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Impact of contaminated water and soil by copper and zinc on market garden products in Cotonou (Benin)

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Abstract Agriculture represents a highlight activity in Benin but this activity faced many environmental issues. The main objective of this study is to determine physicochemical parameters of the water used in market gardening in Fidjrossè and concentrations of copper and zinc in the watering waters, soils and plants grown. This study is initiated to assess the level of copper and zinc pollution of the most consumed leaf vegetables. For this purpose, the total metal contents in irrigation water, soil and in the main market garden crops such as big nightshade and amaranth were analyzed. To more assess the contamination, the bioaccumation factors were also calculated. The results of these analyze show a contamination of vegetables in metals. For copper, the values range from 13.06 mg/kg to 17.89 mg/kg for large nightshade and from 9.90 mg/kg to 11.58 mg/kg for amaranth. For zinc, these values range from 27.83 mg/kg to 87.69 mg/kg for the large nightshade and from 5.94 mg/kg to 33.73 mg/kg for amaranth. These values are well above the maximum allowable standard of 3.3 mg/kg for copper and 5 mg/kg for zinc. The contamination is linked to the presence of these metals in the water and in the soil. The bioaccumulation factors of metals in relation to water and soil revealed that these metals are more available in water than in soil. It is therefore recommend improving the agricultural practices to clean up the environment in order to limit water and soil pollution and water and consequently ensure a good quality of vegetable crops.

Keywords Pollution, vegetable crops, contamination, bioaccumulation, metal

1. Introduction

Urban and peri-urban agriculture is a sub-sector of agriculture. It has undergone an evolution following the urban demographic explosion [1]. This agricultural sub-sector includes market gardening and the breeding of small ruminants and poultry. Vegetable production is developing on the outskirts of large African cities and contributes to food security. Market gardening is practiced in all regions of Benin, on the tray, in the alluvial plains, in the valleys, and in the shallows. They consist on the one hand of traditional crops (tomato, chilli, okra, onion) and on the other hand, leafy vegetables and exotic crops (carrot, cabbage, lettuce, cucumber, leek, green bean...) practiced in urban and peri-urban areas. In fact, southern Benin is watered all year round because it enjoys a favorable subequatorial climate. Vegetable production is higher in southern Benin [2].

Through its domestic production, Benin does not manage to cover its food needs in market gardening products. The observation is that Benin continues to import a good part of its consumption of market garden products from neighboring countries such as Burkina Faso and Nigeria [3] while market gardening has the potential to gain foreign exchange.

Vegetable production is an activity that responds to urban food preferences and demand [4]. It represents an important source of income and employment [5]. Vegetables production in southern Benin is mainly intended for marketing on the markets of Cotonou, Porto-Novo and Abomey-Calavi. However, it is confronted with numerous constraints and generates nuisances which limit its durability [6]. Among the constraints that hamper the production of market gardening, are insecurity of land, lack of control of pests and diseases, poor control of water, conservation difficulties and the low level of organization of stakeholders sector [7]. The fundamental question of this dissertation is whether vegetable production in Fidjrossè in southern Benin is part of a sustainable development perspective if it is ecologically healthy and if the products are of good quality.

Market gardening in southern Benin is practiced all the time throughout the year and depends on large quantities of water for irrigation. Producers do not adopt good irrigation practices [8]. Good irrigation practices would optimize production while saving water. The motorized drilling and sprinkler system allows more efficient application of irrigation water and contributes to a significant reduction in the waste of water resources [7]. This system ensures social sustainability by reducing arduous work and environmental sustainability.

In Benin, vegetables being consumed a lot by the populations in general and those of Fidjrossè in particular, a study on the contamination of cultures by metallic pollutants and the consequences of these pollutants on the health of populations is necessary.

2. Material and methods

2.1. Presentation of the study environment

Cotonou is located on the coastal cord which extends between Nokoué Lake and the Atlantic Ocean, made up of alluvial sands of approximately five meters in maximum height. It represents the only municipality in the Littoral department and is limited to the north by the municipality of Sô-Ava and Nokoué Lake, to the south by the Atlantic Ocean, to the east by the municipality of Sèmè-Kpodji and to the west by that of Abomey-Calavi. It covers an area of 79 km^2, 70% of which is located west of the channel. The eastern districts are connected to the western part by three bridges. West of Cotonou is the Port Autonome and the International Airport, which make the city the most important gateway into and out of Benin, while the East has a large industrial area.

