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Trace Metal Contamination of Sediments in Naviundu River Basin, Luano and Ruashi Rivers and Luwowoshi Spring in Lubumbashi City, Democratic Republic of Congo

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Abstract: As (Arsenic), Ba (Barium), Cr (Chromium), Cu (Copper), Fe (Iron), Mne (Manganese), Pb (Lead) and Zn (Zinc) concentrations were investigated in sediments collected from fifteen sampling locations in Naviundu river basin, Luano and Ruashi rivers and Luwowoshi spring in Lubumbashi city from February to April 2016. Chemical analyses of the samples were carried out using a portable X-ray fluorescence spectrometer. Mean pH values ranged from 4.2 to 5.8. The sediment highest mean levels of As (40 $mg \cdot kg^{-1} \cdot dw$) and Cu (3,723 $mg \cdot kg^{-1} \cdot dw$) were noted in Chemaf (Chemicals of Africa) hydrometallurgical plant effluent, those of Pb (51.5 $mg \cdot kg^{-1} \cdot dw$) and Zn (335 $mg \cdot kg^{-1} \cdot dw$) were recorded in Kabecha river and those of Ba (657.5 $mg \cdot kg^{-1} \cdot dw$), Cr (75 $mg \cdot kg^{-1} \cdot dw$), Mn (591 $mg \cdot kg^{-1} \cdot dw$) and Fe (88,450 $mg \cdot kg^{-1} \cdot dw$) were respectively found in Naviundu river at Cimenkat (Katanga's Cement factory) exit, Naviundu river under bridge on De Plaines avenue, Mukulu river and Foire channel. Mean As, Cu and Zn levels of sediments exceeded the corresponding SQGs (Sediment Quality Guidelines), PELs (Probable Effect Levels) in some of the studied rivers. They could have adverse effects on aquatic organisms in those rivers and on the health of people who depend on the rivers for water supply, irrigation and/or recreation.

Key words: Trace metals, pH, sediments, effluent, rivers, spring, Lubumbashi.

1. Introduction

Water quality deterioration from heavy metal pollution is a major issue of concern in the D.R. Congo Copperbelt, particularly given the considerable environmental legacy from 100 years of intensive industrial scale mining [1]. In the D.R. Congo Copperbelt, which includes the provinces of Upper-Katanga and Lualaba, and in other eastern D.R. Congo provinces such as Ituri, Maniema, North-Kivu, South-Kivu and Tanganyika, atmosphere, soils, surface waters, sediments and groundwater are severely contaminated with trace metals and other contaminants as a result of abandoned and ongoing artisanal and industrial mining and ore processing activities [2-9]. In many locations in those provinces, mining is typically done through artisanal mining which is a

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small scale mining method that takes place in river beds and it can be very environmentally damaging. Artisanal mining destroys landscapes and degrades riparian zones, creating erosion and heavy silting of the water [10]. Moreover, the tailings are often dumped into the rivers and could be contaminated with mercury and cyanide, thus degrading the health of the river systems and putting the wildlife and people at risk [10-12]. As sediments have a high storage capacity of chemical pollutants [10, 11], trace metals accumulated in sediments may persist in the environment long after their primary source has been removed [12] and create a potential for continued environmental degradation [7, 9-12] even where water column contaminant levels comply with established water quality criteria [11]. Indeed, resuspension events from natural or anthropogenic origin can disturb the biogeochemistry of sediments and potentially result in the remobilization of trace metals from sediment particles to the water column [7, 8, 13, 14]. Sediment-associated trace metals represent a risk for organisms living in the sediments and in the water column, especially invertebrates and fish, but also for humans through human food chain [1, 3, 8, 15-17].

The current study aims to investigate trace metal contamination of sediments in Naviundu river basin, Luano and Ruashi rivers and Luwowoshi spring in Lubumbashi city and to compare the sediment metal levels with the SQGs (Sediment Quality Guidelines)—TELs (Threshold Effect Levels) and PELs (Probable Effect Levels)—for freshwater sediments [18] to know the risk of the sediment trace metal toxicity to aquatic organisms. No such an assessment was previously carried out in Naviundu river basin, Luano and Ruashi rivers and Luwowoshi spring.

