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Geochemical Characteristics and Their Environmental Implications for the Water Regime of Hulun Lake, Inner Mongolia, China

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Abstract: The overall geochemical composition of natural-water regimes reflects the response to long-term interactions between the water and the surrounding environment in the process of its circulation. Their characteristics can reflect both aquatic ecological health and the tracer of the water source, as well as the water budget. In this study, Hulun Lake, a remote lake in a cold and arid area of China, was chosen in order to analyze its geochemical characteristics, including the major ions, stable isotopes (δD and $\delta^{18}O$) and dissolved organic matter (DOM) in its lake water, river water and groundwater. The major ions in the water were dominated by $Na^+ + Ca^{2+}$-CO_3^{2-} and the concentration of ions in the groundwater was significantly higher than that in the lake and river water, implying a dry climate and relatively little human disturbance. The δD and $\delta^{18}O$ values for both the groundwater and the river water were similar and both were close to the global meteoric water line (GMWL), indicating that their sources were mainly supplied by atmospheric precipitation. However, the δD and $\delta^{18}O$ values for lake water were below the GMWL, indicating strong evaporation. The concentration of DOM in the lake water was significantly higher than that in the river water and groundwater, which was affected by the growth of aquatic organisms, and the three-dimensional fluorescence spectrum characteristics also proved that the contribution of biomass sources was greater.

Keywords: geochemical characteristics; dissolved organic matter; source; Hulun Lake

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Citation: Zhang, Y.; Wang, S.; Xu, W.; Zhang, B.; Yi, L.; Lu, X. Geochemical Characteristics and Their Environmental Implications for the Water Regime of Hulun Lake, Inner Mongolia, China. *Water* **2022**, *14*, 3696. https://doi.org/10.3390/w14223696

Academic Editor: Domenico Cicchella

Received: 30 September 2022
Accepted: 9 November 2022
Published: 16 November 2022

1. Introduction

The chemical composition of natural water is generally determined by the result of long-term interaction between water and its surroundings in the process of circulation [1,2]. In the process of the mutual transformation and migration of water bodies, substances dissolved in water are exchanged synchronously with the amount of water [3]. Among them, K^+, Ca^{2+}, Na^+, Mg^{2+}, HCO_3^-, CO_3^{2-}, SO_4^{2-} and Cl^- in lake water are the most basic and key water-chemistry-characteristic indicators [4]. The composition of these natural elements affects other elements in the water body, such as fluorine and arsenic [5,6]. The study of lake-water chemistry, including its chemical content characteristics and spatial distribution, is of great significance to determine the geochemical source of water ions, the chemical weathering effects of the region and their relationship with the hydrogeochemistry [7,8]. In addition to the content characteristics of ions, the ratio characteristics of different ions and the total ionic salinity can also reflect the source and exchange characteristics of water bodies [9].

In addition to the natural-water-chemical-ion characteristics of water bodies, Dissolved Organic Matter (DOM) in water is also another kind of water body index with important environmental significance [10]. DOM is a mixture of soluble organic compounds with specific chemical compositions and complex structures, which generally exists in environmental media such as water bodies and sediments [11,12]. Its content and composition directly or indirectly affect the quality of the water environment, the growth and metabolism of aquatic organisms, the migration and transformation of chemicals and pollutants and the bioavailability [13–15].

Lakes are important ecological nodes in the water ecosystem, and a key factor in ensuring their ecological health is having sufficient water [16]. The water in lakes is replenished from sources such as rainfall, river inputs and groundwater [17]. At the same time, lakes also serve as sources of water to replenish surrounding groundwater and lose water due to transpiration [18]. In the process of the recharge and loss of lake water, the chemical characteristics of natural water in lake-water bodies also change. For the source and destination of lake water, the hydrogen and oxygen isotopes of the water and natural-water chemistry are usually used for analysis [19–21]. The chemical method is mainly used to distinguish different natural-water sources through the distribution characteristics of potassium, calcium, sodium, magnesium and inorganic anions carried by different water sources, while hydrogen and oxygen isotopes are mainly used to retrieve the transpiration of lake water. However, there are still some uncertainties in these two methods. The chemical method can be used to distinguish water bodies from different sources, but it cannot effectively identify recharge dynamics, while the hydrogen-and-oxygen-isotope method is not effective in identifying the transpiration of flowing rivers and buried water bodies. DOM from different sources have different material composition, chemical structure and functional groups. These natural organic products are produced in and migrate with the water source; they are not affected by transpiration [22]. The use of DOM in tracing can compensate for the two methods above to identify the flow dynamics.

A popular method for the characterization of dissolved organic matter in natural water is the use of three-dimensional excitation—emission-matrix fluorescence spectra (3D-EEM) combined with the PARAFAC method [23]. Fluorescence spectroscopy coupled with parallel-factor analysis (PARAFAC) has been widely used to characterize DOM. Characterization is based on the intensity and location of independent fluorescent components identified in models constructed from excitation-emission matrices (EEMs) [24]. In the ideal case, in which fluorescence conforms to Beer's Law, this process can lead to the mathematical identification and quantification of independently varying fluorophores [25].The main characteristics of three-dimensional fluorescence-spectroscopy-analysis technology are its fast analysis speed, reduced sample consumption, lack of damage to samples and large amount of information, which can be used to qualitatively or semi-quantitatively analyze the organic matter in samples to a certain extent and can effectively identify the sources and destinations of water bodies combined with the PARAFAC method [26,27].

Hulun Lake is the fifth-largest freshwater lake in China and the largest lake in the north of China, with a maximum water depth of about 8 m and a water-storage capacity of 13.85 billion m^3 [28]. It has special hydrological, hydro-chemical and hydro-ecological characteristics. It is a very rare natural-lake ecosystem with biodiversity and ecological functions in a cold and arid area. According to the water-level-monitoring data for Hulun Lake from the past 50 years [29], from 2001 to the present, the water supply of the lake has been much lower than the water consumption and the water level has been continuously decreasing with the shrinking lake area, which has seriously affected the biodiversity and ecological balance of the lake regime. This rapid decline in the water level may have been caused by the interaction between artificial factors (such as grassland degradation due to overgrazing) and natural factors (such as rainfall, runoff, evaporation, etc.). Therefore, it is of importance to identify the status and causes in the Hulun Lake regime. The purpose of this paper is to analyze the sources and destinations of Hulun Lake's water regime in depth from multiple perspectives, using the traditional natural-water-chemistry characteristics and stable isotopes combined with the novel DOM analysis method in order to provide technical support for the protection of Hulun Lake. Furthermore, this study may also offer insights into water chemistry and its environmental implications for remote-lake regimes in cold and arid areas.

2. Materials and Methods

2.1. Sampling

In July 2021, samples were collected from Hulun Lake and its inflow rivers and groundwater (Figure 1). Lake-water samples and river-water samples were collected from 10 cm under the water surface. The groundwater was collected from the wells around Hulun Lake and two parallel samples were collected from each location. After the sample collection, the basic physical and chemical properties, including temperature, pH value, dissolved oxygen (DO) and other basic parameters, were measured on site using an in situ multi-parameter instrument (IQ150, Spectrum, the US) and the field environment was recorded. The collected samples were brought back to the laboratory for analysis in a portable refrigerator at 0–4 °C.

