



Hydrogeochemical processes between surface and groundwaters on the northeastern Chinese Loess Plateau: Implications for water chemistry and environmental evolutions in semi-arid regions



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ABSTRACT

A large area of the continents is covered by loess that is subject to fast erosion, but detailed research is lacking about processes influencing the hydrogeochemistry in loess-covered regions. This study presents the first $\delta^{18}\text{O}$ and δD , and major ion contents of various waters (rain, rivers, lake, springs and wells) from Daihai Lake catchment on the Chinese Loess Plateau (CLP). In combination with historical hydrological and meteorological data during the past 60 years, we investigate factors affecting water chemistry and lake evolution on the CLP, and thereby provide insight into hydrogeochemical processes under semi-arid climatic conditions.

On the northeast CLP, river and groundwaters show elevated TDS (450 and 461 mg/L, respectively), about ~4 times higher than the global river mean value. Their water chemistry is dominantly influenced by carbonate weathering. Lake waters show even higher TDS at 5758 mg/L, ~50 times of the global mean, which is attributed to strong evaporation and associated with precipitation of calcite and dolomite. The order of carbonate (calcite and dolomite) saturation indexes follows lake water > river water > groundwater. Downstream rivers to the west of Daihai Lake are characterized by elevated SO_4^{2-} , indicating high lake levels in the past. Comparison of $\delta^{18}\text{O}$, δD , TDS and ion contents of river and groundwaters implies that shallow groundwaters are derived from surface runoff via fast infiltration, a hydrological process different from limited infiltration of groundwater on the Tibetan Plateau. Water quality assessment indicates that all river and 79% of well waters belong to moderately hard to hard-fresh waters, suitable for drinking and irrigation of plants with moderate salt tolerance. In contrast, all lake and spring waters and 21% of well waters belong to very bad water quality, and hence are not suitable for irrigation or drinking.

Owing to intensified human activities under drying and warming climate, the lake water level of Daihai declined by 4.83 m from 1955 to 2003, and started to accelerate since 1980. As a result, TDS and Cl^- increased by 1.8 times and Mg/Ca rose by 156 times from 1953 to 2010. Our data show that environment degradation poses a great threat to human occupation on the CLP. Considering the uniformity of loess, hydrogeochemical processes between surface and groundwaters on the loess regions may represent a widespread status of the CLP.

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1. Introduction

Globally, about ~10% of land surface is covered by loess and loess-like deposits, and the portion increases to ~30% in China (Derbyshire, 2001; Liu, 1985). The Chinese Loess Plateau (CLP) covers an area of 640,000 km² with a thickness of >250 m, representing the largest and thickest loess regions in the world (Liu, 1985; Wang et al., 1984). Historically, the CLP has been a well-known political, economic and cultural center in China. The population on CLP increased from 10 million during the late Western Han Dynasty (2 A.D.) to 104 million by 2000 (Wang et al., 2006).

Due to the rapid population growth and unprecedented diffusion of human activities, water shortage has become one of the most prominent issues for the sustainable development of the CLP since the last century (He et al., 2003). The limited water resources are thought to greatly slow down the local economy growth. The climate on the CLP is mostly semi-arid, with low annual precipitation ranging from 150–300 mm in the north to 500–700 mm in the south (Li and Xiao, 1992). Sparse and deep groundwater resources result in harsh environments for plants, even in sub-humid regions in the south of the CLP (Zhang and An, 1994), and consequently most of agriculture relies on dryland farming (Li and Xiao, 1992). The Yellow River, as the world's fifth longest rivers, draining the CLP, has been experiencing frequent dry-ups since 1972, owing to increased irrigation, damming, and water diversion activities in the basin (Chen et al., 2003). The increasing

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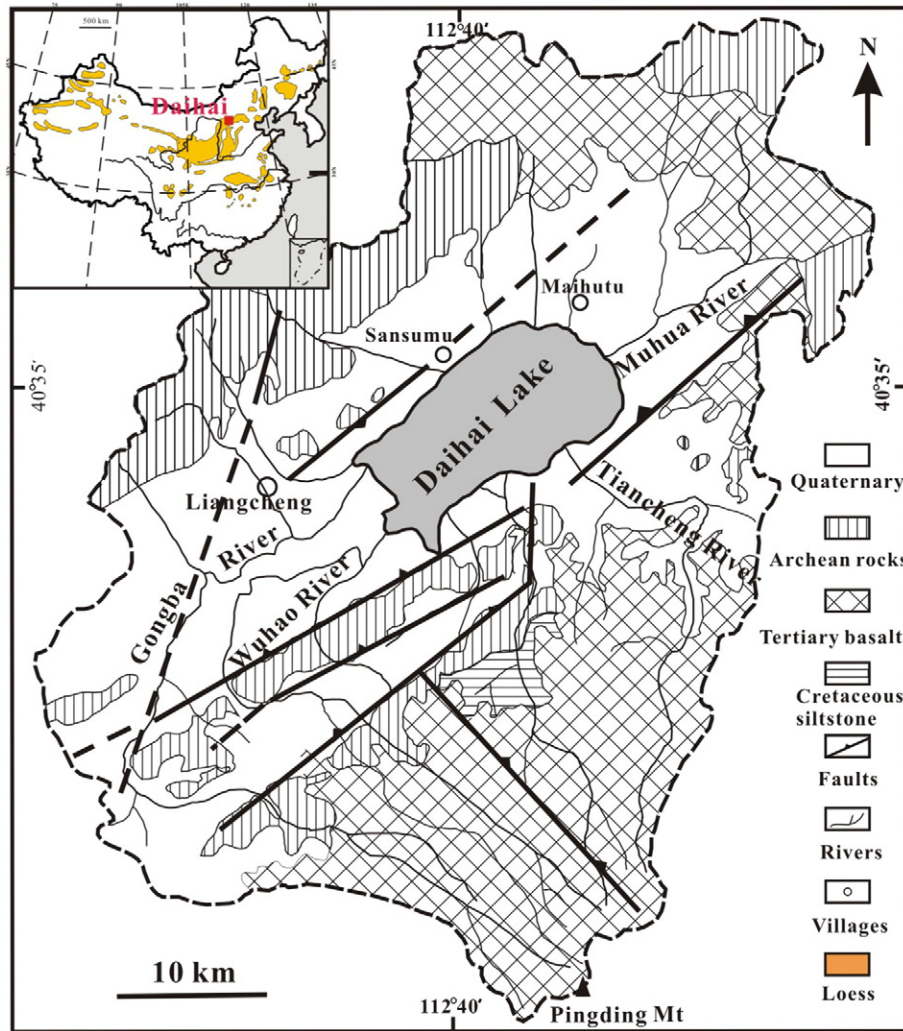


Fig. 1. Sketchy geologic map of the Daihai Lake catchment on the northeastern Loess Plateau. Inserted showing the location of Daihai Lake in China. Modified after Wang et al., 1990; Jin et al., 2006b.

number of flow stoppages has caused great economic and ecological losses. As an example, water supply could only fulfill 33.3% of the total need on the CLP in 2003 (Wang et al., 2006), and water shortage seriously affected the crop yield of dryland farming in the region (Wang et al., 2009; Zhang et al., 2009b). It has been suggested that, given optimum management of water and nutrients, agricultural production could be increased by as much as threefold (Fan and Zhang, 2000).

To date, in such huge regions, no systematical study exists on water chemistry, water cycle, and water quality assessment of surface and groundwaters on the CLP. Located at the northeastern of the CLP, Daihai Lake catchment has drawn great interests due to its potential for high-resolution paleoenvironment research (Jin et al., 2001, 2004, 2006a; Peng et al., 2005; Xiao et al., 2004). Its hydrologically-closed condition facilitates investigation of past hydrogeochemical processes in semi-arid regions. Here, we carried out a comprehensive study on geochemical and isotopic measurements of waters samples collected from Daihai Lake catchment. In combination with time-series records of water chemistry, hydrology, and human activities during the past 60 years, this paper aims to understand: (1) the water chemical characteristics and chemical weathering processes; (2) how natural and human factors affect the hydrology and water quality; and (3) key factors affecting lake evolution in the semi-arid region.

2. Study area

2.1. Geology

Daihai Lake is an asymmetric, east–west oriented graben-type basin, with steep north and gentle south. Outcropping bedrocks are predominantly Archean metamorphosed igneous rocks and Tertiary basalt with minor Cretaceous siltstones (Jin et al., 2006b). The Lake is mainly surrounded by Archean rocks. The lithology includes gneiss and granite (Wang et al., 1990). The Tertiary basalts are widely distributed in the southern mountain areas (Fig. 1) (Peng et al., 2005). Quaternary loess deposits are seen in the lake basin and river valleys, and overlying bedrocks (Fig. 2). The thickness of loess deposits varies from a few meters to more than ten meters (Jin et al., 2006b; Wang et al., 1990).

