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

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Abstract: Aluminum (Al), Vanadium (V), Chromium (Cr), Manganese (Mn), Iron (Fe), Strontium (Sr), Molybdenum (Mo), Silver (Ag), Cadmium (Cd), Tin (Sn), Caesium (Cs), Barium (Ba), Lead (Pb), Bismuth (Bi) and Uranium (U) concentrations were investigated in water samples from fifteen sampling locations in Naviundu river basin, Luano and Ruashi rivers and Luwowoshi spring in Lubumbashi city during February, March and April 2016. Chemical analyses of the samples were carried out using Inductively Coupled Plasma-Mass Spectrometer. Water pH was determined using a pH-meter and mean pH values ranged from 4.2 to 5.8. The highest mean levels of Al (5,961.954 $\mu g \cdot L^{-1}$), Pb (472.287 $\mu g \cdot L^{-1}$), V (21.014 $\mu g \cdot L^{-1}$), Cr (8.185 $\mu g \cdot L^{-1}$), U (4.163 $\mu g \cdot L^{-1}$) and Bi (0.012 $\mu g \cdot L^{-1}$) were recorded in Chemaf (Chemicals of Africa) hydrometallurgical plant effluent, those of Mn (29,714.593 $\mu g \cdot L^{-1}$), Sr (374.377 $\mu g \cdot L^{-1}$), Cd (11.358 $\mu g \cdot L^{-1}$) and Cs (0.107 $\mu g \cdot L^{-1}$) in Naviundu river at Cimenkat (Katanga's Cement Factory) exit, those of Fe (14,258.9 $\mu g \cdot L^{-1}$) and Ba (307.641 $\mu g \cdot L^{-1}$) in Luano river and those of Ag (2.669 $\mu g \cdot L^{-1}$), Mo (0.559 $\mu g \cdot L^{-1}$) and Sn (0.325 $\mu g \cdot L^{-1}$) were respectively noted in Foire channel, Naviundu river under bridge on Kasenga road and Kalulako river. The concentrations of Cd in Naviundu river at Cimenkat exit (11.358 $\mu g \cdot L^{-1}$), Chemaf hydrometallurgical plant effluent (9.697 $\mu g \cdot L^{-1}$), Naviundu river under bridge on De Plaines Avenue (6.95 $\mu g \cdot L^{-1}$) and Kalulako river (3.229 $\mu g \cdot L^{-1}$), Pb concentrations in Chemaf hydrometallurgical plant effluent (472.287 $\mu g \cdot L^{-1}$) as well as the Al, Fe and Mn concentrations recorded in most waters in this study exceeded the WHO (World Health Organization) maximum permissible limits for drinking water. The metal contamination of waters of the studied rivers, channel and spring might be partially attributed to natural processes, unplanned urbanization and poor waste management, and mostly to abandoned and ongoing mining and ore processing activities in Lubumbashi city.

Key words: Trace metal contamination, channel, river, spring, water, pH, Lubumbashi city.

1. Introduction

Industrial and artisanal mineral exploitation and ore processing activities as well as other industrial activities, urban waste, transport and agriculture contribute to the contamination of aquatic environment. 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, North-Kivu, South-Kivu, Maniema and Tanganyika, atmosphere,

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soils, surface waters 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 [2-7]. In many locations in these provinces, mining is typically done through artisanal mining which is a 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 [8]. 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 [8-10]. In those regions, local air and soil environments, surface water and groundwater are deteriorated by factory emanations and dust from artisanal and industrial mining, tailings, discharge of untreated industrial and hospital effluents, discharge of mine water and mining wastewater into rivers, agricultural and urban runoff, and domestic wastewater [2-16]. As millions of people in those provinces largely depend on surface and groundwater to meet their domestic water needs [7, 16], the use of surface and groundwater waters heavily contaminated with trace metals represents a great risk for public health.

The current study aims to investigate trace metal contamination of waters in Naviundu river basin, Luano and Ruashi rivers and Luwowoshi spring in Lubumbashi city and to compare metal levels of the waters with the WHO (World Health Organization) guidelines for drinking-water quality [17], EPA (United States Environmental Protection Agency) drinking water standards and health advisories [18] and EU (European Union) drinking water regulations [19]. Waters of all those rivers, channel and spring are used without prior treatment by the people who live along them to meet their domestic, agricultural and recreational needs.