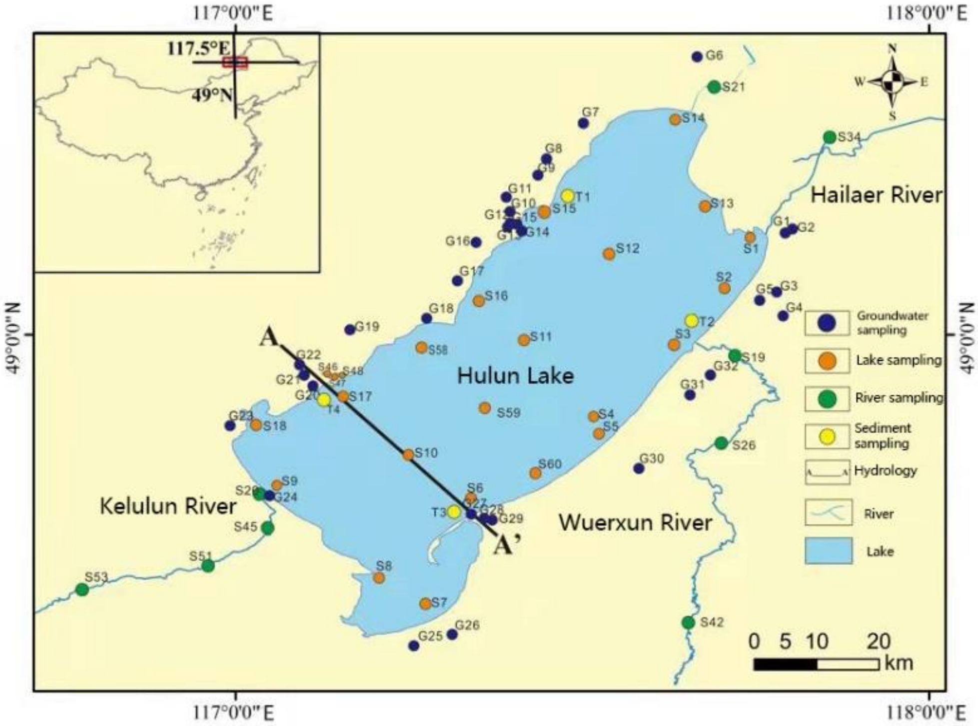


Figure 1. Sampling locations in the Hulun Lake regime.

2.2. Sample Treatment and Analysis

In the laboratory, the collected water samples were first filtered by a 0.45-micrometerfilter membrane. The filtered water samples were used for the determination of DOM content using a Multi N/C 2100s TOC analyzer (calculated by TOC). Each sample was measured 3 times. Potassium hydrogen phthalate solution was used as the standard solution to draw the standard curve, with a detection limit of 0.06 mg/L and a relative standard deviation of less than 3% in the range of 0–100 mg/L. The δD and $\delta^{18}O$ were examined using an isotope-ratio mass spectrometer (L214o-I, Picarro, USA) (measuring range: 1000–50,000 ppm; Precision: $\delta D < 0.100‰$; $\delta^{18}O < 0.0.025‰$). The concentrations of K^+, Ca^{2+}, Na^+, Mg^{2+}, $HCO_3{}^-$, $CO_3{}^{2-}$, $SO_4{}^{2-}$ and Cl^- were measured using an ion-chromatography instrument (Metrohm Eco IC, Switzerland).

The 3D-EEM used Edinburgh FS5 fluorescence spectrometer with excitation light source: photodiode (EPL); bandpass: excitation wavelength λ_{Ex} = 5 nm, emission wavelength λ_{Em} = 5 nm; response time set to automatic; scanning-wavelength range: λ_{Ex} = 200 to 500 nm, λ_{Em} = 250 to 600 nm. The 3D-fluorescence spectral data were imported into MATLAB R2019a, and the sample was Raman- and Rayleigh-normalized after subtracting the spectral signal of the blank water sample (ultrapure water). Finally, the DOM Fluor toolkit was used to perform PARAFAC analysis in MATLAB software. A normality test was conducted before extracting components and abnormal values were eliminated after the test. A paired *t*-test was used to assess the differences in components.

2.3. Quality Assurance and Data Analysis

To ensure the accuracy of the method, parallel samples and replicate analysis were conducted on all samples. The relative standard deviation for each group of replicates was less than 10%, and the recovery of the reference material for all metals was between 85% and 110%. All samples had two replicates and each replicate was tested twice for different parameters. Therefore, each parameter had four measured data. For each parameter of measured data, a normal-distribution test was conducted prior to the measurement of mean calculations and comparison. Abnormal values were eliminated through a statistical test. A significance level of 0.05 was used. Calculations and statistical analyses were performed on Surfer 12 and Origin 2019.

3. Results and Discussion

3.1. Water Chemistry

First, the concentration of total ionic salinity (TIS) of the water was calculated based on the concentrations of K+, Ca^{2+}, Na^+, Mg^{2+}, HCO_3^-, CO_3^{2-}, SO_4^{2-} and Cl^- (Figure 2). The results showed that the groundwater had the highest TIS content among the three water bodies, with the average value of 1750.42 ± 132.43 mg/L. Secondly, the average value of TIS in the lake water was 1250.402 ± 55.43 mg/L. The river water had the lowest TIS content, with an average of only 352.89 ± 36.52 mg/L. As a source of drinking water, the TIS in water contains minerals required by the human body, such as calcium, magnesium, sodium and potassium. However, at the same time, it should be noted that in addition to these beneficial cations, the water also contains anions, such as SO_4^{2-} and Cl^-. Therefore, the ion composition must also be analyzed in detail.

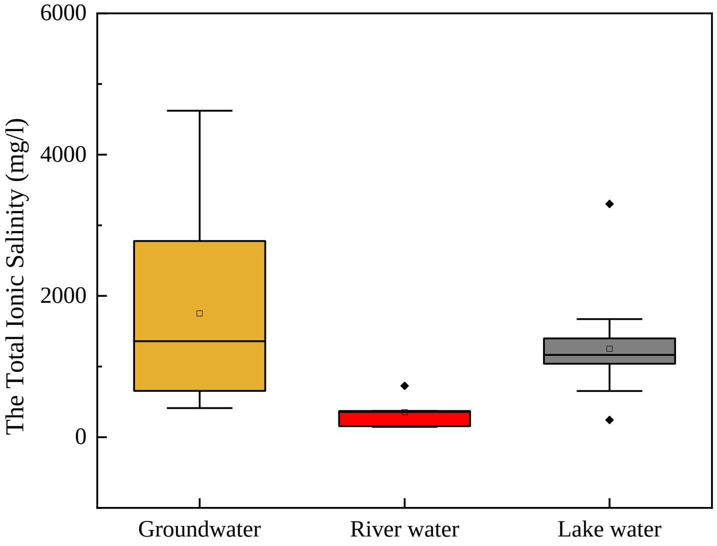


Figure 2. The concentration of total ionic salinity of the water in the Hulun Lake regime.

As shown in Figure 3, the dominant cation in the chemical composition of the groundwater, river water and lake water in Hulun River basin is Na^+, with concentrations of 17.28~1185.69 mg/L, 1.84~22.09 mg/L and 26.58~308.63 mg/L, respectively. The dominant anion in the river water and lake water is HCO_3^-, with concentrations of

95.39~229.78 mg/L and 414.78~641.14 mg/L, respectively. Therefore, the chemical type of the river and lake water is sodium bicarbonate. The dominant anions in the river water and lake water are HCO_3^- and SO_4^{2-}, with concentrations of 23.18~1223.43 mg/L and 17.86~1201.75 mg/L. While there are differences in anion concentrations between the groundwater, river and lake, the order of the average anion concentrations is $HCO_3^- > SO_4^{2-} > Cl^- > CO_3^{2-}$. In the different water bodies, the cation concentrations are generally higher in alkali metal ions (Na^+, K^+) than in alkaline-earth-metal ions (Ca^{2+}, Mg^{2+}). The average concentration order of cations in groundwater and river water is $Na^+ > K^+ > Ca^{2+} > Mg^{2+}$, while that in lake water is $Na^+ > K^+ > Mg^{2+} > Ca^{2+}$.

