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1 Zinc isotope characteristics in the biogeochemical cycle as
2 revealed by analysis of suspended particulate matter (SPM) in
3 Aha Lake and Hongfeng Lake, Guizhou, China.

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Abstract:

Zn isotope is a useful tool for tracing biogeochemical processes as zinc plays important role in the biogeochemistry of natural systems. However, Zn isotope composition in the lake ecosystems has not been well characterized. This study aim to investigate the Zn isotope compositions of suspended particulate matter (SPM) and biological samples collected from the Aha Lake and Hongfeng Lake, and their tributaries in summer and winter, in order to explore the potential of this novel isotope system as a proxy for biogeochemical processes in aqueous environments. Concentration of dissolved Zn ranged from 0.65 to 5.06 $\mu\text{g/L}$ and 0.74 to 12.04 $\mu\text{g/L}$ for Aha Lake and Hongfeng Lake respectively, while the SPM-Zn ranged from 0.18 to 0.70 mg/g and 0.24 to 0.75 mg/g for Aha Lake and Hongfeng Lake respectively. The Zn isotope composition in SPM from Aha Lake and its main tributaries ranged from -0.18‰ to 0.27‰ and -0.17‰ to 0.46‰ respectively, and it varied from -0.29‰ to 0.26‰ and -0.04‰ to 0.48‰ respectively in Hongfeng Lakes and its main tributaries, displaying a wider range in tributaries than lakes. From the results and discussion, they implied that Zn isotope composition mainly affected by tributaries inputting in Aha Lake, while adsorption process by algae was major factor for the Zn isotope composition in Hongfeng Lake, and ZnS precipitation leads to the light Zn isotope composition of SPM in summer. These data and results provide the basic information of the Zn isotope for the lake ecosystem, and promote the application of Zn isotope in biogeochemistry.

Key words: Zn isotope composition; SPM (Suspended particulate matter); Lake;

45 Tributary

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48 **1. Introduction**

49 With the development of MC-ICP-MS, transition metal isotopes have received
50 increasing attention over the last 15 years, and have been successfully applied to trace
51 biogeochemical processes (Luck et al., 1999; Beard et al., 2003; Weiss et al., 2007; Viers
52 et al., 2007; Mattielli et al., 2009; Bigalke et al., 2010; Mathur et al., 2005, 2012; Blätter et
53 al., 2015; Li et al., 2015; Song et al., 2011; Reddy et al., 2015). As one of the second most
54 abundant transition metal elements, Zn occurs widely in the atmosphere, soil, rivers,
55 plants and animals (Hutchinson., 1957; Matthys., 1975; Alloway et al., 2004), and is also a
56 critical element for biological functioning (Brand et al., 1983; Olhaberry et al., 1983;
57 Shankar and Prasad, 1998; Hambidge, 2000; Andreini et al., 2006). It has also been
58 demonstrated that Zn participates in multiple biological processes, notably as cofactor in
59 enzymatic photosynthetic reactions (Frausto J J R, 1991). In particular, Zn is a cofactor in
60 the carbonic anhydrase enzyme that catalyzes the conversion between HCO_3^- and CO_2
61 (Brown et al., 1993, Lippard S J, 1994; Nimer N A, 1995). However, it also has detrimental
62 effects on living organisms when present at high concentration (Cloquet et al., 2006).

63 The fractionation mechanism of Zn isotopes has been studied by many scientists,
64 who have identified three main processes that cause Zn fractionation (Budd et al., 1999;
65 Maréchal et al., 2002a,b; Zhu et al., 2002; Stenberg et al., 2004; Weiss et al., 2005;
66 Pokrovsky et al., 2005; Gélabert et al., 2006; Bryan et al., 2015). Firstly, Zn isotope can be

fractionated during plant uptake (Weiss et al., 2005; Vance et al., 2006) and adsorption processes (Gélabert et al., 2006; Pokrovsky et al., 2005; Kafantaris S C V., 2014). Secondly, zinc adsorption on soil, Mn oxyhydroxide, kaolinite and sediments is an another factor of isotope fractionation (Cacaly et al., 2004; Rousset et al., 2004; Pokrovsky et al., 2005; Bryan et al., 2015; Guinoiseau et al., 2016). Finally, zinc isotope can fractionation during the sphalerite precipitated from the solution or rock material, and also can fractionation during different Zn species, like sulfide, chloride and carbonate (Archer et al., 2004, Wilkinson et al., 2005; John et al., 2008; Jujii., 2011 & 2012). Generally speaking, the range of $\delta^{66}\text{Zn}$ values in geological materials on Earth is between -0.91‰ to 1.04‰ (Luck et al., 1999; Maréchal et al., 2000; Mattielli et al., 2009; Pichat et al., 2003; Dolgopova et al., 2006; Weiss et al., 2007; John et al., 2007; Mason et al., 2005, little et al., 2016), and it is relatively narrow compare to the lunar samples(-3.83‰ to 6.89‰)(Monyier et al., 2006).

The Zn isotope composition of different materials collected from atmosphere, soil, sediment, ocean, and river, has been analyzed and applied to trace sources of Zn (Maréchal et al., 1999; Maréchal et al., 2000; Dolgopolova et al., 2006; Cloquet et al., 2006; Berimin et al., 2006; Weiss et al., 2007; Sivry et al., 2008; Mattielli et al., 2009; Chen et al., 2009; Thapalia, et al., 2010). It was found that the Zn isotope composition in rainfall is lighter than in carbonatite as early as 1999 (Luck et al., 1999). Zn isotope composition were also combined with lead isotope ratios to trace that the Zn in lichen and birch at Orlovka–Spokoinoe mining district, Eastern Transbaikalia, Russia, mainly comes from the mining area (Dolgopolova et al., 2006). Zn isotopes were investigated in a variety of

stream waters draining mining districts located in the United States and estuary in pairs, and it demonstrated that Zn isotopes maybe used to probe biogeochemical processes (Borrok et al., 2008; Chen et al., 2009). The Zn isotope composition of soils shows that mining areas are a source of heavy metal pollution (Bigalke., et al., 2010). Zn isotope composition of snow, ice and atmosphere indicate that $\delta^{66}\text{Zn}$ is useful tool in pollution provenance (Mattielli et al., 2009; Voldrichova., et al, 2014). In addition, Zn isotopes composition was also studied in the Ocean to trace the Zn biogeochemical cycle (John et al., 2004; John et al., 2014; Zhao et al., 2014; Little et al., 2016).

However, Zn isotope composition in the lake ecosystem has not been well characterized, besides the research from the eutrophic Lake Greifen, Switzerland (Peel et al., 2009). Accordingly, there is still much work to be done before using Zn isotopes to unravel biogeochemical cycling of Zn in the lake ecosystem successfully. Lakes are easily accessible natural laboratories with well-established biogeochemical processes (Sigg et al., 1985). This work aims to investigate the Zn isotope composition of suspended particle matter (SPM) in Aha Lake and Hongfeng Lake, both are eutrophic and seasonal anoxic lakes, and located at the southwest suburb of Guiyang, Guizhou Province, China. SPM of lakes is a mixture of organic and inorganic detritus, Fe-Mn oxhydroxides, clay minerals, carbonates, phytoplankton, zooplankton, bacteria, and other particles that are retained on 0.45 μm pore size filter. SPM can affect transportation and transformation of trace contaminants among water, sediment and the food chain, hence it is a critical chemical component of the biogeochemical cycling in lakes (Ödman et al., 1999; Turner and Millward, 2002). The Zn isotopic compositions of SPM in Hongfeng and Aha Lakes and

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4 111 their tributaries were investigated in this research, to assess the behavior of zinc isotopes
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6 112 composition during biogeochemical processes in the aqueous environment.
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9 113 **2. Study background and sample collection**

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11 114 **2.1 study site**

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14 115 Aha and Hongfeng are artificial river interception reservoirs located in southwest of
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16 116 Guiyang city about 8 km and 31.5 km respectively, in a subtropical humid monsoon
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18 117 climate zone. The catchments are characterized by low rainfall and river discharge during
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20 118 winter and spring, whereas high temperatures in summer and autumn bring more rainfall
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22 119 and high river flow (Table1). They are both seasonally anoxic reservoirs. Aha lake covers
23
24 120 an area of 4.5 km², with a total water volume of 4.45×10^7 m³. The average and maximum
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26 121 depths are 13 m and 24 m, respectively. The residence time of lake water is about 0.44
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28 122 year. The watershed area is 190 km² with an average annual precipitation of 1109 mm,
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30 123 and the average annual temperature is 13.8-15.5 °C. Previously, more than 200 coal
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32 124 mines were widely distributed in the watershed, where significant amount of acid mining
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34 125 drainages and dump filtrates were produced. There are six main rivers flowing through the
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36 126 watershed area including five inflowing tributaries, Youyu River (YYR), Caichong River
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38 127 (CCR), Lannigou River (LNR), Baiyan River (BYR) and Sha River (SR), and only one
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40 128 draining river, Xiaoche River (XCR) (Fig1). YYR and BYR are mainly polluted by coal
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42 129 mines, CCR and LNR are mainly polluted by domestic sewerage, and SR polluted by
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44 130 industrial and domestic sewerage. The surface of lake water is colonized by sparse
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46 131 diatoms and cause eutrophication in summer.
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56 132 Hongfeng Lake covers an area of 57.2 km² and much bigger than Aha lake, its
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133 reservoir storage capacity is $6.01 \times 10^8 \text{ m}^3$, with a drainage area of 1596 km^2 , the water
134 residence time is about 0.33 year. The average and maximum water depth is 10.52 m and
135 45 m, respectively. Hongfeng Lake consists mainly of two areas: the North Lake and the
136 South Lake, and there are six main tributaries flowing through the watershed area,
137 including five inflowing tributaries, YCR (Yangchang River), MXR (Maxian River), HLR
138 (Houliu River), MBR (Maibao River), THYR (Taohuayuan River), and one draining river,
139 MTR (Maotiao River) (Fig 1). The discharges of YCR and THYR are larger than others
140 among these tributaries. The industrial wastewater pollution constitutes a more serious
141 impact on the water quality of Hongfeng Lake. In particular, the fertilizer plant of Guizhou
142 is the most serious polluting enterprise, it discharges lots N, P into the lake every year.
143 Accordingly, the lake becomes eutrophic in the spring and summer, as evident from the
144 presence of cyanobacteria and alga.

145 **2.2 Sampling**

146 Samples were mainly collected in Aha Lake and Hongfeng Lake and their tributaries
147 (Fig 1). For the Aha Lake, samples were collected at AHLJK (Liang Jiang Kou) as the
148 upstream site and AHDB (Da Ba) as the downstream site. For Hongfeng Lake, samples
149 were collected along the flow direction from south to north, with HFHW (Hou Wu) site of
150 South Lake and HFDB (Da Ba) site of North Lake. The samples were collected with
151 stratified collection at each site; sampling interval with water depth in each site is slightly
152 different, but generally ranged between 3 and 5 meters. Samples of all tributaries were
153 collected at sites near the lake but far away from living areas. All samples were collected
154 in August 2006 (summer) and January 2007 (winter). The alga samples were collected

155 using nylon net from the surface of the Maxian River (MXR).

