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Copper Concentrations Found from Drinking Water, Soils, and Vegetables

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Abstract: Humans, animals, and plants need copper for growth and development, but it can be an irritant to humans. The daily maximum limit of copper for humans is 10-12 µg day^{-1} and excess concentrations of copper can cause nausea, diarrhea, and anorexia. In plants, excess copper concentrations cause chlorosis, stunted growth, and denaturing of macromolecules. Only 10 mg kg^{-1} of copper can be accumulated by plants. The maximum allowable concentration in agricultural soils is 6.6 mg kg^{-1}. The concentration of copper in drinking water should not exceed 1 mg L^{-1}. When copper concentrations exceed an action level of 1.3 ppm in more than 10% of customer taps sampled, several additional controlling measures must be undertaken. In waste, the allowable concentration is 16 mg kg^{-1}. The hypothesis of the study was that copper would be found in the vegetables grown from the agricultural soils. Cabbage, green pepper, spinach, and tomato were grown for thirteen weeks. The soil and vegetables were digested, and the copper concentrations were measured using an Atomic Absorption Spectroscopy (AAS). The highest total and extractable copper concentrations found in the soil were 73 mg kg^{-1} and 26 mg kg^{-1}, respectively. More than 20 and 32 mg kg^{-1} of copper was found in the shoot and roots of the vegetables, respectively. More than 11 mg L^{-1} of copper was found in the tap water. The results indicated that the copper concentrations from the soil, water, and vegetables exceeded the allowable concentrations.

Keywords: Copper, Vegetables, Tap Water, Extractable, Lugelweni, Soil

1. Introduction

Copper can be detected in the soil, plants, food, beverages, and drinking water at different ranges of concentrations. All organisms need copper at low levels and can be negatively affected by it at high levels. In the soil, an increase in cation exchange capacity, clay, and organic matter content can increase the concentration of copper [1].

In soil, copper can strongly attach to the organic material of the top layers. Soil has 2 to 250 ppm of copper with higher concentrations near facilities that produce copper. The maximum allowable concentration in agricultural soils should not exceed 6.6 mg kg^{-1} [2]. In waste, the allowable concentration is 16 mg kg^{-1}.

According to Agency for Toxic Substances and Disease Registry [3], copper compounds are not found in groundwater. In water, copper is found on the surface and can be bound to suspended particles. The acceptable drinking water standard is 1,300 parts copper per parts of water [4]. The lakes and rivers have copper ranging from 0.5 to 1,000 ppb with an average of 10 ppb. The tap water contains an average concentration of 20 to 75 ppb, and the concentration can be higher when copper is dissolved in copper pipes. The concentration of copper should not exceed 1 mg L^{-1} in drinking water [5] whilst World Health Organization [6] recommends 2 mg L^{-1} of copper in drinking water. In plants excess copper results in leaf chlorosis and stunted growth interfering with photosynthesis and respiration [7-9]. Only 10 mg kg^{-1} of copper can be accumulated by plants.

The recommended dietary allowances range from 340 µg/day for children aged 1 to 3 years, and 900 µg/day for adults. The tolerable upper intake level for copper is 10 mg day^{-1}.

Occupational Safety and Health Administration (OSHA) has the permissible exposure limits set at 0.1 mg/m^3 for copper fumes and 1.0 mg/m^3 for copper dust. Exposure to copper for a long time can irritate the nose, mouth, and eyes. Headaches, dizziness, nausea, vomiting, stomach cramps, and diarrhea are also some of the effects of long-term copper exposure. In the long-term liver, and kidney damage can occur and ultimately death.

Lugelweni Village is in the Former Transkei, Eastern Cape South Africa. It is situated on the N2 route, 140 km away from Walter Sisulu University Mthatha and 3 km from Mt Ayliff. There are attractions such as Ntsizwa Mountain, a Lugelweni waterfall, and a forest found in the same village [10] (Umzimvubu visitors guide 2012). There are entrances on the mountain of the abandoned copper mines.

Lugelweni is a rural area where agriculture is crucial in providing food sources for humans. But at times, agriculture can be negatively affected by the shortage of water or by the runoff from various points and non-points. When using stormwater to irrigate the vegetables for up to ten years [11], found that the metal concentrations increased with the aging of the gardens. They also found out that the sensitivity of the metals from the stormwater was dependent on the type of the vegetables. Although sometimes heavy metals can be caused by various activities such as agriculture, traffic, or industrial activities, agricultural activities were found to be the main source of copper pollution when [12] assessed the spatial distribution of heavy metals in Algeria. In addition to the aforementioned factors, the proximity of the community to the contaminated areas can increase the risk to the residents. In Morocco, when assessing the toxicity of garden soils in the mining area [13] found out the significant values of heavy metals in the cultivated species pose a health risk to the people consuming such species near the contaminated sites.

