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PRELIMINARY ASSESSMENT OF CADMIUM MOBILITY IN SURFACE SEDIMENTS OF A TROPICAL ESTUARY

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ABSTRACT. Cadmium is a toxic metal often found with a strong enrichment factor in coastal sediments. The sequential extraction procedure proposed by the BCR (Community Bureau of Reference) was applied for partitioning of Cd in tropical estuary sediments. The method showed satisfactory recoveries. The repartition of Cd in different phases of sediment was controlled by the residual phase (50.32 to 67.45 %). However, the exchangeable and acid soluble fraction (F1) was in general found to be the second most abundant fraction in the surface sediments (11.14 to 15.24 %), indicating that an important portion of Cd could be remobilized, thus becoming available to aquatic biota. Cd also showed different distribution patterns in the sediment phases due to the heterogeneity of the sediments, as well as the physical and chemical conditions along with the different sources of Cd in the bays. The risk assessment code investigation showed a medium risk of Cd in the estuary.

KEY WORDS: Cadmium, Mobility, Sediment toxicity, Sequential extraction

INTRODUCTION

Heavy metal environmental pollution is a worldwide problem primarily because the metals are not biodegradable, and the majority of them have toxic effects on living organisms when concentrations are elevated [1-5]. Heavy metals are introduced into the environment through natural phenomena and human activities such as agriculture, transport, industrial processes and waste disposal [6-11]. Estuarine and coastal sediments are generally considered a sink for metals. It is recognized that sediments play an important role in the pollution scheme of the aquatic systems because they are less susceptible to flow conditions compared to the water column, and they affect the transport of heavy metals in the aquatic system. Recent data on metal speciation has shown an increase in metal mobility as a result of increasing total metal concentrations in the coastal and estuarine sediments of the central east coast of India [12]. Because the mobility of a metal in the sediment is a good indicator of its bioavailability, studies on metal speciation in sediments are important for understanding potential risks of metals to benthic organisms and aquatic systems.

It is well understood that the determination of total metal concentration in sediments is inadequate for predicting the bioavailability, mobility, and toxicity of metals [12-15]. In contrast, sequential fractionation procedures, which distinguish non-residual metal phases from the residual phase, are more reliable for assessing metal mobility and bioavailability in sediments and soils [16]. Among them, the procedure proposed by the Community Bureau of Reference (BCR) has been widely used, due to its high reproducibility [17-21]. The BCR protocol allows the determination of the amount of metals associated with four phases of the sediments: the exchangeable (including carbonates), reducible, oxidizable, and residual phases. The residual phase is known to be part of the crystalline structure of the sediment, and it is

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considered as having no ecological risk. In contrast, the three other phases are susceptible to be remobilized in the overlying water under certain physical, chemical, and biological conditions. A risk assessment code (RAC), which is based on the percentage fraction of metals associated with the exchangeable and carbonate phases, has recently been used to predict the potential threat of metals to aquatics organisms [22]. While total metal concentration provides limited information on the toxicity of metals in the environment, the RAC method targets the labile exchangeable metal fraction, which is the most bioavailable fraction.

Cadmium is one of the toxic metals found mostly in coastal sediments with a strong enrichment factor [23-25]. Pollution of sediments and waters with Cd causes its incorporation into the food chain, which could result in a wide variety of adverse effects in animals and humans.

Studies on metal fractionation and ecological risk assessment in some tropical sediments have shown that Cd is more mobile than other metal elements, and thus, it may present a high risk to local environment [26-28]. However, more studies are needed to better understand the mobility and the toxicity of Cd in tropical aquatic systems, since its fate may vary in different aquatic environments. For example, along the southwestern coast of Spain, it was reported that Cd showed low mobility in the eastern area, intermediate mobility in the western area, and high mobility in the central area [15]. In addition, studies are concentrated primarily in Asia and South America, and limited data is available on West African estuaries [21, 27, 29-31]. As an example, no study has been conducted in the Ebrie lagoon, even though it is the largest lagoon in West Africa, where almost 70% of industries of Cote d'Ivoire are concentrated.

