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Distribution of Trace Elements in the Aquatic Ecosystem of the Thigithe River and the Fish *Labeo victorianus* in Tanzania and possible risks for human consumption.

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Abstract

The aim of the present study was to assess the distribution of trace elements in the aquatic ecosystem of the Thigithe river. Samples of surface water, sediment and fish were collected up- and downstream of the North Mara Gold Mine (Tanzania) and following trace elements were analysed: As, Cd, Co, Cr, Cu, Hg, Ni, Pb and Zn. Trace element concentrations in surface water were below or near the detection limit. Regarding the sediments, relative high concentrations of arsenic at all sites and high levels of mercury at a site downstream of the mine where artisanal mining is performed were obseved. Trace element concentrations in Ningu fish tissues (*Labeo victorianus*) were comparable to slightly higher than levels in fishes from unpolluted environments. For none of the measured human health risk by consumption of fish from the Thigithe River is expected when an the Tanzanian average amount of 17g/day is consumed. However, for Hg and As the advised maximum daily consumption of Ningu fish was lower than 100 gram. As a result fishermen and people living along the shores of the river consuming more fish than the average Tanzanian fish consumption set by the FAO (2005) are possibly at risk.

Capsule abstract

High levels of As and Hg were observed in sediment. However, these sediment levels were not found to pose risk to the benthic aquatic fauna, since all elements were below the PEC values. For none of the measured metals human health risk by consumption of Ningu fish from the Thigithe River is likely to occur.

Key words

gold mining, trace element, fish, human health risk

1. Introduction

Anthropogenic activities contribute to trace element pollution of aquatic ecosystems by deliberately discharging or accidentally releasing trace elements into the environment (Mdegela *et al*., 2009). When trace elements are entering aquatic environments some are adsorbed onto suspended matter and sediments which lower their dissolved concentrations and bioavailability as they settle to the bottom. Re-suspension of sediments might cause release of trace elements back into the water column posing potential threat to ecosystems (Yi et al., 2011). Thus sediments may act both as a sink and secondary source of trace element contaminants in the aquatic environment with high levels often found in sediments with high clay and organic carbon content (Florence, 1982). Sediment-bound trace elements enter the food chain via feeding of the benthic fauna and benthopelagic feeders (Yi et al., 2011). Fish have been widely used as indicators of contamination in aquatic environments, because they are considered as top consumers that bioaccumulate and biomagnify pollutants in their tissues. The accumulated pollutants may represent potential risk, not only to the fish themselves but also to piscivorous birds and mammals including humans (Bervoets and Blust, 2003; Verhaert et al., 2013). Contaminant accumulation in various fish tissues is therefore used as a measure of contaminant exposure and effect (Evans et al., 1993) with higher accumulation of pollutants being found in demersal fish compared to pelagic fish, due to their direct contact with polluted sediments and feeding on zoobenthic prey (Yi et al., 2011).

Large-scale gold mining takes place in many parts of the world. Generally mining activities have been proved to contaminate the surrounding and distant aquatic environment with trace elements that occur together with gold in the crust (Ntengwe and Maseka, 2006; Almas and Manoko, 2012). An additional potential source of trace element contamination is the use of mercury for gold extraction through the process of amalgamation used by artisan miners

contributing to the contamination of water bodies through direct disposal of processing water and tailings into the environment (Ikingura et al., 1997; Ogola et al., 2002; Chibunda, 2008). Currently, gold mining in Tanzania is dominating the mining industry and export trade, (URT, 2011). The open-pit mine North Mara Gold Mine (NMGM) is the largest Gold mining project installed in the north western part of the country. It has been claimed that the mining operations of NMGM are polluting the surrounding environment, including the aquatic ecosystem of the Thigithe river flowing along the mine (Almas and Manoko, 2012).

To the best of our knowledge, very few studies have been done to assess the distribution of trace elements in aquatic ecosystems in Tanzania in general and in the aquatic system of the Thigithe river in particular (Almas and Manoko, 2012). In addition, the trace element content in fish from this river has never been determined so the health risk of human consumers of contaminated fish is unknown. Although no information is available on the frequency, accidental spills from the mine tailing pond are likely to occur as reported by Almas and Manoko (2012). In this way, the present study was imperative and its main purpose was to assess the distribution of trace metals in the aquatic ecosystem of river Thigithe up- and downstream of a gold mine. The specific objectives were to (1) establish the extent of trace element contamination in the surface water, sediment and fish sampled along the Thigithe river; (2) investigate the relationship between trace element levels in the environment (water and sediment) and in fish tissues; (3) assess the ecological and human health risks associated with concentrations of trace elements in the river and (4) assess the human health risk associated with the consumption of contaminated fish.

2. Materials and Methods

2.1 Study Area

The study has been performed on the river Thigithe, a narrow (width: 3.2-3.8m) and shallow (depth: 0.3-1.3m) river, serving as the main community source of water for human and livestock consumption in over 15 villages of Ingwe division. It originates in Kenya and crosses the Ingwe division in Nyamongo area before it joins the Mara river that pours into lake Victoria. The current study was done on the river section that flows between the Nyabigena and Gokona mining pits. At a certain point the river passes very close to Nyabigena pit at a distance of not more than 500m (Figure 1). Sediment, water and fish samples were collected along the river course during the dry season in August 2013 from five sites with two sampling sites considered as control sites located upstream (about 2 Km) and three downstream of the Nyabigena gold

mine (Figure 1). The sites were approximately 1km apart from each other and their positions were recorded by GPS 60 Garmin, the coordinates are shown in Table SI1 in Supplementary information.

2.2 Sample collection

Water samples were collected in duplicate from each site using sterile 50ml polyethylene vials. The samples were taken at the middle of the river at 5cm depth and the water scooped against the current flow. Sediment samples from the river were collected using a hand sediment core with 2.5 inch inside diameter. The sediment samples were taken from the same locations where water was sampled. From each site three replicates were randomly sampled. One fish species "*Labeo victorianus"* commonly known as Ningu was sampled. *L. victorianus* (Boulenger, 1901) is the most abundant pelagic fish species in the study area (Personal communication with villagers). From each site, fishes were caught using a hand net of mesh size 20mm and five representative individuals were selected within a length range of 9 to 12cm standard length. From each individual, liver, gills and muscle were collected and placed in clean plastic polyethylene bags. The fish is a bottom-feeding omnivorous (feeds on detritus and algae) freshwater cyprinid endemic to Lake Victoria drainage basin including the tributary rivers. The fish is a migratory species that spends most of its life in the lake and ascends the rivers to breed during the rainy seasons (Abwao et al., 2014). In 2006 *L. victorianus* was included in the IUCN red list of threatened species (Bayona, 2006). All samples in the field were stored in a cool box and immediately transferred into the freezer at -20°C upon arrival in the laboratory. Afterwards the samples were shipped to the laboratory at the University of Antwerp, Belgium for trace element analysis, and stored again at -20 °C until the digestion process.

2.3 Sample preparation

After thawing from each water sample 10 ml was collected with a sterile syringe and water was filtered over a 0.20µm cellulose acetate filter and transferred into a 14 ml polypropylene tube. To each sample 150 µl of pure HNO_3 (69%, Merck, Darmstadt Germany) was added and samples were stored at -20°C until trace element analysis.