2.2. Geography and climate

Geographically, Daihai Lake (40°29'–40°37'N, 112°33'–112°46'E) is located in Inner Mongolia on the northeastern CLP. The catchment area is 2289 km². Four large and 18 small intermittent rivers drain into the lake. The four large rivers are the Gongba and Wuhao Rivers in the West, the Tiancheng River in the south, and the Muhua River in

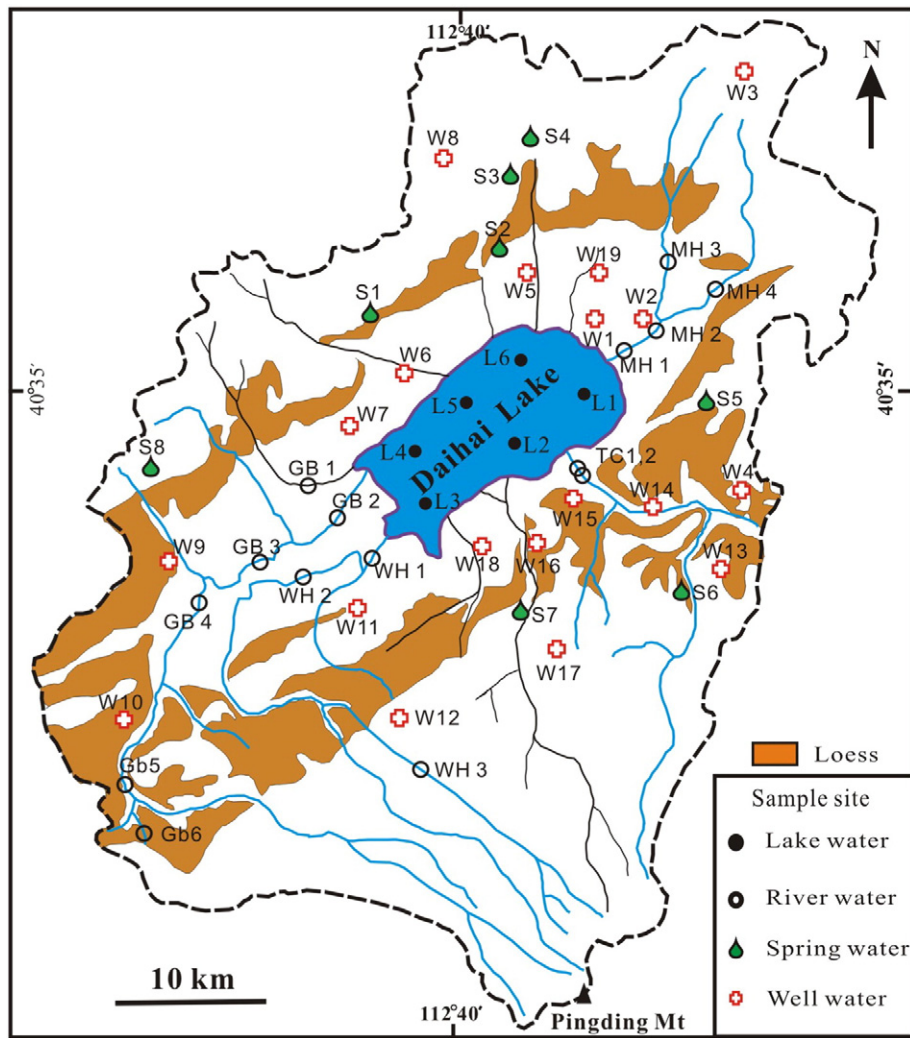


Fig. 2. Map showing rivers, sample locations and loess coverage area within the Daihai Lake catchment.

the east (Fig. 1). The water sources of the lake are mainly from surface and subsurface runoff, and precipitation. The average annual surface water discharge flux from these rivers is $9.98 \times 10^7 \text{ m}^3/\text{yr}$ (Han et al., 2007; Wang and Li, 1991).

Climatically, Daihai Lake is located at the transition between semi-humid and semi-arid areas in the middle of the temperate zone of China, sensitive to climatic changes in the East Asian summer monsoon oscillations. Mean annual temperature during 1959–1999 was only 3.5 °C with averages of -15 °C and 20.5 °C in January and July, respectively. The annual mean evaporation is 1938 mm (Jin et al., 2006b; Xiao et al., 2004). Rainfall during June–August accounts for ~66% of the annual precipitation of 350–450 mm. Vegetation in the lake drainage is influenced by hydrothermal and topographical conditions, showing a range from arid forest, shrub grass-land to semiarid grassland when moving from mid-low mountains in the northwest to the hills (Sun et al., 2006; Wang and Li, 1991).

3. Materials and methods

Water samples from rivers, springs, drinking water wells, lake and rain were collected within the Daihai Lake catchments in August 2008. River waters were sampled from four largest rivers in the catchment, namely the Gongba, the Wuhao, the Muhua, and the Tiancheng Rivers. The locations of sampling sites are shown in Fig. 2. Water samples

were *in situ* filtered on collection through $0.2 \mu\text{m}$ Whatman® nylon filters. For cation analyses of the lake and rain waters, 60 mL filtered water of each sample was stored in a pre-cleaned polyethylene bottle and was acidified to $\text{pH} < 2$ using 6 M quartz-distilled HNO_3 . The cation data of river and groundwaters were published in Zhang et al. (2013). For oxygen ($\delta^{18}\text{O}$) and hydrogen (δD) isotopes and anion measurements, 30 mL filtered sample was stored but not acidified. These 30 mL samples were first used for $\delta^{18}\text{O}$ and δD measurements, and the remaining parts were then used for anion measurements. Temperature and pH were *in situ* measurements. Bottles were wrapped by parafilm surrounding the capes to prevent any leakage. All samples were kept chilled at 4 °C until analysis.

Major cations (Ca^{2+} , K^+ , Mg^{2+} , Na^+ , and Sr^{2+}) of the water samples were analyzed by Leeman Labs Profile ICP-AES at State Key Laboratory of Lake Science and Environment. Major anions were determined using a Dionex-600 ion chromatography at the Institute of Earth Environment, CAS. The average reproducibility was 0.5–1% (2σ). Alkalinity was measured by Gran titration.

The oxygen and hydrogen isotopic compositions of water samples were analyzed by a Finnigan Delta V Plus gas isotope mass spectrometer, combined with a Gas Bench II automated device at the Laboratory of Geochemistry and Isotope, Southwest University. The isotopic ratios are reported as per mill (‰) relative to the Vienna Standard Mean Ocean Water (V-SMOW) for all water samples. Repeated analyses of

Table 1

Major cations, anions, oxygen and hydrogen isotopes, and saturation index data of spring, drinking well, river, lake and rain waters in the Daihai Lake catchment.

Sample no.	Longitude (N)	Latitude (E)	pH	T (°C)	EC ^a (μS/cm)	Ca ²⁺ +b (μmol/L)	K ⁺ +b (μmol/L)	Mg ²⁺ +b (μmol/L)	Na ⁺ +b (μmol/L)	Si ⁴⁺ (μmol/L)	Sr ²⁺ +b (μmol/L)	F ⁻ (μmol/L)	Cl ⁻ (μmol/L)	NO ₃ ⁻ (μmol/L)	SO ₄ ²⁻ (μmol/L)	CO ₃ ²⁻ (μmol/L)	HCO ₃ ⁻ (μmol/L)
Spring water																	
SW-1	40°37'33.2"	112°38'16.9"	8.07	35.1	1230	251	170	116	14,100	649	6.91	716.41	3675	–	1394	–	7326
SW-2	40°41'12.8"	112°42'16.1"	8.00	14.2	374	1339	36	555	579	296	3.42	13.68	134	334	378	–	2921
SW-3	40°41'47.8"	112°42'22.5"	7.63	15.3	482	1775	43	737	861	339	4.05	17.49	326	279	363	–	4307
SW-4	40°41'57.6"	112°42'33.1"	7.50	20.4	439	1652	26	588	926	380	3.63	24.10	214	126	312	–	4208
SW-5	40°34'17.4"	112°50'19.4"	8.23	15.7	494	1210	38	894	1608	339	4.66	46.62	360	482	210	–	4703
SW-6	40°27'19.6"	112°49'43.3"	8.01	15.5	414	1000	63	556	1511	496	3.27	26.62	387	179	229	–	4010
SW-7	40°27'14.7"	112°41'46.4"	7.84	17.1	500	1381	62	764	1477	294	4.08	–	589	87	416	–	4653
SW-8	40°31'52"	112°22'50.6"	7.71	11.8	329	1113	25	423	535	412	2.52	9.79	236	108	216	–	3218
Well water																	
WW-1	40°37'0.1"	112°46'7.8"	8.14	13.0	547	1668	32	937	1326	367	5.25	26.87	473	709	226	–	4901
WW-2	40°36'59.7"	112°47'56.5"	8.13	9.3	624	1577	30	1067	1520	397	5.17	28.83	686	447	316	–	6930
WW-3	40°44'35.8"	112°57'0"	8.00	8.5	549	1946	31	786	778	343	4.56	23.85	886	935	291	–	3911
WW-4	40°30'31.6"	112°51'4.0"	7.91	10.4	410	1120	24	636	1203	294	4.07	47.31	231	329	126	–	4208
WW-5	40°38'27.5"	112°42'30.1"	7.93	9.5	469	1545	34	750	932	339	4.26	23.73	419	379	213	–	4356
WW-6	40°36'23.6"	112°38'44.7"	7.82	10.0	463	1497	42	501	1406	332	3.45	55.25	556	233	253	–	4109
WW-7	40°34'8.8"	112°34'49.4"	7.91	11.6	434	1556	44	485	871	309	3.35	37.24	355	402	239	–	3861
WW-8	40°46'6"	112°40'8.8"	7.74	6.9	442	1693	27	592	599	329	2.79	11.12	321	401	287	–	3911
WW-9	40°28'17.6"	112°25'42"	8.14	8.3	615	2182	25	1026	1381	267	6.09	33.08	376	354	366	–	6089
WW-10	40°23'36.5"	112°23'23.8"	7.82	10.5	394	1207	29	650	816	290	3.32	26.57	238	218	121	–	4133
WW-11	40°27'44.5"	112°33'42"	7.91	9.7	919	1761	60	1087	5670	307	7.32	25.95	2334	33	1198	–	6287
WW-12	40°22'34.3"	112°34'9.5"	8.07	13.2	541	1829	46	899	1304	264	2.46	26.66	524	56	411	–	4950
WW-13	40°27'35"	112°49'52.6"	7.92	15.1	429	1200	53	634	1241	371	3.46	21.58	464	171	273	–	3911
WW-14	40°30'17.6"	112°47'10.8"	7.85	9.2	512	1011	55	881	2186	350	5.43	36.65	595	309	366	–	4505
WW-15	40°31'35.4"	112°44'16.2"	7.89	15.8	541	786	23	972	2740	224	4.26	63.45	787	683	209	–	4554
WW-16	40°28'42.1"	112°42'30.4"	7.69	17.1	469	1256	52	763	1308	308	3.65	26.91	590	162	369	–	4208
WW-17	40°26'39.3"	112°42'21.1"	7.77	13.6	464	1303	96	583	1459	394	3.76	26.93	524	193	340	–	4208
WW-18	40°30'11"	112°39'17.9"	7.89	9.2	590	926	32	1572	2091	319	6.37	102.46	723	315	292	–	5742
WW-19	40°38'8.4"	112°45'12.8"	8.06	9.4	499	1568	35	864	1133	372	4.59	23.73	538	443	189	–	4455
River water																	
GB-1	40°32'15.5"	112°33'7.4"	8.71	18.3	451	1593	75	535	964	282	3.73	27.99	501	78	250	–	4406
GB-2	40°31'45.6"	112°33'29.3"	8.40	18.1	495	1104	154	874	1594	170	3.94	19.01	605	72	542	–	4133
GB-3	40°28'59"	112°29'34.4"	8.44	21.3	563	1405	107	1122	1649	296	4.69	19.19	507	37	521	–	5445
GB-4	40°28'0.2"	112°25'53.4"	8.70	22.5	455	1098	142	954	1283	359	3.53	21.00	466	66	136	–	4703
GB-5	40°20'29.9"	112°22'38.4"	8.42	18.8	468	1457	64	784	1101	223	4.01	20.58	476	51	326	–	4356
GB-6	40°20'22.8"	112°22'34.4"	9.42	25.1	269	499	63	296	1016	135	1.82	25.67	351	–	299	–	1931
WH-1	40°28'24"	112°35'20.7"	8.43	19.2	470	751	119	927	1807	65	2.63	17.79	733	–	597	–	3564
WH-2	40°27'49.6"	112°30'24.1"	8.82	21.8	522	1212	95	1044	1714	233	3.18	22.63	653	36	539	–	4406
WH-3	40°22'25.9"	112°34'18.1"	8.69	19.9	296	899	52	479	584	196	1.56	20.48	223	24	229	–	2574
MH-1	40°36'7.1"	112°46'23.2"	8.55	18.9	495	1585	51	745	1272	303	3.89	33.58	527	78	305	–	4752
MH-2	40°37'6.5"	112°48'22.5"	8.41	26.4	498	1608	52	723	1251	329	3.90	35.32	489	165	290	–	4802
MH-3	40°37'14.8"	112°48'30.9"	8.13	26.6	500	1653	52	755	1153	350	4.12	33.18	439	202	275	–	4851

