Elevated iron and manganese concentrations in groundwater derived from the Holocene transgression in the Hang-Jia-Hu Plain, China

Huan-Xin Weng · Ya-Chao Qin · Xun-Hong Chen

Abstract Groundwater in the Hang-Jia-Hu Plain, eastern China, is a drinking water source for local residents. Groundwater samples were collected from large-diameter hand-dug wells and boreholes for comparison of their iron and manganese concentrations, as well as other ions. The results show that iron and manganese concentrations are relatively high, exceeding drinking water standards by several times. Aquifer sediment samples contain abundant iron (30,790 mg kg^{-1}) and manganese (602 mg kg^{-1}). The results of correspondence factor analysis of the hydrochemistry data and the liberation experiments (using seawater and rainwater as leachants) suggest that iron and manganese in shallow groundwater come from the sediment in the Holocene aquifer. A reductive environment involving relatively high total dissolved solids and organic carbon in the aquifer system is favorable to iron and manganese transferring from the sediment to groundwater and stabilizes these ions. Shallow, large-diameter hand-dug wells provide oxic conditions that decrease the concentrations of dissolved iron and manganese in the well water.

Résumé Dans la Plaine de Hang-Jia-Hu, à l'Est de la Chine, les eaux souterraines constituent une ressource en eau potable pour les autochtones. Des échantillons d'eau souterraine ont été prélevés dans des puits de large diamètre creusés manuellement et dans des forages, afin de confronter leurs concentrations en fer, manganèse et autres ions. Les résultats montrent des concentrations en fer et manganèse relativement hautes, souvent au-delà des limites de potabilité. Les échantillons de sédiments de l'aquifère contiennent des quantités abondantes de fer (30,790 mg kg^{-1}) et de manganèse (602 mg kg^{-1}). Les résultats de l'analyse factorielle de correspondance des données hydrochimiques et des tests de libération (utilisant l'eau de mer et l'eau de pluie comme vecteurs) suggèrent que le fer et le manganèse contenus dans les aquifères superficiels proviennent des sédiments de l'aquifère holocène. Un environnement réducteur, impliquant une quantité élevée de solides dissous et de carbone organique dans le système aquifère, est favorable à un transfert du fer et du manganèse depuis les sédiments vers les eaux souterraines, et stabilise les ions considérés. Les puits peu profonds, de large diamètre et creusés à la main créent des conditions oxydantes qui abaissent les concentrations en fer et manganèse dissous dans l'eau du puits.

Resumen El agua subterránea en la Llanura de Hang-Jia-Hu, al este de China, es una fuente de agua potable para los residentes locales. Las muestras de agua subterránea fueron recogidas en pozos de gran diámetro excavados a mano y en pozos barrenados con el objeto de comparar las concentraciones de hierro y manganeso, y también las de otros iones. Los resultados muestran que las concentraciones de hierro y manganeso son relativamente altas, excediendo varias veces los límites para agua potable. Las muestras de sedimentos tomadas del acuífero contienen abundante hierro (30,790 mg kg^{-1}) y manganeso (602 mg kg^{-1}). Los resultados del análisis de correspondencia de los datos hidroquímicos y experimentos de liberación (usando agua de mar y agua de lluvia como lixiviantes) sugieren que los iones hierro y manganeso en las aguas subterráneas someras provienen de los sedimentos acuíferos del Holoceno. Un ambiente reductor que contiene relativamente alta cantidad de sólidos totales disueltos y carbono orgánico en el sistema acuífero es favorable para la transferencia de hierro y manganeso desde los sedimentos al agua subterránea y para estabilizar estos iones. Los pozos poco profundos, de gran diámetro, excavados a mano, suministran condiciones de oxidación que disminuyen las concentraciones de hierro y manganeso disueltos en el agua del pozo.

Keywords Hydrochemistry · Iron/manganese liberation experiments · Holocene transgression · Correspondence factor analysis · China

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Introduction

The Hang-Jia-Hu Plain is one of the most rapidly developing economic areas in eastern China. With population expansion and modern industry development, the demand on the quantity and the quality of groundwater resources has significantly increased over the last two decades. The Quaternary sediment of the Hang-Jia-Hu Plain, China (Fig. 1), constitutes the principal aquifer that serves as a drinking water source for local residents. However, groundwater chemistry measurements indicate that the iron and manganese concentrations in the groundwater are relatively high and often exceed the national standard for drinking water in China (BGECSP 1991). While Fe and Mn are essential for both plants and animal life forms (Hem 1989), their presence in excessive amounts forms red and black stains. The national secondary drinking water regulations of the US Environmental Protection Agency list a standard of 0.3 mg L^{-1} for Fe and 0.05 mg L^{-1} for Mn (EPA 2006). The Fe standard for water is generally not a concern for health reasons; rather, concern relates to its appearance aesthetically and its staining of plumbing fixtures; Mn is rarely found in a water source alone, but it is generally found in conjunction with dissolved iron. A concentration as high as 0.1 mg L^{-1} of Mn is considered troublesome (Edstrom Industries 2003). According to the report by Brown et al. (1999), a high concentration of dissolved Fe (>0.5 mg L^{-1}) in groundwater leads to fouling in public supply wells, for which treatment and remediation are difficult. High concentrations of Fe and Mn in drinking water are also considered harmful to human health over a long time (Liap 1992). Fe concentration up to 2–3 mg L^{-1} in drinking water might pose a problem for individuals who suffer Fe storage disease (hemochromatosis; Donohue et al. 2004). Numerous methods have been developed to remove Fe and Mn in water supply systems. Fan (1988) reported that the Vyredox method was used in numerous waterworks of Chinese cities to partially remove Fe from groundwater.

Commonly, only low concentrations of Fe or Mn are present in surface water because an oxygen-rich atmosphere enables them to precipitate and become subjected to sorption by suspended particles (Lemley et al. 1999). Fe and Mn concentrations present in groundwater generally vary from place to place. Water penetrating through soil and sediment dissolves Fe and Mn ions, carrying them into the saturated zone. According to the studies of Hem (1989) and Brown et al. (1999), the redox condition and pH are critical factors that dominate the migration of Fe and Mn into groundwater.

The objective of this study is to identify the origin of the high concentrations of Fe and Mn in the groundwater for a study area in the Hang-Jia-Hu Plain (Fig. 1). Groundwater samples were collected from large-diameter dug-wells and boreholes for chemical analysis; surface water samples from the Grand Canal and rainwater samples were also analyzed for a comparison. Sediment samples were retrieved from several bore cores for the analysis of Fe and Mn as well as the general mineral composition. Correspondence factor analysis (CFA) was used to determine the oxidation-reduction conditions of the water, which are related to the concentrations of Fe and Mn. This work provides important information for effective protection and rational utilization of the groundwater resources in this area.

Hydrology in the study area

The study area, 23.7 km long and 2 km wide, is situated in the north of Hangzhou City, which represents a small portion of the Hang-Jia-Hu Plain, China (Fig. 1). This area is located in a subtropical zone with a warm and wet climate. The average annual precipitation and potential evaporation are 1,398.8 and 1,309.6 mm, respectively. Geographically, the study area lies in the south of the Hang-Jia-Hu Plain, where the ground surface is relatively flat and its elevation is only several meters above the mean sea level. Numerous rivers and lakes in the surrounding areas form a complex river network. The Grand Canal, connecting Beijing and Hangzhou with a total length of 1,794 km, flows from south to north within the study area. The building of the canal began in 486 BC during the Wu Dynasty. It was extended during the Qi Dynasty, and later by Emperor Yangdi of Sui Dynasty during 6 years of furious construction from AD 605–610. It is generally regarded as the oldest and longest man-made canal in the world.

