

Study of the mobility of trace elements at the water-sediment interface in coastal and estuarine areas

Étude de la mobilité des éléments traces à l'interface eau-sédiment en zone côtière et estuarienne

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Volume 32, numéro 4, 2020

URI : <https://id.erudit.org/iderudit/1069578ar>

DOI : <https://doi.org/10.7202/1069578ar>

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Éditeur(s)

Université du Québec - INRS-Eau, Terre et Environnement (INRS-ETE)

ISSN

1718-8598 (numérique)

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Citer cet article

Diop, C. & Ouddane, B. (2020). Study of the mobility of trace elements at the water-sediment interface in coastal and estuarine areas. *Revue des Sciences de l'Eau / Journal of Water Science*, 32(4), 463–474.
<https://doi.org/10.7202/1069578ar>

Résumé de l'article

Dans les milieux côtiers et estuariens, les éléments traces piégés dans les sédiments peuvent être relargués dans la colonne d'eau en cas de remise en suspension lors de marées ou de crues. C'est ainsi que ce travail est réalisé pour déterminer la mobilité des éléments traces lorsque ces phénomènes se produisent sur les côtes sénégalaises soumises à des marées de forte énergie. L'extraction séquentielle réalisée selon la procédure du Bureau communautaire de référence (BCR) européen a été utilisée pour déterminer la fraction mobilisable des éléments traces dans les sédiments. Ensuite, des expériences en laboratoire de remise en suspension des sédiments ont été réalisées afin d'évaluer leur capacité à libérer des éléments traces dans l'eau dans le but de mieux comprendre l'effet naturel de la remise en suspension pendant les cycles de marée et de mouvement de l'eau sur la côte. La libération d'éléments dans l'eau a été suivie sur une période de 24 h, ainsi que le potentiel redox (Eh), l'oxygène dissous et le pH. Les pourcentages de biodisponibilité du Cd, Ni, Pb et Zn ont montré une forte affinité avec la fraction soluble dans l'acide, suggérant une mobilité facile de ces éléments. Les résultats des tests de suivi cinétique de la libération d'éléments traces dans l'eau montrent que pendant les premières minutes, la désorption est très importante avec des pics qui peuvent atteindre 90 % selon l'élément, ce qui peut potentiellement provoquer des effets aigus sur les organismes aquatiques. Toutefois, la biodisponibilité des éléments traces dans les sédiments contaminés n'influence la mobilité qu'au début de la remise en suspension. Les tests de remobilisation seraient donc une indication de la capacité des sédiments à libérer des éléments traces lors d'un changement rapide des conditions physicochimiques du milieu aquatique.

STUDY OF THE MOBILITY OF TRACE ELEMENTS AT THE WATER-SEDIMENT INTERFACE IN COASTAL AND ESTUARINE AREAS

Étude de la mobilité des éléments traces à l'interface eau-sédiment en zone côtière et estuarienne

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Received 15 January 2020, Accepted 17 April 2020

ABSTRACT

In coastal and estuarine environments, trace elements trapped in sediments can be released back into the water column if resuspended during tides or floods. This is how this work is carried out to determine the mobility of trace elements when these phenomena occur on Senegalese coasts subjected to high energy tides. Sequential extraction carried out according to the European Community Bureau of Reference (BCR) was used to determine the mobilizable fraction of trace elements in sediments. Subsequently, laboratory sediment resuspension experiments were conducted to evaluate the ability of sediments to release trace elements into the water in order to better understand the natural effect of resuspension during tidal cycles and water movement on the coast. The release of elements into the water was monitored over a 24 h period along with redox potential (Eh), dissolved oxygen and pH. Bioavailability percentages of Cd, Ni, Pb and Zn showed a strong affinity with the acid soluble fraction, suggesting

easy mobility of these elements. The results of the kinetic monitoring tests of the release of trace elements in water show that during the first minutes, desorption is very important with peaks that can reach 90% depending on the element that could potentially cause acute effects on aquatic organisms. However, the bioavailability of trace elements in contaminated sediments only influences mobility at the beginning of resuspension. Remobilization tests would therefore provide an indication of the ability of sediments to release trace elements during rapid changes in the physico-chemical conditions of the aquatic environment.

Key words: *trace elements, water column, sediment, mobility, bioavailability, Senegal.*

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RÉSUMÉ

Dans les milieux côtiers et estuariens, les éléments traces piégés dans les sédiments peuvent être relargués dans la colonne d'eau en cas de remise en suspension lors de marées ou de crues. C'est ainsi que ce travail est réalisé pour déterminer la mobilité des éléments traces lorsque ces phénomènes se produisent sur les côtes sénégalaises soumises à des marées de forte énergie. L'extraction séquentielle réalisée selon la procédure du Bureau communautaire de référence (BCR) européen a été utilisée pour déterminer la fraction mobilisable des éléments traces dans les sédiments. Ensuite, des expériences en laboratoire de remise en suspension des sédiments ont été réalisées afin d'évaluer leur capacité à libérer des éléments traces dans l'eau dans le but de mieux comprendre l'effet naturel de la remise en suspension pendant les cycles de marée et de mouvement de l'eau sur la côte. La libération d'éléments dans l'eau a été suivie sur une période de 24 h, ainsi que le potentiel redox (Eh), l'oxygène dissous et le pH. Les pourcentages de biodisponibilité du Cd, Ni, Pb et Zn ont montré une forte affinité avec la fraction soluble dans l'acide, suggérant une mobilité facile de ces éléments. Les résultats des tests de suivi cinétique de la libération d'éléments traces dans l'eau montrent que pendant les premières minutes, la désorption est très importante avec des pics qui peuvent atteindre 90 % selon l'élément, ce qui peut potentiellement provoquer des effets aigus sur les organismes aquatiques. Toutefois, la biodisponibilité des éléments traces dans les sédiments contaminés n'influence la mobilité qu'au début de la remise en suspension. Les tests de remobilisation seraient donc une indication de la capacité des sédiments à libérer des éléments traces lors d'un changement rapide des conditions physicochimiques du milieu aquatique.