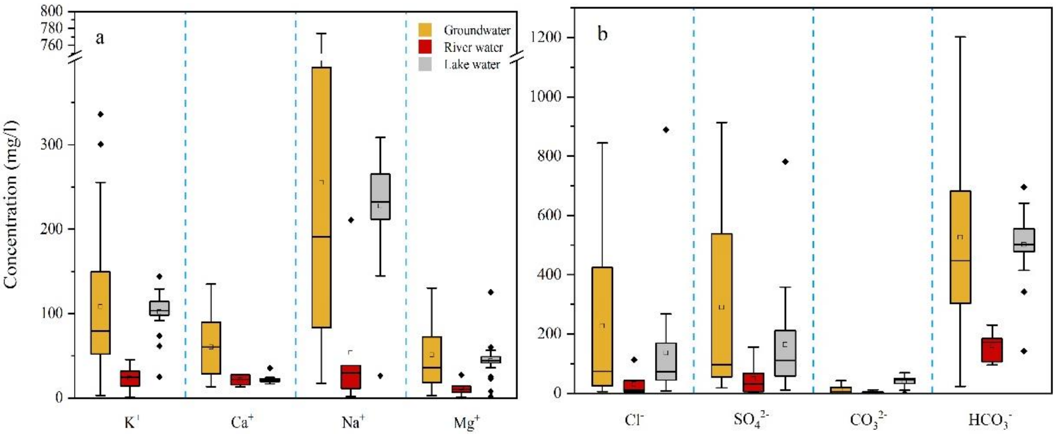


Figure 3. Cations (**a**) and anions (**b**) in the water in the Hulun Lake regime.

The order of the average concentration of the same cation is groundwater > lake water > river water and the average concentration of CO_3^{2-} is in the order of groundwater > lake water > river water, which is the same as that of cations. For the mean value of the same ion concentration, the order of the three water bodies is essentially the same, except for CO_3^{2-}. The ion concentration in the river water is significantly lower than those in the groundwater and lake water, which is due to the long transport distance and flow time of the river, the small fluctuation in the annual flow and the strong self-purification ability of the river. The reason for the narrow variation range of ion concentration and the high ion concentration is that Hulun Lake is a closed lake, and the ion concentration of the lake water increases after long-term evaporation and concentration. The ion-concentration standards of the groundwater around Hulun Lake are quite different, which indicates that there are significant differences in the chemical composition of the groundwater.

Piper diagrams are often used to examine the chemical composition and chemical phases in water samples in hydrogeological studies. Figure 4 shows that there is no significant difference in the anion- and cation-composition characteristics in the Hulun Lake regime, indicating that the hydrological connectivity in the Hulun Lake regime is good. Overall, the cations in the waters of the basin are mainly $K^+ + Na^+$ and the anions are mainly $HCO_3^- + CO_3^{2-}$. However, it is worth noting that the concentrations of anions at different locations in the groundwater are more dispersive than those of the cations. Furthermore, the concentrations of SO_4^{2-} and Cl^- in some of the groundwater are higher, which may be related to the geological background and human activities [30,31]. In order to further elucidate the ionic-composition characteristics of the three water bodies, the Langelier saturation index (LSI) was used to characterize the saturations of the water bodies. The results showed that the LIS values of the groundwater ranged from 1.32 to 4.37 and that the average value was 2.7, indicating that the $CaCO_3$ in the water body was in a supersaturated state, while the LIS values of the lake water and river water were 1.5 and 1.2, respectively, suggesting a relatively balanced state.

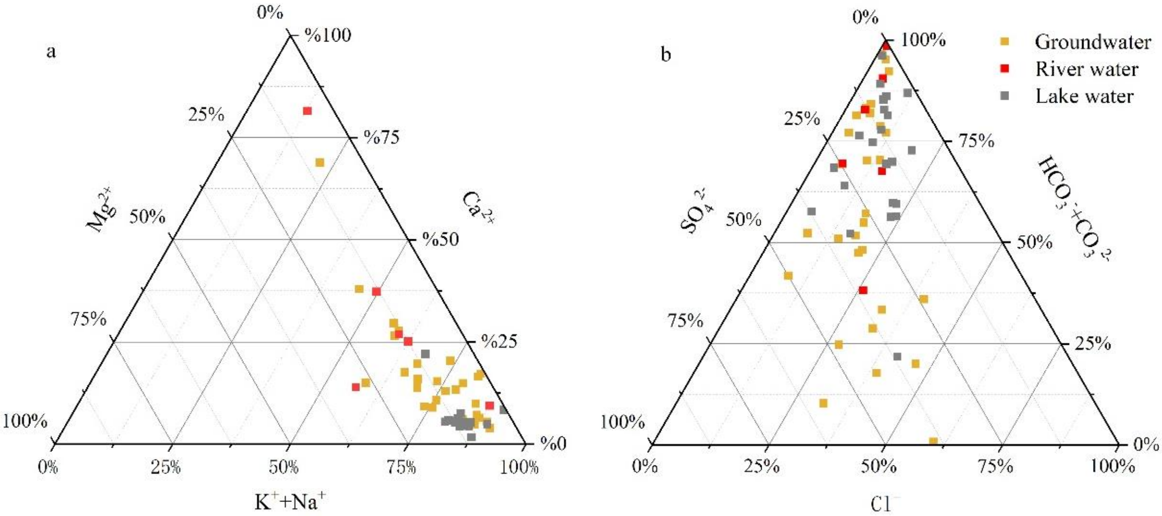


Figure 4. Cations (**a**) and anions (**b**) diagram for the water in the Hulun Lake regime.

3.2. δD and $\delta^{18}O$

Figure 5 shows that the δD value of the river water is −103.72~−83.47‰, the δ^{18}O value is −13.69~−9.89‰ and the average values are −90.85‰ and −11.40 ‰, respectively. The δD value of the groundwater is −115.98~−84.51‰, the δ^{18}O value is −15.03~−10.25‰ and the average values are −93.04‰ and −12.22‰. The δD value of the lake water is −98.08~−57.49‰, the δ^{18}O value is −13.21~−5.15‰ and the average values are −67.04‰ and −7.15‰, respectively. The δD and δ^{18}O values of the lake water are the highest, followed by those of the river water. The δD and δ^{18}O values of the groundwater are the lowest, indicating that the δD and δ^{18}O in the lake water are concentrated with the evaporation of surface water. Although they are both derived from the surface water, the δD and δ^{18}O values in the lake water are significantly higher than those in the river water. This is because the upstream river water may be recharged by the groundwater and the river water is significantly influenced by the groundwater.

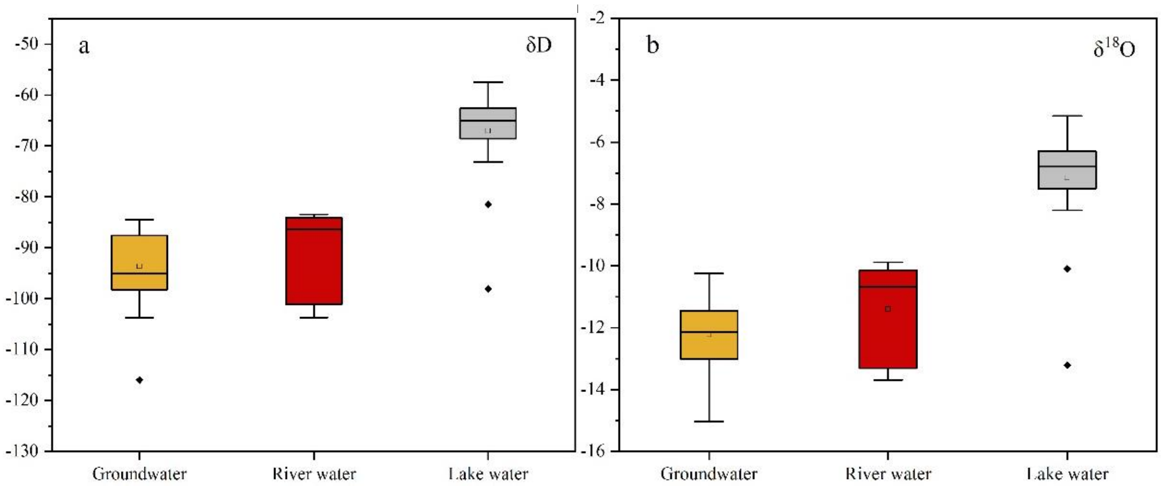


Figure 5. δD and δ^{18}O for the water in the Hulun Lake regime.

