



The mobility of the trace metals copper, zinc, lead, cobalt, and nickel in tropical estuarine sediments, Ebrie Lagoon, Côte d'Ivoire

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Abstract

Purpose Trace metals accumulate in the food web and can pose high risks to human health and aquatic biota. We investigated seasonal and spatial variations of Cu, Zn, Pb, Co, and Ni mobility in surface sediments (0–5 cm) and their potential toxicity.

Materials and methods The sampling was carried out in three embayments of the Ebrie Lagoon (Côte d'Ivoire) during the rainy and dry seasons. The sequential and kinetic extraction methods were used to assess Cu, Zn, Pb, Co, and Ni mobility and their potential toxicity. Analysis of variance (ANOVA) was performed to ascertain spatial and seasonal differences.

Results and discussion The results showed that contrarily to Co, distribution patterns of Zn and Cu in the sediment fractions showed no spatial and seasonal variability. On the other hand, Pb and Ni distribution patterns varied highly across the bays but not seasonally. Nevertheless, repeated measurements over a long period of time should be carried out to better understand the seasonal variability of metal distribution in sediment phases. Cu, Pb, Co, and Ni were abundant in residual fraction (56.93–71.66%) in the bays. On the contrary, a very high portion of Zn (up to 70%) could be remobilized. Cu, Pb, Co, and Ni formed mainly inert complexes in sediments, while Zn formed labile complexes. Zn could pose high risk to biota, Co and Ni a medium risk, and Cu and Pb a low risk.

Conclusions A combination of both sequential and kinetic methods revealed that both Zn and Pb formed labile complexes in the exchangeable and iron/manganese oxide fractions. Sequential extraction showed high Pb concentrations in the iron/manganese oxides. Thus, Zn and Pb may be highly available, which confirmed fish Pb concentrations exceeding WHO safe limits found by previous studies. Therefore, potential mobility of metals could be better assessed by the exchangeable and iron/manganese oxide fractions obtained by sequential extraction methods.

Keywords Heavy metal mobility · Kinetic extraction · Sediment toxicity · Sequential extraction

1 Introduction

Trace metals are of environmental concern because they persist in the environment, incorporate into the food web, and can

pose adverse effects to wildlife and humans (Bonanno and Giudice 2010; Zheng et al. 2010; Du et al. 2013; Qiu 2015). Sediments are an important sink for trace metals (Kouassi et al. 2015; Mahu et al. 2015; Zhang et al. 2016). They are considered as appropriate indicators of metal pollution in aquatic systems. However, to what extent sediments can release trace metals into the water column is unknown in many watersheds in the world. Metals can be released from sediment through many processes, such as sediment resuspension and release, diffusion and advection from sediments, and biotransfer through organisms. Metals form both residual complexes and non-residual complexes in sediment systems. While the former are inert, non-residual complexes show gradual levels of mobility in the water column depending on their thermodynamic stability. The partition of metal ions between the aqueous and particulate phases critically controls the migration behavior and bioavailability of trace metals (Chakraborty et al. 2015). Bioavailability of a metal refers to the portion

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of metal solubilized from an environmental compartment and ready for uptake by biota. Determining total metal concentration alone in sediments cannot provide information about their mobility, bioavailability, and toxicity (Chakraborty 2012; Arfania and Asadzadeh 2015; Fernandes and Nayak 2015; Ma et al. 2016). In addition, the distribution scheme of metals in sediments can vary with time under the variation of physical, chemical, and hydrological conditions (e.g., tides, pH, ionic strength). Therefore, studying the dynamics of trace metal concentrations and complexes into different sediment phases is of critical importance to understand the potential adverse effects of contaminated sediments on regional or local scale.

Metal mobility in sediments (and soils) is estimated through kinetic and sequential extraction methods (Santos et al. 2010; Chakraborty 2012; Chakraborty et al. 2012a, b; Hamdoun et al. 2015), Diffusive Gradients in Thin Films technique, flow techniques, and Batch techniques. Each method/technique has its limits; however, combining two techniques or methods is more efficient than studying one alone (Gismera et al. 2004). Kinetic extraction study provides information about the concentrations and dissociation rate constants of weak and strong metal–sediment complexes (Bermond and Varrault 2004; Fangueiro et al. 2005). Sequential extraction procedures operationally estimate metal concentrations in different phases of the sediment system. The procedure proposed by the Community Bureau of Reference (BCR) is one of the most used due to its high reproducibility. It describes four phases of the sediments. The exchangeable (including carbonates) fraction (F1) and reducible fraction (F2) are identified as direct effect fractions because they are readily absorbed in plants or released into the water column. The oxidizable fraction (F3) is an approximate indication of the less mobile metal pool (Chen et al. 2008). Finally, the residual fraction (F4) is inert and not mobile. Since kinetic and sequential extraction methods are sensitive and easy to implement, they can be used together in developing countries where there is little access to research facilities. This could be of great help in understanding the geochemical speciation of elements in soils and sediments.

Coastal waters, such as lagoons, contribute worldwide to the social and economic well-being of the inhabitants. Such ecosystems are threatened in terms of water pollution, conservation, and management, especially in West Africa because of an intense increase in anthropogenic pressures, including mining operations and agricultural, industrial, and urban activities. This is true for the Ebrie Lagoon, the largest lagoon system in Western Africa. Recent data suggest that sediments from this mangrove ecosystem are heavily contaminated in Cd, Zn, Pb, and Cu (Bakary et al. 2015; Kouassi et al. 2015). An abundant literature is available for metal speciation in tropical estuaries (Cuong and Obbard 2006; Chakraborty et al. 2015; Fernandes

and Nayak 2015; Ma et al. 2016). However, trace metal fate varies with aquatic environments and little information on metal mobility is available in the Ebrie Lagoon for predicting their potential toxicity.

This study investigated the seasonal and spatial variations of Cu, Zn, Pb, Co, and Ni mobility in sediments and their potential ecological risks in the Ebrie Lagoon (Cote d'Ivoire). To address this objective, the BCR sequential and the kinetic extraction protocols were used. The relevance of this study is that remobilization of trace metals and low thermodynamic metal complex stability in sediments may increase their bioavailability in the water column.

2 Material and methods

2.1 Study area and samplings

The Ebrie Lagoon system (3°25' N, 4°45' W) has a total area of 566 km² with a length of 130 km and a maximum width of about 7 km. It 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 (Fig. 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 (Affian et al. 2009; Kouassi et al. 2015). The waters around Abidjan are highly eutrophicated, and frequent oxygen depletion occurs as a result of the discharge of untreated sewage and industrial waste (Bakary and Yao 2015). Human pressures are numerous including urbanization, industrialization, agricultural, fishing, ship building, transport, sand extraction, aquaculture, and tourism. The geology of the study area has been well-described in Kouassi et al. (2015) and Tastet and Guiral (1994). Tertiary and Quaternary Period sediment basins overlay the Precambrian basement. Along the southern edge of the Ebrie Lagoon, marine sand, river–lagoon clay and sand, as well as clayey sand derived from the Quaternary continental plateaus, form a coastal strip that separates the Lagoon from the Atlantic Ocean. The sediments in the northern region of the Ebrie Lagoon include clayey sands and sandstone weathered from high continental plateaus that originate from the Quaternary period (Tastet and Guiral 1994). The stratigraphic column coarsens downward, with clayey, medium-grained, and coarse-grained sand overlaying Precambrian basement rocks (Kadio et al. 2010). Although no distinct stratigraphic sequence can be observed in the south, the sediment cover includes medium to very fine and coarse sands, muddy sediments, and silt (Tastet and Guiral 1994; Kouame et al. 2010).

The sediment samples were collected from three embayments in the estuarine part of the Ebrie Lagoon: Cocody, Banco, and Bietri Bays (Fig. 1). Three environmentally

