Nutrients induction on lead, cadmium, manganese, zinc and cobalt speciation in the sediments of *Aby* lagoon (Côte d'Ivoire)

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ABSTRACT
This study reported nitrogen and phosphorus leverage on lead, Cadmium, Manganese, Zinc and Cobalt speciation in the *Aby* lagoon sediments. The trace elements and water samples were collected from eleven sites located within the four lagoon sectors. Sequential extraction was carried out in five fractions: exchangeable (F1), bound to the carbonates (F2), bound to iron and manganese (oxy) hydroxides (F3), bound to the organic matters (F4) and residual (F5). Heavy metals chemical fractionation followed the four-step Zerbe and *al*. (1999) process, completed with an acid digestion method for residual (F5) extraction. Co-inertia analysis monitored with ADE4 package showed that nitrite and Kjeldhal nitrogen (TKN) mainly influenced Co speciation and especially the compounds (total lead, total Cd, total Zn, Co-F1 and Co-F4) tend to accumulate on sediment surface. However, their higher influence than nitrates on previous metals was too lower than the other nitrogen compounds which they were very negatively correlated. As the phosphorus compounds which showed a greatest impact on lead, Cd, Mn, and Zn speciation. The respective resulted factorial values were about -1 and 1. Total and inorganic phosphorus portion showed a similar influence range than total nitrogen on the various studied heavy metals speciation in sediment.

Keywords: Heavy metals, Nutrients, *Aby* lagoon, sequential extraction, sediment.

INTRODUCTION

High productivity of tropical lagoons, sustained by nutrients variability (Albaret and *al.* 2004), often leads to pollution (Kouassi and *al*., 2005). Insidious metal pollution, specifically submit the sediments to various studies (Issola and *al.* 2009; Yao and *al.* 2009). Fate of this metal pollution, often array, depends on physico-chemical environment (INERIS, 2007). These define mobility and chemical differentiation generating the risks associated with metal presence in the sediments (Kirpichtchikova and *al.* 2006).

Metal in the soils can be divided into two fractions (Rachou and Sauvé, 2008): (i) inert fraction, assumed as non-toxic fraction, and (ii) labile fraction, assumed to be potentially toxic. For the heavy metals availability assessment, only soil labile fraction is considered because often called, by extension, bioavailable fraction (Gray and *al*., 2004).

Cadmium and lead are deemed to be the most important environmental pollutants in the agricultural soils because of their adverse effects on food quality and health of soils (Onweremadu and Duruigbo, 2007). In the aquatic environments, these metals are transferred to the bodies in situ and men through the food chain in certain circumstances.

Nitrogen, phosphorus (Salvia-Castellvi M. and *al*. 2002) and the heavy metals (Yobouet and *al*. 2010) speciation is investigated using sequential fractionation. The resulting five fractions are: exchangeable fraction (F1), bound to - carbonates (F2), (oxy) hydroxides of iron and manganese (F3), -organic matter (F4) and residual fraction (F5).

In terms of mobility, following classification of these fractions can be made: mobile fraction, mobilizable fraction, pseudo-total fraction and immobile fraction (Gupta and *al*. 1996). However, even if process is linked to time, it remains that residual fraction (immobile) mobilization is possible under the effects of watering (Venkateswaran and *al*. 2007). Thus, this concept may be significantly important because of the physico-chemical variability in the lagoons of Côte d'Ivoire (Durand J.R. and Skubich M., 1982).

In addition, reactivity of an element depends on cons-ion (INERIS, ibid.). Indeed, the carbonates, suspended solids, halogenated compounds, nitrogen and phosphorus are the major cons-ion in the heavy metals chemical differentiation in the soils and sediments.

This study aims to fix influence of the physico-chemical on lead, cadmium, manganese, zinc and cobalt speciation as a function of hydrology in *Aby* lagoon. To do this, the co-inertia analyses were carried out with ADE4 package. The results pointed out that nitrogen and phosphorus were the key cons-ion in the studied heavy metals speciation in the sediments of this lagoon. Static and dynamic analysis of these influences have been made and mapped in this work to aid understanding.

