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ORIGINAL ARTICLE

Some factors affecting TDS and pH values in groundwater of the Beihai coastal area in southern Guangxi, China

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Abstract Groundwater of low total dissolved solids (TDS) of 10 mg/L and low pH ranging commonly from 4.0 to 7.0 occurs in the unconsolidated unconfined and confined aquifers in the coastal plain near Beihai, Guangxi, China. Minerals in the unconsolidated sediment of Quaternary are predominated by quartz (more than 50%) with small amount of clay minerals, such as kaolinite, illite and chlorite. SiO_2 accounts for most (more than 70%) of the chemical compositions of the sediments. The sediments contain low concentrations of soluble constituents (below 300 μg/g) and are predominated by SO_4. Abundant recharge from low-TDS precipitation and a long time's dissolution of the unconsolidated sediments containing small amount of soluble compositions lead to low TDS of the groundwater in the area.

Keywords Coastal aquifer · Rainwater · Acidic groundwater · TDS · pH · Soluble ion

Introduction

Relatively abundant fresh groundwater occurs in unconsolidated sediments in the coastal plain near Beihai in southern Guangxi, China. Monitoring data of groundwater quality of nearly 20 years show that groundwater in the coastal aquifers is of low TDS (commonly less than 100 mg/L) and low pH (with average value of about 5, even a bit lower than that of the local rainwater). Although hydrogeological studies have been carried out for this area (Chen et al. 1990; Zhou et al. 1997a, 2000a, b, 2006), the geochemical and hydrochemical aspects of the coastal area near Beihai have seldom been examined. Studies of acidic groundwater by many researchers focus on acid mine drainage waters (Herbert 1996; Keith et al. 2001), whereas little is known about natural low pH groundwater in unconsolidated sediments. Lång and Swedberg (1990) reported the occurrence of acidic groundwater in pre-Cambrian crystalline bedrock aquifers in the southwestern Sweden which receives recharge of acidic surficial water. Preda et al. (2000, 2001) suggested that the oxidation and hydrolysis of pyrite are responsible for the low pH water of the Pimpama River in the southeast Queensland, Australia. A number of hydrogeochemical studies indicate that various physical and chemical processes may occur and lead to changes in chemical compositions of groundwater and their concentrations in the course of groundwater flow from recharge areas, where groundwater receives recharge from precipitation, to discharge areas (Stollenwerk 1994; Wicks and Herman 1996; Giménez 1997; Rosen and Jones 1998; Petalas and Diamantis 1999). TDS and pH in groundwater are affected by many environmental factors such as rainwater, soil, water content and gas in the unsaturated zone, and lithology and configuration of aquifer systems. This paper presents a preliminary investigation of some environmental factors that exist in the coastal area near Beihai and may be responsible for the occurrence of the groundwater of low TDS.

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Hydrogeologic setting and sample collection

The city of Beihai lies in the western part of the coastal plain facing the Beibuwan Gulf in southern Guangxi, China. The coastal line is of peninsula-shape. The coastal plain is generally flat and the elevation ranges from 8 to 25 m. Rivers are sparse and short. The climate of the study area is subtropical humid and monsoon, with a hot summer. The precipitation varies between 849 and 2,382 mm, with a mean annual value of 1,677 mm. Rainfall occurs mainly during the summer wet season from May to October, accounting for more than 80% of the total precipitation of a year. The average annual evaporation is 1,756 mm. The subtropical temperature ranges from 2 to 37°C, with a mean annual temperature of 22.6°C.

Impervious basement rocks consist of mudstone with sandstone and granite, and outcrop in the southwestern tip and the northeastern part of the study area. The coastal plain is underlain by Quaternary and Neogene unconsolidated sediments with a total thickness of 5–350 m. The Quaternary and Neogene sediments consist of sand with gravel and scattered lenses of clay or sandy clay. One unconfined aquifer and three confined aquifers can be grouped in the unconsolidated sediments in the south of the area, whereas one unconfined aquifer and one confined aquifer exist in the north of the study area, depending on the relieves of basement rocks. The unconfined aquifer (2–18 m thick) consists mainly of sand with gravel in the lower part and clayey sand in the upper part of the Beihai Group of the Middle Pleistocene (Q_{2b}). The upper confined aquifer, consisting of sand with gravel of the Zhanjiang Group of the Lower Pleistocene (Q_{1z}), occurs at elevation from 2 to –10 m with a thickness of 8–30 m. The middle and lower confined aquifer, which are composed of sand with clayey sand, correspond to the Shangcun Group (N_{2sh}) and Huangniuling Group (N_{1h}) of Neogene age. Good hydraulic connections exist among the aquifers, especially among the confined aquifers, owing to the semiperviousness and termination of clay (Zhou et al. 2000a).

