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Groundwater hydrochemical characteristics in a plain river network region: Effects of dissolved organic carbon and possible traceability of pollution sources

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Abstract

The chemical composition of groundwater indicates the water quality and provides useful information for identifying pollution sources. The aim of this study was to explore the effects of dissolved organic matter inputs on the ionic composition of groundwater and identify ions that can be used as indicators of pollution sources. Descriptive statistics, a Piper diagram, a Gibbs plot, major ion ratios, and Pearson's correlation coefficients were used to analyze the chemical data of 40 groundwater samples collected from the shallow aquifer surrounding Lake Taihu. The results showed that the water quality index values of most sampling points were less than 50 (excellent water quality), except for one point in the southeast direction of the lake basin (good water quality). The dominant hydrochemical type of groundwater was Ca–Mg–HCO₃ type, and rock dominance was the major mechanism controlling the groundwater chemistry. With an increasing concentration of dissolved organic carbon, the Na⁺, Mg²⁺, and HCO₃[−] concentrations all showed a sharp increase followed by a slow increase, while the NO₃[−] concentration initially decreased sharply and then decreased slowly. The K⁺ concentration was positively correlated with total dissolved nitrogen and phosphorus, nitrate, As, and Cd concentrations ($p < 0.05$). The Ca²⁺, Na⁺, Mg²⁺, Cl[−], HCO₃[−], and CO₃^{2−} concentrations were all positively correlated with Pb concentration ($p < 0.001$). The results indicated that high organic matter inputs can directly or indirectly change the hydrochemical type of groundwater, and K⁺ can be used as a tracer ion for the sources of As and Cd in groundwater in the study area.

Keywords: freshwater eutrophication, groundwater chemistry, water quality index, tracer ion, heavy metal, dissolved organic matter.

Declarations

Ethics approval and consent to participate

Not applicable

Consent for publication

Not applicable

Availability of data and materials

All data generated or analyzed during this study are included in this published article.

Competing interests

The authors declare that they have no competing interests.

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Authors' contributions

ML conceived the study. LG and EH designed the experiment. NM and ZG conducted sample collection. NM and ZG analyzed the sample. NM carried out the data analysis. NM, LG and ML wrote the paper. ML, BP and JW revised the paper. All authors read and approved the

final manuscript.

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Introduction

Groundwater is an important water resource and has become a vital reserve source of domestic water, agricultural irrigation, and industrial water. Particularly in arid and semi-arid areas, groundwater might be the only source of water supply (Konikow et al. 2005). However, climate change and human activities have severely affected the quality and ionic composition of groundwater, which has influenced the use of groundwater resources and poses a threat to human health (Bam and Bansah 2020; Ravikumar et al. 2011). Therefore, understanding changes in the quality and ionic composition of groundwater, and determining possible pollution sources for the utilization and protection of groundwater resources, are essential.

Groundwater quality is mainly measured using physical indicators, such as total dissolved solids (TDS) and electrical conductivity (EC), chemical indicators, such as chemical oxygen demand, nitrate (NO_3^-) concentration, and heavy metal concentrations, and biological indicators, such as total coliforms and total bacteria (Brezonik and Arnold 2012). The water quality index (WQI), which incorporates multiple indicators, is often used to evaluate groundwater quality globally (Vasanthavigar et al. 2010; Tiwari et al. 2015; Lagnika et al. 2016). The hydrochemical characteristics of groundwater refer to the composition, concentration, and proportion of major ions (K^+ , Ca^{2+} , Na^+ , Mg^{2+} , Cl^- , SO_4^{2-} , HCO_3^- , and CO_3^{2-}), which comprehensively indicate the regional effects of various factors, such as geology, geomorphology, hydrology, and biochemistry (Chen et al. 2002). The ionic composition of groundwater is useful for evaluating the hydrochemical type of groundwater, monitoring changes in the water chemical structure, and predicting ion sources (Brezonik and Arnold 2012).

Groundwater recharge directly affects the quality and ionic composition of groundwater (Alyamani and Hussein 1995; Chen et al. 2019). Shallow groundwater can be recharged either by precipitation infiltration or surface water (Keesari et al. 2021; Wang et al. 2021). In shallow aquifers, rainfall infiltration leaches migratory ions (such as NO_3^- , Cl^- , K^+ , and Na^+) from the vadose zone, causing the ion concentrations in groundwater to increase (Ma et al. 2021). Surface water carries pollutants and major ions into shallow aquifers, which alters the quality and ionic composition of groundwater (Alyamani et al. 1995; Subramani et al. 2010).

