How phytoplankton biomass controls metal(loid) bioaccumulation in size-fractionated plankton in anthropogenic-impacted subtropical lakes: A comprehensive study in the Yangtze River Delta, China

Siwen Zheng [a], Rui Wang [a,b,*], Martin J. Kainz [c,d], Chengying Liu [a], Pengwei Li [a], Zixuan Li [a], Haiyu Yan [e], Daqiang Yin [a,b]

[a] *Key Laboratory of Yangtze River Water Environment, Ministry of Education, College of Environmental Science and Engineering, Tongji University, Shanghai 200092, China*
[b] *Shanghai Institute of Pollution Control and Ecological Security, Shanghai 200092, China*
[c] *WasserCluster Lunz - Biologische Station, Inter-University Center for Aquatic Ecosystem Research, Lunz am See, Austria*
[d] *Department of Biomedical Research, Danube University Krems, Krems 3500, Austria*
[e] *State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550081, China*

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ABSTRACT

Phytoplankton biomass can significantly affect metal(loid) bioaccumulation in plankton, but the underlying mechanisms are still controversial. We investigated the bioaccumulation of eight metal(loid)s (As, Co, Cu, Hg, Mn, Pb, Se, and Zn) in three size categories of planktonic organisms – seston (0.7–64 μm), mesozooplankton (200–500 μm), and macrozooplankton (>500 μm) – sampled from six freshwater lakes in two seasons in the Yangtze River Delta, China. Our results highlight phytoplankton biomass is the major driver on metal(loid) bioaccumulation in the studied anthropogenic-impacted subtropical lakes, mainly via affecting site-specific water physiochemical characteristics and plankton communities. However, such impact is highly dependent on chlorophyll *a* (Chl-*a*) concentration. The bioaccumulation of metal(loid)s in size-fractionated plankton declined significantly with increasing phytoplankton biomass when Chl-*a* was below ~50 μg L^{-1}, mainly owing to the reduced metal(loid) bioavailability and subsequent bioaccumulation at more productive sites (with elevated pH and dissolved organic carbon), rather than algal bloom dilution. To a lesser extent, phytoplankton growth dilution and the smaller body-size of zooplankton at more productive sites also contributed to the lower metal(loid) bioaccumulation. The bioaccumulation of metal(loid)s was enhanced under severe algal bloom conditions (when Chl-*a* concentration was higher than ~50 μg L^{-1}). Although the underlying mechanisms still require further investigations, the potential risks of metal(loid) bioaccumulation under severe algal bloom conditions deserve special attention.

1. Introduction

Heavy metals and metalloids have been widely recognized as hazardous pollutants, including biologically essential (e.g., cobalt (Co), copper (Cu), manganese (Mn), selenium (Se), zinc (Zn)) and non-essential (e.g., arsenic (As), mercury (Hg), lead (Pb)) elements (Duffus, 2002; Noger-Huet et al., 2022). Metal(loid)s could pose threats to the environment and human health due to their bioaccumulation and toxicity in aquatic biota (Ali and Khan, 2018; Anandkumar et al., 2019). In aquatic ecosystems, metal(loid) bioconcentration (via dissolved uptake) in phytoplankton and bioaccumulation (via dissolved uptake and dietary ingestion) in zooplankton, as the primary entry point of metal(loid)s into pelagic food webs, could be further transferred to predators (Chen and Folt, 2000; Griboff et al., 2018; Kainz et al., 2006; Wang et al., 2011). It appears that metal(loid) burdens in pelagic fish could not be simply predicted by aqueous metal(loid) concentrations, but are highly dependent on metal(loid) contents in plankton (Chen et al., 2000; Fang et al., 2019; Wu et al., 2019).

Among aquatic ecosystems, there are often significant variations in metal(loid) bioaccumulation in plankton across lakes, which were

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highly associated with varying intrinsic water physicochemical characteristics and plankton communities. For example, the dissolved organic carbon (DOC) and pH of water could alter metal(loid) bioavailability and subsequent planktonic bioaccumulation, as supported by both field investigations (MacMillan et al., 2019; Ogorek et al., 2021) and bio-kinetic studies (Komjarova and Blust, 2009; Vigneault and Campbell, 2005; Yu and Wang, 2002a). Site-specific phytoplankton density (Chen and Folt, 2000) and zooplankton taxa (Long et al., 2018) could also contribute to the site-to-site variations in metal(loid) bioaccumulation. In addition, diet quality and food abundance have been recognized as crucial factors in altering dietary metal(loid) accumulation by modulating diet-specific assimilation and elimination processes in zooplankton (Tsui and Wang, 2007; Yu and Wang, 2002b), while high growth rate could reduce metal(loid) bioaccumulation via growth dilution (Karimi et al., 2007; Sunda and Huntsman, 1998). Therefore, it is challenging but critical to identify the driving factors in metal(loid) bioaccumulation in size-fractionated plankton across lakes for understanding the large regional variations in metal(loid) burdens in pelagic fish.

Metal(loid) contents (especially widely reported for Hg) in plankton and fish are commonly higher in cold and low productive lakes compared to those in eutrophic lakes (Chen et al., 2008; Lavoie et al., 2013; Skei et al., 2000; Wu et al., 2019). To explain such intriguing worldwide observation, previous studies examined the relationships between metal(loid) contents (i.e., As, Pb, Hg) in plankton and plankton density/biomass across lakes with different trophic status in North America (Chen and Folt, 2000; 2005), and ascribed the observed negative correlations to a phenomenon termed as "algal bloom dilution", assuming that the pool of a certain contaminant is finite and uptake by individual cells is constant. The important role of algal bloom dilution on regulating mass-specific Hg burdens in plankton was further verified under laboratory conditions with varying nutrient additions (Pickhardt et al., 2002). Nevertheless, such negative correlations between metal(loid) contents and plankton biomass were not observed in many subtropical and tropical regions, such as within Baihua Reservoir (for Hg, Long et al., 2018), across three lakes in Southwestern China (for Zn, Cu, Fe, Mn, Pb, Cr, Cd, and Ni, Long et al., 2016), and across eight African lakes with different trophic status (for Hg, Poste et al., 2015). Considering that algal bloom is always associated with alterations in water physiochemical characteristics and planktonic communities (Amorim and Moura, 2021; Sim et al., 2020), we hypothesize that the above inconsistent findings might be attribute to the impacts of algal biomass associated confounding factors (i.e., pH, DOC, and planktonic communities) on metal(loid) bioaccumulation process, which may counteract with the phenomenon of algal bloom dilution.

Here, we conducted a comprehensive field study to explore how phytoplankton biomass controls metal(loid) bioaccumulation in size-fractionated plankton in six anthropogenic-impacted subtropical lakes with varying trophic status, located in the Yangtze River Delta (YRD), China. The primary objectives of this study were: (1) to examine metal(loid)- and biota-specific bioaccumulation of metal(loid)s (As, Co, Cu, Hg, Mn, Pb, Se, and Zn) from lake water to three size categories of planktonic organisms, including seston (0.7–64 μm), mesozooplankton (200–500 μm), and macrozooplankton (> 500 μm); (2) to investigate the role of water physiochemical characteristics (including water temperature, pH, chlorophyll a (Chl-a), total phosphorous (TP), total nitrogen (TN), DOC) and planktonic communities (including phytoplankton and zooplankton densities, species compositions, and zooplankton body size) on metal(loid) bioaccumulation; (3) to explore how phytoplankton biomass controls metal(loid) bioaccumulation and whether algal bloom dilution plays the key role in regulating planktonic metal(loid) bioaccumulation in anthropogenic-impacted lakes in subtropical regions.

