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RESEARCH ARTICLE

Distribution and enrichment of mercury in Tibetan lake waters and their relations with the natural environment

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Abstract Mercury (Hg) in aquatic ecosystems is of great concern due to its toxicity, bioaccumulation, and magnification in the food web. The Tibetan Plateau (TP) is endowed with the highest and largest lakes on earth, whereas Hg distribution and behavior in lake waters are least known. In this study, surface water samples from 38 lakes over the TP were collected and determined for the total Hg (THg) concentrations. Results revealed a wide range of THg concentrations from <1 ng to 40.3 ng L^{-1}. THg in lake waters exhibited an increasing trend along the southeast to northwest transect over the TP. Strong positive correlations were observed between THg concentrations and salinity and salinity-related environmental variables, especially for total dissolved solids (TDS) and some of the major ions such as Na^+, K^+, and Cl^-, suggesting the enrichment of Hg in saline lakes. The large-scale geographical pattern of climatic and environmental factors shows a decreasing precipitation and an increasing evaporation northwards and westwards and thereby induces gradient-enhanced enrichment of soluble substances in lake waters, which are likely to complex more Hg in northwestern TP. Our study provides the first comprehensive baseline data set of Hg in Tibetan lake waters and highlights the concurrent high Hg and salinity, representing valuable references and fundamental rules in further understanding the behavior and fate of Hg in lakes over the TP and perhaps high-altitude regions beyond.

Keywords Lake · Water · Mercury · Tibetan Plateau · Distribution · Enrichment

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Introduction

Mercury (Hg) is an ubiquitous environmental contaminant derived from both natural and anthropogenic sources (Mason et al. 1994; Nimick et al. 2013). Owning to its gaseous existence and long retention time in the atmosphere, Hg can be widely dispersed and transported over thousands of kilometers affecting oceanic and terrestrial environments in remote areas (Fitzgerald et al. 1998). Among diverse terrestrial ecosystems, lakes act as sentinels and integrators for environmental variations in their watersheds and airsheds and beyond (Schindler 2009) and represent important habitats for fish that can accumulate Hg to hazardous levels for human consumption (Mergler et al. 2007). Therefore, there is increasing attention being paid to Hg distribution, transformation, and bioaccumulation as well as their environmental implications in lake ecosystems all over the world. In the last few decades, efforts

have been devoted to reveal consistent co-variation of Hg background levels in lake waters and sediments as well as rapid changes in fish Hg in response to regional/global atmospheric Hg deposition (Fliedner et al. 2014; Harris et al. 2007; Swain et al. 1992). Particularly, remote high-altitude lakes are further recognized as Hg-sensitive ecosystems to Hg inputs (Krabbenhoft et al. 2002) and, therefore, are hotspots for understanding the modern cycling and historical changes of Hg in a regional and global context (Phillips et al. 2011).

The Tibetan Plateau represents the highest and largest landforms on earth and is one of the few areas globally that has remained untouched by local human disturbances. Owing to its cold climate and integration of diverse environments, there has been increasing interest in Hg contamination in the TP environments (Zhang et al. 2014). Despite Hg levels that were reported at natural background in the atmosphere, precipitation, soils, and glacier snow (Fu et al. 2012; Huang et al. 2012; Sheng et al. 2012; Zhang et al. 2012), historical reconstruction of atmospheric Hg using lake sediments revealed a clear and consistent increase of Hg induced by Asian Hg emission over the last few decades (Yang et al. 2010), underlining the importance of an integrated consideration of Hg cycle over the TP. The TP is endowed with the world's highest and largest group of high-altitude lakes, whereas the baseline of Hg and its behavior and fate in such unique environment remain almost non-existent, representing a major gap in fully understanding the background and cycle of Hg in the TP environments and the further linkage to regional and global environmental changes.

This study represents the first attempt to establish the comprehensive data set for Hg levels in lake waters over the TP and to reveal their distribution and potential influencing factors. The results represent valuable references and fundamental rules for further investigation on the behavior and fate of Hg in lake ecosystems and regional Hg biogeochemical cycling over the TP.

Materials and methods

Site description

The TP extends an area of more than 2×10^6 km^2 with an elevation well above 4000 m a.s.l. (Liu and Chen 2000) and is surrounded by massive mountain ranges with Himalayan Ranges and Kunlun Ranges at its south and north, respectively. Climatically, the TP is dominated alternately by the Indian monsoon in summer and the westerly in winter, resulting a dramatic contrasting climate with warm–wet summer and cold–dry winter, respectively. The annual mean precipitation varies a large range from >4000 mm in the southeast to <50 mm in the northwest (Sun et al. 1990). Owing to sparse population density and almost negligible industrial activities, the TP is considered one of most remote and pristine regions in the world and therefore serves as an ideal natural laboratory for studies in environmental change at a range of scales.

