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Geochemical composition of fluvial sediments in the Milo River basin (Guinea): is there any impact of artisanal mining and of a big African city, Kankan?

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A B S T R A C T

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For the first time, the bed sediments of the Milo River and its tributaries were sampled and analyzed to characterize their geochemical signature in terms of major, trace and rare earth elements and to determine the potential impacts of artisanal mining and of the anthropogenic activities of Kankan city. 24 sites have been sampled along the Milo river from upstream to downstream and on its tributaries during one sampling campaign to assess the spatial variations of the geochemical signature. During one year, the bed sediments have been sampled monthly on the Milo river upstream and downstream Kankan to determine the seasonal variations of their chemical composition and to investigate the potential impacts of Kankan on the fluvial sediment quality. The geochemical signatures of the sediments are mainly controlled by the geological substratum and the lateritic soil cover, showing that there is no impact of the artisanal mining and very few impacts of Kankan, except for As and Sb on two small tributaries draining the urban agglomeration. All the sediments are more concentrated and naturally enriched in Zr, Hf, U and Th compared to PAAS, due to the regional geochemical background. REE distribution patterns show LREE and HREE enrichments and positive Ce and Eu anomalies. The La/Yb ratios are positively correlated to Al and Fe-oxides and negatively to silica. The non-residual fractions (labile) extracted with EDTA represent less than 20% of the total concentration, showing that the threats for aquatic ecosystems and human populations are limited. This study can represent a reference with regard to the potential development of industrial mining and increase of population due the abundant mineral resources within this catchment.

1. Introduction

The eastern part of Guinea is drained by the upper Niger river and its tributaries, among them the Milo river is one of the most important on the right side (Fig. 1). Guinea and particularly the Milo river basin have many mineral resources (bauxite, diamonds, gold and iron), which are under-exploited. These nonfuel minerals are mainly extracted by artisanal mining. Moreover the Milo river is flowing through the big urban agglomeration of Kankan which is the largest city in Guinea in land area and the second after Conakry in number of inhabitants (around 200 000).

Nevertheless, no data exists until now on the potential impacts of artisanal mining and of urban activities on the quality of the waters, sediments and aquatic ecosystems of the rivers draining this West African region, particularly on the Milo river which is flowing through this large agglomeration of Kankan. In the Milo river basin, the artisanal mining (Annexes-Fig. 14) mainly concerns the gold extraction

(south-eastern and north-eastern parts of the Milo river basin), the diamonds (south-western of the Milo river basin) and iron exploitation in the upper Milo river basin. These mining activities cause many damages to the environments (deforestation soil erosion, groundwater resources) but we do not know if there is any impact of these activities on the river systems, particularly on the quality of suspended matters and bed sediments. Concerning the agglomeration of Kankan, there are few industrial activities, mainly agri-food industry for bottling fruit juices and some artisanal manufactures of bricks (Annexes-Fig. 14). For the rest, there are all the classical activities of a big African city: the domestic effluents are neither collected nor treated, the domestic wastes are little collected and commonly accumulated and burned in the city and around the city, the vehicule traffic is very important and source of many pollutions (from gasoline, motor oil, brake pads, lead batteries ...) and some vegetable crops are cultivated around the city using mineral fertilizers and pesticides.

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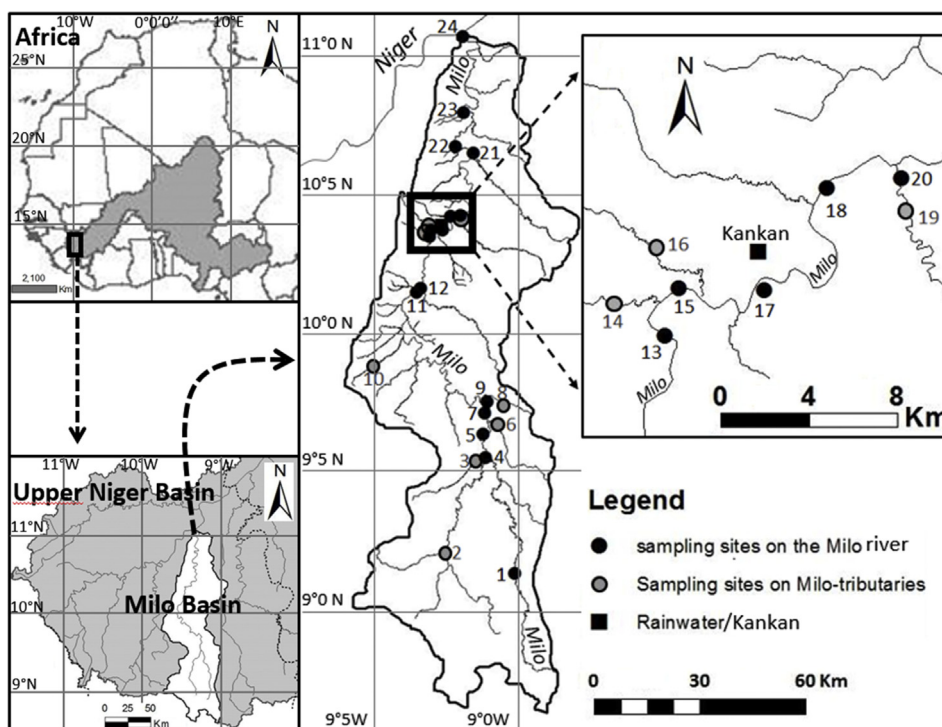


Fig. 1. Geographic situation of the Milo drainage basin and location of the main discharge gauging station at Kankan and of the sampling stations along the Milo river main channel and on the different tributaries (see also [Annexe-Table 5](#)).

Moreover, Guinea is a sub-saharan region of Africa regularly affected by the climate change, particularly by severe droughts in the last century ([Aguilar et al., 2009](#)), but we do not know the impact of such hydro-climatic fluctuations on the river water and sediment quality.

Then it was interesting to investigate this area to have a picture of the present situation and to get a geochemical reference before the potential development of industrial mining and consequently, of the population increase in this region, particularly around the city of Kankan.

As shown previously in different regions of the world ([Casas et al., 2003](#); [Gaiero et al., 2004](#); [Singh et al., 2005](#)), one of the best way to assess the potential contamination of rivers and aquatic ecosystems is first to analyse the fluvial sediments deposited in the main channel. These bed sediments are integrators of the geochemical signature of the different soils and rocks and of what is happening in the river basin, as found by [Cabral Pinto et al. \(2016, 2017\)](#). Indeed, they are good recorders of various pollution sources from domestic, agricultural or industrial activities developed within the catchment ([Valette-Silver, 1993](#); [Singh et al., 2002](#); [Wildi et al., 2004](#); [N'Guessan et al., 2009](#); [Benabdelkader et al., 2018](#)). The stream bed sediments are mainly originating from the physical erosion of the soils, even if the bank erosion could contribute to supply some sediments to the river loads, and their subsequent transport into the hydrographic network by the different rivers draining the upper parts of the catchment. Moreover the finest fractions of the bed sediments present a chemical and mineralogical composition which is very close to the suspended matter transported by the river ([Gaiero et al., 2003](#)). Then analysing the bed-sediments is an integrative method to assess the river suspended loads and it is finally a good strategy to get simply and rapidly a first diagnosis of the « health » of the fluvial system.

