

Water chemistry of the headwaters of the Yangtze River

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Abstract A total of 31 river water samples were collected from the headwater of the Yangtze River and its tributaries across Shigu Town to Mt. Tangua region. Water chemistry analysis was carried out to investigate water quality in the upstream Yangtze River. The results show that the headwaters of Yangtze River are turbid and have an alkaline environment with pH ranges from 8.3 to 9.3. The oxidation reduction potential (ORP) of the water varies from -77.1 to -134.2 mv with an average of -88.8 mv, indicating an anoxic water surface. Based on the ions analysis, the water chemistry of headwaters of the Yangtze River is affected by mineral (magnesium and calcium sulfate) weathering, evaporation–crystallization processes and ground water discharge. Concentrations of ions and elements except Hg in the headwaters of Yangtze River presented a trend of decreasing with the downward of altitude. All heavy metals and other toxic elements concentrations in this study were under the WHO and GB (China national standards) guidelines. But attention should be given to Hg because the concentration of Hg (2.6 ng/l) was much higher than the world average (0.07 ng/l) and it

increased as the river flows down, which may become a threat to the inhabitants in the downstream area of the river.

Keywords Major ions · Heavy metals · Water quality · Yangtze river · Tibetan plateau

Introduction

The Yangtze River is the third longest (6300 km) river in the world, with the fourth largest water discharge ($900 \text{ km}^3 \text{ a}^{-1}$), draining nearly one-fifth of China. It originates from glaciers of the Geladaindong Peak (6621 m.a.s.l.), Tibetan Plateau (TP), flows southwards through the eastern TP, makes a large bend (110°) at Shigu Town in Yunnan Province (Fig. 1), and then flows eastwards until runs into the East China Sea of the Pacific Ocean. The Yangtze River, together with the Yellow River is called the “Mother River” of China for it is feeding more than 400 million people living in China; therefore, the water quality is an essential issue for the local people in the basin

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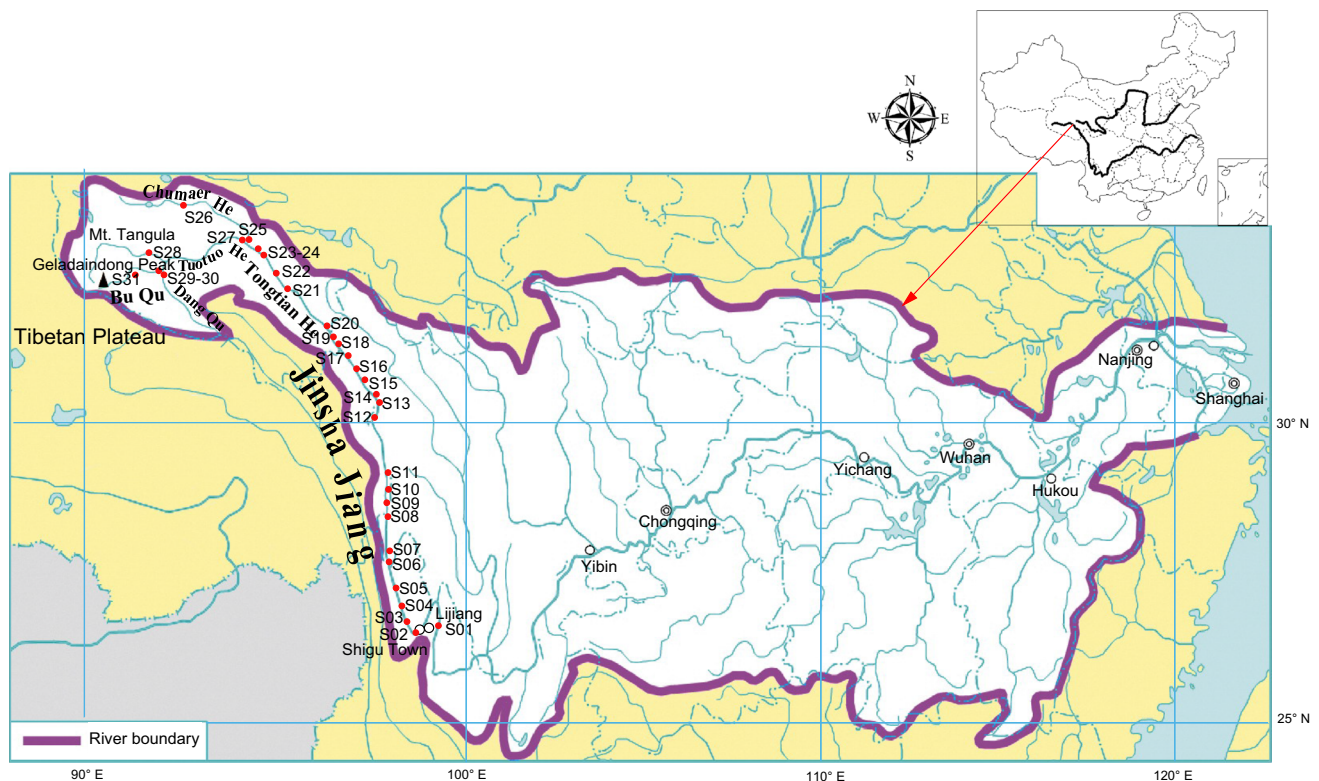


Fig. 1 Study area and sampling sites

regions. The rivers on TP are generally considered as free of contamination (Zheng et al. 2010). However, a recent study suggested that geothermal springs on TP can cause arsenic contamination of the rivers in this area (Li et al. 2014). The TP is bordered by the two largest developing countries in the world, China and India; atmospheric transport of pollutants from the varying human activities in these countries may constitute a source of a wide spectrum of pollutants which are deposited on the plateau (Balerna et al. 2003; Kaspari et al. 2009; Lee et al. 2008; Cong et al. 2007; Cong et al. 2010; Wang et al. 2008; Xiao et al. 2001) and then released to the waters of rivers on TP (Li et al. 2007; Li et al. 2009; Li et al. 2011; Zhang et al. 2012). On the other hand, glacier meltwater on TP is an important water source of Yangtze River (Immerzeel et al. 2010). As a consequence of global warming, the temperature on TP has increased significantly (IPCC 2013), resulting in an increased melting of accumulated ice and snow (Barnett et al. 2005; Kang et al. 2010), which will also affect the river water quality.

So far, a considerable number of studies have been done on waters in the middle stream and downstream of Yangtze River, which have given a wealth of knowledge on the effects of anthropogenic activities (e.g., agriculture and reservoir built) on the water quality and chemistry (Ran et al. 2013; Shi et al. 2013; Zhang et al. 2013; Zhou et al.

2013). However, in the upstream of Yangtze River, an area almost without anthropogenic influence, human health hazard elements such as Hg, As and Pb did not receive sufficient attention in previous studies. In this research, we have investigated not only the major ions in the headwater of Yangtze River, but also some health hazard elements such as Hg, as a contribution to further studies on water chemistry so that it can contribute to the future study of water chemistry under the background of climate change and the change of water quality for human health.