Mots-clés : *éléments traces, colonne d'eau, sédiment, mobilité, biodisponibilité, Sénégal.*

1. INTRODUCTION

Increasing urban, industrial and mineral wastes affect marine coastal and estuary environments in Senegal with metal pollution pressures (AMARA *et al.*, 2019; DIOP *et al.*, 2012). Metallic contamination in aquatic environments has received great attention due to its toxicity and potential long-term accumulation in sediments and organisms (GAO *et al.*, 2018). Sediments have been considered as a well for contaminants discharged to the aquatic environment (DIOP *et al.*, 2015; KALNEJAIS *et al.*, 2015), however, trace elements may be remobilized allowing for diffusion back to the water column. Various factors such as redox, pH, and sulfide influence the distribution of trace elements between

particulate and liquid phase and can help determine whether an element is sequestered in the sediments or remobilized to overlying water (LIU *et al.*, 2019). It has long been established that the toxicity, bioavailability, and mobility of heavy metals depend on their speciation rather than solely on their total concentrations (FLORENCE, 1986). In sediments, the speciation of metals is their distribution in sulfide species, organic matter, Fe and Mn oxides/hydroxides and, to a smaller degree, in carbonates and less reactive mineral fractions (SANTSCHI *et al.*, 1997). Indeed, metals sequestered in sulfide and clay are in binding forms, limiting their mobility (ZOUMIS *et al.*, 2001). However, HAMZEH *et al.* (2014) reported that anoxic sediment resuspension is the most effective factor for mobilizing trace elements sequestered in sulfide phase. Low shear stresses with tides can lead to sediment resuspension, sufficient enough to cause a significant release of metals especially from the surface (KALNEJAIS *et al.*, 2010). When sediments are resuspended, trace elements previously accumulated in sediments may remobilize into the water column due to the drastic change in environmental conditions of the area (redox, conductivity, pH, dissolved oxygen, solid/liquid ratio, degree of contamination, duration, and intensity of resuspension) (BORDAS and BOURG, 2001; FDEZ-ORTIZ DE VALLEJUELO *et al.*, 2014). These dissolved metals are the most bioavailable; thus, metal potential toxicity for aquatic life is likely to be intensified (CALMANO *et al.*, 1993). In Senegal, the few studies that have been carried out along the coast have shown high pollution of the sedimentary compartment by trace elements (AMARA *et al.*, 2019; DIOP *et al.*, 2015). However, no studies have looked at the fate of these pollutants in the event of resuspension of sedimentary particles during tides or floods. Along the Dakar coast and in the Saint Louis estuary, water masses are subject to high-energy currents and tides. Sedimentary particles can therefore be put back into suspension. Since sediments are considered to be a source of metallic contaminants, it appears necessary to study in terms of remobilization the reactivity of the superficial sedimentary layers through laboratory experiments. The main objective of this work is to determine the distribution of trace elements in sediments in order to estimate their mobility and the potential risk posed by these trace elements in the event of sediment resuspension during floods or tides.

2. MATERIALS AND METHODS

2.1 Study sites and sampling

Senegal is a coastal country located in Western Africa characterized by an extended dry season, cool from November to March and warm from April to June, and by a short wet and warm season from July to October (SIMIER *et al.*, 2004).

Although receiving rains in the south, most of Senegal is very dry with few rivers that all have a low flow rate. These low flow rate associated with the very flat level of the country lead the rivers to have salty estuaries with mangroves (DACOSTA *et al.*, 2002). Three sites were selected based on a previous study (DIOP *et al.*, 2015). Two sites along the Dakar coast, site 1: Camberene (unpolluted) and site 2: Hann (highly polluted), and one in Saint-Louis estuary, site 3: Guet Ndar (highly polluted). The choice of these three sites for remobilization tests is justified, apart from the level of pollution, by the fact that these sediments are subject to either flooding, tidal or even dredging phenomena. Some characteristics of the sampling sites are reported in table 1. Surface sediment samples (0-5 cm) were collected into polyethylene bags during low tide period. Sediment samples were placed in a cooler, and transported to the laboratory immediately for sample preparation and storage at -4°C until analysis.

2.2 Analytical procedures

2.2.1 Bioavailable element concentration

In order to determine trace elements associated with the bioavailable fractions of sediment, considered as reactive fractions, we used the method of HUERTA-DIAZ and MORSE (1990). For this, 400 ± 0.5 mg of crude sediment (as opposed to total mineralization) was leached during 24 h with 20 mL of $1 \text{ mol}\cdot\text{L}^{-1}$ HCl at room temperature with continuous agitation. After leaching, the solution was filtered for analysis. Reagents blanks and Canadian International Standard (MESS-3) were used to validate the extraction procedure. Certified and measured results were in good agreement, and the recoveries for all elements analyzed were found to be higher than 90%.

