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# Water and sediment quality in Qinghai Lake, China: a revisit after half a century

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Abstract Qinghai Lake, situated on the Qinghai-Tibet plateau, is the largest lake in China. In this study, the water and sediment quality were investigated in Qinghai Lake, three sublakes, and five major tributaries. Both Na<sup>+</sup> and Cl<sup>-</sup> were found to be the major ions present in Oinghai Lake and the three sublakes, while Ca<sup>2+</sup> and HCO<sup>3-</sup> dominated the tributaries. Compared with historical data from the 1960s, the concentrations of  $NH_4^+$ , NO<sub>3</sub><sup>-</sup>, and soluble reactive silica have increased considerably, likely caused by increased human activities in the area. Compared to the historical data, chemical oxygen demand has increased and lake water transparency has decreased, likely related to an increase in nutrient levels. Relatively high concentrations of total nitrogen (TN) and total phosphorus (TP) were observed in Qinghai Lake sediments, although P fraction types and low water concentrations of these two indicate low possibility of transfer into the water column. The ratios

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X. Xiong · L. Jing · X. Huang · K. Zhang University of Chinese Academy of Sciences, Beijing 100039, People's Republic of China of C/N suggest that the organic matter in the sediments are primarily from autochthonous sources. TN and total organic carbon in the sediment cores increased slowly up the core while TP and total inorganic carbon have been fairly constant.

Keywords Water and sediment quality · Qinghai Lake · Ion composition

## Introduction

Qinghai Lake (36°32′-37°15′N and 99°36′-100°47′E) is a remote closed semisaline inland lake situated on the Qinghai-Tibet plateau at an altitude of about 3,200 m. It is the largest lake in China, with a surface area of roughly 4,500 km<sup>2</sup> and a catchment area of over 30,000 km<sup>2</sup>. The average and maximum water depths of the lake are 19 and 29 m, respectively. Forty rivers flow into the lake, most of which are seasonal. Seven major rivers account for about 95 % of the total discharge into the lake. Decreases in the main lake water levels over recent decades have created three sublakes (Li et al. 2007; Colman et al. 2007). Currently, Gahai and Erhai are hydrologically independent while Jinshawan is still partially connected to the main lake through a narrow channel. The Qinghai Lake area is located at the crossroads of several bird migration routes in Asia, and many species, including several endangered ones, use the lake as an intermediate stop during their migration. For the protection of wildlife and the lake

ecosystem, Qinghai Lake Natural Reserve was established in 1975. Now the lake is considered one of the most scenic places in China and attracts tourists from all over the world every year.

In 1961, the Chinese Academy of Sciences organized the first comprehensive field survey of Qinghai Lake with a purpose to understand the lake geology, water physicochemical properties, hydrodynamics, hydrobiology, sedimentology, geochemistry, and diagenesis. The collected data was primarily used to target petroleum geology-related questions and was published in 1979 (CAS 1979). Further studies have been conducted since the original survey, although the focus has been on paleoclimate. Qinghai Lake is located in a transitional zone affected by East Asian and Indian monsoons and westerly atmospheric flow (Jin et al. 2010). As a result, the lake has been an ideal place for studying past global climate changes (Colman et al. 2007; Liu et al. 2011; Shen et al. 2005).

Since the original survey in 1961, water quality research has been limited at Qinghai Lake due to the remote location. However, the rapid development of the local economy near the lake, as well as climate change, has begun to raise concerns over water quality issues in the area. Between 1959 and 2000, lake water levels have decreased 3.35 m (Li et al. 2007) and overgrazing has caused the degradation of the surrounding grassland (Zhang et al. 2006). The tourism industry is increasing rapidly in the area, with tourist arrivals increasing from roughly 400,000 in 2007 to over one million in 2012. The stark changes since 1960s to this once remote area are possibly putting negative pressure on the local ecosystem. Therefore, the objective of this study was to generate updated water and sediment quality data for Qinghai Lake, several tributaries, and the sublakes. The results will provide a current dataset to be used as a management tool for assessing change to the lake area.

