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Concentrations of heavy metals in raw wastewaters of Cotonou city (Benin)

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Key words: Heavy metals; wastewater, main sewers; Cotonou.

Abstract

The current study aims to determine the concentration of heavy metals in raw wastewaters of Cotonou. Waters of three main sewers dumping their contents in Cotonou lagoon have been bimonthly sampled at their discharge point. Heavy metals analysis were carried out by colorimetric methods using molecular absorption spectrophotometer HACH DR 2800 for iron (Fe), zinc (Zn), copper (Cu), chromium (Cr), manganese (Mn), aluminium (Al), cadmium (Cd) and lead (Pb) and by Wagtech Digital Arsenator Wag-WEI 0500 for Arsenic (As). Total mean heavy metals concentration registered in effluents were 0.269; 0.951; 0.340; 0.064; 0.270; 0.035; 0.024; 0.730 and 1.776 mg/L respectively for Fe, Zn, Cu, Cr, Mn, Al, As, Cd and Pb. These heavy metals mean concentrations were generally found to be within Beninese standards as well as Moroccan and Egyptian acceptable limits for direct discharge with exception of Cd and Pb mean concentrations which exceeded these standards. Raw effluents drained by open main sewers are thereby contaminated by many toxic heavy metals and constitute a threat for lagoon ecosystem and consequently humans who are halieutic products consumers. It is hence necessary to undertake their purification including heavy metals removal before pouring it in aquatic environment.

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Introduction

The pollution of the environment due to discharge of contaminated wastewater is a worldwide problem. This situation is more serious in developing countries like Benin where wastewaters were not often purified before their discharge. Pollutants carried by wastewaters include heavy metals which are known to be responsible for many health problems (Liu *et al.,* 2008) and for unwanted ecological effects increasingly remarked in less developed regions despite their slight industrialization (Edorh, 2007). In urban area like Cotonou, throwaways and run-off flood water from industrial, municipal and domestic set-ups transported through impermeable surfaces (streets, asbestos roofs), drains and water-ways were implicated as sources of heavy metal pollutants in aquatic environment (Ellis *et al.,* 1986; Yong *et al.,* 1992; Hammi, 2010). Several heavy metals including manganese (Mn), zinc (Zn), mercury (Hg), copper (Cu), chromium (Cr), nickel (Ni), aluminium (Al), lead (Pb), cadmium (Cd) and arsenic (As) have attracted researchers'attention in aquatic ecosystem, by reason of their toxicity on organisms and hazard they constitute for human health (Kaiser, 2001). These pollutants even found mostly in very small quantity in most environments, are dangerous for living beings because they are non-biodegradable, bio-available and can consequently be concentrated along the food chain (Fernandez *et al.,* 2000).

Several studies conducted on Cotonou lagoon have revealed abnormal amounts of heavy metals especially lead, cadmium, mercury and zinc in different compartments including water, sediment and animal species such as fish, oysters and shrimp (Vissin *et al.,* 2010; Youssao *et al.,* 2011; Yèhouénou, 2013). In all of these studies, wastewaters drained by both mains sewers and gutters, and dumped into the lagoon, are indexed among the sources of this heavy metals pollution.

The current study aims to determine the iron (Fe), zinc (Zn), copper (Cu), chromium (Cr), manganese (Mn), aluminium (Al), Arsenic (As), cadmium (Cd) and lead (Pb) concentrations in raw wastewaters of Cotonou, in order to assess their input to the lagoon pollution by heavy metals.

Material and methods

Study area

The current study has been carried out in Cotonou, economic capital and the most populated city of Benin, positioned between latitudes 6°20' and 6°23'N and longitudes 2°22' and 2°30'E. Limited in west and east by Abomey-Calavi and Sèmè-Kpodji townships respectively, Cotonou has two natural frontiers linked by a channel called lagoon of Cotonou: Nokoué lake in North and Atlantic ocean in South (Fig.1). This lagoon, 4 Km long, is the outlet of many gutters and main sewers erected in the city, normally to canalize storm waters, but which receive permanently raw wastewaters coming from human activities.