Differences in δD and δ^{18}O in water bodies are mainly due to the influence of precipitation origin, precipitation type and isotope-fractionation degree. There are always some differences in slope and intercept between the local atmospheric precipitation line and the global atmospheric precipitation line in different areas. The global meteoric water line (GMWL) in this study was obtained through the regression fitting of the δD and δ^{18}O data of the precipitation from 1988 to 1992 at Qiqihar Station of the Global Network of Isotopes in Precipitation (GNIP, https://www.iaea.org/services/networks/gnip) (Figure 6), which is close to the study area and has similar climatic conditions. The equation is $\delta D = 7.59\delta^{18}O - 0.03$ (n = 50, R2 = 0.98).

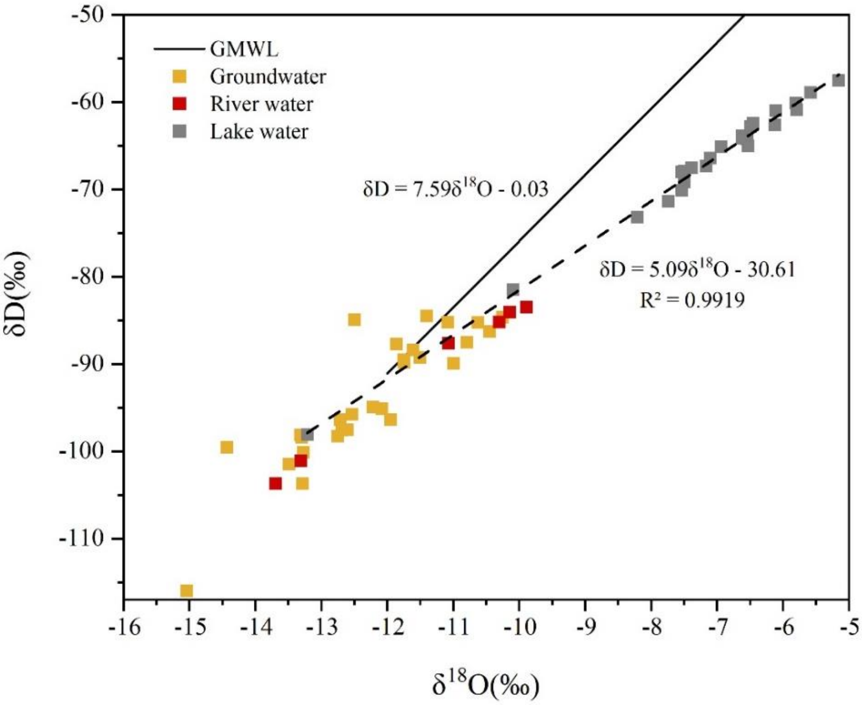


Figure 6. The relationship with the meteoric water line for the δD and $\delta^{18}O$ in the water from the Hulun Lake regime (the dotted line is fitted with data from Hulun Lake).

According to the relationship between the δD and the $\delta^{18}O$ in the lake water, river water and groundwater in the Hulun Lake regime, it can be seen that the δD and $\delta^{18}O$ in the river water and groundwater can generally fall on the GMWL in the Hulun Lake area, indicating that the main water source of each water body is derived from atmospheric precipitation. However, the lake water is significantly different from the two types of water above and its δD and $\delta^{18}O$ values are below the atmospheric precipitation line, GMWL. Through fitting the δD and $\delta^{18}O$ data of the Hulun Lake water, it was found that the line slope of the lake-water fit was 5.09, which was lower than the slope of the GMWL. This shows that the open-water environment of Hulun Lake makes the lake water subject to strong evaporation, which can lead to excessive isotope fractionation. This is consistent with the fact that Hulun Lake is located in an arid and semi-arid region, where the evaporation is greater than the rainfall.

3.3. DOM

As shown in Figure 7, the mean value of DOM is 15.44 ± 2.14 mg/L. The concentrations of DOM in the lake water are significantly higher than those in the river water and groundwater, ranging from 14.49 mg/L to 38.04 mg/L, with an average of 21.69 ± 5.14 mg/L, followed by the river water, ranging from 12.17 mg/L to 18.62 mg/L. The concentration of DOM in the groundwater is similar to that in the river water, with an average value of 13.87 ± 4.32 mg/L, but there is a large difference between the different sites, with values ranging from 3.58 mg/L to 35.20 mg/L.

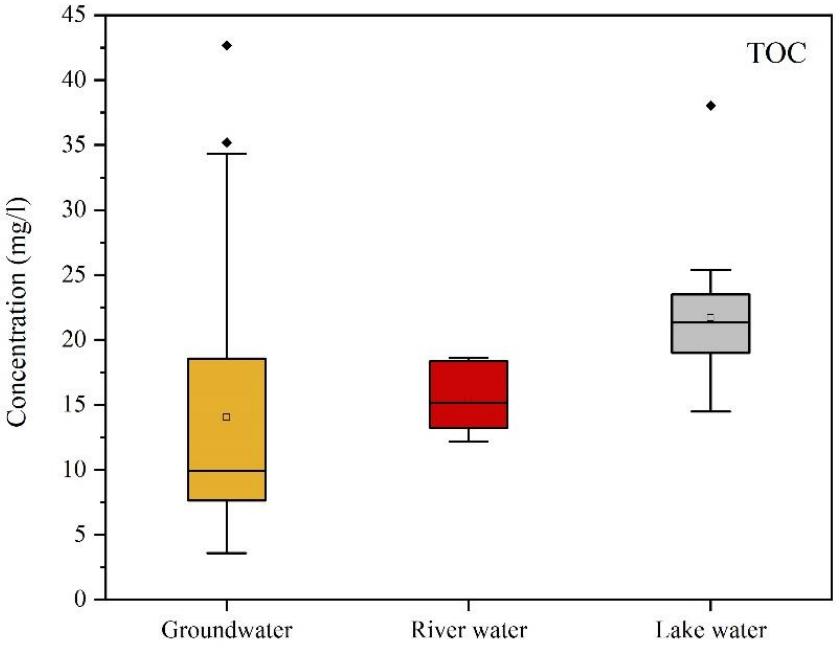


Figure 7. The TOC concentrations in different waters.

EEM-PARAFAC is used to characterize the fluorescence components of groundwater, river water and lake water. The fluorescence components in this study were compared with the previously reported PARAFAC components in the natural environment, and the sources of groundwater, river water, and lake water were effectively evaluated (Table 1).

Table 1. Comparison of peaks for each fluorescence component in different waters.