2.2.2 Sequential extraction of trace elements

Sequential extraction (RAURET *et al.*, 2000) determining the distribution of elements into different binding solid phases was used to assess the fraction of trace elements that can be mobilized from sediment to water. To do this, we used the procedure described by HAMZEH *et al.* (2014). Briefly, we used 1 g of crude sediment for the fractionation of some elements (Cd, Zn, Ni, Pb, Cr and Cu) in several groups of particulate solid fractions: 1) exchangeable and associated to carbonate ($0.11 \text{ mol}\cdot\text{L}^{-1}$ acetic acid extractable under N_2 atmosphere in a closed system), 2) reducibly bound to Fe-Mn oxyhydroxides ($0.5 \text{ mol}\cdot\text{L}^{-1}$ hydroxylamine extractable under N_2 atmosphere in a closed system), 3) bound to organic matter and sulfides ($8.8 \text{ mol}\cdot\text{L}^{-1}$ H_2O_2 + $1.0 \text{ mol}\cdot\text{L}^{-1}$ NH_4COOH extractable), and 4) residual fraction. The residues from the three-step extraction procedure were digested by the method described previously by OUDDANE (1990) and modified by BILLON (2001). After each step, the suspension was centrifuged and the supernatant was decanted and stored in plastic tubes at

4°C until analysis using inductively coupled plasma-optical emission spectrometer (ICP-OES, Thermo ICAP, 6000 Series).

2.2.3 Remobilization tests

To assess the capacity of sediments to release trace elements in water during tidal cycles and water movement on the coast, remobilization tests of sediment resuspension were performed. The mobility of some elements (Cd, Zn, Ni, Pb, Cr and Cu) was measured according to the method described by HAMZEH *et al.* (2014), slightly modified to use autochthonous water from the coast and estuary as extractant. The main advantages of this approach in batch are its simplicity and the ability to simulate natural conditions. Thus, sediments were resuspended in water. In the experiment, the suspension was shaken at constant low stirring rate in polyethylene flasks at room temperature and atmospheric pressure. During the course of the experiment, redox potential (Eh), oxygen and pH were measured at close time intervals during the first hours of the experiment and every hour during manipulation by continuously introducing the electrodes for each parameter. Aliquots of 7 mL were sampled, filtered, acidified, and stored at 4°C until element analyses by ICP-MS (ICP-MS, Varian, 820 MS). The accuracy and precision of the analyses were assessed using procedural blanks, replicated analyses and analyses of standard reference material (MESS-3). Procedural blanks were less than 2% of the signal and the coefficient of deviation of three replicate measurements was consistently below 10% (data not shown). Table 2 shows experimental conditions.

2.3 Statistical analysis

Statistical analysis was performed with SPSS 17.0 for Windows (SPSS, Paris, France). A test (Mann-Whitney *U*) was used to observe the significant differences in parameters between the sites and/or the different tests. In all tests, the significance level for differences values was set at $p < 0.05$. Thereafter, we used single linear regression models (Pearson's test) to study the link between bioavailability and mobility of trace elements.

3. RESULTS AND DISCUSSION

3.1 Bioavailable trace elements concentrations

Table 3 shows bioavailable trace elements concentrations and percentages of bioavailable fractions in surface sediments on the Dakar coast and in the Saint Louis estuary. In sites 1 and 2 respectively, bioavailability percentages of Cd (21%, 50%), Ni (63%, 88%), Pb (17%, 64%) and Zn (22%, 85%) showed a strong affinity with the acid-soluble fraction suggesting

Table 1. Locations and description of sampling sites selected on the Dakar coast and in the Saint Louis estuary (Senegal).**Tableau 1.** Localisation et description des sites d'échantillonnage sélectionnés sur la côte de Dakar et dans l'estuaire de Saint-Louis (Sénégal).

Area	Site N°	Site name	Coordinates	Sediment category ^a
Dakar coast	1	Camberene	14°46'16"N 17°25'54"W	Low polluted (2 < SPI < 5)
	2	Hann	14°42'54"N 17°25'51"W	Highly polluted (10 < SPI < 20)
Saint Louis estuary	3	Guet Ndar	16°01'35"N 16°30'26"W	Highly polluted (10 < SPI < 20)

^a Based on Sediment Pollution Index (SPI) (DIOP *et al.*, 2015)**Table 2.** Experimental conditions of sediment remobilization.**Tableau 2.** Conditions expérimentales de remobilisation des sédiments.

Experimental parameter	Test 1	Test 2	Test 3
Ratio m/v (g·L ⁻¹)	1	2.5	5
Sample volume (mL)	7	–	–
Sample time (min)	0, 1, 2, 5, 10, 30	60, 120, 240, 480, 720, 1 440	
Parameters measured	pH, Eh, dissolved O ₂		
Water quantity (L)	2	–	–
Stirring rate (rpm)	200	–	–

Table 3. Mean values of bioavailable trace elements concentrations (± SD) and percentages of bioavailable fraction in surface sediments.**Tableau 3.** Valeurs moyennes des concentrations (± écart-type) des éléments traces biodisponibles et pourcentages de la fraction biodisponible dans les sédiments de surface.

Site	Cd		Cu		Ni		Pb		Zn	
	(µg·g ⁻¹)	(%)								
1	0.04 ± 0.01	21	1.93 ± 0.78	15	1.42 ± 3.59	63	0.48 ± 0.08	17	1.54 ± 0.43	22
2	0.16 ± 0.07	50	2.79 ± 0.74	17	1.03 ± 2.01	88	4.25 ± 0.76	64	20.4 ± 7.4	85
3	0.26 ± 0.14	19	29.8 ± 23.7	36	4.39 ± 3.76	43	663 ± 468	50	73.1 ± 30.1	83

an easy mobility and bioavailability of these elements in the aquatic medium. Cu bioavailability percentage was below 20%. Differences in bioavailability among elements appeared similar in site 3 with very low bioavailability percentages except for Ni (43%), Pb (50%), Zn (83%) and Cu (36%) showing a strong affinity with the acid-soluble fraction. Comparing the two polluted sites (2 and 3), the higher percentage of bioavailable fraction on the coast than in the estuary can be explained by salinity and particularly high Ca concentrations on the coast compared to the estuary. According to TAM AND WONG (1999), an increase in salinity is associated with an increase in the concentrations of major elements (Na, K, Ca, Mg) that compete with trace elements for the sorption sites in sediments. Indeed, addition of Ca salts results in a higher release of exchangeable

elements in the soil solution compared to the addition of Na salts, which are less competitive for sorption (KHATTAK and JARRELL, 1989). Moreover, DU LAING *et al.* (2008) reported that such effects of salinity on the trace element mobility and availability only occur in surface sediments.