MH-4	40°37'12.5"	112°48'36.2"	8.80	27.4	454	965	49	778	1804	334	3.52	45.59	575	157	297	-	3960
TC-1	40°31'54.5"	112°44'25.7"	8.46	23	564	1286	81	989	2101	252	4.89	31.19	663	200	412	-	5247
TC-2	40°31'54.5"	112°44'25.7"	8.16	18.4	691	1412	87	1697	2723	290	9.12	42.14	697	-	396	-	7128
Lake water																	
L-1	40°33'12.29"	112°38'31.05"	-	-	6977	858	305	5466	82,851	7	8.63	-	79,539	280	1541	1648	10,296
L-2	40°33'58.45"	112°40'14.53"	9.00	21.8	6903	848	298	5384	81,959	7	8.48	-	78,778	-	1472	1748	10,247
L-3	40°35'25.89"	112°40'33.81"	9.03	22	6946	860	307	5477	83,536	7	8.68	-	78,838	-	1393	1598	10,296
L-4	40°34'31.38"	112°42'29.84"	9.02	21.9	6995	866	307	5536	83,945	7	8.72	-	79,572	-	1452	1623	10,420
L-5	40°35'26.71"	112°43'39.16"	9.02	22.1	6993	870	309	5504	83,029	7	8.76	-	79,749	296	1516	1698	10,395
L-6	40°34'10.9"	112°44'25.83"	9.02	22.6	6975	851	310	5467	83,502	7	8.63	-	79,597	-	1501	1947	9900
Rainwater																	
RW	40°31'25.5"	112°29'8.8"	7.66	20.06	47	94	8	22	67	12	0.25	-	36	36	66	-	396

Sample no.	TDS ^c (mg/L)	NICB ^d (%)	$\delta^{18}\text{O}$ (‰)	δD (‰)	Saturation index ^e					Hardness	SAR ^f
					Calcite	Dolomite	Gypsum	Halite	Magnesite		
Spring water											
SW-1	1107	3.32	-12.318	-95.309	0.39	1.43	-2.55	-6.02	-0.53	37	23.29
SW-2	340	5.56	-10.072	-75.546	0.49	1.44	-2.23	-8.76	-0.74	190	0.42
SW-3	457	4.59	-10.199	-78.285	0.39	1.26	-2.18	-8.22	-0.82	251	0.54
SW-4	428	4.38	-9.680	-76.193	0.29	1.04	-2.26	-8.38	-0.92	224	0.62
SW-5	479	-2.66	-8.157	-61.219	0.88	2.49	-2.58	-7.91	-0.07	211	1.11
SW-6	412	-8.01	-9.753	-77.696	0.52	1.66	-2.57	-7.89	-0.56	156	1.21
SW-7	478	-5.67	-9.115	-74.373	0.55	1.72	-2.23	-7.73	-0.51	215	1.01
SW-8	325	-10.23	-10.592	-79.656	0.13	0.68	-2.52	-8.54	-1.17	154	0.43
Well water											
WW-1	525	0.11	-9.539	-75.357	0.89	2.39	-2.43	-7.87	-0.21	261	0.82
WW-2	654	-27.61	-8.418	-67.458	0.93	2.53	-2.32	-7.64	-0.13	265	0.93
WW-3	493	-1.01	-9.317	-74.111	0.66	1.75	-2.24	-7.81	-0.65	273	0.47
WW-4	404	-6.92	-8.975	-73.955	0.42	1.42	-2.78	-8.20	-0.72	176	0.91
WW-5	448	-0.87	-10.090	-76.434	0.56	1.64	-2.45	-8.06	-0.65	230	0.62
WW-6	436	-0.31	-10.482	-80.560	0.42	1.20	-2.37	-7.75	-0.95	200	0.99
WW-7	411	-2.75	-10.180	-77.979	0.53	1.40	-2.38	-8.16	-0.85	204	0.61
WW-8	419	-0.41	-10.117	-77.842	0.33	1.00	-2.26	-8.35	-1.07	229	0.40
WW-9	603	3.06	-9.274	-71.722	1.01	2.52	-2.13	-7.94	-0.23	321	0.77
WW-10	387	-6.52	-9.216	-76.364	0.36	1.27	-2.77	-8.36	-0.80	186	0.60
WW-11	832	3.06	-10.490	-81.748	0.67	1.98	-1.76	-6.55	-0.42	285	3.36
WW-12	506	6.26	-8.870	-67.715	0.86	2.27	-2.14	-7.83	-0.30	273	0.79
WW-13	408	-3.06	-9.557	-75.210	0.49	1.56	-2.43	-7.90	-0.62	184	0.92
WW-14	486	-2.53	-9.134	-75.094	0.30	1.37	-2.39	-7.53	-0.66	189	1.59
WW-15	501	-3.63	-9.037	-70.480	0.34	1.63	-2.75	-7.33	-0.39	176	2.07
WW-16	443	-6.06	-9.165	-72.447	0.32	1.30	-2.30	-7.78	-0.70	202	0.92
WW-17	447	-5.70	-9.302	-73.590	0.37	1.25	-2.31	-7.78	-0.83	189	1.06
WW-18	569	-4.88	-9.352	-71.522	0.39	1.84	-2.57	-7.48	-0.28	250	1.32
WW-19	470	3.19	-9.851	-73.981	0.70	1.98	-2.50	-7.86	-0.46	243	0.73

(continued on next page)

Table 1 (continued)

Sample no.	TDS ^c (mg/L)	NICB ^d (%)	$\delta^{18}\text{O}$ (‰)	δD (‰)	Saturation index ^e					Hardness	SAR ^f
					Calcite	Dolomite	Gypsum	Halite	Magnesite		
River water											
GB-1	435	-4.07	-9.065	-67.629	1.46	3.34	-2.39	-7.99	0.21	213	0.66
GB-2	448	-3.69	-9.606	-72.181	0.97	2.73	-2.21	-7.69	0.08	198	1.13
GB-3	546	-3.53	-8.984	-70.190	1.25	3.32	-2.17	-7.77	0.42	253	1.04
GB-4	444	0.06	-8.676	-67.346	1.37	3.61	-2.86	-7.90	0.59	205	0.90
GB-5	436	1.61	-8.976	-68.545	1.15	2.92	-2.32	-7.96	0.10	224	0.74
GB-6	220	-8.88	-9.304	-74.486	1.35	3.43	-2.75	-8.11	0.45	80	1.14
WH-1	403	-4.28	-9.428	-75.206	0.79	2.57	-2.32	-7.55	0.11	168	1.39
WH-2	477	2.01	-8.828	-75.444	1.46	3.78	-2.22	-7.64	0.67	226	1.14
WH-3	263	2.74	-10.769	-79.667	1.04	2.69	-2.60	-8.55	0.00	138	0.50
MH-1	474	-0.29	-9.613	-75.357	1.34	3.25	-2.32	-7.85	0.24	233	0.83
MH-2	481	-1.80	-9.439	-74.679	1.32	3.23	-2.34	-7.91	0.29	233	0.82
MH-3	485	-0.93	-9.916	-72.974	1.07	2.74	-2.35	-7.99	0.05	241	0.74
MH-4	422	0.14	-10.208	-76.150	1.40	3.66	-2.53	-7.67	0.65	174	1.37
TC-1	538	-3.48	-9.083	-71.860	1.25	3.31	-2.30	-7.55	0.42	228	1.39
TC-2	679	4.08	-8.094	-67.869	1.04	3.05	-2.32	-7.41	0.34	311	1.54
Lake water											
L-1	5700	-0.72	1.331	-20.493	1.45	4.70	-2.54	-4.01	1.61	633	32.94
L-2	5623	-0.79	-	-	1.43	4.66	-2.56	-4.02	1.58	624	32.83
L-3	5660	1.45	1.697	-16.400	1.46	4.73	-2.58	-4.01	1.62	634	33.18
L-4	5710	0.94	-	-	1.46	4.72	-2.56	-4.00	1.62	641	33.18
L-5	5718	-0.81	1.917	-18.709	1.46	4.73	-2.54	-4.01	1.62	638	32.89
L-6	5672	0.05	-	-	1.44	4.69	-2.55	-4.01	1.61	632	33.22
Rainwater											
RW	41	-95.03	-11.258	-87.370	-1.66	-3.06	-3.88	-10.24	-3.06	12	0.20

"-" not analyzed.

