Mwesigye Abraham R.[1], Young Scott D.[2], Bailey Elizabeth H.[2] and Tumwebaze Susan B[1]. 2016. Population exposure to trace elements in the Kilembe copper mine area, Western Uganda: a pilot study. Science of the Total Environment 573, 366–375.
http://dx.doi.org/10.1016/j.scitotenv.2016.08.125

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The mining and processing of copper in Kilembe, Western Uganda, from 1956 to 1982 left over 15 Mt of tailings containing cupriferous and cobaltiferous pyrite dumped within a mountain river valley. This pilot study was conducted to assess the nature and extent of risk to local populations from metal contamination arising from those mining activities. We determined trace element concentrations in mine tailings, soils, locally cultivated foods, house dust, drinking water and human biomarkers (toenails) using ICP-MS analysis of acid digested samples. The results showed that tailings, containing higher concentrations of Co, Cu, Ni and As compared with world average crust values had eroded and contaminated local soils. Pollution load indices revealed that 51% of agricultural soils sampled were contaminated with trace elements. Local water supplies were contaminated, with Co concentrations that exceeded Wisconsin (US) thresholds in 25 % of domestic water supplies and 40 % of Nyamwamba river water samples. Zinc exceeded WHO/FAO thresholds of 99.4 mg kg^{-1} in 36% of *Amaranthus* vegetable samples, Cu exceeded EC thresholds of 20 mg kg^{-1} in 19% of *Amaranthus* while Pb exceeded WHO thresholds of 0.3 mg kg^{-1} in 47% of *Amaranthus* vegetables. In bananas, 20% of samples contained Pb concentrations that exceeded the WHO/FAO recommended threshold of 0.3 mg kg^{-1}. However, risk assessment of local foods and water, based on Hazard Quotients (HQ values) revealed no potential health effects. The high external contamination of volunteers' toenails with some elements (even after a washing process) calls into question their use as a biomarker for metal exposure in human populations where feet are frequently exposed to soil dust. Any mitigation of Kilembe mine impacts should be aimed at remediation of agricultural soils, regulating the discharge of underground contaminated water but also containment of tailing erosion.

Key words: Trace elements; Kilembe mine; tailings; copper

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Introduction

Uncontrolled and illegal mining activities in developing countries have exposed the environment to serious hazards through the generation of large amounts of toxic waste materials, which can impact human health and the ecosystem (Tomov and Kouzmova, 2005). The source of contamination of soils and vegetation is not only the dust fallout from mining operations and from dry parts of tailings ponds, but also the dust emissions from smelters (Ettler et al., 2011). Peplow (1999) reported that hard rock mines typically operate for 5-15 years until the minerals are depleted but metal contamination that occurs as a consequence of such mining activities can persist for centuries after the cessation of mining operations. During mining processes, metal-enriched material is distributed locally as tailings, typically scattered in open and partially covered pits, and transported more widely through wind and water erosion (Habashi, 1992). Exposure of the local population may be both environmental and occupational through air, food or drinking water (Kakkar and Jaffery, 2005).

The health of soil and quality of food crops cultivated in areas affected by mining are subjects of great concern (Musah et al., 2013). Numerous studies have documented trace metal uptake by food crops, vegetables and fruits, and subsequent risk to human health, in many parts of the world (Fernando et al, 2010; Nabulo et al., 2011). Excessive accumulation of trace elements can impair natural soil functions and endanger the wider biosphere by bio-accumulation through the food chain. Metal toxicity is exacerbated in some cases because seemingly healthy plants may (i) systemically accumulate sufficiently large concentrations to endanger human health if ingested (Andrea et al., 2009) and (ii) retain metal particles on external leaf surfaces (Nabulo et al., 2012). If the rate of metal accumulation in humans exceeds that of excretion, a progressive increase in metal body burden will occur (Ezejiofor, 2012). In addition, the severity of adverse health effects is related to the chemical form of

trace metals and is also time and dose-dependent (Alissa et. al, 2011). Metal toxicity may result in serious health consequences, causing low productivity with declining economic development and increased health expenditure (Jarup, 2003). Some common health implications of excessive trace element intake include kidney disease, damage to the nervous system, diminished intellectual capacity, diseases of the heart, gastrointestinal system and skeleton, cancer and death (Jarup, 2003). Unfortunately, the extent of chronic metal poisoning is often difficult to assess in developing countries due to resource limitations.

In the Kilembe area (Western Uganda), the mining and processing of copper from 1956 – 1982 left a legacy of metalliferous material (tailings etc.) dumped mainly within a mountain river valley. Up to 15 Mt of waste was generated during the processing of Cu, Co pyrite ores. There are currently numerous tailing sites of various sizes distributed around the Kilembe mine and Nyamwamba River valley which have the potential to contaminate the regional soils and water bodies through acid mine drainage and erosion by wind and water. The biggest tailing site (> 20 ha) is on the banks of the River Nyamwamba and is visibly eroded whenever the river bursts its banks. There has been substantial mobilisation of sulphate and metallic elements into surrounding river basins and soils (Owor et al., 2007). In addition, potentially contaminated underground mine water discharges into the River Nyamwamba which is a major source of domestic water for local people. Previous studies in the greater Rwenzori region have all found elevated concentrations of trace elements including Cu, Co, Ni and Zn in the soils, lake water and sediments (Edroma, 1974; Muwanga et al., 1997; Ssenku et al., 2014). However no previous study has explicitly investigated trace elements in the Kilembe mine catchment and estimated the extent of metal transfer to food crops and to local populations. Therefore, the aims of this pilot study were to assess the nature and degree of risk to local populations from metal contamination arising from mining activities. The

project objectives included multi-element analysis of metal *sources* (tailings, soils), *environmental media* (soil, river water), *exposure media* (food samples, drinking water, house dust) and *human biomarkers* (toenails).

2. Materials and methods

2.1 Site description

Kilembe mine (0^o 12' N; 30^o 0' E), is located 10 km west of Kasese town on the slopes of the Rwenzori mountain range (0^o 15' N; 29^o 56' E) in Western Uganda. The study area covered Kilembe valley and surrounding hills, an area bisected by the River Nyamwamba which originates from the Rwenzori mountain range (Fig. 1). The study area was divided into three zones. Zone 1 was the upper course of the River Nyamwamba before it reaches Kilembe mine, Zone 2 encompassed the Kilembe mine and tailing sites while Zone 3 was located downstream of the mine and tailing deposits. The area around the Kilembe mine is densely populated, mainly with former mine workers who could not return to their homes when the mine closed in 1982. Most of the residents are subsistence farmers who depend on agriculture for their livelihoods. The food crops grown include bananas, maize, cassava, yams and Irish potatoes. Vegetables such as *Amaranthus spp,* tomatoes, onions, avocados, beans and fruit trees, especially mangoes, are also grown. Most crops are grown downstream of the Kilembe mine and the tailing sites within Zone 2 (Fig. 1), an area that is frequently flooded by the River Nyamwamba which deposits eroded soil and sediments which are enriched with tailing wastes.

2.2 Sample collection and analysis

Sampling was carried out between June and October 2014, cutting across a dry and wet season.

99 *2.2.1 Soils, tailings and household dust: sampling, analysis and indices*

100 Throughout the study area, a total of 18 transects were located along the River Nyamwamba
101 and River Rukoki for collection of soil samples at intervals of 500 m. This enabled
102 assessment of contaminant levels in the entire catchment but focussed on the river as the
103 principal mechanism of mine spoil dispersal. For each transect along the river, 3-5 sampling
104 points were located on either side of the river, separated by an interval of approximately 500
105 m. At each of the tailing sites, 2 transects were established horizontally and vertically where
106 soil samples were taken immediately after the tailings and then after every 500 m to establish
107 dispersion patterns. A total of 89 samples were collected from the study area of which 79
108 were top soils (0-20 cm) and 10 sub soils (20-35 cm). Out of 79 top soils, 73 were sampled
109 from the mining zone and downstream (Zone 2 and Zone 3) while 6 were from control sites
110 upstream (Zone 1). In total, 30 sample plots were occupied by food crops at the time of
111 sampling. At each sampling point, 5 auger borings were taken at the 4 corners and centre of a
112 square with a side length of 10 m (referred to as a 'sample support'), using a standard
113 stainless steel auger, and combined to form a composite sample weighing around 0.5 kg
114 (adapted from British Geological Survey, 2013). Soil samples were also taken from 3
115 recreational grounds used by local schools and communities; 2 were from the mining zone
116 and 1 control sample was taken about 3 km North West from the ore processing centre (Fig.
117 1). Each playground sample was a composite of 5 sub-samples collected from 4 corners of
118 the playground and the centre point. All soil samples were packed in labelled polythene bags
119 and transported to Makerere University where they were air-dried for 2 weeks in the lab,
120 sieved to < 2 mm and stored in plastic zip lock bags. Mine tailing samples were taken from 6
121 tailing sites (Tailings 1-6, Fig. 1), by homogenising 5-7 sub samples from each site to get
122 composite samples which were processed as soil samples**.** Samples of floor dust were
123 collected from 5 private homes (of which one was a control) and 9 public buildings (of which

