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## Journal of Geochemical Exploration

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# The geochemical signature of rare-metal pegmatites in the Central Africa Region: Soils, plants, water and stream sediments in the Gatumba tin–tantalum mining district, Rwanda

Rolf Nieder <sup>a,\*</sup>, Tobias K.D. Weber <sup>a</sup>, Inga Paulmann <sup>b</sup>, Andrew Muwanga <sup>c</sup>, Michael Owor <sup>c</sup>, Francois-X Narambuye <sup>d</sup>, Francis Gakwerere <sup>e</sup>, Michael Biryabarema <sup>f</sup>, Harald Biester <sup>a</sup>, Walter Pohl <sup>g</sup>

<sup>a</sup> Institute of Geocology, Technische Universität Braunschweig, Langer Kamp 19c, 38106 Braunschweig, Germany

<sup>b</sup> Golder Associates GmbH, Vorbruch 3, 29227 Celle, Germany

<sup>c</sup> Department of Geology and Petroleum Studies, Makerere University, PO Box 7062, Kampala, Uganda

<sup>d</sup> Faculty of Agronomy, National University of Rwanda, PO Box 117, Butare, Rwanda

<sup>e</sup> Kigali Institute of Education, PO Box 5039, Kigali, Rwanda

<sup>f</sup> Rwanda Geology and Mines Authority, Kigali, Rwanda

<sup>g</sup> Austrian Academy of Sciences, Vienna, Austria

## ARTICLE INFO

## Article history:

Received 11 July 2013

Accepted 28 January 2014

Available online xxx

## Keywords:

Coltan mining

Rare-metal pegmatites

Toxic elements

Mining impacts on the environment

Geochemical signature

## ABSTRACT

We studied trace elements in soils, plants, water and stream sediments in the Gisuma–Kibilira catchment of the Gatumba area of western Rwanda which has a long tradition of artisanal to small-scale tin–tantalum mining from rare-metal pegmatites. The geochemical fingerprint of soil, plant, water (springs and surface water in dry and rainy seasons) and stream sediment samples reveals elevated concentrations of Li, Rb, Cr, and Cs, but low As and U abundances at or below the global average. Trace element contents of soils and most plant materials are below internationally accepted guideline values. All water samples analyzed meet the World Health Organization (WHO) drinking water guidelines, and the stream sediments are below critical values of Dutch environmental standards. These data provide a baseline for environmental impact studies for rare-metal mining projects in the Central Africa Region.

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## 1. Introduction

There are numerous sources of trace elements in soils, plants, stream sediments and waters. Trace elements in naturally occurring soils accumulate during the weathering of rocks and ores that compose geologic parent materials. Background concentrations of trace elements in soils are thus determined by the concentrations in the underlying parent materials. Most trace elements in soils exhibit strong adsorption by clays. However, under certain conditions, small portions become soluble. Among the factors that determine trace element solubility and bioavailability are pH, cation exchange capacity (CEC), anion exchange capacity (AEC), soil organic matter (SOM) content, clay content and quality, oxide content and type, and redox potential (Adriano, 1986; Gregor, 2004). Humans cause accumulation of trace elements in soils from different sources. They have been added to soils from atmospheric deposition, by land application of (in)organic fertilizers and pesticides, and are

common in industrial goods, as components of paints, as a constituent of industrial waste or by mining activities.

Toxic elements in soils, with residence times of up to thousands of years, pose numerous health hazards to higher organisms. They are known to affect plant growth and have a negative impact on soil microflora (Castaldi et al., 2004; Giller et al., 1998; Lasat, 2002; McGrath et al., 2001). In view of the health risks posed by metals entering the food chain, the elements Ag, Cr, Sn and Ti may pose little risk because owing to their low solubility in soil, uptake and translocation by plants may be negligible (McLaughlin et al., 1999). Elevated concentrations of these elements in foods usually indicate direct contamination by soil or dust. The elements As, Hg and Pb are strongly sorbed by soil colloids. While they may be absorbed by plant roots, they are not readily translocated to aboveground plant tissues and therefore pose risks to human health only when root vegetables are grown on contaminated sites. In contrast, elements such as Cd, Cu, Mn, Ni and Zn are readily taken up by plants (McLaughlin et al., 1999).

A significant relationship exists between the presence of toxic elements and the incidence of serious human diseases (Lottermoser, 2007; Magbagbeola and Oyeleke, 2003). Toxic elements are known to be persistent in the human body, with excretion half-lives that last for decades and can lead to a wide range of toxic effects (Järup et al., 2000; Putila and Guo, 2011; Thomas et al., 2009; Tong et al., 2000).

\* Corresponding author. Tel.: +49 531 3915917; fax: +49 531 3915637.

E-mail addresses: [r.nieder@tu-bs.de](mailto:r.nieder@tu-bs.de) (R. Nieder), [to.weber@tu-bs.de](mailto:to.weber@tu-bs.de) (T.K.D. Weber), [ingapaulmann@gmx.de](mailto:ingapaulmann@gmx.de) (I. Paulmann), [amuwanga@sci.mak.ac.ug](mailto:amuwanga@sci.mak.ac.ug) (A. Muwanga), [mowor@sci.mak.ac.ug](mailto:mowor@sci.mak.ac.ug) (M. Owor), [fnarambuye@nur.ac.rw](mailto:fnarambuye@nur.ac.rw) (F.-X. Narambuye), [gakfira@yahoo.fr](mailto:gakfira@yahoo.fr) (F. Gakwerere), [mbiryabarema@yahoo.com](mailto:mbiryabarema@yahoo.com) (M. Biryabarema), [h.biester@tu-bs.de](mailto:h.biester@tu-bs.de) (H. Biester), [walter13pohl@gmx.net](mailto:walter13pohl@gmx.net) (W. Pohl).

Mining of ores has drastically increased the prevalence and occurrence of toxic elements, through mine drainage, discharge of mine or processing waste, tailings dam failures and remobilization from mining-contaminated floodplains (Hongyu et al., 2005; Osher et al., 2006). Toxic elements originating from mining activities have been widely found in various environmental media, including soil, water, air and food products (Nadal et al., 2005). Sites affected through mining waste disposal are considered specific areas that require environmental risk assessment including metal toxicity monitoring, especially for land reclamation and recultivation for agriculture.

The Great Lakes region of Central Africa hosts one of the major tantalum–tin ore provinces of the world (Pohl, 1994). Rwanda has hundreds of mostly small-sized deposits of tantalum, tin, tungsten, and gold (Pohl et al., 2013). The minerals are mainly extracted via artisanal (small-scale) mining. Tin occurs as cassiterite [ $\text{SnO}_2$ ] and tantalum as tantalite [(Fe,Mn)(Ta > Nb) $_2\text{O}_6$ ], commonly referred to as coltan. The tin–tantalum mineralization is related to granite pegmatites (e.g. Varlamoff, 1954, 1972) of the rare-metal lithium–cesium–tantalum (LCT) class (Cerny and Ercit, 2005).

We studied the environmental impact of coltan mining in the Gatumba area of western Rwanda which has a history of about 80 years of artisanal and semi-industrial tin–tantalum mining. Specifically, we tested soils, spring and stream waters, stream sediments and vegetation for a number of environmentally relevant elements (including As, U, base metals) from the Gisuma–Kibilira catchment within the Gatumba mining district. As the local population in the Gatumba mining district lives directly on what is cultivated on farmland in and adjacent to coltan mines and consumes untreated water from springs, the aims of this study were to systematically investigate the trace element status of i) soils (total amounts in different soil units and horizons) under

direct, indirect, and no mining influence, ii) plants (vegetable, fruit, animal feed and wild plants) currently growing on the respective sites, and iii) spring water, stream water and stream sediments from sampling sites homogeneously distributed over the study area. As western Rwanda has dry and rainy seasons, we also tested whether the seasonality had an influence on the trace element status of soils, plants, water and stream sediments. The results are important to clarify if there is any toxic element enrichment in this mining area, and may also provide a baseline for environmental impact studies for other coltan mining areas in Central Africa.

## 2. Material and methods

### 2.1. Study area and sampling sites

The Gisuma–Kibilira catchment has an area of approximately 20 km<sup>2</sup> (Fig. 1). It is located in the Muhororo Sector of the Ngororero District (western part of the Central Plateau of Rwanda, ca. 50 km west of Kigali), between the longitudes 29°37' and 29°40' E and the latitudes 1°53' and 1°56' S. The altitudes range from 1600 to 2100 m AMSL and the annual mean temperature is about 19 °C (Verdoordt and van Ranst, 2003). The Ruhanga tin–tantalum mine is located in the upper part of the catchment where water is transported via a network of small artificial canals for the typical mining method of the region, i.e. ground sluicing. The Gisuma joins the Kibilira in the middle of the catchment after approximately 3 km (Fig. 1). Gisuma and Kibilira are relatively small streams with no more than 2 m and 4 m, respectively, in width, and, except after heavy rain falls, not deeper than 30 cm. To the west of Gatumba, mountains rise to the Congo–Nile watershed divide at around 3000 m altitude. The study area is part of an east-dipping flank of a

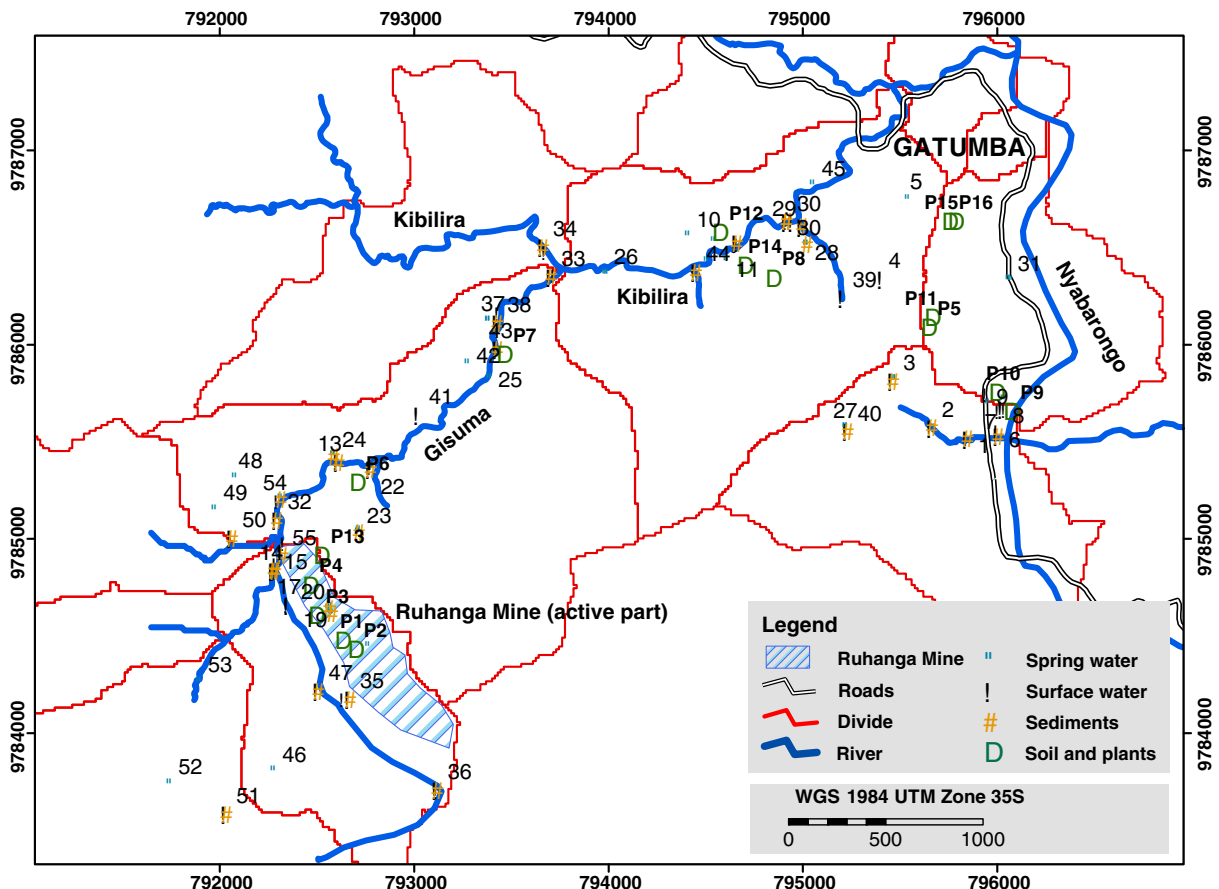


Fig. 1. Soil, plant, water and stream sediment sampling sites in the Gisuma–Kibilira catchment of the Gatumba Mining District, Rwanda.

