Fractionation, mobility and environmental risk of trace metals in the sediments from N'zi River, Côte d'Ivoire

Abstract

Despite increasing human activities, such as agriculture, little information is available on the status of trace metals contamination in rivers in developing countries including Côte d'Ivoire (West Africa). In this study chemical fractions of Cu, Pb, Zn, and Ni has been studied to identify mobility, sources and evaluated ecological risks of traces metal in sediment of N'zi River using modified BCR sequential extraction procedure. The results showed that all metal were dominated by residual fractions. Labile fractions of Pb accounted for 0.0 – 68% of total contents indicating significant anthropogenic sources for Pb, while for Cu, Ni and Zn results suggesting natural sources. The potential mobility of the metals manifested following order: Ni > Zn > Cu > Pb. Risk assessment code indicated low to medium risk for Pb and low risk for other metals in the sediments.

Keywords: Trace metals, BCR extraction, mobility, availability, risk assessment.

1. Introduction

Environmental pollution by metals is a worldwide problem and is considered to be serious threat to the human and aquatic ecosystem because metals are resistant to biodegradation and persistence nature, toxic and have the ability to be incorporated into food chains **[1 – 9]**. Metals are introduced into the environment through natural phenomena (volcanic eruption, weathering of rocks) and anthropogenic activities such as agriculture, transport, industrialization and urbanization **[10 – 17]**.

In rural areas, agricultural activities, through the massive use of fertilizers and pesticides, represent the main sources of contamination of trace metal elements in aquatic environments **[18 – 22]**.

Once in the aquatic environment, metals can bind to different fraction of sediments and can accumulate in sediments. Sediment act as a reservoir of trace metals and provide information on the state of pollution of the aquatic system and the impact of human activities **[23 – 26]**. When environmental conditions change, sediments-bound metals may be released into water and caused deterioration of water quality and/or accumulation of metals in plants and animals and finally also humans **[10; 27-29]**. Sediment have been used as an important tool to assess the level pollution of aquatic ecosystems.

It has been reported that determining the total concentration of a metal in sediments provides little information regarding its mobility, bioavailability, or toxicity **[13; 30-32]**. Metal speciation in sediments is very important tool as it provides additional information related to potential mobility, bioavailability and chemical nature of a particular element **[23; 27; 33-36]**.

The N'zi River, is the most important left bank tributary of Bandama River located in Agneby-Tiassa, South of Côte d'Ivoire (West Africa) (Fig. 1).

The N'zi River hydrographic basin (3°49' - 5°22' W and 6° - 9°26' N) covers an area of 35,500 km^2, is a sub-basin of Bandama River catchment area which covers an area of 98,500 km^2, or 30 % of the area of Côte d'Ivoire. The N'zi River takes its source at an altitude of 400 m to the East of Ferkéssédougou, stretches over 750 km long and merges with Bandama River upstream of Tiassalé. Four climatic seasons occur in the study areas: a high dry season (December–March), a high rainy season (April–July), a low dry season (August to mid-September), and a low rainy season (mid-September to November) (**Fig. 1**). The average monthly air temperature ranges between 25 and 32 °C **[18]**. This agricultural region is known for its exportation products cultivation such as cocoa, coffee oil palm, rubber, and banana plantain. Moreover, since the 2002 crisis, the South of Côte d'Ivoire has experienced rapid population growth. The rapid demographic growth has been accompanied by an intensification of agricultural, industrial, urban and gold mining activities.

