components do not appear in groundwater under natural conditions and their baseline values should be zero. The groundwater is polluted when the detected levels of unnatural pollutants exceed the baseline values [42].

A screening method was established for priority pollutants in groundwater by using the index classification evaluation method and by combining the detection frequency with the pollution degree score. The process for the screening method is shown in Figure 1.

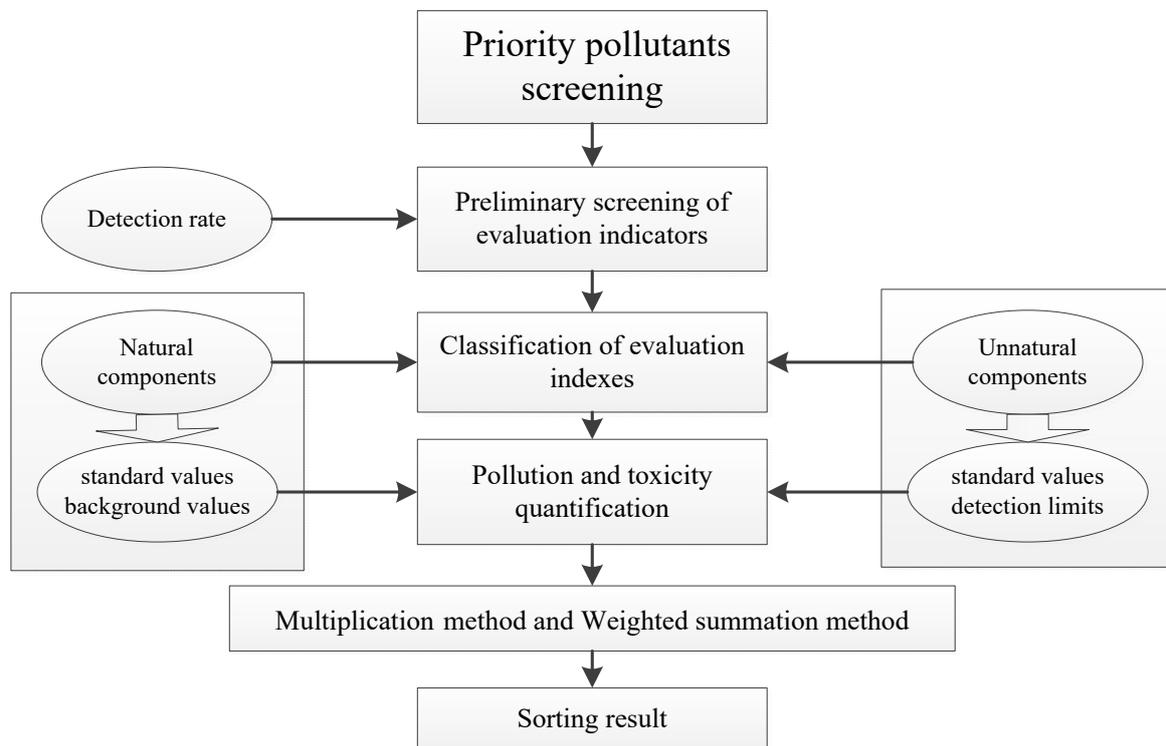


Figure 1. The process flow of the screening method.

2.1.1. Pollution and Health Risk Assessment

The pollution assessment for natural components and unnatural components is shown in Formulas (1) and (2).

$$P_{ij} = C_{ij} \div B_j \quad (1)$$

$$P_{ik} = C_{ik} \div X_k \quad (2)$$

where P_{ij} is the j th index pollution degree of the i th sample, C_{ij} is the monitoring concentration of j th index of i th sample, B_j is the baseline value of the j th index, P_{ik} is the k th index pollution degree of the i th sample, C_{ik} is the monitoring concentration of the k th index of the i th sample, X_k represents the detection limit value for the k th index, i is any groundwater sampling point, and j and k are any indices [43].

The US EPA method was adopted to calculate the incremental lifetime cancer risk (ILCR) associated with drinking groundwater:

$$\text{ILCR} = \frac{\text{TEQ}_{\text{BaP}} \times \text{DR} \times \text{CSF} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT} \times 10^6} \quad (3)$$

where DR is the daily water intake (L/d), CSF is the carcinogenic slope coefficient of BaP (10 (kg d)/mg), EF is the number of days of exposure per year (set to 365 d), ED is the exposure duration (in this study, the time unit was a year), BW is body weight (kg), and AT is averaging time for life (d). A value of $\text{ILCR} > 1 \times 10^{-4}$ indicates carcinogenic unacceptable, and $1 \times 10^{-6} < \text{ILCR} < 1 \times 10^{-4}$ indicates carcinogenic acceptable, while a value of $\text{ILCR} < 1 \times 10^{-6}$ indicates no carcinogenic risk [6].

$$\text{ILCR}_T = \text{ILCR}_{\text{PAHs}} + \text{ILCR}_{\text{Pesticide}} + \text{ILCR}_{\text{VOCs}} \quad (4)$$

where ILCR_T is the total incremental lifetime cancer risk, represented by the sum of the incremental lifetime cancer risk from PAHs, Pesticide, and VOCs.