narrow synclinorium between two large granitic batholiths of the northern Kibara orogen (Gérards, 1965). The geology is dominated by Mesoproterozoic phyllites and quartzites of low- to medium-grade metamorphism. The rocks are primarily schists and sandstone of a clastic, marine sedimentary sequence intruded by mafic dykes and sills (meta-gabbro), and by granites (Dewaele et al., 2010). Pegmatites and hydrothermal quartz veins are associated with the granites. The pegmatites mainly consist of alkali feldspar, muscovite and quartz. Miners extract only weathered, commonly kaolinitic parts of the pegmatites. The water courses in the Gatumba mining district are small to medium-sized creeks that drain into the major Nyabarongo River. Alluvial deposits of the valleys are between 1 and 6 m thick. Farming takes place in most parts of the catchment, including the mine-waste covered areas of the Ruhanga mine. Mining and/or processing activities have released waste material into rivers and surrounding agricultural land (mainly alluvial soils), thus potentially affecting human health and the quality of plant and animal products. Moreover, waters carry a large load of suspended particles (kaolinite, mica) from mining activities and from farming that disturbs natural soils. Entrained iron hydroxide phases give the streams a red-brown color. While coarse materials are deposited next to the mining sites, the finer fractions are transported over long distances.

## 2.2. Soil, plant, water and sediment sampling

### 2.2.1. Soil sampling and sample preparation

The Reference Soil Groups (according to WRB; IUSS Working Group, 2007) selected are representative for the investigated area and we categorized them into directly mining-affected soils (Technosols on mining materials (commonly pegmatite)), soils indirectly influenced by mining (Fluvisols in alluvial sediments located underneath mining areas) and reference soils (Cambisols, Nitisols, Lixisols, Umbrisols), i.e. soils that were not affected by mining (Fig. 1).

In August 2010 (dry season), soils were classified after preparing deep and broad profiles (from soil surface to parent material). Sixteen soil profiles, commonly adjacent to farmers' fields or fallow plots, were sampled by horizon at three different positions along the profile (minimum horizontal distance between positions: 0.5 m) using a shovel. At least three more sampling points, homogeneously distributed on the adjacent field plot, were sampled using a 1 m corer (3 cm inner diameter). From each location almost the same amount of soil was sampled from one horizon. Soil material from one horizon was combined to a mixed sample. The samples were air-dried in Rwanda at a temperature of about 25 °C, subsequently sieved to <2 mm, the fraction which was used for analyses. Prior to analyses in Braunschweig (Institute of Geocology) the soil material was pestled and ground with a pulverizer of zirconium oxide and thoroughly homogenized. In March 2011 (rainy season), 9 of the 16 sites with expected toxic element accumulations through the influence of mining (sites 1–4, 6–10), were sampled again (soil and plant samples). Trace elements from soils were extracted by microwave assisted aqua regia digestion. Before analyses the eluates were diluted with highly purified water.

### 2.2.2. Plant sampling and sample preparation

Simultaneously to the soil sampling campaigns, plant samples, separated into plant parts (roots of root vegetables, leaves of leafy vegetables, fruits, whole plants of animal feed and wild plants) were taken during the dry (August 2010) and the rainy (March 2011) seasons from the plots adjacent to the sampled profiles (at least from five locations). The plant material of one plot was combined to a mixed sample, air-dried at 25 °C and subsequently oven-dried at 40 °C. The plant material (plant parts or whole plants) was coarsely cut and ground. The samples were subsequently pulverized with a tungsten carbide swing mill and thoroughly homogenized. For chemical element analysis, digestion was carried out on 0.2 g finely homogenized plant material with super pure nitric acid (Rotipuran® Supra, 69%) (5 ml) and a

subsequent microwave heated extraction procedure. The extracts were diluted with bi-distilled water and remaining solid matter separated by centrifugation. The analyses were carried out on the extracts.

### 2.2.3. Water and stream sediment sampling and sample preparation

Water samples were taken at locations given in Fig. 1 according to standard procedures (DIN EN ISO 5667-1, 2007; DIN EN ISO 5667-15, 2010; DIN EN ISO 5667-3, 2011; Selent, 1998). The samples were taken in 50 ml polyethylene flasks, stored cool and dark in transportable cooling boxes and subsequently refrigerated. Spring water samples were taken from the flowing source. Surface water samples were taken from the middle of the stream at medium depth. The samples were filtered using cellulose acetate filters < 0.2 µm. Subsequently samples were acidified with ultrapure nitric acid. In all water samples temperature, pH, Eh, EC (electrical conductivity) and DO (dissolved oxygen) were measured in situ with portable devices.

Stream sediments were sampled in proximity to the stream water sample sites. At each site >2 kg of sediment was collected from a minimum of 3 locations within a radius of 10 m. The collected material (>200 g) was homogenized and stored in sterile polyethylene bags during transport. In the laboratory, the water content was reduced at a temperature of 35 °C. Subsequently, the sediment was separated into a fraction of <63 µm which was analyzed. Trace elements from the sediments were extracted analogously to the procedure described for soils.

## 2.3. Analyses

### 2.3.1. Basic properties of soils, waters and sediments

Soil acidity (pH) was analyzed in deionized water and in 0.01 M CaCl<sub>2</sub> using a pH electrode. The electrical conductivity of the suspensions was measured by using a conductivity electrode. The cation exchange capacity was determined by using the BaCl<sub>2</sub> extraction method (basic cations) and subsequent measurement with atomic absorption spectrometry. For the determination of Al, the NaOH titration procedure was applied. Soil texture was determined using the sedimentation method according to Moschrefi (1983). Total C and N in soil samples were determined by dry combustion with an elemental analyzer Carlo Erba NA 1500 at 1020 °C. Anions in water samples were determined using ion chromatography.

### 2.3.2. Trace elements

Total contents of the trace elements As, Bi, Cd, Cr, Cs, Cu, Li, Ni, Pb, Rb, Sb, Zn, and U in soils, sediments, plants and waters were analyzed by inductively coupled plasma mass spectroscopy (ICP-MS) (Agilent 7700), except for Li, Cr, Cu, As, and Pb in the sediment samples which were analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES) (Varian 715-ES) which was also used for the major cation detection. The ICP-MS returned averages of three measurements for each sample, which yielded only small standard deviations throughout all measurements. Reference materials were used to follow up on precision and accuracy.

Reference solutions (river water standard (certified reference material Ontario-99, lot 1109 – lake water samples)) and a Fluka standard solution (Sigma-Aldrich) were measured to follow up on accuracy and precision of the ICP-MS and ICP-OES measurements. The recovery rates resulted in an <5% error for Li, Ni, Zn, Rb, Cd, Pb, and Cs, an error of <10% for Cr, Cu, and U, and an overestimation of As by 25%. All measurements showed a residual standard deviation (RSD) of <0.05, except for As and Cs with 0.25 and 0.23, respectively. Recovery rates for plant material standards (apple leaves) ranged between 95.2% and 99.3% for Cu, Pb and Rb. They were smaller for Cd (63.8%), U (72.8%) and Zn (75.7%). Standard apple leaf values for other trace elements were not given. Reference material for the quality of the aqua regia extractions for a Chinese reference soil (WQB-3, lot 001) showed errors in recovery rates in the range <5% for Cd, Cu, Ni, and Zn, <12% for As and Rb, <20% for underestimated U concentrations, and <30% for Li, Cs, and Cr.

Measurements were carried out with an RSD of <0.06, except for Li (0.19), As (0.15), U (0.16), Rb (0.38), and Cs (0.32). The percentage recoveries of our study are in a normal range and are similar to those found in other studies (e.g. Mganga et al., 2011).

### 2.3.3. Statistics

Statistically significant differences of trace element concentrations and physico-chemical properties in waters and sediments between the two seasons were determined using a Wilcoxon Rank Sum (WRS: Mann and Whitney, 1947). Ranks, as supposed to values, were compared after a Shapiro–Wilk-test. Descriptive statistics (mean, standard deviation, maximum and minimum, and interquartile ranges) and statistical tests were carried out with R-2.12.0 (R Development Core Team, 2010).

## 3. Results

### 3.1. Basic soil properties

Results of the major soil properties are given in Table 1. Due to limited age, on the Spolic Technosol of site 4, an A horizon up to present could not develop. Technosols exhibiting shallow A horizons (Ahi of soils P1 and P3; Ap of P2) represent only weak soil development. In contrast, the shallow Ahi horizons of P11, P13 and P14 reflect the strong influence of erosion on soil formation. The Fluvisols of the study area were commonly deeply developed (P6 to P10) and some were covered by either fresh colluvial (MAp of P7 and P8) or alluvial (MAh of P9 and P10) material.

Most of the sampled soils, independent of their parent material and management, were strongly acidic (soils 1 to 14), with pH values

**Table 1**  
Characteristics of soil profiles directly (1 to 5: Technosols on mining material), indirectly (6 to 10: Fluvisols on mining-contaminated alluvial material) and not (11 to 16) influenced by mining.