The study area is covered with a layer of Quaternary Holocene deposits (Q_4). Based on the depositional environments, this layer is divided into three units. The middle (Q_4^{1-2}) and upper (Q_4^3) units are explored as part of this study, with a total depth of less than 30 m (Fig. 2). They were deposited in fluvial-marine and limnic environments. The sediment consists of clays and fine-grained sands. The two units form an important aquifer for drinking water, fulfilling residential and industrial needs. The lower unit of the Holocene is composed of marine clays, acting as an impermeable layer.

Depth to the water table is small and generally varies from 1 to 3 m. The horizontal hydraulic conductivity, determined using permeameter tests in the laboratory, is between 2.2×10^{-8} and 2.0×10^{-5} cm s^{-1}, and the vertical hydraulic conductivity ranges from 1.5×10^{-8} to 9.4×10^{-4} cm s^{-1}. The chemical type of the groundwater mainly is HCO_3–Ca, and secondly is HCO_3–Na. Aquifer recharge is primarily through precipitation. The regional hydraulic gradient of the water table is less than 1:1000. Given the low hydraulic conductivity and a relatively flat hydraulic gradient, the average groundwater velocity is slow. Evaporation, plant transpiration, and groundwater withdrawal are the main pathways discharging groundwater.

There are numerous domestic wells owned by villagers in the study area. They were hand-dug and often have a long history. The diameter of the wells is usually greater than one meter. Rocks and stone blocks are the main materials for making the circular wall of these wells.

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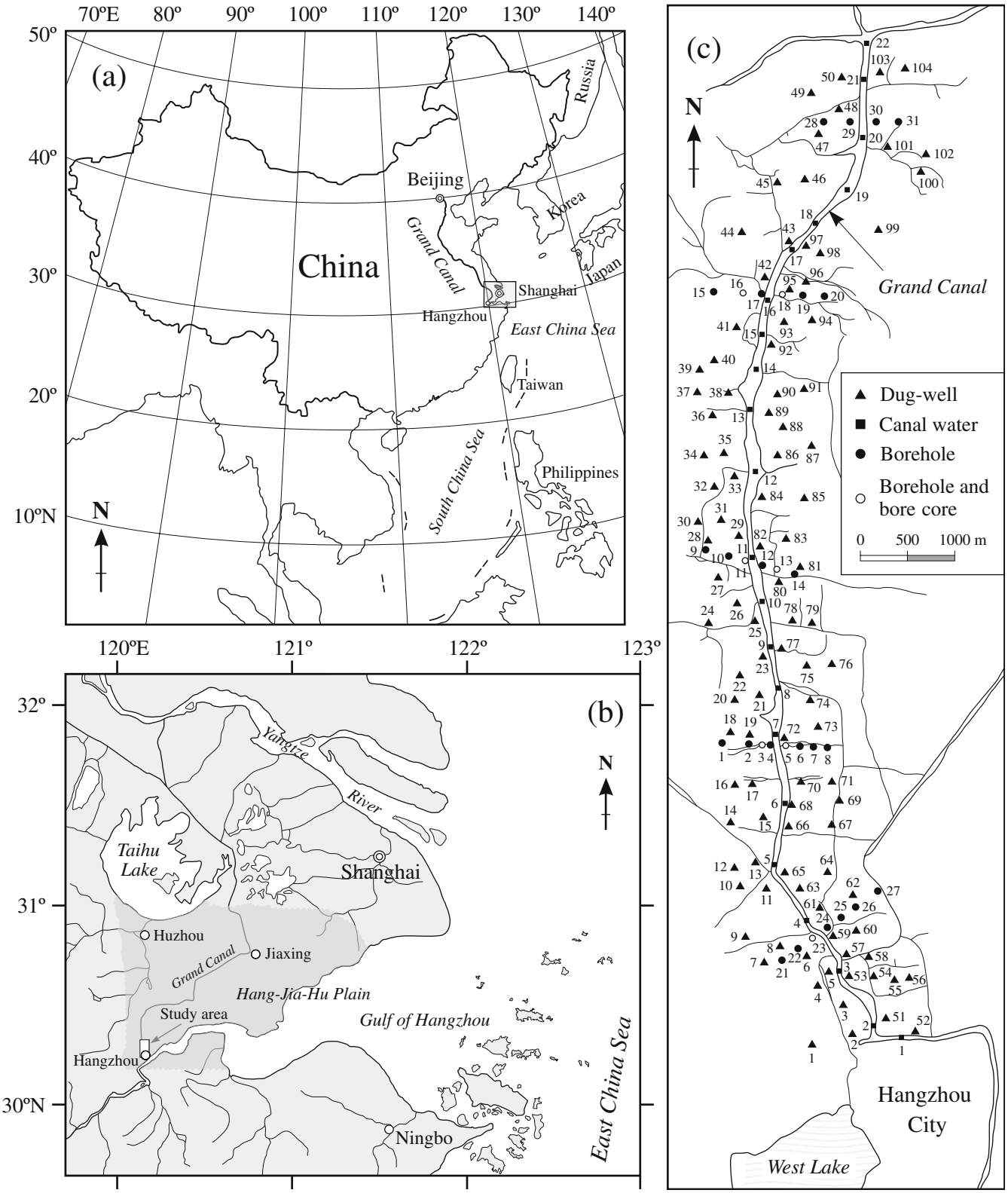

Fig. 1 **a** Map of China, showing the Grand Canal from Beijing to Hangzhou; **b** the location of the study area situated in the south of the Hang-Jia-Hu Plain; **c** the sampling locations along the Grand Canal

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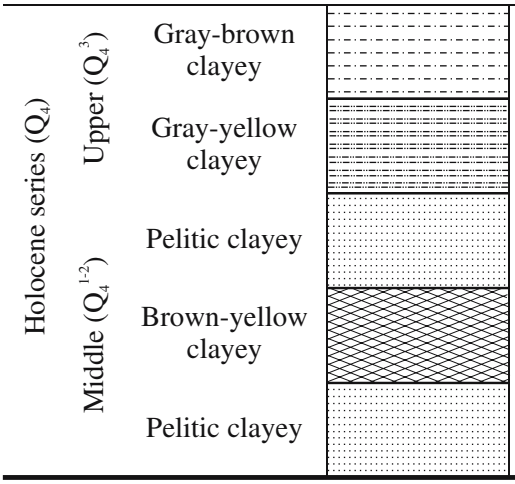

Fig. 2 Stratigraphic profile of the middle and upper Holocene Series in the study area

These wells are often open to the atmosphere. Local residents withdraw water from them for domestic uses. The depth of the wells ranges from 2 to 10 m.