156 All collection wares used in the field were carefully cleaned. Polyethylene bottles,
157 tubes for sample collectors were all soaked in 6 N HCl (GR) for more than three days and
158 then rinsed with 18.2 Ω Milli-Q water. Bottles for sampling were pre-rinsed with the
159 corresponding water samples three times prior to sampling. A multi-parameter sensor was
160 used for determining the pH, water temperature (T), and DO (dissolved oxygen). Water
161 samples for measurement of Zn isotope composition of SPM were collected in 10 liters
162 polyethylene barrels; water samples for determining the concentration of SPM,
163 concentration of Zn and Al in SPM, and speciation of SPM were collected in 1.5 L
164 polyethylene bottles; water samples for analyzing chlorophyll were collected in 50 ml
165 brown glass bottles with two drops of HgCl_2 to prevent metabolic activity. Samples for
166 analyzing the dissolved Zn were filtered with 0.45 μm Millipore membrane filter in the field
167 and acidified to $\text{pH} < 2$ with ultra-pure HNO_3 . All samples were transported to laboratory as
168 soon as possible after collection.

169 3. Sample preparation for Zn isotope analysis

170 The sample preparation work was carried out in a clean room. All the critical work
171 including sample filtration, digestion and purification was completed in class 100 laminar
172 flow hoods. Hydrochloric acid (HCl) was distilled twice in quartz sub-boiling still,
173 Hydrofluoric acid (HF) and Nitric acid (HNO_3) were distilled with Teflon two-bottle setup.
174 Milli-Q water (18.2 $\text{M}\Omega$) was used throughout the procedures. The filters were treated
175 three times with 1 N HCl (double-distilled), rinsed with Milli-Q water (18.2 $\text{M}\Omega$), and then
176 dried at 50°C in an oven and weighted. After those processes, the blank of filters is as low

177 as 0.001 µg/L and can be negligible.

178 **3.1 Sample preparation**

179 The SPM for measurement of Zn isotope composition was isolated by collecting SPM
180 both deposited either on Millipore HA membrane filter (100 mm, 0.45 µm) or particulate
181 matter that settled at the bottom of the container. The filters with SPM were stored in
182 polyethylene tubes in a fridge. The sample for measuring the concentration of SPM, the
183 speciation of SPM and concentration of Zn and Al in SPM was also filtered through
184 Millipore HA membrane filter (45 mm, 0.45 µm), then dried at 50°C in the oven, and
185 weighed. The volume of water filtered was recorded to calculate the concentration of SPM.

186 Samples for determination of chlorophyll were filtered and chlorophyll quantified following
187 the acetone extraction spectrophotometric method (Barnes et al., 1992). Algae samples
188 were cleaned and dried in a freeze dryer, and then ground to 50 meshes for digestion and
189 $\delta^{66}\text{Zn}$ analysis.

190 The speciation of SPM was determined following a sequential extraction procedure
191 (Tessier, et al, 1979). For this, we only extracted three fractions, including adsorption,
192 exchangeable and carbonate bound (AEC) fraction using pH=2 HCl, bound to organic
193 matter fraction using 30% H₂O₂ (pH=2), and residual fraction. The extracted solution was
194 evaporated on a hot plate and the solid residue was digested, and then all of them were
195 dissolved in 2% HNO₃ for analysis.

196 **3.2 Sample digestion**

197 All SPM and algae samples for zinc isotope measurement, concentration of Zn, Al, and
198 the residual fraction of SPM were digested. These samples were soaked with 3 ml aqua

199 regia and 0.5 ml concentration HF for 48h in acid-cleaned Teflon beakers (7 ml, Savillex).
200 The beakers were placed on a hot plate and dried at 80°C. Another 3 ml aqua regia and
201 0.5 ml concentration HF were added and the closed beaker was placed on a hot plate for
202 72h at 140°C for digestion. The procedure was repeated until the particles were
203 thoroughly digested. After samples were digested thoroughly, solutions of sample were
204 left on the hot plate to dry at 80°C. For the zinc isotope measurement samples, the last
205 step was sequentially repeated three times with 0.5 ml concentrated HCl to eliminate
206 HNO₃ and HF, and then the residue re-dissolved in 7 N HCl+0.001% H₂O₂ for chemical
207 purification. Other samples were just re-dissolved in 2% HNO₃ for analysis.

208 3.3 Chemical purification

209 Chemical purification was carried out using procedures similar to those of Maréchal
210 et al. (1999), Ding et al., (2006) and Tang et al. (2006), with slight modifications. Details
211 are as follow: Anion-exchange chromatography was performed with polypropylene
212 column (Bio-Rad, diameter: 6.8 mm, height 4.3 cm) filled with AG MP-1 resin (Bio-Rad,
213 100–200 mesh, chloride form). The resin was first cleaned with 2 ml 0.5M HNO₃
214 alternating with 10 ml 18.2 MΩ Milli-Q water three times. Then 5 ml Milli-Q water was used
215 to ensure that the HNO₃ was thoroughly removed. The resin was then continuously
216 pre-conditioned with 5 ml 7 N HCl+0.001%H₂O₂ and 4 ml 7 N HCl+0.001%H₂O₂. Then the
217 prepared samples were loaded on the resin and the matrix were striped with 35 ml 7 N
218 HCl+0.001%H₂O₂; Fe was eluted with 20 ml 2 N HCl+0.001%H₂O₂, and Zn was eluted
219 with 10 ml 0.5 N HNO₃. The Zn eluate was evaporated to dry on a hot plate at 80°C and
220 dissolved in 0.1 N HNO₃ to a concentration of 100 to 200 µg/L for isotope analysis. The

221 recoveries of Zn for all samples were nearly 100%, so the Zn isotope fractionation can be
222 avoid during the purification process (Maréchal et al., 2002b). The procedural blanks
223 including digestion, column purification and evaporation were always less than 0.11% of
224 the total Zn extracted from the samples.

225 **3.4 Mass spectrometry**

226 The concentration of dissolved Zn was analyzed on Quadrupole ICP-MS (GV
227 Instruments), and the concentration of Zn and Al in SPM was analyzed on ICP-OES
228 (Varian vista MPX). The Zn isotope composition was analyzed on Nu Plasma instrument
229 HR MC-ICP-MS at Laboratory of isotope Geology, MLR, Institute of Geology, CAGS,
230 Beijing, China. The Zn samples and standard Zn sample, with concentrations ranging
231 from 100 to 200 µg/L in 0.1 N HNO₃, were introduced to the argon plasma via a
232 desolvation nebulizer DSN-100 system, with gas flow rates of 50-100 µL/min. The typical
233 ion beams for 200 µg/L Zn solutions of both standards and samples were 4-6 V on ⁶⁴Zn
234 and the blanks were always below 0.005 V. The standard-sample bracketing (SSB)
235 method has been used throughout the study to minimize the instrumental mass bias and
236 the standard-sample concentrations matched within 5%. The performance of the
237 instrument was assessed by repetitive measurements of an internal lab standard (GSB-Zn)
238 relative to the Zn isotope reference material Romil. The average Zn isotope values for
239 GSB Zn is δ⁶⁶Zn =6.96±0.11‰, δ⁶⁷Zn =10.4±0.23 δ⁶⁸Zn=13.2‰±0.22 (2SD) in high
240 resolution mode under optimized conditions. The long-term instrumental reproducibility
241 defined from the 7 months' replicate analyses are 0.11‰ for δ⁶⁶Zn, 0.23‰ for δ⁶⁷Zn and
242 0.22 for δ⁶⁸Zn. The detailed conditions and the performance of isotope measurements

were described in Li et al. (2008) and Gao et al. (2014).

Zn isotope data was reported in $\delta^x\text{Zn}$ ($\delta^{66}\text{Zn}$, $\delta^{68}\text{Zn}$) as parts per thousand deviations relative to JMC 3-0749. All the $\delta^{64}\text{Zn}$ and $\delta^{66}\text{Zn}$ values obtained in this study followed the theoretical mass-dependent fractionation line, with a formula of $\delta^{68}\text{Zn}=1.976\times\delta^{66}\text{Zn}+0.0005(R^2=0.9998)$.

$$\delta^{66}\text{Zn}_{JMC} = \left[\frac{\left(\frac{{}^{66}\text{Zn}}{{}^{64}\text{Zn}} \right)_{\text{sample}}}{\left(\frac{{}^{66}\text{Zn}}{{}^{64}\text{Zn}} \right)_{JMC}} - 1 \right] \times 1000$$

4. Results

4.1 Temperature, DO (Dissolved Oxygen), pH and chlorophyll in Aha Lake and Hongfeng lakes, and their tributaries.

Environment parameters are summarized in Table 1, and plotted in Figs. 2 and 3. In summer thermal stratification was observed in August with a temperature gradient of ca. 10°C in Aha Lake. The thermoclines were located at a water depth ca. 10m for AHDB and ca. 6m at for AHLJK station. Dissolved oxygen declined sharply below the thermoclines, with average concentration ca.1.2 mg/L in Aha Lake, and there was also a marked decrease in pH of ca. 0.5 units below the thermocline for AHDB profile. However, there were no clear depth-dependent variations in temperature, DO and pH in the winter both for AHDB and AHLJK profiles (Fig 2). Moreover the temperature gradient was ca. 6°C from surface water to thermocline for Hongfeng Lake, and the thermocline was located at a water depth ca. 12m for HFHW station in summer. DO was also almost depleted under the thermocline, with average concentration of 2.0 mg/L, and hypoxic conditions prevailed

264 in summer. There was also marked decrease of ca. 2 units in the deep layers at Hongfeng.
265 However, there were also no clear depth-dependent variations in temperature, dissolved
266 oxygen and pH in the winter for Hongfeng Lake in winter (Fig 3).

267 The concentration of chlorophyll was measured for both Aha Lake and Hongfeng
268 Lake. In summer, the concentration of chlorophyll was very high, reaching 42.1 $\mu\text{g/L}$ at
269 surface water, with marked decreasing to 5.2 $\mu\text{g/L}$ at the bottom for HFHW station, while
270 the concentration of chlorophyll varied from 11.1 to 2.1 $\mu\text{g/L}$ for AHDB station. It is
271 apparent that eutrophication occurred at the surface of Hongfeng Lake in summer (Figs 2
272 and 3).

273 Temperature, DO and pH were also measured for all tributaries. The temperatures of
274 most tributaries were similar to that of the thermocline of the lake, and concentrations of
275 DO for most rivers in summer were lower than in winter.