However, bioavailable trace elements concentrations are higher in the estuarine site than coastal sites. Among the elements studied, Cr was in the lowest percentage in the acid-soluble fraction (5-8%) (Figure 1), indicating that Cr cannot be remobilized into the aquatic medium under (bio)geochemical conditions normally occurring in nature (EL-BILALI *et al.*, 2002; GAO *et al.*, 2018).

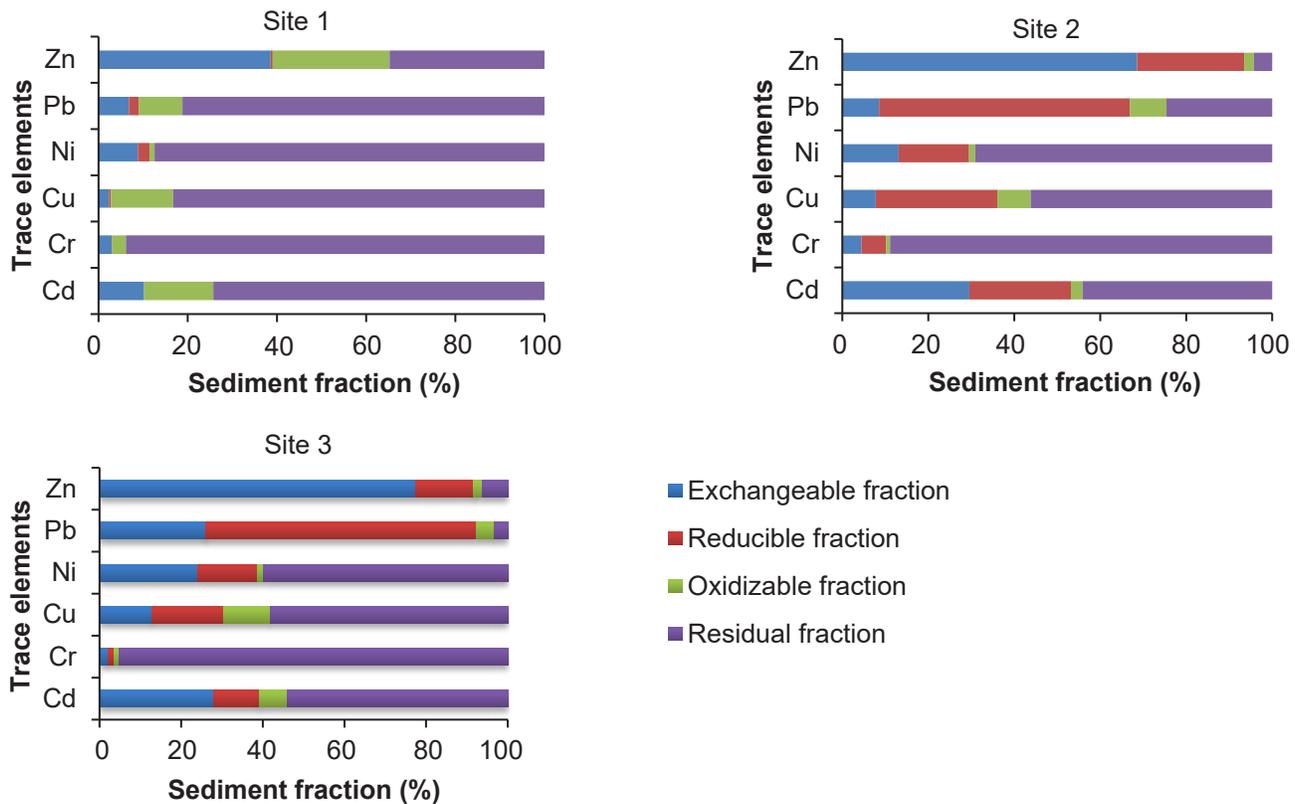


Figure 1. Distribution of trace elements in the four sediment fractions.
Distribution des éléments traces dans les quatre fractions sédimentaires.

3.2 Element speciation in sediments

The profile of the chemical fractionation of trace elements in the superficial sediment is shown in figure 1. The most polluted sites (site 2, Hann and site 3, Guet Ndar) have relatively large reducible fractions for almost all elements; on the other hand, Cambrene (site 1) has a reducible fraction of almost zero for most elements. The residual fraction for all elements is generally higher at the unpolluted site (1) than at highly polluted sites. Pb has very different distribution profile if we compare the three sites. On the other hand, Zn, Ni, Cu and Cd have relatively similar distribution profiles in the sediments of Hann and Guet Ndar, this distribution being totally different from that observed at Camberene. For example, Zn is present in the exchangeable/carbonate fraction at more than 70% at Hann and Guet Ndar while it is present at less than 50% at Camberene. However, heterogeneity is observed for the same elements when their profiles are more accurately compared for the two polluted sites. The exchangeable/carbonate fraction of Ni is higher, for example in Guet Ndar sediments, it is about 30% while it is only about 10% in Hann. Similarly, the exchangeable/carbonate fraction is higher than the reducible fraction at Guet Ndar, while the opposite is true at Hann. Due to the heterogeneous behaviour of elements in different fractions at different sites, it would be preferable to study each element separately. The distribution of Cd in the different

