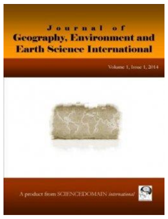

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Determination of Heavy Metal Concentration in Surface Waters of the Western Highlands of Cameroon

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Authors' contributions

This work was carried out in collaboration between all authors. Authors DNT and VMB designed the study, wrote the protocol. Authors VMB, MYCM and DF carried out the laboratory analysis. Authors DNT and VMB managed the literature searches, performed the analysis and wrote the first draft. All authors read and approved the final manuscript.

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ABSTRACT

Heavy metals originating from the use of fertilizers and pesticides are toxic pollutants that limit the beneficial use of water for agricultural, domestic and industrial applications. Three vegetable production basins in the Western Highlands of Cameroon (Bafou, Foumbot and Santa) were surveyed in March 2013, to determine the concentration of heavy metals (Pb, Cd, Cu, Fe, Mn) in

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surface water. A total of 21 surface water samples were collected and transported to the laboratory where heavy metals were analyzed with a flame Atomic Absorption Spectrometer (AAS). Analysis of variance was carried out to show differences in the heavy metal concentrations from the different basins using SPSS. Results showed that surface water was slightly acidic pH (6.2-7.0). Cd, Pb, Fe, Cu and Mn concentrations ranged between 0.002-0.042, 0.016-1.555, 0.001-0.200, 0.026-1.506 and 0.001-0.519 mg/L respectively. Highest mean concentrations of Cd (0.019 mg/L) and Cu (0.122 mg/L) were observed in Foumbot, Fe (0.420 mg/L) and Mn (0.054 mg/L) in Bafou and Pb (0.322) in Santa. Results showed no significant differences (p>0.05) in mean concentrations of Pb, Cu, Fe and Mn in these basins. Concentrations of heavy metals in water were significantly higher (p<0.05) than those of their control. Generally, results revealed that some heavy metals (Pb, Fe and Mn) were higher than WHO permissible limits while Cd was detected above both the World Health Organization and Food and Agriculture Organization of the United Nations safe limits which can pose health risks to the consumers. Consequently, regular monitoring is needed to alert farmers when heavy metal concentration in water is above safe limits.

Keywords: Heavy metals; western highlands; surface waters; vegetables.

1. INTRODUCTION

Heavy metals are metals with high atomic weight and a density much greater (at least 5 times) than that of water. For instance, the specific gravity of As, Cd, Fe, Pb and Hg is 5.7, 8.7, 7.9, 11.3 and 13.5 respectively [1]. There are 35 metals of concern because of their occupational, residential and dietary exposure and 23 environmental pollutants (Sb, As, Bi, Cd, Ce, Cr, Co, Cu, Ga, Ag, Fe, Pb, Mn, Hg, Ni, Pt, Ag, Te, Tl, Sn, U, V and Zn). They are non-degradable, highly toxic and can cause damaging effects even at very low concentrations, accumulate in the food chain, body, stored in soft (kidney) and hard tissues (bone) of human beings. Twelve poisonous heavy metals, such as Pb, Hg, Al, As, Cd, Cr, Cu, Se, Zn, Fe, Mn and Ni exist. They interfere with the enzyme systems and metabolic pathways [1,2].

Heavy metals are priority toxic pollutants that severely limit the beneficial use of water for domestic and industrial application [2]. Their excessive release into the environment and their determination in natural waters is a major concern and important task worldwide. They can enter a water supply by industrial and urban waste or can be released from acidic rain into natural water bodies causing deleterious effects. Land and water pollution with heavy metals includes point sources (emission, effluents and solid discharge from industries) and nonpoint sources (use of pesticides, disposal of industrial and municipal wastes in agriculture and fertilizer applications) [3,4]. Each source of contamination has its own damaging effects to plants, animals and ultimately to human health, but those that add heavy metals to soils and waters are of serious concern [5] because the water is ultimately used for many agricultural practices such as irrigation and mixing of chemicals. The agricultural water containing pesticides and fertilizers supply the water bodies and sediments with huge quantities of heavy metals thus remaining in the environment.

With sufficient surface water infiltration, heavy metals can leach through the soil into underlying groundwater. Heavy metals may be found in the soil, water and sediments. Once these heavy metals are introduced to the environment, they may spread to various environmental components, depending on the nature of interactions occurring in the natural system [6]. Metals can also enter the soil and water where they bind strongly to soil particles and dissolve in water, thus remaining in the environment. Exposure can then occur from drinking contaminated water. Fish, plants and animals take up the heavy metals from their polluted surroundings. Humans are exposed to heavy metal contamination when these animals and plants are eaten [7]. Frequent use of heavy metal contaminated water in agricultural fields gradually enriches the soil with heavy metals leading to soil pollution. Plants take up these heavy metals from the soil through the roots [2].

