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Levels of Heavy Metals Contamination (As, Cd, Hg, Pb) in Some Human Consumption Water Sources in Agbangnizoun and Za-Kpota Town Halls, Southern Benin

Emmanuel Azokpota[1,2], Alassane Youssao Abdou Karim[1,2], Alphonse Sako Avocefohoun[2], Abdoul Kader Alassane Moussa[2], Constant Adandedjan[3], Virgile Ahyi[4], Jean Christian Alowanou[2] , Julien Adounkpe[1], Daouda Mama[1], Dominique Sohounhloue[2]

[1]Laboratory of Applied Hydrology (LHA)/University of Abomey - Calavi, Bénin

[2]Laboratory for Study and Research in Applied Chemistry (LERCA) / University of Abomey-Calavi, 01 BP 2009 Cotonou, Bénin

[3]Water and Food Quality Control Laboratory, BP 01-882 Cotonou, Bénin

[4]Inter-Regional University of Industrial Engineering, Biotechnology and Applied Sciences (IRGIB-Africa University

Correspondence: Alassane Youssao Abdou Karim, Laboratory of Applied Hydrology (LHA)/University of Abomey - Calavi, Bénin; Laboratory for Study and Research in Applied Chemistry (LERCA) / University of Abomey-Calavi, 01 BP 2009 Cotonou, Bénin.

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Abstract

In the current decades, the increasing presence of metallic contaminants in water for human consumption has become a major public health concern. This concern is even more pronounced in rural areas such as in the Town Halls of Agbangnizoun and Za-Kpota where the majority of households use surface water, wells and tanks to satisfy their daily drinking water needs, without any prior treatment, due to the low level of access to drinking water supplied by the State. This study aims at assessing the levels of contamination of these resources in mercury (Hg), cadmium (Cd), lead (Pb) and arsenic (As). The mercury was determined using the cold vapor technique by the Direct Mercury Analyzer (DMA-80) while lead and cadmium were analyzed by molecular absorption spectrophotometry by the DR 3900. The Arsenic was extracted by distillation using the silver diethyldithiocarbamate method then measured by molecular spectrophotometry technique. The results show that surface waters contain great quantities of metals than well and cistern waters. Lead (220.97 $\pm$9.45 µg/L) and cadmium (20.13 $\pm$0.17 µg/L) in surface waters have levels above WHO guidelines and Bénin standards. On the other hand, there is no significant difference between the metal concentrations of well and cistern waters at the 5% threshold. Significant correlations are established between toxic metals (Pb and Cd) and physical parameters (turbidity and suspended matters) at the threshold of 1 %. As for mercury (Hg) and arsenic (As), the concentrations are very lower than these of Cd and Pb and below the quantification limit of the device. These results confirm that the surface waters consumed by the populations of the Town Halls of Agbangnizoun and Za-Kpota do not respect drinking water standards.

Keywords: metals, drinking water, Agbangnizoun, Za-Kpota

1. Introduction

Heavy metals are naturally present in the environment in trace amounts. Their toxicity is much greater in the event of chronic or acute contamination, generally resulting in serious physiological and neurological effects (Grandjean, 1984; Fergusson, 1990; Plumlee and Ziegler, 2003).

Regarding lead for example, sensitivity to toxic effects is more marked in young children. This is related to the permeability of their blood-brain barrier. These are exposed to lead poisoning which results in clinical disorders, biological abnormalities and various histopathological alterations, cognitive and neurobehavioural damage; this pathology is manifested by anorexia, vomiting, irritability, behavioral problems, abdominal pain, coma, and death (INSPQ, 2003; Degbey et al., 2010; Laurent et al., 2013 Beauchamp, 2003).

Mercury poisoning in humans can also cause hydrargyria or hydrargyrism, which is characterized by damage to the nerve center. It is also a nephrotoxic toxic element.

The toxicity of arsenic depends on its degree of oxidation: As (O) > As (III) > As(V) (Callender, 2003). Toxicity increases with the degree of arsenic methylation (Fergusson, 1990; Alloway and Ayres, 1997; Chung et al., 2002). Arsenious oxide, or white arsenic (improperly called arsenic), As2O3 is a violent poison.

Cadmium is also very toxic in all its forms (metal, vapour, salts, and organic compounds); it is one of the few elements with no known function in the human body or in animals. In humans, it causes kidney problems in particular; this can result in irreversible nephropathy, which can lead to renal failure with renal tubular functional impairment from certain concentrations in the renal cortex and to increased blood pressure (Plumlee and Ziegler, 2003). The digestive system is the first to be affected following cadmium poisoning. The symptoms observed are gastroenteritis, vomiting, diarrhea and myalgia (striated skeletal muscle pain).Among the nine (09) Town Halls in the Zou Region the Town Halls of Agbangnizoun and Za-Kpota are the two with a low drinking water coverage rate. 25.2% of households have access to drinking water in the Town Hall of Agbangnizoun and 21.5% of households have access to it in the Town Hall of Za-kpota (INSAE, 2016) against an average Zou Region coverage of 53.4 %. The majority of households, therefore often use rainwater collected in tanks, wells and surface water without any prior treatment to satisfy their daily drinking water needs. Surface water and traditional wells are, for the most part, unfit for consumption because of their level of contamination and may contain toxic pollutants for humans (WHO, 2003, Babadjidé, 2011). In these two Town Halls, agriculture holds an important place with the use of pesticides and chemical fertilizers. The water consumed is therefore exposed to pollutants originating from agricultural sources because the contamination of surface or underground water by toxic substances is closely linked to that of the soil and to the use of pesticides, in this case fungicides which contain heavy metals (Coats, 1991; Deluisa et al., 1996; Bourrelier and Berthelin, 1998). This situation of degradation of water resources is exasperated by poor management of household waste in the two Town Halls where 94.8% of households in Agbangnizoun and 91.6% of households in Za-Kpota discharge waste directly into nature (INSAE, 2016). Indeed, urban wastes contain sources of heavy metals such as batteries (Hg, Zn, Pb, Cd), paints (Cr, Cd, Pb), plastics (Cd, Ni), cardboard paper (Pb) (De Miquel, 2001; Aloueimine, 2006). This study aims to assess the level of contamination in toxic metals (Hg, Pb, Cd and As) of surface water, wells and cisterns consumed by the populations of the concerned areas.

