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SURVEY OF HEAVY METALS CONCENTRATIONS IN WATER AND SEDIMENTS OF THE ESTUARY BIETRI BAY, EBRIE LAGOON, COTE D'IVOIRE

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ABSTRACT

To provide information on heavy metals mercury (Hg), cadmium (Cd), lead (Pb), copper (Cu) and zinc (Zn) concentrations in water and sediments, monthly samples were collected in five sites in the Betri Bay from February 2008 to January 2009. The average values of water physicochemical parameters temperature, pH, dissolved oxygen, transparency, salinity and MES ranged between 28.12 - 30.49 °C; 7.46 -8.17; 5.10 - 6.62 mgL^{-1}; 0.39 -0.95 m; 7, 21 -30.28 ‰ and 13, 78 - 65, 53 mgL^{-1} respectively. The average mean water concentrations of heavy metals ranged between 0.01 - 0.03 μgL^{-1} (Hg), 0.02 - 0.26 mgL^{-1} (Cd), 2.40 - 4.80 mgL^{-1} (Pb), 9.05 - 9.68 mgL^{-1} (Cu) and 12.05 - 19.87 mgL^{-1} (Zn). The average mean sediments concentrations of heavy metals ranged between 0.35 - 1.33 μgkg^{-1} (Hg), 0.11 - 1.25 $mgkg^{-1}$ (Cd), 26.53 - 120.05 $mgkg^{-1}$ (Pb), 21.12 - 86.21 $mgkg^{-1}$ (Cu) and 106.32 - 509.73 $mgkg^{-1}$ (Zn). Results showed significant differences in levels of some water physicochemical parameters (salinity and MES) and heavy metals in water and sediments among dry, rainy and swelling seasons. The annual mean heavy metals were in the order of Zn > Cu > Pb > Cd > Hg and Zn > Pb > Cu > Cd > Hg respectively in water and sediments. The correlation analysis showed a strong positive relationship between heavy metals and physicochemical parameters in water. The concentrations of water metals were influenced by temperature, salinity and dissolved oxygen; while the concentrations of sediments metals were influenced by water metal levels. The exchange factor determined to assess the extent of metal accumulation in the sediments showed a higher value of exchange between water and sediments. Deleterious water quality levels of , Pb, Cd, Cu and Zn, above recommended levels, in both water and sediments of Bietri Bay poses potential health hazards to the aquatic organisms and the inhabitants of the area that use this water resource directly for domestic or agricultural purpose without treatment.

Keywords: Bietri Bay, heavy metals, physicochemical parameters, seasonal variation, sediment, water

1. INTRODUCTION

Heavy metals are common pollutants which are distributed in aquatic environment. There are some sources from which water bodies are getting polluted through heavy metals. They may occur due to industrial, anthropogenic and agricultural wastes [1] [2]. Most heavy metals in coastal waters are leached to rivers by industrial, urban and agricultural discharges [3]. This compounds the fact that coastal lagoons generally have a low water exchange [4], favoring the accumulation of heavy metals in the ecosystem. Some of these are essential for living organisms, such as Cu and Zn, however, some others like Pb, Cd, Al, etc. are toxic to living organisms [3]. They impose serious damage to metabolic, physiological and structural systems of organisms when present in high concentrations in the environment. Metals such as Zinc and Copper are essential elements for normal metabolism of aquatic organisms in low concentrations, while mercury is nonessential without any recognized role in aquatic systems [5]. They may have direct effects on organisms by accumulating in their body or indirectly through food web to the next trophic level [6]. One of the most serious consequences of this transfer is biological amplification through the food chain [7].

The distribution processes of the metals entering natural waters are controlled by a dynamic

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set of physicochemical interactions and their solubility are principally controlled by pH, concentration, type of metal species, organic ligands, the oxidation state of mineral components and the redox environment of the aquatic system [8]. After being introduced into the aquatic environment via various sources and paths, metals are adsorbed onto inorganic and organic particulates and are incorporated into sediment resulting in elevated levels of heavy metals in bottom sediment [9] [10]. Physicochemical parameters play an important role to determine the water quality. The accumulation of metals from the overlying water to the sediment is dependent on a number of external environmental factors such as pH, dissolved oxygen, electrical conductivity and the available surface area for adsorption caused by the variation in grain size distribution [11]. However, metals cannot always be fixed by sediments permanently. Some of the sediment-bound metals may remobilize and be released back to waters via the variation of environmental conditions such as acidification, redox potential conditions, the organic ligand levels and impose adverse effects on living organisms [10].

In Ivory Cost, recent studies revealed that the concentrations of heavy metals have increased in lagoon [4] [12]. Abidjan coastal waters are under increasing pressure from industrial pollution and urbanization [13]. Such pressures pose potential threat to entire ecosystems not only to wildlife but also for the economy and human well-being. The Bietri Bay serves as receptor for domestic and industrial wastes likely going to introduce heavy metal into the water bodies. It is therefore imperative to continuously monitor the levels of metal pollution in the Bietri Bay system of the Ebrié Lagoon. The aim of this study is to monitor the levels of metals – mercury (Hg), cadmium (Cd), lead (Pb), copper (Cu) and zinc (Zn) in water and sediments collected in the Bietri Bay and the influence of the physicochemical parameters of water on these heavy metals.