Known as "the Roof of the World," the TP holds the most extensive area of glaciers outside the polar regions, acting as the source of many major rivers in Asia, including the Yangtze River, the Yellow River, the Yarlung Zangbu/Brahmaputra, and the Mekong River. Besides considerable glacial aggregates and rivers, the TP is endowed with the world's highest and largest group of high-altitude lakes, with 1091 lakes larger than 1 km^2 and 346 lakes larger than 10 km^2, accounting for over half of the lake area in China (Ma et al. 2011; Wang and Dou 1998). Lakes over the TP are different in size, altitude, and shape, with most of which embedded in intermountainous basins and valleys as endorheic lakes (Wang and Dou 1998). Owing to the atrocious climate and environment, lakes over the TP have been less investigated.

In this study, water samples were collected from 38 lakes interspersed over a large geographical scale on the TP. Basically, these lakes were chosen for sampling based on their geographical location (relative ease of access) and the representative of regional surface lake water chemistry. The catchment of the studied lakes is mostly covered by desert vegetation or high frigid meadow. These lakes varied contrastively in characteristics with the lake areas from 0.10 km^2 (no. 34, Qiangyong Co.) to 2015 km^2 (no. 33, Nam Co.) and the altitudes from 3469 m (no. 38, Basom tso) to 5145 m a.s.l. (no. 14, Dajia Co), representing one of the most comprehensive and representative lake clusters for investigating the distribution of Hg in lake waters over the TP (Table 1; Electronic supplementary material Table S1).

Field sampling

During the summer of 2010 and 2011, an interdisciplinary research on Tibetan lakes were conducted along the southeast–northwest transect across the TP (Fig. 1). For Hg sampling, at each lake site, at least one offshore surface water sample (10–15 cm) was collected. All Hg samples were taken in replicates with two persons following strictly the "Clean hands-Dirty hands" sampling protocol (Fitzgerald 1999). Operators were worn non-powder vinyl clean room gloves all times to minimize potential contamination. Hg samples were stored in 50-mL new polypropylene Falcon tubes and were acidified to 0.4 % with ultrapure hydrochloride acid (BV − III grade from Beihua Chemical, China) on site (Zhang et al. 2012). Field blank samples were obtained by filling ultrapure water in situ for each sampling lake and were handled as samples. All samples were tightly sealed, double-packed in Ziploc bags, and then stored in a cooler before transported back laboratory.

Major ionic samples were collected using 100-ml precleaned PET vials and were transported and kept frozen before