Field sampling campaigns were carried out in 2012,

June 15-18 and August 25-28. Surface water sam-

ples were collected from 27 sites at Oinghai Lake,

#### Materials and methods

# Sampling

five major tributary rivers (Heima, Caiji, Buha, Quanji, and Shaliu). Most of the sampling sites were referred to the survey in 1960s with few more sampling sites added at the estuarine areas of the major tributaries. Sampling locations and an overall map of the area are provided in Fig. 1. Water samples were collected using an acrylic water sampler (5 L). Surface sediment samples (0-10 cm) were collected in June using a Peterson sampler (25 L) from sites 01-03, 05-12, and 15-17. Three short sediment cores from sites 01, 08, and 09 (lengths of 9, 15, and 15 cm, respectively) were collected in August using a gravity sediment core sampler and were sliced at 1-cm intervals on-site. Water samples were stored in polyethylene bottles and analyzed within 24 h of collection. Sediment samples were stored in polyethylene plastic bags and kept frozen (-20 °C) until analysis.

# Analysis

Water transparency (Secchi depth, SD) was measured using a Secchi dish. Water pH and temperature (T) were measured using a YSI pH60 pH meter. Dissolved oxygen (DO) and conductivity (EC) were measured with a Mettler SevenGo Duo meter. Major ions (K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>) were analyzed using an ion chromatograph (883 Basic IC plus, Metrohm). Total phosphorus (TP) was determined by ammonium metamolybdate spectrophotometry after a potassium persulfate digestion. Chemical oxygen demand (COD<sub>Mn</sub>) was determined using the potassium permanganate alkaline method. Soluble reactive silica (SRSi) was determined using the yellow silicomolybdate method. Total dissolved solids (TDS) were measured gravimetrically. NH4<sup>+</sup>-N was determined by Nessler's reagent spectrophotometry. NO3-N was determined by ultraviolet spectrophotometry. NO2-N was determined by naphthylethylenediamine spectrophotometry.  $HCO_3^{-1}$  and  $CO_3^{2-1}$  were determined by titration. Chlorophyll a (Chl.a) was determined using a spectrophotometric method after extraction with acetone. All the analysis was performed following standard protocols (SEPA 2002). The method detection limits were 0.01 mg  $L^{-1}$  for TP, 0.02 mg  $L^{-1}$  for NH<sub>4</sub><sup>+</sup>-N,  $0.08 \text{ mg } \text{L}^{-1}$  for NO<sub>3</sub><sup>--</sup>N, 0.001 mg L<sup>-1</sup> for NO<sub>2</sub><sup>--</sup>N, and  $0.04 \text{ mg L}^{-1}$  for SRSi.



Fig. 1 Geographic location of Qinghai Lake and sampling sites in Qinghai Lake, three sublakes (Gahai, Jinshawan, and Erhai), and five major tributary rivers (Heima, Caiji, Buha, Quanji, and Shaliu)

Sediment samples were lyophilized, sieved to <2 mm, digested at 450 °C in a muffle furnace for 3 h, and analyzed for TP following the methods described in Paludan and Jensen (1995). Phosphorus fractions in the surface sediment samples were extracted according to the sequential fractionation methods described in Hupfer et al. (1995) and Pettersson et al. (1988). These methods allow phosphorus to be fractionated into loosely sorbed phosphorus (NH<sub>4</sub>Cl-P), reductant soluble phosphorus (BD-P), metal oxide-bound phosphorus (NaOH-SRP), organic phosphorus (NaOH-NRP), calcium-bound phosphorus (HCl-P), and residual phosphorus (RP). Total nitrogen (TN) was determined using a Kjeldahl analysis system (S5, Behr Labor Technik). Total carbon (TC) and total organic carbon (TOC) were analyzed using a TOC analyzer (Vario TOC cube, Elementar), and total inorganic carbon (TIC) was calculated as the difference between TC and TOC.

For both water and sediment quality test, blank samples, duplicates, and standards were routinely checked during the sample analysis for data quality assurance and quality control purposes. Generally, no target analyte was detected in blank samples, with the variation of duplicate samples being less than 12 %. Analysis of standards showed analytical accuracy to be over 90 %.

