Occurrence and removal of dissolved metals in surface drinking water sources from Yangtze River Delta Region, East China

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ABSTRACT

Multiple factors such as temperature, human activity, climate and hydrochemistry conditions affect water quality of drinking water sources. This research mainly focused on monitoring the dissolved trace metal concentrations from water samples in several important drinking water sources including the Huangpu River, Qingcaosha Reservoir and several reservoirs for West Tai Lake from spring to summer in 2013. The changes of trace metal concentrations and removal efficiencies in four typical water treatment plants (WTPs) in China corresponding to these water sources were also investigated. Results indicated that Qingcaosha Reservoir, Hengshan Reservoir and Youche Reservoir were less influenced by anthropogenic activities, therefore the change of dissolved metal concentrations was not significant except for local geochemical elements such as Sr and Ba. The other two water sources that flow through large industrial areas were greatly affected with elevated trace metal concentrations such as Fe, Mn, Zn, Ni, P, which can be attributed to anthropogenic and socio-economic impacts. High Fe and Mn concentrations were observed at low pH while high electric conductivity gained relevance with high geochemical metal concentrations. The occurrence of high dissolved Ni, Cu, Co and Zn was associated with high ammonia concentration and low pH, which might result from the formation of metal ammine complexes. In addition to the raw water information, dissolved metal concentrations after the treatment by individual WTP processes indicated that biological activated carbon and sand filtration achieved significant removal of Mn and Fe, while coagulation/flocculation efficiently reduced the concentrations of As, Pb and Zn. However, oxidation processes might form highly toxic Cr(VI) and increase the dissolved Cr concentrations which posed a potential threat to human safety. These preliminary results showed the necessity of control technology for dissolved trace metals in micro-polluted water sources for providing safe water.

Keywords: Dissolved trace metals; Surface drinking water sources; Water treatment plant; Yangtze River Delta

1. Introduction

Heavy metals pollution is one of the significant surface water pollution issues worldwide because of the high acute and chronic toxicity, concealment, persistence and biological accumulation [1]. Particularly in developing countries, heavy metals have already caused adverse effects on the safety of drinking water [2–4]. Heavy metals may originate from different sources such as minerals, sediments, scour, bedrock, industrial, agricultural and municipal effluents [5,6]. The factors affecting the concentrations, distribution and speciation

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of heavy metals include temperature, pH conditions, organic matter, electrochemical conditions, ammonia and many other aqueous chemical and biological parameters [7,8].

The speciation of heavy metals in water changes through three processes: (i) removal from dissolved phase through precipitation–dissolution processes [9]; (ii) combination with organic matter and other ligands through complex-dissociation processes [10]; (iii) sorption on solid phase through adsorption–desorption processes [11]. The pH level may be one of the most important water quality parameters that has significant effect on all three processes, and exerts observable effects on dissolved metal fractions [12,13]. However, it is difficult to predict the concentration change of heavy metals in surface water only by pH values as the water environment becomes more and more complex. It is well documented that the low pH conditions may result in the higher metal concentrations and the higher toxicity [4].

For many heavy metals, such as Cr and As, occurrence in dissolved phase seems to show higher toxicity [14,15]. Previous research has already proved that copper in ionic form is more toxic for microalga in freshwater [16]. Due to the poor removal in conventional drinking water treatment plants (WTPs), dissolved heavy metals bring potential risks to human health. In surface water sources, trace heavy metals in dissolved fraction are consisted in vast majority of complexes, which may also flocculate with colloids or adsorb onto minerals, algae and sediment. The ligands for metal complexes may be either naturally sourced (e.g., humic acid) or anthropogenically sourced (e.g., ethylene diamine tetraacetic acid [EDTA]) [17,18]. Metal complexes also exhibit

a certain toxicity, and seem to accumulate and be transported by microorganisms more easily [19].

As the most industrial and developed region in China, rivers and lakes in the Yangtze River Delta region which flow through high population areas may be affected by human activities. Previous work has focused on the concentrations and distributions of different heavy metals in various surface water systems [20–22]. Although this research has presented an overview of metal concentrations in urban regions, the relationships between water quality parameters and dissolved metals are unavailable. For WTPs, monitoring of all dissolved metals is neither practicable nor economical. Therefore, this research collected samples from several typical drinking water sources in the Yangtze River Delta region and focused on the relationships between the hydrological conditions and the concentrations of several representative heavy metals which may be used as guidance for WTP operation.

2. Materials and methods

2.1. Study sites

Six important drinking water sources or backup drinking water sources in the Yangtze River Delta region were investigated (Fig. 1). Qingcaosha Reservoir is a protected drinking water source that feeds about 80% of Shanghai's population. It is located in Yangtze River estuary and covers an area of 66.26 km². The Huangpu River is the main river crossing Shanghai and is used for transportation, fishing,
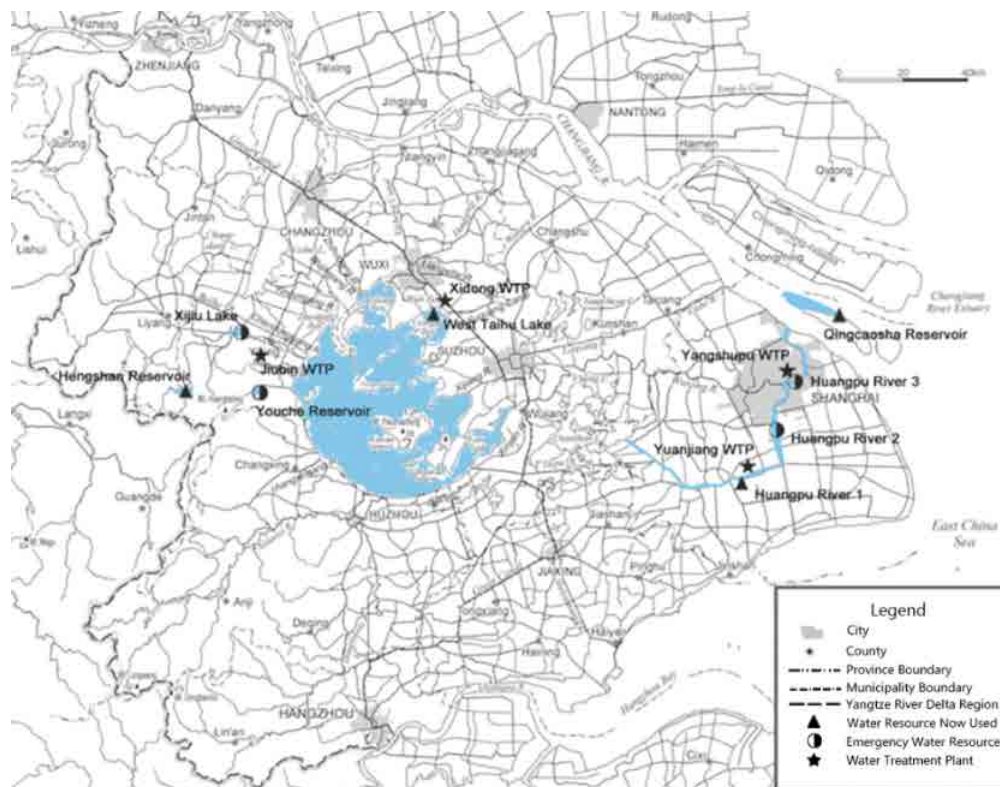

Fig. 1. Study sites.

tourism, wastewater effluent discharge and as a drinking water source. Since many industries such as manufacturing, food production, dyeing, etc. are located in the Huangpu River basin, the river is influenced by human activities. Hengshan and Youche Reservoirs are similar to Qingcaosha Reservoir and supply the majority of the population in Yixing City. West Taihu Lake is another important water source studied in this research and is a well-known polluted water source.

