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Concentrations of arsenic, copper, cobalt, lead and zinc in cassava (*Manihot esculenta* Crantz) growing on uncontaminated and contaminated soils of the Zambian Copperbelt

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ABSTRACT

The concentrations of arsenic (As), copper (Cu), cobalt (Co), lead (Pb) and zinc (Zn) in washed leaves and washed and peeled tubers of cassava (*Manihot esculenta* Crantz, Euphorbiaceae) growing on uncontaminated and contaminated soils of the Zambian Copperbelt mining district have been analyzed. An enrichment index (*EI*) was used to distinguish between contaminated and uncontaminated areas. This index is based on the average ratio of the actual and median concentration of the given contaminants (As, Co, Cu, mercury (Hg), Pb and Zn) in topsoil. The concentrations of copper in cassava leaves growing on contaminated soils reach as much as 612 mg kg^{-1} Cu (total dry weight [dw]). Concentrations of copper in leaves of cassava growing on uncontaminated soils are much lower (up to 252 mg kg^{-1} Cu dw). The concentrations of Co (up to 78 mg kg^{-1} dw), As (up to 8 mg kg^{-1} dw) and Zn (up to 231 mg kg^{-1} dw) in leaves of cassava growing on contaminated soils are higher compared with uncontaminated areas, while the concentrations of lead do not differ significantly. The concentrations of analyzed chemical elements in the tubers of cassava are much lower than in its leaves with the exception of As.

Even in strongly contaminated areas, the concentrations of copper in the leaves and tubers of cassava do not exceed the daily maximum tolerance limit of 0.5 mg kg^{-1}/human body weight (HBW) established by the Joint FAO/WHO Expert Committee on Food Additives (JECFA). The highest tolerable weekly ingestion of 0.025 mg kg^{-1}/HBW for lead and the highest tolerable weekly ingestion of 0.015 mg kg^{-1}/HBW for arsenic are exceeded predominantly in the vicinity of smelters. Therefore, the preliminary assessment of dietary exposure to metals through the consumption of uncooked cassava leaves and tubers has been identified as a moderate hazard to human health. Nevertheless, as the surfaces of leaves are strongly contaminated by metalliferous dust in the polluted areas, there is still a potential hazard of ingesting dangerous levels of copper, lead and arsenic if dishes are prepared with poorly washed foliage.

1. Introduction

Trace elements and their compounds are important components of the biotic environment and several are essential for the health of plants. Metals such as copper and Zn are essential to plant metabolism. However, elevated concentrations of both essential and non-essential metal/metalloids can result in growth inhibition and toxicity symptoms (Hall, 2002; Yruela, 2009). Metals and metalloids may accumulate to toxic levels in the environment through the natural weathering of surface ore-bodies, as well as human activities such as mining or processing of ores (Harrison and Johnson, 1987; Basta and Gradwohl, 2000; Conder et al., 2001; Kachenko and Singh, 2006).

The mobilization of different trace elements at toxic levels in the environment, especially in mining and metal processing areas, can result in their bioaccumulation at various trophic levels. To monitor the trend and spatial distribution of both natural and anthropogenic sources of trace elements in the environment, it is essential to obtain and maintain a database of the proportion of chemical elements in soils and plants.

Cassava tubers and leaves in Zambia and many other tropical countries are important components of human diet, particularly in rural areas. Moreover, leaves of cassava are commonly

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consumed as a cooked vegetable. Data on the concentrations and dietary loads of elements in tropical root and tuber crops such as, for instance, cassava (*Manihot esculenta*), sweet potatoes (*Ipomoea batatas*) and yams (*Dioscorea spp.*) were published for Nigeria, where these crops are widely cultivated (Chukwuma, 1995a; Nganje et al., 2010; Iyaka, 2007; Ukhum et al., 1990). Enhanced concentrations of heavy metals in West African leaf and tuber crops as a consequence of soil and atmospheric contamination by mining and related activities have also been described. Increased concentrations of cadmium, zinc and lead were detected in the leaves of cassava growing near the Enyigba base metal deposit in Nigeria (Chukwuma, 1995b), in the tubers of cassava in the environs of the Arufu base metal deposit in Nigeria (Nganje et al., 2010) as well as in the tubers of cassava, sweet potato and yam in other districts in the same country (Onyedika and Nwosu, 2008). Concentrations of arsenic in cassava tubers were also investigated in areas where gold is extracted from arsenopyrite bearing ore bodies (the Obuashi region in Ghana; Amondo-Neizer et al., 1996; alluvial gold mine at Dunkwa-on-Offin in Ghana; Golow and Adzei, 2002). Crop plants cultivated in areas affected by metal mining and processing industries were found to contain higher concentrations of metals/metalloids when compared with those grown in uncontaminated areas.

The Zambian Copperbelt region has been heavily impacted by mining and processing of copper and cobalt ores (Kříbek et al., 2007, 2010; Ettler et al., 2011, 2012). The area is also characterized by cultivation of cassava which forms a substantial component of human diet, particularly rural populations.