276 **4.2 SPM concentration, Zn in dissolved and SPM, and speciation Zn in SPM for Aha**
277 **Lake and Hongfeng Lake.**

278 The average concentration of SPM was 1.88 and 2.73 mg/L in summer for AHDB and
279 AHLJK profiles respectively, it was higher than in winter(average is 1.02 and 0.98 mg/L for
280 AHDB and AJLJK respectively), and it decreased with increasing water depth in summer.
281 Similarly, the average concentration of SPM was 2.79 mg/L in summer for HFHW, it was
282 also higher than in winter (average is 1.96 mg/L), and the concentration was higher at the
283 surface than bottom in summer (Tables 1 and 2, Figs 2 and 3.).

284 Dissolved Zn ranged from 0.65 to 5.06 $\mu\text{g/L}$ and 0.74 to 12.04 $\mu\text{g/L}$ for Aha Lake and
285 Hongfeng Lake respectively, the SPM-Zn ranged from 0.18 to 0.70 mg/g and 0.24 to 0.75

286 mg/g (Figs 2 and 3). Generally speaking, the concentration of Zn in Hongfeng Lake was
287 higher than in Aha Lake, but dissolved Zn concentration did not exceed regulatory limits in
288 both lakes, in contrast to Yellow River and Greece Kalloni bay (Hong et al, 2006; Gaverill
289 et al., 2005). Dissolved Zn was slightly higher in winter than in summer, but there was no
290 significant variation with water depth for Aha Lake. Meanwhile, average of SPM-Zn in
291 summer was very similar to that in winter. Dissolved Zn in winter was higher than in
292 summer for Hong Lake, which was similar to Aha Lake; while average of SPM Zn in
293 summer was slightly higher than in winter for Hongfeng Lake (Fig 2 and 3).

294 The speciation of Zn in SPM also was determined. It was found that AEC-bound Zn
295 ranged from 57.4 to 94.7% and 29.1 to 90.1% for Aha and Hongfeng Lake respectively
296 (table2 and Fig4). The percentage of organic bound Zn averaged 17.1% in summer,
297 higher than average 7.4% in winter for AHDB station. In addition, the percentage of
298 organic bound Zn reached 53.1% at subsurface water and averaged 14% in summer for
299 HWFW station, higher than the average 7.4% in winter at Hongfeng Lake, which is
300 analogous to HFHW station.

301 Concentration of SPM, dissolved Zn and SPM-Zn varied significantly in time and
302 space (Table 3). For Aha Lake, SR and YYR had the higher SPM (78.03 mg/L and 65.93
303 mg/L) and YYR (18.07 $\mu\text{g/L}$) had the highest dissolved Zn content than other rivers. The
304 concentrations of SPM and dissolved Zn in summer were higher than in winter for most
305 rivers, and concentration of SPM-Zn varies between summer and winter. In addition,
306 average dissolved Zn (5.3 $\mu\text{g/L}$) and SPM-Zn (0.51 mg/g) of Aha tributaries were higher
307 than Aha Lake (2.03 $\mu\text{g/L}$ and 0.36 mg/g, respectively). For Hongfeng Lake, THYR had

highest SPM (9.4 mg/L) and dissolved Zn content (14.78 $\mu\text{g/L}$) concentration than other rivers. The concentration of dissolved Zn in winter was higher than in summer for most of rivers, and THYR also had the highest SPM-Zn content (2.9 mg/g). Moreover, average dissolved Zn (4.63 $\mu\text{g/L}$) in Aha lake was similar to that in Hongfeng Lake (5.73 $\mu\text{g/L}$), but average SPM-Zn (0.70 mg/g) was higher than in the Hongfeng lake (0.40 mg/g).

4.3 Zn isotope composition in Hongfeng, Aha lakes and their tributaries

The Zn isotope composition of SPM varied significantly in time and space. Generally speaking, $\delta^{66}\text{Zn}$ of SPM ranged from -0.29‰ to 0.55‰ for these samples which collected from Aha Lake and Hongfeng Lake and their tributaries, the variation is about 9-10 times compared to precision of determination. This falls largely within the previously determined isotope range of particle Zn from Greifen Lake (-0.66‰ to 0.21‰) and Seine river (-0.08‰ to 0.30‰), but slightly lighter than terrestrial geological material (0.4‰ to 1.4‰)(Peel et al., 2009; Chen et al., 2009; Cloquet et al., 2006; litter et al., 2016). All the $\delta^{66}\text{Zn}$ data for SPM from Aha Lake and Hongfeng Lake are given in Table 1 and $\delta^{66}\text{Zn}$ data for SPM from tributaries are given in Table 3.

The Zn isotope composition of SPM for Aha Lake ranged from -0.18‰ to 0.27‰, slightly lighter than Aha tributaries. The Zn isotope composition in the summer (-0.18‰ to 0.19‰) was lighter than in winter (0.03‰ to 0.27‰) for Aha Lake. The Zn isotope composition of SPM for Hongfeng Lake ranged from -0.29‰ to 0.26‰, and it was also slightly lighter than the Zn isotope composition of SPM in Hongfeng tributaries (-0.04‰ to 0.48‰). Similarly, the $\delta^{66}\text{Zn}$ varied from -0.29‰ to 0.20‰ for Hongfeng Lake in summer, also slightly lighter than the $\delta^{66}\text{Zn}$ in winter (Figs 2, 3, Table 1).

For Aha Lake, there were no discernible trends with increasing water depth both in AHDB and HALJK stations in winter, but it was apparent that the heavier $\delta^{66}\text{Zn}$ appeared at the surface for AHDB, which was similar to the HFHW in summer. Whereas, there was also a clear increase of $\delta^{66}\text{Zn}$ with water depth for AHLJK station in summer. For the Hongfeng Lake, there were no clear trends with depth in winter for both sites HFHW and HFDB. However, a pronounced decrease of $\delta^{66}\text{Zn}$ was observed with increasing water depth to -0.29‰ at a depth of 12 m in summer at HFHW station. Lower $\delta^{66}\text{Zn}$ appeared at the thermocline while the higher $\delta^{66}\text{Zn}$ appeared at the surface. This trend was similar to that of particles collected from Atlantic and Pacific Oceans (Maréchal et al., 2000).

The Zn isotope of SPM in tributaries also varied significantly in time and space. For Aha Lake, the $\delta^{66}\text{Zn}$ of YYR and BYR were -0.09‰ and -0.17‰ in summer respectively, which were isotopically light relative to sphalerite (0.02‰ to 0.44‰), but same as the pyrite (-0.19‰ to -0.19‰) (Maréchal et al., 1999). In addition, YYR and BYR have lighter $\delta^{66}\text{Zn}$ in summer than in winter. However, the $\delta^{66}\text{Zn}$ of CCR was 0.34‰ in summer, which was isotopically heavier than in winter (0.10‰). For the only draining river of the Aha Lake, XCR had similar $\delta^{66}\text{Zn}$ value in summer and winter.

For Hongfeng Lake, THYR and YCR had slightly heavier Zn isotope of 0.40‰ in summer than in winter (0.25‰ and 0.04‰), and the $\delta^{66}\text{Zn}$ of MXR in summer (0.30‰) was slight lighter than in winter (0.48‰) in contrast. Moreover the MTR and HLR had similar $\delta^{66}\text{Zn}$ value in summer and winter. Two algae samples had similar Zn isotope composition of 0.41‰ and 0.40‰ respectively, and the $\delta^{66}\text{Zn}$ of algae collected from MXR was 0.21‰.

5. Discussion

SPM in lake water is mainly supplied by fluvial input, plankton and inorganic materials produced within the lake (autochthonous material), and sediment resuspension (Hakanson and peters, 1995, Sigg et al., 1995; Riemann et al., 2005). Aha Lake and Hongfeng Lake have surface area of 4.5 km² and 57.2 km², water depth of 14 to 24 m and 10 to 45 m respectively, as well as temperature gradients of >10 °C (Fig 2 and 3), which implied that wind induced resuspension of sediment will have limited contributions. Furthermore, Aha and Hongfeng both are seasonal anoxic lakes, therefore our discussion will focus on fluvial, plankton and seasonal anoxic controls.

5.1 Effect of Zn fluvial input from Tributaries on $\delta^{66}\text{Zn}$ of SPM

The Zn contents were normalized to Al to determine Zn enrichment due to non-detrital inputs since Al concentration is a good indicator of detrital input (Chen et al., 2009). Here we investigated the relation between $\delta^{66}\text{Zn}$ and Zn/Al (Fig 5). The Zn/Al ratio of Aha Lake ranged from 0.007 to 0.153 and average was 0.045, it was much higher than Zn/Al in Hongfeng Lake (average was 0.0145), and indicating SPM Zn was more enriched in Aha Lake than in Hongfeng Lake.

For the Aha Lake, including AHDB and AHLJK Profile in summer, a clear negative relationship between $\delta^{66}\text{Zn}$ and Zn/Al can be observed (Fig 5). Samples in summer showed higher Zn/Al ratio and lighter Zn isotope composition, whereas samples in winter showed lower Zn/Al ratio and heavier Zn isotope composition. As the discharge of YYR, BYR and SR are relatively bigger than other rivers, the $\delta^{66}\text{Zn}$ of SPM for Aha Lake maybe controlled by these rivers. The discharge (1.18 m³/s) of YYR is largest of any other rivers, and it mainly contaminated by coal mine and with bigger discharge and high SPM

concentration, displays a higher Zn/Al and lighter Zn isotope in summer, and represents the detrital input from the coal mine, thus the $\delta^{66}\text{Zn}$ of SPM maybe effected by inputting of the YYR with the coal mine. By contrast, SR displayed lower Zn/Al ratio and heavier Zn isotope, and represents input from domestic and industrial activities, Its $\delta^{66}\text{Zn}$ (0.05‰ and 0.29‰) were close to anthropogenic samples, ranging from 0.08‰ to 0.31‰ (Chen et al., 2009). Comparing the discharge and concentration of SPM of SR (0.83 m³/s and 78.03 mg/L respectively) river with BYR (0.90 m³/s and 4.53 mg/L) (Table 2), shows that the discharge of them were similar, but the concentration of SPM of SR was almost 18 times higher than BYR. Therefore the main SPM source was likely to be SR, and $\delta^{66}\text{Zn}$ of SPM likely to be affected by the inputting of SR with domestic and industrial waste water. Consequently, $\delta^{66}\text{Zn}$ of SPM for Aha Lake mainly be affected by mixing of YYR and SR process (Fig 5).

We further investigated the relationship between $\delta^{66}\text{Zn}$ of SPM and the Residual Zn of SPM (Fig 6), since the residual fraction of metals comes mainly from primary and secondary minerals in which trace metals are not expected to be released in solution over a reasonable time under natural conditions (Tessier et al., 1979). Thus, the residual form of SPM may represent the material from background or terrigenous sediment (Ödman et al, 1999; Turner and Millward, 2002; Tessier, 1979).

