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EVALUATION OF THE CONTENTS OF TRACED METAL ELEMENTS (LEAD, CADMIUM AND MERCURY) OF PEPPER (CAPSICUM SPP) AND PEPPER (PIPER NIGRUM) FROM THE MARKETS (YOPOUGON, ADJAME AND PORT-BOUET) OF ABIDJAN (COTE D'IVOIRE).

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ABSTRACT
Spices are present in human food daily as flavor enhancers and sources of biochemical compounds with beneficial effects on health. Given the unprecedented involvement of spices in food, the sanitary quality of this category of food is a paramount parameter for the health of consumers. This work intends to assess the lead, cadmium and mercury contents of dried chilli and pepper marketed in Abidjan. Samples of dried peppers and peppers were collected in the communes of Adjamé, Port-Bouët and Yopougon of the district of Abidjan. These samples were digested with nitric acid (HNO_3) sulfuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2), then the metal contents were determined by atomic absorption spectrometry. These average metallic contents of the two foodstuffs were from 1.36 mg / kg to 1.42 mg / kg of mercury; 0.79 mg / kg to 1.03 mg / kg of lead; 0.13 mg / kg to 0.18 mg / kg of cadmium. In addition, the values for lead and cadmium were well above the tolerance thresholds established by the European Commission and the Codex Alimentarius (lead: 0.3 mg / kg; cadmium: 0.2 mg / kg). For mercury, we referred to the limit of quantification of 0.157 mg / kg.

KEYWORDS: MTE, contamination, spices, chilli, pepper.

INTRODUCTION
Spices are actively involved in the human diet due to their beneficial effects on health. The value of these plants for food is recognized around the world.[1,2] Chili and pepper are popular all over the world. They are essential in African dishes, in particular in Ivorian dishes such as "*kédjénou*" and "*biokesseu*" which are very spicy soups.[3] The chilli can be eaten fresh in the "*garba*" directly, in fries, in sauce or canned. In the dehydrated state, these spices are also used in powder form and are used in seasoning dishes, braised meats, braised fish.[4] The production of spices and more precisely that of peppers and peppers played an important part in agricultural activity in Ivory Coast.[5]

However, this major activity is now facing enormous difficulties, including land tenure insecurity, access to agricultural inputs and the lack of specialized technical supervision. In addition, there is the problem of pollution due to the proximity of the production sites to major urban and industrial traffic axes, the use of wastewater for irrigation of plants and the fertility of market garden soils with poultry manure. Among the undesirable elements in poultry manure and wastewater are trace metal elements including Cadmium (Cd), Lead (Pb) and Mercury (Hg) which are hazardous to health.[6] Indeed, metallic trace elements (MTE), as well as persistent organic compounds (Dioxins, Polychlorobiphenyls, Polybromodi phenylethers) represent a group of toxic substances important for plants as well as for humans and animals.[7] The threat to the environment, especially urban, by MTE is accentuated by the presence of fine dry atmospheric particles deposited by the wind or which fall to the ground in wet form during rains. The aim of this present work is

therefore to assess the level of contamination of spices (chilli and pepper) in the markets (Yopougon, Adjamé and Port-bouët) of Abidjan by MTE.

EQUIPMENT

Plant material

The plant material consists of dried chilli and pepper, shown in Figs. 1 and 2. These spices were purchased in the markets of Yopougon, Adjamé and Port-Bouët in the district of Abidjan in Ivory Coast.

Fig. 1: Dry pepper

Fig. 2: Dry chilli.

METHODS

Sampling

A sampling plan and sampling missions were carried out. The sampling plan was based on.[8]

The samples of dried chilli (*Capsicum*) and pepper (*Piper nigrum*) were purchased in the markets of Yopougon, Adjamé and Port-Bouët in the district of Abidjan. The composite sample obtained is made up of a mixture of several sub-samples of the same spice taken from different places so that the sampling is representative of the environment. The samples were then each conditioned in a sachet (Stomacher), then placed in an adiabatic chamber and transported to the laboratory, for the determination of their content of metallic trace elements. Once in the laboratory, the different samples are ground using a blender before storage.