2.1.2. Baseline Value Calculation

Baseline value is important in assessing groundwater pollution. Its determination methods mainly include sequential statistical regression modeling [44], probability graphs [45], hierarchical clustering analyses [46], and pre-screening methods [47]. Based on the results obtained by these methods, a high percentile is further used to calculate groundwater baseline values. In our study, the piper trilinear diagrams were used to analyze hydrochemical types, and the cumulative frequency plot method was then used to calculate the baseline value. The index concentration was ranked from low to high, and the concentration corresponding to a cumulative frequency of 90% was the baseline value of the natural component in the region [48].

2.1.3. Screening Methods for Main Pollutants

In order to measure the degree of pollution for each component in the entire study area, the total degree of pollution for all sampling points of each component was selected as a screening index. In addition, to avoid the effect caused by the high local concentration of groundwater components in individual sampling points, the median pollution degree of sampling points was also selected as a screening index. Toxicity was also listed as a screening index to reflect the physiochemical property of the component. In summary, the total and the median pollution degree and toxicity of each component were selected, and the multiplication method and weighted summation method were used to screen priority pollutants [43].

(1) Multiplication method

The multiplication method calculated the pollution degree using the following formula.

$$S_i = Q_i \times M_i \times C_i \quad (5)$$

where S_i is the pollution degree of a component, representing the comprehensive score of the harmfulness of this component in groundwater. Q_i represents the total of the i th component pollution degree in all sample points. M_i represents the median value of the pollution degree. C_i represents the toxicity of a component, using the inverse concentration limit value [43].

The score for each substance is calculated and the substance is ranked according to its score to identify the main pollutants in groundwater.

(2) Weighted summation method

The weighted summation method is one of the most commonly used decision-making methods. The selected factors are graded and assigned, then each factor is given a weight value according to the hierarchical analytical process. Finally, the assigned value of each factor is multiplied with the weight of the factor and all factors are summed. The calculated value is the quantified result of the harmfulness of pollutants to the groundwater environment.

$$S_i = Q_i \times W_Q + M_i \times W_M + C_i \times W_C \quad (6)$$

where S_i represents the pollution degree of a component, indicating the comprehensive score of the harmfulness of this component in groundwater; Q_i represents the total of the i th component pollution degree in all sample points; W_Q is the weight value of Q ; M_i represents the median value of the pollution degree W_M is the weight value of M ; C_i represents the toxicity of a component, using the inverse concentration limit value; and W_C is the weight value of C [43]. All quantities in the equation are dimensionless.

In this study, W_C , W_Q , and W_M were assigned using different assignment combinations in order to reduce the influence of subjective factors on the ranking of priority.

2.2. Sampling and Measurements

Sixty groundwater samples were collected in July 2019 in the Xiong'an New Region by taking full account of hydrogeology conditions and under a uniform distribution (Figure 2).

A total of 156 substances were analyzed. A well was pumped for approximately 3 min before sampling to collect fresh groundwater. The samples collected at each point were filtered through a 0.22 mm membrane, and the samples were treated with different protective agents according to the target pollutants to be tested. The tested categories of pollutants are shown in Table S2.

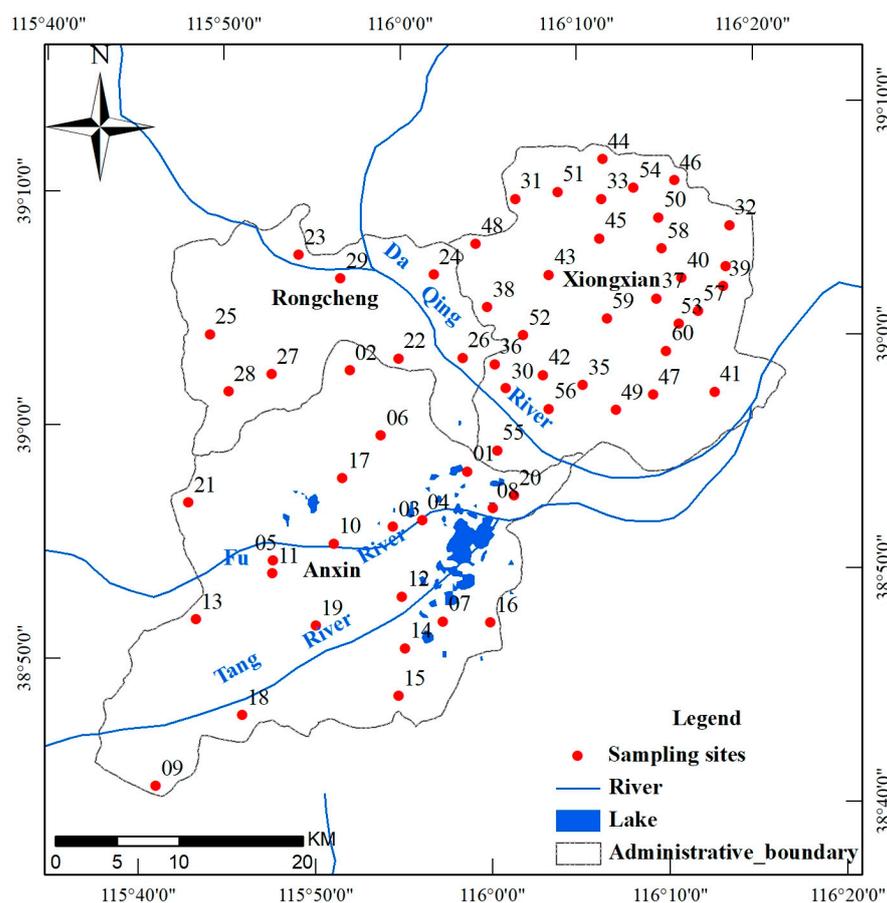


Figure 2. Distribution of sampling sites in the study area.