2. Materials and methods

2.1. Study sites

The YRD region covers 211,000 km^2 with over 153 million people. There are over 200 lakes widely distributed in the YRD, making this region known as "the land of fish and rice" over thousands of years. As one of the most socially and economically developed regions in China, the YRD is also recognized as one of the world-class mega city clusters, which endures strong impacts of urbanization. Anthropogenic inputs of nutrients have largely elevated the nutrient levels in the surrounding aquatic ecosystems, resulting in widespread eutrophication in lakes of the YRD.

The field study was conducted in six important freshwater lakes located in the YRD (Fig. 1, see more details in Table 1). Four natural shallow lakes were sampled, including Dianshan Lake (DS), Gehu Lake (GH), Hongze Lake (HZ), and Taihu Lake (TH), with average water depth < 2 m (Table 1). Among them, TH and HZ are the third and fourth largest freshwater lakes in China. Two reservoir-type lakes were also sampled, including Tianmu Lake (TM) and Qiandao Lake (QD), with average water depth of 19 and 37 m, respectively (Table 1). The lakes HZ, QD, and TH (each > 500 km^2, Table 1) were sampled from one offshore (A) and one nearshore (B) site (Fig. 1 and Table 1), while the other three lakes were sampled at one site close to the center. Each site was sampled twice in fall 2018 (October and November) and spring 2019 (April and May) respectively. All the studied lakes are important sources of drinking water and aquatic products for the surrounding cities, as well as popular recreational venues for local people. Nevertheless, most of the selected lakes are facing metal(loid) contamination problems (especially those shallow lakes, Li et al., 2011; Niu et al., 2020; Wu et al., 2017), owing to the massive industrial wastewater inputs from the surrounding highly industrialized cities.

2.2. Field sampling

Water and plankton samples were collected using nonmetallic sampling apparatus and following trace metal(loid) clean procedures (details provided in Text S1). Considering the vertical migration of zooplankton, water samples were collected from different layers at each sampling site using a plexiglass sampler (10 L) for water physiochemical characteristics and aqueous metal(loid) concentration analyses. For the shallow lakes (DS, HZ, GH, and TH), water samples were collected from two layers (0.5 m below the surface and 0.5 m above the bottom). For the deep lakes (QD and TM), water samples were collected from three layers, i.e., at 0.5 m below the surface, mean depths (9.5 m and 18.5 m, respectively), and at 0.5 m above the bottom. At each site, unfiltered water samples (n = 3 for each water layer) were used to measure TN and TP, while filtered water samples (n = 3 for each water layer) were collect by filtering through 0.45 μm Teflon syringe filters (JET BIOFILM, Canada) for DOC and dissolved metal(loid) analysis. For quality assurance, blank samples were collected at each site by filtering Milli-Q water following the same processes as filtering lake water. For Chl-a measurement of water sample from each layer, 200 mL (1200 mL for QD) of lake water was filtered through pre-combusted (450 °C, 4 h) Whatman GF/F filters (pore size 0.7 μm) in the field, with three replicates for each layer. Additionally, 1 L of surface water (0.5 m below the surface) at each sampling site was collected and preserved with 5% (v/v) Lugol's iodine in the dark for phytoplankton community analysis.

Zooplankton were collected by using a 55 μm plankton net (HYDRO-BIOS, Apparatebau GmbH, Germany) via horizontal tows from 0.5 m below the lake surface (for the shallow lakes), and vertical tows from 0.5 m above the bottom to the surface (for the deep lakes). The collected zooplankton samples were rinsed with filtered (0.7 μm) lake water to remove the adhered particles and then separated successively by using 500 μm and 200 μm mesh filter cups to obtain macro- (> 500 μm) and meso-zooplankton (200–500 μm) for metal(loid)s analyses. For seston
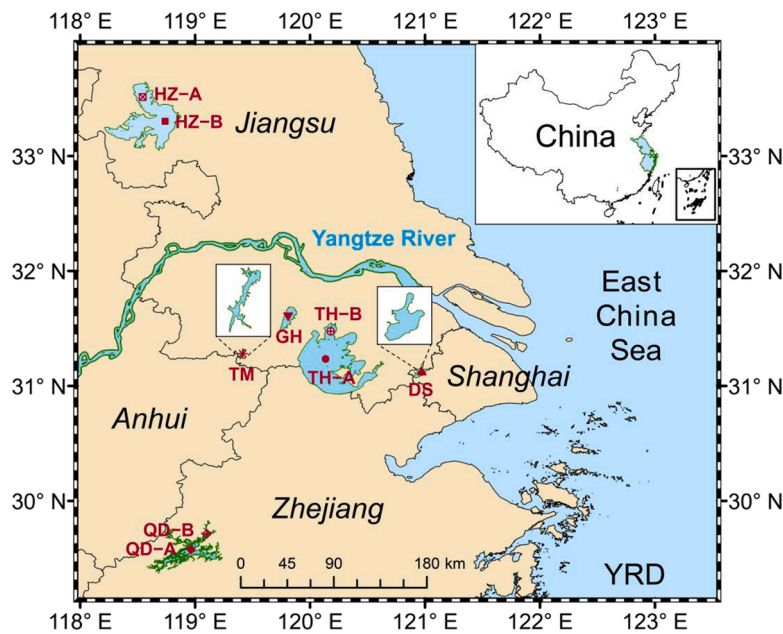
Fig. 1. Locations of the sampling sites in six lakes in the YRD.

Table 1

Characteristics of the sampling sites in six lakes in the Yangtze River Delta (YRD), China.

Lake	Code	Location	Closest city	Population in 2018 (million)	Lake area (km^2)	Average depth (m)
Gehu	GH	31° 35′ 57″ N, 119° 47′ 34″ E	Changzhou	4.7	167	1.3
Tianmu	TM	31° 17′ 47″ N, 119° 25′ 16″ E	Changzhou	4.7	18	19
Dianshan	DS	31° 07′ 40″ N, 120° 58′ 24″ E	Shanghai	24.8	62	2.1
Hongze-A	HZ-A	33° 16′ 56″ N, 118° 41′ 55″ E	Huai'an	4.9	1600	4.5
Hongze-B	HZ-B	33° 25′ 37″ N, 118° 35′ 01″ E	Huai'an	4.9	1600	1.5
Taihu-A	TH-A	31° 12′ 17″ N, 120° 09′ 55″ E	Suzhou	10.7	2300	3.3
Taihu-B	TH-B	31° 21′ 52″ N, 120° 11′ 45″ E	Wuxi	6.6	2300	1.9
Qiandao-A	QD-A	29° 35′ 51″ N, 118° 57′ 38″ E	Hangzhou	11.3	580	104
Qiandao-B	QD-B	29° 40′ 57″ N, 119° 05′ 40″ E	Hangzhou	11.3	580	30

(0.7–64 μm) collection, the mixed lake water from the sampled two or three different water layers were filtered using a 64 μm mesh filter cup. The remaining particles were then collected onto pre-weighed and pre-combusted (450 °C, 4 h) Whatman GF/F filters. In order to determine zooplankton (> 200 μm) biomass and density, extra tows were collected at each site using a plankton net equipped with a mechanical flow meter (HYDRO-BIOS, Apparatebau GmbH, Germany). More details regarding the preservation of all the collected samples are provided in Text S2.

