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Research article

Groundwater quality assessment based on entropy weighted osculating value method

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ABSTRACT

In view of provide scientific basis for groundwater resources protection and rational utilization, osculating value method was used to perform groundwater quality assessment in No. 2 water source site of Dawukou District and information entropy was used to determine the weight of each assessment parameter. The steps for water quality assessment with entropy weighted osculating value method were depicted in detail. The single index assessment showed that NH₄⁺, F⁻ and Mn in some of the groundwater samples are beyond the permissible limits slightly, but the comprehensive assessment showed that groundwater quality in the study area was basically fit for drinking and the most influencing indices affecting the groundwater quality were Tfe, pH and NH₄⁺. Special attention should be paid to these indices to prevent groundwater pollution. The entropy weighted osculating value method was proved an easy and effective method for groundwater quality assessment.

Keywords: Osculating value method, entropy weight, groundwater quality assessment, water resources, water quality

1. Introduction

Groundwater is an important and limited resource in many parts of the word and it is extremely important and heavily used in North China and Northwest China. Groundwater quality assessment is a part of environment assessment and groundwater quality is closely related with human health. The rationality and visualizability of the assessment results are the key points for study. There have been many methods for water quality assessment. For example, fuzzy mathematical method, gray model method, water quality index method and set pair analysis method, et al. for groundwater assessment. Each method has its merit and defect.

The osculating value method is a multiple objective decision-making optimization method which has been widely used in economics, business, management, land treatment and water resources management (Zhang, 2010; Wang et al., 2007a; Wang et al., 2007b; Chen, 2010; Lu and Tang, 1997; Lu and Han, 2009; Zhou and Chen, 2008). This method has been proved an effective method in these fields and in this paper it is introduced into groundwater quality assessment. Information entropy is used to determine the weight of each parameter, which can reduce the error caused by ignoring the weight.

No. 2 water source site of Dawukou District, built in 1997, is a large water source site which supplies drinking water for over 0.2 million of people in Dawukou District, Northwest China. The groundwater quality is closely related with people's health here. However, due to located in an underdeveloped area, little work has been done on the groundwater quality study, and

the existing monitoring system in the area is old and out of date, which command close and immediate actions to solve these problems. Before these actions can be taken, it is urgent and important to understand the state of groundwater quality here. This study mainly deals with the problem.

2. Materials and method

2.1 Data collection

In this study, 10 groundwater samples were collected in water supply wells in No. 2 water source site of Dawukou District during September 2009. Of the 10 samples, sample 4-1, 5-1, 6-1 and 11-1 were collected in the shallow aquifer (80-150 m) and the other 6 samples were collected in deep aquifer (170-240 m). Samples were collected in pre-cleaned plastic polyethylene bottles for physicochemical analysis of sample. Prior to sampling, all the sampling containers were washed and rinsed thoroughly with the groundwater to be taken for analysis. All these samples were analyzed for carbonate, bicarbonate, chloride, sulphate, phosphate, calcium, magnesium, sodium, potassium, pH, chemical oxygen demand (COD), total dissolved solid (TDS), total hardness (TH), nitrate, ammonia nitrogen (NH₄⁺), fluoride (F), total iron (Tfe), total alkalinity, color, arsenic (As), iodine, nitrite, metasillicio acid, manganese (Mn), mercury (Hg) and free carbon dioxide by Laboratory of Urban Water Quality Monitoring Network of Shizuishan Station. During sample collection, handling, and preservation, standard procedures recommended by the Chinese Ministry of Water Resources were followed to ensure data quality and consistency. In this study, 11 parameters are used for groundwater quality assessment and the chemical analysis results are shown in Table 1. Quality standards for groundwater are shown in Table 2. Rank 1 represent excellent quality water, rank 2 represent good quality water, rank 3 represent drinkable quality water, rank 4 represent poor quality water and rank 5 represent extremely quality water.