Sample digestion

The digestion of the samples was carried out at the Central Laboratory for Food Hygiene and Agro-Industry (LCHAI) according to AOAC methods. For the determination of lead and cadmium, the[9] was used. As for mercury, the[10] which was adopted. These different methods have been adapted to laboratory conditions in order to optimize the results. For mineralization, a test sample of 0.5 g of the ground material was introduced into a Teflon tube under a hood, then 5 ml of nitric acid and 2 ml of hydrogen peroxide were added thereto. After 5 min of reaction in the hood, the tubes were brought to 200 ° C using a microwave oven (ETHOS Milestone) for 45 min. After this time, the mineralized material was collected in a 25 ml flask and then made up to the mark with double-distilled water.

Quantification of metallic trace elements

After the mineralization carried out for cadmium and lead, a test portion of 10 ml was taken. For mercury, the,[10] was applied. After bromination, the assay was carried out by atomic fluorescence after formation of cold vapors in the presence of stannous chloride. The MTEs were determined using an atomic absorption spectrophotometer (SPECTRA AA110) previously calibrated at 5 points for each MTE. This spectrophotometer was calibrated in cold vapor mode using a hydride generator (VGA 77) during the determination of mercury. The device's background noise was corrected using a deuterium lamp. The tests were taken in triplicate with a measurement time of four seconds, the value retained being the average of the three measurements. For each run of analysis, a digestion blank and a reference sample of known concentration were analyzed to ensure the quality of the results.

The metal contents are obtained from computer processing of the measurements using the incorporated control software. Then they are expressed mg / L. The metal contents of the samples in mg / kg were calculated from the relation (1):

$$C_m = ((Cl\text{-}Cb)f)/ M \quad (1)$$

C_m: Concentration in parts per million (mg / kg); Cl: Concentration given by the device (mg / L) ; Cb : White concentration (mg / L);
F: Dilution factor;
M: Mass of mineralized matrix (g).

Assessment of the contamination level of samples

To assess the level of contamination of peppers and peppers, the average metal contents are compared with each other first, then secondly against official standards of the European Union (EU).[11] and,[12] the maximum residue limits (MRLs) for lead and cadmium in edible peppers and peppers, are respectively 0.3 mg / kg and 0.2 mg / kg. As for mercury, the tolerance threshold was not established for spices, the values obtained were compared with the Limit of Quantification (LQ) which was 0.157 mg / kg.

Statistical analysis

For statistical analysis, Excel software was used to determine the mean contents and standard deviations of each sample.

RESULTS

Average content of metallic trace elements

The results obtained indicate that the metallic trace elements (Pb, Cd and Hg) are present in both types of spices (peppers and peppers), and this at various concentrations. These average MTE contents are shown in Tab. 1.

Table 1: Assessment of the level of contamination of peppers by MTE.

Matrices	Areas	Metallic trace elements (mg / Kg)		
		Pb	Cd	Hg
Chilli	Adjamé	1,004 ± 0,122	0,138 ± 0,215	1,412 ± 0,057
	Yopougon	1,0297 ± 0,136	0,139 ± 0,019	1,417 ± 0,059
	Port-Bouët	0,788 ± 0,02	0,179 ± 0,028	1,365 ± 0,084
Pepper	Adjamé	1,003 ± 0,35	0,136 ± 0,016	1,390 ± 0,047
	Yopougon	0,825 ± 0, 041	0,125 ± 0,008	1,377 ± 0,037
	Port-Bouët	0,788 ± 0,020	0,145 ± 0,019	1,417 ± 0,041
Standard		0,3	0,2	0,157

Assessment of the level of contamination of peppers by MTE Lead

All of the results obtained from the analysis of the average Pb contents are shown in the figure below.