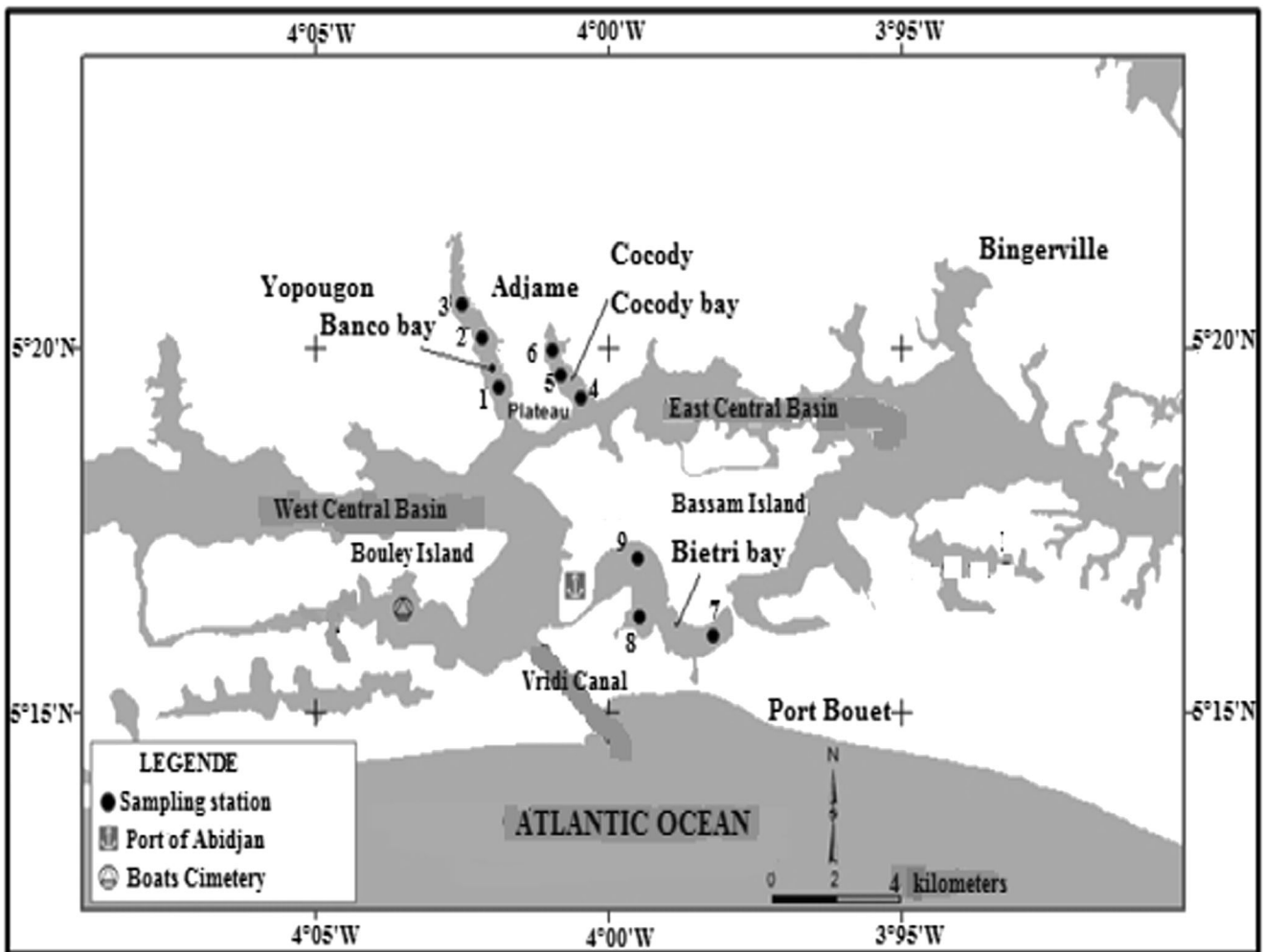


Fig. 1 Study area and sampling sites

significant stations representative of each bay were selected upstream, midstream, and downstream. These stations receive industrial or domestic wastewaters from highly populated Abidjan communes including Yopougon, Adjame, Cocody, and Port Bouet (Fig. 1).

A total of 36 surface sediment samples (0–5 cm) were sampled from the dry (February–March) to the rainy season (April–May). About 500 g of sediment was taken at each station using a Van Veen stainless steel grab of 0.02 m² area, following the USEPA (2001). 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. The samples were sealed in plastic bags, transported to the laboratory at 4 °C, oven-dried at 60 °C, homogenized, and stored at 4 °C until analysis (Chakraborty 2012; Canuto et al. 2013; Qiao et al. 2013; Chakraborty et al. 2014; Fernandes and Nayak 2015). Each sample was sieved through a stainless steel mesh to remove any particle larger than 63 µm in size.

Additionally, overlying sediment waters (0.5 m from the sediments) were sampled with a Niskin bottle, and pH,

salinity, and dissolved oxygen were immediately determined with a multiparameter (pH/ORP/EC/DO/Temp) HANNA HI9828.

2.2 Procedure, reagents, and quality assurance

All chemicals and reagents used in the study were of analytical grade. Glass, plastics, and other laboratory ware were cleaned by soaking in 10% HNO₃ solution overnight and then thoroughly rinsed with de-ionized water. Three replicates of each sample were analyzed, and the samples presented an error within 6%. 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. The reliability of the sequential extraction protocol (modified BCR) was checked by comparing the sum of the four fractions (F1 + F2 + F3 + R) with the total metal concentration measured using GIF-AAS (Qiao et al. 2013; Liu et al. 2018; Saleem et al. 2018). The recovery rates for heavy metals ranged from 93.5 to 109%.

The sediment sand fraction ($< 63 \mu\text{m}$) was determined by mechanical sieving; then, the silt and clay fractions were separated by laser-size particle analyzer (LPSA, Mastersizer 2000) following procedure described in Ramaswamy and Rao (2006). Total organic carbon concentrations were obtained from Kouassi et al. (2015).

2.3 Sequential extraction procedure

Sequential extraction was performed using a three-stage modified procedure recommended by BCR plus the residual fraction (Canuto et al. 2013; Qiao et al. 2013). 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 deionized water, mechanically shaken for 15 min on an end-over-end shaker (model Rotospin, Tarsons), and centrifuged for 20 min at 3000 rpm. The liquid aliquots were analyzed using an air–acetylene flame atomic absorption spectrometer (AAS, Spectr AA100/Varian, Tokyo, Japan). The three extraction steps performed in this study can be broadly summarized as follows.

Step 1 (exchangeable and bound to carbonates). 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 (iron and manganese fraction). Exactly 40 mL of freshly prepared hydroxyl ammonium chloride solution 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 (organic matter and sulfide 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 $85 \pm 2^\circ\text{C}$ 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 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 $85 \pm 2^\circ\text{C}$ for another 1 h. Heating was continued as before until 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.

2.4 Kinetic extraction procedure

Kinetic extraction experiments were conducted for sediments collected in February. Two (2) grams of sediments was added to 200 mL of 0.05 M EDTA solution (at pH 6) in a 400-mL Teflon beaker, and the mixture was continually stirred with a Teflon-coated magnetic stirring. The ratio of the mass sediment to the volume of EDTA solution was set at 0.01, as the ratio provides sufficiently high metal concentrations in the extract to be accurately quantified, while requiring a minimum amount of sediment. A special effort was made to maintain a homogeneous suspension in order to avoid changing the mass/volume ratio during sampling. Larger mass/volume ratios would be undesirable, as they could cause problems with filtration (Chakraborty 2012). At set time intervals (0, 2, 4, 6, 8, 10, 15, 20, 25, 30, 45, 60, 120, 300, 420, 600, 1440, 1800, 2160 min), 2 mL of aliquots of suspension was filtered through a 0.2- μm syringe filter (Millex, Millipore) and analyzed by AAS. The initial time for the kinetic measurement (i.e., $t = 0$) was taken as the time just before the sediment was added to the EDTA solution. The liquid aliquots were analyzed using an air–acetylene flame atomic absorption spectrometer (AAS, Spectr AA100/Varian, Tokyo, Japan).

2.5 Theory: the kinetic model

Kinetic model proposed by Fangueiro et al. (2005) was used to investigate the kinetic speciation of Zn, Cu, Pb, Co, and Ni in surface sediments of the Ebrie Lagoon. According to Fangueiro et al. (2005), multiple first-order extraction reactions may take place simultaneously, having rates that are assumed to be independent on each other. Each reaction rate can, thus, be expressed as:

$$dq_i/dt = k_i(Q_i - q_i) \quad (1)$$

where q_i represents the quantity of desorbed metal from binding location $\langle i \rangle$, Q_i represents the quantity of desorbed metal from binding location $\langle i \rangle$ at equilibrium, and k_i is the rate constant of the extraction reaction for compartment $\langle i \rangle$. Integrating Eq. (1) for the initial conditions $Q_1(t=0) = 0$ and $Q_2(t=0) = 0$ and rearranging the solution yield:

$$q = Q_1(1 - \exp(-k_1 t)) + Q_2(1 - \exp(-k_2 t)) \quad (2)$$

The use of Eq. (1) allows the characterization of the three fractions, as follows:

Q_1 ($\mu\text{g g}^{-1}$): fraction of metal readily extractable with the rate constant k_1 .

Q_2 ($\mu\text{g g}^{-1}$): fraction of metal less extractable, associated to the rate constant k_2 .

Q_3 ($\mu\text{g g}^{-1}$): fraction of metal not extractable. Q_3 is obtained by difference between the total concentration of metal in sediment (Q_{total}) and the concentration extracted at equilibrium:

$$Q_3 = Q_{\text{total}} - (Q_1 + Q_2) \quad (3)$$

The parameters Q_1 , Q_2 , k_1 , and k_2 in this equation were evaluated using Excel's Solver optimization package by an iterative approach. As fitting criterion, the sum of squares of residuals between experimental metal concentration data and calculated data led to a minimum by changing progressively Q_1 , Q_2 , k_1 , and k_2 values. In order to facilitate the comparison of Q_1 , Q_2 , and Q_3 values obtained for metals in sediment samples, those values were re-calculated as proportions ($\%Q_1$), ($\%Q_2$), and ($\%Q_3$) of total content:

$$Q_1(\%) = Q_1/Q_{\text{total}} \times 100 \quad (4)$$

$$Q_2(\%) = Q_2/Q_{\text{total}} \times 100 \quad (5)$$

$$Q_3(\%) = Q_3/Q_{\text{total}} \times 100 \quad (6)$$

2.6 Statistical analysis

Analysis of variance (ANOVA) was performed to ascertain spatial and seasonal differences. Differences at the $p < 0.05$ level (95% confidence interval) were considered statistically significant.