The objective of the present study was to assess the distribution, mobility, and potential ecological risks of Cd in the sediments from Ebrie lagoon. To address this objective, the BCR sequential extraction protocol was used in combination with the risk assessment code (RAC). The influence of organic carbon on the distribution of Cd was also investigated.

EXPERIMENTAL

Study area

The Ebrié lagoon system (3°25 N, 4°45 W), with a total area of 566 km^2, a length of 130 km, and a maximum width of about 7 km, is the largest lagoon bordering the eastern equatorial Atlantic Ocean in West Africa. The average depth is of 4.8 m, with a few deeper areas especially around Abidjan. The study area (Figure 1) is surrounded by Abidjan City (6 million inhabitants) the capital of Côte d'Ivoire. In this area, intense human activities constitute sources of chemical contamination to surrounding waters that may cause public health problems. The waters around Abidjan are highly eutrophicated and frequently oxygen deplete as a result of the discharge of untreated sewage and industrial wastes. Human pressures are numerous and include urbanization, industrialization, agriculture, fishing, ship building, transport, sand extraction, aquaculture, and tourism.

In this study the sediment samples were collected from Cocody, Banco, Bietri and Abou-Abou bays of the estuarine part of the Ebrie lagoon (Figure 1). Cocody, Banco, and Bietri bays receive direct discharges of urban and industrial wastes while Abou-Abou bay is 25 km farther from wastewater discharges.

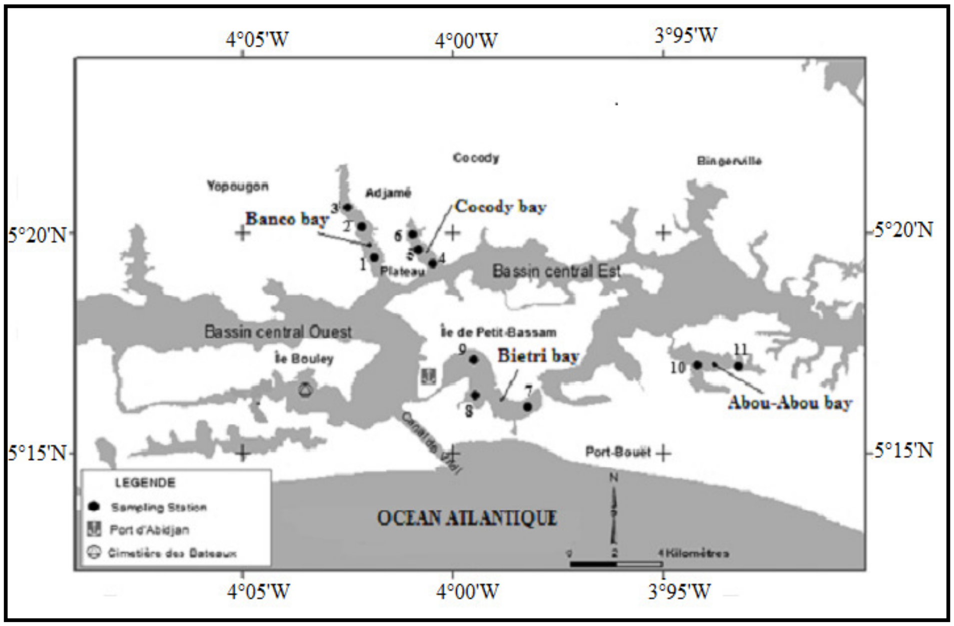

Figure 1. Studied area and sampling sites.

Sampling scheme and sample conservation

Sediment samples were collected between February 2012 and May 2012. A Van Veen stainless steel grab (with an area of 0.02 m^2) was used to collect surface sediment (0-5 cm); without emptying the grab, a sample was taken from the center with a polyethylene spoon (acid washed) to avoid contamination by the metallic parts of the dredge. Three samplings were done at each station. The samples were transported to the laboratory at 4 ^{o}C, dried at 60 ^{o}C in a forced air oven, gently homogenized and stored at 4 ^{o}C until analysis. Each sample was sieved through a stainless steel mesh to remove any particle larger than 63 µm in size.