124 2 were controls) which included a church, a hospital and 7 public schools. Floor dust
125 samples were collected using brushes and plastic dustpans from 3-4 rooms inside residential
126 houses and 4 corners inside public buildings; these were homogenised and processed as soil
127 samples. Control house-dust samples were collected from Nyakazinga village which is 10
128 km South East of Tailing site 1 and therefore presumed to have no aerial or river deposition
129 of tailings material.
130
131 Soils, tailings and household dust (c. 0.2 g) were fully digested in perfluoroalkoxy (PFA)
132 vials using 2.5 mL hydrofluoric acid (HF; 40% Analytical Reagent-AR), 2.0 mL HNO_3
133 (70%, Trace Analytical Grade-TAG), 1.0 mL $HClO_4$ (70%, AR) and 2.5 mL Milli-Q water in
134 a 48-place Teflon-coated graphite block digester (Model A3, Analysco Ltd, UK). Elemental
135 concentrations in digest solutions were analysed by inductively coupled plasma mass
136 spectrometry (ICP-MS; Thermo-Fisher iCAP-Q model).
137
138 The extent of trace element pollution in the affected soils was assessed using the Pollution
139 Load Index (PLI) of Liu et al. (2005). This index is based on the Concentration Factors (CF_i)
140 of each element in the soil where CF is the ratio of soil elemental concentration (C_s) to an
141 appropriate background concentration (C_{bs}) in an uncontaminated soil.

142 $$CF_i = \frac{C_s}{C_{bs}} \qquad \text{Eq. 1}$$

143 Values of C_{bs} were estimated from the mean concentrations of trace elements in soils from
144 Zone 1 (Fig. 1) that were judged to be uncontaminated. For each sampling site, values of PLI
145 at one soil depth were calculated as the *n*th root of the product of *n* CF values:

146 $$PLI = \sqrt[n]{(CF_1 \ x \ CF_2 \ x \ CF_3 \ x \ CF_n} \qquad \text{Eq. 2}$$

147 This index provides a simple, comparative means of assessing the overall level of trace
148 element pollution; values of PLI in excess of 1.0 indicate the presence of trace element
149 contamination.
150
151 *2.2.2 Food crops and human biomarkers: sampling, analysis and indices*
152 Food samples were collected from 30 cultivated plots where soil sampling was undertaken, in
153 addition to 14 samples from household gardens where no soils were sampled. Most of the
154 food sampling was conducted in Zone 2 of the study area, because it was the most densely
155 populated and cultivated zone. They included *Amaranthus tricolour* (n = 31), maize (n = 4),
156 bananas (n = 5), mangoes (n = 2) and cassava (n = 2). The control samples collected
157 included Amaranthus tricolour (6), maize (3), bananas (3) and cassava (2). All samples were
158 washed in clean tap water, rinsed in distilled water, cut up with a stainless steel knife and
159 oven dried at 80ºC for 24 hours before being packed in polythene zip lock bags. Following
160 importation to the UK, samples were ground in a centrifugal mill with a titanium screen
161 (Retsch ZM 200, Germany).
162
163 Toenails were chosen as biomarkers because they are easy to collect and are not invasive.
164 Concentrations of potentially toxic metals in nail tissue have been reported to be an order of
165 magnitude higher than those of body fluids and other accessible tissues (Rodushkin and
166 Axelsson, 2000; Sukumar and Subramanian, 2007). Human nails contain keratin-rich
167 proteins, which incorporate trace elements in proportion to their dietary intake, and other
168 forms of exposure, by mechanisms such as chemical binding with sulfhydryl groups (He,
169 2011). Toenails were collected from 27 volunteer residents of the study area, including 12
170 school-going children aged between 8-14 years and 15 adults aged between 17 and 70 years.
171 Ten volunteers from Kampala City, comprising 5 children aged 9-14 years and 5 adults aged

between 20-60 years who had never lived in the study area also provided toenails as controls. The volunteers were provided with consent forms which they read and signed; children were asked to consult their parents for permission to participate in the study, in which case both the parent and the child signed the consent form. The protocol was approved by the Uganda National Council of Science and Technology. Prior to toenail collection, the subjects had their feet washed with clean tap water. The nails were then clipped using a stainless steel nail clipper. The cut nails were washed three times in distilled water while resistant dirt and extraneous material were scraped off using a brush and acetone. They were dried at room temperature and sealed in polythene zip lock bags prior to exportation to UK for analysis.

Approximately 0.2 g of finely ground food crop and toenail samples were microwave digested (Anton Paar, Multiwave 3000) in 2 mL HNO_3 (70% TAG), 1 mL Milli-Q water and 1 mL H_2O_2 (40% AR). A certified reference material (NIST 1573a) was included for quality assurance. The digested solutions were diluted to 15 mL with Milli-Q water and stored prior to analysis by ICP-MS following a further 1:5 dilution with Milli-Q water. Dry weight concentration data for foods were converted to a fresh weight basis using vegetable and food-specific conversion factors calculated from the measured fresh and dry weights at harvest.

Hazard quotients (HQs) have been widely used to express 'non-cancer' health risk from consumption of food, such as vegetables grown in contaminated soils (e.g. Hough et al., 2004). Values of trace element-specific HQ were calculated according to Equation 3 (Datta & Young, 2005):

$$HQ = \frac{C_p \times ADI \times F_{wc}}{RfD \times BW} \quad \text{Eq. 3}$$

where C_p is the trace element concentration in the edible portion of vegetables (mg kg^{-1} dry weight-DW), ADI is the average daily intake (fresh weight) of vegetable and foods

(established from survey to be 0.2 kg d^{-1}), FWC is a dry-to-fresh weight conversion factor. It is possible to compile an average 'basket' of produce making up the ADI but we chose instead to calculate produce-specific HQ values as a comparative assessment. The reference dose (RfD) is a numerical estimate of a daily exposure to the human population, including sensitive subgroups, that is not likely to cause adverse health effects during a lifetime (EPA, 2002). Finally, the average body weight (BW in equation 3) of 12 children between 8 – 14 years was measured in the study area at 29.6 kg while 15 adults above 18 years had an average of 65.5 kg.

2.2.3 Soil dust contamination of food and toenails

Although toenail samples were washed in water and acetone, it was considered that they could still have soil dust particles on the substrate surface or embedded inside the nail structure, resulting from prolonged exposure to local soil, especially among local people who walk bare footed. Some trace elements have very poor bioavailability and can be used to estimate the likely proportion of the metal content of plants or toenails arising from external contamination from soil dust. Vanadium (V) may be a reliable indicator of extraneous contamination with soil dust because (i) vanadyl (VO^{2+}) and vanadate (VO_4^{3-}) ions are poorly available to plants in soil, (ii) neither species is likely to follow a similar uptake path to that of Fe^{3+} but (iii) trivalent V^{3+} ions substitute for Fe^{3+} in soil iron hydrous oxide particles and vanadate anions are strongly adsorbed by iron oxides (Joy et al., 2015). Thus, a strong correlation between Fe and V concentrations is more likely to reflect structural inclusion of Fe oxide particulates within the nail matrix rather than systemic uptake of V and Fe.

The levels of soil dust contamination in foods and toe nails were estimated, for each element, from the soil V concentration. Equation 4 (Joy et al, 2015) uses plants as an example:

$$P_y\ (\%) = \frac{(V_p\ \ X\ M_S\ )\ 100}{V_S\ X\ M_p} \qquad \text{Eq. 4}$$

Where Py (%) is the percentage contamination from soil dust for a given element (M) in a plant sample, Vp and Vs are the vanadium concentrations in the plant and in the local soil, Mp and Ms are the concentrations of the test element in the plant and the local soil respectively. It must be stressed that this approach provides only an approximate estimate of Py because it assumes (i) no systemic uptake of V and (ii) that the ratio of M:V in the local soil also applies to fine dust particles embedded in plant tissue (and toenails).

2.2.4. Water sampling and analysis

A total of 61 water samples were collected from (i) the Kilembe valley along the River Nyamwamba and Rukoki tributary (n = 30, Fig. 1), (ii) mine and leachate water (n = 4) and (iii) public water sources (n = 9) which included tap water (n = 5), gravity flow water (n = 2), and community water wells (n = 2). Additional samples were taken from the tributaries flowing into the River Nyamwamba (n = 6) as well as samples from household water containers (n = 12). River and stream water samples were composites taken across the width of the river from 2-4 points at a depth of 5 cm below the surface while mine water, leachate, and community water well samples were grab-samples taken from one point below the surface. House hold water containers were vigorously shaken and water poured into the sampling container. All water samples were immediately filtered using 0.45 µm syringe filters to remove suspended solids and stored in plastic bottles. Samples for trace element analysis were acidified, following filtration, using 0.2 M HNO_3 to prevent sorption on containers. Water samples for anion analysis were not acidified but were kept refrigerated at 4^{o}C and assayed using ion chromatography.