3. Results and Discussion

3.1. Groundwater Quality

3.1.1. Groundwater Quality Assessment

The water quality in the study area was evaluated according to the Groundwater Quality Standard (GB/T 14848-2017) [49]. The single index evaluation method was adopted to determine the groundwater quality category according to the limit range of the index. When the index limit values of two quality categories (such as Class II and III) are the same, the higher quality category (Class II) is assigned. As the groundwater in this area is mainly used for drinking, the Class III water quality values were used as the basis for judging whether the standard is exceeded. The evaluation showed that there were 11 samples with water quality belonging to Class II, accounting for 18% of the total number of samples; 41 samples had water quality belonging to Class III, accounting for 68% of the total water samples; and 8 water samples had water quality belonging to Class IV, accounting for 13% of the total. The fluoride, chromium, sodium, and iodide levels exceeded the limit value for drinking water at some collection sites. There were 1, 2, and 5 samples in Anxin, Rongcheng, and Xiongxian Counties, respectively, with water qualities all belonging to Class IV (Figure 3).

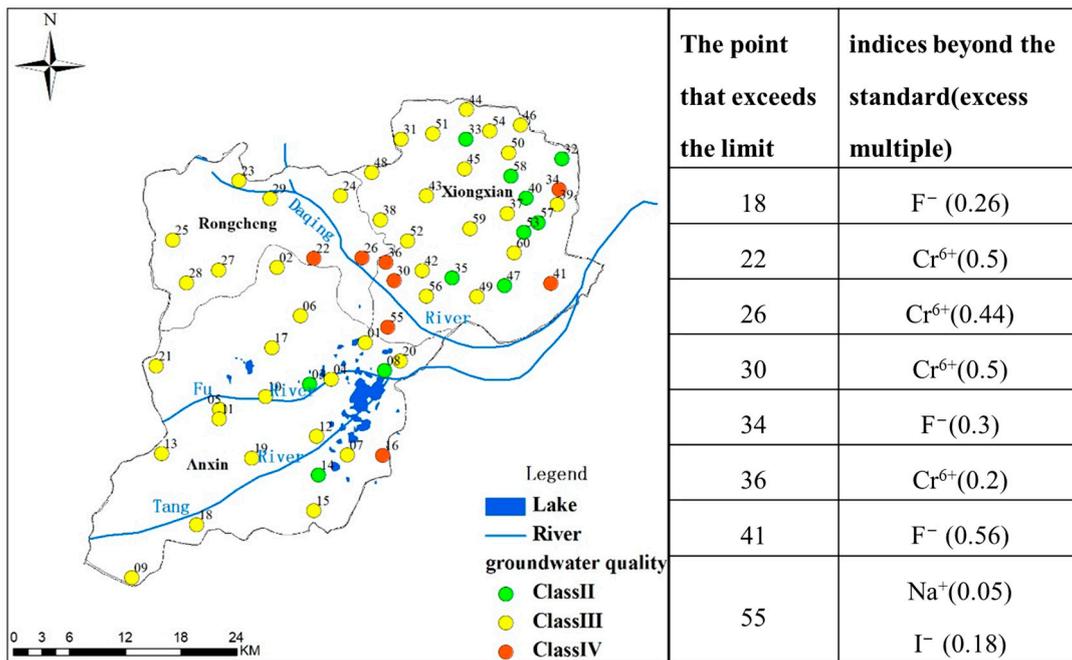


Figure 3. Distribution of water quality categories in the study area.

3.1.2. Concentration of Organic Pollutants

Among the organic pollutants, polycyclic aromatic hydrocarbons and pesticides were detected most frequently. A total of 52 of the 102 tested organic pollutants were detected. All of the 16 PAHs were detected, and the detection rates were all above 70% except for dibenzo[a,h]anthracene (17%) and acenaphthene (42%). The detection rates of fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzene, and fluoranthene were 100%. The concentrations of benzo[a]pyrene at two sites were 5.5 ng/L and 8.7 ng/L, respectively, more than 50% of the Class III standard (5.0 ng/L). The sites were No. 28 in Rongcheng County and No. 38 in Xiongqian County (Figure 4A). The three pesticides with the highest detection rates were hexachlorobenzene, dieldrin, and parathion with detection rates of 98.33%, 88.33%, and 17%, respectively. The concentration of methyl parathion at No. 20 site in Anxin County was more than 50% of the standard of Class III, with a detected concentration of 0.92 µg/L. The distribution patterns of hexachlorobenzene and dieldrin were similar, mainly in the eastern part of Rongcheng County and the central and southern parts of Anxin County. The concentration distribution patterns were mainly affected by agricultural activities (Figure 4B). There were nine perfluorochemicals detected, and the three pollutants with the highest detection rates were PFOA (53.33%), PFHxA (30%), and PFBA (21.67%). However, the concentrations were all low and only slightly above the detection limit (Figure 4C). For volatile organic pollutants, there were 19 types detected, and the 3 with the highest detection rates were 1,2-dibromo-3-chloropropane, 1,2,4-trichlorobenzene, and 1,3-trichlorobenzene, with detection rates of 39.66%, 25.86%, and 24.14%, respectively. The concentrations of 1,2-dibromo-3-chloropropane, 1,2,4-trichlorobenzene, and 1,3-trichlorobenzene were relatively low within the range of 0–161.8 ng/L, 0~14 ng/L, and 0~9.7 ng/L, respectively. The total concentration of volatile organic pollutants was higher around a contiguous area of the three counties (Figure 4D).

