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1 **Mobile Trace Elements in Sediments from Lakes Hawassa, Koka, and Ziway in the Ethiopian Rift Valley**

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23

24 **Abstract**

25 The present work focuses on total concentrations of trace elements such as chromium (Cr), manganese (Mn), cobalt
26 (Co), nickel (Ni), copper (Cu), zinc (Zn), arsenic (As), selenium (Se), cadmium (Cd), and lead (Pb) and their
27 operationally defined speciation in surface sediments from three Ethiopian Rift Valley Lakes (Hawassa, Koka, and
28 Ziway). Total concentrations were determined using Inductively Coupled Plasma-Mass Spectrometer (ICP-MS). A
29 six-step sequential extraction was also applied to evaluate the mobilization potential of these elements. Compared
30 with the consensus-based sediment quality guidelines (SQGs) developed for freshwater ecosystems, the total Zn
31 concentration in sediments from Lakes Hawassa and Ziway, as well as Cr, Ni, and Zn in sediments from Lake Koka
32 were higher than the probable effect concentration (PEC), suggesting that these elements could have a negative
33 effect on benthic organisms. The sequential extraction results showed that Cd, Mn, and Se were to a certain extent
34 associated with the reversible fractions (F1–F3) in sediments, and thereby more mobile than the other investigated
35 trace elements. Predictions of mobility of trace elements using the distribution coefficients (K_d) values were also in
36 agreement with the sequential extraction results. Furthermore, multivariate statistical analyses showed that redox-
37 sensitive fractions (F4 and F6) and the residual fraction (F7) were the dominant factors controlling most trace
38 element mobility. Finally, applying the Risk Assessment Code (RAC) classification system, results showed that Mn
39 in Lake Koka could pose a high risk, while Cd and Mn in Lake Hawassa as well as Cd, Mn, and Se in Lake Ziway
40 sediments could pose medium risk to benthic organisms.

41

42 Key words: Rift Valley, lake sediments, sediment quality guidelines, sequential extraction, multivariate statistical
43 analysis

44

45

46 **Introduction**

47 The Ethiopian Rift Valley Lakes (ERVL), located in the Great East Africa Rift Valley (GEARV), are considered to
48 be very important for the economy of the region, to the livelihood of the local population, and to the biodiversity
49 conservation of the water bodies. The lakes have mostly been used for commercial fisheries, irrigation, recreation,
50 and some domestic purposes (Gebre-Mariam and Desta 2002; Zinabu 1998). However, due to increased human
51 activities, there is a concern that severe contamination of these scarce fresh water resources could go unnoticed and
52 eventually lead to irreversible degradation. There are already indications that long-term changes have occurred in
53 the water qualities of some of these lakes (Zinabu et al. 2002). These changes have mainly been attributed to human
54 activities such as intensive agriculture in the watersheds of the lakes, land use and modification, as well as municipal
55 and industrial discharges into the lakes and their inflows (Gebre-Mariam and Desta 2002; Zinabu 1998)

56 Evaluation of trace element levels in water, sediment, and biota is an essential component of environmental
57 monitoring and assessment. For the ERVL considered in this study (Hawassa, Koka, and Ziway), information on the
58 total concentrations of trace elements in water (Masresha et al. 2011; Zinabu and Pearce 2003), aquatic macrophytes
59 (Amare et al. 2014; Kassaye et al. 2016), and different organs of selected fish species (Ataro et al. 2003; Kebede and
60 Wondimu 2004; Desta et al. 2006, 2007, 2008; Tadiso et al. 2011; Dsikowitzky et al. 2013; Deribe et al. 2014; Sorsa
61 et al. 2016; Samuel et al. 2020; Tessema et al. 2020) have been documented. Speciation of selected trace elements in
62 the lake waters have also been studied (Masresha et al. 2011). Besides, total concentrations of selected trace
63 elements in sediments from Lake Hawassa (Amare et al. 2014; Yohannes et al. 2013), and from Lakes Hawassa and
64 Ziway (Mekonnen et al. 2015; Mekonnen et al. 2012) have also been studied. However, proper assessment of trace
65 elements in lake sediments requires determination of not only their total concentrations, but also of their different
66 geochemical associations controlling their potential mobility and bioavailability (Fytianos and Lourantou 2004;
67 Gibbs 1973; Hass and Fine 2010; Tessier and Campbell 1987; Tessier et al. 1979).

68 In this regard, to the best of our knowledge, speciation studies of trace elements in sediments from ERVL in general
69 and Lakes Hawassa, Koka, and Ziway in particular have not been reported to date. Therefore, the main objective of
70 the present study was to apply chemical sequential extractions to assess the mobility, bioavailability, and possible
71 environmental risks associated with selected trace elements in surface sediments from these three freshwater lakes of
72 the Ethiopian rift valley.

73 **Materials and methods**

74 Description of study area

75 The study area included three lakes (Hawassa, Koka, and Ziway) located in the ERVL region (Fig.1). The Ethiopian
76 Rift Valley extends over 750 km from the southwest to the northeast and is dominated by acidic silica-rich
77 (rhyolites, ignimbrites, pumices and ash) volcanic rocks (Gizaw 1996).

78 Lake Hawassa (Lat: 6°58'–7°8'N; Long: 38°22'–38°27'E) is a terminal lake with no visible surface outflow. It is
79 located at an altitude of 1680 m above sea level (a.s.l), and has a maximum depth of about 22 m (Wood & Talling,
80 1988) with surface and catchment areas of 90 and 1250 km², respectively (Kebede et al. 1994). Lake Hawassa is

81 fed by the River Tikur Wuha, the only perennial inflow, which drains a swampy wetland - a remnant of the former
82 old Lake Shallo (Makin et al. 1975). The Hawassa Industrial Zone which has a cluster of factories, including a
83 textile factory, is situated upstream of the lake and the effluents from these factories are discharged into the swampy
84 area from which River Tikurwhua originates (Gebre-Mariam and Desta 2002; Samuel et al. 2020). A more detailed
85 description of Lake Hawassa and its catchment can be found in Desta et al. (2006, 2007, 2008).

86 Lake Koka (Lat: 8°17'–8°29'N; Long: 38°55'–39°79'E) is an artificial lake situated in the Awash River Basin and
87 has been referred to as the Koka Reservoir in some literature (Mesfin et al. 1988; Zinabu and Pearce 2003). The lake
88 is located at an altitude of 1660 m a.s.l and has a surface area of 200 km². The reservoir was created after
89 construction of the Koka Dam across the River Awash in 1960 (Hughes 1992) for irrigation and hydroelectric power
90 development purposes. River Mojo and River Awash are the main inflows; while River Awash also drains the lake.
91 The Little and Big Akaki Rivers, being tributaries of the River Awash, have been identified as the most polluted
92 rivers in the country (Alemayehu 2001). The Ethiopian Tannery, the largest in the country, is also situated within the
93 Lake Koka catchment area.

94 Lake Ziway (Lat: 7°51'–8°07'N; Long: 38°43'–38°56'E) is fed by River Meki from the west and River Katar from
95 the east; and it is drained by the River Bulbula which finally joins Lake Abiyata (Fig.1). It is situated at 1636 m a.s.l
96 and has maximum depth of 7 m. The surface and catchment areas of the lake are 442 and 7025 km², respectively (E.
97 Kebede et al. 1994). The town of Ziway is situated at the western shore of the lake and, as a result, there is intensive
98 human activity such as the use of lake water for irrigation, excessive expansion of floriculture farms (greenhouses),
99 and commercial fish farming (Ayenew 2007).