Soil profile (site) Nr. with WRB soil unit (IUSS Working Group, 2007)/soil parent material	Soil horizon/ depth (cm)	pH (CaCl <sub>2</sub> )	Corg <sup>a</sup> (%)	TN <sup>b</sup> (%)	C/N <sup>c</sup>	CEC <sup>d</sup> (cmol kg <sup>-1</sup> soil)	Texture		
							Clay (%)	Silt (%)	Sand (%)
P1 Spolic Technosol/pegmatite dump material	Ahi (0–2)	nd <sup>e</sup>	nd <sup>e</sup>	nd <sup>e</sup>	nd <sup>e</sup>	nd <sup>e</sup>	nd <sup>e</sup>	nd <sup>e</sup>	nd <sup>e</sup>
	C (2–50)	3.8	0.1	0.01	9.6	1.6	17	29	54
P2 Spolic Technosol/pegmatite dump-soil mixture	Ap (0–5)	3.9	0.2	0.01	13.9	1.8	7	28	65
	C (5–53)	4.1	0.2	0.02	11.5	2.5	8	36	56
P3 Spolic-gleyic Technosol/pegmatite dump material	Ahi (0–2)	nd <sup>e</sup>	nd <sup>e</sup>	nd <sup>e</sup>	nd <sup>e</sup>	nd <sup>e</sup>	nd <sup>e</sup>	nd <sup>e</sup>	nd <sup>e</sup>
	C (2–80)	4.0	0.2	0.02	10.8	2.2	16	30	54
	Bg (80–120)	4.6	0.1	0.02	9.7	1.7	12	28	60
	Cr (>120)	4.0	0.3	0.02	16.3	2.4	14	42	44
P4 Spolic Technosol/pegmatite dump material	C (0–>200)	4.2	0.1	0.01	9.9	2.5	4	32	64
P5 Spolic Technosol/dolerite dump material	Ah (0–4)	3.2	1.9	0.08	24.0	8.5	13	41	46
	C (>4)	3.6	0.2	0.02	12.6	10.9	30	44	26
P6 Cambic Fluvisol/alluvial sediment (Gisuma–Kibilira)	Ap (0–13)	4.0	0.7	0.07	10.2	2.7	15	20	65
	Bw (13–45)	4.2	0.6	0.06	10.4	2.9	9	22	69
	BgBw (45–110)	4.2	0.1	0.01	10.4	1.0	12	16	82
	Bg (110–240)	4.3	0.1	0.01	11.0	1.0	15	5	80
P7 Dystric Fluvisol/alluvial sediment (Gisuma–Kibilira)	MAp (0–28)	4.5	0.3	0.03	9.3	1.8	4	12	94
	BwBg (28–60)	4.4	0.2	0.02	12.4	1.4	4	9	87
	Bg (60–79)	4.1	0.2	0.02	13.2	1.3	12	32	56
P8 Cambic Fluvisol/alluvial sediment (Gisuma–Kibilira)	MAp (0–55)	4.0	0.3	0.03	11.3	1.7	5	14	81
	Bw (55–83)	4.2	0.2	0.03	10.0	1.7	11	14	75
	BgBw (83–103)	4.9	0.3	0.03	9.3	2.2	8	18	74
	Bg (>103)	4.1	0.2	0.02	7.6	2.4	17	11	72
P9 Cambic-gleyic Fluvisol/alluvial sediment (Nyabarongo)	MAh (0–6)	4.7	1.2	0.08	14.5	3.8	15	61	24
	Bw (6–66)	4.3	0.5	0.04	11.5	2.4	8	26	66
	BwBg (66–90)	4.4	0.5	0.04	11.1	2.0	7	32	61
	Cr (>90)	4.5	0.7	0.06	10.7	2.5	10	48	42
P10 Cambic-gleyic Fluvisol/alluvial sediment (Nyabarongo)	MAh (0–12)	4.6	1.3	0.11	12.0	4.9	18	61	21
	BwBg (12–28)	4.3	1.8	0.16	11.3	4.6	32	64	4
	BgCr (28–77)	4.4	1.6	0.15	10.9	5.0	29	66	5
P11 Dystric Cambisol/weathered dolerite	Ahi (0–1)	nd <sup>e</sup>	nd <sup>e</sup>	nd <sup>e</sup>	nd <sup>e</sup>	nd <sup>e</sup>	nd <sup>e</sup>	nd <sup>e</sup>	nd <sup>e</sup>
	Bw (1–35)	4.4	0.3	0.02	13.1	12.6	31	42	27
	Cw (>35)	4.2	0.1	0.01	13.6	18.7	3	50	47
P12 Dystric Cambisol/weathered schist	MAp (0–35)	4.7	1.0	0.08	13.0	2.9	16	23	61
	Ap2 (35–54)	4.3	1.0	0.08	11.8	3.0	20	22	58
P13 Dystric Nitisol/weathered dolerite	Bw (54–100)	4.2	1.0	0.08	11.6	2.9	22	21	57
	Ahi (0–1)	nd <sup>e</sup>	nd <sup>e</sup>	nd <sup>e</sup>	nd <sup>e</sup>	nd <sup>e</sup>	nd <sup>e</sup>	nd <sup>e</sup>	nd <sup>e</sup>
	E (1–50)	3.8	1.3	0.10	12.6	3.5	45	15	40
P14 Haplic Lixisol/weathered schist	Bt (50–175)	3.9	0.5	0.07	7.2	6.4	73	12	15
	Ahi (0–1)	nd <sup>e</sup>	nd <sup>e</sup>	nd <sup>e</sup>	nd <sup>e</sup>	nd <sup>e</sup>	nd <sup>e</sup>	nd <sup>e</sup>	nd <sup>e</sup>
	E (1–50)	3.8	1.1	0.08	13.1	3.3	34	13	53
P15 Umbric Leptosol/weathered dolerite	Bt (50–106)	3.8	0.7	0.06	11.1	3.8	41	13	46
	Ap (0–20)	5.3	0.6	0.06	10.0	11.5	21	33	46
P16 Vertic Umbrisol/weathered dolerite	Ap (0–20)	5.0	1.6	0.15	10.9	13.5	21	41	38
	Ah (20–55)	5.1	0.7	0.08	8.8	16.5	30	41	29

<sup>a</sup> Organic carbon.

<sup>b</sup> Total nitrogen.

<sup>c</sup> C:N ratio.

<sup>d</sup> Cation exchange capacity.

<sup>e</sup> Not determined.

ranging between 3.2 (P5 in Ah horizon) and 4.9 (P8 in BgBw horizon). Only P15 and P16 were less acidic (pH > 5) which might have been mainly due to the still operating H<sup>+</sup> buffer system of the formerly base-rich parent material (dolerite). The generally low pH in soils of the study area can be attributed to the local climatic conditions which are responsible for intensive chemical weathering of soil minerals and leaching of base cations. Even soils under agricultural use (all soils with Ap and MAp horizons) were acidic. This is because liming, which would counteract soil acidification, up to now has not been very common in Rwandan agriculture.

Apart from a few sites with organic carbon contents > 1% in Ah, MAp and MAh horizons (P5, P9, P10, P12 and P16), most soils were very poor in Corg, especially young Technosols developed on pegmatite dump material (sites P1 to P4). Total nitrogen (TN) contents in soils as well were commonly low. Except for soils developed on dolerite (P11, P15 and P16) and dolerite dump material (5), with CEC > 10 cmol kg<sup>-1</sup>, CEC in all of the other soils was very low and did not exceed 10 cmol kg<sup>-1</sup>. The soils developed on dolerite may still exhibit a portion of “high activity clays” (e.g. vermiculite, montmorillonite) contributing to higher CEC (Reetsch et al., 2008). The texture varied greatly among the soils, particularly between the different Fluvisols. It seems that, except for site P7, on average of the Fluvisol profiles (sites P6 to P10) the clay plus silt fractions increased and the portion of sand decreases tentatively with increasing length of the stream flow path (compare

texture data in Table 1 with sampling sites in Fig. 1). However, the CEC did not increase in this order which may be mainly due to differences in the clay mineral composition.

For most agricultural soils in Rwanda, the only sources of organic matter and nutrients are through recycling of relatively small amounts of manure (animal and/or human kind) as well as biological N<sub>2</sub> fixation, commonly via leguminous crops. However, as the amounts of organic matter applied are very limited, there is only a small potential for build-up of soil organic matter (SOM). Moreover, soil erosion, which is strongly enhanced by agricultural activities, has caused serious SOM and soil nutrient depletion (Reetsch et al., 2008).

### 3.2. Trace element contents in soils

The results on trace element contents in soils are categorized according to soils which were directly (Table 2: P1 to P5), indirectly (Table 2: P6 to P10), and not (Table 3) influenced by mining activities. Besides analytical data, internationally accepted guideline values are also given in Tables 2 and 3. Values presented for Bi, Cd and Sb in all the soils examined (Tables 2 and 3) are extremely low, in some cases below instrumental detection.

The Technosols on pegmatite dump material (soils P1 to P4) also show extremely low contents of As, Cu, Ni, Pb, U and Zn, comparable to or even lower than those of the “reference soils” (soils P11 to P16

**Table 2**

Mean trace element contents in soil profiles directly (1 to 5) and indirectly (6 to 10) influenced by mining.

Site	Soil horizon	As	Bi	Cd	Cr	Cs	Cu	Li	Ni	Pb	Rb	Sb	U	Zn
mg kg <sup>-1</sup> soil														
P1	Ahi	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>
	C	2.8	0.2	0.4	40.1	12.6	3.0	20.3	9.5	12.5	49.0	0.1	2.3	16.5
P2	Ap	2.7	0.1	0.1	52.4	25.2	6.2	20.2	15.6	4.9	68.7	<lod <sup>b</sup>	2.5	<lod <sup>b</sup>
	C	2.4	0.1	0.1	55.6	21.2	7.0	16.4	17.9	4.9	72.3	<lod <sup>b</sup>	2.9	3.1
P3	Ahi	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>
	C	3.5	0.1	0.1	47.2	45.9	2.4	45.2	14.9	10.1	149.9	<lod <sup>b</sup>	3.0	8.0
	Bg	2.3	0.1	0.1	53.4	10.7	7.3	12.3	12.2	7.0	43.2	<lod <sup>b</sup>	1.9	<lod <sup>b</sup>
	Cr	4.2	0.2	0.4	81.8	31.2	5.4	35.8	21.3	7.8	107.0	<lod <sup>b</sup>	2.9	3.7
P4	C	1.8	0.1	0.6	66.9	41.1	3.5	336.8	18.8	7.1	419.6	<lod <sup>b</sup>	5.5	15.6
P5	Ah	2.2	0.2	0.3	30.4	27.9	36.3	190.9	25.1	3.2	422.7	<lod <sup>b</sup>	7.0	27.6
	C	2.0	0.1	0.1	45.5	20.4	40.9	113.5	26.2	4.2	232.3	<lod <sup>b</sup>	5.8	26.7
P6	Ap	6.2	0.7	0.1	30.3	5.9	14.4	12.0	11.4	7.1	47.8	<lod <sup>b</sup>	1.9	9.5
	Bw	6.3	0.3	0.1	31.7	6.0	14.2	12.1	11.5	6.8	56.6	<lod <sup>b</sup>	2.1	9.1
	BgBw	3.6	0.4	0.1	20.2	2.4	6.5	5.5	4.9	4.9	19.4	<lod <sup>b</sup>	1.3	<lod <sup>b</sup>
	Bg	5.6	0.2	0.1	30.5	3.4	7.4	9.9	8.5	8.2	27.3	<lod <sup>b</sup>	1.6	<lod <sup>b</sup>
P7	MAp	8.1	0.2	0.2	33.0	7.0	17.8	21.5	14.6	5.3	58.4	<lod <sup>b</sup>	1.4	14.7
	BwBg	9.8	0.3	0.1	33.8	5.2	20.0	10.3	15.8	5.6	39.3	<lod <sup>b</sup>	1.3	13.6
	Bg	5.7	0.3	0.2	26.0	6.7	8.3	18.3	11.9	9.6	52.0	<lod <sup>b</sup>	1.8	1.5
P8	MAp	6.5	0.5	0.1	40.4	5.4	25.0	6.4	12.5	6.4	40.	<lod <sup>b</sup>	1.4	7.0
	Bw	7.0	0.5	0.1	39.8	5.2	29.9	6.7	14.2	5.9	644.8	0.1	1.6	11.1
	BgBw	6.1	0.7	0.1	41.8	6.7	24.5	8.3	15.1	6.2	60.0	<lod <sup>b</sup>	1.4	10.2
	Bg	6.3	0.6	0.1	39.1	9.2	26.8	10.0	16.2	6.4	54.2	<lod <sup>b</sup>	1.6	11.7
P9	MAh	9.2	0.6	0.2	45.7	4.8	25.3	11.1	18.2	12.0	60.3	0.1	2.4	25.7
	Bw	6.2	0.3	0.1	32.1	4.0	15.7	13.2	12.6	7.6	42.9	0.1	1.6	25.5
	BwBg	7.2	0.4	0.1	36.2	4.4	17.7	11.2	14.1	9.2	49.6	<lod <sup>b</sup>	2.0	15.6
	Cr	9.0	0.7	0.1	44.0	5.2	22.7	12.7	17.8	12.3	60.0	<lod <sup>b</sup>	2.3	29.8
P10	MAh	9.0	0.7	0.2	49.4	5.4	26.7	13.1	21.0	13.6	73.1	0.1	2.6	30.9
	BwBg	12.4	0.9	0.2	66.0	5.7	34.7	12.2	26.2	20.9	81.2	0.1	3.2	39.8
	BgCr	8.3	0.4	0.2	64.7	5.4	31.5	15.6	23.6	18.8	73.0	<lod <sup>b</sup>	2.7	54.0
	Mean (M)Ah/(M)Ap horizons (±SD)	6.3	0.4	0.2	40.2	11.7	21.7	39.3	16.9	7.5	110.2	0.03	2.74	16.5
	Mean subsoil horizons (±SD)	(2.9)	(0.3)	(0.1)	(9.2)	(10.2)	(9.8)	(67.0)	(4.9)	(3.9)	(138.2)	(0.005)	(1.94)	(11.8)
	Range all horizons	5.6	0.4	0.2	44.8	12.6	16.5	36.3	15.7	8.8	86.7	0.02	2.4	15.6
	Guideline values BBodschV <sup>d</sup>	(2.9)	(0.2)	(0.1)	(15.7)	(12.8)	(11.8)	(74.7)	(5.6)	(4.4)	(91.8)	(0.04)	(1.2)	(14.1)
	Dutch target values <sup>e</sup>	1.8–	0.1–	0.1–	20.2–	2.4–	2.4–	5.5–	4.9–	3.2–	19.4–	<lod <sup>b</sup> –	<lod <sup>b</sup> –	<lod <sup>b</sup> –
		12.4	0.9	0.6	66.9	41.1	40.9	336.8	26.2	20.9	422.7	0.1	7.0	54.0
	Guideline values BBodschV <sup>d</sup>	25	ni <sup>c</sup>	10	200	ni <sup>c</sup>	ni <sup>c</sup>	ni <sup>c</sup>	70	200	ni <sup>c</sup>	ni <sup>c</sup>	ni <sup>c</sup>	ni <sup>c</sup>
	Dutch target values <sup>e</sup>	29	ni <sup>c</sup>	0.8	100	ni <sup>c</sup>	36	ni <sup>c</sup>	35	85	ni <sup>c</sup>	3	ni <sup>c</sup>	140