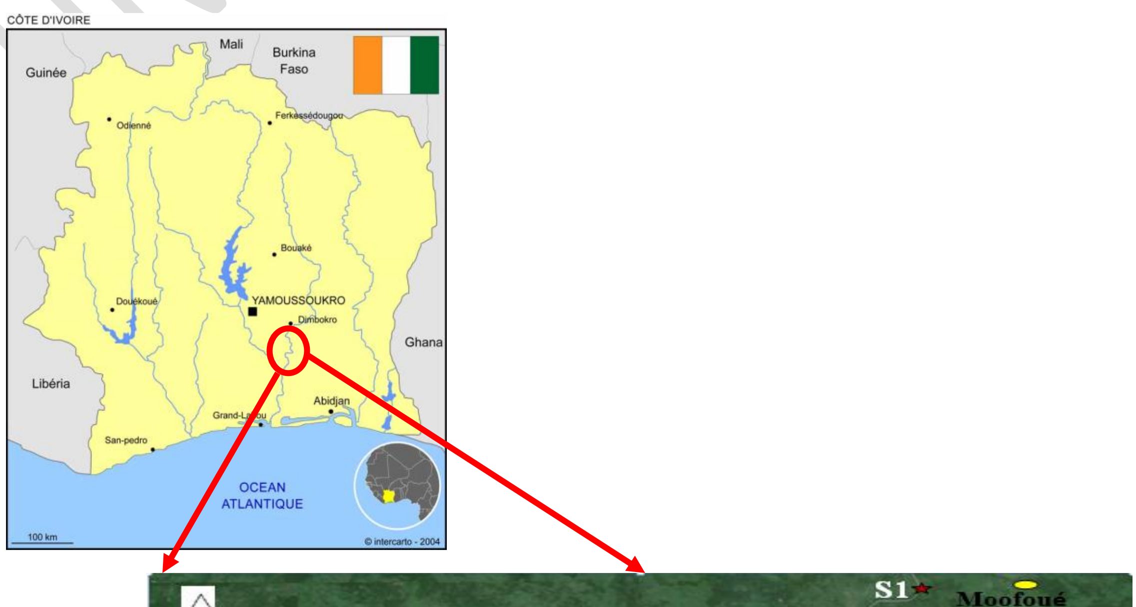

Fig. 1. Map of the study area.

This activities have adversely affected the water quality in the area. It should be noted that the majority of the local population uses untreated water from these rivers for household consumption and bathing.

There is evidence that the concentrations and potential mobility of some metals in the surface sediments from N'zi River adversely impact aquatic organisms and human health.

In this context, we investigated the potential mobility and bioavailability of the metals in various fractions of sediments using BCR protocol, and risk assessment code (RAC) of the metals in sediments. This study would offer useful information pertaining to fractioning of the metals, and assist the environmental control actions for the anthropogenic pollutants in the studied aquatic ecosystem.

2. Material and Methods

2.1. Sampling

Five sites located in rural, forest, domestic, and agricultural zones of the area (**Table 1**), were selected for sampling of sediments in N'zi River during March 2015.

Surface sediment samples were collected using a Vann Veen grab. From each site, a composite samples of four samples were collected. Every composite sample were well mixed and homogenized. Sediment samples were taken at 0-50 cm depth and then immediately transferred into polyethylene bags. Prior to sampling, the polyethylene were washed with 10% HNO_3 acid solution and ringed with distilled water. Sediments samples were transported using ice box to the laboratory and preserved in a refrigerator at 4°C temperature. Sediment samples were dried in a dry and dust-free place at room temperature, ground into fine powder using pestle and mortar before sieving under 63 μm sieve. The samples were then stored in plastic container **[37]**.

Table 1: Geographical location, pH and total organic carbon (TOC) contents of the sediment samples

Station No	Station	Longitude (E)	Latitude (N)	pH	TOC%	Stations details
1	Moofoué	4°44’44.1"	6°07’05.9"	6,83	4,39	residential village, Agriculture
2	Apiamoh	4°45'54.4"	6°06'01.3"	7,12	1,24	Agricultural area, residential village
3	Djibi	4°45'81.2"	6°05'23.6"	8,26	0,64	Luxuriant vegetation
4	N’zianouan	4°49’21.0"	6°00’12.5"	6,94	2,16	Agricultural area, urban area
5	SCB	4°49'56.6"	5°59'42.8"	7,01	1,06	Agricultural activity, residential village

2.2. Analytical Methods

2.2.1. Total metals extraction

The total trace metals were extracted from the sediment samples using an acid digestion mixture of nitric acid HNO_3 concentrated at 65% pure (Panreac, USA) and 37% pure concentrated hydrochloric acid HCl (Scharlau, Spain) at a correspondence of 1/3 (v/v) and with hydrofluoric acid HF concentrated 48%, pure (Merck, Germany) in an open system. A sediment sample (about 0.5 g) was placed in a Teflon crucible and digested in 15 mL HF and 10 mL of a 1:1 (v/v) mixture of HNO_3 and $HClO_4$ on a hot plate up to dryness. After digestion, the final residue was dissolved in 5 mL of 2 mol/L HCl, and the volume made up to 25 mL.

2.2.2. Sequential extraction procedure

In present study a four-step BCR sequential extraction procedure was applied to fractionate the trace metals into four fractions: Exchangeable and bound to Carbonates (F1), which are easily released to the water column; Bound to Fe-Mn oxides (reducible) (F2), which can be released when redox conditions change; Bound to Organic Matter (F3), that represents the metal bound to organic matter and sulfides, which can be released under oxidizing conditions and Residual (F4) is components of the sediment matrix (Fig. 2).

After each successive extraction, samples were centrifuged at 4000 rpm for 20 min to separate the extract from sediments. The concentrations of Cu, Pb, Ni and Zn in the leachates of total extraction and sequential extraction were determined by AAS (Perkin Elmer AAS 3110) in flame mode.

An internal check on the sequential extraction method was performed by comparing the total amount of metal extracted by different reagents using sequential extraction procedure with the results of the total metal concentration **[38]**. The internal check recovery of the sequential extraction procedure was computed by the following equation:

$$Recovery\ (\%) = \frac{C_{ex}+C_{red}+C_{ox}+C_{res}}{C_{total}} \quad (1)$$

Where Cex, Cred, Cox, Cres and Ctotal refer to the metals concentration in exchangeable, reducible, oxidisable, residual and total fractions, respectively. Generally, the recovery are approximately equal to 100%, results shown a good and acceptable agreement between metal levels extracted **[39]**.