3 Results

3.1 Overlying water and surface sediment characteristics

During the sampling period, the water pH, salinity, and dissolved oxygen did not vary significantly between the dry (February–March) and rainy (April–May) seasons at the water–sediment interface ($p < 0.05$, $N = 36$) as shown in Tables S1 and S2 of the Electronic Supplementary Material. On the contrary, water pH, dissolved oxygen, and salinity varied significantly ($p < 0.05$, $N = 36$) between the bays (Tables S1 and S2 in the Electronic Supplementary Material). The average water pH followed the order Cocody (8.05 ± 0.27) > Banco (7.98 ± 0.22) > Bietri (7.51 ± 0.22), the average water salinity order was Banco (31.9 ± 2.72 psu) > Bietri (28.1 ± 4.96 psu) > Cocody (27.2 ± 3.74 psu), while the average dissolved

oxygen concentration was higher at Cocody (4.24 ± 2.56 mg L⁻¹), followed by Banco (2.07 ± 2.50 mg L⁻¹) and Bietri (0.54 ± 0.60 mg L⁻¹).

Sediment texture results showed that sediments were dominated by sand fraction (83–86%) irrespective of the bays (Table S3 in the Electronic Supplementary Material). No spatial or seasonal difference was observed within and among the bays.

3.2 Seasonal and spatial distributions of Zn, Cu, Pb, Co, and Ni in sediment fractions

3.2.1 Seasonal and spatial distributions of Zn

The geochemical fractionation of Zn in sediments from Banco, Bietri, and Cocody Bays (all bays combined) during the dry and rainy seasons is shown in Fig. 2; the spatial variations are depicted in Fig. 3. The results showed that a major portion of Zn is highly associated with the exchangeable fraction (F1) with percentages varying from 43.5 to 50.7% of total concentration (Figs. 2a and 3a) irrespective of the bay and the season. This is equivalent to 70.7–100 $\mu\text{g g}^{-1}$ of Zn concentration out of total of 163–198 $\mu\text{g g}^{-1}$. On the contrary, Zn bounded to the residual fraction (R) (Figs. 2d and 3d) showed very low percentages (24.6–30.8%). One-way ANOVA analysis ($p < 0.05$) showed no significant difference in all fractions between the seasons. With regard to spatial variation, only Zn concentration in the iron/manganese oxide fraction showed a significant difference ($p < 0.05$) between Banco and Bietri Bays and between Bietri and Cocody Bays.

A similar Zn chemical fractionation distribution scheme: exchangeable and bound to carbonates (F1) > residual (R) > iron/manganese (F2) > organic matter and sulfides (F3) was observed during the two seasons in all the bays.

3.2.2 Seasonal and spatial distributions of Cu

As shown in Figs. 2d and 3d, the residual phase was found to be the most abundant Cu fraction with an average percentage varying between 62.1 and 69.8%. Among the non-lithogeneous phase, organic matter was the major Cu scavenger with an average percentage ranging between 16.0 and 25.3% (Figs. 2c and 3c). This corresponds to 12.1–26.0 $\mu\text{g g}^{-1}$ out of total Cu concentration of 75.6–103 $\mu\text{g g}^{-1}$. There was no significant difference (ANOVA, $p < 0.05$) between the seasons for Cu concentrations in sediment fractions. Similarly, there was no significant difference ($p < 0.05$) between different bays for Cu concentrations in the residual and exchangeable fractions. As for the iron and manganese oxide phase (F2) (Fig. 3b), the average Cu concentration was significantly higher ($p < 0.05$) in Banco and Cocody Bays compared to that in Bietri Bay. Furthermore, the fraction of the total Cu associated with the organic matter binding

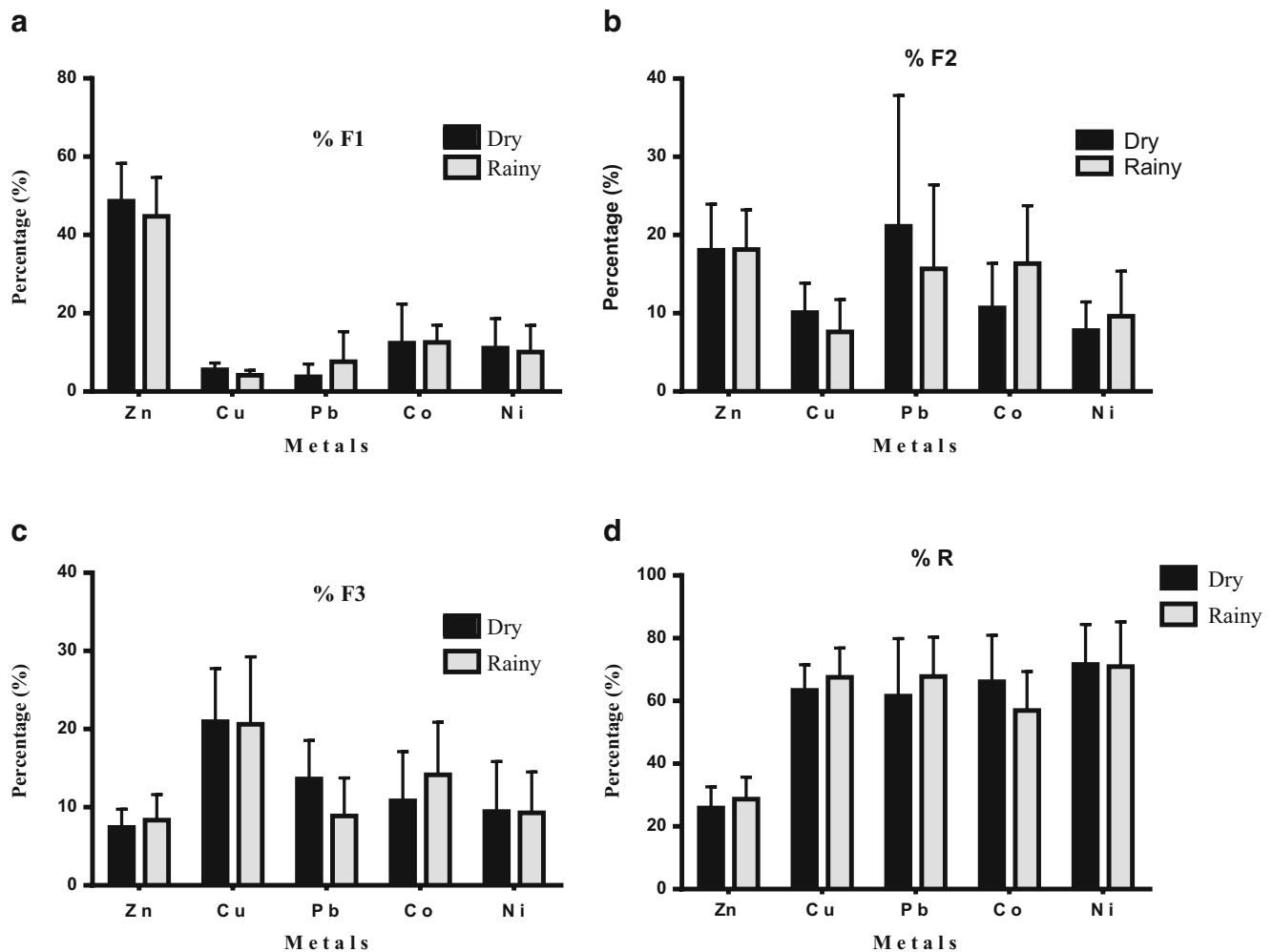


Fig. 2 Seasonal variations in average percentages of metal concentrations in sediment binding phases (all stations of the Banco, Bietri, and Cocody Bays combined). Vertical bars indicate variations among the stations

phase (Fig. 3c) was significantly higher in Bietri Bay than that in Banco Bay. The Cu fractionation showed similar distribution pattern in all bays and seasons: residual (R) > organic matter and sulfides (F3) > iron/manganese (F2) > exchangeable and bound to carbonates (F1).

3.2.3 Seasonal and spatial distributions of Pb

Figures 2d and 3d showed that Pb was primarily associated with the residual fraction with an average percentage ranging from 61.5 to 68.2%. The iron/manganese phase was the most important non-residual fraction, with an average proportion varying between 12 and 22% (Figs. 2b and 3b). In terms of concentration, this is equivalent to 7.30–10.8 $\mu\text{g g}^{-1}$ out of total Pb concentration of 61.1–49.3 $\mu\text{g g}^{-1}$. The Pb percentages in the sediment fractions showed no significant spatial and seasonal variability ($p < 0.05$). Moreover, the Pb chemical fractionation pattern was residual (R) > iron/manganese (F2) > organic matter (F3) > exchangeable and bound to carbonates (F1) irrespective of the season.