Groundwater in the unconfined aquifer receives recharge from precipitation and seepage from canals and discharges to rivers and to the confined aquifers through leakage. Groundwater in the confined aquifers receives recharge from the unconfined aquifer, flows towards northwest and south, finally discharges into the sea. In recent decades, however, artificial withdrawal for water supply has become an important way of discharge. With the increase in the abstraction rate due to the rapid population growth, continual falling in groundwater levels and depression cones in the exploitation centers in the southern part have existed since 1986. During 1989–1993, seawater intrusion had occurred in the northwestern coast where old wellfields are located (Zhou et al. 2000b). Seawater has stopped to intrude since 1994 as a result of the decrease in withdrawal of groundwater in the northwestern coast and the shift of the main wellfilds.

Sampling of groundwater, rainwater, seawater and soil were conducted in the field in August 2002. In the following year, rainwater and groundwater samples from representative wells in the unconfined aquifer (wells WB9 and WB11) and confined aquifer (wells WP9 and WP12) were collected at every 3 months. Soil samples (TB1 to TB6) were collected at depths of 1.5, 3.1, 4.1, 5.1, 6.0 and 8.5 m below the land surface near the northern coast, where both the Q_{2b} and Q_{1z} sediments outcrop. Another two soil samples of Q_{2b} sediments (TQ1 and TQ2, very close to wells WP9 and WP12, respectively) were collected at a depth of 1 m below the land surface in the northern part. The soil samples were dried and ground for determination of minerals, chemical compositions (expressed as oxides) and soluble ions. Location of sampled sites is shown in Fig. 1, and results of analyses of samples are recorded in Tables 1 and 2. Soil samples TQ1, TQ2 and TB1