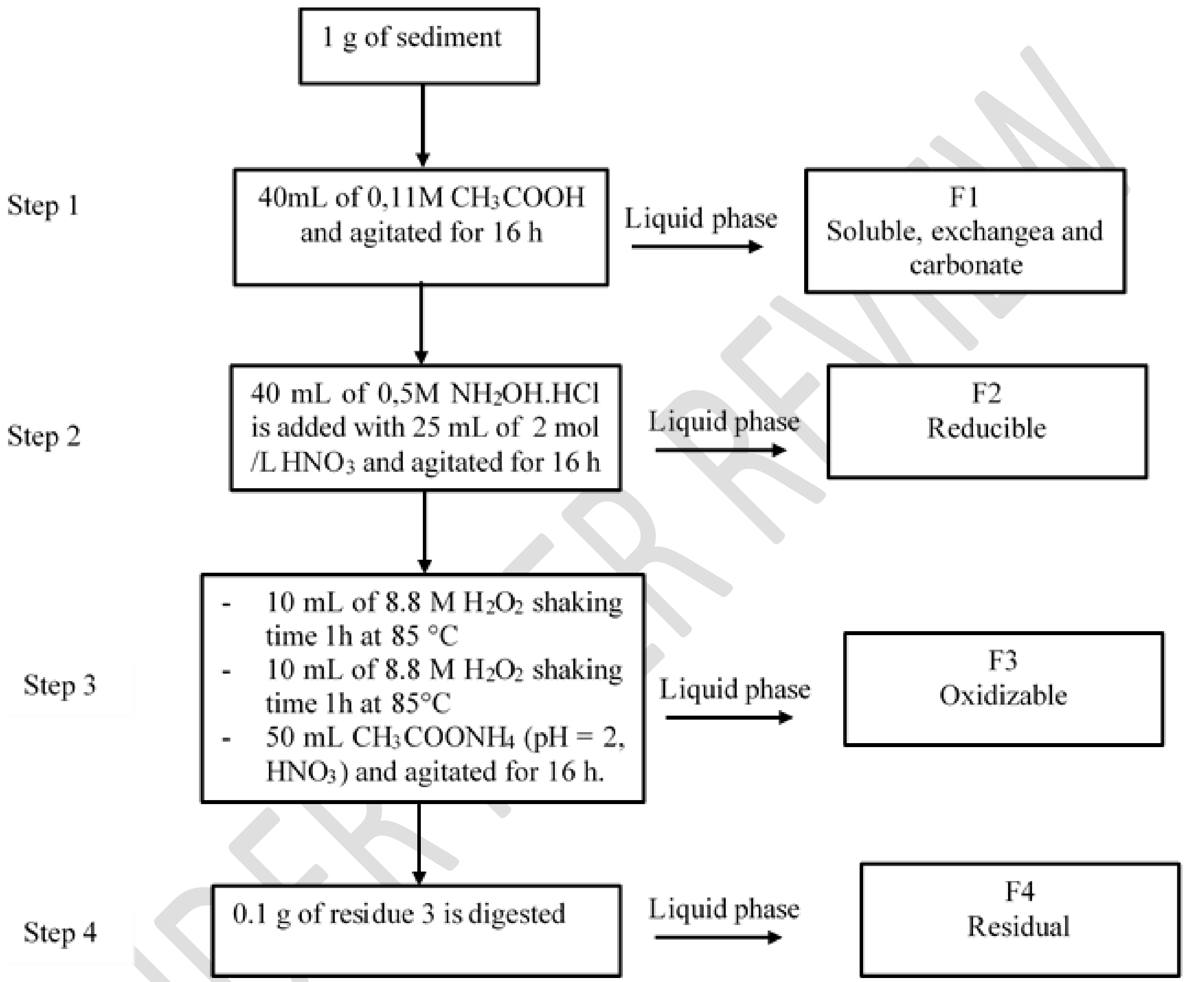

Fig. 2: Flow charts for speciation scheme of sediments.

2.3. Control quality and Statistical analysis

All instruments used were calibrated before use. Tools and work surfaces were carefully cleaned for each sample. Replicate sample were analysed to check precision of the analytical method and instruments. To validate the analytical procedures used, the spike recovery test was conducted on some samples for Cu, Pb, Ni and Zn. Blanks were analysed in each batch of samples throughout the entire analytical procedure. Statistica (version 7) was used to process the data. One way ANOVA (at 5% level of significance) was used to test for significance differences in metal concentrations in water samples. Metals concentrations were also compared to the stipulated world health organization (WHO) **[40]**.

3. Results and Discussion

3.1. Partitioning of trace metals in the sediments

The spatial distributions of metals are illustrated in Figure 3 and Table 2 shown values of trace metal concentration for each step of the BCR sequential extraction procedure.

