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Trace Element Distribution and Enrichment in the Stream Sediments of the Lake Togo Watersheds (South of Togo)

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Abstract: To evaluate the level of sediment contamination in watershed of lake Togo (south of Togo), the concentrations of twelve trace elements, TE (As, Sn, Cr, Co, Ni, Cu, Zn, Zr, Cd, Pb, Th, U) are analyzed using inductively coupled plasma-mass spectrometry (ICP-MS) in eighteen stream sediment samples from Zio and Haho rivers draining into the lake Togo and from lake Togo itself. The results obtained allow to characterize each sediment sample by its TE geochemical distribution pattern. Average TE concentration in the finest fractions (< 63 μm) is ranked from the highest to the lowest content: Cr>Ni>Zn>Cu>Co>Pb> Th> Sn>U>As>Cd. The degree of contamination of these stream sediments is evaluated by calculating sediment quality parameters such as enrichment factors (EF), anthropogenic and naturel contribution. Globally, 70% of TE have an EF lower than 1.5, particularly for As, Sn, Co, Cu, Zn, Pb, Th and U. However, 30% of the samples are more contaminated ($1.5 < \text{EF} < 6$), particularly for Ni, Cr, Cd from one sampling point to another. Nevertheless, the anthropogenic contribution could represent only 18% of the total content, 82% originating from natural rock weathering processes. A single chemical extraction by EDTA allows to assess the non-residual (labile) fractions for Zio and Haho river sediments. For Co, Cu, Cd and Pb, the EDTA extracted fractions represent respectively 38%, 32%, 25% and 24% of the total concentration. The EF values are subjected to multivariate statistical analysis in order to evaluate the origins of TE in the study area. Most of TE are controlled by clay, oxi-hydroxide minerals and organic matter.

Key words: Trace metals, stream sediments, enrichment factor, labile fraction, natural and anthropogenic contributions.

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1. Introduction

Trace element (TE) are natural constituents of stream sediments, whose concentrations depend on different factors such as lithology, geomorphology and structural setting of the catchment area. It also depends on the climate, which controls the rate of weathering, hydrologic characteristics, vegetation type and density (Salomons and Förstner 1984). These elements can also be introduced into the river channels by anthropogenic effluents, which are the products of human activities, like for instance domestic, industrial and agricultural wastewaters, fossil fuel combustion and atmospheric pollutant deposition (Mantei and Foster 1991, Benamar *et al.*, 1999). Most of the metals released into aquatic systems are generally bound to particulate matter, which eventually settles and becomes incorporated into sediment. Sediment acts as a potential scavenger and after becomes a source of contamination in an aquatic system. This is affecting the water quality, and therefore is bring up the question of the effects of human activities in the pollution of lakes (Salomons and Forstner, 1984) and rivers (Helios-Rybicka, 1992). In fact, metals are not permanently stored in sediments, they could be released as a response to the environmental condition changes (James, 1978; Wen and Allen, 1999). Different factors, such as pH, clay fractions, iron and manganese oxides, organic matter etc. can influence the sorption of trace elements onto the particles (Serpaud *et al.*, 1994; Alloway and Ayres 1997; USEPA, 2005).

Aquatic ecosystems in farming areas like the Lake Togo Basin are subjected to disturbance of trace elements due to the use of fertilizers and pesticides. Indeed, farming activities like for example the use of the mineral and organic fertilizers (mainly phosphates), which are added to soil to improve plant growth and yield, add a considerable amounts of trace metals into the soils, depending on the rates and types of fertilizers applied. The streams of Lake Togo basin contain a huge amount of nutrients from anthropogenic wastes including domestic wastes, non-rational use of fertilizers, which are in turn leached to the waters of lagoon areas whose banks are already heavily polluted (Bruce *et al.*, 2015). Beside these inputs, the outlets of the Zio and Haho rivers are confronted with a permanent contamination in trace elements from the sea, coming from Aneho and the mining of trace metal rich phosphorite in Kpogame and Hahotoe, located in the northern side of the lake. The pollutants come from industrial effluents and phosphate washing residues coming from the South of the lagoon system (Gnandi and Tobschall, 1999; Gnandi, 2002).

The work in this paper focuses on the pollution status and distribution of trace metals in the suspended matters and streambed sediments of Zio and Haho rivers, which are the main rivers (85% of the total water supply) draining into the Lake Togo. To evaluate the ecological risk of trace metal in the environment, it is

today, widely admitted that determination of their total concentration is not sufficient. Chemical speciation, distribution, partitioning of trace metals between dissolved phases, suspended particulate matters and bottom sediments, are essential to better understand their availability and potential ecotoxicity (Förstner, 1993; N'Guessan *et al.*, 2009). Unfortunately, for river sediments in Togo, little information is available for these processes and the controlling parameters. Then, the objectives of this study are to:

- Determine the level of trace metal contamination of Zio and Haho river sediments and to evaluate the enrichment factor (EF).
- Determine the respective contribution of anthropogenic and natural sources to the total concentration.
- Evaluate the non-residual (labile) fractions for each ET using an EDTA chemical extraction;

2. Materials and Methods

2.1 Study Area

The Lake Togo watershed (Figure 1) covers an area of 8000 km² (14% of the country land area), with approximately 50% of the Togolese population against 20% living in the capital Lome and it has a complex coastal lagoon system and a fragile marine environment. It contains on one hand, perennial surface water resources but limited and highly variable and the other hand abundant (coastal sedimentary) or limited (base) groundwater resources. Located in southern Togo, the watershed of Lake Togo is drained by a complex hydrosystem consisting of the Zio, Haho and Boko rivers and the lagoon system which is located in a depression of the coastal sedimentary basin. The entire lagoon system communicates with the sea through the Aneho channel opening portion, which has been opened continuously since 1989 because of the coastal erosion. Except for the direct runoff of the banks, the Lake Togo itself, is fed by its two major tributaries, the Haho and the Zio rivers. These two rivers basins drain on 85% of their surface, ferralitic and ferruginous soils coming from the alteration of the crystalline basement, where dominate gneisses and migmatites accompanied to the north-west by quartzite, amphibolite and marble dolomitic as well as of numerous micaschists (Millet 1986). The climate is subtropical, warm and humid with an annual average rainfall which varies between 800 and 1000 mm. Four climatic seasons can be observed : two dry seasons (from December to March and from August to September) and two rainy seasons (from April to July and from October to November). The average air temperature varies between 24°C and 29°C. The area has been continuously used to grow corn, beans, cassava, rice, yam, sugar cane, cotton and coffee, cocoa being grown in upstream. Following anthropic pressures, protected forests have been turned into farms. All these

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environmental characteristics make the Lake Togo basin area vulnerable to surface runoff and physical erosion processes, which might contribute to supply rivers with pollutions.

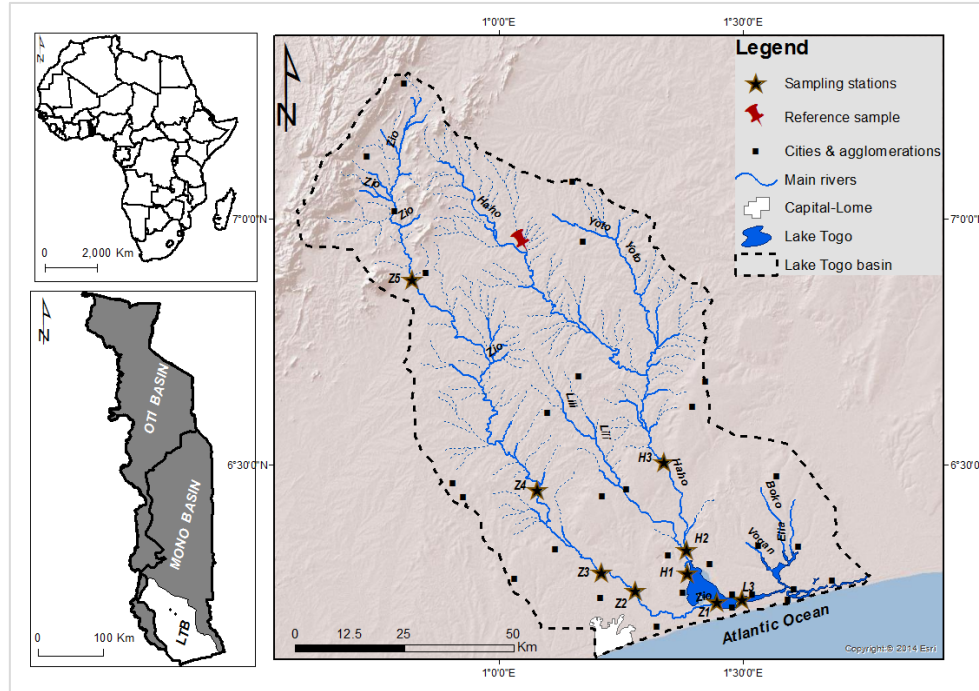


Figure 1 : Map of the study area, the Lake Togo and its drainage basin, and sampling sites in the lake and on the two main rivers, Zio and Haho, flowing into the Lake Togo.