2. MATERIALS AND METHODS

Physicochemical parameters, sediments and water samples were collected monthly in Biétri Bay (05°16'N-03°58'W, Fig. 1) from February 2008 until January 2009. Water samples were collected at 1m depth below water surface in 250 ml capacity Niskin bottles. Water is collected in plastic bottles to assess water quality. Physicochemical parameters such as pH was determined using a digital pH meter (WTW pH 192), temperature, dissolved oxygen and salinity were measured using a multi parameter (TURO T-611). Transparency was measured *in situ* using Secchi disc. The water was preserved in plastic bottles by the addition of few drops of nitric acid to laboratory analyses. The surface sediments were collected using a Van Veen snapper in 5 points of the bay (Fig. 1) during the same journey near to the outlets of the main industrial effluents and the drainage and sewage systems of Biétri City. All samples were dried at 50 °C. Large rock debris; mollusk skeletons and organic debris were removed before sieving. The fraction smaller than 1 mm was ground to a fine powder (<63 µm) in an agate mortar. The pulverized samples were newly dried at 60 °C until obtaining a constant weight. The water was preserved in plastic bottles by the addition of few drops of nitric acid.

Water samples were collected at each site for the laboratory analysis of total suspended solids (MES), which was analyzed as follows; Whatman number 1 glass-fiber filter disks were dried at 450-500°C cooled in desiccators and weighed. A well-mixed sample of water was vacuum-filtered through the weighed filter paper and the filter was then removed and dried at 450-500°C, after which it was cooled in desiccators and weighed. Total suspended solids analysis was performed in triplicate. The MES (mgL^{-1}) was calculated according to [14] as follow: MES = $[P_2-P_1]/V$, with P_1 (mg) weight of the filter paper before filtration (mg); P_2 (mg) weight of the filter paper after filtration (mg); V sample volume (mL).

Chemical analyses of sediments and water were done in accordance with standard procedures established by the [15]. Dried sediments samples were prepared and analyzed using a mixture of hot nitric and hydrochloric acids, followed by ICP-Atomic Emission Spectrometry according to EPA Method 200.2 [15]. Water samples were digested according to the method described in [16]. Lead (Pb) and zinc (Zn) analyses were carried out using an atomic absorption spectrophotometer (Varian SAA Pb), cadmium (Cd) and copper (Cu) (air-acetylene flame). Wavelengths for Pb, Cd, Cu, and Zn were 283.3, 228.8, 324.7, and 213.9 nm respectively. Determination of mercury (Hg) was atomic absorption spectrophotometer (Shimadzu AA 660) equipped with a continuous cold vapor generator connected to an electrically heated quartz tube

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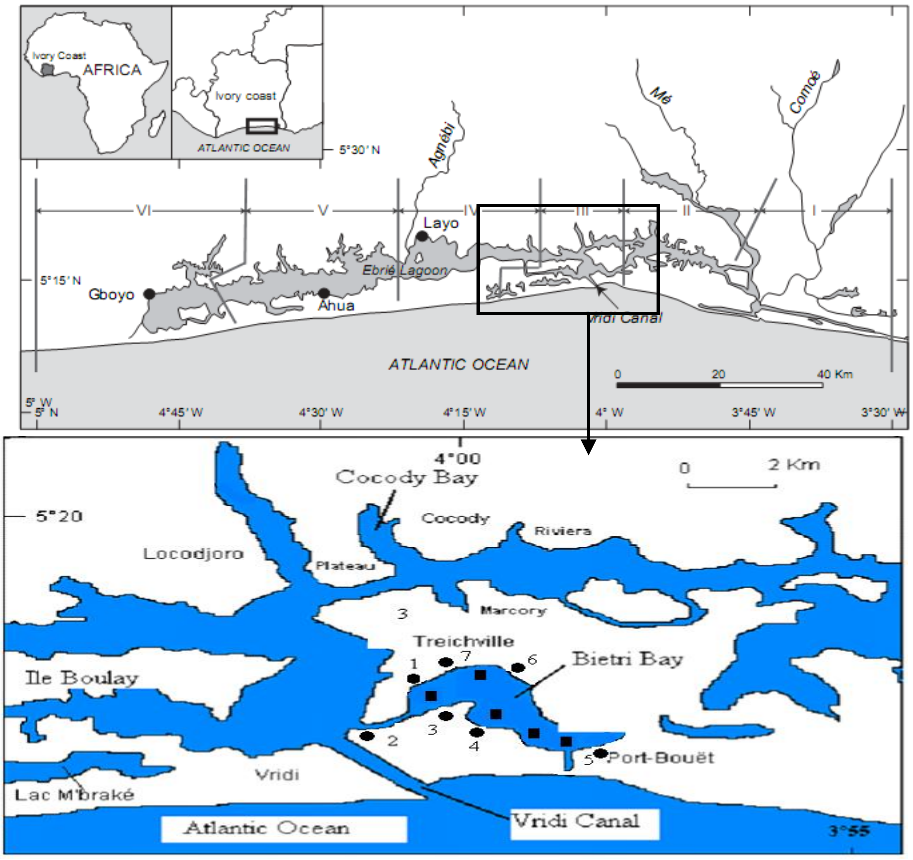