The main objectives of this study were to make a global geochemical screening of the fluvial sediments in this West African region, to generate first data on the chemical composition (major and trace elements, rare earth elements) of the river bed sediments to establish a basic reference and to get a first diagnosis of the geochemical status of these sediments. Then, it was to assess for the first time:

- The spatial variability of the geochemical signature of the fluvial sediments along the Milo river and its different tributaries from upstream to downstream
- The temporal variability of the chemical composition of the bed sediments deposited upstream and downstream the urban agglomeration of Kankan
- The spatial and temporal variabilities of the Rare Earth Elements (REE) distribution patterns and any positive or negative anomalies, particularly for Ce and Eu, and any fractioning or enrichment in Light (LREE) or Heavy (HREE) REE using La/Yb normalized ratios.
- The enrichment factor to determine any natural or anthropogenic impact on the Trace Elements (TE) concentrations
- For each TE, the distribution of the total content within the residual and the non-residual (labile) fractions of the sediments in order to assess any potential threat for the aquatic ecosystems and for the human populations living along the rivers.

2. Material and methods

2.1. Geological and geomorphological settings, soils, vegetation and cultures

The Milo river is a tributary of the Niger ([Fig. 1](#)). It takes its source at 658 m, close to Kerouane village. It flows between two mountains (Langbalma and Traorekonke) going from the South to the North. It drains an area of 13810 km² until the confluence with the Niger, 50 km upstream the city of Siguiri. At the gauging station of Kankan, the drainage basin covers an area of 9700 km². The Milo drains the upper part of the Niger basin on the right bank. It flows South-North from the high plateaus North East of Macenta and the chain of Simandou-Gbing in the region of Kerouane-Beyla where the Pic de Fon reaches 1656 m.

It crosses the contact area between the granite outcrops and the schist regions. There are also some dolerite outcrops which mark the Southern limit of the « Niandan-Banie » chain ([Goloubinow, 1950](#); [Gregoire and Kohl, 1986](#)).

The Milo catchment is included in the Guinean dorsal which is formed by important rolls of highlands with altitude higher than

1000 m. The relief forms are various with gentle slopes covered by ferralitic soils and rounded croups. Along the rivers, the alluvial plains are covered by hydromorphic soils.

The passage from the granite area (upstream) to the schist area (downstream) is accompanied by a fairly sharp change in the type and density of the vegetation cover which decreases from the South to the North, going progressively from peri-forested areas (due to high altitude and high precipitation) to grassy savannas (Diop, 2000).

Along the rivers, the alluvial plains are cultivated, mainly with cereals, tubers, truck farming and fruit crops. The rice is also cultivated without any specific land use arrangement and the cotton is mainly cultivated in the North-East (Diakit  and Doumbouya, 2000). It is also important to note that the itinerant agriculture which is developed in different parts of the basin exposes the soils to the physical erosion, to the fertility decrease and to the acidification. Moreover since 2011, the Guinean government sets up a new agriculture policy to support the use of fertilizers and pesticides without any preliminary study.

2.2. Hydro-climatology

The mean interannual discharge for the Milo River at Kankan averages $170 \text{ m}^3 \text{ s}^{-1}$, i.e a specific water discharge of 550 mm y^{-1} , for the period 1938–2015. Nevertheless, the annual discharge fluctuations exhibit a general decreasing trend as seen in Fig. 2. The interannual fluctuations of the mean annual precipitation follow the same pattern, even if one can notice very dry periods from 1970 to 1993 and since 2010, while the mean air temperature increases during the same period.

The hydrological regime of the Milo river is pluvial and the seasonal discharge is greatly variable (Fig. 3), going from 10 to $80 \text{ m}^3 \cdot \text{s}^{-1}$ during the dry season to 100 – $500 \text{ m}^3 \cdot \text{s}^{-1}$ during the wet period, with the maximum occurring in September or October.

2.3. Sampling strategy, field analyses and pre-treatment of the samples

The sampling strategy was based on a spatial and temporal assessment of the chemical composition variability of the fluvial sediments in the Milo river basin. For the spatial variability, we have collected the river bed sediments during the sampling campaign of June–July 2013 (end of the low water period) along the Milo main channel (12 stations) from upstream to downstream (Fig. 1 and annexe-Table 5) and on the different tributaries (12 stations). For temporal variability, we sampled the river bed sediments each month at Kankan (Fig. 3), upstream and downstream the city, during one hydrological year (June 2014–May 2015).

For each sampling station, pH, temperature, conductivity and dissolved oxygen were measured in the field. The river bottom sediments are collected using a polypropylene bottle in the 2 first centimeters of the sediment layers. Then, the samples were dried in the laboratory at 45°C in a clean oven to avoid any contamination during the drying period. For each sample, the aggregates were crushed in an agate

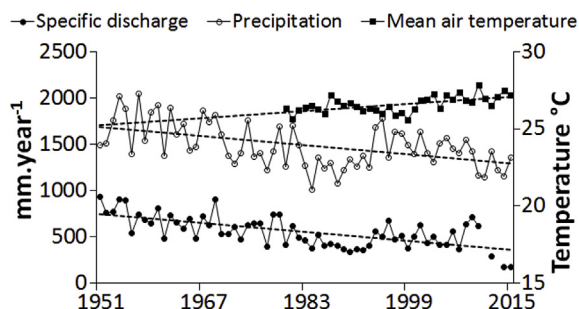


Fig. 2. Interannual fluctuations of mean annual air temperature ($^\circ\text{C}$), annual precipitation ($\text{mm}\cdot\text{year}^{-1}$) and Milo river specific discharge ($\text{mm}\cdot\text{year}^{-1}$) at the station of Kankan for the period 1951–2015.

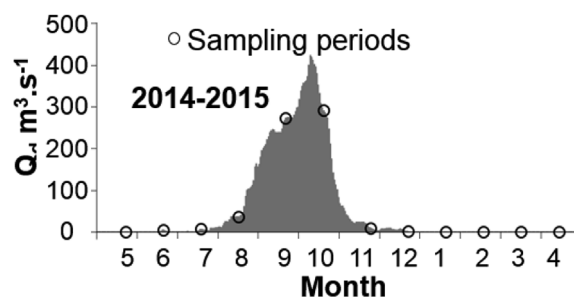


Fig. 3. Annual hydrograph (mean daily discharges, Q_d) of the Milo river at Kankan for the hydrological year 2014–2015 with the position of the monthly sampling periods (white circles) of the bed sediments, upstream and downstream Kankan city.

mortar to separate the grains and then, quartered to extract a representative sub-sample for analyses.

Then, the sediment samples have been sieved at 2 mm , $200 \mu\text{m}$ and $63 \mu\text{m}$ on nylon sieves (to avoid any metal contamination) to separate the different granulometric fractions: clays and silts ($< 63 \mu\text{m}$), fine sands (63 – $200 \mu\text{m}$), coarse sands ($200 \mu\text{m}$ – 2 mm). For each fraction, the grain size distribution has been determined using laser micro-granulometer (HORIBA Partica LA-950V2) going from $0,01 \mu\text{m}$ until $3000 \mu\text{m}$. Before the sediment sample was treated with solution of sodium hexa-meta-phosphate to improve the particle dispersion in the solution.

All the chemical analyses (major and trace elements) have been made on the finest fractions, clays and silts ($< 63 \mu\text{m}$) in order to normalize each sediment sample with regard to their granulometric distribution and because the concentration of trace elements are highest in the finest particles due to their high specific surface area which increases their capacity to adsorb trace elements (Salomons and F rstner, 1980; Horowitz and Elrick, 1987; Probst et al., 1999).

2.4. Chemical analyses of major and trace elements

2.4.1. Total concentrations

For the total content in the river bed sediment, all the chemical analyses have been realized by the National Service of Rock and Mineral Analyses (SARM: <http://helium.cprg.cnrs-nancy.fr/SARM/>) in Nancy, using ICP-AES and ICP-MS. Before analyse, each sample (at least 200 mg) has been digested using an alcalin fusion technique with lithium metaborate (see Carignan et al., 2001). To verify the recovery rate for each element, 4 international reference materials have been used following the same protocol of digestion: LKSD-3, WQB-1, SUD-1 and SRM 1646–2. For all the material, the recovery rates are very good going for example, from 85% to 110% for LKSD-3 and from 86% to 107% for SRM 1646–2, according to the elements.