All the monitoring points studied are in drinking water sources that are either the primary or alternative source for an existing WTP. Four WTPs locates in Shanghai, Yixing and Wuxi were investigated. Fig. 2 shows the relationship between water sources and WTPs as well as treatment processes of each WTP. Due to the same or analogous treatment processes and operation conditions (e.g., the same ozone dose), the removal efficiency is comparable.

2.2. Sampling and treatment

In order to monitor and assess dissolved metal concentrations in WTPs, samples were collected near WTP intakes in the water sources weekly from April to August 2013. Samples were collected in plastic containers from 10 to 15 cm below the water surface [23]. 500 mL plastic containers were soaked with HNO_3 solution (10% v/v, analytical grade) and rinsed thoroughly with ultrapure water (18.2 MΩ cm) produced by Milli-Q Water Purification System (Millipore, Molsheim, France). Samples were also collected from WTPs after each step in the treatment process. Tap water samples were collected in the laboratory, which represented treated water from YP (Yangshupu WTP). During sampling at the WTPs, the samples were taken from flowing water and that three replicate samples were taken.

Water samples were collected in 1% HNO_3 solution and kept at 4°C before use. Dissolved trace metal concentrations were determined after samples were filtered by 0.45 μm nitrocellulose membrane filter then immediately acidified with HNO_3 solution to pH = 2 (2 mL HNO_3 per 1 L sample). The determinations of dissolved organic carbon (DOC) and ammonia were based on water samples collected separately. Glass containers were cleaned by ultrasound and rinsed with ultrapure water. The collected samples were immediately filtered by glass fiber membrane (Whatman, GF/F). All sample analyses for dissolved trace metals were done within 14 d of sample collection, while those for DOC and ammonia were kept less than 24 h [23].

2.3. Analytical method

Dissolved metals (Li, Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Sr, Cd, Ba, Pb) were analyzed by an inductively coupled plasma mass spectrometer (ICP-MS, Agilent 7700, USA). Method validation and quality control of samples were done using certified standard reference material (SRM, SPEX CertiPrep Inc, USA). Specimens were divided into different batches in chronological order and all batches included SRM standard material and a procedural blank. The recovery percentages were satisfactory within a range of 94%–109%. All determined values were obtained from the average value of three replicates, and the standard deviations of triplicate experiments were less than 5% as required. DOC was measured by a total organic carbon analyzer (TOC-VCPH, Shimadzu, Japan) using combustion method with a detection limit around 0.1 mg C/L (derived from replicate measurements of blank samples).

Ammonia was measured by colorimetric method (DR2800, HACH, USA). An infrared thermometer (ST20, Raytek, USA),
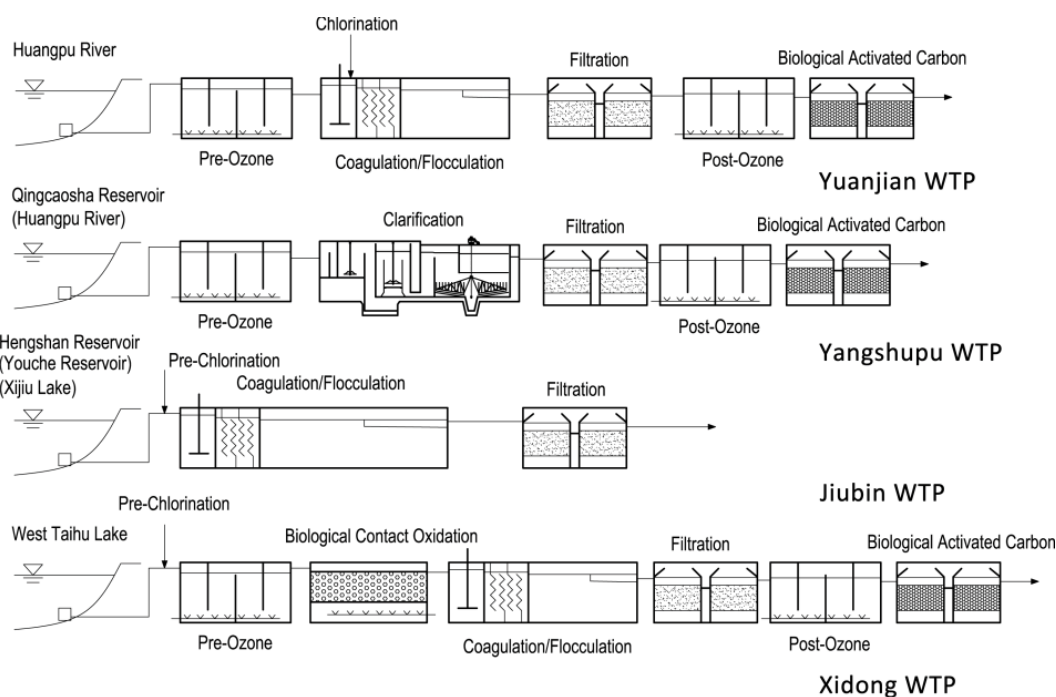

Fig. 2. Relationship between water sources and WTPs, treatment processes of every WTP.

pH meter (PHS-3G, Leici Corp., China) and conductivity meter (SevenEasy S30, Mettler Toledo, Switzerland) were used for in situ measurement of temperature, pH and electrical conductivity, respectively.

2.4. Statistical analyses

Regression and variance analysis were used to examine relationships between dissolved metals concentrations and water qualities as well as the relationships between different elements. The levels of significance were $p < 0.05$ for significant, $p < 0.01$ for highly significant, and $p < 0.001$ for very highly significant. All calculations were made according to SPSS 15.0.

3. Results and discussion

3.1. Water chemistry

The water temperature (Table 1) of all water sources monitored in the Yangtze River Delta region distributed in a relatively high range (23°C–33°C) in summer. Affected by ocean monsoon, water temperatures in Qingcaosha Reservoir and Huangpu River were a little higher than the other monitoring points. Temperature had a complex effect on complex formation (exothermic reaction), sorption (endothermic reaction) and precipitation reactions (exothermic reaction) with mineral and organic phases and/or other reactions related to

dissolved metal stability [8,24]. Nevertheless, high temperature might result in the enhancement of heavy metal toxicity to aquatic organisms [25].

The electrical conductivity tended to increase substantially from spring to summer. All maximum values of different water sources occurred in late July. The influence of electrical conductivity on river water was greater than lake and reservoir water, which was mainly because the major ions were derived from rock-weathering. The increase of bed load in summer was due to increased water supply demand and the effect of arid periods on Huangpu River. The electrical conductivity in Qingcaosha Reservoir was mainly affected by seawater backtracking, while the electrical conductivity in West Taihu Lake was mainly affected by biological activity. Relatively high pH and stable flow were conductive to natural precipitation, which was beneficial to the lower electrical conductivity of West Taihu Lake compared with Xijiu Lake located upstream. Low electrical conductivity was often observed in spring and on rainy days potentially due to the dilution.