100 Sample collection and storage

101 Sampling of sediments from all the three lakes was carried out between July and September 2009. A gravity corer
102 (diameter = 4.5 cm) made from hard plastic (Plexiglass) was used to collect surface sediment samples. Sampling
103 was performed at about the center of each lake in order to minimize any disturbance that could occur from the shore
104 and hence could represent accumulation sites for bottom sediments. The depths of all the sediment cores obtained
105 were less than 10 cm, and results are reported for the upper surface layer (upper 6 cm).

106
107 After sampling, the sediment cores were immediately sliced into 2 cm sections with a clean plastic cutter and then
108 transferred to a clean and dry self-sealing polyethylene bags. The samples were then marked and kept in an ice-box
109 until they were transported to the laboratory at Hawassa University (within 24 hrs), where they were kept in the deep
110 freezer at -20°C. It is believed that freezing samples at -20 to -30°C is the most dependable method of sediment
111 storage especially for trace elements and potentially for chemical speciation purposes (Förstner and Wittmann
112 1981), although perturbations due to freezing must be taken into account (Hlavay et al. 2004; Kersten and Förstner
113 1995). The samples were again transferred to an ice-box for transport to The Norwegian University of Life Science
114 (NMBU), Norway, and kept in the deep freezer at -20°C prior to sequential extractions and the determination of total
115 concentrations of the trace elements.

116

117 Sample preparation, pH, and loss on ignition (LOI)

118 The samples were defrosted and excess water was removed by vacuum filtration. A 1 gram sub-sample from each 2
119 cm section was dried overnight at 105°C in a muffle furnace to determine the water content. The organic matter
120 content of the sediment was determined by loss on ignition (LOI) using a temperature of 550°C for 12 hrs.
121 Subsequently, the wet weight equivalent to the required 1 or 2 gram dry weight was determined based on water to
122 dry sediment ratio. The wet sediment weighing was done shortly after vacuum filtration to avoid water loss by
123 evaporation due to exposure to air. The sediment pH was determined by using a glass electrode (Mettler Toledo,
124 SenTix 21) after the samples were mixed with deionized water in a ratio (1:5) and allowed to settle for overnight.

125 For determination of total concentrations of the trace elements, subsamples were freeze dried, homogenized, sieved
126 (2 mm) and dried samples of about 0.2 and 0.3 g were generally collected for analyses.

127 Sequential extraction procedure (SEP)

128 The sequential extraction of sediment samples was carried out according to the procedure described by Oughton et
129 al. (1992) with slight modifications (Salbu 2000; Skipperud et al. 2009). Wet sediment samples were used in order
130 to preserve as much as possible the original trace element speciation, as drying techniques would influence trace
131 element speciation in sediments and should therefore be avoided (Rapin et al. 1986). The sediment samples were
132 accurately weighed in centrifuge tubes (50 mL, Nalgene Centrifuge Ware) and subjected to sequential extraction by
133 applying the operating conditions and reagents summarized in Table 1. For convenience, the fractions were referred
134 to as F1–F7 (Table 1) where F7 was the residue. The supernatants from each step were separated from undissolved
135 sediments by high speed centrifugation (10,000 g) using the Beckman Avanti 30 Centrifuge. The trace elements in
136 the residual fractions (F7) were determined after acid digestion using UltraClave (Milestone Microwave Laboratory
137 Systems, USA).

138

139 The Risk assessment code (RAC) system was applied to assess the potential environmental risk of the elements
140 investigated. According to this system, the environment risk caused by a trace element is judged to have no risk, low
141 risk, medium risk, high risk and very high risk if the relative (%) sum of the water soluble and exchangeable fraction
142 was <1, 1-10, 11-30, 31-50, and >50%, respectively (Jain 2004).

143

144 Chemical analysis

145 All sediment extracts were heated to dryness on sand bath at 80–90°C and the residue left after dryness was re-
146 dissolved using 2 mL ultrapure HNO₃. This procedure was repeated three times. The residues left after final drying
147 were later re-dissolved in 2.5 mL ultrapure HNO₃ and transferred into a 50 mL clean brand new test tubes.
148 Subsequently, 250 µL of internal standard containing 4 mg/L of rhodium (Rh), indium (In), tellurium (Te) and
149 thalium (Tl) was added for measurement purposes, and then the samples were diluted with deionized water
150 (Barnstead, >18 MΩ.cm⁻¹). Calibration blanks and standard solutions were used for calibrating the Inductively

151 Coupled Plasma-Mass Spectrometer - ICP-MS. (Perkin Elmer Sciex, ELAN 6000). The residues obtained from the 7
152 M HNO₃ acid treatment were further diluted ten times prior to analysis. The total trace element concentrations were
153 determined following acid digestion by the UltraClave (Milestone Microwave Laboratory Systems, USA) using the
154 same procedure as described for the residual fraction. A mixture of 5 mL HNO₃ and 1 mL of HF were added to
155 accurately weighed 0.2–0.3 g samples and digested at high temperature (maximum 260°C) and pressure (max. about
156 160 bar) in an UltraClave. Samples were taken after about 2 hours, and 6 mL of saturated boric acid (H₃BO₃) was
157 added to each digested sample and heated again at a temperature of 85°C in ultrasonic bath for 30 minutes. .

158 The accuracy of the determination of trace elements was evaluated by using standard reference material (National
159 Institute of Standards and Technology, SRM-1646 estuarine sediment). The precision of the total digestion
160 procedure was estimated from replicates (n = 5) each weighing about 0.2–0.3 g. The accuracy of the sequential
161 extraction procedure was evaluated by comparing the sum of the trace element concentrations of all fractions
162 (Σ SEP) with the total concentrations obtained from UltraClave digestion using HF-HNO₃-H₃BO₃ mixture. The
163 precision of the method for the sequential extraction procedure was estimated from replicates (n = 5) of 1 g dry
164 sediment samples subjected to the same sequential extraction procedure as the samples.

165 The limits of detection (LOD) for the residual fractions and total concentrations of trace elements were determined
166 by 3 times the standard deviation of 18 blanks, while the LOD for the other sequential extracts were determined by 3
167 times the standard deviation of 13 blanks. The accuracy, i.e. deviations of measured values (n = 2) from the certified
168 value(s) of the reference material (SRM-1646) (Table 2) was < 10 % for all elements except Cr (12 %), while the
169 precision for total and residual trace element determinations were all less than 5 %, indicating that our data should
170 be considered reliable.

171 172 **Statistics**

173 Arithmetic and geometric mean values were calculated for the trace element concentrations in sediments. If the
174 mean and geometric mean values were similar, the distributions were assumed to be near normal.

175 Dixon's Q-test was applied to test outliers, and results showed that one of the replicate values for the H₂O₂-
176 extractable fractions obtained for precision determination was actually an outlier, and thus not included in the mean
177 calculation. The distribution coefficients (K_d) between surface sediment and the lake water were calculated
178 according to

$$179 \quad K_d = C_{\text{sediment}} / C_{\text{water}} \cdot C_{\text{sediment}}$$

180 where **C_{sediment}** refers to concentration (µg/g d.w.) of a trace element in sediment, while **C_{water}** refers to the
181 concentration (µg/mL) of the same trace element in surface water of the lakes studied. Concentrations of trace
182 elements in water used for the K_d calculation have previously been published by our group (Masresha et al. 2011).