2.2 Sampling and Pre-treatment of the Samples

Sediments from the bottom of the stream were collected from nine different sampling points (Figure 1), in February (low flows) and October (high flows) 2015. Sediment samples are placed in plastic bags and registered. Samples were collected in the first centimeters of the bottom sediments using plastic tube of 1000 ml then, they were air-dried in laboratory for two weeks. After the two weeks, samples are carefully homogenized in an agate mortar, quartered, and separated by sieving into four fractions ($< 63 \mu\text{m}$; $63 \mu\text{m}$ - $200\mu\text{m}$; $200 \mu\text{m}$ - 2mm ; $> 2\text{mm}$). A micro-granulometry analysis is then performed with a Horiba LA 950 laser micro-granulometry at EcoLab Laboratory, Toulouse France.

2.3 Chemical Treatments and Analysis

Mineralization is performed on the fine fraction (<63 μm) of sediments because trace elements are known to be preferentially associated to fine fractions (Probst et al., 1999). Alkaline fusion has been selected as the digestion method for the determination of the total concentration of trace and major elements by ICP-MS at the SARM (Service d'Analyse des Roches et des Minéraux) in CRPG-Nancy (Carignan et al., 2001; Garzanti et al., 2010; Loustau Cazalet, 2012). To find the percentage of carbon and nitrogen in sediments, experiments were running using the Thermo Fisher NA 2100 Protein elemental analyzer at EcoLab. This analyzer is of gas chromatographic (GC) type with TCD (thermal conductivity or cathetometer) detector which allows the simultaneous determination of carbon and nitrogen.

The chemical extraction method with Ethylene Diamine Tetra Acetic Acid (EDTA) is selected to evaluate the labile fraction. One gram of dried sediment was leached with 10 mL of extract solution 0.05 mol.L^{-1} EDTA (Chao, 1984; Sahuquillo et al., 2003, Leleyter et al., 2005), shaken for 1h. The resulting mixture is filtered at $0.22 \mu\text{m}$ and the filtrate is analyzed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) respectively at the geochemical platforms of EcoLab and OMP Toulouse.

2.4 Enrichment Level Assessment

Trace elements in stream bottom sediments come mainly from soil/bedrock weathering and anthropogenic sources. To evaluate the level of contamination in the environment, the enrichment factor (EF) and the TE anthropogenic contribution in the stream sediments are evaluated by comparing their average abundance in reference materials, such as the widely used “shale PAAS” (Harikumar et al., 2009, Karageorgis and Hatzianestis 2003) or “a local uncontaminated material” (N’Guessan et al., 2009, Roussiez et al., 2005). The choice of a reference material is thus not universal and depends on geological and physicochemical characteristics of the study area (Reimann and De Caritat, 2005). In our case study, Post Archean Australian Shales (PAAS) of Taylor and McLennan (1985) and the concentrations of one unpolluted Creek sediment sample from Haho (Figure 1 – reference material) were respectively used as a reference material for comparison purposes in the samples of Zio and Haho. Concerning the reference element, some authors have tried to select the most appropriate element by using some statistics or sequential extraction methods (Loring, 1991; Summer et al., 1996; Tam and Yao, 1998; Aloupi and Angelidis, 2001; Liu et al., 2003; Roussiez et al., 2005). In our case study, scandium (Sc) was chosen as the normalizing element for the determination of the EF because of its attributes of high immobility in an oxidizing surface environment, low occurrence variability and frequent usage as reference element

(Hernandez et al., 2003; Hissler and Probst, 2006). Moreover, Sc presents a better correlation with the majority of the studied trace elements than Cs, Al and Fe.

The following equation was applied to calculate EF and the % of anthropogenic contribution (AC), taking Sc as a reference element :

$$\mathbf{EF} = ([\mathbf{X}]/[\mathbf{Sc}])_{\text{sample}} / ([\mathbf{X}]/[\mathbf{Sc}])_{\text{ref mat}} \quad \text{Equation 1}$$

$$\% \mathbf{AC} = ([\mathbf{X}]_{\text{sed}} - [\mathbf{Sc}]_{\text{sed}} * [\mathbf{X}/\mathbf{Sc}]_{\text{ref mat}}) / [\mathbf{X}]_{\text{sed}} * 100 \quad \text{Equation 2}$$

Where $([\mathbf{X}]/[\mathbf{Sc}])_{\text{sample}}$ is the ratio of concentration of the considered element X to that of Sc in the stream sediment sample; $([\mathbf{X}]/[\mathbf{Sc}])_{\text{ref mat}}$ is the same ratio in the reference material.

Five degrees of contamination are commonly defined according to EF values (Sutherland, 2000) : EF < 2 deficiency to low enrichment; 2 < EF < 5 moderate enrichment; 5 < EF < 20 significant enrichment; 20 < EF < 40 very high enrichment; EF > 40 extremely high enrichment.

TE are usually included in two large sets of geochemical phases. The residual phase (crystalline structure of the minerals) of the particles, where the elements are considered inert, released in the very long term by the processes of alteration, and the non-residual phase or labile fractions where the elements can interact with their environment because they are potentially available for the environment and living organisms. The non-residual (NR) concentration was determined by single chemical extraction with EDTA. The percentage of this fraction is calculated for a given element X as follows:

$$\% \mathbf{NR} = ([\mathbf{X}]_{\text{extraction}}) / ([\mathbf{X}]_{\text{total}}) * 100 \quad \text{Equation 3}$$

The residual fraction results from the difference between the total sample and the labile fractions (NR).

3. Results and Discussions

3.1 Physical Characteristics of Sediments

TE contamination in sediments is often related to the distribution of particle sizes. In streams, clay fraction, colloidal oxides and some insoluble organic compounds that are characterized by high electrically-charged surface areas have the high capacity to adsorb and to co-precipitate soluble TE (Probst et al., 1999). TE associated to abundant clays and silts travel long distances adsorbed onto suspended sediments. The investigated sediments are very fine in general and the less than 63 μm fraction represents on average 90% of the bulk sediment. The distribution patterns of the relevant fractions that compose the sieved sediments are illustrated in Figure 2 for the different sediment samples. Except for Z4 and Z5, the sediment samples are principally composed by clay (<2μm) and silt particles (2-63μm), which represent

favorable conditions for TE adsorption. Indeed, the grading distribution of sediments shows globally a variation from 34% to 94% of clays and silts.

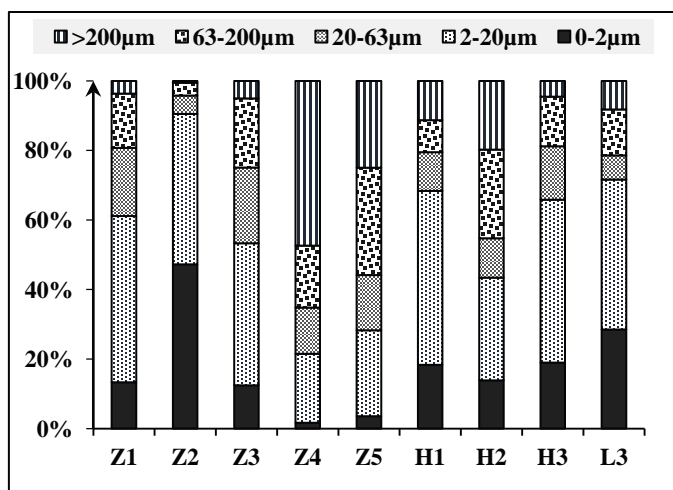


Figure 2 : Abundances (% of bulk sediment) of the different granulometric fractions in the stream sediments: Z1 to Z5 for the Zio, H1 to H3 for Haho and L3 for Lake Togo.