2. Material and Methods

2.1 Study Framework

The Town Halls of Agbangnizoun and Za-kpota are located in southern Bénin (Figure 1), in the Region of Zou. There are two rainy seasons, from March to July for the high season, from August to October for the low one and two dry seasons, December to March for the high season, July to August for the low one. The average annual rainfall varies between 900 mm and 1200 mm of water.

Table 1. Geographical coordinates of the water sampling villages

Town Halls	***Districts***	***Villages***	***Geographical coordinates***
AGBANGNIZOUN	SAHE	SAHETO	7°03'42.2"N 1°56'51.0"E
		COUFFONOU	7°02'21.4" N 1°55'28.0" E
		ADJAHA	7°06'51.5" N 1°54'17.7" E
ZA-KPOTA	KPAKPAME	YABA	7°18'23.5"N 2°06'11.8"E
		TOGA	7°20'29.3"N 2°09'38.2"E
	ZA-KPOTA	OUMGBEDIHO	7°13'30.7"N 2°14'00.9"E

Limited to the north and west by the Town Hall of Abomey, to the south by the Couffo River, to the east by the Town Halls of Bohicon and Zogbodomey, the Town Hall of Agbangnizoun has an area of 244 km^2 and a density of 1,116 inhabitants/Km^2.

According to the General Census of Population and Housing carried out by the National Institute of Statistics and Economic Analysis in 2013 (RGPH, INSAE, 2013), its population is 72,549 inhabitants, of which 34,782 are male and 37,767 females distributed in 16,763 households including. Administratively, the Town Hall is divided into ten (10) Dstricts and fifty-one (51) villages.

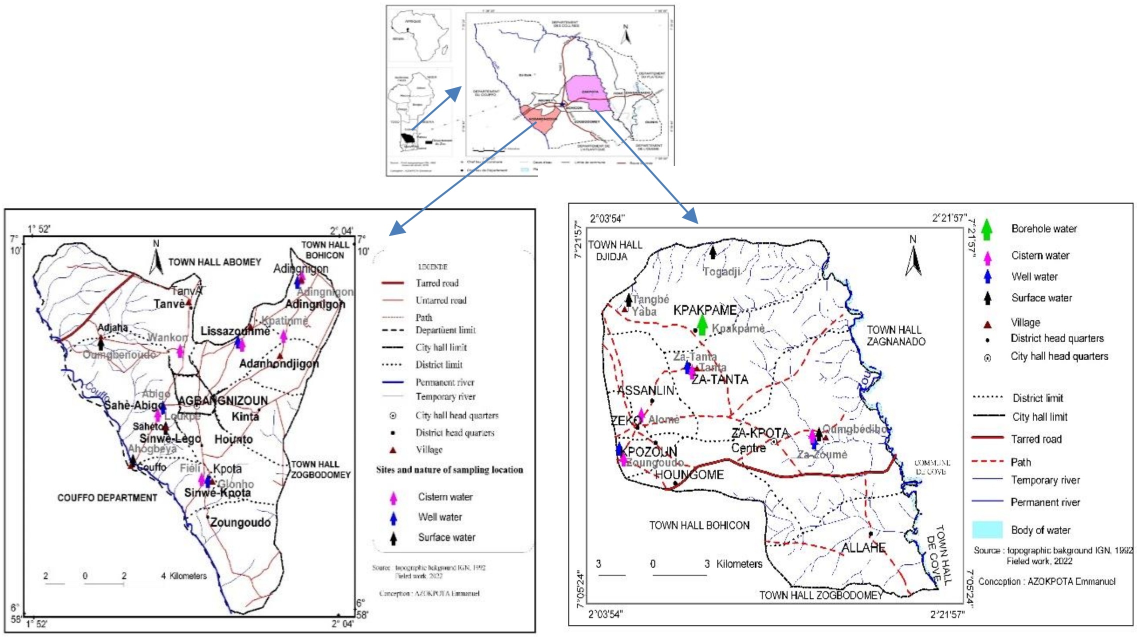

Figure 1. Maps of Zou Region, Agbangnizoun (to the left) and Zakpota (to the right) Town Halls showing the water sampling sites

As for the Town Hall of Za-Kpota, it is limited to the northwest by the Town Hall of Djidja, to the northeast by the Town Hall of Zagnanando, to the southwest by the Town Hall of Bohicon, to the east by the Town Hall of Covè and to the south-east by the Town Hall of Zogbodomey. It covers an area of approximately 600 km2 on which live 132,818 inhabitants, including 61,945 males and 70,873 females, distributed in 29,240 households, of which 15,199 are agricultural (RGPH4, 2013). According to the same source, the Town Hall of Za-Kpota is made up of 56 villages grouped into eight (8) districts from which we have choice six villages for this study (Table 1).

2.2 Water Sampling

The sampling method used for the campaigns is consistent with that used by the same authors in the previous article (Azokpota et al., 2022). The water from a borehole serves as a control sample because its composition is assumed to be close to that of natural water (low concentration of contaminants). The water samples were taken from plastic bottles previously washed and rinsed in the laboratory using the so-called "ultra-clean" method, then dried in an oven at 105°C. This protocol consists of: cleaning with nitic acid (HNO_3) 15%, HCI 1% (ACS reactive grade, J. T. Baker, Phillipsburg, U.S.A.) followed by seven rinses with ultra-pure water (Milli-Q system; > 18 MΩ.cm). These flasks were also rinsed with the water to be sampled in the field. The water sample was taken about 5 cm from the surface. Then, these samples were acidified by adding concentrated nitric acid (HNO_3) (v/v). These bottles were half filled before adding 2ml of HNO_3 (65%) then completely filled before being hermetically sealed to prevent any gas leaks. These samples were then labeled before being placed in a cooler containing cold packs.