2. Material and Methods

2.1 Study Area and Sampling Locations

The study area encompasses various water courses of Naviundu river basin, Luwowoshi spring, Luano and Ruashi rivers in Lubumbashi city. The Naviundu river basin includes Naviundu, Kabesha, Kalulako, Kamasaka, Ma-Vallée and Mukulu rivers, Foire channel and Chemaf (Chemicals of Africa) hydrometallurgical plant effluent. Luwowoshi spring is the source of Ruashi river. 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 water samples were collected from twelve sampling sites in the Naviundu river basin (sample and sampling site codes 21ER, 22ER, 23ER to 32ER) and from one site in each of Ruashi river (33ER), Luano river (34ER) and Luwowoshi spring (35ES) 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, effluent and spring (Fig. 1). The samples were collected in clean 100-milliliter polyethylene bottles after rinsing the bottles three times with the water to be sampled. A sample code as well as the sampling site and the sampling date were written on each bottle and on the bottle lid. To prevent the sample code, sampling site and date from being erased, a transparent plastic sticker was stuck on the bottle and on its lid. 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 pH was determined using

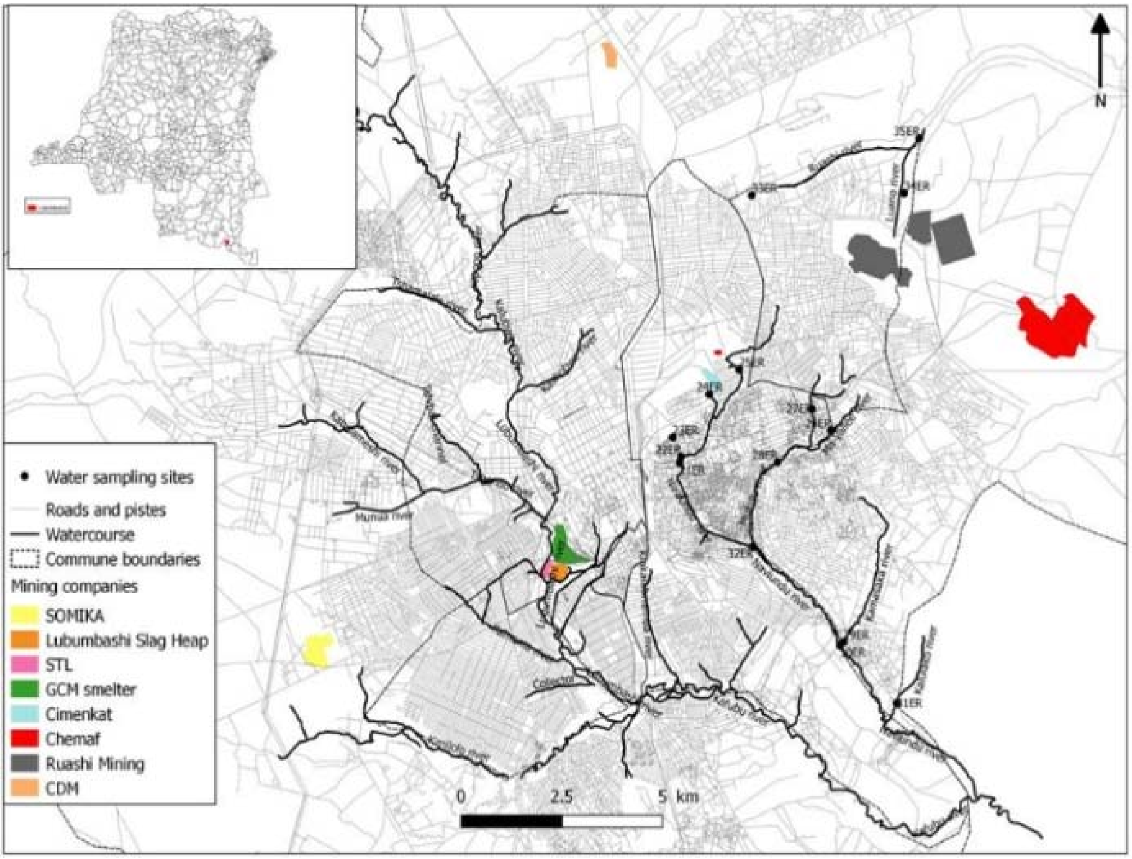

Fig. 1 Map of water sampling locations in Naviundu river basin, Luano and Ruashi rivers in Lubumbashi city during February, March and April 2016.

a pH-meter. After pH determination, samples were acidified with two to three drops of concentrated ultrapure hydrochloric acid. Then they were stored in a clean place at room temperature in the laboratory until they were analyzed for trace metals' content.