2.2.5. Determination of trace elements in all samples

247 The concentrations of 28 elements, including Zn, Cu, Co, Ni, As, Cd, Cr, As and Pb were
248 measured by ICP-MS with 'in-sample switching' between three operational modes: standard
249 mode and kinetic energy discrimination with either He or H_2 as the cell gas to reduce
250 polyatomic interferences. Internal standards included Sc (10 μg L^{-1}), Ge (10 μg L^{-1}), Rh (5
251 μg L^{-1}) and Ir (2 μg L^{-1}) in 2% trace analytical grade (TAG) HNO_3. External multi-element
252 calibration standards (Claritas-PPT grade CLMS-2, Certiprep) included elements in the
253 concentration range 0 – 100 μg L^{-1}.
254
255 For quality control, all samples were prepared and tested in duplicate. The reagents used for
256 sample preparation were analytical reagent grade (AR) or TAG supplied by Fisher Scientific,
257 UK. Digestion blanks and certified reference materials were included in all sample batches.
258
259 The extent of recovery of trace elements from all the samples was assessed through
260 recoveries of trace elements from certified reference materials. Recoveries (%) for NIST
261 1573a (tomato leaves) were As (146), Cd (103), Co (101), Cu (99), Fe (99), Mn (108), Ni
262 (101), Zn (102). Average recoveries (%) for NIST 2711 (soil) were As (95), Cd (126), Co
263 (78), Cu (93), Fe (92), Mn (82), Ni (85), Pb (122), Zn (100).
264
265 *2.2.6 Social Survey*
266 Qualitative data was collected through a survey using questionnaires which were distributed
267 to 60 respondents randomly selected from seven villages within the Kilembe valley
268 (supplementary information). The survey collected information on the life-style of local
269 people, the proximity of their houses to Kilembe mine and tailing sites, occupational
270 exposure to the Kilembe mine, sources of domestic water, cultivation of soil contaminated
271 with tailings and awareness of mine waste dangers.

2.2.7 Statistical analysis

Survey data was assessed for precision and entered into SPSS version 16 to generate descriptive statistics for water sources and foods consumed. Data for tailings, soils, house dust, foods and toenails were analysed using Pearson's correlation, to determine whether there was a linear association between the trace elements. A two sample T-test was conducted to assess differences between trace elements in contaminated and control samples of soils, house dusts, foods, toe nails and water using Minitab version 14. All the statistical tests were conducted at a 5% significance level.

3. Results and discussion

3.1 Tailings dumps

Concentrations of trace elements in the six tailings dumps sampled (Fig. 1) are presented in Table 1. Compared with average crust values, elevated trace elements in the tailings were found in the decreasing order Cu > Ni > Co > As, but there was no correlation between the four elements ($p > 0.05$). Bird (1968) and Davis (1969) identified the primary sulphides at Kilembe to be pyrite (FeS_2), chalcopyrite ($CuFeS_2$) and pyrrhotite ($Fe_{(1-x)}S$) in an approximate ratio of 12:7:1. Rare minerals included linnaeite ($Co^{2+}Co^{3+}{}_2S_4$), sphalerite (Zn,Fe)S), diegenite (Cu_9S_5), pentlandite ($(Fe,Ni)_9S_8$) and molybdenite (MoS_2). The higher concentrations of Co, Cu and Ni measured in tailings compared with world crust average elemental concentrations therefore appear to reflect the known mineralogy of the mine.

3.2. Agricultural soils

The tailings dumped in the vicinity of Kilembe mine have been re-distributed into the neighbouring soils, as suggested by elevated concentrations of Cu, Co and Ni, in soil samples

297 from around the mining and tailings sites in Zone 2 and 3 (Fig. 1) compared with control soils
298 in Zone 1 and 'world average' values (Table 2). The levels of all trace elements in Kilembe
299 mine soils were lower than those found in agricultural soils of Chinese mining zones (Guo et
300 al., 2008). Over 48% of cultivated soils had Co concentrations exceeding recommended
301 thresholds for agricultural soils (Nova Scotia Environment, 2014), 33% exceeded agricultural
302 soil thresholds for Cu (Riccardo et al., 2008) and 53% exceeded thresholds for Ni (Riccardo
303 et al., 2008). The concentrations of Cu, Co and Ni in the Kilembe mine and tailing site soils
304 (Zone 2) and downstream soils (Zone 3) were significantly higher from those in upstream
305 soils (Zone 1); (Cu: $p = 0.003$, Ni: $p = 0.001$, Co: $p = 0.01$). There were strong and positive
306 correlations ($p < 0.001$) between Cu and Co ($r = 0.929$), Ni and Co ($r = 0.534$), Cu and Ni (r
307 $= 0.383$) and Cu and Zn ($r = 0.411$) reflecting the known mineralogy of the area.
308
309 The calculated PLI for soils (Eq. 2) ranged between 0.83 and 3.74 (Fig. 2), with an average of
310 1.72 indicating significant contamination of the area. The data also suggests a possible
311 binary distribution with some relatively highly contaminated sites (PLI > 2) against a
312 background of low level contamination for the majority of sites (PLI = 1.0 – 1.5). Based on
313 the PLI, 51 % of the soils where food crops were grown could be considered contaminated
314 with trace elements, notably Cu, Co and Ni (Table 2).
315
316 ***3.3 Playgrounds***
317 Trace element concentrations in two playgrounds used by communities and schools exhibited
318 high concentrations of Cu (38.2 - 525 mg kg^{-1}), Co (19.7 - 65.3 mg kg^{-1}), Ni (51.7 - 84 mg kg^{-1})
319 and Zn (53 - 167 mg kg^{-1}) compared with a control playground which contained 11.6 mg
320 kg^{-1} for Cu, 5.87 mg kg^{-1} for Co, 12 mg kg^{-1} for Ni and 26.4 mg kg^{-1} for Zn. The mean
321 outdoor Co concentrations (44.5 mg kg^{-1}) were lower than reported for the Katanga copper

322 mine (DRC) of 330 mg kg^{-1} which were found to be elevated and of potential risk to children
323 (Cheyns et. al, 2014) . The 2 contaminated playgrounds were located in Zone 2 (Fig. 1) on
324 top of tailing sites that had been levelled and a thin layer of soil added to plant lawn grass or
325 sports turf. The playgrounds were particularly contaminated by ore-derived metals (Co, Ni,
326 Zn and Cu) with 45 times the Cu concentration of the control site, located upstream 3 km NW
327 from the ore processing centre where contamination from mining activities was negligible.
328 The high concentration of trace elements in contaminated play grounds can be attributed to
329 the tailing residues forming sections of the profile which were sampled in the top soils.
330
331 ***3.4 Interior dust in houses and public buildings***
332 Concentrations of trace elements in house dusts are presented in Table 3. The dust collected
333 from the interiors of private homes and public buildings had concentrations of Cu, Co, Zn
334 and As that were greater than elemental concentrations in control house dusts taken 10 km
335 North East of Tailings site 1. Cobalt concentrations in public buildings and Cu concentrations
336 in both public and private buildings were significantly different from elemental
337 concentrations in control house dusts ($p<0.05$). The mean concentration of Co (23.9 mg kg^{-1})
338 in house dust was significantly lower than mean Co concentrations in the Katanga-DRC
339 mining area of 490 mg kg^{-1} (Cheyns, 2014) which was considered to pose a health risk to
340 children. Nickel concentration was higher in public buildings and slightly lower in private
341 homes but the concentrations were not significantly different from controls collected from
342 uncontaminated sites. However, the mean Cu concentrations of 143 mg kg^{-1} for private
343 homes and 283 mg kg^{-1} for public buildings were significantly greater ($p < 0.001$) than those
344 of control house dust samples (13.3 mg kg^{-1}). The highest Cu concentration measured (699
345 mg kg^{-1}) was in a school located 800 m from Tailings site 4 (Zone 2), just 10 metres from the
346 Nyamwamba river bank on a flat area prone to flooding. Based on Nova Scotia limits for

trace elements in residential soils (Nova Scotia Environment, 2014), Co exceeded the recommended limits of 22 mg kg^{-1} in 75% of the dust samples collected from private residences (n = 4) and 86 % of public buildings (n = 7). Other trace elements were below the Nova Scotia thresholds. Trace elements in house dust were possibly originating from contaminated construction sites, windborne tailings dust, sediments from the River Nyamwamba, eroded tailings, sand collected from the River Nyamwamba which is used to plaster houses and tailings used as an abrasive material by some households to wash cooking utensils.

3.5 Food products

Trace element concentrations in the foods, on a dry weight basis, are given in Table 4. Through the dietary survey, it was established that of all locally grown crops; maize, cassava, bananas, mangoes and *Amaranthus species (*vegetables) were the most abundant and widely consumed foods. Mangoes were consumed fresh while cassava, maize, bananas and vegetables were steamed in saucepans. The food preparations identified are not expected to affect trace element concentrations in food consumed. Over 19% of *Amaranthus tricolour* sampled (n = 31) had Cu concentrations above the EC threshold of 20 mg kg^{-1}, Zn concentrations exceeded WHO/FAO thresholds of 99.4 mg kg^{-1} in 36% of vegetables while Pb concentrations were higher than the WHO/FAO threshold value of 0.3 mg kg^{-1} in 47% of vegetable samples. The concentrations of Cu in *Amaranthus tricolour* were significantly different from control samples ($p < 0.001$). In bananas, 20% of samples (n = 5) exhibited Pb concentrations exceeding the WHO/FAO recommended threshold of 0.3 mg kg^{-1}. The mean concentration of Cu, Ni and Zn in food crops grown in the River Nyamwamba catchment exceeded the concentrations in similar crops grown along the Pearl River estuary, China (Le et al., 2012) which originated from parent materials and river sediments. Strong correlations

($p < 0.001$) were observed between the ore-derived metals Co and Ni ($r = 0.769$) and Cu and Co ($r = 0.563$) in the food samples, suggesting a common source for systemic uptake or possibly soil dust contamination from ore-body metals.