Type of Water	This Study		Compared with Traditional Peaks	
	Component	**Ex(max)/Em(max)**	**Traditional Peaks**	**Substance Represented**
Groundwater	CU1	240,325/400	A, M	Humus-like, aquatic organisms
	CU2	255,365/475	A, C	Humus-like
River Water	CR1	235,310/415	A, M	Humus-like, aquatic organisms
	CR2	260,370/485	A, C	Humus-like
Lake Water	CL1	250,330/435	A, C	Humus-like
	CL2	225,280/345	T	Tryptophan-like, protein-like
	CL3	270,400/495	No correspondence	High molecular weight, aromatic group, fulvic acid, etc.

The fluorescence spectra of the groundwater, river and lake water were analyzed by EEM-PARAFAC. Two fluorescence components (CU1, CU2 and CR1, CR2) of the groundwater and river water and three fluorescence components (CL1, CL2, CL3) of the lake water are obtained. Corresponding to the traditional fluorescence peak [32], as shown in Figure 7, the selection of each component number does not mean that EEMs only contain these fluorophores, but selects the most representative fluorophores, which effectively characterize the compositions of different water samples.

The spectra of fluorescence components of groundwater, river water and lake water analyzed by PARAFAC and their excitation-emission-wavelength loads are shown in Figure 8. Two fluorescence components, CU1 (Ex/Em = 240,325/400) and CU2 (Ex/Em = 255,365/475), are released from the groundwater. CU1 has two excitation peaks when the emission wavelength Em is 400 nm, representing the traditional A peak and M peak, respectively; the M peak is considered to be related to the humus that may come from aquatic organisms [33]. However, some studies have shown that marine humus may not de derived from the ocean and, rather, that they may be a kind of substance that is terrestrial or spontaneously produced by terrestrial (or aquatic) organisms or organic matter in the aquatic environment [34]. The component CU2 corresponds to the mixture of peak A and peak C of the traditional humic-like peaks. They are often the main fluorescence peaks in the low-salinity waters of the terrestrial environment, mainly derived from terrestrial humus. Their spectral characteristics are similar to those of terrestrial higher plants and are also related to organic matter degraded by microorganisms [13,35,36]. The two fluorescence components released from river water are very similar to those from groundwater, among which the component CR1 (Ex/Em = 235,310/415) is similar to the groundwater component CU1 and the component CR2 (Ex/Em = 260,370/485) is similar to the groundwater component CU2, which mainly arises from the discharge of humic-like waste water and microbial degradation [37]. Three fluorescence components are resolved from the lake water; the component CL1 (Ex/Em = 250,330/435) is similar to the groundwater component CU2 and the river-water component CR2, both of which are common terrestrial humus components [38,39]. The component CL2 (Ex/Em = 225,280/345) is a protein-like fluorescence peak [40], which is associated with a tryptophan-like fluorophore (traditional T peak) [41]. Component CL3 (Ex/Em = 270, 400/495) represents a class of high-molecular-weight substances, including aromatics, fulvic acid and some substances that can be chemically degraded by light, but no corresponding traditional peaks were found [42]. In summary, the groundwater and river water are homologous and mainly composed of humus-like substances, which are derived from the discharge of human factors, terrestrial input and microbial transformation, while the lake water is composed not only of humus-like substances, but also of protein-like substances and some high-molecular-weight substances.

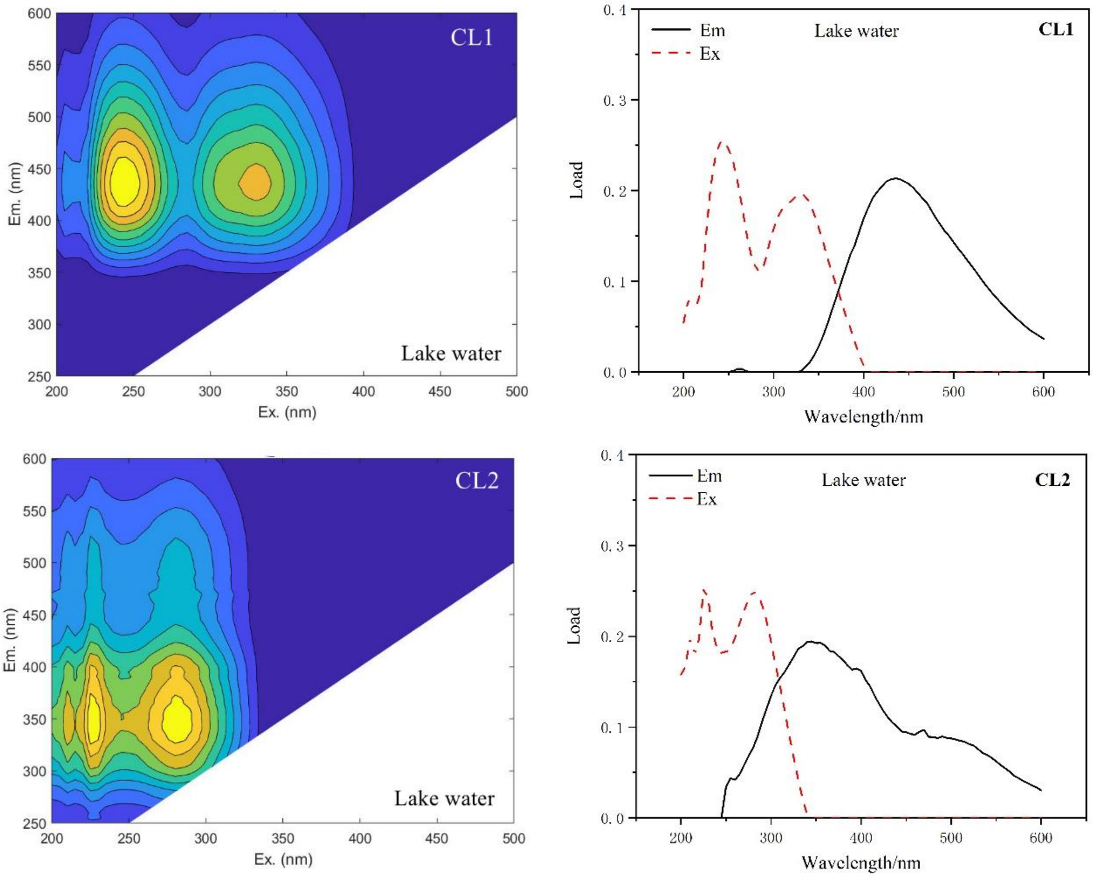
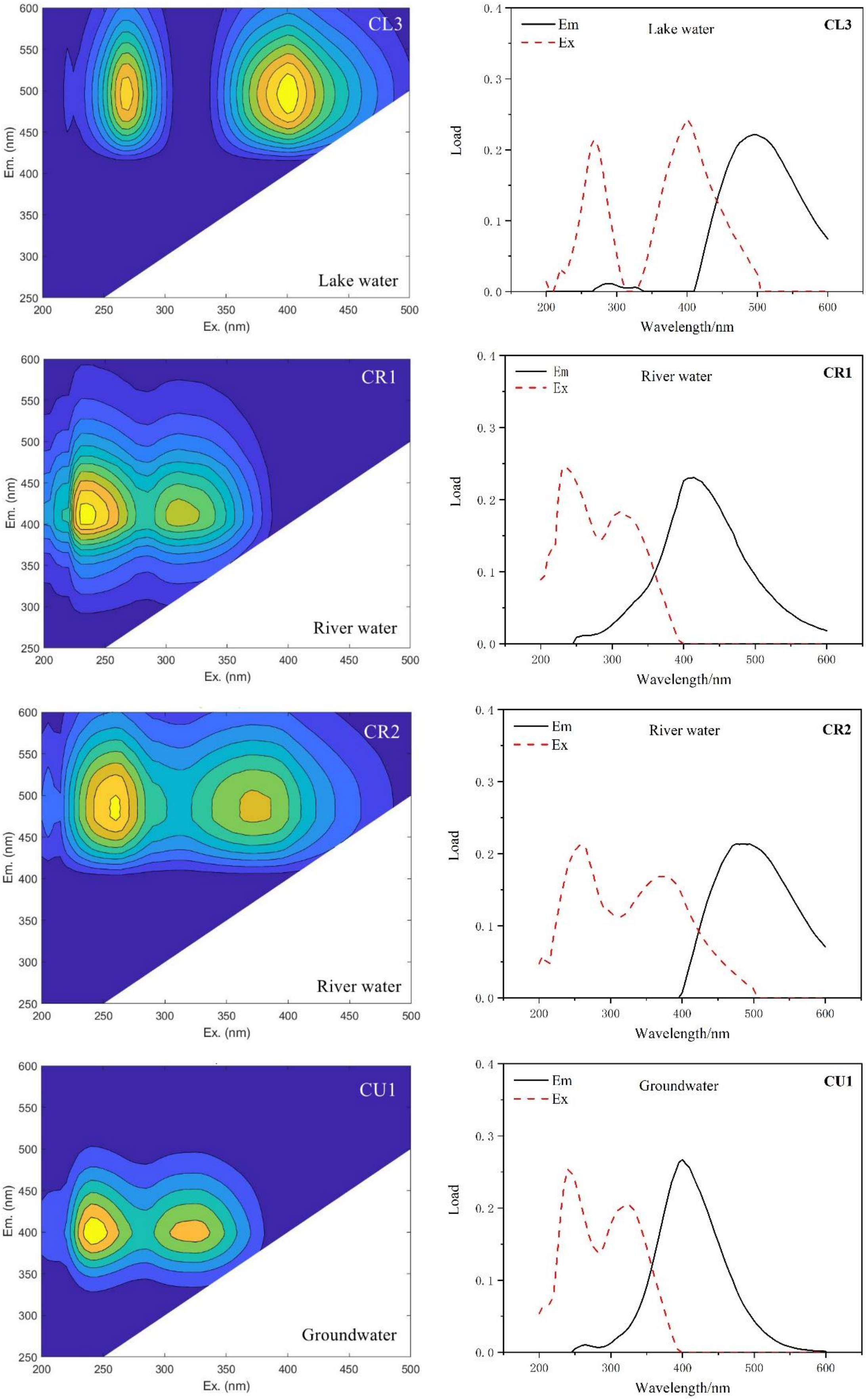


