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ORIGINAL ARTICLE

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Genetic relation between Holocene transgression and chemical composition of the shallow groundwater in Hangzhou, China

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Abstract The shallow groundwater in Hangzhou area has the characteristics of high mineralization, high salinity and high contents of iron and manganese. Statistical analyses and the experiments of simulation show that the Holocene transgressive strata has a crucial effect on the formation of chemical composition of the shallow groundwater in the plain area of Hanghzhou. The degree of transgression is in consonance with the variation tendency of the thickness of the transgressive strata. The chemical compositions of the subsurface water in the hilly area depend on the lithology of the aquifers.

Keywords Hangzhou China · Shallow groundwater · Chemical compositions · Transgressive strata · Clustering analysis · Simulation experiment · China

Introduction

Hangzhou, China, is a world-famous tourist city. With the increase of the urban population and the development of tourism, the requirement of the quantity and quality of groundwater is steadily increasing. Hangzhou region evolved from the ancient shallow sea gulf. According to the local chronicle (Compilation Commission on Hangzhou Chorography (CCHC) 2000), the subsurface water was not potable due to salinity content before Wu-Yue Period (before 476 BC). After the large-scale dykes and dams were built, the encroachment of seawater was kept within limit. The drainage river and ditch were extricated from the encroachment of the tide. Moreover, the West Lake was dredged several times and the fresh lake water was discharged into the rivers, which resulted in gradual desalination of the groundwater. Up to now, although the quality of the shallow groundwater has obviously been improved, the degree of mineralization, the salinity, and the contents of the iron and manganese are still high, so that the groundwater cannot be used directly as drinking water or industrial water. To understand why the quality of the shallow groundwater is poor, the chemical composition of the modern phreatic water has been determined, and the relationships between the sedimentary environment and geochemistry of the aquifers and the chemical components of groundwater have been studied by mathematical statistical methods and simulating experiments. Such a study is very important to exploit and protect the groundwater resources properly and efficiently.

Setting of the survey area and experiments

Hangzhou City is in the coastal area of southeastern China. Qianjiang River, a strongly tide-influenced river, flows through the city proper and discharges into the Gulf of Hangzhou.

According to nature of the geography (Fig. 1), the survey area can be divided into two geographical units of the northeastern plain and the southwestern hilly area. The topography declines gradually from the southwest to the northeast. The area is located in a subtropical climate region with a warm, wet climate and plentiful precipitation. The average annual temperature is 16.2 °C, and the average annual precipitation and evaporation are 1,398.9 mm and 1,309.6 mm, respectively. Because of abundant precipitation, the level of groundwater is rather high. Usually, the level of ground water is between 1 m and 3 m below the ground surface in the plain area, whereas in the hilly area the level is not more than 10 m below the ground surface. The major recharge source of subsurface water is precipitation.

The acreage of the plain area is about threefourths of the whole survey area and is covered with Quaternary sediments from the Upper Pleistocene to the Holocene. Because of the neo-tectonic subsidence movement and the diversity of the basal geological conditions, the thickness of the sediments increases gradually from 40 m in the southwest to 200 m in the northeast. The genesis types of sediments include fluviolacustrine, marine and transitional facies sedimentation. In the Quaternary Period, three marine transgressions had occurred in the study area which was in the transition zone of sea and land, hence there were three marine facies strata in the stratigraphic section (Fig. 2). The shallow groundwater concerned in this paper exists in the range from surface to 15 m depth. The shallow aquifers are the sedimentary strata formed in the Middle-Late Holocene Period, in which the sedimentary types include fluvial-marine and marine-limnetic facies. The sediments are mostly fine and consist of clay, clayey and sand in the form of lamination and cross-interbedding. The hydrous capacity of sediments is poor, which is called ‘‘hydrous viscose layer’’.

The hilly area is the major scenic spot in Hangzhou. The emergence strata and their lithological characters in this region are described as follows: Devonian System (D) terrigenous clastic deposits being composed of quartz sandstone, fine sandstone, siltstone and mudstone; Lower Carboniferous Series (C_1) terrigenous clastic deposits consisting of violet-red sandstone and shale, and littoral-lagoon facies deposits consisting of clastic quartz sandstone, sandy mudstone and carbonaceous shale etc.; Middle-Upper Carboniferous ($C_{2\text{-}3}$) carbonatite formation consisting mainly of limestone; Permian System (P_1) neritic carbonatite deposits composed mainly of chert-bearing bioclastic limestone, interbedding with marlite and siliceous rock; Upper Jurassic Series (J_3) effusive rock being mainly composed of ignimbrite, tuff, breccia, etc.; Quaternary System (Q) eluvial slope wasp and fluvial, fluviolacustrine and lagoon facies loose sediments.