fractions is quite similar at Hann and Guet Ndar sites with a presence of 30% in the exchangeable/carbonate fraction, 10-15% in the reducible fraction, about 5% in the oxidizable fraction and less than 50% in the residual fraction. According to NELSON (2019), surface (oxic) sediments have a significant distribution of Cd in the exchangeable/carbonate fraction. In addition, the formation of CdCaCO_3 by precipitation or by incorporation of Cd into calcite as a substitute for Ca as shown by some authors (KORFALI and DAVIES, 2004; REEDER, 1996) may explain the high percentage distribution of this element in the carbonate fraction. At the Guet Ndar and Hann sites, Pb is mainly associated with the reducible fraction ranging from 58% to 66%. This affinity of Pb to the reducible fraction has been reported in many studies in the literature (CARTER *et al.*, 2006; DONG *et al.*, 2000; HAMZEH, 2012). The latter author shows that almost 70% of Pb is associated with oxides. LESVEN *et al.* (2009) reported that iron oxide is the preferred phase for Pb fixation. ALLOWAY (1995), YONG *et al.* (1992) have established that oxides are the main component elements involved in metal-specific adsorption reactions and the affinity order for oxides is defined by MASON *et al.* (1999): $\text{Pb} > \text{Cu} > \text{Zn}$. Unlike Pb, which is more present in the reducible phase, Zn is more distributed in the exchangeable/carbonate fraction at the three sites. The distribution of Zn in the different fractions, however, varies from site to site. While the carbonate fraction is higher

at Guet Ndar (77%) followed by Hann (69%) and Camberene (39%), the reducible fraction is more represented at Hann (25%) followed by Guet Ndar (14%). The oxidizable fraction is very low in polluted sites (2-3%) while it is relatively high in Camberene (26%). In our study, Zn is the element most present in the carbonate fraction, followed by Cd and Ni. This order of affinity of these elements to the carbonate fraction has been described in other studies, including that of TUSSEAU-VULLEMIN *et al.* (2007). In surface sediments, Zn is also quite bound to the reducible fraction (oxide fraction). Many authors (BARUAH *et al.*, 1996; BOUGHRIET *et al.*, 2007; RANU *et al.*, 1993) have observed a high percentage of Zn in the oxide fraction of surface sediments, which is in line with our results (reducible fraction of Zn in contaminated sites: 14-25%). Among all the metallic trace elements studied, Cu has the highest oxidizable fraction (organic and sulphide, 5-10%) at contaminated sites. This situation is not observed in the unpolluted site (Camberene). The large presence of Cu in the organic fraction in polluted sites can be explained by the fact that this element has a high affinity for organic compounds (LUOMA and RAINBOW, 2008) and that it forms stable complexes with them (LESVEN *et al.*, 2009). In addition, the treatment of wastewater discharged at Camberene contributes to a reduction of dissolved organic matter, which is not the case in polluted sites. However, the organic matter that forms complexes with Cu in the sedimentary compartment is from urban sources (PRABAKARAN *et al.*, 2019).

The quantity of elements in fractions sensitive to changes in the physico-chemical conditions of the environment (variation in pH, redox potential, salinity) are those that are likely to be released into the water column. The bioavailable fraction, such as elements extracted by HCl at 1 mol·L⁻¹, was comparable to the sum of the first three reactive fractions in the Tessier extraction scheme (TESSIER *et al.*, 1979). The mobilizable elements are concentrated in these fractions, which correspond to the carbonate, oxide and organic phases of the sediments. By considering in this study the elements most sensitive to changes in the physico-chemical conditions of the environment, in other words, the most mobile metals, a ranking in decreasing order of lability of elements can be established in the three study sites (Figure 2). This figure shows that Pb and Zn are the most mobile elements at the polluted sites (>75%), followed by Cd and Cu (>40%). At Camberene (the least polluted site), only Zn has a mobilizable fraction of about 60%. The other elements, namely Cd, Pb, Cu, have a mobilizable fraction of less than 30%. These observations show that trace elements are generally linked to residual fractions in clean sediments and that they are highly mobilizable in the case of contaminated sediments.

3.3 Monitoring of water physico-chemical parameters during sediment resuspension

Physico-chemical parameters (pH, redox potential, dissolved oxygen, etc.) play an important role in the behaviour of trace metals. A follow-up of these parameters in the remobilization tests is therefore useful to be able to describe the reactivity of the medium constituted by the water/sediment mixture. Since the remobilization experiments were performed under oxic conditions, only the pH and oxidation-reduction potential were monitored kinetically. Nevertheless, dissolved oxygen was measured at the beginning and end of each experiment. The evolution of the redox potential and pH over time for the different remobilization tests (different sediment/water volume mass ratios: 1, 2.5 and 5 g·L⁻¹) is shown in figure 3. This figure shows that, regardless of the site studied and the ratio of sediment mass to water volume used, there are no significant differences in the evolution of pH over time ($p > 0.1$). A slight increase in pH in the first few minutes (less than 0.3 units) is observed at all sites and then the evolution is stable over time. This stability is due to the fact that the pH is relatively buffered by the carbonates in the marine waters used for remobilization tests. Decreased water pH can induce, for example, oxidation of organic matter or sulphides, and promote the release of elements into the water column (SCHROEDER *et al.*, 2019; SILVA *et al.*, 2013; ZOUMIS *et al.*, 2001). Indeed, the reaction medium is more alkaline than acidic, which suggests that pH will not increase the mobility of trace elements in remobilization tests. The oxidation-reduction potential shows a relatively common evolution at all sites. It includes a first phase characterized by a free fall of redox potential within the first 30 min following the dispersion of the sedimentary material and a second phase resulting in a progressive increase of this potential beyond the first half hour. This increase in potential results from the oxidation of the reaction medium which made it possible to recover after about 24 h oxidizing conditions close to those of the waters used during the remobilization tests. Such observations are similar to those described in the literature (CANTWELL and BURGESS, 2004; HAMZEH, 2012). The variations in redox potential observed particularly in the first few minutes of water-sediment contact reflect the presence of highly reactive species within this two-phase water-sediment system (CANTWELL *et al.*, 2002). These variations are all the more important, especially in the first few minutes, as the ratio of sediment mass to water volume is high. At all sites, it was found that the 1 g·L⁻¹ tests showed a smaller decrease in redox potential than that noted in the 5 g·L⁻¹ tests. The mass of sediment therefore plays a significant role in the contribution of reactive species. This could have an impact on the bioavailability of trace elements. Indeed, when the environment is in a reduced state, the trace elements are trapped by sulphides, which make them less mobile (WANG and WANG, 2017). It appears from the rapid variations in