The uptake of heavy metals by plants results in growth inhibition, structure damage, and a decline of physiological, biochemical activities as well as of the function of plants. Different studies have revealed that the presence of toxic heavy metals like Fe and Pb reduces soil fertility and agricultural output [2,8]. Human health hazards resulting from exposure to heavy metals in water includes: kidney problems, headaches and both cardiovascular and nervous system problems [7]. The toxicity of these metals has also been demonstrated throughout history. Greek and Roman physicians diagnosed symptoms of acute lead poisoning long before toxicology became a science [9]. Learning where these metals can be found and decreasing one's exposure to them is vital to staying healthy and goes a long way in protecting our planet.

Consumers' demand for better quality vegetables is increasing and studies have shown that heavy metals rank high amongst the chief contaminants of vegetables [10,11,8]. These vegetables have greater potential of accumulating heavy metals in their edible parts than grain crops. Contamination of the human food chain is by bioaccumulation in those parts that are directly consumed [12].

Concerns of water pollution within these basins is therefore not limited to potable water criteria but also includes their effects on human health through bioaccumulation in livestock, crops, vegetables and aquatic food. These crops produced in the area are supplied all over the national territory and neighbouring countries such as Gabon and Equatorial Guinea. Therefore, knowledge of the concentrations and distribution of heavy metals and their compounds in various compartments of the environment is a priority for environmental management programs all over the world.

The objective of this study was to determine the concentration of heavy metals in surface waters in the Western Highlands of Cameroon. These concentrations were compared with World Health Organisation (WHO) and Food and Agriculture Organization of the United Nations (FAO) permissible limits for drinking and irrigation.

2. MATERIALS AND METHODS

2.1 The Study Area

Bafou (5°35'N- 5°38'N, 10°03'E -10°05'E), Foumbot (5.45-5.47 °N, 10.07 - 10.08 E) and Santa (5°80' – 5°82'N, 10°17' – 10°18'E) are agrarian environments with high population growth (Fig. 1). Soils are intensively cultivated to meet the increasing demand for food production. The choice of these production basins was based on their intensive agricultural practice precisely vegetables (crops as potatoes, carrots, onions, cabbages, tomatoes and pepper) with the high use of pesticides and fertilizers to improve crop yields. Surface waters in these areas serve purposes of drinking, bathing, irrigation, and household watering with the focus of this study being drinking and irrigation water.

2.2 Sample Collection

In each of the three selected basins, seven sampling sites were identified. Water samples were collected using pre-rinsed plastic containers (washed with detergents, then with distilled water) of 1500 ml by immersing the container to depth between 2 to 3 cm below surface before collection. Immediately after collection, 3 drops of nitric acid were added to each sample to preserve and also prevent precipitation [13]. The samples were labelled and preserved in ice coolers, then transported to the laboratory for analysis. Surface water flowing into the farming areas was collected as control samples. The physical parameter, pH, was measured *in situ* using an electronic pH meter. This instrument was rinsed with distilled water after each measurement. Therefore, a total of 21 surface water samples were collected in March 2013 from the different sampling sites. These water samples were taken to the Laboratory of Soil, Plant, Water and Fertilizer Analyses in the Institute of Agricultural Research for Development in Nkolbisson-Yaounde.

2.3 Experimental Procedure

Before analyses, the water samples were filtered using Whatman number 40 filter papers. Concentrations of Cd, Cu, Pb, Mn and Fe in the filtrate of water samples were detected using the flame Atomic Absorption Spectrophotometer AAS (Model 2380, Perkin Elmer, Inc., Norwalk, CT, USA). The instrument was fitted with a specific column for a particular metal. The instrument was calibrated using standard solutions of the respective heavy metals as well as drift blanks. These solutions were diluted to desired concentrations to calibrate the instrument. Acetylene gas was used as the fuel and air as the support. The coefficients of variation of replicate analysis were determined for different determinations for precision of analysis and variations below 10% were accepted. During analysis, 100 ml of each solution were aspirated into the analyzer for the analysis of the five elements. To confirm the coherence and accuracy of the results, sample analyses were performed in triplicates.

