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Research Paper

Heavy metals pollution in bottom surface sediments, and metal fluxes through the sediment/ water interface, Milliardaires bay, Ebrie lagoon (Côte d'Ivoire)

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ABSTRACT

Milliardaires Bay, Ebrie Lagoon, bottom surface sediments and near bottom waters were sampled and analysed for cadmium, lead, zinc and copper using atomic absorption spectrophotometry. Contents of these four metal elements were determined, also, in interstitial water sediment, obtained by centrifugation at 4000 rpm for 20 min. Statistical analysis using the Pearson correlation matrix showed that there is a significant relationship between metals on the one hand, and on the other hand metals and certain physico-chemical parameters of the sediments. The toxic capacity of the heavy metals analyzed in the sediments was evaluated by using the index of geoaccumulation (I_{geo}). The results obtained revealed high indices of I_{geo} for all metals. The concentrations of Cd and Pb belong to classs (4-5) of Müler and vary from strongly to extremely polluted. Those of Zn and Cu indicate a pollution of the area studied with average values of I_{geo} which vary from class 2 to class 3. Net metals input, calculated on the basis of sedimentation rate and concentration in the uppermost sediments, gave mean values fluctuating between 17 and 646 ng/m^2/h. Concentrations of metals (Cd, Pb, Zn and Cu) remobilized from sediments due to diffusion were calculated. The results showed that the diffusion of these elements, from sediments towards overlying water, represents a substantial proportion of the input (Cd: 29.5%; Pb: 5.8%; Zn: 8.7%; Cu: 4.1 %).

Key words: Heavy metals, correlation, potential toxicity, remobilisation, Ebrié Lagoon

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INTRODUCTION

The Ebrie Lagoon is a brackish tropical lagoon communicating with the Atlantic Ocean by a broad channel artificial (channel of Vridi) on the level of Abidjan. The lagoon stretches along 120 km and drains a surface area of 566 km^2 with an average depth of 4.8 m (Lemasson and Pagès, 1982). The annual total of its hydrous contributions represents 75% sea water, 19% Comoé water (river) and other sources 6% (Varlet, 1978). The climate is of subequatorial type with four seasons including two wet and two dry (Rancurel, 1971; Bakary et al., 2009).

This lagoon is confronted by serious problems of pollution by heavy metals, specific to the aquatic ecosystems of the great agglomerations in general and African in particular (Reyms-Keller et al., 1998; Briton et al., 2006). Indeed the lagoon receives the domestic and industrial effluents of the city of Abidjan, often without preliminary treatment (Yao et al., 2007; Yao et al., 2009). Demographic expansion and industrial development of the town of Abidjan accentuated the degradation of the lagoon over these last decades (Briton Bi et al., 2006). This anthropic pollution significantly affects all the compartments of this aquatic medium (water, sediment, fauna and flora).

In the study of environmental pollution, the sediments constitute privileged targets (Chen and Jiao, 2009). Indeed, the sediments have the capacity to be useful not only as vectors of transport of heavy metals but also as places of storage and accumulation (Silva and Rezende, 2002). These heavy metals adsorbed by the sediments can be desorbed and cause a second pollution under the effect of certain physical disturbances, biogeochemical transformations in the vicinity of the interface and/or of change of the physicochemical conditions (pH, potential redox, salinity, temperature, organic decomposition of matter) (Serpaud et al., 1994; Ramirez et al., 2005). The result can be the creation of gradients of concentration which give rise to diffusive flux. Thus, many elements present in the solid part of the sediment can pass into solution in pore waters (Lourino-Cabana et al., 2012). The profile of vertical changes in the concentrations of elements dissolved in the interstitial medium, indicate the quantitative importance of their flux to the sediment- water interface. Flux of metals (cadmium. lead. zinc and copper) from the sediments towards the overlying column of water can thus be established.

MATERIALS AND METHODS

Stations localization and sediments sampling

During seasonal campaigns (February, April, June, August and October) of 2008 bottom surface sediments (top 5 cm) and near bottom water samples were collected in several areas of the "Milliardaires Bay" in Ebrie Lagoon (4°19' W - 4°27' W; 5°8' N - 5°10' N). Figure 1 shows the location of the sampling stations. The sediments were sampled in polyethylene bags using a Van Veen type bucket. Then the samples were preserved in a refrigerator at (-20°C) until their treatment at INP-HB laboratory of Yamoussoukro (Côte d'Ivoire).

Hydroclimatic data

Figure 2 represents the principal oceanic and river contributions to the Ebrie Lagoon (Varlet, 1978; Bakary et al.. 2009). GDS is the great dry season (December - April); GRS is the great rainy season (May - July); SDS is the small dry season (August - September); SRS is the small rainy season (October - December).

Treatment of the samples and analyses of heavy metals

Near bottom waters interface were acidified without filtration. The total metal concentrations of the solution were measured by atomic absorption spectrophotometry.

One fraction of the sediment sample was oven-dried at 80°C for 24 h, crushed in an agate mortar. Samples were homogenized and filtered on a sieve of 63 µm; the smaller size fractions were used (Dassenakis et al., 2003). About 0.3 g of this fine sediment was mineralized at 120°C for 4 h in the presence of 4 ml of HF and 2 ml of a mixture (HCl + HNO_3). The sample obtained after dilution was filtered on Whatman 0.45 µm paper to separate the insoluble fraction (siliceous compounds). Concentrations of metals were then determined in the supernatant.

