

Research Article

Assessment of Groundwater Quality Based on Matter Element Extension Model

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The basic theory and calculating processes of matter element extension method are discussed in detail. Mass balance simulation is used to study the changes of groundwater chemistry. Results show that calcite and dolomite are oversaturated, while gypsum, fluorite, and halite are unsaturated in the simulation path; so calcite precipitates, while gypsum, fluorite, halite, and dolomite dissolve. The changing tendency of $\text{Ca}^{2+}/\text{Na}^+$ is apparent. Because of the dissolution and precipitation of minerals, the content of each ion changes. Parameters of groundwater are basically within the permissible limits and meet the requirement of drinking water standards. By comparing the evaluation results obtained from matter element extension method, osculating value method based on entropy weight, and principal component analysis method, it is proved that matter element extension is an effective and reasonable method for groundwater quality assessment. The converting tendency of groundwater quality is judged based on the extension indexes; this characteristic is unique of matter element extension method.

1. Introduction

Groundwater is the most important water resource for human. Groundwater quality problems have intensified through the ages in response to the increased growth on concentration of populations and industrial centres and unreasonable exploitation and utilization of groundwater. Thus finding an objective and reasonable method to evaluate water quality is a hot issue at the present time.

Today there are a lot of methods to evaluate groundwater quality, such as water quality index method [1], grey correlation method [2], principal component analysis method [3], and fuzzy theory method [4] and fuzzy synthetic evaluation method [5]; every method has its weakness, such that water quality index evaluation method is subjective, and grey clustering method and fuzzy theory method neglect some important information in the process of calculation and need special program to finish the complicated calculation. Matter element extension method can solve the realistic contradiction qualitatively and quantitatively [6]. It has been applied to many fields, such as environmental quality assessment

[7], land suitability evaluation [8], and risk assessment of urban network planning [9], but the application on evaluating groundwater quality is less. In this paper, we combine the method and information entropy to evaluate groundwater quality of water source of Shizuishan city NW China; the grade of groundwater quality is obtained by calculating the comprehensive correlation degrees and extension indexes [6]. The comprehensive analysis is done based on parameters analysis and mass balance simulation.

2. Method

Matter element extension, incorporating the matter element theory with extension theory [3], was proposed by Mr. Cai in the 1980s. Its basic theory is outlined below.

2.1. Definition of Matter Element. A given thing is named M , whose characteristic c is valued v , the orderly ternary group $R = (M, C, V)$ is named as the matter element. M has n characteristics c_1, c_2, \dots, c_n and the corresponding values are

v_1, v_2, \dots, v_n ; thus the matter element can be expressed as [7–11]:

$$R(x) = \begin{bmatrix} M & c_1 & v_1 \\ & c_2 & v_2 \\ & M & M \\ & c_n & v_n \end{bmatrix} \quad (1)$$

according to the definition of matter element, the classical domain R_0 and section domain R_c can be determined.

2.2. Construction of the Correlation Function. The correlation degree of each characteristic to each class can be calculated by using the following functions [7–11]:

$$K_j(x_i) = \begin{cases} \frac{\rho(x_j, x_{ij})}{|x_{ij}|} & x_j \in x_{ij} \\ \frac{\rho(x_j, x_{pj})}{\rho(x_j, x_{pj}) - \rho(x_j, x_{ij})} & x_j \notin x_{ij} \end{cases} \quad (2)$$

where $|x_{ij}| = |a_{ij} - b_{ij}|$,

$$\rho(x_j, x_{ij}) = \left| x_j - \frac{1}{2}(a_{ij} - b_{ij}) \right| - \frac{1}{2}(b_{ij} - a_{ij})$$

$$i = 1, 2, \dots, m, \quad j = 1, 2, \dots, n \quad (3)$$

$$\rho(x_j, x_{pj}) = \left| x_j - \frac{1}{2}(a_{pj} - b_{pj}) \right| - \frac{1}{2}(b_{pj} - a_{pj})$$

$$j = 1, 2, \dots, n.$$

2.3. Weight Determination. There are many widely used methods, such as principal component analysis [3], and AHP [12]. These methods are subjective and random to some extent. Information entropy [13] is used to determine the weights of evaluated indexes in this study; it minimizes the subjective influence, and the result is more objective and reasonable.