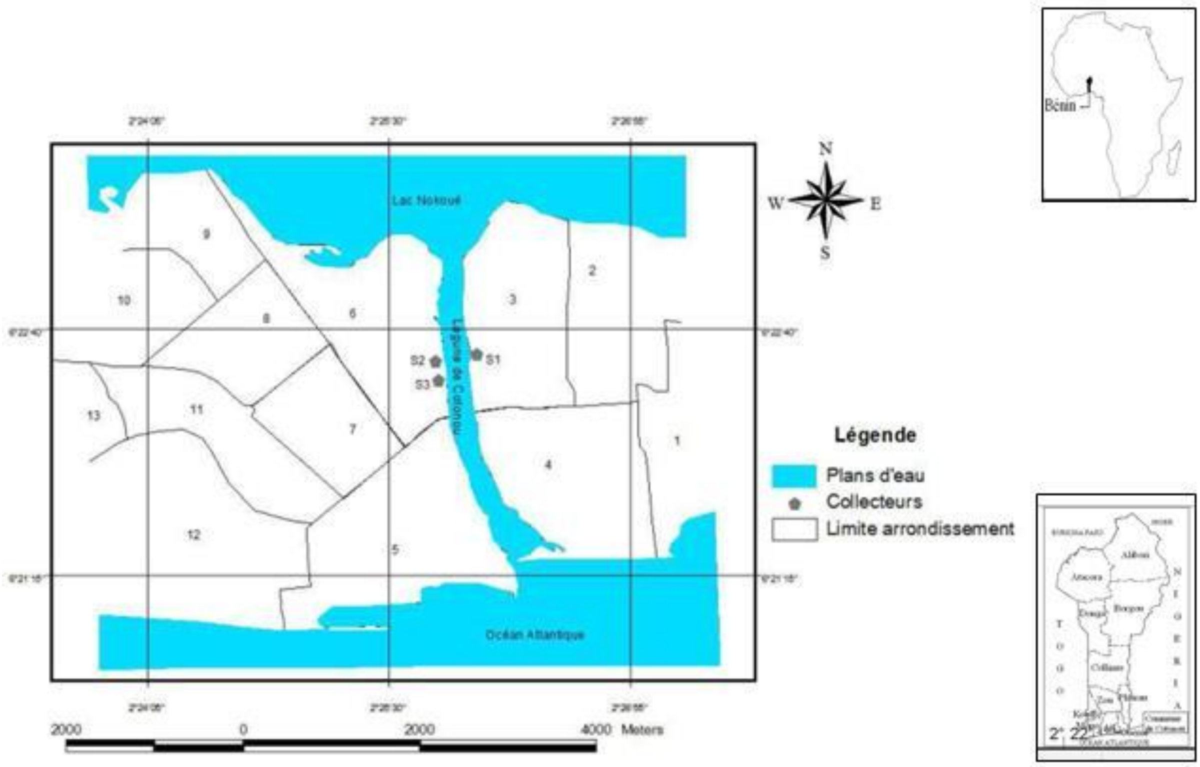

Fig. 1. Map of Cotonou city showing sampling stations.

The area study, because of its geographic position, is subjected to subequatorial climate characterized by four (4) seasons including a long dry season (LDS) from december to March, a long rainy season (LRS) from april to july, a short dry season (SDS) from august to september and a short rainy season (SRS) from october to november (Adam and Boko, 1993).

Sampling and analysis methods

In this study, three main sewers dumping their content in Cotonou lagoon have been prospected, in consideration of their size and anthropic pressure on them. Thus, from January to November 2012, Water Samples were bimonthly (once every two months) collected at three stations corresponding each one to discharge point of one main sewer as indicated in Table1.

Table 1. Characteristics of main sewers and geographic coordinates of sampling stations.

Main sewers	Length	Covered area	Stations	Geographic coordinates	
				Latitude	Longitude
T1	1km	Midombo and vicinity	S1	06°22'38"N	002°26'18"E
B	2km	Gbéto and Dantokpa market	S2	06°22'34"N	002°26'06"E
A	4km	Hindé, Djidjé, Aïdjèdo, Jéricho and Gbégamey.	S3	06°22'55"N	002°26'02"E

Waters were sampled in Cleaned 1L polyethylene bottles and stored in cooler containing ice until their transfer to laboratory. When analysis could not be immediately possible, samples were conserved in fridge at 4°C and acidified until a pH less than 2 with concentrated nitric acid (HNO_3) in order to inhibit the biodegradation of heavy metals (HACH, 2004).

Before the analysis of heavy metals, samples were digested by peroxide oxidation in sulfuric medium, using HACH Digestion apparatus Digesdahl model

23130-20 (HACH, 2004). The concentrations of Fe, Zn, Cu, Cr, Mn, Al, Cd and Pb were determined by colorimetric methods (Hammi, 2010) using molecular absorption spectrophotometer HACH DR 2800. HACH Analysis methods used for this purpose (table 2) are adapted to Standard Methods for the Examination of Water and Wastewater (APHA *et al.,* 2012). The analysis of As was undertaken using Wagtech Digital Arsenator Wag-WEI 0500.

Table 2. Summary of methods used for heavy metals analysis.