2.4.2. Extractible fractions

To get the total extractible fractions which correspond to the non-residual fractions (or labile phases) adsorbed onto the particles, we used a single chemical extraction with EDTA (Wear and Evans, 1968; Leleyter et al., 2012). The protocol is to leached 1 g of sediment with 10 ml of an EDTA solution ($0,05 \text{ mol}\cdot\text{L}^{-1}$) at room temperature with agitating during 1 h . Then the solution is filtrated at $0,22 \mu\text{m}$ to separate the residual fractions on the filter and the non-residual fractions in the filtrate.

Then the chemical analyses of major and trace elements extracted in the solution using EDTA, have been realized using an ICP-MS at the analytical platform of Midi-Pyrenees Observatory (OMP-Toulouse University).

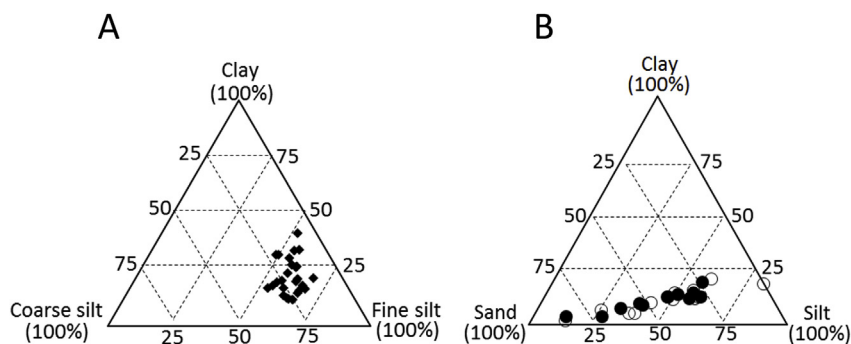


Fig. 4. Granulometric distributions (%) of the particles. A- Ternary diagram for the distribution of the finest fractions (clays < 2 μm, 2 μm < fine silts < 20 μm and 20 μm < coarse silts < 63 μm) in the bed sediments of the Milo river and its tributaries, going from upstream to downstream. B- Distribution of the total fractions (clays < 2 μm, 2 μm < silts < 63 μm and 63 μm < sands < 2 mm) in the bed sediments of the Milo river at Kankan, upstream (black circles) and downstream (white circles) the city.

3. Results and discussion

3.1. Physical characterization and major element composition of the sediments

3.1.1. Particle size distribution

The bed sediments are mainly composed of sand fractions which represent 46%–70% of the total sediment, except for the Milo at the confluence with the Niger. Clays (5–34%) and silts (14–35%) are present in the same proportion and vary around 20% each. Among the finest particles (< 63 μm), the dominant fractions are the fine silts (2–20 μm) (Fig. 4A).

For the two sampling stations of Kankan, located upper and lower the city, the granulometric distributions of the particles are greatly variable according to the seasons (Fig. 4B), going to coarse fractions during the high flow period (August to October) to fine fractions during the low flows (November to July). On the contrary, for the finest fractions (< 63 μm) the distribution is less variable and the most abundant fraction is also the fine silts like for the upper Milo and its tributaries.

3.1.2. Major element composition

The chemical composition of the fluvial sediments reflects that of the lateritic soils which cover the Milo River catchment. They are mainly composed of silica and aluminium and iron oxides (Fig. 5A and B). The cations represent generally less than 10% and their percentages vary few. Spatially (Fig. 5A), the composition varies from the silica pole to the Al and Fe-oxides which can represent until 30%. Concerning the seasonal variations at the station of Kankan (Fig. 5B), it can be seen that the composition is few variable.

3.2. Rare earth element (REE) composition

3.2.1. Total concentrations and distribution patterns

The rare earth element (REE) concentrations are reported in Table 1 and compared to the world average of fluvial sediments and to the chemical composition of the Post Archean Australian Shales (PAAS) and of the Upper Continental Crust (UCC) taken in the literature as references. The REE concentrations are higher in the Milo, particularly for

Table 1

REE concentrations in the fluvial sediments of the Milo catchment compared with some literature references: ^a-World average for the river sediments from Bowen, 1979, ^b-PAAS and ^c-UCC from Taylor and Mc Lennan (1985).

REE μg.g ⁻¹	Sediments of Milo basin (n = 30)				World average ^a	PAAS ^b	UCC ^c
	Min.	Max.	Median	Mean			
La	24.90	86.22	60.70	57.37	41.00	38.20	30.00
Ce	69.16	302.30	135.05	135.09	83.00	79.60	64.00
Pr	6.18	16.23	12.72	12.22	–	8.83	7.10
Nd	22.82	56.30	44.63	42.96	32.00	33.90	26.00
Sm	4.91	10.48	7.95	7.83	6.40	5.55	4.50
Eu	1.03	2.11	1.73	1.69	1.20	1.08	0.88
Gd	4.66	8.82	6.37	6.45	–	4.66	3.80
Tb	0.60	1.46	0.95	0.99	1.00	0.77	0.64
Dy	3.59	9.49	5.65	6.07	–	4.68	3.50
Ho	0.79	2.17	1.20	1.31	–	0.99	0.80
Er	2.34	6.36	3.43	3.70	–	2.85	2.30
Tm	0.40	1.05	0.53	0.58	–	0.40	0.33
Yb	3.04	8.11	4.02	4.27	3.60	2.82	2.20
Lu	0.47	1.40	0.64	0.71	0.70	0.43	0.32

Ce, even if the concentration is greatly variable from one sediment to another. This Ce increase is mainly due to the adsorption of Ce onto Fe-oxides which are abundant in the fluvial sediments eroded from lateritic soils.

If we normalized the REE distribution pattern for each station to the PAAS (Taylor and Mc Lennan (1985)), we can distinguish 4 groups (Fig. 6):

- Group I: the upper Milo main channel until station 13 (stations 1, 5, 7, 9, 11 and 13),
- Group II: the lower Milo river until the confluence with the Niger (stations 15, 17, 18 and 22),
- Group III: the different tributaries going from upstream to downstream (stations 2, 6, 8, 10, 14, 16 and 19)
- Group IV: all the other stations which correspond to a mixing sediments at the confluence between one tributary and the Milo (stations 3, 4, 12, 20, 21, 23) or between the Milo and the Niger (station 24).

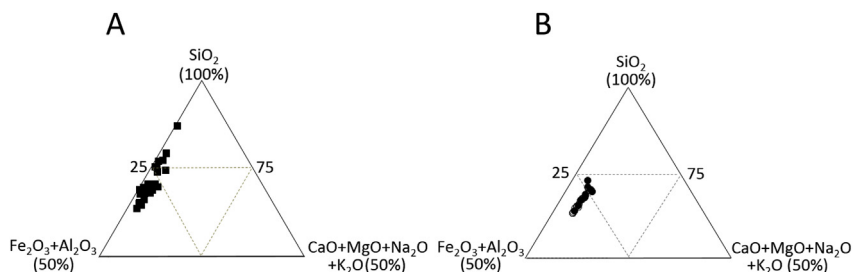


Fig. 5. Ternary diagrams showing the chemical composition of the finest fractions (< 63 μm) of the sediments. A- Spatial variations for the different stations of the Milo and of its tributaries. B- Temporal variations for the stations of Kankan, upstream (black circles) and downstream (white circles).