#### **Results and discussion**

Physicochemical parameters and major ion composition in water

The physicochemical parameters and major ion composition of the surface water samples from Qinghai Lake, three sublakes, and five major tributary rivers are summarized in Table 1 and provided in full in the Supplementary material. All water samples were weakly basic with pH values of 8–9. The pH was slightly higher in August than in June and can be attributed to the growth of phytoplankton consuming more  $CO_2$  in summer (August) compared to the spring (June). The pH of tributary water samples was about half a unit lower than that of Qinghai Lake and sublakes, presumably related

Site	Month	μd	DO	SD	EC	SQT	Chl.a	Major ions (n	$ m lg~L^{-1})$						
			$(mg \ L^{-1})$	(m)	$(mS \ cm^{-1})$	$(g L^{-1})$	$(\mu g \ L^{-1})$	$\mathbf{K}^+$	$Na^+$	Ca <sup>2+</sup>	${\rm Mg}^{2+}$	Cl	$\mathrm{SO_4}^{2-}$	$\mathrm{CO_3}^{2-}$	$HCO_3^-$
Qinghai Lake	Jun.	8.88	7.87	3.2	19.1	12.9	0.57	128	3,280	19.89	570	5,117	2,179	763	792
		(8.67 - 8.91)	(5.69 - 10.2)	(0.3 - 4.7)	(1.53–21.2)	(0.77–15.9)	(0.44-0.71)	(3.41 - 158)	(69.5-4,022)	(5.09-42.8)	(12.8–832)	(1, 612 - 5, 776)	(691–2,454)	(51.7–946)	(209-902)
	Aug.	9.06	6.97	2.94	18.4	12.7	1.44	131	3,190	26.0	654	5,137	2,043	680	790
		(9.0 - 9.11)	(6.60 - 10.03)	(0.5-4.4)	(4.77-20.9)	(2.85–14.7)	(0.91 - 2.03)	(74.0–150)	(698 - 3, 684)	(10.8 - 107)	(160 - 770)	(1,211–5,946)	(426-2,318)	(150-828)	(292–953)
Gahai	Jun.	8.74	7.46	n.d.	42.8	33.1	1.33	322	7,166	169	1,183	10,754	5,609	962	850
	Aug.	8.76	7.55	n.d.	43	33.2	10.5	444	8,884	85.7	1,361	13,742	6,009	810	1,063
Erhai	Jun.	8.73	7.0	n.d.	1.75	0.93	1.09	7.6	129	116	28.8	162	7.77	10.0	152
	Aug.	9.22	9.27	n.d.	1.58	0.94	29.5	11.2	209	118	57.7	263	151	98.0	354
Jinshawan	Jun.	8.84	6.78	n.d.	26.5	18.8	1.29	165	4,318	17.2	822	6,785	2,899	893	973
	Aug.	8.98	6.92	n.d.	26.4	17.3	2.87	183	4,472	16.4	881	7,355	2,806	686	1,116
Tributary rivers	Jun.	8.33	7.87	n.d.	0.42	0.26	n.d.	5.56	75.7	47.3	25.8	89.6	59.7	.p.u	192
		(8.27 - 8.38)	(6.60–7.77)		(0.36 - 0.53)	(0.05-0.57)		(2.14–16.1)	(11.3–291)	(7.29-80.69)	(17.8-46.9)	(6.92 - 360)	(25.3–170)		(181 - 229)
	Aug.	8.46	7.0	n.d.	0.48	0.23	n.d.	2.38	25.1	84.6	14.8	33.41	41.1	.p.u	244
		(8.42–8.55)	(6.41 - 7.78)		(0.39 - 0.54)	(0.11 - 0.36)		(1.59–3.57)	(8.49 - 31.6)	(78.4-89.3)	(11.1–17.1)	(13.3 - 49.6)	(24.0-52.9)		(230–267)

Table 1 Physicochemical parameters and major ion composition of the surface water samples from Qinghai Lake, sublakes, and tributary rivers

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n.d. no data, u.d. undetected

to their major ion compositions. Qinghai Lake and sublake water samples had considerably higher concentrations of alkali and alkaline earth metals. The DO in surface water samples varied between 6 and 10 mg  $L^{-1}$ . The DO is nearly saturated, considering the atmospheric pressure at this altitude, and can be attributed to the photosynthesis of phytoplankton. The windy conditions in the study area during sampling may have also enhanced the air exchange between surface water and atmosphere. Water transparency was only measured in Qinghai Lake and was about 3 m in average. The EC and TDS of surface water from Qinghai Lake averaged 19 mS cm<sup>-1</sup> and 12.9 g L<sup>-1</sup>, respectively. In the three sublakes, EC and TDS were the highest in Gahai, followed by Jinshawan and Erhai. The EC and TDS of water samples from tributary rivers averaged 0.45 mS cm<sup>-1</sup> and 0.25 g L<sup>-1</sup>, respectively. Chl.a averaged 0.57  $\mu$ g L<sup>-1</sup> in June and 1.44  $\mu$ g L<sup>-1</sup> in August. Chl.a was considerably higher in the three sublakes, especially in Erhai in August. This might be attributed to a warmer temperature in August and a higher nutrient level in Erhai Lake (see below).