<sup>a</sup> Not determined.

<sup>b</sup> Limit of determination.

<sup>c</sup> Not indicated.

<sup>d</sup> Bundesbodenschutz- und Altlastenverordnung (BBodschV) (German soil protection ordinance) (1999).

<sup>e</sup> According to Dutch Ministry of Housing (DMH, 2000).

**Table 3**  
Mean trace element contents in soil profiles not influenced by mining (11 to 16).

Site	Soil horizon	As	Bi	Cd	Cr	Cs	Cu	Li	Ni	Pb	Rb	Sb	U	Zn
mg kg <sup>-1</sup> soil														
P11	Ahi	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>
	Bw	1.6	0.2	0.2	36.5	22.3	55.4	63.4	31.5	4.1	152.5	0.1	2.9	33.7
	Cw	0.9	0.1	0.1	27.9	18.3	44.4	53.4	52.2	1.8	126.6	<lod	2.0	41.5
P12	MAp	1.3	0.1	0.1	16.4	0.9	7.1	2.1	9.6	5.2	50.5	0.1	0.7	6.2
	Ap2	1.6	0.1	0.1	28.3	1.1	8.4	2.2	11.0	6.8	51.0	<lod	0.7	5.1
	Bw	1.7	0.1	0.1	32.5	1.2	9.0	2.6	11.8	7.2	60.1	0.1	1.0	6.4
P13	Ahi	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>
	E	3.7	0.3	0.3	94.2	7.5	38.1	12.7	20.9	13.0	53.0	0.1	1.9	16.3
	Bt	2.4	0.1	0.1	121.1	7.7	49.0	11.1	30.6	11.4	25.6	<lod <sup>b</sup>	1.5	24.4
P14	Ahi	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>	nd <sup>a</sup>
	E	2.4	0.1	0.1	43.3	1.6	8.0	1.8	9.7	9.3	71.0	0.1	1.2	5.1
	Bt	2.8	0.1	0.1	49.5	2.1	11.3	2.8	12.3	9.4	85.5	0.1	1.3	9.6
P15	Ap	0.9	0.2	0.3	83.4	19.4	47.5	52.1	48.0	2.6	134.9	<lod <sup>b</sup>	0.7	11.0
P16	Ap	1.1	0.2	0.2	84.2	17.8	44.8	85.4	52.2	4.8	146.0	<lod <sup>b</sup>	0.6	21.8
	Ah	1.1	0.2	0.2	107.2	20.5	46.5	80.0	56.7	4.6	140.8	<lod <sup>b</sup>	0.7	19.9
	Mean (M)/Ah/ (M)Ap horizons (±SD)	1.1 (0.2)	0.2 (0.01)	0.2 (0.1)	72.8 (39.2)	14.7 (9.2)	36.5 (19.6)	54.9 (38.1)	41.6 (21.6)	4.3 (1.2)	118.1 (45.3)	0.03 (0.01)	0.68 (0.05)	14.7 (7.4)
	Mean subsoil horizons (±SD)	2.1 (0.9)	0.1 (0.07)	0.1 (0.07)	54.2 (34.6)	7.7 (8.3)	28.0 (20.7)	18.8 (24.9)	12.3 (14.9)	7.9 (3.7)	78.2 (42.2)	0.06 (0.05)	1.6 (0.7)	17.8 (14.0)
	Range all horizons	0.9–3.7	0.1–0.3	0.1–0.3	16.4–121.1	1.1–20.5	7.1–55.4	1.8–85.4	9.6–56.7	1.8–13.0	25.6–152.5	<lod <sup>b</sup> –0.1	0.6–2.9	5.1–41.5
	Guideline values BBodschV <sup>c</sup>	25	ni	10	200	ni	ni	ni	70	200	ni	ni	ni	ni
	Dutch target values <sup>d</sup>	29	ni	0.8	100	ni	36	ni	35	85	ni	3	ni	140

<sup>a</sup> Not determined.<sup>b</sup> Limit of determination.<sup>c</sup> Bundesbodenschutz- und Altlastenverordnung (BBodschV) (German soil protection ordinance) (1999).<sup>d</sup> According to Dutch Ministry of Housing (DMH, 2000).

in Table 3). However, compared to the Technosols on pegmatite, the Technosol on dolerite (soil P5 in Table 2) is higher in Cu, Ni and Zn. On the other hand, the Technosols, compared to all other soils, are higher in Cs and some of them (soils P4 and P5) show increased contents of Rb. Concerning the Fluvisols (soils P6 to P10) it seems that the contents of As, Cr, Cu, Ni, Pb, Rb and Zn increase in the same direction as the silt plus clay contents in the alluvial sediments increase with increasing transport distance downwards the stream.

It is obvious that the trace element content variations are commonly greater between different soils than within one soil profile. Concerning the Technosols, except for Li and Rb, the contents of all other elements show relatively low variation of the single trace elements between soil horizons (see sites P2 and P3). The same applies to the variation of single trace elements between the different horizons of Fluvisols (sites P6 to P10). The trace element contents in Fluvisol topsoils (Ap, MAp and MAh horizons) are similar to those of subsoil horizons and the differences between subsoil horizons in one and the same Fluvisol are small.

Although the mining-influenced soils (Table 2), compared to the “reference soils” (Table 3), have slightly higher mean contents of As, Pb and U (A and subsoil horizons), the concentrations are still quite low. In contrast, “reference soils” compared to mining-affected soils show higher mean values of Cu (A and subsoil horizons) and Ni (A horizons). “Reference soils” exhibit similar values for Zn compared to mining-influenced soils (means of A and subsoil horizons in Tables 2 and 3). Soils developed on dolerite (soils P13, P15 and P16), compared to all other soils, show the highest contents of Cr. However, guideline values were not exceeded in any soil for any toxic element.

The comparison of element contents in the upper horizons of nine soil profiles during the dry and rainy seasons shows very similar median values data variance for As, Bi, Cd, Ni, Pb, Sb and U (Fig. 2). The values for Cr vary more in the rainy season but the median is lower compared to the dry season. Cesium shows similar median values for both seasons but slightly more variance for the dry season. Copper exhibits similar variance in both seasons but a slightly higher median in the dry season. Similar to Zn, the Li median is slightly lower in the dry season. The Rb

median of the dry season exceeds that of the rainy season. However, in none of the cases the difference between dry and rainy seasons is significant.

The medians of trace element contents in subsoil horizons hardly show any difference in the dry and rainy seasons (Fig. 3). Except for the elements Cr, Li and Rb, that exhibit high data variances, the variances are similar for all other trace elements.

### 3.3. Trace element contents in plants

The results on trace element contents in plants were grouped according to their use, i.e. as leaf and root vegetables (Table 4), and as animal feed, fruit and wild plants (Table 5). Some of the plant species are also used as medicinal plants (Table 4) or green manure (Table 5). The site numbers in Tables 4 and 5 correspond to those given in Tables 1 to 3. The trace element contents correspond to the parts of plants which are commonly being consumed, i.e. leaves or roots in case of leaf or root vegetables (Table 4), fruits in case of fruit plants and whole plants in case of animal feed and wild plants (Table 5). Values of As, Cd and U, independent on the sampling site, in all plant materials

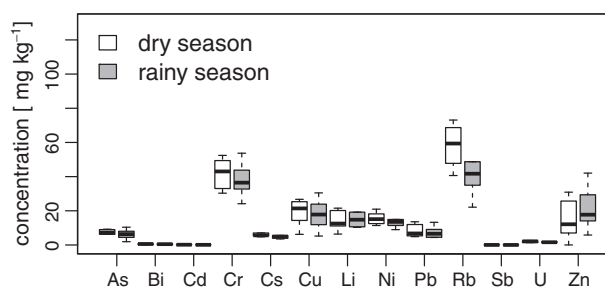
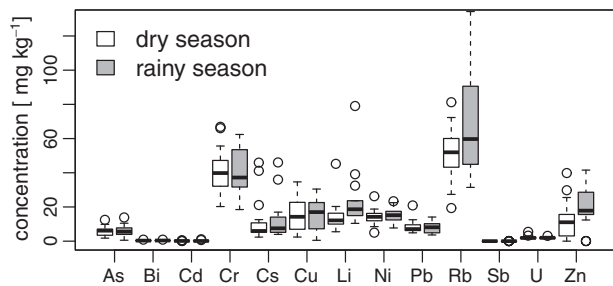


Fig. 2. Comparison of trace element contents in upper horizons of nine soil profiles (1, 2, 3, 4, 6, 7, 8, 9 and 10; medians, minima and maxima) of the dry (August 2010) and rainy (March 2011) seasons.