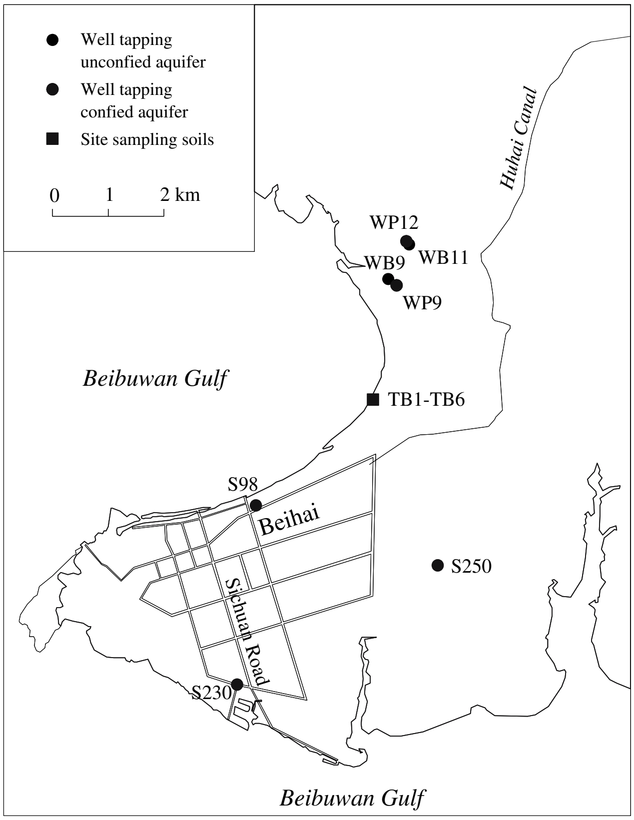


Fig. 1 Location of samples

Table 1 Minerals, chemical compositions and soluble ions of soil samples

Sample		TQ1	TQ2	TB1	TB2	TB3	TB4	TB5	TB6
Period		Q_{2b}	Q_{2b}	Q_{2b}	Q_{2b}	Q_{2b}	Q_{2b}	Q_{1z}	Q_{1z}
Lithology		Yellowish-brown clayey sand	Yellowish-brown clayey sand	Yellowish-brown clayey sand	Yellowish-brown sandy clay	Yellowish sand	Yellowish-brown medium to coarse sand with gravel	Red clay with sandy clay	Gray-white coarse sand with gravel
Minerals (%)	Quartz	70	75	70	70	70	80	50	80
	Illite				15	5	10	20	15
	Kaolinite						10	30	5
	Chlorite + Kaolinite	30	25	30	15	25			
Chemical compositions (%)	SiO_2	76.83	76.16	76.28	86.76	76.58	89.41	73.55	95.25
	Al_2O_3	11.35	11.03	10.06	3.94	11.17	4.55	16.59	2.51
	Fe_2O_3	4.06	4.45	6.13	5.66	4.84	2.29	1.31	0.24
	FeO	0.47	0.46	0.43	0.45	0.47	0.58	0.17	0.35
	MgO	0.51	0.42	0	0.085	0.14	0.16	0.24	0.11
	CaO	0.64	0.062	0.65	0.31	0.25	0.25	0.19	0.24
	Na_2O	0	0	0.18	0	0	0	0	0
	K_2O	0.23	0.19	0.24	0.14	0.23	0.15	0.94	0.15
	H_2O^+	4.35	3.85	4.02	1.49	4.52	1.87	6.37	0.71
	H_2O^-	1.03	1.71	0.98	0.32	0.78	0.26	0.59	0.095
	TiO_2	0.62	0.73	0.55	0.23	0.66	0.22	0.47	0.03
	P_2O_5	0.078	0.078	0.056	0.042	0.066	0.048	0.059	0.037
	MnO	0.019	0.026	0.02	0.025	0.018	0.033	0.023	0.036
Soluble ions (μg/g, except pH)	K	9.38	19.5	23.2	59.3	24.9	33.8	26.0	37.6
	Na	16.5	23.7	24.5	130.5	39.2	18.4	42.5	32.1
	Ca	27.8	24.6	34.0	24.4	39.6	27.6	25.5	41.7
	Mg	22.0	28.6	37.3	36.9	37.2	30.9	11.9	12.7
	Fe^{3+}	1.8	64.7	44.1	8.53	74.4	19.6	18.5	7.81
	Fe^{2+}	37.9	67.2	42.6	0.733	76.3	10.5	13.0	0.793
	Mn	23.2	42.7	36.3	21.6	38.1	50.8	6.27	18.4
	HCO_3	52.2	50.2	37.0	44.9	53.0	49.4	45.7	63.1
	SO_4	137.1	199.0	204.6	258.1	306.2	169.7	98.2	44.9
	Cl	11.1	11.3	11.0	11.2	12.2	10.3	12.7	10.1
	NO_3	0	0	0	0	0	0	0	0
	pH	6.59	6.37	6.66	6.7	6.47	6.53	6.13	6.88

Table 2 Chemical compositions of water samples (in mg/L, except pH)