We can see clearly that there was linear relationship between Zn isotope composition and residual fraction of Zn in Aha Lake (Fig 6). There were a positive relationship between Zn isotope composition and residual fraction of Zn in summer for AHDB, and a negative relationship in summer and positive relationship in winter for AHLJK. Although there were

little data, and they are not significantly correlated with each other, we still can obtain some information from these data. As mentioned above, the main input tributarie was SR for AHDB profile, therefore the main SPM source of AHDB is likely to be SR. According to the Zn isotope composition of SR (0.29‰) and AHDB profile (-0.05‰ to 0.19‰), the Zn isotopic composition of SR are heavier than AHDB profile in summer, thus it lead to positive relationship between Zn isotope composition and residual Zn at AHDB. Consequently, we can draw the Zn isotope composition of SPM for AHDB was mainly affected by input of SR. Similarly, YYR was the main source of AHLK profile according the table 3. Comparing the Zn isotope composition of YYR in summer (-0.09‰) to that in winter (0.46‰), we can obtain that YYR had light Zn isotopes in summer and acts as a heavy Zn isotope source in winter, consistent with a negative correlation in summer and positive correlation between $\delta^{66}\text{Zn}$ and Zn/Al in winter for AHLJK profile(Fig 6). Accordingly we can draw the Zn isotope composition of SPM for AHLJK was mainly affected by inputting of YYR. These conclusions were agree with these from the relation between $\delta^{66}\text{Zn}$ and Zn/Al of SPM, and further approved that Zn isotope composition of Aha Lake was mainly affected by SR and YYR, and it is a mixing of endmember process.

By contrast, there was no correlation between Zn/Al and Zn isotope composition of SPM in HFHW and HFDB both in summer and winter and there were no significant variations of Zn/Al ratio for all samples in Hongfeng Lake. Furthermore, there still was no clear correlation between $\delta^{66}\text{Zn}$ and residual Zn of SPM in Hongfeng Lake

The $\delta^{66}\text{Zn}$ of MXR, THYR and YCR in summer were isotopically heavier than $\delta^{66}\text{Zn}$ in Hongfeng lake, however there was no clear relationship between tributaries and the

418 Hongfeng Lake (Fig5 and Fig6). Therefore there was no significant effect on Zn isotope
419 composition come from fluvial input in Hongfeng Lake.

420 From above discussion, we accordingly draw the conclusion that Zn isotope
421 composition at Aha Lake was mainly controlled by inputting of YYR with coal mine input
422 and SR with the domestic and industrial particulate input, whereas the Zn isotope
423 composition was not necessarily affect by fluvial inputting for Hongfeng Lake.

424 5.2 Effect of algal activities on Zn $\delta^{66}\text{Zn}$ of SPM

425 The $\delta^{66}\text{Zn}$ of SPM depth profile above the thermocline at HFHW profile in summer
426 showed surface SPM had the heaviest Zn isotope composition, and $\delta^{66}\text{Zn}$ gradually
427 decreasing with depth. Similarly for AHDB profile, the heaviest $\delta^{66}\text{Zn}$ of SPM appeared at
428 the surface in summer, and then there was a drop at the sub-surface. These similar
429 phenomena that $\delta^{66}\text{Zn}$ decreased with depth were found for particle samples in Central
430 Atlantic Ocean (Maréchal et al., 2000), and that $\delta^{66}\text{Zn}$ of seawater decreased with water
431 depth above 100 m in the North east Pacific Ocean (Bermin et al., 2006), were thought to
432 be mainly related to the activity of phytoplankton. In addition, the $\delta^{66}\text{Zn}$ of seawater
433 increased with water depth in North Atlantic Ocean, it was also related to phytoplankton
434 and organic matter (John et al., 2014).

435 In summer, the lake water was stratified; the temperature, pH and dissolved oxygen
436 decrease with depth, and the algal proliferate in the surface water of Hongfeng Lake (Fig
437 3). Therefore, the variation in $\delta^{66}\text{Zn}$ in Hongfeng Lake may be related to the algal
438 activities.

439 Zn isotope fractionation by biological processes occurs by preferential adsorption of

the heavy Zn isotope onto the surface of diatoms, and by the preferential incorporation of the light isotope into biological material (Gélabert et al., 2006; Weiss et al., 2005). Hence, we examined whether there was a correlation between Zn isotope composition and chlorophyll, as chlorophyll is an important indicator of primary producers of phytoplankton biomass, and is the main pigment of photosynthetic phytoplankton (Reynold, 1984; Kasprzak et al., 2008) .

Figure 7 showed that that when the concentration of chlorophyll was low in winter, the Zn isotope composition of SPM was heavy, when concentration of chlorophyll was high in summer, the Zn isotope composition of SPM was light($\Delta\delta^{66}\text{Zn}_{\text{winter}-\text{summer}}=0.17\text{‰}$ for Aha Lake, $\Delta\delta^{66}\text{Zn}_{\text{winter}-\text{summer}}=0.07\text{‰}$ for Hongfeng Lake). Moreover, a significant positive relationship was evident between $\delta^{66}\text{Zn}$ and chlorophyll at HFHW profile in summer, and there was no relationship between $\delta^{66}\text{Zn}$ and chlorophyll in AHDB and AHLJK profiles in summer. It was notable that the biomass of phytoplankton in Hongfeng Lake was much higher than in Aha Lake in summer (Fig. 7), suggesting that phytoplankton play a major role in controlling Zn isotope variability for Hongfeng Lake in summer.

How the algae affect the Zn isotope composition during the biogeochemical process remains unclear? Maréchal et al (2000) thought $\delta^{66}\text{Zn}$ of particle decreasing from surface to bottom may be caused by activity of phytoplankton and remineralization, and John was aware that the incorporation by phytoplankton mainly accounts for the $\delta^{66}\text{Zn}$ of seawater increasing with the depth of water(John et al., 2014). At here, we can discuss from absorption and adsorption processes to explain the Zn isotope variation of SPM for Hongfeng Lake in summer, and to compare which one is the major control factor.

Firstly, the Zn isotope composition of SPM in Hongfeng Lake in summer whether affected by incorporation into algal process? On one hand, as algal incorporation is expected to produce lighter Zn isotope composition of SPM in surface water relative to bottom water according to other research (Gélabert et al., 2006; Weiss et al., 2005). However, our data showed that the Zn isotope of SPM at surface water was heavier than bottom water at HFHW and AHDB in summer (Figs 2 and 3). Hence it was contradictory that absorption was major control factor on the Zn isotope composition. On the other hand, Organic-bound Zn was 12.53% on average, which is much lower than AEC-bound Zn (69.87% on average) (Fig 4), and this further illustrates that effect of algal absorption process on the Zn isotope is minor than adsorption process.

Secondly, the Zn isotope composition was possible affected by the adsorption onto the surface of algae. AEC-bound Zn accounts for 69.87% of the total SPM Zn (Table 2) for HFHW profile, which indicated the Zn isotope composition of SPM being controlled by adsorption process. Generally speaking, the adsorption processes contain abiotic adsorption onto the mineral particle (goethite, hematite and birnessite) and biotic adsorption onto the surface of phytoplankton (Pokrovsky et al., 2005a, b; Gélabert et al., 2006; Weiss et al., 2005). The Zn isotope fractionation exceeds 0.5‰ from surface water to deeper water at HFHW profile, as Zn isotope fractionation does not exceed 0.5‰ during adsorption onto most mineral particles (Pokrovsky et al., 2005; Guinoiseau et al., 2016), thus adsorption onto abiotic surfaces was not the main cause for the variation in Zn isotope composition, whereas adsorption onto algae can be the major factor. Zn isotope can be fractionated during preferential adsorption heavy Zn onto diatoms and plankton

(Maréchal et al., 2000; Pokrovsky et al., 2005; Gélabert et al., 2006; Balistrieri et al., 2008; Juillot et al., 2008). This occurs because during adsorption onto diatoms surfaces, Zn reduces its coordination number from six (octahedrally coordinated to H₂O in bulk solution) to four (oxygen and nitrogen tetracoordinated complexes), so the bond distance becomes shorter while bond strength increases, hence the heavy isotope preference join with stronger metal binding species (Criss, et al., 1999; Young and Ruiz et a., 2003). Therefore, an increase of alga led to heavier Zn isotope composition at surface of HFHW in summer (Fig.3). In addition, the $\delta^{66}\text{Zn}$ of alga in MXR ranged from 0.21 to 0.41‰ (table2), and it was isotope heavier than in Hongfeng Lake, also can explained by adsorption process. Consequently, adsorption onto alga is the major effect factor for the Zn isotope composition in Hongfeng Lake in summer.

For Aha Lake, algal biomass was relatively small in summer, so there was no relationship between Zn isotope composition and chlorophyll. However, this interpretation remains to be confirmed given that our data were reported firstly for lake water column. In the absence of isotope data on dissolved Zn due to the low concentration, it is premature to argue about whether isotope fractionation between biologic particles and lake water takes place at equilibrium or by purely kinetic control. Therefore, much work is still required to develop a full understanding of the use of Zn isotope in lake biogeochemistry and material recycling processes.

5.3 The effect of seasonal anoxia and ZnS predicated on Zn isotope composition.

So far, we can conclude from sections 5.1 and 5.2 that Zn isotope composition was mainly affected by the tributary input for Aha Lake, whereas the Zn isotope composition

for Hongfeng Lake was mainly affected by algal adsorption. However, we saw in Fig 3 that the Zn isotope composition of SPM in summer was lighter than in winter for both Hongfeng and Aha Lakes. This result was very similar to $\delta^{66}\text{Zn}$ seasonal variation in SPM from Lake Greifen, Switzerland (Peel et al., 2009), and $\delta^{56}\text{Fe}$ value of SPM were also lower in summer than in winter in Aha Lake (Song et al., 2011). Nevertheless, both of the tributary input and algal adsorption can't account for this phenomenon. Instead, it implied that the Zn isotope composition of Hongfeng and Aha Lake in summer may be affected by another factor.

As previous studies that Zn isotope can fractionation during process of sphalerite precipitation, and sphalerite preferential incorporation of light Zn isotope (Archer et al., 2004; Wilkinson et al., 2005; Kelley et al., 2004; John et al., 2008; Fujii et al., 2011 & 2012). Archer investigated that ZnS precipitated in an anoxic environment at room temperature can fractionate the Zn isotope, and the $\Delta\delta^{66}\text{Zn}_{\text{ZnS-dissolved}} = 0.36\text{‰}$. (Archer et al., 2004); Wilkinson and Gagnevin also found the rapid sphalerite precipitation from the fluid or ore system result in light Zn isotope (Wilkinson et al., 2005; Gagnevin et al., 2012; Kelley et al., 2009); John studied that subsurface cooling of hydrothermal fluids leads to precipitation of isotopically light sphalerite (Zn sulfide), and this process is a primary cause of Zn isotope variation in hydrothermal fluids (John et al., 2008); Fujii investigated the $\delta^{66}\text{Zn}$ in different species, like aqueous sulfide, chloride, and carbonated species using ab initio methods, and negative $\delta^{66}\text{Zn}$ down to at least -0.6‰ can be expected in sulfides precipitated from solution with $\text{pH} > 9$ (Fujii et al., 2011 & 2012).