DOC varied from water source to water source and rarely common interval covered samples except for Huangpu River and West Taihu Lake that were affected by industrial and anthropogenic activities. DOC concentrations in Qingcaosha Reservoir were stable (1.71 ± 0.12 mg L^{-1}) and lower than in its source, Yangtze River [26]. Analogously, DOC in the upstream of Xijiu Lake was higher than West Taihu Lake. High DOC values were observed in rainy days at almost all

Table 1
Average hydrochemical conditions during sampling times

Drinking water source	Water Temp. (°C)		Conductivity (μS cm^{-1})		DOC (mg C L^{-1})		NH$_3$–N (mg L^{-1})		pH	
	N	Mean ± SD[b] range	n	Mean ± SD range	n	Mean ± SD range	n	Mean ± SD range	n	Mean ± SD range
Huangpu River										
HP1[a]	18	24.2 ± 5.7 15.8–33.2	15	672 ± 28 623–713	15	5.38 ± 0.43 4.75–6.22	13	0.61 ± 0.50 0.01–1.83	18	7.53 ± 0.10 7.29–7.68
HP2	16	25.2 ± 4.7 17.6–33.0	15	701 ± 32 641–758	15	5.42 ± 0.47 4.59–6.23	–	– –	16	7.48 ± 0.18 7.04–7.72
HP3	16	24.2 ± 5.0 15.5–33.0	15	661 ± 44 568–727	15	4.95 ± 0.49 4.02–5.60	14	1.43 ± 0.49 0.48–2.09	16	7.50 ± 0.09 7.38–7.65
Qingcaosha Reservoir										
QCS	16	24.0 ± 6.2 12.5–34.5	16	327 ± 34 291–391	16	1.71 ± 0.12 1.54–1.97	16	0.16 ± 0.08 0.03–0.37	16	8.08 ± 0.25 7.77–8.69
Hengshan Reservoir										
HS	9	22.5 ± 8.6 10.3–30.8	9	226 ± 42 152–254	9	2.45 ± 0.36 2.07–2.92	8	0.12 ± 0.04 0.06–0.17	9	7.88 ± 0.40 7.28–8.53
YC	9	22.5 ± 8.5 10.5–30.7	8	207 ± 34 146–227	8	2.01 ± 0.21 1.68–2.24	8	0.13 ± 0.04 0.08–0.19	9	7.88 ± 0.46 7.14–8.53
West Taihu Lake										
XJ	13	23.0 ± 6.1 10.2–30.8	11	774 ± 215 573–1 295	11	5.57 ± 1.04 4.34–7.48	11	0.52 ± 0.30 0.05–1.23	13	7.77 ± 0.37 7.23–8.76
WTH	6	26.7 ± 5.2 18.3–30.8	6	565 ± 103 418–659	7	4.09 ± 0.71 3.11–4.66	6	0.47 ± 0.24 0.18–0.75	6	7.92 ± 0.14 7.80–8.16

[a]HP1, QCS, etc. represent for monitoring points corresponded to Fig. 1.
[b]Mean indicates average value, SD indicates standard deviation, *n* indicates the number of samples collected.

sources as discharge/precipitation characteristics were the primary controls for DOC concentration by flushing soil in agricultural or mixed agricultural/urban areas [27]. Overall, there was a 5%–35% variation of DOC concentration between water sources.

Ammonia is mainly derived from human activities. Extremely low ammonia concentrations in Hengshan Reservoir, Youche Reservoir and Qingcaosha Reservoir showed that these water sources were more influenced by meteorology, microorganism activity, vegetation, etc. than anthropogenic factors. However, for the other two water sources, especially at the lower watershed, high ammonia concentrations caused by industrial and/or municipal wastewater effluent were detected. In most cases, ammonia concentrations in the Huangpu River were lower than Chinese local surface water classification grade III, which meets the use function of drinking water source [28]. West Taihu Lake possessed high algal organic matter characteristic of eutrophication, and ammonia beyond grade II but lower than Huangpu River [29]. Urban land use in the watershed and industrial effluent might be the main contributors to high ammonia concentrations in Huangpu River and West Taihu Lake.

The pH values revealed that all water resources, no matter river or lake, tended to be slightly alkaline (7.04–8.76). The pH values of Huangpu River were just above 7 and fell to a relatively narrow range. The pH values in the lakes and reservoirs were higher (around 8.0) than that in the rivers due to strong microbial photosynthesis [30]. Neal et al. reported that the increased photosynthetic activity in the early spring resulted in carbon dioxide depletion and a change to higher pH [30]. Accordingly, high pH values were found in all water sources in April.

3.2. Dissolved metal concentrations in waters

Dissolved metal concentrations varied on account of different water sources, time, pH, ammonia, organic matter and other factors. Table 2 shows summary statistics of dissolved metal concentrations in drinking water sources. The concentrations of all dissolved metal in Huangpu River showed progressive increases (HP1 < HP2 < HP3) along the flow, which was similar to ammonia variation from anthropogenic inputs. The concentrations of dissolved Al, Mn and Fe in Huangpu River were generally much higher than other sources partly due to the lower pH and effluent influence. The concentrations of Cr, Cu, Cd, Pb were a little lower than the values reported in previous work [32]. Metal concentrations in other rivers that flowed through urban or industrial areas, such as some parts of Thames River in UK and the St. Lawrence in France, have similar findings to this research [33,34]. As a drinking water source in Shanghai, most metal concentrations, especially high toxicity metals such as Cr, As, Ni, Cd, Pb were under World Health Organization (WHO) guidelines and Chinese local standards for drinking water sources. However, metals (Al, Mn, Pb) at the HP3 sampling point, in backup water source for Yangshupu WTP, may sometimes surpass WHO guidelines. Fe concentrations were far beyond the requirement for drinking water sources in GB3838-2002, which might cause taste, odor, color and bacteria problems [35].

Metal concentrations in West Taihu Lake were close to those in Huangpu River. The concentrations of Cr, Ni, Cu, Zn, As, Cd and Pb (Table 2) were around the range reported previously according to the position of the intake structure [23]. Dissolved Mn and Fe still became the major drinking water pollutants. Low levels of the majority of dissolved metal concentrations were detected in reservoirs as they were less affected by anthropogenic activities. Qingcaosha Reservoir showed slightly higher concentrations of Fe, Zn, Ni, Cu, Co, Cd and Pb than reported in the previous research on Yangtze River Estuary, where Qingcaosha Reservoir water came from [36]. It indicated that geologic factors in the reservoir might partly contribute to metals concentrations. All metal concentrations in the three reservoirs were below WHO guidelines and grade I according to GB3838-2002. Hence, the three conventional water sources were not impacted by heavy metals.

3.3. Relationships between water quality parameters and dissolved metals

As befitting different environmental conditions and diverse land uses in the basins of water sources, dissolved metal concentrations varied spatially and temporally. The following research aimed to examine variations in the dissolved metals using linear regression, power regression and binary nonlinear regression. Integrative action of precipitation–dissolution equilibrium, complex-dissociation equilibrium, adsorption–desorption equilibrium and aggregation–dissociation equilibrium contributed to the final concentrations of dissolved metals.

3.3.1. pH and dissolved metals

The pH value may be the most prominent aquatic chemistry parameter affecting metal speciation. Significant correlations between dissolved concentrations of Fe, Mn, Cu, Co, Ni, V and pH were determined (Fig. 3). Dissolved metal concentrations declined sharply within a narrow pH range (2 pH units) for Mn, Ni, and to a lesser extent for Fe, Cu, Co and V.