The present study was performed to investigate the concentrations of copper found in the garden soils, water, and vegetables from Lugelweni. To reach the goal of the study, the physicochemical properties of the garden soils, the concentrations of copper from the garden soils, water, and the shoot and root of the vegetables were investigated and measured.

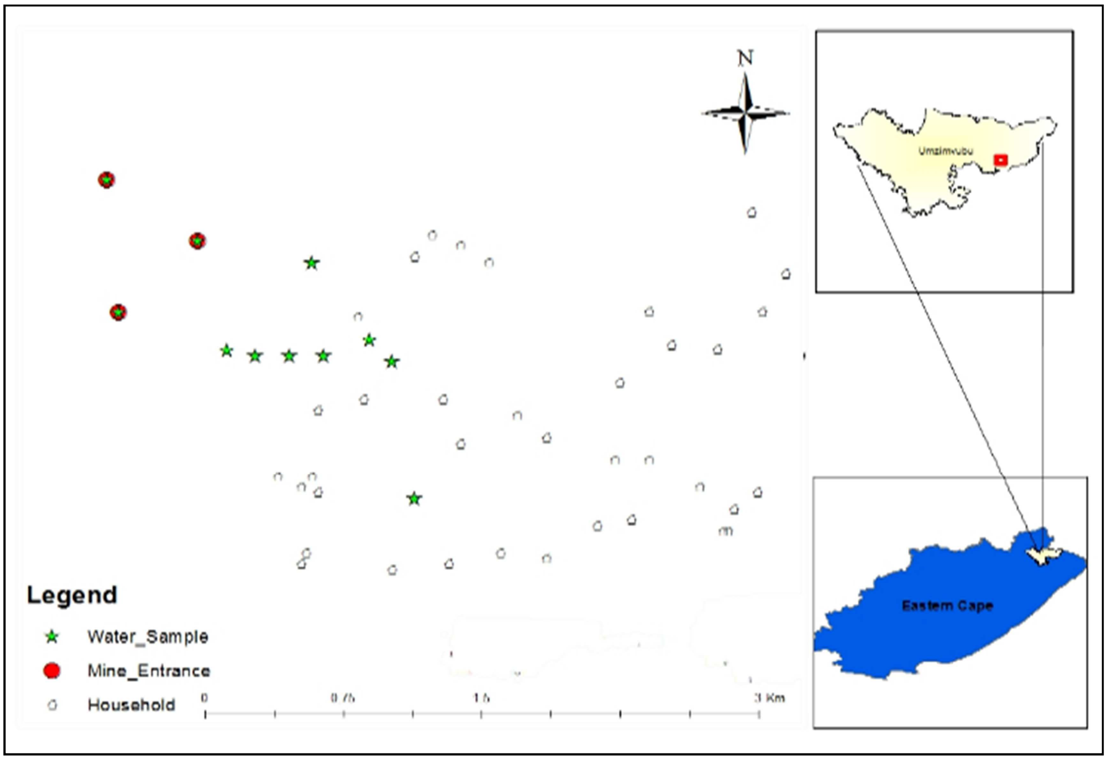

Figure 1. *Study area showing the sampling sites.*

2. Materials and Methods

2.1. Sampling of Soil

Soil sampling for soil copper concentrations analyses and soil classification were conducted using a sampling method by [14]. Systematic sampling was used for soil sampling. There were 429 households, and the desired sampling size was 40 with a soil sampling interval ratio of 10. The soil was collected using an auger. All the sampled soils were collected into clean sterile labeled bags and transported to the Department of Botany at Walter Sisulu University for further analysis.

2.2. Sampling of Water

Water samples were collected from four different sources of water: the river, the two mine entrances, the dam, and the taps. Clean sterile sample bottles were used to collect all the water samples at the study site. The samples were transported to the Department of Botany at Walter Sisulu University for further analysis.