**Fig. 3.** Comparison of trace element contents in subsoil horizons of nine soil profiles (1, 2, 3, 4, 6, 7, 8, 9 and 10; medians, minima and maxima) of the dry (August 2010) and rainy (March 2011) season.

are extremely low, in some cases below detection limit (Tables 4 and 5). In contrast, values of Rb are relatively high in most plant species. Except for Pb on sampling site P8 (Table 5) and Zn on sampling sites P1 and P6 (Table 4), P8 and P10 (Table 5), guideline values for toxic elements recommended by German Health Authority, EU or FAO/WHO were not exceeded.

Fig. 4 compares median, minimum and maximum trace element contents in plants sampled from nine sites during the dry and rainy seasons (see also Figs. 2 and 3). Median values as well as the data variation of As, Cd, Cs and U are very similar in the dry and rainy seasons. Median values of Cu, Li and Pb are also quite similar in the dry and rainy seasons, but a higher data variation can be observed. Only in the case of Rb and Zn it seems that the concentrations are lower in the rainy season compared to the dry season. However, the data variation is very high (Fig. 4) and the differences between dry and rainy seasons are not significant.

### 3.4. Trace element contents in waters and stream sediments

For evaluation purposes, the water and sediment data are presented as different subsets according to season (dry and wet) and according to sample type (spring water, surface water and stream sediments). The seasons were then statistically compared. For several trace elements and physicochemical properties a WRS test exhibited a statistically significant ( $p < 0.05$ ) decrease in mean values from dry to rainy season.

The groundwater samples show a significantly higher concentration in the dry compared to the wet season for the elements Cr, Cu, Zn, Cd, and Pb. In the surface waters Cr, Ni, Zn, Cd, and Pb also show this

trend (Table 6). Near neutral conditions and fully oxidized waters did not promote high element concentrations. Low electric conductivity during the rainy season coincided with reduced loads of dissolved salts and trace element cations. A concise list of data is presented in Tables S1 and S2 (to be added as Supplementary material).

Table 7 summarizes the surface water analyses. Analogous to the groundwater samples, they show near neutral conditions and fully oxidized waters which do not promote high element concentrations. The seasonal dilution pattern is similar to that of the groundwater. In comparison to global means Li, Cs, and Rb are considerably elevated. Means of Ni are close to global means and all other elements are lower than global abundance levels. A full list of stream water analysis results is presented in Tables S3 and S4 (to be added as Supplementary material).

In comparison to global background values in the upper continental crust, the sediments show distinct features (Table 8). Li, Rb, Cs, Cd, and U are found to be enriched. Means of Cr seem to be below and those of As slightly above global means. All other elements are below global abundance values. Cesium, Rb, and U are possibly underestimated by ~20% due to low recovery rates. However, high values of As can be attributed to analytical overestimation. None of the samples revealed accumulation of trace elements above the Holland List (DMH, 2000). A complete list of results of the sediments is presented in Tables S5 and S6 (to be added as Supplementary material).

Fig. 5 shows concentration gradients in stream water (a) and sediments (b) of Li, Rb, and Cs, along the Gisuma river. Site 36 is located 1 km upstream of the Ruhanga mine, site 33 ~2 km downstream, and sites 12 and 29 downstream of the conjunction of Gisuma and Kibilira. The alkali elements are selected as they show an enrichment tendency downstream of the Ruhanga mine and are diluted by the Kibilira joining the river. This could not be shown for any of the other analyzed elements and characteristics. Site 35 is a little downstream of an abandoned part of the Ruhanga mine where farmers let the stream meander through their plots on tailings for irrigation purposes. The stream is in contact with large amounts of tailing material.

## 4. Discussion

### 4.1. Soils

In the sampled soils, trace element concentrations are low compared to guideline values (Tables 2 and 3). However, in some soils there are

**Table 4**  
Mean trace element contents in leaf and root vegetables of different sites.

Site	Plant species	Main use/additional use	As	Cd	Cs	Cu	Li	Pb	Rb	U	Zn
			mg kg <sup>-1</sup> plant								
P1	Centella asiatica	Leaf vegetable/medicinal use	0.2	0.3	4.2	9.9	2.6	1.0	142.9	0.1	80.3
P2	Ipomoea batatas	Root vegetable	<lod <sup>a</sup>	<lod <sup>a</sup>	11.3	10.4	3.9	0.4	174.8	<lod <sup>a</sup>	23.7
P3	Vernonia amygdalina	Leaf vegetable/medicinal use	0.1	<lod <sup>a</sup>	4.8	18.9	12.0	0.7	148.5	0.1	29.2
P6	Manihot esculenta	Root vegetable	<lod <sup>a</sup>	<lod <sup>a</sup>	0.4	6.8	0.8	0.5	38.8	<lod <sup>a</sup>	114.5
P7	Commelina benghalensis	Leaf vegetable/medicinal use	0.1	0.1	0.2	10.1	1.8	0.3	18.9	<lod <sup>a</sup>	51.8
P7	Colocasia esculenta	Root vegetable/medicinal use	<lod <sup>a</sup>	0.2	0.2	6.8	0.8	1.0	54.1	<lod <sup>a</sup>	24.3
P11	Polyscias fulva	Leaf vegetable/medicinal use	0.1	0.1	0.1	5.7	0.1	0.3	15.6	<lod <sup>a</sup>	46.3
P12	Leonotus nepetifolia	Leaf vegetable/medicinal use	<lod <sup>a</sup>	<lod <sup>a</sup>	0.1	19.3	<lod <sup>a</sup>	0.3	54.9	<lod <sup>a</sup>	31.9
Range leaf vegetable			<lod <sup>a</sup> -0.2	<lod <sup>a</sup> -0.3	0.1-4.8	5.7-19.3	<lod <sup>a</sup> -12.0	0.3-0.7	15.6-142.9	0-0.1	29.2-80.3
Range root vegetable			<lod <sup>a</sup>	0-0.2	0.2-11.3	6.8-10.4	0.8-3.9	0.4-1.0	38.8-174.8	<lod <sup>a</sup>	24.3-114.5
ZEBS (1990) guideline values for leaf (and root) vegetables <sup>c</sup>			ni <sup>b</sup>	0.4	ni <sup>b</sup>	ni <sup>b</sup>	ni <sup>b</sup>	3.0	ni <sup>b</sup>	ni <sup>b</sup>	ni <sup>b</sup>
EC 1881/2006 (2006) guideline values for leaf (and root) vegetables <sup>d</sup>			ni <sup>b</sup>	0.7	ni <sup>b</sup>	ni <sup>b</sup>	ni <sup>b</sup>	1.1	ni <sup>b</sup>	ni <sup>b</sup>	ni <sup>b</sup>
FAO/WHO guideline values for metals in food and vegetable <sup>e</sup>			ni <sup>b</sup>	1.0	ni <sup>b</sup>	30	ni <sup>b</sup>	2.0	ni <sup>b</sup>	ni <sup>b</sup>	60

<sup>a</sup> Limit of determination.

<sup>b</sup> Not indicated.

<sup>c</sup> Zentrale Erfassungs- und Bewertungsstelle für Umweltchemikalien (ZEBS) (Central Registration and Evaluation Office for Environmental Chemicals of the German Health Authority) (1990).

<sup>d</sup> European Commission (EC) 1881/2006 (2006).

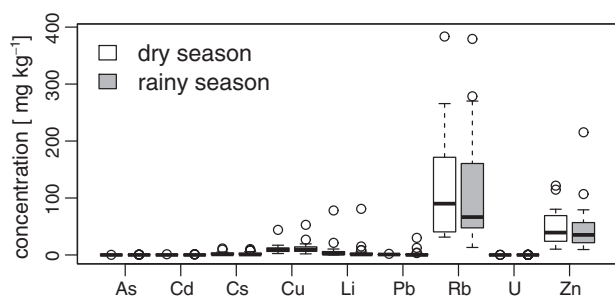
<sup>e</sup> FAO/WHO (1976).

**Table 5**  
Mean trace element contents in fruit, animal feed and wild plant species of different sites.

Site	Plant species	Main use/additional use	mg kg <sup>-1</sup> plant dry matter								
			As	Cd	Cs	Cu	Li	Pb	Rb	U	Zn
P1	<i>Digitaria abyssinica</i>	Animal feed	0.1	<lod <sup>a</sup>	1.2	8.3	2.3	1.2	38.9	<lod <sup>a</sup>	20.8
P1	<i>Hoslundia opposita</i>	Fruit	0.1	<lod <sup>a</sup>	26.7	29.7	2.8	0.2	412.5	<lod <sup>a</sup>	86.6
P2	<i>Indigofera arrecta</i>	Animal feed/green manure	0.2	<lod <sup>a</sup>	1.0	10.1	0.4	0.5	39.1	<lod <sup>a</sup>	28.2
P3	<i>Crotolaria recta</i>	Animal feed/green manure	<lod <sup>a</sup>	0.2	5.2	10.2	21.2	0.3	265.8	<lod <sup>a</sup>	36.3
P4	<i>Sesbania sesban</i>	Animal feed/green manure	0.1	<lod <sup>a</sup>	9.2	5.1	78.3	0.5	383.3	<lod <sup>a</sup>	49.5
P8	<i>Tithonia diversifolia</i>	Wild plant/green manure	<lod <sup>a</sup>	0.5	0.1	10.7	0.8	3.3	39.8	<lod <sup>a</sup>	154.1
P9	<i>Pennisetum purpureum</i>	Animal feed	<lod <sup>a</sup>	0.1	0.3	5.5	0.1	0.9	118.4	<lod <sup>a</sup>	22.4
P10	<i>Polygonum pulchrum</i>	Wild plant	0.2	0.2	0.4	8.6	0.6	1.9	106.3	<lod <sup>a</sup>	42.3
P10	<i>Ludwigia abyssinica</i>	Wild plant	0.1	<lod <sup>a</sup>	0.3	17.1	0.8	1.0	70.3	<lod <sup>a</sup>	64.5
P10	<i>Cyperus papyrus</i>	Wild plant	<lod <sup>a</sup>	<lod <sup>a</sup>	0.3	2.5	0.3	0.7	34.5	<lod <sup>a</sup>	10.2
P12	<i>Mangifera indica</i>	Fruit	<lod <sup>a</sup>	<lod <sup>a</sup>	0.1	11.8	0.3	0.3	71.0	<lod <sup>a</sup>	54.0
P13	<i>Rubus rigidus</i>	Fruit	0.1	<lod <sup>a</sup>	0.7	7.8	2.8	0.3	47.5	<lod <sup>a</sup>	25.7
P14	<i>Psidium guajava</i>	Fruit	<lod <sup>a</sup>	<lod <sup>a</sup>	0.1	2.5	0.2	0.3	7.4	<lod <sup>a</sup>	18.7
P14	<i>Eragrostis exasperata</i>	Fruit	<lod <sup>a</sup>	<lod <sup>a</sup>	0.1	2.6	0.2	0.3	7.5	<lod <sup>a</sup>	25.7
Range animal feed			<lod <sup>a</sup> –0.2	0–0.2	1.0–9.2	5.1–10.2	0.4–78.3	0.3–1.2	38.9–383.3	<lod <sup>a</sup> –0.1	20.8–49.5
Range fruit			<lod <sup>a</sup> –0.1	<lod <sup>a</sup>	0.1–26.7	2.5–29.7	0.2–2.8	0.2–0.3	7.4–412.5	<lod <sup>a</sup>	18.7–86.8
Range wild plant			<lod <sup>a</sup> –0.1	0–0.5	0.1–0.3	2.5–10.7	0.3–0.8	0.7–1.9	34.5–106.3	<lod <sup>a</sup>	10.2–64.5
ZEBS (1990) guideline values for fruits <sup>c</sup>			ni	0.2	ni <sup>b</sup>	ni <sup>b</sup>	ni <sup>b</sup>	1.8	ni <sup>b</sup>	ni <sup>b</sup>	ni <sup>b</sup>
EC 1881/2006 (2006) guideline values for fruits (and animal feed) <sup>d</sup>			(2.0)	(1.0)	ni <sup>b</sup>	ni <sup>b</sup>	ni <sup>b</sup>	0.4	ni <sup>b</sup>	ni <sup>b</sup>	ni <sup>b</sup>
FAO/WHO guideline values for metals in food and vegetable <sup>e</sup>			ni <sup>b</sup>	1.0	ni <sup>b</sup>	30	ni <sup>b</sup>	2.0	ni <sup>b</sup>	ni <sup>b</sup>	60