2. Material and Methods

2.1 Study Area and Sampling Locations

The study area encompasses various water courses of Naviundu river basin as well as Luano and Ruashi rivers and Luwowoshi spring in Lubumbashi city. Luwowoshi spring is the source of Ruashi river. The Naviundu river basin includes Naviundu, Kabesha, Kalulako, Kamasaka, Ma-Vallee and Mukulu rivers, Foire channel and Chemaf (Chemicals of Africa) hydrometallurgical plant effluent. Kamasaka and Mukulu rivers are tributaries of Naviundu river which is in turn a tributary of Kafubu river. All those water courses flow through Lubumbashi, the capital city of the Upper-Katanga province in south-eastern D.R. Congo (Fig. 1).

Surface sediment samples of 25-centimeter depth were collected from twelve sampling sites in the Naviundu river basin (sample and sampling site codes 21 SD (Sediment), 22 SD, 23 SD to 32 SD) and from one site in each of Luano river (33 SD), Ruashi river (34 SD) and Luwowoshi spring (35 SD) during February, March and April 2016 sampling campaigns. Of the fifteen sampling sites, five were in Naviundu river and one in each of the other rivers, channel and effluent (Fig. 1).

The samples were collected using a sediment corer and they were stored in clean plastic bags rinsed three times with the water overlying the sediment to be sampled. A sample code as well as the sampling site and the sampling date were written on each bag containing the collected sample. To prevent the sample code, sampling site and date from being erased, a transparent plastic sticker was stuck on each plastic bag. Geographic coordinates of each sampling location were determined using a Garmin Etrex GPS and later on they were used for elaborating the map of sampling locations (Fig. 1).

2.2 Sample Preservation

After collection, the samples were immediately taken to the laboratory where they were stored in a deep freezer. Later on, they were thawed and dried in an oven at 35 °C for 5 days [19]. They were then grinded in a porcelain mortar and sieved trough a