Study area

The headwater drainage basins of the Yangtze River extend from 32°26'N 90°33'E to 35°45'N 95°20'E, with an area of $103 \times 10^3 \text{ km}^2$ (Fig. 1). The three source branches for Yangtze River flow with a very gentle slope in the TP hinterland. The 358-km-long Tuotuo He basin ('He', 'Jiang' and 'Qu' in this paper are all Chinese for 'river') is cold and dry with intense evaporation. The annual mean temperature is below 4 °C and annual precipitation ranges from 200 to 500 mm. The Tongtian He basin is 828 km and has a cold climate and less rainfall. The Jinsha Jiang is 2290 km long with a drainage area of $362 \times 10^3 \text{ km}^2$. It flows from NW to SE through deep valleys in the

mountains east of the TP and shows a fall of approximately 3300 m over the 2290 km and the deepest gorge has a very steep slope (~ 14 m/km). The annual mean precipitation varies dramatically with elevation, and is about 450 mm at the river catchments on the TP above Shigu Town (CWRC 2007; Wu et al. 2008b), and the annual evaporation is 2–6 times greater than that of annual precipitation (Zheng 1997). Geologically, the source area of the Yangtze River drainage basin between the Bayan Har fold belt and the Tanggula fold belt, is composed of Quaternary fluvial deposits, Mesozoic clastic rocks, and carbonate rocks intercalated with evaporite and volcanic rocks. The Tongtian He basin is covered with Triassic low-grade metamorphic rocks, clastic rocks and volcanic rocks. The Jinsha Jiang drains the Tethyan Himalayan tectonic belt and the Sanjiang fold belt. The volcanic rocks and ophiolitic mélangé discontinuously distribute along the Jinsha Jiang suture zone and are intercalated with minor Permian limestone fragments. Neoproterozoic meta-volcanic rocks and crystalline limestone are found near Shigu Town (CWRC 2007; ISSAS 1986; The China Geological Survey 2004).

Sampling and analysis

Six tributaries (Chumaer He, Tuotuo He, Dang Qu, Bu Qu, Tongtian He and Jinsha Jiang, Fig. 1) in this area were chosen to investigate their water quality. The expedition on the upper reaches of the Yangtze River started on August 30th 2012 at Lijiang, Yunnan, proceeded more than 2000 km upstream to the source region near the Geladaindong Peak, Mt. Tanggula, ending on September 11th, 2012. A total of 31 river water samples were collected along the source region of the Yangtze River (Fig. 1). General water quality parameters (including water temperature, pH, ORP, conductivity, TDS and turbidity) were detected in the field using the portable water testing kits of Wagtech CP1000 along with the sampling work. Water samples for elements analysis were filtered using 0.2 μm polypropylene membrane and stored in 15-ml polypropylene bottles. All samples were taken against the water flow direction at approximately 10 cm depth below the surface. The samples were acidified with ultrapure HNO_3 and HCl ($\text{pH} < 2$) for elemental and Hg measurement, respectively, and stored in containers at 4 $^{\circ}\text{C}$ until analysis.

The concentrations of cations (Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+}) and anions (F^- , Cl^- , NO_3^- , SO_4^{2-} , HCO_3^-) in water were detected by Dionex ICS 2000 and Dionex ICS 2500, respectively. The elements S, Sr, Tl, B, Rb, Ti were measured using inductively coupled plasma-atomic emission spectrometer (ICP-AES) within 40 days of sample collection. The instrument was initially calibrated using standards of the different elements; standards were routinely

run after the initial calibration and every 10 samples during the whole analysis process. The wavelengths used for each element and the corresponding limit of detection (LOD) are listed in Appendix 1. Analysis of Hg in the water samples was performed according to the US EPA Method 1631(version E) (USEPA 2002). The samples were analyzed by cold vapor atomic fluorescence spectroscopy (CVAFS) with an Analytik-Jena Hg analyzer (Analytik-Jena Corporation Inc., Jena, Germany) in metal-free class 100 ultra-clean laboratory room. Mercury concentrations are reported as ng per liter. The LOD was lower than 0.2 ng L^{-1} and recovery percentage was 95–105 % of the certified values for Hg (Huang et al. 2012).

Results and discussion

General chemical characteristics

The sampling information and general chemical characteristics of the river water samples collected during September 2012 along the source region of the Yangtze River are listed in Table 1. Water temperature of the river and its tributaries averaged 14 $^{\circ}\text{C}$. The pH, TDS, EC and ORP also increased from Shigu Town to the source area. The ORP values were all negative, which indicates a severely reducing aquatic environment. And the turbidity of headwaters of the Yangtze River was also fairly high. Over the whole area, pH ranged from 8.3 to 9.3 and EC ranged from 162 to 3290 mS m^{-1} with an average of 967.3 mS m^{-1} (Table 1) indicating an alkaline environment. It appears that these waters have a high buffering capacity for acid dry and wet deposition. Thus, acidification, due to acid rain precipitation, might not be a future problem for the rivers on the plateau. The results are comparable to those of the previous study on the other rivers on TP (Huang et al. 2008; Li et al. 2011; Zheng et al. 2010). The ORP of Yangtze River waters in this study varies from -77.1 to -134.2 mv with an average of -88.8 mv. There exists a significant negative relationship between ORP and pH ($r = -0.83$, sig. at the 0.01 level), indicating that the pH has certain potential influence on the chemical forms and distribution of the metals in water (Gambrell et al. 1977).

Ions in the headwaters of the Yangtze River

Ions concentrations and ionic source of headwaters of the Yangtze River

The most ions concentration of samples collected at site 29 (Dang Qu) exceeded the detection limit in the laboratory. Thus, the data from this point are not discussed in detail.

Table 1 Sampling information and parameters selected by Wagtech CP1000

Location	Site	Date	Elevation (m)	Temp (°C)	ORP (mV)	Turbidity (NTU)	pH	EC (us/cm)	TDS (mg/L)	Total alkalinity (mg/L)
Jinsha Jiang	S01	2012/8/30	1350	20.1	−77.1	668	8.3	520	261	-
	S02	2012/8/31	1817	17.8	−81.5	502	8.4	302	605	340
	S03	2012/8/31	1836	17.2	−83.3	594	8.4	599	304	360
	S04	2012/8/31	1873	17.2	−81	507	8.48	572	289	340
	S05	2012/8/31	1924	21.2	−84.6	631	8.39	580	296	500
	S06	2012/9/1	1999	17.2	−83.8	589	8.51	580	284	460
	S07	2012/9/1	2042	16.7	−91.7	547	8.53	547	278	500
	S08	2012/9/2	2368	15.6	−87.8	790	8.56	672	336	>max
	S09	2012/9/2	2409	15.3	−83.8	579	8.52	658	332	>max
	S10	2012/9/2	2478	15.1	−86.5	476	8.55	691	340	340
	S11	2012/9/2	2485	14.5	−89.8	492	8.53	638	319	320
	S12	2012/9/4	2958	11.9	−87	560	8.57	748	-	380
	S13	2012/9/4	2995	13.1	−92.1	656	8.55	830	-	>max
	S14	2012/9/5	3048	11.9	−87.6	644	8.57	1130	579	>max
	S15	2012/9/5	3057	11.8	−86.5	755	8.48	1089	535	>max
	S16	2012/9/5	3097	11.9	−87.4	724	8.57	1166	587	>max
	S17	2012/9/6	3290	12.3	−87.9	520	8.48	1058	522	420
	S18	2012/9/7	3367	11.9	−86.7	603	8.57	1204	601	420
	S19	2012/9/7	3474	12	−87	549	8.5	1137	566	480
	S20	2012/9/8	3518	12.6	−89.1	453	8.39	1090	542	420
Tongtian He	S21	2012/9/8	4274	11.9	−78.6	316	8.43	1271	644	280
	S22	2012/9/8	4191	12.8	−87.4	361	8.52	1191	589	200
	S23	2012/9/9	4180	14.1	−91.9	212	8.64	162	532	80
	S24	2012/9/9	4185	10.2	−90.3	56	8.58	579	283	<min
Chumaer He	S25	2012/9/9	4221	15.3	−82.8	167	8.47	1535	774	0
	S26	2012/9/10	4536	8.2	−98.7	758	8.78	1120	998	>max
Tuotuo He	S27	2012/9/9	4261	14.2	−94.3	846	8.63	2040	998	>max
	S28	2012/9/10	4491	15.1	−92.1	229	8.6	3290	1650	110
Dang Qu	S29	2012/9/10	4492	17.2	−134.2	6.7	9.33	>max	>max	<min
Bu Qu	S30	2012/9/10	4540	10.8	−96	212	8.7	1517	758	70
	S31	2012/9/11	4717	6.6	−84.1	83.2	8.52	503	251	<min

