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

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Abstract:

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24   Zn isotope is a useful tool for tracing biogeochemical processes as zinc plays

25   important role in the biogeochemistry of natural systems. However, Zn isotope

26   composition in the lake ecosystems has not been well characterized. This study aim to

27   investigate the Zn isotope compositions of suspended particulate matter (SPM) and

28   biological samples collected from the Aha Lake and Hongfeng Lake, and their

29   tributaries in summer and winter, in order to explore the potential of this novel isotope

30   system as a proxy for biogeochemical processes in aqueous environments.

31   Concentration of dissolved Zn ranged from 0.65 to 5.06 µg/L and 0.74 to 12.04 µg/L

32   for Aha Lake and Hongfeng Lake respectively, while the SPM-Zn ranged from 0.18 to

33   0.70 mg/g and 0.24 to 0.75 mg/g for Aha Lake and Hongfeng Lake respectively. The

34   Zn isotope composition in SPM from Aha Lake and its main tributaries ranged from

35   -0.18‰ to 0.27‰ and -0.17‰ to 0.46‰ respectively, and it varied from -0.29‰ to 0.26‰

36   and -0.04‰ to 0.48‰ respectively in Hongfeng Lakes and its main tributaries,

37   displaying a wider range in tributaries than lakes. From the results and discussion,

38   they implied that Zn isotope composition mainly affected by tributaries inputting in Aha

39   Lake, while adsorption process by algea was major factor for the Zn isotope

40   composition in Hongfeng Lake, and ZnS precipitation leads to the light Zn isotope

41   composition of SPM in summer. These data and results provide the basic information

42   of the Zn isotope for the lake ecosystem, and promote the application of Zn isotope in

43   biogeochemistry.

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

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45   Tributary

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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 a., 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

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67   fractionated during plant uptake (Weiss et al., 2005; Vance et al., 2006) and adsorption

68   processes (Gélabert et al., 2006; Pokrovsky et al., 2005; Kafantaris S C V., 2014).

69   Secondly, zinc adsorption on soil, Mn oxyhydroxide, kaolinite and sediments is an another

70   factor of isotope fractionation (Cacaly et al.,2004; Rousset et al., 2004; Pokrovsky et

71   al.,2005; Bryan et al., 2015; Guinoiseau et al., 2016). Finally, zinc isotope can

72   fractionation during the sphalerite precipitated from the solution or rock material, and also

73   can fractionation during different Zn species, like sulfide, chloride and carbonate (Archer

74   et al., 2004, Wilkinson et al., 2005; John et al., 2008; Jujii., 2011 & 2012). Generally

75   speaking, the range of δ^{66}Zn values in geological materials on Earth is between -0.91‰ to

76   1.04‰ (Luck et al., 1999; Maréchal et al., 2000; Mattielli et al., 2009; Pichat et al., 2003;

77   Dolgopova et al., 2006; Weiss et al., 2007; John et al.,2007; Mason et al., 2005, little et al.,

78   2016), and it is relatively narrow compare to the lunar samples(-3.83‰ to 6.89‰)(Monyier

79   et al., 2006).

80   The Zn isotope composition of different materials collected from atmosphere, soil,

81   sediment, ocean, and river, has been analyzed and applied to trace sources of Zn

82   (Maréchal et al., 1999; Maréchal et al., 2000; Dolgopolova et al., 2006; Cloquet et al.,

83   2006; Berimin et al., 2006; Weiss et al., 2007; Sivry et al., 2008; Mattielli et al., 2009; Chen

84   et al., 2009; Thapalia, et al., 2010). It was found that the Zn isotope composition in rainfall

85   is lighter than in carbonatite as early as 1999 (Luck et al., 1999). Zn isotope composition

86   were also combined with lead isotope ratios to trace that the Zn in lichen and birch at

87   Orlovka–Spokoinoe mining district, Eastern Transbaikalia, Russia, mainly comes from the

88   mining area (Dolgopolova et al., 2006). Zn isotopes were investigated in a variety of

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89   stream waters draining mining districts located in the United States and estuary in pairs,

90   and it demonstrated that Zn isotopes maybe used to probe biogeochemical processes

91   (Borrok et al., 2008; Chen et al., 2009). The Zn isotope composition of soils shows that

92   mining areas are a source of heavy metal pollution (Bigalke., et al., 2010). Zn isotope

93   composition of snow, ice and atmosphere indicate that $\delta^{66}Zn$ is useful tool in pollution

94   provenance (Mattielli et al., 2009; Voldrichova., et al, 2014). In addition, Zn isotopes

95   composition was also studied in the Ocean to trace the Zn biogeochemical cycle (John et

96   al., 2004; John et al., 2014; Zhao et al., 2014; Little et al., 2016).

97   However, Zn isotope composition in the lake ecosystem has not been well

98   characterized, besides the research from the eutrophic Lake Greifen, Switzerland (Peel et

99   al., 2009). Accordingly, there is still much work to be done before using Zn isotopes to

100   unravel biogeochemical cycling of Zn in the lake ecosystem successfully. Lakes are easily

101   accessible natural laboratories with well-established biogeochemical processes (Sigg et

102   al., 1985). This work aims to investigate the Zn isotope composition of suspended particle

103   matter (SPM) in Aha Lake and Hongfeng Lake, both are eutrophic and seasonal anoxic

104   lakes, and located at the southwest suburb of Guiyang, Guizhou Province, China. SPM of

105   lakes is a mixture of organic and inorganic detritus, Fe-Mn oxhydroxides, clay minerals,

106   carbonates, phytoplankton, zooplankton, bacteria, and other particles that are retained on

107   0.45 μm pore size filter. SPM can affect transportation and transformation of trace

108   contaminants among water, sediment and the food chain, hence it is a critical chemical

109   component of the biogeochemical cycling in lakes (Ödman et al., 1999; Turner and

110   Millward, 2002). The Zn isotopic compositions of SPM in Hongfeng and Aha Lakes and

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111   their tributaries were investigated in this research, to assess the behavior of zinc isotopes

112   composition during biogeochemical processes in the aqueous environment.