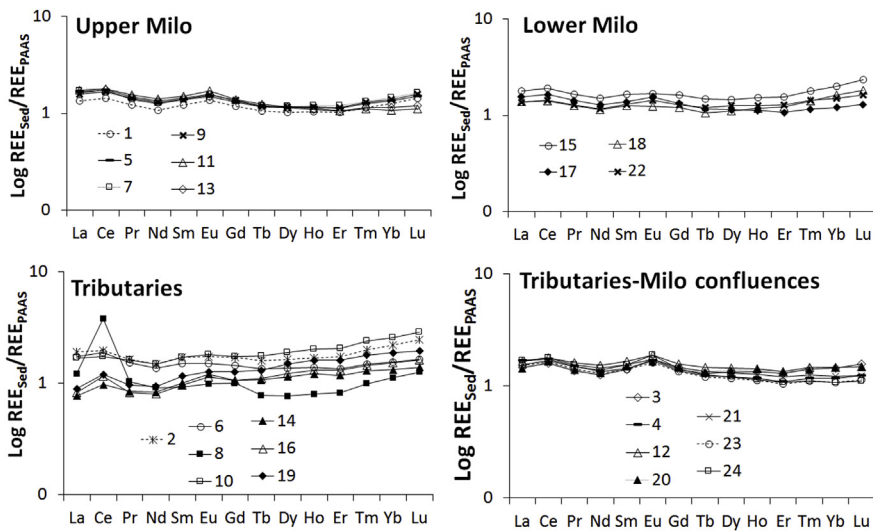


Fig. 6. Distribution patterns of REE concentrations normalized by the PAAS concentrations, in the bed sediments of the Milo river basin at the different stations (1–24). The stations are grouped according to their REE pattern (see text): upper Milo (Group I), lower Milo (Group II), tributaries (Groupe III) and confluence between Milo and its tributaries (Group IV^o).

For Group I (upper Milo), the REE patterns are close to the PAAS but they are slightly enriched in Light REE (LREE) with positive anomalies for Ce and Eu (see next section). For Heavy REE (HREE), we can observe a slight enrichment for the upper stations (1, 5, 7 and 9) while for the lower stations (11 and 13) there is no HREE enrichment.

For Group II (lower Milo), the patterns are more dispersed but they present the same LREE slight enrichment with Ce and Eu anomalies (see next section). Compared with the upper Milo, the HREE enrichment is more pronounced, particularly for stations 15, 18 and 22.

Most of the tributary sediments (Group III) exhibits HREE enrichments, particularly those produced by the upper tributaries (stations 2 and 10) draining the granitic rocks, except station 6 on the Djassa river on the left side in which the LREE are more enriched. As for the upper and lower Milo, the Ce anomalies are present, except for station 2 and 10, while the Eu presents no anomaly. For the Wassa river (station 8), the Ce anomaly is very important (see next section).

Finally for the last Group, the confluence sediments which are generally a mixing between the Milo sediments and the sediments supplied by the different tributaries, the REE distribution patterns are very close to the Milo sediment patterns.

At Kankan (Annexe-Fig. 12), the REE seasonal concentrations are less variable downstream the city (Station B) than upstream (Station A), but the distribution patterns are the same for both stations, showing a positive anomaly for Eu (see next section) and enrichments for LREE and HREE. This pattern is close to the patterns already described for the other stations of the Milo main channel. There is a very good relationship between REE concentrations measured upstream and downstream the city of Kankan ($Y = 0.976x - 0.1587$ with $R^2 = 1$). Consequently, we can say that there is no impact of Kankan anthropogenic activities on the REE concentrations and pattern distributions which may be recorded downstream the city in the Milo river bed sediments.

Nevertheless, it is interesting to note that between upstream and downstream, there is a slight decrease of the HREE concentrations normalized to PAAS (Fig. 7) probably due to a slight difference of the particle size distribution (finer fractions downstream) and of chemical composition (lower sediments enriched in Al and Fe-oxides).

3.2.2. Ce and Eu anomalies and La/Yb ratios

Among the REE, Eu and Ce are especially interesting to study because they have different oxidation degrees (contrary to the other REE) and then, different ionic radius which allow the substitution of other elements in minerals. For example in reducing conditions, Sr or Ca can be substituted by Eu in feldspars and Ca-plagioclases (McLennan, 1989). The redox conditions can also change their availability for living

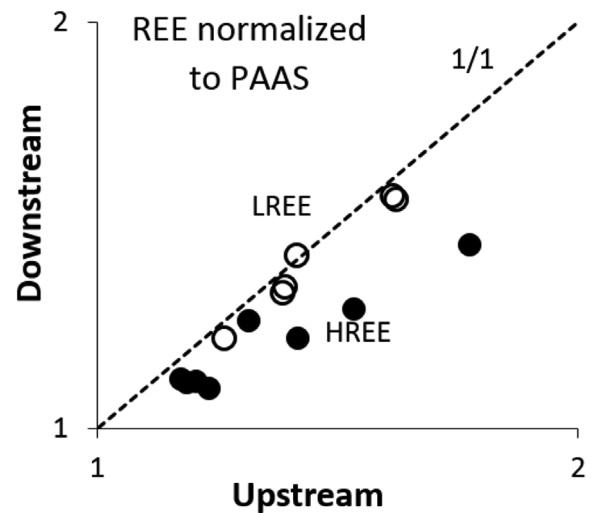


Fig. 7. Relationships between the logarithms of mean REE concentrations normalized by the PAAS concentrations in the Milo sediments at station A (upstream the city) and B (downstream the city) of Kankan (white circles for LREE, black circles for HREE).

organisms. For example, Ce^{4+} is less available than Ce^{3+} in oxidizing conditions (Kabata-Pendias and Pendias, 1992). Consequently, these changes of oxidation states modify their biogeochemical behaviour in the environment and cause positive or negative anomalies of Eu or Ce compared to the other REE. The Eu and Ce anomalies (Ce^* and Eu^*) are calculated as follows (McLennan, 1989; Leleyter et al., 1999) by normalizing the REE concentrations to PAAS values:

$$Ce^* = Ce_N / (2La_N + Nd_N) + 2/3$$

$$Eu^* = Eu_N / (Sm_N \times Gd_N)^{1/2}$$

With X_N = PAAS normalized concentration of the element X.

The anomaly is positive or negative when Ce^* or $Eu^* > 1$ or < 1 respectively.

The REE fractionation between Light REE (LREE) and Heavy REE (HREE) can be assessed by the normalized ratio $(La/Yb)_N$, classically used by the geoscience community. Then, when the ratio is > 1 there is a LREE enrichment and when the ratio is < 1 there is a HREE enrichment.

As seen in Table 2, almost all the sediments present positive Ce anomalies, mainly due to its very low mobility in such environments

Table 2

Ce and Eu anomalies and La/Yb ratios calculated from REE concentrations normalized to PAAS for the bed sediments of the Milo river and its tributaries (1), and for the upstream (2) and downstream (3) stations of Kankan.

Ce & Eu anomalies and Ratios La/Yb		PAAS Normalization		
		Min	Max	Mean
Ce*	1	0.99	1.80	1.07
	2	1.01	1.06	1.03
	3	1.02	1.04	1.03
Eu*	1	0.99	1.27	1.12
	2	0.98	1.13	1.06
	3	1.04	1.15	1.10
(La/Yb) _N	1	0.32	1.62	1.06
	2	0.85	1.32	1.08
	3	1.05	1.51	1.22

1- Milo and tributaries, 2- Milo at Kankan, upstream the city, 3- Milo at Kankan, downstream the city.

because of its strong adsorption onto Mn and Fe-oxides (Braun et al., 1990; Laveuf et al., 2008). This positive Ce anomaly has been shown already by Leleyter et al. (1999) in the sediments of the Piracicaba river draining also lateritic environments, but they clearly demonstrated also that this Ce anomaly in the total sediment could be attributed to the non-residual fraction of Ce adsorbed onto Fe-oxides.