Many studies have shown that groundwater is seriously polluted by organic matter from wastewater and fertilizers (Chen et al. 2010; Li et al. 2014; Shen et al. 2015). In particular, high organic matter inputs alter groundwater quality and ion concentrations (Ham and Tamiya 2006; Halim et al. 2009). Ham et al. (2006) analyzed groundwater samples in an alluvial fan area in Tsukui, Central Japan, between 1999 and 2003. The authors found that the Se concentration was significantly positively correlated with the dissolved organic carbon (DOC) concentration in groundwater, with the main factors influencing Se concentration being DOC concentration, groundwater level, and recharge source. Therefore, exploring the relationship between pollutants and DOC is crucial for the protection and rational use of groundwater.

Local human pollution activity is also an important factor affecting groundwater quality and ionic composition (Lee and Song 2007; Wisitthammasri et al. 2020; Vaiphei and Kurakalva, 2021). Wisitthammasri et al. (2020) showed that, in an aquifer located in Saraburi, Thailand, the PO_4^{3-} concentration in groundwater was not only related to apatite dissolution, but also closely linked to human activities, such as sewage irrigation and fertilizer application. Similarly, Vaiphei and Kurakalva (2021) found that serious nitrate pollution of groundwater

occurred in an intensive agricultural region of India, and that leaching of agricultural fertilizers was among the most important sources of nitrate. The hydrochemical characteristics can show the potential sources of groundwater pollutants. As early as 1993, the Eastern Coal Geology Corporation found that the groundwater in Hunchun Basin was polluted by Fe, Mn, and NO_3^- -N. Subsequently, Woo et al. (2000) showed that the Cd and F concentrations in groundwater in the same area also exceeded the standard levels, with groundwater pollution often associated with anthropogenic activities.

Lake Taihu is often referred to as ‘the land flowing with milk and honey’ in China. This lake basin is a typical plain river network region that includes the third largest freshwater lake in China and nourishes more than 20 million people (Qin et al. 2007). Owing to the high intensity of industrial and agricultural production, rivers and lakes in this region are facing serious problems from eutrophication. Therefore, analyzing the groundwater quality and identifying potential pollution sources in this region is imperative for protecting water resources. Therefore, the aim of this study was to: investigate whether organic matter inputs from recharge sources around Lake Taihu affect the ionic composition of shallow groundwater, and explore whether specific ions can be used as tracers to indicate the sources of pollutants in groundwater.

Methods and Materials

Study area and sample collection

The Lake Taihu Basin is located in the middle and lower reaches of the Yangtze River, with a mean water depth of 1.9 m (Qin et al. 2007). The Yangtze River basin comprises various

sedimentary rock systems from the present Cambrian period to the Quaternary period, mainly carbonate, evaporite, and terrestrial clastic rocks, with carbonate rocks being dominant (Xia et al. 2008).

In August 2018, groundwater samples were collected from 40 wells located in the northeast (NE), northwest (NW), southeast (SE), and southwest (SW) directions of Lake Taihu (Fig. 1). The depth of these wells was approximately 5 m, and the sampling depth was 0.5–1 m below the water surface. Ten sampling points were selected in each direction, and the distance from the sampling point to the shore of Lake Taihu was in the range of 0–43.09 km.

Chemical analysis

A portable multifunctional parameter meter (Mettler Toledo AG, Zurich, Switzerland) was used to measure the pH, EC, and TDS of groundwater *in situ*. *In situ* determination of biocarbon (HCO_3^-) was performed using the titration method with 0.02 mol L^{-1} HCl (Wei et al. 2020). Groundwater samples were collected using 1,000-mL polyethylene bottles, stored at $<16^\circ\text{C}$, and transported back to the laboratory as soon as possible. The water samples were filtered through precleaned $0.45\text{-}\mu\text{m}$ Millipore membranes and the filtrates were stored at 4°C for two weeks to complete all chemical analyses.

