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Evaluation of the bioaccumulation of mercury (Hg) and fluorine (F) in garden produce in south Benin

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ABSTRACT

Objectives: The richness of the soils in metallic trace elements (MTEs) and Fluorine, which are potentially toxic elements, makes it necessary to pay attention to the risks of transfer of these elements to the food chain. The aim of this study is to evaluate the content of mercury and fluorine in soils, irrigation water and market garden products in South Benin.

Methodology and Results: A total of 21 composite soil samples (0-20cm), 21 samples of irrigation water per growing area and 87 plant samples were collected. After sampling under aseptic conditions, they were sent for analysis in laboratories. The Excel spreadsheet calculated the contents and the GraphPad Prism 8.0 calculated the averages and tests of two ways. Before determining the bioaccumulation, the contents were compared to the minimum concentration referenced by international standards. All matrices were contaminated with mercury and fluorine. The minimum reference concentration (0.55mg/Kg) was higher than the average levels of the study soils in Mercury (0.11±0.1. 10^{-2} to 0.164±0.345 .10^{-3} mg/Kg) and in Fluorine (8.123±1.772 to 23.5±1.126mg/Kg). Mercury and Fluorine levels in site irrigation water were below the standards. The levels of mercury (0.46 .10-3 ±0.13 .10^{-4} to 0.001±0.38. 10^{-4} mg/L) and fluorine (0.15±0.07 to 2.17±0.41mg/L) in the irrigation water of the sites are lower than the standards, except for the Houéyiho borehole. In leaves such as amaranth, there was a very significant difference ($0.001 < p < 0.01$) at Sème-kpodji and Grand-popo. Amaranth is a leaf that is in direct contact with the chemicals used in the environment and could absorb mercury. Fluorine levels exceed the maximum recommended concentration (0.05 mg/Kg) so the vegetables are polluted with fluorine.

Conclusion and application of results: In Houéyiho, a medium bioaccumulation in amaranths and carrots was observed while in chili peppers bioaccumulation was low. On the other hand, in Sèmè-kpodji and Grand-popo, a low bioaccumulation of mercury in all the vegetables was observed. Fluorine bioaccumulation is medium in amaranth and carrot at Houéyiho and Sèmè-kpodji and low in chilli peppers at both sites. While bioaccumulation is low in vegetables produced at the Grand-popo site.

Key words: bioaccumulation, soil contamination, vegetable contamination, mercury, fluorine, MRC, Benin

INTRODUCTION

In Benin's coastal cities, urban and peri-urban vegetable production plays a major role in supplying households with fruit and vegetables. It provides the populations of the cities of Cotonou, Sèmè-kpodji, Grand-Popo and surrounding areas with 64% of annual consumption for certain vegetables (Adorgloh-Hessou, 2006; Adifon *et al.,* 2015). Among the vegetables grown in these zones, amaranth, chilli pepper and carrot are the most cultivated in terms of area by market gardeners (Ouikoun *et al.,* 2019). The parasitic pressure associated with the decrease in soil fertility leads market gardeners to use mineral fertilizers and synthetic phytosanitary products in an abusive or inappropriate way with ecological problems through the risks of contamination of water, market garden products and soil by pesticide residues and metallic trace elements. (Adriano, 2001). Soil contamination presents a risk of toxicity for living beings and man through the food chain. Consequently, the establishment of crops is difficult or even impossible, depending on the degree of pollution, but also risky due to the accumulation of contaminants in the plant and its transfer in the food chain (Bourrelier & Berthelin, 1998; Mench & Baize, 2004). Some research work has been carried out in recent years in Benin in order to know the level of contamination of the components of the environment including the soil, consumer products, drinking water, in the face of environmental and toxicological risks and public health concerns associated with organic and inorganic pollutants, especially heavy metals. Mercury is identified as a toxic element, and more particularly nephrotoxic (acting on the kidneys) and neurotoxic. Therefore, the general objective of this study is to evaluate the bioaccumulation of mercury and fluorine in vegetable products.

MATERIALS AND METHODS

Study area: The study area is part of the geomorphological complex of the coastal area of South Benin, which is a very complex area due to the diversity and dynamism of the elements it associates: the sea, lagoons, lakes, swamps and coastal cordons. This study was conducted in three Districts of south of Benin republic (Figure 1) namely *Sèmè-kpodji* in the Ouémé department, *Cotonou* in the Littoral department and *Grand-popo* in the Mono department. The choice of these Districts was based on the importance according to market gardening and the importance of activities contributing to the contamination the market gardening sites.