<sup>a</sup> Limit of determination.<sup>b</sup> Not indicated.<sup>c</sup> Zentrale Erfassungs- und Bewertungsstelle für Umweltchemikalien (ZEBS) (Central Registration and Evaluation Office for Environmental Chemicals of the German Health Authority) (1990).<sup>d</sup> European Commission (EC) 1881/2006 (2006).<sup>e</sup> FAO/WHO (1976).

variations within soil profiles. For example, compared to other soils, Li and Rb show higher variation in the Technosols (Table 2). In most Technosols there are higher Li (sites P2, P3 and P5) and Rb (sites P3 and P5) contents in surface horizons compared to subsoil horizons. These differences may be probably due to heterogeneities in the distribution of Li and Rb in the deposited pegmatite dump material. Because of the limited age of the Technosols weathering of the parent material and displacement of metals might not have occurred to a significant extent up to now. On the other hand, pedogenic processes might have contributed to displacement of several trace elements in soils not influenced by mining, i.e. soils with a longer phase of development (Table 3). For example, Cu, Ni and Zn show higher concentrations in subsoil horizons compared to surface soil horizons (Cu: sites P12, P13, P14; P16; Ni: sites P11, P12, P13, P14, P16; Zn: sites P11, P13, P14). The latter elements might have been released due to weathering of the parent material, subsequently displaced downwards within the soil profiles under acidic conditions and finally fixed in deeper soil horizons. The fate of trace elements in soils (e.g. mobilization, displacement and fixation) is generally regulated by the interactions between different physical (e.g. water flux) and biogeochemical processes such as solution and formation of secondary minerals including sesquioxides (Cox et al., 1995; Malpas et al., 2001).

**Fig. 4.** Comparison of trace element contents in plants of nine sites (1, 2, 3, 4, 6, 7, 8, 9 and 10) of the dry (August 2010) and rainy (March 2011) seasons.

For the Fluvisols (soils P6 to P10), a distinct spatial distribution pattern of trace elements was found. Except for the elements which have generally low (Cs) or very low (Bi, Cd, Sb) concentrations, there is a tendency of increasing concentrations for all other trace elements in the Fluvisol profiles with increasing distance from the river head, in analogy to the increase of the fine particle size fractions (Table 1). This may be because trace elements besides organic matter mainly accumulate in fine particles of soils (clay and silt) due to their large surface areas and negative charge (Acosta et al., 2011a,b).

As arsenopyrite is a mineral known to occur in tin deposits, arsenic contents were expected to be high in the mining-influenced soils of the GKC, particularly in Technosols. However, in our study the highest As concentrations occur in the Fluvisols where it may be associated with fine particles and/or bound to SOM (Reimann et al., 2009). However, all the values measured are below the internationally accepted guideline values and within the average range in soils of 1–40 mg As kg<sup>-1</sup> (Visioli and Marmiroli, 2013). Our mean values of 6.3 ± 2.9 mg As kg<sup>-1</sup> in (M)Ah and (M)Ap horizons and 5.6 ± 2.9 mg As kg<sup>-1</sup> in corresponding subsoil horizons (Table 2) are similar to median As concentrations found in a study by Tarvainen et al. (2013) of ca. 2200 soil samples covering western Europe each from arable soils (0–20 cm Ap: 5.7 mg As kg<sup>-1</sup>) and grazing land (0–10 cm Ah: 5.8 mg As kg<sup>-1</sup>).

Cadmium and Pb contents in soils of the GKC were also expected to be high because sulfides and sulfosalts of Cd and Pb may be associated with tantalum pegmatites. Nevertheless, Cd and Pb values are generally below guideline values and in the range of average soil Cd and Pb contents of 0.06 to 1.1 mg kg<sup>-1</sup> (De Vos and Tarvainen, 2006) and 2 to 300 mg kg<sup>-1</sup> (Agyarko et al., 2010), respectively. Sulfates and sulfosalts of zinc as well can be associated with tantalum pegmatites. However, the measured Zn values of the GKC range from below detection limit to 54 mg Zn kg<sup>-1</sup> which is within the normal range in soils of 1 to 900 mg Zn kg<sup>-1</sup> (Agyarko et al., 2010). Although background values for Zn were found to be relatively high (105 mg kg<sup>-1</sup>) in basaltic rocks such as dolerite (De Vos and Tarvainen, 2006), the highest concentrations in our study occur in Fluvisols.

Uranium is associated with tantalum pegmatites and is both radiotoxic and carcinogenic. However, guideline values are neither

**Table 6**

Spring water physico-chemical properties and trace element concentrations for both seasons. Analyzed maximum values compared to the WHO drinking water guideline values (WHO, 2011).

		Dry season (n = 16)			Wet season (n = 21)			WHO guideline
		Mean	(SD)	Range	Mean	(SD)	Range	
pH	[–]	6.17	(0.59)	5.70–7.62	5.80	(0.58)	5.00–7.25	na <sup>e</sup>
T <sup>a</sup>	[°C]	22.23	(1.07)	20.60–25.20	24.63	(1.84)	19.70–25.50	na <sup>e</sup>
Eh <sup>b</sup>	[mV]	348.0	(119.0)	* 165.2–467.10	430.7	(114.3)	* 77.80–606.00	na <sup>e</sup>
EC <sup>c</sup>	[μS cm <sup>-1</sup> ]	268.7	(263.8)	67.00–1045.00	114.3	(160.9)	37.00–778.00	na <sup>e</sup>
Σ <sub>cations</sub>	[meq l <sup>-1</sup> ]	1.08	(1.19)	0.11–4.60	0.86	(1.60)	0.08–7.77	na <sup>e</sup>
Σ <sub>anions</sub>	[meq l <sup>-1</sup> ]	0.52	(0.24)	0.23–1.15	0.42	(0.17)	0.18–0.74	na <sup>e</sup>
Li	[μg l <sup>-1</sup> ]	46.78	(87.10)	* 0.67–357.29	34.24	(63.89)	* 0.88–228.18	na <sup>e</sup>
Cr	[μg l <sup>-1</sup> ]	0.57	(0.28)	0.15–1.09	0.46	(0.63)	<lod <sup>d</sup> –2.54	50
Ni	[μg l <sup>-1</sup> ]	2.73	(1.35)	* 1.03–6.82	2.86	(1.78)	* 0.36–7.19	70
Cu	[μg l <sup>-1</sup> ]	2.56	(2.50)	0.37–8.23	1.33	(1.86)	<lod <sup>d</sup> –8.50	2000
Zn	[μg l <sup>-1</sup> ]	19.28	(13.93)	* <lod–48.13	6.60	(4.50)	* <lod <sup>d</sup> –20.36	3000
As	[μg l <sup>-1</sup> ]	1.06	(0.60)	* 0.37–2.57	0.20	(0.33)	* <lod <sup>d</sup> –1.51	10
Rb	[μg l <sup>-1</sup> ]	9.32	(7.99)	* 1.21–23.99	8.41	(12.38)	* 0.17–57.28	na <sup>e</sup>
Cd	[μg l <sup>-1</sup> ]	0.04	(0.02)	<lod–0.08	0.02	(0.01)	<lod <sup>d</sup> –0.06	3
Cs	[μg l <sup>-1</sup> ]	0.85	(1.29)	* 0.01–5.26	0.70	(1.11)	* <lod <sup>d</sup> –4.32	na <sup>e</sup>
Pb	[μg l <sup>-1</sup> ]	0.15	(0.10)	0.04–0.37	0.06	(0.05)	<lod <sup>d</sup> –0.13	10
U	[μg l <sup>-1</sup> ]	0.14	(0.18)	<lod–0.45	0.05	(0.09)	<lod <sup>d</sup> –0.32	15

Different letters in the same row indicate significant differences ( $p < 0.05$ ) among means.

As extreme outliers, Zn values from site 23/24 in dry season and 24 in wet season not included.

<sup>a</sup> Temperature.

<sup>b</sup> Redox potential.

<sup>c</sup> Electrical conductivity.

<sup>d</sup> Limit of determination.

<sup>e</sup> Not available.

\* Indicate significant differences in concentrations between dry and wet seasons.

given in the German soil protection ordinance nor in the Dutch target list (DMH, 2000). Values in the GKC soils range from 0.6 to 7.0 mg U kg<sup>-1</sup> and are thus within the mean range of soils of 0.79 to 11 ppm (De Vos and Tarvainen, 2006). Soils exhibiting U contents within this range are considered non-hazardous for cultivation (Flügge et al., 2007). Cesium as well is a co-product of tantalum pegmatites and the highest contents can be found in pegmatite mica. The measured Cs values (0.9 to 45.9 mg kg<sup>-1</sup>) apply to the estimated average soil content of 0.3 to 26 mg kg<sup>-1</sup> (De Vos and Tarvainen, 2006). Guidance values are not given for Cs.

Chromium exists in several minerals and mafic rocks. Due to its high binding affinity to fine particle size fractions and oxides, the highest Cr contents were found in soils derived from dolerite (sites 13, 15 and 16). The values, ranging from 16.4 to 121.1 mg kg<sup>-1</sup>, are lower compared to guideline values of the German soil protection ordinance, but on some sites, the Dutch target value for Cr as well as the average soil Cr content of 54 mg kg<sup>-1</sup> (De Vos and Tarvainen, 2006) was exceeded. Even the intervention value of the Dutch list (DHM, 2000) of 380 mg kg<sup>-1</sup> (not given in Tables 2 and 3) is still higher.

**Table 7**

Surface water physico-chemical properties and trace element concentrations for both seasons. Analyzed means compared to global means in pristine rivers.