Figure 1. Location of sampling sites (■) in Bietri Bay, Ebrié Lagoon, Ivory Coast
● Industrial factories (1 Unilever; 2 SHELL; 3 Village of fishermen; 4 SIR; 5 Slaughterhouse; 6 SIVOA; 7 Marina).

atomizer, at absorbance resonance line of 253.7 nm. All extractions were carried out in triplicate and blanks were processed as the samples. Results are expressed as mg L^{-1} for water, mg kg^{-1} dry weight for sediments, excepted mercury concentrations which were expressed µg L^{-1} or for water, µg kg^{-1} dry weight respectively for water or sediments.

The exchange factor (CE) water-sediment for each heavy metal was calculated according to [17] as the heavy metal level in water (Cw) divided by the heavy metal level in sediment (Cs): CE = Cw/Cs

The Pearson correlation coefficient of variation was used to measure the strength of a linear relationship between any two variables on a scale of -1 (perfect inverse relation) through 0 (no relation) to +1 (perfect sympatric relation). In this study, the correlation was applied to physicochemical parameters and water and sediments heavy metals data to understand the underlying variability and to assess the relationship between variables. Three seasons dry (from January to April), rainy (from May to August) and swelling (from September to October) were determined. ANOVA was used to evaluate the effect of season over the physicochemical parameters and heavy metal accumulation in water or sediments. Then, Duncan multiple range test was performed if significant difference found in ANOVA. Differences were considered significant at p values <0.05. Statistical analyses were carried out with Statistica 7.1

3. RESULTS AND DISCUSSION

The physicochemical parameters of surface water in the Bietri Bay recorded from February 2008 to January 2009 (Fig. 2) show that temperature range from 28.12 to 30.49 °C with highest value recorded in February (dry season) and lowest value in May and June (rainy season). The water pH is slightly basic, pH-value range from

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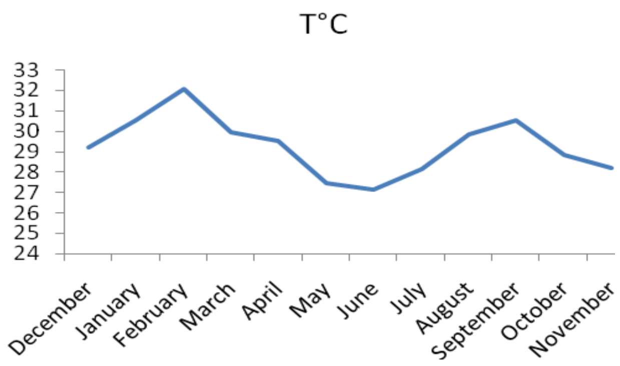
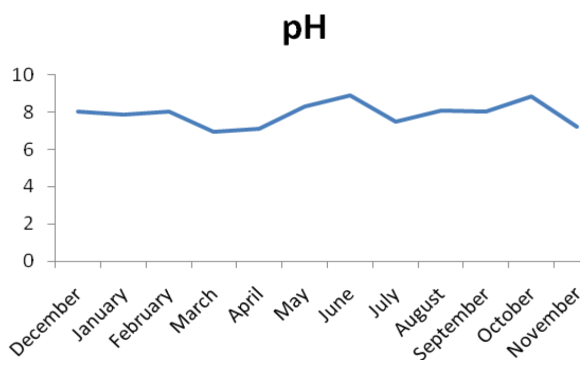
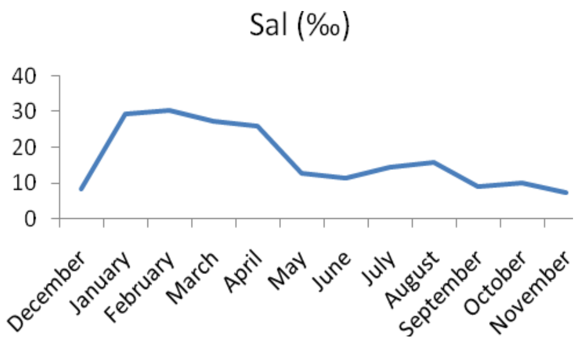
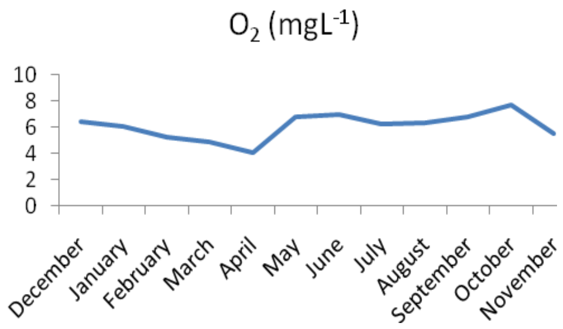
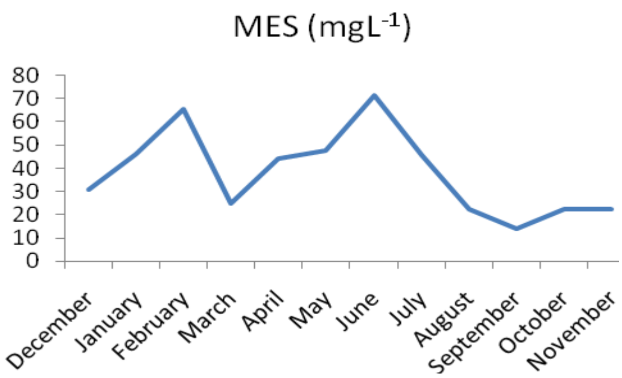
7.46 in March to 8.17 in June. Dissolved oxygen shows the range value of 5.10 to 6.62 mgL^{-1} with the mean values of 5.10 ± 0.18; 6.60 ± 0.36 and 6.62 ± 1.09 mgL^{-1} respectively in dry, rainy and swelling seasons. The values of Secchi disc transparency ranged from 0.39 m in February to 0.95 m in June. There were no significant differences ($p > 0.05$) between seasons for temperature, pH, Dissolved oxygen and Secchi disc transparency. The salinity of Bietri Bay waters range from 7.21 ‰ in November to 30.28‰ in February. Seasonal values showed significant difference ($p < 0.05$) among seasons. Lower value of salinity (8.51 ± 1.30 ‰) was recorded in swelling season while the highest value (28.10 ± 2.18 ‰) was observed in dry season. The value of raining season (13.49 ± 2.30 ‰) was intermediate. For the Suspended Matter (MES), the values ranged from13.78 mgL^{-1} in September to 65.53 mgL^{-1} in February. Seasonal data shows that during the study period the MES content was lower in swelling season (22.18 ± 8.40 mgL^{-1}) compared to the values of dry (45.23 ± 20.30 mgL^{-1}) and rainy (46.84 ± 24.68 mgL^{-1}) seasons.