2.3 Analytical Method

The samples were analyzed using ICP-MS (Inductively Coupled Plasma-Mass Spectrometry) at the AMGC (Analytical, Environmental and Geochemical) laboratory at VUB (Vrije Universiteit Brussel) in Belgium.

3. Results and Discussion

Mean water pH values and mean water concentrations of fifteen trace metals including Ag, Al, Ba, Bi, Cd, Cr, Cs, Fe, Mn, Mo, Pb, Sr, Sn, U and V ($mg \cdot L^{-1}$) at different sampling locations as well as the WHO guidelines for drinking-water quality [17], EPA drinking water standards and health advisories [18] and EU drinking water regulations [19] are presented in Table 1. Mean water pH values were very low and ranged from 4.2 to 4.9 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 and Fig. 2). The water pH values were low in the other rivers, channel and Chemaf hydrometallurgical plant effluent and ranged from 5.1 to 5.8 (Table 1 and Fig. 2). All those water pH values were out of the WHO [17], EPA [18] and EU [19] pH range of 6.5 to 8.5 for drinking water, suggesting that waters of the studied spring, channel and rivers were improper for human consumption. Moreover, the low water pH increases metal bioavailability to aquatic

Table 1 Mean trace metal concentrations in waters (µg·L^{-1}) of the Naviundu river basin, Luano and Ruashi rivers and Luwowoshi spring in Lubumbashi city during February, March and April 2016.

Rivers, channel, spring	Sample code	pH	Sr-88 (µg·L^{-1})	Mo-98 (µg·L^{-1})	Ag-107 (µg·L^{-1})	Cd-114 (µg·L^{-1})	Sn-118 (µg·L^{-1})	Cs-133 (µg·L^{-1})	Ba-137 (µg·L^{-1})	Pb-208 (µg·L^{-1})	Bi-209 (µg·L^{-1})	U-238 (µg·L^{-1})	Al-27 (µg·L^{-1})	V-51 (µg·L^{-1})	Cr-52 (µg·L^{-1})	Mn-55 (µg·L^{-1})	Fe-56 (µg·L^{-1})
	WHO	6.5-8.5	Na	Na	Na	3	Na	Na	1,300	10	Na	30	200	Na	50	50	300
	EPA	6.5-8.5	Na	Na	100*	5	Na	Na	2,000	15	Na	30	50-200*	Na	100	50*	300*
	EU	6.5-8.5	Na	Na	Na	5	Na	Na	Na	10	Na	30	200*	Na	50	50*	200*
Naviundu river under bridge on De Plaines avenue	21ER	5.1	286.037	0.451	0.452	6.95	0.029	0.103	94.147	8.18	0.008	1.16	501.641	2.204	1.183	16,687.622	2,678.391
Naviundu river under bridge on Kasenga road	22ER	5.3	168.013	0.559	1.522	0.356	0.038	0.061	89.575	2.712	0.003	1.042	133.83	1.482	0.865	2,071.28	4,687.757
Naviundu river at Cimenkat (Katanga's Cement Factory) exit	23ER	4.7	374.377	0.238	0.311	11.358	0.008	0.107	92.431	5.607	0.005	0.886	400.5	1.731	0.797	29,714.593	962.45
Chemaf (Chemicals of Africa) hydrometallurgical plant effluent	24ER	5.8	242.301	0.329	1.86	9.697	0.068	0.082	255.788	472.287	0.012	4.163	5,961.954	21.014	8.185	2,104.966	5,152.054
Kabecha river	25ER	5.3	235.054	0.264	0.627	0.181	0.059	0.088	119.462	2.207	0.005	0.438	147.826	2.181	0.891	570.083	1,239.863
Ma-Vallée river	26ER	5.1	63.275	0.071	2.359	0.138	0.026	0.043	158.897	2.486	0.003	0.109	417.806	3.907	0.858	118.47	1,496.352
Foire channel	27ER	5.7	91.263	0.312	2.669	0.099	0.012	0.02	78.264	1.476	0.002	0.258	178.076	2.084	0.681	211.415	1,254.168
Mukulu river	28ER	5.5	30.849	0.042	1.16	0.072	0.019	0.015	40.759	0.985	0	0.095	318.921	1.273	0.449	69.596	1,044.442
Kamasaka river	29ER	5.3	138.936	0.043	2.2	1.309	0.018	0.056	85.286	3.164	0.003	0.844	572.538	3.723	1.653	2,714.81	2,056.599
Naviundu river at its confluence with Kamasaka river	30ER	4.2	31.604	0.027	0.851	0.246	0.005	0.028	41.183	3.348	0.001	0.226	601.693	3.09	0.824	154.322	3,398.445
Kalulako river	31ER	4.6	276.153	0.423	1.536	3.229	0.325	0.103	115.618	2.466	0.006	1.073	202.248	1.267	1.161	14,893.741	2,085.919
Naviundu river at its confluence with Mukulu river	32ER	4.9	41.149	0.091	0.911	0.07	0.019	0.016	29.211	0.434	0	0.139	45.121	2.137	0.339	62.228	221.785
Ruashi river	33ER	5.3	151.458	0.093	1.069	0.047	0.021	0.01	64.829	1.059	0	0.101	398.272	0.064	0.495	3,985.105	789.124
Luano river	34ER	4.8	55.064	0.029	0.96	0.365	0.003	0.071	307.641	8.846	0.001	1.15	2,329.495	6.698	1.772	3,606.887	14,258.9
Luwowoshi spring	35ES	5.8	118.378	0.193	1.226	0.133	0.09	0.031	71.578	5.188	0.002	0.31	316.923	2.196	0.944	510.649	5,098.152