An amount of 0.5g wet weight (ww) of fish tissue and sediment samples were accurately weighed. After freeze drying, the dry weight (dw) was determined. To each sample 500µl of concentrated HNO_3 (69%), 1500µl of HCl (37%), 200 µl of H_2O_2 and a magnetic stirrer were

added. Sample digestion was done by a SP-Discover Microwave (CEM, USA) in two steps. The first step was set to run at 120°C, ramp time of five minutes, hold time of five minutes, pressure of maximum 34bars at 300W and low stirring. Step 2 was ran at 160°C, ramp time of five minutes, hold time of five minutes, pressure of maximum 34bars at 300W and low stirring. Samples were diluted upon 5-6% acid for Hg analysis and to 1-2% acid for the other elements. For quality control blanks and certified reference materials (CRM) were added and prepared in the same way as the samples. Reference materials were channel sediment (BCR 320R) and lyophilised Cod Muscle (BCR 422) from the Institute for Reference Materials and Measurements (IRMM, Geel Belgium) and freeze dried mussel tissue (no 2976) from NIST (National Institute of Standards and Technology-USA). The number of samples collected at each site is indicated in table SI2.

2.4 Trace elements analysis

Analysis of total mercury in all samples was performed in cold plasma mode by a High Resolution Inductively Coupled Mass Spectrometry (HR-ICP-MS) (Thermo scientific Finnigan element 2, Waltham, MA, USA). All other elements; Arsenic , Cadmium , Cobalt , Chromium, Copper, Nickel, Lead and Zinc were analysed by an Inductively Coupled Plasma-Mass Spectrometer (ICP-MS, Varian UltraMass 700, Victoria, Australia). The instrumental detection limit for mercury was 0.01µg/l and for other trace elements 0.1µg/l. The measured concentrations agreed well with the certified concentrations in the reference materials, ranging from 90-110% .

2.5 Total Organic Carbon (TOC)

Total organic matter content (TOM) in the river sediments in each respective sample was determined by the loss on ignition (LOI) method as described in Heiri *et al*., (2001). Oven dried sediment samples (2 replicates per sampling station) were weighed and incinerated in a muffle furnace at 550°C for four hours. After cooling down, samples were weighed again and the weight loss was considered to be proportional to the organic carbon content in the sample. Since it is assumed that organic matter contains 58% organic carbon a conversion factor of 1.724 was used to calculate the total organic carbon (TOC); i.e. TOC= TOM/1.724.

2.6 Data analysis

2.6.1 Statistical analysis

One way analysis of variance (ANOVA) was performed to test differences among sites in TOC in the sediments and in trace element concentrations in surface water, sediment and fish tissues. Non-parametric ANOVA by rank (Kruskal–Wallis test) was performed whenever data did not show a normal distribution. Tukey (HSD) or Dunn post hoc test were applied to determine which sites significantly differed from each other for each matrix and tissue. Correlation and regression analyses were performed to determine the degree of association between organic matter and trace element concentrations in sediments and between trace elements in different matrices. The non-parametric Spearman rank correlation test was performed whenever assumptions for normality were not fulfilled. When samples were found to be below the limit of detection (BDL), the value was transformed to BDL/2 to calculate the mean value (Bervoets et al., 2004; Custer et al., 2000). Descriptive statistics and graphical representation were done by Microsoft excel while all other statistics were done by the software R.

2.6.2 Ecological and human health risks associated with level of trace elements in the river

To determine whether the observed trace element concentrations in the river sediments potentially have adverse ecological effects to aquatic benthic fauna, the measured concentrations in the sediments were compared to the USA consensus based sediment quality guidelines (SQGs) in MacDonald et al. (2000) for fresh water (Table SI 3 in Supplementary information), presenting TEC (Threshold Effect Concentration) and PEC (Probable Effect Concentration) values (MacDonald et al., 2000). Likewise for assessment of human health risks associated with concentrations of trace elements in running water, the measured trace element concentrations were compared to water quality standards of trace elements in water (WHO water quality standards - WHO, 2006).

2.6.3 Assessment of human health risk by the consumption of contaminated fish

To assess the human health risk associated with the consumption of contaminated fish, hazard quotients (HQ) were calculated. The HQ is the ratio of the estimated daily intake dose (EDI) of a pollutant (µg/kg body weight a day) and the tolerable daily intake dose (TDI) of a pollutant (µg/kg body weight a day). The EDI is based on the average fish consumption per inhabitant of Tanzania (17g/day, FAO/WHO, 2005), the average body weight of 70 kg for an adult person

and the 50th and 95th percentile of the observed concentration of a trace element in the fish muscle (µg/g ww). The TDI is based on international guidelines for oral consumption of trace elements by the Agency of toxic Substances and Disease Registry (ATSDR, 2013) and the WHO (2002; 2007; 2011). For fish tissues, it is assumed that 80-100% of total mercury is methylmercury and a conversion factor of 1.0 based on the methylmercury/total mercury proportion has been suggested (EFSA, 2012).

It can be expected that subsistence fishermen and people living along the shores of the river consume more fish than the average Tanzanian fish consumption set by the FAO (2005). Therefore, the amount of fish which can be consumed by a person of 70 kg without potential human health risks was calculated, in addition to the HQs using the following equations:

$$Y = (W * M)*1000 \quad \text{and} \quad Q = Y/C \quad \text{Thus} \quad Q = (W * M) / C$$

Where:

M = Minimum Risk Level (MRL) for oral intake of a trace element (mg/kg body weight/day)

W = Weight of an average person of 70Kg

Y = Maximum amount of a trace element (µg) a 70kg person can consume per day without posing health risk

C = 50th and 95th percentile of the observed concentration of a trace element in the fish muscle (µg/g ww)

Q = Maximum amount (g) of contaminated fish muscle a 70kg person can consume per day without posing health risks

3. Results and discussion

3.1 Trace elements in surface water and sediment

The dissolved trace element concentrations are summarized in Table 1. Generally, the concentrations of As, Cd, Co, Cr, Hg, Pb and Zn were BDL. Nickel and Cu could be detected at all sites, ranging from 0.19 - 2.1 µg/l and 0.03 – 1.3 µg/l respectively. The dissolved trace element levels were unexpected low which might be due to adsorption to suspended matter and sediment particles which rapidly remove the elements from the water column (Doong et al., 2008; Yu et al., 2012). However, we did not measure metals in the suspended matter. Levels were comparable or only slightly higher than recorded by Almas and Manoko (2012) from the same river at a site not influenced by NMGM. Nyairo et al. 2015 who measured Cd, Cu, Cr, Pb and Zn in surface water of other tributaries of the Mara River, recorded much higher levels.

Levels of Regarding human health, the measured concentrations for all trace elements are also lower than WHO (2006) water quality standards for drinking water (Table 1).
The median values and ranges of concentrations of trace elements in sediments are presented in Figure 2 and Table SI 3 respectively. Significant differences in trace element concentrations in sediments among sites were found for Cr, Cu, Hg and Zn. For Co, Cr, Cu, Ni, Pb, and Zn highest levels were found at site S1 and levels decreased downstream, whereas for Hg the highest levels were measured at site S4. Arsenic showed no definite distribution pattern being lowest at S2 and highest at S3. Cadmium concentration followed a decreasing gradient from site S1 to site S5 with the exception of site S4, where the concentration increased again.