2.3. Growing and Analysis of the Vegetable

Four different types of vegetables, namely, *Brassica oleracea* (cabbage), *Capsicum annuum* (green pepper), *Spinacia oleracea* (spinach), and *Solanum lycopersicum* (tomato) were grown at Lugelweni for thirteen weeks. After thirteen weeks the vegetables were harvested into sterile plastic bags which were transported to the Department of Botany at Walter Sisulu University for further analysis. The harvested vegetables were cleaned using distilled water to remove the soil particles. The plants were separated into shoots and roots, dried, and digested for analysis of copper concentrations using the [15] method with some modifications by [16].

3. Results

3.1. Physicochemical Properties of the Soil

The analyses of the physicochemical properties of the soil were performed on the soil sampled from gardens at Lugelweni, Mount Ayliff. The results (Table 1) indicated that the pH ranged from 3.8 to 7.2. The soil density varied as it ranged from 1 g ml^{-3} to 1.2 g ml^{-3}. The percentage of acid saturation ranged from 0 to 37. The total cations ranged from 6.02 to 21 cmol L^{-1}. Phosphorus (P) showed varied concentrations ranging from 0 to 141 g ml^{-1}. Ten percent of the soil had phosphorus ranging from 100 to 130 mg L^{-1}. Sixty-three percent of the samples had potassium between 100 and 450 g ml^{-1}. The low level of potassium was 3.8 g ml^{-1}. The highest concentrations of calcium, magnesium, and zinc were 3493 g ml^{-1}, 696 g ml^{-1}, and 2.8 g ml^{-1}, respectively. The lowest amounts of magnesium and zinc were 147 g ml^{-1}, and 1.0 g ml^{-1}, respectively.

Table 1. *The physicochemical properties of the soil.*

Physicochemical properties	Minimum	Maximum	Average
Sample density g mL	1	1.25	1.1228
P gml^{-1}	0	141	32.975
K gml^{-1}	3.8	540	168.27
Ca gml^{-1}	518	3493	1941.6
Mg gml^{-}	147	696	377.1
Exch. Acidity $cmoll^{-}$	0.09	2.35	0.4485
Total cation $cmolk^{-1}$	6.02	21.89	13.670
Acid sat%	0	37	4.75
pH (KCl)	3.87	7.24	4.99
Zn gml^{-1}	0	2.8	0.655

Extractable and total copper concentrations in soil.

The results (Table 2) indicated that there were significant differences, $p<0.05$ at 0.000, in the extractable and the total copper from soil samples. The average concentrations for the extractable and total copper concentrations were 20.66 and 34.05 mg/kg, respectively.

Table 2. *Total and extractable copper concentrations from the soil.*

Copper concentration (mg/kg)	Minimum	Maximum	Average
Total	11.71	73.6	34.05
Extractable	1.93	26.19	20.66

Copper concentrations in vegetables.

3.2. Shoot and Root Copper Concentrations

The highest shoot copper concentration was observed in the green pepper and tomato at 10 mg/kg (Figure 2). The cabbage displayed the lowest amount of copper among the four types of vegetables. Tomato had the highest amount of copper in the roots at 23 mg/kg (Figure 2), whilst the spinach had the lowest amount of copper in the roots.

Copper concentration from the drinking water samples from the forty households was 3.56 mg/kg (data not shown).

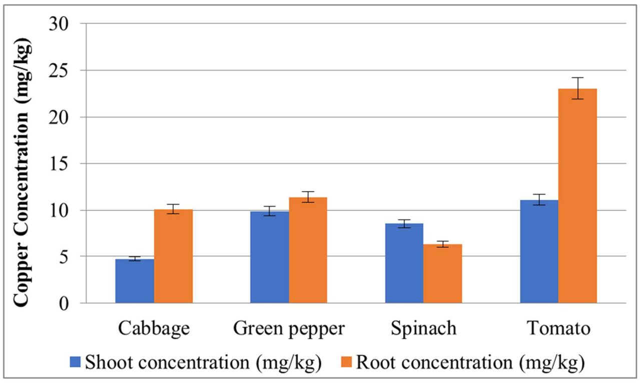

Figure 2. *Copper concentration (mg/kg) from vegetables grown for thirteen weeks. Values and error bars represent means.*

4. Discussion

4.1. Physicochemical Properties

The soils from the present study indicated that the soils had low pH and densities of slightly more than 1 g ml^{-3}. When the density and the pH of the soil are low, there is a tendency for an increase in metal mobility. Similar results were observed from the research work conducted by Bech et al. [17], where they showed that acidic soils influence and mobilize metals from the immobile state. The study by Anjos, Magalhaes, and Abreu [18] showed a similar trend when the soil pH was acidic with few neutral samples.