2.3. Sample analyses

At each sampling site, water physiochemical characteristics and aqueous metal(loid) concentrations were measured from the sampled two or three different water layers, with three replicates for each layer. Water temperature and pH were measured in the field with a portable multi-parameter water quality analyzer (HQ40d, Hach, USA). TP and TN were quantified using the potassium persulfate oxidation method GB 11893-89 and GB 11894-89 respectively. Chl-*a*, as a proxy for phytoplankton biomass, was extracted with 95% ethanol (Lorenzen, 2003) and analyzed by UV-Visible spectrophotometer (EVOLUTION 201, Thermo Fisher Scientific, USA). DOC was analyzed directly using a TOC analyzer (TOC-LCPH, Shimadzu, Japan). Phytoplankton identification and enumeration were conducted at 400 × magnification under a microscope (BX51, Olympus, Japan) based on the taxonomic information of freshwater algae in China (Hu and Wei, 2006). Zooplankton was counted and identified with an Olympus microscope BX51 (40 × magnification) according to the taxonomic information provided by

Wang (1961), Jiang and Du (1979), and Shen and Song (1979). To quantify zooplankton biomass at each site, the filters with zooplankton (> 200 μm) were dried at 60 °C in the oven for 24 h before weighing. For each zooplankton taxa (i.e., Copepod, Cladocera, and Rotifera), zooplankton abundance was converted to biomass using length-weight regressions following the methods described by Zhang and Huang (1991).

Total Hg concentrations in filtered lake water and size-fractionated plankton samples were analyzed by cold vapor atomic fluorescence spectrometry (CVAFS, MERX, Brooks Rand, USA) following US EPA Method 1631. For plankton, seston (on filters) and zooplankton (~0.05 g) were freeze-dried, homogenized, and digested by freshly mixed ultrapure nitric acid and sulfuric acid (3:1, v/v) at 95°C for 3 h before going to automated analytical system for Hg (MERX, Brooks Rand, USA). For As, Co, Cu, Mn, Pb, Se, and Zn, metal(loid) concentrations in water and size-fractionated plankton samples were determined by inductive coupled plasma mass spectrometry (ICP-MS, Agilent 7700, USA; USEPA Method 200.8, 1994). Seston (on filters) and zooplankton samples were freeze-dried and digested in 10 mL 30% nitric acid (v/v) for 12 h at 60 °C in the oven. External quality control for all the tested metal(loid)s was performed by digesting and analyzing comparable amount of standard reference materials (plankton, BCR-414, IRMM) with known metal(loid) contents. Recovery rates for all the tested metal(loid)s ranged between 90% and 109%. Blanks, certified reference materials, and sample duplicates were measured every twenty samples. The relative standard deviations of the measured parallel samples were mostly within ±10%.

2.4. Statistical analyses

To better reflect the whole column water characteristics of each site, water physiochemical characteristics and aqueous metal(loid) concentrations used in the following calculation or statistical analyses were all mean values calculated from the sampled two or three different water layers. The trophic status of each sampling site was assessed based on TP concentrations (Lampert and Sommer, 2007) according to the following classifications: TP < 5 µg L^{-1} indicates ultra-oligotrophic, 5 µg L^{-1} $<$ TP ≤ 10 µg L^{-1} indicates oligotrophic, 10 µg L^{-1} $<$ TP ≤ 30 µg L^{-1} indicates mesotrophic, 30 µg L^{-1} $<$ TP ≤ 100 µg L^{-1} indicates eutrophic, and TP $>$ 100 µg L^{-1} indicates hypereutrophic. Metal(loid) bioconcentration factor (BCF, mL g^{-1}, considering uptake from water) for seston, and bioaccumulation factor (BAF, mL g^{-1}, considering the contributions of both waterborne and dietborne pathways) for mesozooplankton and macrozooplankton were calculated by dividing metal(loid) concentrations in seston or zooplankton (µg g^{-1}, dry wt) by aqueous metal(loid) concentrations (µg L^{-1}, mean value of different water layers).

Significant differences among metal(loid) BCF and BAF (meso- and macro-) were performed through one-way ANOVA followed by Tukey's post-hoc test. To evaluate the effects of seasonal variations on metal(loid) bioaccumulation, paired *t*-Test analysis was performed to examine the difference of lake water characteristics and metal(loid) BCF or BAF between the two seasons. Considering no significant seasonal variations were observed for the tested water characteristics and metal(loid) BCF or BAF across the sampling sites, seasonal variations were not further discussed in this study. Pearson's correlation analysis was conducted to test the relationships among water characteristics and between water characteristics and metal(loid) BCF or BAF. Linear regressions were performed to test the relationships between phytoplankton biomass (indicated by Chl-*a* and phytoplankton density) and metal(loid) BCF or BAF. The vertical migration of zooplankton would result in ingestion of phytoplankton from the whole water column. Therefore, in this study, the mean value of Chl-*a* at each site (calculated from the data of two or three different water layers, with three replicated for each layer) was considered as a better indicator, rather than phytoplankton density data (measured only in surface water). Canonical correspondence analysis (CCA) was performed to assess the differences among phytoplankton species on seston metal(loid) BCF, as well as zooplankton community compositions on zooplankton metal(loid) BAF. All statistical analyses were conducted using SPSS 22.0. The significance levels for all tests were set at $p < 0.05$. The distribution map of sampling sites was drawn using ArcGIS 10.7. The data graphs were plotted using R script 1.3.959 and GraphPad Prism 7.0.

3. Results and discussion

3.1. Metal(loid) bioaccumulation in plankton

Aqueous dissolved metal(loid) concentrations in the current study, as shown in Table S1 for mean values of two or three water layers and Table S2 for detailed concentrations of each water layers, are generally comparable to previous reports in lakes of eastern China (Guo et al., 2020; Razavi et al., 2015). Among the tested metal(loid)s, Zn (11.2–93.0 µg L^{-1}, based on data of all studied sites, same below) and Mn (3.66–93.0 µg L^{-1}) exhibited the highest values, while Hg showed the lowest concentrations (range: 0.21–2.73 ng L^{-1}, mean: 1.14 ng L^{-1}). The metal(loid) contents in size-fractionated plankton (seston, meso-, and macro-zooplankton) varied largely across different sites (Table S3), but were generally comparable with those reported in lakes (Table S4) within the same geographic regions (e.g., Lake Taihu, Yu et al., 2012); seven reservoirs in eastern China (Razavi et al., 2015), or lakes of other countries/regions (e.g., Lake Yeniçaga in Turkey, Saygi and Yigit, 2012; three lakes in Southwestern China, Long et al., 2018, 2016; Lake Bolshoy Vudyavr in Russia, Pavlova et al., 2019), except that Zn (average 5800 µg g^{-1}) and Mn (average 736 µg g^{-1}) contents in seston were noticeably

higher in our study. Such higher Zn and Mn contents in seston might be highly attributed to the higher Zn and Mn concentrations in lake water, but also related to the different size fractions used for seston/phytoplankton sampling across studies (Table S4). In the current study, we used 0.7–64 µm as the size fraction for seston sampling. This seston size fraction incorporated a certain proportion of smaller phytoplankton or other particles (with higher surface area-to-volume ratios) compared to those size fractions of seston/phytoplankton in most of previous studies (> 30 µm, Saygi and Yigit, 2012; > 74 µm, Yu et al., 2012; > 29 µm, Pavlova et al., 2019), thus might partly accounting for the observed higher metal(loid) burdens.