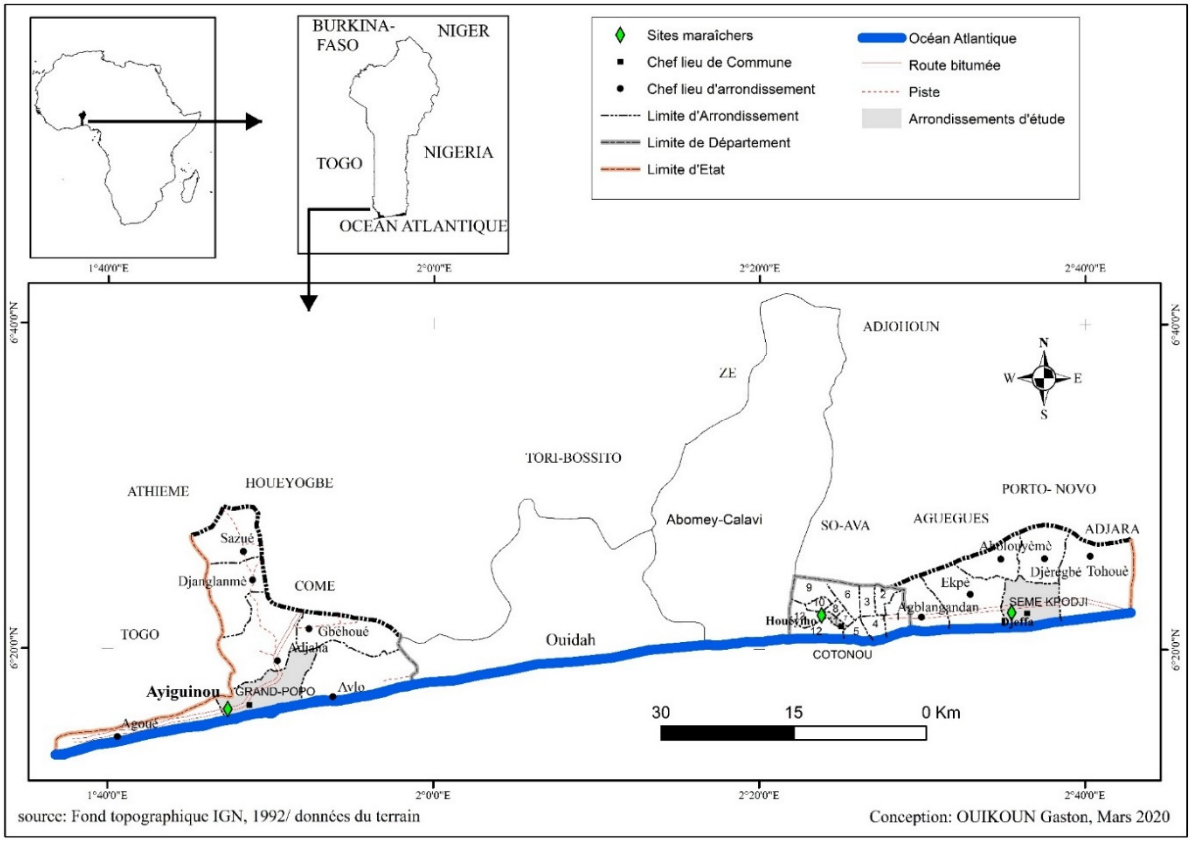

Figure 1: Map showing the study sites.