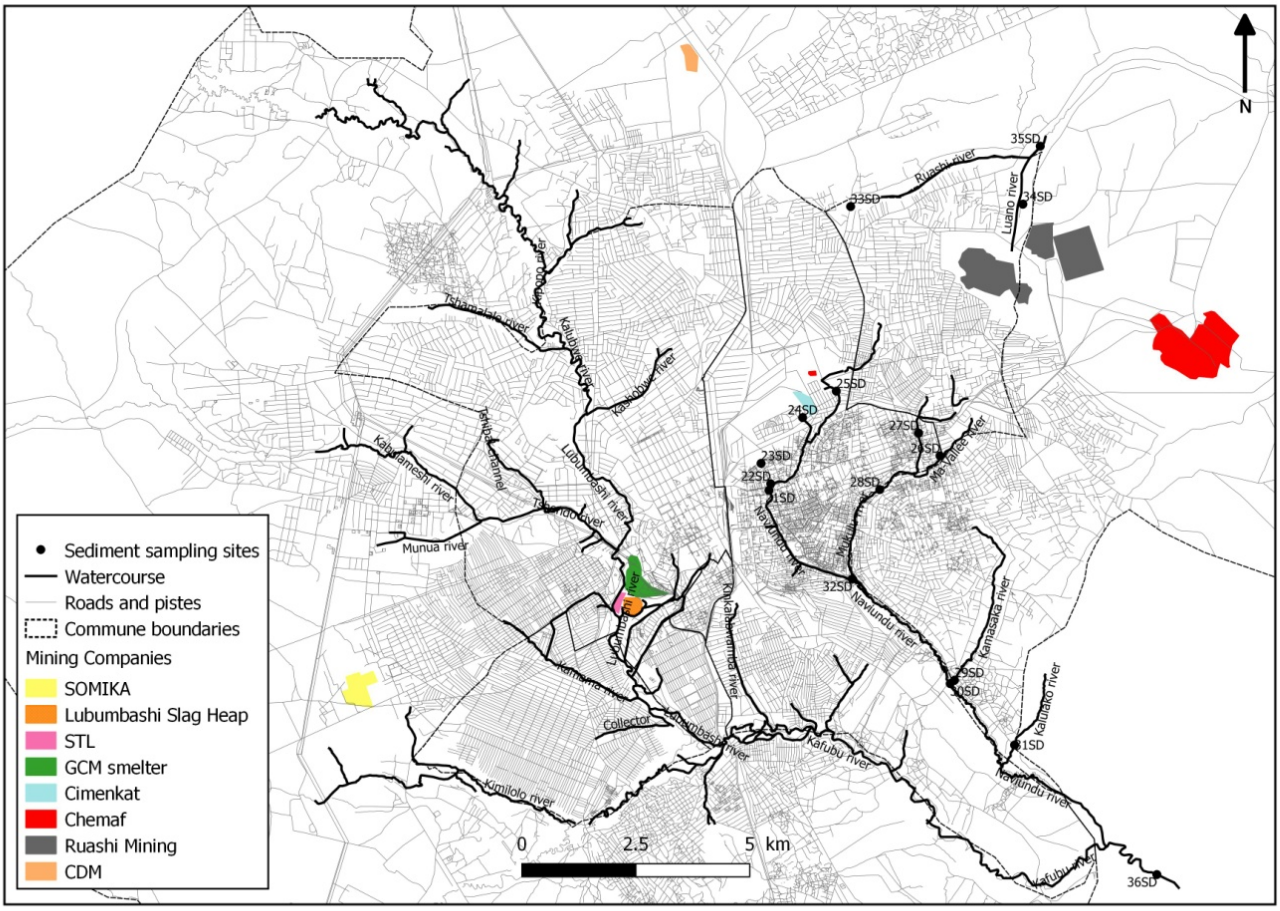

Fig. 1 Map of sediment sampling locations in Naviundu river basin, Luano and Ruashi rivers and Luwowoshi spring in Lubumbashi city during February, March and April 2016.

2-mm sieve to obtain fine grain size. The grinded and sieved samples were then stored into 25-mm diameter sealed glass vials [X-RFS (X-Ray Fluorescence Spectrometer) sample cells] until they were analyzed for trace metals' content.

2.3 Analytical Method

The sediment samples were analyzed using an X-RFS. The accuracy and precision of the X-RFS measurements were evaluated by analyzing a standard reference material (soil). That indicated an acceptable quality of this method as a screening tool.

3. Results and Discussion

Mean water pH values of the sediment samples and mean concentrations of eight trace metals including As, Ba, Cr, Cu, Fe, Mn, Pb and Zn ($mg \cdot kg^{-1} \cdot dw$) at different sampling locations as well as the SQGs' TELs and PELs values [18] are presented in Table 1. Mean water pH values were very low and ranged from 4.2 to 4.9 respectively in Naviundu river at its confluence with Kamasaka river (4.2), Kalulako river (4.6), Naviundu river at the exit of Cimenkat (Katanga's Cement Factory) (4.7), Luano river (4.8) and Naviundu river at its confluence with Mukulu river (4.9) (Table 1, Fig. 2). The pH mean values were low in the other sampling locations and ranged from 5.1 to 5.8 respectively in Naviundu river under bridge on De Plaines avenue as well as Ma-Vallee river (5.1), Naviundu river under bridge on Kasenga road, Kabecha river, Kamasaka river as well as Ruashi river (5.3), Mukulu river (5.5), Foire channel (5.7) and Chemaf hydrometallurgical plant effluent as well as Luwowoshi spring (5.8) (Table 1, Fig. 2). The low pH

Table 1 Mean trace metal concentrations in sediments (mg·kg^{-1}·dw) of Naviundu river basin, Luano river, Ruashi river and Luwowoshi spring in Lubumbashi city during February, March and April 2016.