The carcinogenic risk of organic indicators was assessed, and the results showed that there were six sites with lifetime carcinogenic risk far lower than the acceptable level recommended by EPA (10^{-6} ~ 10^{-4}), among which, five sites were located in Xiongqian County, and the rest of the sites were in the acceptable level recommended by US EPA. The highest overlapping risk site was No. 28, located in Rongcheng County. These results show that attention should be paid to the detection of organic pollutants.

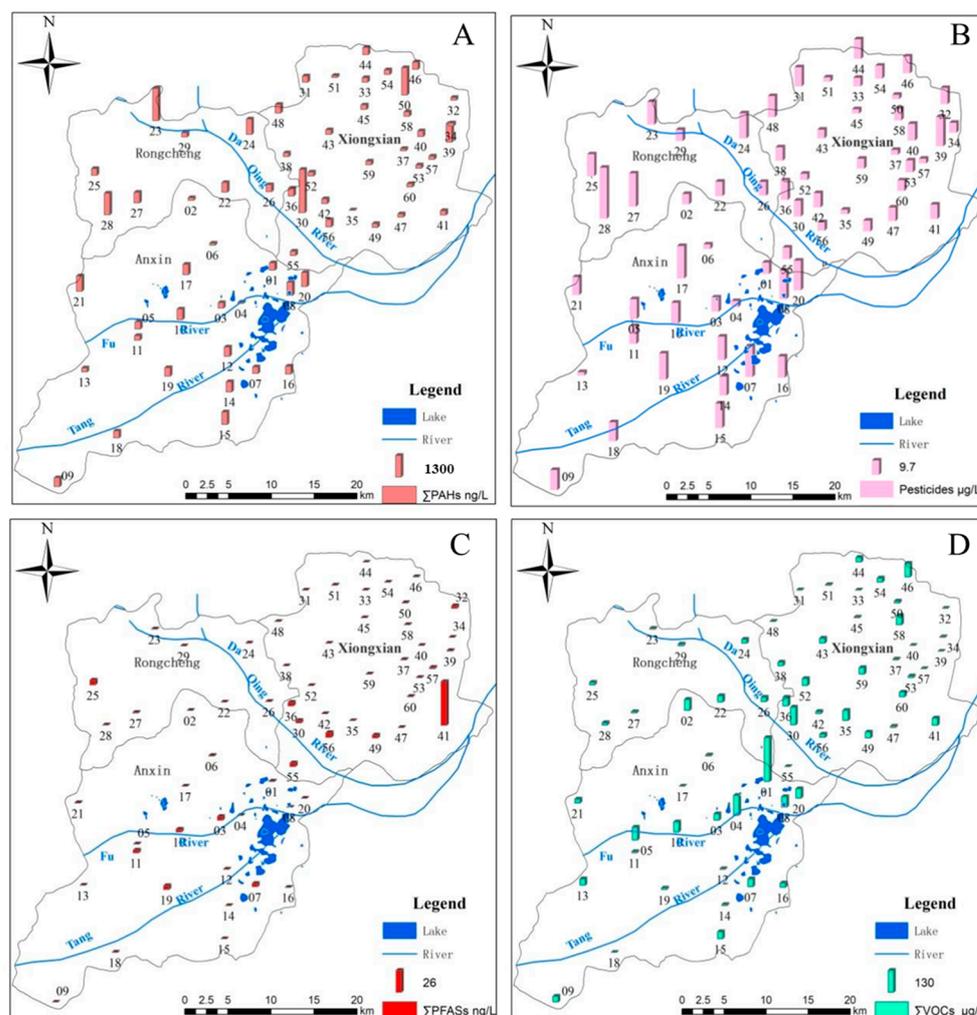


Figure 4. Distribution of PAHs, pesticides, PFASs and VOCs. (A) The distribution of PAHs; (B) The distribution of pesticides; (C) The distribution of PFASs; (D) The distribution of VOCs.

3.2. Quantification of Groundwater Pollution

3.2.1. Classification of Pollutants

The undetected pollutants and those not included in the standard of groundwater quality were eliminated in the preliminary screening process. There was a total of 50 pollutants tested in the evaluation process. The pollutants were divided into natural and unnatural as shown in Table S3.

3.2.2. Assessment of Natural Components

RockWare Aq-QA software (RockWare AqQA 1.1.4.1 CD) was used to analyze the hydrochemical characteristics of groundwater in the study area. The results indicated that Na-HCO₃ type of water accounted for almost 97% of the tested samples, and no obvious outliers were observed (Figure 5A). Therefore, the baseline levels were calculated using the current data.