113   **2.   Study background and sample collection**

114   **2.1 study site**

115   Aha and Hongfeng are artificial river interception reservoirs located in southwest of

116   Guiyang city about 8 km and 31.5 km respectively, in a subtropical humid monsoon

117   climate zone. The catchments are characterized by low rainfall and river discharge during

118   winter and spring, whereas high temperatures in summer and autumn bring more rainfall

119   and high river flow (Table1). They are both seasonally anoxic reservoirs. Aha lake covers

120   an area of 4.5 km^2 ,with a total water volume of 4.45×10^7 m^3. The average and maximum

121   depths are 13 m and 24 m, respectively. The residence time of lake water is about 0.44

122   year. The watershed area is 190 km^2 with an average annual precipitation of 1109 mm,

123   and the average annual temperature is 13.8-15.5 °C. Previously, more than 200 coal

124   mines were widely distributed in the watershed, where significant amount of acid mining

125   drainages and dump filtrates were produced. There are six main rivers flowing through the

126   watershed area including five inflowing tributaries, Youyu River (YYR), Caichong River

127   (CCR), Lannigou River (LNR), Baiyan River (BYR) and Sha River (SR), and only one

128   draining river, Xiaoche River (XCR) (Fig1). YYR and BYR are mainly polluted by coal

129   mines, CCR and LNGR are mainly polluted by domestic sewerage, and SR polluted by

130   industrial and domestic sewerage. The surface of lake water is colonized by sparse

131   diatoms and cause eutrophication in summer.

132   Hongfeng Lake covers an area of 57.2 km^2 and much bigger than Aha lake, its

133 reservoir storage capacity is $6.01 \times 10^8 \, m^3$, 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 algea.

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 algea samples were collected

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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 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 MΩ) 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 MΩ), and then

176 dried at 50°C in an oven and weighted. After those processes, the blank of filters is as low

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177   as 0.001 μg/L and can be negligible.

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, 045 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). Algea samples

188   were cleaned and dried in a freeze dryer, and then ground to 50 meshes for digestion and

189   δ^{66}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% H_2O_2 (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% HNO_3 for analysis.

3.2 Sample digestion

197   All SPM and algea 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

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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   HNO_3 and HF, and then the residue re-dissolved in 7 N HCl+0.001% H_2O_2 for chemical

207   purification. Other samples were just re-dissolved in 2% HNO_3 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 HNO_3

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 HNO_3 was thoroughly removed. The resin was then continuously

216   pre-conditioned with 5 ml 7 N HCl+0.001%H_2O_2 and 4 ml 7 N HCl+0.001%H_2O_2. Then the

217   prepared samples were loaded on the resin and the matrix were striped with 35 ml 7 N

218   HCl+0.001%H_2O_2; Fe was eluted with 20 ml 2 N HCl+0.001%H_2O_2, and Zn was eluted

219   with 10 ml 0.5 N HNO_3. The Zn eluate was evaporated to dry on a hot plate at 80°C and

220   dissolved in 0.1 N HNO_3 to a concentration of 100 to 200 μg/L for isotope analysis. The

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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 HNO_3, 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 ^{64}Zn

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 $\delta^{66}Zn$ =6.96±0.11‰, $\delta^{67}Zn$ =10.4±0.23 $\delta^{68}Zn$=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 $\delta^{66}Zn$, 0.23‰ for $\delta^{67}Zn$ and

242   0.22 for $\delta^{68}Zn$. The detailed conditions and the performance of isotope measurements

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

244   Zn isotope data was reported in δ^xZn (δ^{66}Zn, δ^{68}Zn) as parts per thousand deviations

245   relative to JMC 3-0749. All the δ^{64}Zn and δ^{66}Zn values obtained in this study followed the

246   theoretical   mass-dependent   fractionation   line,   with   a   formula   of

247   δ^{68}Zn=1.976×δ^{66}Zn+0.0005(R^2=0.9998).

248
$$\delta^{66}Zn_{JMC} = \left[\frac{\left(^{66}Zn \big/ _{64}Zn \right)_{sample}}{\left(^{66}Zn \big/ _{64}Zn \right)_{JMC}} - 1 \right] \times 1000$$

249

250   **4. Results**

251   **4.1 Temperature, DO (Dissolved Oxygen), pH and chlorophyll in Aha Lake and**

252   **Hongfeng lakes, and their tributaries**.

253   Environment parameters are summarized in Table 1, and plotted in Figs. 2 and 3. In

254   summer thermal stratification was observed in August with a temperature gradient of ca.

255   10°C in Aha Lake. The thermoclines were located at a water depth ca. 10m for AHDB and

256   ca. 6m at for AHLJK station. Dissolved oxygen declined sharply below the thermoclines,

257   with average concentration ca.1.2 mg/L in Aha Lake, and there was also a marked

258   decrease in pH of ca. 0.5 units below the thermocline for AHDB profile. However, there

259   were no clear depth-dependent variations in temperature, DO and pH in the winter both

260   for AHDB and AHLJK profiles (Fig 2). Moreover the temperature gradient was ca. 6°C

261   from surface water to thermocline for Hongfeng Lake, and the thermocline was located at

262   a water depth ca. 12m for HFHW station in summer. DO was also almost depleted under

263   the thermocline, with average concentration of 2.0 mg/L, and hypoxic conditions prevailed

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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 µg/L at

269   surface water, with marked decreasing to 5.2 µg/L at the bottom for HFHW station, while

270   the concentration of chlorophyll varied from 11.1 to 2.1 µg/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 µg/L and 0.74 to 12.04 µg/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

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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 μg/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 μg/L) and SPM-Zn (0.51 mg/g) of Aha tributaries were higher

307   than Aha Lake (2.03 μg/L and 0.36 mg/g, respectively). For Hongfeng Lake, THYR had

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308   highest SPM (9.4 mg/L) and dissolved Zn content (14.78 μg/L) concentration than other

309   rivers. The concentration of dissolved Zn in winter was higher than in summer for most of

310   rivers, and THYR also had the highest SPM-Zn content (2.9 mg/g). Moreover, average

311   dissolved Zn (4.63 μg/L) in Aha lake was similar to that in Hongfeng Lake (5.73 μg/L), but

312   average SPM-Zn (0.70 mg/g) was higher than in the Hongfeng lake (0.40 mg/g).

313   **4.3 Zn isotope composition in Hongfeng, Aha lakes and their tributaries**

314   The Zn isotope composition of SPM varied significantly in time and space. Generally

315   speaking, δ^{66}Zn of SPM ranged from -0.29‰ to 0.55‰ for these samples which collected

316   from Aha Lake and Hongfeng Lake and their tributaries, the variation is about 9-10 times

317   compared to precision of determination. This falls largely within the previously determined

318   isotope range of particle Zn from Greifen Lake (-0.66‰ to 0.21‰) and Seine river (-0.08‰

319   to 0.30‰), but slightly lighter than terrestrial geological material (0.4‰ to 1.4‰)(Peel et

320   al., 2009; Chen et al., 2009; Cloquet et al., 2006; litter et al., 2016). All the δ^{66}Zn data for

321   SPM from Aha Lake and Hongfeng Lake are given in Table 1 and δ^{66}Zn data for SPM from

322   tributaries are given in Table 3.