This paper presents (1) data on the concentrations of metals in cassava tissues from areas of the Zambian Copperbelt contaminated by metal extraction and smelting activities, by comparison to the natural geochemical backgrounds, (2) concentrations of these elements in cassava tissues in relation to soil total concentrations in these locations, and finally (3) a preliminary assessment of whether food prepared from cassava growing in contaminated areas contains concentrations of metals/metalloids in excess of the recommended dietary limits, and thus poses a potential hazard to human health.

A particular focus of the study was to determine the extent of surface contamination of cassava leaves cultivated in the immediate vicinity of smelters in the Copperbelt.

2. The area studied

2.1. General information

The area studied is the Copperbelt region, which lies in northern Zambia (Fig. 1). Within the study area, the city of Kitwe has the largest population of 866,646, followed by Chingola (177,445), and Mufulira (152,664). Other important towns are Chililabombwe (84,866), Kalulushi and Chambishi.

Three climatic seasons are defined: (i) a rainy season, (ii) a cool dry season, and (iii) a hot dry season. The rainy season lasts roughly from the beginning of November until the end of April and is characterized by tropical thunderstorms. The cool dry season lasts from the first half of May until the end of August and is characterized by light winds. Precipitation during this season is negligible. The wind flow field is dominated by strong winds from the south-easterly quadrant from March until October. During January, February, November and December, wind flow is dominated by light north-easterly winds.

According to the FAO-UNESCO (1997) classification freely drained soils of the Copperbelt can be assigned to the ferralsol group (acric, orthic or rhodic ferralsols). Ferralsols in the surveyed area are highly leached and acidic (pH_{KCl}: 3.94–7.15), with variable concentrations of soil organic carbon (<0.2–7.2 wt%), nitrogen (<0.5–1.59 wt%) and cation exchange capacities ranging from 0.09 to 1.26 mmol g^{-1} (Kříbek et al., 2010).

The riparian soils and soils of the dambo-type (poorly drained soils, cambisols according to the FAO-UNESCO (1997) classification that occur locally along the riverbanks were not sampled.

2.2. Mining and ore processing

The Copperbelt sediment-hosted strata-bound and stratiform deposits are characterized by finely disseminated copper-, cobalt- and iron sulfides. The principal minerals are chalcopyrite, cobalt-rich pyrite, bornite and minor carrolite. The host rocks include quartzite (arkose), shale and dolomite. The grades average 3 wt% Cu and 0.18 wt% Co in ore deposits from which both metals are extracted. Trace amounts of gold (Au), platinum (Pt) and silver (Ag) are recovered from the copper slimes during the refining process (Kamona and Nyambe, 2002).

In 2008, the annual production of copper in the whole of the Copperbelt mining district amounted to ca. 569,891 metric tons and that of cobalt was ca. 5275 metric tons. Significant volumes of selenium (17 t) and silver (8 t) together with minor gold and platinum group elements were also produced in 2008 (BMI, 2009). Ores are processed by flotation at Kitwe (the Nkana ore treatment plant), Chingola, Chililabombwe, Chambishi, Chibuluma and Mufulira ore treatment plants, and for a long time were smelted and refined at the Mufulira, Kitwe and Chingola smelters. The Kitwe Smelter was decommissioned in 2008 and a new smelter was commissioned in Chingola in the same year. The Chambishi Smelter re-processes old slag from the Kitwe (Nkana) Smelter, which is rich in copper and cobalt.

3. Materials and methods

3.1. Sampling

Cassava was selected for this study because of its ubiquitous distribution; it constitutes staple foods in rural parts of the Zambian Copperbelt. Whereas other types of vegetables, for example, cabbage or giant rape, are cultivated in the environs of large cities and on large farms in the Copperbelt region, cassava is grown in many places, particularly in small villages in the rural area. Samples of cassava were collected on June and July, during the cool and dry seasons in the years 2005–2009. The upper 0–10 cm of rhizosphere soil was sampled at the same time as plant collection. Altogether 54 samples of cassava leaves, 50 samples of cassava tubers and 54 soil samples were collected. All data are presented in supplements electronically available with this publication.

The sampling sites for the soil and vegetation were selected so as to cover both contaminated and uncontaminated areas. Because of the very variable lithological and geochemical character of the bedrock and soils in the Zambian Copperbelt, it is very difficult to distinguish contaminated from uncontaminated areas. Since the uppermost part of the soil horizon (topsoil) is mostly affected by metalliferous dust fallout, an enrichment index (*EI*; Kříbek et al., 2010) was used to distinguish between contaminated and uncontaminated areas. This index is based on the average ratio of the actual and median concentration of the given contaminants (As, Co, Cu, Hg, Pb and Zn) in topsoil:

$$EI = \frac{\left(\frac{As}{m_{As}} + \frac{Co}{m_{Co}} + \frac{Cu}{m_{Cu}} + \frac{Hg}{m_{Hg}} + \frac{Pb}{m_{Pb}} + \frac{Zn}{m_{Zn}}\right)}{6}$$

The enrichment index actually shows a higher-than-median or lower-than-median average concentration of the six elements and to a large extent it also reflects the enrichment of topsoil from