2.4 Statistical Analysis

Analysis of variance (ANOVA) was conducted using the Statistical Package for Social Sciences (SPSS Version 16.2) to check for mean differences ($p < 0.05$) between heavy metals and locations. Differences between the mean concentrations of heavy metals in water samples and reference water samples were conducted with the Student's t-test. The mean concentrations of the heavy metals were compared with the FAO and WHO permissible limits for heavy metals in irrigation and drinking water, respectively.

3. RESULTS

3.1 pH and Heavy Metal Levels in Water from the Western Highlands of Cameroon

Concentrations of the various heavy metals as well as pH values varied at different sites (Table 1). The water samples had an average pH range of 6.3 to 6.8 in the different collection sites with different mean values varied from 6.8 – 6.9 in Santa. In Bafou, overall mean concentrations in the two divisions stood at 0.012, 0.122, 0.004, 0.429 and 0.168 mg/L for Cd, Pb, Cu, Fe and Mn, respectively and concentration range of 0.002-0.04, 0.028-0.212, 0.000-0.017, 0.026-0.506 and 0.004-0.519 mg/L for Cd, Pb, Cu, Fe and Mn, respectively. In Foumbot, there were mean heavy metal concentrations of 0.019, 0.122, 0.041, 0.397 and 0.051 mg/L for Cd, Pb, Cu, Fe and Mn respectively and in the range 0.006-0.041, 0.057-0.211, 0.000-0.200, 0.104-1.324 and 0.001-0.139 mg/L for Cd, Pb, Cu, Fe and Mn respectively. Mean concentrations of the heavy metals were in the order at Fe>Pb>Cu>Cd>Mn.

Overall concentration of Cd ranged from 0.002 to 0.042 mg/L with the highest and lowest concentrations (0.042 and 0.002 mg/L) registered in the Bafou. The mean concentration of Cd also varied in these three areas with the highest mean concentration registered in the Foumbot (0.019 mg/L). However, there were no significant differences ($P=0.692$, df =2) in the concentration of Cd in these three areas.

Overall concentration of Pb ranged from 0.016 to 1.555 mg/L with the highest concentration registered in Santa (1.550 mg/L).However, mean concentration of Pb varied in these three areas with the highest mean concentration recorded in the Bafou (0.283 mg/L) and the lowest in the Santa (0.066 mg/L). Also, no significant differences (df= 2, $P=0.126$) were registered for Pb concentrations in Bafou, Foumbot and Santa.

Mean concentration of Cu varied in these three areas with the highest mean concentration recorded in Foumbot (0.042 mg/L) and the lowest in the Santa (0.002 mg/L).No significant differences (df= 2, $P= 0.181$) existed between Cu concentrations in these localities.

At various points of sample collection, there was a variation in the concentration of Fe metal. Overall concentration ranged from 0.021 to 1.324 mg/L with its highest concentration recorded in Foumbot (1.324 mg/L). However, Bafou and Foumbot recorded high and outstanding levels of Fe contaminants of 1.306 and 1.324 mg/L, respectively. Mean concentrations of Fe varied in the three different areas with the highest mean concentration recorded in Foumbot (0.415 mg/L) and the lowest recorded in the Bafou (0.026 mg/L). There were differences in mean concentrations of these metals but however no significant differences ($P= 0.207$, df =2) were shown.

Manganese being one of the micronutrients also experienced some variation in concentrations. The concentration of Mn in the different points of study varied greatly from one point to the other and from one area to the other. Concentrations ranged from 0.001 to 0.519 mg/L with the highest concentration recorded in the Bafou (0.519 mg/L).

Moreover, the mean concentration of Mn in these areas was not the same but also varied from one area of study to the other with the highest mean concentration recorded in the Bafou (0.168 mg/L) $P=0.068$.

Water pH varied from one site to the other in one area of study and from one site to the other in the different areas of study. However, pH ranged from slightly acidic (6.2) to slightly alkaline (pH=7.2), with the highest pH recorded in Foumbot (pH = 7.3).