323   The Zn isotope composition of SPM for Aha Lake ranged from -0.18‰ to 0.27‰,

324   slightly lighter than Aha tributaries. The Zn isotope composition in the summer (-0.18‰ to

325   0.19‰) was lighter than in winter (0.03‰ to 0.27‰) for Aha Lake. The Zn isotope

326   composition of SPM for Hongfeng Lake ranged from -0.29‰ to 0.26‰, and it was also

327   slightly lighter than the Zn isotope composition of SPM in Hongfeng tributaries (-0.04‰ to

328   0.48‰). Similarly, the δ^{66}Zn varied from -0.29‰ to 0.20‰ for Hongfeng Lake in summer,

329   also slightly lighter than the δ^{66}Zn in winter (Figs 2, 3, Table 1).

15

330   For Aha Lake, there were no discernible trends with increasing water depth both in

331 AHDB and HALJK stations in winter, but it was apparent that the heavier δ^{66}Zn appeared

332 at the surface for AHDB, which was similar to the HFHW in summer. Whereas, there was

333 also a clear increase of δ^{66}Zn with water depth for AHLJK station in summer. For the

334 Hongfeng Lake, there were no clear trends with depth in winter for both sites HFHW and

335 HFDB. However, a pronounced decrease of δ^{66}Zn was observed with increasing water

336 depth to -0.29‰ at a depth of 12 m in summer at HFHW station. Lower δ^{66}Zn appeared at

337 the thermocline while the higher δ^{66}Zn appeared at the surface. This trend was similar to

338 that of particles collected from Atlantic and Pacific Oceans (Maréchal et al., 2000).

339   The Zn isotope of SPM in tributaries also varied significantly in time and space. For

340 Aha Lake, the δ^{66}Zn of YYR and BYR were -0.09‰ and -0.17‰ in summer respectively,

341 which were isotopically light relative to sphalerite (0.02‰ to 0.44‰), but same as the

342 pyrite (-0.19‰ to -0.19‰) (Maréchal et al., 1999). In addition, YYR and BYR have lighter

343 δ^{66}Zn in summer than in winter. However, the δ^{66}Zn of CCR was 0.34‰ in summer, which

344 was isotopically heavier than in winter (0.10‰). For the only draining river of the Aha Lake,

345 XCR had similar δ^{66}Zn value in summer and winter.

346   For Hongfeng Lake, THYR and YCR had slightly heavier Zn isotope of 0.40‰ in

347 summer than in winter (0.25‰ and 0.04‰), and the δ^{66}Zn of MXR in summer (0.30‰) was

348 slight lighter than in winter (0.48‰) in contrast. Moreover the MTR and HLR had similar

349 δ^{66}Zn value in summer and winter. Two algea samples had similar Zn isotope composition

350 of 0.41‰ and 0.40‰ respectively, and the δ^{66}Zn of algea collected from MXR was 0.21‰.

351 **5. Discussion**

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352   SPM in lake water is mainly supplied by fluvial input, plankton and inorganic materials

353   produced within the lake (autochthonous material), and sediment resuspension

354   (Hakanson and peters, 1995, Sigg et al., 1995; Riemann et al., 2005). Aha Lake and

355   Hongfeng Lake have surface area of 4.5 km^2 and 57.2 km^2, water depth of 14 to 24 m and

356   10 to 45 m respectively, as well as temperature gradients of >10 °C (Fig 2 and 3), which

357   implied that wind induced resuspension of sediment will have limited contributions.

358   Furthermore, Aha and Hongfeng both are seasonal anoxic lakes, therefore our discussion

359   will focus on fluvial, plankton and seasonal anoxic controls.

5.1 Effect of Zn fluvial input from Tributaries on δ^{66}Zn of SPM

361   The Zn contents were normalized to Al to determine Zn enrichment due to

362   non-detrital inputs since Al concentration is a good indicator of detrital input (Chen et al.,

363   2009). Here we investigated the relation between δ^{66}Zn and Zn/Al (Fig 5). The Zn/Al ratio

364   of Aha Lake ranged from 0.007 to 0.153 and average was 0.045, it was much higher than

365   Zn/Al in Hongfeng Lake (average was 0.0145), and indicating SPM Zn was more enriched

366   in Aha Lake than in Hongfeng Lake.

367   For the Aha Lake, including AHDB and AHLJK Profile in summer, a clear negative

368   relationship between δ^{66}Zn and Zn/Al can be observed (Fig 5). Samples in summer

369   showed higher Zn/Al ratio and lighter Zn isotope composition, whereas samples in winter

370   showed lower Zn/Al ratio and heavier Zn isotope composition. As the discharge of YYR,

371   BYR and SR are relatively bigger than other rivers, the δ^{66}Zn of SPM for Aha Lake maybe

372   controlled by these rivers. The discharge (1.18 m^3/s) of YYR is largest of any other rivers,

373   and it mainly contaminated by coal mine and with bigger discharge and high SPM

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374 concentration, displays a higher Zn/Al and lighter Zn isotope in summer, and represents

375 the detrital input from the coal mine, thus the δ^{66}Zn of SPM maybe effected by inputting of

376 the YYR with the coal mine. By contrast, SR displayed lower Zn/Al ratio and heavier Zn

377 isotope, and represents input from domestic and industrial activities, Its δ^{66}Zn (0.05‰ and

378 0.29‰) were close to anthropogenic samples, ranging from 0.08‰ to 0.31‰ (Chen et al.,

379 2009). Comparing the discharge and concentration of SPM of SR (0.83 m^3/s and 78.03

380 mg/L respectively) river with BYR (0.90 m^3/s and 4.53 mg/L) (Table 2), shows that the

381 discharge of them were similar, but the concentration of SPM of SR was almost 18 times

382 higher than BYR. Therefore the main SPM source was likely to be SR, and δ^{66}Zn of SPM

383 likely to be affected by the inputting of SR with domestic and industrial waste water.

