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Distribution and Enrichment of Trace Metallic Elements in the Sediments of the Kaswa/Mahagi Thermal Waters of (North-East of the Democratic Republic of the Congo)

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ABSTRACT

Sediments contamination by trace metals constitutes one of the major problems in aquatic environments worldwide. This work aimed to study the distribution and evaluate the level of contamination of trace metallic trace elements (TMEs) in the sediments of the thermal waters of Kaswa/Mahagi in the North-East of the Democratic Republic of Congo. The indexes and statistics method allowed the assessment of sediment quality. Six surface sediment samples, collected in January and April 2022, were analysed using the FAAS Perkin Elmer brand-Analyst 400 spectrometer. The TMEs identified were lead (Pb), copper (Cu), zinc (Zn), manganese (Mn), chromium (Cr), cadmium Cd) and nickel (Ni), the abundance being Mn>Zn>Pb>Fe> Cu>Cr>Ni>Cd. The concentrations of Cd (0.83±0.14 μ g/g) and Pb (43.22±5.76 μ g/g) were beyond the standards considered. The geo-accumulation index (Igeo) and enrichment factor (EF) showed moderate pollution of the sediments and serious enrichment in Cd (2<Igeo<3, 10<EF<25), enrichment of anthropogenic origin (FE>1.5). The sites were unpolluted to slightly polluted and moderately enriched in Pb, Cu and Zn (Igeo<1, 1<FE<3). Polymetallic toxicity revealed a considerable degree of contamination (12<DC<24) and a progressive deterioration of sediment quality (Pollution load index-PLI>1) in all sites.

Keywords: Contamination, Indexes, Mahagi, Sediments, Thermal water, Trace metals

INTRODUCTION

Sediments undergo considerable anthropogenic pressures in addition to natural processes including rock degradation and soil leaching, constituting serious threats throughout the world (Gopal et al., 2018; Ali et al., 2022). Trace metals and other dangerous and persistent contaminants can reach the aquatic and sedimentary environment, posing worrying environmental problems. Considering the morphology of the particles, the sediments constitute an important reservoir, place of concentration of inorganic and organic pollutants (Behra and Probst, 2015).

Indeed, most micro pollutants, including trace metals, have considerable affinities for particles which have the property of sedimentation. Trace metals are adsorbed onto fine sediments, most of which accumulate as bottom sediments (Zheng *et al.*, 2008, Donald Lougheed *et al.*, 2020). Sediments can thus store contaminants for several years, even decades. These micro pollutants are redistributed again from time to time in the water, resulting in the deterioration of their quality. Contaminants thus become undesirable when they occur beyond admissible standards. (Carmen *et al.*, 2016).

The thermal waters of Kaswa/Mahagi emerge at the foot of the Blue Mountains near Lake Albert in the Albertine Rift and are located near the fracture lines which border the escarpment, at the places of dislocation of the earth's crust. They accumulate in places used by the natives, in no way escaping contaminations (Omasombo et al., 2021, Budiu et al., 2023a). In the Albertine Rift, the sediments are allogenic and characterized by a dual origin: the fluvio-lacustrine sediments of Kaïso and the fluvial-torrential sediments of the Semliki (Mbuluyo and Faidance, 2018). The indigenous people make daily use of the thermal waters of Kaswa/Mahagi and their sediments for sanitary and hygienic purposes, mainly in the treatment of their skin conditions (Budju et al., 2023b).

Agricultural activities in the area through the use of chemical fertilizers and pesticides, walking or visiting paths, the passage of fishermen and traffickers, the presence of illegal dumping observed around these ecosystems, are the different

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anthropogenic pressures constituting the main source which may to cause contamination of these thermal waters. Thus, heavy metals, can reach thermal waters through several channels including runoff water and lake water in the event of a rise in these waters in certain periods, these lake waters constituting a receptacle for countless discharges and inflow of continental waters.

When sediment quality monitoring is not carried out, the risks induced by contaminants can go unnoticed, reaching aquatic fauna and flora (fishes, plants etc) (Mohammed *et al.*, 2023).

Considering the surrounding anthropogenic and natural pressure, the sediments of the thermal waters of Kaswa/Mahagi would be contaminated by heavy metals likely to deteriorate their poor quality. The present work aimed to study the distribution and evaluate the level of contamination of trace metals in the sediments of the thermal waters of Kaswa/Mahagi. Due to the lack of data on the sediments of the thermal waters of Kaswa/Mahagi, this study will provide for the first time the main essential information serving as a guide for practitioners and for subsequent researches.

MATERIALS AND METHODS Study site

The study took place in the locality of Kaswa, a fishermen's camp on the coast of Lake Albert at 55 km South of Mahagi-Port (North-East of the Democratic Republic of Congo). The minimum temperature of the area is 22°C and maximum 32°C with an annual average of 26°C, the annual rainfall is 600.8 mm. The region enjoys a tropical climate with two distinct seasons: dry season and rainy season (Omasombo *et al.*, 2021; CAID, 2022). Kaswa is located at 2°00'46.678 North and 31°04'57.829 East, at an altitude of 735 m. The coordinates of the different sampling sites were taken using the GARMIN "eTrex®10" GPS device (Figure 1).