Aha Lake and Hongfeng Lake both are seasonal anoxic lakes. The concentration of

DO (dissolved oxygen) were range from 1.60 to 7.80 mg/L, and average was 4.2 mg/L for Aha Lake in summer, which was much lower than in winter(the concentration of DO were range from 7.7 to 9.0 mg/L and average is 8.6 mg/L). For Hongfeng Lake, The concentration of DO were range from 1.0 to 8.1 mg/L and average was 3.6 mg/L in summer, which was also much lower than in winter(average was 12.7 mg/L). In addition, the concentration of DO deceased from surface to bottom rapidly for all profiles(AHDB, AHLJK, HFHW and HFDB), and the DO only 1.0 mg/L and depth of 15 m in HFHW in summer, the bottom of Lakes were depleted oxygen in summer. This seasonal anoxic characteristic was also appeared in Baihua Lake and Black Sea (Bai et al., 1996; Sun and Wakeham, 1994). At this anoxic condition in summer, SRB (sulfate reducing bacterial) can reduce the SO_4^{2-} to S^{2-} (Sass et al., 1997; Bailey et a., 2017), thus Zn can be precipitated from the water, and exist as the species of the sphalerite (ZnS) in the SPM, and this can be approved by the concentration of dissolved Zn was lower in summer than in winter (Fig2 and Fig3). As discussed above, The sphalerite (ZnS) preferential incorporated the light Zn isotope during the precipitation process, therefore the Zn isotope composition of SPM should be light in summer than in winter, and this conclusion coupled with our $\delta^{66}\text{Zn}$ data for both Aha Lake and Hongfeng Lake. This maybe account for why the $\delta^{66}\text{Zn}$ in summer was lower than in winter.

6. Conclusion

This study described seasonal variation of $\delta^{66}\text{Zn}$ values for Hongfeng and Aha Lakes, as well as data for tributaries and biological samples, and arrived following conclusions.

Concentration of dissolved Zn ranged from 0.65 to 5.06 $\mu\text{g/L}$ and 0.74 to 12.04 $\mu\text{g/L}$ for Aha and Hongfeng Lake respectively, while the SPM-Zn ranged from 0.18 to 0.70 mg/g and 0.24 to 0.75 mg/g for Aha and Hongfeng Lake respectively. The $\delta^{66}\text{Zn}$ of SPM ranged from -0.29‰ to 0.26‰ for the Hongfeng Lake and its tributaries respectively, the $\delta^{66}\text{Zn}$ of SPM ranged from -0.18‰ to 0.27‰ and -0.17‰ to 0.46‰ for the Aha Lake and its tributaries, displaying a wider range in tributaries than lakes.

From the relation of $\delta^{66}\text{Zn}$ versus Zn/Al and $\delta^{66}\text{Zn}$ versus residual-bond Zn, we conclude that Zn isotope composition of Aha Lake is mainly affected by SR and YYR, and it is a mixing of endmember process. Discussion the relation of $\delta^{66}\text{Zn}$ versus chlorophyll and proportion of AEC-bond Zn, it suggests that Zn isotope composition of Hongfeng Lake mainly controlled by the adsorption process of algae. As sphalerite (ZnS) preferential incorporated the light Zn isotope during the precipitation process, this can account for why the $\delta^{66}\text{Zn}$ in summer is lower than in winter.

In summary, Zn isotopes composition in Aha Lake and Hongfeng Lake are reported firstly, and the major affect factors are discussed, this providing the basic information of Zn isotope in lake system, and promoting the application of Zn isotope in biogeochemistry.

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575 **References**

576 Archer, C.D., Vance, D., Butler, I., 2004. Zn isotopes fractionation upon sorption and
577 precipitation. Goldschmidt Conference Abstracts 68, A325.

578 Alloway, B.J., 2004. Zinc in soil and Crop Nutrition. Belgium: International Zinc Association
579 Brussels, Belgium.

580 Andreini, C., Banci, L., Bertini, I., Rosato, A., 2006. Counting the zinc-proteins encoded in
581 the human genome. J. Proteome Res. 5(1), 196–201.

582 Bai, Z.G., Wu, F.C., Zou, W.X., Qing, S., Jiang, W.G., 1996. Mechanism of seasonal
583 deterioration of water quality in Lake Baihua, China. Chinese Journal of
584 Geochemistry 15, 185-188.

585 Bailey, L.T., Mitchell, C.P.J., Engstrom, D.R., Berndt, M.E., Coleman Wasik, J.K., Johnson,
586 N.W., 2017. Influence of pore water sulfide on methylmercury production and
587 partitioning in sulfate-impacted lake sediments. Science of the Total Environment 580,
588 1197-1204.

589 Balistrieri, L.S., Borrok, D.M., Wanty, R.B., Ridley, W.I., 2008. Fractionation of Cu and Zn
590 Isotopes During Adsorption onto Amorphous Fe(II) Oxyhydroxide: Experimental
591 Mixing of Acid Rock Drainage and Ambient River Water. Geochimica et
592 Cosmochimica Acta 72(2), 311-328.

593 Barnes, J.D., Balaguer, L., Manrique, E., Elvira, S., Davison, A.W., 1992. A reappraisal of

- the use of DMSO for the extraction and determination of chlorophylls a and b in lichens and higher plants. *Environmental and Experimental Botany*, 32(2), 85-100.
- Beard, B.L., Johnson, C.M., Skulan, J.L., Nealson, K.H., Cox, L., Sun, H., 2003. Application of Fe isotopes to tracing the geochemical and biological cycling of Fe. *Chemical Geology*, 195, 87–117.
- Bermin, J., Vance, D., Archer, C., Statham P.J., 2006. The Determination of the Isotopic Composition of Cu and Zn in Seawater. *Chemical Geology*, 226, (3-4): 280-297.
- Bigalke, M., Weyer, S., Kobza, J., Wilcke, W., 2010. Stable Cu and Zn Isotope Ratios as Tracers of Sources and Transport of Cu and Zn in Contaminated Soil. *Geochimica et Cosmochimica Acta* 74, (23): 6801-6813.
- Blättler, C.L., Miller, N.R., Higgins, J.A., 2015. Mg and Ca Isotope Signatures of Authigenic Dolomite in Siliceous Deep-Sea Sediments. *Earth and Planetary Science, Letters* 419: 32-42.
- Borrok, D.M., Nimick, D.A., Wanty, R.B., Ridley W.I., 2008. Isotopic Variations of Dissolved Copper and Zinc in Stream Waters Affected by Historical Mining. *Geochimica et Cosmochimica Acta* 72, (2), 329-344.
- Brand, L.E., Sunda, W.G., Guillard, R.R.L., 1983. Limitation of marine phytoplankton reproductive rates by zinc, manganese, and iron. *Limnol. Oceanol.* 28 (6), 1182–1198.
- Brown, P.H., Cakmak, I., Zhang, G., 1993. Form and function of zinc in plants. In: Robson, A.D. (Ed.), *Zn in soils and plants*. Kluwer Academic Publishers, pp. 93–106.
- Bryan, A.L., Dong, S., Wilkes, E.B., Wasylenki, L.E., 2015. Zinc isotope fractionation

616 during adsorption onto Mn oxyhydroxide at low and high ionic strength. *Geochimica*
617 *et Cosmochimica Acta* 157, 182-197.

618 Budd, P., Lythgoe, P., McGill, R.A.R., Pollard, A.M., Scaife, B., 1999. Zinc Isotope
619 Fractionation in Liquid Brass (Cu-Zn) Alloy: Potential Environmental and
620 Archaeological Applications." *Geological Society London Special Publications* 165,
621 (1): 147-153.

622 Cacaly, S., Marechal, C., Juillot, F., Guyot, F., Benedetti, M., 2004. Zn Isotopes
623 Fractionation Upon Sorption and Precipitation. *Goldschmidt Conference Abstracts* 68,
624 (11): A366.

625 Chen, J.B., Jérôme, G., Pascale, L., Sylvain, H., 2009. Zn Isotopes in the Suspended
626 Load of the Seine River, France: Isotopic Variations and Source Determination.
627 *Geochimica et Cosmochimica Acta*, 73, (14): 4060-4076.

628 Cloquet, C., Carignan, J., Libourel, G., 2006. Isotopic Composition of Zn and Pb
629 Atmospheric Depositions in an Urban/Peri-Urban Area of Northeastern France.
630 *Environmental science & technology* 40, (21), 6594-6600.

631 Criss, R.E, 1999. *Principles of Stable Isotope Distribution*: Oxford University Press New
632 York.

633 Ding, X., Nomura, M., Suzuki, T., Sugiyama, Y., Kaneshiki, T., and Fujii, Y., 2006.
634 Chromatographic Zinc Isotope Separation by Phenol Formaldehyde Benzo Crown
635 Resin. *Journal of Chromatography*, 1113, (1): 182-185.

636 Dolgoplova, A., Weiss, D.J., Seltnann, R., Kober, B., Mason, T.F.D., Coles, B., Stanley,
637 C. J., 2006. Use of Isotope Ratios to Assess Sources of Pb and Zn Dispersed in the

- 638 Environment During Mining and Ore Processing within the Orlovka–Spokoinoe
639 Mining Site (Russia). *Applied Geochemistry*, 21 (4), 563-579.
- 640 Fujii, T., Moynier, F., Pons, M.L., Albarède, F., 2011. The origin of Zn isotope fractionation
641 in sulfides. *Geochimica et Cosmochimica Acta* 75, 7632-7643.
- 642 Fujii, T., Albarede, F., 2012. Ab initio calculation of the Zn isotope effect in phosphates,
643 citrates, and malates and applications to plants and soil. *PloS one* 7, 2, e30726, 1-5.
- 644 Frausto J.J.R. *Chemistry of Elements: The Inorganic Chemistry of Life*, Clarendon Press,
645 Oxford, 1991, 206 pp.
- 646 Gagnevin, D., Boyce, A.J., Barrie, C.D., Menuge, J.F., Blakeman, R.J., 2012. Zn, Fe and S
647 isotope fractionation in a large hydrothermal system. *Geochimica et Cosmochimica*
648 *Acta* 88, 183-198.
- 649 Gao, Z.F., Zhu, X.K., 2014. Lateral Variation of Zinc Isotopes in Dongshengmiao Ore
650 Deposit, Inner Mongolia, China. *Acta Geologica Sinica (English Edition)*, 88,
651 1563-1564.
- 652 Gavrill, A.M., Angelidis, M.O., 2005. Metal and organic carbon distribution in water column
653 of a shallow enclosed Bay at the Aegean Sea Archipelago: Kalloni Bay, island of
654 Lesbos, Greece. *Estuarine, Coastal and Shelf Science*, 2005, (64), 200-210.
- 655 Gélalbert, A., Pokrovsky, O.S., Viers, J., Schott, J., Boudou, A., Feurtet-Mazel, A., 2006.
656 Interaction between Zinc and Freshwater and Marine Diatom Species: Surface
657 Complexation and Zn Isotope Fractionation. *Geochimica et Cosmochimica Acta*, 70
658 (4), 839-857.
- 659 Guinoiseau, D., Gelalbert, A., Moureau, J., Louvat, P., Benedetti, M.F., 2016. Zn Isotope

660 Fractionation during Sorption onto Kaolinite. *Environ Sci Technol* 50, 1844-1852.

661 Håkanson, L., Peters, R.H., 1995. *Predictive Limnology Methods for Predictive Modelling*.
662 SPC Academic Publishing, Amsterdam, pp. 1–464.