MATERIALS AND METHODS

This study was conducted on Côte d'Ivoire rural *Aby* lagoon located between 2°51 - 3°21 eastern longitude and 5°05 – 5°22 northern latitude. The two main tributaries (*Bia* and *Tanoe*) are escape routes from anthropogenic and mining operations within its watershed in Côte d'Ivoire and Ghana (Claon, 2004). The investigations were conducted according to the two main seasons (December to April and May to November) that shape system of the rivers *Bia* and *Tanoe* (Durand and Chantraine, 1982). Eleven sampling sites within the four sectors (North *Aby*, South *Aby*, *Tendo* and *Ehy*) of *Aby* lagoon were selected (Figure 1). Water and the sediments samples were collected from the stations previously defined.
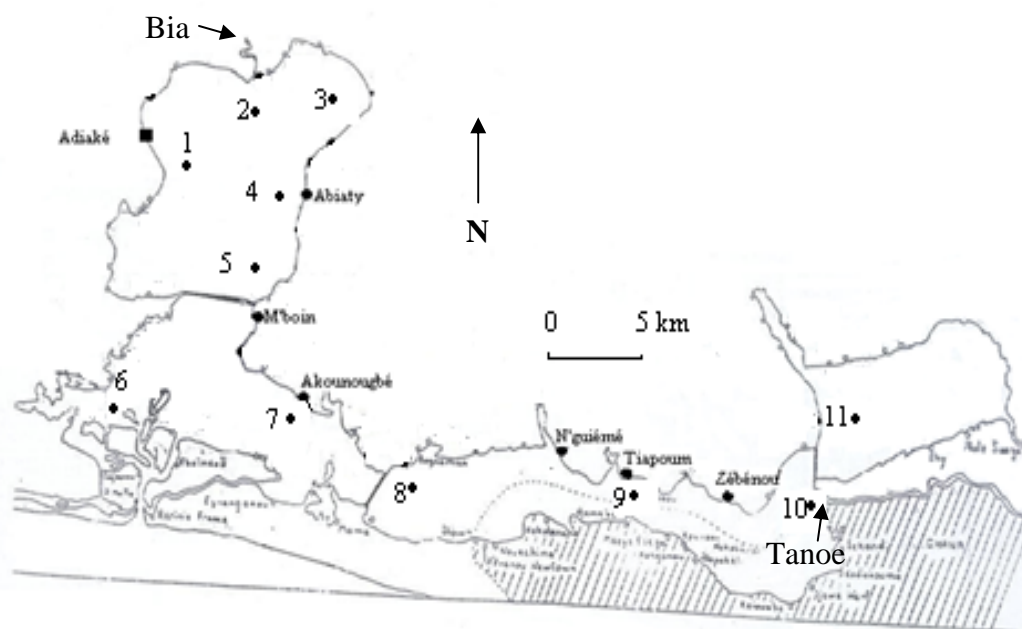

Figure 1: *Aby* lagoon geomorphology and the sampling sites location.

Physico-chemical data, e.g. pH, salinity, dissolved oxygen, suspended solids, % sand, % organic matter, nitrogen and phosphorus, were collected to water-sediment interface. While the sediments sampling was conducted within the layer 5 cm using a sediment pliers. The sediment samples previously stabilized with 3 mL of concentrated nitric acid, were air-dried, crushed, sieved and the fraction < 2 mm was used for the heavy metals analysis. The heavy metals total concentration analysis were performed with UNEP (2007) method. The Zerbe and *al*. (1999) four-step extraction process was followed to fractionate the heavy metals, including solvable and exchangeable metals (F1), mobile and bound to carbonates (F2), mobilizable and bound to (oxy) hydroxides (F3), pseudo-total and bound to organic matters (F4).

The heavy metals fifth fraction (residual) extraction, immobile and bound to silica matrix (F5), was performed from F4 residue with an acid digestion method in dry evaporation conditions. 5 mL of HNO_3, 5 mL of HF and 1.5 mL $HClO_4$ were successively added and heated on a sand bath at 180°C. The resulted dry residues were dissolved with 2 mL of HNO_3 and collected in glass tube, added of de-ionized water with a total volume of about 50 mL, stored for a night at 4°C before supernatant analysis.

Analysis of the nitrogen compounds were conducted following the NF T90-012 standard and related. For the phosphates, NF T90-023 guided the analyses. The organic and total fractions of the both compounds were

previously mineralized in presence of acids (H_2SO_4/K_2SO_4 at 400 ° C) using blue molybdenum method (Murphy and Riley, 1962). Finally co-inertia analysis was conducted between the average of physico-chemical at water-sediment interface and the total/specied metal content of sediments. Total co-inertia observed value (69.45) was more than all the calculated co-inertias set of random permutations. In fact, relations were established between the physico-chemical and heavy metals behavior in the *Aby* lagoon sediments.

RESULTS AND DISCUSSION

The co-inertia analysis results were presented in table 1. Besides, information contained in the original tables was expressed by f1 factor for 90.57 %. It was consequently used to assess physico-chemical influence on the heavy metals speciation in the *Aby* lagoon sediments.