The measured sediment concentrations of some elements in this study were lower (Cr, Ni, As) and some were slightly below (Zn, Cu) to within the range (Co, Pb) of the values recorded by Almas and Manoko (2012) in the same study area (Table 2). The comparable levels found at all sites for Co, Cu, Pb and Zn suggest that concentrations of these trace elements in the sediments of river Thigithe are not changing. The study of Almas and Manoko (2012) was done when an accidental spill of mining waste water from tailing pond of NMGM at Nyabigena pit occurred in May 2009 five years before the present study. This episode might have contaminated the river sediments leading to immediately recorded high levels of As, Cr and Ni in the sediments of the river Thigithe. The fact that in the present study the concentrations of As, Cr and Ni are lower than those recorded in Almas and Manoko (2012) suggests pollution is decreasing in the river sediment. Different results were observed for Hg with high levels in the sediments at S4 and for Pb at S1, S2, S3 and S4 which are higher than levels recorded by Almas and Manoko (2012) (Table 2). This indicates that Hg and Pb levels are increasing at these sites. However, no information is available on the grain size distribution in both sampling periods. So we cannot exclude the possibility that in the present study sediments were coarser grained sediment and as a result adsorbed less metals.

The measured sediment concentrations in the present study were comparable to the levels measured by Mdegela et al. (2009) in the sediments from rivers and Mindu dam in Morogoro, Tanzania except for Hg and As. According to Mdegela et al. (2009) the low concentrations of trace elements in the studied sediments suggest natural background sources such as soil erosion, weathering of rocks, and deposition from air rather than anthropogenic sources. The findings of the present study are further consistent with the concentrations of trace elements except for

As in the sediments of Pangani river basin in Tanzania found by Hellar-Kihampa et al., (2012) (Table 2) who also concluded that the measured concentrations were mostly from natural sources because they showed no significant difference with crustal background values.
In addition, comparison to crustal background concentrations (Taylor and McLennan 1985; Wedepohl 1995), suggests that the river Thigithe sediments are not anthropogenic enriched with the trace elements Cd, Co, Cr, Cu, Ni, Pb and Zn. The measured concentrations of As in sediments at all sites were up to 15 times higher than the background crustal As concentration. This may suggests a significant enrichment of arsenic into the river. Previous study by Almas and Manoko (2012) found very high concentrations of As (up to 126 µg/g dw and 45µg/g dw), in the top and sub-soils. However, at sites farther away from the mine, levels in top soils were < 10 µg/g dw. Site S2, upstream of the pollution source was also sampled by Almas and Manoko (2012). At that site they found an As concentration of 45 µg/g dw. So probably, As contamination has another source, additional to the NMGM resulting in relative high levels at all sampled sites. The high Hg level at site S4, exceeding the background levels up to more than 5 times, suggests an anthropogenic pollution at that site, possibly caused by artisanal gold extraction at that site using mercury.
The levels of Co, Cr, Cu, Ni, Pb and Zn in sediments showed a marked decrease from upstream to downstream. A possible explanation could be that some metals are leached from the sediment due to effluent of the mine. This however has to be investigated more in depth.

When comparing the median concentrations of trace elements in sediments to the US consensus based SQGs (TEC and PEC values) (MacDonald et al., 2000) (Table 3 and Table SI3), the concentrations of As at all sites, Cr and Ni at S1 and Hg at S4 were higher than their TEC counterparts. However, the concentrations of all trace elements at all sites were lower than the corresponding PEC values indicating that the trace element concentrations in the sediments at these sites are not toxic to the aquatic benthic fauna.

The TOC levels ranged from 2.0% at S1 to 3.7 % at site S4 (Figure 3) but did not differ significantly among the sites ($p > 0.05$). All TOC levels were lower than the T qOC levels (5% - 21%) obtained by Hellar-Kihampa et al. (2013) from the sediments of Pangani river in Tanzania but within the range of the levels in river Mabubi sediments in Tanzania (0.56 – 5.0 %) (Chibunda et al., 2010).

3.2 Trace elements in fish

Ranges and medians of trace element levels in muscle, gill and liver tissues of *L. victorianus* are presented in tables and boxplots respectively. Figure 4 for muscles, Figure 5 for gills, Figure 6 for livers and in Table SI4. At all sites, Co in liver, Cr in gills and liver and Pb in muscle were BDL. In general, significant differences were observed among sites. For As and Cd, the concentrations in liver, gills and muscle tissue differed significantly among sites (As: liver; $K_w\chi^2_{(4)}$=15, p=0.0054; gills; $K_w\chi^2_{(4)}$=14, p=0.0082; muscle; $F_{(4,17)}$=3.8, p=0.023; Cd: liver; $K_w\chi^2_{(4)}$=10, p=0.036, gill; $K_w\chi^2_{(4)}$=21, p=0.00031; muscle; $K_w\chi^2_{(4)}$=11, p=0.022), whereas for Co, Cr, Hg and Pb no significant differences were observed between the location for any of the fish tissues. The concentrations of Cu were significantly different among sites in the muscle and gills (muscle; $K_w\chi^2_{(4)}$ =12, p= 0.021; gill; $K_w\chi^2_{(4)}$ =19, p= 0.00094) but not in liver. Zinc concentrations were found to be significantly different among sites in the gills and livers (gill; $K_w\chi^2_{(4)}$ =13, p= 0.01, liver; $K_w\chi^2_{(4)}$ =13, p= 0.012) but not in muscle. Nickle concentrations differed significantly among sites for muscle and liver (muscle; $F_{(4,17)}$=3.7, p= 0.025, liver; $K_w\chi^2_{(4)}$ =13, p= 0.0092) but not for gills. Significant differences between sites are indicated in figure 4 with letters.

Regarding tissue specific accumulation by *L. victorianus*, for As, Cd, Ni, Pb and Zn the average concentrations decreased as follows: liver ≥ gill > muscle. This pattern has been found in many other studies for these trace elements (e.g. Bervoets et al., 2001; Bervoets and Blust 2003, Türkmen *et al*., 2004). For Co, the order was gill > muscle > liver and for Hg, Cr and Cu, muscle > liver=gills. The higher accumulation of trace elements in livers and lower in muscles could be attributed to the role of liver in toxicant accumulation and detoxification. In fish blood passes through the liver before reaching systemic circulation, in doing so the liver can remove toxicants from the blood, biotransform them or excrete them into the bile and thus prevent their distribution to other parts of the body (Rosabal et al. 2015). The observation of higher Cr and Cu levels in muscle compared to gills or liver is contradictory to several other studies (e.g. Bervoets and Blust 2003; Oguz and Yeltekin, 2014; Wei et al. 2014) but could be species specific (Djedjibegovic et al., 2012). The possible explanation for this difference in muscle trace element concentration among species can be the different physiological regulatory mechanisms that influence trace element uptake and elimination among species (Allen-Gil and Martynov, 1993). The higher Hg levels in muscle are in line with findings of other studies (Wei et al. 2014).