Table 1 THg concentrations, water parameters and sampling site information

No.	Lake name	Location	Elevation m a.s.l.	Lake area km^2	THg ng L^{-1}	pH	DO mg L^{-1}	Salinity ppt	Conductivity S cm^{-1}	TDS g L^{-1}
1	Pangkog Co	89° 26.39′ E, 31° 45.09′ N	4520	140	4.09±0.63, n=4	8.7	4.53	20.66	33.05	21.15
2	Zige Tangco	90° 49.56′ E, 32° 02.94′ N	4561	191.4	2.08±0.28, n=8	10.1	3.26	13.43	22.36	14.33
3	Nganggun Co	85° 27.29′ E, 31° 11.01′ N	4658	22.6	2.01±0.09, n=2	9.58[a]	–	–	–	1.7[a]
4	Dawa Co	85° 03.38′ E, 31° 14.72′ N	4626	114.4	2.42±0.20, n=2	9	6.43	15.43	25.37	16.24
5	Qigai Co	85° 29.81′ E, 31° 12.14′ N	4663	20.3	2.12±0.14, n=2	10.43[a]	–	–	–	0.1[a]
6	Zhari Namco	85° 24.34′ E, 31° 04.71′ N	4613	996.9	2.23±0.02, n=2	9.6[a]	–	–	–	8.8[a]
7	Qingmuke Co	85° 04.22′ E, 31° 14.49′ N	4638	6	2.26±0.80, n=2	9.76[a]	4.75	3.32	6	3.8
8	Serbug Co	88° 16.82′ E, 32° 01.21′ N	4516	62.7	1.47±0.11, n=6	9.6	5.16	3.18	5.73	3.69
9	Dong Co	84° 44.22′ E, 32° 07.44′ N	4396	87.7	7.21±0.17, n=2	8.9	4.76	38.79	57.98	37.11
10	Merqung Co	84° 34.25′ E, 31° 06.22′ N	4666	62.3	5.02±0.09, n=2	9.4[a]	–	–	–	6.7[a]
11	Taro Co	84° 18.59′ E, 31° 07.65′ N	4566	486.6	0.51±0.06, n=4	8.7	5.47	0.48	0.9	0.6
12	Chabyer Caka	84° 04.17′ E, 31° 21.58′ N	4421	243	40.26±1.70, n=2	9.17–9.31[a]	–	–	–	439.8[a]
13	Ngangla Ringco	83° 22.08′ E, 31° 26.65′ N	4715	512.7	1.71±0.15, n=2	9.53[a]	–	–	–	14.5[a]
14	Dajia Co	85° 44.77′ E, 29° 53.37′ N	5145	114.5	3.91±0.03, n=2	9.4	4.64	13.63	22.67	14.5
15	Garing Co	84° 58.65′ E, 30° 48.34′ N	4650	66	0.87±0.27, n=2	7.4	6.21	2.13	3.9	2.5
16	Yunbo Co	84° 49.31′ E, 30° 49.35′ N	4638	64.3	1.34±0.08, n=2	9.7[a]	7.12	0.17	0.32	0.2
17	Dogze Co	87° 30.33′ E, 31° 51.18′ N	4459	244.7	2.22±0.28, n=12	9.6	4.47	14.81	24.45	15.65
18	Kunggyu Co	82° 08.11′ E, 30° 39.02′ N	4786	66.2	0.82±0.15, n=4	9.5[a]	–	–	–	–
19	Bangong Co	79° 45.64′ E, 33° 26.31′ N	4241	604	1.10±0.69, n=56	8.73	6.02	0.37	0.9	0.57
20	Rawu Co (middle)	96° 48.35′ E, 29° 25.46′ N	–	–	1.61±0.55, n=20	–	–	–	–	–
21	Rawu Co (up)	96° 49.62′ E, 29° 23.90′ N	3850	22	3.02±0.85, n=4	–	–	–	–	–
22	Rawu Co (down)	96° 43.78′ E, 29° 29.86′ N	–	–	0.81±0.22, n=16	–	–	–	–	–
23	Along Co	81° 43.52′ E, 32° 45.76′ N	4427	58.6	4.91±0.54, n=8	9.2	5.35	25.03	40.59	25.98
24	Songmuxa Co	80° 14.98′ E, 34° 35.98′ N	5051	24.6	0.99±0.29, n=6	8.53	6.32	0.32	0.51	0.32
25	Eshui Co	80° 33.91′ E, 33° 22.44′ N	4292	22.4	3.24±0.06, n=2	–	–	–	–	–
26	Lubu Co	80° 09.75′ E, 33° 06.43′ N	4342	8.4	0.75±0.07, n=4	9.39	6.21	1.84	2.99	1.91
27	Kunzhong Co	80° 22.62′ E, 33° 07.09′ N	4338	15	4.00±0.51, n=4	–	–	–	–	–
28	Rabang Co	80° 29.05′ E, 33° 02.25′ N	4324	31.6	8.18±0.40, n=2	9.2[a]	–	–	–	–
29	Bero Zeco	82° 57.20′ E, 32° 25.43′ N	4395	33.2	4.55±0.37, n=8	8.97	4.98	25.31	40.15	25.7
30	Lang Co	87° 23.91′ E, 29° 12.61′ N	4300	12.1	1.10±0.20, n=4	9.5[a]	–	–	–	–
31	Chagcam Caka	82° 12.86′ E, 32° 34.80′ N	4326	128.3	2.05±0.39, n=4	7.9[a]	–	–	–	–
32	Longmu Co	80° 22.06′ E, 34° 35.29′ N	5002	97	17.10±1.15, n=2	7.8[a]	–	–	–	173.6[a]
33	Nam Co	90° 58.53′ E, 30° 47.27′ N	4718	2015.4	1.09±0.73	9.2	8.9	–	1.85	0.86
34	Qiangyong Co	90° 13.53′ E, 28° 53.44′ N	4870	0.1	0.83±0.36, n=12	–	–	–		–

Table 1 (continued)

No.	Lake name	Location	Elevation m a.s.l.	Lake area km^2	THg ng L^{-1}	pH	DO mg L^{-1}	Salinity ppt	Conductivity S cm^{-1}	TDS g L^{-1}
35	Mapam Yumco	81° 37.02′ E, 30° 42.36′ N	4586	412	1.39±0.76, n=2	8–8.4[a]	–	–		–
36	La'nga Co	81° 19.65′ E, 30° 39.02′ N	4572	268.5	1.51	8.6[a]	–	–		–
37	Yamdrok Tso	90° 32.12′ E, 29° 10.59′ N	4441	650.5	1.97±0.15, n=2	9.08[a]	–	–		1.1[a]
38	Basom tso	93° 54.75′ E, 30° 00.45′ N	3469	37.5	2.32±0.38, n=2	7.2[a]	–	–		0.12[a]

[a] Cited from (Wang and Dou 1998)

analysis. Water parameters, including pH, temperature, salinity, and salinity-related variables (total dissolved solid (TDS) and electrical conductivity) were measured in situ using a HACH Hydrolab multi-parameter probe.

Analysis of Hg and major ions

Hg concentration was quantified by cold vapor atomic fluorescence spectrometry following USEPA Method 1631 (USEPA 2002) using an Analytik-Jena Hg analyzer (Analytik-Jena Corporation Inc., Jena, Germany) in a metal-free Class 100 laminar flow hood placed in a Class 1000 ultra-clean laboratory at the Key Laboratory of Tibetan Environment Changes and land surface processes (TEL). Quality assurance and quality control of the analysis were made through an integrated measurement and assessment of replicates, method blanks, field blanks, and ongoing precision and recovery (OPR) standards. In this study, the method detection limit (MDL), defined as three times the standard deviation of ten replicate measurements of a blank solution, was less than 0.2 ng L^{-1}. During Hg determination, a method blank and an OPR standard of 5 ng L^{-1} were loaded with a batch of 10–15 samples to check instrument operation. Results showed that method and field blanks were below the MDL with only few of field blank samples lower than 0.3 ng L^{-1}, indicating negligible contamination during sampling, transport, and analysis. The recovery percentage of OPR was 95–105 % of the certified value. The relative standard deviations for all the replicate samples were <5 %. Additionally, sampling and analyzing materials (e.g., Ziploc bags, Falcon tubes, and acid-cleaned glass bottles in Jena MERCUR) were randomly tested for Hg concentrations, and they were always below the MDL.