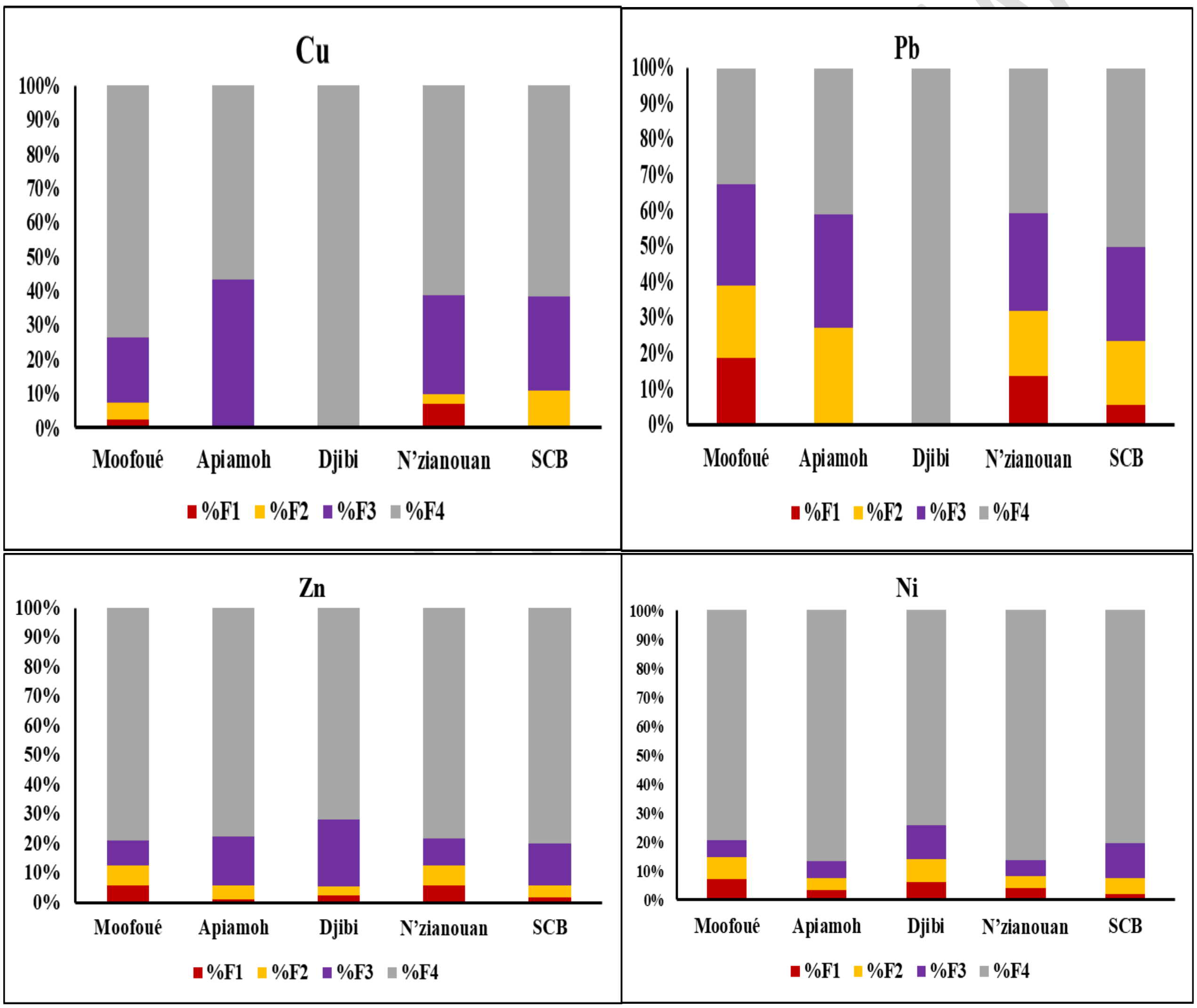

Fig. 3. Distribution of trace metal content in various fractions for all samples.

According to the results, the highest fraction of Cu was obtained in residual fraction (57 – 73 %). This variation corresponded to a concentrations varied from 0.03 µg/g to 28.6 µg/g on a total ranged between 0.05 µg/g and 38.8 µg/g (Table 2). These results suggested that a significant part of the Cu is bound to the crystalline structure of the sediment. The percentage of the fraction (F3) of copper bound to organic matter and sulphides varied between 19 % (Moofoué) and 43 % (Apiamoh). This fraction represented the most important reactive fraction of Cu in sediments. This marked distribution for the organic phase reflect the affinity of copper with organic matter. The affinity of copper with organic matter result in the formation of stable organic complexes, reducing the bioavailability of copper in the water column.

The fraction (F2) of Cu bound to iron and manganese oxides varied between 0.00 % (Apiamoh) and 5.09% (SCB).