However, it should be noticed that only NO_3^- was detected here and the concentration was fairly low, 0.19 mg/L. Concentrations of NO_3^- in the study area were also much lower than those of midstream and downstream Yangtze River waters (Müller et al. 2008). In addition, no NH_4^+ was detected in the headwaters of the Yangtze River, indicating that the effect of human activities on river waters in this area is irrelevant. Other common ions such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} , F^- , Cl^- , NO_3^- , SO_4^{2-} and HCO_3^- were detected (Fig. 2).

HCO_3^- concentration in Jinsha Jiang was lower than that of the source area, decreasing with pH. The concentrations of other ions decreased from the source area of the Yangtze River to Shigu Town (Fig. 2b), mainly due to the greater

precipitation and the larger runoff in lower reaches. The ions can be discussed based on the fairly clear differences in spatial distribution (Figs. 2, 3). Even though the results show a clear dilution of ions (except HCO_3^-) in Jinsha Jiang, it should be noted that there is still an extremely high level of dissolved salts in the water of the whole study area, in particular Na^+ (146.6 mg/L), SO_4^{2-} (120.6 mg/L), Cl^- (267.5 mg/L) and HCO_3^- (116.8 mg/L). The concentrations of dissolved ions reached the highest values at site 28, Tuotuo He (Fig. 2). The four ions were the main components in the water and made up over 87 % of the total ions. Among them, concentrations of Na^+ and Cl^- were much higher than world average level. Cl^- had the highest mole concentration with an average of 7.71 mmol/L. Over 70 %

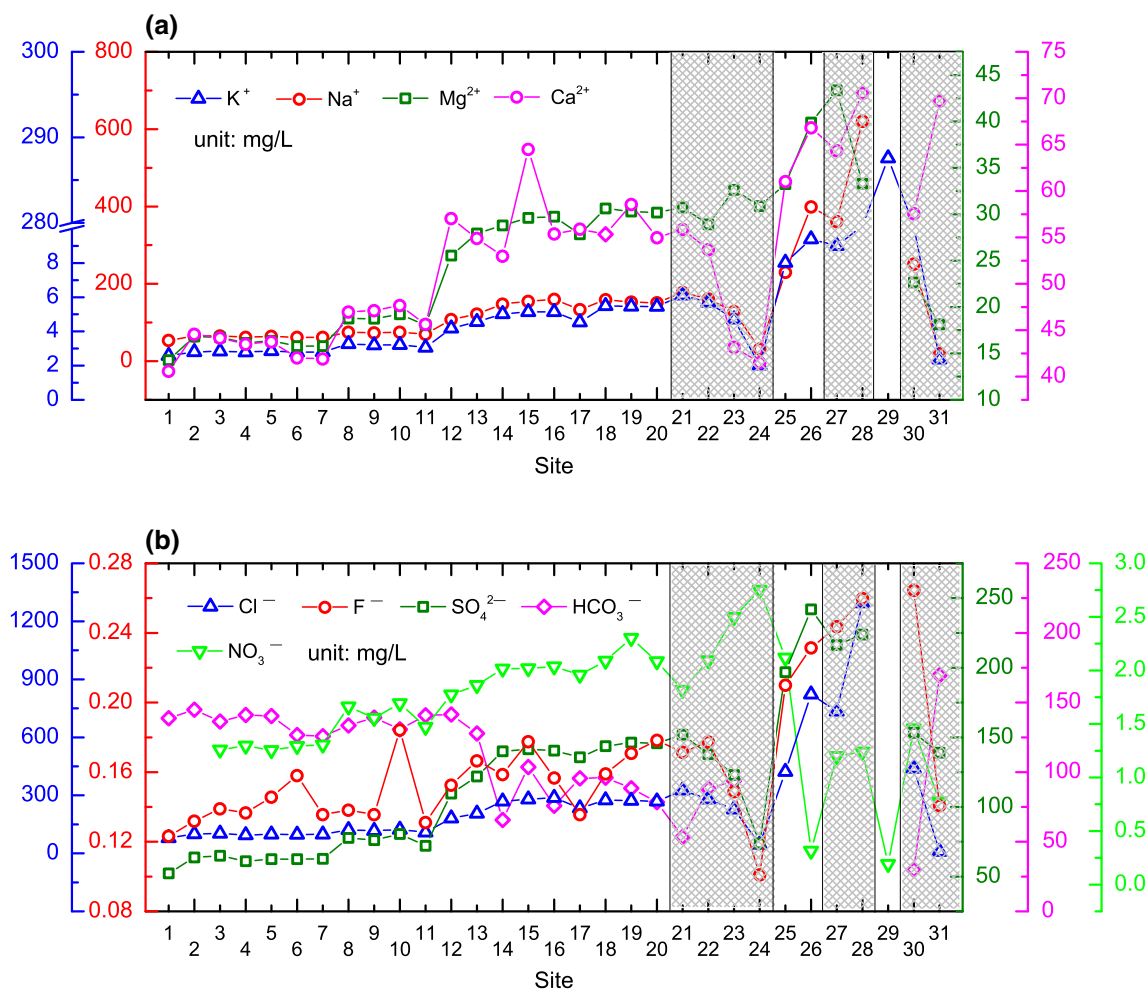


Fig. 2 Concentrations of ions in upstream of Yangtze River (**a** for cations and **b** for anions). S01–S30, Jinshajiang; S21–S24, Tongtian He; S25–S26, Chumaer He; S27–S28 Tuotuo He; S29, Dang Qu; S30, Bu Qu. Same to Fig. 6

of the cations were made up by Na⁺ and more than 71 % of the anions were Cl⁻. The total cationic charge ($Tz^+ = Na^+ + K^+ + 2Mg^{2+} + 2Ca^{2+}$) ranged between 5.6 and 13.3 meq/l with an average of 9.3 meq/l, which is seven times more than the average for the world's rivers (1.25 meq/l) (Meybeck 1981), and also higher than the average of the whole Yangtze River (2.8 meq/l) (Han and Liu 2004).