183 Multivariate analysis was conducted by using the CANOCO 4.5 software package, including the diagram software

184 CanoDraw 4.14. Partial redundancy analysis (pRDA) was performed to evaluate the overall variation and patterns in
185 the data related to the trace element concentrations obtained from the various sequential extraction steps. In addition,
186 an initial pRDA was also performed to identify if there were any differences in trace element concentrations among
187 the different lakes and sediment depths.

188
189 The concentrations of trace elements in some of the samples, 19 out of 140 (14 %), were below the limits of
190 detection (LOD). Hence, we considered the substitution of samples having trace element concentrations below LOD
191 with half of LOD in our data set as valid, in accordance with (Antweiler and Taylor 2008) stating that substituting
192 left-censored data below LOD with $LOD \cdot 0.5$ is an adequate method if the amount of censored data is not too high.

193 The various samples were classified according to their respective sequential extraction step, lake, and depth. The
194 classifications were further applied to make a set of categorical explanatory variables, i.e. seven sequential
195 extraction steps, three lakes, and three sediment depths. The categorical explanatory variables were coded by
196 dummy-values, i.e. 1 and 0. Prior to the analyses, the data was $\log(x+1)$ transformed to reduce the effects of extreme
197 values, and in addition, centered and standardized (i.e. bringing their means to zero and their variance to one).

198 Since the variables lake and depth are not independent, it was decided to use the interaction between the two
199 variables (lake x depth) as the explanatory variable in the initial pRDA. In addition, the seven sequential extraction
200 steps were included as co-variables (i.e. removing the effect of the various sequential extraction steps). Samples
201 belonging to specific sequential extraction steps were defined as blocks in the permutation set-up (i.e. the blocks
202 were defined by the co-variable). Samples within each block were freely permuted and between-block variation was
203 thus excluded from the test.

204 To evaluate if there were any overall differences between the various sequential extracts in terms of trace element
205 concentrations, partial redundancy analysis (pRDA) was performed. In this model, the seven sequential extracts
206 were used as explanatory variables and the interaction between lake and sediment depth was used as co-variable. A
207 total of nine blocks were defined using the co-variable lake x sediment depth as criteria, and the permutations were
208 only performed on samples within these blocks. Hence, between-block variation was excluded from the test.

209 The permutation tests were performed by the Monte Carlo permutation test and results with $p < 0.05$ were assigned
210 statistically significant. We used 499 permutations under reduced model, which is preferable with small data sets.

211 **Results and discussion**

212 Data quality

213 The precision of the sequential extraction procedure was in the range: 2–25 % for As, 3–12 % for Cd, 1–14 % for
214 Cr, 4–11 % for Co, 1–20 % for Cu, 2–23 % for Pb, 1–17 % for Mn, 2–11 % for Ni, 8–17 % for Se, and 4–19 % for
215 Zn. The measurement uncertainties varied according to the concentrations of the elements in the different extracted
216 fractions.

217 The sum of concentrations in seven sequential extracts (Σ SEP) is compared with the total concentrations obtained
218 from a single step dissolution of the same samples in Table 3. The differences between total trace element
219 concentrations and Σ SEP values were mostly <20 %. Higher deviations could occasionally be observed for trace
220 elements with concentrations close to LOD due to higher uncertainties associated with measurements and possibly
221 also due to higher relative loss due to sorption processes during extractions. Taking the lack of sediment
222 homogeneity into account, the agreement between total concentrations from the single step digestion and sequential
223 extractions (Σ SEP) was judged to be acceptable.

224 Sediment characteristics

225 Tudorancea and Zullini (1989) reported that the type and size of particles in the deeper sediment parts of Lakes
226 Hawassa, Koka, and Ziway were medium and fine silt, having particle size in the range 2–63 μ m (Förstner and
227 Wittmann 1981). Sediment characteristics such as water content, percent loss on ignition (% LOI) and pH are
228 presented in Table 4. The mean pH of the sediment samples from all the three lakes varied between 8.0 and 8.5, and
229 the sediments could be categorized as weakly alkaline. The water content (weight %) in the sediment was in general
230 close to or more than 50 %; and the 2-cm top sediment layers appeared to have similar water contents as the lakes.
231 The mean LOI (%) values of the sediments from the three lakes varied between 7 and 34 %, and the LOI (%) values
232 were the lowest for sediments from Lake Koka (% LOI₅₅₀ = 7.3–7.6). In agreement with this study, Mesfin et al.
233 (1988) and Tudorancea and Zullini (1989) reported that LOI (%) values for Lake Koka were in the ranges 7.4–11.5
234 %. Although the mean LOI (%) values reported for Lake Ziway in the present study (8.3–11 %) were within the
235 range (4.7–21.4 %) reported by Tudorancea and Zullini (1989), they were nearly two times lower than the maximum
236 LOI reported by these authors. The LOI (%) determined in this study for sediments from Lake Hawassa (29–34 %) appeared to be higher than the results reported in a previous study (5–23 %) (Telford et al. 1999). However, the LOI (%) reported in this study for Lake Hawassa was comparable with the maximum LOI (%) previously reported (3.8–31.4 %) by Tudorancea and Zullini (1989).

240 Total concentrations of trace elements

241 The vertical distribution of the trace element concentrations in the 6 cm core were quite even (Table 3). For that
242 reason, the concentrations in the top 2 cm were chosen for comparisons. The average total concentrations of trace
243 elements decreased in the order: Mn > Zn > Cr > Ni > Pb > As > Cu > Co > Se > Cd in Lake Hawassa, Mn > Zn >
244 Cr > Ni > Cu > Co > Pb > As > Cd > Se in Lake Koka, and Mn > Zn > Cr > Ni > Cu > Pb > Co > As > Se > Cd in
245 Lake Ziway (Table 3). The sequence was surprisingly similar, especially in sediments from Lakes Koka and Ziway,
246 possibly reflecting sources of natural origin of the trace elements in these lakes.

247 The mean concentrations of Cr and Co in the three lakes, and Cu in Lakes Koka and Ziway were higher than values
248 reported for five Kenyan Rift Valley Lakes - KRVL (Ochieng et al. 2007) by factors of about 5–20, 5–14, and 2,
249 respectively. However, the average concentrations of Cd, Pb, Mn and Zn in sediments from all the three lakes, and
250 Ni and Cu in sediments from Lake Hawassa were all within the ranges reported for the five KRVL (Ochieng et al.
251 2007). As both the Kenyan and the Ethiopian lakes are located within the same geological settings, higher

252 concentrations of some of the trace elements could be attributed to inputs from both local point and diffuse sources.