The relative abundance of major ions on an equivalent basis is given in ternary diagrams in Fig. 2. Samples from Qinghai Lake and sublakes plotted in the K<sup>+</sup>+Na<sup>+</sup> corner for cations and in the Cl<sup>-</sup> corner for anions except the sample from Erhai. Na<sup>+</sup> was the dominant cation in surface water from Qinghai Lake followed by  $Mg^{2+}$ ,  $K^+$ , and Ca<sup>2+</sup>, whereas Cl<sup>-</sup> was the dominant anion followed by  $SO_4^{2+}$ ,  $HCO^{3-}$ , and  $CO_3^{2-}$ . Based on concentration values, Na<sup>+</sup> and Cl<sup>-</sup> account for about 82 and 58 % of the major cations and anions, respectively. In the three sublakes, the concentrations of these major ions were the highest in Gahai, followed by Jinshawan and Erhai. Gahai is separated from the main lake with no surface water supply. High evaporation and little freshwater supply (precipitation and groundwater only) lead to an increase of EC, TDS, and major ion concentrations. The concentrations of  $K^+$ ,  $Na^+$ ,  $Cl^-$ , and  $SO_4^{2-}$  were two to three times higher in Gahai than in Qinghai Lake. Jinshawan is still partially connected to Qinghai Lake through a narrow channel. EC, TDS, and the concentrations of K<sup>+</sup>, Na<sup>+</sup>, Cl<sup>-</sup>, and SO<sub>4</sub><sup>2-</sup> increased 50 % roughly, compared to those of Qinghai Lake. In contrast, Erhai is supplied by the Daotang River, and EC, TDS, and the concentrations of  $K^+$ ,  $Na^+$ ,  $Cl^-$ , and  $SO_4^{2-}$  were less than one-tenth those of Qinghai Lake. This is likely due to dilution by freshwater from Daotang River after separating from the main lake.

Chemical and/or biological precipitation of  $CaCO_3$  is an important process governing lake water and sediment compositions. The degree of supersaturation of  $CaCO_3$  and MgCO<sub>3</sub> can be used to determine if precipitation is occurring and was estimated using the following equations:

$$\frac{S_{CaCO_3}}{K_{sp(CaCO_3)}} = \frac{[Ca^{2+}][CO_3^{2+}](f)^2}{K_{sp(CaCO_3)}}$$
$$\frac{S_{MgCO_3}}{K_{sp(MgCO_3)}} = \frac{[Mg^{2+}][CO_3^{2+}](f)^2}{K_{sp(MgCO_3)}}$$
$$\log f = -0.5Z^2 \frac{\sqrt{I}}{1 + \sqrt{I}}$$

At 7.5 °C (average water temperature), the values of  $K_{sp(CaCO_3)}$  and  $K_{sp(MgCO_2)}$  are  $4.5 \times 10^{-9}$  and  $5 \times 10^{-5}$ , respectively. I is the ionic strength and f is the activity coefficient. The degrees of supersaturation for CaCO<sub>3</sub> in Qinghai Lake, Gahai, Erhai, and Jinshawan were 365, 267, 6.7, and 314 in June and 373, 105, 58, and 228 in August, respectively. The degrees of supersaturation for MgCO<sub>3</sub> were 1.54, 2.8, 0.002, and 2.25 in June and 1.59, 2.51, 0.043, and 1.83 in August, respectively. These results suggest that CaCO<sub>3</sub> is oversaturated in Qinghai Lake and the sublakes, leading to chemical precipitation of CaCO<sub>3</sub>. MgCO<sub>3</sub> is also oversaturated in the lake waters, with Erhai being the only exception. The precipitation occurring can remove Ca<sup>2+</sup> and  $Mg^{2+}$  from the water into the sediment. Saturation of CaCO<sub>3</sub> has also been observed in other semiarid closed lakes in the Qinghai-Tibet plateau (Ju et al. 2010; Wang et al. 2010).