Baseline levels of groundwater refer to the concentrations of chemical composition in groundwater without the influence of human activities, which reflect the chemical compositions in groundwater under a natural state [50]. The determination of baseline levels of groundwater allows for more scientific and reliable assessment of groundwater pollution [51]. The baseline levels of Al, Cu, Cd, and Volatile Phenols were all below the detection limit. Therefore, the detection limits were used as the baseline levels in the evaluation process. The baseline values of the natural components are shown in Figure 5B–D.

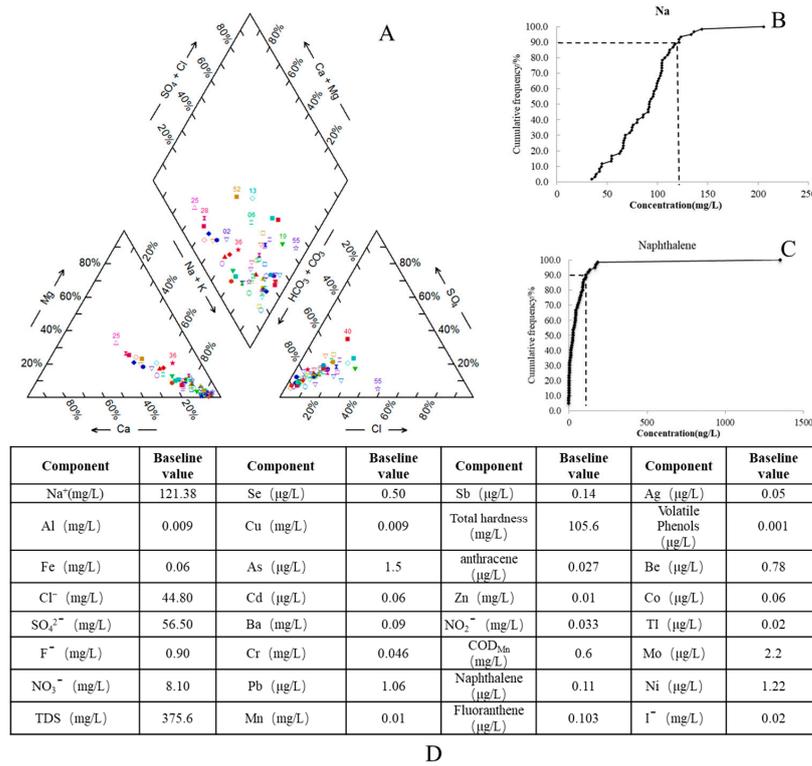


Figure 5. The baseline levels of natural components. (A) The hydrochemistry of groundwater in the study area; (B) The frequency of Na⁺ accumulation; (C) The frequency of Nap accumulation; (D) The baseline levels of natural components.

The pollution degree of natural components was calculated using Formula (1) and the results were analyzed. The total pollution degrees of natural components ranged from 1.11 to 48.37, with an average value of 26.22. Of the 32 indicators, the pollution degree of TDS, COD_{Mn}, Na⁺, Ba, and SO₄²⁻ were relatively high, with values of 48.37, 46.67, 43.91, 41.1, and 36.04, respectively. The total pollution degree of Volatile Phenols, Cd, and Cu were the lowest of the 32 indicators. The median pollution degrees of natural components ranged from 0 to 0.83. COD_{Mn}, TDS, Na⁺, Ba, and SO₄²⁻ were the five highest indicators, and the median pollution degree of NO₂⁻, Ti, Sb, Pb, Co, Al, Ag, Be, Volatile Phenols, Cd, and Cu were all 0 (Figure 6).

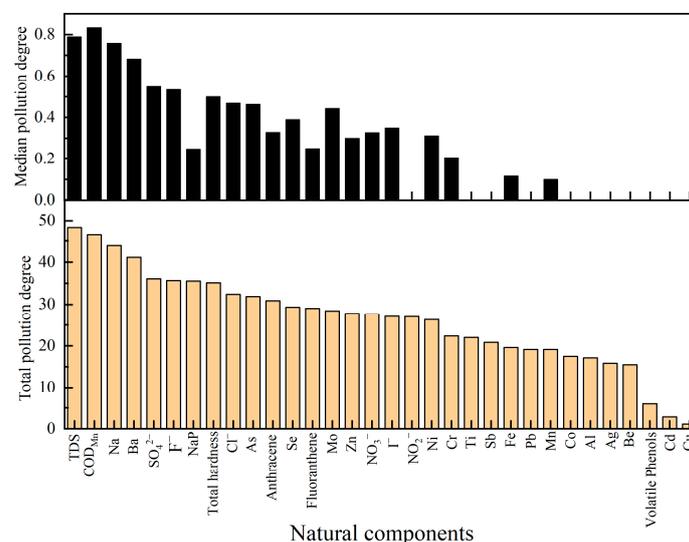


Figure 6. The pollution degree of natural components.

3.2.3. Assessment of Unnatural Components

The levels of the unnatural components in groundwater reflect the degree of pollution. Once an unnatural component is detected, the groundwater is polluted. Therefore, the detection limit of the unnatural component is treated as its baseline value. In this study, the detection limits were derived from laboratory test results, as shown in Table S4.