253 When comparing the present data with values assigned to unpolluted sediments (Förstner and Wittmann 1981), the
254 concentrations of Cr, Mn, Ni, and Zn in Lake Koka, and Mn, Zn, and Se in Lakes Hawassa and Ziway were higher
255 than concentrations considered to be unpolluted. Similarly, comparison of our data with consensus-based freshwater
256 sediment quality guidelines - SQGs (Table 3) developed by MacDonald et al. (2000), indicated that the
257 concentrations of Cr, Ni and Zn in sediments from Lake Koka, and Zn in sediments from Lakes Hawassa and Ziway
258 could potentially induce harmful effects to the benthic organisms as the values exceeded probable effect
259 concentrations (PEC). The total concentrations of As, Cd, and Pb were all lower than the Threshold Effect
260 Concentration (TEC) suggesting that it was unlikely that these trace elements could cause any negative effects on
261 benthic organisms. The consensus-based SQGs are derived from sediment quality guidelines developed by matching
262 sediment chemistry with toxicity tests which implies that the bioavailability has been taken into account. However,
263 SQGs developed for North America cannot directly be utilized at other continents due to: 1) the influence of
264 temperature variation on biochemical reaction rates, metabolic rates, and biological activity (Chapman et al. 2006),
265 2) differences in benthic communities in different regions, and 3) variations in sediment chemistry (mixtures of
266 contaminants), etc. (De Deckere et al. 2011). Since there are no SQGs developed for Ethiopia, information on
267 mobility of the trace elements in bottom sediments, rather than total concentrations, could therefore be used for
268 ecological risk assessment.

269 Sequential extraction of sediments

270 The relative distribution (%) of trace elements in the different sequential extracts (F1–F7), as compared to the total
271 concentrations of all extracts, is presented in Fig. 2. The relative fractions of trace elements extracted by H₂O (F1)
272 were in general low (0–2 %) for all elements investigated; however, somewhat higher in sediments from Lake Koka
273 (0.3–1.8 %) as shown in Fig. 2. The relative fraction of trace elements in the F2 extract (pH 7 NH₄OAc) was also
274 low (<1 %), except for Cd (6 %) and Mn (17%) in sediments from Lake Koka (Fig. 2). The low trace element levels
275 in the F1 and F2 reflected low mobility of the elements. In this study, the mean pH of the lake sediments was
276 between 8.0 and 8.5 indicating that the sediments were slightly alkaline. Generally, solubility of many trace metals
277 in water decreases as a result of increasing pH (Avila-Pérez et al. 1999).

278 The relative fraction of trace elements in the F3 fraction (pH 5 NH₄OAc) varied from 0.1–22 % which suggested a
279 large variation among the different trace elements (Fig. 2). The dominating trace elements in this fraction were Mn
280 (16–20 %), Cd (10–17 %), and Se (5–17 %) indicating that a considerable proportion of these elements were
281 reversibly associated to the lake sediments. Trace elements in the F1-F3 fractions are normally considered to be
282 reversibly associated (physical and/or electrostatic sorption) to sediment surfaces (Salbu 2000). In contrast, trace
283 elements in the F4–F7 fractions are assumed to be irreversibly associated with sediments due to irreversible
284 chemisorption (Salbu 2000) as redox agents are needed for dissolution.

285 The relative fraction of trace elements in the F4 extract (NH₂OH.HCl) varied from 1–33 %, and the dominating trace
286 elements were Mn (20–30 %), Cd (15–33 %), Se (8–15%), Ni (10–15 %), and Pb (7–14 %). For Co (2–22 %), the

287 highest extractable fraction was observed in Lake Koka; while for As (2–15 %), the highest fraction was observed in
288 sediments from Lake Hawassa. As a weak reducing agent was applied in F4, the fraction extracted was assumed to
289 be associated with amorphous LOI materials or hydroxides/oxides of elements such as Fe, Mn, or Al.

290 The relative fraction of trace elements in the F5 extract, where H₂O₂ was used as a weak oxidizing agent, varied
291 from 0.1–87 % in the different lakes. The dominating trace elements were Se (48–87 %) and Ni (10–39 %), while
292 large variations were found for As (1–36 %) and Co (2–22 %) among the study lakes. The highest fractions were in
293 general found in sediments from Lake Hawassa, probably due to the relatively higher LOI (%) values of the
294 sediments (Table 4) indicating association to organic material. In general, lake sediments with high organic matter
295 due to the presence of stable high molecular mass humic substances could release relatively higher fractions of trace
296 metals under oxidizing conditions (**Jain et al. 2007; Singh et al. 1998**). The sum of the F6 (7 M HNO₃) fraction and
297 the F7 (residual fraction) were 44–96 % for As, 40–65 % for Cd, 91–95 % for Cr, 68–75 % for Co, 88–96 % for Cu,
298 76–90 % for Pb, 30–56 % for Mn, 47–72 % for Ni, 0–24 % for Se, and 91–95 % for Zn, indicating that most of the
299 trace elements were strongly bound to the sediments. Similar to our findings, most of the trace elements investigated
300 in the sediment of Badvci lake (Kosovo) were found in the residual fraction (**Malsiu et al. 2020**). This metal
301 fraction was of detrital and lattice origin which originates from natural sources (**Salomons and Förstner 1980**). It
302 is very unlikely that these trace element fractions would be mobilized and become bioavailable to aquatic biota
303 under the natural conditions found in the lakes. If the sediments are used as food sources by bottom-dwelling
304 organisms, bioavailability could be controlled by assimilation efficiency which, in turn, depends on the type of
305 metal, the physico-chemical form, and distribution in prey, species digestive physiology, environmental conditions,
306 food quality, food ingestion rate, and metal concentration in the diet (Wang and Fisher 1999). In such a case,
307 consensus-based SQGs could be of significance for detritus feeding organisms.

308 To evaluate the relationship between the various fractions (F1–F7) and the trace element concentrations,
309 multivariate statistical analysis using partial redundancy analysis (pRDA) was performed. The pRDA showed that
310 the differences in concentrations among the various sequential extraction steps could significantly ($p = 0.002$)
311 explain 80 % of the total variation in the sequential extraction data from all study lakes. Lake and sediment depth
312 interactions significantly ($p=0.002$) explained only 5.5 % of the variance.

313 The relationship between the concentrations of trace elements and the respective fractions are shown using the RDA
314 bi-plot (Fig. 3). The RDA bi-plot (Fig. 3) shows that the first extraction steps were generally associated with low
315 leachability/mobility (small sized sample symbols); whereas the later extraction steps were associated with trace
316 elements strongly bound to the sediment phases that were dissolved using agents of high dissolution power (large
317 sized sample symbols). In particular, the concentrations of most of the trace elements were negatively correlated
318 with their concentrations extracted in F1, F2, and F5, but positively correlated with the concentrations extracted in
319 F4, F6, and F7, and partially to F3. This implies that relatively large concentrations of the trace elements were found
320 in F4 (NH₂OH.HCl-extractable), F6 (HNO₃-extractable), and F7 (residual) fractions, i.e. the redox and temperature
321 influenced fractions. Cadmium (Cd) and Mn displayed another release pattern compared to the other trace elements,
322 i.e. were more related to F3 (pH 5 NH₄OAc-extractable) and F4 (NH₂OH.HCl-extractable) and agreed with results

323 (Fig. 2) that these trace elements were more mobile than the others.