The acid-soluble fraction (F1 fraction) corresponding to the fraction exchangeable of Cu bound to carbonates was very low in all the sediments (0.00 - 6.79 %). This range was equivalent to nd –0.95 µg/g out of a total of 0.05 - 38.8 µg/g. The Cu fractioning followed the order:

Moofoué and SCB: Residual fraction (R) > fraction bound to organic matter and sulphides (F3) > fraction bound to oxides (F2) > exchangeable fraction bound to carbonates (F1).

Apiamoh: Residual fraction (R) > fraction bound to organic matter and sulphides (F3) > fraction bound to oxides (F2) = exchangeable fraction bound to carbonates (F1).

N'zianouan: Residual fraction (R) > fraction bound to organic matter and sulphides (F3) > exchangeable fraction bound to carbonates (F1) > fraction bound to oxides (F2).

The results showed that high proportion of Pb was bound to the residual fraction (32.5 – 50.1 %) for the concentrations varying from 0.09 to 0.92 µg/g of total content. The fraction (F3) bound to organic matter was the largest mobile fraction (26.3 – 31.8 %) followed by fraction (F2) bound to iron and manganese oxides (17.1 – 27.2 %) and acid soluble fraction (F2) (0.00 – 18.9 %). The Pb fractioning followed the order: Residual fraction (R) > fraction bound to organic matter and sulphides (F3) > fraction bound to oxides (F2) > exchangeable fraction bound to carbonates (F1).

The residual fraction (F4) mainly controlled the distribution of zinc in all sediments (77.6 – 79.8 %). These proportions corresponded to the concentrations between 0.93 µg/g and 5.09 µg/g and on a total content of Zn in the sediments.

The fraction (F3) bound to organic matter varied between 8.47 and 16.6 %. It represented the largest non-residual fraction in the stations. A change in the environmental conditions would lead to the solubilization of the zinc by the dissolution of these organic materials.

The fraction (F2) of zinc bound to iron and manganese oxides varied from 4.28 % to 6.78 %.

The F1 proportion of Zn concentration ranged from 1.22 to 5.93.

The retention of zinc by the different phases of the sediments followed order: residual fraction (R) > fraction bound to organic matter and sulphides (F3) > fraction bound to oxides (F2) > exchangeable fraction bound to carbonates (F1) for all stations.

Ni was strongly present in the residual fraction (F4) regardless of the sampling site. The content varied from 79.55 to 86.60 %.

The acid soluble fraction (F1) of nickel oscillated between 2.01 and 7.10% which corresponded to concentrations varying between 0.03 µg/g to 0.25 µg /g on total content (1.07 µg/g – 3.12 µg/g). These values was lower than the average value for the earth's crust (18.6 µg/g), implying that Ni content posed no threat to aquatic life.

The fraction bound to iron and manganese oxides (F2) was in the range of 4.08 % to 7.39%.

The fraction linked to organic matter (F3) was between 5.44% and 12.06%. The highest proportion was obtained in SCB station.

The distribution of Ni in the different phases of sediment followed the order:

Moofoué: Residual fraction (R) > fraction bound to oxides (F2) > exchangeable fraction bound to carbonates (F1) > fraction bound to organic matter and sulphides (F3).

Apiamoh and SCB: Residual fraction (R) > fraction bound to organic matter and sulphides (F3) > fraction bound to oxides (F2) > exchangeable fraction bound to carbonates (F1).

N'zianouan: Residual fraction (R) > fraction bound to organic matter and sulphides (F3) > fraction bound to oxides (F2) = exchangeable fraction bound to carbonates (F1).

Table 2: Trace metal concentrations (µg/g, dry weight) in sediments obtained by BCR sequential extraction method and by total extraction

Site	Fraction	Cu	Pb	Ni	Zn
Moofoué	Fraction 1	0.95	0.06	0.25	0.07
	Fraction 2	1.91	0.06	0.26	0.08
	Fraction 3	7.33	0.09	0.21	0.10
	Fraction 4	28.6	0.10	2.80	0.93
	Total (F1+F2+F3+F4)	38.8	0.32	3.52	1.18
	Total	38.8	0.30	3.12	1.16
	Recov %	99.9	106	113	102
Apiamoh	Fraction 1	0	0	0.03	0.08
	Fraction 2	0	0.06	0.04	0.30
	Fraction 3	0.02	0.07	0.06	1.09