The concentrations of most ions decreased from Mt. Geladaindong to Shigu Town, which results from the higher runoff as the river flows down (Huang et al. 2009; Ramanathan 2007). There is a positive correlation between Mg²⁺ and Ca²⁺ concentrations with the content of the dissolved ions (expressed as electrical conductivity, $r^2(Mg/EC) > 0.36$, $r^2(Ca/EC) > 0.49$, see “Appendix”). The ions, Na⁺ and Cl⁻, have a significant consistence with each other ($r^2(Na/Cl) > 0.99$), and the correlation between Ca²⁺, Mg²⁺ and SO₄²⁻ are also fairly good [$r^2(Ca/SO_4) > 0.77$; $r^2(Mg/SO_4) > 0.75$], indicating that they have a common

origin. It should be noticed that the waters studied here were rich in sulfate ions, with significantly higher SO₄²⁻ than the average of other rivers in the world (Table 2). Sulfate ions in river waters may have several sources. It is often suspected of having anthropogenic origin as well as being the result of dissolution of evaporites such as gypsum, oxidation of sulfides, and atmospheric input (Han and Liu 2004). However, there are almost no industrial activities around Mt. Geladaindong. So the sulfate ions here probably also have a natural source. Stoichiometry can be used to identify the sources of several ions (Han and Liu 2004; Stallard and Edmond 1983). The equivalent mole ratio of $(Ca^{2+} + Mg^{2+})/(SO_4^{2-} + HCO_3^-)$ of approximately 1 (Fig. 3a), along with the good relationship between Ca²⁺, Mg²⁺ and SO₄²⁻, are indicative that the ions were contributed by sulfate minerals rather than silicate weathering. Additionally, the equivalent ratios above the gypsum dissolution line suggest a contribution of gypsum to sulfate. The SO₄²⁻ in the

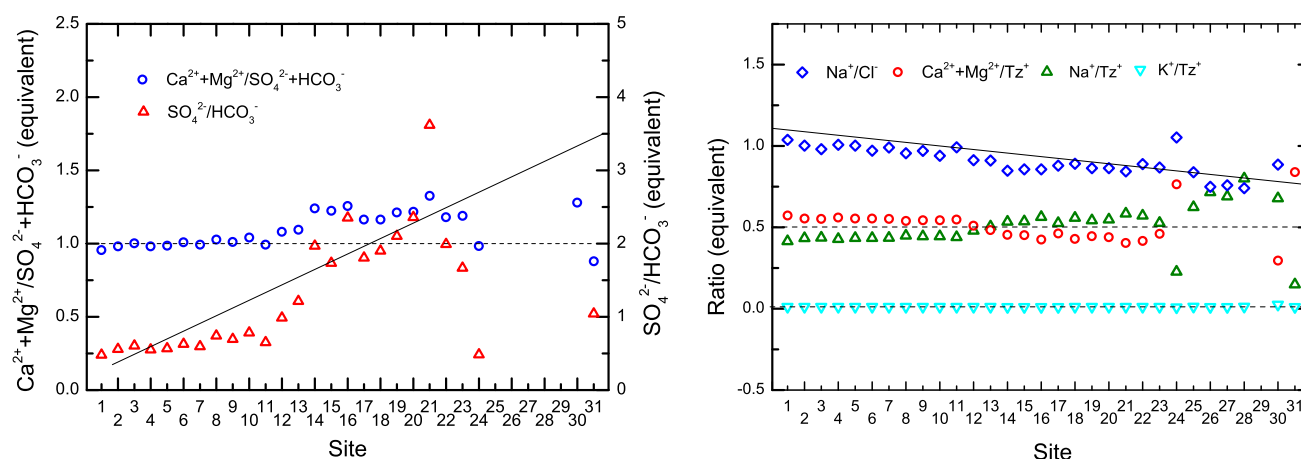


Fig. 3 Scatter plots of $(\text{Ca}^{2+} + \text{Mg}^{2+})/(\text{SO}_4^{2-} + \text{HCO}_3^-)$ (a) and Na^+/Cl^- , $(\text{Ca}^{2+} + \text{Mg}^{2+})/\text{Tz}^+$, Na^+/Tz^+ (b) in the Yangtze River, China

Yangtze River was likely affected by magnesium and calcium sulfate. Though it has been reported that sulfate concentrations in the Yangtze River basin have been increasing in the past 50 years due to the increase in industrial and agricultural activities (Chen et al. 2002), it is found that the natural process was the dominant factor controlling the water chemistry of the headwaters of the Yangtze River. $\text{SO}_4^{2-}/\text{HCO}_3^-$ ratios increased from site 1 to site 31 (Fig. 3a), demonstrating that carbonate mineral dissolution was not as strong as sulfate mineral as the altitude (actually pH) increases. Further, the equivalent ratio of Na^+/Cl^- was close to one, indicating that the ions come from mineral source such as halite or ground water/spring sources, rather than sodium and potassium aluminosilicate weathering or anthropogenic emissions. Previous study showed that there exists a large number of springs in this area, most of which have Na–Cl– HCO_3 type chemistry (Zhou 2012), suggests a possible source of Na^+ and Cl^- . Furthermore, most SO_4^{2-} -type springs have a deep source, so they cannot be responsible for significant recharge to the river water (Han and Liu 2004). Investigations of hot springs in the central TP (Zhao 2000; Zhou 2012) showed that there are fairly high concentrations of F^- in the ground waters. Furthermore, there is also a good correlation between F^- , Cl^- and Na^+ [$r^2(\text{F}/\text{Cl}) > 0.73$, $r^2(\text{F}/\text{Na}) > 0.76$]. So the high concentration of F^- could mainly come from ground water rather than precipitation or chloride bearing minerals weathering or anthropogenic emissions. Moreover, equivalent mole ratios of K^+/Tz^+ were almost as low as 0 (Fig. 3b) indicates that the weathering of sylvinit is very low in the upstream areas of the Yangtze River.

In summary, mechanisms controlling riverine water chemistry include atmospheric precipitation, rock weathering, evaporation–crystallization processes (Gibbs 1970),

and anthropogenic activities. The factors affecting the chemical composition of the waters are different along the upstream of the Yangtze River. The ratios of Na^+/Cl^- ($\text{Na}^+ + \text{Ca}^{2+}$) (avg. 0.60) and TDS (avg. 578.1 mg/l) increases from S01 to S31 in Gibbs plots (Fig. 4) and the position of Ca^{2+} , Mg^{2+} and HCO_3^- are in the middle position of the cation ternary plots in S01–S24, Jinsha Jiang and Tongtian He (Fig. 5), while Na^+ is at the apex of Cl^- based on the samples from S25–S31 (source tributaries, Chumaer He, Tuotuo He, Dang Qu and Bu Qu). All of the plots indicate that the water chemistry of headwater of Yangtze River is likely to be dominated by the chemical weathering of magnesium and calcium minerals from S01 to S24, and the major ion chemistry in S25–S31 is mainly influenced by evaporation–recrystallization and the ground water (fairly high concentration of Na^+ and Cl^-).