663 Hambidge, M., 2000. Zinc and health: current status and future directions. *Nutrition*. 130,
664 1344–1349.

665 Hong, S., Chen, J.S., Cheng, B.Q., 2006. Research on Suspended Matter and Sediment
666 Quality Criteria for Metals in Yellow River Using Equilibrium Partitioning-biological
667 Effect Approach. *Journal of Wuhan university of technology*, 28(12), 61-65.

668 Hutchinson, G.E.A., 1957. *Treatise on Limnology, Introduction to Lake biology and*
669 *limnoplankton*. New York: John Wiley & Sons, 1115.

670 John, S.G., Bergquist, B.A., Boyle, E.A., 2004. Zinc isotope variations in natural and
671 cultured marine phytoplankton. *AGU Fall Meeting Abstract*, vo53B, 04.

672 John, S.G., Rouxel, O.J., Craddock, P.R., Engwall, A.M., Boyle, E.A., 2008. Zinc stable
673 isotopes in seafloor hydrothermal vent fluids and chimneys. *Earth and Planetary*
674 *Science Letters* 269, 17-28.

675 John, S.G., Conway, T.M., 2014. A Role for Scavenging in the Marine Biogeochemical
676 Cycling of Zinc and Zinc Isotopes. *Earth and Planetary Science Letters*, 394,
677 159-167.

678 John, S.G., Rouxel, O.J., Craddock, P.R., Engwall, A.M., Boyle, E.A., 2008. Zinc stable
679 isotopes in seafloor hydrothermal vent fluids and chimneys. *Earth and Planetary*
680 *Science Letters* 269, 17-28.

681 Juillot, F., Maréchal, C., Ponthieu, M., Cacaly, S., Morin, G., Benedetti, M., Hazemann, J.

- 682 L., Proux, O., Guyot, F., 2008. Zn Isotopic Fractionation Caused by Sorption on
683 Goethite and 2-Lines Ferrihydrite. *Geochimica et Cosmochimica Acta*, 72, (19),
684 4886-4900.
- 685 Kafantaris, F.A., Borrok, D.M., 2014. Zinc Isotope Fractionation During Surface Adsorption
686 and Intracellular Incorporation by Bacteria. *Chemical Geology*, 366, 42-51.
- 687 Kasprzak, P., Judit, P., Rainer, K., Lothar, K., Frank, G., 2008. Chlorophyll a Concentration
688 across a Trophic Gradient of Lakes: An Estimator of Phytoplankton Biomass.
689 *Limnologia - Ecology and Management of Inland Waters*, 38, (3–4), 327-338.
- 690 Kelley, K., Wilkinson, J., Chapman, J., Crowther, H., Weiss, D., 2009. Zinc isotopes in
691 sphalerite from base metal deposits in the Red Dog district, Northern Alaska.
692 *Economic Geology* 104, 767-773.
- 693 Li, D.D., Liu, S.A., Li S.G., 2015. Copper Isotope Fractionation During Adsorption onto
694 Kaolinite: Experimental Approach and Applications. *Chemical Geology*, 396, 74-82.
- 695 Li, S.Z., Zhu X.K., Tang, S.H, He X.X., Cai, J.J., 2008. The application of MC-ICP-MS to
696 high-resolution measurement of Zn isotope ratios. *Acta Petrologica Et Mineralogica*,
697 27(4), 273-278.(In chinese with English abstract)
- 698 Lippard, S.J., Berg, J.M., 1994. *Principles of Bioinorganic Chemistry*, University Science
699 Books, Mill Valley, 411.
- 700 Little, S.H., Vance, D., Mcmanus, J., Severmann, S., 2016. Key role of continental margin
701 sediments in the oceanic mass balance of Zn and Zn isotopes. *Geology* 44, 207-210.
- 702 Luck, J.M., Ben, O.D., Albarède, F., Telouk, P., 1999. Pb, Zn and Cu Isotopic Variations
703 and Trace Elements in Rain. *Proc. 5th Int. Symp. Geochemistry of the Earth's*

704 Surface, 199–202.

705 Maréchal, C.N., Telouk, P., Albarede, F., 1999. Precise Analysis of Copper and Zinc
706 Isotopic Compositions by Plasma-Source Mass Spectrometry. *Chemical Geology*, 156,
707 251–273.

708 Maréchal, C.N., Emmanuel, N., Chantal, D., Francis, A., 2000. Abundance of Zinc Isotope
709 as a Marine Biogeochemical Tracer. *Geochemistry, Geophysics, Geosystems* 1,
710 1999GC00029.

711 Maréchal, C.N., and Sheppard, S.M.F., 2002a. Isotopic Fractionation of Cu and Zn
712 between Chloride and Nitrate Solutions and Malachite or Smithsonite at 30 Degrees
713 and 50 Degrees C. In *Geochimica et Cosmochimica Acta*, 66, A484.

714 Maréchal, C.N., and Francis, A., 2002b. Ion-Exchange Fractionation of Copper and Zinc
715 Isotopes. *Geochimica et Cosmochimica Acta*, 66, (9), 1499-1509.

716 Mason, T.F.D., Weiss, D.J., Chapman, J.B., Wilkinson, J.J., Tessalina, S.G., Spiro, B.,
717 Horstwood, M.S.A., Spratt, J., Coles, B.J., 2005. Zn and Cu isotopic variability in the
718 Alexandrinka volcanic-hosted massive sulphide (VHMS) ore deposit, Urals, Russia.
719 *Chemical Geology* 221, 170-187.

720 Mathur, R., Ruiz, J., Titley, S., Liermann, L., Buss, H., Brantley, S., 2005. Cu Isotopic
721 Fractionation in the Supergene Environment with and without Bacteria. *Geochimica
722 et Cosmochimica Acta*, 69, 22: 5233-5246.

723 Mathur, R., Jin L., Prush, V., Paul, J., Ebersole, C., Fornadel, A., Williams, J.Z., Brantley,
724 S., 2012. Cu Isotopes and Concentrations During Weathering of Black Shale of the
725 Marcellus Formation, Huntingdon County, Pennsylvania (USA)." *Chemical Geology*,

- 726 304–305: 175-184.
- 727 Matthys, W., 1975. Enzymes of heavy-metal-resistant and non-resistant populations of
728 *Silene cucubalus* and their interaction with some heavy metal in vitro and in vivo.
729 *Physiol. Plant* 33, (2): 161-165
- 730 Mattielli, N., Petit, J.C.J., Deboudt, K., Flament, P., Perdrix, E., Taillez, A.,
731 Rimetz-Planchon, J., Weis, D., 2009. Zn Isotope Study of Atmospheric Emissions
732 and Dry Depositions within a 5 Km Radius of a Pb-Zn Refinery. *Atmospheric
733 Environment*, 43, (6), 1265-1272.
- 734 Moynier, F., Beck, P., Yin, Q.Z., Ferroir, T., Barrat, J.A., Paniello, R., Telouk, P., and Gillet,
735 P., 2010. Volatilization Induced by Impacts Recorded in Zn Isotope Composition of
736 Ureilites. *Chemical Geology*, 276, (3-4), 374-379.
- 737 Nimer, N.A., Dong, L.F., Guan, Q., Merrett, M.J., 1995. Calcification rate, dissolved
738 inorganic carbon utilization and carbonic anhydrase activity in *Emiliania huxleyi*, *Bull.
739 Inst. Oceanogr. Monaco* 14, 43-50.
- 740 Ödman, F., Ruth, T., Ponter, C., 1999. Validation of a Field Filtration Technique for
741 Characterization of Suspended Particulate Matter from Freshwater. Part I. Major
742 Elements. *Applied Geochemistry* 14, (3), 301-317.
- 743 Olhaberry, J., Leary, W., Reyes, A., Lockett, C., 1983. Biochemistry of zinc. *S. Afr. Med. J.*
744 64, 894–895
- 745 Peel, K., Weiss, D., Sigg, C.L., 2009. Zinc isotope composition of settling particles as a
746 proxy for biogeochemical processes in lakes: Insights from the eutrophic Lake
747 Greifen, Switzerland. *Limnology and Oceanography* 54, 1699-1708.

748 Pichat, S., Douchet, C., Albarede, F., 2003. Zinc isotope variations in deep-sea
749 carbonates from the eastern equatorial Pacific over the last 175 ka. *Earth and*
750 *Planetary Science Letters* 210, 167-178.

751 Pokrovsky, O.S., Viers, J., Freydier, R., 2005. Zinc Stable Isotope Fractionation During Its
752 Adsorption on Oxides and Hydroxides. *Journal of Colloid and Interface Science* 291,
753 no. 1: 192-200.

754 Pokrovsky, O.S., Pokrovski, G.S., Gélabert, A., Schott, J., Boudou, A., 2005. Speciation of
755 Zn Associated with Diatoms Using X-Ray Absorption Spectroscopy. *Environmental*
756 *science & technology*, 39, (12), 4490-4498.

757 Reddy, T.R., Andrew J.F., Brian, L.B., Clark, M.J., 2015. The Effect of Ph on Stable Iron
758 Isotope Exchange and Fractionation between Aqueous Fe(II) and Goethite. *Chemical*
759 *Geology*, 397: 118-127.

760 Reynolds, C.S., 1984. *The Ecology of Freshwater Phytoplankton*: Cambridge University
761 Press.

762 Rousset, D., Henderson, G.M., Shaw, S., 2004. Cu and Zn Isotope Fractionation During
763 Sorption Experiments. *Goldschmidt Conference Abstracts*, 68, (11), A360.

764 Sass, H., Cypionka, H., Babenzien, H.D., 1997. Vertical distribution of sulfate-reducing
765 bacteria at the oxic-anoxic interface in sediments of the oligotrophic Lake Stechlin.
766 *FEMS Microbiology Ecology* 22, 245-255.