The hilly area lies on the West Lake synclinorium. The compression rifts, trending NE 45° with a dip angle about 70°, are the chief fracture tectonics of the West Lake synclinorium. The extension rifts trending NW also developed. They created the favorable conditions for the development of the carbonatite karst crevice and the fractures in clastic sedimentary rock and volcanic effusive rock. The geological conditions mentioned above control the aquifer types in the hilly area, which are the karst crevice aquifer, fractured aquifer consisting of clastic sedimentary strata and volcanic effusive rock, as well as the porous aquifers in the Quaternary deposits.

Two hundred and seventeen groundwater samples were collected with a sampling density of one sample per km^2 in the survey area. A total of 164 samples were collected from drinking wells in the plain area and 53 samples were collected from boreholes and springs in the hilly area. The pH value and the temperature of the groundwater samples were determined in situ. All samples were chemically analyzed. The samples were

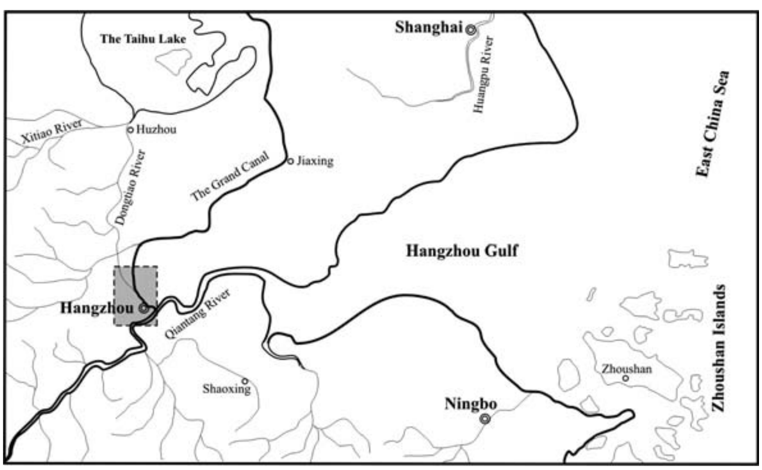

Fig. 1 The position map of the survey area

Fig. 2 The generalized section

Stratum		Lithology	Genetical type	Depth (m)	Thickness (m)	Lithological column	Paleogeography land ⇔ sea	Paleoclimate cold ⇔ warm
Holocene series (Q_4)	Upper (Q_4^3)	Grey-brown clayey	Limnetic facies	0—2	0—2			
		Grey-yellow clayey	Fluvio-lacustrine facies	2—5	1—3			
	Middle (Q_4^{1-2})	Politic clayey	Littoral limnetic facies	3—30	1—30			
		Brown-yellow clayey	Estuarine facies	12—18	8—10			
		Politic clayey	Littoral facies	15—30	5—10			
Upper Pleistocene series (Q_3)	Upper (Q_3^3)	Brown-yellow clayey	Fluvio-lacustrine facies	25—30	0—15			
	Middle (Q_3^2)	Grey-yellow clayey	Littoral limnetic facies	30—35	2—5			
		Grey, pale, yellow-brown clayey	Fluvio-lacustrine facies	40—50	10—20			
		Sand-gravel	Fluvial facies	50—60	5—15			
	Lower (Q_3^1)	Gravel-bearing clayey	Alluviofluvial facies	60—70	0—8			

acidized before analysis. The content of iron and manganese in the samples collected from the plain area were determined.

To understand the geochemical characteristics of shallow groundwater, several sediment samples were collected based on different lithology and depth of aquifers in the plain area. The compositions of the clay minerals in the sediments were determined by means of X-ray diffraction (XRD) and infrared spectrum. The contents of iron and manganese in the sediment samples were analyzed by atomic absorption spectrophotometer (AAS). The mathematical statistical methods, including clustering analysis and factor analysis, were applied to reveal the geochemical information from the samples.

The lixiviation experiments were designed to reveal the interaction process between the chemical compositions of groundwater and that of the aquifer media. The lixiviation experiments were performed under the hermetical sealed condition. Two hundred and fifty grams sediment samples were placed in the bottom of the lixiviation container, and 1,000 mL lixiviant were slowly added, then the container was sealed. After 2, 4, 8, 16, 32 and 480 h, respectively, 100 mL lixivium was removed each time. The precipitate water and the seawater were chosen as the lixiviants, which were collected locally and from the East China Sea, respectively. The chemical components of the lixiviants and lixiviums, including the contents of iron and manganese, were determined. To understand the lixiviation effect on the groundwater compositions in the open condition, sample No.7 was also experimented under the open condition at the same time. A replicate analysis of samples gave a precision of $>8\%$.