The calculated metal(loid)-specific seston BCFs and zooplankton (meso- and macro-) BAFs are presented in Fig. 2 and Table S4. The metal(loid) seston BCF exhibited large differences among metal(loid)s, mainly due to the metal(loid)-specific bioaccumulation processes. The seston BCF and zooplankton BAF for Hg (Fig. 2 and Table S4) were significantly higher than those of other metal(loid)s, which was in accord with the widely observed high bioaccumulation potential of Hg owing its specific chemical properties (Bjørklund et al., 2017). The seston BCF values (Fig. 2 and Table S4) of essential elements (Zn, Mn, Cu, and Co) were generally higher than those of non-essential elements (Pb and As, except for Hg), which may be largely explained by the physiological requirements for essential elements. The seston BCF of all the tested metal(loid)s (except Se) were significantly higher than the corresponding zooplankton (meso- and macro-) BAF across the sampling sites (Fig. 2 and Table S4), probably owing to the greater contribution of metal(loid) adsorption onto the surface of seston (with higher surface area-to-volume ratio than zooplankton). In contrast, there was no significant differences in metal(loid) BAF between the two size-categories of zooplankton (Fig. 2 and Table S4). Importantly, the seston BCF and zooplankton (meso- and macro-) BAF of the tested eight metal(loid)s showed large variations across sites (Table S4), which could be highly attributed to the site-specific water characteristics and plankton communities (discussed in detail below).

3.2. Impacts of water characteristics on metal(loid) bioaccumulation in plankton

The average water temperature of these lakes in fall 2018 and spring 2019 were $18.6 \pm 1.0°C$ and $19.1 \pm 0.8°C$ respectively, as shown in Table S5 for mean values of two or three water layers and Table S6 for detailed water characteristics of different water layers, same below for other water characteristics if not otherwise specified. All lakes were alkaline (pH values ranging from 7.1 to 9.3), but varied greatly in TP (40–240 µg L^{-1}), TN (1.1–2.7 mg L^{-1}), Chl-*a* (1.2–160 µg L^{-1}), DOC (2.9–9.5 mg L^{-1}), phytoplankton density (3.9×10^5–9.2×10^8 cells L^{-1}), zooplankton density (127–570 cells L^{-1}), and zooplankton biomass (0.33–1.26 mg L^{-1}).

The seston BCFs of the tested eight metal(loid)s showed 5–36 times variations across sites (calculated based on the data range of metal(loid)-specific BCF as shown in Table S4), which can be partly explained by the differences of water characteristics among each sampling site. The site-specific seston BCFs were significantly negatively correlated with pH ($p < 0.05$ for all metal(loid)s, except Zn) and DOC (for Cu, $r = -0.486$, $p < 0.05$), but showed weaker relationships with other environmental variables (Fig. 3 and Table S7), indicating that pH and DOC played key roles in reducing metal(loid) bioavailability and subsequent bioconcentration in seston (mostly phytoplankton). The negative relationships between pH and metal(loid) BCF could not be explained by the competition between protons and metal(loid) ions to biotic ligands (as expected in biotic ligand model, Slaveykova and Wilkinson, 2005), but may related with the increase of total free metal(loid) concentrations due to protonation of complexing agents and the impact of pH on the formation of potentially bioavailable metal(loid) complexes can also account for the negative relationships between pH and metal(loid) BCF (Xu et al., 2012). The lower metal(loid) BCF in seston at sites with higher DOC levels
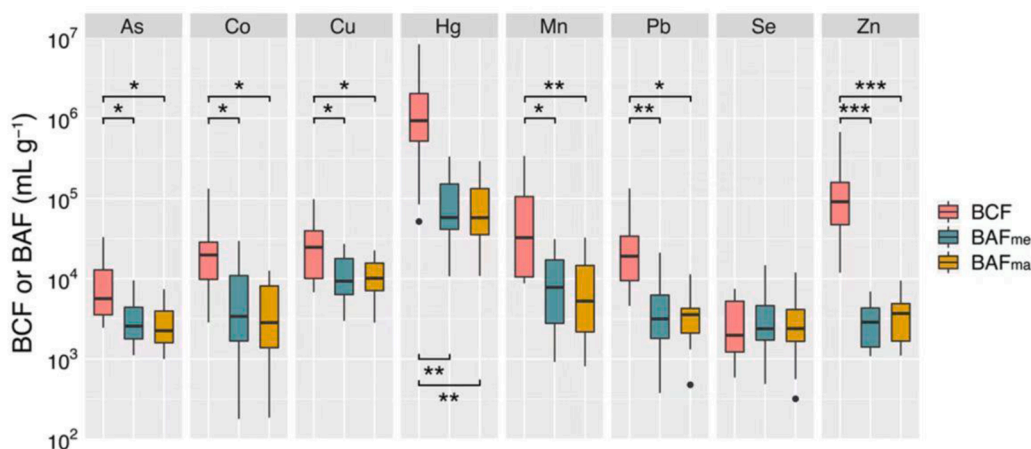
Fig. 2. Seston metal(loid) (As, Co, Cu, Hg, Mn, Pb, Se, and Zn) bioconcentration factor (BCF, mL g^{-1}) and zooplankton metal(loid) bioaccumulation factor (meso-, BAF$_{me}$; macro-, BAF$_{ma}$, mL g^{-1}) of the sampling sites in six lakes in the YRD. Significant differences between groups are indicated by single asterisk (*, $p < 0.05$), double asterisks (**, $p < 0.01$), or triple asterisks (***, $p < 0.001$).
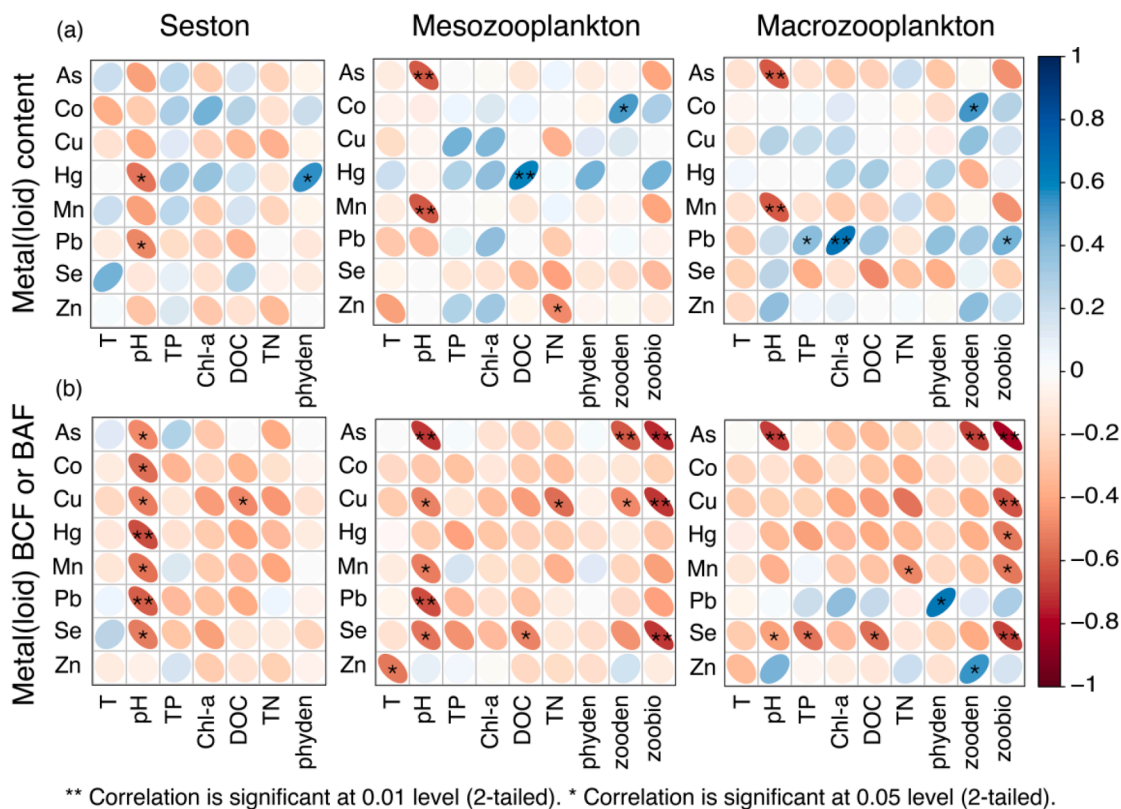