2.4. Comprehensive Correlation Degree $K_i(P)$ and Extension Index j^* Calculation. The comprehensive correlation degrees of evaluated samples can be obtained

$$K_i(p) = \sum_{j=1}^n W_j \cdot K_j(x_i) \quad i = 1, 2, \dots, m; \quad j = 1, 2, \dots, n. \quad (4)$$

Suppose

$$\overline{K_i(p)} = \frac{K_i(p) - \min K_i(p)}{\max K_i(p) - \min K_i(p)} \quad i = 1, 2, \dots, m. \quad (5)$$

The formula for calculating the extension index j^* is

$$j^* = \frac{\sum_{i=1}^m i \cdot \overline{K_i(p)}}{\sum_{i=1}^m \overline{K_i(p)}} \quad i = 1, 2, \dots, m. \quad (6)$$

The grade of evaluated object and the attributive degree of the evaluated matter element tend to convert into adjacent levels can be judged from j^* [14, 15].

3. Case Study and Materials

3.1. Study Area. The water source of Shizuishan City is located between latitude $38^\circ 57' 18'' - 39^\circ 04' 04''$ N and longitude $106^\circ 25' 09'' - 106^\circ 33' 33''$ E. It covers an area of about 75.23 km^2 , 10.03 km from east to west, and 7.50 km from north to south. It is situated in the arid continental climate area with little rain and intensive evaporation. The average annual rainfall is 160.94 mm and the average annual evaporation value is 1792.64 mm. The maximum and minimum temperatures are 25.18°C and -6.73°C , respectively. The ground elevation varies from 1120 m to 1123 m and tilts smoothly from northwest to southeast. The area consists of diluvial inclined plain and flood-lacustrine plain.

3.2. Materials. The water source of Shizuishan City pumps water from the confined aquifer, so we must evaluate the groundwater quality to make sure whether the groundwater is drinkable. Ten groundwater samples were collected from the water source in April 2009, which were taken from the third confined aquifer. Samples were collected in precleaned plastic polyethylene bottles for physicochemical analysis. Prior to sampling, all the sampling containers were washed and rinsed thoroughly with the groundwater to be taken for analysis.

4. Result and Discussion

4.1. Parameters Analysis. Groundwater quality depends on various chemical constituents and their concentrations, which are mostly derived from the geological stratum of the particular region. Thus it is necessary to find some useful indicators, both chemical and physical, to monitor groundwater quality changes. The individual parameters are given as minimum, maximum, average, and standard deviation of the collected samples in the specific area.

Seen from Table 1 and Figure 1, there are mainly six ions in the groundwater (Na^+ , Mg^{2+} , Ca^{2+} , Cl^- , SO_4^{2-} , HCO_3^-). They have indirect influence on other parameters of groundwater, such as TDS, TH, and conductivity, thus they can affect groundwater quality to some extent.

Total hardness (TH) is closely related to daily life and industry; water with high TH is not suitable for drinking, washing, and industry. Besides, it may lead to some diseases. The maximum TH is 400.05 mg/L in W741; the minimum is 84.1 mg/L in W44. TDS reflects the total concentration of dissolved solids; the high TDS is maybe caused by mineral weathering. The TDS ranges from a minimum of 259.31 mg/L in W279 to a maximum of 665 mg/L in W75.

COD reflects the organic matter's concentration; whether water is polluted by organics can be judged from the value of COD. The highest value of COD is 2.84 mg/L in W44; the lowest value is 0.44 mg/L in W279. COD is slightly higher, which may be due to the organic pollution.

Fluoride in small amount is good for preventing dental caries, but high concentration causes health risk such as dental fluorosis and skeletal fluorosis [16]. Fluoride-bearing minerals in the rocks and their interaction with water and

TABLE 1: Statistical analysis for physicochemical parameters of groundwater.

Parameters	Max	Min	Average	Std. Dev.
TH	400.05	84.1	199.08	102.43
TDS	665	259.31	504.67	132.05
COD	2.84	0.44	1.37	0.79
Na ⁺	200	57	123.5	48.52
K ⁺	4.87	0.94	2.25	1.33
Mg ²⁺	29.68	7.8	17.29	8.98
Ca ²⁺	103.67	20.8	49.44	26.15
Cl ⁻	160.9	34.09	89.79	33.93
SO ₄ ²⁻	213.4	2.45	98.91	81.08
HCO ₃ ⁻	395.96	192.2	264.22	57.41
F ⁻	1.13	0.1	0.58	0.46

Note: Unit mg/L for all parameters.