3.2 pH and Heavy Metal Levels in Reference Samples

Control samples were collected from streams, springs and rivers leading to farmlands. These surface waters are mostly used for irrigation, mixing of chemicals and drinking. Variation was noticed in heavy metal concentrations as well as pH. Highest pH was recorded in water samples of the Santa (pH = 7.0) and the lowest recorded in the Foumbot (pH = 6.5). Therefore, pH followed the variation Santa>Bafou>Foumbot. Heavy metal concentrations ranged from 0.002 to 0.012, 0.099 to 0.297, 0.008 to 0.017, 0.026 to 0.234 and 0.002 to 0.006 mg/L for Cd, Pb, Cu, Fe and Mn, respectively. Highest concentration of Cd was recorded in the Santa (0.012 mg/L). Bafou recorded highest concentrations of Cu (0.017 mg/L) and Mn (0.006 mg/L) while the Foumbot recorded highest concentrations of Pb (0.297 mg/L) and Fe (0.234 mg/L). Most of the metal concentrations except Cd and Pb were below recommended safe limits for drinking by WHO and irrigation by FAO (Table 2).

4. DISCUSSION

4.1 pH and Heavy Metal Levels in Surface Waters

Results indicated the presence of heavy metals in surface waters with Cd, Pb, Fe and Mn present in all 21 water samples and Cu present in 14 water samples. Low levels of some heavy metals in this study may be due to dilution, from the influence of water waves in their surface waters and rainfall but the continuous use of these heavy metal polluted water for irrigation results into accumulation of heavy metals into the soil [13]. These heavy metals will bio accumulates and persist in the environment thereby increasing in concentrations that will subsequently be above the safe limits for irrigation [14]. Also, observed pH ranged from slightly acidic (pH =6.8) for the Santa through the Foumbot to slightly alkaline for the Bafou transects. These average pH values however were within recognized World Health Organisation [15] permissible limits for drinking and Food and Agricultural Organisations [16] permissible limits for irrigation. No significant differences were observed between the various pH values in Foumbot, Santa and Bafou.

Foumbot recorded the highest average concentrations (mg/L) of Cd (0.019), Cu (0.122) while the Bafou transect recorded highest average concentrations (mg/L) of Fe (0.420) and Mn (0.054) and the highest average concentration of Pb (0.322) was recorded in Santa. Therefore highest mean concentrations of heavy metals in these three areas therefore followed the trend Foumbot>Bafou>Santa. The existence of a positive significant correlation between Cd and Pb, Mn and Cu indicated that pollution of these surface waters with these metals was from the same source. No significant differences were observed between the various heavy metals from the various areas. No significant differences (P>0.005) were recorded between the heavy metal concentrations in the different parts of the Western Highlands. This can be justified by the fact that the same agricultural practices are carried out and agricultural chemicals are the main sources of heavy metal pollution. Implementation of Good Agricultural Practices (GAP) is needed to ensure a sustainable management of fertilizers and pesticides throughout the Western Highlands.

4.2 pH and Heavy Metal Levels in Control Samples

There were significant differences (p>0.05) between the heavy metals in these areas compared to those around intensive agricultural activities. The concentrations of heavy metals in surface water representative samples were significantly higher than those in reference water samples. In reference or control samples, most of the heavy metal concentrations were below the safe limits except metal, Pb, had level greater than safe limits for drinking. This therefore can be attributed to the fact that there were little or no agricultural activities around these areas of control. Cd concentrations on the other hand exceeded the advocated limits for drinking and irrigation in the Santa. However, sequences indicated that heavy metal content of surface waters were higher than in reference samples with little or no agricultural activities around. Heavy metal contents in waters around agricultural zones are as a result of farm irrigation with heavy metal polluted water and also as a result of seepage from crops sprayed with pesticides and chemical fertilizers [17]. Use of heavy metal contaminated water for irrigation leads to accumulation of large quantities in soils which persist for an indefinite period and are later on taken up by plants. ANOVA showed that concentrations of individual heavy metals in the surface waters were significantly higher than in reference samples indicates that agricultural activities increased the heavy metal content in water.

Table 1. pH and heavy metal levels in surface waters in Western Highland of Cameroon

Basin	pH	Concentration of metals (mg/L)				
		Cd	Pb	Cu	Fe	Mn
Foumbot	6.400±0.402	0.019±0.013	0.122±0.013	0.041±0.079	0.397±0.0466	0.051±0.047
Santa	6.800±0.231	0.012±0.008	0.322±0.062	0.012±0.015	0.147±0.481	0.024±0.037
Bafou	6.500±0.241	0.012±0.150	0.122±0.605	0.004±0.007	0.429±0.230	0.168±0.229
Mean	6.570±0.291	0.014±0.570	0.189±0.227	0.019±0.037	0.324±0.183	0.081±0.104