On the contrary, Pb chemical fractionation pattern varied with the bay. In Bietri and Cocody Bays, the pattern was residual (R) > reducible (F2) > organic matter (F3) > exchangeable and bound to carbonates (F1), while that of Banco bay was residual (R) > organic matter (F3) > iron and manganese (F2) > exchangeable and bound to carbonates (F1).

3.2.4 Seasonal and spatial distributions of Co

The results of seasonal and spatial variations of Co percentages in sediment fractions are shown in Figs. 2 and 3. The residual fraction was the most important Co binding phase with an average percentage varying between 56.9 and 66.1% (Figs. 2d and 3d). The percentages of Co in the non-residual fractions were comparable. Only the Co concentrations in the iron and manganese oxide fraction (Fig. 2b) were significantly higher ($p < 0.05$) in the rainy season than in the dry season. The average Co concentration in the all fractions did not vary significantly ($p < 0.05$) among the bays. On the contrary, the

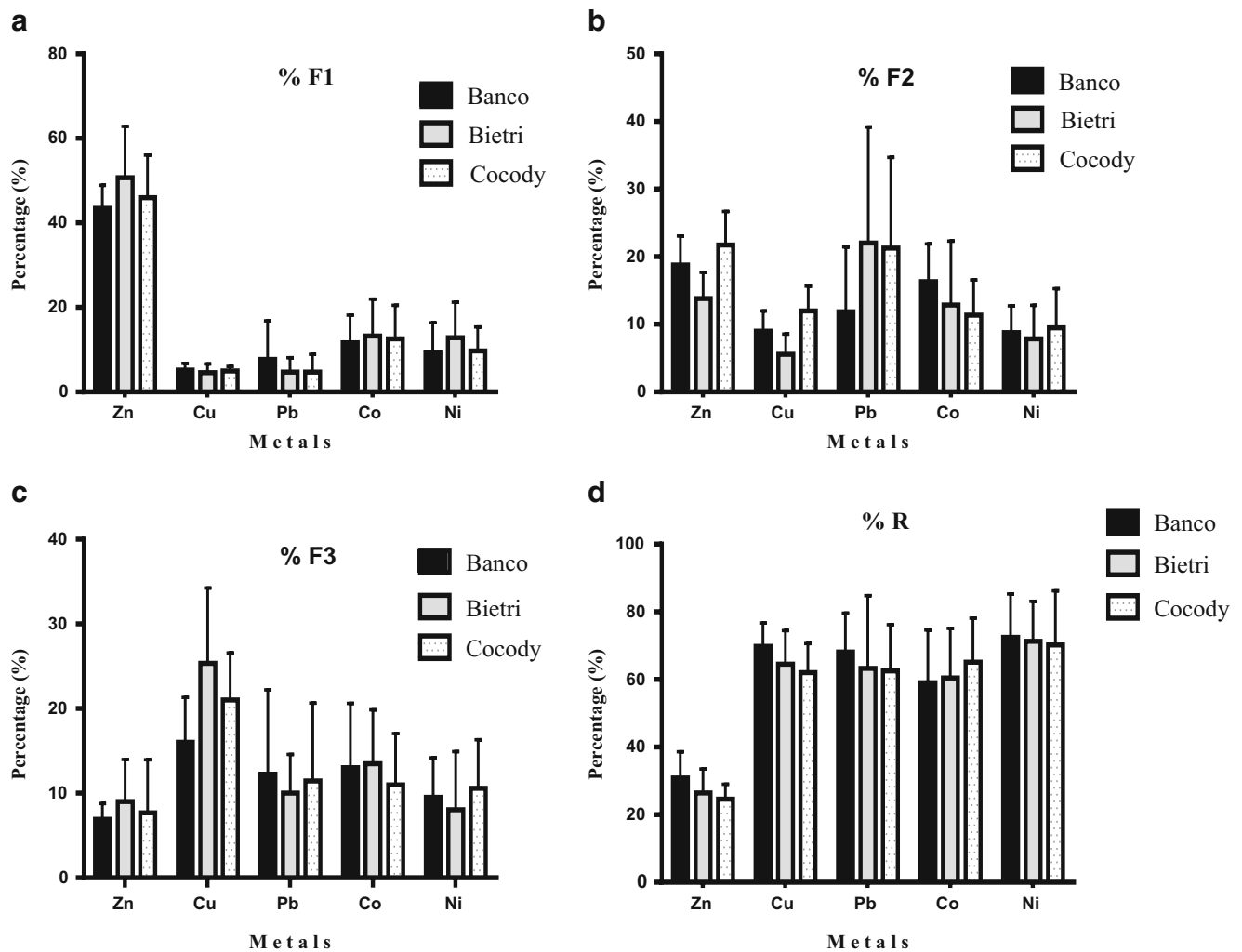


Fig. 3 Spatial variations of metal fractions in sediments from the Ebrie Lagoon. Vertical bars indicate the temporal variability at the stations during the sampling period

seasonal chemical fractionation pattern of Co varied with the season and the bay. The fractionation pattern in sediment was residual (R) > exchangeable and bound to carbonates (F1) > organic matter (F3) > iron and manganese oxides (F2) in the dry season and residual (R) > organic matter (F3) > iron and manganese (F2) > exchangeable and bound to carbonates (F1) in the rainy season. As for spatial variations, different cobalt distribution patterns were observed in the bays: residual (R) > iron/manganese (F2) > organic matter (F3) > exchangeable and bound to carbonates (F1) in Banco Bay, residual (R) > organic matter (F3) > exchangeable and bound to carbonates (F1) > iron/manganese (F2) in Bietri Bay, and residual (R) > exchangeable and bound to carbonates (F1) > iron/manganese oxides (F2), > organic matter (F3) in Cocody Bay.

3.2.5 Seasonal and spatial distributions of Ni

Figures 2 and 3 illustrate the geochemical partitioning of Ni in sediment fractions. The dominant Ni phase was

the residual fraction with an average percentage ranging from 70.2 to 72.4% (Figs. 2d and 3d). The Ni percentages in the non-residual fractions were comparable, although F1 fraction showed slightly higher values (11%; equivalent to $4.08 \mu\text{g g}^{-1}$ out of Ni total concentration of $37.05 \mu\text{g g}^{-1}$). ANOVA analysis showed no significant spatial and seasonal variability ($p < 0.05$) in Ni percentages in all sediment fractions. Ni distribution schemes varied across the bays but not seasonally. During both the dry and rainy seasons, the Ni distribution pattern was residual (R) > exchangeable and bound to carbonates (F1) > organic matter (F3) > iron/manganese oxides (F2).

The spatial distribution patterns of Ni were residual (R) > organic matter (F3) > exchangeable and bound to carbonates (F1) > iron/manganese (F2) in Banco and Cocody Bays and residual (R) > exchangeable and bound to carbonates (F1) > organic matter (F3) > iron/manganese oxides (F2) in Bietri Bay.

3.3 Mobility of Zn, Cu, Pb, Co, and Ni based on sequential extraction

The average concentrations of non-residual Zn, Cu, Pb, Co, and Ni in sediments varied between 114 and 148 $\mu\text{g g}^{-1}$, 22 and 39 $\mu\text{g g}^{-1}$, 20 and 26 $\mu\text{g g}^{-1}$, 4 and 5 $\mu\text{g g}^{-1}$, and 7 and 12 $\mu\text{g g}^{-1}$, respectively (Table S4 in the Electronic Supplementary Material). The sum (%F1 + %F2 + %F3) representing the percentage of the non-residual fraction was calculated to assess Zn, Cu, Pb, Co, and Ni mobility (Fig. 4). For all bays combined, Zn had the highest non-residual fraction proportion during the dry (74.1%) and rainy (71.3%) seasons. During the whole study period, the percentage of Zn non-residual fraction varied from 69.1 at Banco to 75.4% at Cocody and was much higher than the ones at Cu, Pb, Co, and Ni (less than 40%). The mobility percentage of the elements followed the order dry > rainy for Zn, Co, and Pb and rainy > dry for Cu and Ni. With regard to the potential mobility of each metal in the bays, the decreasing mobility trends were Cocody > Bietri > Banco for Zn, Cu, Pb, and Ni and Banco > Bietri > Cocody for Co with no significant difference.

3.4 Mobility assessment by kinetic extraction

The extraction curves obtained from the kinetic extraction are given by Figs. 5, 6, and 7. Two distinguishable features can be distinguished. The first part of all the curves: $t < 45$ min in Cocody Bay and $0 < t < 60$ min in Banco and Bietri Bays for Zn, $0 < t < 60$ in all the bays for Cu and Co, and $0 < t < 45$ min in all the bays for Pb and Ni, represents the concentrations of readily extractable weak metal complexes (Q_1) with low thermodynamic stability and dissociation rates k_1 . The second

part of all the curves: $t > 45$ min in Cocody Bay and $t > 60$ min in Banco and Bietri Bays for Zn, and $t > 60$ min in all the Bays for Cu and Co, $t > 45$ min in all the bays for Pb and Ni, corresponds to the fraction (Q_2) of less extractable metals with moderate thermodynamic stability and dissociation rates k_2 . The k_1 values ranged from 9.3×10^{-2} to 10^{-1} min^{-1} for all metals, while those of k_2 varied between 10^{-6} and $13 \times 10^{-3} \text{ min}^{-1}$ (Table 1). Thus, k_1 values were higher than k_2 values.