Analysis of major ions was also carried out in TEL. Major cations (Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}) were performed on a Dionex ISC 2000 ion chromatograph equipped with a CSES suppressor using an IonPac CS12A column and 20 mM methanesulfonic acid (MSA) as the eluent. Major anions (Cl^{-}, NO_3^{-}, HCO_3^{-}, and SO_4^{2-}) were quantified on a Dionex ISC 2500 ion chromatograph equipped with an ASRS suppressor using an IonPac AS11-HC column and 25 mM KOH as the eluent. The detection limits were 1 μg L^{-1} for all ions, and the analytical precision was within 5 %.

Results

Mercury concentrations in lake waters over the TP

Average THg concentrations in surface waters of the sampling lakes varied over a wide range from <1 ng to 40.3 ng L^{-1} (Table 1). THg concentrations in most lakes (33 of 38 lakes)

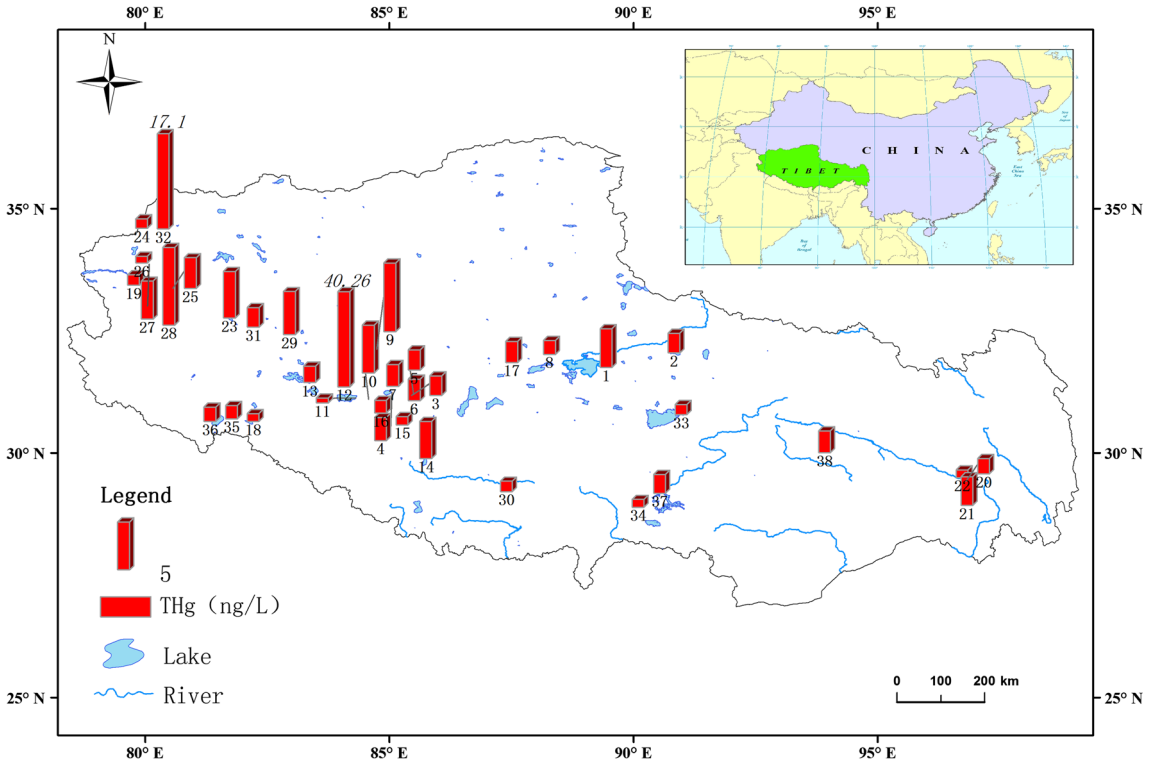

Fig. 1 Map showing the sampling lakes and their averaged THg concentrations in surface waters over the Tibetan Plateau

were lower than 5 ng L^{-1}. Notably, THg concentrations exhibited higher values in Lake Chabyer Caka (no. 12, 40.3 ng L^{-1}) and Lake Longmu Co (no. 32, 17.1 ng L^{-1}). Measured water parameters such as salinity, conductivity, TDS, and major ionic concentrations also displayed wide ranges (Table 1). For example, TDS ranged between <0.1 and 439.8 g L^{-1}; pH values were consistently alkaline and ranged from 7.2 to 10.4.