Major cations (K^+ , Ca^{2+} , Na^+ , Mg^{2+}) and heavy metal(loid)s (Cr, Cu, Zn, As, Cd, and Pb) were determined by inductively coupled plasma–mass spectrometry (ICAP Qc; ThermoFisher, Waltham, MA, USA). Major anions (Cl^- , SO_4^{2-} , and NO_3^-) were analyzed by ion chromatography (ICS–1100; Dionex, Sunnyvale, CA, USA). Total dissolved nitrogen (TDN) and total dissolved phosphorus (TDP) concentrations were measured in accordance with the Standard Methods for the Examination of Wastewater (APHA, 2005). DOC concentration

was measured using a total organic carbon analyzer (TOC–L CPN; Shimadzu, Kyoto, Japan).

All reagents used in this study were analytically pure, and standard solutions were prepared using Milli-Q water. Furthermore, all experimental devices were precleaned using 5% concentrated nitric acid solution and rinsed with Milli-Q water.

Water quality index calculation

Groundwater quality was evaluated using the WQI, which was calculated as follows (Saleh et al. 2017; Derdour et al. 2020).

(1) Calculation of proportional weight (W_i):

$$W_i = w_i / \sum_{i=1}^n w_i \quad (1)$$

where W_i is the proportional weight of the i th chemical parameter, w_i is the weight of the i th parameter, and n is the number of parameters tested in this study ($n = 17$; Table S1).

(2) Calculation of the quality rating scale:

$$q_i = (C_i / S_i) \times 100 \quad (2)$$

where q_i is the quality rating based on the i th chemical parameter, C_i is the value of the i th parameter, and S_i is the drinking water standard for the i th parameter.

(3) Determining the sub-index value:

$$SI_i = W_i \times q_i \quad (3)$$

(4) Calculation of the WQI value:

$$WQI = \sum_{i=1}^n SI_i \quad (4)$$

where SI_i is the sub-index of the i th chemical parameter and n is the number of parameters tested ($n = 17$).

The water quality was classified into five classes according to the calculated WQI values

(Vasanthavigar et al. 2010; Derdour et al. 2020), as follows: Excellent ($WQI < 50$); good ($WQI = 50\text{--}100$); poor ($WQI = 100\text{--}200$); very poor ($WQI = 200\text{--}300$); and unsuitable for drinking ($WQI > 300$).

Hydrochemical analysis

To identify the hydrochemical type of groundwater, a Piper diagram was constructed based on the concentrations of Mg^{2+} , Ca^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} , CO_3^{2-} , and HCO_3^- . The diamond part of the Piper diagram was divided into four regions, representing $Ca\text{--}Mg\text{--}HCO_3$, $Ca\text{--}Mg\text{--}SO_4$, $Na\text{--}SO_4$, and $Na\text{--}HCO_3\text{--}SO_4$ types of groundwater (Piper, 1944). A Gibbs plot was used to distinguish the factors influencing groundwater hydrochemistry, which mainly included precipitation dominance, rock dominance, and evaporation crystallization dominance (Gibbs, 1970). In the Gibbs plot, the weight ratio of $Cl^-/(Cl^-+HCO_3^-)$ or $Na^+/(Na^++Ca^{2+})$ was plotted on the x-axis and the TDS was plotted on the y-axis.

Statistical analysis

Statistical analyses were performed using the IBM SPSS Statistics software 25.0 (IBM Corp. Armonk, NY, USA). Pearson's correlation and regression analyses were used to examine the relationships between variables, with a p-value of 0.05 used to determine significance. Origin 2017 (OriginLab Corp. Northampton, MA, USA) and Microsoft Excel 2020 were used to analyze data and draw graphs. Correlation matrices were graphed using the corrplot package in R 4.0.2 (<http://www.r-project.org/>). A map of the sampling points was created using ArcGIS 10.6 (ESRI Inc. Redlands, CA, USA).

Results

Water quality characteristics

The DOC concentrations in groundwater samples ranged from 0.70 mg L⁻¹ (SW6) to 51.67 mg L⁻¹ (SW10), with a mean value of 7.73 mg L⁻¹ (Fig. 2a). The TDN (Fig. 2b) and NO₃⁻ (Fig. 2d) concentrations were in the range of 0.18–8.62 mg L⁻¹ (mean, 2.61 mg L⁻¹) and 0.00–11.50 mg L⁻¹ (mean, 2.92 mg L⁻¹), respectively. The TDP concentrations (Fig. 2c) ranged from 0.00–0.49 mg L⁻¹, with a mean value of 0.07 mg L⁻¹, and values in the SE direction were significantly higher ($p < 0.05$) than those in the SW direction of Lake Taihu.