Major components and total organic carbon (TOC) determination

Major components of the sediments samples were determined using a scanning electron microscope (SEM) (D.C.AR MEB FEG Supra 40 VP Zeiss) coupled with an energy dispersive spectrometer (EDS) (INCA Dry Cool, without nitrogen liquid). The sediment sample was finely crushed using an agate mortar, sieved through a stainless steel mesh 63 µm, and then 0.3 g sediment was placed on an aluminum stub using conductive carbon before processing. The spectrum was analyzed by the EDS.

TOC concentrations in sediments were determined using the Walkey-Black method [32], followed by an application of a factor of 1.4 to the results. This method has been widely used for the determination of TOC in soil and sediments because it is simple, rapid, and has minimal equipment need [33]. A large scale comparison showed good recoveries close to 88 to 106%, when a correction factor of 1.4 was applied to the results [34].

Procedure and reagents

All chemicals and reagents used in the study were of analytical grade. Glass, plastics, and other laboratory ware were cleaned by soaking in 10% HNO_3 solution overnight and then thoroughly rinsed with de-ionized water.

Pseudo total metal digestion

All digestions were performed in Teflon containers. Approximately 0.2 g of each of the homogenized sediment was digested with a mixture of 1 mL of aqua regia (HNO_3: HCl; 1:3, v/v) and 3 mL of HF in loosely capped Teflon vessels on a hot plate to dryness and left for 15 min at room temperature. Next, 20 mL of H_3BO_3 (140 g/L) were added to each vessel to mask free fluoride ions in the solution and re-dissolve fluoride precipitates. The final digests were diluted to 50 mL with 2% ultrapure HNO_3. The liquid aliquots were filtered through 0.45 μm pore size membrane (Millex millipore) prior to air-acetylene flame atomic absorption (spectrometer, SpectrAA100 Varian spectrophotometer, Japan) analyses. Three replicates of each sample were analyzed and the samples presented an error within 6%. The limit of detection was calculated as three times the deviation standard of the blank values, and was found to be 0.005 ng/L. Duplicate blanks were prepared and analyzed with each batch of digested samples. The operational conditions for the AAS were adjusted in accordance with the manufacturer's guidelines to obtain optimal determination.

Sequential extraction procedure

Sequential extraction was performed using a three-stage modified procedure recommended by BCR plus the residual fraction. All extractions were carried out for 16 h (overnight) at room temperature, using a mechanical shaker. The extract was then separated from the solid residue by centrifugation for 20 min at 3000 rpm, and the resultant supernatant liquid was transferred into a polyethylene volumetric flask. The residue was washed by adding 20 mL of deionised water, shaken for 15 min on the end-over-end shaker (model Rotospin, Tarsons), and centrifuged for 20 min at 3000 rpm. Subsequently, the supernatant was decanted. The three extraction steps performed in this study can be broadly summarized as follows.

Step 1 (acid extractable/exchangeable fraction). Exactly 40 mL of 0.11 M acetic acid was added to 1 g of sediment sample in a centrifuge tube and shaken for 16 h at room temperature. The extract was then separated from the solid residue by centrifugation and filtrate was separated by decantation as previously described.

Step 2 (easily reducible fraction). Exactly 40 mL of freshly prepared hydroxyl ammonium chloride was added to the residue from step 1 in the centrifuge tube, and re-suspended by mechanical shaking for 16 h at room temperature. The separation of the extract collection of the supernatant, and rinsing of residues were the same as described in step 1.