Data for trace element levels in fish tissues from rivers and lakes in Tanzania are rather limited. Particularly data for trace element burdens in *L. victorianus* were not available. However, levels could be compared with levels in the other species captured from different countries in Africa (Table SI5). The concentration distribution patterns of most trace elements among tissues in the present study were generally similar to what was observed by Dsikowitzky *et al*. (2012) in fishes from Koka and Awassa lakes in Ethiopia. Moreover, the concentrations in present study were within the range of or slightly higher than the concentrations measured by Ikingura and Akagi (1996), Mdegela et al. (2009) and Dsikowitzky et al. (2012) in fish of lake Victoria, and Mindu dam, Tanzania and lake Koka and Awassa, Ethiopia respectively.

However, the tissue concentrations of As in the present study were higher than what was recorded by Dsikowitzky *et al*., (2012) in all fish species. And the tissue concentrations of Hg in *L. intermedius* recorded by Dsikowitzky et al. (2012) were higher than the levels measured during the present study. The tissue levels in the current study are lower than trace element levels in the tissues of fish from river Niger Nigeria (Nwajei et al., 2012) (Table SI5).

Relationship between trace element levels in tissues and environmental trace element levels

The relative contribution of water and food to the uptake of trace elements depends on the levels in the habitat of the fish (Yi et al., 2011; Mdegela et al., 2009). In the present study, the levels of most trace elements measured in water were negligible (BDL), making it impossible to establish relationships between tissue and water concentrations. Concerning the relationships between trace element levels in sediment and in fish tissues only for As a significant positive relationship was found between sediment and muscle ($R^2 = 0.85$, $p=0.03$, $F_{(1,3)}=17$) suggesting that sediments are a source of As in fish. However, we do not have information on the mobility of the fish, nor on the bioavailability of the sediment bound metals at the different sites. TOC normalization of trace element levels in sediments did not change any of the relationships.

The absence of clear differences in metal levels in *L. victorianus* among the different sites, might be due to the reproductive behaviour of this species. *Labeo victorianus* spends most of its life span in lake, but spawns in shallow waters beside streams that are connected to the lake (www.fishbase.org). As a result it could be possible that the specimens captured in the present study, are returning from Lake Victoria and that the measured levels reflect the contamination of the lake. However, as mentioned above, the As and Hg levels in the present study were

higher than in fish from lake Victoria. Campbell et al. (2003) reviewed the mercury levels in fish from lake Victoria and levels in muscle ranged from 0.006 to > 0.500 µg/g ww being well above the maximal level we measured (0.12 µg/g ww). However, when comparing species from the same trophic level (between 2 and 3) the levels found in our study were comparable to slightly higher to levels in fish from Lake Victoria). Since we captured specimens with a length of 9 to 12 cm and since length at first maturity is 15.1 cm (www.fishbase.org) we can assume that we captured juveniles that are not originating from Lake Victoria and that reflect the local contamination, or from more upstream.

3.3 Human health risk

Table 4 reports the maximum amount of Ningu fish from the Thigithe River that is recommended to eat on a daily basis for a person weighing 70 kg, without posing a risk on poisoning with the measured metals. In addition the calculated HQ is reported. The lowest edible amount found was for As and the highest was for Ni. Lead was below the limit of detection in all analysed fish, so no limit of fish consumption could be derived for Pb.

Considering the average fish intake for Tanzania of 17g/day/person documented by FAO/WHO, (2005), the calculated maximum recommended daily fish intake is far above this value resulting in a HQ of < 1 for all metals (table 4).

It can be expected however, that subsistence fishermen and people living along the shores of the river consume more fish that this average Tanzanian fish consumption. For As the maximum recommended amount of fish to consume is 45 gram and for Hg 85 gram so this may pose a risk for subsistence fisherman that consume more fish than an average Tanzanian. However, in fish and shell fish 80%-95% of total As is in organic form which is non-toxic (Benramdane et al., 1999). Therefore, the observed As concentrations in fish muscles suggest that consumption of maximal 50 gram (FAO/WHO, 2005) of Ningu fish a day from river Thigithe by an average 70kg human consumer should not pose a risk (Banerjee et al., 2014). However, given the levels of Hg, a daily consumption of more than 100 gram Ningu fish is not recommended. It has to be emphasised that these recommended maximum amounts are only valid for the measured metals and only in Ningu fish.

4. Conclusions and Recommendations

Generally, the measured concentrations of trace elements in the water of the river Thigithe were very low to negligible. Results suggest that the distribution of most of the measured trace elements in the sediments of the river Thigithe is not affected by the mining activities (NMGM) but rather by the natural background concentrations in the upper earth's crust. Most concentrations of trace elements in the sediments were below and some were very comparable to crustal background levels. However, concentration of arsenic was up to 15 times higher than the background concentration in all collected sediment samples. In order to fully understand the source of the metals and arsenic in the sediment and to investigate the effect of the gold mine in depth, more research is needed. The mercury concentration in the sediments was above the crustal value at S4 where extraction of gold using mercury by artisanal miners is undertaken. The concentrations of trace elements in the sediments did not exceed the consensus based PEC sediment quality guidelines proposed by MacDonald et al. (2000), hence they were considered not toxic to aquatic fauna.

Concentrations of most trace elements in fish tissues were low and typical of levels in fish tissues from unpolluted environments. For most trace elements concentrations in muscles were lower than in gills and livers. For all measured metals the HQ was < 1, indicating that an average person of 70 kg with an average fish consumption of 17g/d is not at risk will not be poisoned by the measured metals. It can be expected that subsistence fishermen and people living along the shores of the river consume more fish than the average Tanzanian fish consumption set by the FAO (2005). So to clearly assess the human health risk by the consumption of contaminated fish, it is recommended to investigate the consumption habits of the local population by conducting consumption questionnaires. In addition, it is recommended that an extended research should be done; (1) covering the whole stretch of the river Thigithe so as to identify the source and characterize the distribution of arsenic in the sediments of the river. (2) To assess the extent of trace element levels in other fish species in the river and in different seasons.

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Figures and tables

Figure 1. Map of the study area at Nyabigena-Gokona project site of NMGM indicating sampling sites (Maps were obtained from google earth and google search and modified to suit the purpose of this study).

Figure 2. Boxplots of concentrations of trace elements in the sediments of the river Thigithe (µg/g dw). Different letters indicate significant differences among sites. The concentrations of trace elements in the sediments of river Thigithe are compared to background concentrations of trace elements in the upper crust of the earth. *****UCC = Upper Continental Crustal concentrations of trace elements (ppm) (Wedepohl, 1995) and S1 – S5 = Sampling sites.

Figure 3. Boxplots of percentage total organic carbon in the sediments of the Thigithe river

Figure 4. The boxplots of concentrations of trace elements in muscle of Ningu fish (*Labeo victorianus*) from the Thigithe river (µg/g dw). Letters indicate significant differences between sites and S1 – S5 are sampling sites.