The other fraction of the sediment was centrifuged at 4000 rpm for about 20 min. After centrifugation, the supernatant was filtered using a Nuclepore filter 0.4 5 µm to separate the dissolved phase. Just after filtration, about 2/3 of the filtrate was acidified (HNO_3 suprapure, 65%) (Klump and Martens, 1981; Klump, 1987). The Cd, Pb and Cu concentrations were measured by graphite furnace atomic absorption spectrophotometry (Perkin-Elmer. model 3100), that of Zn by flame atomic absorption spectrophotometry.

Statistical analysis

The calculation of the coefficients of variation for each metal analysis, based on reproducibility of replicates analyse on one sample, gave the following relative coefficients of variation (that is, $\text{standard deviation} \times 100 / \text{averange}$): Cd 10% ,Pb 11%, Zn 7%, Cu 9%, that is, a mean reproducibility of about 90.2% . The accuracy of the analytical method was checked by using certified sediment of reference (Bcss-1), provided by the National Council of Research of Canada. The error brackets obtained for the various metals analyzed ranged from 7 to 9%. The detection limits were 8, 6, 4 and 9 $ng.g^{-1}$(dry weight) for Cd, Pb, Zn, and Cu respectively. The test of correlation of Pearson ($p < 0.05$) was used to check the possible relations between various parameters by using software STATISTICA 7.1

Index of geoaccumulation

The index of geoaccumulation I_{geo} presented the first time by Müller (1969) is a criterion of determination of the metal degree of pollution of the marine sediments (Table 1). He distinguishes six (6) classes from I_{geo} and has been calculated as follows (Equation 1):

$$\mathbf{I_{geo} = \log_2(C_{sr} / \lambda \times C_{Br})} \qquad \text{(Equation 1)}$$

Where, C_{Sr} is the measured concentration of heavy metal r in the sediment; C_{Br} is the concentration of heavy metal r in the earth's crust / or geochemical background noise of the Ebrié Lagoon for heavy metal r (Aoua et al., 2010); λ is a constant which makes it possible to take into account at the same time the natural fluctuations of the content of a substance given in an environment as well as weak anthropic influences (λ = 1.5).

The average index of geo accumulation I_m (geo) which allows one to quantify the total pollution of a site is given by the mathematical relation (Equation 2):

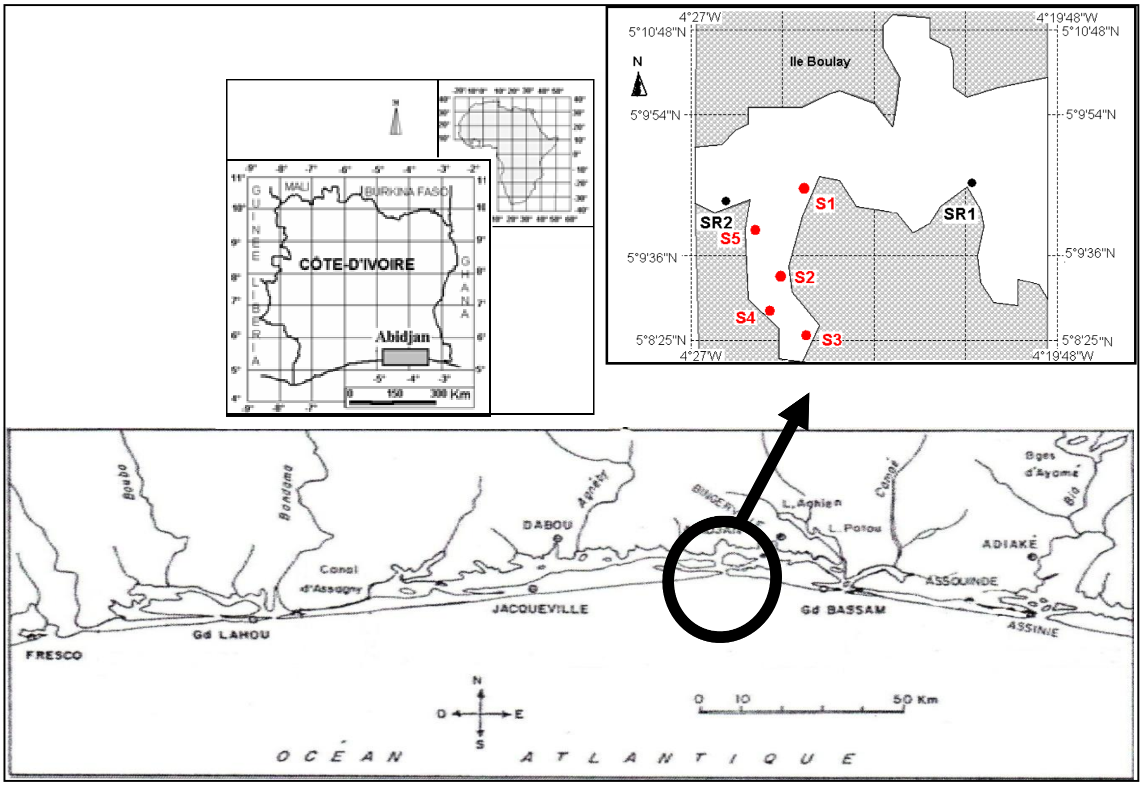

Figure 1. Localization of the sampling stations of the bottom surface sediments of Milliardaires Bay in Ebrie Lagoon.