Notwithstanding the clear evidence of environmental contamination, a risk assessment of locally grown foods (HQ values; Eq. 3) indicated no evidence of potentially negative health effects to consumers (Table 5). Hazard quotients are relatively crude indices of the potential for adverse health effects; it is only reasonable to assume that for values less than 1.0 no adverse health effects are expected. The apparent contradiction suggested by low HQ values calls for further studies into the specific dietary habits of local people to ascertain risks based on actual dietary surveys and a more thorough assessment of contact between contaminated soil and those engaged in cultivation operations. Depending on (assumed) consumption rates, the simple hazard quotient index suggests that children are more exposed to health risks compared to adults, due to their smaller body mass.

3.5.1 Soil dust contamination of foods

Estimates of percentage dust contamination (Eq. 4) in all foods revealed that the proportions of Co arising from soil dust in cassava, mangoes, maize, bananas and *Amaranthus tricolour* were 7%, 13%, 8%, 23% and 13% respectively. Copper from soil dust was 2% for cassava and bananas, 2.5% for maize and mangoes while Cu from soil dust in *Amaranthus* tricolour was 12%. Nickel from soil dust averaged only 1.7% in cassava, 1.7% in mangoes, 0.8%, in maize, 6% in bananas but 16% in *Amaranthus tricolour*. Mean Pb from soil dust in Amaranthus tricolour was 35%, 17% in cassava, 5% in mangoes, 13% in maize and 22% in bananas while mean Zn contribution from soil dust was 0.61 in *Amaranthus* tricolour, 0.2% (cassava), 0.7% (mangoes), 0.1 % (maize) and 0.4 % in bananas. Dust estimations in foods suggested that most of the trace elements in the washed edible parts of foods sampled were

systemically taken up by plants via roots during growth. Kabata- Pendias (2011) also observed that the major route for trace elements in plants is via root uptake. Nevertheless, there were some examples, particularly *Amaranthus* tricolour, where approximately one fifth of the Co, Cu and Pb concentrations apparently originated from soil dust, in qualitative agreement with the Kampala (Uganda) study of Nabulo et al (2012).

3.6 Water quality in the Kilembe catchment

Through the social survey (Section 2.2.6), it was established that more than half the households in Kilembe (51%) depended on tap water for their water sources; 38% depended on the River Nyamwamba while 11% collected water from community water sources such as streams, water wells and gravity water systems.

3.6.1 Trace elements in water samples

Compared with control waters from Zone 1 upstream (Fig. 1), elevated concentrations of trace elements were found in water samples collected from (i) the underground mine (mine water) (ii) the River Nyamwamba along the mine area and downstream (Zones 2 and 3; Fig. 1) and (iii) leachate from mine and tailing sites (Table 6). The concentrations of Cu, Co and Ni in upstream water samples were significantly lower than the concentrations along the mine area and downstream ($p<0.001$). This confirmed trace element input to natural water systems, originating from the mine and tailings sites. In particular, trace element concentrations for the mine water and leachate samples were in excess of the drinking threshold limits for Co, Ni, Cu and Pb specified in Table 6, although these sources are not likely to be utilised for domestic water supply. Over 25 % of domestic water samples collected (n = 12) and 40% of River Nyamwamba waters along the mine area and downstream (n = 20) exhibited Co concentrations exceeding the Wisconsin (USA) thresholds of 40 $\mu g\ L^{-1}$. By contrast, apart

422 from Co concentrations in a small number of samples downstream of the mining area, all
423 samples upstream of the mining area and from public and domestic supplies were well below
424 the WHO (2008) specified limits for other trace elements. Angelova et al., (2004) and
425 Duruibe et al., (2007) observed that trace elements from mine sites are leached and carried by
426 acidic water downstream but distance from the mining sites, suspended solids loadings, pH
427 perturbations and dilution ultimately control the quality of water sources in individual
428 locations. The rate of decrease in trace element concentrations (Zone 3) was not consistent
429 with distance downstream, perhaps due to multiple trace element inputs from several
430 localised point sources and dilution of River Nyamwamba water with non-contaminated
431 inputs from several tributaries.
432
433 Water samples showed strong correlations ($p < 0.001$) between Cu and Ni ($r = 0.989$), Cu and
434 Zn ($r = 0.934$), Cu and Co ($r = 0.810$), Ni and Co ($r = 0.989$), Zn and Co ($r = 0.918$), Pb and
435 Ni ($r = 0.543$, $p < 0.05$). Trace element correlations in water corresponded qualitatively to
436 those found for soils. This may reflect the presence of trace elements adsorbed to
437 nanoparticulate (< 0.45 μm) oxides of Mn, Fe, Al and organic ligands that passed through the
438 water filters used (Kimball et al., 1992; Concas et al., 2006) rather than truly dissolved metal
439 species.
440
441 *3.6.2 Anions in water samples*
442 Sulphate (SO_4^{2-}) was the dominant anion in waters around Kilembe copper mine with a mean
443 concentration of 0.3 mg L^{-1} upstream, 104 mg L^{-1} along the mine and tailing sites and 4.02
444 mg L^{-1} downstream, corroborating findings by Bird (1968) and Davis (1969) who identified a
445 number of primary sulphides at Kilembe. However the sulphate concentrations were below
446 the USEPA recommended drinking water threshold of 250 mg L^{-1}. Fluoride was only found

447 along the mine and tailing zone with a mean value 0.17 mg L^{-1}, below the USEPA threshold
448 of 4 mg L^{-1}. Chloride (mean concentration of 0.62 mg L^{-1}) was measureable upstream, but not
449 along the mining and tailings sites, while downstream chloride concentration was 0.32 mg L^{-1},
450 well below the USEPA threshold of 250 mg L^{-1}. Nitrate (NO_3^-), with mean concentrations
451 of 8.2 mg L^{-1} and 1.4 mg L^{-1} upstream and downstream respectively, did not exceed the
452 USEPA threshold of 10 mg L^{-1}. Along the mine and tailing zones, NO_3^- was not
453 measureable. There were measureable concentrations of sulphate in 86% of the samples;
454 corresponding figures for the other anions were chloride (43%), nitrate (30%) and fluoride
455 (9%) but none of the water samples contained measureable phosphate.
456
457 ***3.7 Toenail biomarkers***
458 The elemental concentrations in toenails are shown in Table 7. Compared with control
459 samples from volunteers who lived more than 400 km from the Kilembe mine, and had never
460 lived in the study area, trace element concentrations in toenails of children were significantly
461 different in the case of Co ($p = 0.009$), Ni ($p = 0.01$), Cu ($p = 0.002$) and As ($p = 0.035$). By
462 contrast, the concentrations of Cu, Co Ni and As in toenails of resident adults and control
463 volunteers were not significantly different ($p > 0.05$). A comparison of Kilembe resident
464 children and adults revealed that concentrations of Co and Cu were significantly different (p
465 < 0.01) with greater trace element concentrations found in the toenails of children. Overall
466 Kilembe residents' toenails contained more than double the control concentrations of Co in
467 50% of samples, Cu and Pb in 30% of samples and As in 62 % of samples. Slotnick et al.,
468 (2005) found similar toenail trace element concentrations (mg kg^{-1}) in Detroit USA for Co
469 (0.17), Cu (5.1), As (0.1), Pb (0.74) in adults, and Co (0.27), Cu (5.7), As (0.14) and Pb
470 (1.6) in children. However the Detroit study found higher mean Ni concentrations at 32.9 mg
471 kg^{-1} for adults and 45.2 mg kg^{-1} for children compared with the mean Ni concentrations in

children from the Kilembe mine area of 4.2 mg kg $^{-1}$ and adults 5.07 mg kg $^{-1}$. In Kilembe mine area toenail samples, there were strong and positive correlations ($p < 0.001$) between the primary ore metals Cu and Co ($r = 0.845$), Pb and Zn ($r = 0.726$). However, it was evident that extraneous soil on toenails was a major contributor to toenail elemental concentrations with more than 70% of the toenail samples indicating contamination with extraneous dust (Eq. 4). The presence of soil dust in toenails was also very strongly indicated by correlating toenail V and Fe as shown in Fig. 3 ($r = 0.987$). It seems highly unlikely that V and Fe are biochemically processed together and accumulate systemically in toenails which would suggest that the majority of the Fe (and V) in toenails has been derived from inclusion of extraneous Fe oxide particulates within the toenail structure. The Fe:V mole ratio was 460:1 in the toenails which differed by about 25% from the ratio for soils in the area ($n = 90$) with an Fe:V mole ratio of 344:1 ($r = 0.818$). This discrepancy may reflect differences in the composition of whole soils and the soil dust fraction thought to be included within the toenails. Nevertheless, the apparent inclusion of soil particles within toenails has significant implications for the proportion of soil-derived trace metals in this important human biomarker, estimated from Eq. 4. The mean elemental contribution to toenails from soil dust was 19% for Co, 20 % for both Ni and Cu, 18% for As, 9.6% for Cd, 16% for Pb and only 0.8% for Zn. However, with the exception of Zn, estimated soil dust contributions to toenail elemental concentrations in some samples were as high as 82%. This probably calls into question the use of (cleaned) toenail samples from Kilembe residents as biomarker indicators of dietary ingestion. Trace elements from possible extraneous soil dust on toenails further imply potential risks from dermal absorption, inhalation and direct ingestion.