Figure 5. The boxplots of concentrations of trace elements in gill of Ningu fish (*Labeo victorianus*) from the Thigithe river (µg/g dw). Letters indicate significant differences between sites and S1 – S5 are sampling sites.

Figure 6. The boxplots of concentrations of trace elements in liver of Ningu fish (*Labeo victorianus*) from the Thigithe river (µg/g dw). Letters indicate significant differences between sites and S1 – S5 are sampling sites.

Fig.1

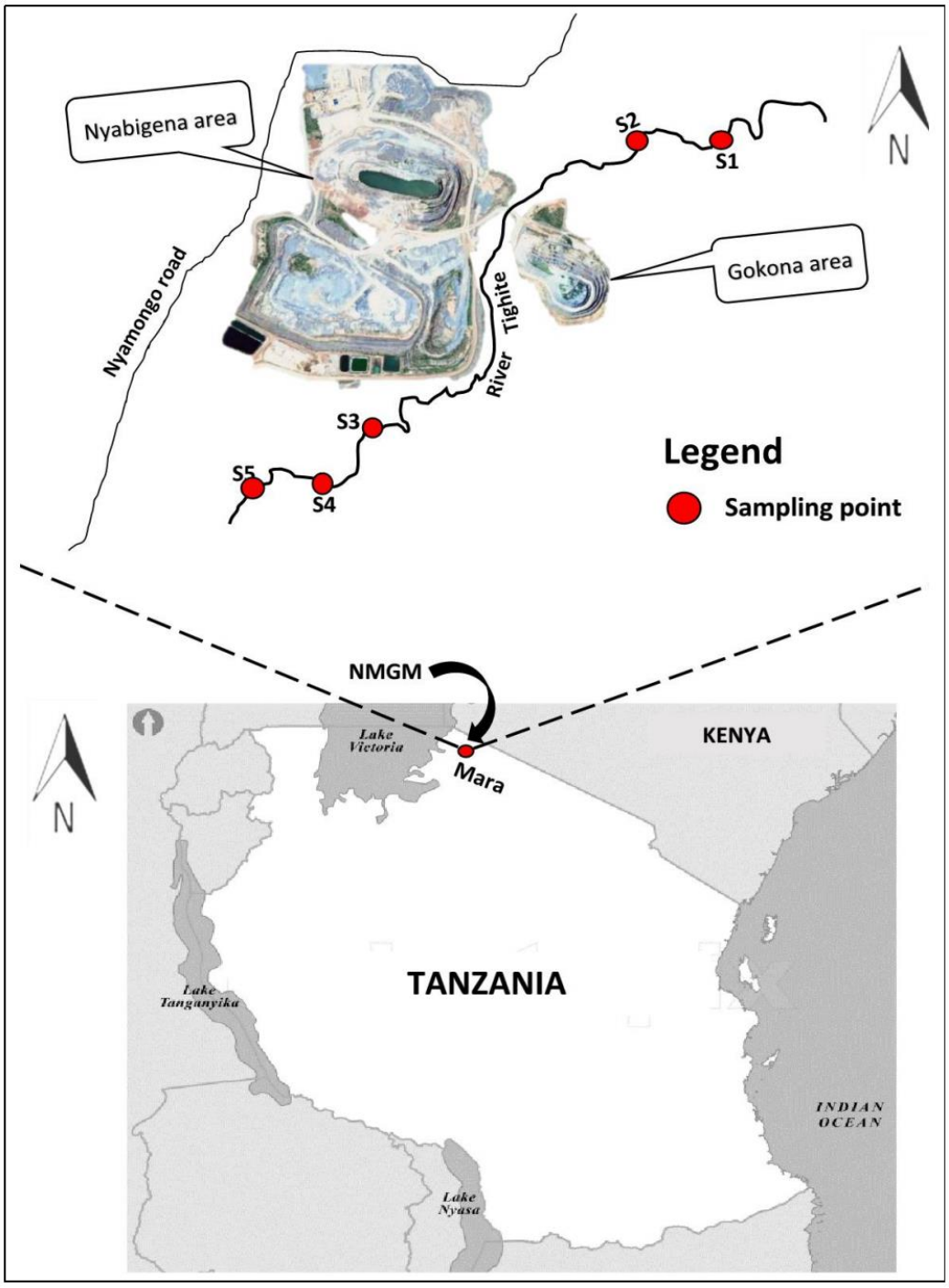
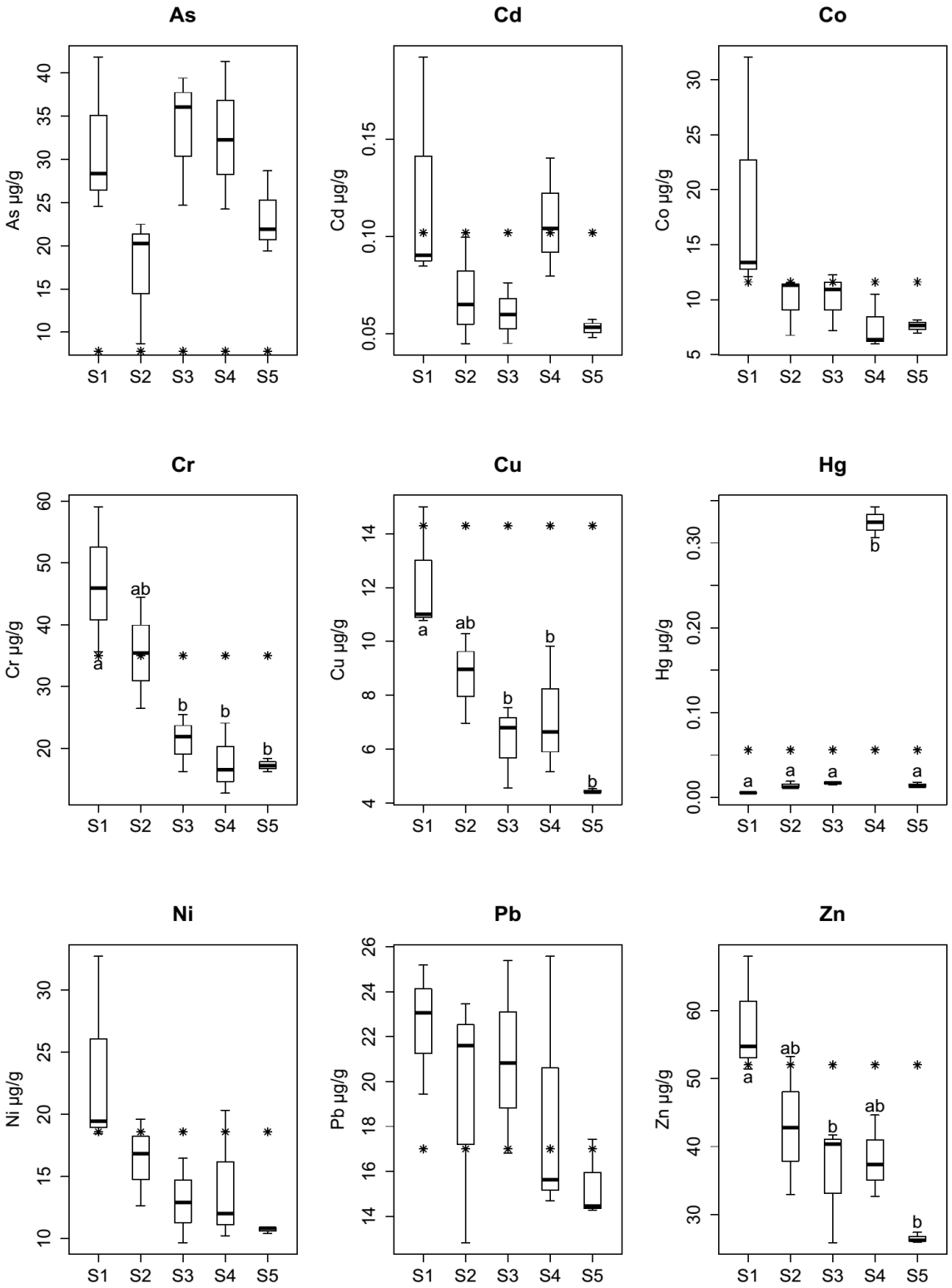