Study methods

Sampling and analyses

In the study area, 104 groundwater samples were collected from large-diameter dug-wells and 31 groundwater samples were retrieved from boreholes. These sampling sites are evenly distributed either side of the Grand Canal and within a 1-km band width. In addition to measurements of Fe and Mn concentrations, concentrations of Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+, Cl^-, SO_4^{2-}, HCO_3^-, CO_3^{2-}, NO_2^-, and NO_3^-, pH value, total dissolved solids (TDS), and chemical oxygen demand (COD) were also determined (pH was measured in situ).

To understand the effect of the aquifer materials and the ambient conditions on the groundwater chemistry, seven sediment samples were retrieved from bore cores in the aquifer and 22 surface water samples were taken from the Grand Canal. A sequential extraction procedure proposed by Tessier et al. (1979) was adopted to separate the speciation of Fe and Mn in the sediment into five fractions: exchangeable (I), bound to carbonates (II), bound to Fe-Mn oxides (III), bound to organics (IV), and residual (V). The clay mineral and organic carbon contents were also determined.

The concentrations of Na, K, Ca, Mg, total Fe (TFe), and total Mn (TMn) were determined by atomic absorption spectrometry (AAS). Their detection limits are 0.01 mg L^{-1} Na, 0.05 mg L^{-1} K, 0.05 mg L^{-1} Ca, 0.02 mg L^{-1} Mg, 0.01 mg L^{-1} Fe, and 0.01 mg L^{-1} Mn, respectively. Fe^{2+} and Fe^{3+} were measured sequentially by 1,10-phenanthroline spectrophotometry with a detection limit of 0.05 mg L^{-1} in a 50-ml water sample (BGECSP 1997). Chloride was determined using argentometric (Mohr's) method, where the minimum aliquot to be titrated must contain above 0.1 mg Cl (Philbert 1982). Sulfate was measured using a turbidimetric method with a detection limit of 1 mg L^{-1} (BGECSP 1997). Ammonium, nitrite, and nitrate were analyzed using spectrophotometric methods, where the minimum aliquots to be detected must contain above 1 μg N, 0.165 μg N, and 2.5 μg N, respectively (BGECSP 1997). Bicarbonate and carbonate were measured by acid-base titration (BGECSP 1997). Total hardness was calculated from the individual hardness-causing cations that have already been determined by AAS (Philbert 1982). Procedural blanks and replicate samples were also analyzed in a similar way to check the accuracy of analysis. Analytical errors were <5%.

Table 1 Fe and Mn concentrations in the groundwater (mg L^{-1}) and their exceedance relative to the US EPA secondary standards for drinking water (EPA 2006)

Element	Sample type	No. of samples	Conc. range	Mean	Distribution type	Over-standard[a]		
						No. of samples	Rate (%)	Max. ratio
Fe	Dug-well	104	0–8.0	0.9	Skewed normal	59	67.8	25.7
	Borehole	31	0–12.0	4.2	Normal	30	97	39.0
Mn	Dug-well	104	0.03–3.87	0.44	Skewed normal	56	59.6	37.7
	Borehole	30	0.002–4.69	0.95	Normal	24	80.0	45.9

[a] Drinking water secondary standard for Fe is 0.3 mg L^{-1}, and for Mn is 0.05 mg L^{-1}

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Table 2 Vertical variations of Fe and Mn concentrations in the groundwater (mg L^{-1})

	Depth (m bgl)	Fe^{2+}	Fe^{3+}	Mn^{2+}	pH
Borehole water	0–3.5	3.10	1.11	0.95	6.75
	3.5–15.0	3.99	2.55	1.36	6.78
Dug-well water	0.0	0.50	0.70	2.15	6.60
	3.5	1.20	1.00	2.13	6.70
	8.0	2.50	4.00	2.93	6.75

Fe and Mn liberation experiments

Liberation experiments were performed to evaluate the relationship between the Fe and Mn concentrations in the groundwater and the groundwater chemistry represented by redox, organic matter, and TDS. The experimental procedure was as follows: 250 g of freeze-dried sediment collected from the bore core were homogenized with 1-L leachant and placed into a 1-L capped glass bottle. The change in dissolved Fe and Mn concentrations was monitored by subsampling the container at appropriate time intervals of 2, 4, 8, 16, 32, and 48 h, respectively. Rainwater and seawater collected from the East China Sea were chosen as leachants, as the former is the main source that recharges the groundwater system and the impact of marine water invasion during the Holocene remains evident in the chemical components of the groundwater, though not as remarkable as thousands of years ago; according to the local chronology, 2,500 years ago the shallow groundwater was brackish and was unfit for drinking. As a result of long-term leaching by precipitation, the impact of marine invasion has been reduced.

Correspondence factor analysis

Correspondence factor analysis (e.g., Greenacre 1983, 1993) was conducted for 10 variables of the 27 borehole water samples, including Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}, Cl^{-}, SO_4^{2-}, HCO_3^{-}, TDS, total hardness, and pH, so that variables and samples can be projected on one factorial map for classification and interpretation. CFA is a graphic multivariate technique that provides objective distribution maps of the data after reduction and filtering of redundant information and noise. The key to the analysis of very complex data tables is the formation of barycenters into correspondence analysis used as mathematical models. This is possible in CFA because the method uses χ^2-metrics and is based on the distributional equivalence of the rows and columns of the transformed data matrix. A good reason for choosing CFA for the hydrochemistry analysis is that it considers the two fields formed by the rows of variables and columns of samples in a totally symmetrical fashion. In other words, two sets of properties—one set of chemical variables and the other samples—are placed on a par and confronted without having to consider a unidirectional link whereby the chemical types of groundwater are the result of the aquifer environment. In this respect, it can be likened to a two-fold principal component analysis where the samples are classified with respect to the variables and the variables with respect to the samples. This symmetry in CFA has several useful practical consequences (e.g., Greenacre 1983, 1993).

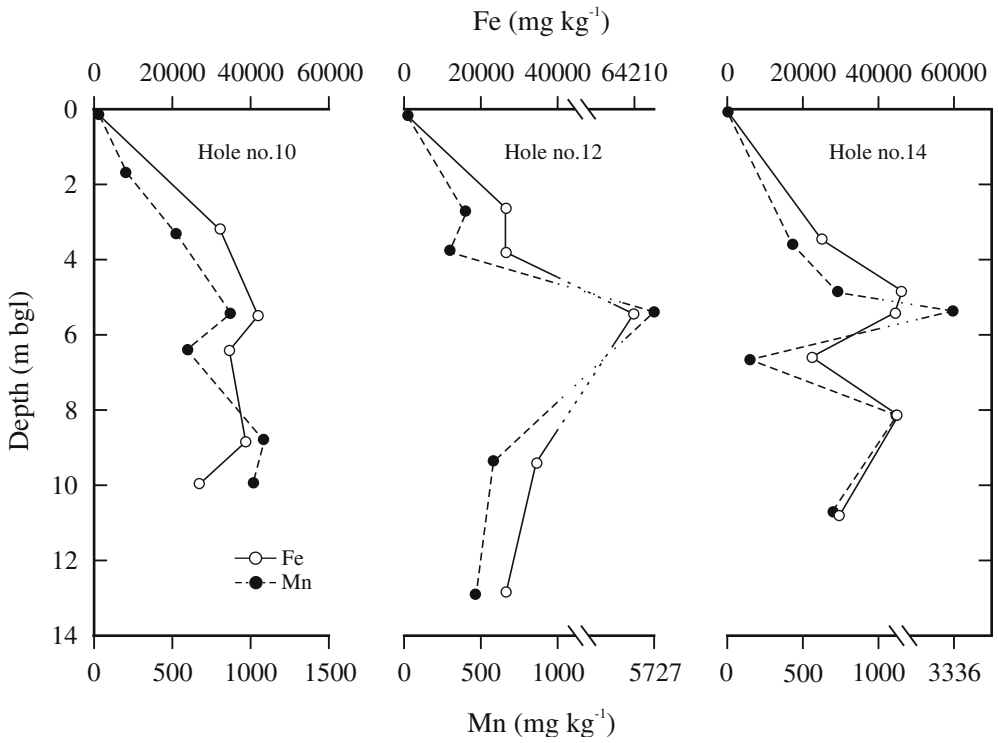

Fig. 3 Vertical variation in the Fe and Mn concentrations in the aquifer sediment