The total mobility (%) of Zn, Cu, Pb, Co, and Ni was estimated by the sum (% Q_1 + % Q_2). The results are shown in Table 1. In all the bays, the Zn total mobility was the highest, varying between 77.62 and 88.53%. Table 1 also indicated that an important portion (65 to 94%) (% Q_3) of Cu, Pb, Co, and Ni was not extracted by EDTA. Using values of total mobility percentage (% Q_1 + % Q_2) in different bays, it can be observed that the order of metal mobility was Zn > Pb > Co > Ni > Cu in Bietri and Cocody Bays, while the one in Banco Bay was Zn > Co > Ni > Pb > Cu.

4 Discussion

4.1 pH, salinity, dissolved oxygen, and sediment grain sizes

In the Ebrie Lagoon, the dry season corresponds to intrusion of marine waters from the Atlantic Ocean, which increases water salinity, pH, and redox potential values. On the contrary, during the rainy season, precipitations and freshwaters from the Comoe River dilute lagoon waters and decrease water salinity, pH, and redox potential values. The absence of significant seasonal

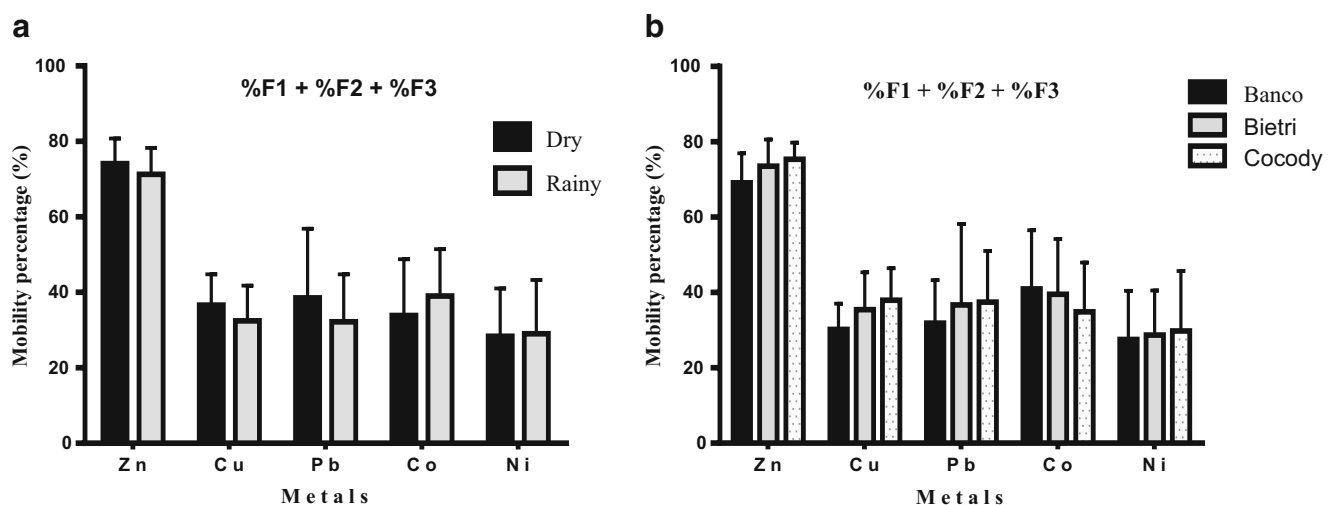


Fig. 4 Seasonal (a) and spatial (b) variations in the non-residual fraction (%F1 + %F2 + %F3) of studied trace metals (all bays combined)

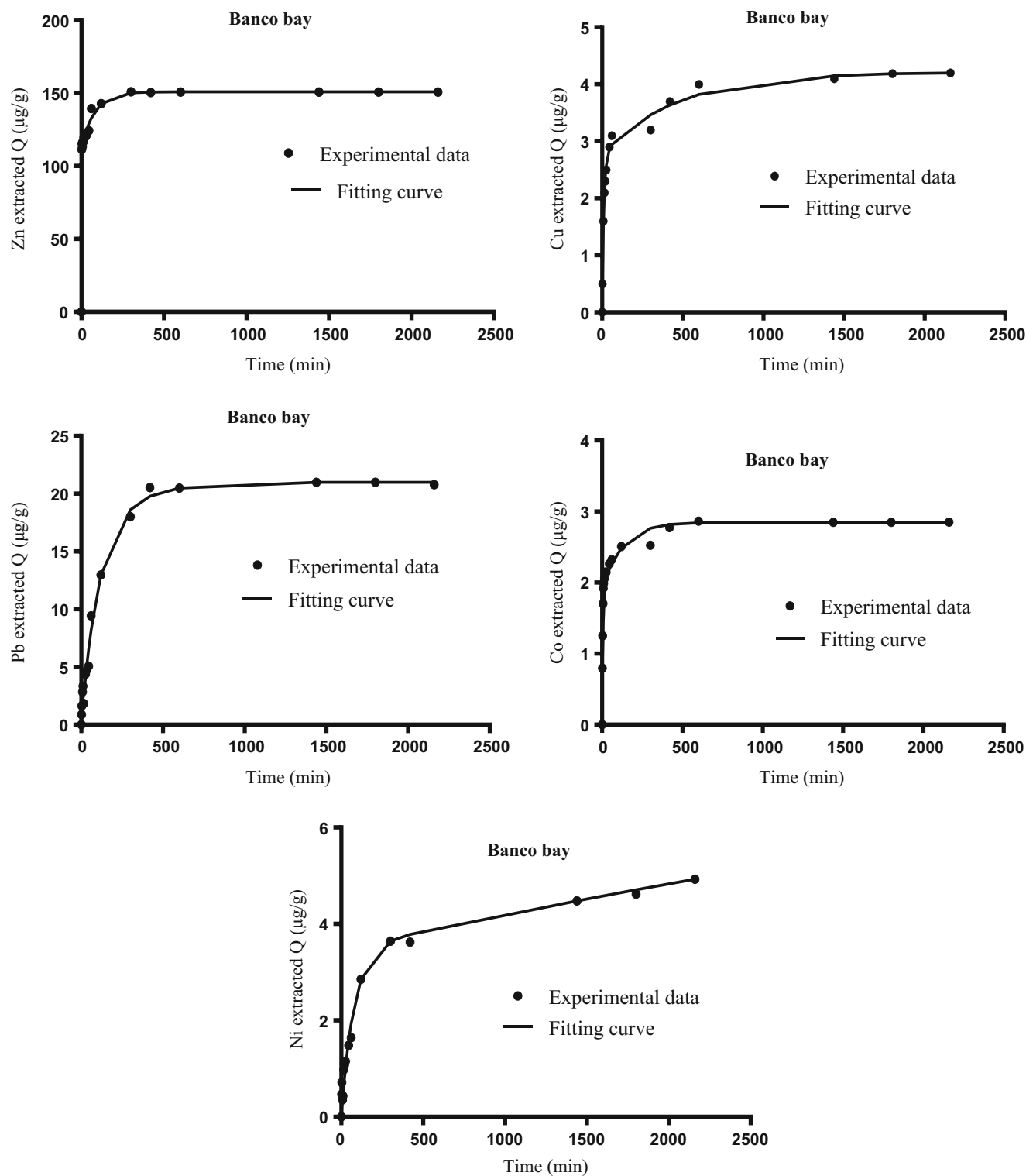


Fig. 5 Kinetic extraction curves for metals in the Banco Bay

variability in water characteristics found in this study could be attributed to the fact that the high rainy season did not reach its peak over the study period. On the contrary, the observed significant spatial variability in water pH, dissolved oxygen, and salinity results from

differences in the proximity of the bays to seawater or freshwater discharges, difference in water bathymetry and wastewater inputs as reported by Kone et al. (2009). The results also underlined a relatively permanent anoxia at most stations in Banco and Bietri Bays