		Dry season (n = 20)			Wet season (n = 28)			Global mean <sup>f</sup>
		Mean	(SD)	Range	Mean	(SD)	Range	
pH	[–]	7.29	(0.55)	5.65–8.04	7.38	(0.35)	6.83–8.31	na <sup>e</sup>
T <sup>a</sup>	[°C]	22.93	(2.41)	19.50–26.60	24.10	(2.19)	19.60–25.50	na <sup>e</sup>
Eh <sup>b</sup>	[mV]	401.9	(43.97)	* 346.20–469.00	389.4	(69.59)	* 215.7–495.30	na <sup>e</sup>
EC <sup>c</sup>	[μS cm <sup>-1</sup> ]	95.13	(56.40)	31.00–247.00	44.71	(12.70)	28.00–79.00	na <sup>e</sup>
Σ <sub>cations</sub>	[meq l <sup>-1</sup> ]	0.33	(0.26)	0.00–1.01	0.25	(0.15)	0.05–0.65	na <sup>e</sup>
Σ <sub>anions</sub>	[meq l <sup>-1</sup> ]	0.35	(0.11)	0.00–0.64	0.22	(0.07)	<lod <sup>d</sup> –0.40	na <sup>e</sup>
Li	[μg l <sup>-1</sup> ]	29.22	(43.18)	* 2.11–187.50	16.55	(20.29)	* 0.52–74.39	3.2
Cr	[μg l <sup>-1</sup> ]	0.47	(0.44)	0.14–1.73	0.28	(0.45)	<lod <sup>d</sup> –2.47	0.7
Ni	[μg l <sup>-1</sup> ]	1.98	(0.87)	* 1.00–4.12	1.57	(0.91)	* 0.39–4.50	0.8
Cu	[μg l <sup>-1</sup> ]	2.88	(3.02)	* 0.75–15.33	1.78	(1.12)	* 0.14–4.94	1.5
Zn	[μg l <sup>-1</sup> ]	16.08	(12.79)	* 4.05–48.52	10.58	(23.59)	* <lod <sup>d</sup> –128.35	0.6
As	[μg l <sup>-1</sup> ]	1.32	(0.82)	* 0.44–3.53	0.19	(0.09)	* 0.03–0.51	0.6
Rb	[μg l <sup>-1</sup> ]	5.97	(5.08)	* 1.42–23.76	5.51	(3.05)	* 2.59–13.85	1.6
Cd	[μg l <sup>-1</sup> ]	0.04	(0.02)	<lod <sup>d</sup> –0.10	0.02	(0.01)	<lod <sup>d</sup> –0.04	0.1
Cs	[μg l <sup>-1</sup> ]	0.36	(0.40)	* 0.02–1.70	0.25	(0.28)	* 0.01–1.21	0.01
Pb	[μg l <sup>-1</sup> ]	0.20	(0.16)	0.04–0.72	0.07	(0.08)	<lod <sup>d</sup> –0.27	0.1
U	[μg l <sup>-1</sup> ]	0.05	(0.05)	<lod <sup>d</sup> –0.19	0.03	(0.04)	<lod <sup>d</sup> –0.18	0.4

Different letters in the same row indicate significant differences ( $p < 0.05$ ) among means.

As extreme outliers, Zn values from site 1/33 in dry season and 32 in wet season not included.

<sup>a</sup> Temperature.

<sup>b</sup> Redox potential.

<sup>c</sup> Electrical conductivity.

<sup>d</sup> Limit of determination.

<sup>e</sup> Not available.

<sup>f</sup> World average reference (Gaillardet et al., 2003).

\* Indicate significant differences in concentrations between dry and wet seasons.

**Table 8**  
Sediment trace element concentrations for both seasons. Analyzed means compared to global means and maximum values to the Holland List.

	Dry season (n = 22)			Wet season (n = 29)			Global mean <sup>c</sup>	Holland List <sup>d</sup>
	Mean	(SD)	Range	Mean	(SD)	Range		
Li [ $\mu\text{g g}^{-1}$ ]	148.4	(122.2)	<lod <sup>a</sup> –485.87	139.5	(158.3)	13.87–594.32	21	na <sup>b</sup>
Cr [ $\mu\text{g g}^{-1}$ ]	73.14	(30.16)	21.80–142.57	74.08	(32.07)	14.74–157.35	92	180
Ni [ $\mu\text{g g}^{-1}$ ]	28.06	(7.97)	16.63–46.99	30.65	(13.79)	8.12–68.88	47	100
Cu [ $\mu\text{g g}^{-1}$ ]	29.85	(15.71)	<lod <sup>a</sup> –71.57	34.20	(21.96)	<lod <sup>a</sup> –95.39	28	190
Zn [ $\mu\text{g g}^{-1}$ ]	55.65	(24.94)	22.93–138.72	53.73	(19.72)	23.13–110.51	67	720
As [ $\mu\text{g g}^{-1}$ ]	17.48	(4.60)	<lod <sup>a</sup> –28.12	16.44	(6.60)	<lod <sup>a</sup> –33.58	4.8	76
Rb [ $\mu\text{g g}^{-1}$ ]	120.4	(73.30)	29.47–387.53	92.93	(62.55)	15.71–266.84	84	na <sup>b</sup>
Cd [ $\mu\text{g g}^{-1}$ ]	0.70	(0.52)	0.12–2.24	0.68	(0.46)	0.06–1.49	0.1	13
Cs [ $\mu\text{g g}^{-1}$ ]	15.63	(14.35)	2.41–69.39	10.34	(8.75)	1.28–32.90	4.9	na <sup>b</sup>
Pb [ $\mu\text{g g}^{-1}$ ]	28.96	(37.28)	7.67–179.29	15.64	(6.08)	5.96–32.51	17	530
U [ $\mu\text{g g}^{-1}$ ]	5.05	(1.67)	2.66–9.63	4.78	(2.66)	1.31–12.17	2.7	na <sup>b</sup>

Different letters in the same row indicate significant differences ( $p < 0.05$ ) among means.

<sup>a</sup> Limit of determination.

<sup>b</sup> Not available.

<sup>c</sup> World average upper crust (Rudnick and Gao, 2003 and cited references).

<sup>d</sup> According to Dutch Ministry of Housing (DMH) (2000).

Lithium is a common element in tantalum pegmatites and may reach exploitable concentrations (e.g. in spodumene). Contents of Li are elevated in some soils, ranging from 2 to 337 ppm, with the highest values in a Technosol, reflecting the high Li content of the pegmatite. There are no guideline values given for Li, however, the Li contents of some Technosols (sites P3, P4 and P5) exceed average contents of soils that range between 1.3 and 56 mg kg<sup>-1</sup> (De Vos and Tarvainen, 2006).

Rubidium is of minor toxicity and is known to have no negative impact on the environment. Accordingly, there are no guideline values given for Rb. Relatively high values of Rb (range: 19.4 to

422.7 mg kg<sup>-1</sup>) were found in the Technosols of the GKC. However, this range is close to average values in soils that vary between 2 and 390 mg Rb kg<sup>-1</sup> (De Vos and Tarvainen, 2006). Similar to Li, values of Rb in our study reflect the geogenic accumulation in the parent pegmatite (sites 1 to 5).

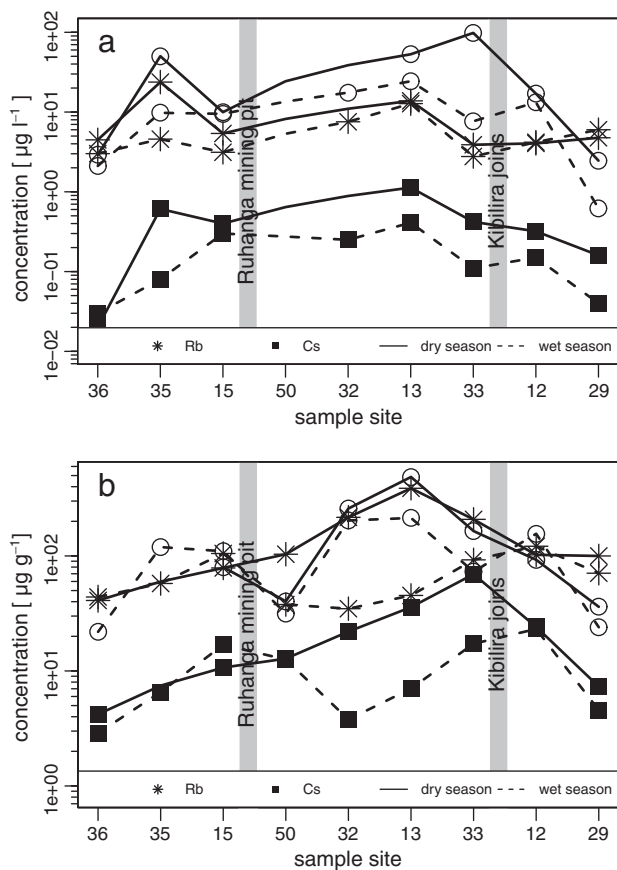
4.2. Plants

In the current study, a large spectrum of plant species was found on the different farmers' field plots or fallow plots, respectively (Tables 4 and 5). With some exceptions (e.g. Rb and Zn), the levels of most trace elements were limited in both soils (Tables 2 and 3) and plant tissues (Tables 4 and 5), to a large extent being below detection limits. Thus, it was not possible to classify plants on the basis of their relations to trace element contents in soils, e.g. to develop soil to plant transfer factors. Moreover, almost all the sites were grown with different species and transfer factors are known to depend on species (Edeogu et al., 2007). In addition, in most of the published studies (including the present one) total amounts of trace elements in soils were analyzed, while only the plant-available fractions are prone for plant uptake.

In contrast to other vegetable crops, *Ipomoea* spp. are known to have the ability to tolerate trace element-rich environments such as contaminated landfills (Agamuthu et al., 2007). In the current study, *Ipomoea batatas* roots only exhibited elevated values of Rb (175 mg Rb kg<sup>-1</sup>; Table 4). However, as Rb is only moderately toxic and guideline values for Rb are not common, these concentrations may be of minor importance. Among the vegetable crops examined, the highest values for Zn (115 mg Zn kg<sup>-1</sup>) were found in *Manihot esculenta* roots (cassava tuber), followed by *Centella asiatica* leaves (80 mg Zn kg<sup>-1</sup>). Of the plants examined, only Zn exceeds the FAO/WHO guideline values. It is well-known that compared to other trace elements cassava tuber hyperaccumulates Zn (Bouka et al., 2012).

Relatively high values of Rb were also found for other plants (Tables 4 and 5), especially for the fruit plant *Hoslundia opposita* (412.5 mg Rb kg<sup>-1</sup>) and the animal feed plants *Sesbania sesban* (383 mg Zn kg<sup>-1</sup>) and *Crotalaria recta* (266 mg Rb kg<sup>-1</sup>; Table 5). Rubidium (Rb<sup>+</sup>) in soils strongly interacts with K<sup>+</sup>. Plant-available K<sup>+</sup>, however, is a limiting factor in soils of the GMD (Reetsch et al., 2008). It is known that both pH and K<sup>+</sup> supply of soils is inversely related to plant uptake of Rb<sup>+</sup> and relatively more Rb<sup>+</sup> compared to K<sup>+</sup> which is becoming more plant-available at further increase in soil acidity (Grobner and Tyler, 1998).

Although *Cyperus* spp. have been identified as Cd hyperaccumulators (Mganga et al., 2011), Cd was not found in *Cyperus papyrus* (Table 5). This may be mainly because the corresponding soil Cd contents were very low (Table 2). In contrast, *Tithonia diversifolia*, commonly known as



**Fig. 5.** Concentration profiles of a) surface waters and b) sediments along a 3 km stretch starting top stream of the active Ruhanga mine until downstream where the Gisuma flows into the Kibilira river.

“Mexican sunflower”, demonstrated a strong accumulative potential for Pb and Zn. While the soil contents of Pb and Zn were below mean values of the GKC (Table 2, site P8), Pb and Zn contents in *T. diversifolia* tissue exceeded FAO/WHO guideline values. Similar results were obtained by Adesodun et al. (2010) who confirmed high heavy metal uptake efficiency for both of the sunflower species *T. diversifolia* and *Helianthus annuus*. This implies that sunflowers are suitable for the phytoremediation of Pb- and Zn-contaminated soils.