^a EC, electrical conductivity.

^b Cation data of river and groundwater is from Zhang et al. (2013).

^c TDS, total dissolved solids.

^d Normalized Inorganic Charge Balance (NICB) = $(\text{TZ}^+ - \text{TZ}^-) / \text{TZ}^+$, where $\text{TZ}^+ = \text{Na}^+ + \text{K}^+ + 2\text{Mg}^{2+} + 2\text{Ca}^{2+}$, $\text{TZ}^- = \text{Cl}^- + 2\text{SO}_4^{2-} + \text{HCO}_3^- + \text{NO}_3^-$ in $\mu\text{Eq/L}$.

^e Saturation Index was calculated using Geochemist's Workbench V.8.0 (Bethke and Yeakel, 2009).

^f SAR, sodium absorption ratio.

samples and laboratory standards show that the 1σ uncertainties were 0.15‰ for $\delta^{18}\text{O}$ and 1.5‰ for δD , respectively.

4. Results and discussion

4.1. Water chemical characteristics

Table 1 lists pH, Total Dissolved Solids (TDS), major ions and the Normalized Inorganic Charge Balance (NICB) of water samples of rivers, springs, wells, lake, and rain sampled within the Daihai Lake catchment. The TDS is calculated by $\text{TDS} = \text{Na}^+ + \text{K}^+ + \text{Mg}^{2+} + \text{Ca}^{2+} + \text{SiO}_2 + \text{Cl}^- + \text{SO}_4^{2-} + \text{HCO}_3^- + \text{NO}_3^-$ in mg/L. The Normalized Inorganic Charge Balance ($\text{NICB} = (\text{TZ}^+ - \text{TZ}^-) / \text{TZ}^+$) is used to estimate overall analytical uncertainties (Table 1), and is expected to be close to zero unless one or more ions have been overlooked during the analyses. For almost all samples measured, the total dissolved cationic charge ($\text{TZ}^+ = \text{Na}^+ + \text{K}^+ + 2\text{Mg}^{2+} + 2\text{Ca}^{2+}$ in $\mu\text{Eq/L}$) and the total dissolved anionic charge ($\text{TZ}^- = \text{Cl}^- + 2\text{SO}_4^{2-} + \text{HCO}_3^- + \text{NO}_3^-$ in $\mu\text{Eq/L}$) are well balanced with $\text{NICB} < \pm 10\%$. All of the 15 river water samples show $\text{NICB} < \pm 5\%$, with the exception of GB-6 ($\text{NICB} = -8.88\%$). These suggest that the dissolved ions are responsible for the major charge balance of samples measured in this study.

4.1.1. River waters

Our data show that river waters are mild alkaline with pH values ranging from 8.16 to 8.55. The water temperature and electrical conductivity (EC) show variations of 7.1–19.3 °C and 269–691 $\mu\text{S/cm}$, respectively. The TZ^+ ranges from 2699 to 9027 $\mu\text{Eq/L}$, which is higher than the world average of ~1250 $\mu\text{Eq/L}$ (Meybeck, 1979). The TDS of the river waters in the Daihai Lake catchment varies from 220 to 679 mg/L with an average of 450 mg/L. This value is higher than most of rivers draining the Himalayas and the Tibetan Plateau (from low to high, TDS = 71, 164, 175, 187, 208, and 274 mg/L in Brahmaputra, Indus, Red River, Ganges, Upper Yangtze River, and Upper Yellow River, respectively), but is very similar to the lower reaches of the Yellow River (460 mg/L) (Dalai et al., 2002; Gaillardet et al., 1999; Galy and France-Lanord, 1999; Karim and Veizer, 2000; Moon et al., 2007; Qin et al., 2006; Wu et al., 2005).

On average, Ca^{2+} , K^+ , Mg^{2+} , and Na^+ account for 43.7%, 1.5%, 29.0%, and 25.7% of the TZ^+ of the measured river water samples, respectively. The molar cation concentrations follow an order of $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$, or $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$, and this trend is shown by the ternary diagram for cations (Fig. 3a). Na^+ is significantly higher than Cl^- , with Na^+/Cl^- molar ratios ranging from 1.91 to 3.91. This suggests that dissolution of halite is not the sole Na^+ source in river waters. The average Si concentration is 254 μM , nearly 2 times of the world average (145 μM , Meybeck, 2003). The high Si values in the river waters may indicate influences of silicate weathering and/or evaporation under the semi-arid climate condition in the Daihai catchment.

HCO_3^- is a major anion of measured river waters, accounting for 64.7%–85.1% of the TZ^- in charge equivalent units. The molar anion concentrations listed in Table 1 follow an order of $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^- > \text{F}^-$. The ternary diagram (Fig. 3b) clearly shows that most data plot around the alkalinity apex leaning towards ($\text{Cl}^- + \text{SO}_4^{2-}$). This indicates that dissolution of evaporites and/or pyrite oxidation supplies Cl^- and SO_4^{2-} to the rivers. NO_3^- ranges from 24 to 202 $\mu\text{mol/L}$. One of the sources of nitrate to rivers is fertilizers (Bernier and Bernier, 1996). The influence of agriculture on NO_3^- abundance in the Daihai Lake catchment is difficult to assess, as the knowledge on agriculture practice and fertilizer use in the catchment is limited. However, in the Muhua River samples which have the $\text{NO}_3^- > 150 \mu\text{mol/L}$, anthropogenic contribution could be a reason.

4.1.2. Groundwaters

Groundwaters sampled in the Daihai Lake catchment include springs and drinking wells. These samples are all alkaline with pH values ranging from 7.50 to 8.23. The temperature of well waters ranges from 6.9 to 17.1 °C, lower than the values of spring water (11.8–35.1 °C). The EC of spring waters varies from 329 to 1230 $\mu\text{S/cm}$, showing a slightly wider range than that of well waters (394–919 $\mu\text{S/cm}$). The TDS concentrations of the groundwater range from 325 to 654 mg/L with an average of 461 mg/L, with the exception of the two high values of 832 mg/L and 1107 mg/L (Table 1). The average TDS is lower than those of groundwater in the semi-arid/arid Lake Qinghai catchment in the northeastern Tibetan Plateau (average 672 mg/L, Xiao et al., 2012), and those of rivers in more arid Tarim River basin in the northwestern Tibetan Plateau (0.75–4.62 g/L, Zhu and Yang, 2007).

Ca^{2+} , K^+ , Mg^{2+} , and Na^+ account for 48.0%, 0.7%, 25.4%, and 25.9% of the TZ^+ of the groundwater, respectively. The molar cation concentrations follow the same order as those of the river waters. The cationic concentrations of the groundwater are also close to those of the river waters. In the ternary diagram (Fig. 3a), the data of groundwaters and river waters are largely overlapped, with the groundwaters relatively closer to the Ca^{2+} apex due to their higher Ca^{2+} proportions. The dominant anion, HCO_3^- , accounts for 74.6% of the TZ^- in the groundwaters. The molar anion concentrations of the groundwaters follow an order of $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^- > \text{F}^-$. The ion concentrations of the groundwaters, as well as their proportions of each ion to the total ions, are very close to the river waters. This phenomenon is shown in the ternary diagram (Fig. 3a, b, c) in that the data points of the river waters and the groundwaters are overlapped, indicating exchange of waters via mutual permeation between the two water types.

4.1.3. Lake waters

Six lake water samples from Daihai Lake show pH values between 9.00 and 9.03, temperatures between 21.8 and 22.6 °C, and EC between 6903 and 6995 $\mu\text{S/cm}$ (Table 1). The TDS of the lake waters vary from

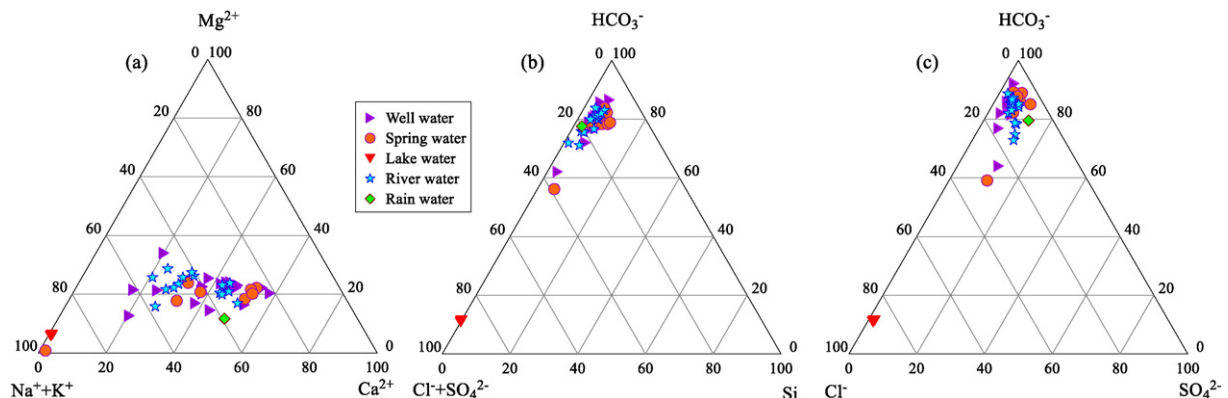


Fig. 3. Ternary diagrams for cations and anions of river, rain, lake, and groundwaters (including well and spring waters) within the Daihai Lake catchment.