Step 3 (oxidizable fraction). The residue in step 2 was treated twice with 10 mL of 8.8 M hydrogen peroxide. First 10 mL of hydrogen peroxide was added to the residue 2 in the centrifuge tube. The digestion was allowed to proceed at room temperature for 1 h with occasional manual shaking, followed by digestion at 85±2°C for another 1 h. During the digestion, the centrifuge tube was loosely covered to prevent substantial loss of hydrogen peroxide. Next, the centrifuge tube was uncovered and heating was continued until the volume reduced to about 2-3 mL. An additional 10 mL of hydrogen peroxide was added to the tube, covered, and digested with cover at 85±2°C for another hour. Heating was continued as before until the volume reduced to 2-3 mL. Finally, 50 mL of 1 M ammonium acetate was added to the cold mixture and shaken for 16 h at room temperature. The separation of the extract, collection of the supernatant, and rinsing of residues were the same as described in step 1.

Step 4 (residual fraction). The residue from step 3 was digested using a mixture of aqua regia and HF.

An internal check was performed on the results of the sequential extraction by comparing the total amount of metal extracted by different reagents during the sequential extraction procedure with the results of the total digestion.

	Major element relative contents (%) (mean ± SD)											
Station	Na	Al	Si	S	Cl	K	Ca	Ti	Fe	Cu	Mg	P	O
Banco 1	1.59±0.07	14.0±0.4	21.7±0.3	2.09±0.05	2.75±0.07	0.48±0.06	0.38±0.04	1.31±0.02	10.39±0.06	0.17±0.15	-	-	45.07±0.03
Bietri 1	2.9±0.4	10.49±0.02	18.8±1.3	5.1±0.3	3.7±0.6	1.2±0.3	0.33±0.05	0.55±0.08	11.6±1.2	0.36±0.05	0.94±0.04	-	44.0±0.7
Bietri 2	4.0±0.3	9.23±0.10	20.1±0.4	5.10±0.13	6.6±0.4	1.01±0.03	0.19±0.03	0.44±0.04	8.3±0.5	-	1.32±0.05	-	43.9±0.5
Cocody 1	1.12±0.02	14.7±0.3	21.8±0.3	0.35±0.01	1.72±0.07	0.42±0.01	0.90±0.01	1.47±0.10	13.1±0.4	0.3±0.3	-	-	44.1±0.3
Cocody 3	9.4±0.8	10.2±0.3	15.9±0.9	1.52±0.03	12.3±0.9	0.9±0.3	0.5±0.2	0.75±0.05	9.6±1.1	0.4±0.1	0.82±0.05	0.29 ±0.05	37.4±0.9
Abou-Abou 2	1.53±0.06	11.91±0.12	18.25±0.10	5.75±0.11	2.00±0.13	0.95±0.04	0.56±0.05	0.54±0.05	11.67±0.10	0.37±0.06	1.31±0.02	-	45.33±0.05

Table 1. Major element relative contents (%) in selected sediments collected from the Ebrie lagoon.

RESULTS AND DISCUSSION

Major constituents in sediments

Major elements content (%) observed by SEM/EDS in surface sediments from the bays of the Ebrie lagoon bays are shown in Table 2. The results show that, the sediments of Ebrie estuary bays are dominated by silicon (Si) (15.9-21.81%) which suggests the abundance of quartz (SiO_2). The next important elements are aluminum (Al) (9.23-14.70%) and iron (Fe) (8.26-13.11%), indicating the presence of Al and Fe oxides. The quartz and Al oxides may go through several cycles of deposition, erosion, and accumulation. It is important to note that phosphorus (P) was only found in sediments from station Cocody 3 and had an average percentage of 0.29%. P concentrations may be related to the presence of organic matter while that of potassium and magnesium is related to the presence of clay phases. The presence of sulfur (S) (0.3-5.6%) suggests that the sulfates ion reduction may also underway. The mineral composition of the studied sediments also showed spatial variability, indicating sediment heterogeneity. The observed mineral phases may enhance the accumulation of trace metals in sediments.

Table 2. Pseudo total and total concentrations of Cd (µg/g) in sediments collected from the Ebrie lagoon.