Sample	Rain water				WB9					WB11				
Aquifer					Unconfined aquifer					Unconfined aquifer				
Sampling date (D/M/Y)	*	23/3/2003	11/6/2003	12/8/2003	24/8/2002	21/11/2002	5/3/2003	10/6/2003	30/8/2003	25/8/2002	21/11/2002	5/3/2003	10/6/2003	30/8/2003
K	0.50	0.1	0.1	0.2	1.2	0.8	0.8	0.9	1.0	0.6	0.8	3.6	5.4	1.0
Na	0.42	0.18	0.49	0.18	8.5	3.57	3.26	3.26	15.52	2.5	2.65	4.18	3.57	2.34
Ca	2.47	3.1	0.8	3.1	11.9	9.6	5.8	6.9	13.8	7.1	6.9	5.0	3.8	3.8
Mg	0.93	0.5	0.5	0.5	1.3	0.7	0.9	0.9	2.6	0.8	9.0	1.6	1.2	0.9
NH_4	0.19	0.01	0.01	0.07	0.052	0.01	0.01	0.01	0.01	0.32	0.01	0.06	0.01	0.01
Cl	4.17	1.6	3.2	2.4	17.9	12.7	8.7	9.5	26.1	10.3	11.1	25.3	22.1	9.5
SO_4	2.13	0.5	0.5	0.5	2	0.5	0.5	0.5	8.8	2.5	0.5	0.5	0.5	0.5
HCO_3	7.97	6.8	8.1	9.4	35.8	27	16.2	20.3	20.3	17.2	23	2.7	6.8	12.2
NO_3	0.72	0.06	0.06	0.56	1.69	0.06	0.06	0.006	26.0	0.3	0.44	6.0	0.72	1.08
NO_2	0.01	0.014	0.001	0.001	0.004	0.001	0.001	0.001	0.006	0.004	0.001	0.008	0.001	0.001
Mn	0.02	0.005	0.005	0.005	0.025	0.02	0.02	0.005	0.02	0.025	0.005	0.005	0.005	0.005
Fe	0.043	0.01	0.01	0.035	0.05	0.01	0.01	0.01	0.01	0.05	0.065	0.105	0.045	0.01
Al	–	0.4	0.14	0.12	0.15	0.14	0.16	0.11	0.16	0.13	0.37	5.6	1.2	0.16
F	0.021	0.005	0.005	0.05	0.05	0.005	0.005	0.005	0.005	0.05	0.005	0.005	0.010	0.005
HPO_4	0.05	0.012	0.012	0.012	0.05	0.012	0.012	0.012	0.012	0.05	0.012	0.012	0.012	0.012
H_2SiO_3	2.60	0.65	0.65	0.65	7.31	6.5	5.85	5.2	10.4	6.24	6.5	8.45	6.5	7.15
Free CO_2	5.80	3.88	2.91	4.85	18.7	0.97	1.94	3.88	26.18	25.6	1.94	4.85	5.82	19.39
TDS	14.10	8.94	9.2	11.64	69.7	47.43	33.47	36.82	114.4	36.44	40.79	49.54	46.69	31.87
Hardness	9.83	9.8	4.06	9.8	35.07	26.85	18.19	20.94	45.17	21.02	20.94	19.07	14.43	13.2
Alkalinity	6.5	5.58	6.64	7.71	29.36	22.15	13.29	16.65	16.65	14.11	18.86	2.21	5.58	10.01
pH, lab	5.56	6.35	5.73	6.48	5.97	7.64	7.04	6.81	5.86	5.85	7.37	4.68	5.74	5.1

Sample	WP9					WP12					Sea water
Aquifer	Confined aquifer					Confined aquifer					
Sampling date (D/M/Y)	24/8/2002	21/11/2002	5/3/2003	10/6/2003	30/8/2003	25/8/2002	21/11/2002	5/3/2003	10/6/2003	30/8/2003	26/8/2002
K	1.0	0.8	1.2	0.8	1.4	0.005	0.2	0.2	0.2	0.4	158.2
Na	3.9	3.88	2.65	2.34	3.26	5.1	3.26	2.34	2.34	3.26	4670.0
Ca	6.6	6.9	2.3	3.1	2.3	7.5	2.3	3.1	3.8	3.1	194.4
Mg	0.8	0.7	1.2	0.9	0.9	1.3	2.8	1.9	1.9	1.9	597.6
NH_4	0.125	0.01	0.01	0.01	0.01	0.135	0.01	0.01	0.01	0.01	0.071
Cl	9.6	10.3	7.9	7.9	8.7	14.4	21.4	16.6	14.2	15.8	8539.9
SO_4	5.2	0.5	0.5	0.5	0.5	2.5	0.5	0.5	0.5	0.5	1429.7
HCO_3	19.9	21.6	10.8	13.5	9.4	19.9	2.7	2.7	5.4	6.8	76.9
NO_3	0.29	0.06	1.4	1.5	0.16	0.95	0.04	0.05	0.92	0.06	0.1
NO_2	0.004	0.014	0.024	0.04	0.001	0.004	0.001	0.001	0.001	0.001	0.079
Mn	0.025	0.005	0.005	0.005	0.005	0.025	0.005	0.005	0.005	0.005	0.53
Fe	0.05	0.01	0.01	0.01	0.01	0.05	0.01	0.01	0.01	0.01	0.05
Al	0.01	0.3	0.9	0.5	3.4	0.01	0.46	0.42	0.64	0.3	0.01
F	0.05	0.005	0.005	0.005	0.005	0.05	0.005	0.005	0.005	0.005	0.488
HPO_4	0.05	0.012	0.012	0.012	0.012	0.05	0.012	0.012	0.012	0.012	0.05
H_2SiO_3	5.49	4.55	5.2	4.55	6.5	9.3	7.15	6.5	6.5	7.15	7.01
Free CO_2	19.73	0.97	0.97	5.82	16.48	33.5	17.45	1.94	4.85	43.63	2.0
TDS	42.83	37.99	27.25	27.84	21.42	48.5	38.5	32.04	32.5	35.07	16031.4
Hardness	19.78	20.11	10.69	11.45	9.45	24.08	17.27	15.57	17.31	15.57	2946.64
Alkalinity	16.32	17.71	8.86	11.07	7.71	16.32	2.21	2.21	4.43	5.58	63.07
pH, lab	6.08	7.64	6.99	6.34	5.7	5.4	4.32	5.7	6	4.89	7.9