2.3 Analysis Method

The determination of lead and cadmium is done in three stages: mineralization (Digestion according to HACH), extraction with pure chloroform recta and molecular absorption spectrophotometer (DR 3900). As for mercury, the dosage was carried out by the MILESTONE Direct Mercury Analyzer (DMA-80) using the cold vapor technique.

Digestion according to HACH

The stages of mineralization are for Cd and lead are:

- measure 40 mL of liquid sample in a 100 mL digesdahl flask.

Add 3 mL of concentrated sulfuric acid and bring to 440°C on the mineralizer;

- let it char for 3 to 5 minutes;

- add 10 mL of hydrogen peroxide 30 to 50% volume using a capillary funnel. If the sample is not completely clear, continue adding 5mL fractions;

- let the hydrogen peroxide evaporate completely and remove the vial from the mineralizer;

- after cooling (approximately 15 min), top up with distilled water up to the 100 mL line.

Filtering

Filtration is done using a GF/C membrane, with a porosity of 0.45 µm for dissolved metals analyses.

Prior treatment for mercury determination

The water samples did not undergo any treatment before the Hg analysis phase.

Prior treatment for arsenic determination

Finally, the arsenic was extracted by distillation using ISO 2590: 1973 (the silver diethyldithiocarbamate method) and then quantified by molecular spectrophotometry with DR 3900 device.

2.4 Statistical Processing of Analysis Results

All statistical analyses were performed in the R statistical software package, version 4.0.0 (R Core Team, 2020). We calculated descriptive statistics on the data and used barplot to explore the variation in water parameters (lead concentrations, cadmium concentrations, mercury concentrations and arsenic concentrations) among the water sources and campaigns. We then tested for significant effects of water parameters on water sources and collection campaigns using separate Kruskall-Wallis test since assumptions for Multivariate Analysis Of Variance were violated. When the null hypothesis is rejected in a validation, Wilcoxon multiple comparisons test is performed using multicomp package. When the influence is significant from the analysis of variance, the separation of the two metals averages has been made with the Student - Newman Keuls test. The relationship between the different water parameters was evaluated with the Pearson correlation test. The one-sample t-test was used to compare the three water sources. The concentration of each type of water have been compared with Beninese standards and those of the World Health Organization for drinking water. For all statistical analyses, the significance threshold used is 5%.

3. Results and Discussion

Spatial evolutions of median values of metal concentrations

The Kruskal Wallis test was carried out to study the evolution of the median values of the concentrations. The results show the p-value is less than 0.05 (P-value =0.0001). So there is a difference in significance at the 5% threshold between the median values of the concentrations of metals in the waters of the different localities studied. The multivariate analysis of variances (Figure 2) made it possible to see that the concentrations of mercury (Hg) and arsenic (As) are very lower than these of cadmium (Cd) and lead (Pb) and below the quantification limit of the device for the arsenic.

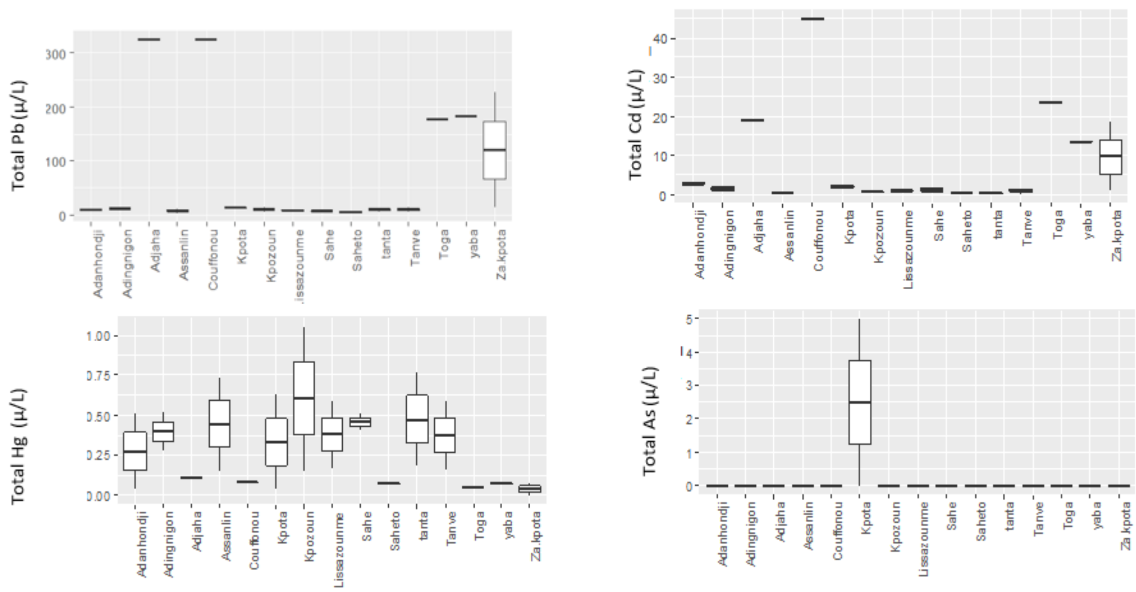

Figure 2. Comparison of median values of metal concentrations according to localities for the first campaign; Pr(>F)=0.0001

These results show two trends of variations of metals concentrations in water samples. Cadmium and lead concentrations are in the order of micrograms per liter to a few tens and hundreds micrograms per liter. While mercury and arsenic concentrations are in the order of a few tenths of micrograms per liter or in the state of traces (below the quantification limit).

Influence of water sources on Pb, Cd and As concentrations variations between the two campaigns

Lead, Cd and As concentrations did not vary significantly ($p<0.05$) in cistern, surface and well water between the two sampling campaigns despite a slight upward trend (Figure 3). On the other hand, surface waters have concentrations of Pb and Cd higher than those of cisterns at the 5% threshold. While cistern water is more contaminated with arsenic compared to surface and well water.