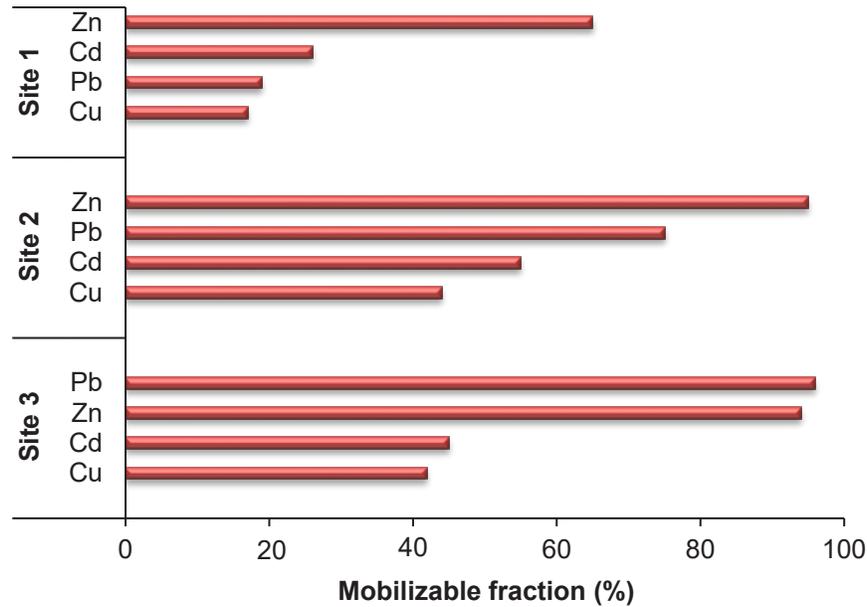


Figure 2. Ranking in descending order of the mobilizable fraction of trace elements.
 Classement par ordre décroissant de la fraction mobilisable des éléments traces.