2.2. Samples collection

A preliminary investigation was carried out in order to target the areas of vegetable production, the sources of water supply for irrigation, the various cultural practices used by market gardeners and the use of agricultural inputs. The sites were located and identified using a GPS and presented in Table 1 below. The samples consisted of taking water samples, sediment and plants at the various points. To achieve this, some measures have been taken beforehand at the laboratory level, namely the cleaning of field equipment and the calibration of measuring instruments. The water samples to be analyzed were taken about 5 cm from the surface of the water points in plastic bottles. These bottles were previously washed and rinsed. The bottles are filled and sealed to prevent gas leakage. The soil samples are composite samples taken using a hoe to collect the soil. Vegetables samples are taken at maturity stage, one on boards of amaranth and the other of the large nightshade at each site. Vegetables and sediment samples are collected in sterile stomaching bags. The figure 1 shows the location of the study area.

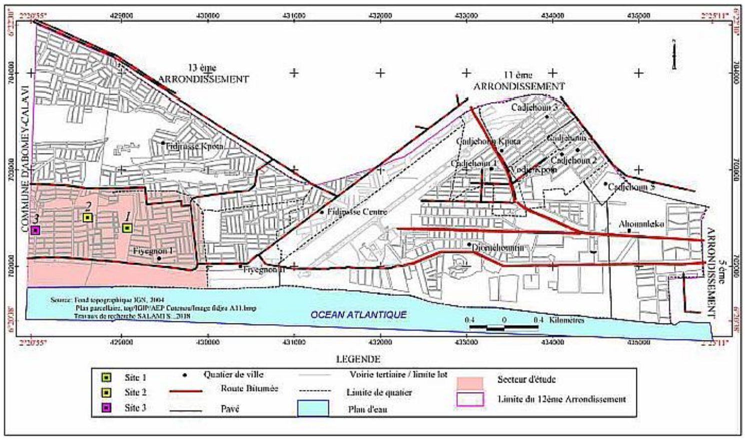

Figure 1: Location of the study area and sampling points

2.3. Physico-chemical analysis of water

The pH was determined using a WTW 3110 pH meter. The temperature, conductivity, TDS, resistivity and salinity are determined using a WTW 3210 conductivity meter.

2.4. Copper and zinc determination

The plants underwent a preliminary treatment which consisted of grinding the fresh leaves and taking a precise weight of 0.5 grams for the mineralization. The mineralization of the sediment and of the plant was made according to HACH and the aqueous samples obtained are taken to the spectrophotometer DR2800 for the measurement of copper and zinc. Copper and zinc in the waters were also analysis using a DR2800 spectrophotometer with a detection limit of 0.01 mg/L. Copper is determined by the CuVer method and zinc by the ZincoVer method.

2.5. Physico-chemical analysis of the soil

In order to know the acidic, neutral or basic character of the sediments, the pH was measured. The protocol is summarized as follows: 10 g of fine sediment sieved to 0.2 mm in a beaker was weighed using an electronic balance, and then 25 ml of distilled water and 1/3 of 3N KCl were added. Then, the whole was stirred with a magnetic stirrer for 1 hour at an ambient temperature of 20 ± 2 °C. This made it possible to suspend the entire sample and thus obtain equilibrium between the solid phase and the aqueous one. The beaker was then left to stand for 2 hours in the absence of air, and then the pH of the suspension was measured.

2.6. Total organic carbon (TOC) content

For the measurement of the total organic carbon content, the TOC persulfate method was used. The COD reaction chamber is used for heating.

2.7. Nitrogen content

After sample mineralization, the nitrogen and phosphorus contents were measured with the DR2800 spectrophotometer by the Nessler method. The protein level is a function of the nitrogen level and is obtained by multiplying the total nitrogen (NTK) by a general factor which is 6.25 in the absence of a specific factor for the species of the leaf.