324 Sources, mobility and bioavailability of the trace elements

325 In previous studies (Izquierdo et al. 1997; Turki 2007), it was reported that the relative distribution between residual
326 and non-residual fractions (exchangeable, “carbonates”, reducible and oxidizable fractions) could be used to predict
327 whether the primary sources of the trace elements would be of anthropogenic or lithogenic origin. According to
328 Samanidou and Fytianos (1987), trace metals from anthropogenic sources are usually present in relatively more
329 mobile forms than those from natural sources. Thus, trace elements found mainly in the residual fraction could be
330 considered to originate from lithogenic minerals, and as a result, did not have a remobilization potential under
331 normal changing environmental conditions encountered in nature. Applying this approach to the present data, the
332 non-residual (F1–F5) fractions (sum total of H₂O-, pH 7 NH₄OAc-, pH 5 NH₄OAc-, NH₂OH.HCl- and H₂O₂-
333 extractable fractions) of As, Cd, Ni, and Se in sediments from Lake Hawassa, Cd, Mn, and Se in sediments from
334 Lake Koka, and Se in sediments from Lake Ziway exceeded 50 % of the total concentrations, indicating a
335 contribution from a local anthropogenic sources possibly such as agricultural runoff, municipal and industrial wastes
336 etc.

337 The assumed reversible fractions could also be used to assess potential mobility of trace metals (Salbu 2000;
338 Skipperud et al. 2009). Therefore, it can be assumed that the F1–F3 fractions (H₂O-, pH 7 NH₄OAc-, and pH 5
339 NH₄OAc-extractable fractions) represent the mobile fractions in the present study. Accordingly, the sum of the
340 concentrations of trace elements in the first three sequential extracts accounted for 2–6 % for As, 11–24 % for Cd,
341 <1% for Cr, 1–8 % for Co, 1–3 % for Cu, 2–6 % for Pb, 20–35 % for Mn, 3–4 % for Ni, 5–17 % for Se, and <1 %
342 for Zn in all the three lakes considered in this study. These results suggested that most of the trace elements
343 investigated were strongly associated to the sediments, indicating that their remobilization potentials were very low.
344 Thus, based on results obtained from sequential extraction, trace elements of highest mobility were Cd, Mn and Se,
345 while Zn and Cr were elements of extremely low mobilization potential.

346 Application of risk assessment code (RAC)

347 According to the RAC classification system, a scale was developed based on the sum of the relative (%) fraction of
348 trace elements in the assumed exchangeable and “carbonate” fractions (**Jain 2004; K. P. Singh et al. 2005**) in the
349 upper 6-cm sediment as this is expected to be the most reactive part of the sediment with overlying surface water
350 (Sallade and Sims 1997). Accordingly, trace elements accumulated in sediments could be considered safe to the
351 environment if the sediment releases <1 % of their total concentrations in the assumed exchangeable and
352 “carbonate” fractions. In addition, trace elements in sediments are considered to easily enter the food chain and pose
353 a risk to the aquatic environment if the sediments could release more than 50 % of total concentrations in these
354 fractions.

355 Based on the RAC criteria, the risk from the trace elements in the study lakes could be arranged as follows:

356 Lake Hawassa: Cd and Mn (Medium risk) >As, Co, Cu, Pb, Ni, and Se (Low risk) > Cr and Zn (No risk)
357 Lake Koka: Mn (High risk) > Cd (Medium risk) > As, Co, Cu, Pb, Ni, and Se (Low risk) > Cr and Zn (No risk)
358 Lake Ziway: Cd, Mn, and Se (Medium risk) > As, Co, Cu, Pb, and Ni (Low risk) > Cr and Zn (No risk)

359 It is important to emphasize that these conclusions are derived barely from sequential extraction results which are
360 contradictory to the predictions made by comparing total concentrations with consensus-based SQGs. However, diet
361 related exposure of mobile trace elements at high total concentrations may be of importance if the benthic organisms
362 use sediments as a source of food.

363
364 The distribution coefficients (K_d)

365 To estimate the transfer of trace elements from sediment to the overlying waters the distribution coefficients, K_d ,
366 based on total concentrations in sediments and water are frequently applied (Lee et al. 1997; AaPGCC Tessier and
367 Campbell 1987) in impact assessment models. The mean K_d values for the trace elements included in this study are
368 shown in Table 5. The distribution coefficients ranged in general from 10^3 to 10^5 d.w. with highest transfer (K_d of
369 10^3 d.w.) of Se, As, and Cu in Lake Hawassa, Se and most other elements in Lake Koka and Se as well as As, Cu,
370 and Cd in Lake Ziway. Low mobility (K_d of 10^5 d.w.) were obtained for Cr, Cu and Zn in Lakes Hawassa and Ziway.
371 As the K_d concept is based on the assumption that equilibrium/pseudoequilibrium exists between the sediment
372 surface and the water phase, the data from Lake Koka was recalculated as the water contained a high load of
373 particles. Thus, the total concentration of trace elements in water was replaced with the concentration of potentially
374 interacting low molecular mass (LMM) species in water (Table 5, column 4). Recalculation showed that As and Se
375 could be considered as mobile (10^3 d.w.), while Cu, Cr and Zn were inert (K_d of 10^5 d.w.) which was in agreement
376 with results from the other lakes. Therefore, it appeared that K_d values based on total concentrations of trace
377 elements in sediments (Σ SEP) and the concentrations of LMM (<10 kDa) species in water rather than total sediment
378 concentrations and total water concentrations should better predict the potential sediment–water transfer of trace
379 elements in the studied lakes.

380 Predictions of mobility of trace elements using the K_d values and sequential extraction results were partly in
381 agreement. Trace elements such as Se as well as also Cd in Lake Ziway were predicted to be the most mobile
382 elements by both methods. On the other hand, Mn was predicted as one of the most mobile together with Cd and Se
383 using sequential extraction but was not supported by the K_d values. A possible reason could be that the
384 concentrations of trace elements in surface waters did not only reflect the sediment transfer concentrations, but also
385 includes contribution from other sources.

386 **Conclusions**

387 The present study provides baseline information with respect to the total concentrations and operationally defined
388 speciation of a series of trace elements in surface sediments from Lakes Hawassa, Koka, and Ziway situated in the
389 Rift Valley. This information is of paramount importance as this study is the first of its kind from these tropical

390 lakes that are exposed to many different anthropogenic sources. Comparisons of total concentrations with both
391 reference values for unpolluted sediments and consensus-based SQGs gave predictions that trace elements such as
392 Cr, Ni and Zn in Lake Koka could bring about adverse biological effects in benthic organisms. As sequential
393 extraction demonstrated that desorption of these elements was rather limited, the expected biological effects may
394 occur only if the sediments are directly ingested by bottom feeding organisms. The results obtained from sequential
395 extraction indicated also that the mobility of the trace elements present in relatively high concentrations (e.g., Cr, Ni
396 and Zn) were very low and the corresponding K_d values were very high (K_d of 10^5 d.w.), except for Mn being
397 somewhat more mobile (K_d of 10^4 d.w.). The low mobility of the trace elements investigated could also suggest that
398 natural sources were more relevant than anthropogenic sources in these lakes, although a series of anthropogenic
399 sources are situated in the catchments. Cadmium has concentrations corresponding to unpolluted sediments, but
400 such results must be interpreted with caution as Cd has high remobilization potential ($F_1+F_2+F_3 = 11-24$ %, K_d of
401 10^4 d.w.). Based on the risk assessment code (RAC) system for sediments, Cd, Mn and Se were predicted to
402 represent medium to high risk to bottom-dwelling organisms in the lakes. Although sequential extraction and
403 calculation of K_d values seem most useful to predict potential mobility of trace elements from sediments to pore and
404 overlying waters, exposure of trace elements to biota such as benthic organisms depends not only on mobilization
405 and speciation, but also on ingestion of sediments and uptake of bioavailable trace elements. Therefore, future work
406 should compare results from toxicity tests of relevant sediment living exposed organisms with predictions associated
407 with trace elements in sediments and their potential adverse biological effects derived from the consensus based
408 SQGs.