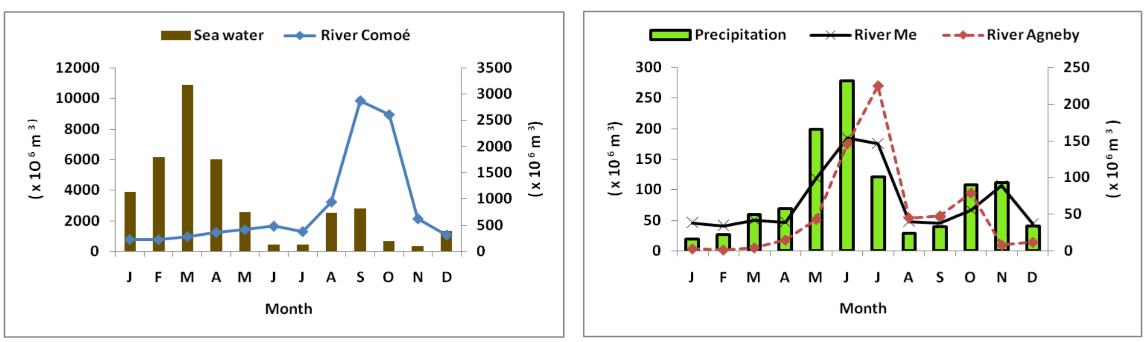

Figure 2. Principal Histograms of the hydrous contributions of the Ebrié Lagoon (Varlet, 1978; Bakary et al., 2009).

$$\mathbf{I_m(geo)} = \sum(\mathbf{Igeo})_r / \mathbf{n} \qquad \text{(Equation 2)}$$

Where, n is the number of analyzed elements; I_{geo} is the index of geoaccumulation of heavy metal r.

Metals fluxes calculation for the sediments

Net input

Many authors connect the importance of the remobilisation of heavy metals of the sediments to their net input in sediments (Gaznon et al., 1997; Covelli et al., 1999). These net inputs can be calculated according to Beldowski et al. (2009) by the formula of Equation 3:

$$\mathbf{F_S} = \frac{\mu}{10}\left(1 - \frac{\beta}{100}\right)\rho_S C_S \qquad \text{Equation 3}$$

Where, F_S is the net metals input to the bottom sediments (ng/m^2 hour); μ is the sedimentation rate (μ = 0.5 mm/year); β is the water content in sediments (%); ρ_S is the

Table 1. Relationship between I_{geo} and pollution level (**Müller, 1969**)

I_{geo} value	Class of I_{geo}	Pollution level
≤ 0	0	Unpolluted
0 - 1	1	Unpolluted to moderately polluted
1 - 2	2	Moderately polluted
2 - 3	3	Moderate to strongly polluted
3 - 4	4	Strongly polluted
4 - 5	5	Strongly to extremely polluted
> 5	6	Very strongly polluted

dry sediment density; and C_S is the total metal concentrations in surface sediments.

Diffusive fluxes at sediment/ water interface

The diffusive fluxes of different metals at the sediment water interface were calculated using Fick's first law from concentration gradients in the interstitial waters and near-bottom waters (Beldowski et al., 2009; Mamdouh and Ehsan, 2011) (Equation 4):

$$J_z = -\varphi D_s \left(\frac{dC}{dz}\right) \quad \text{(Equation 4)}$$

Where, J is diffusive fluxes (ng/m^2 hour); φ (dimensionless) is the porosity at sediment-interface (φ = 0. 34); D_S is the molecular diffusion coefficient (m^2/ hour); (dC/dz) is the concentration gradient of metal in the interstitial water (ng.m^{-4}); and (dz = 0.05 m; the negative sense towards the sediment).

Values of the molecular diffusion coefficient were calculated using the Equation 5 (Boudreau, 1997):

$$D_S = D_0/1 - \mathrm{Log}(\varphi^2) \quad \text{Equation 5}$$

Where, D_0 is the coefficient of metal in water at infinite dilution (m^2/s); φ is the porosity (dimensionless). Diffusion coefficients, D_0 of ions were calculating for porewater at 30°C by using Stokes-Einstein equation (Einstein, 1905):

$$D_0 = k_B T/6\pi\eta R_0 \quad \text{Equation 6}$$

Where k_B = 1.38 x 10 $^{-23}$ kg m^2/s K is Boltzmann's constant, T is temperature, η is the shear viscosity, and R_0 the radius of the ion. In addition D_0 values were adjusted for viscosity and temperature effects according to the following (Li and Gregory, 1974):

$$(D_0\eta/T)_1 = (D_0\eta/T)_2 \quad \text{Equation 7}$$

Where η represents the viscosity of the interstitial water at the temperature T. D_0 (x10^{-9} m^2/s): Pb^{2+} = 2.32; Cd^{2+} = 2.86; Zn^{2+} = 3.76; Cu^{2+} = 3.86

Metals remobilization

The metals remobilization can be roughly approximated by the following formula:

$$R_M(\%) = J_z \times 100/F_S \quad \text{Equation 7}$$

Where R_M is the rate of metal remobilization, J_z is the diffusive fluxes and F_S is the net metals input.