2.8. Determination of Dry Matter and Organic Matter

To find out the total organic matter in the plant samples, the loss on ignition (PAF) method or calcination loss method was used. It is determined from the following formula:

$$\% \text{ MO} = \frac{[\text{dry soil weight (g)} - \text{cremated soil weight (g)}] * 100}{\text{dry soil weight (g)}}$$

2.9. Bioaccumulation factor

Bioaccumulation factor FBc (water) = $\frac{[\text{Metal content}]\ (mg/kg)\ \text{in vegetables}}{[\text{Metal content}]\ \text{in water}\ (mg/l)}$

Bioaccumulation factor FBc (soil) = $\frac{[\text{Metal content}]\ (mg/kg)\ \text{in vegetables}}{[\text{Metal content}]\ \text{in soil}\ (mg/l)}$

3. Results

3.1. Analysis of water intended for watering plants

The results of the physicochemical analyzes and metallic trace elements in the water intended for the watering of vegetables are presented in Table 1.

Table 1: Parameters studied on water intended for watering vegetables

Sites	Water pH	Temperature (°C)	TDS (mg/L)	Conductivity (µS/cm)
Site 1	6.3	26.3	428.5	857
Site 2	6.34	26.4	292	579.99
Site 3	6.8	26.4	241	484
Average	6.48	26.37	320.5	640.33

The pH values vary from 6.3 to 6.8 with an average of 6.48. The highest value was observed at site 3 and the lowest value at site 1.

The temperatures of the irrigation water are between 26.3 ° C and 26.4 ° C with an average of 26.37 ° C. Sites 2 and 3 have the same values which are the largest and the smallest of the values observed on site 1. The measured temperature values are influenced by the climatic conditions at the time of the samples. The conductivity of the irrigation water varies from 484 µs/cm to 857 µs/cm with an average value of 640.33 µs/cm and the TDS varies from 241 mg/L to 428.5 mg/L with an average value of 320.5 mg/L. The highest conductivity and TDS values of the three sites were found at site 1 and the lowest at site 3.

For copper, the contents vary from 0.011 mg/L to 0.058 mg/L with an average value of 0.027 mg/L (Figure 1). The largest of the values was obtained at site 1 and the lowest at site 3 for zinc, the contents varied from 0.12 mg/L to 0.27 mg/L and the largest was obtained at site 1 also and the same values were obtained on the two other sites. The copper and zinc contents of the waters comply with the Canadian recommendation for the water quality of agricultural purposes. The figure 2 shows the copper and zinc distribution in water

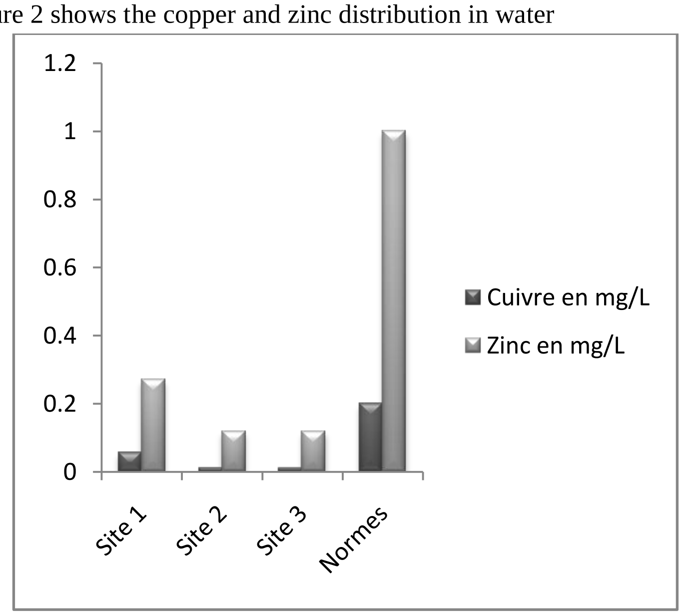

Figure 2: Copper and zinc contents in the water

3.2. Soil analysis

The results of the physicochemical, chemical and metallic trace element analyzes carried out on the ground are shown in Table 2.

Table 2: Parameters studied on the ground

Sites	Soil pH	KCl pH	Carbon (%)	Matter Organic (%)	Azote (mg/kg)
Site 1	7.28	7.18	0.62	1.07	33.15
Site 2	7.58	7.36	0.48	0.84	51.54
Site 3	7.73	7.55	0.28	0.28	66.53
Average	7.53	7.36	0.46	0.73	50.41

For Water pH and KCl pH on vegetable plank soils, the largest values were observed at site 3 and the smallest values at site 1.