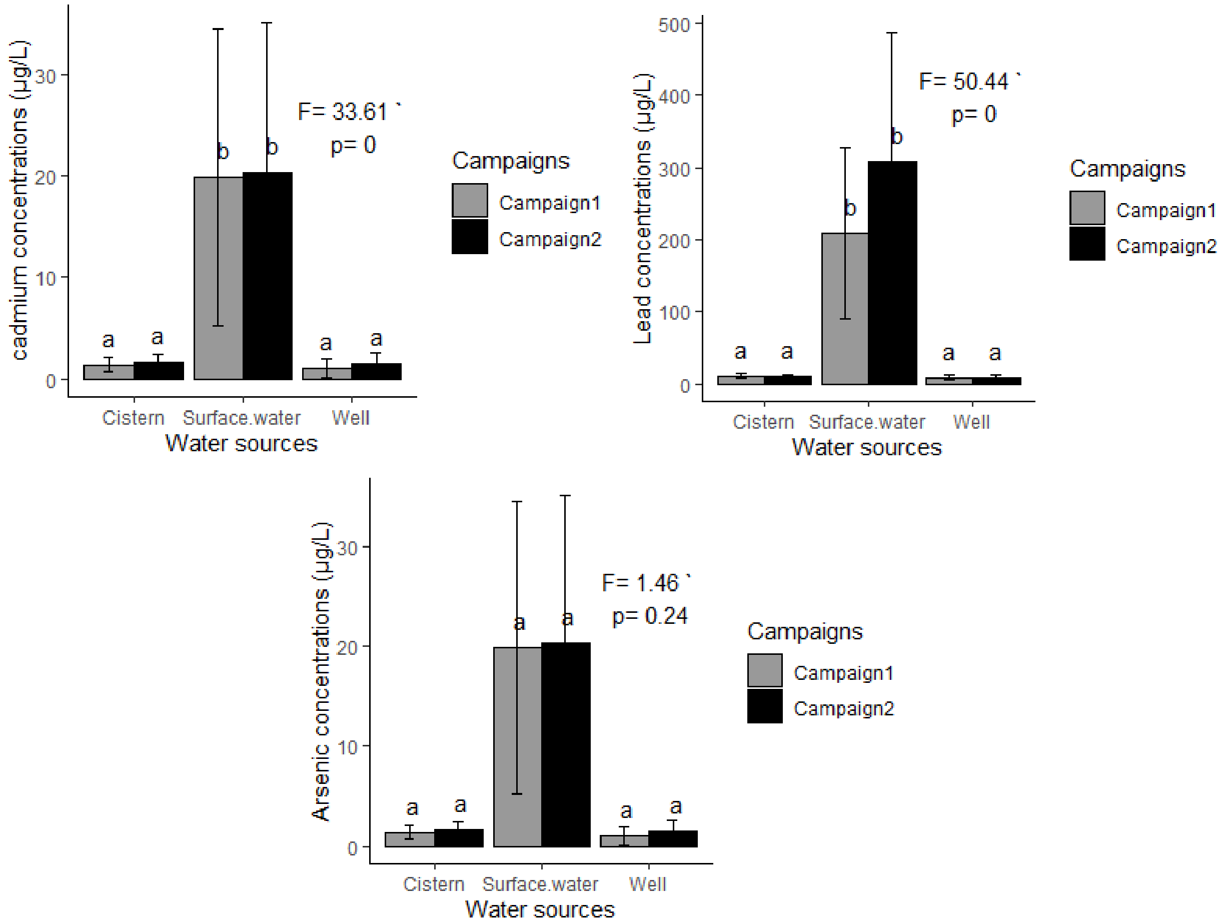

Figure 3. Variations in the concentrations of Pb, Cd and As according to the water sources between the two sampling campaigns

Variations of mercury residues

As for mercury (Hg) residues, the highest concentration of Hg was recorded in Kpozoun (1,060 µg/L) and the lowest in Za-Kpota with a concentration below the detection threshold in cistern water samples. Indeed, the cisterns are left open and exposed to bad weather throughout the rainy period while waiting for the drought period. The average concentrations recorded are 0.580; 0.077 and 0.186 µg/L in cistern, surface and well water, respectively. After cistern water, well water is the most contaminated with Hg. This indicates a local source like from using material as the thermometer, cosmetics products and pomades for women, etc. Indeed, the populations are frequently in contact with these waters for their daily needs by plunging all kinds of containers into them. These wells are also left open; which also exposes them to the weather.

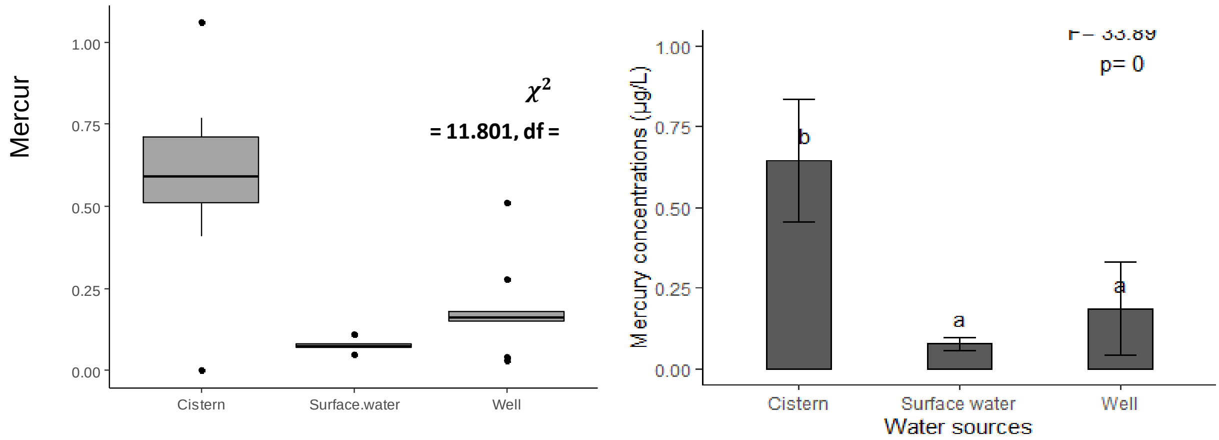

Figure 4. Comparison of median values (at the left) and means (at the right) of Hg concentrations according to water sources

The Kruskal Wallis test was carried out to study the evolution of median values of mercury concentrations (Figure 4). The results show the p-value is less than 0.05 (P-value =0.003). So there is a difference in significance at the 5% threshold between the median values of the concentrations of cistern, surface and well water.