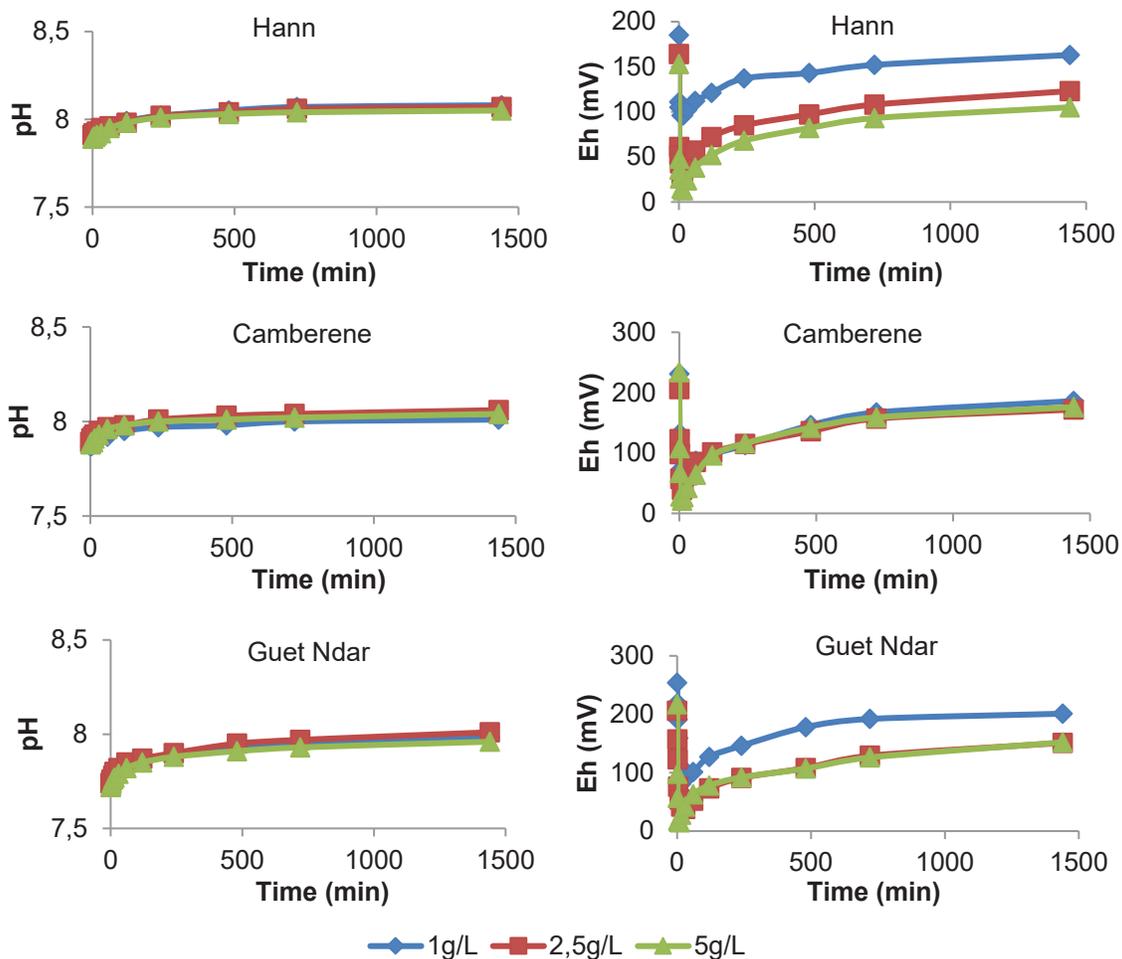


Figure 3. Evolution as a function of time of pH and redox potential (Eh) at the different sites for the three remobilisation tests.
 Évolution en fonction du temps du pH et du potentiel d'oxydoréduction (Eh) dans les différents sites pour les trois essais de remobilisation.

physico-chemical parameters noted in the first few minutes of the 1 g·L⁻¹ tests that a disturbance of the environment (high tide, flood, dredging) can induce at the sediment water interface a more or less significant release of trace elements.

3.4 Kinetics of the release of trace elements into water

In order to be able to compare the behaviour of trace elements at the different sites, kinetic monitoring was carried out in terms of the element mobility and not concentration in water. Element mobility is expressed as the ratio between the amount of element extracted from the sediment at a given time (during resuspension) and the concentration of the element in the sediment obtained after total mineralization. Therefore, the percentage mobility of a given element at a time t is calculated according to the following expression:

$$M = (C_t - C_0)/C_0 \quad (1)$$

where M is mobility, C_0 and C_t are the respective concentrations ($\mu\text{g}\cdot\text{g}^{-1}$) of a given element in the sediment before and after resuspension at a given time.

Figure 4 shows the evolution over time of the percentage mobility of trace elements in the three sites studied. The results of the kinetic monitoring tests of the release of trace elements into the water show that during the first few minutes, the desorption of trace elements is very important with peaks that can reach 90% depending on the element and the site. The tests were carried out under oxic conditions, the oxidation of sulphides by oxygen in the medium leads to a significant release of metals. The considerable reduction of the oxidation-reduction potential in the first few minutes makes the reducing medium reducing, which would promote the solubilization of metal oxides. In addition, the suspension of calcite-rich sediments (CaCO_3) will lead to a dissolution of the carbonates. These three phenomena (oxidation of sulphides and dissolution of carbonates and oxides) could be at the origin, according to some authors (RICKARD and MORSE, 2005; SCHROEDER *et al.*, 2019), of the significant release of trace elements into the water in the first minutes. The increase in trace element mobility is quickly followed by a decrease in mobility for all elements and sites that could be explained by adsorption and precipitation (VIDAL-DURÀ *et al.*, 2018). The kinetics of desorption are much slower than that of adsorption, so the longer the contact time, the greater the adsorption becomes (SPARKS *et al.*, 1999), which reduces the mobility of trace metals.

From 1 min to 8 h of sediment resuspension, Ca concentrations in water increase from 4.4 to 7.3 mg·L⁻¹ for Camberene, 2.5 to 3.5 mg·L⁻¹ for Guet Ndar, and

0.26 to 0.8 mg·L⁻¹ for Hann. The same observations were made with Mg whose concentrations in water increased during the same period from 0.07 to 0.96 mg·L⁻¹ for Guet Ndar, 0.34 to 0.35 mg·L⁻¹ for Hann and 0.16 to 0.89 mg·L⁻¹ for Camberene. We can therefore see that at the moment when the mobility of trace elements decreases over time, that of major elements increases. The negativity of the Pearson correlation coefficients calculated between Ca/Pb (-0.05), Ca/Co (-0.46), Ca/Cu (-0.34), Ca/Ni (-0.01), Ca/Zn (-0.08), Mg/Co (-0.41), Mg/Ni (-0.19), Mg/Cr (-0.05) and Mg/Zn (-0.17) confirms the reverse evolution between major and trace elements. It is reported in the literature that some elements such as Ca compete with trace elements at resorption sites in sediments (TAM and WONG, 1999; ZHAO *et al.*, 2013). It appears that the decrease in trace element mobility over time is related to the greater desorption of cations such as Mg and Ca. This is because as the major elements release their sorption sites, they would be occupied by trace elements, which reduces their mobility. Similar observations have been reported by DU LAING *et al.* (2008) who indicated that the effects of salinity on trace element mobility occur only in surface sediments.

Given the complexity of all phenomena (adsorption, competition) and parameters (sediment characteristics) that may be involved in laboratory remobilization tests, it would be important to compare these results with field data. However, remobilization tests provide an indication of the ability of sediments to release trace elements during a rapid change in the physico-chemical conditions of the environment.

3.5 Relationship between mobility and bioavailability of trace elements

The study of processes that govern the presence of metals in sediments and water is of critical importance for understanding mobility, reactivity and, therefore, bioavailability of toxic trace metal elements (DU LAING *et al.*, 2009). The mobility and bioavailability of trace elements are largely related to their speciation, *i.e.* the different phases under which the element is present in the sediment compartment (KERSTEN, 2002). It is therefore important to study the relationships between the reactive and therefore bioavailable fraction of trace elements and the ability to remobilize sediments during resuspension events. The relationships between mobility and bioavailability of trace elements are demonstrated by the regression coefficients determined between these two parameters. The Camberene site which is the least polluted shows very low regression coefficients (0.0047 at 1 min and 0.0004 at 1 h of resuspension). This shows that in “clean” sites, the remobilization of trace metals is not related to their bioavailability. At the Hann and Guet Ndar sites, which are more contaminated by trace elements, relatively good regression coefficients are noted at the first