It is found that the carbon contents vary from 0.28% and 0.62% with an average of 0.463% and the organic matter contents vary from 0.28% to 1.07% with an average of 0.73%. The highest values of these two parameters were found on site 1 and the lowest on site 3. The high value at site 1 in organic matter is due to the decomposition of the waste leaked into the soil.

Following the analyzes, it appears that the nitrogen concentrations vary between 33.15 mg / kg and 66.53 mg / kg with an average of 50.41 mg / kg. Analysis of the nitrogen in the soil shows that, whether on the plate of the large nightshade and that of the amaranth, site 3 has a higher nitrogen rate and site 1 is the one that has lower nitrogen levels.

The concentration of copper in soils varies from 42.33 to 250.46 mg / kg with an average of 115.76 mg / kg (Figure 3). The highest concentration was observed at site 1 and the lowest at site 2; the same is true for zinc, the contents of which vary from 78.43 mg / kg to 83.33 mg / kg with an average of 80.38 mg / kg.

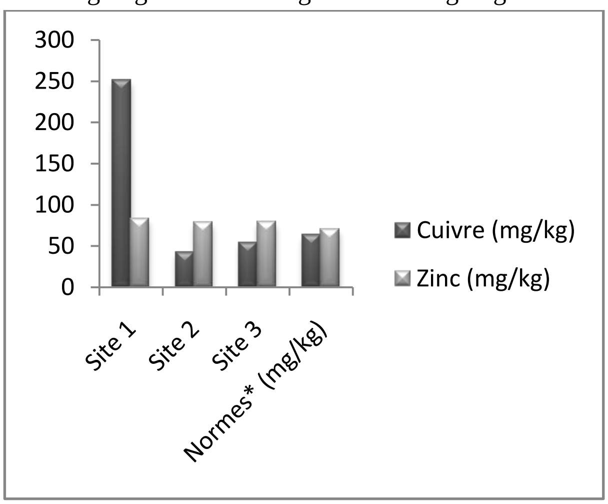

Figure 3: Copper and zinc contents in soils

3.3. Vegetables analysis

The results of the chemical analyze and metallic trace elements carried out on the vegetables are presented in Table 3.

Table 3: Parameters studied on the sampled vegetables

Sites	NTK (mg/kg)		Protein (mg/kg)		Phosphorus (%)	
	GM	A	GM	A	GM	A
Site 1	70.23	78.18	438.93	488.66	624.25	1119.69
Site 2	58.91	22.13	368.18	138.33	835.82	344.01
Site 3	56.60	37.28	353.74	232.98	682.16	574.26
Average	61.91	45.87	386.95	286.66	714.08	679.32

GM: Large nightshade; A: Amaranth

The nitrogen content varies from 28.91 mg kg to 70.23 mg/kg on the nightshade with an average of 61.91 mg/kg. For amaranth, it ranges from 22.13 mg/kg to 78.18 mg/kg with an average of 45.86 mg/kg. The protein level is proportional to the nitrogen level, the higher the nitrogen concentration is, the higher the protein concentration is.
On the nightshade, the phosphorus contents vary from 624.25 mg/kg to 835.82mg/kg with an average of 714.08 mg/kg and on the amaranth, the phosphorus contents vary 344.01 mg / kg at 1119.69 mg/kg with an average of 679.32 mg/kg. The highest rate is found on amaranth which accumulates more phosphorus than the nightshade.
The copper content varies from 13.06 mg/kg to 20.45 mg/kg on the nightshade with an average of 17.13 mg/kg and on the amaranth it varies from 9.90 mg/kg to 11.58 mg/kg with an average of 10.53 mg/kg (Figure 4). The zinc content in the nightshade the content varies from 27.83 mg/kg to 87.69 mg/kg with an average of 55.23 mg/kg and on amaranth from 5.94 mg/kg to 33.73 mg/kg with an average of 22.87 mg/kg. Analyzes point out that all plant speculations have very high levels of zinc and copper. The values obtained show that the concentrations exceed the maximum limits admissible standards required by Codex Alimentarius [9].