Contrary to the sediment samples of Z4 and Z5 where the sand dominate with respectively 65 % and 56 % of the total sediment, silt is the major granulometric fraction with up from 33% to 67%. The highest proportions of silts are observed in the mouths of rivers Zio (Z1: silt = 67%; clay = 13%) and Haho (H1: silt = 61%; clay=18%) with the lake Togo. The percentage of clay is below 20 % in the samples of rivers, except for station Z2 (47%) and for the lake (L3 = 28%). The reactivity of the sediment towards the processes of surface being bound to the total specific surface area of the particles (Salomons and Förstner, 1980; Probst et al., 1999), which is inversely proportional to the average diameter of the particles; brings us to say that the TE contents in our sampled sediments will be higher in the stations where the silt and clay fractions are dominating.

3.2 Geochemistry of Major and Trace Elements

3.2.1 Average Concentrations

Concerning major elements, the results of sediment chemical composition on the Table 1 shows that among oxides, silica, aluminum, iron and manganese are more concentrated in river sediments as well as in lake ones. These high contents are due to the erosion of the ferruginous soil materials recovering the basin and the sub-sequent sedimentation in the rivers and in the lake. The concentrations of major cations

(Ca, Mg, Na, K) are very weakly represented in the whole of the pond (3 % - 9 %). For TE analyses in our basin, Cd, As, Sn and U present the lowest mean concentrations ($0.06 \mu\text{g.g}^{-1}$ - $2.53 \mu\text{g.g}^{-1}$) while the highest contents are for Zr (188.8 - $1285 \mu\text{g.g}^{-1}$) follow by Cr (143.70 - 280.32) and Ni ($42.73 \mu\text{g.g}^{-1}$ - $280.32 \mu\text{g.g}^{-1}$). For other elements, concentrations vary between $8.53 \mu\text{g.g}^{-1}$ (Th) and $105.20 \mu\text{g.g}^{-1}$ (Zn). As a whole, the order of TE abundance is $\text{Zr} > \text{Cr} > \text{Ni} > \text{Zn} > \text{Cu} > \text{Co} > \text{Pb} > \text{Th} > \text{Sn} > \text{U} > \text{As} > \text{Cd}$. By comparing the sum of the average TE concentrations, we notice that the fluvial sediments of the Haho basin are more concentrated in the Haho river ($\Sigma\text{TE} = 1258 \mu\text{g.g}^{-1}$) than in the creek ($921 \mu\text{g.g}^{-1}$) considered as the local reference sediment, but they are also more concentrated than in the Zio ($\Sigma\text{TE} = 1093 \mu\text{g.g}^{-1}$) and in the Lake Togo ($\Sigma\text{TE} = 1081 \mu\text{g.g}^{-1}$). The high contents in the Haho river might result from the geographic localization of this river. Indeed, the TE concentration in the reference creek sediment, situated upstream and considered as non-polluted sediment, is 1.4 times (but 1.8 for Sn, 3 for Cr and 3.7 for Ni) less concentrated than sediments of the main course of the Haho river which is situated in the area of phosphate exploitation and which is more exposed to contamination by this industrial mining activity. These high contents in the Haho can also result from the agriculture which uses fertilizers and pesticides. In addition, most of the mean TE contents in studied sediments are higher than the corresponding literature values of the reference materials (UCC and PAAS from Taylor and McLennan, 1985)), except for Cu, Zn, Pb, Th, U. Also, the contents of TE such as Cr, Ni, Cu and Pb seems more important in sediments of Haho and Lake Togo analyzed by Gnandi (2002) while the values of the major elements are more important in this present study.

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Table 1 : Concentrations of major (%) and trace elements ($\mu\text{g.g}^{-1}$) in the bottom sediments of Zio (n=9) and Haho (n=6) rivers and in the creek taken as a reference, in the Lake Togo (n=2), compared with UCC and PAAS (Taylor and MacLennan, 1985); Gnandi's results in 2002 for Haho (n=13) and Lake Togo (n=21) sediments.

	Zio stream sed.			Haho stream sed.			Lake sed.	Creek sed.	UCC	PAAS	Gnandi, 2002		
	Min	Max	Mean	Min	Max	Mean	Mean	Mean	Mean	Mean	Mean	Mean	Mean
												Lake	Haho
Major elements (%)													
SiO₂	45.67	70.29	57.72	52.16	64.11	58.23	48.96	59.22	28.80	62.80	-	-	
Al₂O₃	11.23	21.37	15.55	13.28	16.18	14.66	14.52	13.47	7.96	18.90	8.53	15.96	
Fe₂O₃	4.79	8.03	6.74	5.77	8.17	7.06	9.15	5.38	4.32	6.50	13.85	7.02	
MnO	0.03	0.25	0.11	0.12	0.24	0.17	0.23	0.20	0.07	0.11	1.30	0.11	
MgO	0.58	1.82	1.10	1.35	1.77	1.59	1.81	0.99	2.20	2.20	0.30	1.26	
CaO	0.56	2.79	1.32	0.95	1.67	1.29	2.49	1.81	3.85	1.30	1.66	1.23	
Na₂O	0.29	1.72	1.04	0.75	1.16	0.99	1.66	0.79	2.36	1.20	0.83	0.67	
K₂O	0.59	1.02	0.82	1.12	1.38	1.26	0.95	1.73	2.14	3.70	1.47	0.70	
TiO₂	0.98	2.89	1.53	1.18	1.26	1.23	1.26	1.12	0.40	1.00	1.21	1.41	
P₂O₅	0.10	0.18	0.14	0.10	0.21	0.16	0.31	0.18	0.08	0.16	0.12	0.20	
Traces elements ($\mu\text{g.g}^{-1}$)													
As	1.15	4.23	2.06	1.69	2.64	2.05	3.50	1.60	1.50	-			
Sn	1.97	9.02	4.23	2.49	6.75	3.96	9.35	2.20	2.70	4.00			
Cr	143.70	277.62	180.53	184.30	280.32	228.44	145.22	75.26	35.00	110.00	177	232	
Co	16.28	33.22	23.19	26.44	36.45	31.00	25.98	21.00	10.00	23.00			
Ni	42.73	110.72	78.05	100.20	170.69	126.76	93.51	34.40	20.00	55.00	114	142	
Cu	22.09	62.05	39.55	27.36	40.31	34.09	32.70	35.81	25.00	50.00	42	42	
Zn	49.77	105.20	76.80	62.54	77.64	70.19	79.23	58.97	71.00	85.00	55	49	
Zr	188.8	1285.0	658.2	427.1	1079.0	725.4	659.0	650.6	190	210	126	175	
Cd	0.06	0.73	0.30	0.14	0.87	0.43	0.57	0.14	0.09	-	0,02	0,06	
Pb	13.52	25.36	17.40	16.16	24.38	19.66	19.00	21.28	20.00	20.00	69	56	
Th	8.53	11.61	10.25	12.13	15.90	13.87	10.93	16.65	10.70	14.60			
U	2.07	3.01	2.46	2.53	3.48	3.00	2.94	3.49	2.80	3.10			

3.2.2 *Spatial and Temporal Distribution Patterns*

The distribution graphs plotted for each TE in the different sediments of the study area are presented in Figure 3. Excepted As, Sn and Cd, the variation of TE concentrations between the two campaigns of sampling (February and October) is low for each station. In addition, TE study are rather widely distributed in the area. The concentrations of TE, except Cd and Sn, are generally slightly higher during the period of the high-water (October) than in low-water (February). Indeed, the streamflow being very low during August and September 2015, it favors on one hand, the deposit of fine particles to supply bottom sediments, and on the other hand, the adsorption of TE in solution onto particles, so pulling higher concentrations of TE in thorough sediments. However, the insignificant duration between these deposits and the beginning of the high-water of October which also corresponds to the small rainy season with the increase of the flow favors the re-suspension and the transfer of TE associated to the finest particles towards the downstream. This could be at the origin of these higher TE concentrations in the sediments in October 2015.