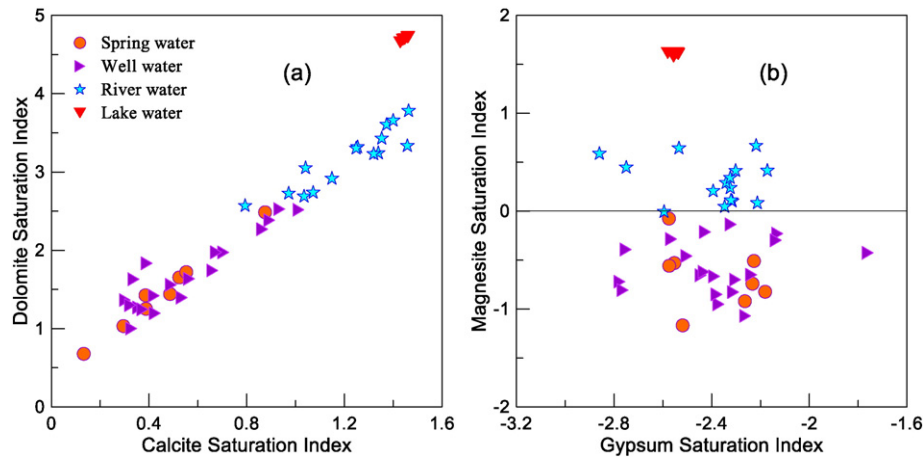


Fig. 4. Plots of saturation index for (a) dolomite vs. calcite, and (b) magnesite vs. gypsum of water samples in the Daihai Lake catchment.

5623 to 5718 mg/L (mean 5681 mg/L), much higher than those of the global rivers (115 mg/L). The lake water chemistry is dominated by Na^+ and Cl^- (Fig. 3a, b, c) with Na^+ accounting for 86% of the TZ^+ and Cl^- for 82% of the TZ^- . The molar cation concentrations follow an order of $\text{Na}^+ \gg \text{Mg}^{2+} > \text{Ca}^{2+} > \text{K}^+$ and the molar anion concentrations follow $\text{Cl}^- \gg (\text{HCO}_3^- + \text{CO}_3^{2-}) > \text{SO}_4^{2-}$. In addition, Ca^{2+} concentrations in the lake waters are much lower than Mg^{2+} , suggesting that Ca^{2+} is removed from the water by precipitation of authigenic carbonates whereas Mg^{2+} is accumulated in the lake (see Section 4.2.2).

4.1.4. Rainwater

The chemical component of rainwater reflects the local chemical background, and is a crucial means to trace the atmospheric material sources and transportations. The pH of the rain water is 7.66 and its TDS content is 41 mg/L, within the general range of the rainwater salinity (20–50 mg/L) (Shen et al., 1993). The Na^+/Cl^- molar ratio of the rainwater sample is 1.85, higher than that of the seawater, indicating that the chemical compositions of rainwater are modified by dissolving the atmospheric dust during transportation.

4.2. Influencing processes for the release of major ions in natural waters

4.2.1. Saturation index

The saturation index data calculated with the software of Geochemist's Workbench V.8.0 (Bethke and Yeakel, 2009) are listed in Table 1 and displayed in Fig. 4. The calcite, dolomite, magnesite and gypsum saturation indices are defined by:

$$\text{Calcite Saturation Index} = \log \left(\frac{\{\text{Ca}^{2+}\} \times \{\text{CO}_3^{2-}\}}{K_{\text{calcite}}} \right)$$

$$\text{Dolomite Saturation Index} = \log \left(\frac{\{\text{Ca}^{2+}\} \times \{\text{Mg}^{2+}\} \times \{\text{CO}_3^{2-}\}}{K_{\text{dolomite}}} \right)$$

$$\text{Magnesite Saturation Index} = \log \left(\frac{\{\text{Mg}^{2+}\} \times \{\text{CO}_3^{2-}\}}{K_{\text{magnesite}}} \right)$$

$$\text{Gypsum Saturation Index} = \log \left(\frac{\{\text{Ca}^{2+}\} \times \{\text{SO}_4^{2-}\}}{K_{\text{gypsum}}} \right)$$

where K values are the thermodynamic solubility product constants and “{ }” denotes activities of ions. We find that all waters are supersaturated with respect to calcite and dolomite, but are undersaturated with respect to gypsum. In addition, all lake and river waters besides groundwaters are supersaturated with respect to magnesite (Fig. 4a, b). The carbonate (calcite and dolomite) saturation index follows lake water > river water > groundwater.

4.2.2. Mechanisms controlling water chemistry

Weathering and erosion of rocks/minerals are crucial to influence water chemical compositions. Gibbs (1970) proposed that the $\text{TDS} - \text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ could be used to explore the relative importance of the major natural mechanisms controlling water chemistry. Three types of controls may be classified based on the diagram: (1) rock weathering, (2) atmospheric precipitation, and (3) evaporation/crystallization. Fig. 5a shows that, with the exception of the spring water S1, all the water samples fall within the Gibbs model, and their distributions exhibit following features.

- (1) The lake waters plot within the evaporation/crystallization dominance field. Their TDS contents are higher than the river and groundwaters and most large global rivers. The $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ values close to 1, similar to the seawater endmember, indicate that the chemical compositions of the lake water are controlled by evaporation/crystallization.
- (2) The river and the groundwater data plot within the rock dominance field, indicating that these waters are dominated by parent material weathering. Moreover, these samples are close to the boundary of the rock and the evaporation dominances, suggesting a secondary role of evaporation. Furthermore, the points of the river and the groundwaters overlap in the rock dominance with the same level of the TDS contents and $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ ratios. Compared with the global rivers (115 mg/L), the river waters within the Daihai Lake catchment exhibit higher TDS concentrations (450 mg/L), showing different water chemistry developed under semi-arid environment.
- (3) The rainwater data plots within the lower end of the rock dominance field, close to the boundary of the rock and the precipitation dominances, indicating that the rainwater potentially dissolves local dust during the processes of long distance transportation to the catchment, resulting in an increase in TDS contents. When carbonate dust dissolves in the rainwater (Zhang et al., 2009a), its $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ value decreases, and hence the data point moves left to the rock dominance field.

The plot of $\text{Mg}^{2+}/\text{Ca}^{2+}$ versus $\text{Mg}^{2+}/\text{Na}^+$ (Fig. 5b) is used to reflect the evolution process of water chemistry in arid environments (Webster et al., 1994). The increase of $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio from rain to river waters and finally to lake waters in semi-arid Daihai Lake catchment shows obvious evaporation influences, in particular for the lake waters (Fig. 5b). During such process, calcite precipitation occurs. It was reported that CaCO_3 abundances in the lake sediments ranged from 10.4% to 14.5% (Jin et al., 2001). The carbonate saturation index (CSI) shows that the lake waters are calcite over-saturated with respect

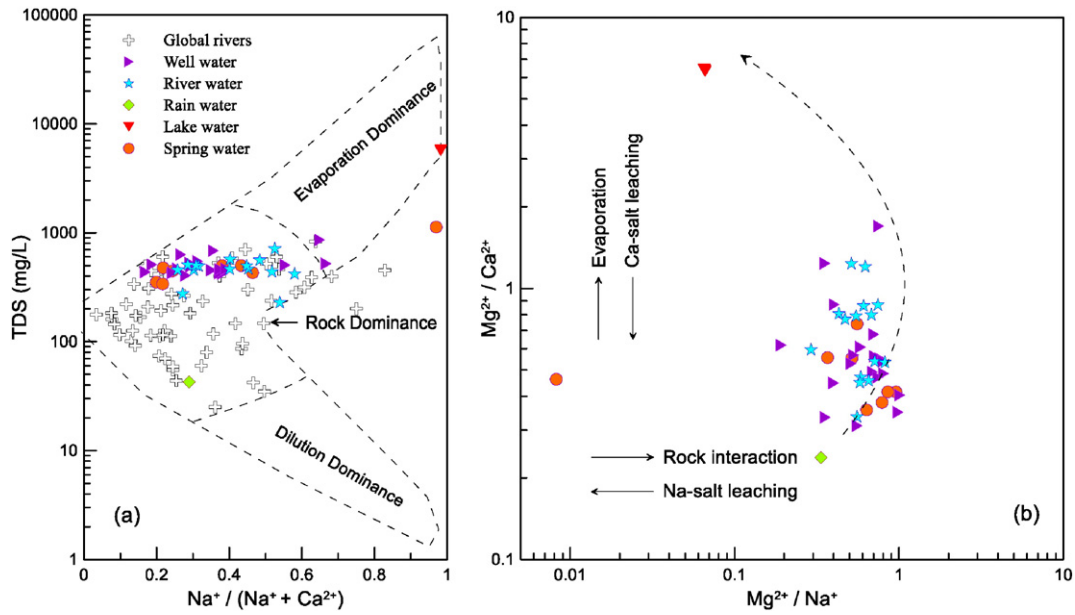


Fig. 5. Plots of (a) TDS vs. $Na^+ / (Na^+ + Ca^{2+})$ (after Gibbs, 1970), and (b) Mg^{2+} / Ca^{2+} vs. Mg^{2+} / Na^+ molar ratios (after Webster et al., 1994).