Simply Methods: The soils (0-20cm), vegetables such as amaranth, chilli pepper and carrot and then the irrigation water were sampled. A total of 21 composite soil samples were taken from three market gardening sites according to the AFNOR X 31 - 100 standard for soils, 21 samples of irrigation water per growing area were taken under aseptic conditions from three study sites (about 1.5 L) for irrigation water and 87 plant samples were taken from the study sites. The Houéyiho site is divided into nine plots, the Sèmè-kpodji site is divided into six plots and Grand-popo is divided into 6 plots via the Cotonou-Lomé Inter-State road. On each plot, the three matrices were sampled. After sampling under aseptic conditions, they were sent for analysis in the laboratories. The solubilisation method is used to mineralize soils and vegetables according to the NF ISO 11466: 1995 standard (aqua regia method). It is carried out in closed and hot (150°C) environment. The mineralization of all samples was carried out at the Laboratory of Soil, Water and Environmental Sciences (LSSEE) of the National Institute of Agricultural Research of Benin and then the Laboratory of Management, Treatment and Valorization of Waste (GTVD) of the Faculty of Sciences of the University of Lomé was used for the analysis of MTEs in irrigation water, soil and vegetables. Mercury determinations were made using the Atomic Absorption Spectrometer (AAS) coupled with a thermo scientific VP100 flameless cold vapour emitter. The SPADNS method is used for the determination of fluorine is based on the reaction of fluorine with zirconium red. Before determining the level of bioaccumulation, a comparison was done with the minimum concentration referenced by international standards. The Excel spreadsheet to calculate the contents and the Graph Pad Prism 8 software to calculate the averages and tests of two ways comparison.

RESULTS AND DISCUSSION

Mercury (Hg) and fluorine (F) content in soils: The table 1 shows the results of the assessment of mercury and fluorine contents at the study sites and that the soils are contaminated. The maximum reference concentration is higher than the average soil mercury and fluorine contents. These results confirm those of Koumolou *et al.* (2009). The pH values at all sites ranged from 5.60 to 7.25 and the percentage of organic matter was less than 3%. It can be concluded that the soils of the sites are polluted with mercury. Given that the sites are the rubbish dumps for all kinds of garbage and the reckless use of pesticides by the producers, it can be concluded that mercury comes from the waste deposited on the sites, so these results confirm the results of Alkaa *et al.* (2012) and Has-Schon *et al.* (2008). It can be said that the pollution of a soil does not depend on its physical form nor its limitation of the always-animated roads. Thus, the study soils are not polluted with mercury or fluorine..

Table 1: Mercury (Hg) and fluorine (F) content in soils

Sites	Soils (0 – 20cm)	
	Hg (mg /Kg)	F (mg/Kg)
HOUEYIHO	0.132± 0.010	23.5± 1.13
SEME KPODJI	$0.119 \pm 0.1.\ 10^{-2}$	8.123± 1.77
GRAND POPO	$0.164 \pm 0.345.10^{-3}$	15.06± 1.44
MRC*	0.55 mg/Kg (1)	700 mg/Kg (2)

*Maximum Recommended Concentration

Content of chemical elements in irrigation water: The table 2 shows the average concentrations of mercury and fluoride in irrigation water. The irrigation water is contaminated with mercury and fluoride. Mercury and fluorine levels in the irrigation water at the sites are below the standards except for the Houéyiho borehole. The contamination of Houéyiho's irrigation water could be expressed by the filtration of Cotonou city garbage dumped on the site and that the soil has a very low retention capacity and therefore filtration in the water table.

Table 2: Mercury (Hg) and fluorine (F) content in irrigation water

Sites	**Mercury (mg/L)**	**Fluorine (mg/L)**
Boring water		
HOUEYIHO	$0.784\ .10^{-3} \pm 0.56\ .10^{-4}$	2.170 ± 0.410
SEME KPODJI	$0.001 \pm 0.38.\ 10^{-4}$	0.313 ± 0.040
GRAND POPO	$0.46.\ 10^{-3} \pm 0.13.\ 10^{-4}$	0.150 ± 0.070
Swamp water		
HOUEHIYO	$0.88.\ 10^{-3} \pm 0.28.\ 10^{-4}$	0.577 ± 0.067
MRC*	**1**. 10^{-3} **mg/L**	**1.5 mg/L**

*Maximum Recommended Concentration

Mercury and Fluorine contents in market garden products intended for consumption

Mercury content. : The table 3 shows the mercury levels in vegetables produced by market gardeners for consumption. Vegetables are contaminated with mercury at the production sites but the levels are below the standard. In the row of leaves such as amaranth, noticed a very significant difference ($0.001 < p < 0.01$) in Sème-kpodji and Grand-popo. These sites are close to inter-state voices that come alive in the days and not fenced. Amaranth is a leaf that is in direct contact with the chemicals used; could absorb mercury so this may confirm an elevation of mercury in the leaves. According to Bourrelier and Berthelin (1998), trace elements such as mercury can be absorbed directly by the aerial parts; they would follow the same foliar penetration routes as nutrients (N, P) by the ectoderms of the cuticle.