Variations in concentrations of arsenic (As) residues

Most of the results obtained for arsenic residues are below the detection limit. Only the water samples taken from Kpota (5.00 µg/L) during the first sampling campaign and from Adingnigon (10 µg/L) in cistern water and Assanlin (3 µg/L) during the second sampling campaign in well water have showed concentrations above quantification limit (Table 2).

Evolution of the concentrations of Pb and Cd

The results of the analyses carried out for the metals are presented in Table 2.

Lead residues are mainly represented in the surface water collected during the first sampling campaign on the sites of Adjaha (in Agbangnizoun), Couffonou (in Agbangnizoun) and Za-kpota (in Za-kpota) then in Toga and Yaba (in Za-Kpota). The Sahèto (in Agbangnizoun) site has the lowest lead concentration among the surface waters studied. The highest lead concentrations are obtained during the second sampling campaign with a value of 611 µg/L in Yaba, 296.25 µg/L in Za kpota and 261 µg/L in Adjaha.

As for rainwater stored in cisterns and water from traditional wells, the trends in lead residue variations are similar with concentration values ranging from 5.82 µg/L at Sahe to 13.77 µg/L at Kpozoun (in Za-kpota) for cistern water and 3.53 µg/L at Assanlin (in Za-kpota) to 12.70 µg/L at Adingnigon (in Agbangnizoun) for the first sampling campaign.

Correlations between the parameters studied

From the analysis of tables 3 and 4, it appears that:

- The concentration of suspended solids in the water is very strongly correlated with the concentration of lead ($r = 0.98$ with $p < 0{,}0001$) on the one hand, and very strongly correlated with the concentration of cadmium ($r = 0.99$ with $p < 0{,}0001$) on the other hand ;

- The colour of the water is very strongly correlated with lead concentrations ($r = 0.96$ with $p < 0{,}0001$) on the one hand and strongly correlated with cadmium concentrations ($r = 0.93$ with $p < 0{,}0001$) on the other hand;

- Water turbidity is correlated with cadmium concentrations ($r = 0.74$ with $p < 0{,}0001$).

From these significant correlations, it can be deduced that the large part of lead and cadmium (in particulate phase) is kept by suspended solids in the water, as shown by the results of the phase speciation of said metals (Table 3). The turbidity of the water depends on the suspended solids which are at the origin of the water colour. This justifies the strong correlations observed between lead and cadmium fixed on suspended matter and the colour of the water. The correlation between suspended solids and metals also explains that established between turbidity, lead and cadmium.

Legend

Cond	TDS	Turbo	SM	NO2-	NO3-	PO43-	bp	CD	Col	ammo	Sulp
Conductivity	TDS	Turbidity	Suspended Matter	Nitrites	Nitrates	Orthophosphate	Lead	Cadmium	Colour	Ammonium	Sulphates

Table 2. Correlation matrix (Pearson)

Variables	pH	Temp	Cond	TDS	Turbo	SM	NO2-	NO3-	PO43-	Pb	Cd	Colo	ammo	Sulp
pH	1													
Temp	**-0.5320**	1												
Cond	**-0.6039**	**0.5608**	1											
TDS	-0.4112	0.3955	**0.8878**	1										
Turbo	-0.0149	0.1410	-0.1753	-0.1439	1									
MY	-0.0395	-0.2443	0.2941	**0.4608**	**0.7763**	1								
NO2-	-0.0080	-0.1039	0.3466	**0.5038**	**0.5775**	**0.9112**	1							
NO3-	**-0.4315**	**0.6381**	**0.6577**	**0.4292**	-0.0963	-0.2183	-0.2261	1						
PO43-	-0.2562	0.3606	0.1774	0.0937	0.0545	-0.0367	-0.0907	**0.6227**	1					
Pb	-0.0329	-0.2320	0.2874	**0.4621**	**0.6843**	**0.9801**	**0.9244**	-0.2273	0.1997	1				
Cd	0.0288	-0.2643	0.2604	**0.4327**	**0.7478**	**0.9904**	**0.9274**	-0.2581	-0.0803	**0.9642**	1			
Colo	-0.0383	-0.2031	0.2659	**0.4475**	**0.5949**	**0.9512**	**0.9207**	-0.2355	**0.5790**	**0.9650**	**0.9380**	1		
ammo	0.1386	-0.1831	0.2729	**0.4723**	**0.5115**	**0.8274**	**0.9447**	-0.2187	**0.7342**	**0.8638**	**0.8441**	**0.8383**	1	
Sulp	-0.1130	0.0722	0.0534	0.0155	0.1573	0.3728	**0.4538**	-0.1433	-0.2123	0.3771	0.3981	0.4038	0.0250	1

Values in bold are different from 0 at significance level alpha=0.05

Table 3. Probability values associated with the correlation between water parameters