Eu anomalies are also significant (Table 2), particularly for the bed sediments of the upper Milo river and for some tributaries draining the granitic substratum in the upstream part of the basin. Then Eu anomaly is probably derived from the minerals (plagioclase and

orthoclase) of granitic parent rock as already shown by Aubert et al. (2001), due to a substitution of Ca, Sr and Na by Eu, but also from some residual minerals like zircon (Braun et al., 1993).

Concerning the ratio between LREE and HREE calculated from La and Yb normalized concentrations, one can see in Table 3, that there is on average a fractionning and an enrichment in LREE in the sediments of the Milo river basin. As seen previously there is also a fractionning between Kankan upstream and downstream and then, the La/Yb normalized ratio is lower in the upper station where the sediments are more enriched in HREE than in the lower station.

As seen in Fig. 8, there are very good positive relationships between La/Yb normalized ratios and the percentage of Al and Fe-oxides. On the contrary, this relationship is negative with the percentage of silica and cations, except for the Milo and its tributaries where there is no significant relationship. That means that for the Milo river and its tributaries, when the chemical weathering rate of the sediments derived from lateritic soil erosion increases, i.e the percentage of silica and cations decreases while the percentage of Al and Fe-oxides increases, the sediments are progressively enriched in LREE, relative to HREE. These results are comparable to those obtained by Braun et al. (1990) for lateritic profiles in Cameroon, Silva et al. (2016) for the sediments of the lower Catumbela river in Angola, Li et al. (2013) for the sediments of the rivers draining Taiwan and to those of Leleyter et al. (1999) for the sediments of the Piracicaba river which also drains lateritic soils in the Sao Paulo State, Brazil.

Whereas for the Milo at Kankan, the difference one can observe between the upper and the lower stations can not be attributed to chemical weathering fractionning because both stations are controlling the same drainage basin, but rather, as previously mentioned, to

Table 3

Trace element concentrations (Min, Max, Mean) in the sediments (fractions < 63 µm) of the Milo river and its tributaries, compared to PAAS, UCC and SQGs concentrations.

TE (µg.g ⁻¹)	Sediments (< 63 µm) of the Milo river basin, n = 30			PAAS	UCC	SQGs for TE (µg.g ⁻¹)								
	Min	Max	Mean			TEL	ERL	LEL	MEL	PEL	ERM	SEL	TET	CB PEC
Be	1.09	2.87	1.97	–	3									
Sc	12.57	19.76	16.42	16	13.6									
V	78.47	194.80	114.38	150	107									
Cr	80.50	244.00	148.41	110	83	37.3	80	26	55	90	145	110	100	111
Co	7.07	33.44	18.24	23	17									
Ni	20.23	83.65	44.46	55	44	18	30	16	35	36	50	75	61	48.6
Cu	22.06	50.96	37.81	50	25	35.7	70	16	28	197	390	110	86	149
Zn	35.11	93.00	69.12	85	71	123	120	120	150	315	270	820	540	459
Ga	14.63	34.31	26.80	17.5	17									
Ge	1.32	1.84	1.63	–	1.6									
As	1.51	14.46	2.92	–	1.5	5.9	33	6	7	17	85	33	17	33
Rb	27.30	76.18	59.32	160	112									
Sr	24.10	139.90	74.01	200	350									
Y	20.95	58.09	35.31	27	22									
Zr	551.30	3526.00	1540.75	210	190									
Nb	18.97	43.47	26.61	19	12									
Mo	0.63	3.18	1.17	–	1.5									
Cd	0.31	2.10	0.91	–	0.98	0.6	5	0.6	0.9	3.53	9	10	3	4.98
In	0.07	0.09	0.08	–	0.5									
Sn	2.03	4.00	2.73	–	5.5									
Sb	0.21	1.03	0.37	–	0.2									
Cs	1.08	3.49	2.20	15	4.6									
Ba	126.20	1049.00	597.54	650	550									
Hf	13.69	94.94	41.22	–	5.8									
Ta	1.37	4.07	2.21	–	1									
W	0.70	3.87	1.76	–	2									
Pb	12.83	33.19	25.83	20	17	35	35	31	42	91.3	110	250	170	128
Bi	0.12	0.35	0.18	–	0.13									
Th	13.05	48.43	28.05	14.6	10.7									
U	3.48	13.33	6.50	3.1	2.8									

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).

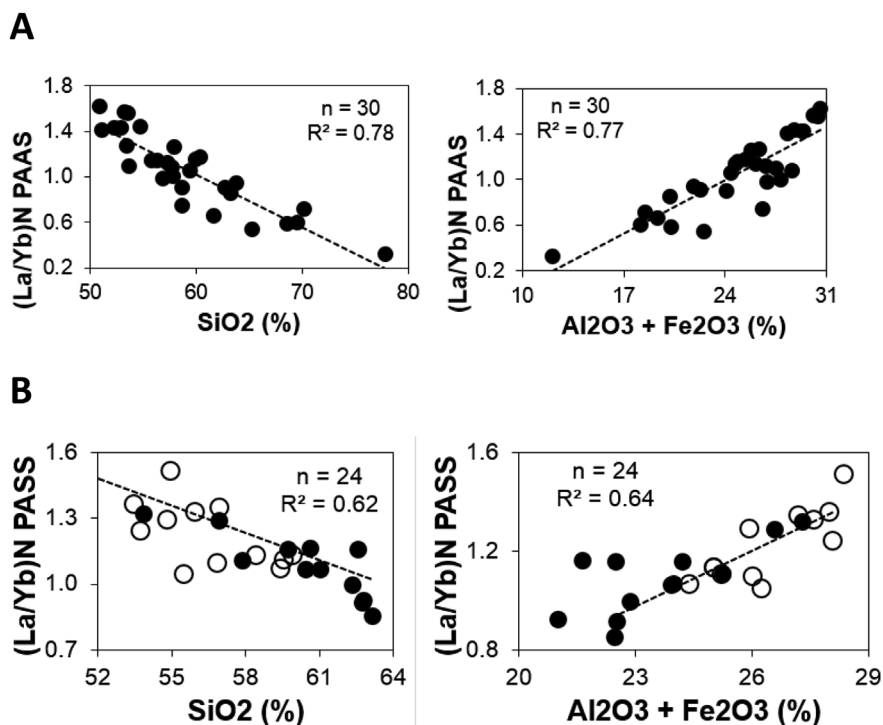


Fig. 8. Relationships between the PAAS normalized ratios La/Yb and the percentages of silica, and aluminium plus iron oxides in the sediments of the Milo river and its tributaries (A) and of the Milo river at Kankan (B), upstream (black circles) and downstream (white circles) the city.

granulometric distribution of the particles which are finer (higher % of clay fractions) downstream than upstream, i.e. lower percentage of silica and higher percentage of Al and Fe-oxides in the lower sediments.

Finally it is important to underline that there is no impact of the anthropogenic activities of Kankan city on the granulometric distribution of the particles in the Milo river bed sediments, even if we have some artisanal sand extraction in the lower station. The differences that can be observed between upstream and downstream the city are mainly due to « natural » sedimentation processes of the finest particles downstream the city. Consequently this difference has also an impact on the REE concentrations and distribution patterns in the sediments, with lower HREE normalized concentrations, higher La/Yb normalized ratios and higher Eu anomalies in the downstream station. It is also well known that in non-carbonated environments, the HREE are preferentially complexed by residual mineral (Cao et al., 2001; Compton et al., 2003) which are more abundant in the upstream station where silica contents in the sediments are higher.