RESULTS AND DISCUSSION

Physicochemical and metallic characteristics of sediments

The results of the physicochemical parameters of the surface sediments presented in Table 2 line up as follows: Temperature (29. 32 – 31.05°C), salinity (3.41 – 4.35‰), pH (6.80 -7.71), conductivity (4.01 – 5.77 mS/cm), organic matter rate (0.68 – 2.88), rate faction < 63 µm (0.92-1.85), and water content (16.88 – 19. 85). These values are characteristic of the sandy and/or sandy-argillaceous sediments (Lemasson and Pagès, 1982; Zabi et al., 1990).

The background concentration of heavy metals is very important and useful for determining the anthropogenic impact on the aquatic ecosystems. In this study the description of the metal contamination of the sediments, is deduced from the comparison of the space average contents measured and those recorded on the level of the references sediments BF-LE (Aoua et al., 2010) and UCC (Weldephol., 1995). The local background (BF-LE) was selected in Ebrié Lagoon, far from all disturbances of anthropic origin. The results of these measurements are reported to Table 3.

The cadmium content measured in this study is higher than those of the references BF-LE and UCC, by a factor of 29 and 15, respectively. The lead concentration exceeds that of the reference BF-LE by 23 times and 3 times that of

Table 2. Physicochemical parameters of the surface sediments in "Milliardaires Bay".

Sampling sites	T (°C)	S (‰)	pH	Cond (mS/Cm)	% M.O	% < 63	% T.E
S1	29.32	3.41	7.05	4.01	0.98	1.25	18.31
S2	30.73	4.35	7.71	5.77	0.95	0.92	18.95
S3	31.02	4.17	7.46	5.41	0.68	1.54	18.88
S4	29.71	4.12	6.8	5.67	2.88	1.8	16.88
S5	29.79	3.95	6.99	4.65	0.74	1.83	17.24
SR1	30.55	3.87	7.54	4.88	1.21	1.31	18.58
SR2	31.05	3.93	7.6	5.18	1.27	1.85	19.85
Mean values	30.31	3.97	7.31	5.08	1.24	1.50	18.38

Table 3. Total metal concentrations in surface sediment in "Milliardaires Bay", compared with reference values (UCC and BF-LE).

Sampling sites	Cd (µg/g)	Pb (µg/g)	Zn (µg/g)	Cu (µg/g)
S1	1.24	60.97	52.38	15.32
S2	1.41	56.88	56.2	14.16
S3	1.41	60	53.42	15.71
S4	1.36	56.43	54.7	14.9
S5	1.33	56.89	55.45	13.69
SR1	1.32	58.7	56.2	15.11
SR2	1.04	50.97	42.44	13.92
Mean values	1.30	57.26	52.97	14.69
BF-LE	0.05	2.4	11.18	1.51
UCC	0.1	17	52	14

UCC: Upper continental crust (Weldephol, 1995); BF-LE: Background of the lagoon (Aoua et al., 2010).

the reference UCC. As for metals zinc and copper, their concentrations represent 5 times and 11 times those of reference BF-LE, respectively. The results of these quantitative measurements emphasized the existence of a significant enrichment of the sediments by metals cadmium and lead. This pollution could be of an anthropogenic origin. This assumption is supported by many authors in particular Briton Bi et al. (2006) and Yao et al. (2009).

Correlation between metals and physicochemical parameters of the sediments

The calculation of correlation coefficients allows having an idea on the possible relations between physicochemical parameters: common origin, homogeneous distribution, behavior identical with respect to the physicochemical processes, influences one on the other (Chouti et al., 2010). The correlation coefficients matrix between heavy metal concentrations and certain physicochemical and granulometric parameters of the sediments are presented in Table 4. The results show the heavy metals Cd, Pb, Zn and Cu were significantly and positively correlated with each other (Cd and Pb: 0.65; Cd and Zn: 0.91; Pb and Zn: 0.70; Pb and Cu: 0.73), indicating that they mostly came from the same source. It was also found that relationships between Cd and %T.E, Pb and F.P, Zn and F.P were significantly negative and the Pearson's correlation coefficients achieved -0.48 ($p < 0.05$), -0.49 ($p < 0.05$) and -0.45 ($p < 0.05$), respectively. Table 3 also indicates that the four physicochemical parameters temperature, salinity, pH and conductivity, are significantly correlated with each other, indicating that these physicochemical parameters probably have similar characteristics in the sediments. The Pearson correlation results also show a strong association between pH and M.O, F.P and T.E.

Geoaccumulation index of heavy metals in surface sediments

The index of geoaccumulation and the related classes of various studied metals were calculated and consigned in Table 4, by using two values of C_{Br} : reference BF-LE (Aoua et al., 2010) and reference UCC (Weldephol, 1995). The detailed analyses of the contamination show that the mode

Table 4. Correlation coefficient matrix between heavy metal concentrations and physicochemical parameters in the sediment of "Milliardaires Bay" in the Ebrie Lagoon.