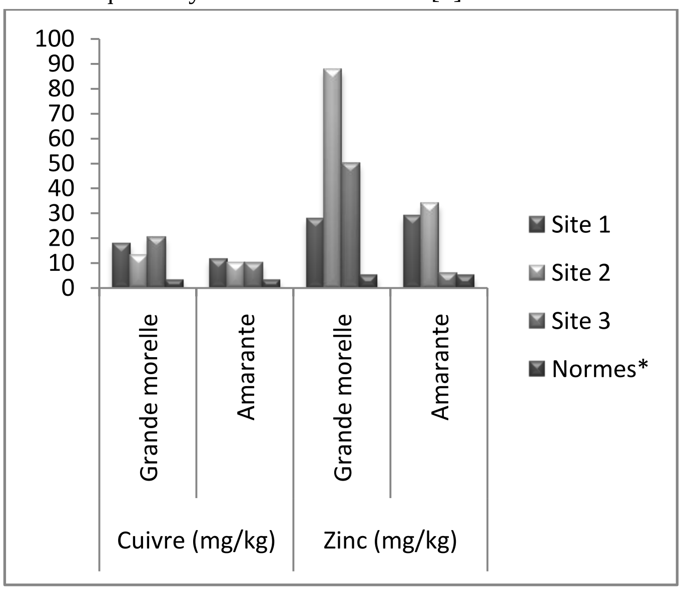

Figure 4: Copper and zinc content in plants

3.4. Bioconcentration factor

To better appreciate how copper and zinc accumulate in water and in soils, we have calculated the bioaccumulation factor which is calculated compared to water and compared to soil (Table 4).

Table 4: Factors of bioconcentration of vegetables with respect to water and soil

		Site 1		Site 2		Site 3	
		GM	**A**	**GM**	**A**	**GM**	**A**
Cu	**FBc Water**	308.50	199.71	1004.62	778.31	1858.73	900.09
	FBc Soil	0.07	0.05	0.31	0.24	0.38	0.18
Zn	**FBc Water**	103.09	107.25	730.73	281.06	418.22	49.51
	FBc Soil	0.33	0.35	1.12	0.43	0.72	0.08

GM: Large nightshade; A: Amaranth

The results obtained show that the factor is higher compared to water than to soil.

4. Discussion

The temperature ranges from 26.3 °C to 26.4 °C. These values are higher than those obtained at the Houéyiho sites which vary between 20.2 ° C and 21.3 °C [10].
Measuring the conductivity makes it possible to assess the quantity of dissolved salts dissolved in the water. The waters of the sites are highly mineralized due to the presence of high contents of cations and anions.

The copper levels in the water at the three sites are below the Canadian Guidelines for sprinkler water. For zinc levels in water, the results are like those of Dahan [11], who obtained very low and undetectable zinc levels in irrigation water at sites in Houéyiho. At pH below 6.5 according to Canadian standards [12], the zinc level should not exceed 1.0 mg/L and for those with a high pH,a limit of 5 mg/L is recommended. In the present work, the content of this element is normal because it varies from 0.12 mg/L to 0.27 mg/L.

For soils, the results of our study show that, on the sites, the pH values are slightly basic. This indicates that the soils are generally basic agricultural soils (alkaline) and will allow good activity of bacteria for the formation of humus. The soils used in vegetable crops are rich in organic matter. Which will allow growth fast plants. The presence of these organic materials could due to animal and vegetable waste decomposition.

The copper contents are above the threshold value of the Canadian Recommendations for the quality of agricultural soil (63 mg/kg). The trace elements contained in the compost, such as copper are essential for the plant. However, at high levels, they become toxic [13]. Zinc contents are above the threshold value of the Canadian Recommendations for the quality of agricultural soil (70 mg / kg). These data are comparable to those collected in the soil of the market garden site of Houéyiho which varied from 42 mg / kg to 185 mg / kg [14].