767 Shankar, A.H., Prasad, A.S., 1998. Zinc and immune function: the biological basis of
768 altered resistance to infection. *Am. J. Clin. Nutr.* 68, 447-463.

769 Sigg, L., 1985. Metal transfer mechanisms in lakes; the role of settling particles. *Chemical*

- Processes in Lakes, John Wiley and Sons, New York New York, 283-310.
- Sigg, L., Kistler, D., Ulrich, M.M., 1995. Seasonal variations of zinc in a eutrophic Lake. *Aquatic Geochemistry* 1, 313-328.
- Sivry, Y., Riotte, J., Sonke, J.E., Audry, S., Schäfer, J., Viers, J., Blanc, G., Freydier, R., Dupré, B., 2008. Zn Isotopes as Tracers of Anthropogenic Pollution from Zn-Ore Smelters the Riou Mort–Lot River System. *Chemical Geology*, 255, (3), 295-304.
- Song, L.T., Liu, C.Q., Wang, Z.L., Zhu X.K., Teng, Y., Liang, L.L., Tang, S.H., Li, J., 2011. Iron Isotope Fractionation During Biogeochemical Cycle: Information from Suspended Particulate Matter (Spm) in Aha Lake and Its Tributaries, Guizhou, China. *Chemical Geology* 280, 1: 170-179.
- Stenberg, A., Andren, H., Malinovsky, D., Engstrom, E., Rodushkin, I., Baxter, D.C., 2004. Isotopic Variations of Zn in Biological Materials. *Anal Chem*, 76, 3971-3978.
- Sun, M.Y., Wakeham, S.G., 1994. Molecular evidence for degradation and preservation of organic matter in the anoxic Black Sea Basin. *Geochimica et Cosmochimica Acta* 58, 3395-3406.
- Tang, S.H., Zhu, X.K., Cai, J.J., Li, S.Z., Wang, J. H., 2006. Chromatographic Separation of Cu, Fe and Zn using AG MP-1 Anion Exchange Resin for Isotope Determination by MC-ICP-MS. *Rock and Mineral Analysis*, 25(1), 5-8.
- Tessier, A., Campbell, P.G.C., Bisson, M., 1979. Sequential Extraction Procedure for the Speciation of Particulate Trace Metals. *Analytical Chemistry*, 51, (7), 844-851.
- Thapalia, A., Borrok, D.M., Metre, P.C.V., Musgrove, M.L., Landa, E.R., 2010. Zn and Cu Isotopes as Tracers of Anthropogenic Contamination in a Sediment Core from an

792 Urban Lake. Environmental Science & Technology, 44,(5), 1544-1550.

793 Turner, A., and Millward, G.E., 2002. Suspended Particles: Their Role in Estuarine

794 Biogeochemical Cycles. Estuarine, Coastal and Shelf Science, 55,(6), 857-883.

795 Vance, D., Archer, C., Bermin, J., Kennaway, G., Cox, E.J., Statham, P.J., Lohan, M.C.,

796 and Ellwood, M.J., 2006. Zn Isotopes as a New Tracer of Metal Micronutrient Usage

797 in the Oceans. Geochimica et Cosmochimica Acta Supplement, A666.

798 Vance, D., Archer, C., Kennway, G., Cox, E., Statham, P.J., 2004. Controls on the

799 transition metal isotopic composition of seawater: diatom culture experiments. Fall

800 Meet. Suppl., Abstract V35B-05, Eos Trans. AGU, vol, 85(47).

801 Viers, J., Oliva, P., Nonell, A., Gélabert, A., Sonke, J.E., Freydier, R., Gainville, R., Dupré,

802 B., 2007. Evidence of Zn Isotopic Fractionation in a Soil–Plant System of a Pristine

803 Tropical Watershed (Nsimi, Cameroon). Chemical Geology, 239, (1-2): 124-137.

804 Voldrichova, P., Vladislav, C., Adela, S., Juraj, F., Martin, N., Marketa, S., Michael, K.,

805 Frantisek, V., Vladimir, B., Eva, P., 2014. Zinc Isotope Systematics in Snow and Ice

806 Accretions in Central European Mountains. Chemical Geology, 388, 130-141.

807 Weiss, D.J., Rausch, N., Mason, T.F.D., Coles, B.J., Wilkinson, J.J., Ukonmaanaho, L.,

808 Arnold, T., Nieminen, T.M., 2007. Atmospheric Deposition and Isotope

809 Biogeochemistry of Zinc in Ombrotrophic Peat. Geochimica et Cosmochimica Acta,

810 71,(14): 3498-3517.

811 Weiss, D.J., Mason T.F.D., Zhao, F.J., Kirk, G.J.D., Coles, B.J., Horstwood, M.S.A., 2005.

812 Rapid Reports Isotopic Discrimination of Zinc in Higher Plants. New Phytologist, 165,

813 (3), 703.

- 1
2
3
4 814 Wilkinson, J.J., Weiss, D.J., Mason, T.F.D., Coles, B.J., 2005. Zinc isotopic variation in
5
6 815 hydrothermal system: preliminary evidence from the IRISH midlands ore field.
7
8 816 Society of Economic Geologists, Economic Geology, 100, 583–590.
9
10
11 817 Young, S., Ruiz, J., 2003. Inorganic control of copper isotope fractionation in Supergene
12
13 818 environmentsin. EGS-AGU-EUG Joint Assembly. Nice France. A2045.
14
15
16 819 Zhao, Y., Vance, D., Abouchami, W., Baar, H.J.W., 2014. Biogeochemical Cycling of Zinc
17
18 820 and Its Isotopes in the Southern Ocean. *Geochimica et Cosmochimica Acta*, 125,
19
20 821 653-672.
21
22
23 822 Zhu, X.K., Guo, Y., Williams, R.J.P., O’Nions, R.K., Matthews, A., Belshaw, N.S., Canters,
24
25 823 G.W., Waal, E.C., Weser, U., Burgess, B.K., 2002. Mass Fractionation Processes of
26
27 824 Transition Metal Isotopes. *Earth Planet. Sci. Lett*, 200, 47–62.
28
29
30
31
32
33
34
35
36
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Fig. 1. Location map of Aha Lake and Hongfeng Lake, southwest of China. Shown together in the map are their main, discharges of tributaries and the sampling sites. The sampling locations were AHDB (Da Ba) and AHLJK (Liang jiang kou) profiles in Aha Lake; HFDB (Da Ba) and HFHW (How Wu) profiles in Hongfeng Lake.

207x239mm (300 x 300 DPI)

Fig. 2. Plots of Temperature, pH, Chlorophyll, DO (Dissolved Oxygen), Concentration of SPM, concentration of dissolved Zn, concentration of SPM Zn and $\delta^{66}\text{Zn}$ of SPM (suspended particulate matter) for AHDB and AHLJK profile of Aha Lakes. For both profiles, green triangle and red triangle refer to date of August 2006 and January 2007 for AHDB, respectively; while green square and red square refer to date of August 2006 and January 2007 for AHLJK, respectively.

351x185mm (300 x 300 DPI)

Fig. 3. Plots of Temperature, pH, Chlorophyll, DO(Dissolved Oxygen), concentration of SPM, concentration of dissolved Zn, concentration of SPM Zn and $\delta^{66}\text{Zn}$ of SPM(suspended particulate matter) for HFHW and HFDB of Hongfeng lake. For both profiles, green circles and red circle refer date of August 2006 and January 2007 for HFHW, respectively, while red diamond refer to date of o January 2007 for HFDB.

356x152mm (300 x 300 DPI)

Fig. 4. The proportion of Zn different speciation of SPM. Plot A is the proportion of Zn different speciation of SPM for Aha Lake, while plot B is for Hongfeng lake. For both of two lakes, the open columns refer to AEC-bound Zn, green columns refer to organic-bound Zn, and slash column refer to the residual-bound Zn.

208x114mm (300 x 300 DPI)

Fig. 5. Relation between Zn isotope composition of SPM and Zn/Al ratio. Plot A is for Aha Lake and plot B is for Hongfeng Lake. For plot A, data points for SPM of AHDB in summer is green triangle, AHDB in winter is red triangle, AHLJK in summer is green square, AHLJK in winter is red square. In addition, the date of YCR, SR and BYR were plotted, as their discharges are bigger than other rivers. For plot B, data points for SPM of HFHW in summer is green circle, HFHW in winter is red circle, HFDB in winter is red diamond, and date of YCR, THYR and MXR are plotted as they are the main tributaries of Hongfeng Lake.

232x121mm (300 x 300 DPI)

Fig .6. The $\delta^{66}\text{Zn}$ versus to residual bound Zn of SPM. The A and B refer to for AHDB and AHLJK profiles respectively, and the C and D refer to HFHW and HFDB profiles. The green triangle and red triangle refer to the data in summer and winter respectively for AHDB respectively, and the green square and red square refer to the data in summer and winter for AHLJK respectively. The green circle and red circle refer to the date in summer and winter for HFHW respectively and red diamond refer to the date in winter for HFDB.

159x101mm (300 x 300 DPI)

Fig. 7. The $\delta^{66}\text{Zn}$ of SPM versus to chlorophyll in Aha and Hongfeng Lakes. Plot A is for Aha and Plot B is for Hongfeng Lake. The green triangle and red triangle refers to the data in summer and winter for AHDB respectively, the green square and red square refer to the data in summer and winter for AHLJK respectively, the green circle and red circle refer to the date in summer and winter for HFHW respectively, and red diamond refer to the date in winter for HFDB.

205x67mm (300 x 300 DPI)

Table1. pH, temperature, DO(dissolved oxygen), concentration chlorophyll, SPM and dissolved Zn in summer and winter for Aha Lake and Hongfeng Lake, southwest of China.