For spatial distribution, TE concentrations vary slightly from one station to another. Co shows decrease of its contents from upstream to downstream of both river basins during the two periods of sampling, except Z1. Like for Cr, Ni, Cu and Zn present a decrease of their contents from stations Z5 to Z3, then an increase from Z3 to Z1, with a peak at Z2. On the other hand, the spatial evolution observed of TE contents in the Haho sediments (from H3 to H1) is less variable. The concentrations of Cu, Zn, Pb, As and Sn are higher at downstream stations like Z1, Z2 and Z3 however Ni, Co and Cr are higher at the upstream station Z5. The increase concentration of Cd observed at H2, H3, Z3, Z4 and Z3 would result from the streaming of farmlands especially rice perimeters of Mission-Tove and Akodessewa which are localized upstream to Z3 and H2. For Sn and As, their concentrations are higher in the lake (station L3) than at the mouth of the rivers (stations Z1 and H1) because of the intrusion of the sea water during the low water period (Julien *et al.*, 2017). Indeed, the oceanic coast of Togo is contaminated by the discharges of effluents stemming from the washing activity of phosphate on the coast.

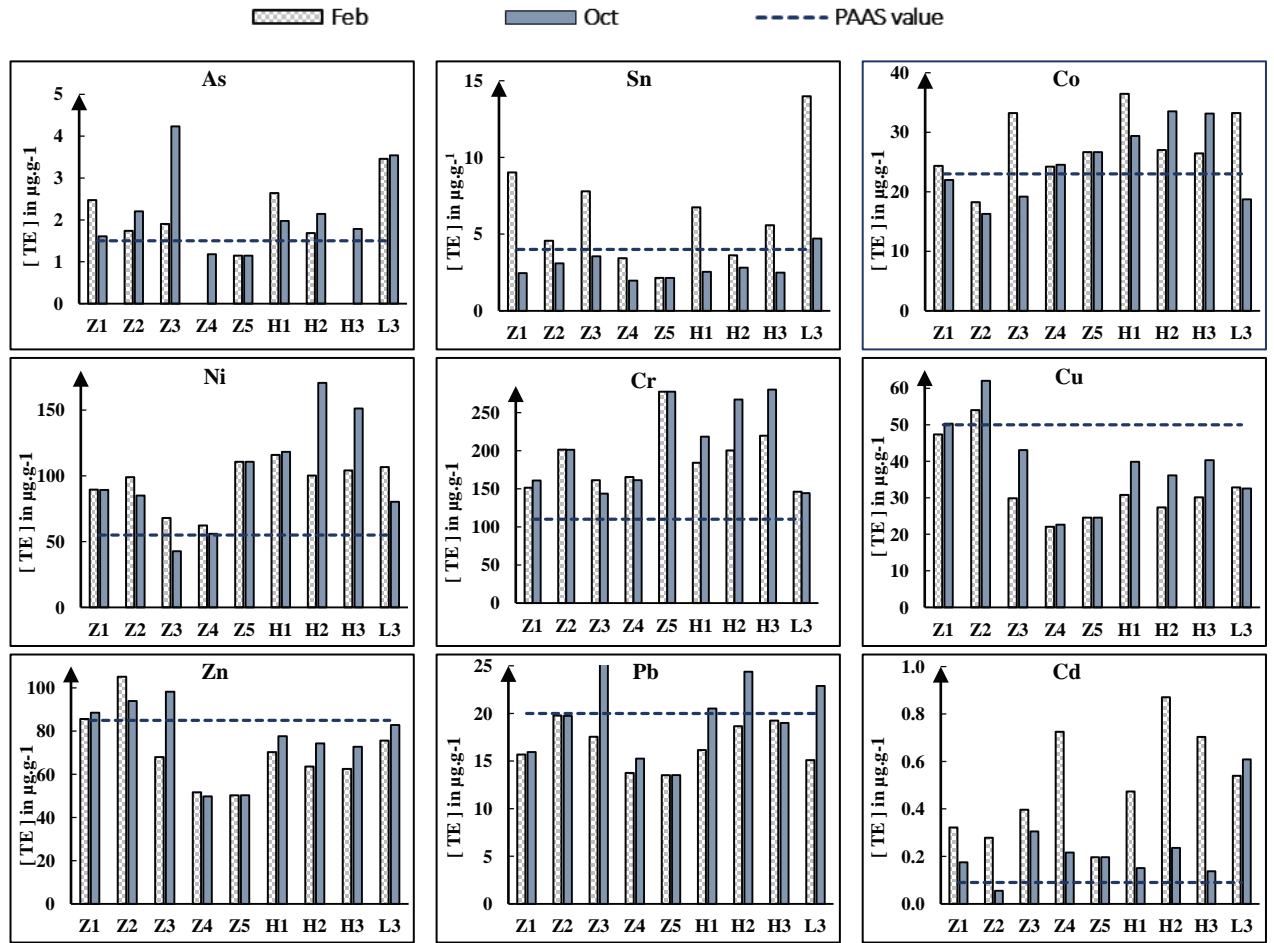


Figure 3 : Spatial and temporal distributions of trace element contents in the finest fractions (<63 μm) of the bottom sediments: Z1 to Z5 for Zio river, H1 to H3 for Haho river and L3 for Lake Togo.

3.2.3 Enrichment Factor

The Enrichment Factor (EF) is a potent tool for TE contamination evaluation. Elements which are naturally derived have an EF value of nearly unity, while elements of anthropogenic origin have EF values of several orders of magnitude. It is generally accepted that $EF < 2$ reflects natural variability of the regional geochemical background and of the mineralogical composition of the bedrocks (Sutherland, 2000; Hernandez *et al.*, 2003). But using the geochemical composition of a local pristine sediment as a reference in EF calculation allows to decrease the EF threshold for natural geochemical background to 1.5 (Soto-Jimenez and Paez-Osuna, 2001; Roussiez *et al.*, 2005).

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As seen in Figure 4, the ratio between TE concentration in sediment and TE content in UCC and PAAS (Taylor and McLennan, 1985), indicates that sediment concentrations always present a significant anomaly for As, Cr, Ni, Zr and Cd elements. On the opposite, normalisation to local pristine sediment (Creek) indicates less anomaly, especially for Zr. The discrimination of Zr using the Creek confirms that its enrichment in the bed sediment of Zio and Haho basins is mainly due to the geological substratum and to the lateritic soils which have been developed and enriched in Zr by chemical weathering processes (Sow *et al.*, 2018). The lateritization of soil profile resulted in an intense chemical unbalance between the granitic parent rock and the weathered product which consists largely of clayey material containing quartz (Boeglin and Probst, 1998) and resistant minerals enriched in Zr (Horbe and Da Costa, 1999).

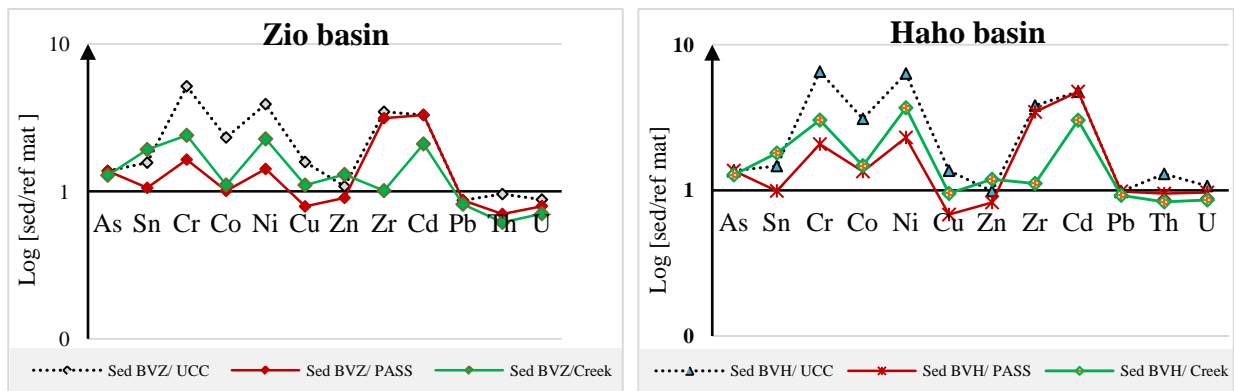


Figure 4: Normalization of TE in Zio and Haho stream bed sediments with the local pristine material (Sed/Creek), UCC (Sed/UCC) and PAAS (Sed/PAAS). Data for PAAS and UCC are from Taylor and McLennan, 1985.

Concerning EF values, the average results obtained in figure 5 show that among the twelve TE analyzed, only Zr and Cd present a moderate enrichment with the PAAS normalization for Haho and Zio sediments. To these, must be added As and Sn for lakeside sediments with PAAS and Creek normalization. In contrast, normalization with the Creek sediment (natural background level of 1.5), Cr, Ni, Cd and Sn present moderate enrichments for sediments of Haho and low enrichments for Zio sediments. Based on Sutherland (2000) classification, the foregoing TE fall in the range of background concentration in a large proportion of the study area. The abundance of those TE from the lithogenic sources tends to return them less sensitive to the human disturbances.