384 Consequently, δ^{66}Zn of SPM for Aha Lake mainly be affected by mixing of YYR and SR

385 process (Fig 5).

386   We further investigated the relationship between δ^{66}Zn of SPM and the Residual Zn

387 of SPM (Fig 6), since the residual fraction of metals comes mainly from primary and

388 secondary minerals in which trace metals are not expected to be released in solution over

389 a reasonable time under natural conditions (Tessier et al., 1979). Thus, the residual form

390 of SPM may represent the material from background or terrigenous sediment (Ödman et

391 al, 1999; Turner and Millward, 2002; Tessier, 1979).

392   We can see clearly that there was linear relationship between Zn isotope composition

393 and residual fraction of Zn in Aha Lake (Fig 6). There were a positive relationship between

394 Zn isotope composition and residual fraction of Zn in summer for AHDB, and a negative

395 relationship in summer and positive relationship in winter for AHLJK. Although there were

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396   little data, and they are not significantly correlated with each other, we still can obtain

397   some information from these data. As mentioned above, the main input tributarie was SR

398   for AHDB profile, therefore the main SPM source of AHDB is likely to be SR. According to

399   the Zn isotope composition of SR (0.29‰) and AHDB profile (-0.05‰ to 0.19‰), the Zn

400   isotopic composition of SR are heavier than AHDB profile in summer, thus it lead to

401   positive relationship between Zn isotope composition and residual Zn at AHDB.

402   Consequently, we can draw the Zn isotope composition of SPM for AHDB was mainly

403   affected by input of SR. Similarly, YYR was the main source of AHLK profile according the

404   table 3. Comparing the Zn isotope composition of YYR in summer (-0.09‰) to that in

405   winter (0.46‰), we can obtain that YYR had light Zn isotopes in summer and acts as a

406   heavy Zn isotope source in winter, consistent with a negative correlation in summer and

407   positive correlation between δ^{66}Zn and Zn/Al in winter for AHLJK profile(Fig 6).

408   Accordingly we can draw the Zn isotope composition of SPM for AHLJK was mainly

409   affected by inputting of YYR. These conclusions were agree with these from the relation

410   between δ^{66}Zn and Zn/Al of SPM, and further approved that Zn isotope composition of

411   Aha Lake was mainly affected by SR and YYR, and it is a mixing of endmember process.

412   By contrast, there was no correlation between Zn/Al and Zn isotope composition of

413   SPM in HFHW and HFDB both in summer and winter and there were no significant

414   variations of Zn/Al ratio for all samples in Hongfeng Lake. Furthermore, there still was no

415   clear correlation between δ^{66}Zn and residual Zn of SPM in Hongfeng Lake

416   The δ^{66}Zn of MXR, THYR and YCR in summer were isotopically heavier than δ^{66}Zn in

417   Hongfeng lake, however there was no clear relationship between tributaries and the

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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.

5.2 Effect of algal activities on Zn δ^{66}Zn of SPM

425 The δ^{66}Zn of SPM depth profile above the thermocline at HFHW profile in summer

426 showed surface SPM had the heaviest Zn isotope composition, and δ^{66}Zn gradually

427 decreasing with depth. Similarly for AHDB profile, the heaviest δ^{66}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 δ^{66}Zn decreased with depth were found for particle samples in Central

430 Atlantic Ocean (Maréchal et al., 2000), and that δ^{66}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 δ^{66}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 δ^{66}Zn in Hongfeng Lake may be related to the algal

438 activities.

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

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440   the heavy Zn isotope onto the surface of diatoms, and by the preferential incorporation of

441   the light isotope into biological material (Gélabert et al., 2006; Weiss et al., 2005). Hence,

442   we examined whether there was a correlation between Zn isotope composition and

443   chlorophyll, as chlorophyll is an important indicator of primary producers of phytoplankton

444   biomass, and is the main pigment of photosynthetic phytoplankton (Reynold, 1984;

445   Kasprzak et al., 2008) .

446   Figure 7 showed that that when the concentration of chlorophyll was low in winter, the

447   Zn isotope composition of SPM was heavy, when concentration of chlorophyll was high in

448   summer, the Zn isotope composition of SPM was light($\Delta\delta^{66}Zn_{winter-summer}$=0.17‰ for Aha

449   Lake, $\Delta\delta^{66}Zn_{winter-summer}$=0.07‰ for Hongfeng Lake). Moreover, a significant positive

450   relationship was evident between $\delta^{66}Zn$ and chlorophyll at HFHW profile in summer, and

451   there was no relationship between $\delta^{66}Zn$ and chlorophyll in AHDB and AHLJK profiles in

452   summer. It was notable that the biomass of phytoplankton in Hongfeng Lake was much

453   higher than in Aha Lake in summer (Fig. 7), suggesting that phytoplankton play a major

454   role in controlling Zn isotope variability for Hongfeng Lake in summer.

455   How the algea affect the Zn isotope composition during the biogeochemical process

456   remains unclear？ Maréchal et al (2000) thought $\delta^{66}Zn$ of particle decreasing from surface

457   to bottom may be caused by activity of phytoplankton and remineralization, and John was

458   aware that the incorporation by phytoplankton mainly accounts for the $\delta^{66}Zn$ of seawater

459   increasing with the depth of water(John et al., 2014). At here, we can discuss from

460   absorption and adsorption processes to explain the Zn isotope variation of SPM for

461   Hongfeng Lake in summer, and to compare which one is the major control factor.

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462   Firstly, the Zn isotope composition of SPM in Hongfeng Lake in summer whether

463   affected by incorporation into algal process? On one hand, as algal incorporation is

464   expected to produce lighter Zn isotope composition of SPM in surface water relative to

465   bottom water according to other research (Gélabert et al., 2006; Weiss et al., 2005).

466   However, our data showed that the Zn isotope of SPM at surface water was heavier than

467   bottom water at HFHW and AHDB in summer (Figs 2 and 3). Hence it was contradictory

468   that absorption was major control factor on the Zn isotope composition. On the other hand,

469   Organic-bound Zn was 12.53% on average, which is much lower than AEC-bound Zn

470   (69.87% on average) (Fig 4), and this further illustrates that effect of algal absorption

471   process on the Zn isotope is minor than adsorption process.