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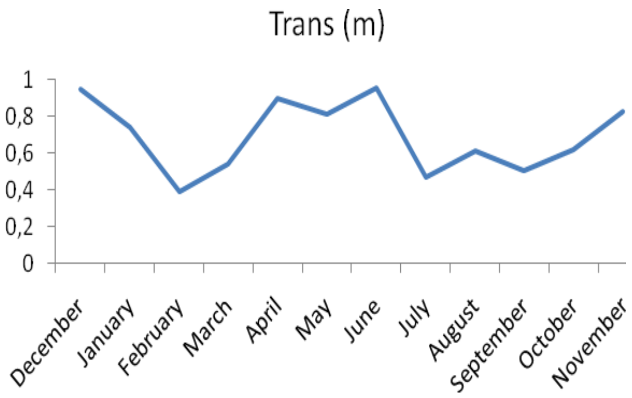
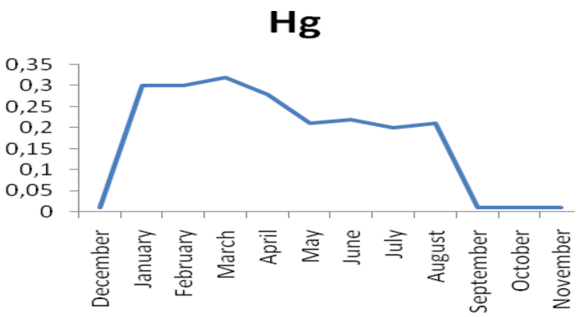
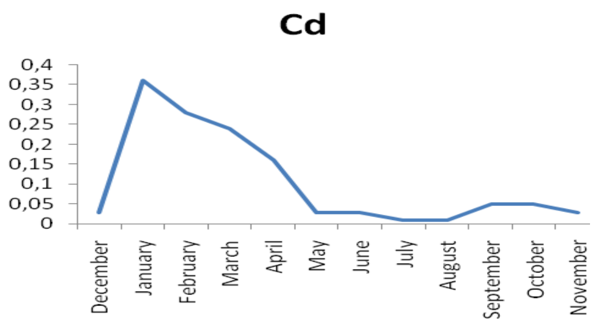


Figure 2. Monthly variations of physicochemical parameters in water of Bietri bay from February 2008 to January 2009. PH: Hydrogen Potential; O_2: Dissolved Oxygen; MES: Suspended Matter, T°C: Temperature, Sal: Salinity, Trans: Transparency