	Fraction 4	0.03	0.09	0.84	5.09
	Total (F1+F2+F3+F4)	0.05	0.22	0.97	6.56
	Total	0.05	0.2	1.07	6.08
	Recov %	106	110	90.7	108
Djibi	Fraction 1	0.00	0.00	0.03	0.06
	Fraction 2	0.00	0.00	0.04	0.08
	Fraction 3	0.00	0.00	0.06	0.60
	Fraction 4	0.02	0.06	0.37	1.88
	Total (F1+F2+F3+F4)	0.00	0.00	0.50	2.62
	Total	0.02	0.06	0.52	2.30
	Recov %	100	100	95.6	114
N’zianouan	Fraction 1	0.79	0.07	0.06	0.10
	Fraction 2	0.33	0.09	0.06	0.07
	Fraction 3	3.39	0.14	0.08	0.09
	Fraction 4	7.12	0.21	1.27	0.93
	Total (F1+F2+F3+F4)	11.6	0.51	1.47	1.19
	Total	11.6	0.48	1.43	1.20
	Recov %	100	106	103	99.2
SCB	Fraction 1	0.03	0.11	0.04	0.08
	Fraction 2	1.04	0.32	0.11	0.21
	Fraction 3	2.69	0.48	0.24	0.70
	Fraction 4	6.08	0.92	1.60	3.92
	Total (F1+F2+F3+F4)	9.84	1.83	1.99	4.91
	Total	8.42	1.63	2.18	5.04
	Recov %	117	112	91.3	97.5

3.2. Potential mobility, bioavailability and Source apportionment of trace metals in sediment

Sequential extraction makes it possible to assessment the mobility and bioavailability of trace metals **[10; 38]**. The percentage of labile fraction (%F1 + %F2 + %F3) provides an indication of mobility and bioavailability of trace metal. High percentage of metal in labile fraction indicate that metal are very mobile and bioavailable for human and aquatic biota such as fish. In additional, among the elements associated with the labile phases, those associated with the exchangeable and carbonated fractions are more easily extractable when the environmental conditions such as pH, redox potential or organic matter change. They are therefore more mobile and potentially more available than those linked to the reducible and oxidizable fractions **[41]**.

The results as illustrated in Fig. 4 showed that Ni, Zn and Cu was associated with more than 60% of the residual fraction in the sediments, which suggested that these metals was less mobile and available in the water column. Pb was the most mobile in sediment with a percentage varying between 49.9 and 68.5 %. Taking into account the proportions of each metal in fraction 1, Pb had the greatest potential for mobility and availability. Pb was the most available in the Moofoué station with a percentage of 67.5 % of labile fraction and 18.9 % of acido-soluble fraction.

The decreasing order of availability of metals in the sediments was as follows:

Ni > Zn > Cu > Pb.