Spatial variation over the surface water sampling points on Qinghai Lake for the major ions was pretty constant (relative standard deviation (RSD) <10 %), excluding samples collected from the estuarine area of the Buha River (sampling points 01, 26, and 27). Lower transparency, EC, and TDS values were also observed in samples from those sites. The Buha River is the largest river entering the lake with 50 % of the total runoff and 70 % of the total sand discharge (Colman et al. 2007; Jin et al. 2010). Discharges of freshwater dilute the lake water at the river mouth, while the input of suspended materials and nutrients increase the growth of plankton, both reducing the water transparency. However, water samples from the estuarine areas of the Heima (11), Quanji (16), and Caiji (18) rivers showed no substantial differences in major ion compositions. The discharge of these rivers is considerably less than that



Fig. 2 Ternary plots of the major dissolved ions for water samples collected from Qinghai Lake (*QH*), five major tributary rivers (*IR*), and three sublakes. **a**, **b** Samples from June 2012. **c**, **d** Samples from August 2012

of the Buha River (<10 %) (Jin et al. 2010), likely causing this lack of considerable difference in the major ion compositions.

Among the five selected major rivers, no substantial difference was observed for pH, DO, and EC in surface water samples. The concentrations of major ions were significantly lower than those in Qinghai Lake. River water samples plotted in the  $Ca^{2+}$  corner for cation and in the  $CO_3^{2-}$ +HCO<sup>-</sup> corner for anion in the ternary diagram (Fig. 2).  $Ca^{2+}$  and HCO<sup>-</sup> were the dominant ions in river water, except the sample from the Heima River in June. Their dominance results primarily from the chemical weathering of bedrock (limestone and sandstones) within the rivers' watershed (Jin et al. 2010; Xu et al. 2010a). Slightly higher K<sup>+</sup>, Na<sup>+</sup>, and Cl<sup>-</sup> were found in the Heima compared to the other rivers in June, while no substantial difference was

observed in August. This is likely caused by lake water intrusion brought on by decreased river discharge observed during the dry season.

#### Nutrients in water

Nutrient concentrations for the surface water samples collected are presented in Fig. 3. In Qinghai Lake, the concentrations of TP,  $NH_4^+$ -N,  $NO_3^-$ -N, SRSi, and  $COD_{Mn}$  averaged 0.02, 0.18, 0.28, 0.21, and 2.10 mg L<sup>-1</sup>, respectively, in June and 0.38, 0.56, 0.30, 0.02, and 2.94 mg L<sup>-1</sup>, respectively, in August (data from 26 and 27 were excluded from the calculation).  $NO_2^-$ -N was detected only at a few sites, with concentrations of 0.001 mg L<sup>-1</sup>. Considerably higher TP,  $NO_3^-$ -N, SRSi, and  $COD_{Mn}$  were observed at sites 26 and 27. These two sites are heavily impacted by the



Fig. 3 Concentrations of nutrients in Qinghai Lake, three sublakes, and five major tributary rivers

discharge from the Buha River. This discharge increases nutrient concentrations in the water and promotes the growth of plankton by nutrient loading. This might have caused the very high TP and COD<sub>Mn</sub> at those two sites (even higher than those in the Buha River). In the three sublakes, the nutrient concentrations were highest in Erhai, due to the nutrient loading from the Daotang River. SRSi, NO3-N and COD<sub>Mn</sub> in lake water samples were higher in August than in June at most of the sampling sites, which can be attributed to a higher loading from tributaries and higher primary productivity in summer compared to the spring. SRSi and NO<sub>3</sub><sup>-</sup>-N were higher in all five major rivers compared to Qinghai Lake, suggesting that the tributary rivers are an important source for nutrient loading. Both SRSi and NO<sub>3</sub><sup>-</sup>-N in the rivers were higher in August, likely caused by erosion and surface runoff during the wet season in the catchment area. TP was higher in the Buha and Caiji rivers compared to Qinghai Lake, likely due to the chemical weathering and surface runoff from the rivers' watersheds. In addition to the natural processes, there is a small town along the Buha River near the sampling site. In the summer, tourists come to the town to visit Qinghai Lake, adding an anthropogenic input likely leading to a higher TP in the river water downstream. The higher TP in the Caiji River may be largely attributed to the input of animal waste. The estuarine delta region of this river is an import habitat for numerous migrant and resident birds. Previously, waterbird feces have been found to be important sources for nutrient input to water bodies (Hahn et al. 2007).