to calcite (Table 1). The increase of Mg^{2+} / Na^+ ratio from rain water to river waters indicates the chemical weathering of parent materials in the Daihai Lake catchment, while the slightly decrease of the ratios from river waters to lake waters may reflect a small amount of Mg

removal by precipitation of dolomite and/or magnesite. These two minerals are over-saturated in the lake water. Microscopic observations on core sediments provide a direct evidence of authigenic carbonate precipitation, which mainly includes micro-grained and spherical calcite,

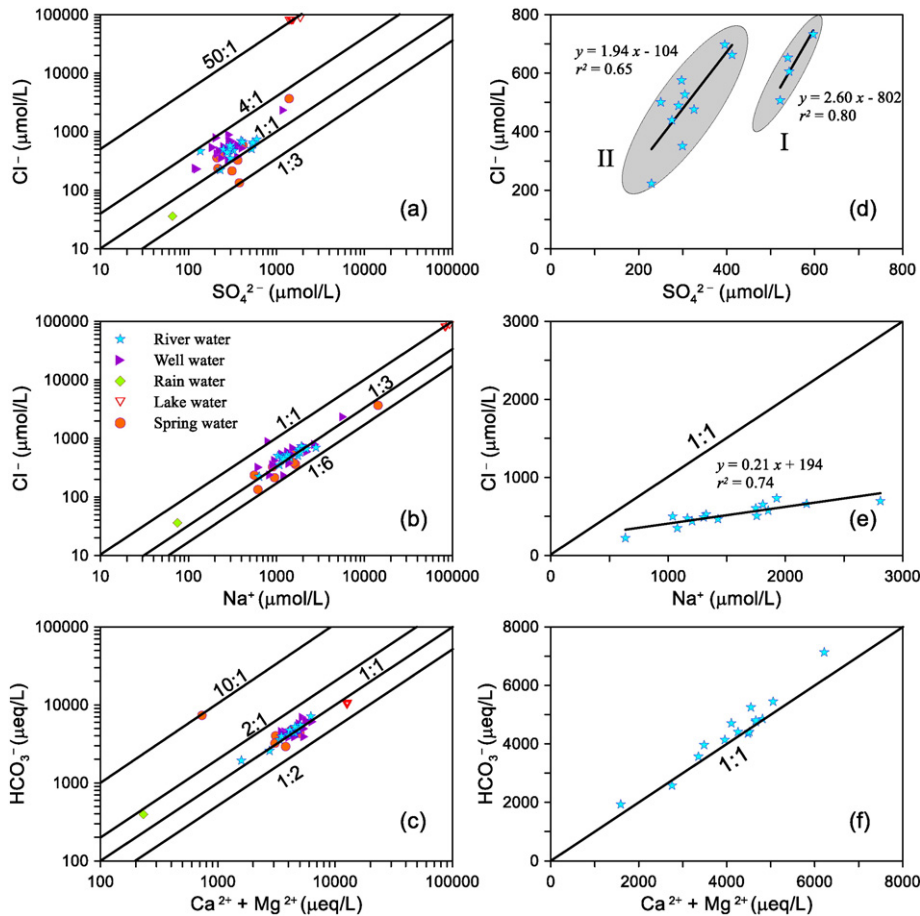


Fig. 6. Plots of Cl^- vs. SO_4^{2-} (a, d), Cl^- vs. Na^+ (b, e), and HCO_3^- vs. $(Ca^{2+} + Mg^{2+})$ (c, f). (a–c) show the major ions variations of waters from rivers, wells, rain, lake and springs, and (d–f) show the major ions variations of river waters in the Daihai Lake catchment.

as well as minor dolomite only found to precipitate on shallow water zone of lake-bay where river water feeds quite limited and evaporation is strong (Wang et al., 1990). The warm spring water with extremely low Mg^{2+}/Na^+ ratio may indicate the Na-bearing salt leaching.

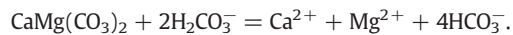
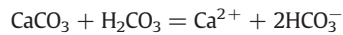
4.2.3. Rock/mineral weathering, evaporation and biological decomposition

In the Daihai Lake catchment, major ions of water samples exhibit large variations in concentrations and ratios (Fig. 6a, b, c), which may indicate different sources, evaporation enrichment and biological decomposition. Like the TDS, the extremely high major ion concentrations of the lake waters reflect evaporation influence, whereas their much higher Cl^-/SO_4^{2-} molar ratios (~50) than those of the river waters (0.97–3.42) indicate that other factors, rather than evaporation enrichment, affect the ion ratios for the lake waters (Fig. 6a). Considering that Cl^-/SO_4^{2-} ratio of rain water (0.55) is lower than that of the river waters, the input from rainfall is excluded to be the reason for the high Cl^-/SO_4^{2-} ratios of the lake waters. Same phenomenon was reported by Wang et al. (1990) that SO_4^{2-} concentration of pore water in sediment core in Daihai Lake decreased with increasing depth, with Cl^- content constant. Therefore, the most possible explanation for high Cl^-/SO_4^{2-} ratios in the lake waters might be that SO_4^{2-} is decomposed by sulfate bacterial activity. In addition, river and most of well waters show similar ranges of ion concentrations and ratios (Fig. 6a, b, c), suggesting infiltration of groundwater from surface water in loess environment. However, different from the river and well waters, warm spring water shows very high contents of Na^+ , Cl^- and SO_4^{2-} but low $(Ca^{2+} + Mg^{2+})$, indicating its different ion source (Fig. 6a, b, c).

For surface weathering processes, good correlations between Cl^- and SO_4^{2-} for river waters indicate their common sources (evaporite dissolution) (Fig. 6d). It is worth noting that the samples in Fig. 6d are divided into two groups. Group I include 4 samples collected at the downstream of the Gongba and Wuhao Rivers, while Group II are the remaining samples collected surrounding Daihai Lake. The higher SO_4^{2-} contents in the Group I relative to the Group II indicate more sulfate dissolution such as thenardite (Na_2SO_4) and gypsum in the downstream of the Gongba and Wuhao Rivers, where gypsum layers were observed in a 79.1 m long core (Liu and Zhou, 2009). Both the more sulfate dissolution and gypsum layers prove a high lake level in historical period. The plot of Na^+ and Cl^- shows a strong correlation ($r^2 = 0.74$) (Fig. 6e). Cl^- content is generally minor in rocks but is rich in evaporite (such as halite). A few previous studies showed that evaporite content was up to 5–10% of loess on the CLP (Zhang and Zhang, 2003), and evaporite dissolution from loess contributed a large proportion of cationic dissolved load to the Yellow River, from 37.6% of cations for the whole river (Zhang and Zhang, 2003), from 1% to 70% in the Upper reaches (Wu et al., 2005), and 50.1% in the middle reaches (Zhang et al., 2015). Zhang et al. (2015) further indicated that among the 50.1% of evaporite contribution, 25.7% was from halite. In this study, all the river samples in Fig. 6e plot below the 1:1 line, suggesting that excess Na^+ to Cl^- is derived from other sources besides halite dissolution. Yokoo et al. (2004) conducted an H_2O -extracted experiment on loess of the CLP, and found that parts of Na content were derived from halite dissolution, while the excess Na to Cl was from thenardite. However, the mean Na^+/Cl^- molar ratio (2.92) for the river waters is still much higher than those of the H_2O -extracted fraction (1.32–1.70) of typical loess (Yokoo et al., 2004). The sources for Na^+ in river water can be evaporite dissolution, atmospheric input, and silicate weathering. Considering that the Na^+/Cl^- molar ratios of river waters are also much higher than that of rain water (1.85) collected in the Daihai Lake catchment, the excess Na^+ in the river waters should be derived from silicate weathering besides evaporite and atmospheric input.

In the river water compositions, Ca^{2+} and Mg^{2+} together constitute 72.7% of the TZ^+ , and HCO_3^- for 76.3% of the TZ^- . The cations Ca^{2+} and

Mg^{2+} in water are mainly supplied by carbonate minerals such as calcite and dolomite. The principal reactions can be illustrated as:



Accordingly, if Ca^{2+} , Mg^{2+} and HCO_3^- in waters are derived from carbonate minerals, the ratio of $(Ca^{2+} + Mg^{2+})/HCO_3^-$ should theoretically equal to 1. Plot of $(Ca^{2+} + Mg^{2+})$ versus HCO_3^- in Fig. 6f shows that the river water samples clearly plot close to the 1:1 line, indicating the important carbonate weathering in the Daihai Lake catchment. This result is consistent with the high carbonate abundance in loess, as illustrated by Liu (1985) that a very important characteristic of loess is the presence of carbonates (dolomite and calcite). Despite that, most of the river water samples fall slightly above the 1:1 line (Fig. 6f), suggesting that an excess of alkalinity of the river waters should be balanced by $(Na^+ + K^+)$ derived from silicate weathering.

Na^+ and K^+ in the river waters account only for 27.2% of the TZ^+ . Compared with the high $(Ca^{2+} + Mg^{2+})/TZ^+$ ratio (72.7%), the low $(Na^+ + K^+)/TZ^+$ ratio along with high $(Ca^{2+} + Mg^{2+})/(Na^+ + K^+)$ ratio (2.89) indicate that silicate weathering is less important relative to carbonate weathering, though the outcropped bedrocks in the Daihai Lake catchment are predominantly Archean metamorphosed igneous rocks and Tertiary basalt, with limited area of loess. A most possible explanation is that carbonate rocks dissolve much more readily than silicate rocks.