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Table 3 Average concentrations of Fe^{2+}, Fe^{3+}, total iron (TFe), and total manganese (TMn) in the rainwater and the Grand Canal water (mg L^{-1})

	No. of samples	Fe^{2+}	Fe^{3+}	TFe	TMn	pH
Rainwater	9	–[a]	–	–	–	6.40
Canal water	22	1.56	0.32	1.88	0.34	6.95

[a] Dash means below detection limit

Results and discussion

Fe and Mn concentrations in the groundwater

In the study area, the spatial distribution of the Fe and Mn concentrations in groundwater is characterized as follows:

1. As shown in Table 1, the Fe and Mn concentrations in groundwater are relatively high, where 'over-standard' means samples exceeding the secondary standards for drinking water in the USA and 'max. ratio' stands for ratio of the maximum concentration detected versus the secondary standards. The average Fe concentrations are 0.9 and 4.2 mg L^{-1} for dug-well and borehole water, respectively, which are as high as 3 and 14 times the secondary Fe standard for drinking water (0.3 mg L^{-1}; EPA 2006). Similarly, the Mn concentrations average 0.44 and 0.95 mg L^{-1}, for dug wells and boreholes respectively, which are 8.8 and 19 times the secondary Mn standard for drinking water (0.05 mg L^{-1}; EPA 2006). The Fe and Mn concentrations of the borehole water are higher than those of the well water. The percentage in excess of the required standard (over-standard rate) and the maximum ratio are also larger than those of the dug-well water. Their distribution types and their variation ranges in the borehole water are different from those in the dug-well water. The Fe and Mn data show a normal distribution in the borehole water, which indicates a normal material exchange between aquifer and groundwater in boreholes, where the deeper and more restricted water is least affected; whereas for the well-water samples, Fe and Mn distribution is skewed, which implies that the Fe and Mn concentrations have been influenced by local conditions in open wells.

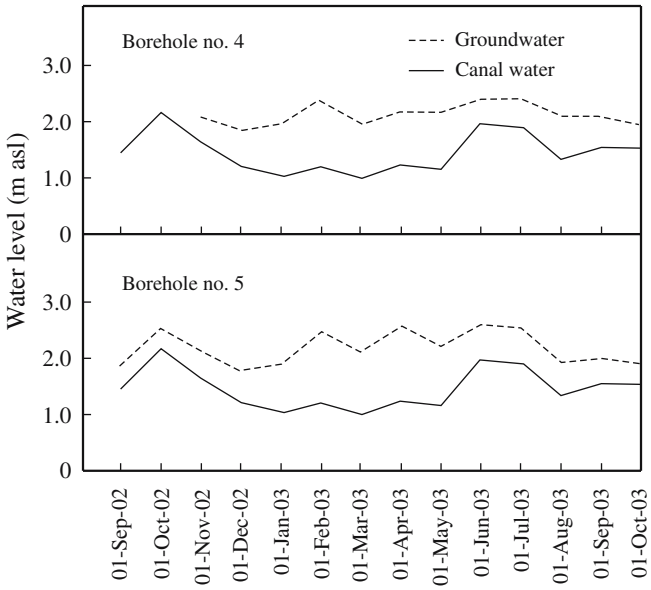

Fig. 5 Phreatic fluctuation in borehole nos. 4 and 5 compared with the canal water level

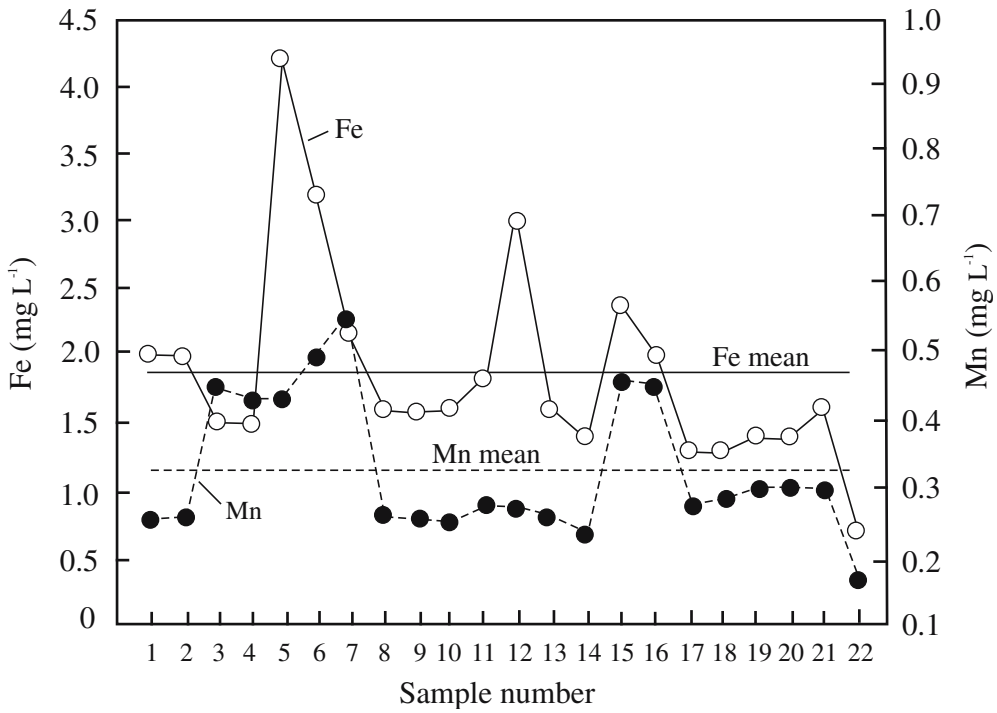

Fig. 4 Variation in Fe and Mn concentrations in the Grand Canal waters. Sampling sites are ascendingly sequenced from south to north

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Table 4 Fe and Mn concentrations in the aquifer sediment (mg kg^{-1}, depth 15 m bgl)

Hole no.	1	4	5	6	10	12	14	15	17	19
Fe	39,360	40,020	26,300	30,570	30,740	34,600	31,290	23,620	30,040	26,880
Mn	600	730	1,000	610	660	630	850	490	480	580

2. Horizontally, the Fe and Mn distributions in the groundwater do not show a spatial trend, but vertically, their concentrations increase with the groundwater depth (meters below ground level: m bgl; Table 2), which corresponds to the vertical variation tendency of the Fe and Mn contents in the sediment (Fig. 3). This result agrees with a study in the Kathmandu Valley of Nepal (Warner et al. 2001).
3. There is certain correlation between Fe and Mn concentrations in groundwater, with a correlation coefficient r=0.86 (the critical value is 0.195, significant at the 0.05 level). It suggests that Fe and Mn have a homologous source in terms of geochemical properties. Furthermore, the Fe and Mn concentrations have an exponential correlation with the TDS of the groundwater (Wu and Weng 1987).