High pH would increase the adsorption and/or co-precipitation fraction of metals on different particles and colloids including minerals, metal oxides, algae, etc. [37–41]. Moreover, nearly neutral conditions commonly found in natural water sources, imperceptible reduction of pH would cause conspicuous change of metal speciation. On the contrary, for geochemical elements Ba and Sr, poor relationship between geochemical elements Ba and Sr with pH were found because metal cations were soluble in a wide range of pH values.

3.3.2. Conductivity and dissolved metals

Heavy metals including Sr, Ba, Cr and Cd may enter the water body through geological pathways such as dissolution of bedrock and sediments. It may also be the case for conductivity where there is little or no anthropogenic influence [33]. As shown in Fig. 4, a striking relationship was found between increased dissolved Sr, Ba, Cr and Cd concentrations and high conductivity in Qingcaosha Reservoir. As for Taihu Lake, the relationship was not prominent owing to the effect of human discharge. Cd in Qingcaosha Reservoir

Table 2
Dissolved metal concentrations of several main drinking water resources and comparison with different guidelines of surface water for drinking use, Yangtze River Delta, China

Drinking water source samples		HP1[a] (n[b] = 15)	HP2 (n = 15)	HP3 (n = 15)	QCS (n = 16)	HS (n = 9)	YC (n = 8)	XJ (n = 11)	WTH (n = 7)	WHO guideline[d]	Chinese standard (GB3838-2002)[e]				
											I	II	III	IV	V
Li (μg L⁻¹)	Mean ± SD[b]	7.73 ± 2.50	8.82 ± 2.94	8.20 ± 1.57	5.06 ± 1.73	1.27 ± 0.62	1.37 ± 1.18	5.96 ± 1.56	6.66 ± 0.79						
	Range	4.82–12.94	6.59–17.72	6.73–12.10	2.89–9.47	nd–2.94	nd–4.04	4.37–8.97	5.49–8.63						
Al (μg L⁻¹)	Mean ± SD	249 ± 116	530 ± 209	1,332 ± 670	47 ± 28	20 ± 4	37 ± 22	417 ± 254	565 ± 383	900					
	Range	93–451	268–1,046	357–2,791	11–101	17–29	16–71	179–943	280–1,114						
V (μg L⁻¹)	Mean ± SD	2.90 ± 0.73	4.22 ± 0.90	5.05 ± 1.62	2.01 ± 0.44	0.78 ± 0.32	nd[c]	4.14 ± 1.84	4.04 ± 0.82		50[f]				
	Range	1.99–4.41	2.96–6.03	2.73–8.57	1.45–2.92	nd–1.21	nd	2.34–7.92	2.18–5.14						
Cr (μg L⁻¹)	Mean ± SD	1.28 ± 0.39	1.70 ± 0.63	2.50 ± 1.13	0.52 ± 0.17	nd	nd	1.74 ± 0.80	1.57 ± 0.42	50	10	50	50	50	100
	Range	0.72–2.27	0.79–2.99	1.00–4.63	0.31–0.95	nd	nd	0.78–3.64	1.10–2.12						
Mn (μg L⁻¹)	Mean ± SD	144.5 ± 40.6	178.2 ± 51.1	234.4 ± 68.5	11.6 ± 4.0	95.5 ± 65.8	91.6 ± 91.3	147.1 ± 68.6	60.4 ± 22.4	400	100[f]				
	Range	51.2–210.2	84.0–293.0	159.4–431.1	1.7–17.4	17.0–185.8	8.8–209.3	85.3–281.0	44.5–93.7						
Fe (μg L⁻¹)	Mean ± SD	339 ± 141	772 ± 333	1,401 ± 860	38 ± 20	16 ± 2	37 ± 17	626 ± 369	645 ± 294		300[f]				
	Range	101–569	380–1,572	614–3,492	12–77	15–20	16–55	249–1,354	430–1,079						
Co (μg L⁻¹)	Mean ± SD	0.49 ± 0.13	0.85 ± 0.20	1.30 ± 0.66	nd	nd	nd	0.64 ± 0.35	0.70 ± 0.18		1,000[f]				
	Range	0.19–0.69	0.58–1.34	0.69–3.20	nd	nd	nd	0.24–1.33	0.42–1.08						
Ni (μg L⁻¹)	Mean ± SD	5.99 ± 1.45	6.79 ± 1.22	7.07 ± 1.48	0.72 ± 0.40	0.43 ± 0.09	0.46 ± 0.09	5.54 ± 2.54	3.88 ± 0.74	70	20[f]				
	Range	3.38–7.74	5.09–9.85	5.41–10.15	nd–1.65	0.32–0.54	0.38–0.61	3.01–10.55	3.13–4.58						
Cu (μg L⁻¹)	Mean ± SD	5.1 ± 1.2	5.7 ± 2.2	9.1 ± 4.7	2.1 ± 1.3	1.0 ± 0.3	1.0 ± 0.2	5.7 ± 3.3	4.2 ± 1.2	2,000	10	1,000	1,000	1,000	1,000
	Range	2.9–8.0	2.6–9.9	3.6–19.5	1.2–6.4	nd–1.3	nd–1.2	1.0–12.2	2.8–5.8						
Zn (μg L⁻¹)	Mean ± SD	13.0 ± 5.0	26.3 ± 22.0	29.7 ± 16.2	8.8 ± 6.7	9.1 ± 6.6	13.6 ± 11.0	28.4 ± 12.1	17.1 ± 1.9		50	1,000	1,000	2,000	2,000
	Range	7.2–26.2	6.3–87.0	7.0–62.0	nd–24.2	3.9–20.6	6.1–33.0	15.4–48.0	14.6–19.2						
As (μg L⁻¹)	Mean ± SD	2.78 ± 0.57	3.39 ± 0.58	4.76 ± 1.31	3.52 ± 0.74	0.90 ± 0.38	nd	3.38 ± 1.42	2.71 ± 0.87	10	50	50	50	100	100
	Range	2.16–3.94	2.62–4.46	2.98–7.11	1.97–4.80	nd–1.48	nd	2.09–7.60	1.57–3.62						
Sr (μg L⁻¹)	Mean ± SD	215.2 ± 35.8	231.5 ± 39.4	228.3 ± 35.3	192.0 ± 36.9	172.1 ± 24.6	138.8 ± 20.0	280.5 ± 60.1	196.4 ± 15.5						
	Range	142.7–270.1	154.8–300.3	163.8–297.0	135.7–280.8	159.6–216.1	118.2–172.2	204.8–370.3	180.9–214.6						
Cd (ng L⁻¹)	Mean ± SD	20 ± 8	37 ± 20	65 ± 33	14 ± 7	nd	nd	125 ± 88	90 ± 27	3,000	1,000	5,000	5,000	5,000	10,000
	Range	6–39	13–90	23–135	7–30	nd	nd	23–343	67–128						
Ba (μg L⁻¹)	Mean ± SD	51.6 ± 7.0	52.0 ± 8.2	58.0 ± 9.6	45.9 ± 6.6	40.6 ± 4.9	29.2 ± 2.2	91.0 ± 11.2	72.5 ± 10.3	700	700[f]				
	Range	36.8–61.8	42.2–73.8	44.4–78.4	33.9–63.0	34.2–46.9	26.6–31.3	76.8–108.5	57.4–79.9						
Pb (μg L⁻¹)	Mean ± SD	1.05 ± 0.36	2.34 ± 0.74	4.36 ± 2.41	0.49 ± 0.32	0.33 ± 0.12	0.62 ± 0.44	2.71 ± 1.35	2.66 ± 0.66	10	10	10	50	50	100
	Range	0.36–1.57	1.08–3.35	1.57–10.40	nd–1.40	nd–0.51	0.29–1.39	0.88–5.78	1.66–3.96						