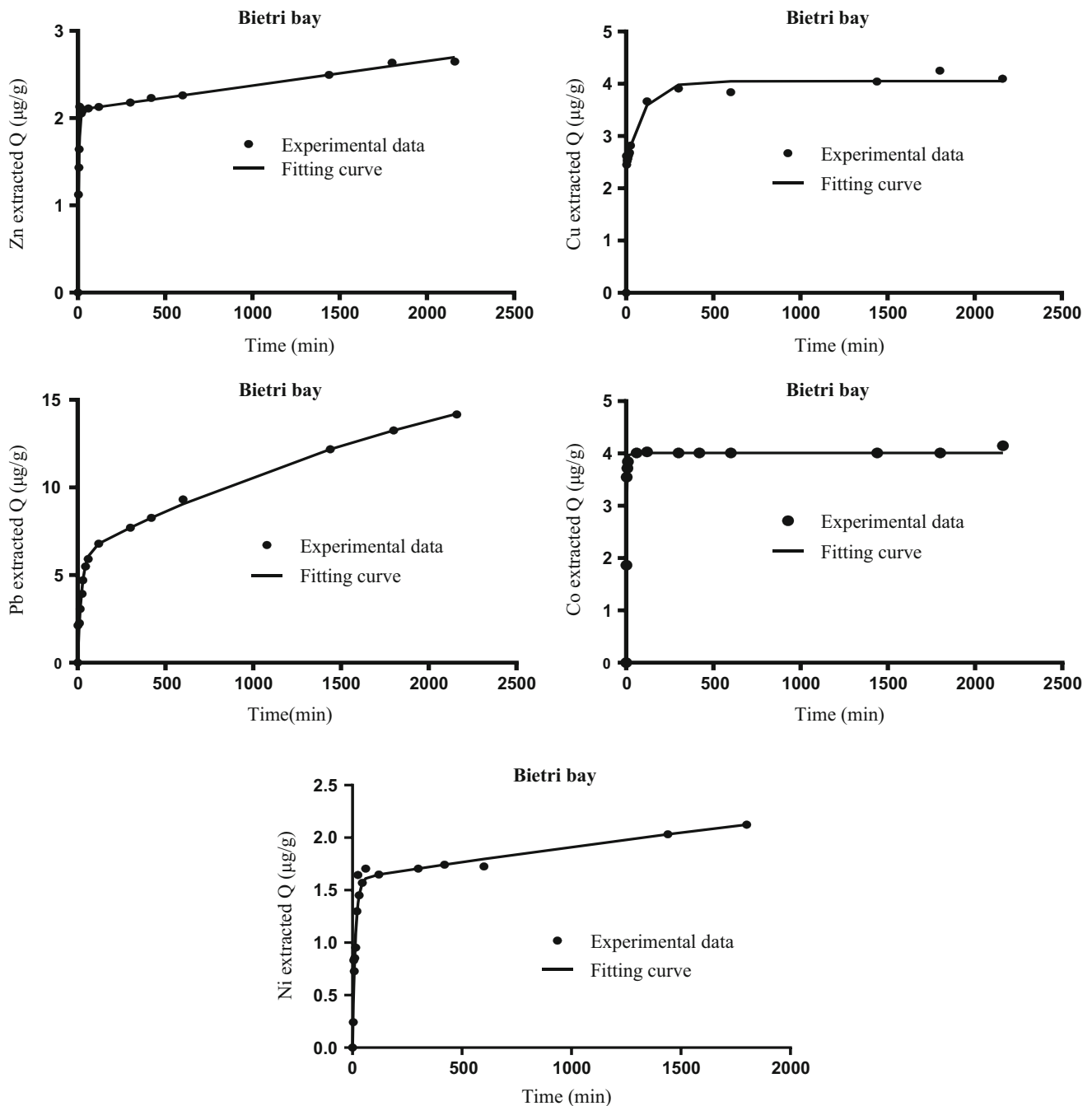


Fig. 6 Kinetic extraction curves for metals in the Bietri Bay

and occasional hypoxia in few stations in Cocody Bay. This indicates that the sediments of Cocody, Banco, and Bietri Bays were predominated by reducing conditions. The observed deoxygenation of the Ebré Lagoon waters is attributive to anthropogenic nutrient inputs, which can result in primary production and subsequent high oxygen consumption (Altieri and Gedon 2015). In addition, water stratification could be a complementary cause of the observed deoxygenation. The local geology consists of sediment deposit. Our results showed that the

sediments were sandy, and the proportion of sand, silt, and clay was similar irrespective of the seasons and the bays. This could indicate that the bays are not environmentally different in terms of sediment discharges. The relative spatial homogeneity in sediment composition could also be related to the position and the similar depths of the sampled stations. Moreover, Kouassi et al. (2015) found that the TOC content in the sediments from the present study ranged between 2.42 and 3.25% and did not vary among the

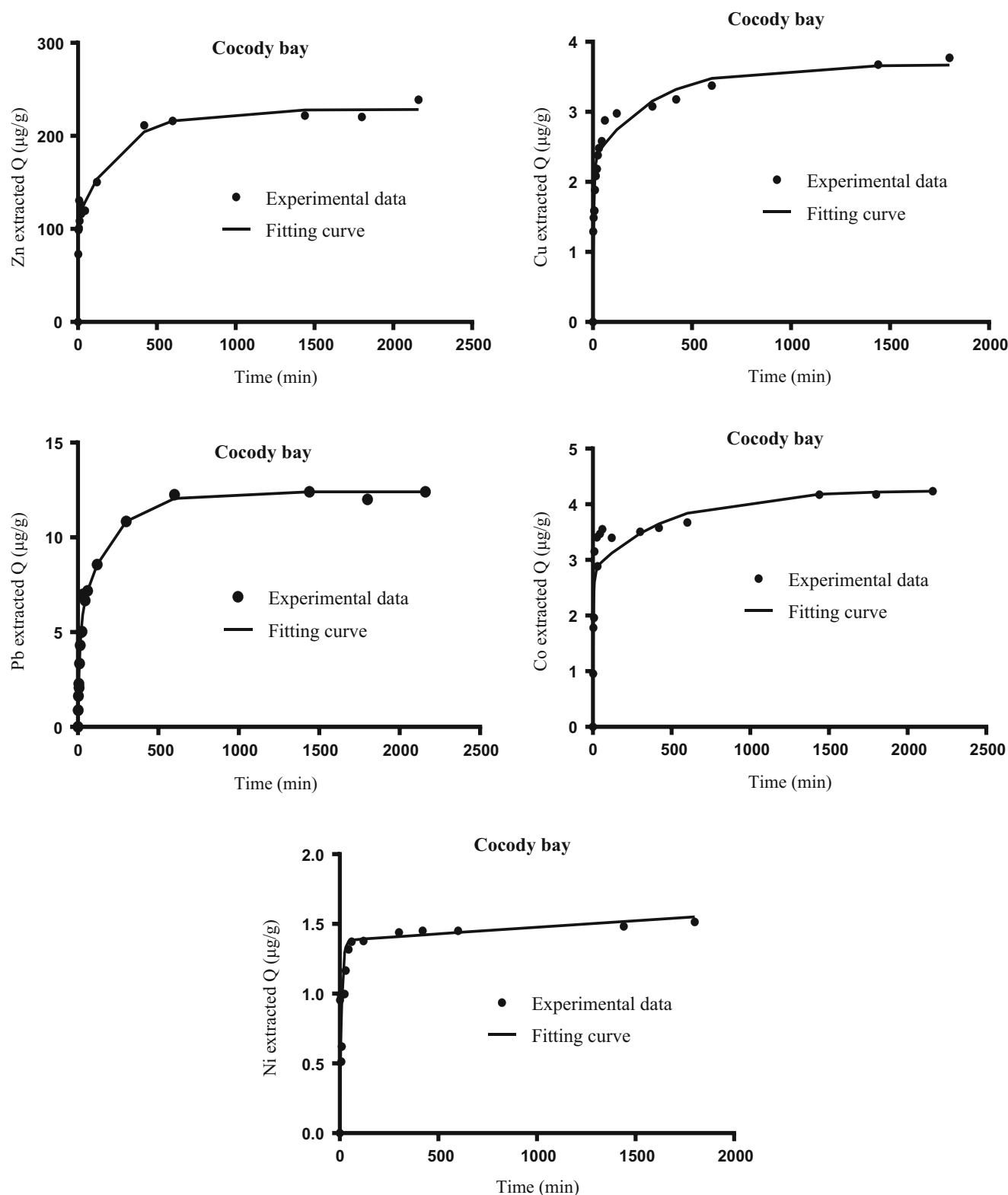


Fig. 7 Kinetic extraction curves for metals in the Cocody Bay

Cocody, Banco, and Bietri Bays (Table S3 in the Electronic Supplementary Material). It has been reported that TOC increases with finer particles; thus, the lack of

significant variation in TOC content between the bays could be a consequence of the relative spatial homogeneity of sediment texture.