#### Comparison with historical data

The water quality data from Qinghai Lake, Erhai, Gahai, and the three tributaries were compared with historical data from 1960s in Table 2. Jinshawan was still part of the Qinghai Lake at the time of the original survey. Some difficulty in data comparison does exist. The analytical methods used for the measurement of several water quality parameters are different from the current methods used. The water pH was measured using colorimetry in 1960s while a pH probe and meter was used in this study. The colorimetric method for pH measurement can be affected by water quality such as color, turbidity, and salinity. Therefore, the pH measurement in 1960s might be less accurate than the results obtained in the current study. Major ions Ca<sup>2+</sup> and Mg<sup>2+</sup> were analyzed by complexometric titration with EDTA, Na<sup>+</sup> and K<sup>+</sup> by flame atomic absorption spectrophotometry,  $Cl^-$  by the Mohr method, and  $SO_4^{2-}$  by iodometry titration. For major ion measurement, those methods used in 1960s should be comparable to the ion chromatograph method used here.

In all lakes and rivers, the water pH differs slightly from the historical data. The water transparency of the lake has also decreased from 5 to 10 m to less than 5 m over time. This decrease of transparency is likely caused by the increase of lake productivity and suspended particle loadings from tributary rivers. The annual average cell density of phytoplankton in the Qinghai Lake has increased from 58,847 cells  $L^{-1}$  in the 1960s to 68,500 cells  $L^{-1}$  in 2012 (unpublished data provided by Dr. Yu Gongliang).

The major ion composition in Qinghai Lake shows no substantial difference from the 1960s, with the exception of Ca<sup>2+</sup>. Previous research has shown that the residence time of Cl<sup>-</sup>, Na<sup>+</sup>, K<sup>+</sup>, and Mg<sup>2+</sup> in Qinghai Lake is 15,643, 12,020, 3,858, and 2,492 years, respectively, while the time of  $Ca^{2+}$  is much less at 6.1 years (Jin et al. 2010). Therefore, no significant changes in concentrations for  $Cl^{-}$ ,  $Na^{+}$ ,  $K^{+}$ , and  $Mg^{2+}$  would be expected over 50 years. The change of lake water levels is likely the predominant reason for the limited variation in concentration observed. The input from the rivers can increase the  $Ca^{2+}$  concentration. As CaCO<sub>3</sub> is supersaturated, precipitation can remove  $Ca^{2+}$  from the water column. As a result, the Ca<sup>2+</sup> concentration in the lake water is regulated by the balance between Ca<sup>2+</sup> input and precipitation. An increase in Ca<sup>2+</sup> concentration suggests that the rate of loading is higher than the rate of precipitation. The concentrations of Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup>, and K<sup>+</sup> decreased in Erhai while they increased in Gahai. These results agree well with the idea that Erhai is diluted by freshwater from the Daotang River while Gahai is under evaporative conditions, lack of surface water supply. The major ion concentrations were higher than they were in the 1960s in the Buha and Heima rivers, but lower in Shaliu River. This difference might be caused by the change of river discharge and land use patterns in the rivers' watershed.

In all three lakes, the concentrations of nutrients increased considerably in the last 50 years, especially for  $NO_3^-$ -N and  $NH_4^+$ -N. These increased nearly 10-fold, likely due to the input from rivers and atmospheric depositions. In the three rivers available for comparison, the concentrations of  $NO_3^-$ -N and  $NH_4^+$ -N also increased anywhere from 2 to 78 times, which is likely caused by human activities in these watersheds. TP is not directly comparable as dissolved phosphate was