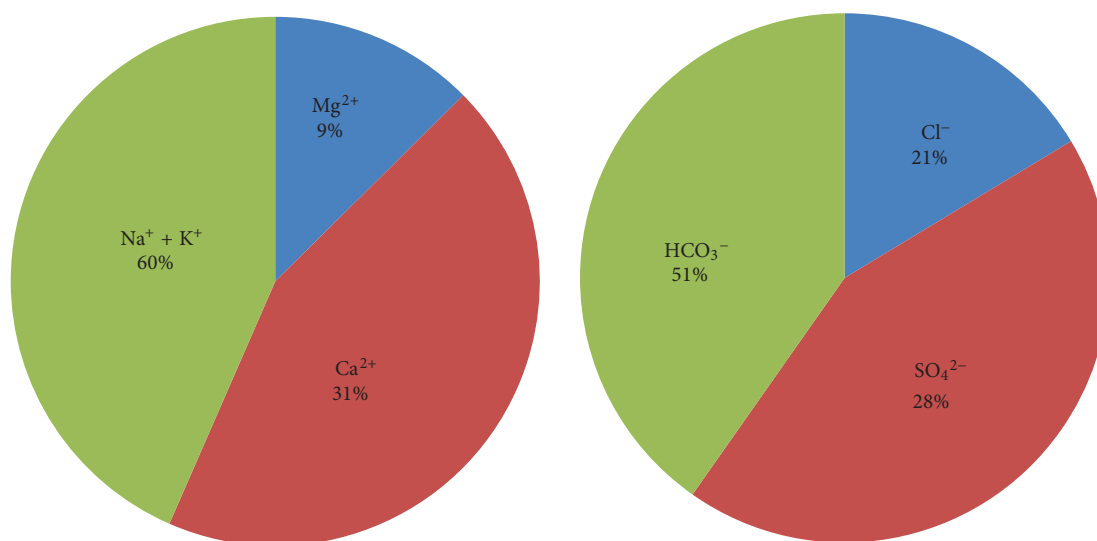


FIGURE 1: Pie chart of groundwater ions equivalents.

agricultural activities are considered to be the main cause for fluoride in groundwater. In this case, the fluoride ranges from 0.1 mg/L to 1.13 mg/L, and there is no values exceed the permissible limits.

Volatile phenol, As, Hg, Cr, Ag, and other heavy metals are important for assessing groundwater quality; if their concentrations are too high, human health will be under threat. Fortunately, these indexes in this study are all within the permissible limits.

Hydrochemical concepts help to elucidate mechanisms of flow and transport in groundwater systems. In this paper, Piper plot is used to infer hydrogeochemical facies of groundwater. Seen from Figure 2 that the major chemical types of water samples fall into Cl-HCO₃-Na type, Cl-HCO₃-Na-Ca type, Cl-SO₄-HCO₃-Na-Ca, Cl-SO₄-HCO₃-Na-Ca-Mg type and some mixed. Seen from the plot, alkalis (Na and K) exceed alkaline earths (Ca and Mg) and strong acids (Cl and SO₄) exceed weak acids (HCO₃ and CO₃).

4.2. Mass Balance Simulations. Mass balance simulation is mainly used for studying the chemical reaction during the

process of groundwater flow. In the method, two points (e.g., A and B) in the flow path are considered to be the study subjects. The chemistry of A in the upstream is considered to be the initial water quality, and the chemistry of B in the downstream is considered to be the final water quality. According to the chemical reactions between groundwater and aquifer, the quantities of mineral dissolution and precipitation between A and B can be calculated using the mass balance principle. On the basis of that, the chemistry changes in groundwater can be analyzed. In general, mass balance simulation is based on the following equation [17]:

$$\sum_{j=1}^n a_{ij} x_j = b_i, \quad (7)$$

where a_{ij} is the stoichiometric number of the i th element in the j th mineral. x_j is the dissolved mole of the j th mineral, if the value is positive, it means that the j th mineral is dissolved, whereas the negative value indicates the j th mineral is precipitated. b_i is the increments of the i th element between A and B.