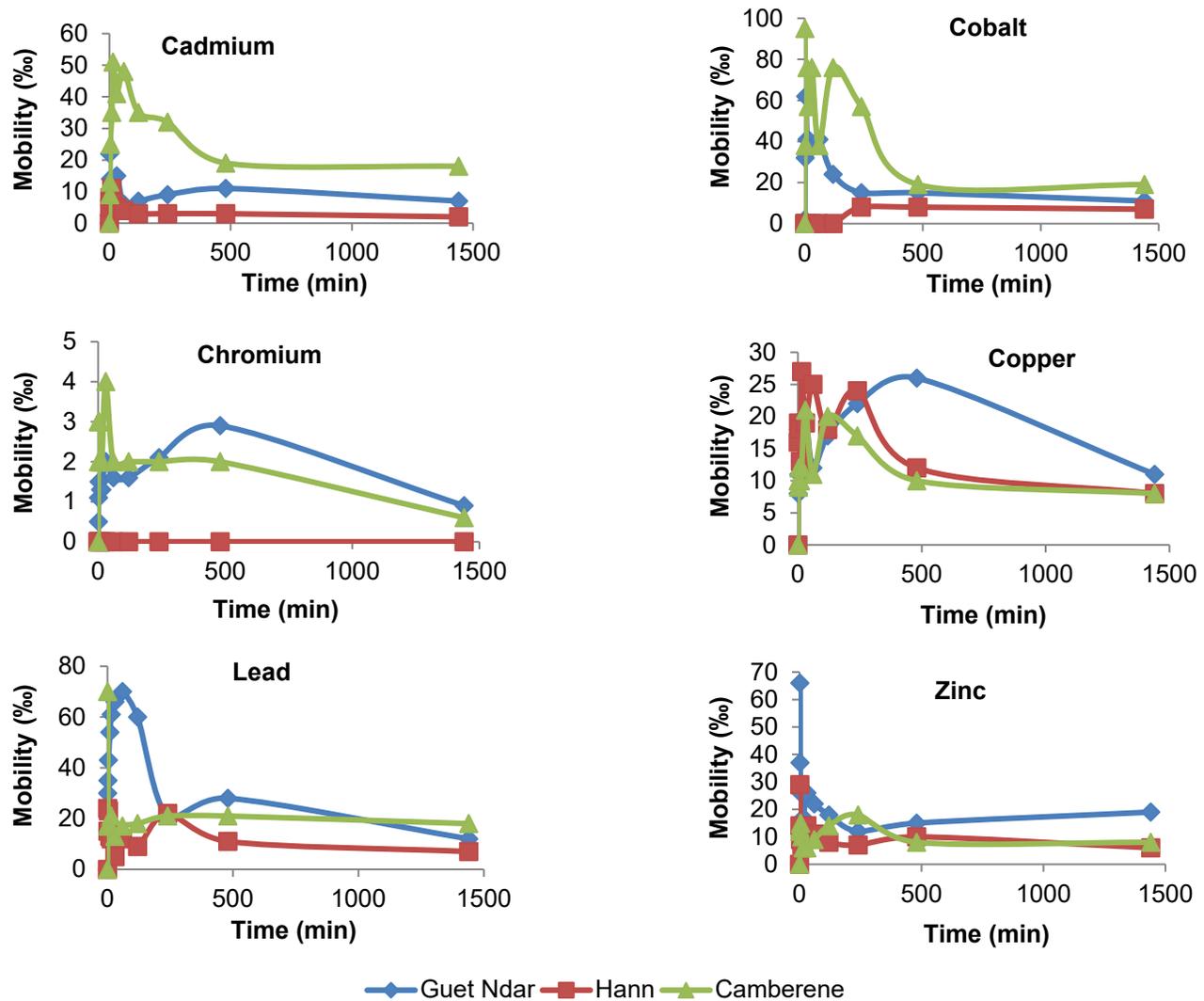


Figure 4. Kinetics of trace element mobility for the 1 g·L⁻¹ remobilization test.
Cinétique de la mobilité des éléments traces pour l'essai de remobilisation de 1 g·L⁻¹.

minute of sediment resuspension with a regression coefficient of 0.84 at Guet Ndar and 0.60 at Hann; these coefficients decrease to 0.09 and 0.31 respectively after 1 h of resuspension. These observations suggest that the bioavailability of trace elements in contaminated sediments influences mobility only at the beginning of the resuspension. LIU *et al.* (2019) showed that higher element bioavailability in sediments could facilitate the release of elements. It should therefore be noted that at the beginning of the tide or flood, the bioavailable trace elements in polluted sites are strongly released and the risk to aquatic organisms increases. However, these phenomena do not last long and in less than an hour, bioavailable metals are re-adsorbed by sediment particles.

4. CONCLUSION

Our study showed that the mobilizable fraction is around 75% in polluted sediments, whereas it is less than 30% in less polluted sediments. The kinetic monitoring of the release of trace elements into the water shows that during the first minutes, the desorption of trace elements is very important with peaks that can reach 90% depending on the element. The regression coefficient of 0.84 in the first minute between the mobility and bioavailability of trace elements indicates that at the beginning of the tide or during flooding, mobilizable trace metals are strongly released, which increases the risk for aquatic organisms. Thus, remobilization tests provide an idea of the capacity of sediments to release trace elements when the physico-chemical conditions of the environment change. These results will have to be confirmed by carrying out additional field studies during floods or tides.

ACKNOWLEDGMENTS

This work was supported by the Common Centre of Measurements (ULCO) and the Laboratory of Analytical and Marine Chemistry (Université Lille 1, France). We are grateful to the France Embassy in Senegal for their help and thank the Government of Senegal for their support.

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