Variables	pH	Temp	Cond	TDS	Turbo	MY	NO2-	NO3-	PO43-	Pb	Cd	Color	ammo	Sulf
pH														
Temp	**0.0090**													
Cond	**0.0023**	**0.0054**												
TDS	0.0513	0.0618	**< 0.0001**											
Turbo	0.9501	0.5532	0.4599	0.5450										
SM	0.8581	0.2614	0.1732	**0.0269**	**< 0.0001**									
NO2-	0.9711	0.6370	0.1051	**0.0143**	**0.0039**	**< 0.0001**								
NO3-	**0.0398**	**0.0011**	**0.0006**	**0.0410**	0.6621	0.3170	0.2995							
PO43-	0.2379	0.0909	0.4180	0.6705	0.8051	0.8680	0.6806	**0.0015**						
Pb	0.8817	0.2868	0.1837	**0.0264**	**0.0003**	**< 0.0001**	**< 0.0001**	0.2969	0.3987					
Cd	0.8962	0.2229	0.2300	**0.0392**	**< 0.0001**	**< 0.0001**	**< 0.0001**	0.2344	0.7366	**< 0.0001**				
Color	0.8623	0.3526	0.2201	**0.0323**	**0.0028**	**< 0.0001**	**< 0.0001**	0.2794	**0.0075**	**< 0.0001**	**< 0.0001**			
ammo	0.5281	0.4031	0.2077	**0.0229**	**0.0126**	**< 0.0001**	**< 0.0001**	0.3161	**0.0002**	**< 0.0001**	**< 0.0001**	**< 0.0001**		
Sulf	0.6076	0.7432	0.8088	0.9439	0.4735	0.0798	**0.0296**	0.5141	0.3689	0.0761	0.0599	0.0560	0.9167	

Values in bold are different from 0 at significance level alpha=0.05

Lead concentration's variations

The Student - Newman Keuls test of the results shows that the concentration of total lead in water varies significantly ($p<0.05$) depending on the alternative water sources (Table 4). On average for the two targeted campaigns, the total lead in surface water is significantly higher (220.97µg/L) than in cistern waters (10.90µg/L), wells (10.37µg/ L) and drillings (8.22µg/L) (witness). There is a significant difference between the lead concentration obtained in the sampled surface waters and the guidelines regulated by the WHO and the Bénin standards. The lead concentration in the well and cistern waters is significantly lower than Beninese standards. On the other hand, surface waters have a high concentration which significantly exceeds the guideline values set by the WHO and the standards of Bénin.

Table 4. Variation of metals according to water sources

Parameters	***Water sources***			
	Cisterns	***Wells***	***Surface waters***	***Drilling (witness)***
Cadmium (µg/L)	2.42± 0.19[b]	1.28± 0.17[b]	20.13± 1.46[a]	0.82± 0.17[c]
Lead (µg/L)	10.90 ± 0.61[b]	10.37 ± 0.10[b]	220.97± 9.45[a]	8.22± 0.66[b]

Legend: The same letters (a or b) mean that there is no significant difference between the values.

Cadmium concentration's variations

Regarding cadmium, the statistical analysis has showed that the results obtained are similar to those of lead. The average total cadmium, for the two years, is the lowest (0.82 µg/L) in the drilling waters (witness) compared to surface waters which have a total cadmium concentration of 20.13 µg/L, an increase of more than 95%. Moreover, the total cadmium concentrations vary significantly ($p<0.05$) from one alternative water source to another. The cistern and well waters concentrations in cadmium are significantly lower than the WHO guideline values and the Bénin standard. On the other hand, surface waters contain a cadmium concentration significantly higher than the reference values.

The concentrations represent the average values of the waters of the different sources. the same letters (a or b) mean that there is no significant difference between the values.

The presence of metal concentrations (Pb and Cd) in the water consumed above the witnesses and standards indicates a contribution of anthropogenic activities (agriculture, solid and liquid wastes). The results obtained are in agreement with those of African researchers (Table 5) who have devoted research to the metallic contamination of waters where the values of lead vary from 0.02 to 70.4 mg/L in surface waters (Kakulu et al., 1992; Chitou et al., 2010; Youssao et al., 2011; Blinda et al., 2013; Kabunga et al., 2013; Onivogui et al., 2013; Yapi et al., 2014; Fouad et al., 2014; Traore et al., 2015; Wanga et al., 2015; Greichus et al., 2015; Mohiuddin et al., 2015; Fahssi et al., 2016; Edward et al., 2017; Kadriua et al., 2017; Agbandou et al., 2018). On the other hand, our results are in disagreement with those obtained by researchers where the values of Cadmium vary from 0.1 to 20.49 mg/L in surface waters (Chitou et al., 2010; Yapi et al., 2014; Fouad et al., 2014; Wanga et al., 2015; Greichus et al., 2015; Mohiuddin et al., 2015). For the well waters, the cadmium values obtained (0.0010 mg/L) are contrary to those obtained by researchers and which are in the range of 0.02 mg/l to 0.23 mg/l exceeding the standards for cadmium (Tanouayi et al., 2015; Yapi et al., 2014; Gbamele et al., 2020); those of lead (0.010 mg/L) are lower than the values (0.03 mg/l to 4.8 mg/l) obtained by other researchers (Peliba et al., 1991; Creppy et al., 2003; Tanouayi et al., 2015; Chaïeb et al. , 2016; Gbamele et al., 2020 ; Yapi et al., 2014). As for the cistern waters, the average values obtained for lead (0.010 mg/L) and cadmium (0.002 mg/L) are lower than the values obtained respectively by Legret et al.,1994 and Hebabaze et al., 2015 in rainwaters collected in cisterns for lead (0.078 mg/L and 0.016 mg/L) and cadmium (0.017 mg/L and 0.011 mg/L).

Health effects linked to the presence of these toxic metals in drinking water are known. Mention may be made, for lead, of lead poisoning, which results in clinical troubles, biological anomalies and various histopathological alterations, cognitive and neurobehavioural damage, increased sensitivity to the toxic effects of lead in young children linked to blood-brain barrier permeability, anorexia, vomiting, irritability, behavioral disturbances, abdominal pain, coma, and death; in pregnant women, there is harm to the development of the central nervous system of the fetus (INSPQ, 2003; Degbey et al., 2010; Laurent et al., 2013). The health effects linked to cadmium are: kidney pains, bone alterations and arterial hypertension; " Itai Itai " characterized by bone decalcification, proteinuria and glucosuria (Botta and Bellon, 2004; Rodier et al., 2009).