The soil pollution by these metals can be linked to several factors, the numbers of which, we can list the geographic location of the site and agricultural inputs. The geographical location of the site is revealed to be a factor in bringing metals into the soil since it is in the heart of the city of Cotonou. In large cities, there is a strong automobile traffic and an industrialization which often generate a significant emission of gases highly charged in the air. Thus, metallic elements can be found in the atmosphere at significant rates. There is a correlation between traffic density, industrial activities and the rate of metals in city air [15-17]. Likewise, large quantities of household waste, poultry droppings, pork and cottonseed brought to the soil also constitute a direct source of metal accumulation. The use in raw agriculture of this organic waste increases the risk of soil contamination through the elements it contains such as batteries, iron, cans and other toxic substances etc [18]. This is confirmed by Bagbila [19] and Yé [20] who showed that urban solid waste is polluted by metals and therefore their use as an amendment can lead to increasing pollution of the soil by these metals.

From the above, the soils used in crops in Fidjrossè are contaminated with copper and zinc which are trace elements bioaccumulative by the organism.

The plants showed residual toxicity in metals beyond the standards defined by Codex Alimentarius 3. They all accumulated copper and zinc. These are trace elements necessary for the plant. However, levels beyond the standards become toxic to the plant [21].

Analyzes show that plants have a high level of copper which exceeds the limit accepted by the Codex Alimentarius standard (0.3 mg/kg). Site analyzes show that leafy vegetables contain zinc residues beyond Codex Alimentarius standards (5 mg/kg). With regard to those revealed by Agbossou *et al* [10] in the vegetable crops of Houéyiho, the leafy vegetables of the present study are less contaminated. Eating these zinc-rich vegetables can cause health problems, such as stomach cramps, skin irritations, vomiting, nausea and anemia. Very high levels of zinc can damage the pancreas and disrupt protein metabolism and cause arteriosclerosis. Intensive exposure to zinc chloride can cause respiratory disorders [11]. The presence of metals in the plant is linked to the presence of metals in the soil. Apart from absorption by the soil, we can note the atmospheric fallout where particles are blown away by the wind to settle directly on the surface of the leaves [15]. Referring to the work of Kozlowski *et al* [22] which state that excessive amounts of heavy metals inhibit plant growth and development, we can say that the values obtained are not yet lethal for the plant although they are higher than the norm because the growth data and development records showed good plant growth [22]. So it would be impossible to believe that a well-developed crop is free from contamination. These heavy metal levels, which are not yet lethal for crops, may prove to be a risk to human health by bioaccumulation.

For the plant, nitrogen is the fuel and therefore plays a fundamental role in the constitution of plant matter. It makes proteins so the more nitrogen the plant has, the more protein it has. The nitrogen content found in plants is higher than the norm, therefore nitrogen has a chemical origin; it comes from chemical fertilizers used in large doses by market gardeners.

The presence of metals in plants is explained by the bioaccumulative capacity of leafy vegetables. The calculated bioaccumulation factors helps to evaluate the bioavailability of the metal considered in one of the compartments of the biotope in relation to the organism or plant studied [23]. By comparing the FBc (water) and FBc (soil) in the different metals, it follows that the FBc of copper is higher than that of zinc. It therefore appears that compared to the bioavailability of each of the metals in water and soil, leafy vegetables tend to accumulate relatively much more copper than zinc. The bioaccumulation factor also shows that plants tend to accumulate copper and zinc by water than by soil. The origin of copper and zinc found in plants is therefore irrigation water.

In general, vegetable crops grown in Fidjrossè are contaminated in copper and zinc contained in water. Plants accumulate these metallic elements which are present in water. The bioaccumulation of these metals by vegetables intended for consumption endangers populations because these metallic elements also accumulate in our organism to create degenerations.

5. Conclusion

Analysis of the physico-chemical parameters and trace elements of the soil, plants and irrigation water is essential for determining the risks to the environment and health. The study of the vegetable crops quality of the produced in Benin and specifically atthe Fidjrossè market gardening highlights strong metallic contamination of the finished product. The rates of the various pollution indicator parameters illustrate the risk linked to the use of poor quality irrigation water and compost with a high residual content for soil improvement, in agriculture and mainly in market gardening. This is added to the uncontrolled use of synthetic chemical substances clearly leading to a high toxicity of vegetable crops. It is therefore urgent to control the quality of agricultural inputs used in market gardening as well as the need to set a waiting period before harvesting. Finally, for public health reasons, it is necessary to continuously monitor the garden market products, quality in order to set up a warning and alert system.

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