* EPA Secondary Drinking Water Regulations [18], * EU Indicator Parameters [19]; EPA: United States Environmental Protection Agency Drinking Water Standards and Health Advisories, 2011 [18]; EU: European Union (Drinking-water) Regulations, 2014 [19]; Na: no available data; WHO: World Health Organization Guidelines for Drinking-Water Quality, 2017 [17].

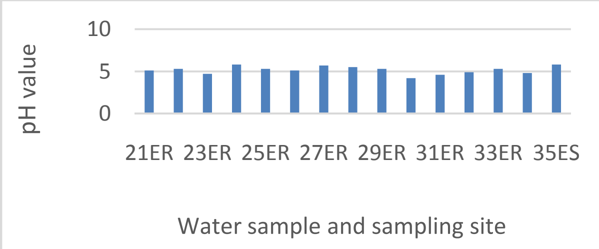

Fig. 2 Mean water pH values of water samples from Naviundu river basin, Luano and Ruashi rivers and Luwowoshi spring in Lubumbashi city during February, March and April 2016.

organisms [6, 20-25] living in the rivers, channel and spring and to human beings who depend on those waters to meet their domestic and recreational needs.

The highest mean concentrations of Al (5,961.954 μg·L^{-1}), Pb (472.287 μg·L^{-1}), V (21.014 μg·L^{-1}), Cr (8.185 μg·L^{-1}), U (4.163 μg·L^{-1}) and Bi (0.012 μg·L^{-1}) were recorded in Chemaf hydrometallurgical plant effluent, those of Mn (29,714.593 μg·L^{-1}), Sr (374.377 μg·L^{-1}), Cd (11.358 μg·L^{-1}) and Cs (0.107 μg·L^{-1}) were noted in Naviundu river at the exit of Cimenkat, those of Mo (0.559 μg·L^{-1}) and Sn (0.325 μg·L^{-1}) were found in Kalulako river, those of Fe (14,258.9 μg·L^{-1}) and Ba (307.641 μg·L^{-1}) were recorded in Luano river and that of Ag (2.669 μg·L^{-1}) was noted in Foire channel (Table 1 and Figs. 3-6).