410 Table 1. Extracted fractions, reagents and conditions employed in the current sequential extraction procedure from
 411 Oughton et al. (1992).

Fractions	Reagents	pH	Temp. (°C)	Time (h)
F1 H ₂ O	20 mL H ₂ O	7.0	20	1
F2 pH 7 NH ₄ OAc	20 mL 1 M NH ₄ Ac	7.0	20	2
F3 pH 5 NH ₄ OAc	20 mL 1 M NH ₄ Ac (adjusted to pH 5 with HAc)	5.0	20	2
F4 NH ₂ OH.HCl	20 mL 0.04 M NH ₂ OH.HCl in 25 % v/v HAc (adjusted to pH 3 with HNO ₃)	3.0	80	6
F5 H ₂ O ₂	15 mL 30 % H ₂ O ₂ (adjusted to pH 3 with HNO ₃), then 5 mL 3.2 M NH ₄ Ac in 20 % v/v HNO ₃	2.0	80	5.5
F6 HNO ₃	20 mL 7 M HNO ₃	1.0	80	6
F7 Residual	5 mL HNO ₃ + 1 mL HF + 6 mL H ₃ BO ₃			

412

413

414
 415 Table 2. Comparison of measured concentrations of the trace elements with the certified/given values ($\mu\text{g/g d.w.}$) of
 416 the certified reference material (Estuarine Sediment, CRM-1646, $n = 2$)

Trace elements	Measured values	Certified values
As	10.8 ± 0.2	11.6 ± 1.3
Cd	0.34 ± 0.00	0.36 ± 0.07
Cr	85 ± 2	76 ± 3
Co	9.8 ± 0.4	10.5 ± 1.3
Cu	18 ± 0.4	18 ± 3
Pb	27.1 ± 0.1	28.2 ± 1.8
Mn	345 ± 21	375 ± 20
Ni	32 ± 2	32 ± 3
Se	0.6 ± 0.3	0.6^1
Zn	134 ± 1	138 ± 6

417 ¹**Given** value - a measured value for which uncertainty of the measurement is not known.

418 Table 3. Total trace element concentrations ($\mu\text{g/g}$ d.w.) from single step Ultra Clave digestion and the sum of concentrations in the sequential extracts (ΣSEP).

419 SQGs = Sediment Quality Guidelines, TEC = Threshold Effect concentration, and PEC = Probable Effect Concentration (MacDonald et al., 2000).

Lake	SQGs		Sample	Lake Hawassa			Lake Koka			Lake Ziway		
	TEC	PEC		0–2 cm (n = 3)	2–4 cm (n = 3)	4–6 cm (n = 1)	0–2 cm (n = 3)	2–4 cm (n = 3)	4–6 cm (n = 3)	0–2 cm (n = 2)	2–4 cm (n = 1-2)	4–6 cm (n = 1)
As	9.79	33	Total	10.98 ± 0.04	11.6 ± 0.2	12.5	5.9 ± 0.2	5.9 ± 0.2	6.0 ± 0.2	5.1 ± 0.3	4.8	3.8
			ΣSEP	10 ± 2	11.1 ± 0.3	12.0	5.9 ± 0.4	5.74 ± 0.16	5.65 ± 0.07	5.2 ± 0.6	4.6 ± 0.3	3.8
Cd	0.99	4.98	Total	0.25 ± 0.03	0.25 ± 0.01	0.27	0.13 ± 0.01	0.13 ± 0.01	0.14 ± 0.01	0.15 ± 0.04	0.19	0.23
			ΣSEP	0.32 ± 0.02	0.32 ± 0.01	0.30	0.11 ± 0.01	0.12 ± 0.02	0.10 ± 0.01	0.17 ± 0.04	0.24 ± 0.01	0.24
Cr	43.4	111	Total	26 ± 7	24 ± 5	20	115 ± 8	116 ± 4	116 ± 3	60 ± 4	46	33
			ΣSEP	28 ± 3	23 ± 1	22	107 ± 6	107 ± 8	96 ± 6	60 ± 6	42 ± 1	32
Co	N/A	N/A	Total	6.8 ± 1.3	5.7 ± 0.1	5.4	18.8 ± 0.3	19.2 ± 0.4	19.1 ± 0.7	14.1 ± 0.7	13	11.8
			ΣSEP	5.7 ± 0.4	5.1 ± 0.1	4.8	15.9 ± 0.6	16.8 ± 1.2	15 ± 1	13 ± 1	12 ± 0	11
Cu	31.6	149	Total	10 ± 1	8.7 ± 0.3	8.5	43 ± 2	42 ± 1	42.2 ± 0.8	27 ± 2	21.0	14.5
			ΣSEP	12 ± 1	9 ± 0	9	38 ± 2	39 ± 3	33 ± 4	26 ± 2	26 ± 2	26 ± 2
Pb	35.8	128	Total	14 ± 3	11.1 ± 0.1	10	18.1 ± 0.6	18.3 ± 0.6	18.9 ± 0.2	19 ± 2	19	19
			ΣSEP	15 ± 2	13.1 ± 0.3	12	15.3 ± 0.3	16 ± 1	14 ± 2	18 ± 1	19 ± 1	20
Mn	N/A	N/A	Total	1050 ± 163	940 ± 35	740	1330 ± 457	1310 ± 224	1240 ± 57	1710 ± 71	1740	1590
			ΣSEP	1084 ± 107	1000 ± 25	797	1145 ± 376	1172 ± 206	1068 ± 49	1642 ± 59	1601 ± 44	1651
Ni	22.7	48.6	Total	22 ± 7	17.8 ± 3.5	15.1	85 ± 6	85 ± 3	85 ± 6	47 ± 3	36.8	27.1
			ΣSEP	27 ± 4	23 ± 2	20	80 ± 5	82 ± 7	75 ± 8	55 ± 4	43 ± 2	38
Se	N/A	N/A	Total	1.0 ± 0.3	1.34 ± 0.05	1.4	<LOD	<LOD	0.39	0.71 ± 0.03	0.74	0.8
			ΣSEP	1.2 ± 0.6	1.08 ± 0.09	1.2	0.4 ± 0.1	0.4 ± 0.1	0.3 ± 0.1	0.7 ± 0.2	0.49 ± 0.06	0.41
Zn	121	149	Total	158 ± 22	144 ± 6	137	201 ± 5	203 ± 4	207 ± 4	207 ± 13	211	215
			ΣSEP	178 ± 15	170 ± 5	152	170 ± 6	171 ± 12	157 ± 15	195 ± 7	210 ± 10	221

420 Table 4. Moisture content, loss on ignition (LOI), and pH determined in sediment samples (mean \pm SD)

Lake	Hawassa			Koka			Ziway		
	0–2 cm (n = 3)	2–4 cm (n = 3)	4–6 cm (n = 1)	0–2 cm (n = 3)	2–4 cm (n = 3)	4–6 cm (n = 3)	0–2 cm (n = 2)	2–4 cm (n = 2)	4–6 cm (n = 1)
Water (%)	72 \pm 1	73 \pm 4	76	45 \pm 4	48 \pm 3	48 \pm 2	5 \pm 3	59 \pm 1	49
LOI (%)	29 \pm 4	30.9 \pm 0.8	34	7.6 \pm 0.0	7.3 \pm 0.2	7.4 \pm 0.1	11 \pm 1	8.9 \pm 0.3	8.3
pH (H ₂ O)	8.10 \pm 0.02 (n = 2)			7.99 \pm 0.12 (n = 3)			8.50 \pm 0.04 (n = 2)		