Station	Pseudo total*	Total
Banco 1	0.83 ± 0.30	0.80 ± 0.28
Banco 2	0.92 ± 0.53	1.17 ± 0.44
Banco 3	0.91±0.51	0.91 ± 0.64
Bietri 1	0.80 ± 0.18	0.87 ± 0.17
Bietri 2	1.00 ± 0.43	1.22 ± 0.30
Bietri 3	0.69 ± 0.42	0.85 ± 0.48
Cocody 1	0.99 ± 0.31	1.05 ± 0.22
Cocody 2	1.08 ± 0.28	1.21 ± 0.43
Cocody 3	**1.32** ± 0.48	**1.23** ± 0.31
Abou-Abou 1	**0.49** ± 0.33	**0.65** ± 0.55
Abou-Abou 2	0.56 ± 0.60	0.80 ± 0.29
Upper Continental Crust (UCC)		0.1
Lower Continental Crust (LCC)		0.1

*Pseudo total = F1 + F2 + F3 + R. Minimum and maximum values are in bold.

Distribution of Cd in sediments

Cd concentrations measured in surface sediments collected from the bays of the Ebrie lagoon are shown in Table 3. The range of Cd concentration was 0.65-1.23 µg/g with an average concentration of 0.99 µg/g. The general levels of Cd concentrations were relatively high in all the studied sediments compared with both the average values of the Lower and Upper Continental Crusts [35]. This suggests that sediments contaminated with Cd. The high contents of Cd could be explained by anthropogenic activities. Cd may be derived from several sources in this area. These include, fuel combustion, phosphate fertilizers, road traffic, sewage sludge, and waste disposal, all related to demographic pressure in the vicinity of Ebrie lagoon.

Sequential extraction for Cd fractionation in surface sediments

In order to validate the extraction method, we compared the sum of the four fractions (F1 + F2 + F3 + R) with total metal concentration measured using AAS. All the recoveries were approximately 100%, except for the samples from Abou-Abou, where the recovery for all the samples was found to be 57.66±20.37%. This may be attributed to losses during step 3, indicated by the appearance of spattering. The percentages of total Cd concentration obtained from the application of the BCR method in different phases of the surface sediments are shown in Figure 2. A major portion of Cd was bound to the residual fraction, varying between 50.32 and 67.45%. This is equivalent to a range of 0.37-0.65 µg/g out of total Cd concentrations of 0.14-1.29 µg/g. It appears that the non-residual fraction of Cd in the Ebrie lagoon are higher than the average continental crust value (0.1 µg/g) suggesting that significant amount of Cd is associated with the crystalline structure of the Ebrie lagoon surface sediments. In addition, an important extraction percentage of Cd (11.14-15.24%) was found to be bound to the exchangeable and acid soluble fraction (F1). In term of concentration, 0.08-0.15 µg/g out of 0.16-0.30 µg/g of Cd was associated to F1. In comparison with the average continental crust value (0.1 µg/g), the amount of Cd bound to F1 was very high. The F1 phase may pose the main environmental risk for aquatic systems [15, 36] because metals in this fraction are easily leached in neutral or slightly acidic waters. Furthermore, F1 was found to be the second most abundant fraction of Cd in the surface sediment in Banco, Bietri and Cocody bays. This indicates that an important portion of Cd could be remobilized, becoming available to aquatic biota following a slight decrease in pH or change in ionic strength. The proportion of the most mobile phase of

Cd bound to sediments found in this study is consistent with findings from the western area of the southwestern coast of Spain (15-25%) [15], but lower than those from the Pearl River Estuary in China (>50%) [27] and from the Mahanadi estuary in India (31%) [26]. On the contrary, Cd concentration associated with fraction F1 of surface sediments of the Ebrie lagoon was higher than those in the Akyatan lagoon (undetectable), Turkey [37].

The reducible fraction F2 was the second most abundant non-residual fraction for Bietri, Cocody, and Abou-Abou bays. This finding indicates the important role of high Fe oxides content found with SEM measurements in binding trace metals, especially Cd. The association of Cd with Fe and Mn oxides has also been reported in others studies [38, 39].

It is worth noting that the proportion of Cd in the oxidizable fraction in Abou-Abou bay, 0.19 µg/g out of a total concentration of 0.38 µg/g, is two to threefold of those found in Banco, Bietri and Cocody bays. This could be explained by the accumulation of organic matter in Abou-Abou bay, which is the deepest of the Ebrie estuary. In this sediment fraction, Cd is strongly complexed and may be released following either degradation of organic matter or oxidation of sulfides to sulfates.