Nyabigena area
Nyamongo road
S2
S1
N
Gokona area
River Tighite
S3
S5
S4
Legend
Sampling point
NMGM
Lake Victoria
Mara
KENYA
N
TANZANIA
Lake Tanganyika
INDIAN OCEAN
Lake Nyasa

Fig 2.


As
As µg/g
10 15 20 25 30 35 40
S1 S2 S3 S4 S5
Cd
Cd µg/g
0.05 0.10 0.15
S1 S2 S3 S4 S5
Co
Co µg/g
5 10 15 20 25 30
S1 S2 S3 S4 S5
Cr
Cr µg/g
20 30 40 50 60
a ab b b b
S1 S2 S3 S4 S5
Cu
Cu µg/g
4 6 8 10 12 14
a ab b b b
S1 S2 S3 S4 S5
Hg
Hg µg/g
0.00 0.10 0.20 0.30
a a a b a
S1 S2 S3 S4 S5
Ni
Ni µg/g
10 15 20 25 30
S1 S2 S3 S4 S5
Pb
Pb µg/g
14 16 18 20 22 24 26
S1 S2 S3 S4 S5
Zn
Zn µg/g
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S1 S2 S3 S4 S5

Fig. 3

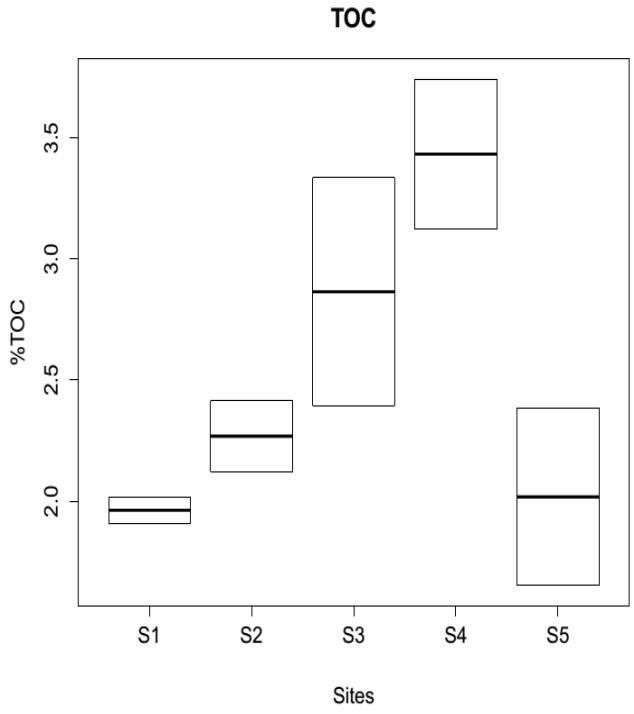
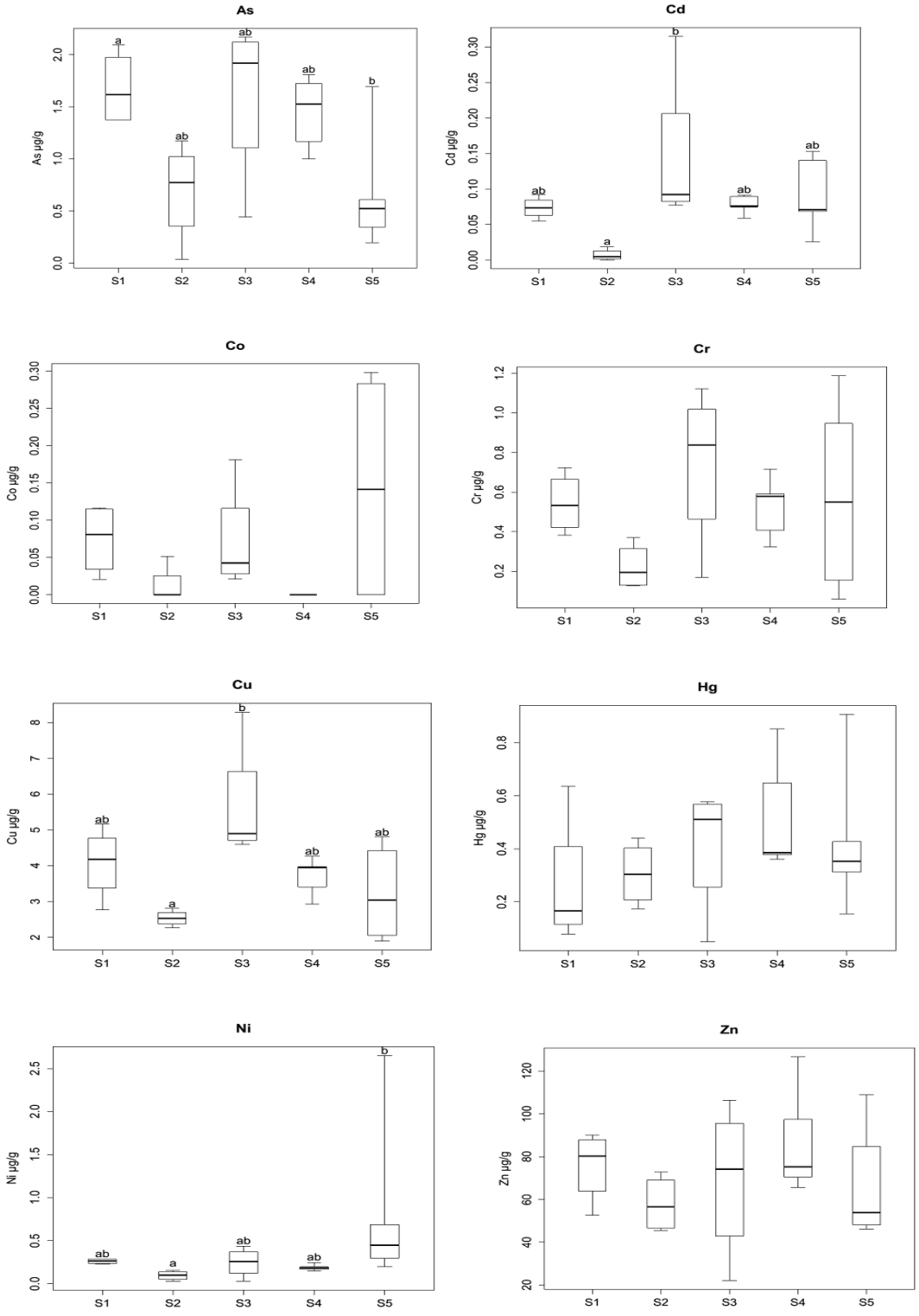


Fig 4.