The pollution by unnatural components was assessed. The total pollution degree ranged from 1.12 to 460.18. Benzo[a]pyrene, Hexachlorobenzene, and Atrazine showed the highest total pollution degree, which were all greater than 100. There were 9 chemicals with total pollution degree below 10. Methylbenzene, 1,2-Dichloroethylene, and Carbon tetrachloride showed the lowest total pollution degree (Figure S1).

3.3. Screening of Priority Pollutants

3.3.1. Quantification of Toxicity

The toxicity of a pollutant is defined according to the Class III water standard of GB/T 14848-2017 and Standards for Drinking Water Quality (GB5749-2022). The concentration limits are shown in Table S4. The toxicity of each component was characterized by the reciprocal of its concentration limit. The higher the limit of a pollutant concentration, the less toxic it is. Taking the logarithm of the reciprocal of a concentration limit was used for evaluation of toxicity. Benzo(a)pyrene has the highest toxicity with a toxicity value of 6. TDS has the least toxicity with a toxicity value of -3 (Figure 7).

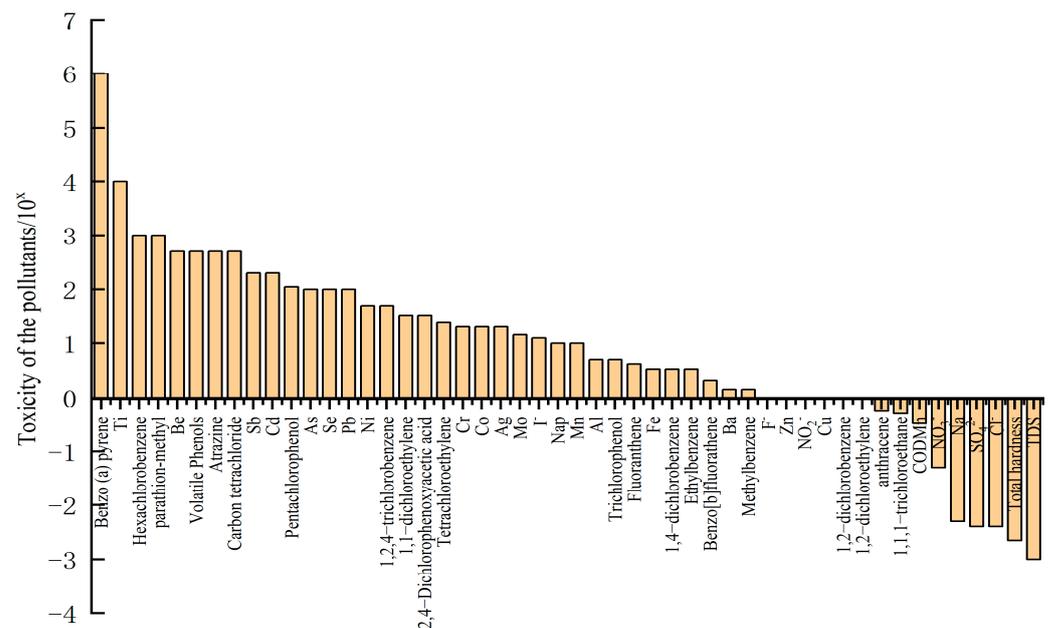


Figure 7. The toxicity scale of the pollutants.

3.3.2. The Multiplication Method

The 26 chemicals with a median pollution degree of 0 were not considered when sorting the pollutants because the multiplication method calculates the pollution degree directly using the actual values of a pollutant. Direct multiplication amplifies the pollution degree of a given pollutant, because the total and median pollution degrees are from the same pollutant. The indicators need to be quantified first before being used by the multiplication method.

Considering that the total and median pollution degrees reflect the pollution degree of the same pollutant, and 26 pollutants had a median value of 0, the ranking assignment method was adopted to assign a value for each pollutant. As a result, the differences within the screened pollutants were reduced. The total pollution degree, median pollution degree, and toxicity of the 50 pollutants were ranked from 1 to 50, respectively. For the

26 pollutants with a median pollution degree of 0, a rank of 1 was assigned for all of them; therefore, the other pollutants were ranked from 27 to 50. Benzo[a]pyrene had the highest total pollution degree, median pollution degree, and toxicity. Ti, Sb, Pb, parathion-methyl, volatile phenols, and many other pollutants had relatively high toxicity values, whereas their pollution degrees were relatively low (Figure 8A).