The concentrations of heavy metals in the water samples are shown in Fig. 3. Hg was in the range 0.01-0.32 µgL^{-1}, with mean concentration of 0.30 ± 0.02; 0.21 ± 0.01 and 0.01 ± 0.00 µgL^{-1} for dry, rainy and swelling seasons respectively. In an increasing order, it is dry > rainy > swelling. In this study it was found that mean concentration of Cd ranged between 0.02 ± 0.01 mgL^{-1} (rainy season) and 0.26 ± 0.02 mgL^{-1} (dry season). Fig. 3 shows maximum concentration of Cd (0.36 mgL^{-1}) in January and low concentration (0.01 mgL^{-1}) in July. The mean concentration of Pb ranged from 2.40 ± 0.02 mgL^{-1} to 4.80 ± 1.03 mgL^{-1} respectively in rainy and dry seasons. Relatively higher concentration of Pb was recorded in February and October while the lower values were observed in May, Jun and July (Fig. 3). The highest concentration of 12.70 mgL^{-1} for Cu was recorded in October during the swelling season, while the lowest value was 6.66 mgL^{-1} in July in the rainy season. The mean concentrations of Cu were 9.56 ± 2.03 mgL^{-1}; 9.05 ± 1.85 mgL^{-1} and 9.68 ± 3.02 mgL^{-1} for dry, rainy and swelling seasons respectively. No significant difference ($p > 0.05$) was observed in levels of Cu among seasons. Zn recorded its highest concentration of 21.88 mgL^{-1} in December during the dry season and its lowest concentration of 10.73 mgL^{-1} in May during the rainy season. The mean concentrations for dry, rainy and swelling seasons were 19.22 ± 1.08; 12.05 ± 1.32 and 19.87 ± 2.01 mgL^{-1} respectively.





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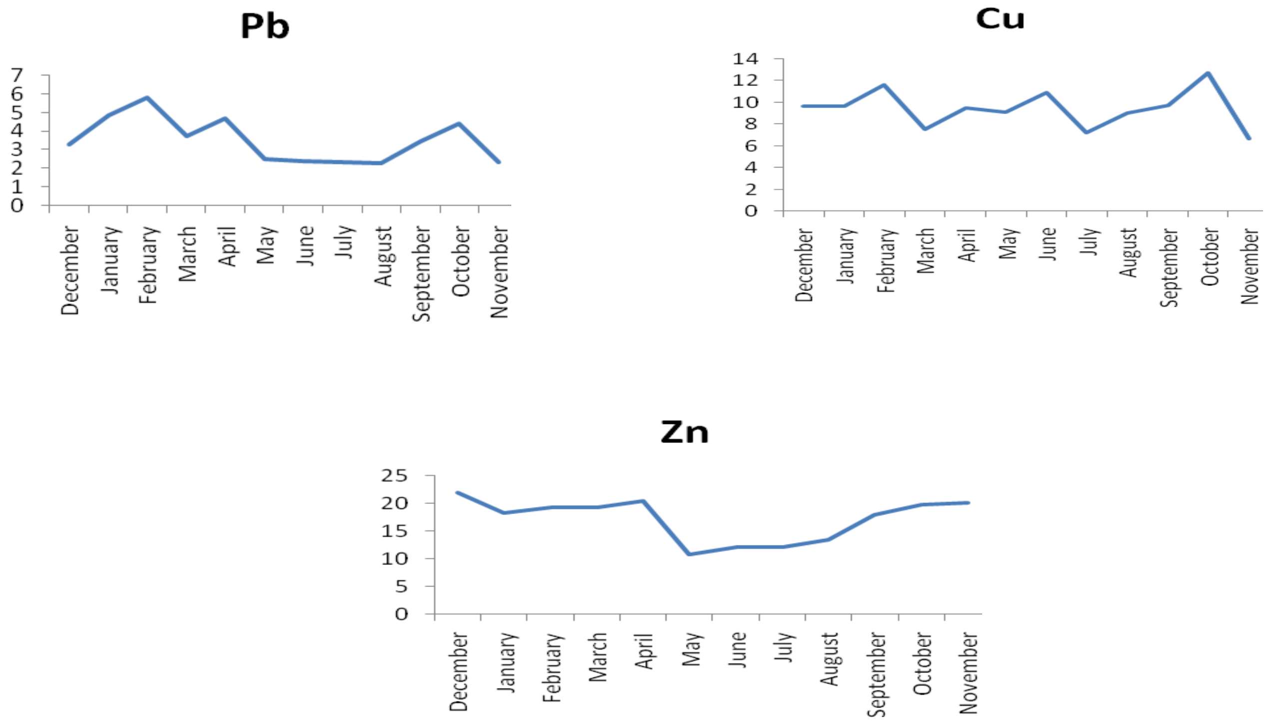

Figure 3. Monthly variations of heavy metal concentrations in water (mgL^{-1} dry weight, except Hg (µgL^{-1})) of Bietri Bay from February 2008 to January 2009.