Sampling site	Sample code	pH water	As (mg/kg/dw)	Ba (mg/kg/dw)	Cr (mg/kg/dw)	Cu (mg/kg/dw)	Mn (mg/kg/dw)	Pb (mg/kg/dw)	Zn (mg/kg/dw)	Fe (mg/kg/dw)
	SQGs									
	TELs	Na	5.9	Na	37.3	35.7	Na	35	123	Na
	PELs	Na	17.0	Na	90.0	197	Na	91.3	315	Na
Naviundu river under bridge on De Plaines avenue	21 SD	5.1	ND	542	75	ND	ND	ND	ND	39,900
Naviundu river under bridge on Kasenga road	22 SD	5.3	ND	429	ND	1,254	264	48	321	63,000
Naviundu river at Cimenkat exit	23 SD	4.7	ND	657.5	38	149.5	76.5	ND	46.5	39,050
Chemaf hydrometallurgical plant effluent	24 SD	5.8	40	216	ND	3,723	93	36	ND	59,000
Kabecha river	25 SD	5.3	20	141.5	ND	470.5	154	51.5	335	32,050
Ma-Vallee river	26 SD	5.1	ND	544.5	24	227.5	199	ND	44.5	33,000
Foire channel	27 SD	5.7	ND	591.5	ND	104	222.5	ND	36	88,450
Mukulu river	28 SD	5.5	ND	512	56	540	591	ND	71	26,700
Kamasaka river	29 SD	5.3	18	248	56	151	162	ND	ND	45,700
Naviundu river at its confluence with Kamasaka river	30 SD	4.2	ND	305.5	69	529.5	148.5	ND	232.5	20,300
Kalulako river	31 SD	4.6	ND	461.5	58.5	142.5	142.5	34	56.5	31,550
Naviundu river at its confluence with Mukulu river	32 SD	4.9	ND	431	61.5	36	82	24	33	17,650
Luano river	33 SD	5.3	ND	426.5	ND	791.5	240	ND	150.5	38,600
Ruashi river	34 SD	4.8	ND	326	69.5	762.5	221	ND	48	12,300
Luwowoshi spring	35 SD	5.8	ND	453	67	167	111	ND	ND	9,700

Chemaf: Chemicals of Africa; Cimenkat: Katanga's cement factory; dw: dry weight; Na: no available data; ND: Not Detected; PELs: Probable Effect Levels refer to concentration levels above which adverse effects are likely to occur; SD: Sediment; SQGs: Sediment Quality Guidelines (Canadian Council of Ministers of the Environment, 2001); TELs: Threshold Effect Levels represent concentrations below which a toxic effect on aquatic organisms will rarely occur.

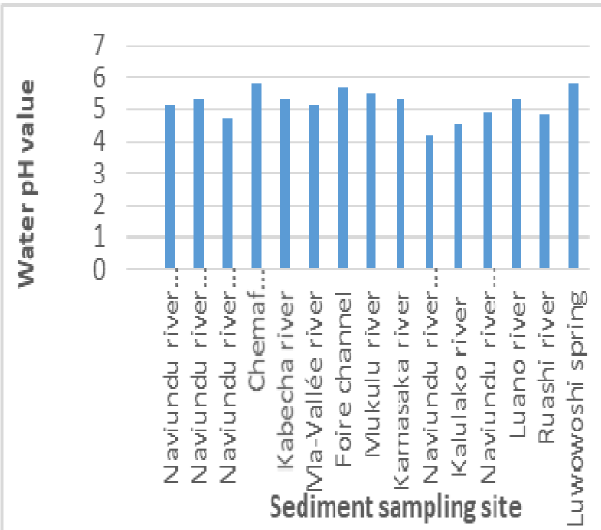

Fig. 2 Mean water pH values of sediment samples from Naviundu river basin, Luano and Ruashi rivers and Luwowoshi spring in Lubumbashi city during February, March and April 2016.

increases metal bioavailability to aquatic organisms [6, 7, 20, 21] living in the rivers, channel and spring and to human beings who depend on those waters to meet their domestic, irrigation and recreational needs. It has been reported that mobilization of Al, Fe, Zn, Co, Pb and Cu increases with acidification and that acidification also influences the speciation of metals, transforming metals and metalloids, like As, into species much more toxic to biota [21].