[a] Mean values of rainwater of three samples collected on August 16, 1997; September 7, 1998 and September 8, 1999

represent the upper Q_{2b} sediments, and TB2, TB3 and TB4 are the lower Q_{2b} sediments. Soil samples TB5 and TB6 stand for the upper clay and the lower sand with gravel of the Q_{1z} sediments, respectively. All the soil and groundwater samples are believed to be unaffected by land use and seawater. Groundwater exploitation was negligible near the sampled sites compared to what was in the southern part of the study area.

Results and discussion

Soil minerals

Minerals present in the soil samples are quartz and clay minerals detected with x-ray diffraction analyses. Quartz accounts for 50% of the mineral compositions of the upper clay of the Q_{1z} sediments and more than 70% of the other Q_{2b} and Q_{1z} sediments (Table 1). Clay minerals include kaolinite and chlorite and small amount of illite. The upper Q_{2b} sediments (samples TB1, TQ1, TQ2) contain chlorite with kaolinite but do not contain illite. Samples TB2 and TB3 contain illite and chlorite with kaolinite. Samples TB4, TB5, TB6 contain illite and kaolinite but do not contain chlorite. Pyrite was not detected in the soil samples. The minerals of soil samples are believed to be typical products of long time weathering.

Soils chemistry

The chemical compositions (expressed as oxides) of soil samples show that SiO_2 is the main oxides of the soil (Table 1), ranging from 73.55% (TB5) to 95.25% (TB6). Al_2O_3 varies between 3.94% (TB2) and 16.59% (TB5) and Fe_2O_3 is in the range of 0.24% (TB6)–6.13% (TB1). In addition, H_2O^+ ranges from 0.71% (TB6) to 4.52% (TB3), and H_2O^-, from 0.0961% (TB6) to 1.71% (TQ2). Other oxides are rare or absent in soil samples (Table 1). Concentrations of these four major oxides do not show any systematic change in the soil profile (Fig. 2). Insoluble compositions account for most of the chemical compositions of the Q_{2b} and Q_{1z} soils, indicating that the sediments have undergone dissolution in the local water circulation under natural conditions for a long time and extensive leaching of soluble compositions from soils have taken place.

The soil samples have low levels of soluble ions; almost all of the ions are less than 300 μg/g (Table 1). SO_4 predominates in the anions, ranging from 44.9 μg/g (TB6) to 306.2 μg/g (TB3). HCO_3 varies between 37.0 μg/g (TB1) and 63.1 μg/g (TB6) and Cl, between 10.1 and 12.2 μg/g. K, Na, Ca and Mg have similar concentrations of several tens of μg/g, while Mn, Fe^{2+} and Fe^{3+} also have concentrations of several tens of μg/g close to those of the above four cations. In the soil profile, Na is the highest at TB2, Fe^{2+} and Fe^{3+} are high at TB3, and SO_4 increases from TB1 to TB3 and decreases from TB3 to TB6 (Fig. 3). Low levels of soluble ions in the soil samples also indicate extensive leaching of soluble compositions from soils.

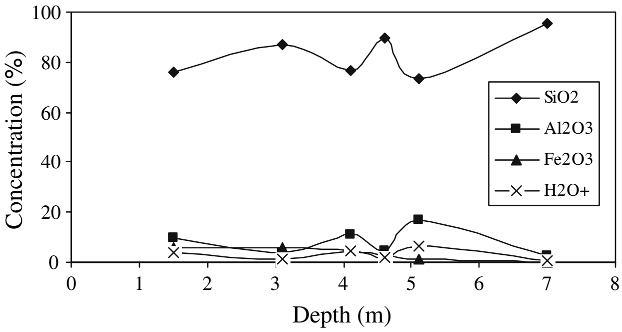


Fig. 2 Changes in major oxides in soil profile

Rainwater

Chemical analyses of rainwater sampled seven times from August 1997 to August 2003 show that it has very low TDS (Table 2), ranging from 7.3 to 21.2 mg/L with an average value of 11.34 mg/L. The water type is mainly of Ca·HCO_3-Cl type. The pH ranges from 5.29 to 6.48 with an average value of 5.88. Relationship between monthly precipitation and pH in groundwater at selected wells S98, S230 and S250 from 1989 to 1996 is shown in Fig. 4. Increasing monthly precipitation has little effect on the pH of the groundwater. Change in pH in groundwater show that pH in the rainy seasons is