Table 1 Kinetically distinguishable components of Zn, Cu, Pb, Co, and Ni complexes in the Ebrie Lagoon sediments obtained by kinetic extraction

Metals	Bays	%Q ₁	%Q ₂	%Q ₃	%Q ₁ + %Q ₂	k ₁ (min ⁻¹)	k ₂ (min ⁻¹)
Zn	Banco	63.7	22.8	13.5	86.47	7.9 × 10 ⁻²	13 × 10 ⁻³
	Bietri	0.67	87.9	11.5	88.53	1.9 × 10 ⁻²	10 ⁻⁶
	Cocody	37.5	40.1	22.4	77.62	5.3 × 10 ⁻²	4 × 10 ⁻³
Cu	Banco	6.05	3.11	90.8	9.16	9 × 10 ⁻²	2.2 × 10 ⁻³
	Bietri	3.99	2.64	93.4	6.63	9.3 × 10 ⁻²	2.8 × 10 ⁻³
	Cocody	3.61	2.15	94.2	5.76	9 × 10 ⁻²	1.9 × 10 ⁻³
Pb	Banco	13.3	4.71	82.0	17.97	10 ⁻¹	41 × 10 ⁻⁴
	Bietri	6.37	15.5	78.1	21.89	4 × 10 ⁻²	3.5 × 10 ⁻⁴
	Cocody	5.40	7.01	87.6	12.41	8 × 10 ⁻²	5 × 10 ⁻³
Co	Banco	20.0	10.0	70.0	30	1.6 × 10 ⁻²	8 × 10 ⁻³
	Bietri	10.1	20.8	69.1	30.85	8 × 10 ⁻²	2.8 × 10 ⁻³
	Cocody	23.3	12.1	64.6	41.87	2.5 × 10 ⁻²	2.1 × 10 ⁻³
Ni	Banco	6.37	15.4	78.2	21.84	1.3 × 10 ⁻²	8.5 × 10 ⁻³
	Bietri	9.16	12.3	78.5	21.51	8 × 10 ⁻²	15 × 10 ⁻³
	Cocody	2.39	3.45	94.2	5.84	1.1 × 10 ⁻²	5 × 10 ⁻⁵

4.2 Seasonal and spatial variations of Zn, Cu, Pb, Co, and Ni in sediment fractions

It should be noted that total metal concentrations in sediments from this study, their sources, and spatial distributions have been previously described in Kouassi et al. (2015) (Table S4 in the Electronic Supplementary Material). The ranges of metal concentrations in the Cocody, Banco, and Bietri Bays were as follows: 61.1–418 µg g⁻¹ for Zn, 33.25–182 µg g⁻¹ for Cu, 9.19–132 µg g⁻¹ for Pb, 8.20–18.4 µg g⁻¹ for Co, and 1.35–73.1 µg g⁻¹ for Ni. These results showed that Ebrie Lagoon was one of the most contaminated tropical estuaries in trace metals. However, total concentration cannot provide information about the fate, bioavailability, and toxicity of sediments. Therefore, the results of the present study focused on the potential mobility of trace metals from the sediments to the overlying waters.

The proportions of Zn, Cu, Pb, Co, and Ni concentrations in the exchangeable and bound to carbonates, iron/manganese oxides, organic matter, and residual phases of the Ebrie Lagoon sediments did not vary significantly among the seasons from February to May. The sorption of metals on sediment phases is a complex physical–chemical process. Changes in environmental conditions, such as pH, salinity, redox potential, organic matter, and temperature could influence metal distribution in sediment fractions (Chakraborty and Babu 2015; Wang et al. 2015). For example, under reducing conditions, iron/manganese oxides can dissolve and be released into the water column. Similarly, part of metal bound to organic matter fraction can be released into the water column in anoxic conditions (Feng et al. 2014). At lower pH (< 4), metal adsorption efficiency decreases while at higher pH metal adsorption increases. In addition, high water salinity may increase metal desorption.

During the sampling period, the average water pH, dissolved oxygen, and salinity did not differ significantly among the seasons. This may in part explain why metal concentrations in sediment binding phases did not vary between the seasons from February to May 2012. On the contrary, pH, dissolved oxygen, and salinity at the water–sediment interface varied significantly between the bays, but no significant spatial variation was observed in metal levels in the sediment phases among the bays.

Sediment texture plays a key role in trace metal distribution in sediments. Trace metal concentrations in sediment increase with finer particles (Yao et al. 2015). Consequently, the clay fraction accumulates more metal than the silt and sand fractions because of their larger specific surface and higher TOC content. However, the influence of sediment size fractions on metal mobility is hardly predictable. In this study, both the sedimentary metal proportions and the sediment grain size composition did not show significant seasonal and spatial changes (Table S5 in the Electronic Supplementary Material). Furthermore, we found moderate to significant correlations between grain size composition and percentages of metal bound to sediment phases (Table S6 in the Electronic Supplementary Material). For example, with regard to Zn, moderate to significant correlations were obtained between iron/manganese oxides and silt ($r = 0.54$) and clay ($r = 0.40$) in May; organic matter and sand ($r = 0.57$) and clay ($r = -0.62$); exchangeable and bound to carbonates and sand ($r = -0.49$) in February; between organic matter and sand ($r = 0.68$) and silt ($r = -0.56$) and clay ($r = -0.52$), exchangeable and bound to carbonates and sand ($r = -0.42$) in April. These correlations may indicate a relative link between metal proportion in sediment phase fractions and sediment texture. Nevertheless, additional studies taking other factors, such as

physical transport, solid–liquid equilibrium of trace metals between pore water and sediment, larger geographic areas, and longer study periods, into account should be carried out to better explain the seasonal variability of metal fractionation observed in this study. Koretsky et al. (2006) showed similar Zn, Cu, Pb, and Co fractions in sediments from the Asylum Lake (USA) between winter and summer. In contrast, Iwegbue et al. (2007) observed that Zn and Pb levels in the Ase River sediment phases (Nigeria) were influenced by the season, which is in stark contrast with our observations. These findings show that seasonal and spatial variations of metal distribution in sediment binding phases are local specific.

Contrary to Co, Zn and Cu distribution patterns in the sediment fractions showed no spatial and seasonal variability. On the opposite, Pb and Ni distribution schemes varied highly across the bays but not seasonally. The different distribution patterns observed among the metals could result from different affinities of metals for sediments and different metal sources. Sediment heterogeneity (grain size composition) in time and space could explain spatial variability as it has been reported by Kang et al. (2017) in the Jiaozhou Bay. In addition, dredging activities in the Bietri Bay may have released bottom sediments to the surface during the sampling period. According to Kouassi et al. (2015), the major sources of metals in the bays of the Ebrie Lagoon are water runoffs and diffuse residential water discharges from neighborhoods close to bays. The diffuse sources of metals in these bays could result in similar metal distribution patterns as mentioned by Fonseca et al. (2013). The seasonal changes in Co chemical distribution pattern in the sediment could be attributed in part to mutual transformations of sediment fractions as mentioned by Feng et al. (2014).

Zinc partitioning in the sediment phases was controlled by the exchangeable fraction in the Ebrie Lagoon bays during the study period. This may indicate that carbonates are major scavengers of Zn in the Ebrie Lagoon sediments. Previous studies have shown that anthropogenic metals are predominantly found in the exchangeable and carbonate fraction (Cárdenas et al. 2010; Gao and Chen 2012), which are vulnerable to small changes in environmental conditions, such as those caused by human activities. Kouassi et al. (2015) mentioned anthropogenic sources of Zn in the Ebrie Lagoon. Thus, high percentages of Zn obtained in the exchangeable fraction in our study could result from the anthropogenic sources of Zn. The proportion of the most mobile phase of Zn (26.7–70.0%) bound to sediments found in this study is comparable to the one obtained in systems under anthropogenic influences like the Shantou Bay in China (41%) (Qiao et al. 2013), but higher than those measured in systems in which Zn was from natural origin like in the Bohai Bay in China (8.2%) (Gao and Chen 2012) and the Sal Estuary in Brazil (12%) (Canuto et al. 2013). On the contrary, Pb and Ni showed high proportions in the residual phase of the

sediments suggesting that these metals derived mainly from natural sources.

4.3 Mobility of Zn, Cu, Pb, Co, and Ni

Kinetic extraction results revealed that Zn was rapidly extracted by EDTA, while Cu, Pb, Co, and Ni were slowly extracted. Up to 65–94% of Cu, Pb, Co, and Ni complexes were not extracted by EDTA. This finding indicates that Cu, Pb, Co, and Ni formed mainly inert complexes in sediments, while Zn formed labile complexes. Thus, Cu, Pb, Co, and Ni may be less available for biota, while Zn may be highly available. Kinetic results also showed that the order of metal mobility in the Bietri Bay was similar to that in the Cocody Bay, but it was different to the one in the Banco Bay. For example, Pb ranked as the second most mobile element in the Bietri and

Table 2 Correlation coefficient matrix for dynamic (% Q_1 + % Q_2) and inert (% Q_3) fractions obtained by the kinetic extraction and sequential extracted non-residual (%F1, %F2, and %F3) fractions

	Cu	% Q_3	% Q_1 + % Q_2	%F1	%F2	%F3
Cu						
% Q_3		1.00				
% Q_1 + % Q_2		−1.00	1.00			
%F1		0.52	−0.52	1.00		
%F2		0.40	−0.40	0.98	1.00	
%F3		0.76	−0.76	0.52	0.32	1.00
Zn		% Q_3	% Q_1 + % Q_2	%F1	%F2	%F3
% Q_3		1.00				
% Q_1 + % Q_2		−1.00	1.00			
%F1		−0.97	0.97	1.00		
%F2		−0.72	0.72	0.69	1.00	
%F3		0.82	−0.82	−0.83	−0.98	1.00
Pb		% Q_3	% Q_1 + % Q_2	%F1	%F2	%F3
% Q_3		1.00				
% Q_1 + % Q_2		−1.00	1.00			
%F1		−0.80	0.80	1.00		
%F2		−0.80	0.80	0.40	1.00	
%F3		0.98	−1.00	−0.77	−0.89	1.00
Ni		% Q_3	% Q_1 + % Q_2	%F1	%F2	%F3
% Q_3		1.00				
% Q_1 + % Q_2		−1.00	1.00			
%F1		−0.40	0.40	1.00		
%F2		0.80	−0.80	−0.85	1.00	1.00
%F3		0.80	−0.80	−0.85	1.00	1.00
Co		% Q_3	% Q_1 + % Q_2	%F1	%F2	%F3
% Q_3		1.00				
% Q_1 + % Q_2		−1.00	1.00			
%F1		−0.10	0.10	1.00		
%F2		−0.70	0.70	−0.66	1.00	
%F3		0.30	−0.30	0.93	−0.89	1.00