Mean metal concentrations in sediments ranged from not detected in various rivers, channel and spring to 40 mg·kg^{-1}·dw in Chemaf hydrometallurgical plant effluent for As, from 141.5 mg·kg^{-1}·dw in Kabecha river to 657.5 mg·kg^{-1}·dw in Naviundu river at Cimenkat (Katanga's cement factory) exit for Ba and from not detected in Naviundu river under bridge on

Kasenga road, Chemaf hydrometallurgical plant effluent, Kabecha river, Foire channel and Luano river to 75 mg·kg^{-1}·dw in Naviundu river under bridge on De Plaines avenue for Cr. Sediment mean levels of Cu ranged from not detected in Naviundu river under bridge on De Plaines avenue to 3,723 mg·kg^{-1}·dw in Chemaf hydrometallurgical plant effluent, those of Mn from not detected in Naviundu river under bridge on De Plaines avenue to 591 mg·kg^{-1}·dw in Mukulu river, those of Pb from not detected in various rivers, channel, effluent and spring to 51.5 mg·kg^{-1}·dw in Kabecha river, those of Zn from not detected in Naviundu river under bridge on De Plaines avenue, Chemaf hydrometallurgical plant effluent, Kamasaka river and Luwowoshi spring to 335 mg·kg^{-1}·dw in Kabecha river and those of Fe ranged from 9,700 mg·kg^{-1}·dw in Luwowoshi spring to 88,450 mg·kg^{-1}·dw in Foire channel (Table 1, Figs. 3-6).

Sediment mean As levels in Chemaf hydrometallurgical plant effluent (40 mg·kg^{-1}·dw), Kabecha river (20 mg·kg^{-1}·dw) and Kamasaka river (18 mg·kg^{-1}·dw) exceeded the SQGs' PEL value (17 mg·kg^{-1}·dw), suggesting that aquatic organisms living in those effluent and rivers are at high risk related to their exposure to As. Similar As exposure risk was reported for aquatic organisms dwelling in Lubumbashi river at its confluence with Tshondo river (37 mg·kg^{-1}·dw), Munua river (29.5 mg·kg^{-1}·dw), Tshondo river (23.5 mg·kg^{-1}·dw), Kimilolo river (22 mg·kg^{-1}·dw), Kafubu river 1.36 km downward its confluence with Naviundu river (21.5 mg·kg^{-1}·dw) and Kamama river (17 mg·kg^{-1}·dw) [7]. It was reported that As can adsorb on various solid phases encountered in sediments, including aluminum, iron and manganese (hydr)-oxides, clays and organic matter and that the distribution between the liquid and the solid phases depends on arsenic concentration, arsenic speciation, competing ions, pH and adsorption properties of the solid surface, e.g. coating or isomorphic substitution [22, 23]. At pH 4, it was experimentally shown that the affinity of As(V) for several minerals decreases as follows: iron (hydr)-oxides (40 to 2,100 mmol·kg^{-1})-aluminum (hydr)-oxides (20 to 1,700 mmol·kg^{-1}) > manganese (hydr)-oxides (16 mmol·kg^{-1}) > aluminosilicates (0.4 to 0.5 mmol·kg^{-1}). The results confirmed that Fe and Al (hydr)-oxides are the main host phases for As(V) adsorption in sediments [24, 25]. Sorption processes of As(III) are more complex because $H_3As^{+III}O_3$, which is the main species at pH 5-9, is electrically neutral. As(III) essentially adsorbed on iron (hydr)-oxides, and its adsorption is not pH-dependent