421

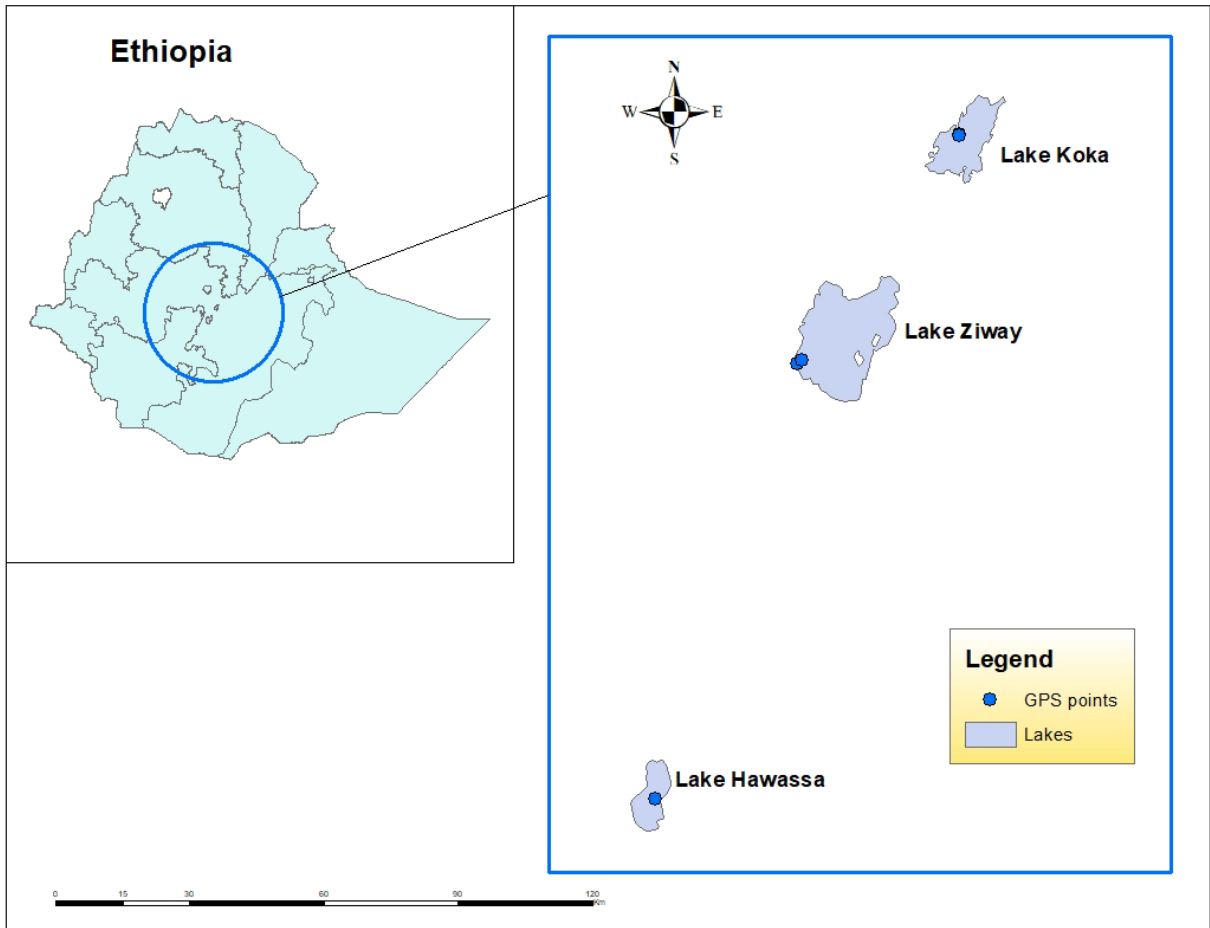
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423 Table 5. The mean distribution coefficients (K_d) calculated as a ratio between the total concentration ($\mu\text{g/g}$ d.w.) of
 424 trace element in 0-6 cm sediments (ΣSEP_{1-7}) and the total trace element concentrations in water ($\mu\text{g/mL}$) assuming
 425 equilibrium conditions. As the water in Lake Koka contained sediment particles, K_d is also calculated using the
 426 concentration of low molecular mass (<10 kDA) species in water.

	Distribution coefficients (K_d) (unitless)			
	Hawassa ^a (n = 1-3)	Koka ^a (n = 3)	Koka ^b (n = 3)	Ziway ^a (n = 1-2)
As	4.6×10^3	2.0×10^3	8.3×10^3	2.5×10^3
Cd	2.3×10^4	2.2×10^3	1.6×10^4	1.2×10^4
Cr	2.7×10^5	2.0×10^3	2.6×10^5	1.7×10^4
Co	7.4×10^4	2.1×10^3	1.1×10^5	1.7×10^4
Cu	7.7×10^3	1.7×10^3	3.8×10^4	5.9×10^3
Pb	1.5×10^5	1.8×10^3	7.5×10^5	1.6×10^4
Mn	8.0×10^4	2.7×10^3	3.5×10^4	1.2×10^4
Ni	4.7×10^4	2.0×10^3	3.3×10^4	1.5×10^4
Se	1.1×10^3	3.5×10^2	1.6×10^3	4.4×10^2
Zn	8.4×10^5	1.7×10^3	2.1×10^5	3.0×10^4

427 ^a K_d values were calculated by dividing the average of the sum of trace element concentrations in seven sequential
 428 extracts (ΣSEP , $\mu\text{g/g}$) by the total water concentration of each lake; ^b K_d values were calculated by dividing the
 429 average of the sum of trace element concentrations in seven sequential extracts (ΣSEP , $\mu\text{g/g}$) by the LMM
 430 concentrations ($\mu\text{g/mL}$) concentration of each lake.