The concentration ranges of heavy metal(loid)s in the groundwater samples are shown in Fig. S1. A significant difference ($p < 0.05$) in Cr concentrations was observed between the NE and NW, SW, or SE directions of Lake Taihu. Furthermore, the Pb concentration in the SW direction was significantly lower ($p < 0.05$) than those in the SW, NE, and SE directions of Lake Taihu.

To assess the groundwater quality, the WQI was calculated for groundwater at the 40 sampling points. The WQI values were in the range of 13.29–56.25, with a mean value of 29.32 (Fig. S2). Among the 40 sampling points, only SE10 had WQI > 50, which indicated good water quality. At the other sampling points, the WQI values were <50, indicating the excellent quality of shallow groundwater in the study area.

Groundwater hydrochemical characteristics

The K⁺ concentrations in groundwater samples ranged from 0.95 mg L⁻¹ (SW6) to 57.18 mg L⁻¹ (SE7), with a mean value of 15.09 mg L⁻¹. A significant difference ($p < 0.05$) in K⁺ concentrations was observed between the SE and NW, NE, or SW directions of Lake Taihu (Fig. 3a). The SO₄²⁻ concentrations varied from 18.40 (SW8) to 223.89 mg L⁻¹ (NE6), with a mean value of 70.41 mg L⁻¹, and the values in the NE direction were significantly higher than

those in the SW direction ($p < 0.05$; Fig. 3f). No significant differences were observed in the concentrations of Ca^{2+} , Na^+ , Mg^{2+} , Cl^- , HCO_3^- , and CO_3^{2-} among the four directions of Lake Taihu.

The Piper diagram (Fig. 4) showed that there was no significant difference in the groundwater type among the four directions of Lake Taihu. Most sampling points were located in area IV, meaning that the hydrochemical type of shallow groundwater in the study area was predominantly Ca–Mg– HCO_3 type. The Gibbs plots (Fig. 5) showed that rock dominance was the major mechanism controlling groundwater chemistry. The TDS concentrations were in the range of 89.70–337.84 mg L^{-1} , with $\text{Cl}^-/(\text{Cl}^- + \text{HCO}_3^-)$ and $\text{Na}^+/(\text{Na}^+ + \text{Ca}^{2+})$ in the ranges of 0.04–0.43 and 0.12–0.59, respectively.

Relationships between water quality parameters, major ions, and heavy metals

Correlations between the relative proportions of major ions in groundwater samples are shown in Fig. 6. A significant negative correlation was observed between the relative proportions of Na^+ , Cl^- , and Ca^{2+} , and between the relative proportions of HCO_3^- , CO_3^{2-} , and SO_4^{2-} . Furthermore, the relative proportion of Mg^{2+} was negatively correlated with those of K^+ , Ca^{2+} , and SO_4^{2-} ($p < 0.01$), while the relative proportion of Na^+ was positively correlated with that of Cl^- ($p < 0.001$), and the relative proportion of CO_3^{2-} was positively correlated with that of HCO_3^- ($p < 0.001$).

Regression analysis was conducted between the concentrations of DOC and major ions in groundwater samples. With increasing DOC concentration, the Na^+ , Mg^{2+} , and HCO_3^- concentrations all showed a rapid increase followed by a slow increase ($R^2 = 0.5652, 0.6631$, and 0.4621 , respectively); conversely, the NO_3^- concentration showed a rapid decrease

followed by a slow decrease ($R^2 = 0.2826$; Fig. 7).

Correlations between the major ions and water quality parameters or heavy metals are shown in Fig. 8. The concentrations of most ions (except SO_4^{2-}) were significantly positively correlated with EC, TDS, and pH ($p < 0.001$). The SO_4^{2-} concentration was also significantly correlated with EC and TDS ($p < 0.05$), but not with pH. Furthermore, a significant positive correlation was observed between the concentrations of K^+ and TDN, TDP, NO_3^- , As, or Cd ($p < 0.05$). The concentrations of all major ions (except K^{2+}) were significantly positively correlated with the Pb concentration ($p < 0.001$), while the concentrations of Na^+ , HCO_3^- , and CO_3^{2-} were positively correlated with the Zn^{2+} concentration ($p < 0.05$).