Results and discussion

Characteristics of the chemical compositions of groundwater

The average chemical components of the shallow groundwater in Hangzhou are listed in Table 1. It shows that the characteristics of the shallow groundwater in the plain area are quite different from those in the hilly area. The former has medium hardness of water with relatively strong mineralization, and the latter has low hardness of water with relatively weak mineralization. The contents of the major ions in the plain groundwater are higher than those in the hilly area except Mg^{2+}. The contents of Na^+, SO_4^{2-} and Cl^- in the plain area are 10.6, 5.1 and 5.9 times, respectively, higher than those in the hilly area. The average content sequence of the major cations in groundwater in the plain area is $Ca^{2+} > Na^+ > Mg^{2+} > K^+$, and the anions $HCO_3^- > SO_4^{2-} > Cl^-$. The chemical type of groundwater is described by the Kurlov formula (Ren 1986) as $M_{0.71}\frac{HCO^3_{52}SO^4_{28}Cl_{20}}{Ca_{45}Na_{34}Mg_{13}[K_8]}$. Although it belongs to HCO_3–Ca, it has an obvious disparity with the typical water of HCO_3–Ca: $M_{0.24}\frac{HCO^3_{95}[SO^4_5]}{Ca_{81}Mg_{11}[Na_8]}$.

Table 1 Chemical composition characteristics of groundwater

Sample sources	Cation and anion (mg/L)							Mineralization (g/L)	Hardness (German)	pH
	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	HCO_3^{-}	SO_4^{2-}	Cl^{-}			
Plain	106.87	31.23	81.18	12.13	268.55	148.59	101.56	0.709	23.6	7.2
Hill	63.32	40.09	7.68	1.67	183.72	25.04	16.99	0.236	9.84	6.9

The chemical type of groundwater in the survey area has the features of relatively high proportions of Na^{+}, SO_4^{2-} and Cl^{-}, and obviously low proportion of HCO_3^{-}. Comparing the HCO_3–Na type groundwater formed in littoral plain $M_{0.7}\frac{HCO^{3}_{68}Cl_{18}SO^{4}_{14}}{Na_{93}[Ca_4Mg_3]}$, the mineralized degree and content percentage of Cl^{-} in this area are consistent. This shows that the shallow groundwater in the plain area has dissolved the chemical substances of terrigenous and marine sediments in the aquifers.

The analytical results of the soluble salts in sediments show that the salinity in marine sediment is up to 1,709 mg/100 g_{sample}, while that in the fluviolacustrine sediment is only 109.5 mg/100 g_{sample}. It is obvious that the fluviolacustrine sediment cannot result in the ionic contents of groundwater so high level listed in Table 1. The chlorides and sulfates retained in the marine sediment during the Holocene transgressions may provide plenty of Na^{+}, Cl^{-} and SO_4^{2-} to groundwater.

The correlation analysis indicates that there are significant correlations between the contents of Na^{+} and Cl^{-} in the groundwater in the plain area with a correlation coefficient = 0.86 (the critical value is 0.195 at 95% significant level of 100 samples). It further confirms that the contents of the Na^{+}, Cl^{-} in groundwater have direct relation with the dissolution of the NaCl in the marine sediments. There is a significant correlation between the major ionic contents and mineralized degree of the groundwater in the plain area (Table 2), in which the correlation between chloride (Cl^{-}) and mineralized degree is the most significant (Fig. 3) and sulfate (SO_4^{2-}) is second. This illustrates that the marine deposits formed in the Holocene transgressions played a significant role in increasing the mineralization of the groundwater, and that chloride content made an important contribution to the mineralization.

The hilly groundwater samples are collected, respectively, from the clastic rock aquifer, Quaternary loose sediment aquifer, volcanic rock aquifer and carbonatite aquifer. The average contents of major cations and anions in groundwater range, respectively, $Ca^{2+} > Na^{+} > Mg^{2+} > K^{+}$ and $HCO_3^{-} > SO_4^{2-} > Cl^{-}$. The contents of major ions in aquifers vary with lithological characters (Fig. 4). By and large, the chemical type of the groundwater in the hilly area belongs to HCO_3–Ca, for which the Kullov formula (Ren 1986) is $M_{0.24}\frac{HCO^{3}_{81}SO^{4}_{11}[Cl_8]}{Ca_{55}Mg_{35}[Na_7K_4]}$.

Table 2 The correlation coefficients between mineralized degree and the major ions

	HCO_3^{-}	SO_4^{2-}	Cl^{-}	Na^{+}	Ca^{2+}	Mg^{2+}	K^{+}
Mineralized degree	0.642	0.656	0.837	0.77	0.771	0.738	0.367

The content proportion of ions in groundwater in the hilly area is different from that in groundwater in the plain area. The chemical type of groundwater and content proportions of the ions in the groundwater in the hilly area are controlled by the protogenic geochemical environment, the lithological characters of limestone, sandstone and volcanic rock distributed widely in this area, and the geological and hydrogeological conditions (Wu and Weng 1984).