4.3. Oxygen and hydrogen isotopes

The $\delta^{18}O$ and δD values for river waters vary from -10.8‰ to -8.1‰ and -80‰ to -67‰ , respectively, with mean $\delta^{18}O$ and δD values of -9.3‰ and -72.6‰ , respectively (Table 1). The shallow groundwater samples from drinking wells have $\delta^{18}O$ and δD values varying from -10.5‰ to -8.4‰ and -82‰ to -67‰ , respectively, with mean $\delta^{18}O$ values of -9.5‰ and mean δD of -74.4‰ , respectively (Table 1). Waters from rain and warm spring have the most negative isotopic values ($\delta^{18}O$: -11.3‰ and -12.3‰ ; δD : -87‰ and -95‰), and the lake waters have the most positive values ($\delta^{18}O$: from 1.3‰ to 1.9‰ ; δD : -16‰ and -20‰), both differing significantly from the river and well waters.

Fig. 7 illustrates the relationship of $\delta^{18}O$ and δD of rainwater, river, lake and groundwaters, along with Global Meteoric Water Line (GMWL; $\delta D = 8 \delta^{18}O + 10$, Craig, 1961). All these waters plot to the right of the GMWL. The $\delta^{18}O$ and δD in the well waters fall in the

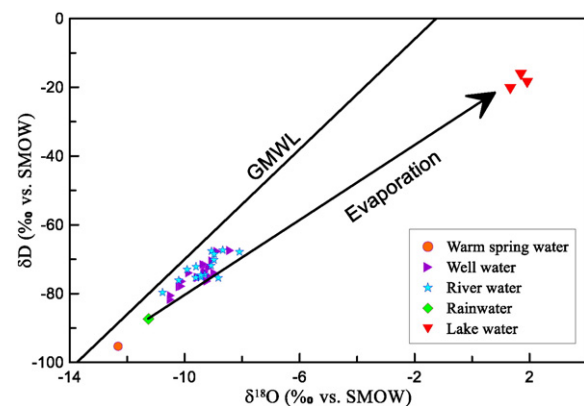


Fig. 7. Plot of δD versus $\delta^{18}O$ of waters from warm spring, wells, rivers, rain and lake in the Daihai Lake catchment. Global Meteoric Water Line (GMWL) is from Craig (1961). Lake waters are enriched in heavy isotopic compositions due to evaporation.

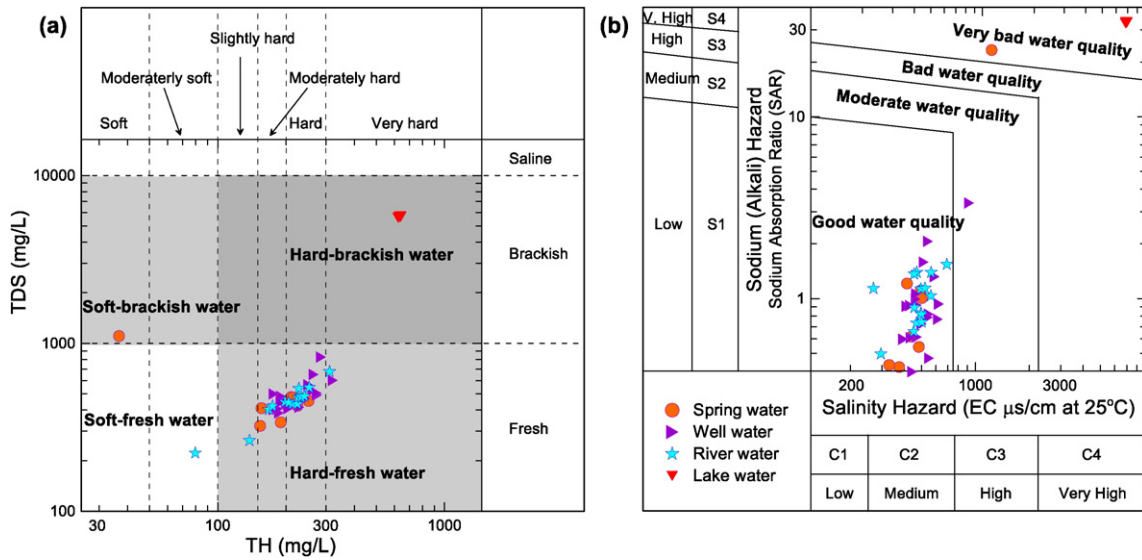


Fig. 8. Diagrams for classification of drinking (a) and irrigation waters (b; after Richards, 1954) in the Daihai Lake catchment, northeastern Chinese Loess Plateau.

range of the river waters (Fig. 7). Their similarity of $\delta^{18}\text{O}$ and δD in these two water types, along with the similar major ion concentrations and TDS (Figs. 3 and 5a), demonstrates that: (1) shallow groundwater is derived from infiltration of surface runoff, and (2) this infiltration process is very fast, resulting in minor variations of $\delta^{18}\text{O}$, δD , TDS and ion compositions between river water and groundwater. The fast infiltration is determined by local lithological characteristics, because both of the loose physical structure of loess and the porosity of basalt facilitate the fast infiltration of surface to groundwaters. This phenomenon in the CLP is very different from that in the northeastern Tibetan Plateau. For example, the TDS of river water in the semi-arid Lake Qinghai catchment (243–405 mg/L for the main rivers, Zhang et al., 2009a) is obviously lower than that of groundwater (average 672 mg/L, Xiao et al., 2012), since the lithology is not conducive to water infiltration. For the rainwater within the Daihai Lake catchment, its more negative $\delta^{18}\text{O}$ and δD values indicate that both of the river and groundwaters are originally derived from local precipitation. On the other hand, the warm spring water has most negative $\delta^{18}\text{O}$ and δD values, suggesting that the warm spring water is likely derived from deeper aquifers rather than local precipitation. It is further supported by its extremely high Na^+ , HCO_3^- and F^- , but very low Ca^{2+} and Mg^{2+} (Table 1). The most positive $\delta^{18}\text{O}$ and δD values of the lake water reflect the clear effect of evaporative enrichment, consistent with its several orders of magnitude higher Na^+ and Cl^- contents than those of the river waters.

4.4. Water quality assessment

The Daihai Lake catchment is located at the semi-arid northeastern CLP, where the water resources are scarce. Better understanding of water quality in such region is critical to the viability of irrigation and domestic water use.

4.4.1. Drinking water

The natural water quality for drinking purpose in this study is assessed based on the recommended National Standard of the People's Republic of China (NSPRC, 2002), from which the highest desirable limits of TDS, TH, pH and the concentrations of Ca^{2+} , Mg^{2+} , Na^+ , F^- , Cl^- , NO_3^- and SO_4^{2-} are 1000 mg/L, 450 mg/L, 8.5, 1871, 1234, 8700, 79, 7052, 806, and 2603 $\mu\text{mol/L}$, respectively. The TDS versus TH plot shows that all of the lake water samples are very hard-brackish water, and one warm spring sample is soft-brackish water, and almost all of other surface and subsurface samples are moderately hard to hard-

fresh water, with only one river water sample (GB6) belonging to soft-fresh water (Fig. 8a). Among 19 drinking well samples, the NO_3^- concentration of one well (W3) and Ca^{2+} and/or Mg^{2+} contents of 3 wells exceed the desirable limits of NSPRC. Long-term drinking of those wells may lead to some diseases. For example, high NO_3^- concentrations could result in birth malformation, hypertension and high-Fe hemoglobin (Carpenter et al., 1998). Therefore, 4 of 19 drinking wells (21%) cannot be used for drinking, whereas other wells (79%) and all river water samples have all the ions below the limits of NSPRC, suitable for drinking.

4.4.2. Irrigation water

The diagram of EC versus sodium absorption ratio (SAR) is widely used to assess the water quality for irrigation purposes (Richards, 1954) and is shown in Fig. 8b. The salinity hazard expressed in terms of EC can be classified as low (<250 $\mu\text{s/cm}$), medium (250–750 $\mu\text{s/cm}$), high (750–2250 $\mu\text{s/cm}$) and very high (2250–5000 $\mu\text{s/cm}$) salinity zones. The interpretation of the EC classification of irrigation waters is summarized as follows: Low salinity water (C1) can be used for irrigation with most crops on most soils. Medium salinity water (C2) can be used if a moderate amount of leaching occurs. Plants with moderate salt tolerance can be grown in most cases without special practices for salinity control. High salinity water (C3) cannot be used on soils with restricted drainage. Even with adequate drainage, special management for salinity control may be required and plants with good salt tolerance should be selected. Very high salinity water (C4) is not suitable for irrigation under ordinary conditions (Richards, 1954). The sodium (alkali) hazard is often expressed as SAR and it can be estimated by the formula:

$$\text{SAR} = \text{Na}^+ / ((\text{Ca}^{2+} + \text{Mg}^{2+}) / 2)^{0.5}$$

where the ion concentrations are expressed in mEq/L. High sodium water used for irrigation may produce harmful levels of exchangeable sodium in most soil, which destroys the soil structure owing to dispersion of the clay particles and finally reduces plant growth (Richards, 1954; Singh et al., 2005). Fig. 8b shows that almost all of the river and well waters within the Daihai Lake catchment belong to low sodium–medium salinity water which can be used for irrigating plants with moderate salt tolerance, whereas lake water and one warm spring water, both with very high sodium (14,100–83,945 mEq/L), belong to very bad water quality and are not suitable for irrigation. Therefore, compared with the Yellow River in which 70% of the total length of the river is classified

as bad water (Wang et al., 2006), most waters in the Daihai Lake catchment are still suitable for drinking and irrigation.