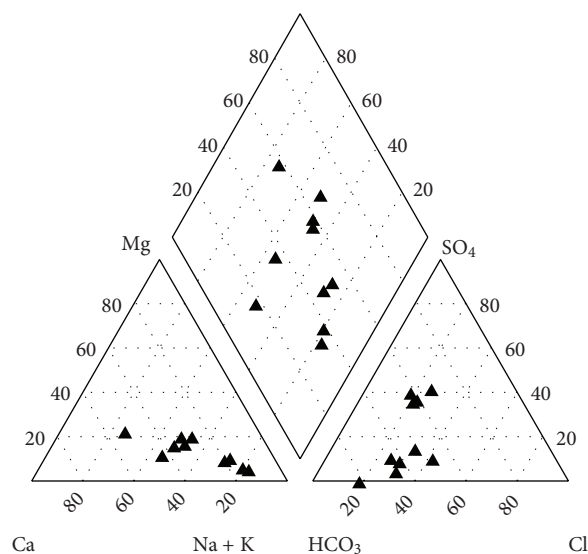


FIGURE 2: Piper plot of groundwater samples.

TABLE 2: Groudwater chemical analysis results in the simulation path (mg/L).

	pH	K ⁺	Na ⁺	Ca ²⁺	Mg ²⁺	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	F ⁻
W279	8.15	1	57	34.56	10.47	238.83	34.09	2.45	0.12
W75	7.91	1.88	128	65.7	29.2	219.2	102.1	213.4	1

TABLE 3: Reaction equations.

	Reaction equation
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} = \text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O}$
Fluorite	$\text{CaF}_2 = \text{Ca}^{2+} + 2\text{F}^-$
Calcite	$\text{CaCO}_3 = \text{Ca}^{2+} + \text{CO}_3^{2-}$
Halite	$\text{NaCl} = \text{Na}^+ + \text{Cl}^-$
Dolomite	$\text{CaMg}(\text{CO}_3)_2 = \text{Ca}^{2+} + \text{Mg}^{2+} + 2\text{CO}_3^{2-}$
Ion exchange	$2\text{NaX} + \text{Ca}^{2+} \leftrightarrow 2\text{Na}^+ + \text{CaX}_2$

In this case, groundwater flows from northwest to southeast, W279 is in the upstream, W75 is in the downstream, so the simulation path is from W279 to W75. The chemical analysis results of sample W279 and W75 are showed in Table 2. Saturation index (SI) is the common index to do the hydro-geochemical research, and it is applied to determine the saturation state of minerals in groundwater [17].

The mineral facies are chosen based on the analysis result of groundwater quality, the main components of groundwater, and the occurrences conditions [18]. In the study area, the main cations are Na⁺, Ca²⁺, Mg²⁺, the main anions are HCO₃⁻, SO₄²⁻, Cl⁻; thus halite, gypsum, calcite, and dolomite are chosen to be the mineral facies. Although fluoride is the required element for human body, considering its pathogenetic role, fluorite is also decided to be analyzed. Above all, there are five minerals selected.

During the process of groundwater flow, the cations existed in groundwater can be exchanged by other cations existed in the surface of aquifer media. The cation exchange reactions plays important role in the chemical evolution

of groundwater [17], so it is included in the mass balance simulation. If the ratio of Ca²⁺ to Na⁺ decreases in the flow path, it indicates that Ca²⁺ existed in groundwater may exchange with Na⁺ existed in clay; if the ratio of Ca²⁺ to Na⁺ increases, it indicates that Na⁺ existed in groundwater may exchange with Ca²⁺ existed in clay [19]. The reactions which may occur in the simulation path are listed in Table 3.

Seen from Table 4, Na⁺, Ca²⁺, and Cl⁻ increase in the simulation path, and the increase degree of Na⁺ is greater than that of Cl⁻, which indicates that there are some other reactions related to Na⁺ occur in the simulation path besides halite's dissolution. The value of Ca²⁺/Na⁺ in W279 is 0.3486, and the value of Ca²⁺/Na⁺ in W75 is 0.2951; it indicates that the cation exchange reaction may occur in the path.