Fig. 3. Pearson correlations (a) among water characteristics (T, pH, Chl-*a*, TP, TN, DOC, phytoplankton density (phyden), zooplankton density (zooden), zooplankton biomass (zoobio) and metal(loid) contents in size-fractionated plankton (seston, meso-, and macro-zooplankton); and (b) water characteristics and BCF, BAF$_{me}$, and BAF$_{ma}$ of each metal(loid) of the sampling sites in six lakes in the YRD. The blue color indicates positive correlations and the red color indicates negative correlations (*r* scale on the right). See Table S8 for the detailed Pearson correlation coefficients.

(Figs. 3 and S1) might be attribute to the formation of less bioavailable metal(loid) complexes with organic matter (Macoustra et al., 2019; Vigneault and Campbell, 2005).

The BAFs of the tested eight metal(loid)s in zooplankton exhibited 4–165 times differences across sites (calculated based on the data range of metal(loid)-specific BAF as shown in Table S4). Biokinetic studies have predicted that both dietary ingestion and dissolved uptake are important metal(loid) exposure pathways for zooplankton (Wang and Fisher, 1998; Yu and Wang, 2002a). First, similar with the results for seston, the varying pH and DOC across sites were crucial factors in

controlling the dissolved uptake of metal(loid)s in zooplankton (Fan et al., 2012; Komjarova and Blust, 2009; Wu et al., 2019), which can be explained by the negative relationships of pH (mostly $r < -0.5$, $p < 0.05$) and DOC (mostly $r < -0.2$, $p > 0.05$) with metal(loid) BAF in zooplankton (Fig. 3 and Table S7). Although TN generally exhibited negative correlations with metal(loid) BAF in zooplankton (mostly $r < -0.2$, Fig. 3 and Table S7), N additions could not lead to significant effect on metal(loid) accumulation in zooplankton (Yu and Wang, 2004). Second, ingestion of seston could largely account for the lower metal(loid) BAF in zooplankton at productive sites, as supported by the

similar patterns between metal(loid) BCF in seston versus metal(loid) BAF in zooplankton with environmental variables (such as Chl-*a*, pH, and DOC, Fig. 3). Although there were strong negative correlations between zooplankton density/biomass and metal(loid) BCF (mostly $r < -0.5$, $p < 0.05$, Fig. 3) or BAF (mostly $r < -0.2$, $p > 0.05$, Fig. 3), such relationships should be spurious correlations ascribing to the positive correlations between metal(loid) concentrations in water and zooplankton density/biomass (Table S7a).

3.3. Impacts of plankton community on metal(loid) bioaccumulation in plankton

Phytoplankton community compositions differed across lakes and showed site-specific seasonal variations (Fig. 4a). The prominent phytoplankton of the sampled two sites at TH was cyanobacteria both in fall and spring (85–99%), whereas diatoms were the most abundant (about 90%) phytoplankton at GH in both seasons. The site-to-site differences in dominant phytoplankton species might be attribute to complex impacts of site-specific environmental variables (such as light, nutrients, water temperature, etc., Kakouei et al., 2022). In contrast, the phytoplankton community compositions at other lakes exhibited strong seasonal variations (Fig. 4a). For example, the dominant phytoplankton at DS shifted from cyanobacteria (about 98%) in fall to diatoms (about 77%) in spring, while the main species at TM tended to change from diatoms (about 75%) in fall to cyanobacteria (about 78%) in spring. At QD, chlorophytes and cryptophytes contributed more than 90% of the total phytoplankton in fall, but the major phytoplankton species shifted to diatoms and cyanobacteria (99% in total) in spring. Such large seasonal variations might be related with seasonal changes of site-specific environmental drivers for each phylum. For example, N/P ratio showed significant effects on seasonal dynamics of chlorophytes (Li et al., 2021), while pH, dissolved oxygen, transparency, and colored DOC have been reported to influence seasonal variations of diatoms in subtropical lakes (Li et al., 2021; Sullivan et al., 2022).

Lake-to-lake differences and seasonal shifts in phytoplankton species (Fig. 4a) can be a crucial factor in regulating seston BCF across sites. Testing the relationships between species-specific phytoplankton abundance and metal(loid) seston BCF via CCA (Fig. 5a), it was evident that the dominance of cyanobacteria was markedly contributed to Zn bioaccumulation, while pyrophyte, cyanobacteria, and cryptophyte positively were related to As bioaccumulation. For the bioaccumulation of other tested metal(loid)s, cryptophyte and chlorophyte turned out to be the most important contributors. Such differences can be highly attributed to the species-specific bioaccumulation of phytoplankton, owing to its differences in cell size, shape, surface area-to-volume ratios (Cottingham, 1999; Kim et al., 2014).

The community compositions of zooplankton differed across lakes, but remained relatively constant between the two seasons (Fig. 4b). Rotifers dominated zooplankton community in the six lakes, contributing 40–84% of the total zooplankton abundance. In contrast, the biomass share of rotifers (Fig. S2) was markedly lower than those of cladocerans and copepods across all the sampling sites owing to the smaller biovolume of rotifer in relative to crustacean. For crustaceans, the relative abundance and biomass share of cladocera were higher than those of copepoda at GH and DS compared to the other four lakes (Figs. 4b and S2).