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	Qinghai Lake	c	Erhai		Gahai		Buha River		Heima River		Shaliu River	
	This study <sup>a</sup>	1960s <sup>b</sup>	This study	1960s	This study	1960s	This study	1960s	This study	1960s	This study	1960s
Hq	8.97	9.3	8.97	9.0	8.75	9.4	8.39	8.5	8.43	8.5	8.38	8.5
SD (m)	1.5-4.7	5 - 10	I	I	I	I	I	I	I	I	I	I
$COD_{Min} (mg L^{-1})$	2.52	1.41	13.2	1.85	5.01	8.36	2.68	3.73	4.35	4.01	2.31	4.12
$K^+$ (mg $L^{-1}$ )	142	146	9.40	19.2	383	309	3.3	22.3°	9.84	$107^{c}$	1.94	$188^{\rm c}$
$Na^+$ (mg $L^{-1}$ )	3,535	3,258	169	268	8,025	6,721	37	Ι	161	I	21.2	I
$Ca^{2+}$ (mg L <sup>-1</sup> )	21.9	9.87	117	11.63	127	15.1	58	50.2	47.2	59.3	70.0	40.8
$Mg^{2+}$ (mg $L^{-1}$ )	667.3	821.8	43.3	86.27	1,272	1,469	20	20.1	32.0	19.8	16.0	36.4
$CI^{-}$ (mg $L^{-1}$ )	5,461	5,274	212.5	291.7	12,248	10,661	41	70.5	204	53.5	14.4	192
${\rm SO_4}^{2^-} ({\rm mg}{\rm L}^{-1})$	2,246	2,034	114.4	207.9	5,809	4,588	47	36.6	103	261	39.2	234
${\rm CO_3}^{2-} ({\rm mg}\;{\rm L}^{-1})$	765.9	419.4	54.0	175	886	573	u.d.	17.01	u.d.	1.51	u.d.	19.40
$HCO_3^-$ (mg L <sup>-1</sup> )	827.2	525.0	253	87.4	956	520	206	110	226	140	206	141
SRSi (mg $L^{-1}$ )	0.30	0.16	1.81	0.94	0.24	0.18	3.34	1.18	3.68	2.83	2.93	1.18
$NO_{3}^{-}-N \text{ (mg L}^{-1})$	0.24	0.036	0.596	0.052	0.581	0.024	0.765	0.069	2.61	0.128	0.75	0.112
$\mathrm{NH_4}^+$ -N (mg L <sup>-1</sup> )	0.41	0.040	0.835	0.071	0.268	0.052	2.975	0.038	0.305	0.160	0.3	0.036
TP (mg $L^{-1}$ )	0.020	Ι	0.079	I	0.023	Ι	0.145	Ι	0.035	Ι	0.04	I
$PO_4^{3+}-P \text{ (mg } L^{-1})$	I	0.007	Ι	0.002	I	0.003	I	0.042	Ι	0.106	Ι	0.012
<sup>a</sup> Samples from sites <sup>b</sup> Data from CAS (15 cr++27+	26 and 27 were ( 979)	excluded from	m the calculation	n for Qingh	ai Lake							
$\mathbf{N} \pm \mathbf{N}\mathbf{a}$												

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measured in the 1960s. In Qinghai Lake and Erhai, COD<sub>Mn</sub> increased considerably, suggesting an overall increase of lake productivity, likely promoted by the increase of nutrient levels. However, COD<sub>Mn</sub> decreased in Gahai, a possible result of increased salinity. As salinity increases, the growth of certain aquatic organisms can be inhibited. Based on the current TP and water transparency (Secchi), the trophic status of Qinghai Lake is mesotrophic to eutrophic according to the OECD classification (OECD 1982). Although situated in a pristine area, the rapid increase of nutrient concentrations in Qinghai Lake should raise concern over the health of the lake. Overgrazing and the development of the local tourism industry are likely contributing to the rise of nutrient levels.

#### Sediment quality

The concentrations of TN, TP, TIC, and TOC in surface sediments collected from Qinghai Lake in June are presented in Fig. 4. TN, TP, TIC, and TOC average 2.63, 0.61, 59.3, and 18.9 g kg<sup>-1</sup>, respectively. Their spatial distributions were fairly constant with RSD

<20 % except for TP, of which RSD was 25 %. TN and TP in Qinghai Lake sediment were found comparable to those in the sediment from other highly eutrophicated lakes in China, such as Taihu Lake (TP 0.29-0.96 g kg<sup>-1</sup>, TN 0.72-1.01 g kg<sup>-1</sup>) (Wang et al. 2006; Zhang et al. 2010) and Dianchi Lake (TP 0.98-4.74 g kg<sup>-1</sup>, TN 4.13-5.41 g kg<sup>-1</sup>) (Chen et al. 2007a; Chen et al. 2007b). Although the concentrations of TP and TN were considerably high in Qinghai Lake sediment, their concentrations in the lake water were relatively low compared to other eutrophicated lakes, suggesting that the release of P and N from the sediments is limited.