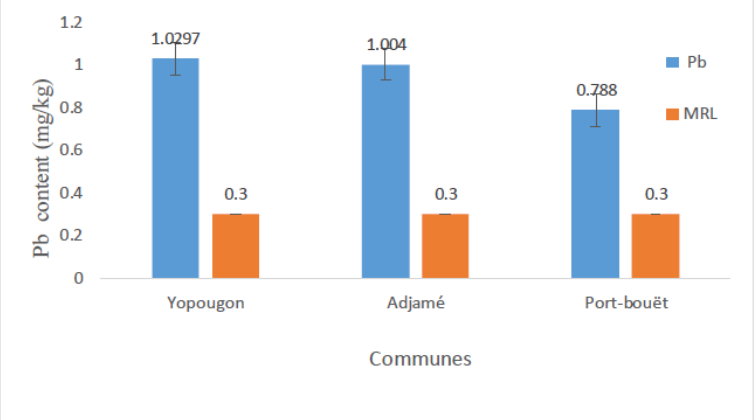

Fig. 1: Comparison of lead contents to the MRL.

The results show that Yopougon peppers contain more lead (1.029 ± 0.136) mg / kg than those of Adjamé (1.004 ± 0.122) mg / kg and Port-Bouët (0.788 ± 0.02) mg / kg. Whatever the study area, the lead content is well above the maximum residue limit (MRL).

Cadmium

Fig. 2 represents the variation of the Cd content according to the municipality. As a result, Port-Bouët peppers contain more Cd compared to Adjamé and Yopougon. However, the Cd concentrations are below the MRL threshold (0.2 mg / kg).

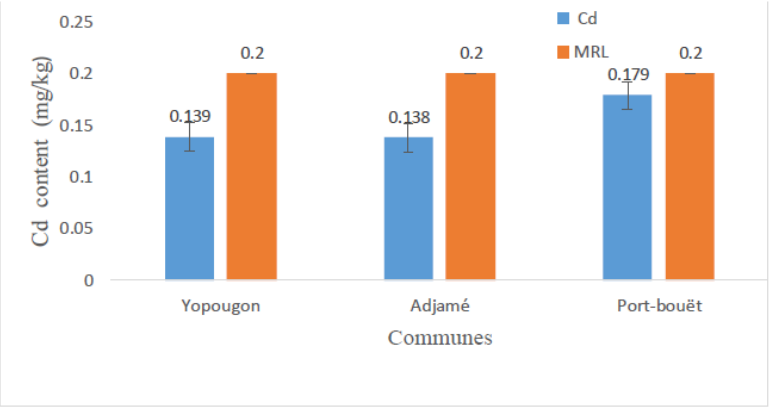

Fig. 2: Comparison of Cadmium levels to the MRL.

Fig. 3 represents the mercury content in the three municipalities compared to the recommended limit.

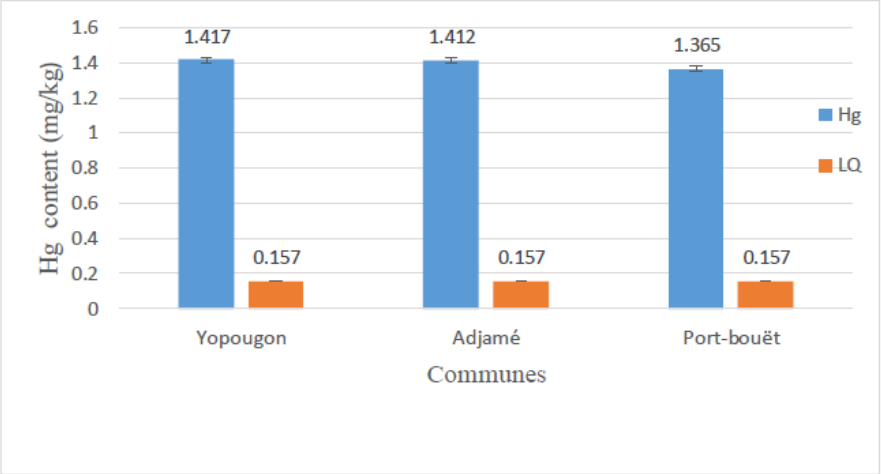

Fig. 3: Comparison of Hg contents to the Limit of Quantification (LQ).