4. Conclusions

A pilot study conducted in Kilembe copper mining area, Western Uganda found that concentrations of Cu, Co, Ni and As in tailings were many times higher than world crustal averages, and had eroded into soils, surface and ground water sources. Over 51% of soils had a pollution load index (PLI) exceeding 1.0. The concentrations of Co, Cu and Ni exceeded agricultural thresholds in 48, 33 and 53 % of the sites sampled respectively. Interior dusts in 75% of residential houses and 86 % of public buildings contained Co concentrations exceeding Nova Scotia Environment thresholds. Playground soils too contained relatively high concentrations of trace elements which in combination with house dusts could expose populations to trace elements through inhalation or accidental ingestion.

Amaranthus vegetables exceeded European Community Cu thresholds in 19% of the samples while FAO/WHO thresholds for Zn and Pb were exceeded in 36 and 47% of samples respectively. In bananas, 20% of samples exceeded the WHO/ FAO Pb thresholds. Exposure of populations through contaminated drinking water was demonstrated. Over 40% of River Nyamwamba waters along the mine area and downstream and 25% of domestic water samples contained Co exceeding the Winsconsin (US) drinking water thresholds. Exposure of populations to Cu, Co Zn and Pb in water and foods exceeding thresholds could pose negative health effects such as gastro-intestinal diseases and increased risks of cancer.

The concentrations of Cu, Co and Ni in the toenails of Kilembe mine area residents were several fold higher compared with controls, possibly from direct contact with soil dust as well as systemic absorption. Children exhibited Cu, Co and Ni concentrations that were significantly higher than adults and controls, implying increased risks of exposure. However a significant proportion of the metal loading of toenails appeared to originate from extraneous soil particles, despite washing of samples. This perhaps calls for use of alternative biomarkers

in future studies in the study area. The overall impression left by this pilot study is of latent risks to the local population which could be avoided through measures such as 'awareness' outreach programs, containment of tailing erosion and treatment of mine water before discharge. Given the acidic nature of the local soils, it is possible that soil amendments such as liming agents may help in limiting bioavailability of metals to locally produced crops. Populations need to make informed locational choices for settlements, cultivation, drinking water supply, construction of playgrounds etc. Considering that risk assessment results were inconclusive, a more thorough risk assessment considering more human subjects (exposed and non-exposed), a greater number of environmental samples and all routes of exposure needs to be carried out to have more accurate risk estimates.

Acknowledgements

The authors thank Saul Vasquez Reina and Lolita Wilson, School of Biosciences, Nottingham University who helped in sample preparation and ICP-MS analysis and several anonymous reviewers for their constructive suggestions. This work was funded by the Carnegie Corporation New York through the Graduate School of Makerere University: Carnegie NGAA II Grant.

538 **References**

539

540 Alissa E.M., Gordon A., Ferns G.A. Heavy metal poisoning and cardiovascular disease: A
541 review. Journal of Toxicology, 2011; 2011: 1-21.

542

543 Andrea F, Iren P, Zsuzsanna S. Human Health Risk Assessment: A case study of heavy metal
544 contamination of garden soil in Szeged. AGD Landscape and Environment, 2009; 3: 11-27.

545 Angelova, V., Ivanova, R., and Ivanov, K. Accumulation of lead, cadmium and zinc from contaminated
546 soils to various plants. J. Balkan Ecol. 2004; 7:83–91

547

548 Bird H.H. Falconbridge's copper operations in Uganda. Can. Min. Metall. Bull. 1968; 61:
549 1075–1082.

550

551 Cheyns K., Banza C., Nkulu L., Ngombe K., Asosa N.J., Haufroid V., De Putter T.,
552 Nawrot T., Célestin M.K., Numbi O.L., Ilunga B.K., Nemery B., Smolders E. Pathways of
553 human exposure to cobalt in Katanga, a mining area of the D.R. Congo. Science of the Total
554 Environment, 2014; 490: 313–321.

555

556 Concas A., Ardau C., Cristini A., Zuddas P., Cao G.. Mobility of heavy metals from tailings
557 to stream waters in a mining activity contaminated site. Chemosphere 2006; 63: 244–253.

558

559 Datta S.P., Young S.D. Predicting metal uptake and risk to the human food chain from leaf
560 vegetables grown on soils amended by the long-term application of sewage sludge. Water,
561 Air and Soil Pollution, 2005; 163: 119–136.

562

563 Davis G.R. Aspects of the metamorphosed sulphide ores at Kilembe, Uganda. In: James C.H.
564 (ed.) Sedimentary ores ancient and modern (revised): proceedings of the 15th inter-University
565 Geology Congress, Leicester 1967, pp 273–29.

566 Duruibe, J. O. , Ogwuegbu, M. O. C. 2 and Egwurugwu, J. N. Heavy metal pollution and human
567 biotoxic effects. International Journal of Physical Sciences 2007; 2 (5): 112-118

568 E. C. Commission Regulation No 1881. Setting maximum levels for certain contaminants in
569 foodstuffs. Official Journal of the European Union, 2006; 346: 18–20.

EPA. A review of the reference dose and reference concentration processes. Technical panel report. U.S. Environmental Protection Agency 2002; Washington DC 20460

E.U. European Union (Drinking Water) Regulations. Statutory Instrument S.I. No. 122 of 2014.

Edroma E.L. Copper pollution in Rwenzori National Park, Uganda. Journal of Applied Ecology, 1974; 11: 1043-1056.

Ettler V,, Mihaljevic M., Kribek B., Majer V., Sebek O. Tracing the spatial distribution and mobility of metal/metalloid contaminants in oxisols in the vicinity of the Nkana copper smelter, Copperbelt province, Zambia. Geoderm,a 2011; 164: 73–84.

Ezejiofor N.T., Udebuani I.A.C., Ezeji E.U., Ayalogbu E.A., Azuwuike C.O., Adjero L.A., Ihejirika C.E., Ujowundu C.O., Nwaogu L.A., Ngwogu K.O. Environmental metals pollutants load of a densely populated and heavily industrialized commercial city of Aba, Nigeria. Journal of Toxicology and Environmental Health Sciences, 2013; 5: 1-11.

FAO/ WHO Codex Alimentarius Commission. Working document for information and use in discussions related to contaminants and toxins in GSCTFF Food Standards Programme, 2011, Rome, Italy.

Fernando G., Anderson R.T., Takashi M., Nericlenes C.M., Solange G.C. Heavy metals in vegetables and potential risk for human health. Sci. Agric., 2010; 69: 54-60.

Guo L., Liao DL., Quan ML. Heavy metals contamination characteristics in soil of different mining activity zones. Trans. Nonferrous Met. Soc. China, 2008; 18: 2007-2011.

Habashi F. Environmental issues in the metallurgical industry – Progress and problems. Environmental Issues and Waste Management in Energy and Mineral Production, 1992; 1143 -1153.

He K. Trace elements in nails as biomarkers in clinical research. European Journal of Clinical Investigations, 2011; 41: 98-102.

Hough R.L., Breward N., Young S.D., Crout, N.M.J., Tye A.M., Moir A.M., Thornton I. Assessing potential risk of heavy metal exposure from consumption of home-produced vegetables by urban populations. Environmental Health Perspectives, 2004; 112: 215–221.

Järup L. Hazards of heavy metal contamination. British Medical Bulletin, 2003; 68: 167–182.

Joy J.M., Broadley M.R., Young S.D., Black C.R, Chilimba A.D.C., Ander E.L., Barlow S.T., Watts J.M. Soil type influences crop mineral composition in Malawi. Science of the Total Environment, 2015; 505: 587–595.

Kabata-Pendias A. Trace Elements in Soils and Plants. CRC Press, Taylor and Francis Group 2011.

Kakkar P., Jaffery F.N. Biological markers for metal toxicity. Environmental Toxicology and Pharmacology, 2005; 19: 335–349.

Kimbal B.A., McNight D.M., Wetherbee G.A., Harnish R.A. Mechanism of Iron photoreduction in metal-rich acidic streams (St. Kevin Gulch, Colorado, USA). Chem. Geol., 1992; 96: 227-239.

Li Q., Yan Chen Y., Fu H., Cu Z.H., Lei Shi Wang L., Liu Z.F. Health risk of heavy metals in food crops grown on reclaimed tidal flat soil in the Pearl River Estuary, China. J. Haz. Mat., 2012; 227– 228; 148-154.