Source of Fe and Mn

As previously stated, precipitation is responsible for recharging the groundwater and the Grand Canal has a potential of interaction with the groundwater system. Samples of rainwater and the Grand Canal water were measured for a comparison, which is summarized in Table 3. Clearly, Fe and Mn were not detected in the precipitation samples. Precipitation is hence unable to supply these ions for the groundwater. However, the Fe and Mn concentrations were high in the canal water, which have been mainly caused by environmental pollution (Wu and Weng 1988). Figure 4 demonstrates that the Fe and Mn concentrations in the canal water tend to decrease from south to north (from left to right in Fig. 4). Although groundwater samples with higher concentrations of Fe and Mn are located closer to the contaminant sources (Wu and Weng 1988), the decreasing trend is not observed horizontally in the groundwater by contrast. Furthermore, the Fe and Mn concentrations between the canal water and the groundwater on both sides of the canal show little correlation, with the correlation coefficients r_{Fe}=−0.09 and r_{Mn}=0.13.

In this area, the average horizontal hydraulic conductivity of the clay sediment is $<10^{-6}$ cm s^{-1}. This low-permeability stratum results in a weak hydraulic connection between the groundwater systems and the canal. The annual water level in the canal within the study area varies from 0.93 to 2.2 meters above the mean sea level (m asl), while the annual groundwater level on both sides of the canal ranges from 1.78 to 2.56 m asl (Weng and Chen 2000). Thus, the adjacent groundwater level is usually higher than that of the Grand Canal, and the variations of the water tables are consistent (Fig. 5). Given the low-permeability layer surrounding the canal and the hydraulic gradient toward the canal, it is hard for Fe and Mn in the canal water to permeate into the adjacent groundwater system.

Groundwater chemistry may be related to aquifer materials (Li and Liu 1989). The analyses of the lithology and paleogeography of the aquifer suggest that the study area was in a transitional depositional environment from fluvial to marine facies. The studies by Sigleo et al. (1982) and Ren and Wang (1981) showed that paralic deposits often have plenty of Fe and Mn substances. Sediment samples from the aquifer contain high concentrations of Fe and Mn, up to 64,210 mg kg^{-1} for Fe and 3,336 mg kg^{-1} for Mn. Table 4 lists the Fe and Mn concentrations in several sediment samples from bore cores, and the average Fe and Mn concentrations are 31,342 and 663 mg kg^{-1}, respectively, which are 2.2 and 4.3 times as much as the background element value of the adjacent basement rock and are similar to the Fe and Mn concentrations in the sediment from the modern East China Sea (Shi and Li 1982). The average ratio of Fe to Mn in the sediment from the bore cores is near 50.

Each species of Fe and Mn was separated and their distribution is shown in Fig. 6. It can be seen that the active component for Fe, involving exchangeable Fe (I) and Fe bound to carbonates (II) accounts for a minor portion; the main Fe species is the residual fraction (V)

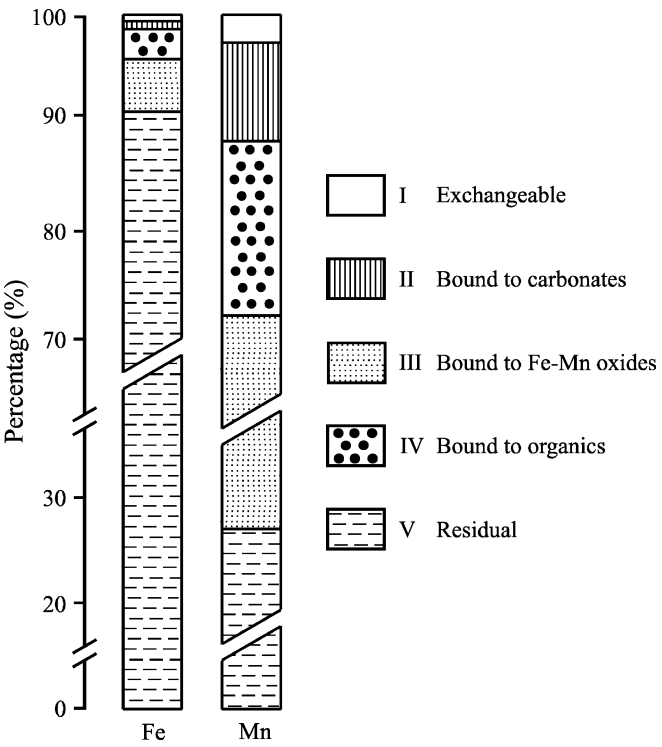

Fig. 6 Fe and Mn speciation distribution in the aquifer sediment

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Table 5 Compositions of the seawater and the rainwater (mg L^{-1})

	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-	Mn	Fe	pH
Seawater	6820.0	330.0	287.0	902.4	12,988.8	1,800.0	112.9	<0.01	<0.01	8.30
Rainwater	0.8	0.5	4.2	3.7	<1	4.3	17.6	–[a]	–	6.40

[a] Dash means below detection limit

and is over 90%. The distribution sequence of each species is ranked as Fe_V>Fe_{III}>Fe_{IV}>Fe_{II}>Fe_I. In contrast, the active component for Mn is a relatively major component, implying that it has a stronger mobility than iron, and the distribution sequence is Mn_{III}>Mn_V>Mn_{IV}>Mn_{II}>Mn_I. The infrared spectrograms and the differential thermal curves of clay minerals from the aquifer indicate that the clay minerals in the aquifer mainly belong to the smectite family (Wu and Weng 1987). These Fe-bearing clays have a relatively strong ability to adsorb cations such as Fe and Mn.

The composition of the seawater and rainwater used as leachants are given in Table 5. Figure 7 demonstrates the liberation of Fe and Mn from the aquifer sediment as a function of time. Since these two types of leachants have different chemical properties, the Fe and Mn release, as well as the chemical types of the extractives, are different. After leaching for 48 h, the rainwater turned from HCO_3–Ca–Mg type to HCO_3–SO_4–Ca and Cl–HCO_3–Na types, whereas the seawater remained in the typical Cl–Ca type. It can be seen from Fig. 7 that the Fe release rapidly reached its maximum and then declined as the leaching continued, for both extractives. After 48 h, the Fe concentrations in the extractives came to the same level. Moreover, the Fe liberated from the aquifer sediment was larger overall using rainwater compared with seawater.