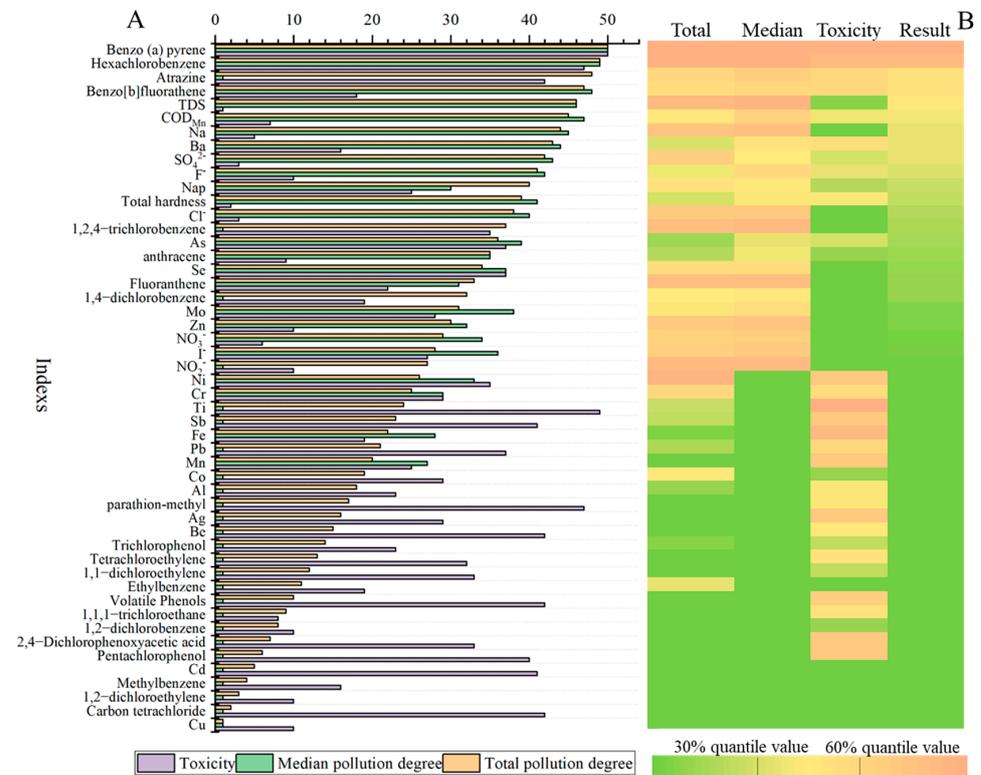


Figure 8. Screening results by the multiplication method. (A) Screening results of each indexes; (B) The heat map of screening results.

As shown in Figure 4, Benzo[a]pyrene, Hexachlorobenzene, As, and Se were the four priority pollutants with both high pollution degree and toxicity, followed by Benzo[b]fluoranthene, Ba, F⁻, and COD_{Mn} with high pollution degree and relatively low toxicity. 1,2-Dichlorobenzene, 1,1,1-Trichloroethane, methylbenzene, 1,2-Dichloroethylene, and Cu were at the bottom of the list with low pollution degree and low toxicity (Figure 8B).

3.3.3. The Weighted Summation Method

The weighted summation method used the same ranking as the multiplication method in Section 3.3.2. However, weights were assigned to total pollution degree (Q), median pollution degree (M), and toxicity (C) based on the importance of each evaluation factor. When Q, M, and C are equally important, each of them is assigned a weight of 0.33. When C is considered to be slightly more important and Q and M are equally important, C is assigned a weight of 0.5, and Q and M are assigned weights of 0.25, respectively. There are five schemes to assign the weights as shown in Table S5.

Relative to the evaluation scores obtained with the same weights for Q, M, and C, opposite trends for the evaluation scores were observed when W_C was greater compared to when W_Q or W_M was greater. When W_M was greater, the calculated scores of the lower ranked pollutants were similar because the same median pollution degree of 1 was assigned to all the pollutants. As the total and median pollution degrees are closely related, it is reasonable to assign a higher weight for toxicity. Comparing the results with weights of 0.5 and 0.6 for toxicity, the weight of 0.5 yielded more differentiation power for the 50 pollutants (Figure 9). Therefore, Scheme b was chosen.

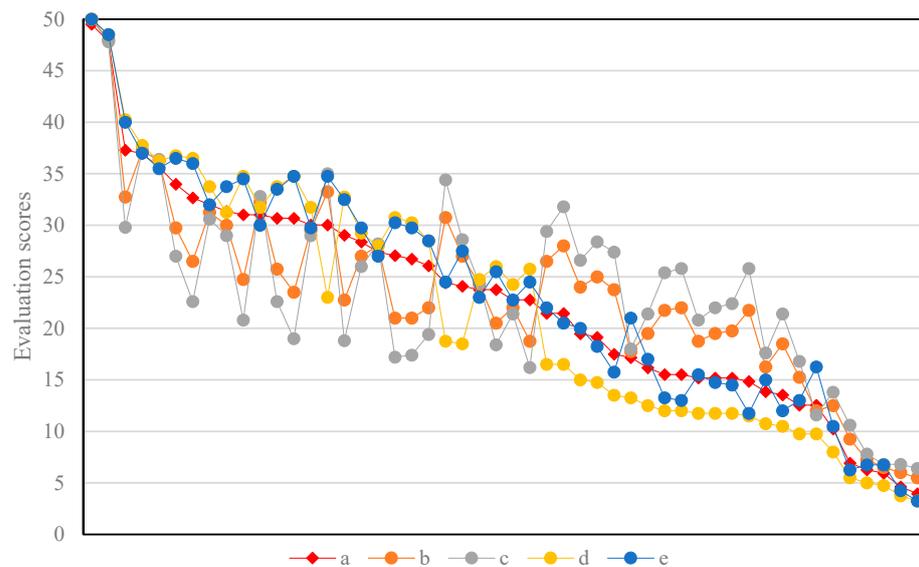


Figure 9. The evaluation scores of different weight assignment schemes.