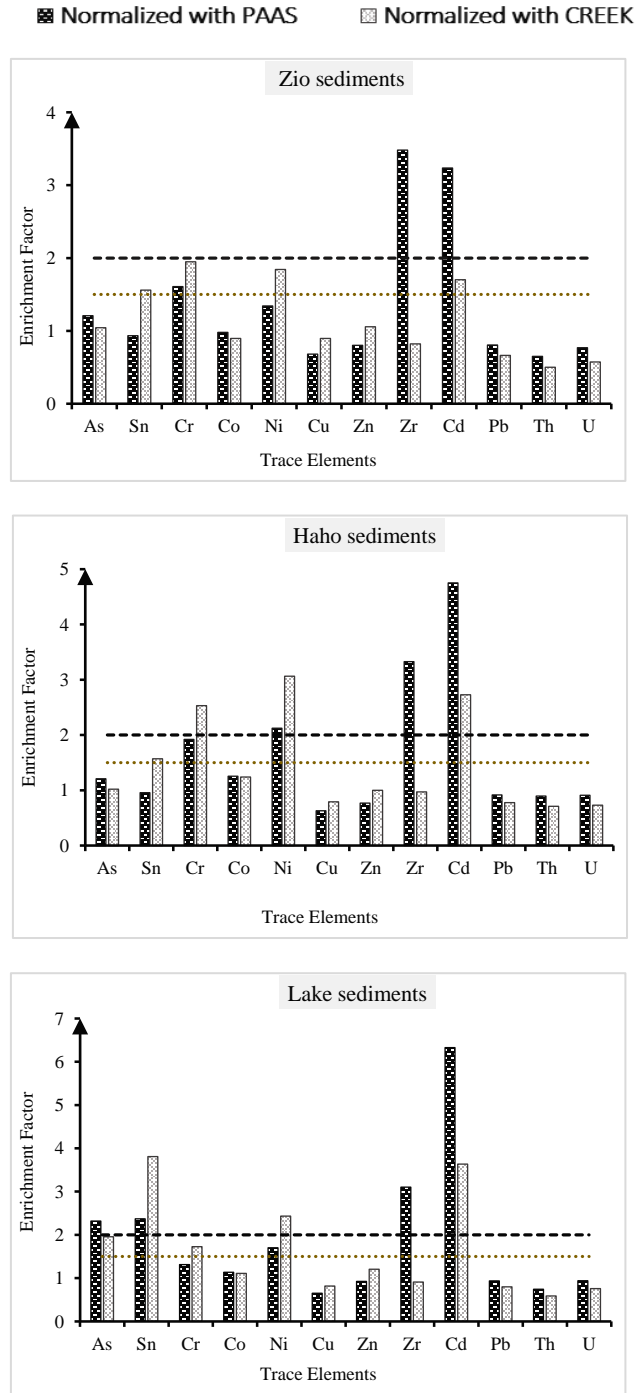


Figure 5 : TE enrichment factors in the finest sediment fractions (<math><63\mu\text{m}</math>). Mean values of trace elements in Zio, Haho and Lake were normalized using the PAAS and local creek sediment as natural references. The dashed lines represent the natural variability thresholds, respectively for PAAS (EF = 2) and local creek sediment (EF = 1.5) normalization.

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With regard to this previous analysis, the EF spatial distribution (Figure 6) based on the local pristine Creek sediment normalization indicates a significant variability among the samples for all elements. Globally, the spatial distribution of EF data reveals that 70% of TE in sampling stations have EF values lower than 1.5. A moderate enrichment is observed for Ni and Cr at all stations; for As at Z3, L3 ; for Sn at Z1, Z3, H1, H3 and for Cd at Z1, Z3, H1, H3 and for Cd at H1, H3, Z3. However significant enrichments in Cd and Sn are respectively observed at L3, Z4, H2 and at L3. Generally Cd and Sn are from the agriculture practices, especially from seasonal agriculture which are practiced in the minor and major river beds of Haho and Zio. The enrichment of Cd and Sn can also be result of the various domestic practices such as the clothes, cars and motorcycles washing with highly concentrated detergents in the bed of the rivers.

However, there is no significant enrichment of trace elements like As, Sn (except L3), Co, Cu, Zn, Pb, Th and U. Nevertheless, it is useful to determine the relative contribution of natural and anthropogenic sources to each TE content in the sediments.

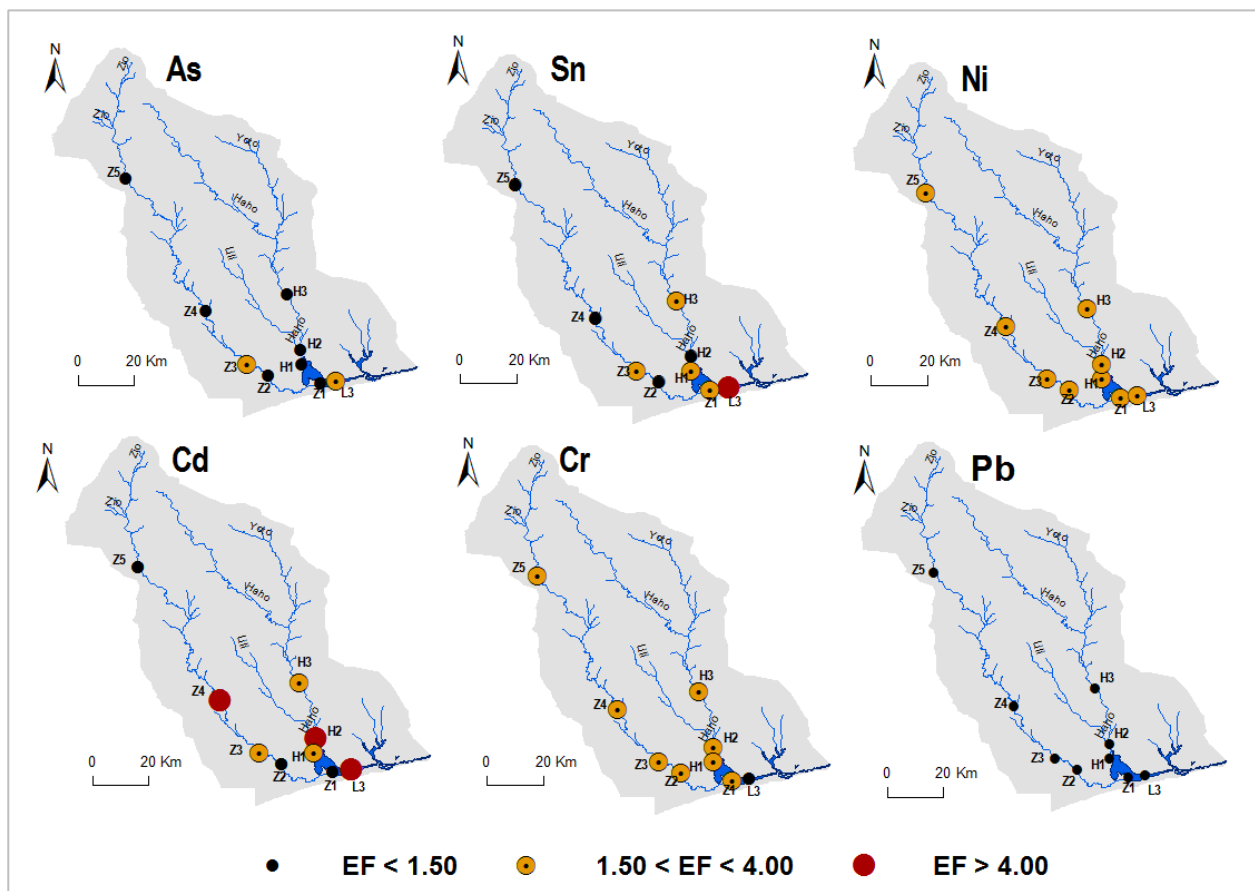


Figure 6 : Maps showing the spatial distribution of the most relevant TE enrichment factors.