472   Secondly, the Zn isotope composition was possible affected by the adsorption onto

473   the surface of algea. AEC-bound Zn accounts for 69.87% of the total SPM Zn (Table 2) for

474   HFHW profile, which indicated the Zn isotope composition of SPM being controlled by

475   adsorption process. Generally speaking, the adsorption processes contain abiotic

476   adsorption onto the mineral particle (goethite, hematite and birnessite) and biotic

477   adsorption onto the surface of phytoplankton (Pokrovsky et al., 2005a, b; Gélabert et al.,

478   2006; Weiss et al., 2005). The Zn isotope fractionation exceeds 0.5‰ from surface water

479   to deeper water at HFHW profile, as Zn isotope fractionation does not exceed 0.5‰

480   during adsorption onto most mineral particles (Pokrovsky et al., 2005; Guinoiseau et al.,

481   2016), thus adsorption onto abiotic surfaces was not the main cause for the variation in Zn

482   isotope composition, whereas adsorption onto algea can be the major factor. Zn isotope

483   can be fractionated during preferential adsorption heavy Zn onto diatoms and plankton

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484   (Maréchal et al., 2000; Pokrovsky et al., 2005; Gélabert et al., 2006; Balistrieri et al., 2008;

485   Juillot et al., 2008). This occurs because during adsorption onto diatoms surfaces, Zn

486   reduces its coordination number from six (octahedrally coordinated to H_2O in bulk solution)

487   to four (oxygen and nitrogen tetracoordinated complexes), so the bond distance becomes

488   shorter while bond strength increases, hence the heavy isotope preference join with

489   stronger metal binding species (Criss, et al., 1999; Young and Ruiz et a., 2003). Therefore,

490   an increase of algea leaded to heavier Zn isotope composition at surface of HFHW in

491   summer (Fig.3). In addition, the $\delta^{66}Zn$ of algea in MXR ranged from 0.21 to 0.41‰ (table2),

492   and it was isotope heavier than in Hongfeng Lake, also can explained by adsorption

493   process. Consequently，adsorption onto algea is the major effect factor for the Zn isotope

494   composition in Hongfeng Lake in summer.

495   For Aha Lake, algal biomass was relatively small in summer, so there was no

496   relationship between Zn isotope composition and chlorophyll. However, this interpretation

497   remains to be confirmed given that our data were reported firstly for lake water column. In

498   the absence of isotope data on dissolved Zn due to the low concentration, it is premature

499   to argue about whether isotope fractionation between biologic particles and lake water

500   takes place at equilibrium or by purely kinetic control. Therefore, much work is still

501   required to develop a full understanding of the use of Zn isotope in lake biogeochemistry

502   and material recycling processes.

503   **5.3 The effect of seasonal anoxia and ZnS predicated on Zn isotope composition.**

504   So far, we can conclude from sections 5.1 and 5.2 that Zn isotope composition was

505   mainly affected by the tributary input for Aha Lake, whereas the Zn isotope composition

23

506 for Hongfeng Lake was mainly affected by algal adsorption. However, we saw in Fig 3 that

507 the Zn isotope composition of SPM in summer was lighter than in winter for both

508 Hongfeng and Aha Lakes. This result was very similar to δ^{66}Zn seasonal variation in SPM

509 from Lake Greifen, Switzerland (Peel et al., 2009), and δ^{56}Fe value of SPM were also

510 lower in summer than in winter in Aha Lake(Song et al., 2011). Nevertheless, both of the

511 tributary input and algal adsorption can't account for this phenomenon. Instead, it implied

512 that the Zn isotope composition of Hongfeng and Aha Lake in summer may be affected by

513 another factor.

514 　　As previous studies that Zn isotope can fractionation during process of sphalerite

515 precipitation, and sphalerite preferential incorporation of light Zn isotope(Archer et al,2004;

516 Wilkinson et al., 2005; Kelley et al.,2004; John et al., 2008; Jujii et al., 2011 & 2012).

517 Archer investigated that ZnS precipitated in an anoxic environment at room temperature

518 can fractionated the Zn isotope, and the $\Delta\delta^{66}$Zn$_{ZnS-dissolved}$= 0.36‰. (Archer et al.,2004)；

519 Wilkinson and Gagnevin also found the rapid sphalerite precipitation from the fluid or ore

520 system result in light Zn isotope (Wilkson et al., 2005; Gagnevin et al., 2012; Kelley et al.,

521 2009); John studied that subsurface cooling of hydrothermal fluids leads to precipitation of

522 isotopically light sphalerite (Zn sulfide), and this process is a primary cause of Zn isotope

523 variation in hydrothermal fluids(John et al., 2008); Fujii investigated the δ^{66}Zn in different

524 species, like aqueous sulfide, chloride, and carbonated species using ab initio methods,

525 and negative δ^{66}Zn down to at least -0.6‰ can be expected in sulfides precipitated from

526 solution with pH>9(Fujii et al., 2011 & 2012).

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

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528   DO (dissolved oxygen) were range from 1.60 to 7.80 mg/L, and average was 4.2 mg/L for

529   Aha Lake in summer, which was much lower than in winter(the concentration of DO were

530   range from 7.7 to 9.0 mg/L and average is 8.6 mg/L). For Hongfeng Lake, The

531   concentration of DO were range from 1.0 to 8.1 mg/L and average was 3.6 mg/L in

532   summer, which was also much lower than in winter(average was 12.7 mg/L). In addition,

533   the concentration of DO deceased from surface to bottom rapidly for all profiles(AHDB,

534   AHLJK, HFHW and HFDB), and the DO only 1.0 mg/L and depth of 15 m in HFHW in

535   summer, the bottom of Lakes were depleted oxygen in summer. This seasonal anoxic

536   characteristic was also appeared in Baihua Lake and Black Sea (Bai et al., 1996; Sun and

537   Wakeham, 1994). At this anoxic condition in summer, SRB (sulfate reducing bacterial) can

538   reduce the SO_4^{2-} to S^{2-}(Sass et al., 1997; Bailey et a., 2017), thus Zn can be precipitated

539   from the water, and exist as the species of the sphalerite (ZnS) in the SPM, and this can

540   be approved by the concentration of dissolved Zn was lower in summer than in winter

541   (Fig2 and Fig3). As discussed above, The sphalerite (ZnS) preferential incorporated the

542   light Zn isotope during the precipitation process, therefore the Zn isotope composition of

543   SPM should be light in summer than in winter,   and this conclusion coupled with our

544   δ^{66}Zn data for both Aha Lake and Hongfeng Lake. This maybe account for why the δ^{66}Zn

545   in summer was lower than in winter.