3.3. Other trace element (TE) composition

3.3.1. Total TE concentrations

The TE concentrations in the Milo river bed sediments are greatly variable according to the element and vary from 10^{-2} – $10^3 \mu\text{g g}^{-1}$ (Table 3), the less concentrated being In and the most abundant being Zr and Ba (Fig. 9). If the TE are ranked in decreasing order of their concentrations in the Milo sediments (10 first TE: Zr > Ba > Cr > V > Sr > Zn > Rb > Ni > Hf > Cu > ...) and compared with the PAAS and UCC concentrations (10 first for PAAS: Ba > Zr > Sr > Rb > V > Cr > Zn > Ni > Cu > Y > ...), we can observe that this order of abundance presents some differences, particularly for Zr, Cr, Sr, Rb and Hf. Nevertheless, the Milo sediments present the same patterns (Fig. 9) than the PAAS and UCC distributions, except for some elements like Rb, Sr, Ba and Cs (less abundant), As, Sb, Zr, Hf, Th and U (more abundant).

The same patterns can be observed for upper and lower stations of the Milo at Kankan and there is a very good relationship between upper

TE concentrations and lower ones ($Y = 0.9654 X^{0.9971}$ with $R^2 = 0.9957$), contrary to what we could observed for HREE. That means also that there is no or few impact of the anthropogenic activities of Kankan city on trace element concentrations in the Milo River bed sediments.

3.3.2. TE enrichment factor (EF)

TE in river bed sediments originate mainly from soil/bedrock weathering and anthropogenic sources. The concept of “enrichment factor” (EF) was developed in the seventies (Chester and Stoner, 1973) to evaluate the anthropogenic contribution. Originally applied to atmosphere and sea water, EF was gradually extended to continental environments, such as soils (Hernandez et al., 2003) or river sediments (Tam and Yao, 1998; N’Guessan et al., 2009). It is defined as the concentration ratio of a considered element to a reference element in a given sample, divided by the same ratio in earth’s crust (Chester and Stoner, 1973).

$$EF = (X/Y)_{\text{sample}} / (X/Y)_{\text{reference material}}$$

With X = concentration of the considered TE; Y = concentration of the reference element.

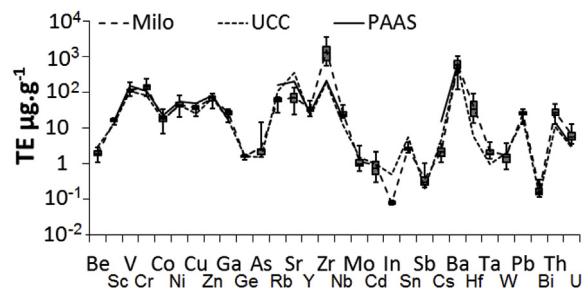


Fig. 9. Trace element concentration patterns for the river bed sediments of the Milo and its tributaries. Comparison with the PAAS and UCC pattern distributions.

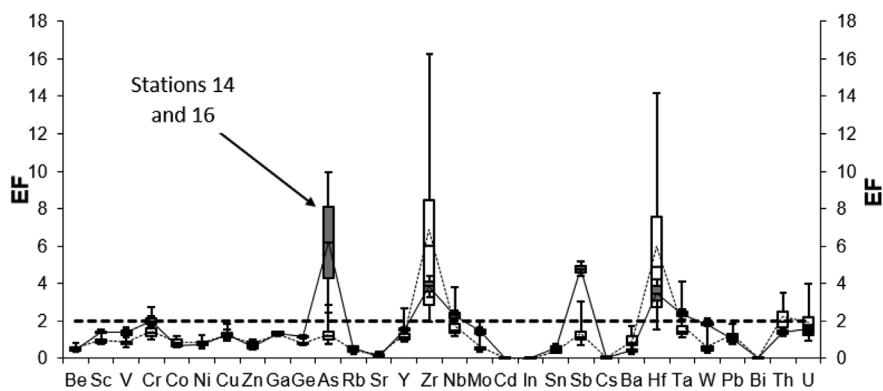


Fig. 10. Distribution patterns of the Enrichment Factor (EF) for all the stations (except 14 and 16) of the Milo river basin (in white) and for 2 tributaries (in grey), the Kounankoro river at station 14 and the Debekoro river at station 16, which drain the urban agglomeration of Kankan. Mean, Min and Max EF are calculated for each TE using PAAS as reference material and Al as reference element. The horizontal dotted line (EF = 2) represents the geochemical naturel background compared to the PAAS.

To normalize TE concentrations, the authors often used the earth crust (UCC from Taylor and Mc Lennan, 1985), as a reference material (Soto-Jimenez and Paez-Osuna, 2001; Pekey, 2006) since it is generally accepted by the scientific community. This normalization is quite correct for large river basins like the Amazon or the Congo river (Gaillardet et al., 1995), where there are various rock outcrops, but for smaller catchments it did not reflect local or regional bedrock chemical composition (Reimann and De Caritat, 2005). Indeed, some authors have tried to circumvent this handicap by using local background values (Hernandez et al., 2003; N'Guessan et al., 2009) and by comparing to calculation using earth crust reference. But, the composition of regional bedrocks is rarely known as it is the case for the river Milo basin. Consequently, it is more appropriate to normalize the Milo river sediments to the composition of shale composites (NASC from Gromet et al. (1984) or PAAS from Taylor and Mc Lennan (1985)) which are classically used for stream sediments (Leleyter et al., 1999; Roussiez et al., 2006; N'Guessan et al., 2009; Benabdelkader et al., 2018) rather than UCC.

The choice of the reference element is constrained by some requirements (Luoma, 1990): (1) the occurrence of a linear relationship between this reference element and the TE; (2) this element must be stable and not submitted to biogeochemical processes such as reduction/oxidation, adsorption/desorption, and diagenetic processes that may alter its concentration (i.e. it must be mainly located in the residual fraction, see section 3.3.3); and finally, (3) it must be of natural origin and its concentration ratio with TE must be conservative during chemical weathering processes. In the literature, Al (Windom et al., 1989; Benabdelkader et al., 2018), Ti (Galuszka and Migaszewski, 2011), Li (Loring, 1990), Cs (Ackermann, 1980; Roussiez et al., 2005; N'Guessan et al., 2009), Sc (Grousset et al., 1995; Hernandez et al., 2003), Fe (Chester and Stoner, 1973; Schiff and Weisberg, 1999), Mn (Zoller et al., 1974) and even organic matter content (Hissler and Probst, 2006), have been used as reference elements, leading to various results from an element to another. The choice of a reference element is thus not universal and depends on geological and physicochemical characteristics of the study area (Reimann and De Caritat, 2005).

In our case study, we used Al, Ti and Sc as reference elements because they mainly originating from natural sources and they are very adapted to such lateritic soil environments where kaolinite ($Al_2Si_2O_5(OH)_4$) and aluminium oxides are formed by natural weathering processes. Moreover Ti, Al and Sc are mainly in the residual fractions of the sediments as we could see in section 3.3.3 using EDTA extraction to get the non-residual fractions (less than 1% for Ti and Al, less than 10% for Sc).

Then, Ti is often used as a chemically conservative element of soils for mass-balance weathering rate studies (Sudom and St. Arnaud, 1971; Hutton, 1977). Al is particularly adapted for clayey sediments containing phyllosilicate minerals and Sc is structurally combined in clay minerals, particularly in sediments containing Al-silicates (Dias and Prudêncio, 2007).

The degree of enrichment varies according to EF value. It is generally accepted that $EF < 1.5$ (Soto-Jimenez and Paez-Osuna, 2001; Roussiez et al., 2005) or < 2 (Sutherland 200; Hernandez et al., 2003) reflects natural variability of the chemical and mineralogical composition of the samples. These low EF values can be considered as the natural geochemical background. According to Sutherland (2000), one can classify the degree of enrichment as follows according to EF Values: $2 < EF < 5$ moderate, $5 < EF < 20$ significant, $20 < EF < 40$ very high and $EF > 40$ extreme.