3.2.4 Anthropogenic Contribution

The average anthropogenic contribution (AC) in the stream bed sediments of lake Togo basin, calculated using equation 2 and the local creek sediment as reference material, is greatly variable according to TE. AC is very high for Ni (54%) and Cr (53%), high for Cd (36%) and Sn (25%), low for Co (12%); As (8%) and ; Zn (6%) and very low for Cu (2%) and Pb (2%). For the other TE (Th, U and Zr), there is no AC. For Ni, Cr and Cd spatial distribution, the anthropogenic contamination of Zio and Haho stream sediments is obvious at Z3, Z4, Z5, H1, H2, H3 with regard to the intensity of the enrichments observed. In the case of As, Sn, Ni and Cr, the anthropogenic signature increases from upstream to downstream in the Haho basin while it is variable in Zio basin where the stations impacted by the anthropogenic signature depend on the TE. Indeed, Z3 station in Zio basin exhibits the highest AC for As, Sn and Pb. In the lake Togo (station L3), the AC shows high to very high levels whatever the TE, except Pb.

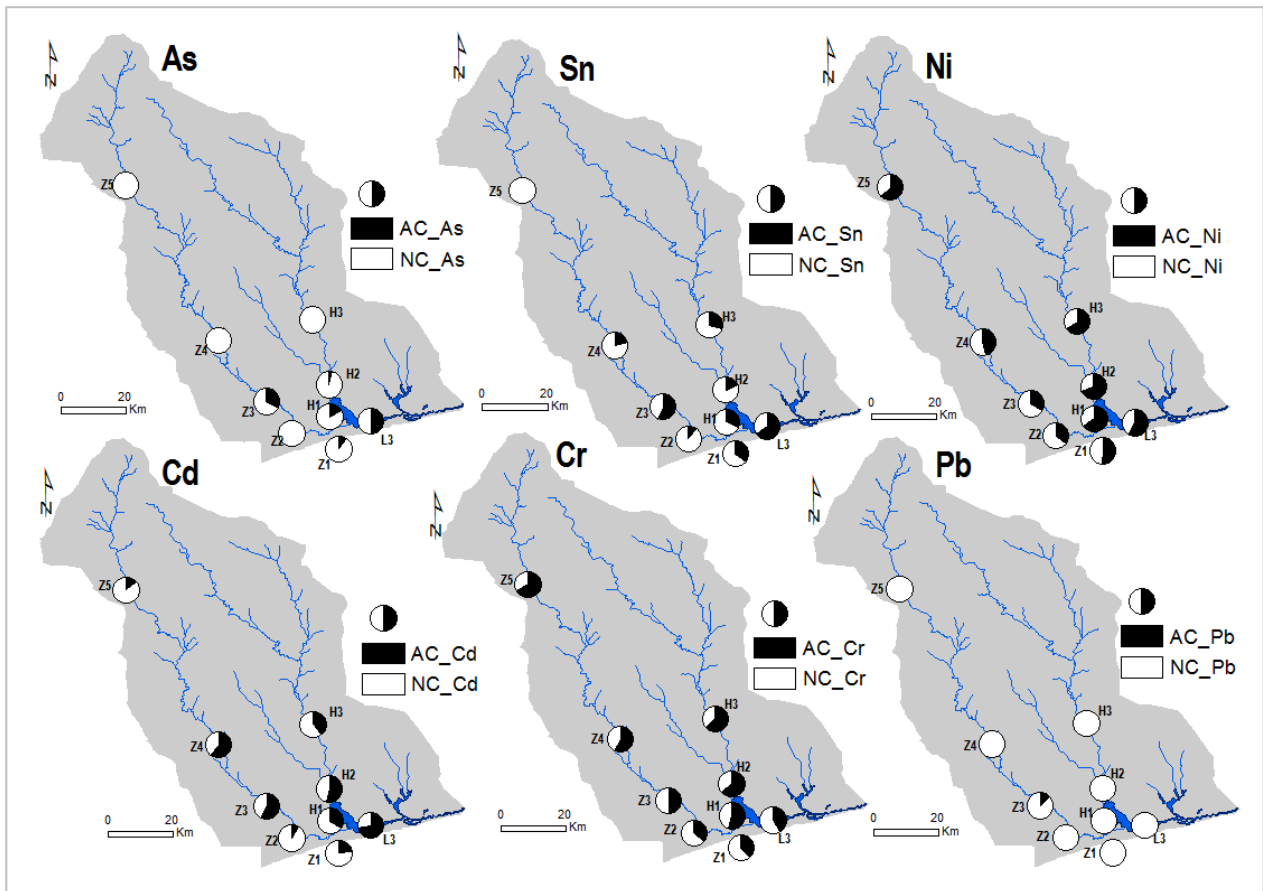


Figure 7 : Maps showing the spatial distribution of anthropogenic (AC) and natural (NC) contributions in percentage of the total concentration for each of the most relevant TE.

Based on the Pearson correlation coefficients, displayed in Table 2, there is a positive significant correlation between EF and AC of each TE. The enrichment increases in run away as the AC becomes important. Moreover, the correlations between EF values of Sn, Co, and Pb, and the anthropogenic contribution of Cd allow to make the hypothesis that those metals may be derived from the same pollution source in the area.

Table 2 : Pearson correlation coefficients between the percentages of AC and EF values for all the stations (n=17 values), including Zio (Z1 to Z5), Haho (H1 to H3) et Lake Togo (L3).

TE	As	Sn	Cr	Co	Ni	Cu	Zn	Cd	Pb
R²	0.83	0.78	0.97	0.81	0.92	0.67	0.92	0.85	0.62

All the value have a significant level of 0.05

3.2.5 EDTA extractable fraction of metal

The total concentration of metals in soils and sediments is not a good indicator of their availability, due to their different and complex distribution patterns among various chemical species or solid phases. Indeed, sorbed elements onto particles are potentially available, as they may be extracted due to changes in the physico-chemical properties of the aquatic environment such as salinity, pH, redox potential, and concentration of chelators (Abollino *et al.*, 2002; Bourg, 1988, 1995; Calmano *et al.*, 1993; Chuan *et al.*, 1996; Ernst, 1996; Forstner, 1993; Forstner and Kersten, 1988; Forstner *et al.*, 1986; Gambrell and Patrick, 1988). The objective consists to determine in the particulate fractions, the distribution of the element between the residual phases and the non-residual phases (labile fractions), and consequently its potential mobility toward the dissolved fractions as well as its potential bioavailability and then, its capacity to contaminate water resources and to infiltrate the food chain.

The figure 8 reports for each ET, the percentage of non-residual fractions (NR = non-residual or labile fraction) which have been extracted using an EDTA single extraction and the percentage of residual fractions (R), for the various studied samples. The relative ordering of elements, in terms of their environmental mobility or bioavailability, is observed from the most mobile to the least as follows: Co>Cu>Cd>Pb>Ni> As>Zn> Th> Sn> U>Cr>Zr.

Comparing the R and NR fractions of TE, the Co, Cu, Pb and Cd are associated more than 24 % to the NR fractions, except Co in sediments of the lake. The percentage of As and Ni in the NR of is between 10% to 16% (Figure 8). Zn, Th, Sn, U, Cr and Zr are rather associated to the residual fraction, which represents

on average 91 to 96 % of total particulate fraction for Zn and Th, and 99 to 100% for Sn, U, Cr and Zr. These results show that Cu, Co, Pb, Cd, are potentially more available and mobile with regard to the variations of the physico-chemical conditions of the aquatic systems than the rest of TE. Among them, Co is although into the available form in the sediments of Zio and Haho rivers with respectively 40% and 36% of NR fractions. Co could be logically considered like the element possessing the highest potential of mobility and toxicity, except in the Lake Togo, followed by Cu (30-33%), Cd (24-25%) and Pb (24-25%) for Haho and Zio, but 39% for the Lake. According to Salomons and Förstner (1980), the mobility and the toxicity of TE are bound to their proportion of non-residual fractions. More an element has a strong proportion of non-residual fraction, more its capacity of mobility and availability for the environment and for the living organisms is high, and *vice versa* if the residual fraction is dominant.