	Cd	Pb	Zn	Cu	T(⁰C)	S (‰)	pH	Cond	%M.O	%FP	%T.E
Cd	1.00										
Pb	0.65[a]	1.00									
Zn	0.91[a]	0.70[a]	1.00								
Cu	0.35	0.73[a]	0.26	1.00							
T(⁰C)	-0.10	-0.40	-0.35	-0.06	1.00						
S(‰)	0.49[a]	-0.29	0.23	-0.23	0.58[a]	1.00					
pH	-0.13	-0.24	-0.24	-0.08	0.86[a]	0.35	1.00				
Cond	0.35	-0.38	0.07	-0.11	0.57[a]	0.94[a]	0.32	1.00			
%M.O	-0.01	-0.26	0.01	0.07	-0.31	0.13	-0.50[a]	0.39	1.00		
% F.P	-0.40	-0.49[a]	-0.45[a]	-0.26	-0.07	-0.05	-0.48[a]	-0.01	0.34	1.00	
%T.E	-0.48[a]	-0.32	-0.61[a]	-0.01	0.77[a]	0.04	0.88[a]	0.09	-0.49[a]	-0.29	1.00

[a]:significant correlation ($p < 0.05$) ; FP : fine fraction of sediments (< 63 µm); MO: organic matter.

of distribution and accumulation of these elements remains different from each other. Thus cadmium presents I_{geo} raised at the level of stations S2, S4 and SR2 (Reference BF-LE). Zinc and copper record high values of I_{geo} on the level of the stations S5 and SR2 (Reference UCC). But as for the element lead the I_{geo} increases significantly on the level of stations S1, S5 and SR2. Figure 3 displays samples percentages in Muller classes for Cd, Pb, Zn and Cu. For Cd, samples mainly fall in class 5 (71.4% of total samples) and the remainder 28.6% in class 4. For Pb, 71.4% of the samples are included in class 4, and the remaining 28.6% fall in class 5. For Zn, concentrations fall mainly in class 2 (100%, of total samples). For Cu, 100% of the samples fall in class 3. These results indicate that the surface sediments of the "Milliardaires Bay" in Ebrie Lagoon can be categorized as follows: moderately polluted with Zn ($1 <$ average $I_{geo} < 2$), moderately to strongly polluted with Cu ($2 <$ average $I_{geo} < 3$), strongly polluted with Pb ($3 <$ average $I_{geo} < 4$), and strongly to extremely polluted with Cd ($4 <$ average $I_{geo} < 5$).

As shown in Table 5 and Figure 3, by considering the reference UCC and according to the scale of Muller, the studied zone is prone to a metal pollution, with an interval of average of I_{geo} which varies from class 0 (unpolluted) to class 4 (strongly polluted).

Metals fluxes

Net metals input in the sediments

Figure 4 presents the spatial and temporal evolution of the net cadmium, lead, zinc, and copper input to sediments from the study area.

The spatial analysis shows that metals net input present values raised at the level of all the stations. This could be, mainly, the result of an industrial activity very diversified in the area without excluding those from agricultural and domestic origins (Briton Bi et al., 2006). The temporal evolution shows a light increase of the sedimentation flux during the great rain season, GRS (May - July), and during the small dry season, SDS (August - September), for the elements cadmium, zinc and copper. For the metal lead, in addition to the small dry season, one observes a relatively significant peak during the great dry season, GDS (December - April), due probably, to one specific and occasional contribution. During, the periods of great dry season and small rain season, SRS (October - November), the dominating entry of marine water into the lagoon increases the turbulence of the medium following a handing-over in causing resuspension of fine materials, and could be the cause of fluxes low values observed. Conversely, during the great rain season and the small dry season, the decantation and the trapping of biogenic salts and organics in the sediments are facilitated in an environment of weak hydrodynamicity.

Diffusive metal fluxes in the sediments

The flux values calculation (Equations 4 and 5) of some metals (Cd, Pb, Zn, and Cu) in pore water of the sediments of "Milliardaires" Bay in Ebrié Lagoon were enumerated in Table 6 and represented in Figure 5.

Cadmium (Cd): The calculated flux of Cd fluctuated between -0.13 to -9.13 ng/m²/hr at stations S1 and S3 during great rain season (May - July) and small rain season (October-November), respectively with an annual average -5.05 ng/m²/h.

Lead (Pb): The calculated fluxes of Pb were found between – 0.68 and – 92.66 ng/m²/h at stations S4 and S1 great rain season (May - July) and great dry season (December –

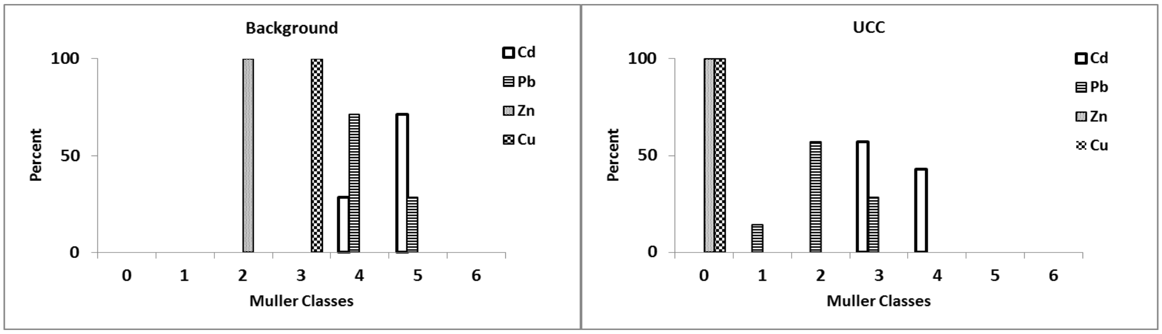

Figure 3. Percentage of samples in Muller class, using local background and Upper Continental Crust as reference material.