Table 5. Calculation of contamination indexes (CI) of lead and cadmium residues

No,	Water sources	Localities	Sample name	Campaign_1_Concentrations in µg/L				Campaign_2_Concentrations in µg/L			
				Pb_tot	CI Pb	Cd_tot	CI Cd	Pb_tot	CI Pb	cd_tot	CI Cd
20	Drilling (Reference)	Kpakpame	BF/AEV(Reference)	10.35	0.00	3.01	0.00	10.35	0.00	3.01	0.00
16	Cistern	Sahe	Cistern 1	5.82	-0.28	1.88	-0.23	6.81	-0.21	1.96	-0.21
17		Adingnigon	Cistern 2	9.7	-0.03	2.13	-0.17	10.2	-0.01	2.25	-0.14
18		Adanhondji	Cistern 3	10.84	0.02	2.15	-0.17	10.75	0.02	2.25	-0.14
19		Kpota	Cistern 4	12.04	0.08	2.29	-0.14	11.97	0.07	1.85	-0.24
20		Tanve	Cistern 5	13.47	0.13	1.75	-0.26	11.32	0.04	0.94	-0.52
21		Lissazounme	Cistern 6	9.28	-0.05	1.37	-0.37	9.88	-0.02	3.26	0.04
22		Kpozoun	Cistern 7	13.77	0.14	0.6	-0.67	9.89	-0.02	1.1	-0.46
23		Assanlin	Cistern 8	10.83	0.02	0.29	-0.82	11.02	0.03	0.5	-0.72
24		tanta	Cistern 9	12.36	0.09	0.71	-0.62	12.63	0.10	0.89	-0.54
25		Za kpota	Cistern 10	13.22	0.12	0.96	-0.52	12.23	0.08	1.52	-0.33
1	Surface water (SW)	Adjaha	SW Adjaha	325.63	0.94	18.75	0.72	261	0.92	13.21	0.63
2		couffonou	SW Couffo	324.38	0.94	45	0.87	325	0.94	46	0.88
3		Za kpota	SW Oung	227.81	0.91	18.44	0.72	296.25	0.93	20.51	0.74
4		saheto	SW Saheto	5.35	-0.32	0.41	-0.76	49.25	0.65	2.11	-0.18
5		Toga	SW Toga	178.44	0.89	23.44	0.77	297	0.93	25.2	0.79
6		yaba	SW Yaba	183.13	0.89	13.44	0.63	611	0.97	15.02	0.67
7	Well (W)	Adanhondji	W Adan	9.92	-0.02	3.46	0.07	8.02	-0.13	3.5	0.08
8		Adingnigon	W Adin	12.7	0.10	0.9	-0.54	12.84	0.11	1.02	-0.49
9		Assanlin	W ASS	3.53	-0.49	0.7	-0.62	2.06	-0.67	2.69	-0.06
12		Kpota	W Kpota	13.44	0.13	1.67	-0.29	5.95	-0.27	1.09	-0.47
10		Kpozoun	W Kpozoun	6.17	-0.25	0.94	-0.52	14.2	0.16	2.1	-0.18
11		Lissazounme	W Lissazou	7.85	-0.14	0.76	-0.60	7.61	-0.15	0.85	-0.56
14		Sahe	W Sahe	7.98	-0.13	0.4	-0.77	7.65	-0.15	1.01	-0.50
15		tanta	W Tanta	6.49	-0.23	0.24	-0.85	6.94	-0.20	51	0.89
13		Tanve	W Tanve	5.96	-0.27	0.36	-0.79	6.01	-0.27	0.34	-0.80

Table 6. Phase speciation of Cadmium and Lead in surface waters

Surface water	*Lead (µg/L)*			*Cadmium (µg/L)*		
	Dissolved(D)	*Particulate(P) (P)*	*P/D* [1]	*Dissolved(D)*	*Particulate(P)*	*P/D*
Adjaha	15.29	245.71	16	2.1	11.11	5
Couffonou	13.75	311.25	23	3.6	42.4	12
Oumgbediho	26.61	269.64	10	1.96	18.55	9
Saheto	27.71	21.54	1	0.5	1.61	3
Toga	13.51	283.49	21	2.91	22.29	8
Yaba	17.54	593.46	34	1.58	13.44	9

P/D represents the particulate Pb / dissolved Pb and the particulate Cd / dissolved Cd ratios

The phase speciation results show that the P/D ratio varies from 1 to 34 for lead and from 3 to 12 for cadmium (Table 6). This relatively high ratio shows that the total lead and cadmium present in the water are found in high proportion in the particulate form retained by suspended matter. This means that most of the lead and cadmium inputs are essentially in the particulate form and there is little mineralization of the organic matter contained in the water. The total lead and cadmium in water are therefore mainly found in the form of particles. These lead and cadmium particles can have as, among other sources, aerial fallout that is drained to surface waters by runoff. Under certain environmental conditions, the mineralization of organic matter having fixed the particulate lead and cadmium could increase the dissolved lead and cadmium which would merge with the total lead and cadmium, as in the case of water sources where suspended matter are low or even non-existent. This is the case of cistern and well waters where the total lead and cadmium practically merge with the dissolved lead and cadmium.

Spatial evolution of total lead levels

Analysis of variance of total lead levels according to Town Hall

Total lead is the only pollution parameter that differs significantly from one Town Hall to another; the highest concentration (78.50 µ/L) has been recorded in the waters of Za-kpota Town Hall (Figure 5).