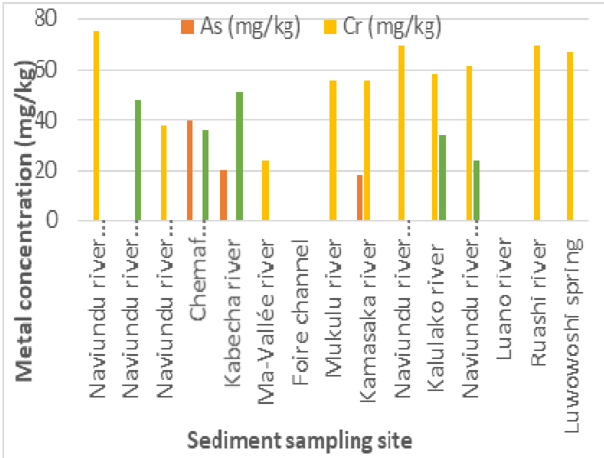

Fig. 3 Mean concentrations of As, Cr and Pb in sediment samples (mg·kg^{-1}·dw) from Naviundu river basin, Luano and Ruashi rivers and Luwowoshi spring in Lubumbashi city during February, March and April 2016.

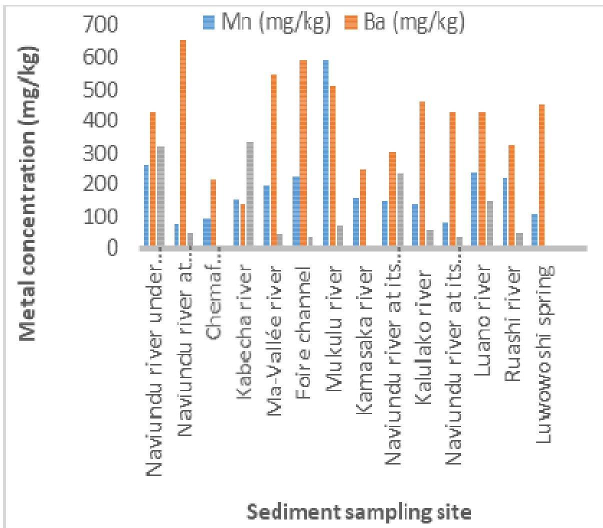

Fig. 4 Mean concentrations of Mn, Ba and Zn in sediment samples (mg·kg^{-1}·dw) from Naviundu river basin, Luano and Ruashi rivers and Luwowoshi spring in Lubumbashi city during February, March and April 2016.

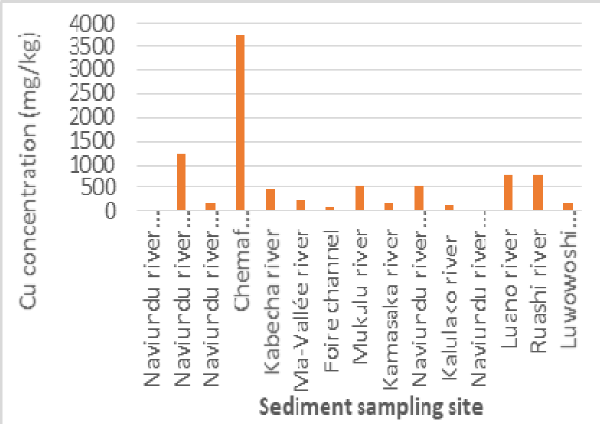

Fig. 5 Mean concentrations of Cu in sediment samples (mg·kg^{-1}·dw) from Naviundu river basin, Luano and Ruashi rivers and Luwowoshi spring in Lubumbashi city during February, March and April 2016.

