Metals and arsenic in cassava: Indicators of contamination in the Zambian Copperbelt mining district

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GEOLOGICAL MAP OF ZAMBIA

Surveyed area

Geological sketch map of Zambian Copperbelt and the scope of the environmental-geochemical survey

Total area: 4700 km²

- 760 composite samples of surface soil
- 264 samples of subsurface soils
- 270 samples of stream sediments
- 120 samples of surface waters
- 60 special samples (slag, tailings, ochres)
SOURCES OF ANTHROPOGENIC CONTAMINATION OF SOILS AND PLANTS:

- Gaseous and solid emissions from smelters
- Dust from dry superficial parts of tailing ponds
- Dust from ore treatment plants and slag deposits
- Transport of concentrates and products
Airborne dust particles from smelters

Dust particles contain:
As, Be, Co, Cr, Cu, Hg, Mo, Se, V, a Zn

Fine-grained airborne particles from the Nkana Smelter
Magnification: 2000x

Slag particles Magn. 800x

Magnetite-rich glass particles

Cu-Fe-S intermediate solid solution particle (ISSN)

Slag particles, Nkana crushers Magnification 600x

the Nkana Smelter
SOURCES OF ANTHROPOGENIC CONTAMINATION

Airborne particles from dry beaches of tailing impoundments contain up to:
- 22 ppm As
- 3,090 ppm Co
- 9,350 ppm Cu
- 0.02 ppm Hg
- 88 ppm Mo
- 124 ppm Ni
- 95 ppm Pb
- 21 ppm Se
- 74 ppm Zn

Sandstorm over the Mindolo Impoundment

Sandstorm over a dry beach of the Mindolo Impoundment
METALS AND ARSENIC IN CROP PLANTS

The objectives of this study were:

(1) To assess contents of As, Cu, Co and Pb in crop plants (cassava, sweet potato, maize) in uncontaminated and contaminated areas

(2) To evaluate the plant-to-soil response

(3) To assess whether food prepared from crop plants grown in contaminated areas endangers the health of the local population

(4) To evaluate superficial contamination of leaves caused by dust fallout in the neighbourhood of smelters
Sampled plant/plant parts

Cassava/leaves, tubers \( (n = 55/49) \)
Sweet potato/leaves, tuber \( (n = 17/18) \)
Maize/grains \( (n = 32) \)
The pseudo-total digests of soil samples were obtained by a standardized *aqua regia* extraction procedure (ISO 11466).

Bioavailable metals in soils:
- 0.01M solution of CaCl$_2$
- 0.1 M solution of ammonium fluoride and complexone III (Mehlich III)
- 0.025 M solution of Na$_2$EDTA
- 0.001M solution of DTPA

Approximately 1-g aliquots of the plant parts were burned down in a muffle oven. Temperature program: from 25 °C to 550 °C.

The Co, Cu, Fe, Pb and Zn were determined in ash leachate using Flame Atomic Absorption Spectroscopy (FAAS), arsenic was determined using Hydride-Generation Atomic Absorption Spectrometry (HGAAS).
Distribution of metals and arsenic in plant parts (uncontaminated area, background data)

Leaf stalk:
As 0.43
Co <0.5
Cu 7.7
Pb 2
Zn 76

Stem:
As 0.27
Co <0.5
Cu 6.5
Pb 1.8
Zn 23

Root:
As 0.37
Co <0.5
Cu 6.7
Pb 1.8
Zn 36

Peeled tuber:
As 0.11
Co <0.5
Cu 1.7
Pb 0.7
Zn 11

Leaf:
As 0.14
Co <0.5
Cu 11.7
Pb 3
Zn 133

Concentration in soil: As: 0.90, Zn: 55 mg kg$^{-1}$, Co: 17, Cu: 48, Pb: 10.6, Zn: 55 mg kg$^{-1}$

Cassava, accumulation factors

Leaf
As: 0.15
Cu: 0.24
Pb: 0.28
Zn: 2.41

Tuber
As: 0.12
Cu: 0.04
Pb: 0.07
Zn: 0.23
Sweet potato

Leaf:
As 0.16
Co <0.5
Cu 16.6
Pb 0.7
Zn 29

Leaf stalk:
As 0.2
Co <0.5
Cu 20.7
Pb 0.7
Zn 18

Stem:
As 0.15
Co <0.5
Cu 17.6
Pb 0.5
Zn 11

Root:
As 0.14
Co <0.5
Cu 15.7
Pb 0.5
Zn 19

Peeled tuber:
As 0.14
Co <0.5
Cu 7.1
Pb <0.5
Zn 10

Peel:
As 0.21
Co <0.5
Cu 0.14
Pb 0.7
Zn 0.52

Concentration in soil: As: 0.90, Co: 17, Cu: 48, Pb: 10, Zn: 55 mg kg⁻¹

Sweet potato, accumulation factors

Leaf
As: 0.21
Cu: 0.36
Pb: 0.06
Zn: 0.52

Tuber
As: 0.15
Cu: 0.14
Pb: 0.03
Zn: 0.18
Contents of metals in plants are governed by a number of factors:

**External factors:**
- content of bioavailable metals in soil
- soil composition and pH
- vegetation period
- climatic conditions

**Internal factors:**
- age of plant
- bioessentiality of elements
- avoidance mechanisms
- antagonism of elements

Concentrations of copper and zinc in leaves and tubers of cassava and sweet potatoes in relation to the age of these crop plants
Metals and arsenic in uncontaminated and contaminated areas

Plant and soils were sampled in contaminated part of the Zambian Copperbelt (CIP > 1)

and,

in the reference, uncontaminated part of the Zambian Copperbelt (CIP < 1)

Coefficient of Industrial Pollution

\[
CIP = \left( \frac{As + Co + Cu + Hg + Pb + Zn}{6 \times m_{As} + m_{Co} + m_{Cu} + m_{Hg} + m_{Pb} + m_{Zn}} \right)
\]

\[m_X - \text{value of the metal concentration}\]
Contents of metals and arsenic in uncontaminated and contaminated soils of the Zambian Copperbelt
Content of metals and arsenic in cassava leaves and tubers (uncontaminated and contaminated area)
Zinc was found to prevail over copper in leaves of cassava growing in uncontaminated areas. The distribution of data is very homogeneous.

In contrast, copper was mostly found to prevail over zinc in leaves of cassava growing in contaminated areas, but the distribution of data is rather very heterogeneous.
**Spearman correlation matrix**

<table>
<thead>
<tr>
<th></th>
<th>Root-Me_{soil}</th>
<th>Leaf-Me_{soil}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td></td>
<td>0.5254</td>
</tr>
<tr>
<td>Zn</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td></td>
<td></td>
</tr>
<tr>
<td>As</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Significant correlation cassava-total metal in soil**

**Significant correlation cassava-biavailable metal in soil (EDTA)**

<table>
<thead>
<tr>
<th></th>
<th>Root-Me_{soil}</th>
<th>Leaf-Me_{soil}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td></td>
<td>-0.3301</td>
</tr>
<tr>
<td>Co</td>
<td></td>
<td>0.4868</td>
</tr>
<tr>
<td>Ni</td>
<td></td>
<td>0.6134</td>
</tr>
<tr>
<td>Cu</td>
<td>0.6134</td>
<td>0.5649</td>
</tr>
<tr>
<td>Zn</td>
<td>0.5262</td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td></td>
<td>0.3701</td>
</tr>
<tr>
<td>As</td>
<td>0.3931</td>
<td></td>
</tr>
</tbody>
</table>

**Bioavailable metals in soils**

- Available metals (in % of total amount of metal in soil)
  - Chemical elements: As, Co, Cr, Cu, Fe, Mn, Ni, Pb, V, Zn
  - Available metals using different extraction methods:
    - 0.01 M CaCl2
    - 0.1 M CaCl2
    - Mehlich III
    - EDTA
    - DTPA

**Correlation between the contents of metals and arsenic in plants and soil**

Correlation is low obviously due to plowing or soil loosening during which the contaminated topsoil is mixed with deeper less contaminated layer of soil profile.
<table>
<thead>
<tr>
<th>Plant Part</th>
<th>Location</th>
<th>Median Cu (mg.kg-1,dw)</th>
<th>Min-Max Cu (mg.kg-1, dw)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cassava leaves</strong>, uncontaminated area, Nigeria</td>
<td>41.6</td>
<td>32.7-58.4</td>
<td>Chukwuma 1995</td>
<td></td>
</tr>
<tr>
<td><strong>Cassava leaves</strong>, uncontaminated area, Copperbelt</td>
<td>20.1</td>
<td>2.1-252.4</td>
<td>This study</td>
<td></td>
</tr>
<tr>
<td><strong>Cassava leaves</strong>, contaminated area, Copperbelt</td>
<td>131.1</td>
<td><strong>12.3-611.9</strong></td>
<td>This study</td>
<td></td>
</tr>
<tr>
<td><strong>Cassava tubers</strong>, uncontaminated area, Ghana</td>
<td>6.2</td>
<td>5.3-8.4</td>
<td>Nganje et al. 2000</td>
<td></td>
</tr>
<tr>
<td><strong>Cassava tubers</strong>, uncontaminated area, Nigeria</td>
<td>10.5</td>
<td>12.4-16.2</td>
<td>Boadi et al. 2009</td>
<td></td>
</tr>
<tr>
<td><strong>Cassava tubers</strong>, uncontaminated area, Nigeria</td>
<td>12.4</td>
<td>10.7-18.9</td>
<td>Iyaka, 2007</td>
<td></td>
</tr>
<tr>
<td><strong>Cassava tubers</strong>, uncontaminated area, Copperbelt</td>
<td>3.9</td>
<td>1.7-17.1</td>
<td>This study</td>
<td></td>
</tr>
<tr>
<td><strong>Cassava tubers</strong>, contaminated area, Copperbelt</td>
<td><strong>8.4</strong></td>
<td><strong>2.3-92.9</strong></td>
<td>This study</td>
<td></td>
</tr>
</tbody>
</table>
The extremely high contents of copper in cassava leaves indicate that cassava is able to tolerate even extremely high contents of copper in soils in which it is grown.