Source of the chemical components of groundwater

Q-type clustering analysis

Fifty-three samples selected randomly from the 217 samples have received Q-type clustering analysis. The

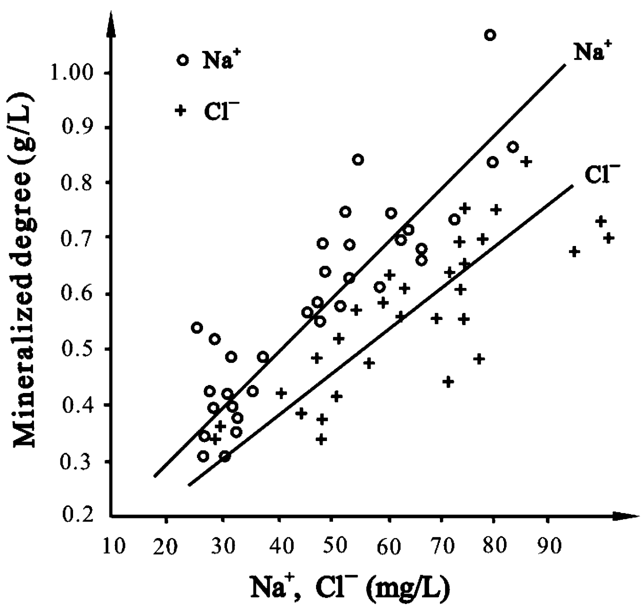

Fig. 3 Correlations between Na^{+}, Cl^{-} and the degree of mineralization in shallow groundwater

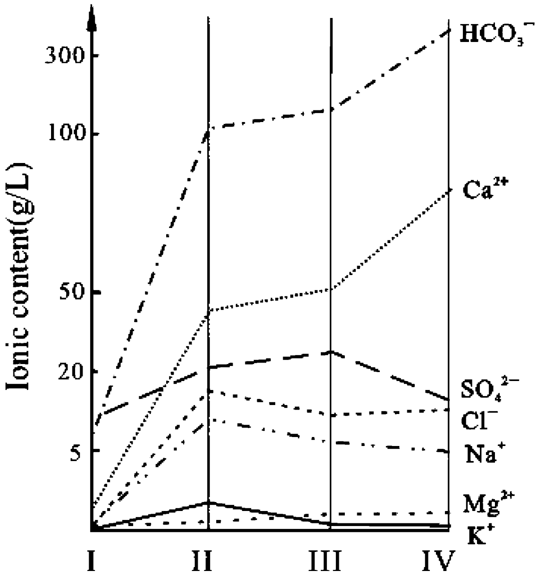

Fig. 4 The distribution of the main ions in hilly groundwater of different aquifers I—Clastic rock aquifer; II—The Quaternary aquifer; III—Volcanic rock aquifer; IV—Carbonatite aquifer

samples were chosen in such a way that the selected samples are distributed evenly over the entire survey area. The analytical results, listed in Fig.5, show that if the distance coefficient is 0.9, the samples will be divided into four groups. The samples in each group have a spatial distribution area of their own (Fig. 6). As is shown in the chart, the samples in Group II distribute along the Jing-Hang Grand Canal in the middle of the survey area; the samples of Group I distribute at both sides of Group II; the samples of Group IV distribute in the east of the survey area; the samples collected from the hilly area (Group III) are distinctly different from other three groups. The chemical components and types of shallow groundwater in different sampling zones have an obvious distinction (Table 3). The mineralized degree of shallow groundwater in the zone where Group I distributes is relatively high, which is 0.807 g/L and 3.5 times as much as that in the hilly zone. The content proportions of Na^+, Cl^- are also relatively high, 32.3% and 19.7%, respectively. The mineralized degree of the shallow groundwater in the zone where Group II samples distribute is 0.566 g/L, and the content proportions of Na^+, Cl^- are 28.7% and 16.4%, respectively. The mineralized degree of groundwater in the zone where Group IV distributes is the highest, which is 1.407 g/L and six times as much as that in the hilly zone. The content proportions of Na^+ and Cl^- are 39.5% and 25.8%, respectively. The chemical type of the groundwater in Group IV sampling zone is HCO_3–Na, which differs from the others. As a whole, the mineralized degree and content proportions of Na^+ Cl^- in groundwater in the plain area horizontally have a tendency of