The heavy metals concentrations recorded in surface sediments of Bietri Bay from February 2008 to January 2009 (Fig. 4) show that Hg ranged from 0.35 in April to 1.33 µgkg^{-1} in December. The Hg mean concentrations were higher in dry (0.88 ± 0.46 µgkg^{-1}) and swelling (0.81 ± 0.52 µgkg^{-1}) seasons compared to rainy season (0.68 ± 0.33 µgkg^{-1}). Cd ranged from 0.11mgkg^{-1} in March to1.25 mgkg^{-1} in October. There was no significant difference ($p > 0.05$) between seasons. The concentration of Pb ranged from 26.53 in June to 120.05 in October with the mean values of 56.83 ± 37.67; 45.30 ± 29.87 and 73.29 ± 46.76 mgkg^{-1} respectively in dry, rainy and swelling seasons. Higher concentration of Pb was recorded in swelling season, while the lower value was observed in rainy season. Surface sediments concentration of Cu ranged from 21.12 mgkg^{-1} in April to 86.21mgkg^{-1} in February. Seasonal values showed significant difference ($p < 0.05$) among seasons. Lower value of Cu (25.45 ± 4.33 mgkg^{-1}) was recorded in rainy season while the highest values were observed in dry (53.94 ± 32.27 mgkg^{-1}) and swelling (47.07 ± 21.61 mgkg^{-1}) seasons. For the sediments Zn concentration, the values ranged from 106.32 mgkg^{-1} in March to 309.73 mgkg^{-1} in October. Seasonal data shows that during the study period the sediments Zn content was lower in rainy season (152.76 ± 46.44 mgkg^{-1}) compared to the values of dry (198.70 ± 86.09 mgkg^{-1}) and swelling (211.27 ± 98.46 mgkg^{-1}) seasons.

The heavy metal mobility in water towards the sediments was characterized by the exchange factor (CE) water-sediments. The results of CE are shown in Table 1. The seasonal CE-values showed higher variations of Hg (2.9 – 81.0), Cd (23.5 – 17000.0), Pb (11839.5 – 22209.0), Cu (2812.1 – 5642.2), and Zn (10348.9 – 12677.1). The results showed that the CE was higher for all heavy metals except Hg.

Table 1. Seasonal exchange factor of water and sediment in the Bietri Bay.

Metal	Dry	Rainy	Swelling
Hg	2.9	3.2	81.0
Cd	2950.0	23.5	17000.0
Pb	11839.5	18875.0	22209.0
Cu	5642.2	2812.1	4362.6
Zn	10348.9	12677.1	10632.6

The Pearson correlation analysis between water physicochemical parameters and heavy metals in the water showed that both Cd and Pb were positively correlated to salinity (Table 2). Cd,

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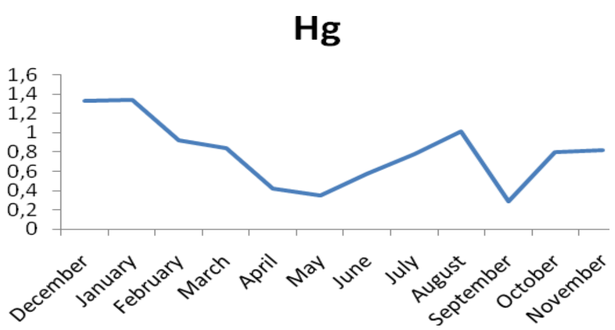
Pb and Zn were positively correlated to water temperature. In addition, Hg was positively correlated to both salinity and MES and Cu was positively correlated to water pH. In contrast, Hg and Cd were negatively correlated to dissolved oxygen. This suggests that different physicochemical parameters influence the concentrations of some heavy metals in the water. The values showed a wide range from -0.50 between dissolved oxygen and cadmium to 0.89 between salinity and cadmium (Table 2).

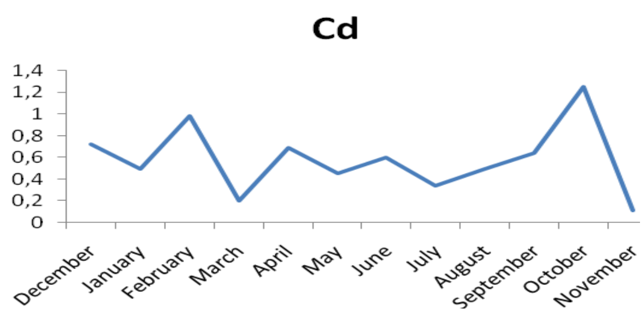
Table 2. Correlation coefficients between heavy metals and physicochemical parameters in water collected in Bietri Bay from February 2008 to January 2009.