We investigated the influence of total organic carbon (TOC) on Cd distribution in the sediments of the studied bays by performing a correlation between Cd in organic matter with sulfides fraction (F3). A significant correlation ($r^2 = 0.45$; $p < 0.01$, $N = 21$) was found between Cd and TOC, indicating that TOC plays an important role in Cd distribution in the sediments of the Ebrie estuary. However, the low value of r^2 indicates that other factors infuence the distribution of Cd as well in the Ebrie lagoon. We also found (Figure 2) that the Cd concentration associated with different fractions varied across the bays. The distribution patterns of Cd concentration in surface sediments collected in Cocody and Bietri bays was residual (R) > exchangeable and bound to carbonates (F1) > reducible (F2) > organic matter and sulfides (F3) while that of Banco bay was residual (R) > exchangeable and bound to carbonates (F1) > organic matter and sulfides (F3) > reducible (F2). Finally the following pattern residual (R) > organic matter and sulfides (F3) > reducible (F2) > exchangeable and bound to carbonates (F1) was found in the Abou-Abou bay. These different distribution patterns of Cd in sediment phases could be explained by the heterogeneity of the sediments along with the different sources of Cd in the bays, as well as the physical and chemical conditions in the medium.

Risk assessment code (RAC)

Metals are bound to different sediment fractions, with the binding strength determining their bioavailability and the risk associated with their presence in aquatic systems. The risk assessment code (RAC) was determined based on the percentage of the total metal content that was found in the exchangeable and acid soluble fraction (F1). This fraction is considered to be the most unstable and reactive phase, which has greater potential for adverse effects on the aquatic environment compare to the other fractions [22]. When the percentage mobility is less than 1 %, the sediment has no risk to the aquatic environment. Percentages of $1 < RAC < 10\%$ may reflect low risk, $11 < RAC < 30\%$ medium risk, and $31 < RAC < 50\%$ high risk. A RAC percentage above 50% poses a very high risk and it is considered dangerous because metals are easily able to enter the food chain [22]. Figure 3 illustrates the results of the risk factor analysis with values for Cd given as percentage for the soluble fraction in acid (% F1). Based on the RAC scale, the sediments collected from the four bays of the Ebrie lagoon could pose a medium risk for Cd, indicated by RAC values ranging between 11 and 30%. However, bioavailability and toxicity of metals can be influenced by a variety of factors including seasonal variations and synergic effects of various elements. Therefore, further studies are needed to fully understand Cd availability in the Ebrie lagoon.

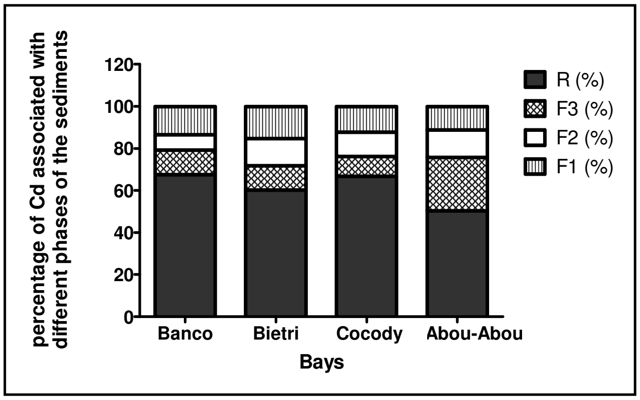

Figure 2. Chemical fractionation of Cd in surface sediments collected in different bays in Ebrie lagoon.