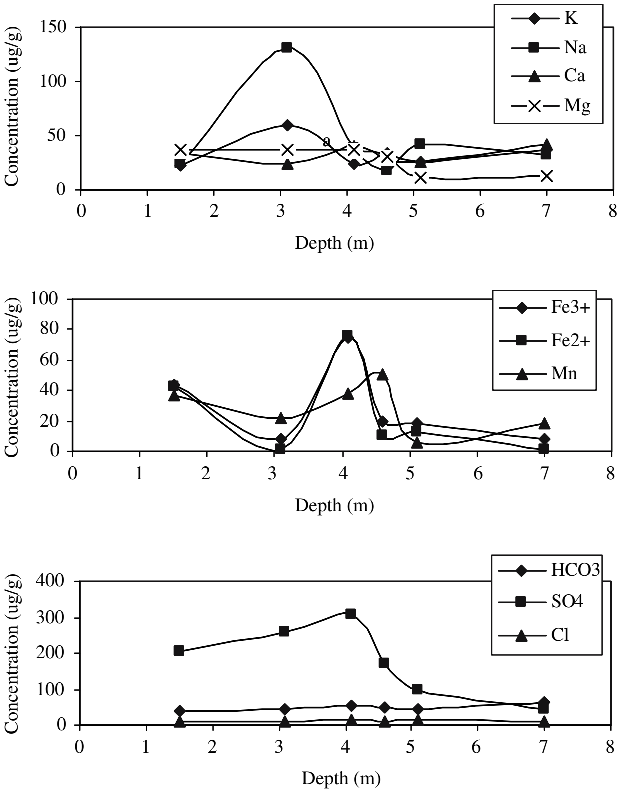


Fig. 3 Changes in soluble ions in soil profile

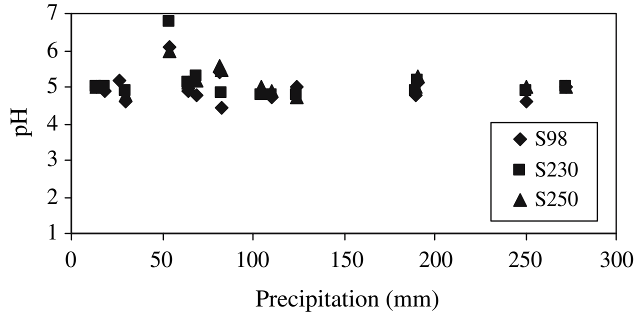


Fig. 4 Precipitation versus pH at wells S98, S230 and S250 from 1989 to 1996

a bit lower than that in dry seasons. The highest values of pH, 6.1, 6.8, 6.0, at wells S98, S230 and S250, respectively, were measured in March 1993 when the precipitation was 54.3 mm. The pH in rainwater does not show any systematic trend with time.