As
As µg/g
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S1
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S3
S4
S5
Cd
Cd µg/g
ab
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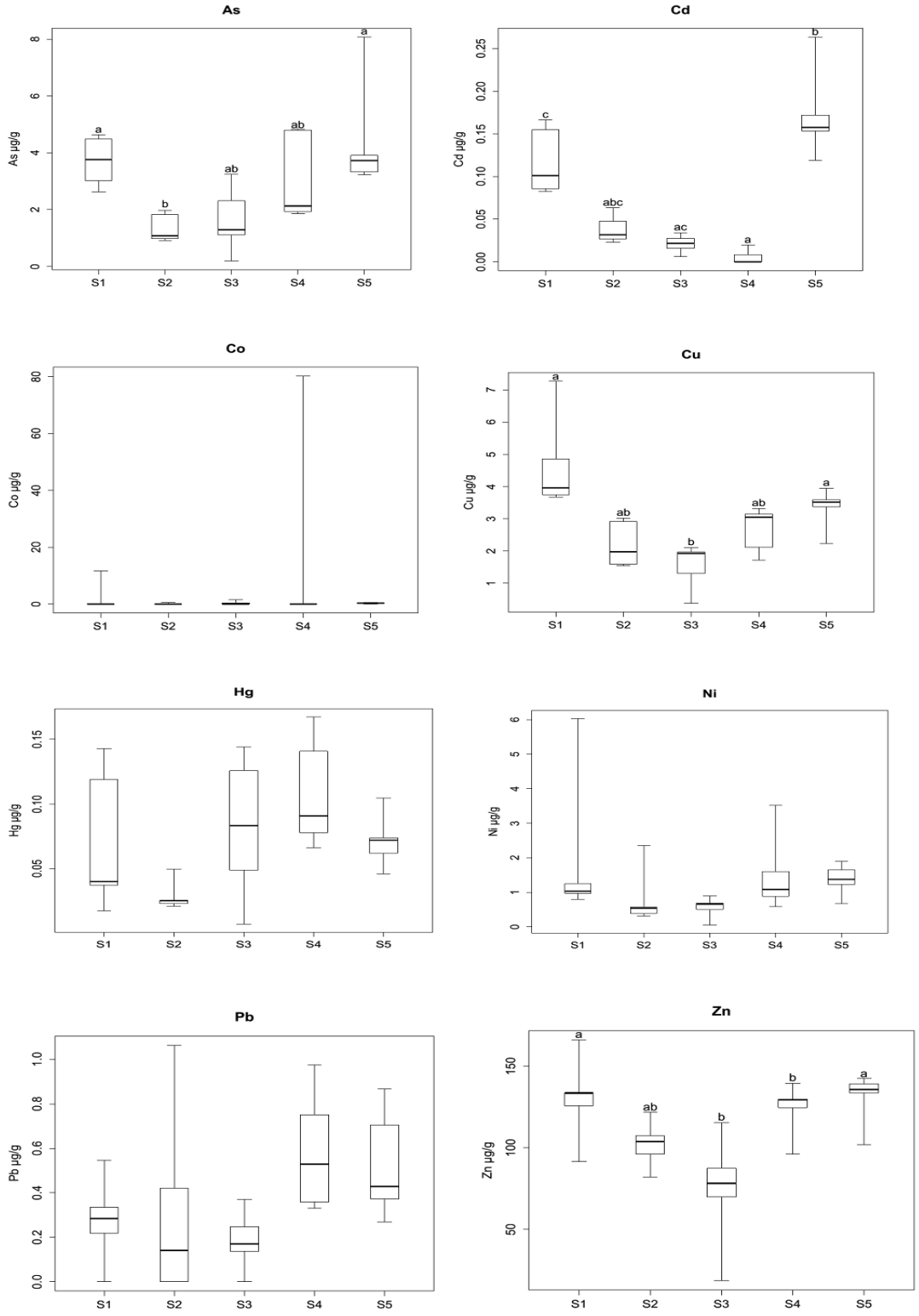
b
ab
ab
Co
Co µg/g
Cr
Cr µg/g
Cu
Cu µg/g
Hg
Hg µg/g
Ni
Ni µg/g
Zn
Zn µg/g

Fig 5.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abc
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a
ab
b
ab
a
Hg
Hg µg/g
Ni
Ni µg/g
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S1
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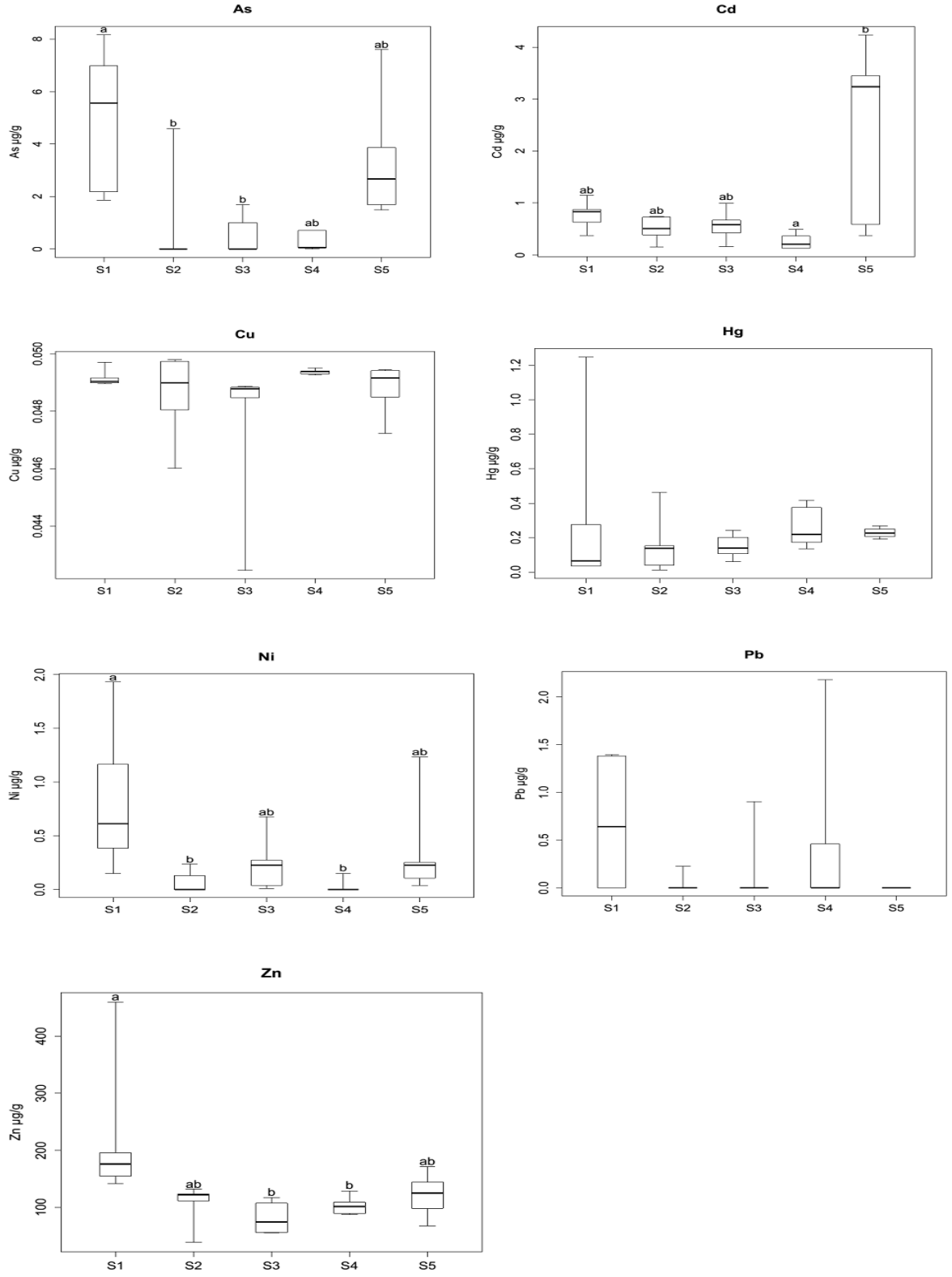
Fig. 6