Table 2. pH and heavy metal levels in reference samples

Area	pH	Concentration of metals (mg/L)				
		Cd	Pb	Cu	Fe	Mn
Santa	7.0	0.012±0.020	0.099±0.001	0.008±0.002	0.177±0.001	0.003±0.001
Bafou	6.8	0.002±0.012	0.283±0.002	0.017±0.001	0.026±0.001	0.006±0.002
Foumbot	6.5	0.002±0.005	0.297±0.001	0.003±0.001	0.234±0.002	0.002±0.002
FAO (1975) safe limits for irrigation	-	0.01	5.0	0.2	5.0	0.2
WHO(1999) safe limits for drinking	-	0.01	0.05	0.05	0.3	0.1

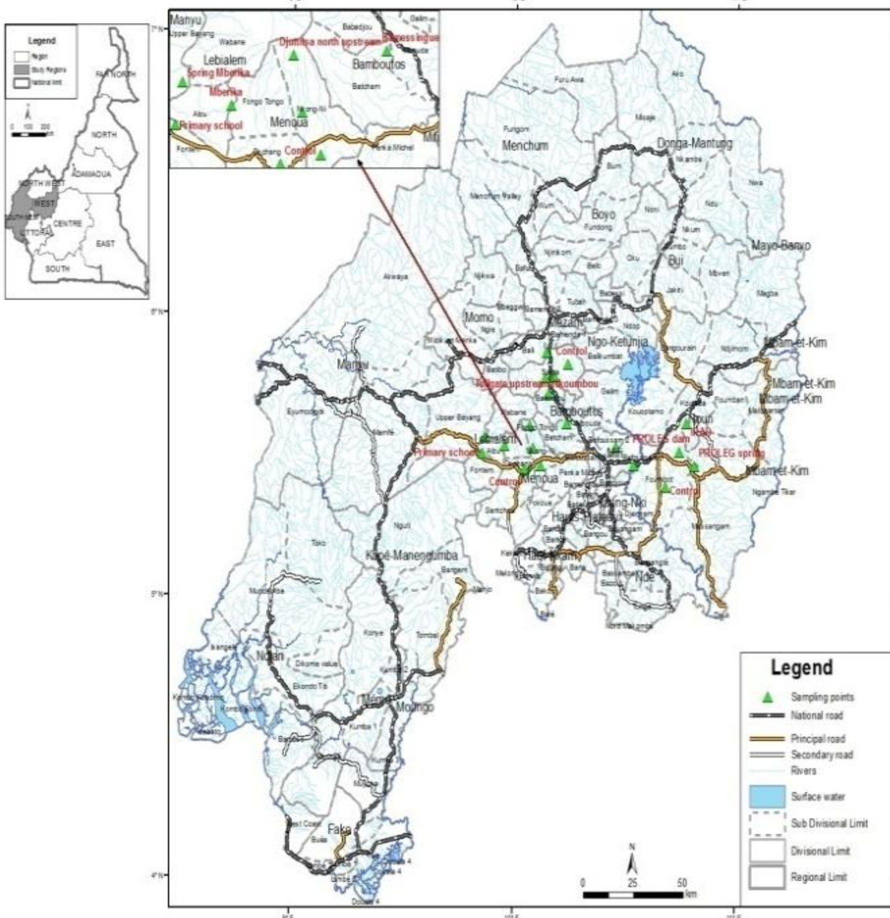

Fig. 1. Map of study area

5. CONCLUSIONS AND RECOMMENDATIONS

Surface water was slightly acidic pH (6.2-7.0). Cd, Pb, Fe, Cu and Mn concentrations ranged between 0.002-0.042, 0.016-1.555, 0.001-0.200, 0.026-1.506 and 0.001-0.519 mg/L respectively. Highest mean concentrations of Cd (0.019 mg/L) and Cu (0.122 mg/L) were observed in Foumbot, Fe (0.420 mg/L) and Mn (0.054 mg/L) in Bafou and Pb (0.322) in Santa. Results showed no significant differences ($p>0.05$) in mean concentrations of Pb, Cu, Fe and Mn in these basins. Concentrations of heavy metals in water were significantly higher ($p<0.05$) than those of their control. Generally, results revealed that some heavy metals (Pb, Fe and Mn) were higher than WHO permissible limits while Cd was detected above both the WHO and FAO safe limits which can pose health risks to the consumers. Concentration of heavy metals in reference samples were lower compared to those at agricultural sites.

The data obtained in this study would present a baseline for the planners, health authorities, scientists and consumers to adopt appropriate remedial measures. Regular monitoring of the ecosystem is suggested to alert vegetable growers on heavy metal accumulation in water.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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