Table 1: Chemical analysis results (Unite: mg/L except pH)

Well No.	NH ₄ ⁺	Tfe	Cl ⁻	SO ₄ ² -	F-	TH	TDS	As (×10 ⁻³)	Hg (×10 ⁻⁴)	Mn	рН
11-1	0.40	0.120	40.4	19.6	0.87	139.1	304	4.54	0.157	0.033	8.27
11-2	0.40	0.128	95.0	82.4	1.05	142.1	470	4.68	0.045	0.034	8.46
4-1	0.36	0.150	78.7	243.0	0.98	286.3	672	0.75	0.289	0.26	8.41
4-2	0.16	0.119	81.3	172.6	1.62	176.8	576	3.94	0.530	0.110	8.51
5-1	0.76	0.022	37.9	18.7	0.78	112.6	303	0.31	0.094	0.040	8.40
5-2	0.28	0.089	51.2	37.8	1.38	107.6	329	2.57	0.047	0.061	8.37
6-1	0.76	0.098	64.9	41.3	0.74	143.2	353	1.07	0.251	0.066	8.40
6-2	0.16	0.060	105.4	71.1	0.72	201.0	422	2.54	0.013	0.012	8.20
8-2	0.60	0.010	72.5	53.7	0.63	105.1	451	2.51	0.740	0.002	7.99
9-2	0.02	0.138	80.0	198.9	1.51	242.9	598	7.54	0.087	0.035	8.18

Table 2 Quality standard for groundwater in China
(Unite: mg/L except pH)

Index	Rank 1	Rank 2	Rank 3	Rank 4	Rank 5
pН	6.5-8.5	6.5-8.5	6.5-8.5	5.5-6.5 or 8.5-9	<5.5 or >9
TH	≤150	≤300	≤450	≤550	>550
TDS	≤300	≤500	≤1000	≤2000	>2000
SO_4^{2-}	≤50	≤150	≤250	≤350	>350
C1	≤50	≤150	≤250	≤350	>350
Tfe	≤0.1	≤0.2	≤0.3	≤1.5	>1.5
Mn	≤0.05	≤0.05	≤0.1	≤1.0	>1.0
$\mathrm{NH_4}^+$	≤0.02	≤0.02	≤0.2	≤0.5	>0.5
F-	≤1.0	≤1.0	≤ 1.0	≤2.0	>2.0
Hg	≤0.00005	≤0.0005	≤0.001	≤0.001	>0.001
As	≤0.005	≤0.01	≤0.05	≤0.05	>0.05

2.2 Method

Osculating value method is an optimization method which determines the water quality by the osculating values ordering of different water samples and the quality standards of different ranks. The steps are as follows (Wu et al., 2010):

(1) Set up standardized dimensionless matrix

Assuming there are m samples and p standard ranks and in each sample or standard ranks there are n indices to be considered. Then we can get an initial matrix $\mathbf{C} = c$ (ij) $(m+p) \times n$, where, c (ij) is the observed values of samples or the standard limits of corresponding ranks, $i = 1, 2 \dots (m+p)$ and $j = 1, 2 \dots n$.

where,
$$c(y)$$
 is the observed values of samples of the standard limits of corresponding ranks, $a = 1, 2 \dots (m+p)$ and $j = 1, 2 \dots n$.

$$C = \begin{bmatrix} c_{11} & c_{12} & \cdots & c_{1n} \\ c_{21} & c_{22} & \cdots & c_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ c_{(m+p)1} & c_{(m+p)2} & \cdots & c_{(m+p)n} \end{bmatrix}_{(m+p)\times n}$$
(1)

Because in the initial matrix, complex relation such as the different dimensions, different order of magnitude or sometimes different unites exists, the initial matrix must be standardized. The initial matrix is standardized with formula (2).

$$r_{ij} = \begin{cases} c_{ij} / \left[\sum_{i=1}^{(m+p)} c_{ij}^2 \right]^{\frac{1}{2}} & \text{efficiency type} \\ -c_{ij} / \left[\sum_{i=1}^{(m+p)} c_{ij}^2 \right]^{\frac{1}{2}} & \text{cost type} \end{cases}$$

$$(2)$$

After standardization, we can get the standardized matrix $\mathbf{R} = (r_{ij})_{(m+p) \times n}$

(2) Determination of the optimum and worst point sets

Let
$$\begin{cases} r_j^+ = \max\{r_{1j}, r_{2j} \dots r_{(m+p)j}\} \\ r_j^- = \min\{r_{1j}, r_{2j} \dots r_{(m+p)j}\} \end{cases}$$
 $(j = 1, 2, ...n)$ (3)

Then we can get the optimum and worst point sets. The optimum set is

$$G = \{r_1^+, r_2^+ \dots r_n^+\}$$
 (4)