Liu W.H., Zhao J.Z., Ouyang Z.Y., Soderlund L., Liu G.H. Impacts of sewage irrigation on heavy metals distribution and contamination in Beijing, China. Environment International, 2005; 31: 805-812.

Musah S.Z., Maxwell A., Boateng A. Health risks of heavy metals in selected food crops cultivated in small-scale gold-mining areas in Wassa-Amenfi-West District of Ghana. Journal of Natural Sciences Research, 2013; 3 (5) 96-108

Muwanga A. Environmental impacts of copper mining at Kilembe, Uganda: a geochemical investigation of heavy metal pollution of drainage water, stream sediments and soils in the Kilembe Valley in relation to mine waste disposal. Bswg. Geowiss. Arb. 21, Institut für Geowissenschaften, TU Braunschweig, 1997, 140 pp.

Nabulo G., Black C.R., Young S.D. Trace metal uptake by tropical vegetables grown on soil amended with urban sewage sludge. Environmental Pollution, 2011; 159: 368-376.

Nabulo G., Black C.R., Craigon J., Young S.D. Does consumption of leafy vegetables grown in peri-urban agriculture pose a risk to human health? Environmental Pollution, 2012; 162: 389-398.

New Jersey Department of Environmental Protection. Health Effects Subcommittee Report, 2008.

Nova Scotia Environment. Environmental Quality Standards for Contaminated sites. Rationale and Guidance Document 2014.

Owor M., Hartwig T., Muwanga A., Zachmann D., Pohl W. Impact of tailings from the Kilembe copper mining district on Lake George, Uganda. Environ. Geol. 2007 ; 51: 1065–1075.

Peplow D. Environmental Impacts of Mining in Eastern Washington. Center for Water and Watershed Studies Fact Sheet 1999. University of Washington, Seattle.

Riccardo S., Gabriella F. Soil trace elements patterns in the Torino Olympic Winter Games venue (E.U.). Soil & Sediment Contamination, 2008; 17: 205–220.

Rodushkin I., Axelsson D. Application of double focusing sector field inductively coupled plasma-mass spectrometry multi-elemental characterization of human hair and nail Part II. A study of inhabitants of northern Sweden. Sci. Total Environ., 2000; 262: 21–36.

Slotnick M.J., Nriagu J.O., Hohnson M.M., Linder A.M., Savoie K.L., Jamil H.J., Hammad A.S. Profiles of trace elements in toe nails of Arab-Americans in the Detroit Area, Michigan. Biological Trace Element Research, 2005; 107: 113-126.

Sukumar A., Subramanian R. Relative element levels in paired samples of scalp hair and fingernails of patients from New Delhi. Sci. Total Environ., 2007; 372: 474–479.

Ssenku J.E., Ntale M., Oryem Origa H. Physico-chemical characteristics of copper tailings and pyrite soils in Western Uganda: Implication for phytoremediation. International Journal of Environmental Monitoring and Analysis, 2014; 3:1-12

Tomov A., Kouzmova K. Exploring possibilities of cultivation of unpolluted plant produce in lead and cadmium contaminated sites, J. Cen. Eur. Agric., 2005; 6: 121-126.

US EPA Iris Database, 2015, http://cfpub.epa.gov/ncea/iris/

Wisconsin Department of Natural Resources. Drinking Water & Groundwater Quality Standards/Advisory Levels, 2011.

WHO (World Health Organization (2008), Guidelines for Drinking-water Quality, 3rd Edition. Geneva, Switzerland

Table 1: Concentration of trace elements in Kilembe mine tailing sites (mg kg^{-1}), Western Uganda. Values are given to three significant figures.

Tailing Site	Cr	Co	Ni	Cu	Zn	As	Ag	Cd	Pb
1	152	79.7	101	2270	29.6	11.7	0.40	0.00	6.30
2	136	148	156	1100	68.3	2.90	0.20	0.30	7.00
3	107	110	118	5470	41.1	11.9	0.90	0.10	16.2
4	113	152	125	10200	36.2	5.00	0.80	0.10	4.80
5	121	101	164	165	52	6.30	0.23	0.03	13.4
6	97.4	78.2	119	691	50.9	13.6	0.60	0.10	21.8
Average Crust[i]	100	1-15	20	25-75	70	1.8	0.06	0.1	15

[i]Kabata-Pendias (2011).

Table 2: Trace elements in cultivated soils from the Kilembe mine area (Western Uganda). Units = mg kg^{-1}.

Elements		Soils (Zones 2 and 3; n= 30)	Control soils (Zone 1; n=5)	World Average [i]	Agricultural limit
Co*	Range	8.39 - 51.9	8.15-15.5	10	22 [iii]
	Mean±SD	22.2 ± 10.2	10.53 ± 8.3		
Ni*	Range	18.8 - 102	7.71-20.3	13-37	35 [ii]
	Mean±SD	39.1 ± 19.3	15.7 ± 14.1		
Cu*	Range	6.78 - 399	12.6-42.7	14-109	100 [ii]
	Mean±SD	90.3 ± 106	22.5 ± 33		
Zn	Range	26.6 - 174	30.8-97.7	60-89	350 [ii]
	Mean±SD	61.9 ± 37.2	60.8 ± 74.6		
As	Range	0.97 - 7.59	1.19-2.36	6.83	31 [iii]
	Mean±SD	2.52 ± 1.98	1.67 ± 1.5		
Cd	Range	0.07 - 0.31	0.1-0.22	0.2-1.1	1.4 [iii]
	Mean±SD	0.18 ± 0.11	0.15 ± 0.18		
Pb	Range	5.95 - 48.4	12.1-16.3	27	80 [ii]
	Mean±SD	14.2 ± 7.15	13.7± 4.4		

[i]Kabata-Pendias (2011), [ii]Riccardo et al. (2008), [iii]Nova Scotia Environment (2014).

*There were significant differences between contaminated sites and controls

Table 3: Trace elements in house dusts around Kilembe copper mines, Western Uganda. Units = mg kg^{-1}.

Element		Public buildings[#] (n=9)	Private homes (n=5)	Mean Control (n=3)	Maximum limit Residential soil [i]
Co*	Range	14.3 - 107	15.8 - 29.7	15.8-26.2	22
	Mean ± SD	33.1 ± 28.8	23.9 ± 4.6	20.4±5.3	
Ni	Range	12.2 - 37.6	27.4 - 72.1	32.4-72.1	130
	Mean ± SD	28.1 ± 7.8	49.8 ± 15.6	51.3±20	
Cu* æ	Range	30.1 - 699	13.3 - 272	13.3-30.1	1100
	Mean ± SD	283 ± 204	143 ± 125	19.6±9.1	
Zn	Range	24.3 - 117	45.1 - 80	45.1-117	5600
	Mean ± SD	49.7 ± 27.9	62.4 ± 15.2	79.8±36	
As	Range	1.2 - 3.68	1.56 - 11.8	1.6-1.98	31
	Mean ± SD	1.86 ± 0.75	3.5 ± 12.3	1.7±0.24	
Pb	Range	9.5 - 16.8	9.92 - 14.7	9.92-16	140
	Mean ± SD	12.7 ± 2.88	11.9 ± 5.5	13.6±3.22	
Cd	Range	0.05 - 0.11	0.08 - 0.22	0.08-0.18	14
	Mean ± SD	0.07 ± 0.03	0.13 ± 0.18	0.11±0.06	

[i]Nova Scotia Environment (2014).

[#]Public buildings included 7 schools, a church and a hospital,

*The elemental concentrations in public buildings and controls were significantly different

æ The elemental concentrations in private buildings and controls were significantly different

Table 4: Trace element concentrations in Kilembe mine area foods, Western Uganda. Units = mg kg^{-1} dry weight (dw)