Spatial distribution of Hg in Tibetan lake waters

As can be seen in Fig. 1, THg concentrations in lake waters showed a general increasing trend along the southeast–northwest transect over the TP. Readers are reminded that relatively less sampling sites are in the southeast TP, and this may reduce the spatial resolution. Nevertheless, it is clear that Hg-enriched lakes concentrated in the northwest region.

Comparison of Hg concentrations in lake waters over the TP and other areas globally

Table 2 presented a comparison of THg concentrations in waters from lakes over the TP and other areas globally. Generally, THg concentrations in Tibetan lake waters (mean = 3.82, median = 2.07) are lower than those in lakes influenced by human activity such as Taihu Lake and Dianchi Lake, while they are comparable to those of remote lakes in French Alps and North America and are higher than that of Antarctic lake. Overall, Hg levels in most Tibetan lakes lie within the background Hg of global natural waters of <10 ng L^{-1} (Fitzgerald and Watras 1989), indicating that Tibetan lake waters are minimally influenced by human activity, which is in agreement with previous studies that Hg levels in various environmental matrix over the TP remain natural background. Nonetheless, Hg concentrations in several lakes are notably high and are comparable to or even exceed those of lakes that suffered from intensive human activities.

Discussion

Mercury and natural environmental variables

The distribution of Hg in aquatic environments is influenced by various chemical and biological parameters in the watershed (Bloom and Effler 1990; Zhang et al. 2009). Principle cluster analysis (PCA) was performed to investigate the interrelations between Hg concentrations and water physiochemical parameters as well as some other relevant environmental variables of lake watersheds summarized in Electronic supplementary material Table S1. As illustrated in Fig. 2, THg, salinity, and salinity-related water chemical parameters (i.e.,

Table 2 Comparison of THg concentrations in waters from lakes in the TP and other areas globally

Region	Lakes/location	Altitude m a.s.l	Period	THg (ng L^{-1})		Remarks	References
				Mean	Range		
Asia	38 lakes, Tibetan Plateau	3850–5145	2010–2011	3.82±6.75	<1–40.3	Remote	This study
	Puding Reservoir, China	1400	2006–2007	2.74±2.07	1.0–11.74	Suburban/ agricultural activity	(Zhang et al. 2009)
	Taihu Lake, China	1887	2009	28±18	6.8–83	Urban/intensive human activity	(Wang et al. 2012a)
	Dianchi Lake, China		2009	30±8.0	18–46	Urban/intensive human activity	(Wang et al. 2012b)
Europe	4 lakes, French Alps	1649–2448	2008		0.1–4.34	Remote	(Marusczak et al. 2011)
	Lake Balaton, Hungary		2000–2011		1.45–6.48	Rural	(Nguyen et al. 2005)
	Plitvice Lakes, Croatia	500–650	2005–2007	1.22	0.73–1.77	Remote/filtered samples	(Vukosav et al. 2014)
North America	Great Lakes		2002–2009	1.0±2.05	0.1–18.2	Rural/urban	(Dove et al. 2012)
	60 Lakes, Northern Canada		1996	3.64±2.52	0.1–14.7	Remote	(Vaidya et al. 2000)
	101 lakes, Western US	1125–3562	1999	1.07±1.41	0.27–14.09	Remote	(Krabbenhoft et al. 2002)
	Great Salt Lake, US	1280	2006–2007	3.6±0.8		Filtered samples	(Peterson and Gustin 2008)
Africa	10 reservoirs, Burkina Faso		2009	5.3	0.4–21.38	Mining activity	(Ouedraogo and Amyot 2013)
Antarctica	Lake Hoare, Taylor Valley		1994		0.66–1.36	Remote	(Vandal et al. 1998)

conductivity, TDS, and most of ions) converged together and were highly loaded in PC1 (Electronic supplementary material Table S2), indicating close relations between Hg and these variables. This is further evidenced by the high correlation coefficients among THg and some of the major ions such as K^+, Na^+, and Cl^- in lake waters (Table 3). Plot of Hg versus TDS clearly illustrated that THg covaries with TDS, and such linear relationship is not solely derived from the low Hg cluster lakes but is also applicable for those high Hg cluster lakes (Fig. 3).

Distribution and enrichment of mercury in lake waters

In surface waters, Hg derives mainly from atmospheric deposition, runoff, and groundwater (Driscoll et al. 2007). Once incorporated into lake water, Hg exists in elemental,