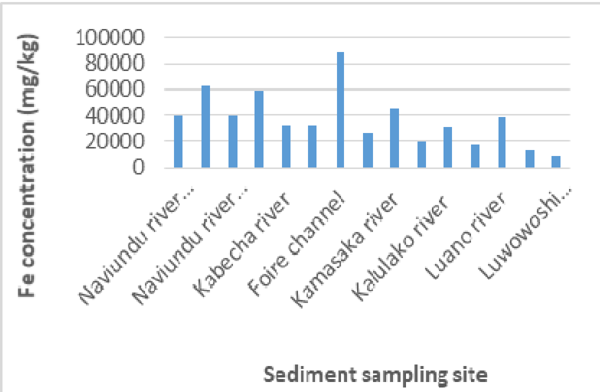

Fig. 6 Mean concentrations of Fe in sediment samples (mg·kg^{-1}·dw) from Naviundu river basin, Luano and Ruashi rivers and Luwowoshi spring in Lubumbashi city during February, March and April 2016.

and not as strong as As(V). It has also been shown that whatever the pH, inorganic As(V) remains the most impacted species by sorption processes with a retention capacity on minerals that decreases in acidic media [23]. Other sediment metal levels exceeding the SQGs' PELs values [18] in this study are Cu in Chemaf hydrometallurgical plant effluent (3,723 mg·kg^{-1}·dw), Naviundu river under bridge on Kasenga road (1,254 mg·kg^{-1}·dw), Luano river (791.5 mg·kg^{-1}·dw), Ruashi river (763.5 mg·kg^{-1}·dw), Mukulu river (540 mg·kg^{-1}·dw), Naviundu river at its confluence with Kamasaka river (529.5 mg·kg^{-1}·dw), Kabecha river (470.5 mg·kg^{-1}·dw) and Ma-Vallee river 227.5 mg·kg^{-1}·dw), and Zn in Kabecha river (335 mg·kg^{-1}·dw) and Naviundu river under bridge on Kasenga road (321 mg·kg^{-1}·dw) (Table 1; Figs. 4 and 5). Except Naviundu river sediments under bridge on Kasenga road, Kabecha and Luano rivers, Foire channel and Chemaf hydrometallurgical plant effluent sediments in which Cr was not detected and Ma-Vallee river sediment where Cr level was 24 mg·kg^{-1}·dw, Cr concentrations in sediments of all the other rivers were higher than the SQGs' TEL value of 37.3 mg·kg^{-1}·dw but they were lower than the PEL value of 90.0 mg·kg^{-1}·dw [18]. Pb concentrations in sediments of Kabecha river (51.5 mg·kg^{-1}·dw), Naviundu river at Cimenkat exit (48 mg·kg^{-1}·dw) and Chemaf hydrmetallurgical plant effluent (36 mg·kg^{-1}·dw) (Table 1, Fig. 3) exceeded the SQGs' TEL value of 35 mg·kg^{-1}·dw but they were lower than the SQGs' PEL value of 91.3 mg·kg^{-1} [18]. The mean concentration of Ba recorded in Kabecha river sediment (657.5 mg·kg^{-1}·dw) and that of Mn in Mukulu river sediment (591 mg·kg^{-1}·dw) in the present study were respectively higher than the highest concentrations of those metals (547 mg·kg^{-1}·dw and 531 mg·kg^{-1}·dw) respectively noted in Kinkalabwamba river and Kimilolo river sediments [7]. On the other hand, the highest Cu level of sediment in Chemaf hydrometallurgical plant effluent sediment (3,723 mg·kg^{-1}·dw), those of Cr in Naviundu river sediment under bridge on De Plaines avenue (75 mg·kg^{-1}·dw), Pb in Kabecha river (51.5 mg·kg^{-1}·dw), Zn in Kabecha river sediment (335 mg·kg^{-1}·dw) and were Fe in Foire channel were respectively lower than the levels of Cu in Lubumbashi river sediment 1.45 km downward the Lubumbashi Slag heap (5,438 mg·kg^{-1}·dw), Cr in Kinkalabwamba river sediment (174.5 mg·kg^{-1}·dw), Pb in Kafubu river sediment at its confluence with Lubumbashi river (342 mg·kg^{-1}·dw), Zn in Kafubu river sediment at its confluence with Lubumbashi river (1,534.5 mg·kg^{-1}·dw) and Fe in Kafubu river sediment 1.3 km downward its confluence with Naviundu river (108,900 mg·kg^{-1}·dw) [7]. The highest concentrations of As, Cu, Pb, Fe and