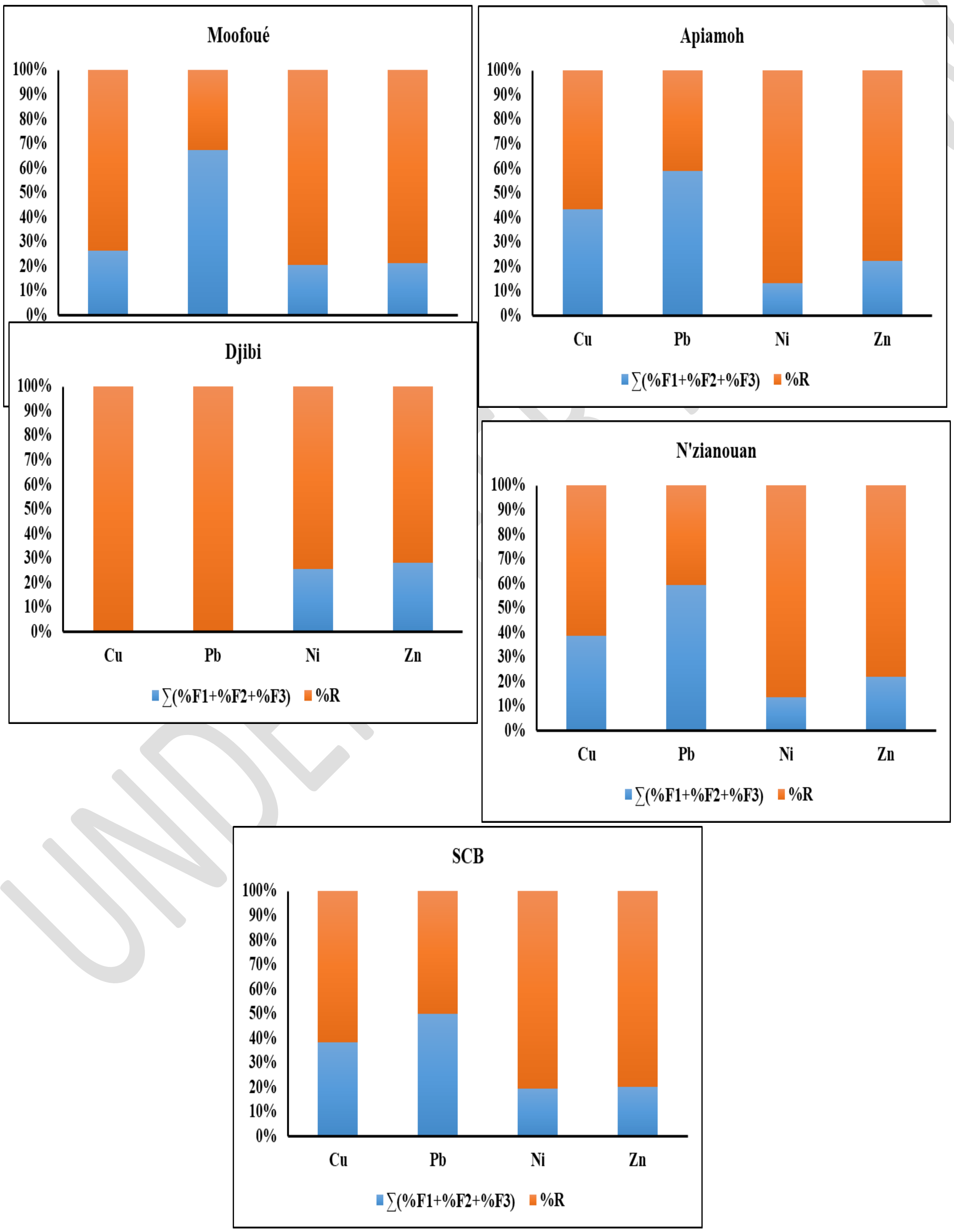

Fig 4: Percentages of labile and residual fraction copper, lead, nickel and zinc in each station.

Chemical fractionation can provide information on sources of trace metals in sediments. High concentrations of metals in the labile fraction indicate that the elements derive mainly from anthropogenic origins. While High concentrations of metals in residual fraction indicate that the metal provide from natural sources. Indeed, labile fraction (carbonates, Fe and Mn oxides, organic matter, and sulfides) is sensitive to variations in environmental conditions **[10; 34; 39]**.

The results showed that Cu, Ni and Zn were basically retained in the residual fraction, suggesting that these metals derived mainly from natural origins and only a low concentrations provided from anthropogenic activities. High percentage of labile fraction for Pb indicated that Pb was mainly from anthropogenic sources. N'zi River is affected by anthropogenic activities which could increase the percentage of labile fractions if the anthropogenic activities intensifies.

3.3. The risk assessment code (RAC)

Labile fraction is the fraction introduced by anthropogenic activities and remain loosely held to sediments as exchangeable fraction (F1) which could be released to aquatic phase and/or could be taken by benthic plants/animals, causing environ-mental toxicity **[27; 33; 38-39]**. The toxicity of metals is bound to their mobility and bioavailability and precisely to their proportions in acid soluble fraction. The toxicity of metal can assessment by applying the criteria of the risk assessment code (RAC).

The results showed that in general, the sediments of all stations could present a low risk of toxicity by the metals Cu, Zn and Ni with RAC values varying between 2 and 10% (**Fig 5**).

For Pb, the RAC results showed no risk in sediments of Apiamoh and Djibi, low risk in sediments of SCB and medium risk in sediments of Moofoué and N'zianouan. The highest RAC values were found at Moofoué (19%) and N'zianouan (14%). These two stations are both agricultural and urban areas. Pb can easily enter the food chain and threaten the aquatic ecosystem in these stations **[33]**. It should also be noted that an intensification of anthropic activities could increase the health risk for humans and aquatic lives.