Table 1: Summary of co-inertia analysis between the physico-chemical and the heavy metals sediments contents of *Aby* lagoon.

Factor	Covariance	Variance 1	Variance 2	Correlation	INER 1	INER 2
f1	7,46	6,452	10,52	**0,9057**	6,625	10,81
f2	2,082	2,876	1,94	0,8814	4,103	3,275

At low water, the average nitrite (NO_2^-) concentrations ranged from 0.46 mol/L to 4.33 mol/L during rainy season with the respective variation amplitudes of 2.42 µmol/L and 21.76 µmol/L.

Nitrates ranged from 0.69 mg/L to 2.04 mg/L for the two seasons with the average values of 0.63 mg/L (low water) and 0.05 mg/L (raw). Similarly, ammonia ranged from 3.12 to 11.61 µmol/L, while Kjeldhal nitrogen (TKN) ranged from 0.09 to 0.47 mg/L for the average concentrations of 0, 4 mg/L and 0.82 mg/L.

Average total phosphorus decreased from 20.34 mg/L (dry season) to 4.84 mg/L (rainy season) with the variation amplitudes of 16.9 mg/L and 18.66 mg/L. While average organic portion varied from 1.01 mg/L to 0.41 mg/L for the respective variation amplitudes of 0.88 mg/L and 1.53 mg/L. As for its inorganic portion, the seasonal averages were in order equal to 19.31 mg/L and 4.43 mg/L for the variation amplitudes equivalent to 16.04 mg/L and 17.57 mg/L. Inorganic phosphorus was about 90% of the total contents in the bottom of the *Aby* lagoon.

At a pH of 7.25 and 8.25, ionized ammonia (NH_4^+) part was 99% and 90% (ATSDR, 2004). pH average value at sediment-water interface had proven almost static (7.31) in *Aby* lagoon for all seasons, despite the high spatial and temporal variability (6.81 to 8.86). Bozkurt and *al.* (2000) reported that pH increasing to an almost neutral level, due to the organic acids degradation, was buffered by the carbonates system. This stability of pH supported ammonia production. However, ATSDR (ibid.) noted that ammonia volatilization to atmosphere reduced residence time in the sediments due to its transformation by micro-organisms to nitrite and nitrate (nitrogen cycle). Dontsova and *al.* (2005) concluded that ammonia adsorption to the ionized particles of the sediment was chemical (more stable) as exchangeable ion. This particularity of ammonia justified its influence on most of the studied metals speciation (Figure 2), especially total Mn, total Co, Ld-F4, Zn-F4 and Co-F5 (low co-inertia); Ld-F1 , Ld-F3, Ld-F5, Cd-F1 to Cd-F4, -Mn-F1 to Mn-F3, Zn- F1 to Zn-F3, Zn-F5, and Co-F3 (high co-inertia). Ammonia had a similar static influence to organic nitrogen and larger than total nitrogen. The nitrite and TKN had significant influences virtually identical, but smaller on lead, zinc, total cobalt, Cd-F5, Mn-F1, Mn-F2, Mn, Co-F1, Co- F2, Co-F4, Co-F5. Unlike nitrate, which had a too low influence limited to Pb-F4, Cd-F2 to Cd-F4, Mn-F5, Zn-F1 to Zn-F4. In fact, dynamic map of co-inertia significantly separated nitrite and TKN from the other parameters.

Regarding to the phosphorus compounds (inorganic, organic and total), they had some qualitatively identical influences to those of total nitrogen and ammonium on metals as before (Figure 2). Nitrogen and phosphorus compounds influence on the studied metals speciation in sediment were controlled by temperature and salinity (Environment Agency, 2007).