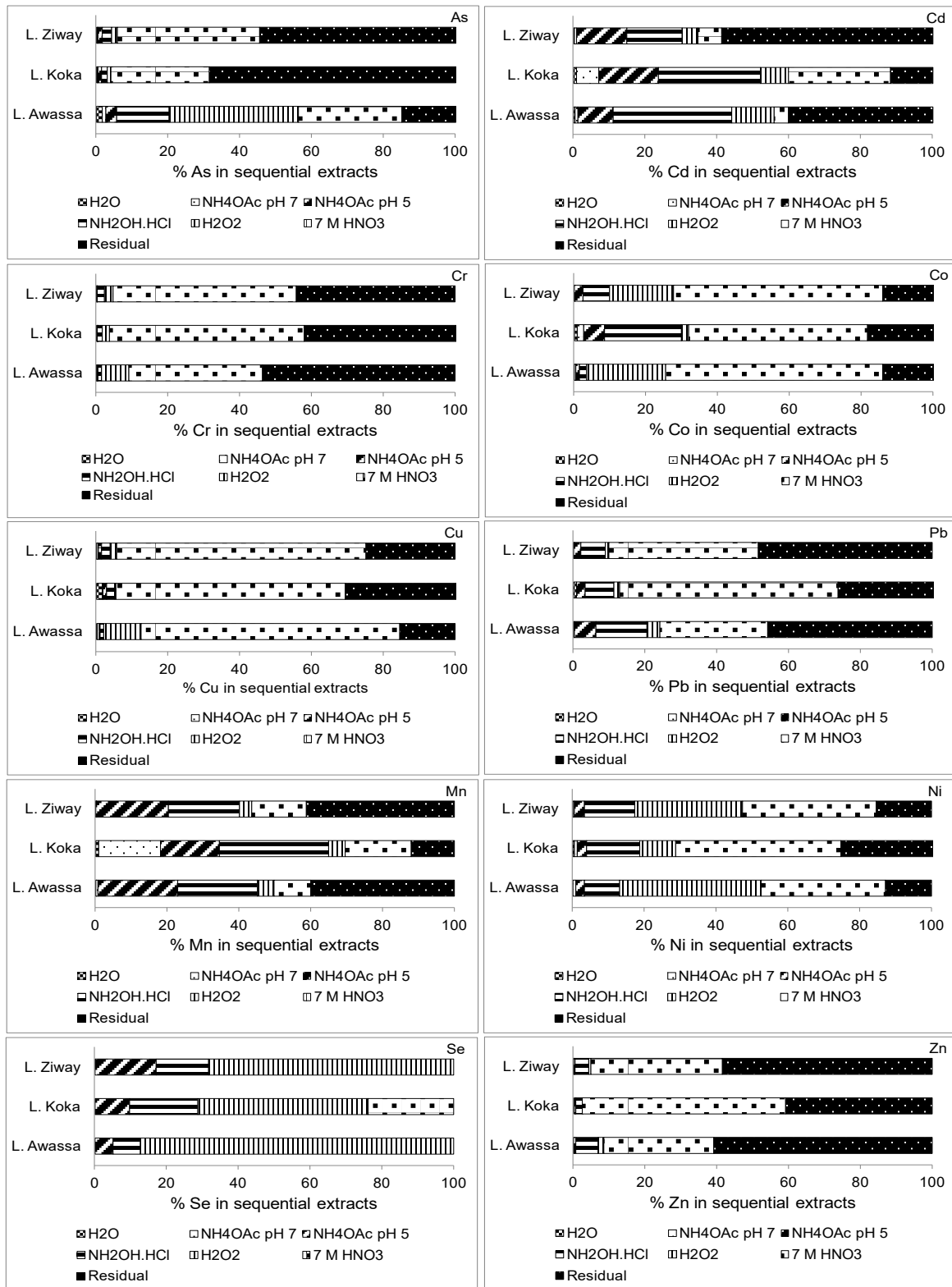
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433 **Fig.1** Map of the study area showing the investigated lakes (L. Hawassa, L. Koka and L. Ziway) and sampling
434 points.

435

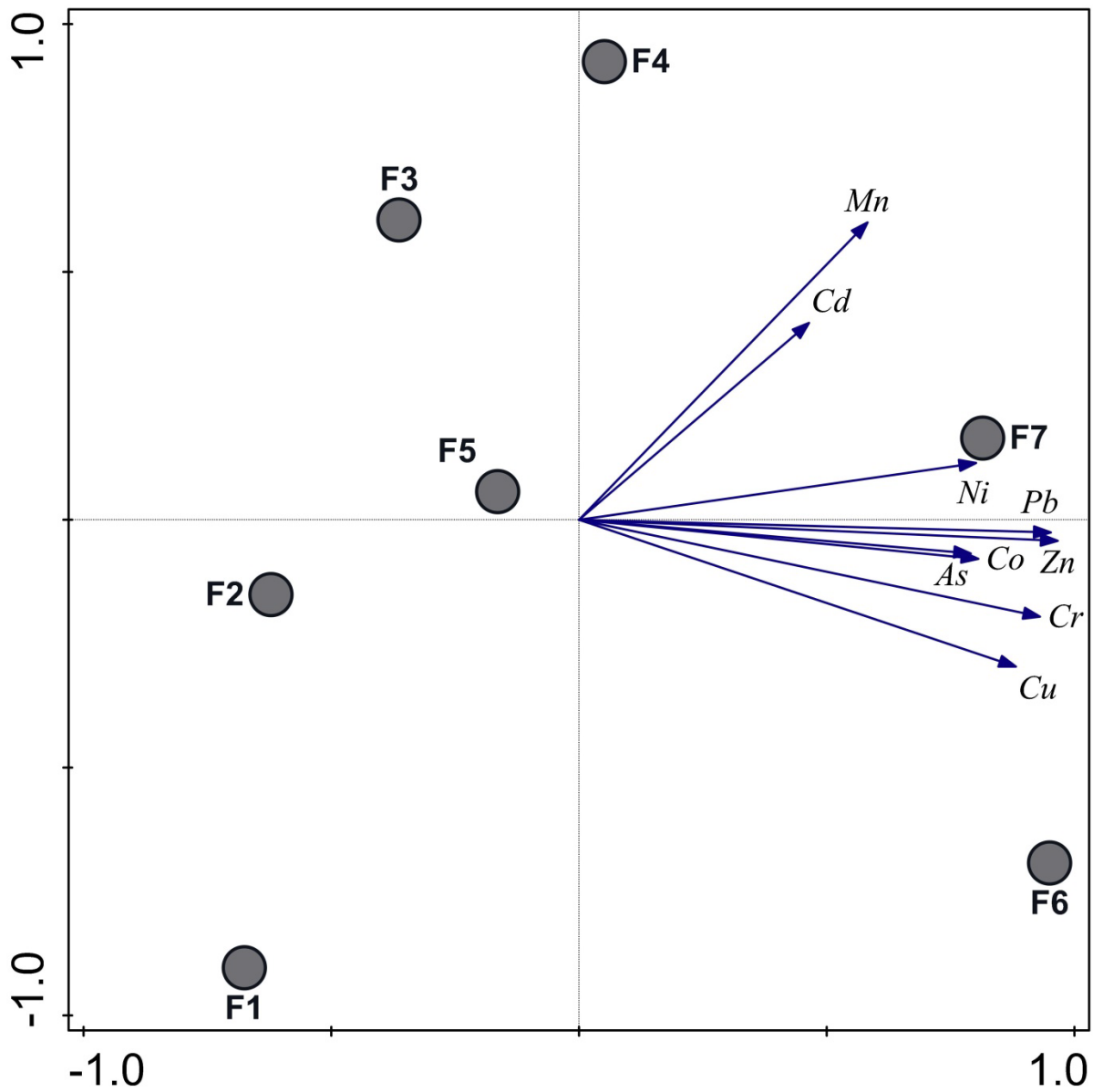
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437

438 **Fig. 2** Relative (%) distribution of some trace elements in sediment cores (0–6 cm) collected from a) Lake Koka (n =
 439 3) b) Lake Ziway (n = 1–2) and c) Lake Hawassa (n = 1–3)

440



441
 442 **Fig. 3** RDA bi-plot showing different sequential extracts (F1–F7) as categorical variables and trace elements
 443 determined in sediments as response variables.
 444

445 **Statements and declarations**

446 **Ethical Approval:** Not applicable.

447 **Consent to participate:** Not applicable.

448 **Consent to publish:** The authors confirm that this manuscript has not been published elsewhere and is not under
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452 Skipperud, and Zinabu Gebremariam closely supervised the work. Sondre Meland did the multivariate statistical
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454 on previous versions of the manuscript.

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