[a]HP1, QCS, etc. represent for monitoring points corresponded to Fig. 1.
[b]Mean indicates average value, SD indicates standard deviation, n indicates the number of samples collected.
[c]nd refers to metal concentrations below detection limits.
[d]Guidelines for Drinking-water Quality, 4th edition WHO [31].
[e]Environmental quality standards for surface water [28], the standard divided water qualities into five grade, only grade I, II and III can be applied as drinking water source.
[f]Concentration guidelines in GB3838-2002 are listed in supplementary terms for drinking surface water source.
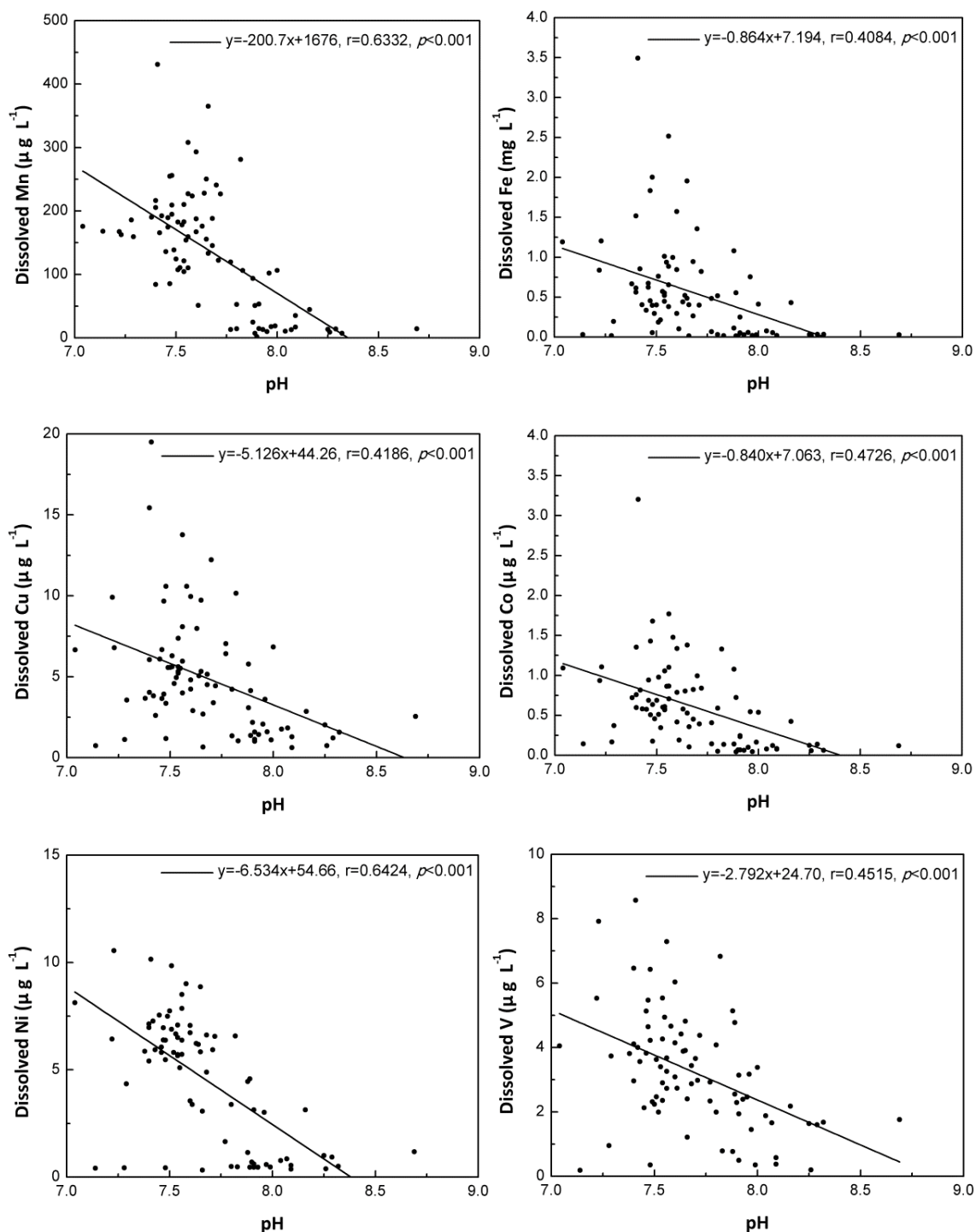
Fig. 3. Relationships between pH values and dissolved metal concentrations (Fe, Mn, Cu, Co, Ni, V).

had the same source as Sr, coming from rocks such as calcite that was dissolved under alkaline conditions [42]. Moreover, low pH promoted the system of $Sr/CO_3^{2-}/HCO_3^-$ transmitting Sr from solid phase to aqueous phase (Fig. 5). The relatively high Cr concentrations at high pH values indicated that Cr in Qingcaosha Reservoir mainly existed in the form of CrO_4^{2-} (Cr(VII)) because Cr(III) was inclined to be polymerized and precipitated at high pH [43]. Cr(VII) had been proven to be

more toxic and carcinogenic to humans and fortunately, Cr in Qingcaosha Reservoir was present at levels less than 1 μg L⁻¹.