Table 3 Correlation of Hg and selected environmental factors in lake waters

	THg	pH	Salinity	Conductivity	TDS	DO	Na^+	NH_4^+	K^+	Mg^{2-}	Ca^{2-}	Cl^-	HCO_3^-	SO_4^{2-}
THg	1.000													
pH	0.127	1.000												
Salinity	0.972*	0.221	1.000											
Conductivity	0.960*	0.249	0.999*	1.000										
TDS	0.960*	0.249	0.999*	1.000 *	1.000									
DO	−0.515	−0.230	−0.621	−0.627	−0.628	1.000								
Na^+	0.935*	0.450	0.918*	0.914*	0.914*	−0.449	1.000							
NH_4^+	0.927*	0.461	0.934*	0.932*	0.932*	−0.632	0.976*	1.000						
K^+	0.990*	0.140	0.939*	0.923*	0.923*	−0.478	0.942*	0.927*	1.000					
Mg^{2+}	0.930*	0.131	0.914*	0.907*	0.907*	−0.281	0.887*	0.818**	0.917*	1.000				
Ca^{2+}	0.546	−0.387	0.581	0.579	0.579	−0.085	0.336	0.272	0.488	0.716**	1.000			
Cl^-	0.956*	0.161	0.879*	0.860*	0.860*	−0.330	0.940*	0.891*	0.984*	0.919*	0.455	1.000		
HCO_3^-	−0.014	0.786**	0.100	0.129	0.129	−0.493	0.209	0.327	−0.041	−0.197	−0.602	−0.102	1.000	
SO_4^{2-}	0.987*	0.168	0.964*	0.954*	0.954*	−0.435	0.945*	0.913*	0.982*	0.973*	0.599	0.966*	−0.068	1.000

*$p \leq 0.01$; **$p \leq 0.05$

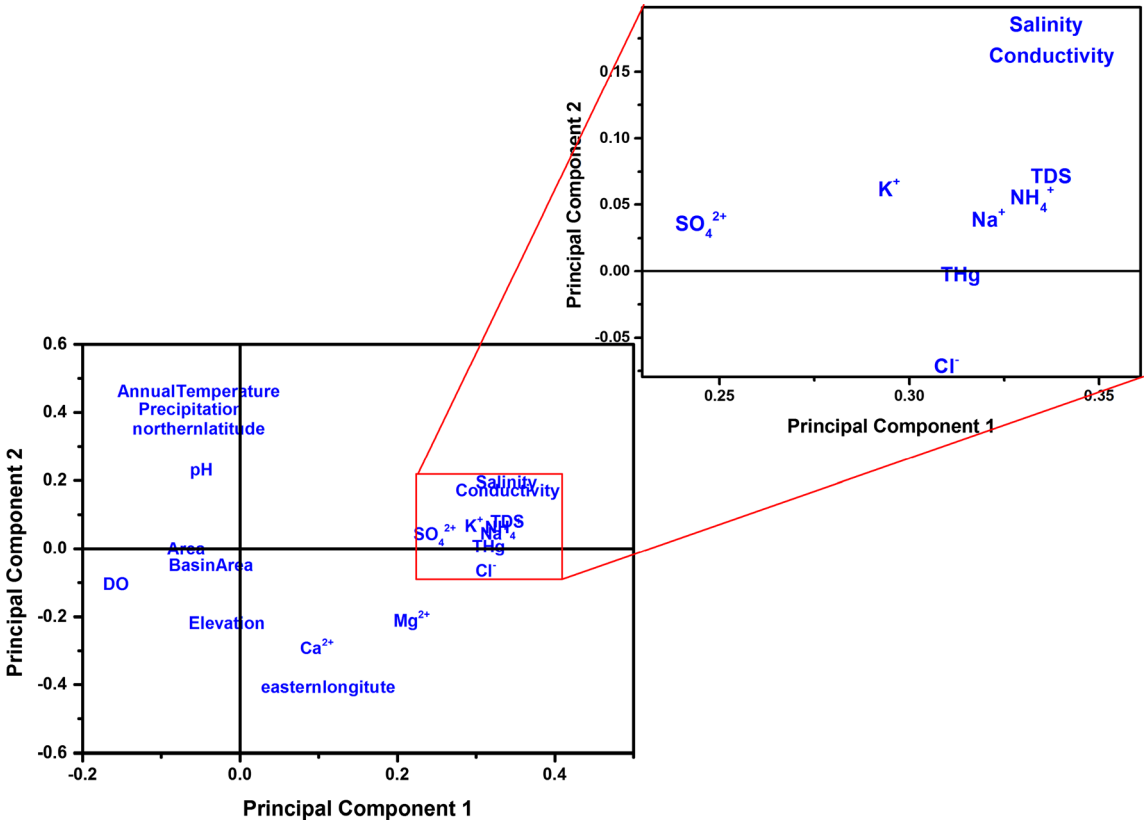

Fig. 2 PCA factors of Hg and relevant environmental variables

inorganic, and organic forms (Wang et al. 2004), while Hg^{2+} is recognized as the dominant form (Mousavi et al. 2011). Hg speciation participates in complex environmental and biological processes, and its distribution and fate in lake waters were influenced by multiple factors. Generally, lakes nearby Hg emission sources, such as industrial and populous areas, are readily receiving more Hg input and thereby exhibited higher Hg levels. For example, Dove et al. (2012) performed a survey on Hg distribution in waters from Great Lakes and observed consistently highest Hg concentrations in the western basin of Lake Erie which is the recipient of intensive urban and industrial inputs. Similarly, Wang et al.