Sample site	Sampling date	Depth	pH	T(°C)	DO	Chlorophyll	SPM	Zn(DIS)
SPM		m		(°C)	mg/L	mg/L	mg/L	μg/L
AHDB	Aug	0	8.19	25	7.00	11.08	2.27	1.28
AHDB	Aug	-4	8.32	25.2	7.04	6.64	2.13	2.21
AHDB	Aug	-8	7.93	24.6	5.11	8.06	1.53	0.77
AHDB	Aug	-12	7.7	22.3	5.32	7.26	1.33	1.97
AHDB	Aug	-16	7.53	17.4	2.09	4.86	2.00	1.94
AHDB	Aug	-20	7.5	14.9	1.98	2.05	1.73	1.70
AHDB	Aug	-23	7.6	14	2.00		2.20	0.65
AHDB	Jan	0	7.49	7.9	8.43	3.79	1.19	2.99
AHDB	Jan	-5	7.49	7.4	7.70	2.97	1.31	2.60
AHDB	Jan	-10	7.97	7.3	8.14	3.05	0.96	2.64
AHDB	Jan	-15	7.95	7.1	8.76	1.46	0.80	2.66
AHDB	Jan	-20	7.92	7.23	8.80	3.21	1.05	2.19
AHDB	Jan	-23	7.9	7.3	8.33	2.56	0.82	2.67
AHLJK	Aug	0	8	25.1	7.80	6.08	3.00	1.65
AHLJK	Aug	-3	7.8	22.1	6.51	5.82	3.20	1.78
AHLJK	Aug	-6	7.6	19.2	2.33	5.75	2.40	1.29
AHLJK	Aug	-9	7.5	18.6	1.65	6.11	2.50	1.20
AHLJK	Aug	-13	7.6	14.2	1.60		2.53	1.05
AHLJK	Jan	0	7.95	7.95	9.00	2.80	0.86	2.01
AHLJK	Jan	-3	7.8	7.8	8.88	3.00	1.26	5.06
AHLJK	Jan	-6	7.87	7.87	8.60	2.50	0.91	1.98
AHLJK	Jan	-10	7.46	7.46	9.20	2.00	0.89	2.32
HFHW	Aug	0	9.37	28.1	8.10	42.10	3.73	1.48
HFHW	Aug	-3	8.49	26.6	7.50	29.23	3.00	0.75
HFHW	Aug	-6	8.42	26.3	5.20	21.06	3.00	1.55
HFHW	Aug	-9	8.21	25.9	1.20	11.74	3.27	1.80
HFHW	Aug	-12	7.66	24.1	1.10	7.50	2.60	1.67
HFHW	Aug	-15	7.54	23.3	1.00	5.23	1.73	1.29
HFHW	Aug	-19	7.44	22.6	1.20		2.20	1.22
HFHW	Jan	0	8.31	8	15.00	9.91	2.59	2.13
HFHW	Jan	-5	7.99	7.8	14.20	10.61	2.48	2.58
HFHW	Jan	-10	8.13	8.1	14.00	10.52	1.40	2.15
HFHW	Jan	-15	7.94	8	13.00	8.36	1.94	2.83
HFHW	Jan	-20	8.18	7.8	12.00	8.34	1.87	5.69
HFHW	Jan	-25	8.08	7.5	12.50	5.58	1.49	12.04
HFDB	Jan	0	7.75	8.1	12.10	7.30	1.09	2.44
HFDB	Jan	-5	7.84	7.7	11.90	5.30	1.72	2.20
HFDB	Jan	-10	7.81	7.8	11.80	6.50	1.27	3.94
HFDB	Jan	-15	7.79	7.7	11.90	5.20	1.82	1.95
HFDB	Jan	-20	7.51	7.7	12.10	4.90	1.54	3.21
HFDB	Jan	-30	7.7	7.6	11.80	5.10	1.58	2.83

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Table2: The Zn isotope composition, SPM Zn and Al₂O₃, and speciation Zn of SPM in summer and winter for Aha Lake and Hongfeng Lake.

Sample site	Date	Depth	Al ₂ O ₃ (SPM)	Zn(SPM)	AEC-Zn(SPM)	organic-Zn(SPM)	Residual-Zn(SPM)	δ ⁶⁶ Zn _{IMC}	Zn/Al
SPM		m	%	mg/g	%	%	%	(‰)	
AHDB	Aug	0	4.44	0.26	70.23	16.05	13.72	0.10	0.0110
AHDB	Aug	-4	0.37	0.30	74.26	19.04	6.69	-0.05	0.1529
AHDB	Aug	-8	3.11	0.32	68.00	23.90	8.10	-0.03	0.0195
AHDB	Aug	-12	1.57	0.40	86.87	9.04	4.09	0.02	0.0481
AHDB	Aug	-16	0.80	0.48	78.59	18.49	2.92	0.01	0.1135
AHDB	Aug	-20	1.57	0.70	66.67	23.25	10.08	0.02	0.0840
AHDB	Aug	-23	1.23	0.32	86.80	9.73	3.47	0.19	0.0490
AHDB	Jan	0	5.14	0.36	86.42	4.04	9.55	0.16	0.0131
AHDB	Jan	-5	5.24	0.57	79.07	15.46	5.47	0.23	0.0205
AHDB	Jan	-10	6.45	0.27	83.66	8.42	7.92	0.27	0.0080
AHDB	Jan	-15	1.28	0.25	87.69	5.43	6.89	0.21	0.0372
AHDB	Jan	-20	4.01	0.40	94.72	3.86	1.42	0.55	0.0187
AHDB	Jan	-23	3.05	0.27				0.20	0.0167
AHLJK	Aug	0	0.62	0.38	59.37	18.38	22.25	-0.18	0.1149
AHLJK	Aug	-3	0.47	0.18	70.89	12.92	16.20	0.05	0.0738
AHLJK	Aug	-6	1.46	0.24	86.92	12.24	0.83	0.12	0.0307
AHLJK	Aug	-9	2.39	0.26	83.21	8.99	7.80	0.16	0.0203
AHLJK	Aug	-13	1.17	0.32	57.36	19.50	23.14	0.09	0.0514
AHLJK	Jan	0	2.15	0.21	81.94	4.76	13.30	0.13	0.0187
AHLJK	Jan	-3	2.65	0.69	76.91	8.83	14.26	0.03	0.0488
AHLJK	Jan	-6	2.99	0.40	71.59	7.31	21.10	0.20	0.0254
AHLJK	Jan	-10	2.85	0.32	75.64	5.56	18.80	0.14	0.0213
HFHW	Aug	0	2.15	0.39	54.69	9.10	36.21	0.20	0.0344
HFHW	Aug	-3	6.44	0.48	52.01	11.26	36.73	0.01	0.0140
HFHW	Aug	-6	3.28	0.34	29.13	53.14	17.73	-0.11	0.0193
HFHW	Aug	-9	5.13	0.60	75.72	7.59	16.69	-0.19	0.0220
HFHW	Aug	-12	6.58	0.35	80.71	5.82	13.47	-0.29	0.0101
HFHW	Aug	-15	5.17	0.29	84.00	5.65	10.35	-0.20	0.0107
HFHW	Aug	-19	5.89	0.52	81.80	7.69	10.50	-0.11	0.0167
HFHW	Jan	0	4.75	0.40	83.39	6.12	10.48	0.15	0.0158
HFHW	Jan	-5	4.29	0.24	78.95	10.84	10.21	0.10	0.0104
HFHW	Jan	-10	5.22	0.31	86.33	5.26	8.40	0.12	0.0112
HFHW	Jan	-15	8.77	0.30	81.88	4.74	13.38	0.22	0.0065
HFHW	Jan	-20	10.41	0.75	84.66	5.97	9.38	0.26	0.0136
HFHW	Jan	-25	12.02	0.48	75.27	12.77	11.95	0.13	0.0075
HFDB	Jan	0	4.76	0.30	89.07	6.01	4.92	0.11	0.0121
HFDB	Jan	-5	4.56	0.34	86.79	5.40	7.80	0.20	0.0141
HFDB	Jan	-10	4.30	0.38	89.36	4.64	6.00	0.07	0.0166
HFDB	Jan	-15	5.37	0.40	90.08	4.63	5.29	0.17	0.0142
HFDB	Jan	-20	5.02	0.35	82.15	12.06	5.79	0.12	0.0132
HFDB	Jan	-30	4.70	0.34	88.66	5.08	6.26	0.22	0.0136
Sampling site station									
Algae	MXR								0.41
Aglea	MXR								0.40
Plant	MXR								0.21

Table3. The pH, temperature, DO(dissolved oxygen), discharges, concentration of dissolved Zn, SPM and SPM Zn, and Zn isotope composition in tributaries of Aha Lake and Hongfeng Lake.

Sampling site	Sampling	Average discharge m ³ /S	Draining In/Out	pH	T (°C)	Do mg/L	SPM mg/L	Zn-DIS μg/L	Zn-SPM mg/g	Al ₂ O ₃ %	δ ⁶⁶ Zn _{JMC} ‰	Zn/Al
Tributaries of Aha Lake												
XCR	Aug	0.65	Out	7.21	12	5.19	0.87	1.07	0.84	1.35	0.20	0.1166
XCR	Jan	0.65	Out	7.66	7.7	8.45	1.03	2.48	0.62	5.57	0.11	0.0212
BYR	Aug	0.90	In	8.14	21.8	7.47	4.53	1.53	0.26	5.64	-0.17	0.0088
BYR	Jan	0.90	In	8.36	7.4	10.32	2.21	5.68	0.26	6.84	0.05	0.0073
CCR	Aug	0.21	In	7.66	21.6	5.19	6.27	1.42	0.93	4.99	0.34	0.0351
CCR	Jan	0.21	In	7.71	9.3	8.8	1.71	7.54	0.43	1.27	0.10	0.0635
SR	Aug	0.83	In	8.28	22.6	7.6	78.03	1.03	0.00			
SR	Jan	0.83	In	8.28	8.7	10.4	3.29	5.13	1.27	8.02	0.29	0.0299
YYR	Aug	1.18	In	8.18	21.6	8.17	65.93	18.07	0.49	1.24	-0.09	0.0744
YYR	Jan	1.18	In	7.88	8.6	9.28	21.53	4.78	0.49	1.24	0.46	0.0744
LNGR	Aug	0.15	In	7.61	21	1.6	27.40	3.56	0.00	4.38		
LNGR	Jan	0.15	In	7.14	8.7	5.11	14.00	11.30	0.51	3.17	-0.04	0.0303
Tributaries of Hongfeng lake												
MTR	Aug	14.74	Out	7.49	20.7	5.98	0.93	1.48	0.19	1.21	0.22	0.0288
MTR	Jan	14.74	Out	7.42	6.9	6.91	1.48	2.95	0.48	5.38	0.10	0.0170
THYR	Aug	4.14	In	7.13	24.5	7.8	9.40	14.78	2.90	10.28	0.40	0.0533
THYR	Jan	4.14	In	7.29	5.6	9.23	4.91	5.31	1.83	7.49	0.25	0.0462
YCR	Aug	12.67	In	7.37	26.5	7.2	3.00	2.59	0.70	9.61	0.40	0.0137
YCR	Jan	12.67	In	7.08	3.4	10.2	3.42	12.42	0.43	5.79	0.04	0.0141
MXR	Aug	5.31	In	8.04	26.3	8.17	3.47	0.24	0.17	6.85	0.30	0.0048
MXR	Jan	5.31	In	7.67	4.2	10.38	0.91	2.46	0.25	6.06	0.48	0.0079
HLR	Aug	1.86	In	8.07	24.9	7.38	1.20	0.65	0.00		0.03	
HLR	Jan	1.86	In	9.72	3.9	9.76	1.74	4.13	0.25	16.70	0.13	0.0028
MBR	Jan	0.32	In	7.44	9	8.32	1.93	3.94	0.46	12.44	0.14	0.0069