The site-specific biomass share of zooplankton (Fig. S2) could at least partly explain the variation in zooplankton BAF across sites. Testing the relationships between species-specific zooplankton biomass (> 200 μm) and metal(loid) zooplankton BAF (meso-, Fig. 5b), the CCA results showed that the biomass share of copepod was positively correlated with the bioaccumulation of most of the tested metal(loid)s (except Zn). In contrast, the biomass share of cladocera was related with Zn bioaccumulation, while rotifer showed no relationship with any of the tested metal(loid)s. Similarly, zooplankton community compositions have also been reported to be strongly correlated with Hg contents in zooplankton (Long et al., 2018), and accounted for the temporal differences in As and Pb bioaccumulation in zooplankton (Chen and Folt,
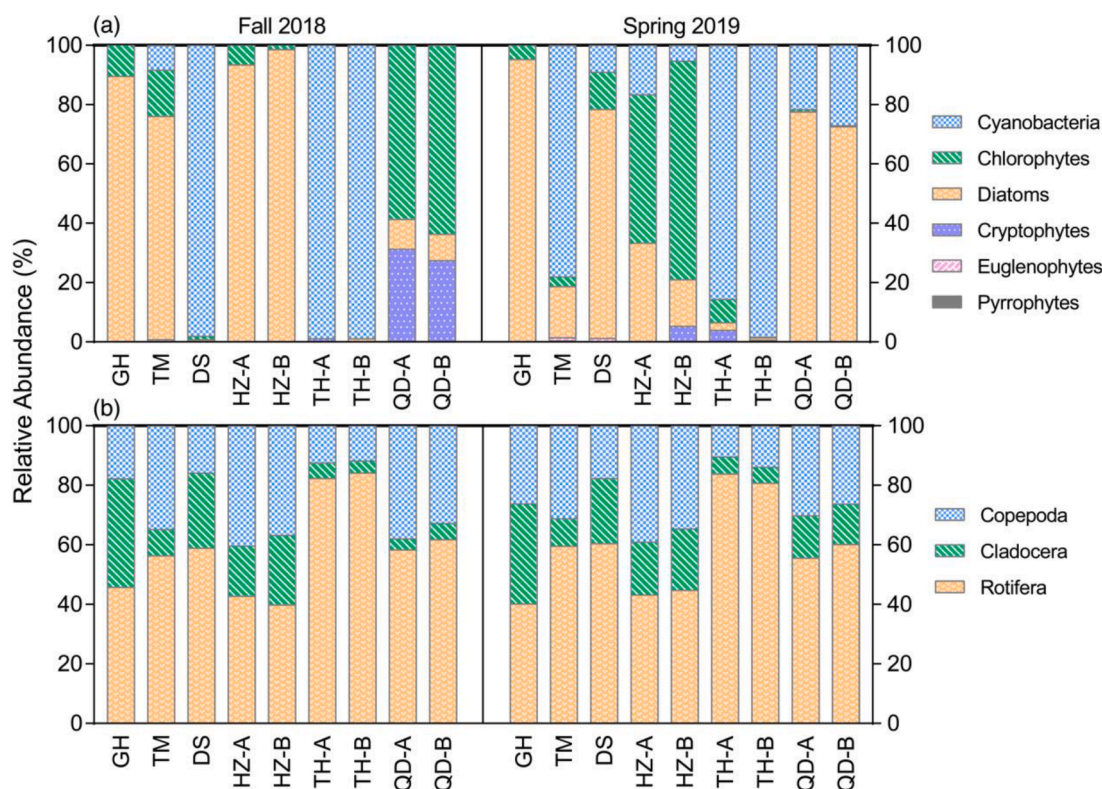

Fig. 4. Phytoplankton (a) and zooplankton (b) community compositions (%) of the sampling sites in six lakes in the YRD in fall 2018 and spring 2019. See Table S1 for lake codes and Fig. 1 for locations.
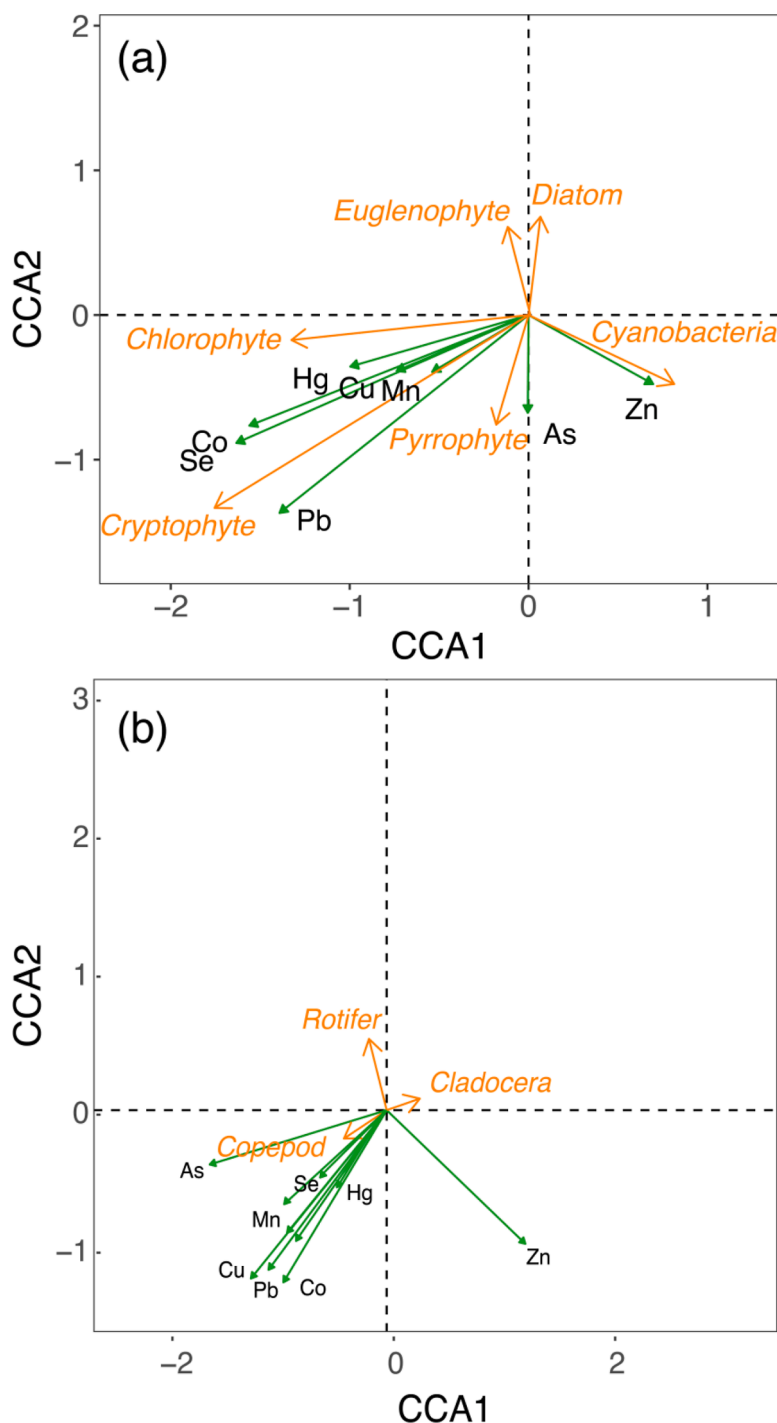
Fig. 5. Canonical correspondence analysis (CCA) biplots representing the relationships between (a) species-specific phytoplankton abundance and metal(loid) seston BCF and (b) species-specific zooplankton biomass and metal(loid) zooplankton BAF (meso-, BAF_{me}) of the sampling sites in six lakes in the YRD.

2000).

3.4. Controlling of phytoplankton biomass on metal(loid) bioaccumulation in plankton

The primary observation of this study was that the metal(loid) BCF or BAF of size-fractionated plankton in the studied six lakes in the YRD decreased (Figs. 6, 7, and S3) with increasing phytoplankton biomass when Chl-*a* concentrations were below ~50 μg L^{-1}. Similar relationships also existed between metal(loid) BCF or BAF in size-fractionated plankton and phytoplankton density (in surface water layer; Fig. S4).