And the worst point set is

$$B = \{ r_1^-, r_2^- ... r_n^- \}$$
 (5)

(3) Determination of weights of indices by information entropy

Suppose there are m water samples taken to evaluate the water quality (i=1, 2... m). Each sample has n evaluated parameters (j=1, 2... n). Then an initial eigenvalue matrix can be constructed. When calculate the weights, the initial matrix must be transformed to eliminate the error caused by different dimensions and different unites or magnitude. After transformation, the standard-grade matrix Y can be obtained.

$$\mathbf{Y} = \begin{bmatrix} y_{11} & y_{12} & \cdots & y_{1n} \\ y_{21} & y_{22} & \cdots & y_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ y_{m1} & y_{m2} & \cdots & y_{mn} \end{bmatrix}$$
 (6)

The **Y** is determined by the following formula:

$$y_{ij} = \begin{cases} \frac{x_{ij} - (x_{ij})_{\min}}{(x_{ij})_{\max} - (x_{ij})_{\min}} & \text{efficiency type} \\ \frac{(x_{ij})_{\max} - x_{ij}}{(x_{ij})_{\max} - (x_{ij})_{\min}} & \text{cost type} \end{cases}$$

$$(7)$$

Where, x_{ij} is the original water quality analysis data, $(x_{ij})_{max}$ and $(x_{ij})_{min}$ are the maximum and minimum of each index in the original water quality analysis data.

The information entropy is expressed by the formula below:

$$e_{j} = -\frac{1}{\ln m} \sum_{i=1}^{m} P_{ij} \ln P_{ij}$$
 (8)

In formula (8), $P_{ij} = y_{ij} / \sum_{i=1}^{m} y_{ij}$. The smaller the value of e_j is, the bigger the effect of j index.

Then the entropy weight can be calculated with the below formula:

$$\omega_{j} = \frac{1 - e_{j}}{\sum_{j=1}^{n} (1 - e_{j})}$$
(9)

In the formula, ω_j is defined as the entropy weight of j parameter.

(4) Calculation of osculating value

The osculating value of each sample can be calculated with formula (10) and (11):

$$\begin{cases} d_{i,G} = \sqrt{\omega_j \sum_{j=1}^{n} [r_{ij} - (r_{ij})_G]^2} \\ d_{i,B} = \sqrt{\omega_j \sum_{j=1}^{n} [r_{ij} - (r_{ij})_B]^2} \end{cases}$$
(10)

$$E_{i} = \frac{d_{i,G}}{\min\{d_{i,G}\}} - \frac{d_{i,B}}{\max\{d_{i,B}\}}$$
(11)

Where, $d_{i,G}$ is the Euclidean distance between optimum point G and water sample i, and $d_{i,B}$ is the Euclidean distance between worst point B and water sample i. E_i is the osculating value of i sample. The min $\{di, G\}$ and max $\{d_{i,B}\}$ are the minimum and maximum of optimum and worst point distances.

(5) Water quality assessment

All samples and standard ranks are ordered from small to big according to the calculated osculating value E_i , and water quality is determined by the osculating value. For example, the water sample locate before rank 1 is classified into excellent quality water, and the water sample locates between rank 1 and rank 2 is good quality water.

3. Results and discussion

3.1 General characteristics of groundwater

 NH_4^+ is an indicator for manual pollution. The NH_4^+ mainly comes from domestic sewage and under proper condition it can transform into NO_2^- which is a carcinogenic matter. The permissible concentration of NH_4^+ is 0.2 mg/L in drinking water quality standard of China. In the study area, NH_4^+ pollution is the most serious and obvious problem. Of the 10 samples, NH_4^+ concentrations in 7 samples exceed the standard limit. The highest NH_4^+ concentration is 0.76 mg/L existing in well 5-1 and 6-1 and the lowest NH_4^+ concentration is 0.02 mg/L existing in well 9-2. Special attention should be paid to NH_4^+ to prevent further pollution.

Fluoride (F⁻) is a widespread element in the nature and is a necessary trace element for human bodies and for the animals. Insufficient or excessive intake of fluorine will cause many health problems. High fluoride concentration water is particularly disastrous to humans, and in the high fluoride water areas, dental fluorosis and skeletal fluorosis caused by high fluoride water are prevalent. The F⁻ concentration for drinkable water is 1.0 mg/L in China. In this study, the highest F⁻ concentration is 1.62 mg/L existing in well 4-2 and the lowest F⁻ concentration is 0.63 mg/L existing in well 8-2. 4 of the 10 samples exceed the permissible limit for F⁻.