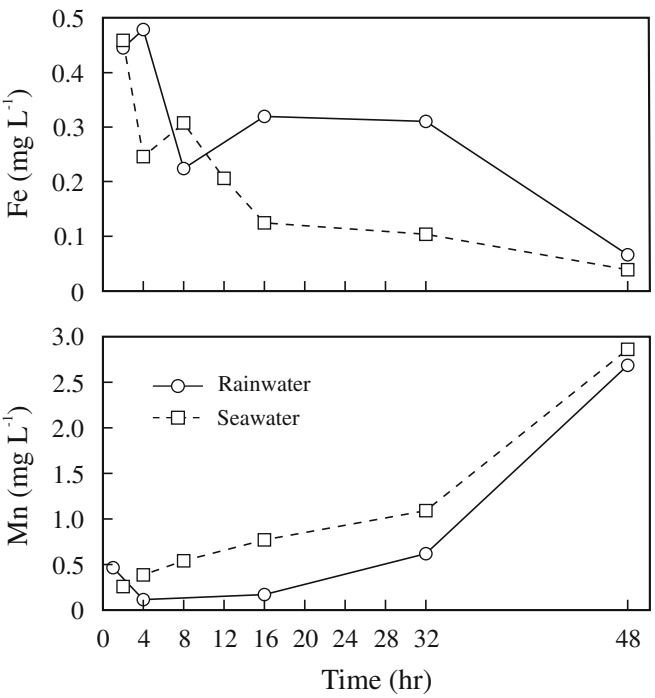

Fig. 7 Variation in Fe and Mn concentrations as a function of leaching time during the liberation experiments

The Mn concentration increased in the extractives as leaching continued. After leaching for 48 h, it seemed that Mn was still being liberated from the aquifer sediment. Although the Fe concentration in the sediment is about 50 times as high as Mn (see Table 4), the active pools of Fe account for only several percent compared with that of Mn, so when water permeates through the aquifer materials, Mn is more subjected to release than iron. As a result, the Fe concentration in the groundwater is only five times more than that of Mn.

Effects of groundwater chemistry on the elevated Fe and Mn

Effect of redox condition

Fe and Mn are both transition metal elements, which have specific stable ranges of pH-Eh in aqueous solution, so the redox condition of groundwater exerts an obvious influence on Fe and Mn behavior. Also, the chemical behavior of Fe and its solubility in water are strongly dependent on the depth of oxygen penetration as well as pH (Hem 1989).

The presence of transition elements in specific form may be used to identify the redox character in the ambient environment (Zhao and Zhang 1988). Hence, variation in the forms of Fe in groundwater can be used to judge whether the environment is oxidative or reductive. The analytical data of groundwater samples from 31 boreholes

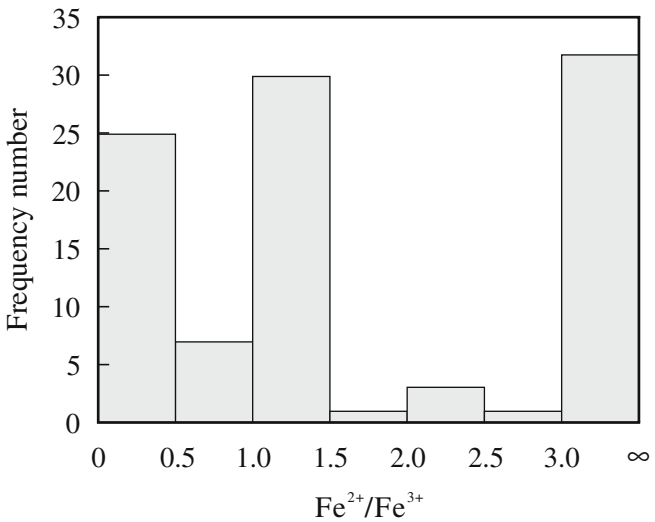

Fig. 8 Frequency histogram of the Fe^{2+}/Fe^{3+} ratio. If Fe^{2+} concentration is below its detection limit, the sum of these samples is counted in the ratio interval of (0, 0.5); similarly, if Fe^{3+} concentration is below its detection limit, the sum of these samples is counted in the interval of (3.0, ∞)

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Table 6 Principal reductive substances in the groundwater

	Dug-well water				Borehole water			
	Fe^{2+}	Mn^{2+}	NH_4^+	NO_2^-	Fe^{2+}	Mn^{2+}	NH_4^+	NO_2^-
No. of samples	104	104	104	104	31	30	27	27
No. of detected samples	71	93	57	77	25	30	17	26
Detected rate (%)	68	89	55	74	81	100	63	96
Average conc. (mg L^{-1})	0.33	0.44	0.55	0.54	3.70	0.95	0.42	0.41

show that Fe^{2+} concentration is higher than that of Fe^{3+}. The Fe^{2+}/Fe^{3+} ratio varies from 1 to 15, indicating that the redox condition of the borehole water ranges from mildly reductive to reductive. The Fe^{2+}/Fe^{3+} ratio histogram of 104 well-water samples shown in Fig. 8 suggests that the well water is in transition from mildly reductive to mildly oxidative. Moreover, the presence of reducing substances, such as NO_2^- and NH_4^+ (Table 6) that commonly occur in groundwater, also reveals the reductive inclination.

Correspondence factor analysis (e.g., Greenacre 1993) was conducted to analyze the relationship among ten chemical variables monitored in borehole water samples (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, HCO_3^-, TDS, total hardness, and pH). As suggested by the eigenvalues listed in Table 7, the cumulative contribution of three former factors accounts for 97.09%, which mainly involve variables of Na^+, Ca^{2+}, Cl^-, and HCO_3^-. These three principal factors, corresponding to three eigenvalues, provide enough precision for explaining the characteristics of the data. Based on three eigenvectors, which correspond to these three eigenvalues, the R-mode and Q-mode factor loading matrixes are obtained. According to these loading matrix transformations, the sites of the variables and the samples have been projected on a factor plane with the first (F_1) and second (F_2) factors used as coordinates (Fig. 9). Clearly, SO_4^{2-} and HCO_3^- are at opposite ends of the F_1 axis, SO_4^{2-} at the upper and HCO_3^- near the lower end of axis F_1. Na^+, Cl^- and Ca^{2+}, HCO_3^- are, respectively, at the opposite ends of axis F_2. Because the cumulative contribution percentage of F_1 plus F_2 is up to 86.51%, F_1 and F_2 are considered as the major factors dominating the chemical composition of the groundwater.

Since SO_4^{2-} and HCO_3^- are, respectively, projected at the opposite ends of axis F_1, it can be inferred that there is a negative correlation between them. In groundwater, SO_4^{2-} could be reduced into H_2S (Wu and Weng 1988) during degradation of organics. Thus, the stronger the reducibility of the environment, the lower the concentration of SO_4^{2-}, and then the more HCO_3^- concentration will increase. It means that F_1 stands for oxidation and reduction. Figure 9 shows that most of the water samples are scattered between SO_4^{2-} and HCO_3^-, and somewhat closer to HCO_3^-, indicating that the borehole water has a strong reducibility. As to F_2, Na^+ and Cl^- are at one end of the axis, and Ca^{2+} and HCO_3^- are at the other end. This result agrees with the paleogeography (Weng 1994), for it reflects the mixing of seawater mainly containing Na^+ and Cl^- with penetrated precipitation mainly containing Ca^{2+} and HCO_3^-.