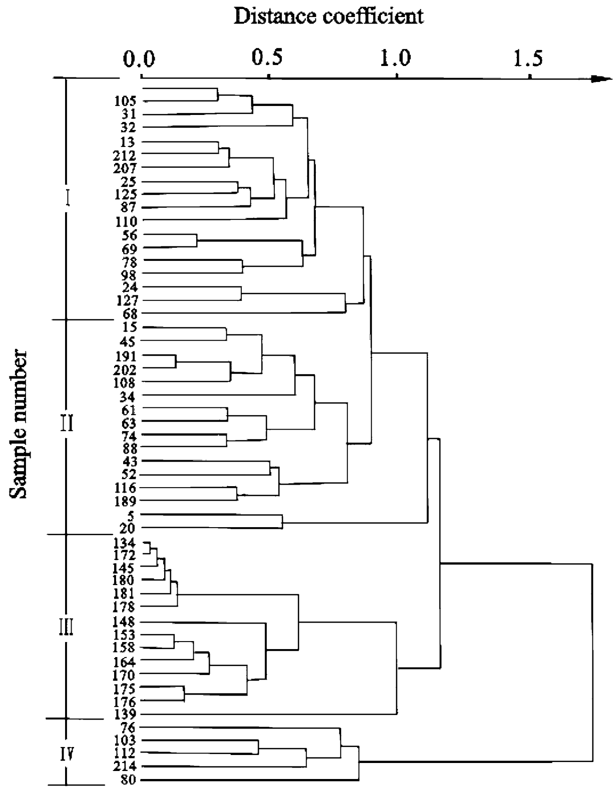

Fig. 5 Q-type clustering analysis diagram

gradually increasing from the southwest to the northeast, which is in accord with the trend of the transgressive strata gradually thickening from the southwest to the northeast, and is just opposite to the direction of paleo-seawater invasion. It indicates that the chemical component of shallow groundwater was influenced directly by the Holocene marine invasion, and the influence intensity was controlled by the invasive degree of paleo-seawater. The mineralized degree and content proportions of Na^+, Cl^- in the shallow groundwater distributed in Group I zone are not only lower than those distributed in Group I zone, but also lower than the average mineralized degree (M = 0.71 g/L) and average content proportions of Na^+ Cl^- in the whole plain area, which has certain relation with the exchange reaction between ground water and surface water (Langmuir 1997). The samples of Group II distribute along the Grand Canal. From the correlation diagrams of the major ionic proportions between groundwater and seawater (Fig. 7), it can be seen that the ionic proportions of Group I and IV are more close to seawater than those of Group II, and the samples of Group III are different from potable groundwater. This also confirms that the results of Q-type clustering analysis manifest the degree of the transgressive strata effect on the chemical components of the shallow groundwater of Hangzhou.