Mn is a trace element on earth helping fight against senium and the permissible concentration in drinking water is 0.1 mg/L. In this study, except well 4-1 and 4-2, the Mn concentrations in all samples are within the permissible limit. The Mn concentrations in well 4-1 and 4-2 are 0.26 and 0.11 mg/L, respectively.

TDS, TH, As, Hg and Tfe are all important parameters for assessing groundwater quality. The permissible concentrations for these parameters are 1000 mg/L, 450 mg/L, 6.5-8.5, 0.05 mg/L, 0.001 mg/L and 0.3 mg/L, respectively. Fortunately, these matters in this study are all within the standard limits which means the groundwater is fit for drinking with respect to these matters.

Hydrochemical concepts can help to elucidate mechanisms of flow and transport in groundwater systems, and unlock an archive of pale environmental information (Vasanthaviga et al., 2010). In this paper, Piper plot is also used for inferring hydrogeochemical facies of groundwater (Fig. 1). The plot shows that the major chemical types of water samples fall into HCO₃·Cl-Na·Ca type, HCO₃ -Na·Ca type and some mixed HCO₃·SO₄·Cl-Na·Ca type. From the plot, alkalis (Na and K) exceed alkaline earths (Ca and Mg) and weak acid (HCO₃) exceed strong acids (Cl and SO₄).

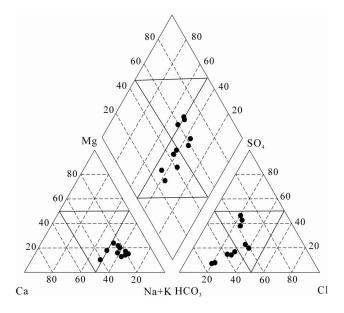


Figure 1: Piper plot of groundwater samples

3.2 Groundwater quality comprehensive assessment

Groundwater quality comprehensive assessment in No. 2 water source site of Dawukou District is performed with the above-mentioned steps. According to formula (1), first an initial matrix is constructed below.

```
139.1
             304
                    40.4
                            19.6
                                   0.40
                                         0.120
                                                0.87
                                                       0.00450
                                                                 0.0000157
                                                                              0.033
                                                                                     8.27
     142.1
             470
                    95.0
                            82.4
                                   0.40
                                         0.128
                                                 1.05
                                                       0.00468
                                                                 0.0000045
                                                                              0.034
                                                                                     8.46
     286.3
             672
                    78.7
                           243.0
                                  0.36
                                         0.150
                                                 0.98
                                                       0.00075
                                                                 0.0000289
                                                                              0.260
                                                                                     8.41
     176.8
             576
                    81.3
                           172.6
                                  0.16
                                         0.119
                                                 1.62
                                                       0.00394
                                                                 0.0000530
                                                                              0.110
                                                                                     8.51
     112.6
             303
                    37.9
                            18.7
                                   0.76
                                         0.022
                                                 0.78
                                                       0.00031
                                                                 0.0000094
                                                                              0.040
                                                                                     8.40
     107.6
             329
                    51.2
                            37.8
                                   0.28
                                         0.089
                                                 1.38
                                                       0.00257
                                                                 0.0000047
                                                                              0.061
                                                                                     8.37
     143.2
             353
                    64.9
                            41.3
                                   0.76
                                         0.098
                                                 0.74
                                                       0.00107
                                                                  0.0000251
                                                                              0.066
                                                                                     8.40
C =
     201.0
             422
                    105.4
                            71.7
                                   0.16
                                                 0.72
                                                       0.00254
                                         0.060
                                                                 0.0000013
                                                                              0.012
                                                                                     8.20
     105.1
             451
                    72.5
                            53.7
                                   0.60
                                         0.010
                                                 0.63
                                                       0.00251
                                                                 0.0000740
                                                                              0.002
                                                                                     7.99
     242.9
             598
                    80.0
                           198.9
                                   0.02
                                                 1.51
                                                       0.00754
                                                                 0.0000087
                                                                              0.035
                                         0.138
                                                                                     8.18
     150
             300
                    50.0
                             50
                                   0.01
                                          0.1
                                                 0.33
                                                         0.005
                                                                  0.00005
                                                                              0.02
                                                                                       7
      300
                    150.0
                                                                               0.05
                                                                                      7.5
             500
                            150
                                   0.02
                                          0.2
                                                 0.66
                                                         0.01
                                                                   0.0005
                                                                                      8.5
      450
             1000
                   250.0
                            250
                                   0.2
                                          0.3
                                                  1
                                                         0.02
                                                                   0.00075
                                                                               0.1
                                                  2
                                                         0.05
                                                                    0.001
                                                                                       9
      550
             2000
                   350.0
                            350
                                   0.5
                                          1.5
                                                                                1
```