Comparison with other rivers in the Tibetan Plateau and the world

Surface water chemistry and dissolved materials in surface water are strongly influenced by the lithological composition of the bed rock, hydro-climatic conditions, plant coverage and human activities (Probst et al. 1994; Stallard and Edmond 1983) as well as the ground water within the drainage basin. Generally, forested land has low concentrations of ions. The specific geological and geographical conditions in the upstream areas of the Yangtze River have clear effects on the water chemistry. Examination of major ions and chemical elements demonstrated that the water chemistry of the upstream areas of the Yangtze River differs significantly from S01 to S31. The headwaters of the Yangtze River also have its own features compared with the midstream and downstream to Shanghai and other

Table 2 Ion concentrations in the Yangtze River compared to waters around the world

	Yangtze River (upstream) ^a	Yangtze River (midstream and downstream) ^{b, c}	Nujiang ^d	Longchuanjiang ^d	Yalung Tsangpo River ^d	Yangbajing Hot Spring ^e	Asia ^d	Europe ^d	Africa ^d	North America ^d	South America ^d
Na ⁺	146.6	14.5	3	12	3	403.5	6	5	11	9	4
K ⁺	5.24	2.7	1	1	1	58.8	4	2	–	1	2
Mg ²⁺	25.4	9	7	14	4	0.1	6	6	4	5	2
Ca ²⁺	53.1	39.8	24	49	21	4	18	31	13	21	7
F [–]	0.16	–	–	–	–	14.1	–	–	–	–	–
Cl [–]	267.5	–	5	14	5	562.1	9	7	12	8	5
NO ₃ [–]	1.63	1024	n.a.	n.a.	n.a.	n.a.	1	1	1	1	1
SO ₄ ^{2–}	120.6	17	31	69	27	38.8	8	24	14	20	5
HCO ₃ [–]	116.8	128.7	66	138	47	–	79	95	43	68	31
TDS	537.6	202.2	141	302	112	–	142	182	121	143	69
n.a. under LOD											
– no report											

n.a. under LOD

– no report

^a This study, ^b Müller et al. (2008); ^c Chen et al. (2002); ^d Huang et al. (2009); ^e Zhao et al. (2000)

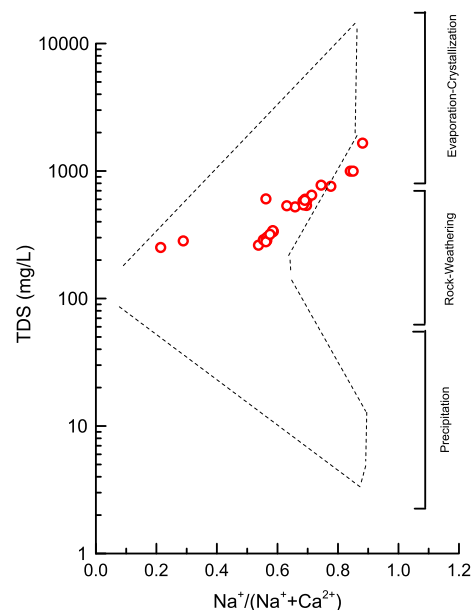


Fig. 4 The Gibbs graph of major ion compositions (TDS was the sum of major ions) in the Yangtze River (upstream), China (x axis represents the ratio of weight concentrations)

rivers in TP such as Nu Jiang, Longchuan Jiang and Yalung Tsangpo River (Table 2). For example, TDS, Na⁺, Cl[–], Mg²⁺ and SO₄^{2–} concentrations were much higher (1–2 orders of magnitudes). The anomalous enrichment of Na⁺ and Cl[–] might be explained by the effects of ground water and springs. High concentrations of Mg²⁺, Ca²⁺ and SO₄^{2–} could occur mainly because of intense evaporation, high weathering rates and the dissolution of evaporates in the source areas of the Yangtze River (Wu et al. 2008a, b). Concentrations of HCO₃[–] in Nu Jiang and Yalung Tsangpo rivers are very low compared with the headwaters of the Yangtze River. K⁺ concentrations were a bit higher in the upstream areas of the Yangtze River due to the weathering of volcanic rocks and granites along the basin. Ca²⁺ concentration in the headwaters of the Yangtze River was similar to all the rivers investigated. NO₃[–] was low in this area (often under LOD) and lower than that of mid-stream and downstream areas of the Yangtze River, which suggests there is almost no effect from human activities.

Anthropogenic activities (e.g., urban expansion) contributed to dissolved solutes, like SO₄^{2–}, the level of which was consistent with the combustion of sulfur-rich coal and acid deposition worldwide. However, when compared with other rivers around the world (Tables 2, 3), the water chemical constitution of upstream areas of the Yangtze River also showed a higher concentration of dissolved solutes, including SO₄^{2–}. The value is not only higher than the average for water of Europe, Africa, and North and South America, but also higher than the Asia average (Huang et al. 2009). All of the detected ions were found

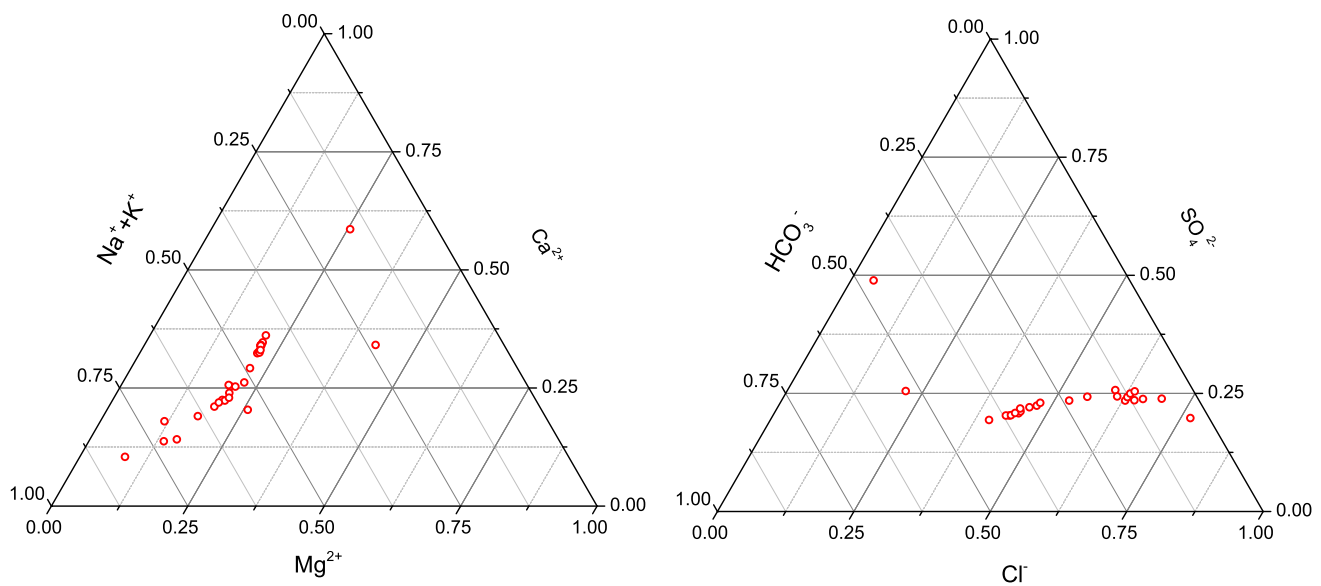


Fig. 5 Ternary plots showing cation compositions in the Yangtze River (upstream), China

in far greater concentrations (1–2 orders of magnitudes) than in the waters of world rivers. In view of the remote location of Tibetan Plateau, a possible explanation could be erosion and weathering conditions resulting from the high elevation and strong topographic relief (from 4700 to 1350 m in a distance over 2000 km) of the upstream Yangtze River. Lithology and hydro-climatic conditions also play a role in the unique water chemical composition. Low precipitation and high evaporation (Wu et al. 2005), as well as the ground water in the area are further factors responsible for the fairly high concentration, in addition to physical characteristics such as land use/land cover, population density, etc.