The mass balance simulation is done by PHREEQC, and the simulation results are listed below.

Seen from Table 5, calcite and dolomite are always oversaturated in the simulation path and have the tendency to precipitate; meanwhile gypsum, fluorite and halite are unsaturated in the simulation path and have the tendency to dissolve into groundwater.

Known from Table 6, calcite precipitates while gypsum, fluorite, halite, and dolomite dissolve in the simulation path. The cation exchange reaction between Na⁺ and Ca²⁺ occurs at the same time. During the process, F⁻ increases due to the fluorite's dissolution, Cl⁻ increases due to the halite's dissolution, Mg²⁺ increases due to the dolomite's dissolution, and SO₄²⁻ increases due to the gypsum's dissolution. Na⁺ increases because of the combined effect of halite's dissolution and the cation exchange reaction. Since the influences of

TABLE 4: Ratios of $\text{Ca}^{2+}/\text{Na}^+$ and Na^+/Cl^- .

	Na^+ (mmol/L)	Ca^{2+} (mmol/L)	Cl^- (mmol/L)	$\text{Ca}^{2+}/\text{Na}^+$	Na^+/Cl^-
W279	2.4783	0.8640	0.9603	0.3486	0.3875
W75	5.5652	1.6425	2.8761	0.2951	0.5168
Difference	3.0870	0.7785	1.9158	-0.0535	0.1293

TABLE 5: Saturation indices.

	Gypsum	Fluorite	Calcite	Halite	Dolomite	$\text{CO}_2(\text{g})$
W279	-3.44	-3.13	0.61	-7.28	1.06	-2.79
W75	-1.42	-1.16	0.48	-6.49	0.96	-2.61

TABLE 6: Dissolution of the mineral facies (mmol/L).

Calcite	Dolomite	Fluorite	Halite	Gypsum	NaX	CaX_2
-1.612	0.781	0.023	1.907	2.199	1.138	-0.569

Note: Positive means dissolution, negative means precipitation.

TABLE 7: Comprehensive correlation degrees and extension indexes.

Samples	$K_i(P)$				j^*	Level
	I	II	III	IV		
W279	0.9374	-0.7077	-0.8589	-0.9026	1.1359	I
W390	0.7434	-0.4621	-0.6973	-0.8297	1.305	I
W719	0.5338	-0.1644	-0.7095	-0.8132	1.4078	I
W741	-0.1117	-0.2959	0.119	-0.4583	2.2124	II
W16	-0.132	0.3749	-0.451	-0.4885	1.7464	I
W43	0.0962	0.3431	-0.5084	-0.7263	1.7135	I
W44	0.4992	-0.2544	-0.5663	-0.7411	1.4398	I
W66	-0.2628	0.0508	0.2968	-0.1565	2.7885	II
W75	-0.1554	0.0453	0.2501	-0.2702	2.4265	II
W69	-0.3968	0.0186	0.2233	-0.1476	2.8706	II

TABLE 8: Comparison of the results of the two methods.

Samples	W279	W390	W719	W741	W16	W43	W44	W66	W75	W69
Matter element extension	I	I	I	II	I	I	I	II	II	II
Osculating value method	I	I	I	II	II	I	I	III	III	III
PCA	I	I	I	II	II	II	III	II	II	II

gypsum, fluorite, and dolomite's dissolution on the content of Ca^{2+} are greater than that of calcite's dissolution and the cation exchange reaction, the concentration of Ca^{2+} increases. The precipitation of calcite and the dissolution of dolomite together decrease HCO_3^- . Because the groundwater in this case is confined water and the burial depth is large, it is less connected with the atmosphere, so pH of the groundwater is mainly affected by the content of alkaline anions, such as HCO_3^- .

Judged from the dissolution of NaX and CaX_2 , the cation exchange reactions is extensive, and the change of Ca^{2+} is smaller, while the change of Na^+ is greater, and the changing tendency of $\text{Ca}^{2+}/\text{Na}^+$ is apparent. Thus we can determine

again that Na^+ increase is due to the combined effect of halite's dissolution and cation exchange reaction.