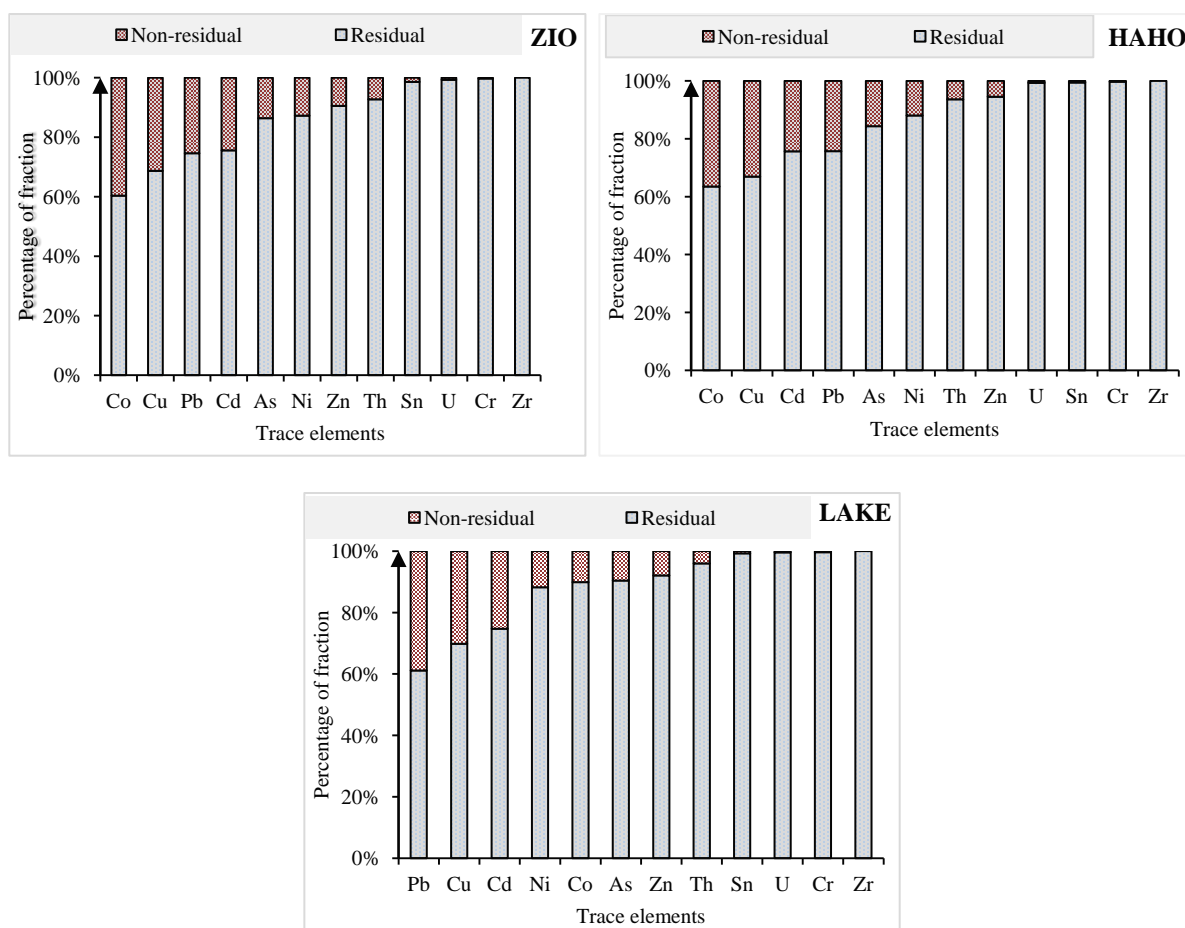


Figure 8 : Proportion of the various fractions (NR = non-residual; R= residual) outcome from the single chemical extraction using EDTA in the sediments of Zio and Haho rivers and of the Lake Togo.

3.3 Origins of Trace Elements in the Sediment Using Multivariate Statistical Analyses

In the absence of sequential extraction analyses which allows to determine the different TE bearing minerals (Leleyter and Probst, 1999), multivariate statistical analyses can provide meaningful information for the identification of the most important bearing geochemical phases (Santos et al., 2005). Principal component analysis (PCA) (Table 3 and Figure 9 A and B) were carried out to identify the origins of the different TE and their relationships with the various bearing phases in the sediment samples. The input data were enrichment factors (EF) for TE and the major element concentrations to represent the main bearing phases. Three principal components (Comp 1, Comp 2 and Comp 3) have been identified, explaining 80.8% and 76.94% of the total variance for Zio and Haho respectively.

In the Zio basin, component 1 distinguished between the metals that are least anthropogenically influenced (As, Sn, Ni, Cu, Zn, Pb, Th) and which are linked to Al and Fe oxides (Filgueiras et al., 2004) and clay-silt minerals (Suresh et al., 2012). The opposite correlation for Ni, demonstrates that there is no affinity for Ni to Al and Fe oxides (Chaillou et al., 2003). Component 2 and 3 isolated the most anthropogenically influenced metals and indicated that Sn, Co and Cd were linked to phosphate minerals (P) and organic matter (C, N). It was proposed that Cd and Sn mostly originated from agricultural sources due to fertilizer or pesticide inputs, particularly associated with organic matter during the erosion. This association is illustrated by the enrichment of Cd, Sn and Cu in Zio sediments at Z3 and Z1 in October (Figure 9-A) after the leaching of soil surface during the small rainy season. The opposite correlation about Pb, Cr, Th, and U with the component 2 reflects that those elements are associated to other sources of pollution. Indeed, contribution of Pb would be due to the accumulation of the old atmospheric pollutions from leaded gasolines and the activities of cleaning and draining of big trucks in the bed of the Zio river especially at Toglekope (Z3).

In the Haho basin, component 1 indicates that Cu and Ni are linked to Al and Fe oxides and also to clay-silt minerals. The anti-correlation to fine minerals for TE like Cd, Th and U, which are highly concentrated in the phosphates of exploited mines, confirms the study of Gnandi (2002) which showed that the Cd concentrations in the Haho sediments increase when the size grading increases. This is one of characteristics of phosphates from mining activities in the basin. Component 2 indicated that Ni, Pb and U were linked to P and organic matter (C, N). The component 3 shows that Pb, Cu and Cr are linked to P. This association shows that the P controlling factor mostly originates from agricultural sources and domestic wastes.

Table 3 : Loadings of experimental variables on significant principal components.

Variables	ZIO			HAHO		
	Component			Component		
	1	2	3	1	2	3
As	0.86	0.13	-0.23	-0.35	-0.13	0.74
Sn	0.46	-0.51	0.62	0.41	0.29	0.58
Cr	-0.24	0.74	0.37	-0.42	0.4	-0.68
Co	0.19	0.35	0.88	-0.31	0.32	0.84
Ni	-0.48	0.01	0.36	-0.78	0.55	-0.13
Cu	0.76	-0.17	-0.55	-0.77	-0.33	-0.47
Zn	0.95	0.12	-0.24	0.03	0.44	0.76
Cd	0.2	0.36	0.66	0.87	0.29	0.11
Pb	0.84	0.51	0.01	0.12	0.81	-0.48
Th	0.51	0.66	0.43	0.76	0.48	-0.22
U	0.44	0.79	0.36	0.71	0.58	-0.25
Al	0.83	-0.39	-0.11	-0.71	0.47	-0.36
Fe	0.76	-0.16	0.16	-0.54	0.44	0.32
P	0.06	-0.66	0.51	-0.05	0.46	-0.45
C	0.09	-0.76	0.56	-0.34	0.83	0.29
N	0.21	-0.70	0.58	0.07	0.81	0.12
CFS	0.83	-0.28	-0.11	-0.72	0.04	0.26
Eigen value	5.97	4.22	3.55	5.03	4.24	3.81
% total variance	35.1	24.8	20.9	29.59	24.94	22.41
Cumulative % variance	35.1	59.9	80.8	29.59	54.53	76.94

Bold values indicate strong and moderate loadings. (CFS =% clay + fine silt)

According to the hydrological periods (F-low flows of February or O-high flows of October) and to the origine of metal contamination, the PCA of major and trace elements compared to sampling stations for component 1 and 3 (Figure 9-A) showed that As, Sn, Co and Zn which are more enriched in sediments of H1 during the period of February, are controlled by hydroclimatic factors. Yet during the low water period

(February), Julien *et al.* (2017) showed the hydrological effect of the lake Togo on the outlets of rivers Zio (Z1) and Haho (H1). TE like As, Sn, Co and Zn may result from the intrusion of the sea water in the lake. Besides, the group of Cd, Th and U in sediments of stations H2 in october (H2-O) and H3 in february (H3-F), both periods in the course of which the grain-size of sand and coarse silt is more important in those stations (50% and 51% of coarse silt and sand for H2-O and H3-F respectively) confirm the results of Gnandi (2002). Contrary to the other TE which increase when the clayey fine fraction increases, the Cd contents increase rather when the size of the grain increases. It is one of the characteristics of the cadmium stemming from the old abandoned exploitation areas. The Cd from this area is preferentially bound to apatite mineral.