These both physico-chemicals were positively correlated to metal species with high positive factorial values (> 0.5) on map (Figure 3). In addition, inorganic suspended solids had a weaker influence, but predominant on the coarse sands.
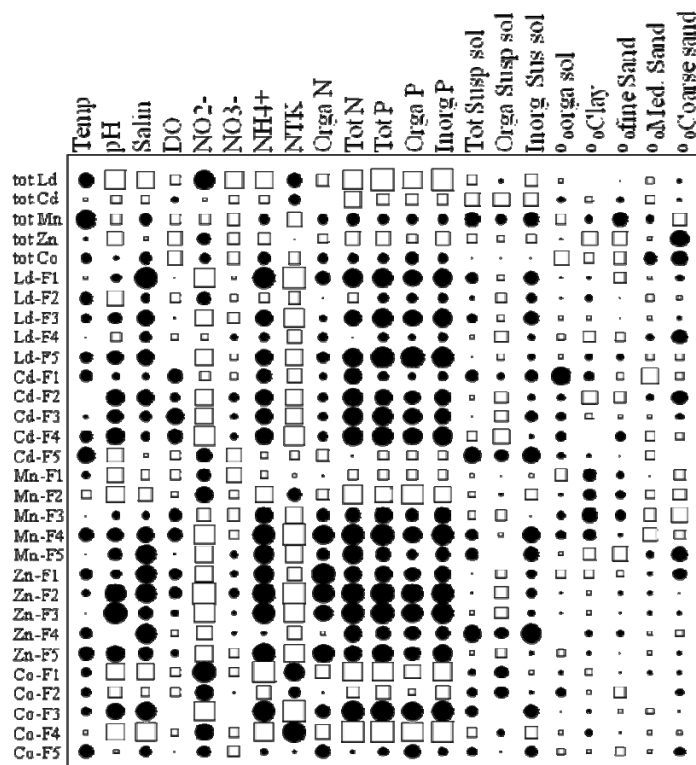
Figure 2: Static seasonal influence of the physico-chemical on the total and specied lead, cadmium, manganese, zinc and cobalt sediments contents in *Aby* lagoon.

●: *Positive co-inertia*

□ : *Negative co-inertia*

Concerning the quantitative aspects of nitrogen and phosphorus compounds influence on the studied metals speciation, it should be noted that their inputs in the basins mainly take place in particulate form, which was heavily dependent on the rivers hydrological and morphological conditions (Salvia-Castellvi and *al*. 2001). But once inside lagoon environment, they were submitted to a high reduction activity (inorganic P/organic P = ~ 90% and predominance of ammonia).

Also, Pb, Cd, Zn, Mn and Co mainly adsorbed to the soil surface (INERIS, 2005, 2006, 2007, ATSDR, 2001) forming complexes with the humic acids. These complexes are unstable because easily leach the heavy metals due to change of pH or redox potential.

This release is particularly related to cobalt for which increased amounts of organic matter decrease its adsorption on sediments, in favor of dissolved cobalt and precipitate or co-precipitate cobalt (ATSDR, ibid.). Dissolved cobalt was then mainly resulted in nitrite and TKN speciation in the sediments in *Aby* lagoon. Just (1995) highlighted that because of adsorption, cobalt did not migrate in solution phase.

These salts of nitrogen were the factors that influenced the heavy metals speciation; especially compounds tend to accumulate on sediment surface (Pb, Cd and total Zn, Co and Co-F1-F4).

But nitrite and TKN competed with ammonia which then formed a chemical bond more stable with the heavy metals, which would not last however, the bonding time in the case of phosphorus and nitrogen. Indeed inorganic phosphorus is final step of oxidation, while nitrites and ammonium (contained among other in TKN) are transitive phases to nitrate and particulate nitrogen. Nitrite increase takes place at the expense of the others. This justified

negative correlation between nitrite, TKN and ammonia, total and organic nitrogen, phosphorus compounds. The respective factorial values were about -1 and 1 (figure 3).
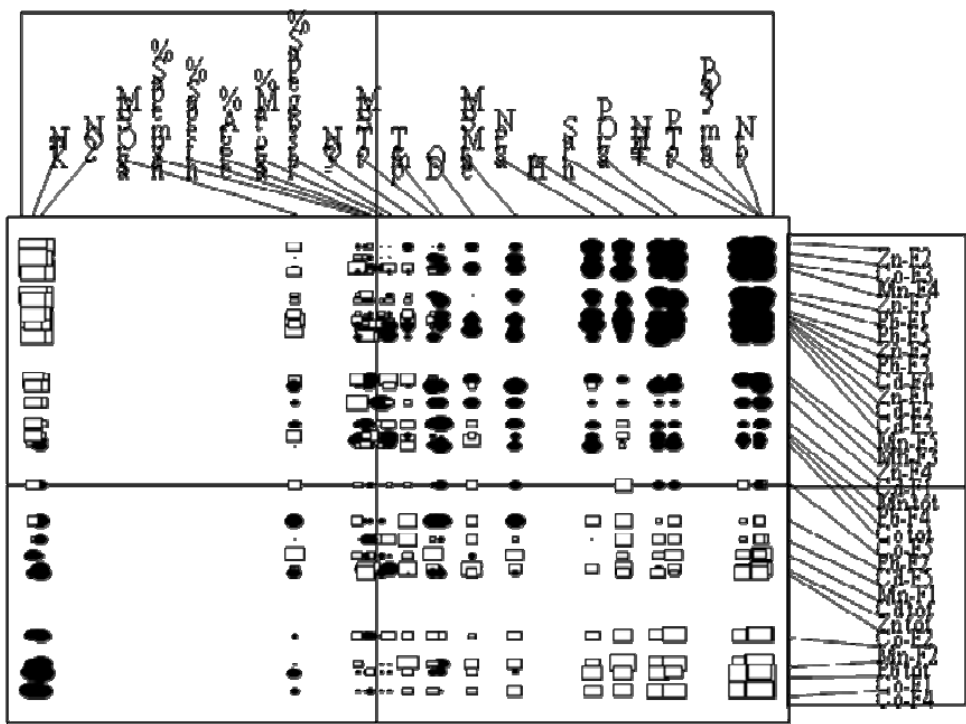