Figure 8. *Cont.*



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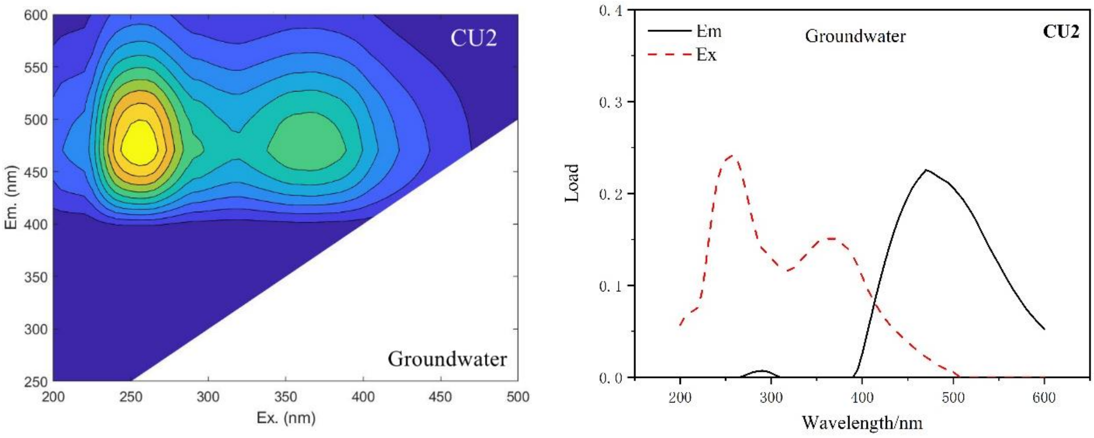

Figure 8. Three-dimensional spectral-fluorescence characteristics of different waters.

3.4. Implications of the Water Geochemstry

Surface water and groundwater are important components in the water cycle and the transformation relationship between them is the key link in the water cycle [43], which affects the formation and structural characteristics of regional water resources [44,45]. In the process of the mutual transformation and migration of water bodies, the geochemical composition and DOM of the natural water in water bodies are also synchronized with the exchange of water volume. In a typical inland lake, the water is replenished by atmospheric precipitation, river water and groundwater, but no river can flow out. A Mg-HCO_3 composition is typical of waters interacting with serpentinite rocks and the Ca-HCO_3 chemical composition can be controlled by the dissolution of Ca-rich phases forming the metabasalts [5,9]. The anions of the river water are all distributed in the rock-weathering area and the cations are between the rock weathering and evaporation, indicating that the dominant ions in the river water are mainly controlled by rock weathering and are affected little by evaporation. The distribution characteristics of groundwater ions are similar to those of the lake water, but they are more discrete than the lake water. From the TIS and anion and cation diagrams of the three types of water, it can be seen that both the TIS and the ionic composition in the river water were characterized by a natural water chemistry, which was mainly affected by natural precipitation. However, the concentration of the TIS in the groundwater was relatively high and the anion is dominated by $HCO_3^- + CO_3^{2-}$. The average $Cl^-/(Cl^- + HCO_3^-)$ values of the groundwater, river water and lake water were 0.28, 0.13 and 0.18, respectively, in the range of 0.1~0.4. They are mainly located in the rock-weathering and evaporative-crystallization areas, which are affected by the combined action of the two, while the dominant ions in groundwater and lake water are the same, indicating that the two are closely related. [9]. Although the concentrations of SO_4^{2-} and Cl^- are high in the groundwater, they may be derived from different sources. SO_4^{2-} may contribute to aqueous solutions only through the oxidative dissolution of pyrite [46], which proceeds very fast in the early stages of granite dissolution (for alkalinity lower than 30 mg HCO_3/Kg), leading to a steep increase in SO_4^{2-} concentration [47]. Cl^- is generally believed to be affected by human activities. The δD and $\delta^{18}O$ in the Hulun Lake regime are below the GMWL, implying strong evaporation, while the river water and groundwater are both above the GMWL, indicating that atmospheric precipitation is the main recharge source for the river water and groundwater. For the DOM in the water, the vast Hulun Lake provides a good ecological water environment. The water body is retained for a long time and a certain amount of microorganisms and plankton in the water body are formed during the growth and death process [48]. The DOM ensures that the TOC content in the water body is the highest and the contribution of its biomass source components is relatively high. Because the river water is in a flowing state and is replenished by fresh atmospheric precipitation, the biomass in the water body is relatively small and the content of DOM is relatively low. For the groundwater, because the water is filtered by rocks and shading inhibits the biological activity, its DOM content is the lowest.

4. Conclusions

The cation concentration of different water bodies is generally formed of alkali metal ions (Na^+, K^+), higher than alkaline-earth-metal ions (Ca^{2+}, Mg^{2+}). The average concentration order of cations in groundwater and river water is $Na^+ > K^+ > Ca^{2+} > Mg^{2+}$ and that of lake water is in the order of $Na^+ > K^+ > Mg^{2+} > Ca^{2+}$. There is no significant difference in the anion and cation composition characteristics for Hulun Lake and its inflow rivers and groundwater, indicating that the hydrological connectivity in the Hulun Lake regime is good. The TIS and LSI results showed that the $CaCO_3$ in the groundwater was supersaturated, indicating that it was greatly affected by underground rock weathering, while the lake and river water were in ion equilibrium. The δD and $\delta^{18}O$ in the river water and groundwater generally followed the GMWL. However, the δD and $\delta^{18}O$ values of the lake water were below the GMWL, implying that the open-water environment of Hulun Lake makes the lake water subject to strong evaporation. The concentration of DOM in Hulun Lake's water is significantly higher than that in the river water and groundwater and, in addition to humus-like substances, it features biodegradable components, indicating that biological growth in lake water is the main source of DOM.