4.5. Lake evolution and anthropogenic effects over the last 60 years

Lake evolution can have a profound impact on the local ecological environment. Great changes have taken place in Daihai Lake over the past decades. One of the most important changes is the lake shrinkage. It is shown that the area and water level of Daihai Lake have been reduced by 41% and 4.83 m, respectively, from 1955 to 2003, and started to accelerate since 1980 (Fig. 9). Lake shrinkage has also been reported in the Tibetan Plateau in northwest China, and climatic factor is considered to be the reason. Lake Qinghai, located in the northeastern Tibetan Plateau, has shrunk by 4 km²/yr in the past 20 years, due to increasing air temperature and decreasing precipitation (Liu and Liu, 2008). In this study, the meteorological data (1954–2011) in Daihai vicinity areas (Datong and Jining) show same trends of air temperature and precipitation as those in the Lake Qinghai catchment, indicating the great climate effect on the Daihai Lake shrinkage (Fig. 10a, b).

In addition, the impacts of human activities cannot be ignored for the lake shrinkage. The human activities in the Daihai Lake catchment mainly include: (1) 25 reservoirs have been built since 1958 and (2) a large number of mechanical wells were used for irrigation in the 1970s when the lake began to shrink fast. These human activities eventually led to the changes of hydrological flowpaths and the decreases of the inflow runoff feeding the lake. As a consequence, Daihai Lake has dramatically shrunk, along with the decline of groundwater table level.

Moreover, Daihai Lake shrinkage has produced a series of environmental problems. (1) Serious soil and water loss. The loss area accounts for 51.8% of the total catchment area (Li, 2011; Sun et al., 2006). (2) Salinization of the lake water (Table 2). Both of the TDS and Cl⁻ concentrations increased by 1.8 times from 1953 to 2010, with the former increasing from 2250 to 6225 mg/L and the latter from 1090 to 3046 mg/L, respectively (Fig. 11a). It is also observed in Fig. 11a that the salinization rate accelerated since 2004, compared to the slow rate during 1952–1984. (3) Great variations of the lake water compositions. The Mg/Ca molar ratio increased by 156 times from 1953 to 2010 with its values varying from 0.05 to 7.87 (Fig. 11b). Since the water chemistry compositions determine the growth of aquatic organisms, such variations may significantly change the ecological structure of Daihai Lake. For example, the pH value (9.1) of the lake water is already close to the upper limit of the fish survival, while the total alkalinity (13.68 mEq/L in 2008) of Daihai Lake has been far higher than the standard (3.5 mEq/L) of aquatic organisms.

Besides lake shrinkages in Qinghai Lake and Daihai Lake, the Yellow River, the second largest in China and the fifth longest in the world, has also suffered sharply decreased runoff and water quantity since the 1950s (Chen et al., 2003). Based on these results, it is reasonably concluded that climate in the northern and northwestern China is

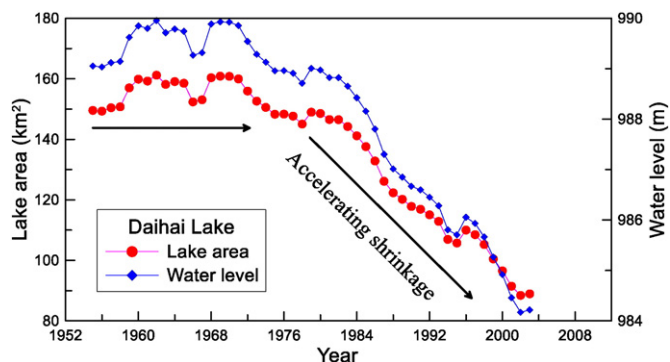


Fig. 9. Temporal evolution of area and water level of Daihai Lake, showing accelerating lake shrinkage.

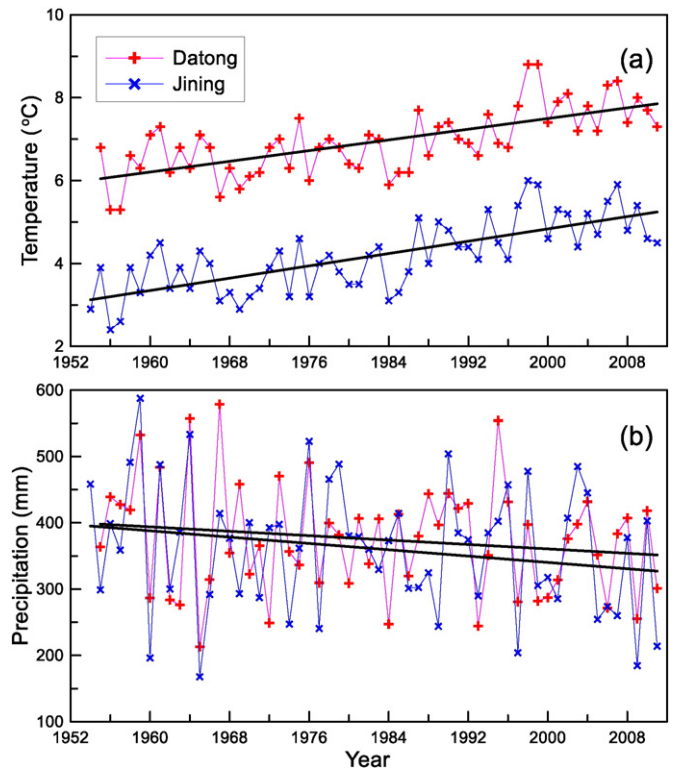


Fig. 10. Temporal variations of air temperature (a) and precipitation (b) in the Daihai vicinity cities (Datong and Jining) from 1953 to 2011, showing the increasing air temperature and decreasing precipitation over the past decades.

becoming more drought and environment degradation is growing rapidly in these semi-arid/arid regions. Considering the uniformity of loess, these results may represent a common status of the CLP.

5. Conclusions

Our measurements show that river and lake waters from the semi-arid loess-covered region on the northeastern CLP are characterized by high TDS, approximately 4–50 times of the global river mean values. Under natural conditions, the river and groundwater chemistry is

Table 2
Temporal variations of water chemistry for the Daihai Lake water over the past 60 years.

Year	TDS mg/L	References	Cl mg/L	Mg/Ca mol/mol	References
1953			1291	0.05	Wang et al. (1990)
1962	2250	Huang et al. (1997)	1190		Wang et al. (1990)
1963	2282	Huang et al. (1997)	1090	0.24	Wang et al. (1990)
1964				2.01	Wang et al. (1990)
1974	2700	Huang et al. (1997)		3.22	Wang et al. (1990)
1985			1448	5.03	Wang et al. (1990)
1986	3310	Huang et al. (1997)	1571		Wang et al. (1990)
1987				5.92	Wang et al. (1990)
1988	3400	Huang et al. (1997)			
1989	3300	Huang et al. (1997)			
1990	3954	Huang et al. (1997)			
1992	3900	Huang et al. (1997)			
1994	4310	Huang et al. (1997)	2107	5.41	Du et al. (1999)
1995	4474	Du et al. (1999)	2148	5.29	Du et al. (1999)
1996	4245	Zhou et al. (2008)	2064	4.88	Du et al. (1999)
1997	4236	Du et al. (1999)	2064	4.91	Du et al. (1999)
2003	4413	Sun et al. (2006)	2199	7.81	Sun et al. (2006)
2004	4659	Zhou et al. (2008)	2135	7.43	Zhou et al. (2008)
2006	4835	Wu et al. (2007)	2240	7.74	Wu et al. (2007)
2008	5681	This study	2813	6.44	This study
2010	6225	This study	3046	7.87	This study

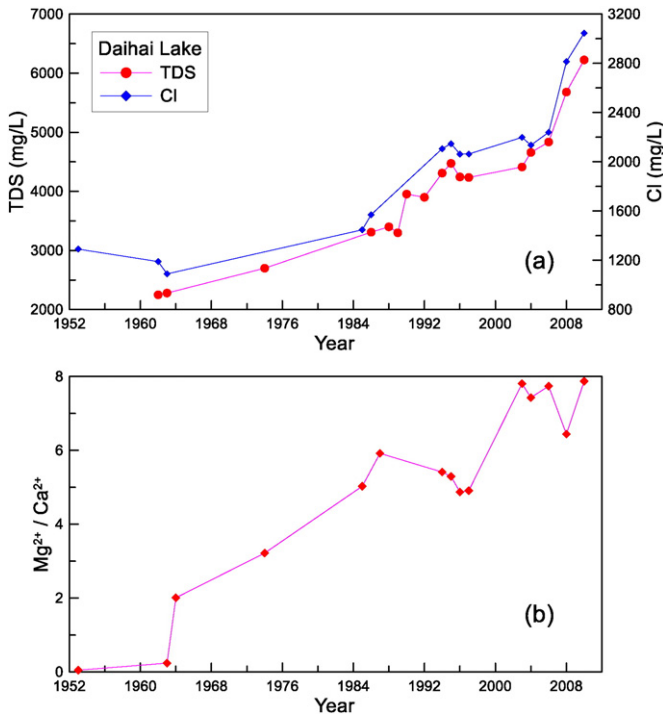


Fig. 11. Temporal evolution of TDS and Cl (a), and Mg/Ca (b) of Daihai Lake water from 1952 to 2010.

dominated by carbonate weathering. The lake water is affected by calcite and dolomite precipitation due to strong evaporation. The water chemistry indicates a fast water infiltration from surface to groundwaters in the loess-covered area. Our water quality assessment shows that all of the river and 79% of well waters are potable and suitable for irrigation of plants with moderate salt tolerance, in contrast to lake and spring waters which cannot be used for drinking nor irrigation.

The TDS and Cl⁻ concentrations increased by 1.8 times, and Mg/Ca increased by 156 times from 1953 to 2010. The salinization rate accelerated since 2004, compared with the slow rate during 1952–1984. The environment on CLP is degrading rapidly, greatly threatening human occupation in the semi-arid regions. Our results provide important information to improve our understanding of processes affecting water chemistry and utilization and probably other loess-covered regions, where water resources are a key factor determining the health and wealth of more than 100 million habitats.

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