Mn in sediments in this study (Table 1, Figs. 3-6) are also lower than those respectively reported by Atibu, E. K., et al. [3] for As (54.4 $mg \cdot kg^{-1} \cdot dw$), Cu (47,468 $mg \cdot kg^{-1} \cdot dw$), Pb (851.9 $mg \cdot kg^{-1} \cdot dw$) and Fe (34,848 $mg \cdot kg^{-1} \cdot dw$) in sediments at KS-15 sampling site and Mn (1,544 $mg \cdot kg^{-1} \cdot dw$) in sediments at KS-20 sampling site of Luilu and Musonoie rivers which receive mining effluent waters. The metal contamination of sediments of various rivers, channel and effluent of the Naviundu river basin, Luwowoshi spring and Luano and Ruashi rivers might be due to atmospheric deposition, runoff from contaminated soils and urban waste discharge and mostly to effluents from artisanal and industrial processing of ores and other industrial activities in Lubumbashi city. Indeed, mining technology used in the Katanga's Copperbelt region over the past decades was not efficient and the resulting waste tailings still contained a relatively high level of metals [26]. Consequently, operators tended to "stockpile" these tailings behind small dams in valleys for later reprocessing. Meanwhile, the tailings became a constant source for releasing leached metals into surface waters, and most likely into groundwater as well [26]. It has also been reported that the exploitation of quartz and brick-making contribute to the remobilization of trace metals through the landscape, soil, air and water [27] and that during rainy season hydromorphic soils in the Lubumbashi city bottom valleys collect waste enriched with trace metals from various plants all around the city, from ore washing carried out by artisanal mining exploiters in their residential parcels, from malachite jewelry-making scattered in the city quarters and from a layer of slag spread on avenues to combat dust during dry season and mud during rainy season [28]. The metal-rich waste discharged into rivers and channel contributes to contaminate the receiving rivers and channel with trace metals. Thus, the metal contamination of waters and sediments of Naviundu river basin, Luano and Ruashi rivers and Luwowoshi spring might be partially due to urban and domestic effluents, runoff from metal-rich soils and mostly to abandoned and ongoing artisanal and industrial mining and ore processing activities in and around Lubumbashi city.

4. Conclusion

This study assessed trace metal contamination of sediments at twelve locations in Naviundu river basin and three respective locations in Luwowoshi spring, Luano and Ruashi rivers in Lubumbashi city. The results showed low mean values of water pH ranging from 4.2 to 5.8 and various concentrations of As, Ba, Cr, Cu, Fe, Mn, Pb and Zn. Chemaf hydrometallurgical plant effluent sediment had the highest As and Cu concentrations whereas the highest levels of Pb and Zn were noted in Kabecha river sediment and those of Ba, Cr, Fe and Mn were respectively found in Naviundu river under Cimenkat (Katanga's Cement Factory) exit, Naviundu river under bridge on De Plaines avenue, Foire channel and Mukulu river.

The trace metal contamination of sediments of the studied channel, effluent, rivers and spring in Lubumbashi city might be partially attributed to natural processes, unplanned urbanization and poor waste management, and mostly to abandoned and ongoing mining and ore processing activities. It presents a risk to organisms living in those sediments and in the water column and to the health of the populations who depend on those rivers, channel and spring to meet their water supply, irrigation and recreational needs.

The authors suggest that regular monitoring of the waters and sediments be carried out and that provincial and national authorities strictly apply the D.R. Congo Mining Regulations to avoid further deterioration of water and sediment quality as well as to allow full recovery of the already deteriorated water systems.

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