Figure 3: Dynamics of the physic-chemical seasonal induction on the total and specied lead, cadmium, manganese, zinc and cobalt sediments contents in *Aby* lagoon.

Soil pH is a parameter that most influences the absorption, retention and movement of heavy metals in them (De Matos and *al*. 2001). A high pH (> 7) allows a better zinc absorption. Salinity increase causes zinc desorption of the sediments (INERIS, 2006).

Salinity influence on speciation results from Cl ability, associated with other ions, in the heavy metals extraction from sediment. The soluble, mobile and mobilizable fractions extraction used as reactants $CaCl_2$ 0.01 M, $CaCl_2$ 0.05 to 0.05 M EDTA pH 7 (Blanchard, 2000), while total extraction occurs as a result of HCl pH 7 (Meunier and *al*. 2004; Masahiro and Shin-Ichiro, 2007). In fact, pH influence resulted from intervals of changes below unity (7.31 to 8.86) in *Aby* lagoon, but which showed a significant factorial value. The positive pH and salinity factorial values (co-inertia coefficient > 0.5) indicated simultaneous increase in both parameters, especially in areas influenced by ocean and high activities of organic matter degradation. Their increases had antagonistic effects on zinc adsorption, which was found in dissolved form and capable of binding to phosphorus and nitrogen. They subsequently led zinc to residual layer in organic matter speciation. All the zinc species (Zn-F1 to Zn-F5) factorial values with phosphorus and nitrogen were significantly positive and high (north-east of the plan). Salvia-Castellvi and *al*. (2001) found that 60-70% of total phosphorus was residual (unextractable), assigned to inert and organic phosphorus in the *Haute-Sûre* basin sediments. In this study, it was rather inorganic, total and organic phosphorus which showed a greatest impact on zinc speciation in the *Aby* lagoon sediments. Nitrogen influence was evenly exercised through its compounds other than nitrite and TKN.

Organic matter rate hampers cadmium mobility in the soils. Otherwise, it could be trebled when pH increases by one unit in the range 4-8 (Adriano, 1986). Thus, pH varied around neutrality and same set of nutrients promoted cadmium distribution in the different fractions (F1 to F4 north-east of plan). This distribution was dominant on its accretion in the lower fractions of sediment. Cd-F5 had negative factorial value and located in south-east of the plan.

Besides Ld-F2, phosphorus and nitrogen influence on lead speciation also appeared to be favored by salinity effect. Its species (Ld-F1, Ld-F3, Ld-F5) had positive factorial values.

As for manganese, Mn-F1 and Mn-F2 seemed not to be influenced by phosphorus. This was due to manganese binding by chemisorptions to $CaCO_3$ particles of up $MnCO_3$ precipitation in the calcareous soils case (Adriano, 1986). In the precipitation case, oxides, hydroxides and oxyhydroxides precipitate manganese and lead to a new phase that will act as a surface on which other substances may adsorb (ATSDR, 2000). Thus the Mn-F1 and Mn-F2 fractions were continuously submerged, leaving untouched the last three fractions (positive factorial values on map).

CONCLUSION

In Aby lagoon, nitrite and TKN influence were significantly higher on lead, zinc and cobalt mobilization, while promoting Pb, Mn and Co binding to exchangeable and residual fractions. Unlike ammonia, organic and total nitrogen as phosphorus compounds which were less effective in Pb, Cd and Zn mobilization process. Their influences seemed also reduced on Cd and Co speciation in residual; as on Mn and Co binding to exchangeable and the carbonates fractions. In contrast, Pb, Cd and Zn speciation in the five fractions was strongly dependent on these salts. Otherwise, these heavy metals chemical differentiation was pH, salinity and temperature dependent. Finally, the reaction intermediates (nitrite especially) dominance reduced the other nitrogen and phosphorus forms influence on the heavy metals speciation in the sediments.

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