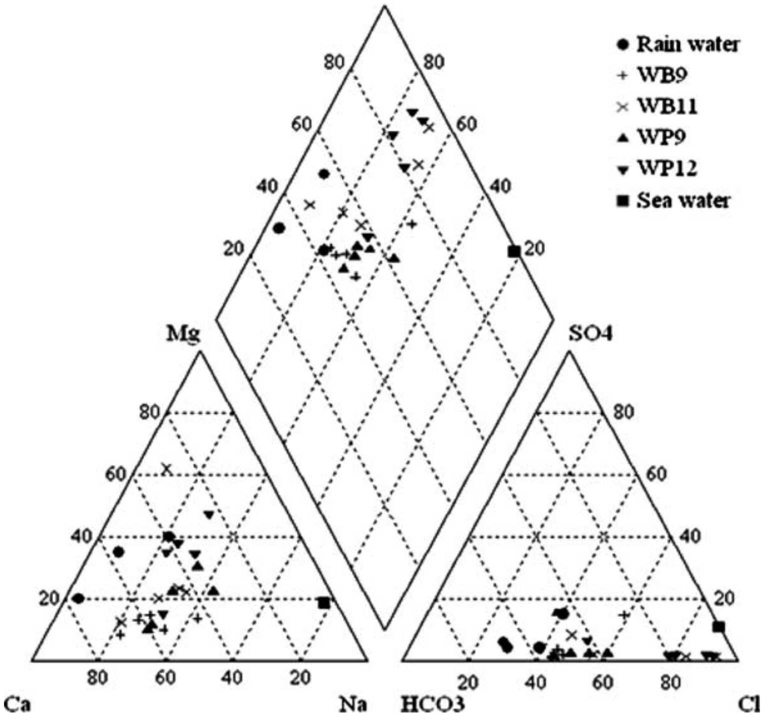
Groundwater

The TDS of the unconfined aquifer ranges from 30 to 70 mg/L (Table 2). The highest TDS in this investigation occurred at well WB9 sampled on August 30, 2003, which was abnormal owing to the high contents of NO_3 of 26.0 mg/L, possibly due to contamination. The TDS values of the confined aquifer were even lower than those of the unconfined aquifer, ranging commonly from 20 to 50 mg/L. Na and Ca are the major cations and HCO_3 and Cl are the major anions. They have always low concentrations. The groundwater has low pH ranging between 4.0 and 7.0. The pH of several groundwater samples are higher than 7.0. The reason for this is that the pH was measured in the lab, giving a higher value than that measured in the filed. The groundwater has a wide variety of water type at different wells at the same time (Fig. 5) or at the same well at different times. Ca·Na-Cl and Ca·Na-Cl·HCO_3 are the dominant water type for the unconfined aquifer, and Ca·Na-HCO_3·Cl is the major water type of the confined aquifer. Ion concentrations of groundwater change with time, but they are in low levels. Little or lack of alkaline substances in the groundwater system is helpful in the accumulation of acidity from rainwater and other sources, resulting in a decrease in pH of groundwater.

Seawater

The seawater sample was taken from the northern bay of the Beibuwan Gulf near the soil profile. It has TDS of 16031.4 mg/L (Table 2), only about half of that of the normal seawater. This is mainly due to the sampled location which is close to the coast and to the estuary. The seawater sample is of Na-Cl type and has pH of 7.9, which is obviously higher than the groundwater and rainwater in the area. The seawater is thought to be unrelated hydrochemically to the groundwater in the coastal aquifers far from the coast under natural conditions.

Fig. 5 Piper diagram of water samples



Summary

The minerals of the Quaternary sediments in the Beihai area are predominated by quartz with small amount of clay minerals, such as illite, kaolinite and chlorite. SiO_2 accounts for most of the chemical compositions of the sediments. The sediments contain small amount of Al_2O_3 and Fe_2O_3, and little of the other oxides. The soluble ions of the soils are at low levels and are dominated by SO_4, with similar contents of K, Na, Ca, Mg, Mn, Fe^{2+} and Fe^{3+}. The high concentrations of insoluble compositions in soils reflect extensive weathering of soils and thorough dissolution and migration of soluble ions. On the other hand, relatively large amount of precipitation (annual 1,677 mm), flat topography, and permeable unsaturated and saturated zones are helpful for groundwater in receiving recharge from precipitation, resulting in significant seasonal fluctuation in groundwater levels in both the unconfined and confined aquifers (Zhou et al. 1997b). Quick water circulation may cause easier dissolution and migration of soluble ions of the Quaternary soils and a long time dissolution and migration of soluble ions have resulted in low concentrations of soluble ions in the soils. Precipitation of low TDS infiltrates such kinds of soils, leading to low TDS and low concentrations of dissolved ions of groundwater in the coastal area (unaffected by land use and sea water intrusion). Thus, the low TDS groundwater in the area is attributed to abundant recharge from low-TDS precipitation, relatively rapid water circulation and sediments containing low concentrations of soluble compositions.

Groundwater in the coastal aquifers in the Beihai area is of low pH, ranging commonly from 4 to 7. The preliminary recognition of the main mechanism is the possibility of dissociation of $H_2CO_{3.}$ Under the natural conditions, H^+ in the groundwater may be derived from dissociation of H_2CO_3 as well as from the acidity of rainwater. The H_2CO_3 in the groundwater is formed by dissolution of CO_2, which comes mainly from the biological contribution. Lack of alkaline substances in the groundwater system is also helpful in the accumulation of acidity, resulting in a decrease in pH of the groundwater. However, the mechanism leading to low pH groundwater in the study area is not fully understood and needs to be examined in detail in future research.

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