Cocody Bays but was the last but one mobile element in the Banco Bay. This finding confirms the spatial variability of Pb mobility revealed by sequential extraction results. The lower mobility of Cu, Co, and Ni has been also reported in other studies (Fangueiro et al. 2005; Chakraborty 2012). In contrast, Hamdoun et al. (2015) obtained high mobility of Cu in marine sediments from Ouistreham and Concarneau Harbors (France) and Pool (UK). Leleyter et al. (2012) reported high and low mobility for Pb and Zn, respectively, in estuarine sediments in France. Overall, these observations show that the mobility of metals can vary widely in estuaries because there are numerous factors that determine their speciation.

4.4 Comparison between sequential and kinetic extraction methods

To better understand metal mobility, we performed correlation analysis between non-residual fractions F1, F2, and F3 obtained by sequential extraction with the labile ($Q_1 + Q_2$) and the inert (Q_3) fractions obtained by kinetic methods (Table 2). A correlation with the labile fraction indicates formation of labile complexes, while a correlation with the inert fraction indicates formation of thermodynamically inert complexes in the sediment phases (Chakraborty et al. 2012a; Chakraborty 2012).

We found that Zn, Cu, Pb, and Ni bound to the organic matter fraction of sediments were strongly correlated with their inert fractions. This suggests that Zn, Cu, Pb, and Ni formed inert complexes with organic matter and are therefore not mobile. Our finding corroborates previous studies reporting that organic matter fraction is an approximate indication of the less mobile metal pool (Chen et al. 2008; Ma et al. 2016). Thus, using the sum of non-residual fractions obtained by sequential extraction to evaluate metal mobility in the Ebrie Lagoon may overestimate the mobile metal pool as

mentioned by Chakraborty et al. (2012a) for the Godavari estuary in India.

Correlation analysis also showed that Cu formed thermodynamically stable complexes in all the sediment phases. Zn and Pb formed labile complexes in the exchangeable and iron and manganese oxide fractions, while Co formed labile complexes in the iron and manganese oxides. These results indicate that a high total concentration of Zn and Pb in the exchangeable and the iron/manganese phases in the Ebrie Lagoon sediments could result in significant bioaccumulation of these elements. Contradictory to the kinetic extraction results, Pb may be available to biota because sequential extraction showed relatively high amounts of Pb in the iron/manganese phase ($7.30\text{--}10.8\text{ }\mu\text{g g}^{-1}$). The significant bioavailability of Pb in the Ebrie Lagoon is consistent with previous studies that found fish Pb concentrations exceed the safe limits (Coulibaly et al. 2012; Yapi et al. 2012). This result shows that combination of both sequential and kinetic extraction methods better explains Pb availability than the kinetic extraction method alone. We concluded that potential mobility of metals in the Ebrie Lagoon could be better assessed through the exchangeable fraction and the iron/manganese oxide fraction obtained using sequential extraction methods.

4.5 Potential risks of Zn, Cu, Pb, Co, and Ni

The Risk Assessment Code (RAC) was determined based on the percentage of total metal concentration in the exchangeable and acid soluble fraction (F1). This fraction is considered the most unstable and reactive phase, which has greater potential for adverse effects on the aquatic environment (Jain 2004). Based on the RAC scale, sediments collected from the Ebrie Lagoon could pose a high risk relative to Zn and a medium risk for Co and Ni. The RAC values of Pb and Cu

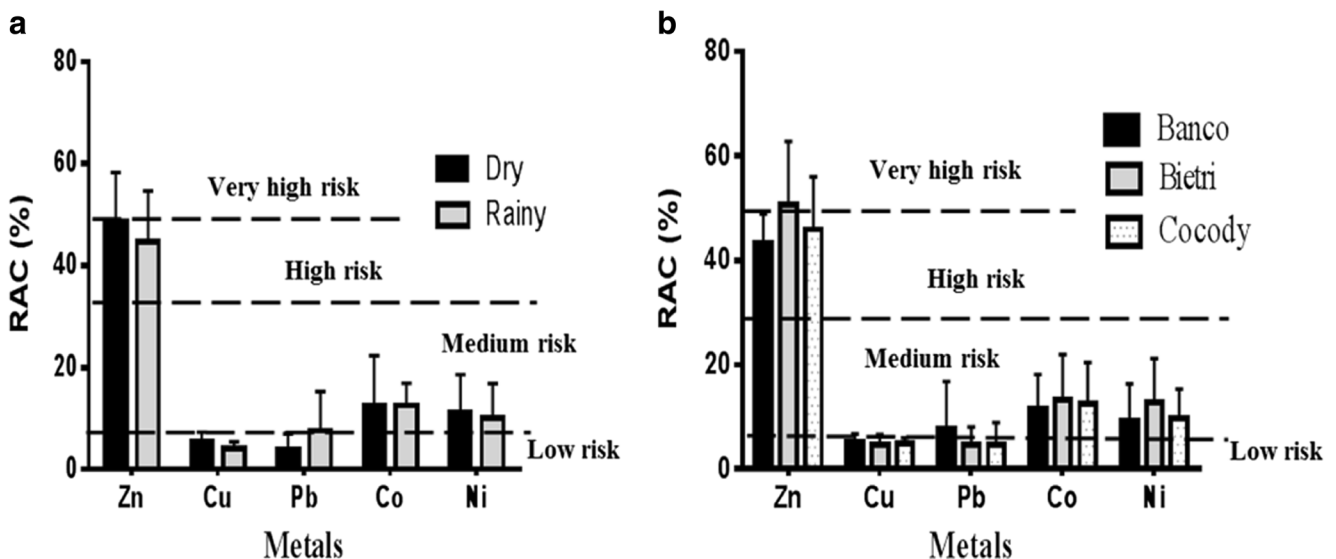


Fig. 8 Seasonal (a) and spatial (b) variations in the Risk Assessment Code (RAC) of studied trace metals (all bays combined)

revealed low risk (Fig. 8). Thus, it can be concluded that Zn was the most bioavailable metal in the Ebrie Lagoon. This is confirmed by previous studies that found high Zn concentrations in fish and mollusks compared to other metals (Coulibaly et al. 2012; Bakary et al. 2015). On the contrary, this study shows that Pb was one of the less available metals in the Ebrie Lagoon system, which does not reflect concentrations exceeding WHO/FAO health limits reported in Cote d'Ivoire lagoon systems (Coulibaly et al. 2012; Yapi et al. 2012; Bakary et al. 2015). RAC evaluates qualitatively the potential risk of metals and does not take into account total metal concentration. The results of sequential extraction and kinetic studies performed in the present work suggest that the high concentrations of Pb found in biota from the Ebrie Lagoon revealed by previous studies resulted from high accumulation of Pb in the iron and manganese oxide phase. Therefore, RAC may underestimate Pb risk in the Ebrie Lagoon because it is limited to the exchangeable fraction in assessing the risk.

5 Conclusions

The mobility and potential risk of Zn, Cu, Pb, Co, and Ni were assessed in the Ebrie Lagoon using kinetic and sequential extraction methods from February 2012 to May 2012. This research demonstrates that percentages of Zn, Cu, Pb, Co, and Ni concentrations in the exchangeable and bound to carbonates, iron/manganese oxides, organic matter, and residual phases did not vary significantly among the bays and the seasons from February to May. Comparing kinetic and sequential extraction results, we found that high concentrations of Zn and Pb in the exchangeable and in the iron/manganese phase in the Ebrie Lagoon sediments could result in significant bioaccumulation of these elements. It was concluded that potential mobility of metals in the Ebrie Lagoon could be better assessed by the exchangeable fraction and the iron/manganese oxide fraction obtained by sequential extraction methods. Our study also revealed that Zn was the most mobile metal followed by Pb, while Co, Ni, and Cu were less available for biota in the Ebrie Lagoon. The Risk Assessment Code (RAC) results showed that Zn could pose high risk to biota, Co and Ni a medium risk, and Cu and Pb a low risk.

Long-term changes in trace metal proportions in sediments may occur; therefore, measurements over a longer study period as well as complementary studies including DGT (diffusive gradients in thin films) method and metal accumulation in organisms should be conducted to better understand the trace metal dynamics and the level of metal pollution.

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Compliance with ethical standards

Conflict to interest The authors declare that they have no conflict to interest.

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