Evaluation of the level of contamination of pepper by MTE

Tab. 1 is the summary of the average of the metallic trace elements studied, namely Pb, Cd and Hg in pepper from the Adjamé, Yopougon and Port-Bouët markets. The values of metals vary from one municipality to another. We used each metal's MRL to discuss these values.

Lead

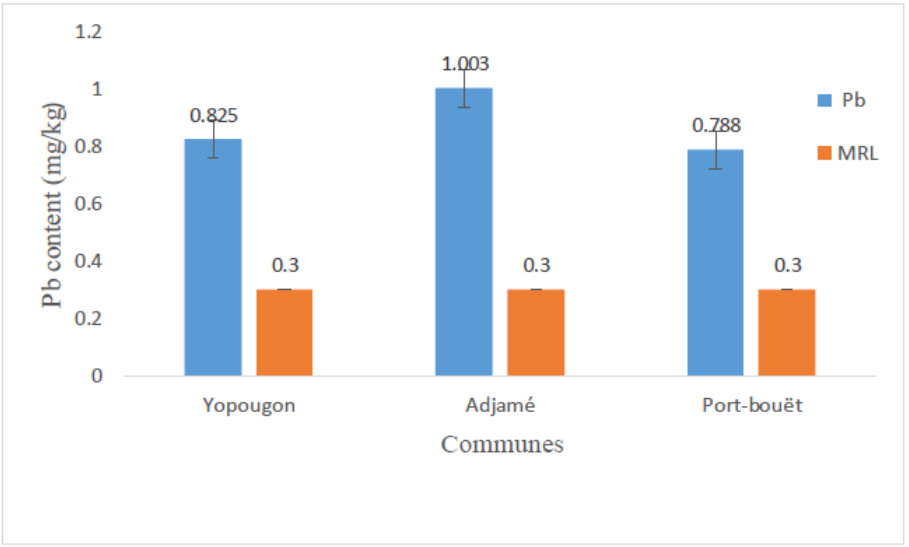

Fig. 4: Comparison of Pb contents to the MRL.

From Fig. 4, the Pb values in the pepper samples from the three municipalities show a minimum recorded in the municipality of Port-Bouët with a value of 0.788 mg / Kg and a maximum in the municipality of Adjamé with 1.003 mg / kg of value. These values are well above the fixed limit.

Cadmium

Fig. 5 shows us the variation of the Cd content in peppers taken from the markets compared to the MRL. The average Cd levels recorded are below the MRL. The average Cd concentrations in the pepper samples range from 0.125 to 0.145 mg / kg. The highest Cd contents in pepper were detected in the town of Port-Bouët with a value of 0.145 mg / kg. However, this content remains below the MRL.

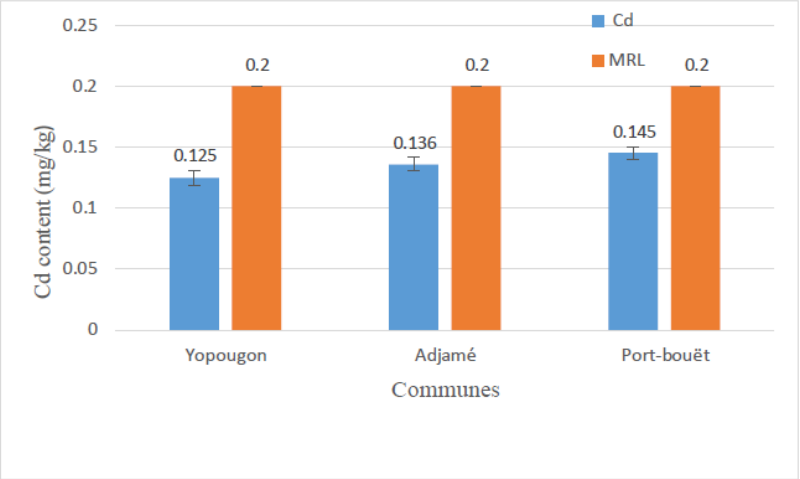

Fig. 5: Comparison of Cd contents to the MRL.