Elements in the headwaters of the Yangtze River

The concentrations of measured chemical elements are shown in Fig. 6. Most of the element concentrations were much higher than the world average level. The concentration of Rb is 654.6 $\mu\text{g/l}$, two orders of magnitude higher than the median value (2 $\mu\text{g/l}$) of the world stream water range (Ivanov 1996). Rb in the headwater of Yangtze River may not be a threat to the environment because it was reported that Rb is not only essential to human health (Meng et al. 1993; Paschalis et al. 1978), but also has an important use in medical technology (Jadvar and Parker 2005). The concentration of Hg is also high in upstream of Yangtze River (2.59 ng/l) when compared with the world average (0.07 ng/l) (Huheey et al. 1993; Porterfield 1993). But unlike Rb, which is beneficial to mankind, Hg is a nonessential heavy metallic element for human health and

is one of the most toxic elements, which is considered to be a global pollutant (Wheatley and Wyzga 1997). There is a significant difference between the distribution of Sr, B, Rb, Ba and that of Tl and Ti. The former group showed a good agreement between its components along the study area, while the concentrations of Tl and Ti fluctuated significantly around the average with no obvious trend. Further, Sr, B, Ba and Rb have a good positive correlation with major ions such as K^+ , Mg^{2+} , and SO_4^{2-} ($r > 0.7$), while Ti correlates only with Mg^{2+} , indicating that these elements may also have come from rock weathering. Hg showed a negative correlation with most of the ions and elements (especially with Ti, Ba, Mg^{2+} and SO_4^{2-}). Moreover, it was also found that the concentration of Hg has a negative correlation with pH. This is because higher acidity could enhance the mobility of mercury in the environment (Singh 2005). The concentrations of dissolved Al and Fe were under the LOD of the ICP-AES (Al_{LOD} is 65.9 ng/l, Fe_{LOD} is 70.8 ng/l, Appendix 1). As the pH of the water is fairly high (around 8.53), Al and Fe would deposit and exist in sediment rather than dissolved in water. The low concentration of Al and Fe is very different from other large rivers the world and rivers in China (Gibbs 1972; Müller et al. 2008; Wetzel 2001).

Conclusions

For the geography, hydrology and geology conditions on Tibetan Plateau, water quality in the upstream areas of Yangtze River is affected significantly by the continuing

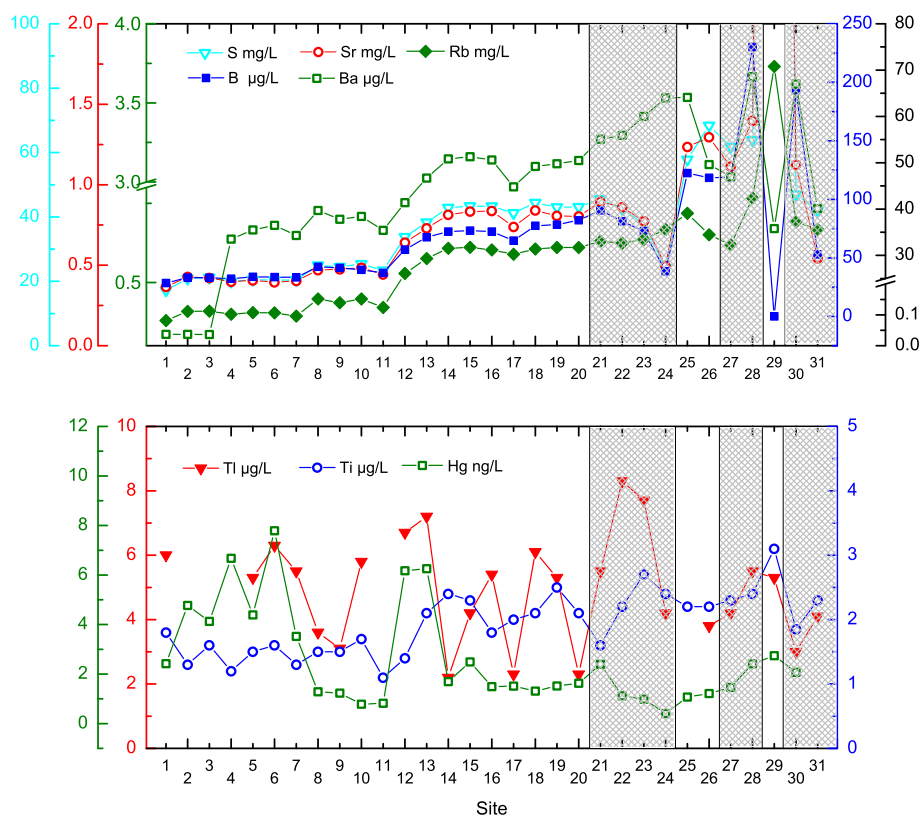
Table 3 Dissolved elements concentrations in the Yangtze River compared to river and lake waters around the world

	Yangtze River (upstream) ^a	Yangtze River (midstream and downstream) ^{b,c}	Nujiang ^d	Longchuanjiang ^d	Yarlung Tsangpo River ^d	World average ^e
Sr mg/l	1.06	221.9	–	–	–	0.06
Rb µg/l	654.6	–	–	–	–	1
Ti µg/l	1.94	–	1	0.55	0.6	3
Tl µg/l	4.16	0.05	–	–	–	–
B µg/l	69.51	71	–	–	–	10
Ba µg/l	46.58	73.3	–	–	–	25
Hg ng/l	2.59	0.09	<1	<1	<1	0.07

n.a. under LOD

– no report

^a This study, ^b Müller et al. (2008); ^c Chen et al. (2002); ^d Huang et al. (2009); ^e The world average composition of stream water are derived by a consensus and averaging process for data abstracted from references Huheey et al. (1993) and Porterfield (1993)

Fig. 6 Concentrations of elements (S, Sr, Rb, B, Ba, Hg, Tl and Ti)

tectonic instability and water chemistry processes. The results show that the headwaters of Yangtze River are turbid and have an alkaline environment and an anoxic water surface. TDS in situ observations showed that the parameter was positively correlated with calcium and magnesium concentrations, indicating that the effect of physical erosion and chemical weathering on local soil and rocks is an important factor in the water quality.

The water chemistry study showed that the headwaters of the Yangtze River is not only affected by mineral (magnesium and calcium sulfate) weathering, but also by ground water and evaporation–crystallization processes, especially around the source area of Mt. Geladaindong. Concentrations of heavy metals and other elements that may harm human health are much lower than WHO and GB guidelines, but both TDS and turbidity are too high for

humans to drink the waters directly. Although the harmful elements in the water are below recommended limits, attention should be paid to Hg. The concentration of Hg was much higher than the world average and the concentration increased as the river flowing down, which may become a threat to the local inhabitants. Further study of mercury in the Yangtze River is required.