As
As µg/g
a
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ab
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S1
S2
S3
S4
S5
Cd
Cd µg/g
ab
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ab
a
b
Cu
Cu µg/g
Hg
Hg µg/g
Ni
Ni µg/g
a
b
ab
b
ab
Pb
Pb µg/g
Zn
Zn µg/g
a
ab
b
b
ab

Table 1. Concentrations of trace elements in the surface water of river Thigithe in µg/l and Lake Victoria in ppm are compared to WHO water quality guidelines for drinking water in mg/l

	S1	S2	S3	S4	S5	River Thigithe[a]	WHO[b]
Cr	BDL	BDL	BDL	BDL	BDL	nd	0.05
Co	BDL	BDL	BDL	BDL	BDL	0.1	
Ni	0.19 - 0.24	0.58 – 0.93	0.87- 0.89	0.82 – 3.6	1.3 – 2.1	0.9	0.07
Cu	0.03 – 0.05	0.36 – 0.82	1.2 – 1.3	0.53 – 0.82	0.07 – 0.32	1.1	2
Zn	BDL	BDL	BDL	BDL	1.5 – 2.2	1.9	
As	BDL	BDL	BDL	BDL	BDL	1.1	0.01
Cd	BDL	BDL	BDL	BDL	BDL	0.01	0.003
Pb	BDL	BDL	BDL	BDL	BDL	0.07	0.01
Hg	BDL	BDL	BDL	BDL	BDL	0.4	0.006

[a]River Thigithe = Almas and Manoko (2012)

[b]WHO = World Health Organisation (2006) - Guidelines for Drinking-water Quality

BDL = Below detection limit of the measuring method; S1 – S5 = Sampling sites; nd = Not determined

Table 2. Comparison of trace element concentrations in the sediments of river Thigithe measured during the present study with other studies

Trace element	Thigithe river along NMGM[a]	Thigithe river along NMGM[a]	Rivers in Morogoro[a]	Pangani river basin[a]
Cr	17 – 47	79 - 85	44 – 100	BDL – 160
Co	7.6 – 19	16 – 34	-	-
Ni	11 - 24	31 – 34	-	11 – 61
Cu	4.4 - 12	13 - 25	22 – 48	16 – 81
Zn	27- 58	59 - 98	37 – 84	63 – 130
As	17 – 32	51 - 520	6 – 11	BDL
Cd	0.05 - 0.12	-	0.4 – 0.8	BDL
Pb	15 – 23	16 - 18	8 – 32	BDL
Hg	0.006 - 0.37	nd - 0.01	0.04 – 0.2	-
	This study	Almas and Manoko (2012)	Mdegela *et al*., 2009	Hellar-Kihampa *et al*., (2012)

- Not available

[a] = Concentrations given in µg/g dw

NMGM = North Mara Gold Mine

BDL = Below detection limit

Table 3. Median concentrations of trace elements in the sediments of river Thigithe per sampling site compared to Sediments Quality Guidelines (SQGs)

	S1	S2	S3	S4	S5	PEC	TEC
As	28	20	36	32	22	33	10
Cd	0.09	0.07	0.06	0.1	0.05	4.9	0.99
Co	13	11	11	6.4	7.7	-	-
Cr	46	35	22	17	17	111	43
Cu	11	9.0	6.8	6.6	4.4	149	32
Hg	0.006	0.01	0.02	0.34	0.01	1.1	0.18
Ni	20	17	13	12	11	49	23
Pb	23	22	21	16	15	128	36
Zn	55	43	40	37	26	459	121

TEC = Threshold Effect Concentration (µg/g dw) (MacDonald *et al*., 2000)

PEC = Probable Effect Concentration (µg/g dw) (MacDonald *et al.*, 2000)

S1 – S5 = Sampling sites concentrations (µg/g dw) of the present study

Table 4. The maximum amount of Ningu fish (*L. victorianus*) from the Thigithe river per contaminant trace element that could be consumed per day without risking the health of an average 70kg person and the hazard quotient for concentration of each trace element in the fish muscle

	Cr	Co	Ni[a]	Cu	Zn	As	Cd	Hg[b]
MRL (mg/kg bw/day)	0.0009	0.01	0.29	0.01	0.3	0.0003	0.0001	0.00023
MRL (mg/day) for person of 70 kg	0.06	0.70	20	0.70	21	0.02	0.007	0.02
50th percentile concentration in Ningu muscle (*L.victorianus*) (µg/g ww)	0.13	0.008	0.06	0.91	18	0.31	0.02	0.09
95th percentile concentration in Ningu muscle *(L.victorianus*) (µg/g ww)	0.24	0.072	0.17	1.14	26	0.47	0.04	0.19
Maximum edible amount of Ningu per day (g) for a person of 70 kg based on 50th percentile levels	485	87500	338333	769	1186	**68**	292	179
Maximum edible amount of Ningu per day (g) for a person of 70 kg based on 95th percentile levels	263	9700	120000	614	808	**45**	159	85
HQ at 50th percentile concentration	0.04	<0.01	<0.01	0.02	0.01	**0.25**	0.06	0.10
HQ at 95th percentile concentration	0.07	< 0.01	< 0.01	0.03	0.02	**0.38**	0.11	0.20

[a]WHO, 2002 = PTWI = 2 mg/kg bw/week

[b]WHO, 2007 = PTWI = 1.6 µg /kg bw/week methyl mercury in fish and sea foods

[c]WHO, 2011 = MRL = 0.36 µg /kg bw/day

PTWI = Provisional Tolerable weekly Intake, WHO = World Health Organisation, HQ = Hazard Quotient, Concentrations for other trace elements are from (ATSDR, 2013)