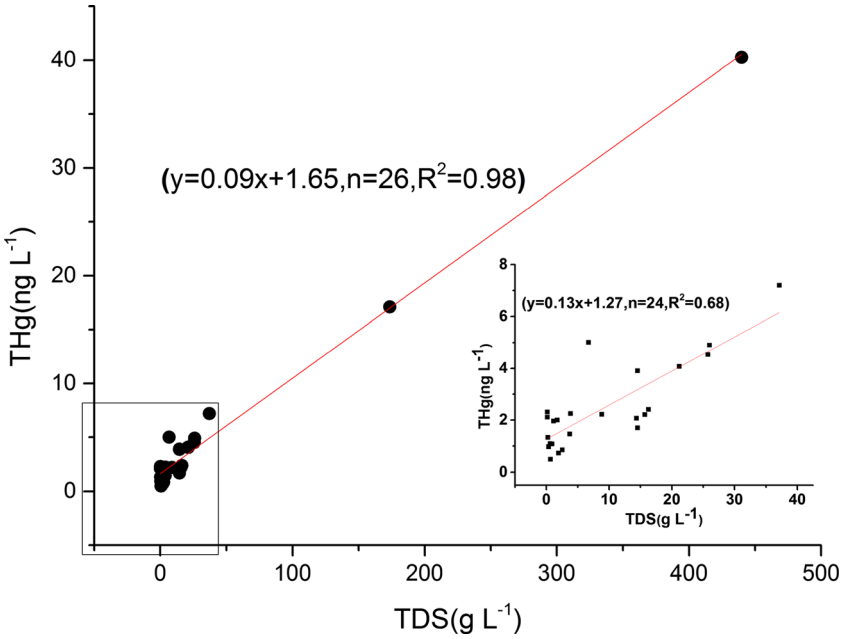

Fig. 3 Correlation between THg concentration and TDS from the sampling lakes

(2012a) reported high Hg concentrations (6.8–83 ng L^{-1}) in waters from Lake Taihu in Eastern China which suffers Hg contamination from nearby agricultural and urban inputs. Hg in waters from the lakes in remote regions generally showed background levels and is from background geologic and/or atmospheric sources. The TP is far from anthropogenic Hg sources, and the Hg in lakes over the TP is generally attributed to the input of runoff and atmospheric deposition; the latter has been considered the primary Hg contributor to the remote lakes over the TP (Yang et al. 2010). As shown earlier, Hg concentrations in lakes across the TP exhibited a wide range, with some values exceeding the global background Hg levels in natural waters. Atmospheric deposition is not likely the major factor resulting in the contrasting Hg distribution in lake waters; this can be argued by the constant low atmospheric Hg depositional fluxes over the TP as indicated by glacier snow and lake sediment records, Hg deposition measurements, and modeling results in the TP (Huang et al. 2012; Wang et al. 2014; Yang et al. 2010; Zhang et al. 2012). Apart from direct atmospheric deposition, Hg concentrations in lakes are usually dependent on the lithological characteristics of the catchment and/or on weathering and leaching of soils (Yang et al. 2002). It has been reported that some particular aquatic systems received runoff Hg as the dominant external Hg input (Gao et al. 2006; Kang et al. 2000). There are insufficient data sets of quantitative runoff Hg input for the large clusters of lakes over the TP, precluding further linkages with the variability of Hg in lake waters to the difference in runoff Hg input on a large scale over the TP. Nevertheless, soil Hg levels exhibited a decreasing trend along the southeast–northwest transect across the TP (Sheng et al. 2012; Zhang et al. 2002), which is exactly the inverse distribution pattern compared with that of Hg in lake waters, possibly suggesting that catchment lithology and runoff Hg input are not major factors controlling the distribution of Hg in lake waters over the TP.

As presented earlier, Hg concentrations showed a strong correlation with salinity and salinity-related parameters in lake waters (Fig. 3 and Table 3). The salinity of the lakes over the TP is closely related to the natural climatic and environmental conditions and exhibits an increasing trend from south and southeast to north and northwest, co-varying closely with the annual precipitation and aridity (expressed as annual evaporation/annual precipitation) of the TP (Zheng and Liu 2009). Consequently, lakes in the TP exhibit transitions in the order of fresh water lakes, saline lakes, and highly saline lakes along the South/East–North/West gradient (CAS 1984; Zhang et al. 2008). This basic distribution pattern of lakes greatly affects the variation of many lake water parameters such as stable isotopes (e.g., deuterium and dissolved inorganic carbon isotope) (Lei et al. 2012; Yuan et al. 2011), organic compounds (e.g., alkenone) (Liu et al. 2011), diatoms (Yang et al. 2001), and bacteria community (Liu et al. 2013). This is typically explained that lake waters can accumulate or regulate substances while undergoing evaporation enrichment. Hg in lake waters is likely regulated by the similar mechanism, as illustrated in Fig. 4. With the decrease of precipitation and increase of evaporation northwards/westwards, lake water evolved to be concentrated with more soluble substances such as salts and dissolved organic matters (DOM) (Hammer 1986); this phenomenon has been observed in many regions as well as the TP itself globally (Anderson and Stedmon 2007; Xu et al. 2013). Hg is known to be readily complexed by various natural organic ligands (Guentzel et al. 1996; Han and Gill 2005), which are prone to enrich in high salinity lakes. Therefore, the concurrent high Hg and salinity in lake waters indicate the effect of the natural environment on the distribution of lake water chemistry over the TP, suggestive of consistent enrichment of Hg and other soluble substances in lake waters induced by evapoconcentration. Therefore, it is the within-lake process, rather than the direct input of Hg, that induced almost uniformly higher Hg levels in lakes in the northwest that those in the southeast of the TP.