Discussion

The WQI results showed that the groundwater around Lake Taihu did not have a serious pollution problem. However, the WQI of one sampling point (SE10) was markedly higher than that of other sampling points, meaning that SE10 was slightly polluted. Although DOC was not included in the WQI calculation, SE10 might be organically polluted when analyzing the water quality indicators.

The Gibbs plot results indicated that the hydrochemical characteristics of groundwater in the Lake Taihu Basin were mainly affected by rock weathering and dissolution. The soil in the study area is often saturated due to high precipitation (Zhai et al. 2020) and, in this case, the minerals in the rock continue to dissolve. Dissolved minerals are then leached into shallow groundwater by the infiltration of rainfall, resulting in differences in the composition of anions and cations in groundwater across different areas (Alyamani et al. 1995; Subramani

et al. 2010; Ye et al. 2010). For example, K^+ is generally derived from the weathering and dissolution of potassium feldspar, salt sedimentary rocks, or silicate in aquifers (Yang et al. 2016). Na^+ is the primary product of the weathering and dissolution of halite, albite, and silicate (Yang et al. 2016), and can be used as an indicator of seawater intrusion or groundwater overexploitation. Ca^{2+} mainly comes from the dissolution of gypsum ($CaSO_4 \cdot 2H_2O$), anhydrite ($CaSO_4$), calcite ($CaCO_3$), and dolomite ($CaMg(CO_3)_2$) (Chen et al. 2002; Yang et al. 2016).

To further explore the possible origin of major ions and the geochemical process controlling groundwater chemistry (Moussa et al. 2009), the proportional coefficient was analyzed (Fig. S3). In the $Na^+ - Cl^-$ ratio diagram (Fig. S3a), some sampling points were distributed around the 1:1 line, indicating that halite dissolution was dominant (Meybeck, 1987). However, the distribution of most samples above the 1:1 line indicated that halite dissolution was not the only source of Na^+ . Indeed, other Na^+ sources included weathering of sodium silicate and human activity (Yang et al. 2016). Furthermore, the proportional coefficient of Ca^{2+} and SO_4^{2-} can be used to determine whether Ca^{2+} and SO_4^{2-} in groundwater originate from the dissolution of gypsum and anhydrite. In the $Ca^{2+} - SO_4^{2-}$ ratio diagram (Fig. S3c), the distribution of most samples was under the 1:1 line. In addition to gypsum dissolution, other sources of Ca^{2+} might exist, such as carbonate rocks.

The bivariate plot of Ca^{2+} versus HCO_3^- (Fig. S3d) showed that most sampling points were near the 1:1 line. This distribution pattern indicated that HCO_3^- in the groundwater mainly originated from the dissolution of carbonates (such as calcite and dolomite), while Ca^{2+} was partly derived from carbonates in the study area. This conclusion was consistent with the

Ca²⁺–SO₄²⁻ ratio results (Fig. S3c). To determine the occurrence of ion-exchange in groundwater, the linear relationship between ((Ca²⁺+Mg²⁺) – (SO₄²⁻+HCO₃⁻)) and (Na⁺+K⁺–Cl⁻) was analyzed (Yang et al. 2016). Most of the groundwater sampling points around Lake Taihu were near the 1:1 line (Fig. S3f), indicating strong ion-exchange occurring in shallow groundwater in the study area.

The results of this study showed that an increasing DOC concentration in groundwater resulted in a rapid increase, followed by a slow increase, in Na⁺, Mg²⁺, and HCO₃⁻ concentrations. Dissolved organic matter (DOM) in groundwater is the main energy source for microbial activity (Vázquez-Suné et al. 2004; Hofmann et al. 2018). Highly soluble organic matter can stimulate the activities of microorganisms, which release a large amount of CO₂ through respiration. As a result, an increased amount of CO₂ enters the groundwater, resulting in higher HCO₃⁻ concentrations in groundwater. This dissolved CO₂ can promote the dissolution of rocks and minerals, which is the reason for the rapid increase in Na⁺ and Mg²⁺ concentrations with increasing DOC concentration. With the increase in rock and mineral dissolution, the ionic concentration in groundwater gradually reaches saturation, leading to a slow increase in Na⁺, Mg²⁺, and HCO₃⁻ concentrations.