Mercury

The average mercury contents in pepper are shown on Fg. 6 compared to the MRL. These contents are very high compared to the Limit of Quantification (LQ).

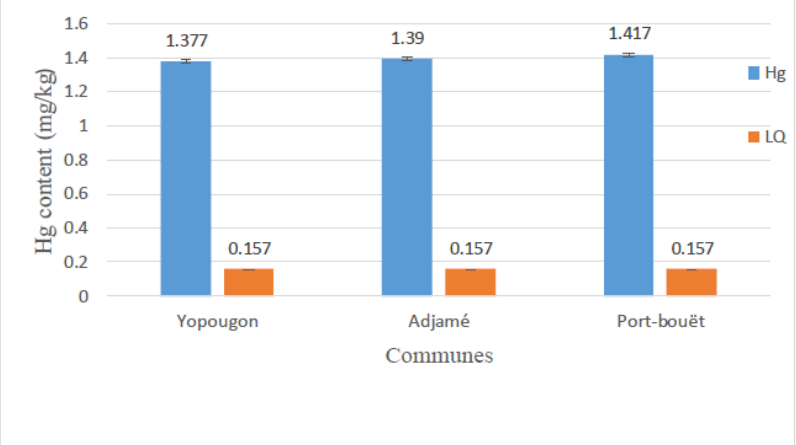

Fig. 6: Comparison of Hg contents to LQ.

DISCUSSION

The results of this study clearly show that the metallic trace elements studied are present in the different matrices. 180 samples analyzed, ie 90 samples of peppers and 90 samples of peppers show TME contents. Thus, the most accumulated metal remains Hg followed by Pb and Cd. Mercury is present in all samples where its maximum and minimum concentrations are respectively 1.58 mg / kg and 1.30 mg / kg recorded on the pepper from the market in the town of Port-Bouët for an average value of 1.396 mg / kg. In all these samples analyzed, the Hg has levels above the limit of quantification which is 0.157 mg / kg. These values remain higher than the Hg data obtained by,[7] in mackerel (0.048 mg / kg) in the region of Sidi Ifni in Morocco. This contamination can find its source in the establishment of hydroelectric complexes, human activities, the combustion of fossil products, mining which produce and release particles of mercury into the environment. Mercury is used for several purposes and as a constituent of several products: batteries, thermometers, barometers, dental amalgam, paints, dyes, switches, thermostats, fungicides, vaccines, and it is still used in some research laboratories.[13]

Pb is omnipresent in both matrices with average concentrations of Pb detected in chillies and peppers which are respectively 1.0297 mg / kg on the Yopougon market and 1.003 mg / kg on the Adjamé market. This is explained on the one hand by the fact that these metals are originally present in the earth's crust,[14] including the soil; and on the other hand by human activities. We can state in our study that the origin of the contamination of these spices is mainly due to the fallout of air particles and water. Lead is an environmental contaminant mainly resulting from emissions of human origin. Food is the main source of exposure to Pb. Most of the lead in spices comes from the air. Similar work carried out in market garden areas located along heavily trafficked roads in

Kinshasa by,[15] reported that the vegetables grown on these sites are polluted by the lead contained in the smoke released by vehicles itself coming from the consumption of gasoline containing tetraethyl lead.[16] revealed that the lead content in both soil and vegetables decreases with increasing distance from the main roads, risky situations arise when the road is close to specialized crops (market gardening, orchards, vineyards, tobacco), organic, industrial under contract or labeled. This is also the case in Grand-Popo and in other large cities of Benin (Cotonou, Sèmè, Porto-Novo and Parakou).