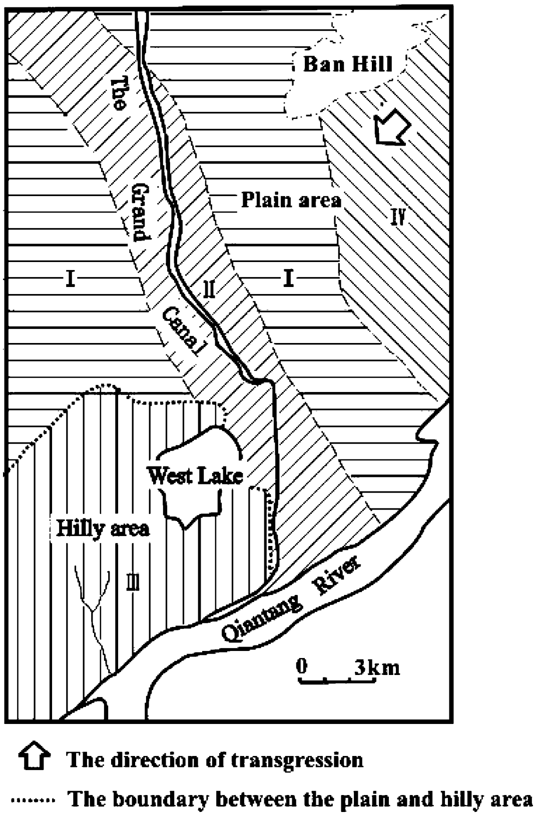

Fig. 6 The distribution of the clustering sampling spot

Factor analysis

To understand each ion effect on the chemical compositions of water, R-type factor analysis was conducted by selecting 14 variables in 53 samples which are Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, HCO_3^-, NO_3^-, H (hardness), SiO_2, M (mineralized degree), pH, Fe and Mn. In general, when the accumulative contribution rate of the chief factors is beyond 80%, over 80% of the entire primitive information will be revealed. Table 4 shows the chief factors carrying matrix, which shows that the variance accumulative contribution percentage of seven factors is 82.26. Table 4 reveals the hydrogeochemical information of the survey area. To get a simplified structure, the maximal variance is rotated and the characteristic coefficients of absolute values smaller than 0.3 are discarded. Finally, and the maximal variance factor solutions are obtained and are presented in Table 5. As is shown in the table, the first chief factor F_1 including Na^+, Cl^-, Ca^{2+}, Mg^{2+}, SO_4^{2-} and HCO_3^- constitute a chief factor solution. The factor F_1 is 33.8% of the gross variance contribution and is the dominant factor controlling the groundwater chemical components. This reveals that the chemical components of groundwater come mainly from lixiviation of the hydrous viscose layer. The characteristic coefficient of HCO_3^- in the chief factor F_1 is 0.90, which indicates that the main supply source of groundwater is precipitation that has a crucial effect on the chemical type of groundwater. Moreover, the characteristic coefficients of Na^+, Cl^- are relatively high, 0.886 and 0.866, respectively, which indicates once more that the Holocene transgressions has an obvious impact on the formation of the groundwater chemical compositions.

Experiments of simulation

Clay minerals in sediments have certain sensitivity to and are indicative of the environment. The analytical results of XRD (Fig. 8) and the infrared spectrum (Fig. 9) show that the clay minerals of the Quaternary sediments in the plain area consist of illite, kaolinite, chlorite, montmorillonite and some mixed texture of chlorite-montmorillonite. The semi-quantitative analyses of the clay minerals prove that the clay components in the studied area are in accord with the sediments collected from the shelf of East China Sea (Shi and Li 1982). It indicates that the Quaternary sedimentary geochemical environment and the material sources of marine sediments are similar to those of the modern shelf of East China Sea.

The lixiviants used in the experiments were collected from the native precipitate water and the seawater of East China Sea. The reasons for selecting them are, on the one hand, the precipitate water being the chief supply of shallow groundwater; and on the other hand, the

Table 3 The average contents of major ions in various sample groups (mg/ L)

Sample group	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-	Chemical type
I	74.73	11.68	102.20	42.48	113.48	160.09	302.44	$HCO_3–CaM_{0.807}\frac{HCO^{3}_{51.4}SO^{4}_{23.4}Cl_{19.7}}{Ca_{44.2}Na_{32.3}Mg_{18.4}[K_{5.1}]}$
II	49.84	22.95	82.63	17.95	64.34	91.64	237.39	$HCO_3–CaM_{0.566}\frac{HCO^{3}_{60.3}SO^{4}_{23.3}Cl_{16.4}}{Ca_{47.7}Na_{28.7}K_{13.2}Mg_{10.4}}$
III	6.74	1.74	50.45	2.68	9.23	13.71	145.89	$HCO_3–CaM_{0.23}\frac{HCO^{3}_{86.4}SO^{4}_{8.1}Cl_{5.5}}{Ca_{81.9}Na_{10.9}[K_{2.8}Mg_{4.3}]}$
IV	156.92	16.0	147.3	77.24	260.24	192.0	557.34	$HCO_3–NaM_{1.407}\frac{HCO^{3}_{55.2}Cl_{25.8}SO^{4}_{14.9}}{Na_{39.5}Ca_{37.1}Mg_{19.4}[K_{4.0}]}$

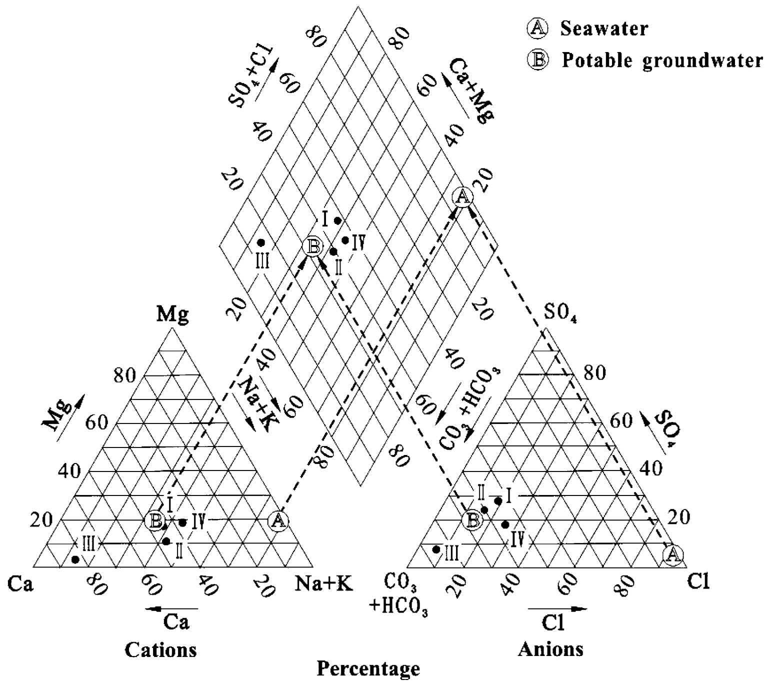

Fig. 7 Chemical analyses of water represented as percentages of total equivalents per liter on the diagram developed by Hill (1940) and Piper (1944) N—native dry slice; E—ethylene glycol saturated slice; H—heated slice

Holocene invasive marine water played an important role in forming the groundwater chemistry of the shallow aquifers. The primordial chemical components of the two lixiviants are listed in Table 6.