Strategy adopted by plants to tolerate excess content of copper in soil:

- chelation of copper in the cytosol by peptides such as phytochelatins,
- repair of stress-damaged proteins,
- the compartmentation of metals in the vacuole by tonoplast-located transporters.
**Dietary risk assessment**

**Highest tolerable intake limits for metals and metalloids**  
(after FAO/WHO Expert Committee on Food’s limits, JECFA, 2007)

- **Arsenic:** weekly intake limit: 0.015 mg.kg\(^{-1}\) of Human Body Weight (HBW)
- **Lead:** weekly intake limit: 0.025 mg.kg\(^{-1}\) HBW
- **Copper:** daily maximum tolerable limit: 0.5 mg.kg\(^{-1}\) HBW

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**Estimation**

- Daily intake of cassava mush is estimated at 300 g.d\(^{-1}\) (single meal).
- The daily intake of cassava vegetable salad is estimated at 70 g.d\(^{-1}\) (single meal).
- The average weight (HBW) of Zambian rural population (adults) was estimated at 70 kg.
Cassava mush and cassava vegetable salad: Daily/weekly intake, Copperbelt

<table>
<thead>
<tr>
<th></th>
<th>Cu (mg.kg⁻¹ HBW, daily intake)</th>
<th>Pb (mg.kg⁻¹ HBW, weekly intake)</th>
<th>As (mg.kg⁻¹ HBW, weekly intake)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum</td>
<td>0.013</td>
<td>0.005</td>
<td>0.002</td>
</tr>
<tr>
<td>Median</td>
<td>0.097</td>
<td>0.017</td>
<td>0.011</td>
</tr>
<tr>
<td>Maximum</td>
<td>0.592</td>
<td>0.063</td>
<td>0.062</td>
</tr>
<tr>
<td><strong>MAX TOLERABLE INTAKE</strong></td>
<td><strong>0.5</strong></td>
<td><strong>0.025</strong></td>
<td><strong>0.015</strong></td>
</tr>
</tbody>
</table>
Surface contamination of the aboveground parts of vegetables by dust

The health risk linked with the intake of metals and arsenic from crop plants might be substantially higher when poorly washed leaves are used for preparation of salads.
CONTAMINATION OF LEAVES BY DUST PARTICLES AND EFFECT OF WASHING

The amount of dust on surface of the leaves can be significantly reduced by their thorough washing when fresh vegetable salads are being prepared.
CONCLUSIONS:

- Because of strong contamination of some parts of the Zambian Copperbelt mining district caused by the extraction and processing of copper ores, the local soils and crop plants in contaminated areas contain high concentrations of copper.

- The leaves of both cassava and sweet potatoes in contaminated areas also contain higher contents of zinc, cobalt and arsenic, whereas the content of lead is low and more or less the same in plants from both contaminated and uncontaminated areas.

- The contents of metals in tubers of cassava and sweet potatoes are much lower than their contents in their leaves.

- The values of correlation coefficients between individual metals and arsenic in soil and crop plants were found to be low at individual sampling sites. This is believed to be due to the mixing of strongly contaminated topsoil with the deeper horizons in the soil profile caused by hoeing.

- The dietary risk assessment has not indicated any excessive intake of copper, but excessive intake of Pb and As was occasionally recorded in contaminated areas of the Zambian Copperbelt.
CONCLUSIONS:

- The surfaces of cassava leaves are strongly contaminated by metalliferous dust particles in polluted areas and there is still a significant risk of ingesting dangerous levels of copper, lead and arsenic if dishes are prepared with poorly washed foliage.

- Compared with cassava tubers and particularly with cassava leaves, the grains of maize contain very low contents of metals and arsenic even in strongly contaminated areas. Therefore, planting of maize is recommended instead of growing cassava or sweet potato in areas strongly affected by contamination.

Comparison of average contents of elements in leaves and tubers of cassava, sweet potatoes and in grains of maize cultivated near the Nkana smelter at the city of Kitwe, Zambia.
Thank you for your attention