But if one compares the TE concentrations with a non-local reference material, as it is the case here with the PAAS, the enrichments that we obtained can be of course from anthropogenic sources, but also from natural origin due to regional geochemical background which is enriched in some TE compared to UCC or PAAS.

For the Milo river bed sediments (Fig. 10), EF calculated by normalizing the TE to PAAS and using 3 reference elements (Al, Sc and Ti) are within the range of natural geochemical background, except for Zr and Hf which exhibit moderate to significant EF values, but also moderate for U and Th and moderate to significant for As and Sb in two small tributaries (Stations 14 and 16) which drain the urban agglomeration of Kankan (Fig. 10). For these two stations, the sampling points are located under the bridges of the National road 6 (N6). Then the bed sediments of these two stations are clearly impacted by the important vehicle traffic on this road. EF calculated using Sc and Al as reference elements are very close while EF calculated with Ti are lower, particularly for Zr and Hf.

The enrichments one can observed for Zr, Hf, U and Th when compared with the PAAS concentrations can be considered in that case as reflecting the regional geochemical background. On the contrary, the enrichments observed for As and Sb in stations 14 and 16 are due to anthropogenic activities in the urban agglomeration of Kankan. Nevertheless, these 2 small tributaries have no impact on As and Sb enrichments in the sediments of the Milo river, downstream their confluences. Their sediment contributions are diluted by the sediment fluxes of the Milo River.

The regional enrichments that can be observed for Zr, Hf, U and Th in the Milo river bed sediments are mainly due to the geological substratum and to the lateritic soils which have been formed by chemical weathering processes. 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 ore minerals enriched in Zr and Th particularly (Horbe and Da Costa, 1999).

Indeed, these TE are associated with heavy minerals as shown by Vital and Statterger (2000) for the Amazon river sediments. Zr and Hf are derived from Zircon, one of the main weathering-resistant minerals which is accumulated in lateritic soil. Then, there is a very good relationship between Zr and Hf concentrations for all the stations of the Milo river basin ($Y = 35.958 X + 56.755$ with $R^2 = 0.9856$) and for the two stations (upstream and downstream) of Kankan ($Y = 43.543 X -$

Table 4

Average percentages for each TE of the non-residual fractions, ranked by % classes and calculated from the % we got for all the sediments (n = 30 samples) we collected in the Milo river basin.

% non-residual	< 1%	1–5%	5–10%	10–20%
TE	Al, Be, Ti, Cr, Ga, Rb Zr, Nb, Sn, Sb, Cs, Hf Ta, W, U,	V, Fe, Ni, Mo, Cd, Bi, Th	Sc, Zn, Ge, Sr, Ba	Co, Cu, As, Y, Pb

211.16 with $R^2 = 0.9858$).

Then Zr and Hf concentrations are very high in all this kind of weathering profiles like lateritic soils (Horbe and Da Costa, 1999), red bauxites (Esmaily et al., 2009) or even kaolins (Baioumy and Gilg, 2011) which are progressively enriched in less mobile elements (Nb, Th, Zr, Mo, Ga and Cr).

3.3.3. TE distribution between residual and non-residual (labile) fractions

In order to evaluate the distribution of each TE between the residual and the non-residual fractions, we used a single chemical extraction with 10 ml of EDTA (0.05 mol.L^{-1}) on 1 g of sediment (Beckett, 1989; Ghestem and Bermond, 1998; Leleyter et al., 2012). The non-residual fractions represent the sum of the TE which are complexed or adsorbed onto different chemical components and mineralogical phases (clays, carbonates, Mn and Fe-oxides, organic matter) and which could be desorbed/released into the river waters if there is any change of physico-chemical conditions (pH, redox potential, dissolved organic or inorganic ligands ...). Then, these non-residual TE represent a threat for the aquatic ecosystems. On the contrary, the residual fractions include all the TE which are in the mineral lattices or which are very difficult to extract for living organisms, assuming that they represent no threat for the aquatic ecosystems.

There is no relationship between the total concentration of TE and the percentage of its non-residual fraction. Nevertheless, TE released into the river water by anthropogenic activities, are mainly adsorbed, when they are adsorbed, onto the sediments as non-residual phases. Consequently, even if the total TE concentrations are low, it is always important with regard to their potential ecotoxicity in the sediments, to check if the non-residual fractions are important or not. Then, that is the case for the Milo river bed sediments, because one could observe relatively low concentrations when compared to PASS or UCC, except for some elements like Zr, Hf, U and Th which seem to be naturally enriched due to lateritic soil covers and As and Sb for two tributaries close to Kankan city which could originate from anthropogenic activities. It was also important to check and to be sure that the reference elements (Al, Ti and Sc) we used to normalize our sediment concentrations to calculate the enrichment factor, are mainly in the residual fractions.

As seen in Table 4 and Fig. 11, the % of labile fractions is relatively low (< 20%) for all TE, compared with river bed sediments highly impacted by anthropogenic activities like for example, mining activities (Benabdelkader et al., 2018). It is important to note that the reference elements we selected to calculate EF are mainly in the residual fractions (> 99% for Al (Fig. 11) and Ti, > 90% for Sc (Annexe-Fig. 13)). The natural origins of Zr, Hf, U and Th are confirmed by the very low percentages of non-residual fractions (Annexe-Fig. 13). On the contrary, As which is enriched for some tributaries located around the Kankan city agglomeration is relatively more distributed in the non-residual

fractions (10–20%).

As already described previously, the TE from anthropogenic sources are fixed/adsorbed onto the sediments as non-residual phases and they can be desorbed/released into the river water column if the physico-chemical conditions change. Then, Assaker (2016) could observe in the bed sediments of the Ibrahim river in Lebanon, a good positive relationship between the enrichment factor (EF) and the percentage of labile fractions for Co, Ni, Zn and Pb which are mainly originating from anthropogenic activities, while for Zr which is of natural origin, this relationship is negative. For the Milo river, one can observe the same kind of results for the bed sediments in which Zr ($Y = 1.1956x^{-0.463}$ with $R^2 = 0.8997$) and Hf present negative relationships between EF and % labile TE, and positive linear relationships for other TE like Co ($Y = 0.1298x + 0.5178$ with $R^2 = 0.7287$), Sb, Zn, Cd, Pb and Cu.

3.3.4. 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 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 Milo 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 2), one can see that, except Cr, our total TE concentrations are lower (Cu, Zn, Cd, Pb) than the SQGs or within the range (Ni, As) of the SQGs.

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 threat to aquatic ecosystems present very low values (see Table 4: less than 20% of the total concentration for Co, Cu, As and Pb, < 10% for Zn, < 5% for Ni and Cd, < 1% for Cr) in the case of the bed sediments of Milo river basin. Then, the total TE concentrations could be divided by 5 for Co to 100 for Cr 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 for which the total concentration is over the SQGs.