Special attention should be focused on F⁻, pH and Hg. Because in the water quality standard for groundwater listed in Table 2, the first three ranks of F⁻ and pH have the same limits respectively and the last three ranks of Hg have the same limit. We manually assigned limits to the three indices so that it is convenient for us to do the calculation. The manual treatment doesn't change the final results. It can be seen from the above initial matrix that the dimension and order of magnitude are different between different samples and even in the same sample, which requires standardization.

According to formula (2), the initial matrix is standardized, and the standardized matrix is listed below. We can see from the standardized matrix the orders of magnitude are the same between different samples and different ranks after transformation. And all these indices are dimensionless.

```
-0.14 -0.11
              -0.08
                      -0.03
                            -0.26
                                    -0.08
                                            -0.21
                                                  -0.08
                                                          -0.01
                                                                  -0.03
                                                                         -0.27
                                                                  -0.03
-0.15 -0.17
              -0.18
                      -0.14
                             -0.26
                                    -0.08
                                            -0.25
                                                   -0.08
                                                           0.00
                                                                         -0.27
              -0.15
                             -0.23
                                            -0.24
                                                                  -0.25
                                                                         -0.27
-0.30 -0.25
                      -0.41
                                    -0.09
                                                   -0.01
                                                          -0.02
-0.18 \quad -0.21
              -0.16
                      -0.29
                             -0.10
                                            -0.39
                                                   -0.07
                                                          -0.04
                                                                  -0.10
                                                                         -0.28
                                    -0.08
-0.12
       -0.11
              -0.07
                      -0.03
                             -0.49
                                            -0.19
                                                   -0.01
                                                          -0.07
                                                                  -0.04
                                                                         -0.27
                                    -0.01
                                                           0.00
-0.11
       -0.12
               -0.10
                      -0.06
                             -0.18
                                    -0.06
                                            -0.33
                                                   -0.05
                                                                  -0.06
                                                                         -0.27
       -0.13
               -0.13
                      -0.07
                             -0.49
                                            -0.18
                                                   -0.02
                                                           -0.02
                                                                  -0.06
                                                                         -0.27
-0.15
                                    -0.06
-0.21
       -0.15
              -0.20
                      -0.12
                             -0.10
                                    -0.04
                                            -0.17
                                                   -0.05
                                                           0.00
                                                                  -0.01
                                                                         -0.27
      -0.16
              -0.14
                      -0.09
                             -0.39
                                    -0.01
                                            -0.15
                                                   -0.04
                                                          -0.05
                                                                  0.00
                                                                         -0.26
-0.11
      -0.22
              -0.16
                      -0.33
                             -0.01
                                            -0.36
                                                   -0.13
                                                          -0.01
                                                                  -0.03
                                                                         -0.27
-0.25
                                    -0.09
      -0.11
              -0.10
                      -0.08
                             -0.01
                                            -0.08
                                                   -0.09
                                                          -0.04
                                                                  -0.02
                                                                         -0.23
-0.16
                                    -0.06
-0.31
       -0.18
              -0.29
                      -0.25
                             -0.01
                                    -0.13
                                            -0.16
                                                   -0.18
                                                          -0.37
                                                                  -0.05
                                                                         -0.24
              -0.49
                      -0.42
                             -0.13
                                    -0.19
                                            -0.24
                                                   -0.36
                                                          -0.55
                                                                  -0.10
-0.47
       -0.37
                                                                         -0.28
-0.57 -0.73
              -0.68
                      -0.59
                             -0.32
                                    -0.95
                                           -0.48
                                                  -0.89
                                                          -0.74
                                                                  -0.95
                                                                        -0.29
```

We can get the optimum and worst point sets according to formula (3) to (5). The optimum point set is $G = \{-0.11, -0.11, -0.07, -0.03, -0.01, -0.01, -0.08, -0.01, 0.00, 0.00, -0.23\}$, and the worst point set is $B = \{-0.57, -0.73, -0.68, -0.59, -0.49, -0.95, -0.48, -0.89, -0.74, -0.95, -0.29\}$.