Table 5. I_{geo} index and Müller class of heavy metals studied in the sediments of each sampling site of the Milliardaires Bay in Ebrie Lagoon (Reference BF-LE).

Stations	Cd		Pb		Zn		Cu		Average	
	I_{geo}	class	I_{geo}	class	I_{geo}	class	I_{geo}	class	Im (geo)	class
S1	4	4	4.1	5	1.6	2	2.8	3	3.1	4
S2	4.2	5	4	4	1.7	2	2.7	3	3.2	4
S3	4.1	5	4	4	1.7	2	2.6	3	3.1	4
S4	4.2	5	4	4	1.7	2	2.6	3	3.1	4
S5	4.1	5	4	4	1.7	2	2.7	3	3.1	4
SR1	3.8	4	3.8	4	1.3	2	2.6	3	2.9	3
SR2	4.2	5	4.1	5	1.7	2	2.8	3	3.2	4
Average	4.1	5	4	4	1.6	2	2.7	3	3.1	4

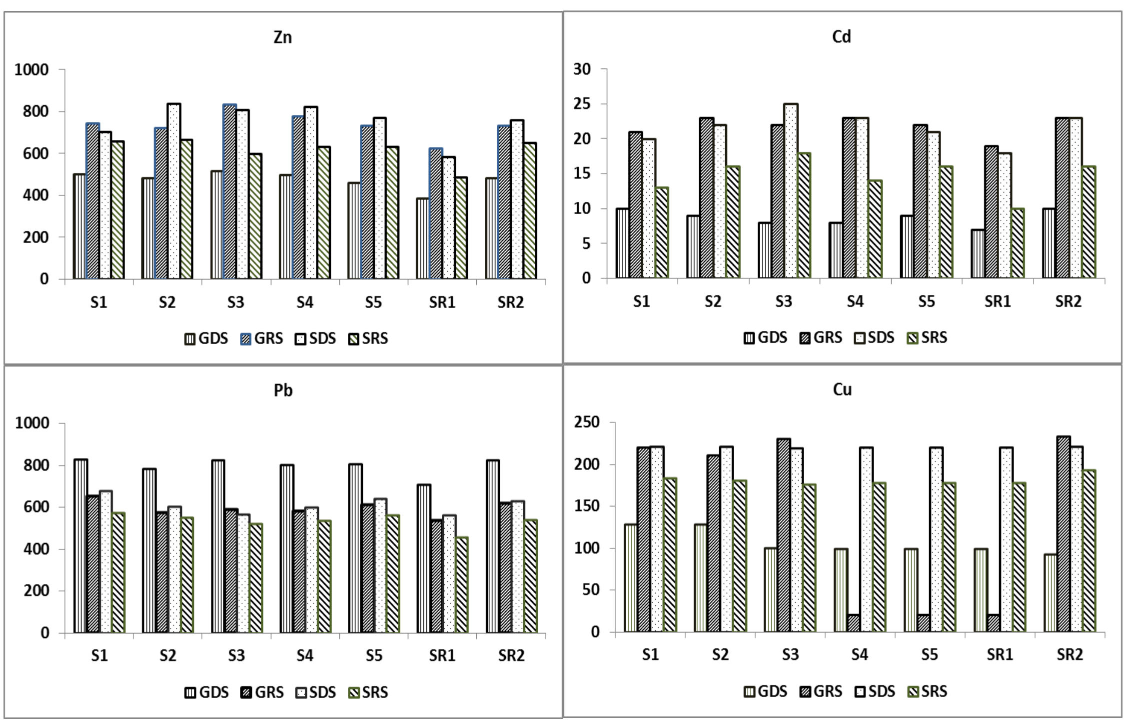

Figure 4. Spatial and temporal variations of metals fluxes (ng/m²/h) of sedimentation in Milliardaires Bay.

Table 6. I_{geo} index and Müller class of heavy metals studied in the sediments of each sampling site of the Milliardaires Bay in Ebrie Lagoon (Reference UCC).

Stations	Cd		Pb		Zn		Cu		Average	
	I_{geo}	class	I_{geo}	class	I_{geo}	class	I_{geo}	class	Im (geo)	class
S1	3	3	1.3	2	-0.6	0	-0.5	0	0.8	1
S2	3.2	4	1.1	2	-0.5	0	-0.5	0	0.8	1
S3	3.1	4	1.2	2	-0.5	0	-0.6	0	0.8	1
S4	2.8	3	1.2	2	-0.5	0	-0.6	0	0.7	1
S5	3.1	4	2.8	3	-0.5	0	-0.5	0	1.2	2
SR1	2.8	3	1	1	-0.9	0	-0.6	0	0.6	1
SR2	2.8	3	2.8	3	-0.5	0	-0.4	0	1.2	2
Average	3.0	1	1.6	2	-0.6	0	-0.5	0	0.9	1