From the present study, the acid saturation which depends on soil pH was found to be less than the total cations. The soils with low acid saturation found in the present study can result in more Al^{3+} that are toxic to plant growth. In addition, soils with low acid saturation have low pH, which makes them less buffered from all the processes that acidify the soil. Moreover, the soils with low acid saturation contain fewer amounts of K^{+}, Ca^{2+}, and Mg^{2+}.

Wang and Nan [19] found that soils with high CEC retained Cu more than the soils with low CEC. Using the agricultural soils near a copper smelter in southeast China, [20] found out that the copper concentrations were controlled by the concentrations of magnesium and iron.

4.2. Extractable and Total Copper Concentrations from Soil

Extractable copper is the mobile and available copper in the soil that is accessible for plant absorption. This study reveals that even the concentration of extractable copper in the soil is elevated beyond permissible levels. In general, a high amount of extractable copper concentration in the soil triggers high absorption of copper in excess amounts by plants. The work by Perlatti et al. [21] demonstrated that the extractable copper or else known as the bioavailable copper was high exceeding the maximum allowable concentrations and was influenced by abandoned mines. The total copper concentration is the amount of extractable copper and immobile copper due to the physical and chemical properties of the soil. In the present study, the concentrations of total copper in soils were twice the extractable concentrations of copper. Therefore, this indicates that the copper concentrations in Lugelweni garden soils were higher than the allowable copper concentration in the soils which is 6.6 mg/ kg. From the study conducted by Obiora, Chukwu, and Davies [22], the agricultural soils around mining areas were contaminated by the mines and the copper concentrations were within the allowable amounts.

4.3. Copper Concentrations in Vegetables

Vegetables are edible plants that provide nutrients to humans. The Eastern Cape Province comprises 609 000 households who are substantial farmers and vegetables are produced largely for family consumption [23].

Consumption of metal-rich crops because of metal accumulation/contamination and drinking metal-rich water trigger physiological complications to human health. The amount of copper absorbed into edible organs of the plants that are over the minimum permissible copper levels threatens humans and causes serious damage according to the concentrations consumed per day.

The present study reveals that Lugelweni household gardens are contaminated with copper as vegetables are grown which include cabbage, green pepper, spinach, and tomato were screened and found to contain copper. The above-listed vegetables contained concentrations of copper that are beyond the allowable amounts of copper which are 10 mg kg^{-1} in the aerial parts of the four vegetables.

Some studies seem not to agree with the present study. The study by Obiora, Chukwu, and Davies [22], showed that the mines situated around the households were not affecting crops grown as the copper concentrations did not exceed the permissible copper. Similar results were found from the studies conducted by Mohod, Usubalieva et al., Opaluwa, et al. [24, 25, 26], screening spinach, tomato, and cabbage all grown close to mining sites and were within the allowable copper concentrations. In contrast, Miclean et al. [27] had the results that were in agreement with the results from the present study where the soil and plants around the mining areas had elevated copper concentrations above permissible concentrations.

From the present study the concentrations of copper in shoots of vegetables were found to be: cabbage<spinach<green pepper<tomato. In the roots, the concentrations of copper were spinach< cabbage <green pepper <tomato. In Germany, [28], when assessing the risk of toxic elements such as As, Cu, Mn, Pb, Zn, and Hg in vegetables such as beans, carrots, and lettuce growing from four gardens found that they contained very high concentrations of the elements. They found out that the beans and the lettuce had more elements than the carrots. With the copper regulation limit of 40 mg kg^{-1} in Germany, the maximum copper concentration from the gardens was 420 mg kg^{-1} and the minimum concentration was 33 mg kg^{-1}. Specifically, they found copper concentrations below 15 mg kg^{-1}, the copper concentrations below the ones found in the vegetables from the present study. In Pakistan, Ur Rehman et al. [29], when working from the garden soils containing 11 to 16 mg kg^{-1} of copper found that the concentrations of copper from the vegetables were up to 19 mg kg^{-1}.

5. Conclusions

Metal mobility in soils from Lugelweni with low pH was increased. There were very high amounts of extractable and total copper in the soil. The high extractable copper from the soils was accumulated by the cabbage, green pepper, spinach, and tomato grown for three months. The leafy vegetables had more copper in their shoots and roots.

The soils, water, and vegetables from Lugelweni Mt Ayliff have more than the permissible amounts of copper, therefore, action needs to be taken by the Departments of Environmental Affairs, Health, Agriculture and Fisheries, and Water and Sanitation.

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