3.3.3. Relationships between dissolved metals

Fig. 6 shows the linear correlation between dissolved metals including Pb, Cu, V and Fe, Mn and Co, Sr and Ba. Since the dissolved Fe and Mn concentrations had a wide
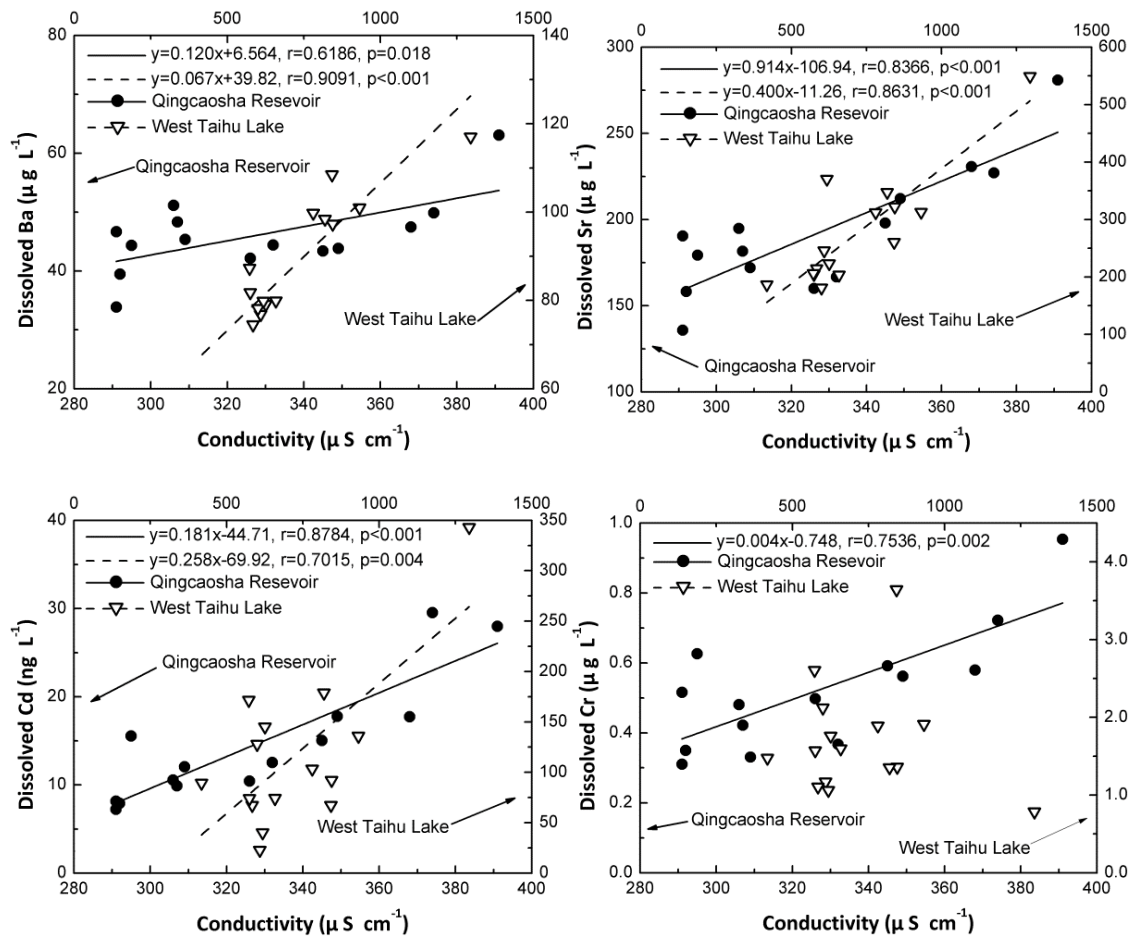
Fig. 4. Relationships between conductivity and dissolved metal concentrations with possible geological sources, for individual drinking water sources.
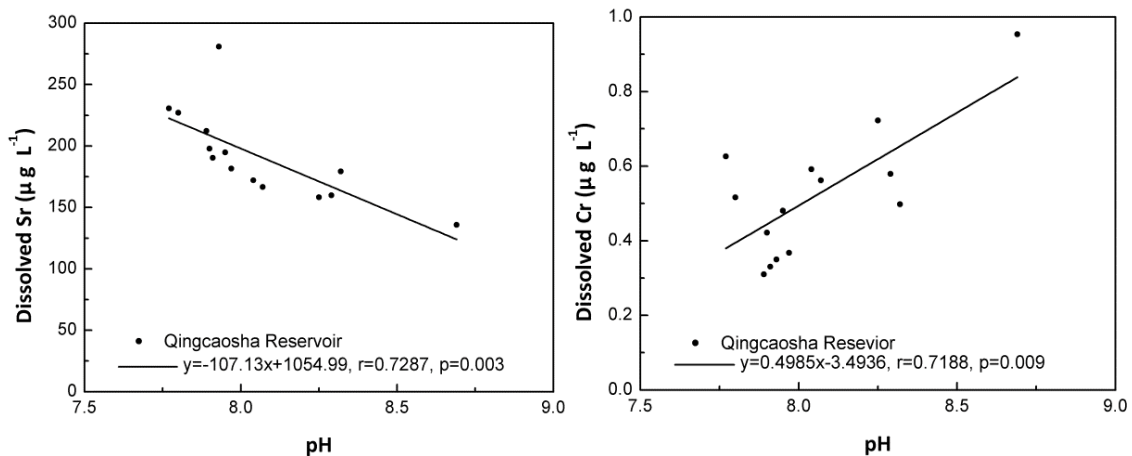

Fig. 5. pH values and dissolved Sr, Cr concentrations in Qingcaosha Reservoir.

range in Huangpu River and West Taihu Lake, the relationship was plotted by data collected from those two water sources. The results suggested that: (i) adsorption and co-precipitation with Fe, Mn oxides, minerals and/or hydroxides played an important role in controlling raw water dissolved metal concentrations [44]. Dissolved Fe concentrations could be an indicator for other dissolved metals which were rarely included in routine monitoring; (ii) elevated pH values might increase the sorbed fraction of metals on Fe and Mn particles and promote the formation of iron hydroxides that caused the decrease of dissolved concentrations of both Fe, Mn and other metals mentioned. (iii) Since the two reservoirs were
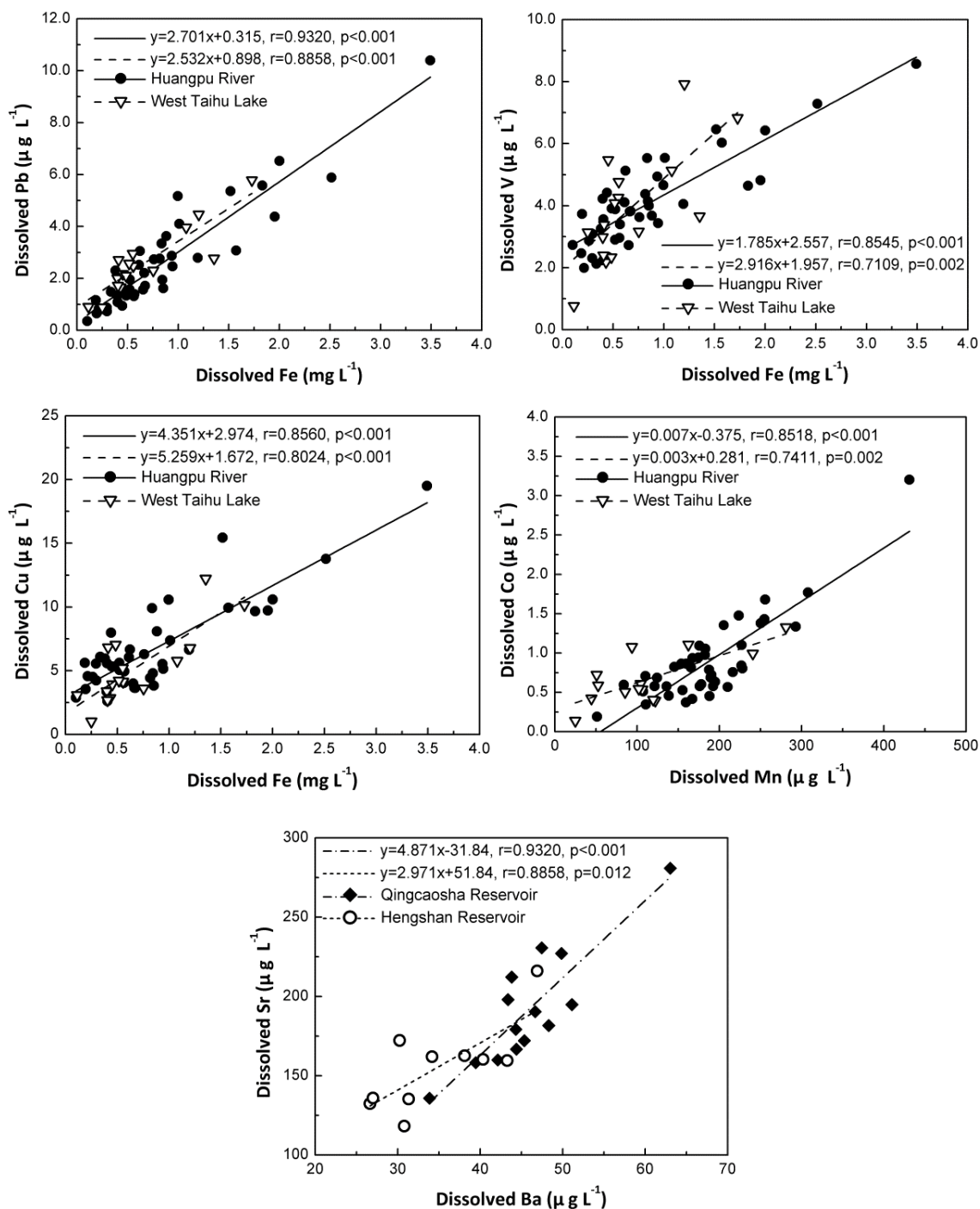
Fig. 6. Relationship between dissolved metals Pb, Cu, V and dissolved Fe, between dissolved Co and Cu, between dissolved geological elements Sr and Ba, for individual drinking sources (For Sr and Ba, strong relationship can only be found at sources less affected by human activities in this research).

less affected by human activities, Sr and Ba were from the geological pathways discussed in section 3.3.2.