Parameters	Hg_w	Cd_w	Pb_w	Cu_w	Zn_w	T°C	pH	Sal	O_2	Trans	MES
Hg_w	1										
Cd_w	0.64*	1									
Pb_w	0.32	0.80*	1								
Cu_w	-0.06	0.14	0.54*	1							
Zn_w	-0.27	0.39	0.60*	0.13	1						
T°C	0.25	0.67*	0.75*	0.24	0.52*	1					
pH	-0.27	-0.30	-0.06	0.76*	-0.34	-0.23	1				
Sal	0.86*	0.89*	0.70*	0,06	0.18	0.63*	-0.40	1			
O_2	-0.53*	-0.50*	-0.35	0.41	-0.39	-0.37	0.84*	-0.66*	1		
Trans	-0.16	-0.24	-0.29	-0.01	0.03	-0.58*	0.13	-0.31	0.01	1	
MES	0.59*	0.28	0.20	0.29	-0.37	-0.11	0.25	0.38	-0.11	0.16	1

Significant levels are indicated by * at $p < 0.05$.

The matrix of linear relationship coefficient between heavy metals in water and sediments is shown in Table 3. The correlation values showed a wide range from 0.53 between Cd_w in water and Cu_s in sediments, to 0.95 between Cu_w in water and Zn_s in sediments. The Pearson correlation data showed that both Cd_s and Zn_s in sediments were strongly correlated with Pb_w and Cu_w in the water. In addition, Cu_s in sediment was correlated positively with Cd_w, Pb_w and Zn_w in water.





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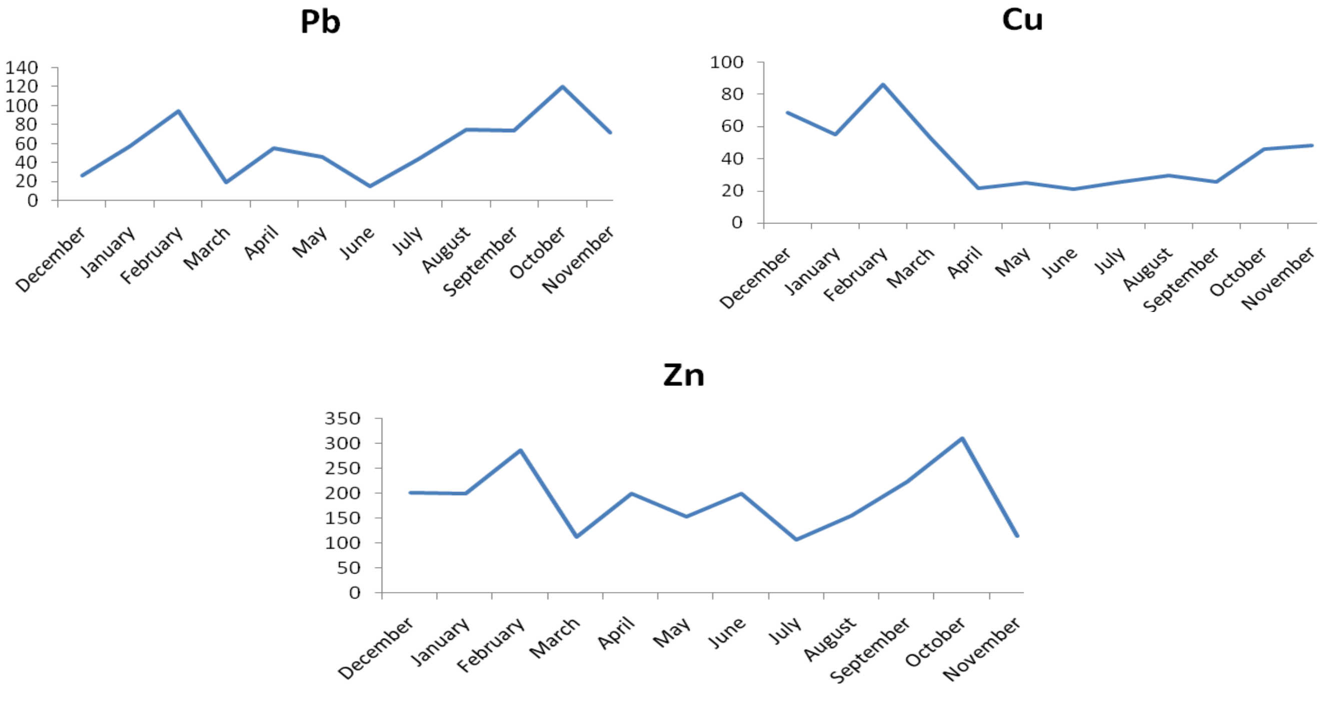

Fig 4. Monthly variations of heavy metal concentrations in surface sediments (mgkg^{-1} dry weight, except Hg (µgkg^{-1}) of Bietri Bay from February 2008 to January 2009.

Table 3. Correlation coefficients between heavy metal of water and sediments collected in Bietri Bay from February 2008 to January 2009.