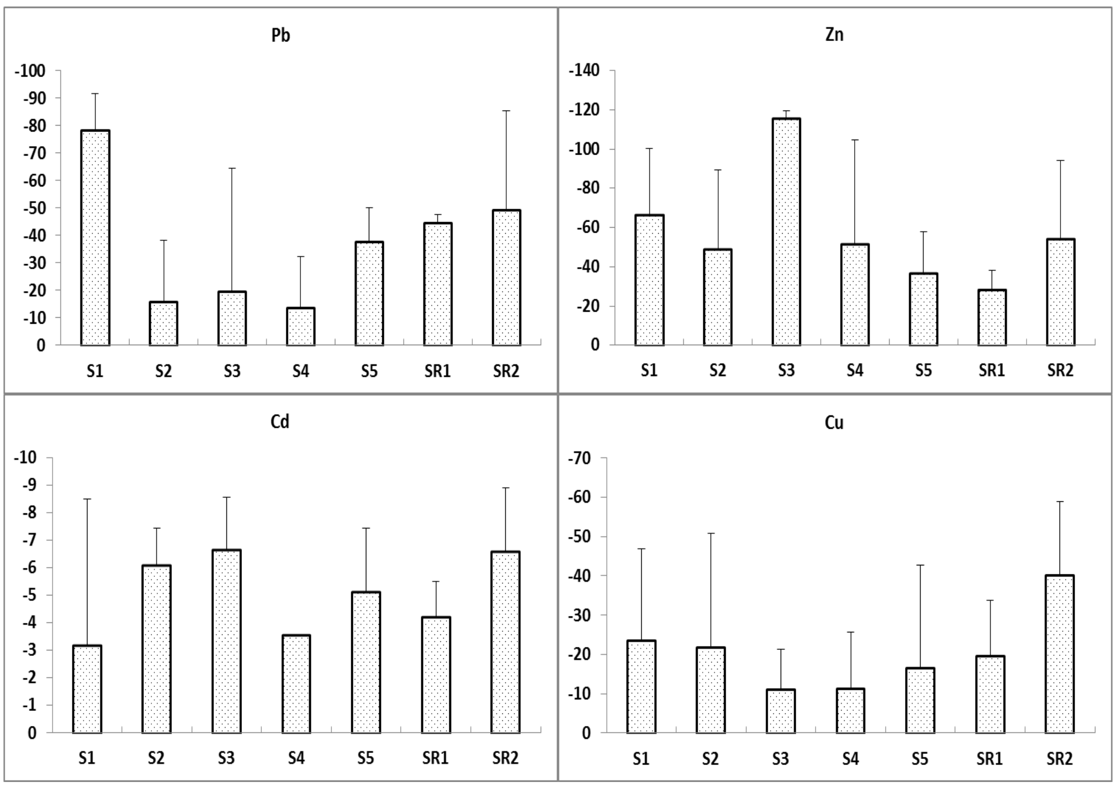

Figure 5. Spatial fluxes variations of some metals ng/m²/h and standards deviations in pore water of the sediments of "Milliardaires" Bay in Ebrie Lagoon.

April), respectively with an annual average of -36.96 ng/m²/h.

Zinc (Zn): The calculated flux of Zn showed variation between -1.05 and -189.82 ng/m²/h at stations SR1 and S3 during small rain season (October-November) and great rain season (May - July) respectively, with an annual average -57.29 ng/m²/h.

Copper (Cu) : The calculated flux of Cu fluctuated between -0.99 to -66.57 ng/m²/hr at stations S4 and SR2 during small rain season (October-November) and great dry season (December - April) respectively, with an annual average -20.59 ng/m²/h.

From the data of the present study it is noticeable that fluxes of studied metals vary according to the sampling stations and are turned from the sediment towards to near bottom water. These physicochemical phenomena depend on the (bio) geochemistry of the sediment and its level of pollution. Average fluxes of studied metals vary significantly from -5.05 to -57.29 ng/m²/h. These values are

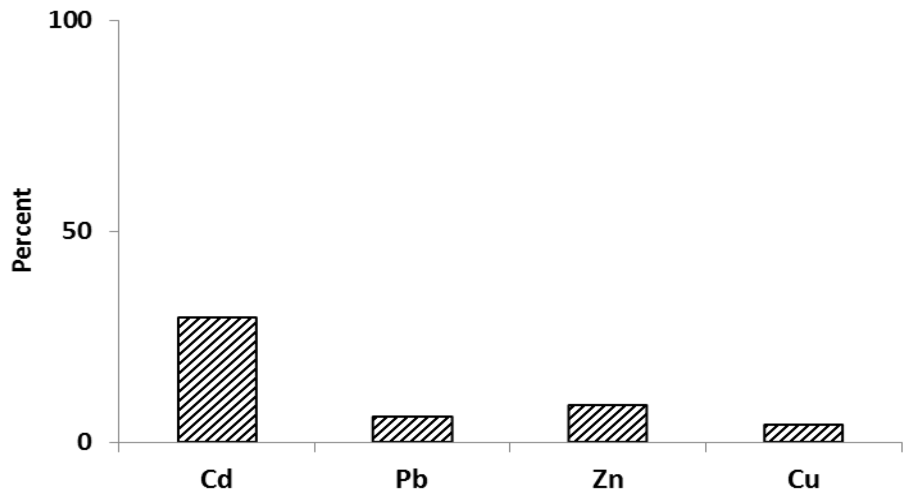

Figure 6. Percentages of the metals remobilized in the water column.

lower compared with those of Mamdouh and Ehsan (2011), who observed in the Rosetta estuary in Egypt -47.59 ng/m^2 h for Cu, -93.33 ng/m^2 h and -4705 ng/m^2 h for Zn. This can be related to the environmental conditions and the nature of the sediment of the study area. Indeed, the water depths of the study area are not very deep (approximately 4.8 m) and the water is oxygenated, thanks to turbulences due to the currents (winds, tides, flux of coastal rivers). This presence of oxygen in the medium will support reactions of metal precipitations of ions in overlying water, particularly oxidative precipitation of Fe^{2+} and Mn^{2+} that diffused from the sediments. It is what Lourino-Cabana et al. (2012) think by affirming that under toxic conditions, ions (Cu^{2+}, Mn^{2+}, Ni^{2+} and Zn^{2+}) present in water column and those released from the sediment through diagenetic processes appeared to be scavenged from the overlying water through adsorption to iron and manganese (hydr)oxide solid phases: these particles then tend to deposit back to the surface sediment.