Contaminants can be wind transported to the glacial region of TP and conserved in snow; glacier melting will release the deposited pollutants into the river. On the other hand, glaciers on the TP are important reservoirs of river waters; ice melting and continuing shrinkage of glaciers due to climate change will increase the runoff of rivers and consequently the sediment yields from mountain ranges which will affect

water chemistry. Therefore, it is reasonable to expect that the river water quality will be affected by climate change in the future.

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Appendix

See Tables 4, 5, 6, 7 and 8.

Table 4 ICP-AES: wavelength used for each element and corresponding limit of detection (LOD)

Three times the standard deviation of replicate blank measurements

Element	Wavelength (nm)	LOD (ng/L)	Element	Wavelength (nm)	LOD (ng/L)
Ag	3280	6.0	Mg	2852	21.3
Al	1670	65.9	Mn	2020	86.8
As	1890	6.2	Mo	2020	3.1
B	2497	10.4	Na	8183	400.2
Ba	4554	1.6	Ni	2216	3.4
Bi	2230	49.7	Pb	2203	9.3
Ca	4226	126.2	Rb	4244	7.2
Cd	2288	1.2	S	1807	59.2
Co	2286	2.1	Sb	2068	22.8
Cr	2835	1.9	Sr	3464	9.9
Cu	3247	6.7	Ti	3349	2.4
Fe	2395	70.8	Tl	1908	14.8
K	7664	12.8	V	3093	2.7
Li	6103	55.8	Zn	2138	5.0

Table 5 Concentrations of ions in the upstream of Yangtze River, China and the world (mg/L)

Site	Na ⁺ (mg/L)	K ⁺ (mg/L)	Mg ²⁺ (mg/L)	Ca ²⁺ (mg/L)	NH ₄ ⁺ (mg/L)	F ⁻ (mg/L)	Cl ⁻ (mg/L)	NO ₃ ⁻ (mg/L)	SO ₄ ²⁻ (mg/L)	HCO ₃ ⁻ (mg/L)
S01	53.53	2.58	14.27	40.61	n.a.*	0.12	79.65	n.a.	52.25	138.76
S02	65.19	2.80	16.82	44.58	n.a.	0.13	100.42	n.a.	63.68	144.84
S03	65.54	2.84	16.74	44.16	n.a.	0.14	103.23	1.26	64.95	136.42
S04	61.84	2.79	16.14	43.51	n.a.	0.14	94.77	1.30	61.02	141.02
S05	64.05	2.86	16.36	43.78	n.a.	0.15	98.65	1.25	62.53	140.34
S06	61.57	2.79	15.78	42.03	n.a.	0.16	97.84	1.29	62.54	126.70
S07	63.47	2.88	16.25	43.11	n.a.	0.13	98.88	1.27	63.21	135.02
S08	75.00	3.27	18.76	46.98	n.a.	0.14	121.22	1.66	77.75	133.50
S09	73.74	3.20	18.74	47.13	n.a.	0.14	117.39	1.56	76.10	139.18
S10	75.01	3.23	19.22	47.66	n.a.	0.18	123.24	1.69	80.54	130.66
S11	69.81	3.06	18.04	45.64	n.a.	0.13	108.63	1.47	72.04	140.79
S12	107.61	4.18	25.56	57.05	n.a.	0.15	182.06	1.77	109.65	141.44
S13	121.61	4.57	27.92	54.89	n.a.	0.17	206.06	1.86	121.85	127.73
S14	147.91	5.00	28.91	61.12	n.a.	0.16	269.25	1.98	140.03	90.42
S15	155.11	5.15	29.61	64.49	n.a.	0.18	279.73	2.02	141.46	103.64
S16	159.79	5.15	29.73	55.37	n.a.	0.16	288.02	2.04	140.47	75.91
S17	133.38	4.54	27.85	55.90	n.a.	0.14	234.27	1.96	135.73	95.49
S18	159.04	5.50	30.63	55.34	n.a.	0.16	275.68	2.09	143.66	96.05
S19	152.60	5.46	30.29	58.55	n.a.	0.17	272.82	2.30	146.23	88.37
S20	150.86	5.46	30.18	54.98	n.a.	0.18	269.71	2.08	145.71	78.51
S21	178.22	6.12	30.73	55.88	n.a.	0.17	326.04	1.82	151.86	53.35
S22	160.89	5.69	28.91	53.70	n.a.	0.18	279.59	2.09	137.91	88.03
S23	128.13	4.71	32.64	43.16	n.a.	0.15	227.96	2.50	122.99	93.79
S24	31.77	2.02	30.89	41.53	n.a.	0.10	46.61	2.75	73.86	194.12
S25	229.79	8.03	33.24	61.05	n.a.	0.21	422.88	2.12	196.76	—
S26	360.70	9.01	43.35	64.34	n.a.	0.24	734.55	1.20	216.39	—
S27	399.58	9.40	39.87	66.83	n.a.	0.23	823.09	0.31	241.94	—
S28	620.77	16.87	33.29	70.53	n.a.	0.26	1294.31	1.24	223.80	—
S29	>max**	>max	>max	>max	n.a.	>max	>max	0.19	>max	—
S30	251.82	15.57	22.66	58.14	n.a.	0.25	438.82	1.55	153.03	33.92
S31	20.36	2.37	18.14	69.69	n.a.	0.14	8.73	0.77	139.03	169.53
Avg. A	66.25	2.94	17.01	44.47		0.14	103.99	1.42	66.96	137.02
Avg. B	137.46	4.89	29.53	54.76		0.16	242.91	2.10	131.65	102.07
Avg. C	313.84	49.83	31.76	65.10		0.22	620.40	1.05	195.16	101.72
Avg.	146.62	5.24	25.38	53.06		0.16	267.47	1.63	120.63	116.83
Avg. (mmol/L)	6.51	0.38	1.02	1.28		0.0087	7.72	0.025	1.26	1.84

—means no data

*n.a. means the concentration is under the LOD of the equipement. >max ** means above detection limit