The fractionation of P in the sediments was studied by sequential extraction. As presented in Fig. 5, HCl-P is the dominant fraction followed by RP. The HCl-P and RP combined account for over 85 % of the TP in the surface sediment. The HCl-P represents P bound to carbonates, apatite phosphorus, and traces of hydrolyzable organic P, while RP consists of organic and other refractory phosphorus (Hupfer et al. 1995; Pettersson et al. 1988). Both fractions are relatively stable and contribute to the permanent burial of P in the sediment



Fig. 4 TN, TP, TOC, TIC, C/N, and TOC/TIC in surface sediment samples from Qinghai Lake

**Fig. 5** Contribution of each P fraction to TP in the surface sediments



(Kaiserli et al. 2002). The high HCl-P is likely attributed to the high carbonate concentration in the Qinghai Lake sediment. BD-P represents the redox-sensitive P forms, which accounts for 4.7 % of the TP on average. This fraction can be released into overlaying water as the sediment changes from oxic conditions to anoxic conditions. The NaOH-SRP and NaOH-NRP are both NaOH-extractable fractions, which account for 1.89 and 3.59 % of the TP, respectively. The NaOH-SRP represents P bound to metal oxides, mainly Al and Fe, while the NaOH-NRP represents P in microorganisms, bound in humic compounds and organic P in detritus (Hupfer et al. 1995). In this fraction, P is exchangeable against OH<sup>-</sup>. The NH<sub>4</sub>Cl-P represents the loosely sorbed P and is the most labile P fraction. This fraction only accounts for 2.2 % of the TP. In highly eutrophicated Taihu Lake and Dianchi Lake, NaOH-P and BD-P, which are more bioavailable to the algae, were found to be more dominant in the sediment (Hu et al. 2007; Zhou et al. 2005). Although TP levels were relatively high in Qinghai Lake sediment, P fractionation suggests that the majority of the P is nonexchangeable. Therefore, the release of P from sediment to water is limited.

The ratio of TOC/TIC varied from 0.16 to 0.41, indicating that inorganic carbon is the dominant carbon source in the sediments, and can be attributed to the precipitation of CaCO<sub>3</sub> from lake water. Correlation analysis indicates that TN and TOC are strongly correlated (p<0.01), suggesting that N in the sediment exists primarily in organic state. The ratios of C/N are often used to indicate sources of organic matter in the sediment. Aquatic plants and lacustrine plankton have C/N ratios ranging 5–12, whereas vascular terrestrial plants have ratios over 20 (Meyers and Lallier-vergés 1999; Meyers 1994). The C/N ratio in Qinghai Lake sediment ranged from 5.47 to 8.08, suggesting that the organic matter is primarily from autochthonous sources.

The vertical distributions of TN, TP, TIC, and TOC in the three sediment cores collected from Qinghai Lake are presented in Fig. 6. The sedimentation rates in Qinghai Lake have been studied extensively and have been found to be higher in estuarine areas and lower in the center of the lake, averaging 1 mm a year (Xu et al.



Fig. 6 Vertical distribution of TN, TP, TOC, and TIC in three sediment cores from Qinghai Lake

2010b). Therefore, these cores represent a sediment record of 80-150 years. A strong positive correlation (p < 0.01) between TN and TOC was also observed in the sediment core. Both TN and TOC show a slow increasing trend from the bottom to the top of the sediment core. This may be related to an increase of lake productivity as a result of the elevation of nutrient levels. As a consequence, the amount of organic materials deposited to the sediment also increased. TP fluctuated in the sediment core, but no increasing trend was observed. TIC indicated an increasing trend at site 01 above 5 cm and at site 08, likely due to the increase of  $Ca^{2+}$  and  $CO_3^{2-}$  concentrations. However, no such trend was observed in the sediment core from site 09, suggesting that the sedimentation pattern varies depending on locations.

# Conclusions

In this study, we provide updated current information on the water and sediment quality of Qinghai Lake, three sublakes, and five major tributary rivers. Major ion composition indicates that weathering and soil erosion are the primary sources of major ions in tributary water while evaporation and CaCO<sub>3</sub> precipitation contribute to the lake water major ion characteristics. Comparison with historical data indicates an increase of nutrient levels in the lake water. In the sediments, TIC is the dominant carbon source, and C/N ratios suggest an autochthonous origin of organic materials. TN and TP in the sediments were found comparable to those from highly eutrophicated lakes but mainly exist in non-exchangeable forms. Vertical distribution of TN and TOC shows a slow upward increasing trend in the sediment, suggesting an increase of lake productivity. Although situated within a remote area, overgrazing and rapid development of tourism industry may have caused the deterioration of lake water quality.

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