Similar conclusions were also obtained from the correspondence factor analysis for 104 dug-well water samples. Figure 10 shows that SO_4^{2-} and HCO_3^- are at the opposite ends of axis F_1, and Na^+ and Cl^- at one end of axis F_2. The accumulative variance contribution rate of F_1 and F_2 accounts for 77.36%. The similarity of these two types of water samples makes it clear that the groundwater is reductive. Furthermore, according to the distinction of these two types of samples illustrated in the correspondence analysis, the borehole water has a relatively stronger reducibility than the well water. A reductive environment creates a favorable condition for stabilization of Fe and Mn ions in groundwater.

Table 7 Eigenvalues of the correspondence factor analysis for the borehole water samples

Eigenvalue (λ)	Cumulative value	Cumulative percentage
0.06153	0.06153	59.69
0.02765	0.08918	86.51
0.01091	0.10009	97.09
0.00162	0.10171	98.66
0.00076	0.10247	99.40
0.00041	0.10288	99.80
0.00013	0.10301	99.93
0.00007	0.10308	100
0.00001	0.10309	100
0.00000	0.10309	100

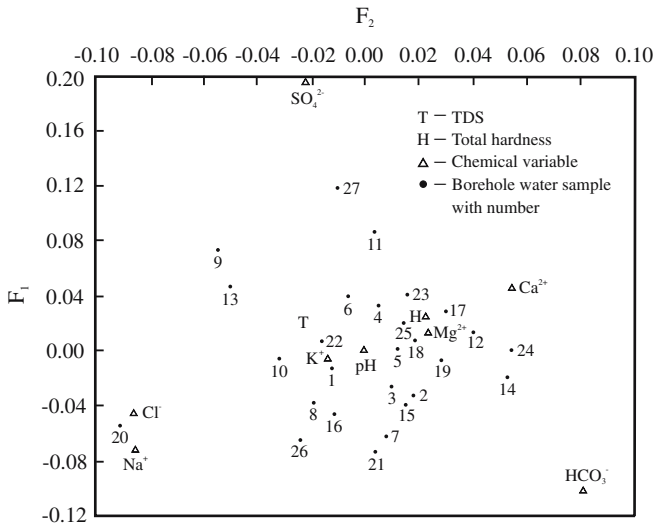

Fig. 9 Projected locations of chemical variables and the borehole water samples on the correspondence factor (CF) analysis map. The sampling locations of these borehole water samples are marked in Fig. 1 in terms of the sample numbers

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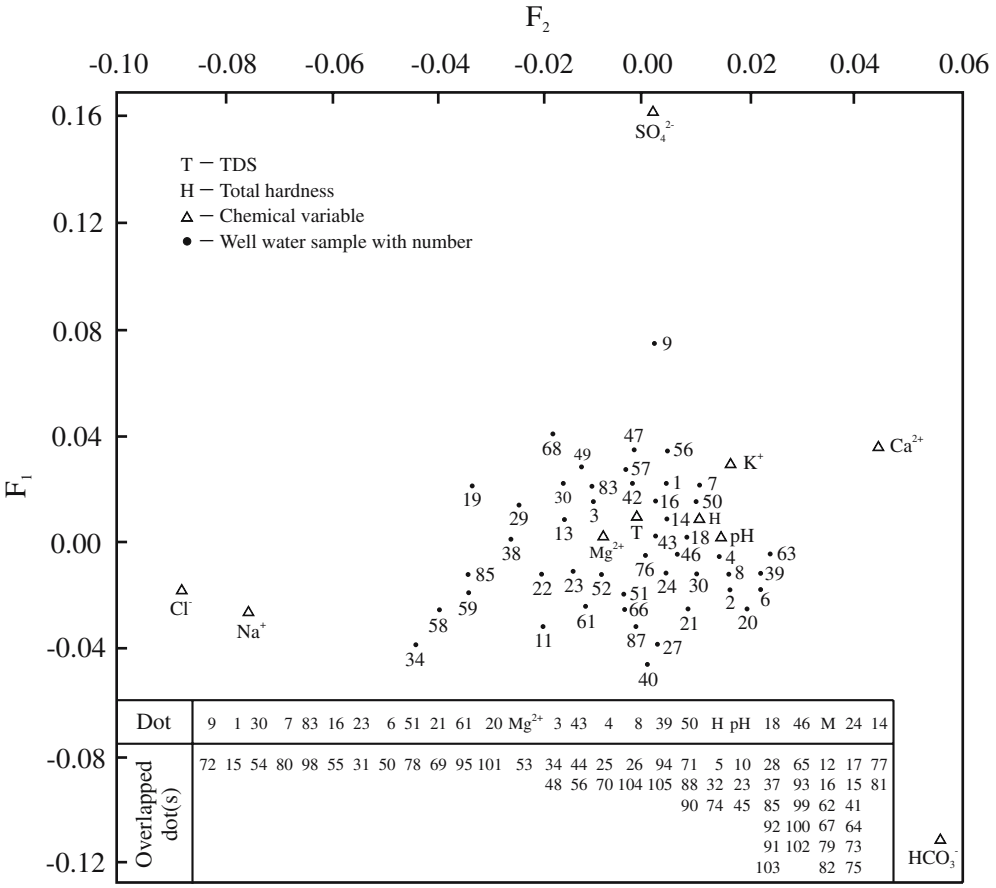

Fig. 10 Projected locations of chemical variables and the dug-well water samples on the correspondence factor analysis map. Some variables and samples were projected at the same locations. The sampling locations of these dug-well water samples are marked in Fig. 1 in terms of the sample numbers

A relatively atmosphere-isolated state is responsible for the stronger reducibility of borehole water, whereas dug-well water is exposed to the atmosphere with extensive interaction. Hence, not only can the oxygen in the air diffuse into well water, but also oxygen-saturated precipitation may mix into well water, resulting in a mildly reductive ambient environment. Dissolved oxygen in well water oxidizes some organic matter and some kinds of transition ions of low valence such as Fe^{2+} and Mn^{2+} transform into Fe^{3+} and Mn^{4+}, respectively, which makes the dissolved Fe and Mn concentrations in well water decrease. Because the oxidation potential of $Mn^{4+}+2e \rightarrow Mn^{2+}$ is larger than that of $Fe^{3+}+e \rightarrow Fe^{2+}$, the oxidation of Mn^{2+} only takes place in some well water with a strong oxidization level, which makes the Fe and Mn concentrations in borehole water higher than those in well water, and the ratio of Fe^{2+} concentration in borehole water versus that of well water is much greater than that of Mn^{2+}. In addition, the dissolved oxygen in well water decreases rapidly with the increase of depth, and Fe concentration in groundwater has a more obvious tendency to increase with depth than that of Mn (Fig. 11).