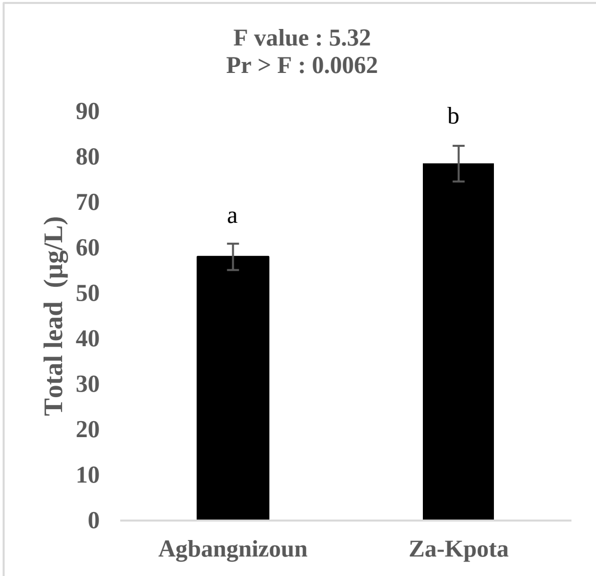

Figure 5. Variation in the average concentration of lead in the Town Halls studied

Analysis of variance of total Pb and Cd concentrations according to the concerned localities

The water samples collected in Adjaha and Couffonou are more polluted in lead (293.32 µg/L and 324.69 µg/L respectively). The lead concentration is lower in the threshold of 0.05 (Figure 6), in the waters of Adanhondjigon Adingningon , Assanlin , Kpota , Kpozoun , Lissazounmè , Tanta and Tanvè. As far as the cadmium is concerned, the highest concentration was recorded in Couffonou (45.50 µg /L).

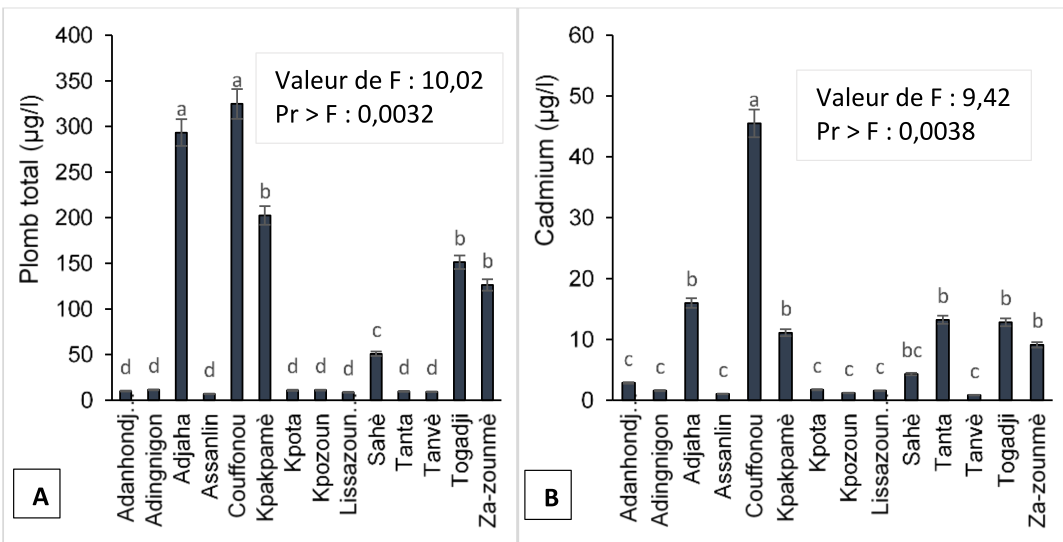

Figure 6. Variation of pollution parameters in the sampled localities

Contamination indexes (CI) of lead and cadmium residues

The contamination index is defined in relation to the reference site, representative of the natural background noise of the study area. For a metal i, it is determined by the formula:

$$IC_i = \frac{(C_i - C_{réf})}{C_i + C_{réf}}$$

Where Ci is the concentration of metal i at the sample site and $Cref$ its concentration at the control sample site which is sample BF/AEF, the drilling water. The results are presented in Table 6 where the abbreviations used are as follows: Pb_tot =Total Lead; Cd_tot = total cadmium; As_tot = Total Arsenic; Hg_tot = Total Mercury.

The analysis of the table 6 makes it possible to deduce that the contamination indexes of lead and cadmium vary from one water source to another and from sampling campaign to another. However, we note some peculiarities within the same source.

Except of the Sahèto water, all the calculated indexes for surface waters sampled, has showed positive contamination indexes for lead and cadmium during the two campaigns.

The probable sources of contamination of these waters are the chemical fertilizers and pesticides used by agriculture in the cotton, maize and groundnut fields located in the slopes of these waters.

With regard to well and cistern water, the cadmium contamination indexes are negative during the first campaign, except for the cistern water sampled at Lissazounmè and the well water sampled at Adanhondjigon and Tanta which presented positive contamination. For the two water sampling campaigns, the lead contamination indexes are positive for water from cisterns sampled at Adanhondjigon , Tanvè , Kpota , Assanlin , Tanta and Za-Kpota. Those from wells sampled at Adingnigon , Kpota for the first campaign and in kpozoun for the second campaign are also positive. The sources of contamination of cistern water by lead would therefore be aerial and probably old sheets and dry palm leaves used to cover cisterns. On the other hand, the probable source of contamination of well water by lead would be the source rock constituting the aquifer. It is the same source which would be at the origin of the presence of cadmium in the water of wells taken from Adanhondjigon and Tanta.

4. Conclusion

The study of metallic contamination of surface, traditional well and cistern waters used for drinking by human populations in Agbangnizoun and Za-kpota Town Halls, southern Bénin, shows that these waters are not suitable for consumption. The heavy metals recorded in surface waters whose average values are higher than the standards accepted for drinking water are:

- Lead with an average value of 220.97 ±9.45 µg/L;
- Cadmium with an average value of 20.13 ±0.17 µg/L.

These metals are found to a large extent, retained by suspended solids in the water. These results reflect the evidence of the poor quality of these surface waters. The influence of human activities and poor sanitation of the study area on water quality has also been picked up.

The populations who consume these waters for drinking are therefore exposed to health risks. However, the consumption of water from cisterns and traditional wells presents less danger for vulnerable populations than that of surface water. We suggest a primary treatment by water filtration before any human consumption to eliminate the particulate phase which is the most abundant.

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