Food crop		Co	Ni	Cu*	Zn*	Pb	Cd	As
Maize (n = 4)	Range	0.01 - 0.47	0.12 - 3.11	1.48 - 16.2	16.3 - 40	0.00 - 0.07	0.00 - 0.03	0.00 - 0.03
	Mean ± SD	0.16 ± 0.22	1.46 ± 1.4	5.92 ± 7.6	26.8 ± 13.4	0.04 ± 0.04	0.02±0.02	0.02±0.02
	Control range (n=3)	0-0.16	0-0.48	1.25-15.8	4.97-114	0-0.1	n.d	n.d
	Control Mean ±SD	0.09±0.08	0.1±0.33	6.33±8.23	42.1±62.4	0.04±0.04	n.a	n.a
Cassava (n = 2)	Range	0.15 - 1.41	1.56 - 2.98	2.99 - 20.47	15.4 - 36.2	0.06 - 0.1	0 - 0.01	0.01
	Mean ± SD	0.78 ± 0.88	2.3 ± 0.99	11.7 ± 12	25.8 ± 14.6	0.08 ± 0.11	0.01 ± 0	0.01 ± 0.01
	Control range (n=2)	n.d.	0.41-0.94	2-2.49	11.5-14.3	0.06±0.01	n.d	n.d
	Control Mean ± SD	n.d	0.68±0.38	2.25±0.34	12.9±1.94	n.d	n.a	n.a
Banana (n = 5)	Range	0.01 - 0.5	0 - 1.1	2.03 - 5.06	6.7 - 19.3	0.01 - 0.37	0.0 - 0.01	0 - 0.01
	Mean ± SD	0.17 ± 0.18	0.59 ± 0.46	3.84 ± 1.2	11.3 ± 5.1	0.1 ± 0.15	0.004 ± 0.005	0.004 ± 0.005
	Control range	n.d.	n.d.	n.d.	4.97-14.3	n.d.	n.d.	n.d.
	Control Mean ± SD	n.a	n.a	n.a	9.84±4.66	n.a	n.a	n.a
Mangoes (n = 2)	Range	0.26-0.41	4.4 - 5.3	5.58 - 7.1	7.14 - 7.5	0.19 - 0.24	0.0 - 0.07	0.01 - 0.01
	Mean ± SD	0.26±0.21	4.4 ± 1.26	5.21 ± 2.1	7.14 ± 0.49	0.19 ± 0.07	0.04 ± 0.05	0.01 ± 0
Amaranthus (n = 31)	Range	0.01 - 81	0.33 - 9.1	1.95- 35.4	25 - 846	0.08 - 2.7	0.0 - 0.22	0.0 - 0.1
	Mean ± SD	4.2 ± 14	1.7 ± 1.68	11.1 ± 9	102 ± 140	0.3 ± 0.45	0.08 ± 0.05	0.04 ± 0.01
	Control range	0.01-2.49	0.07-2.31	5.14-7.33	15.6-54.6	0.01-0.5	0.02-0.11	n.d
	Control Mean ± SD	0.84±1.12	0.93±0.95	6±1.1	40.2±17.3	0.23±0.21	0.07±0.04	n.a
Cassava and Banana guidelines		-	67.9	73.3	99.1	0.3	1	-
Guideline for vegetables		50[i]	66.9[i]	20[ii]	99.4[i]	0.3 [i]	1[i]	-

[i]WHO /FAO (2011); [ii]EC standards (2006), n.d. = not detectable n.a = not applicable

*Significant differences were found with controls in *Amaranthus* species

Table 5: Hazard Quotients (HQ) associated with consumption of food crops and water in the Kilembe mine catchment, Western Uganda.

Element	RfD ($mg\ kg^{-1}\ d^{-1}$)	Consumer	*Amaranthus Tricolour* n = 31 c.f. = 0.13	Bananas n = 5 c.f. = 0.26	Maize n = 4 c.f. = 0.43	Mangoes n = 2 c.f. = 0.19	Cassava n = 2 c.f. = 0.44	Domestic water[$] n = 12	Domestic water[#] n= 12
Cu	0.40[i]	Child	0.02	0.01	0.03	0.01	0.07	0.008	0.027
		Adult	0.01	0.01	0.02	0.008	0.04	0.003	0.012
Pb	0.0035[i]	Child	0.08	0.06	0.02	0.05	0.05	0.017	0.077
		Adult	0.04	0.02	0.01	0.03	0.03	0.008	0.008
Ni	0.02[ii]	Child	0.07	0.05	0.02	0.23	0.03	0.024	0.28
		Adult	0.03	0.02	0.01	0.13	0.02	0.001	0.03
Zn	0.30[ii]	Child	0.30	0.05	0.19	0.02	0.26	0.013	0.045
		Adult	0.13	0.03	0.12	0.01	0.12	0.006	0.02
Co	0.02[iii]	Child	0.18	0.01	0.02	0.01	0.12	0.086	0.28
		Adult	0.08	0.01	0.01	0.01	0.05	0.039	0.13

[i]Hough et al. (2004), [ii]US EPA Iris Database (2009), [iii]New Jersey Department of Environmental Protection (2008).

[$]Calculated using mean concentration, [#]Calculated using maximum concentration.

c.f: dry weight to fresh weight conversion factor, RfD: Reference dose

Table 6: Concentration of trace elements in Kilembe mine catchment waters, Western Uganda. Units = µg L^{-1}.

Sample source		Co*	Ni*	Cu*	Zn	Pb	As	Cd
Nyamwamba water, Zone 1 (n = 6)	Range	0.18 - 0.47	0.5 - 1.1	0.6 - 2.6	2.9 - 5.9	0.2 - 0.4	0.1 - 0.2	0.01 - 0.01
	Mean ± SD	0.25 ± 0.1	0.7 ± 0.25	1.6 ± 1.25	4.2 ± 1.25	0.3 ± 0.1	0.1 ± 0.03	0.01 ± 0
Nyamwamba water, Zone 2 (n= 16)	Range	3.21 - 57.4	1.8 - 13.2	16.2 - 68.1	5.7 - 20.8	0.03 - 0.8	0.1 - 0.17	0.01 - 0.04
	Mean ± SD	43 ± 52	9.2 ± 10	45 ± 52	11.4 ± 16	0.5 ± 1.2	0.13 ± 0.08	0.2 ± 0.01
Nyamwamba water, Zone 3 (n = 4)	Range	4.72 - 66	2 - 13	5.9 - 60	4.6 - 23	0.2 - 1.4	0.1 - 0.15	0.02 - 0.04
	Mean ± SD	38.4 ± 7.4	9.1 ± 1.4	57 ± 6.6	10.8 ± 2	0.3 ± 0.1	0.13 ± 0	0.03 ± 0.06
Mine water and leachate (n = 4)	Range	367 - 5860	89 - 1105	27 - 27793	25 - 752	0.21- 539	0.5 - 4.9	0.2 - 3.32
	Mean ± SD	2824 ± 2588	497 ± 452	7363 ± 13626	289 ± 318	135 ± 270	2.1 ± 2	1.6 ± 1.58
River Rukoki (n = 4)	Range	0.17 - 57.6	0.48 - 19.1	0.61 - 35.4	2.25 - 92.7	0.05 - 0.34	0.03 - 8.13	0 - 0.13
	Mean ± SD	19.5 ± 37	5.22 ± 9	9.77 ± 17	26.7 ± 44	0.13 ± 0.14	2.11 ± 4	0.04 ± 0.08
Nyamwamba tributaries (n = 6)	Range	0.19 - 1000	0.5 - 230	1.25 - 1044	3.98 - 196	0.1 - 0.49	0.16 - 0.66	n.d.
	Mean ± SD	167 ± 418	39.4 ± 95	176 ± 435	37.7 ± 80	0.2 ± 0.15	0.3 ± 0.2	n.d.
Public water sources (n = 9)	Range	0.02 - 2.4	0.02 - 1.3	0.3 - 6.5	0 - 82	0 - 0.6	0 - 0.9	0.0 0.07
	Mean ± SD	0.82 ± 0.9	0.71 ± 0.48	3.4 ± 2.4	25 ± 27	0.3 ± 0.18	0.2 ± 0.27	0.02 ± 0.3
Domestic water (n = 12)	Range	0.03 - 66	0.6 - 16	1.24 - 129	4.9 -160	0.06 - 0.8	0 - 0.9	0.01- 0.04
	Mean ± SD	20 ± 24	5.6 ± 6	36 ± 49	47 ± 49	0.3 ± 0.04	0.13 ± 0.02	0.02 ± 0.01
Thresholds limits:		40[ii]	200[i]	2000[i]	3000[i]	10[i]	10 [i]	5[iii]

[i.]WHO (2008), [ii.]Wisconsin Department of Natural Resources (2011), [iii]EU (2014).

*The concentrations of the elements in control waters and the contaminated waters (along the mine area and downstream) were significantly different

Table 7: Trace elements concentrations (mg kg^{-1} dw) in toenails of 15 adults and 12 children from the Kilembe copper mining district in Western Uganda. Control samples were from 5 children aged 9-14 years and 5 adults aged 20-60 years

Trace element	Age Group	Range	Mean ±SD	Control range (n=5)	Control Mean ±SD
Co*	Children	0.57 - 5.39	2.21 ± 1.75	0.19-1.03	0.49±0.32
	Adults	0.04 - 1.44	0.37 ± 0.39	0.11-1.2	0.42±0.45
Ni* æ	Children	2.1 - 6.7	4.21 ± 1.4	0.65-2.57	1.37±0.76
	Adults	0.92 - 40	5.1 ± 9.8	0.45-3.1	1.73±1.06
Cu* æ	Children	5.3 - 37.6	20.5 ± 11.9	2.20-5.53	3.51±1.39
	Adults	0.93 - 35.4	5.86 ± 18.3	1.84-5.5	3.25±1.42
As*	Children	0.11 - 2.52	0.62 ± 0.8	0-0.08	0.04±0.03
	Adults	0.05 - 5.22	0.76 ± 1.56	0-0.07	0.03±0.03
Zn	Children	75 - 144	114 ± 19.2	69.5-129	92.7±26.6
	Adults	85 - 602	148 ± 129	45-135	97.8±37.6
Pb	Children	0.25 - 2	0.92 ± 0.28	0.4-1.1	0.76±0.4
	Adults	0.4 - 8.76	2.02 ± 1.3	0-0.21	0.62±0.03
Cd	Children	0.01 - 0.07	0.03 ± 0.02	0.1-0.21	0.06±0.03
	Adults	0.02 - 0.024	0.051 ± 0.053	0.4-1	0.16±0.04