The mean Al (5,961.954 μg·L^{-1}), Pb (472.287 μg·L^{-1}), V (21.014 μg·L^{-1}), Cr (8.185 μg·L^{-1}), U (4.163 μg·L^{-1}) and Bi (0.012 μg·L^{-1}) levels of water recorded in Chemaf hydrometallurgical plant effluent were much higher than those respectively reported for Kashobwe river (5,515.816 μg·L^{-1} Al, 3.898 μg·L^{-1} Cr and 1.879 μg·L^{-1} U) and Munua river (140.294 μg·L^{-1} Pb, 12.063 μg·L^{-1} V and 0.008 μg·L^{-1} Bi) [20]. The highest mean concentration of Cd (11.358 μg·L^{-1}) noted in Naviundu river at Cimenkat plant exit exceeded the WHO maximum admissible limit of 3 μg·L^{-1} in drinking-water but it was much lower than that reported for Kafubu river at its confluence with Lubumbashi river (17.994 μg·L^{-1}) [20]. In the studied rivers, spring, channel and effluent, mean Mn and Fe levels of the waters were several orders of magnitude higher than the respective mean Mn and Fe levels of 49 μg·L^{-1} and 25 μg·L^{-1} noted in surface water of Komabangou, a gold mining area in the Tillabéri region, Niger [21]. The mean Pb concentrations in waters in this study (0.434 μg·L^{-1} to 472.287 μg·L^{-1}) were higher than that (below quantification limit) reported for Komabangou surface water [21] and those (< 0.000 μg·L^{-1}) noted in water of Luilu and Musonoie rivers, Kolwezi-Katanga (D.R. Congo) [2],

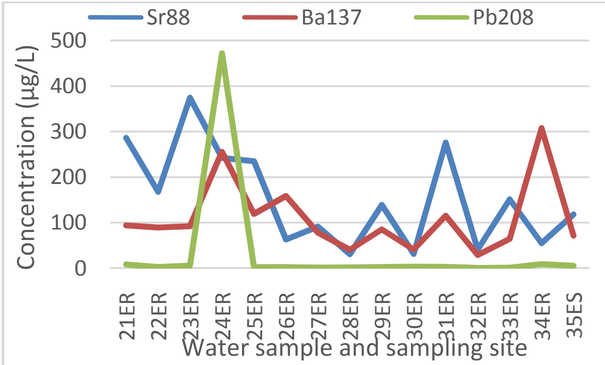

Fig. 3 Mean concentrations of Sr, Ba and Pb in water samples from Naviundu river basin, Luano and Ruashi rivers and Luwowoshi spring (μg·L^{-1}) in Lubumbashi city during February, March and April 2016.

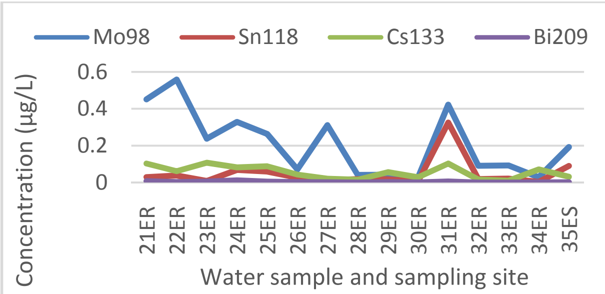

Fig. 4 Mean concentrations of Mo, Sn, Cs and Bi in water samples from Naviundu river basin, Luano and Ruashi rivers and Luwowoshi spring (μg·L^{-1}) in Lubumbashi city during February, March and April 2016.

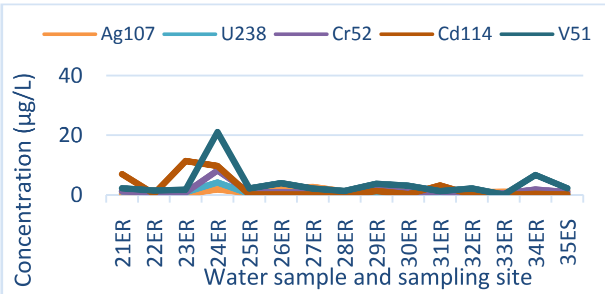

Fig. 5 Mean concentrations of Ag, U, Cr, Cd and V in water samples from Naviundu river basin, Luano and Ruashi rivers and Luwowoshi spring (μg·L^{-1}) in Lubumbashi city during February, March and April 2016.