The plant contents of trace elements in the GKC were generally low in both the dry as well as the rainy seasons, except for Rb and Zn (Fig. 4). Both elements had higher concentrations in soils (Tables 2 and 3) and also showed a tendency of having higher plant contents during the dry compared to the rainy season. Evaporation of water from soil and dehydration of plants by transpiration may have decreased biomass production and thus increased trace element concentration in plant tissue (Oyedele et al., 2008). However, the differences of Rb and Zn concentrations found in the two seasons were not significant.

In summary, except for Pb and Zn in some species, trace element values for most plant samples and sites do not exceed guideline values and correspond to normal ranges in plants which were indicated for Cd ( $<2.4 \text{ mg kg}^{-1}$ ), Cu ( $<25 \text{ mg kg}^{-1}$ ), Pb ( $0.5\text{--}30 \text{ mg kg}^{-1}$ ) and Zn ( $20\text{--}100 \text{ mg kg}^{-1}$ ) (Opalawu et al., 2012).

#### 4.3. Waters and stream sediments

The classification of toxicity, particularly in the light of arsenic was one of the aims of the present study. The analytical results from two extended sampling campaigns in the GKC provide no basis to expect any health risk to the local population concerning possible trace element exposure (Tables 6 and 7). Comparison of our results for Cr, Cu, Ni, Zn, As, Cd, Pb, and U concentrations in spring waters to WHO guideline values and of stream sediment data to the Holland List (DHM, 2000) reveals that no sample exceeded guideline values. The mining and processing activity consists of gravity separation of ore components and barren material only. No form of chemical/metallurgical processing is applied within the district.

Due to the geologic setting, particular focus was put on As. Water is considered as the dominant human As exposure pathway (Abernathy, 1993). Its ascent to today's attention was significantly and essentially propagated by advancing analytical applications in the 1980s with which it was possible to include As in systematic geochemical mapping campaigns and in monitoring (Plant et al., 2003). Arsenic is strongly chalcophile and can attain percentage-range concentrations in sulfide ore assemblages (Greenwood and Earnshaw, 1997). In a review on the provenance of As in the environment Smedley and Kinniburgh (2002) concluded that sufficient knowledge is available to bring together some of the common features and to speculate about the critical factors that can lead to high-As groundwaters of which none of the situations are pertinent to the GKC. Concerning mining, the only known site involving pegmatite veins and high As values is linked to adit and alluvial mining of Sn and W from pegmatites with a distinct Sn–As–W mineralization (Fordyce et al., 1995; Williams, 2001; Williams et al., 1998). The mentioned case concerns Sn mining in Ron Phibun, Thailand, but the geological setting is considerably different from that in the GMD. In Ron Phibun high-grade arsenopyrite tailings from former bedrock mining are the main source of As contamination. FeAsS is oxidized at lowered water tables and As is released to the water by its subsequent rise (ibid). In a study on regions with high As concentrations derived from natural sources Welch et al. (2000) made no connection to pegmatites and As contaminated groundwaters, either (Welch et al., 2000, and references herein). Nevertheless, exceptionally high concentrations of As up to several  $\text{mg l}^{-1}$  were found in groundwaters in areas with apparently near-average source rocks with As at upper continental crust values in oxidizing and reducing conditions (Smedley and Kinniburgh, 2002).

Arsenic can be mobilized under strongly reducing conditions. These were not found during the time of sampling. The mobilization of As due

to a theoretically reducing environment is not apparent. Typically, the kinds of reducing conditions catalyzing arsenic mobilization were frequently reported from Quaternary alluvial, deltaic sediments where various factors have resulted in complex patterns of sedimentation including the quick burial of large quantities of sediments together with fresh organic matter (Plant et al., 2003). Thick sequences of young sediments are quite often the sites of high groundwater arsenic concentrations (Plant et al., 2003). These conditions usually occur in deltaic regions, where rapid development of thick layers of Quaternary sediments occurred. In relation to this and in terms of river continuum, the GMD is a source and not a region of deposition of suspended material. Due to the geologic setting and mining processes, acidification of water courses or acid mining drainage, well known for its potential to leach toxic concentrations of metals, is of no concern in the GKC. This seems clearly to exclude sufficiently large quantities of pyrite and arsenopyrite (Flügge et al., 2007) and is supported by the pH ranges which span from slightly acidic to neutral in groundwaters (pH 5.3 to 7.6 in the dry season and pH 5.0 to 7.2 in the wet season), a picture which is similar in the surface waters with a slight shift to the alkaline side (pH 5.7 to 8.0 in the dry season and pH 6.8 to 8.3 in the wet season). Arsenic never exceeds the WHO target value of  $10 \mu\text{g l}^{-1}$  and shows a mean of  $\sim 1.0\text{--}1.3 \mu\text{g l}^{-1}$  in the water samples and, values up to  $17 \mu\text{g g}^{-1}$  in stream sediments which, in the light of an analytical overestimation of  $\sim 20\%$ , is normal.

According to a WRS test, some trace elements and physicochemical properties show a significant ( $p < 0.05$ ) decrease in mean values from dry to rainy season in the waters (Tables 6 and 7). No trend was established for any of the elements in the stream sediments. None of the elements shows a significant increase from dry to wet season. This fact was primarily attributed to similar pH conditions during both seasons, strongly oxidized waters, swiftly running streams with depths of  $<20 \text{ cm}$ , continuous supply of eroded material and re-deposition of sediments in rain events due to flash floods. These are typical for runoff patterns when the rainstorms set in and lead to large scale repositioning of the river sediments. The reason why Li, Rb, and Cs do not show this trend is likely to be explained by several factors. These elements are available in large abundances, weather readily, and mining at Ruhanga continuously supplies material of pegmatite origin.

Considering the hydro-geochemical signature of the GKC with the rare-metal LCT pegmatite lenses, the Ruhanga pegmatite reveals itself clearly with a distinct geochemical signature in the aqueous environment. This fact is, per se, not all too surprising as lithology is widely seen as an essential factor in determining river chemistry (Drever, 1988). This is particularly true on the local scale in small catchments where streams reflect their immediate environment (Meybeck, 1986).

The partially high standard deviations with SD sometimes as high as 80% for many of the collected parameters, represent the small scale spatial heterogeneity of the four different very distinct rock types present (pegmatite, shales, sandstone, and dolerite). The dolerites are more easily weathered compared to the quartz-rich metasediments but play a minor role in the hydrogeochemistry. The heterogeneous nature of country rocks inhibits successful application of geostatistics, i.e., cluster analyses and ordination procedures to refine the local extent of the hydrogeochemical pegmatite fingerprint. Nevertheless, some interesting findings can be put forward.

The Li, Rb and Cs concentration profiles of stream water and sediment samples during both seasons show an influence of the pegmatite bodies. We stipulate that the weathered pegmatite leachates positively impact the concentration of stream water. It is probable that eroded material from the open cast mining is transported along the stream and deposited in the sediments leading to a non-local phenomenon of elevated Li, Rb and Cs concentrations in stream sediments as well. An accumulation of these elements occurs in the stream sediments until the Gisuma meets the Kibilira where dilution is expressed by a considerable concentration drop from sample sites 33 to 12. Upstream of the river's junction, the Kibilira drains a catchment with deeply weathered pegmatites,

however, with little ongoing mining. This reflects the strong impact of the Ruhanga pegmatite on Li, Rb and Cs concentration levels in the aquatic environment.

Regardless of season and sample type, some samples showed elevated Zn and Cd values. Zn is often elevated in shales, clayey sands and basalts with concentrations of 80 to 120  $\mu\text{g g}^{-1}$  (Alloway, 1990). Zn and Cd occur in association and are quite mobile elements. However, the mean Zn concentrations of stream sediments and soils are below the upper continental crust average.

In summary, a geochemical influence of the pegmatite within a background of a typical shale–sandstone lithology intruded by mafic sills on the chemistry of the water regime can be observed. In both dry and wet seasons, Cd is elevated in the stream sediments, with dry season concentrations at 0.7 ( $\pm 0.5$ )  $\mu\text{g g}^{-1}$  and wet season concentrations at 0.7 ( $\pm 0.47$ )  $\mu\text{g g}^{-1}$ . The Holland List (DMH, 2000) guideline values are not exceeded but enrichment is at about seven times the global abundance level (Rudnick and Gao, 2003). The laboratory determination of Cd was successful so that analytical problems can be excluded.

## 5. Conclusions

Our chemical data on soils, plants, water bodies and stream sediments in the Gatumba mining district reveal no dangerous toxic element levels. Except for Pb and Zn in some plant species, soils, plants, sediments, and waters are below internationally accepted guideline values or in the range of normal concentrations. An exposure of the local population to toxic elements is most probably not the case. However, the *status quo* of trace elements may be different in other mining areas in Rwanda (Haidula et al., 2011).

Based on two sampling campaigns, we show that the seasonal variation in toxic trace element concentrations (Cr, Ni, Cu, Zn, As, Cd, Pb, U) in waters is largely governed by climate. Significantly smaller concentrations during the rainy season can be attributed to the dilution effect by precipitation. High redox conditions and near neutral pH do not act as drivers for increased mobility of the trace elements.

The alkali elements Li, Rb, and Cs show high concentrations in the surface waters irrespective of the season, an effect which we attribute to the active Ruhanga mine. Water is channeled into the open cast mining area and is in contact with the LCT pegmatite body and continuously releases components from the highly weatherable minerals such as feldspar. Stream sediments do not reveal this pegmatite-specific element pattern, probably due to dilution by the much more abundant pelitic country rocks. None of the elements is found to significantly increase from one season to the other.

The physico-chemical properties of waters are comparable to those of weathered sandstone–shale dominated catchments with low major ion concentrations. With regard to global abundance values for the upper continental crust, Li, Rb, and Cs show strong enrichment in waters and sediments alike, as do U and Cd in the sediments only. All other elements are at or below global abundance values. These data reflect the chemical signature of the rare metal pegmatites.

There is a need to critically assess the toxic element concentration values from a consumer point of view. In our study, we abided by standard procedures, i.e., waters were first filtered and then acidified. With regard to the preparation of samples from drinking water sources, i.e., concrete-lined springs, it might be interesting to analyze unfiltered water samples, with acidity similar to that of the intestinal tract. It is thinkable that through dissolution of metals bound to particulate matter in the acidic intestinal tract human exposure could be higher than reported here.

Besides the question of toxicity and seasonality, it is noteworthy that the sediment load in the water courses derived from active and inactive mining sites within the Gatumba mining district is high, although not quantified. The rate of erosion of fertile natural topsoil material from the steep and scarcely vegetated hills is currently unknown. It is

probably this physical impact which poses the major long-term threat for a sustainable agricultural perspective, which calls for additional research.

## Author contributions

RN AM FG FN and MB designed the site research. RN and HB designed the laboratory research. RN and IP carried out the research on plants and soils. TW AM and MO performed the research on water and sediments. RN and TW wrote the paper with contributions of AM WP FG and HB.

## Acknowledgments

This work has been accomplished in the frame of the project “Sustainable Restitution/Recultivation of Artisanal Tantalum Mining Wasteland in Central Africa (2010–2013)” (short title: “Coltan Environmental Management”). The authors are thankful to the Volkswagen Foundation that funded the project.

We wish to thank Jacintha Nayebare and Alain Ndoli for assistance during the sampling campaigns. Additionally, we express our thankfulness to Hans Peter Dauck who patiently supported the work with all GIS-related matters.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.gexplo.2014.01.025>.

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