Parameters	Methods
Total iron (Fe)	Ferrover method using Ferrover (HACH 8008)
Zinc (Zn)	Zincon method using ZincoVer5 (HACH 8009)
Copper (Cu)	Bicinchoninate method using CuVer1 reagent (HACH 8506)
Total Chromium (Cr)	1, 5-Diphenylcarbohydrazide method (HACH 8023)
Manganese (Mn)	PAN method (HACH 8124)
Aluminium (Al)	Aluminion method using AluVer 3 reagent (HACH 8012)
Cadmium (Cd)	Dithizone method (HACH 8017)
Lead Pb	Dithizone method (HACH 8033)

Data analysis

The mean values of heavy metals were compared between sampling stations on the one hand and between seasons on the other hand, by one way analysis of variance (ANOVA 1) after verifying both data normality and homogeneity of variance using "Shapiro-Wilk's test" and "Levene's test" respectively (Scherrer, 2007). Significant differences between stations or season means ($P<0.05$) were then determined using Turkey's test.

When normality and homogeneity conditions were not fulfilled, non-parametric Kruskall-Wallis's test has been used, followed in case of need by Man-Whitney's test in order to highlight the significant differences between the means (Scherrer, 2007). All statistical tests were performed using the statistical software called Mintitab14.

Results

Heavy metals mean concentrations registered at the three sampled stations and their total mean values are shown in table 3. No significant difference was recorded among the sampling stations ($P>0.05$). However, it suits to note that the concentration of studied heavy metals (Fe, Zn, Cu, Cr, Mn, Al, As, Cd and Pb) varied from 0.07 mg/L (S2) to 2 mg/L (S1), 0.13 mg/L (S3) to 0.85 mg/L (S1), 0.025 mg/L (S1) to 0.75 mg/L (S3), 0.007 mg/L (S2) to 0.2 mg/L (S3), 0.05 mg/L (S2) to 0.9 mg/L (S2), 0.011 mg/L (S3) to 0.09 mg/L (S1), 0.008 mg/L (S1 and S3) to 0.067 mg/L (S1), 0.023 mg/L (S1) to 2.02 mg/L (S1) and 0.071 mg/L (S2) to 8.19 mg/L (S1) respectively.

Table 3. Heavy metals mean concentrations ± standard deviation of studied wastewaters at the sampling stations followed by total mean values.

Parameters (mg/L)	S1	S2	S3	Total mean values
Iron (Fe)	1.353±0.666	0.662±0.583	0.837±0.323	0.951±0.594
Zinc (Zn)	0.427±0.220	0.322±0.133	0.283±0.084	0.340±0.160
Copper (Cu)	0.236±0.137	0.267±0.106	0.304±0.267	0.269±0.174
Chromium (Cr)	0.045±0.013	0.063±0.052	0.084±0.062	0.064±0.047
Manganese (Mn)	0.114±0.051	0.483±0.437	0.215±0.129	0.270±0.295
Aluminum (Al)	0.041±0.029	0.039±0.018	0.025±0.010	0.035±0.020
Arsenic (As)	0.032±0.028	0.025±0.017	0.017±0.009	0.024±0.019
Cadmium (Cd)	0.665±0.846	0.551±0.652	0.974±0.976	0.730±0.806
Lead (Pb)	3.580±3.620	0.768±0.745	0.984±1.102	1.776±2.469

Means on the same line are not significantly different ($P>0.05$).

Likewise, Fe, Zn, Mn, Al and Pb concentrations were not significantly different among seasons (P>0.05). In return, a significant difference was noticed for Cu, Cr, As and Cd seasonal mean concentrations (P<0.05) (Table 4). Thus, LRS concentration of Cu was higher than its SRS concentration but no significant difference was noticed between both rainy and dry seasons. For Cr and As, no significant difference was recorded between long and short seasons, but their concentrations were significantly higher during LDS than during LRS. For Cd, no significant difference was observed between both rainy seasons, but LRS concentration was the highest followed successively by SDS concentration and LDS concentration which was the lowest.

Table 4. Heavy metals mean concentrations ± standard deviation of studied wastewaters in different seasons of 2012.

(LDS = Long dry season; LRS =Long rainy season; SDS = Short dry season; SRS = Short rainy season)

Parameters (mg/L)	LDS	LRS	SDS	SRS
Iron (Fe)	0.952±0.812	0.888±0.331	1.243±0.412	0.780±0.849
Zinc (Zn)	0.267±0.119	0.437±0.228	0.310±0.061	0.347±0.040
Copper (Cu)	0.212±0.055^{ab}	0.412±0.195^{a}	0.275±0.189^{ab}	0.092±0.058^{b}
Chromium (Cr)	0.083±0.060^{a}	0.027±0.016^{b}	0.078±0.035^{ab}	0.085±0.04^{ab}
Manganese (Mn)	0.420±0.388	0.143±0.094	0.363±0.434	0.133±0.006^{ab}
Aluminum (Al)	0.026±0.005	0.052±0.028	0.035±0.013	0.021±0.006
Arsenic (As)	0.039±0.024^{a}	0.009±0.001^{b}	0.028±0.019^{ab}	0.022±0.010^{ab}
Cadmium (Cd)	0.039±0.018^{c}	1.621±0.317^{a}	0.280±0.090^{b}	0.782±1.069^{ab}
Lead (Pb)	2.780±4.170	2.027±0.330	0.562±0.264	0.484±0.202

Means on the same line followed by different superscripts are significantly different (P< 0.05).