Note that these values are lower than the values indicated in vegetables in Ivory Coast (8.69 - mg / kg) studied by,[17] and in India (21.59 - 57, 63 mg / kg) by,[18] but relatively higher than the Pb contents reported in plants (0.01 - 0.02 mg / kg) in Lagos, Nigeria. The concentration level accepted by the French higher council of public hygiene for plants in human food is of the order of 0.3 mg / kg for Pb in leafy vegetables.[19]

Cadmium was detected in all samples with an uneven distribution in the different matrices. Its concentration varies between 0.12 mg / kg and 0.21 mg / kg. The Cd contents in this study are lower than the levels obtained in plants grown at the metallurgical sites of Noyelle Godault and Auby in France, which reach up to 1.50 mg / kg.[20] A study carried out on the market gardening sites of Cocody and Marcory in Ivory Coast by.[17] reported Cd levels similar to ours in plants (0.12 - 0.41 mg / kg). Some studies also report very high Cd contents varying from 2.5 to 7.6 mg / kg.[21] It can be noted that these municipalities are under the influence of the Abidjan landfill, which receives all types of domestic and industrial waste. This waste is either composted, buried in the ground or is incinerated in an ambient space. Thus, the pollutants from this buried or incinerated waste will, on the one hand, contaminate the soil where these spices are dried. And on the other hand, by atmospheric fallout from incineration. With regard to the municipality of Port-Bouët, the crops largely receive the gases from air traffic and the fumes from the incineration of waste frequently practiced in the open. However, some pollutants present in these fumes come from the combustion of kerosene from airplanes or the combustion of household waste, while others are inherent in the nature of the waste incinerated.[22] These pollutants will contaminate the spices grown in these areas via the leaves or even the soil. For Cd, the accepted standard is around 0.2 mg / kg in leafy vegetables.[19] The average Cd levels recorded in the various markets are below the threshold set by the standard, but their presence in these spices constitutes a possible source of contamination. It should be noted that Cd is easily absorbed and transported to the various organs of the plant.[23]

The ETM contents recorded in chilli and pepper can be explained in general, either by the soils of crops of the spice species studied, or by the deposits of particles on the spices during drying.[24] One of the main sources of metals in market garden plots is the deliberate application of various exogenous products: fertilizers, phytosanitary products, various wastes incorporated into the soil, wood ash, etc.[25,5] It follows that chilli and pepper thus are unfit for human consumption with regard to the standards set for Hg and Pb. Likewise, with regard to the standards for Cd, all of these spices are unfit for human consumption. It should be noted, for example, that, in cadmium- nickel-based batteries, cadmium represents more than 15 to 20% of the weight of the battery,[26] Thus, the risk assessment for human health will establish the consequences incurred by the exposure of these foods to toxic contaminants, more particularly to cadmium and lead. Indeed, the latter are known to be carcinogenic elements with a non-threshold effect, that is to say they are considered toxic regardless of their doses. Pb and Cd do not play a fundamental role in the body and can therefore, at certain levels, disrupt the growth and proper functioning of the plant.[24]

CONCLUSION

In view of the results of this study, the risks of contamination of the food chain by the consumption of chilli and pepper sold in the various markets of Yopougon, Adjamé and Port- Bouët in the district of Abidjan are not negligible. It is clear that the concentrations of Pb, Cd and Hg in spices (chilli and pepper) sold in these markets exceed the maximum levels permitted in foodstuffs intended for human consumption. This exceedance of standards is explained not only by the strong anthropogenic activities emitting heavy metals around the points of cultivation such as road traffic, deposits and the incineration of various waste but also by the use of inadequate drying techniques, crop irrigation as well as the excessive use of fertilizers.

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