546

547   **6. Conclusion**

548   This study described seasonal variation of δ^{66}Zn values for Hongfeng and Aha Lakes,

549   as well as data for tributaries and biological samples, and arrived following conclusions.

25

550   Concentration of dissolved Zn ranged from 0.65 to 5.06 µg/L and 0.74 to 12.04 µg/L

551   for Aha and Hongfeng Lake respectively, while the SPM-Zn ranged from 0.18 to 0.70 mg/g

552   and 0.24 to 0.75 mg/g for Aha and Hongfeng Lake respectively. The δ^{66}Zn of SPM ranged

553   from -0.29‰ to 0.26‰ for the Hongfeng Lake and its tributaries respectively, the δ^{66}Zn of

554   SPM ranged from -0.18‰ to 0.27‰ and -0.17‰ to 0.46‰ for the Aha Lake and its

555   tributaries, displaying a wider range in tributaries than lakes.

556   From the relation of δ^{66}Zn versus Zn/Al and δ^{66}Zn versus residual-bond Zn, we

557   conclude that Zn isotope composition of Aha Lake is mainly affected by SR and YYR, and

558   it is a mixing of endmember process. Discussion the relation of δ^{66}Zn versus chlorophyll

559   and proportion of AEC-bond Zn, it suggests that Zn isotope composition of Hongfeng Lake

560   mainly controlled by the adsorption process of algea. As sphalerite (ZnS) preferential

561   incorporated the light Zn isotope during the precipitation process, this can account for why

562   the δ^{66}Zn in summer is lower than in winter.

563   In summary, Zn isotopes composition in Aha Lake and Hongfeng Lake are reported

564   firstly, and the major affect factors are discussed, this providing the basic information of Zn

565   isotope in lake system, and promoting the application of Zn isotope in biogeochemistry.

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Acknowledgments

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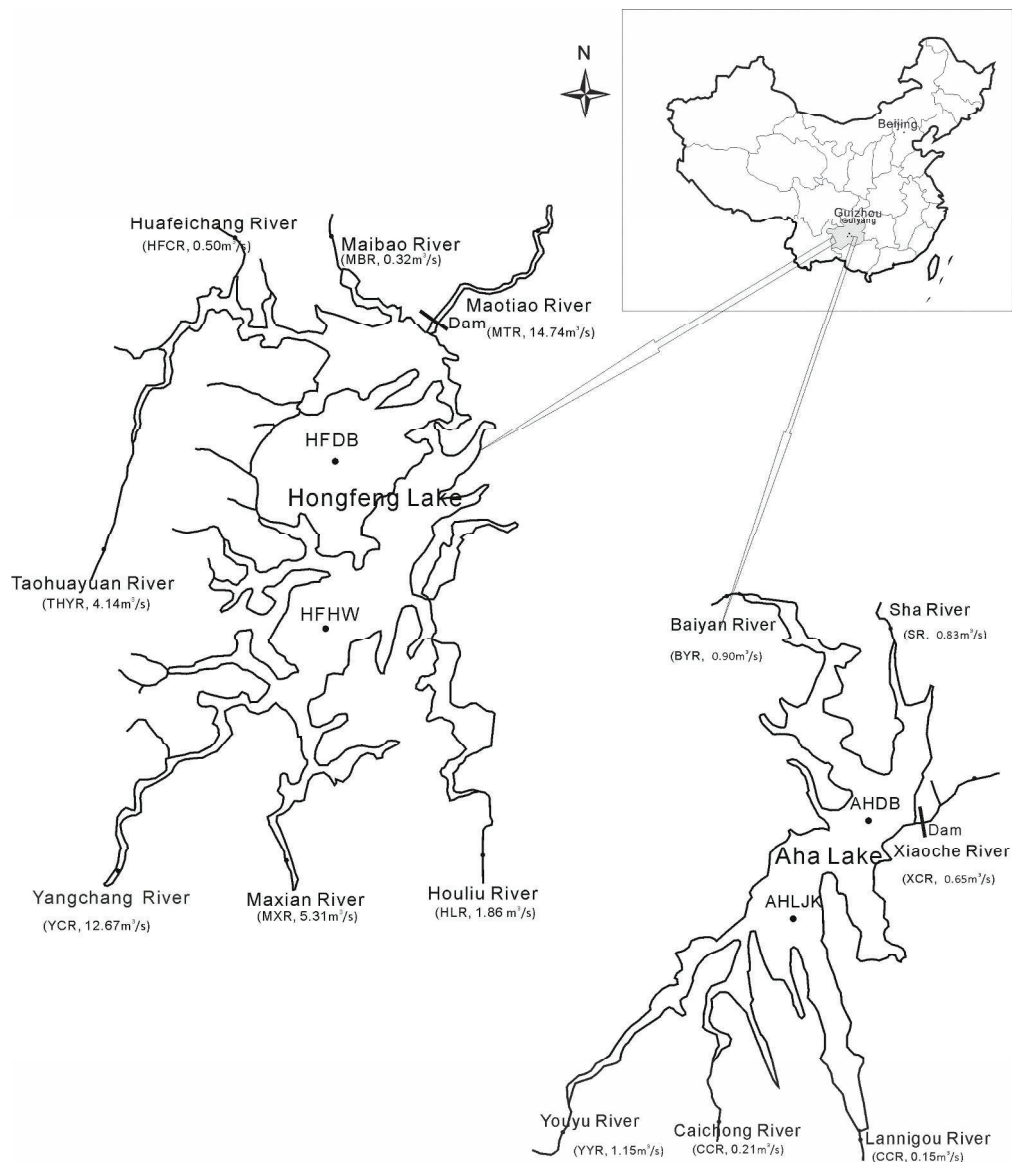
Fig. 1. Location map of Aha Lake and Hongfeng Lake, southwest of China. Shown together in the map are their main, discharges of tributaries and the sampling sites. The sampling locations were AHDB (Da Ba) and AHLJK (Liang jiang kou) profiles in Aha Lake; HFDB (Da Ba) and HFHW (How Wu) profiles in Hongfeng Lake.