3.3.4. Ammonia and dissolved metals

Ammonia concentrations were found to be higher in river water in China, and in this research, ammonia concentrations in Huangpu River were up to 2.09 mg L^{-1} [45]. Ammonia may form metal ammine complexes with several metals such as Ni, Cu, Co, Zn. In addition, the metal ammine complexes usually possessed high stability under aqueous conditions [46]. The transition-metal ammine complexes were usually in cationic forms (e.g., $Cu(NH_3)_4^{2+}$), which meant that carrying positive charges and elevated pH might cause the particles'
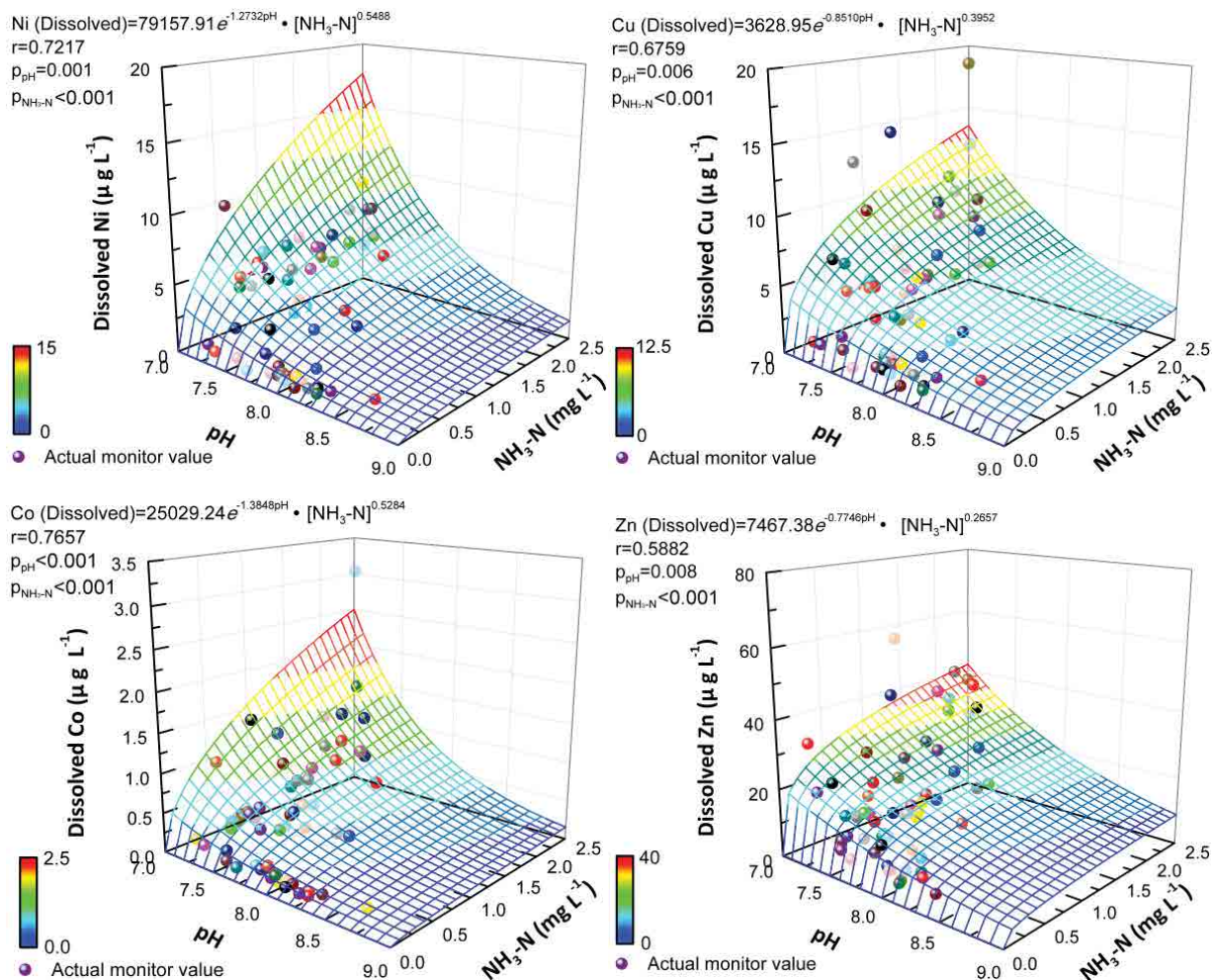
Fig. 7. Relationships between dissolved Ni, Cu, Co, Zn concentrations with pH values, ammonia concentrations and multivariate regression analysis.

surface charges to become more negative. Therefore, the dissolved metal concentrations were controlled by both ammonia concentrations and pH values. Thus, a multivariate regression model derived from complex-dissociation equilibrium and pH effect discussed in section 3.3.1 may be useful in estimating dissolved Ni, Cu, Co, Zn concentrations. The model can be expressed as:

$$\text{Dissolved Ni, Cu, Co, Zn concentrations (mg L}^{-1}) = C_e{}^{a\text{pH}}[\text{NH}_3]^b \quad (1)$$

where C is constant and a, b are index numbers. The model for individual metals is illustrated in Fig. 7. The relevance of the relationship between metal ammine complexes and the dissolved metal fraction was evident in that only the metals plotted in Fig. 7 showed significant relationship with pH and NH$_3$–N through multivariate regression analysis. In natural water sources, ammine complexes of Ni, Cu, Co, Zn may be another important form of these metals dissolved in water other than bound with organic matter [47]. Since ammonia and pH were included in routine water quality monitoring in almost all WTPs, the equation may be used in warning of metal contamination and rough estimation of dissolved

metal concentration ranges. On the other hand, at West Taihu Lake and the lower reaches of Huangpu River, high dissolved Ni, Cu, Co, Zn concentrations were accompanied by elevated ammonia concentrations. As several kinds of industrial wastewater (e.g., dyeing, metal plating, pharmaceutical) may contain high concentrations of metal–ammonia complexes, discharging into water bodies may result in the co-occurrence of higher ammonia and dissolved metal concentrations [48]. Moreover, the solubility of metals may be promoted after the point of discharge for wastewater with high ammonia concentrations.