3.4. Comparison of the Two Screening Methods

The results from the two screening methods were compared. There were 3 significant differences among the top 15 ranked pollutants (Figure 10). The multiplication method calculated the pollution degree directly using the actual value of each pollutant, there was no arbitrary intervention in the calculation process. However, the applicability of this method is poor when the evaluation parameters (Q_i , M_i , and C_i) of a pollutant exhibit large variation. The weighted summation method can effectively avoid the influence caused by the large variation of evaluation parameters, but the weight settings are arbitrary. The total pollution degree ranged from 1.11 to 460.18; the median pollution degree ranged from 0 to 4.9 and the toxicity ranged from 0.001 to 10^6 (Figure S2). In the multiplication method, the total pollution degree and the median pollution degree were closely related. As a result, the effect of pollution level was overestimated. Therefore, it is more appropriate to use the weighted summation method to calculate the ranking of major pollutants in this study.

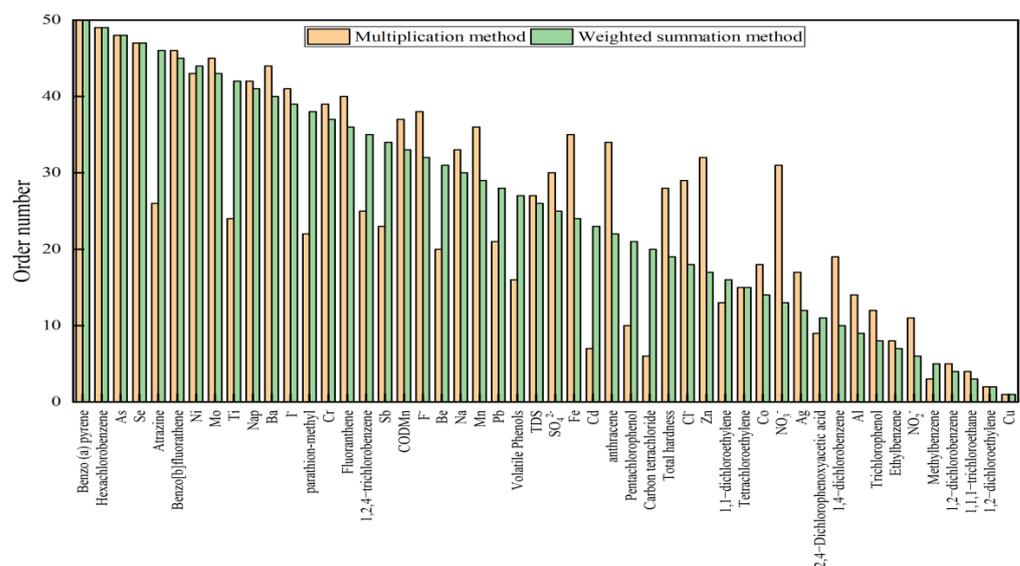


Figure 10. Comparison of screening results between the two methods.

Using the weighted summation screening method, the pollutants in the study area were sorted. The top 10 pollutants were Benzo[a]pyrene, Hexachlorobenzene, As, Se, Atrazine,

Benzo[b]fluoranthene, Ni, Mo, Ti, and Naphthalene. These pollutants should be monitored closely as part of groundwater environment management in the Xiong'an New Region.

4. Conclusions

An efficient priority ranking list is required to focus on the compounds in groundwater that are predicted to be the most hazardous to the environment. The main objective of this study was to develop a screening method for major pollutants based on groundwater pollution assessment. By using this method, the evaluation indexes were divided into natural and man-made components, and pollution evaluation was realized based on the apparent background value and inspection limit, respectively. Additionally, the mean and median of pollution degree were selected, and combined with the toxicity parameters of each component, the product method and hierarchical scoring method were used for coupling calculation. According to the calculated score, the main pollutants in groundwater could be sorted.

Assessment results by using the multiplication method and the weighted summation method were also compared. The unwanted effects caused by the large variation of pollutant evaluation parameters can be effectively avoided when using the weighted summation method. Using the results from comparing different combination of weights, it was more appropriate to use the weighted summation method with weights of 0.5, 0.25, and 0.25 for toxicity, total, and median pollution degrees, respectively. Ten pollutants including Benzo[a]pyrene, Hexachlorobenzene, As, Se, Atrazine, Benzo[b]fluoranthene, Ni, Mo, Ti, and Naphthalene, were selected as priority pollutants in Xiong'an New Region by using the selected screening method, which means more concern is required to strengthen pollution prevention and control of these pollutants.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/w15081565/s1>, Table S1. The reported screening and sorting methods of priority pollutants. Table S2. Tested category. Table S3. Classification of pollutants used for evaluation. Table S4. The detection limits of unnatural components. Table S5. Weight assignment scheme. Figure S1. The pollution degree of unnatural components. Figure S2. The data distribution in the study. (References [19,33–41] are cited in the Supplementary Materials).

Author Contributions: Conceptualization, Y.L.; Methodology, X.Q., X.L. and T.Q.; Formal analysis, X.Q. and X.L.; Investigation, X.Q. and X.L.; Resources, Y.L.; Data curation, X.Q. and Y.L.; Writing—original draft, X.Q.; Writing—review & editing, Y.L.; Visualization, X.Q.; Supervision, Y.L.; Project administration, Y.L.; Funding acquisition, Y.L. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

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