A similar but different phenomenon reported previously was that the increase in phytoplankton biomass could result in lower mass-specific burdens of contaminants in phytoplankton and subsequently transfer to zooplankton, known as algal bloom dilution (Pickhardt et al., 2002). For example, plankton biomass has been observed to be negatively correlated with planktonic organochlorine levels across 33 lakes in Southern Ontario (Taylor et al., 1991) and with planktonic polychlorinated biphenyl concentrations in Lake Ontario (Dachs et al., 2000). Field observations also showed that high plankton densities could reduce Hg biomagnification (Chen and Folt, 2005) and As bioaccumulation in plankton and fish (Chen and Folt, 2000) across 20 lakes
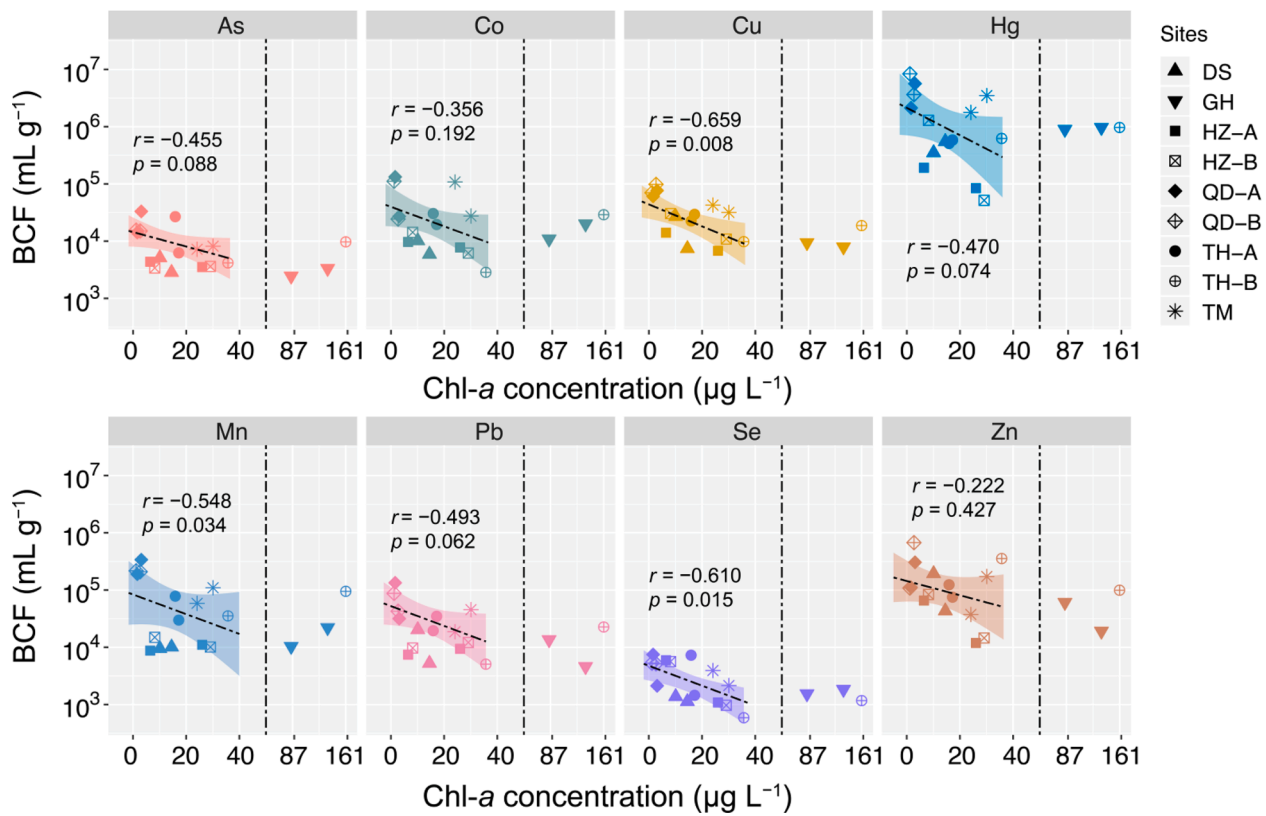
Fig. 6. Relationships between seston BCF of each metal(loid) and Chl-*a* concentration (μg L⁻¹) of the sampling sites in six lakes in the YRD.
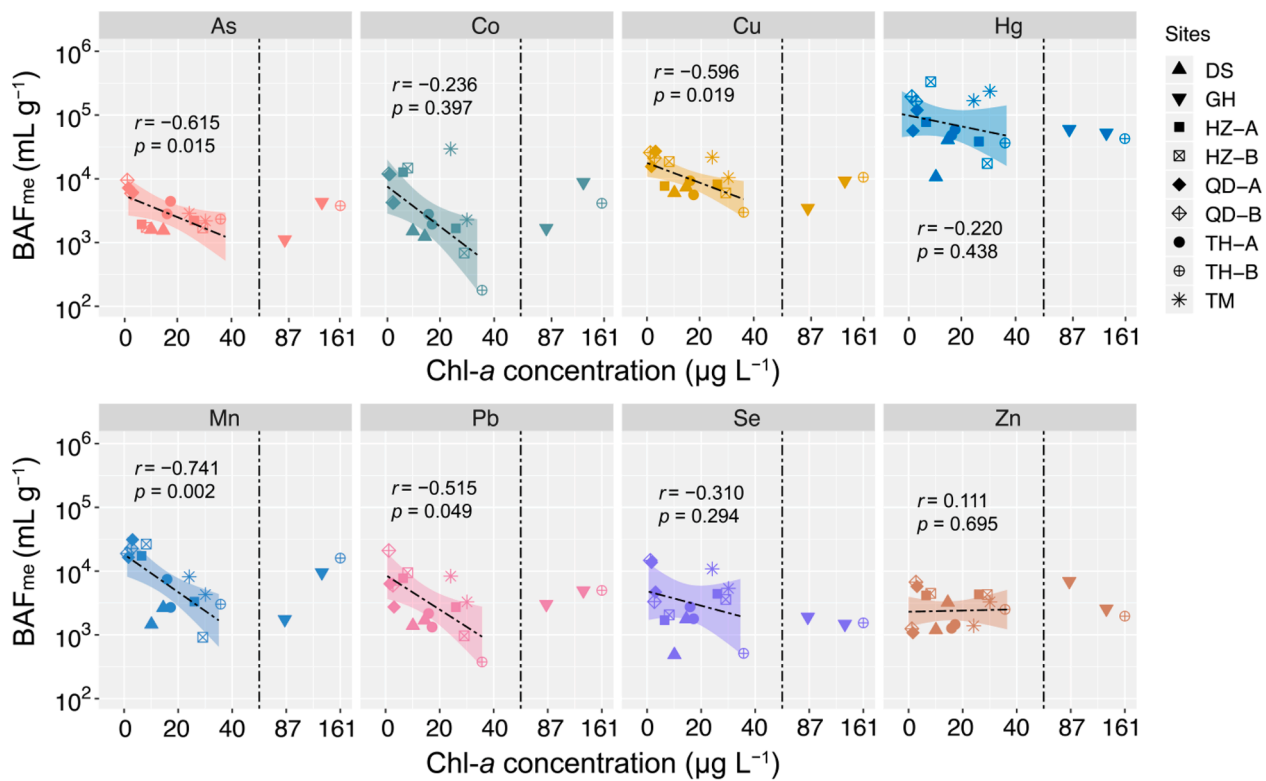

Fig. 7. Relationships between mesozooplankton BAF$_{me}$ of each metal(loid) and Chl-*a* concentration of the sampling sites in six lakes in the YRD. See Fig. S3 for relationships between macrozooplankton BAF$_{ma}$ and Chl-*a*.

in the Northeastern United States.