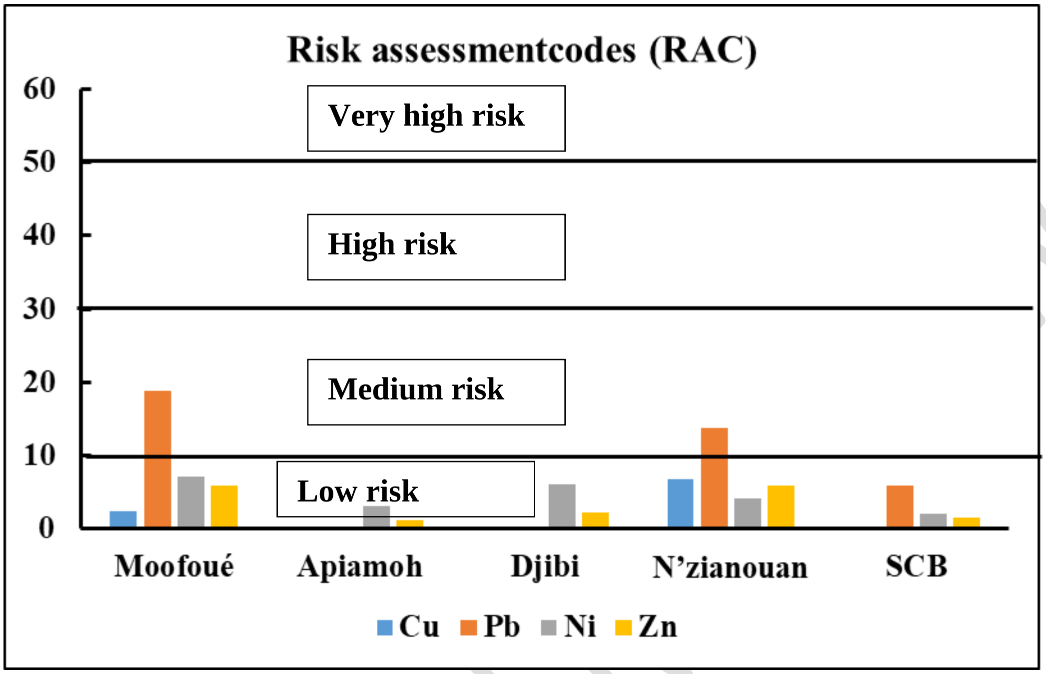

Fig. 5: shows the variations in the toxicity risks of the metals Cu, Pb, Zn and Ni in the sediments of the N'zi River.

3.4. Cluster analysis and Matrix correlation

Cluster analysis was performed to detect the relationship between the studied sampling sites based on the concentration of trace metals in the exchangeable fraction. The obtained dendrogram (Fig. 6) shows that there are two distinct main groups. The first group consists of sampling sites Moofoué, Apiamoh, N'zianouan and SCB. These stations have been located in agricultural and urban areas. The numerous anthropogenic activities in these areas have caused that the trace metals pollution in river sediments be increased and potential risk of metals availability be considerable. The station of Djibi represent the second group which trace metals content in labile fraction is lowly than the first. This station has been located in forest area.

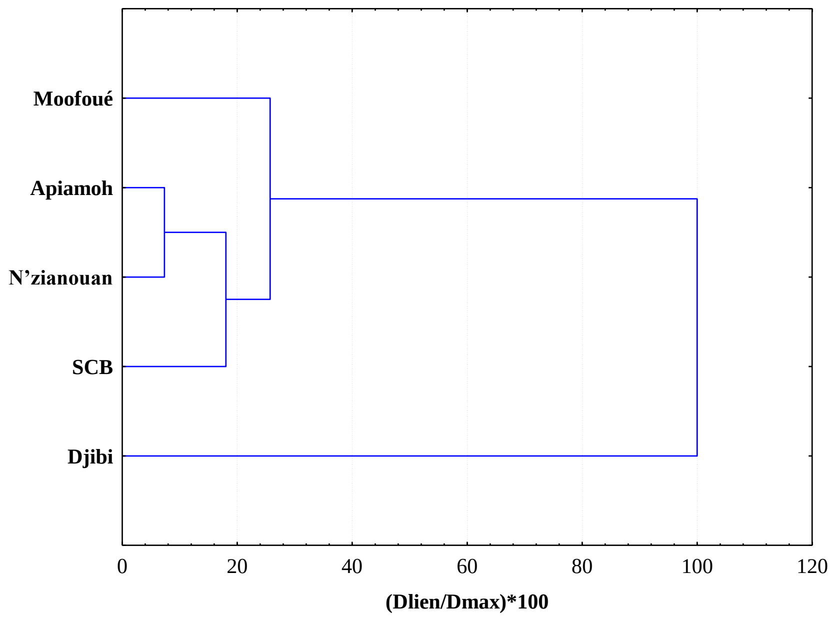

Fig. 6. Dendogram of cluster analysis for the sampling stations based on the metal content in the exchangeable fraction.

Pearson's correlation (PC) matrix for analyzed sediment parameters was calculated to see if some of the parameters interrelated with each trace metal in exchangeable fraction and the results are presented in **Table 3**. Cu and Ni in exchangeable fraction show a high positive correlation with total organic carbon suggesting anthropogenic activities, such as fertilizers and pesticides **[18; 42]** and that the concentrations of these metals in exchangeable fraction are controlled by the same conditions.

Table 3: Correlation between the elements in F1 fraction, pH and TOC%

	F1-Cu	F1-Pb	F1-Ni	F1-Zn	pH	TOC%
F1-Cu	1					
F1-Pb	0.35	1				
F1-Ni	0.78	0.23	1			
F1-Zn	-0.21	0.38	-0.13	1		
pH	-0.56	-0.63	-0.45	-0.7	1	
TOC%	0.9[a]	0.28	0.96[a]	-0.05	-0.6	1

[a] Correlation is significant at the 0.05 level.

4. Conclusions

The results obtained by the BCR sequential extraction method in the present study showed that trace metals were mainly bound to residual fraction. Pb presented higher availability in the labile fraction suggesting high mobility and could pose potential environmental risk. Hence Pb presented risk to aquatic biota particularly because they are very toxic and may accumulate in the overlying flora and fauna. The metals bioavailability showed the following trend: Pb > Cu > Zn > Ni. According to risk assessment code (RAC, %), Cu, Ni and Zn presented low risk and Pb indicated low to medium risk. The highest RAC values were found for Pb (52.3%) at Moofoué.

Statement of Competing Interests

The authors declare that they have no conflict of interest.

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