The lixiviation experiments were conducted under hermetical sealed conditions. The results are listed in Table 7. It can be seen from Table 7 that the main ions, except Ca^{2+}, in the seawater lixivium have distinctly decreased, whereas in the precipitate water they have increased, and the contents of iron and manganese in both, obviously, increased. The experimental results show that the Holocene transgressive aquifers really have the ability to obtain the ions of Na^{+}, Ca^{2+}, etc. from seawater, and the percolated precipitation and surface water have the ability to obtain Na^{+}, Ca^{2+} and iron and manganese ions from hydrous viscose layer as well. In the process of material exchange, the clay minerals played an important role in the cation exchange reaction. Various clay minerals have a different capacity of cation exchange. Because the main clay mineral in the sediments of the aquifer is illite, the sediments have a large exchange capacity (Langmuir 1997). During marine transgression, Na^{+} in the seawater entered into clay minerals and Ca^{2+} entered into the seawater. During marine regression, precipitation and surface water percolated into the shallow aquifers, and Ca^{2+} in the

Table 4 Initial factor carrying matrix

	F_1	F_2	F_3	F_4	F_5	F_6	F_7
Na^{+}	0.828	−0.158	−0.057	−0.232	−0.047	−0.085	−0.226
K^{+}	0.285	0.564	−0.032	−0.353	−0.027	0.383	0.467
Ca^{2+}	0.779	0.073	−0.138	−0.068	−0.117	0.087	−0.006
Mg^{2+}	0.760	−0.025	0.075	0.442	−0.097	−0.129	0.180
Cl^{-}	0.869	−0.124	−0.047	−0.120	−0.073	−0.036	−0.273
SO_4^{2-}	0.713	0.188	−0.291	−0.066	0.100	−0.054	0.055
HCO_3^{-}	0.809	−0.298	0.049	−0.232	−0.302	−0.051	−0.025
NO_3^{-}	−0.044	0.664	−0.279	−0.211	−0.303	−0.192	−0.019
H	0.754	0.185	0.141	0.386	0.122	0.101	0.170
SiO_2	0.161	0.436	0.489	−0.340	0.424	0.194	−0.385
M	0.396	0.422	0.100	0.470	0.383	−0.164	−0.080
pH	0.145	−0.388	−0.507	0.111	0.297	0.604	−0.069
Fe	0.144	−0.274	−0.233	−0.390	0.623	−0.440	0.294
Mn	0.268	−0.393	0.693	−0.158	−0.035	0.104	0.277
Variance contribution	4.737	1.712	1.257	1.170	1.043	0.865	0.732
Accumulative percentage (%)	33.84	46.07	55.04	63.40	70.85	77.03	82.26

H total hardness; M mineralized degree

Table 5 Variance maximal factor solutions

	F_1	F_2	F_3	F_4	F_5	F_6	F_7
Na^+	0.886						0.910
K^+							
Ca^{2+}	0.612						
Mg^{2+}	0.515			0.757			
Cl^-	0.866						
SO_4^{2-}	0.437						
HCO_3^-	0.900						
NO_3^-			−0.758				0.379
H	0.369			0.796			
SiO_2		0.950					
M				0.748			
pH						0.964	
Fe					0.985		
Mn			0.801				
Characteristic value	4.737	1.712	1.257	1.170	1.043	0.865	0.732
Accumulative percentage (%)	33.84	46.07	55.04	63.40	70.85	77.03	82.26

H total hardness; M mineralized degree

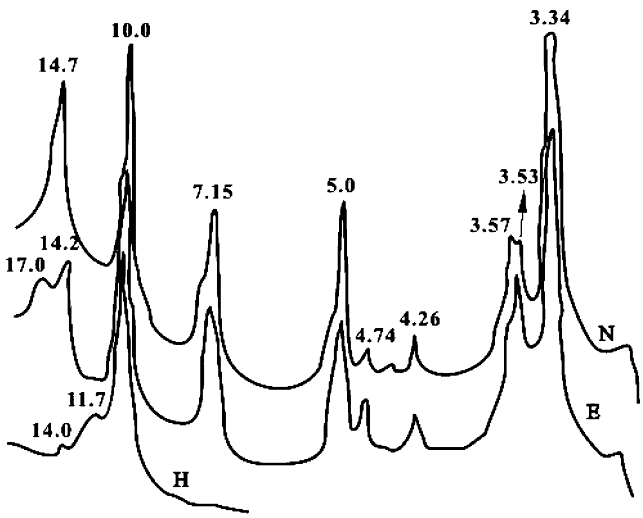

Fig. 8 The X-diffraction diagram of sample T_7 (littoral grey–green clayey)