4.3. Assessment of Groundwater Quality. In this study, eight typical indexes are selected to be the evaluation indexes, which can reflect the physical and chemical characteristics of groundwater. There are TH, TDS, COD, Ca^{2+} , Cl^- , SO_4^{2-} , HCO_3^- , and F^- . The state standard of groundwater quality GB/T14848-93 is chosen to be the evaluation criterion, which is divided into five levels. Considering that there is no evaluation index exceeded the fifth level limit in this study, thus only the first fourth levels are chosen to build the matter elements.

Based on matter element extension method, groundwater quality is evaluated. The comprehensive correlation degree $K_i(P)$ and extension index j^* are calculated and shown in Table 7.

Known from Table 7, groundwater quality of W279, W390, W719, W16, W43, and W44 belong to level I, and W741, W66, W75, and W69 belong to level II. The result indicates that groundwater quality in the study area is good as a whole and can be drinkable. Because of the great depth and the protection of aquitard, the confined water is not easy to be polluted. Judged from the value of extension index j^* , water samples W16 and W43 tend to convert from level I into level II. W741 and W75 tend to convert from level II into level I, while W66 and W69 tend to convert from level II into level III.

Which water sample's quality is better than other's at the same level can be judged by comparing the values of extension indexes. For instance, groundwater quality of both W279 and W16 belongs to level I, but the extension index value of sample W16 is higher than that of W279. It indicates that the attributive degree of W16 to convert into II level water is higher than that of W279. In other words, groundwater quality of W16 is worse than that of W279. The rest can be done in the same way. So groundwater quality of water samples from good to bad can be expressed in the order of $W279 > W390 > W719 > W44 > W43 > W16 > W741 > W75 > W66 > W69$.

Osculating value method based on entropy weight [13] and principal component analysis method (PCA) [20] are the popular methods to assess groundwater quality, so we also use the two methods to assess groundwater quality of study area and then compare the results obtained from the three methods.

Seen from Table 8, the results obtained from the three different methods are basically similar. Principal component analysis method (PCA) neglects some important information, which may lead some result unreasonable; the evaluated result obtained by using osculating value method based on entropy weight is too restrict. Based on the reasons presented above, the evaluated results obtained from the three methods are different from each other more or less. But on the whole the comparison confirms that the results obtained from matter element extension are reliable and scientific.

5. Conclusion

From the mass balance simulation, calcite and dolomite are oversaturated, meanwhile gypsum, fluorite and halite are unsaturated in the simulation path, and the changing tendency of Ca^{2+}/Na^+ is apparent. Calcite precipitates, while gypsum, fluorite, halite, and dolomite dissolve in the simulation path. Because of the dissolution and precipitation of minerals, the contents of chemical compositions are changed. Groundwater quality in the study area is evaluated by using the matter element extension method, and results show the groundwater meets the requirement of drinking water standards. It is proved that matter element extension is a reasonable and effective method to evaluate groundwater

quality by comparing the results obtained from the other methods. The application of information entropy minimizes the subjective interferences and makes the result more objective and accurate. According to the values of extension indexes, groundwater quality of water samples in the same level can be compared and the tendency of conversion can be judged; it is the unique characteristic of matter element extension method used in this study.

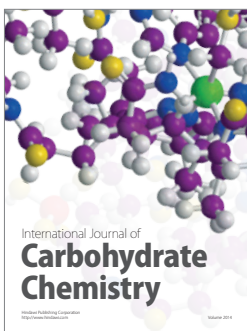
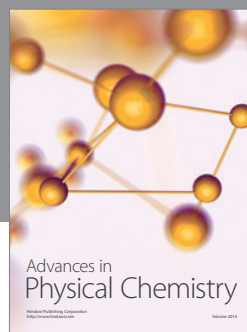
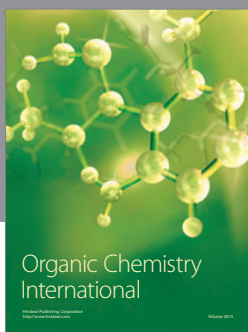
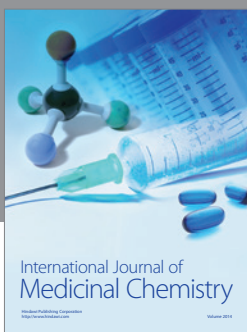
Acknowledgments

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