Author Contributions: Conceptualization, X.L. and L.Y.; methodology, S.W.; software, W.X.; validation, B.Z. and S.W.; formal analysis, S.W.; investigation, L.Y.; resources, Y.Z.; data curation, Y.Z.; writing—original draft preparation, Y.Z.; writing—review and editing, Y.Z. and X.L.; visualization, X.L.; supervision, X.L.; project administration, X.L.; funding acquisition, X.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Tianjin Key R&D Program [21YFSNSN00220] And The APC was funded by the Tianjin Key R&D Program [21YFSNSN00220].

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: This work was supported by the Tianjin Key R&D Program (21YFSNSN00220).

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Jia, H.; Qian, H.; Zheng, L.; Feng, W.; Wang, H.; Gao, Y. Alterations to groundwater chemistry due to modern water transfer for irrigation over decades. *Sci. Total Environ.* **2020**, *717*, 137170. [CrossRef] [PubMed]
2. Liu, F.; Zou, J.; Liu, J.; Zhang, J.; Zhen, P. Factors controlling groundwater chemical evolution with the impact of reduced exploitation. *CATENA* **2022**, *214*, 106261. [CrossRef]
3. Johansson, K.; Wilander, A.; Fölster, J.; Göransson, E. Synchronous variation in water chemistry for 80 lakes in Southern Sweden. *Environ. Monit. Assess.* **2005**, *102*, 389–403. [CrossRef]
4. Tao, Y.; Yuan, Z.; Fengchang, W.; Wei, M. Six-Decade Change in Water Chemistry of Large Freshwater Lake Taihu, China. *Environ. Sci. Technol.* **2013**, *47*, 9093–9101. [CrossRef]
5. Fuoco, I.; Marini, L.; De Rosa, R.; Figoli, A.; Gabriele, B.; Apollaro, C. Use of reaction path modelling to investigate the evolution of water chemistry in shallow to deep crystalline aquifers with a special focus on fluoride. *Sci. Total Environ.* **2022**, *830*, 154566. [CrossRef]
6. Susheela, A.K.; Mudgal, A.; Keast, G. Fluoride in water: An overview. *Water Front* **1999**, *1*, 11–13.
7. Missi, C.; Atekwana, E.A. Physical, chemical and isotopic characteristics of groundwater and surface water in the Lake Chilwa Basin, Malawi. *J. Afr. Earth Sci.* **2019**, *162*, 103737. [CrossRef]
8. Vaiphei, S.P.; Kurakalva, R.M.; Sahadevan, D.K. Water quality index and GIS-based technique for assessment of groundwater quality in Wanaparthy watershed, Telangana, India. *Environ. Sci. Pollut. Res.* **2020**, *27*, 4504–45062. [CrossRef]
9. Apollaro, C.; Di Curzio, D.; Fuoco, I.; Buccianti, A.; Dinelli, E.; Vespasiano, G.; Castrignanò, A.; Rusi, S.; Barca, D.; Figoli, A.; et al. A multivariate non-parametric approach for estimating probability of exceeding the local natural background level of arsenic in the aquifers of Calabria region (Southern Italy). *Sci. Total Environ.* **2021**, *806*, 150345. [CrossRef]

10. Bertilsson, S.; Tranvik, L.J. Photochemical transformation of dissolved organic matter in lakes. *Limnol. Oceanogr.* **2000**, *45*, 753–762. [CrossRef]
11. Liu, D.; Du, Y.; Yu, S.; Luo, J.; Duan, H. Human activities determine quantity and composition of dissolved organic matter in lakes along the Yangtze River. *Water Res.* **2019**, *168*, 115132. [CrossRef] [PubMed]
12. Al-Kharusi, E.S.; Tenenbaum, D.E.; Abdi, A.M.; Kutser, T.; Karlsson, J.; Bergström, A.-K.; Berggren, M. Large-Scale Retrieval of Coloured Dissolved Organic Matter in Northern Lakes Using Sentinel-2 Data. *Remote Sens.* **2020**, *12*, 157. [CrossRef]
13. A Stedmon, C.; Markager, S.; Bro, R. Tracing dissolved organic matter in aquatic environments using a new approach to fluorescence spectroscopy. *Mar. Chem.* **2003**, *82*, 239–254. [CrossRef]
14. Hudson, N.; Baker, A.; Reynolds, D.M. Fluorescence analysis of dissolved organic matter in natural, waste and polluted waters—A review. *River Res. Appl.* **2007**, *23*, 631–649. [CrossRef]
15. Zhang, H.; Zheng, Y.; Wang, X.C.; Wang, Y.; Dzakpasu, M. Characterization and biogeochemical implications of dissolved organic matter in aquatic environments. *J. Environ. Manag.* **2021**, *294*, 113041. [CrossRef]
16. Ye, Z.; Chen, S.; Zhang, Q.; Liu, Y.; Zhou, H. Ecological Water Demand of Taitema Lake in the Lower Reaches of the Tarim River and the Cherchen River. *Remote Sens.* **2022**, *14*, 832. [CrossRef]
17. Ayenew, T.; Gebreegziabher, Y. Application of a spreadsheet hydrological model for computing the long-term water balance of Lake Awassa, Ethiopia. *Hydrol. Sci. J.* **2006**, *51*, 418–431. [CrossRef]
18. Tweed, S.; Leblanc, M.; Cartwright, I.; Favreau, G.; Leduc, C. Arid zone groundwater recharge and salinisation processes; an example from the Lake Eyre Basin, Australia. *J. Hydrol.* **2011**, *408*, 257–275. [CrossRef]
19. Yang, K.; Han, G. Controls over hydrogen and oxygen isotopes of surface water and groundwater in the Mun River catchment, northeast Thailand: Implications for the water cycle. *Appl. Hydrogeol.* **2020**, *28*, 1021–1036. [CrossRef]
20. Che, Q.; Su, X.; Zheng, S.; Li, Y. Interaction between surface water and groundwater in the Alluvial Plain (anqing section) of the lower Yangtze River Basin: Environmental isotope evidence. *J. Radioanal. Nucl. Chem. Artic.* **2021**, *329*, 1331–1343. [CrossRef]
21. Doctor, D.H.; Petrič, M.; Kogovšek, J.; Urbanc, J.; Lojen, S.; Stichler, W. Quantification of karst aquifer discharge components during storm events through end-member mixing analysis using natural chemistry and stable isotopes as tracers. *Hydrogeol. J.* **2006**, *14*, 1171–1191. [CrossRef]
22. Zhang, Y.; Zhang, E.; Yin, Y.; Van Dijk, M.A.; Feng, L.; Shi, Z.; Liu, M.; Qina, B. Characteristics and sources of chromophoric dissolved organic matter in lakes of the Yungui Plateau, China, differing in trophic state and altitude. *Limnol. Oceanogr.* **2010**, *55*, 2645–2659. [CrossRef]
23. Rasmus, B. PARAFAC. Tutorial and applications. *Chemom. Intell. Lab. Syst.* **1997**, *38*, 149–171.
24. Ishii, S.K.L.; Boyer, T.H. Behavior of Reoccurring PARAFAC Components in Fluorescent Dissolved Organic Matter in Natural and Engineered Systems: A Critical Review. *Environ. Sci. Technol.* **2012**, *46*, 2006–2017. [CrossRef] [PubMed]
25. Murphy, K.R.; Stedmon, C.A.; Graeber, D.; Bro, R. Fluorescence spectroscopy and multi-way techniques. PARAFAC. *Anal. Methods* **2013**, *5*, 6557–6566. [CrossRef]
26. Zhang, J.; Song, F.; Li, T.; Xie, K.; Yao, H.; Xing, B.; Li, Z.; Bai, Y. Simulated photo-degradation of dissolved organic matter in lakes revealed by three-dimensional excitation-emission matrix with regional integration and parallel factor analysis. *J. Environ. Sci.* **2019**, *90*, 310–320. [CrossRef]
27. Wang, Z.-G.; Liu, W.-Q.; Zhao, N.-J.; Li, H.-B.; Zhang, Y.-J.; Si-Ma, W.-C.; Liu, J.-G. Composition analysis of colored dissolved organic matter in Taihu Lake based on three dimension excitation-emission fluorescence matrix and PARAFAC model, and the potential application in water quality monitoring. *J. Environ. Sci.* **2007**, *19*, 787–791. [CrossRef]
28. Gao, H.; Ryan, M.C.; Li, C.; Sun, B. Understanding the Role of Groundwater in a Remote Transboundary Lake. *Water* **2017**, *9*, 363. [CrossRef]
29. Zheng, J.; Ke, C.; Shao, Z.; Li, F. Monitoring changes in the water volume of Hulun Lake by integrating satellite altimetry data and Landsat images between 1992 and 2010. *J. Appl. Remote Sens.* **2016**, *10*, 16029. [CrossRef]
30. El-Dars, F.M.S.E.; Salem, W.A.; Fahim, M.M.; Taha, M.M.N. A Comparative Evaluation of Soil Characteristics at the 10th of Ramadan and El-Gabal El-Asfar, Egypt. *Chem. Afr.* **2022**, *5*, 1611–1626. [CrossRef]
31. Sun, Z.; Soldatova, E.; Guseva, N.; Shvartsev, S. Impact of Human Activity on the Groundwater Chemical Composition of the South Part of the Poyang Lake Basin. *IERI Procedia* **2014**, *8*, 113–118. [CrossRef]
32. Coble, P.G. Characterization of marine and terrestrial DOM in seawater using excitation–emission matrix spectroscopy. *Mar. Chem.* **1996**, *51*, 325–346. [CrossRef]
33. Pitta, E.; Zeri, C. The impact of combining data sets of fluorescence excitation—Emission matrices of dissolved organic matter from various aquatic sources on the information retrieved by PARAFAC modeling. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2021**, *258*, 119800. [CrossRef] [PubMed]
34. Murphy, K.R.; Stedmon, C.A.; Waite, T.D.; Ruiz, G.M. Distinguishing between terrestrial and autochthonous organic matter sources in marine environments using fluorescence spectroscopy. *Mar. Chem.* **2008**, *108*, 40–58. [CrossRef]
35. Du, Y.; Lu, Y.; Roebuck, J.A.; Liu, D.; Chen, F.; Zeng, Q.; Xiao, K.; He, H.; Liu, Z.; Zhang, Y.; et al. Direct versus indirect effects of human activities on dissolved organic matter in highly impacted lakes. *Sci. Total Environ.* **2020**, *752*, 141839. [CrossRef]
36. Yamashita, Y.; Cory, R.M.; Nishioka, J.; Kuma, K.; Tanoue, E.; Jaffé, R. Fluorescence characteristics of dissolved organic matter in the deep waters of the Okhotsk Sea and the northwestern North Pacific Ocean. *Deep Sea Res. Part II Top. Stud. Oceanogr.* **2010**, *57*, 1478–1485. [CrossRef]