3.4. Removal efficiency in drinking water treatment plants

Fig. 8 shows the removal efficiency (using box-and-whisker plots) of several dissolved metals in the individual drinking WTP studied in this research. The removal efficiencies of dissolved Mn, Fe, Cu, Zn, Pb by pre-chlorination was poor (below 20% on average). Hypochlorous acid, hypochlorite ion and/or chlorine formed during the chlorination process was a kind of feeble oxidant, which can oxidize Cr(III) to more toxic Cr(VI) [49]. In addition, this process would be
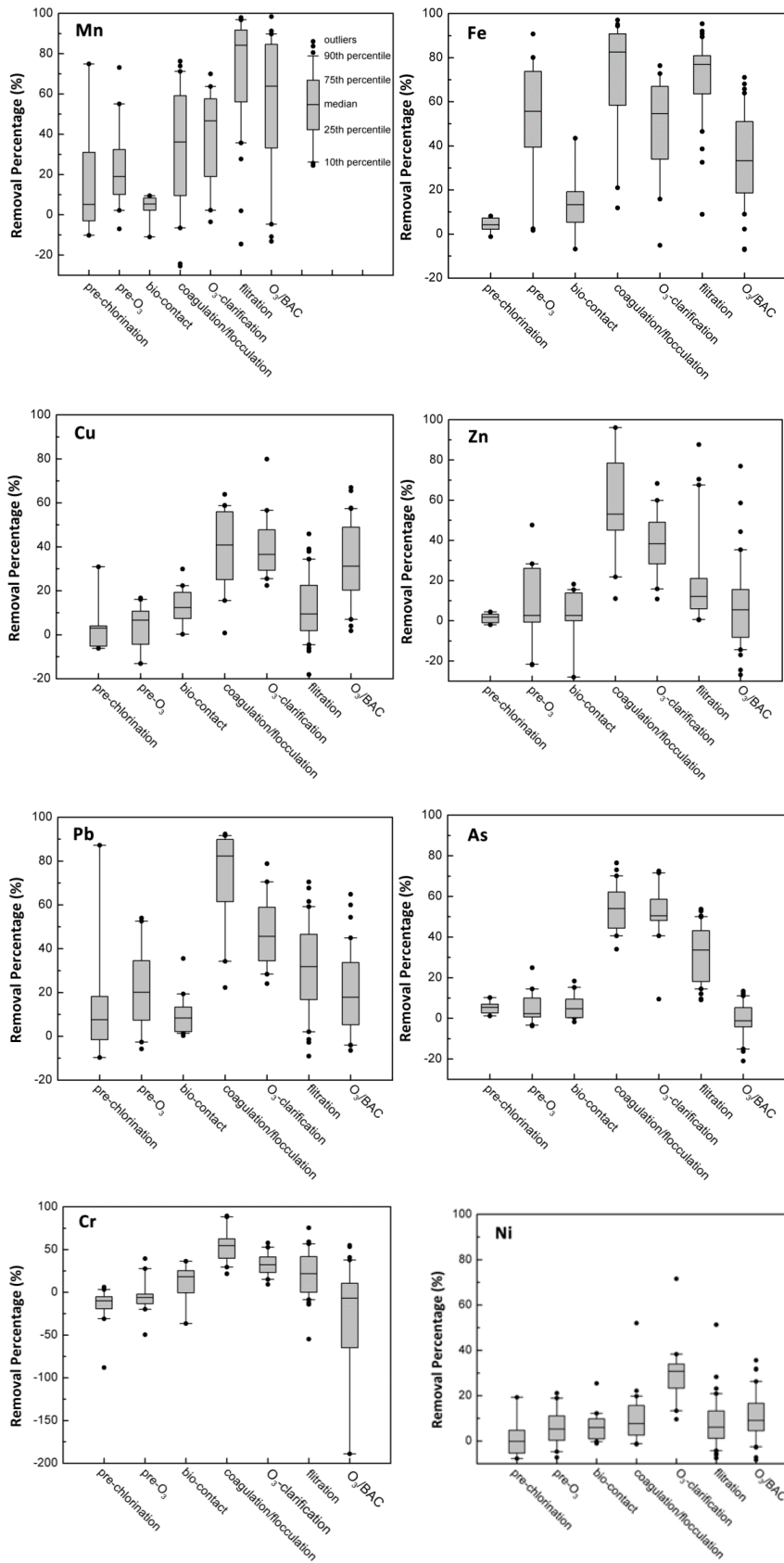
Fig. 8. Removal percentage of several metals studied in drinking water treatment plant (the removal percentage resulted from ratio between input concentrations and outlet concentrations of every individual process).

enhanced under relatively low pH conditions [49]. It may also result in the increased dissolved Cr concentrations after chlorination (about 25% on average). 41% removal of dissolved Fe was obtained during the pre-ozonation process, while the removal percentage was lower for other metals. Stemmler et al. [50] found that ozone was capable to oxidize metal ligands, which forced a portion of dissolved metals to partition to solid phase.

Though microorganisms had the ability to accumulate metals, a strong effect on dissolved metals concentration was not observed in the bio-contact process. Metal speciation variation was complicated in bio-contact processes, and the dissolved organic matter derived from microorganisms might be the ligands for potential metal-complexes. Due to relatively less contact time, uptake by microorganisms may be low. On the other hand, the weather conditions may affect the removal of dissolved metal.

High removal efficiency of dissolved metal occurred in coagulation/flocculation (clarification), filtration and ozonation/biological activated carbon (O_3/BAC) processes. Many researches have shown that hydroxides of Al and Fe formed in coagulation/flocculation process can adsorb and/or co-precipitate with metals [51]. Therefore, the metals dissolved in water can be absorbed by sludge. Adsorption was also the main process which can remove dissolved metals during filtration and BAC processes. Ferric hydroxide and oxides, manganese oxides and minerals that stayed in water after previous treatment processes may persistently gather at the surface of sand or activated carbon [52]. This would enhance the adsorption of dissolved metals during filtration and BAC processes.

Ozone exerts the same effect as chlorination for chromium [53]. However, the ratio between the input and outlet concentrations was highly variable. The chromium concentration in WTP effluent water was two times higher than intake water. Considering that most of the dissolved Cr in finished water was highly toxic Cr(VI), chromium was a potential threat to water safety. For another highly toxic metal As, high removal efficiency was only observed in coagulation/flocculation (clarification) process. Since dissolved Sr and Ba concentrations varied little through all drinking water treatment processes as expected, the results were not shown.

4. Conclusions

This research focused on the distribution, relationship with water quality parameters and removal efficiency of several dissolved metals in some important water sources in Yangtze River Delta region. In most cases, dissolved metal concentrations were well under guidelines proposed by WHO and local standards for raw water whether the watersheds were affected by anthropogenic activities or not. However, the dissolved metal concentrations greatly varied under different meteorological, hydrochemical and anthropogenic conditions. The prominent metals in protected reservoirs were geochemical elements such as Sr and Ba. Due to the same source from bedrock dissolution, these metals were correlated with conductivity. Among several geochemical factors, pH exerted the greatest influence on the concentration of dissolved transition metals such as Mn, Ni, Fe. Significant relationships between dissolved Ni, Cu, Co, Zn with ammonia and pH were proven

by multivariate regression analysis. The above results indicated that the speciation and distribution of dissolved metals can be significantly influenced by pH values, conductivity and ammonia concentrations. The results might also be helpful in simplifying monitoring of dissolved metals for drinking water treatment and controlling of metals through hydrochemical conditions in source water.

The obtained results obtained from drinking water treatment processes indicated that the full-scale treatment plants can achieve high removal efficiency for dissolved Mn, Fe, Pb, Zn, etc. However, there were still some problems in water treatment plants. The concentrations of several metals such as Ni and Cu were only reduced moderately. The highly toxic form of Cr generated in oxidation processes might be a potential threat to water safety. Subsequent research should focus on these problems in drinking water treatment plants.

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