In contrast to the trends of Na⁺, Mg²⁺, and HCO₃⁻ concentrations, NO₃⁻ concentration showed an initial rapid decrease followed by a slow decrease in groundwater as the DOC concentration increased. The reduction of nitrate in groundwater is mainly achieved through denitrification by microorganisms (Spalding and Exner 1993). A higher DOM concentration is the main energy source for denitrifying bacteria, which can promote the occurrence of denitrification. Furthermore, the decomposition of DOM consumes dissolved oxygen in

groundwater and creates an anaerobic microenvironment, which is also necessary for the denitrification process to occur. Therefore, the DOC concentration in groundwater affects the redox conditions and NO_3^- concentration via biotic and abiotic processes.

In this study, Ca^{2+} showed a significant negative correlation with Na^+ , Mg^{2+} , Cl^- , and CO_3^{2-} , while Mg^{2+} showed a significant negative correlation with SO_4^{2-} . This indicated that Ca^{2+} in groundwater had a different source to Na^+ , Mg^{2+} , Cl^- , and CO_3^{2-} . In contrast, significant positive correlations were observed between Na^+ and Mg^{2+} or Cl^- , and between Mg^{2+} and Cl^- or CO_3^{2-} , showing that these ions had the same source. Furthermore, the lack of significant correlation between K^+ and other major ions (except Mg^{2+}) indicated that the source of K^+ was distinctly different to that of other ions.

Datta et al. (1997) studied the effects of long-term fertilizer application on groundwater ions in the alluvial plain of the Ganges River, India. The authors found that long-term fertilizer application led to an increase in the K^+ concentration in groundwater, mainly due to high K^+ input from chemical fertilizers, such as KNO_3 and KH_2PO_4 . Furthermore, Wei et al. (2020) analyzed the ionic composition of soil water extract and domestic sewage in the Dangjiangkou area of China, finding that the relative proportion of K^+ in soil water extract was much higher than that in sewage. The findings of the present and previous studies indicate that K^+ in groundwater is mainly derived from the use of chemical fertilizers in the Lake Taihu Basin.

In this study, a significant positive correlation was observed between K^+ and several water quality parameters (NO_3^- , TDP, and TDN), further suggesting that the K^+ in groundwater mainly originates from chemical fertilizers. Furthermore, the TDN concentration in Lake

Taihu and its surrounding river network is usually 2.00 mg L^{-1} (Yao et al. 2018), and the mean TN concentration in Lake Taihu is 1.55 mg L^{-1} (The Health Status Report of Taihu Lake, 2018). In the present study, the mean TDN concentration in groundwater around Lake Taihu (2.61 mg L^{-1}) was higher than that in Lake Taihu and its surrounding river network. Therefore, NO_3^- leaching from soil in the Lake Taihu Basin might be the main source of NO_3^- in groundwater.

The results of this study also showed a significant positive correlation between the concentrations of K^+ and As or Cd, indicating that the sources of As and Cd in groundwater were similar to that of K^+ . Therefore, both As and Cd might come from the use of fertilizers in agricultural production. The extensive application of fertilizers can increase the content of heavy metal(loid)s, including As and Cd, in soil and groundwater (Nicholson et al. 2003; Atafar et al. 2008; Belon et al. 2012; Kubier et al. 2019). A previous study has shown that ~30%–35% of Cd in the groundwater of an agricultural region comes from mineral fertilizers (Belon et al. 2012). Boudaghi et al. (2012) studied changes in heavy metals in groundwater before and after fertilization of paddy soil, finding an increase in the concentration of heavy metals after fertilization; the results showed a significant positive correlation between the Cd concentration and amount of potassium fertilizers applied.