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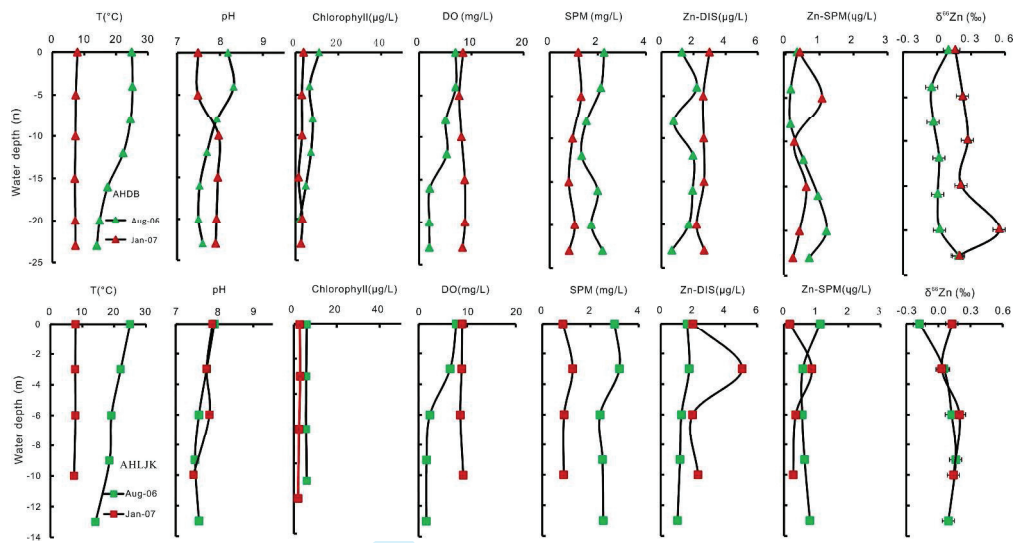
Fig. 2. Plots of Temperature, pH, Chlorophyll, DO (Dissolved Oxygen), Concentration of SPM, concentration of dissolved Zn, concentration of SPM Zn and δ^{66}Zn of SPM (suspended particulate matter) for AHDB and AHLJK profile of Aha Lakes. For both profiles, green triangle and red triangle refer to date 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.

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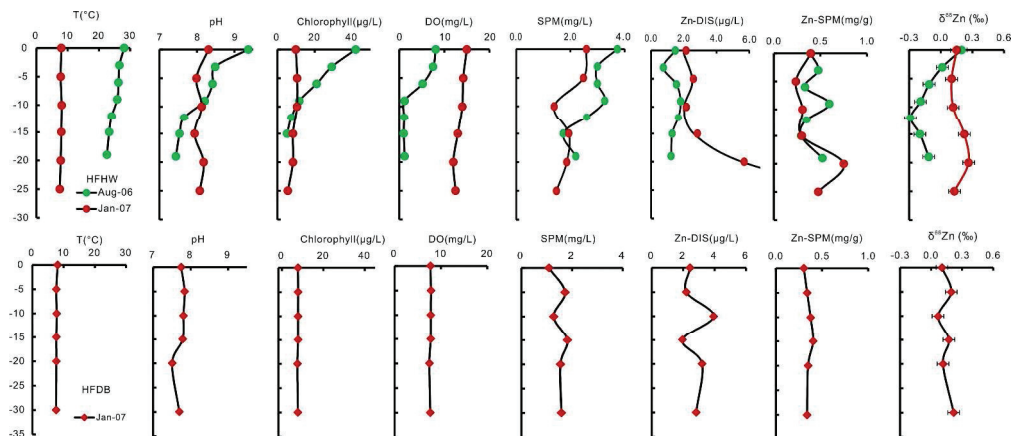
Fig. 3. Plots of Temperature, pH, Chlorophyll, DO(Dissolved Oxygen), concentration of SPM, concentration of dissolved Zn, concentration of SPM Zn and δ^{66}Zn of SPM(suspended particulate matter) for HFHW and HFDB of Hongfeng lake. For both profiles, green circles and red circle refer date of August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

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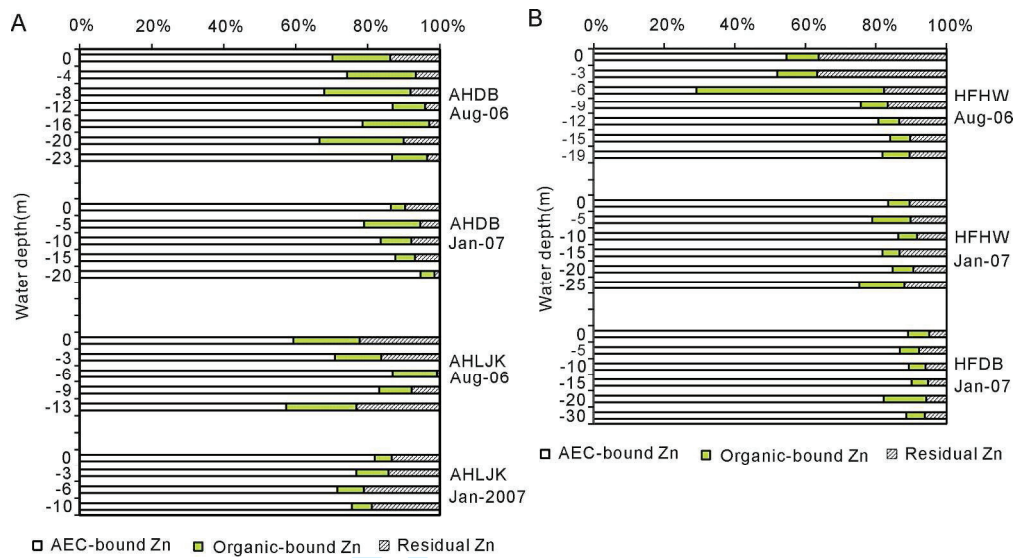
Fig. 4. The proportion of Zn different speciation of SPM. Plot A is the proportion of Zn different speciation of SPM for Aha Lake, while plot B is for Hongfeng lake. For both of two lakes, the open columns refer to AEC-bound Zn, green columns refer to organic-bound Zn, and slash column refer to the residual-bound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