4. Conclusion

For the first time, the river bed sediments of the Milo drainage basin, upper tributary of the Niger, could be analyzed in this study. The sampling strategy, both spatial and temporal, we set up in this study to assess the variability of the chemical composition of the sediments

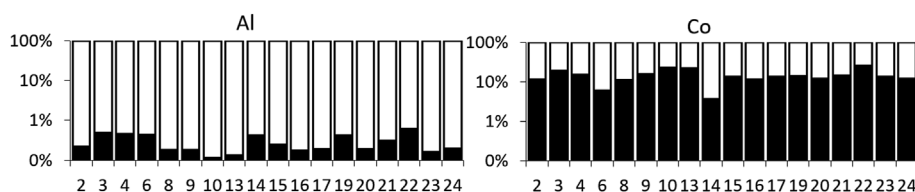


Fig. 11. Distributions (%) of two selected TE (Al and Co) between residual (white) and non residual (black) fractions for the river bed sediments collected at the different stations in Milo river basin. See also Annexe-Fig. 12 for Ti, Zr, U, Zn, Pb and As.

within the catchment during the 2014 campaign and its seasonal variability upstream and downstream the city of Kankan during the hydrological year 2014–2015 allowed us to exhibit some very important results:

- The geochemical signature (major, trace and rare earth elements) of the fluvial sediments is relatively homogeneous within the catchment and highly controlled by the geological substratum (granites and schists) and the lateritic soil cover, even if one can observe some differences between the upper and the lower Milo and its tributaries. Then it appears clearly that there is no impact of any artisanal mining activities on the quality of the fluvial sediments.
- The chemical composition of the Milo river bed sediments is characteristic of a catchment draining lateritic soils with higher concentrations in Zr, Hf, U and Th than the PAAS signature and consequently, high enrichment factors for this TE, due to this regional geochemical background.
- The distribution patterns of REE in the bed sediments are also controlled by the lateritic soils with enrichment in LREE et HREE and lower concentration in MREE, Ce and Eu positive anomalies which are characteristics of fluvial sediments produced by physical erosion of lateritic soils.
- No anthropogenic impact of the Kankan city agglomeration could be measured on the chemical composition of the Milo river bed sediments, except for As and Sb in two small tributaries close to Kankan. Then, there is no enrichment in TE between upstream and downstream the city.
- The seasonal variations one can measure upstream and downstream Kankan city shows that the geochemical signature of the river bed sediments varies few even if the TE concentrations and the granulometric distributions of the particles vary, except for HREE which are impoverished in the lower stations due to finest particles and to higher concentrations in Al and Fe-oxides.

- The percentage of non-residual fractions (i.e. labile phases) for most of TE are relatively low (< 20%) compared with polluted catchment. Consequently these TE concentration levels are globally under the Sediment Quality Guidelines and the enrichment rates represent no threat for the aquatic ecosystems of the Milo River.
- Even if the % of non-residual is low, there is a good positive relationship between this % and the enrichment factor, except for Zr, Hf and Cr for which the relationship is decreasing.

It would be interesting now to measure the chemical concentration of the suspended matter and to follow their seasonal fluctuations in order to estimate their flux contribution to the Niger suspended loads. It would be also important to compare the suspended load with the dissolved load and to calculate for each TE the partitioning coefficient between the two phases and the factors that are controlling this distribution.

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ANNEXES

Table 5
Characteristics of the different sampling stations on the Milo and its tributaries.

Station number	River	Station name	Altitude m	Latitude °N	Longitude °W
1	Milo	Mamadidou	506	9.12652	9.03064
2	Baoule	Banankoro	670	9.19928	9.28706
3	Milo	Fankono	474	9.53247	9.16906
4	Baoule-Milo*	Fankono	474	9.54542	9.13898
5	Milo	Leckro	462	9.62994	9.14854
6	Djassa	Frankonedoukoro	479	9.66509	9.09596
7	Milo	Komana	467	9.70588	9.14138
8	wassa	Fabala	493	9.73463	9.07252
9	Milo	Lelen	470	9.74692	9.13302
10	Wan	Moribaya	418	9.87582	9.54807
11	Milo	Morigbèdou	376	10.14158	9.39210
12	Diaman-Milo*	Koura kignebala	376	10.15576	9.37590
13	Milo	Boussoura	360	10.34340	9.34395
14	Kounankoro	Kounankoro	373	10.35864	9.36808
15	Milo	Kankan Bordo	370	10.36656	9.33713
16	Debekoron	Kankan Bordo	373	10.38576	9.34831
17	Milo	Kankan	361	10.36540	9.29620
18	Milo	Karifamoriah	368	10.41450	9.26621
19	Limbo	Kotèro	364	10.40375	9.22826
20	Limbo-Milo*	Kotero	373	10.41923	9.23057
21	Djesse	Kobako	361	10.64630	9.18285
22	Milo	Bate Nafadji	358	10.66670	9.24847
23	Koba-Milo*	Bate Kofilani	354	10.78739	9.22181

(continued on next page)

Table 5 (continued)

Station number	River	Station name	Altitude m	Latitude °N	Longitude °W
24	Milo-Niger*	Djelibakoro	348	11.07700	-9.23054

*Confluences between two rivers.

Annexes

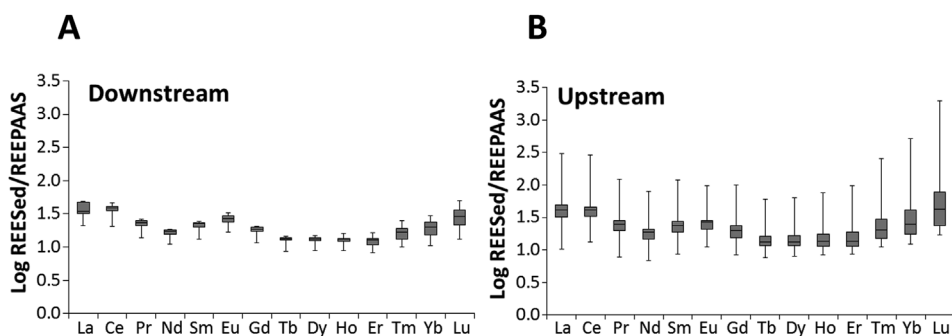


Fig. 12. Average distribution patterns of REE concentrations (monthly samples during one year) normalized by the PAAS concentrations, in the bed sediments of the Milo river basin at Kankan, upstream (A) and downstream (B) the city. Means, medians and standard deviations.

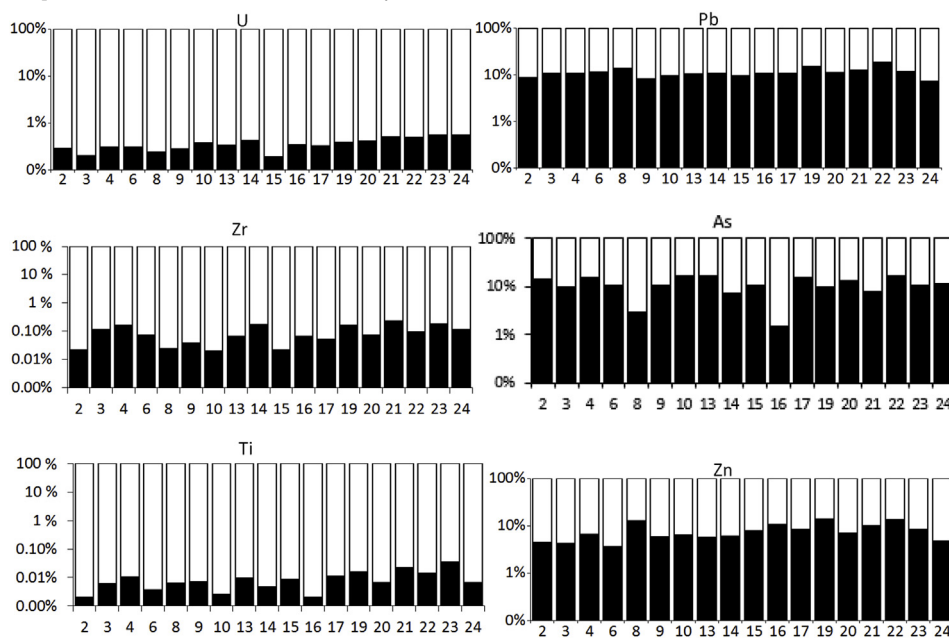


Fig. 13. Distributions (%) of some selected TE between residual (white) and non residual (black) fractions for the river bed sediments collected at the different stations in Milo river basin. Left column: low % for reference element (Ti) and TE from natural origins (Zr and U). Right column: higher % for TE naturally more labile (Zn and Pb) and for TE from anthropogenic activities (As).

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