Uddin and Kurosawa (2011) investigated the effects of nitrogen fertilizer application on As pollution in groundwater in Bangladesh, finding that a high-N environment created by fertilizers led to reducing conditions in the groundwater through microbial activity, which in turn promoted As release from sediment. Furthermore, Campos (2002) studied the influence of phosphate fertilizer application on groundwater pollution by As in Sao Paulo, Brazil, with

the results showing that As element as an undesirable additive in phosphatic fertilizers was a source of As in groundwater. In summary, As and Cd in the groundwater of Lake Taihu have similar sources, and are likely derived from the application of chemical fertilizers in agricultural production. Considering their close relationship, K^+ can be used as a tracer ion for the sources of As and Cd in shallow groundwater in the study area.

In this study, the concentrations of all major ions, except K^+ , were positively correlated with the Pb concentration in groundwater. The sources of dissolved Pb in groundwater mainly include water–rock interactions in aquifers and industrial or agricultural activities (Millot and Négrel 2015). Furthermore, Pb can be emitted into the atmosphere by industries and automobiles, then deposited on the soil in the form of wet or dry sedimentation, and further leached into groundwater (Saby et al. 2006). However, owing to its low solubility and mobility, most exogenous Pb deposited in soil stays on the soil surface, and does not easily enter the groundwater (Saby et al. 2006; Millot and Négrel 2015). Therefore, Pb in the groundwater of Lake Taihu mainly comes from water–rock interactions in the aquifer.

Conclusions

This study investigated the hydrochemical characteristics of groundwater surrounding the Lake Taihu Basin using descriptive statistics, a Piper diagram, a Gibbs plot, proportional coefficients of major ions, and Pearson's correlation coefficients. The main conclusions obtained from this study were as follows:

(i) The quality of shallow groundwater in the study area was excellent, with a mean WQI value of 29.32. Rock dominance was the major mechanism controlling the groundwater

chemistry. The groundwater was mainly Ca–Mg–HCO₃ type, and there was no significant difference in the hydrochemical type of groundwater among the four directions of the lake basin.

(ii) High levels of organic matter were observed in Lake Taihu and its surrounding river network due to eutrophication, and a large amount of organic matter input to groundwater accelerated the activities of microorganisms and altered the redox conditions of the groundwater. These environmental changes, in turn, accelerated the dissolution of rocks and minerals, and changed the concentrations of ions in groundwater, which affected the hydrochemical type of groundwater.

(iii) The concentrations of heavy metal(loid)s in groundwater were closely linked to human activities. K⁺, As, and Cd in the study area were mainly derived from the application of chemical fertilizers, and K⁺ can be used as indicator ion for the sources of As and Cd in groundwater. Pb in the groundwater around Lake Taihu mainly originated from water–rock interactions in the aquifer.

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Figure captions:

Fig. 1 Location map of the study area (Lake Taihu Basin) and groundwater sampling points ($n = 40$).

Fig. 2 Spatial variation in water quality parameters of groundwater in the aquifer surrounding the Lake Taihu Basin: (a) Dissolved organic carbon (DOC); (b) total dissolved nitrogen (TDN); (c) total dissolved phosphorus (TDP); (d) nitrate (NO_3^-). *indicates significant difference between different directions of Lake Taihu ($p < 0.05$). Line within box, transparent square, and box indicate the median, mean, and 25%–75% interquartile range, respectively.

Fig. 3 Spatial variation in major ion concentrations in groundwater: (a) K^+ ; (b) Ca^{2+} ; (c) Na^+ ; (d) Mg^{2+} ; (e) Cl^- ; (f) SO_4^{2-} ; (g) HCO_3^- ; (h) CO_3^{2-} . * indicates significant difference between different directions ($p < 0.05$). Line within box, transparent square, and box indicate the median, mean, and 25%–75% interquartile range, respectively.

Fig. 4 Piper diagram showing the chemical composition of groundwater samples in the study area.

Fig. 5 Gibbs plots indicating the mechanisms controlling groundwater chemistry in the study area.

Fig. 6 Correlations between the relative proportions of major ions in groundwater. * $p < 0.05$, ** $p < 0.01$, and *** $p < 0.001$.

Fig. 7 Correlations between the concentrations of DOC and (a) Na^+ , (b) Mg^{2+} , (c) NO_3^- , and (d) HCO_3^- in groundwater.

Fig. 8 Correlations between the major ions and basic water quality parameters or heavy metals in groundwater. * $p < 0.05$, ** $p < 0.01$, and *** $p < 0.001$.

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