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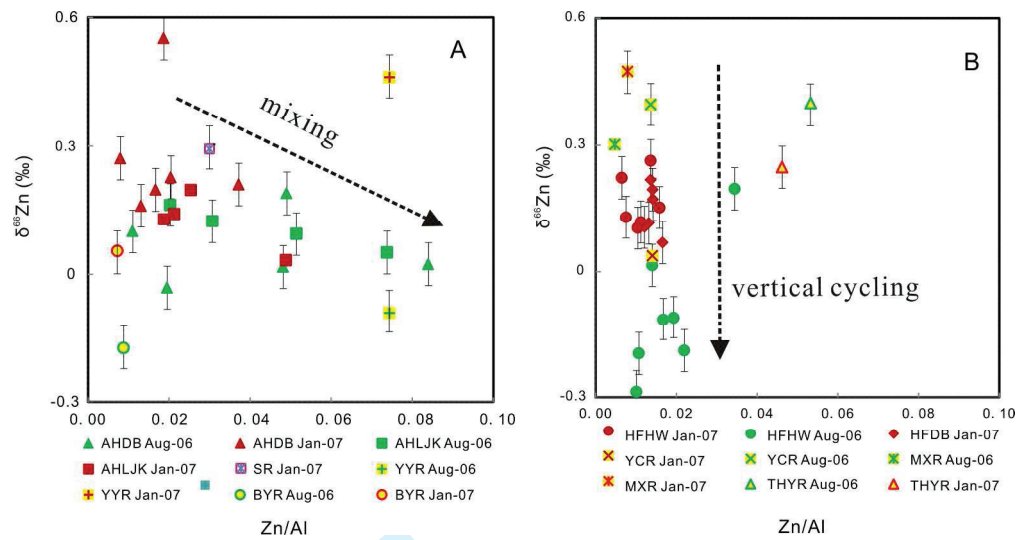
Fig. 5. Relation between Zn isotope composition of SPM and Zn/Al ratio. Plot A is for Aha Lake and plot B is for Hongfeng Lake. For plot A, data points for SPM of AHDB in summer is green triangle, AHDB in winter is red triangle, AHLJK in summer is green square, AHLJK in winter is red square. In addition, the date of YYR, 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.

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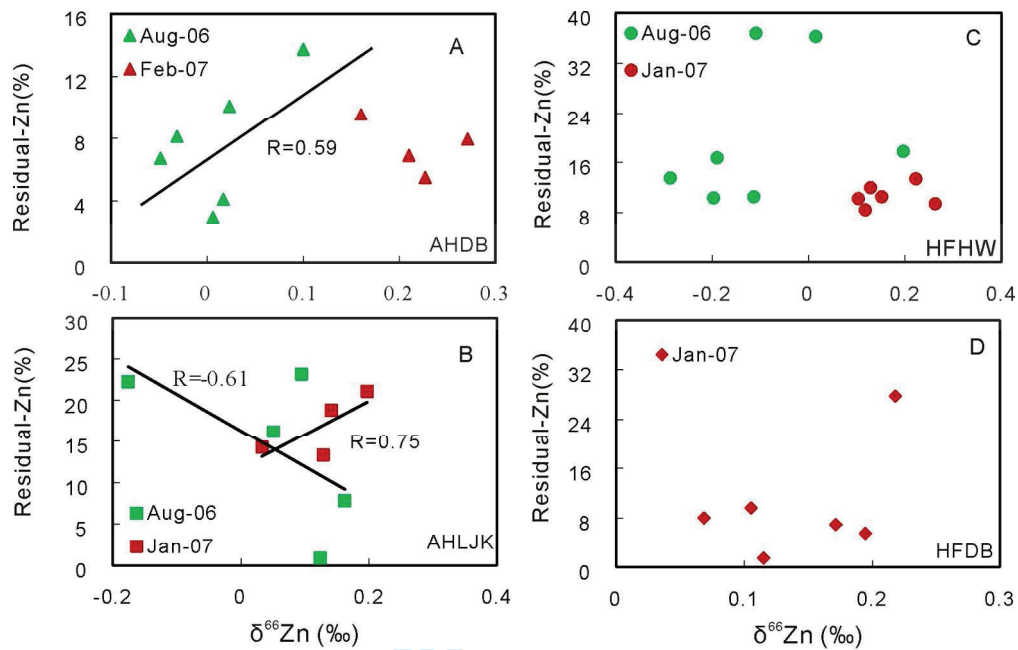
Fig .6. The δ^{66}Zn versus to residual bound Zn of SPM. The A and B refer to for AHDB and AHLJK profiles respectively, and the C and D refer to HFHW and HFDB profiles. The green triangle and red triangle refer to the data in summer and winter respectively for AHDB respectively, and the green square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

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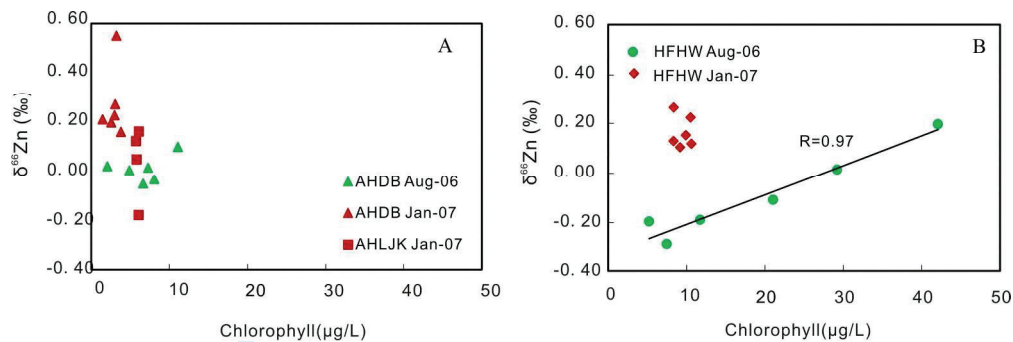
Fig. 7. The δ^{66}Zn of SPM versus to chlorophyll in Aha and Hongfeng Lakes. Plot A is for Aha and Plot B is for Hongfeng Lake. The green triangle and red triangle refers to the data in summer and winter for AHDB respectively, the green square and red square refer to the data in summer and winter for 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 SPM	Sampling date	Depth m	pH	T(℃) (℃)	DO mg/L	Chlorophyll mg/L	SPM mg/L	Zn(DIS) 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

Table2: The Zn isotope composition, SPM Zn and Al_2O_3, and speciation Zn of SPM in summer and winter for Aha Lake and Hongfeng Lake.

Sample site SPM	Date	Depth m	Al_2O_3(SPM) %	Zn(SPM) mg/g	AEC-Zn(SPM) %	organic-Zn(SPM) %	Residual-Zn(SPM) %	$\delta^{66}Zn_{JMC}$ (‰)	Zn/Al
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 m³/S	Draining In/Out	pH	T (℃)	Do mg/L	SPM mg/L	Zn-DIS µg/L	Zn-SPM mg/g	AL₂O₃ %	δ⁶⁶Zn_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
Turbutaries 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