According to formula (6) to (9), we can get the entropy weight of each index, and the calculated results are listed in Table 3.

Table 3: Calculated entropy weight of each index

	TH	TDS	Cl	SO_4^{2-}	$\mathrm{NH_4}^+$	Tfe	F ⁻	As	Hg	Mn	рН
e_i	0.93	0.91	0.90	0.92	0.87	0.85	0.90	0.93	0.92	0.95	0.86
ω_i	0.07	0.09	0.09	0.08	0.12	0.14	0.09	0.06	0.07	0.05	0.13

It can be seen that Tfe, pH and NH_4^+ play the leading roles in influencing the groundwater quality. The weights of these indices are larger than 0.10, while others all are smaller than 0.10. TDS, Cl⁻ and F⁻ have the same influence on groundwater quality and their weights are 0.09. After all these have been prepared, the osculating value can be calculated by formula (10) and (11) and groundwater quality can be assessed. The assessment results are listed in Table 4.

Table 4: Assessment results with entropy weighted osculating value method

Well No.		6-2	5-2	11-1	11-2	4-2	8-2
E_i	0.000	0.993	1.769	1.783	2.273	2.752	2.767
Ranks	rank 1	2	2	2	2	2	2
Well No.	9-2		4-1	5-1	6-1		
$\overline{E_i}$	2.822	3.406	3.603	3.649	3.724	6.866	16.487
Ranks	2	rank 2	3	3	3	rank 3	rank 4

It can be seen from the Table 4 that all samples are located behind rank 1 according the order of osculating value, which means all water samples can not be classified into excellent quality water. However, except sample 4-1, 5-1 and 6-1, all samples are located before rank 2, which means except sample 4-1, 5-1 and 6-1 all samples can be classified into good quality water. Sample 4-1, 5-1 and 6-1 are located between rank 2 and rank 3, so the three samples are classified into drinkable quality water. According to the comprehensive assessment results, the groundwater quality in deep aquifer (170-240 m) is better than that in shallow aquifer (80-150m) and the groundwater quality in the study area is basically fit for drinking and no or little pollution occurs here presently. However, Special attention should be paid to Tfe pollution and NH₄⁺ pollution, because Tfe and NH₄⁺ usually have bigger weights and stress great impacts on groundwater quality. Once the groundwater is polluted by Tfe or NH₄⁺, it is difficult and expensive to be treated and restored.

Not only can we understand which rank a sample is classified into, but also can compare two samples classified into the same rank. For example, sample 6-2 and 4-2 both are classified into rank 2 (good quality water), we can determine that the quality of sample 6-2 is better than that of sample 4-2 because the osculating value of sample 6-2 is smaller than that of sample 4-2. This means we can compare any two or more samples using their osculating values. This is the peculiarity of osculating value method because other methods can not do this clearly. Moreover, the calculation processes are easy and can be calculated merely in Microsoft Excel and doesn't need to construct a complex computing program which is always difficult for junior engineering and students.

4. Conclusions

Groundwater in No. 2 water source site of Dawukou District are assessed with a novel and easy to use method, the following conclusions are obtained.

- (1) NH₄⁺, F⁻ and Mn in some of the groundwater samples are beyond the permissible limits slightly. The comprehensive assessment results show that Tfe, pH and NH₄⁺ are the most influencing factors affecting the groundwater quality and special attention should be paid to these parameters to prevent further pollution. The groundwater quality in the study is classified into good quality rank except well 4-1, 5-1 and 6-1 belonging to drinkable quality. The groundwater in the study area is basically fit for drinking.
- (2) The entropy weighted osculating value method is an effective method for groundwater quality assessment. It can easily compute the groundwater quality ranks and can clearly illustrate the comparison between two samples in the same rank. It can be calculated in Microsoft Excel, which is most fit for junior engineering and students.

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