Metals remobilization

The results of the remobilization of metals due to diffusion are presented in Figure 6 and Table 7. These results show that the return soluble of metals from the sediment to the water column constitute a substantial proportion of the input; they vary between 4.1 and 29.5% and could indicate that the study area is to some extent polluted by heavy metals. The cadmium recorded the strongest proportion (29.5%) followed by zinc (8.7%), lead (5.8%) and coppers (4.1%). The high value, observed in the case of cadmium, is due probably to the considerable mobility of this metal in the sandy sediments of the study area. For organisms living in the lagoon, elevated heavy metal content desorbed may impart a significant impact on health, reproduction and survival. Contaminants may pass through the food chain to human and result in a wide range of adverse effects.

Conclusion

In order to determine the impact of the human activities of the adjacent urban area and industries of Abidjan, on Milliardaires Bay, a physicochemical and study of selected heavy metal was carried out on the surficial bottom sediments and the bottom sediment water interface of this bay. The degree of pollution by heavy metals, based on the Muller geoaccumulation index was evaluated on the sediments. Nets fluxes of metal entries in the sediments, diffusive fluxes of metals to the sediment water- interface and the rate of metal remobilization were also determined in this study.

The results obtained show that the sediments are neutral-basic and are slightly charged out of organic matter. The comparison of the contents of the metals studied with those of the references sediments of the Ebrié Lagoon indicates heavy metal pollution of the bay sediments. This polymetallic contamination of these surface sediments is confirmed by the calculation of the Muller geaccumulation index. With regard to the results of diffusive metals fluxes, they show that all studied metals can be recycled out of the sediments back into the water column. This metal remobilization due to diffusion represents a substantial proportion compared to their net input in the sediments which is approximately 4.1% for copper, 5.8% for lead, 8.7% for zinc and 29.5% for cadmium.

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Table 7. Spatial and temporal metals fluxes variations (ng/m^2/h) in pore water of the sediments of Milliardaires Bay in Ebrie Lagoon.

	Cd					**Pb**				
Station	**GDS**	**GRP**	**SDS**	**SRS**	**Average**	**GDS**	**GRS**	**SDS**	**SRS**	**Average**
S1	-7.63	-0.13	-4.88	-0.11	-3.19	-92.66	-81.77	-64.76	-73.83	-78.26
S2	-7.36	-4.48	-7.09	-5.43	-6.09	-5.62	-11.3	-8.54	-37.52	-15.75
S3	-6.41	-2.28	-8.73	-9.13	-6.64	-66.19	-6.81	-2.63	-3.08	-19.68
S4	-0.89	-4.41	-7.98	-0.91	-3.55	-39.41	-0.68	-1.69	-13.32	-13.78
S5	-7.63	-2.31	-6.16	-4.3	-5.1	-38.06	-39.3	-17.23	-55.59	-37.55
SR1	-6.21	-3.08	-3.19	-4.37	-4.21	-58.64	-53.74	-3.17	-62.75	-44.58
SR2	-8.2	-5.34	-7.87	-4.88	-6.57	-74.6	-47.86	-50.74	-23.25	-49.11
Mean	-6.33	-3.15	-6.56	-4.16	-5.05	-53.6	-34.49	-21.25	-38.48	-36.96
	Zn					**Cu**				
Station	**GDS**	**GRS**	**SDS**	**SRS**	**Average**	**GDS**	**GRS**	**SDS**	**SRS**	**Average**
S1	-56.13	-74.45	-29.61	-104.58	-66.19	-46.11	-29.92	-4.88	-13.19	-23.53
S2	-14.41	-3.79	-104.84	-71.91	-48.74	-47.66	-27.89	-5.21	-6.67	-21.86
S3	-82.24	-189.82	-100.47	-88.54	-115.27	-17.17	-20.02	-4.4	-2.9	-11.12
S4	-26.17	-21.59	-56.71	-101.52	-51.5	-21.45	-20.35	-2.18	-0.99	-11.24
S5	-6.24	-46.76	-57.29	-36.47	-36.69	-47.21	-3.65	-4.88	-10.08	-16.46
SR1	-12.49	6.53	-108.96	1.05	-28.47	-25.49	-2.63	-5.24	-45.33	-19.67
SR2	-42.12	-33.08	-42.71	-98.75	-54.17	-66.57	-28.15	-26.12	-40.18	-40.26
Mean	-34.26	-51.85	-71.51	-71.53	-57.29	-38.81	-18.94	-7.56	-17.05	-20.59

GDS: Great dry season (December - April); GRS: Great rain season (May - July) SDS: Small dry season (August -September); SRS: Small rain season (October-November).

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