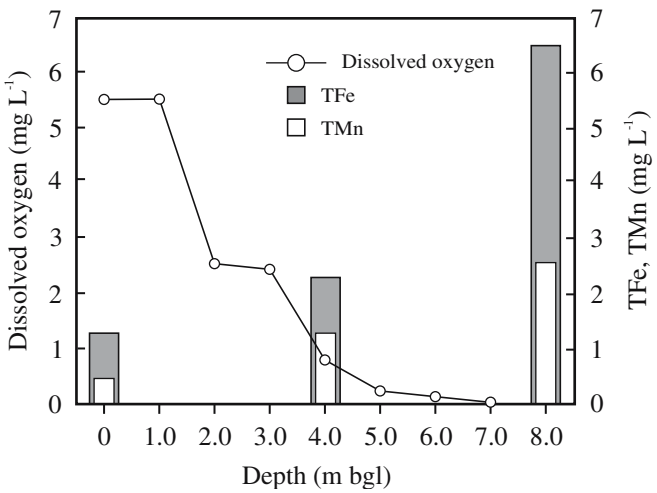

Fig. 11 Variation of dissolved oxygen, total Fe (TFe), and total Mn (TMn) concentrations with depth in the groundwater

Effect of organic matter

The average COD of the groundwater is relatively high, over 3.3 mg L^{-1} (Table 8). The COD of borehole water is

Table 8 Chemical oxygen demand (COD) of the groundwater

	Dug-well water	Borehole water	
		0–3.5 (m bgl)	3.5–15 (m bgl)
No. of samples	104	13	13
Mean COD (mg L^{-1})	3.3	3.6	4.0
Variance of mean (mg L^{-1})	1.9	1.7	2.2

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Table 9 Organic carbon contents in the cultivated soil horizon[a]

	Blue powder mud		Yellow spot earth		Little powder earth		Green purple mud		Yellow loose earth	
Depth (cm)	0–20	20–40	0–20	20–40	0–20	20–40	0–20	20–40	0–20	20–40
No. of samples	19	19	5	5	22	22	21	21	10	10
Mean organic carbon (wt%)	2.97	2.28	2.58	1.67	2.69	1.96	2.85	2.28	1.17	1.7
SD (wt%)	0.52	0.83	0.22	0.42	0.74	0.76	0.69	0.87	0.94	1.05

[a] Data from (Department of Environment Protection, Zhejiang Agriculture University, China, unpublished data, 1998). *SD* standard deviation

more than that of well water and increases with depth. COD can reflect the organic carbon concentration in groundwater. Organic carbon contained in the upper cultivated soils and the aquifer material itself are high (Tables 9 and 10, respectively). In a previous study, Li (1988) indicated that soil is an important source of organic matter for groundwater, and infiltration of precipitation can carry a lot of organics into groundwater. Organics are present in a reducing environment and respond to the geochemistry of the immediate environment (DGNU 1979). On the one hand, organic decomposition in groundwater will consume dissolved oxygen, resulting in a more reductive hydrochemistry; on the other hand, organics can stabilize Fe and Mn in waters by forming organic complexes with them, leading to elevated Fe and Mn concentrations in groundwater.

Effect of TDS

The TDS in the groundwater is high, averaging 0.89 g L^{-1} with a high ionic strength (Zhao and Zhang 1988). Based on the Debye-Hückel Equation, it was calculated that the average ionic strength of the groundwater is 0.016 and the activity coefficient of bivalent ions is 0.60 (Matthess 1982), which means that the solubilities of Fe and Mn in groundwater have obviously enhanced. The elevated ionic strength can drive more Fe and Mn ions into solution in groundwater due to the 'salt effect'. Furthermore, with the increase of complex anions in water, Fe and Mn ions can combine with them as inorganic complexes, also improving their solubility in groundwater (Stumm and Morgan 1981).

Fe and Mn ions in groundwater can combine with Cl^-, SO_4^{2-}, HCO_3^-, or CO_3^{2-}, etc. as inorganic complexes. According to the law of conservation of mass, free ions of Fe and Mn are calculated based on the following formulae derived:

$$\left[Fe^{2+}\right] = TFe^{2+} \Big/ \left(1 + K_{FeSO_4^0}\left[SO_4^{2-}\right] + K_{FeCl^+}\left[Cl^-\right] + K_{FeOH^+}\left[OH^-\right]\right)$$

$$\left[Mn^{2+}\right] = TMn^{2+} \Big/ \left(1 + K_{MnSO_4^0}\left[SO_4^{2-}\right] + K_{MnCl^+}\left[Cl^-\right] + K_{MnOH^+}\left[OH^-\right]\right)$$

where the *K*-values are the complex stability constants of $FeSO_4^0$, $FeCl^+$, $FeOH^+$, $MnSO_4^0$, $MnCl^+$, and $MnOH^+$. After putting the relevant data of the dug-well water into the formulae above, the results yield Fe^{2+}/TFe^{2+}=83% and Mn^{2+}/TMn^{2+}=55%. Thus, the inorganic complexes of Fe and Mn in well water account for 17 and 45% with respect to the total bivalent ions of Fe and Mn, respectively. For the borehole water, the results are Fe^{2+}/TFe^{2+}=84% and Mn^{2+}/TMn^{2+}=55%. These reflect the similarity of the contributions of the inorganic complexes to the total concentrations of Fe and Mn in the borehole and well water. From the formulae above, it can be inferred that with the increase of anions, the effect of inorganic complexes on the Fe and Mn concentrations will increase. A high TDS therefore plays an important role in causing elevated Fe and Mn in groundwater, especially Mn, as the calculations demonstrate that inorganic complexes of Mn are able to increase its concentration by 45%. The exponential correlation between TDS and Fe and Mn concentrations in groundwater (Wu and Weng 1987) suggests that the effects of TDS on Fe and Mn concentrations are also influenced by specific environmental conditions besides the reasons discussed here. TDS in groundwater is directly related to water replenishment. In stagnant or low flow areas, groundwater interacts with

Table 10 Organic carbon contents in the aquifer sediment (wt%)

Hole no.4		Hole no.5		Hole no.6	
Depth (m)	Organic carbon	Depth (m)	Organic carbon	Depth (m)	Organic carbon
2.25–2.65	1.246	1.71–2.02	1.004	1.77–2.07	0.916
4.15–4.45	2.088	3.25–3.35	1.091	2.77–3.07	1.467
6.65–6.95	1.935	4.41–4.71	1.306	5.38–5.66	1.282
9.15–9.45	1.625	7.29–7.59	1.520	8.37–8.67	0.837
–	–	10.17–10.47	1.294	–	–

Dash means not sampled or not measured

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aquifer materials constantly, maintaining a high TDS and reduction capacity. Consequently, combination of the high TDS and the reductive hydrochemistry is responsible, in part, for the partially face-shaped distribution of the high concentration zone of Fe and Mn.

Conclusions

There are four favorable environmental conditions that lead to the high concentrations of Fe and Mn in shallow groundwater of the Hang-Jia-Hu Plain, China. Firstly, the aquifer sediment, containing abundant Fe and Mn substances deposited during the Holocene marine invasions, acts as the supply source for the shallow groundwater through the infiltration of precipitation. Secondly, a reductive ambient subsurface environment is favorable to Fe and Mn ions transferring from the aquifer matrix into groundwater. Thirdly, organic matter in the groundwater and the soil makes the groundwater environment reductive and facilitates dissolving Fe and Mn out of the sediment. Meanwhile, organics can combine with Fe and Mn to form organic complexes that are stable in groundwater. Finally, a high TDS in groundwater enhances the ionic strength and improves the solubilities of Fe and Mn. In addition, Fe and Mn ions can form inorganic complexes with various anions and therefore maintain stability. The shallow domestic hand-dug large-diameter wells provide a primitive but cost-effective approach for reducing the concentrations of Fe and Mn in groundwater.

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