*Significant differences were found between children elemental toe nails concentrations and controls

æ Significant differences were found between children and adults toe nail elemental concentrations

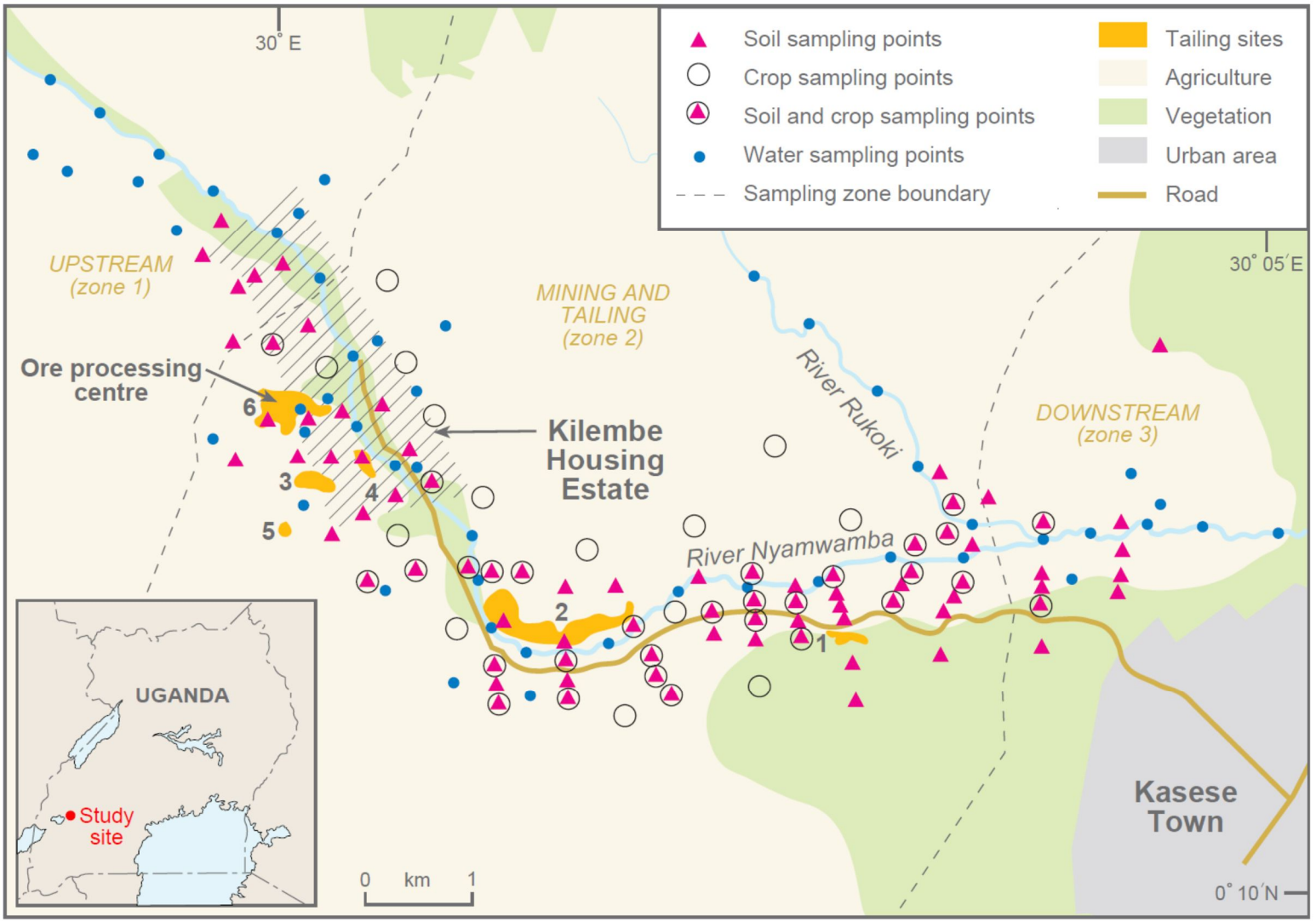

Figure 1: Sketch map of the survey area around the Kilembe mine site in W. Uganda showing sampling locations for soil (red triangle), crop (black circles) and water (blue circle) samples around, and on, the Rivers Nyamwamba and Rukoki. The town of Kasese (population c. 102 k) is shown in the south-east corner of the area.

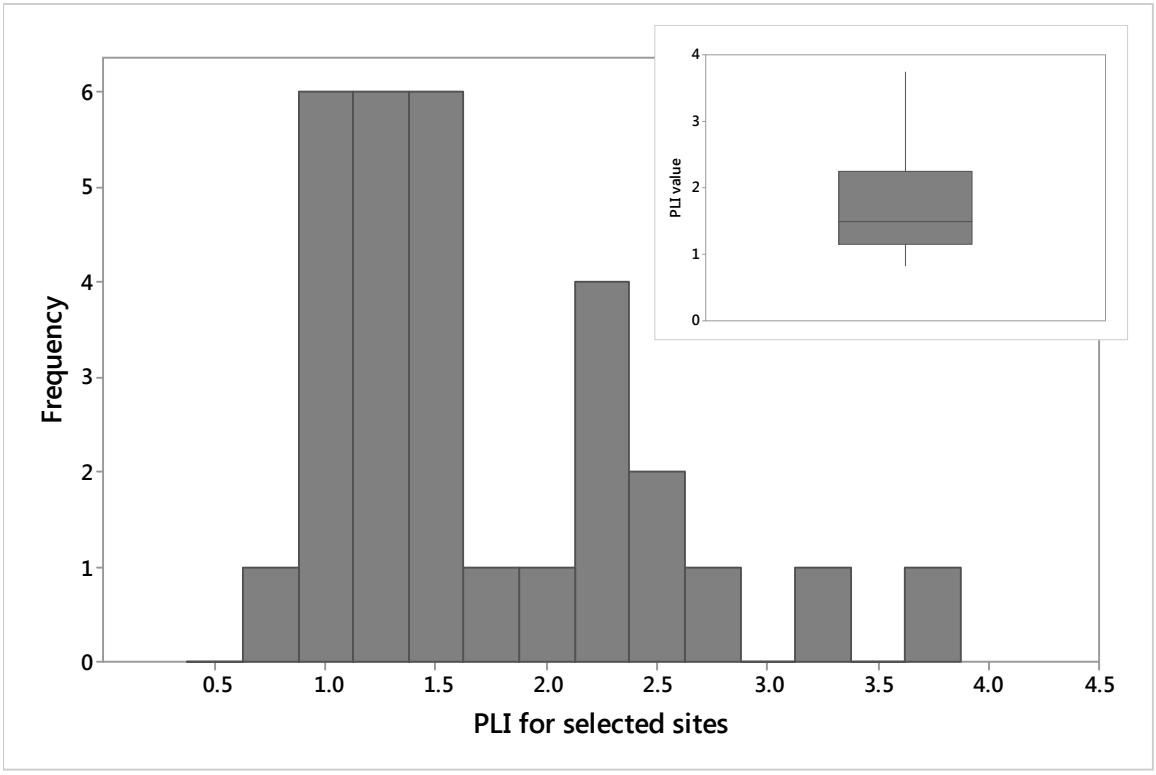

Figure 2: Frequency distribution of Pollution Load Index (PLI) values for agricultural soils; values > 1 indicate contamination relative to background metal concentrations in local soils of the Kilembe area, W. Uganda.

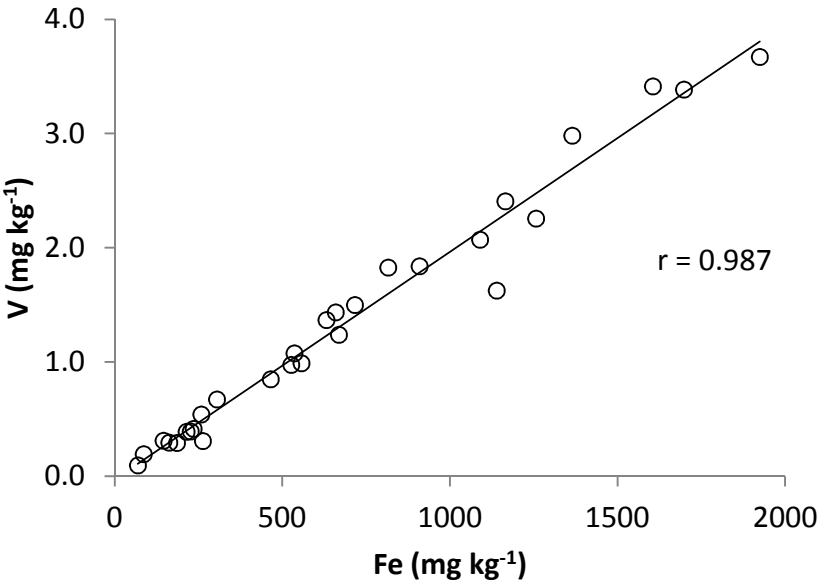

Figure 3: Correlation between iron (Fe) and vanadium (V) concentrations in toenail samples from volunteers in the Kilembe area, W. Uganda.