37. Kim, J.; Kim, Y.; Park, S.E.; Kim, T.-H.; Kim, B.-G.; Kang, D.-J.; Rho, T. Impact of aquaculture on distribution of dissolved organic matter in coastal Jeju Island, Korea, based on absorption and fluorescence spectroscopy. *Environ. Sci. Pollut. Res.* **2021**, *29*, 553–563. [CrossRef]
38. Zhuang, W.-E.; Chen, W.; Cheng, Q.; Yang, L. Assessing the priming effect of dissolved organic matter from typical sources using fluorescence EEMs-PARAFAC. *Chemosphere* **2020**, *264*, 128600. [CrossRef]
39. Jia, F.; Yang, Q.; Liu, X.; Li, X.; Li, B.; Zhang, L.; Peng, Y. Stratification of Extracellular Polymeric Substances (EPS) for Aggregated Anammox Microorganisms. *Environ. Sci. Technol.* **2017**, *51*, 3260–3268. [CrossRef]
40. Garcia, R.D.; Reissig, M.; Queimaliños, C.P.; Garcia, P.E.; Dieguez, M.C. Climate-driven terrestrial inputs in ultraoligotrophic mountain streams of Andean Patagonia revealed through chromophoric and fluorescent dissolved organic matter. *Sci. Total Environ.* **2015**, *521–522*, 280–292. [CrossRef]
41. Soto Cárdenas, C.; Gerea, M.; Garcia, P.E.; Pérez, G.L.; Diéguez, M.C.; Rapacioli, R.; Reissig, M.; Queimaliños, C. Interplay between climate and hydrogeomorphic features and their effect on the seasonal variation of dissolved organic matter in shallow temperate lakes of the Southern Andes (Patagonia, Argentina): A field study based on optical properties. *Ecohydrology* **2017**, *10*, e1872. [CrossRef]
42. Harjung, A.; Sabater, F.; Butturini, A. Hydrological connectivity drives dissolved organic matter processing in an intermittent stream. *Limnologica* **2018**, *68*, 71–81. [CrossRef]
43. Zhang, B.; Song, X.; Zhang, Y.; Han, D.; Yang, L.; Tang, C. Relationship between surface water and groundwater in the second Songhua River basin. *Shuikexue Jinzhan/Adv. Water Sci.* **2014**, *25*, 336–347.
44. Zhan, L.; Chen, J.; Zhang, S.; Li, L.; Huang, D.; Wang, T. Isotopic signatures of precipitation, surface water, and groundwater interactions, Poyang Lake Basin, China. *Environ. Earth Sci.* **2016**, *75*, 1307. [CrossRef]
45. Ratino, S.; Seangmeng, H.; Ratha, D.; Kong, C.; Eam, E.K.; Siev, S.; Thea, S.; Khanal, R.; Yoshimura, C. Groundwater and Surface Water Exchange in the Lake Basin. In *Water and Life in Tonle Sap Lake*; Yoshimura, C., Khanal, R., Sovannara, U., Eds.; Springer: Singapore, 2022; pp. 81–90. [CrossRef]
46. Fan, R.; Qian, G.; Li, Y.; Short, M.D.; Schumann, R.C.; Chen, M.; Smart, R.S.C.; Gerson, A.R. Evolution of pyrite oxidation from a 10-year kinetic leach study: Implications for secondary mineralisation in acid mine drainage control. *Chem. Geol.* **2021**, *588*, 120653. [CrossRef]
47. Fuoco, I.; De Rosa, R.; Barca, D.; Figoli, A.; Gabriele, B.; Apollaro, C. Arsenic polluted waters: Application of geochemical modelling as a tool to understand the release and fate of the pollutant in crystalline aquifers. *J. Environ. Manag.* **2021**, *301*, 113796. [CrossRef]
48. Segovia, B.T.; Pereira, D.G.; Bini, L.M.; De Meira, B.R.; Nishida, V.S.; Lansac-Tôha, F.A.; Velho, L.F.M. The Role of Microorganisms in a Planktonic Food Web of a Floodplain Lake. *Microb. Ecol.* **2014**, *69*, 225–233. [CrossRef]