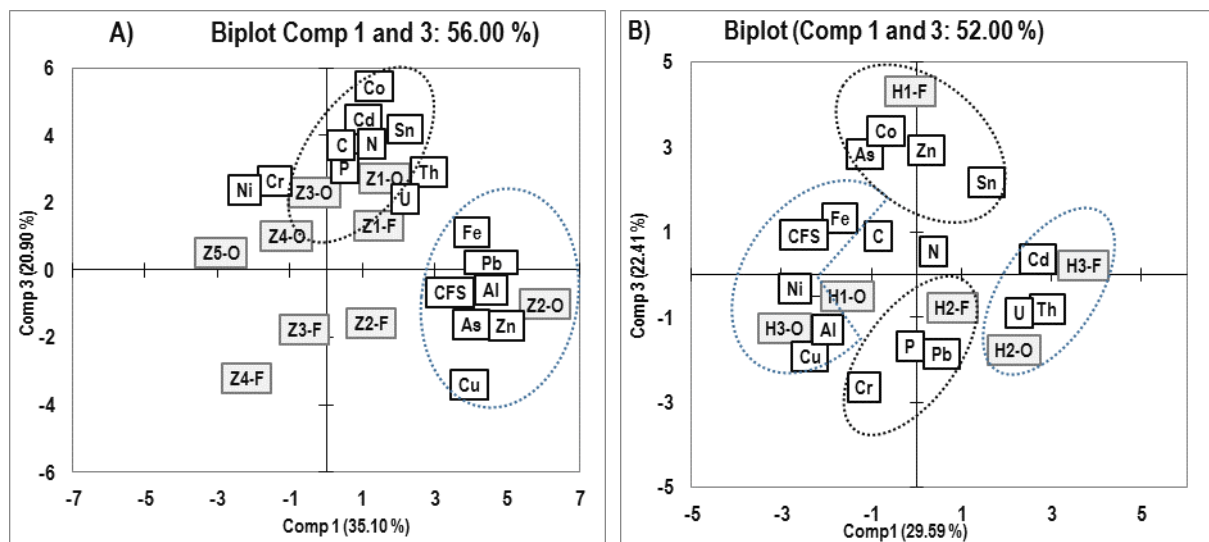


Figure 9 : Loading plots (components 1 and 3) from a PCA of major (C, N, P, Fe, Al), % Clay+Fine Silt (CFS) and TE compared to sampling stations of Zio (A) and Haho (B) stream bed sediments during the period of low flows in February (Z1-F to Z5-F and H1-F to H3-F) and high flows in October (Z1-O to Z5-O and H1-O to H3-O). The variance percentage of each component is mentioned in Table 3.

In the stream sediments of the watersheds draining into the Lac Togo, all TE contents are mainly linked to the geological and lithological nature of the rocks and to the soils. Nevertheless for the Zio riverbed sediments, two groups of elements can be distinguished according to their anthropogenic sources:

- As, Cr, Cu, Zn, Pb, Th and U are enriched by the contributions of atmospheric deposition, domestic effluents, solid waste and traffic in the environment. The exogenic Pb coming from the accumulation

of the old atmospheric pollutions from car gasoline and also from the activities of cleaning and draining of big trucks in the river bed of the Zio;

- Sn, Co and Cd are enriched by fertilizer inputs and are associated to phosphorus. Fertilizers are known to be significantly enriched in Cd associated to phosphates (Avril, 1992; Micó *et al.*, 2006; N'Guessan *et al.*, 2009). Their high concentrations in sediments of the station Z3 in October confirmed the result of soil leaching during rainy seasons in the cultivated areas.

With regard to Haho sediments, one can distinguish three groups of TE:

- Pb, Cr, Ni, Cu, Th, U are enriched by contributions of atmospheric deposition, domestic waste in the environment and the phosphate exploitation area;
- The contents of As, Co, Zn and Sn are influenced by the rise of brackish water of the lake into the rivers under the influence of the sea ;
- Cd, except the agriculture impact, also comes from apatite of phosphate mining.

3.4 Comparison with Sediment Quality Guidelines (SQGs) for Some TE

Sediment quality issues are important focus in the assessment, protection and management of aquatic ecosystems. Then numerous SQGs have been developed during the last decades to assist regulators in dealing with contaminated sediments. The original SQGs which were compared with a reference or with geochemical background, like EF, provided little insight into the potential ecological or ecotoxicological impacts of sediment TE. The new generation of SQGs was developed relying on field sediment chemistry paired with field or laboratory biological effects data. If we compared the TE concentrations in the river bed sediments with different SQGs, particularly for Cr, Ni, Cu, Zn, As, Cd and Pb for which SQGs exist in the literature (see the references in Table 4), one can see that, except Cr and Ni, our total TE concentrations are lower (Cu, Zn, As, Cd, Pb) than most of the SQG values.

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Table 4: TE average concentrations in the sediments (fractions <63µm) of the Zio and Haho rivers and of Lake Togo, compared to SQGs concentrations.

TE (µg.g ⁻¹)	Sediments (<63µm)			SQGs for TE (µg.g ⁻¹)								
	Zio	Haho	Lake Togo	TEL	ERL	LEL	MEL	PEL	ERM	SEL	TET	CB PEC
Cr	180.53	228.44	145.22	37.3	80	26	55	90	145	110	100	111
Ni	78.05	126.76	93.51	18	30	16	35	36	50	75	61	48.6
Cu	39.55	34.09	32.70	35.7	70	16	28	197	390	110	86	149
Zn	76.80	70.19	79.23	123	120	120	150	315	270	820	540	459
As	2.06	2.05	3.50	5.9	33	6	7	17	85	33	17	33
Cd	0.30	0.43	0.57	0.6	5	0.6	0.9	3.53	9	10	3	4.98
Pb	17.40	19.66	19.00	35	35	31	42	91.3	110	250	170	128

Sediment Quality Guidelines for sediments (SQGs): TEL-Threshold Effect Level (Smith et al. 1996), ERL- Effects Range Low (Long and Morgan, 1991), LEL-Lowest Effect Level (Persaud et al., 1993), MEL-Minimum Effect Level (MENVIQ/EC,1992), PEL- Probable Effect Level (Smith et al., 1996), ERM-Effect Range Median (Long and Morgan, 1991), SEL-Severe Effect Level (Persaud et al., 1993), TET- Toxic Effect Threshold (MENVIQ/EC,1992), CB PEC-Consensus-Based for Probable Effect Concentrations (MacDonnald et al., 2000).

Moreover, the issue of bioavailability is not well addressed by the empirical SQGs since they are based on total sediment concentrations (Burton, 2002). As seen in the previous section, the non-residual fractions which correspond more or less to the bioavailable fractions which represent a real threat to aquatic ecosystems present lower values (see Figure 8), particularly for Ni for which the NR fractions represent only 12-13% of the total concentrations and for Cr for which there is no NR, Cr being only in the residual fractions of the sediments. Then, the total TE concentrations could be divided by 2.5 to 3 for Pb and Cu, until 10 for As to get the TE concentrations which indeed represent a real threat for the organisms. Consequently, the non-residual TE concentrations are largely under the SQGs, even for Cr and Ni for which the total concentrations are over the SQGs, mainly because they are mainly associated to residual fractions and then, not at all bioavailable.

4. Conclusions

A study of the occurrence, distribution and enrichment of TE like As, Sn, Cr, Co, Ni, Cu, Zn, Cd, Pb, Th and U in the stream sediments of the watersheds draining into the Lac Togo, reveals the following important results. The levels of total concentrations of trace metals in the study area, in general, do not constitute any serious environmental risk except for Ni, Cr and specially Cd which need to be monitored at the outlet of both rivers, Zio (Z1) and Haho (H1) and also at Togblekope (Z3) and Hahotoe (H2) sites. Nevertheless when compared the TE labile fractions with the Sediment Quality Guideline values, all the TE labile concentrations remain largely under the ecotoxicological limits. Knowing that most of the studies on trace elements more dealt with the coastal zone especially on the discharge of the mining effluents in the sea, the concentration ranges for the different trace metals in the Zio and Haho can serve as baseline environmental data against which the degree of pollution of these trace metals can be evaluated in the future.

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