Discussion

Total mean concentrations (mg/L) recorded for heavy metals were 0.269±0.174; 0.951±0.594; 0.340±0.160; 0.064±0.047; 0.270±0.295; 0.035±0.020; 0.024±0.019; 0.730±0.806 and 1.776±2.469 for Fe, Zn, Cu, Cr, Mn, Al, As, Cd and Pb respectively. Similar results were found for Fe, Cr, Mn and Cd in effluents of Kafr El-Zyat City in Egypt (Daifullah *et al.,* 2003), for Cu and Cr in effluents of Benin City in Nigeria (Oguzie and Okhagbuzo, 2010), for Cr in effluents of Suez province in Egypt (Mohamed *et al.,* 2012) and for Mn in effluents of Iranian municipalities (Mojiri, 2012). Nevertheless, the concentrations registered for Fe, Zn and Cu were lower than the values reported for domestic wastewater in Suez province (Mohamed *et al.,* 2012). In return, studied wastewaters were more loaded in Fe and Mn on the one hand, and in Zn and Cu on the other hand than those of Teheran in Iran (Harati *et al.,* 2011) and Kafr El-Zyat City (Daifullah *et al.,* 2003) respectively. Likewise, the registered values for Cd and Pb were beyond those registered for wastewaters of Benin City (Oguzie and Okhagbuzo, 2010), Suez province (Mohamed *et al.,* 2012) and Iranian municipalities (Mojiri, 2012).

The mean concentrations of Fe, Zn, Cu, Cr, Mn, Al and As in the prospected wastewaters were below the limits recommended by Beninese standards for direct discharge (MEHU, 2001). They were also within Moroccan and Egyptian (EEAA, 1994; MATEE, 2005) standards. In return, the limits recommended by the previous standards for Cd and Pb (at most 0.2 mg/L and 0.5 mg/L respectively) were exceeded.

The high amount registered for Cd could be imputable to mechanic and vulcanization workshops which produce surrounding sampled drains, solid waste coming from wear and tears of vehicles and tyres known as sources of this metal (Lagerweff and Specht, 1970). Furthermore, one notes the highest Cd concentration during the rainy seasons. This could be attributable to run-off flood water which can transport heavy metals through washing of various sources such as rubbish dump of domestic refuse, solid waste, roofs (Biney *et al.,* 1994; Chebbo *et al.,* 2001; Van Metre and Mahler, 2003).

The high concentration of Pb registered in studied wastewaters could be mainly due to adulterated gasoline selling activities conducted surroundings main sewers and gutters (Vissin *et al.,* 2010). Indeed, gasoline contains organic lead very harmful for organisms especially fishes (Oguzie and Okhagbuzo, 2010; Youssao *et al.,* 2011).

Pb and Cd, heavy metals are non-essential for metabolic activities of living organisms including human and express for them toxic properties (Biney *et al.,* 1994). They were mentioned with arsenic, also detected in this study, as heavy metals linked most often to human poisoning (Akpor and Muchie, 2010). Moreover, Pb and Cd inhibit, even at low concentration, photosynthesis and growth of phytoplankton (Biney *et al.,* 1994), major constituent of the base of aquatic food webs. Phytoplankton growth could also be disturbing by Cu of which registered mean concentration exceeds highly 4 µg/l, limit sufficient for this effect (Kaiser, 2001).

Other metals such as Zn, Cr, As, even if they were found in low amount, constitute also a threat for living beings. For instance, these heavy metals, like Cd, Pb and Cu, are phytotoxic at both low concentrations as well as very high concentrations (Singh *et al.,* 2011).

Seeing that increased metal concentrations in water resulted generally in increased metal concentration in biota (Klavins *et al.,* 1998), the heavy metals, even present in low amount, must be considered as potentially dangerous to living organisms including humans.

Conclusions

The results of this study show that the raw effluents of Cotonou are very loaded in heavy metals especially cadmium and lead which are found in abnormal amounts. This confirms these wastewaters coming from main sewers and gutters as one of Cotonou lagoon pollution sources by heavy metals. They constitute therefore a permanent threat for the lagoon living resources and consequently for human health. It is hence necessary to undertake their purification including heavy metals removal before pouring it in aquatic environment.

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