Metals	Hg_s	Cd_s	Pb_s	Cu_s	Zn_s	Hg_w	Cd_w	Pb_w	Cu_w	Zn_w
Hg_s	1									
Cd_s	0.01	1								
Pb_s	-0.02	0.58*	1							
Cu_s	0.67*	0.26	0.21	1						
Zn_s	0.02	0.95*	0.61*	0.35	1					
Hg_w	0.04	-0.18	-0.31	0.03	-0.17	1				
Cd_w	0.35	0.06	0.04	0.53*	0.21	0.64*	1			
Pb_w	0.20	0.58*	0.41	0.58*	0.67*	0.32	0.80*	1		
Cu_w	-0.00	0.93*	0.46	0.22	0.95*	-0.06	0.14	0.54*	1	
Zn_w	0.35	0.27	0.26	0.61*	0.35	-0.27	0.39	0.60*	0.13	1

Significant levels are indicated by * at $p < 0.05$

In the present study, water temperatures vary from 28.12°C to 30.49°C. These values were similar to those reported by [18] [19] in Ebrié Lagoon. The Bietri Bay shows slightly alkaline character with pH ranging from 7.46 to 8.17. This may be attributed to the effect of bicarbonate ions and to penetration of oceanic waters in the bay [20]. Our results were similar to those reported by [21]. The value of dissolved oxygen in water may be due to the abundance of phytoplankton that increases photosynthetic activity leading to production of large amount of dissolved oxygen. Our results showed that dissolved oxygen was correlated positively with pH but negatively with salinity. The values of dissolved oxygen (5.10 -6.62 mgL^{-1}) were comparable with results (4 -7 mgL^{-1}) reported by [22]. The average salinity dropped from 30.28 ‰ in dry season to 7.21 ‰ in swelling season. The increased freshwater input into estuary during swelling season resulted in a reduction of salinity in the Biétri Bay, while the high salinity during dry season resulted in a significant evaporation of water due to the high temperature during this season. The low Secchi disc transparency observed in this study resulted in the increasing of suspended matters like soil particles in rainy season and the abundance of the plankton in the dry reason.

The results of heavy metals in water showed significant differences in the concentrations of Hg, Cd, Pb and Zn among seasons. Seasonal metal means recorded in water showed higher dry season levels than rainy season except Cu. The general increase in mean concentrations of heavy metals in the water during the dry season could be attributed to more bioaccumulation due to the metal concentration arising from reduced water volume during this season. The higher dry season levels of the heavy dependent upon the physicochemical properties of water, such as pH, temperature, salinity, conductivity and dissolved oxygen levels [23] [24]. The correlation analysis applied to assess the relationship between physicochemical parameters and heavy metal concentrations in water shown that contaminations of Cd and Pb were strongly and positivity correlated with salinity. Cd, Pb and Zn concentrations were positively correlated to water temperature. In addition, Hg was positively correlated with both salinity and MES and Cu with pH. In contrast, Hg and Cd were negatively correlated to dissolved oxygen. The concentrations of heavy metals in water were influenced by the variables of mineralization. The water pH, the nature and concentration of organic ligands, oxidation state and redox conditions within the environment could influence metal solubility [20] [23] [8]. Water temperature is one of the most influencing environmental factors affecting estuary dynamics and both the biological processes and water quality [25]. This study revealed that the sediment of Bietri Bay contained very high amounts of heavy metals when compared with their concentration in water. Our results of Pb, Cu and Zn for dry season were higher than the values reported by [4] in early dry season (48.86, 25.72 and 137.33 $mgkg^{-1}$ respectively for Pb, Cu and Zn) in the Bietri Bay. Sediments are considered to be compartments of accumulation of pollutants, brought by the water column, that have their origin in the different uses of soil of the drainage areas basin [26]. Our values are higher than the values observed by [27] considered as normal for the natural environment except for Cd. Cu concentrations represent a unique source of variance in the system. The Cu may thus be from an alternative natural source to all the other metals or from a diffuse anthropogenic source. This indicates that there was enrichment of metals on this bay. The Pearson correlation between heavy metal concentration in the water and the sediments in the Bay of Biétri showed a strong relationship of metal contents in the two components of the Bay. According to [9], aquatic sediments absorb persistent and toxic chemicals to levels of many times higher than the water column concentration. The values of exchange factor water-sediment of all metals (except Hg), were very higher showing greater mobility of Cd, Pb, Cu and Zn in water toward the sediments. The accumulation of metals from the overlying water to sediments is dependent on a number of external environmental factors such as pH, conductivity or salinity [11].

4. CONCLUSION

In Bietri Bay, temperature, salinity and dissolved oxygen influenced positively the levels of Hg, Cd, Pb in water, while pH influenced negatively on Cu. The concentrations of heavy metals in water and sediments in the present study showed that sediments were contaminated by heavy metals water. Significant differences were observed among seasons for both physicochemical parameters and heavy metals in water and sediments. This reflected the contribution of various heavy metals from different watersheds by runoff during rainy and swelling seasons. Highest levels of heavy metals found in the water and sediments were mainly due to the anthropogenic input from the city of Abidjan. This constitutes health hazards to aquatic life.

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