Table 3: Mercury content in plants at the study site level

Sites	Mercury (mg/Kg)		
	Amaranth	Carrot	Chilli pepper
HOUEYIHO	$0.2.10^{-2}$± $0.86.10^{-3}$	$0.7.\ 10^{-3}$± $0.31.\ 10^{-3}$	$0.1.\ 10^{-2}$± 0.00
SEME KPODJI	$0.3.10^{-2}$± $0.2.10^{-3}$**	$0.30.\ 10^{-3}$± 0.00	$0.39.10^{-3}$± $0.105.10^{-3}$
GRAND-POPO	$0.04.10^{-3}$±$0.03.\ 10^{-3}$	$0.7.\ 10^{-3}$± $0.35.\ 10^{-3}$	$0.1.\ 10^{-2}$± $0.1.\ 10^{-2}$
MRC*	0.03	0.03	0.03

Each value represents the average obtained from the plot data. * Maximum Recommended Concentration according to Michel Mench & Denis Baize, (2004). $0.001 < p < 0.01$: Amaranth Sème-kpodji vs Grand-popo Fluorine content

Fluorine content: The table 4 shows the fluorine levels in plants that are contaminated with Fluorine. Fluorine levels exceed the maximum recommended concentration (0.05 mg/Kg) so the vegetables are contaminated with Fluorine. An inter-site comparison reveals that the average total fluorine content in vegetables is lower at the grand-Popo level than at the other sites. A comparison between vegetables (at Houéyiho and Sèmè-kpodji), shows that the average total fluorine content in carrots (respectively 3.1 and 2.55 mg/Kg) exceeds that of amaranth (respectively 2.28 and 1.09 mg/Kg) and chilli pepper (respectively 1.78 and 0.96 mg/Kg).

Table 4: Fluorine content in plants at the study site level

Sites	Fluorine (mg/Kg)		
	Amaranth	Carrot	Chilli Pepper
HOUEYIHO	2.28± 1.593	3.097± 0.985	1.783±0.22
SEME KPODJI	1.097± 0.23	2.553± 0.512	0.967± 0.203
GRAND-POPO	1.03± 0.62	0.38± 0.05	0.2±0.00
MRC*		0.05 mg/kg	

Each value represents the average obtained from the plot data. * Maximum Recommended Concentration according to the Ordinance of the Federal Department of Home Affairs (FDHA, 2015)

Bioconcentration of Mercury: Table 5 shows the results of the bioconcentration of Mercury in vegetable products from the different sites. In Houéyiho, observed a medium bioaccumulation in the amaranths and carrots while in the chilli peppers is low. On the other hand, in Sèmè-kpodji and Grand-popo, we observed a low bioaccumulation in all vegetables. These results show that the production soils are not polluted.

Table 5: Bioconcentration of Mercury

	Bioconcentration factor (FBC) of Mercury		
Sites	Amaranth	Carrot	Chilli Pepper
HOUEYIHO	0.29± 0.013	0.016± 0.004	0.195± 0.015
SEME-KPODJI	0.028± 0.002	0.003±0.0	0.002±0.0
GRAND-POPO	0.01± 0.00	0.025± 0.015	0.013± 0.003

The table 6 shows the results of the bioconcentration of Fluorine in vegetable products from the different sites. Bioaccumulation is medium in amaranth and carrot at Houéyiho and Sème-kpodji and low in chilli peppers at both sites. While bioaccumulation is low in vegetables produced in the Grand-popo site.

Table 6: Bioconcentration of Fluorine

	Fluorine Bioconcentration Factor		
Sites	Amaranth	Carrot	Chilli Pepper
HOUEYIHO	0.77± 0.033	0.083± 0.037	0.214± 0.057
SEME-KPODJI	0.167± 0.094	0.097± 0.027	0.268± 0.088
GRAND-POPO	0.075± 0.045	0.028± 0.003	0.04± 0.00

CONCLUSION

Based on the results of this study, it is clear that all soils are contaminated with mercury and fluorine. In Houéyiho, we noticed pollution in the water used for irrigation in fluorine. The site of Sème-kpodji accumulates more mercury in the moorings. All the vegetables of the three are very polluted in fluorine. Therefore, the bioaccumulation depends on the content of the matrixes, especially in vegetables. In addition, regular monitoring of VTEs in environmental matrices, particularly in soil, water and vegetables should be implemented to avoid excessive accumulation of mercury and fluorine in the food chain.

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