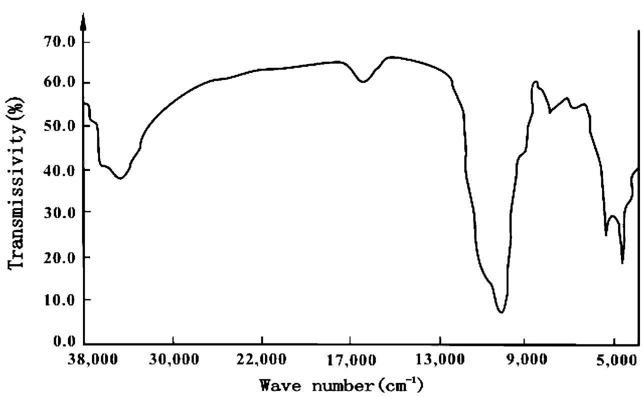

Fig. 9 The infrared spectral diagram of sample T_7 (littoral grey–green clayey)

permeated water exchanged with Na^+ retained in the marine sediments, so that the content of Na^+ in groundwater increased. The processes mentioned above can be formulated as follows:

$$[\mathrm{Clay}-2\mathrm{Na}^+]+\mathrm{Ca}^{2+}\underset{\text{Regression}}{\overset{\text{Transgression}}{\rightleftharpoons}}[\mathrm{Clay}-2\mathrm{Ca}^{2+}]+2\mathrm{Na}^+$$

The results of the simulant lixiviation experiments throw light on the reversible processes. Moreover, a portion of iron and manganese can be absorbed by marine sediments due to clay minerals having strong absorbability, and deposited in the transitional zone with the oxidation state. Once the sediments are buried underground, the iron and manganese oxides were partially reduced in the reducing environment and entered into the groundwater, along with the iron and manganese absorbed re-released into the water, thus the contents of iron and manganese obviously increased in the subsurface water.

Summary

The Holocene transgressions play an important role in the formation of chemical composition of shallow groundwater in Hangzhou, China. The transgressive sediments still contain primitive marine components, especially retaining an amount of chloride and sulfate with high solubility, and some iron, manganese substances formed in the sea–land alternate zone. When they became part of the aquifers and contacted directly the percolated precipitate and surface water, these substances might have entered into groundwater through lixiviation. Hence, the groundwater in the studied area has characteristics of high-mineralized degree, high contents of Na^+, Cl^-, iron and manganese.

Table 6 The primitive contents of major ions in seawater and precipitate water(mg/L)

Sample	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2+}	HCO_3^-	Mn	Fe
Seawater	6,820.0	330.0	287.0	902.4	12,988.8	1,800.0	112.9	< 0.01	< 0.01
Precipitate water	0.8	0.5	–	3.7	–	–	17.6	< 0.01	< 0.01

Table 7 The content change of some components in the lixivium (mg/L)

Lixiviant	Sample number	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-	Mn	Fe
Seawater	T_7	−460.0	−35.0	+95.7	−55.4	−925.0	0	−3.6	+0.44	+0.12
	T_8	−560.0	−46.0	+247.9	−118.7	−977.1	−100.0	+31.7		
Precipitate water	T_7	+10.6	+6.1	+14.8	0	+8.9	+30.0	+31.8	+0.18	+9.62
	T_8	+12.3	+1.7	+14.8	+12.7	+6.8	+70.0	+52.9		

+, − , respectively, for higher or lower than the contents of the primitive water. The major ions were determined after lixiviating for 20 days; the values of Mn and Fe were the average content of seven samples after lixiviating for 6 days

Groundwater, as a constituent part of the hydrosphere, participates in the circulating movements of water. Precipitate water is a supply source to phreatic water and can dilute the composition of groundwater as well. Although dilution has gradually attenuated the effect of marine substances on groundwater, so far the chemical compositions and types of shallow groundwater of Hangzhou still maintain the marine feature. Therefore, before serving as drinking or industrial water, the groundwater has to be treated. When the groundwater resources in the study areas are exploited, it should be done in a proper way; and should not be mixed with other groundwater to avoid affecting other high-quality groundwater resources.

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