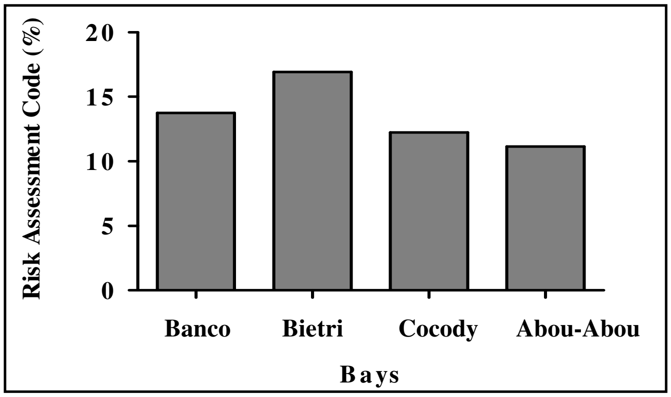

Figure 3. Risk assessment code (RAC) for Cd in surface sediment from Ebrie lagoon.

CONCLUSION

In this study, the distribution, mobility and potential ecological risks of Cd were assessed in four environmentally different bays of the Ebrie lagoon, the largest lagoon in West Africa. Total Cd contents showed higher values (0.65-1.23 µg/g) compared with the upper continental crust average concentrations. Chemical fractionation results revealed that Cd is mostly bound to the residual fraction (50.32 to 67.45%). This suggests that the mineralogical origin of Cd in the sediments of Ebrie lagoon is significant. However, a higher proportion of Cd (0.08-0.15 µg/g out of a total of 0.16-0.30 µg/g) was found in the most mobile fraction (the exchangeable and acid soluble phase). These findings indicate a high mobility of Cd in the surface sediments. Risk assessment code results showed that Cd could pose a medium risk to biota. Different distribution patterns of Cd in the sediment phases were observed among the sites, which could be explained by the heterogeneity of the sediments, as well as the physical and chemical conditions along with the different sources of Cd in the bays. Based on the results of this study, urgent measures should be taken to reduce Cd discharges in the Ebrie lagoon to avoid further ecological catastrophes.

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REFERENCES

1. Morin, S.; Duong, T.T.; Dabrin, A.; Coynel, A.; Herlory, O.; Baudrimont, M.; Delmas, F.; Durrieu, G.; Scha fer, J.; Winterton, P.; Blanc G.; Coste, M. *Environ. Pollut.* **2008**, 151, 532.
2. Bonanno, G.; Giudice, R.Lo. *Ecolog. Indicat.* **2010**, 10, 639.
3. Shi, G.; Xu, S.; Xu, Z.; Chen, S.; Zhang, J.; Wang, L.; Bi, C.; Teng, J. *Environ. Pollut.* **2008**, 156, 251.
4. Storelli, M.M.; Storelli, A.; D'Addabbo, R.; Marano, C.; Bruno, R.; Marcotrigiano, G.O. *Environ. Pollut.* **2005**, 135, 163.
5. Zheng, N.; Liu, J.; Wang, Q.; Liang, Z. *Atmosph Environ.* **2010**, 44, 3239.
6. Sekabira, K.; Origa, H.O.; Basamba, T.A.;Mutumba, G.; Kakudidi, E. *Int. J. Environ. Sci. Technol.* **2010**, 7, 435.
7. N'guessan, Y.M.; Probst, J.L.; Bur, T.; Probst. A. *Sci. Total. Environ.* **2009**, 407, 2939.
8. Micó, C.; Recatalá, L.; Peris, M.; Sánchez, J. *Chemosphere* **2006**, 65, 863.
9. Jayaprakash, M.; Urban, B.; Velmurugan, P.M.; Srinivasalu, S. *Environ. Monit. Assess.* **2010**, 170, 609.
10. Tang, W.;Shan, B.; Zhang, H.; Mao, Z. *J. Hazard. Mat.* **2010**, 178, 945.
11. Aptiz, S.E. *Sci. Total. Environ.* **2012**, 415, 9.
12. Chakraborty, P.; Babu, P.V.R.; Sarma, V.V. *Chem. Geol.* **2012**, 294-295, 217.
13. Haruna, A.; Uzairu, A.; Harrison, G.F.S. *Int J. Environ. Res.* **2011**, 5, 733.
14. Chakraborty, P.J. *Geochem. Explor.* **2012,** 115, 13.
15. Morillo, J.; Usero, J.; Gracia, I. *Chemosphere* **2004**, 55, 431.
16. Tessier, A.; Campbell, P.G.C.; Bisson, M. *Anal. Chem.* **1979**, 51, 844.
17. Quevauviller, P.; Ure, A.; Muntau, H.; Griepink, B. *Int. J. Environ. Anal. Chem.* **1993**, 51, 129.
18. Zhang, W.; Liu, X., Cheng, H.; Zeng, E.Y.; Hu, Y. *Mar. Pollut. Bull.* **2012**, 64, 712.
19. Dundar, M.S.; Altundag, H. Eyupoglu, V.; Keskin, S.C.; Tutunoglu, C. *Environ. Monit. Assess.* **2012**, 184, 33.
20. Kalhori, A.A.; Jafari, H.R.; Yavari, A.R.; Prohić, E.; Kokya, A.T. *Int. J. Environ. Res.* **2012**, 6, 185.
21. Nemati, K.; Bakar, N.K.A.; Abas, M.R.; Sobhanzadeh, E. *J. Hazard. Mat.* **2011**, 192, 402.
22. Jain, C.K. *Wat. Res.* **2004**, 38, 569
23. Kumar, K.S.; Sajwan, K.S.; Richardon, J.P.; Kannan, K. *Mar. Pollut. Bull.* **2008**, 56, 136.
24. Lim, H.S.; Lee, J.S.; Chon, H.T.; Sager, M.J. *Geochem. Expl.* **2008**, 96, 233.
25. Weng, H.X.; Zhu, Y.M.; Qin, Y.C.; Chen, J.Y.; Chen, X.H. *J. Asian Earth Sci.* **2008**, 31, 522.