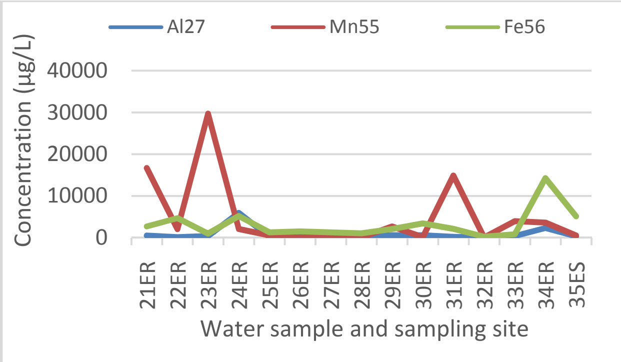

Fig. 6 Concentrations of Al, Mn and Fe in water samples from Naviundu river basin, Luano and Ruashi rivers and Luwowoshi spring (µg·L^{-1}) in Lubumbashi city during February, March and April 2016.

except for water Pb concentration at site KW13 (2,300 µg·L^{-1}) which was higher than those recorded in the present study. Also, water Pb concentration at site KW1 (100 µg·L^{-1}) [2] was higher than those recorded in this study, except for the 472.287 µg·L^{-1} noted in Chemaf hydrometallurgical plant effluent. The water Cd concentrations (0.099 µg·L^{-1} to 11.358 µg·L^{-1}) noted in this study were in the range of 0 µg·L^{-1} to 39,700 µg·L^{-1} reported for waters of the upper Lufira hydrographic basin and Tshangalele lake near Likasi (Upper-Katanga province) [3] and in that reported for Umtata river (1 µg·L^{-1} to 260 µg·L^{-1}), but they were higher than those (0.2 µg·L^{-1} to 4.3 µg·L^{-1}) reported for Mvudi river (South Africa) [16]. Water U and V levels recorded in the present study (0.095 µg·L^{-1} to 4.163 µg·L^{-1} and 0.064 µg·L^{-1} to 21.014 µg·L^{-1}, respectively) were in the ranges of 0 µg·L^{-1} to 23 µg·L^{-1} and 0 µg·L^{-1} to 36 µg·L^{-1} respectively reported for waters of upper Lufira hydrographic basin and Tshangalele lake [3]. The metal contamination of the channel and rivers 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. For the WHO guidelines for drinking-water quality, EPA drinking water standards and health advisories, and EU (drinking water) regulations [17-19], the maximum concentration limits are respectively 200 µg·L^{-1}, 200 µg·L^{-1} and 200 µg·L^{-1} for Al, 1,300 µg·L^{-1}, 2,000 µg·L^{-1} and no standard for Ba, 3 µg·L^{-1}, 5 µg·L^{-1} and 5 µg·L^{-1} for Cd, 50 µg·L^{-1}, 100 µg·L^{-1} and 50 µg·L^{-1} for Cr, 300 µg·L^{-1}, 300 µg·L^{-1} and 200 µg·L^{-1} for Fe, 50 µg·L^{-1}, 50 µg·L^{-1} and 50 µg·L^{-1} for Mn, 10 µg·L^{-1}, 15 µg·L^{-1} and 10 µg·L^{-1} for Pb and 30 µg·L^{-1}, 30 µg·L^{-1} and 30 µg·L^{-1} for U (Table 1).

Over the past decades, mining technology used in Katanga's Copperbelt region 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 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 waters at twelve locations in Naviundu river basin and three locations in Luwowoshi spring, Luano and Ruashi rivers in Lubumbashi city. The results showed low mean water pH values ranging from 4.2 to 5.8 and various concentrations of Ag, Al, Ba, Bi, Cd, Cr, Cs, Fe, Mn, Mo, Pb, Sn, Sr, U and V. Naviundu river under Cimenkat (Katanga's Cement Factory) exit had the highest mean concentrations of Sr, Cd, Cs and Mn and the same river under bridge on Kasenga road had the highest Mo level with Cd and Mn levels which exceeded the WHO maximum concentration limits for drinking water.

The highest Al, Pb, Bi and U levels were found in Chemaf hydrometallurgical plant effluent with Al and Pb levels above the WHO maximum permissible limits for drinking-water. Luano river had the highest levels of Fe and Ba with Fe exceeding the WHO guideline for drinking-water and Naviundu river under bridge on Kasenga road had the highest Mo mean concentration. The trace metal contamination of waters 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 waters and to the health of the populations who depend on those rivers, channel and spring to meet their drinking water, agricultural and recreational needs.

This study recommends regular monitoring of the waters and that provincial and national authorities strictly apply the D.R. Congo Mining Regulations to avoid further deterioration of water quality and to allow full recovery of the already deteriorated water system.

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