Table 6 Concentrations of trace elements in the upstream of Yangtze River

Site	Sr (mg/L)	Rb (mg/L)	Ti (ng/L)	Tl (ng/L)	B (ng/L)	Ba (ng/L)	Hg (ng/L)	As (ng/L)	Pb (ng/L)
S01	0.37	0.38	1.8	6.0	28.6	37	2.42	n.a.	n.a.
S02	0.43	0.41	1.3	n.a.*	33.2	37	4.77	n.a.	n.a.
S03	0.42	0.41	1.6	n.a.	33.1	36.5	4.13	n.a.	n.a.
S04	0.40	0.40	1.2	n.a.	32.2	33.5	6.67	n.a.	n.a.
S05	0.41	0.40	1.5	5.3	33.8	35.5	4.39	n.a.	n.a.
S06	0.39	0.40	1.6	6.3	33.6	36.5	7.79	n.a.	n.a.
S07	0.40	0.39	1.3	5.5	33.45	34.3	3.52	n.a.	n.a.
S08	0.47	0.45	1.5	3.6	42.4	39.7	1.29	n.a.	n.a.
S09	0.48	0.44	1.5	3.1	41.5	37.8	1.23	n.a.	n.a.
S10	0.48	0.45	1.7	5.8	39.9	38.4	0.78	n.a.	n.a.
S11	0.44	0.42	1.1	0	37.2	35.4	0.82	n.a.	n.a.
S12	0.64	0.53	1.4	6.7	57.1	41.4	6.18	n.a.	n.a.
S13	0.73	0.58	2.1	7.2	67.7	46.7	6.25	n.a.	n.a.
S14	0.81	0.61	2.4	2.2	72.5	50.85	1.70	n.a.	10.3
S15	0.83	0.61	2.3	4.2	73.3	51.3	2.49	n.a.	n.a.
S16	0.84	0.60	1.8	5.4	72.5	50.6	1.49	n.a.	n.a.
S17	0.74	0.59	2	2.3	64.8	44.8	1.52	n.a.	n.a.
S18	0.84	0.61	2.1	6.1	77.5	49.2	1.31	n.a.	n.a.
S19	0.81	0.61	2.5	5.3	78.4	49.8	1.52	n.a.	n.a.
S20	0.80	0.61	2.1	2.3	82.2	50.5	1.63	n.a.	n.a.
S21	0.89	0.63	1.6	5.5	90.6	55.1	2.40	n.a.	n.a.
S22	0.86	0.62	2.2	8.3	81.3	55.9	1.12	n.a.	n.a.
S23	0.77	0.64	2.7	7.7	72.8	60	0.99	n.a.	n.a.
S24	0.49	0.67	2.4	4.2	38.5	64	0.41	n.a.	n.a.
S25	1.24	0.72	2.2	0	122.5	64.1	1.08	n.a.	n.a.
S26	1.11	0.62	2.3	4.2	119	47	1.46	n.a.	n.a.
S27	1.30	0.65	2.2	3.8	118.4	49.6	1.22	n.a.	n.a.
S28	1.40	0.77	2.4	5.5	230.2	68.6	2.41	32.8	n.a.
S29	11.29	3.73	3.1	5.3	0	35.8	2.74	14.2	n.a.
S30	1.12	0.69	1.85	3	193.45	67	2.07	38.7	12.25
S31	0.54	0.67	2.3	4.1	53	40.1	—*	n.a.	n.a.
Avg. A	0.43	0.41	1.46	3.24	35.36	36.51	3.44		
Avg. B	0.77	0.61	2.12	5.18	71.48	51.55	2.23		
Avg. C	2.57	1.12	2.34	3.7	119.51	53.17	1.83		
Avg.	1.06	0.65	1.94	4.16	69.51	46.58	2.59		

— means not detect

* n.a. means the concentration is under the LOD of the equipement

Table 7 Pearson Correlation (r) of chemical compositions (ions and elements) in the upstream of Yangtze River China

Sr	Ti	Ti	B	Ba	Rb	Hg	F ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	HCO ₃ ⁻	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	TDS	EC
1																	
Sr																	
Ti	1																
Ti	0.026	1															
B	0.908**	0.476**	1														
Ba	-0.072	0.532**	-0.131	1													
Rb	0.995**	0.579**	0.02	0.768**	1												
Hg	-0.042	-0.403*	0.356	-0.268	-0.075	1											
F ⁻	0.869**	0.395*	-0.076	0.889**	0.604**	-0.176	1										
Cl ⁻	0.872**	0.433*	-0.073	0.882**	0.566**	-0.234	0.859**	1									
NO ₃ ⁻	-0.473**	0.06	0.122	-0.098	-0.425*	-0.293	-0.29	-0.268	1								
SO ₄ ²⁻	0.962**	0.648**	-0.175	0.817**	0.846**	-0.383*	0.823**	0.837**	-0.124	1							
HCO ₃ ⁻	-0.845**	-0.259	0.092	-0.803**	-0.487*	0.263	-0.770**	-0.942**	-0.278	-0.727**	1						
Na ⁺	0.891**	0.438*	-0.073	0.902**	0.639**	-0.241	0.875**	0.998**	-0.249	0.848**	-0.939**	1					
K ⁺	0.995**	0.471**	0.033	0.987**	0.987**	-0.001	0.900**	0.880**	-0.485**	0.763**	-0.796**	0.900**	1				
Mg ²⁺	0.835**	0.721**	-0.055	0.606**	0.802**	-0.454*	0.602**	0.683**	0.238	0.866**	-0.520**	0.689**	0.540**	1			
Ca ²⁺	0.796**	0.556**	-0.28	0.702**	0.770**	-0.262	0.700**	0.677**	-0.227	0.882**	-0.421*	0.688**	0.638**	0.647**	1		
TDS	0.891**	0.458*	-0.028	0.899**	0.672**	-0.234	0.840**	0.973**	-0.144	0.841**	-0.852**	0.977**	0.885**	0.701**	0.699**	1	
EC	0.819**	0.398*	-0.136	0.878**	0.646**	-0.246	0.810**	0.897**	-0.095	0.768**	-0.773**	0.905**	0.859**	0.603**	0.702**	0.894**	1

* Correlation is significant at the 0.05 level (2-tailed)

** Correlation is significant at the 0.01 level (2-tailed)

Table 8 National and international quality standards for drinking water surface water quality (in mg/L)

	WHO ^a	Remark	GB5749 ^b	Remark	GB3838 ^c		Remark
					Grade I	Grade II	
pH	No	Optimum: 6.5–8.5	6.5–8.5		6–9	6–9	
TDS	No		1000		–	–	
Turbidity	5						
EC							
Total alkalinity							
SO ₄ ^{2–}	No		250		–	250	
Ag	No		0.05		–	–	
Al	0.2	Practicable level	0.2		–	–	
As	0.01 (P)		0.01		0.05	0.05	
B	0.5 (T)						
Ba	0.7						
Bi							
Ca					–	–	
Cd	0.003		0.005		0.001	0.005	
Cl	0.05 (P)	For total chromium					
Co	–		–		–	1	
Cr	0.05 (P)	For total chromium	0.05	For Cr(+6)	0.01	0.05	For Cr(+6)
Cu	2		1		0.01	1	
Fe	No		0.3		–	0.3	
Hg	0.001	For total mercury	0.001		0.00005	0.00005	
K							
Li							
Mg							
Mn	0.4 (C)		0.1		–	0.1	Mn
Mo	0.07		0.07		–	0.07	
Na	No		200		–	–	
Ni	0.02 (P)		0.02		–	0.02	
Pb	0.01		0.01		0.01	0.01	
Rb							
S	No						
Sb							
Sr							
Ti	–		–		–	0.1	
Tl							
V							
Zn	No		1		0.05	1	Zn

No no health based guideline value is provided, *P* provisional guideline value as there is evidence of a hazard but the available information on health effects is limited, *T* provisional guideline value because calculated guideline value is below the level that can be achieved through practical treatment methods source protection etc., *C* concentrations of the substance at or below the health-based guideline value may affect the appearance taste or odor of the water resulting in consumer complaints

^a (WHO 2011); ^b (MOH and SAC 2006); ^c (SEPA and AQSIQ 2002)

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