Algal bloom dilution has been widely recognized as the key mechanism for the lower contaminant levels in plankton under more productive conditions in Northern American lakes (Chen and Folt, 2000; 2005), with two important assumptions: (1) the pool of a certain contaminant is finite; (2) uptake by individual cells is constant. However, our study provides evidences that algal bloom dilution is not the key driver for the lower metal(loid) bioaccumulation in plankton at more productive sites in these anthropogenic-impacted lakes in the YRD, China. First, the dissolved metal(loid) concentrations in the studied lakes were not negatively correlated with increasing Chl-*a* (as would be expected under "algal bloom dilution" scenarios), but generally showed positive correlations ($r > 0.1$ for all metal(loid)s; $r > 0.5$, $p < 0.05$ for Cu and Hg, Table S7b). Such positive relationships might be attributed to the impacts of concurrent inputs of anthropogenic metal(loid)s and nutrients, as evidenced by the positive correlations between metal(loid)s and TN (except Zn, Table S7b). This was in disagreement with the first assumption that high phytoplankton biomass would reduce certain contaminants in a certain pool. However, phytoplankton at nutrient-rich sites may experience growth dilution (metal concentration in phytoplankton would be reduced when cellular growth rate exceed metal uptake rate, Sunda and Huntsman, 1998) even if such phenomenon can be obscured under high loads of anthropogenic metal(loid)s. Second, pH and DOC levels were generally negatively related with metal(loid) BCF or BAF across sites (Fig. 3 and Table S7f-h), denoting hampered metal(loid) bioconcentration and bioaccumulation at productive sites (with higher pH and DOC levels). Such observation disagreed with the second assumption of the constant uptake by individual cells. Additionally, we observed that the negative correlations between metal(loid) BCF or BAF in plankton and Chl-*a* were more pronounced than those between metal(loid) contents in plankton and Chl-*a* (Fig. 3 and Table S7c-e), indicating that higher phytoplankton biomass (when Chl-*a* concentrations below ~50 µg L^{-1}) reduced metal(loid) bioaccumulation, rather than algal bloom dilution.

The higher phytoplankton biomass reduced metal(loid) bioaccumulation in plankton (when Chl-*a* concentrations were lower than ~50 µg L^{-1}) mainly by regulating water characteristics and shaping plankton community. First, higher phytoplankton biomass was associated with higher pH and DOC levels in lake water. Specifically, DOC was significantly positively related with Chl-*a* ($r = 0.616$, $p = 0.007$, Table S7a) and phytoplankton density ($r = 0.510$, $p = 0.031$, Table S7a) among the sampling sites. Although the positive relationships between pH and Chl-*a*/phytoplankton density were not significant ($p > 0.05$, Table S7), higher phytoplankton biomass at least partially contributed to the elevated pH levels in productive sites. Such results can be explained by the reduction of carbonate and bicarbonate levels to replenish the lost CO_2 utilized by photosynthesis of phytoplankton. Therefore, higher phytoplankton biomass reduced metal(loid) bioavailability and subsequently bioaccumulation in plankton via elevating pH and DOC levels (possible mechanisms already discussed in section 3.2). Second, plankton community could be shaped under different nutrient levels (Davies et al., 2010; Irwin et al., 2006), thus regulating metal(loid) bioaccumulation in plankton. In our study, the large variations of phytoplankton and zooplankton community across sites contributed greatly to the variations of metal(loid) BCF or BAF across sites (as discussed in section 3.3), although the relationship between phytoplankton biomass and plankton community was complex. In addition, we observed evidences that the smaller body-sizes of zooplankton at more productive sites contributed to their lower metal(loid) BAF. The average body sizes of the main zooplankton species (including six species of cladocerans and four species of copepods, Table S8) at QD (with the lowest phytoplankton biomass) were all larger than those in other lakes. For example, the average lengths of cladocerans *Bosmina longirostris* (one of the dominant cladoceran species) and copepods *Thermocyclops dybowskii* (one of the dominant copepod species) at QD were 693 µm and 1311 µm, respectively, which were both significantly larger than those

in other lakes, such as GH (541 µm and 998 µm) and TH (412 µm and 843 µm). Similar with our observation, smaller sizes of zooplankton at more productive sites have been observed in a number of eutrophic lakes with high cyanobacterial biomass in eastern China (Zhang et al., 2013), owing to both top-down and bottom-up forces. Therefore, the larger body sizes of zooplankton (Table S8) in QD (with the lowest phytoplankton biomass) at least partially accounted for the higher metal(loid) BAF.

The metal(loid) BCF in seston and BAF in zooplankton did not further decrease with increasing phytoplankton biomass when Chl-*a* concentrations were higher than ~50 µg L^{-1} (Figs. 6, 7, and S3), suggesting that the impact of phytoplankton biomass on metal(loid) bioaccumulation might be controlled by other confounding mechanisms. One possible mechanism contributing to the enhanced metal(loid) accumulation might be related with the impacts of more algal-derived extracellular polymeric substances (EPS) under severe algal bloom conditions on metal(loid) adsorption and bioaccumulation. Once bound with algal cells, algal-derived EPS could significantly facilitate the adsorption of metal(loid)s (such as As and Cd, Xie et al., 2020; Zhang et al., 2020), due to its high metal(loid) binding affinity via ion exchange, complexation, and precipitation (Naveed et al., 2019). When released into the water, algal-derived soluble EPS may even enhance metal(loid) uptake via forming organic complexes which can increase metal(loid) sequestration from water. There were evidences that weak complexes may increase metal(loid) uptake by phytoplankton (i.e., Zn and Cd, Xu et al., 2012), and algal-derived DOC could promote Hg uptake by phytoplankton (Zhong and Wang, 2009). Although the above mechanisms still require further investigations, our results demonstrated that the potential risk of metal(loid) bioaccumulation in planktonic food webs under severe algal bloom conditions deserve special attention.

4. Conclusions

Based on a comprehensive field investigation across six anthropogenic-impacted subtropical lakes in the Yangtze River Delta, this study showed great impacts of phytoplankton biomass on controlling metal(loid) bioaccumulation in size-fractionated plankton. Higher phytoplankton biomass (when Chl-*a* concentration was below ~50 µg L^{-1}) associated with lower metal(loid) BCF or BAF in size-fractionated plankton, which was highly attributed to the lower metal(loid) bioavailability at more productive sites (with higher pH and DOC), rather than algal bloom dilution. Phytoplankton growth dilution and the smaller body-size of zooplankton at more productive sites at least partially contributed to the lower metal(loid) bioaccumulation. Site-specific plankton communities also accounted for the large variations in metal(loid) bioaccumulation in size-fractionated plankton. Additionally, this study provided field evidence that metal(loid) bioaccumulation could be enhanced under severe algal bloom conditions (when Chl-*a* concentration was higher than ~50 µg L^{-1}), although the mechanisms still require to be tested under laboratory conditions. Such complex role of phytoplankton biomass in controlling metal(loid) bioaccumulation in planktonic food webs may further exhibit inevitable effects on predators (such as pelagic fish), indicating that algal bloom and plankton communities must be carefully examined in tandem with non-biotic lake conditions to account for metal(loid) bioaccumulation risks in anthropogenic-impacted lakes.

Supplementary materials

Additional information as noted in the main text of the current paper is available, including Text S1–S2, Tables S1–S8, and Figures S1–S4.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

the work reported in this paper.

Data availability

We have shared all the data in the supplementary material.

Acknowledgments

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.watres.2022.119075.

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