Perspectives on Hg biogeochemical study over the TP

Long-range transport of atmospheric Hg to remote regions such as the Arctic and Antarctica has been significantly enhanced due to industrialization, and the subsequent fate of Hg and its potential risk have raised substantial concerns (Bargagli 2008; MacDonald et al. 2000; Poissant et al. 2008). As the low-altitude counterpart of the Polar Regions, the TP and its surrounding mountainous regions as a whole

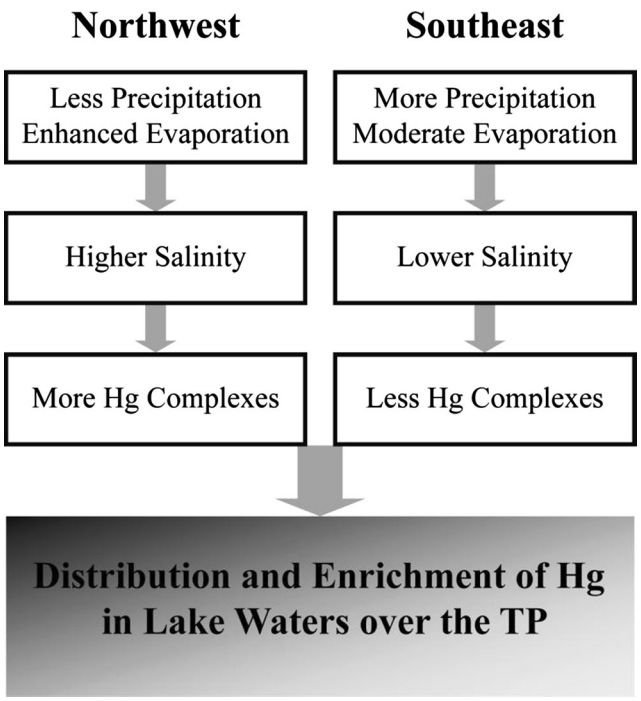

Fig. 4 Illustration of relations between the natural environment and the distribution and enrichment of Hg in lake waters over the TP

are known as "The Third Pole" (Qiu 2008; Yao et al. 2012), while Hg's fate and the basic picture of biogeochemical cycling over this unique region have been less known. The TP boasts the most populous high-altitude lakes globally which are of particular importance as potential sinks of Hg and repositories of historical Hg deposition. Recent studies have revealed altered atmospheric Hg levels in the last few decades via lake sediments in the TP (Wang et al. 2010; Yang et al. 2010); additionally, the TP has been highlighted as ecologically critical environment with the occurrence of high levels of Hg in indigenous wild fishes (Yang et al. 2011; Zhang et al. 2014). Our results provided fundamental background of Hg levels in lake waters for further Hg investigation over the TP. Besides, the high levels of Hg in saline lakes induced by evaporation enrichment represent an important natural mechanism of Hg accumulation within the saline lakes. While much emphasis has been on assessing the impact of direct atmospheric deposition and watershed runoff input of Hg on remote lake ecosystems, the enhancement of Hg in waters induced by within-lake processes, as presented in this study, urges for further attention to probe into additional Hg accumulation mechanisms within the lake itself. Lakes over the TP are generally deep and have long water renewal times (Wang and Dou 1998), allowing long retention and sufficient transformation of Hg therein. The accumulation and potential methylation of Hg within lakes are likely further enhanced in the presence of Cl^- which is typically one of the dominant ions in Tibetan lakes and can suppress the degradation of methyl-Hg (Sun et al. 2013; Zhang and Hsu-Kim 2010). Although methyl-Hg has not been measured in this study, considering that methyl-Hg generally accounts proportionally to THg in natural waters (Hamasaki et al. 1995), the methyl-Hg concentration and its potential accumulation could be substantially higher in saline lakes over the TP. In the future, studies on Hg dynamics and bioaccumulation in lakes are needed to depict a full picture of the fate and environmental significance of Hg in lakes over the TP.

Conclusions

To sum up, Hg in Tibetan lake waters exhibited a wide range from <1 to 40.3 ng L^{-1}. Hg had a strong correlation with salinity and salinity-related water parameters especially for TDS and some of the major soluble ions such as K^+, Na^+, and Cl^-. The spatial distribution of Hg in lake waters showed a general increasing trend along the southeast–northwest transect across the TP, resulting from the increasing evaporation enrichment of lake water chemistry influenced by the natural environment over the TP. The relatively high Hg levels in saline lakes represent a natural accumulation mechanism of Hg. The Hg dynamics and bioaccumulation in lakes over the TP under the changing climate context warrant further study.

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