26. Sundaray, S.K.; Nayak, B.B.; Lin, S.; Bhatta, D. *J. Hazard. Mat.* **2011**, 186, 1837
27. Liu, B.; Hu, K.; Jiang, Z.; Yang, J.; Luo, X.; Liu, A. *Environ. Earth. Sci.* **2011**, 62, 265.
28. Zhao, S.; Feng, C.; Wang, D.; Liu, Y.; Shen, Z. *Chemosphere* **2013**, 91, 977.
29. Ngiam, L.S.; Lim, P.E. *Sci. Total. Environ.* **2001**, 275, 53.
30. Qiao, Y.;Yang, Y.; Gu, J.; Zhao, J. *Mar. Pollut. Bull.* **2013**, 68, 140
31. Rodriguez, M.A.J.; Prego.R.; Willerer, M.A.; Shumilin, E.; Garcia, C.A. *Mar. Pollut. Bull.* **2007**, 55, 459.
32. Walkley. A.; Black, I.A. *Soil Sci.* **1934**, 63, 251.
33. Nelson, D.W.; Sommers, L.E. *Total Carbon, Organic Carbon, and Organic Matter* in *Methods of Soil Analysis*, Sparks, D.L.; Page, A.L.; Helmke, P.A.; Loeppert, R.H.; Soltanpour, P.N.; Tabataba, M.A.; Johnston, C.T.; Sumner, M.E. (Eds.), Part 3, 2nd ed., American Society of Agronomy, Inc.: Madison, WI; **1996**; pp 961-1010.
34. Soon, Y.K.; Abboud, S. *Commun. Soil Sci. Plant Anal.* **1991**, 22, 943.
35. Wedepohl, H.K. *Geochim. Cosmochim. Acta* **1995**, 59, 1217.
36. Delgado, J.; Barba-Brioso, C.; Nieto, J.M.; Boski, T. *Sci. Total. Environ.* **2011**, 409, 3666.
37. Davutluoglu, O.I.; Seckin, G.; Kalat, D.G.; Yilmaz, T.; Ersu, C.B. *Desal.* **2010**, 260, 199.
38. Gao, X.; Chen, C.T.A. *Wat. Res.* **2012**, 46, 1901.
39. Vasile, G.D.; Vlădescu, L. *Environ Monit Assess.* **2010**, 167, 349.