Figure 1: Kaswa/Mahagi thermal water sediment sampling sites. **Legend:** Source 1, 2, 2, 3, 4, 5 and 6 are denoted by K α , K β , K γ , K δ , K ϵ and K λ (K = Kaswa)

Sampling

Six samples of surface sediment were taken by coring at strategic locations for the six thermal water, generally at the points of sediment accumulation and conditioned according to the recommendations provided by CCME (2011). The samples were taken, during the dry season (January 2022) and rain period (April 2022) from the surface to a depth not exceeding 60 cm.

Sample pre-treatment and trace metals determination

In the laboratory, the samples were dried in an oven at 105° C for 2 hours, allowing grinding using the porcelain pilot and mortar and separations: by sieving of the necessary fractions. After washing with 2% nitric acid and rinsing with distilled water, the three fractions were obtained using sieves of different dimensions. Thus, coarse sands were collected between 2 mm-200 µm, fine sands between 200-63 µm, clays and silts less than CSJ 15(1): June, 2024

63 μ m, using the method described by Rodier *et al.* (2009).

A total of eleven (11) trace elements were selected for analysis: lead (Pb), copper (Cu), zinc (Zn), iron (Fe), manganese (Mn), chromium (Cr), cadmium (Cd), nickel (Ni), mercury (Hg), Bismuth (Bi) and scandium (Sc). The Sc will be used as a normalizing element. These trace metals were determined in the clay-silty fraction (<63 µm) which is the most important, the most reactive because the trace metals have an affinity with the particles contained there (Sahli et al., 2014). For the extraction of trace metals. 200 mg of sample was used. The digestion was carried out using hydrofluoric acid (ultra-pure HF, 40%) combined with aqua regia (HNO₃-HCl, 1:3, v/v) in a hot microwave reaching a power of 1800 MW at a temperature of 200°C and maintained for 15 minutes, referring to the methods describes by Krishnamurty et al. (1976); Rodier et al. (2009) and Chakraborty (2012).

The determination of TMEs was carried flame atomic absorption out using the spectrophotometer (FAAS), Perkin Elmer brand, Model Analyst 400. The quality control of the measurements was carried out using blanks and international reference materials. (Lake Sediment Reference Materials, LKSD-1). The values obtained on four measurements were within standards certified by the Canadian Reference Materials Project (CCRMP). The statistical processing of the data, notably the histograms of frequency, minimum, maximum, arithmetic mean and standard deviation, was carried out using Excel 2016 and PAST software.

Determination of metal accumulation indexes Five indexes have been considered:

- *a* Geo-accumulation index (Igeo):calculated by the equation (1) and the degree of pollution was evaluated by the classification used by Müller, 1981; Singh et al., 2002).
- h-Enrichment factor (EF) was obtained from equation (2) and judged according the classification proposed by Pote et.al., (2008) and Zhang et al. (2014)
- с-Contamination factor (CF) and the degree of contamination (DC) were calculated by the

formula (3) and (4) and judged based on the contamination levels described by Sahli et al. (2014) and Hakanson (1980) respectively.

Pollution load index (PLI) was obtained by dthe equation (5) and interpreted by using the classification proposed by Tomlinson et al. (1980) and Kowalska et al. (2018).

$$Igeo = \log_2 \frac{c_n}{1.5*B_n} \tag{1}$$

$$EF = \frac{\binom{[X]/[Sc]}{_{\acute{e}chantillon}}}{\binom{[X]/[Sc]}{_{mat\acute{e}riel\ de\ r\acute{e}f\acute{e}rence}}}$$
(2)

$$CF = \frac{C_{métal}}{C_{bruit de fond métal}}$$
(3)

$$C_i = \sum CF \tag{4}$$

$$PLI = (FC_1 x FC_2 x FC_3 x \dots FC_n)^{1/n}$$
 (5)

Where C_n: concentration of the metal n to be examined in the sediment samples; B_n: the concentration of the metal (n) geochemical background: 1.5: lithospheric factor.

X is the metal studied; scandium (Sc) is the normalizing element.

RESULTS AND DISCUSSION

Total concentration and distribution of trace metal elements (TMEs)

The concentration of metallic trace elements in the sediments varies from one site to another. In the thermal waters of Kaswa/Mahagi, the highest concentration was that of Mn (327.07 $\mu g/g$) observed at Kaswa α and the smallest was that of Cd (0.88 μg/g) at Kaswa ε. The highest cumulative average concentration was observed at the Kaswa α site (68.38 μ g/g), the lowest was noted at the Kaswa γ site (49.75 μ g/g). Considering their average concentrations of TMEs from the surface sediments of the thermal waters of Kaswa/Mahagi, the metallic distribution is presented as follows: Mn > Zn > Pb > Fe > Cu > Cr > Ni > Cd. The concentration of mercury (Hg) and bismuth (Bi) were lower than 0.02 μ g/g. (Table 1).

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ISSN: 2276 - 707X, eISSN: 2384 - 6208 **Table 1**. Total concentration of trace metals (ug/g)

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Tuble 1. Four concentration of frace metals $(\mu E/S)$										
Site de	Pb	Cd	Cu	Fe	Zn	Mn	Cr	Ni	Sc	
Kaswa α	41.54*	0.82*	22.56	32.11	99.35	327.07	13.61	7.11	4.42	
Kaswa β	38.12*	1.03*	22.04	28.85	102.2	294.54	25.22	8.02	3.63	
Kaswa γ	40.66*	0.67*	31.38	25.65	78.98	188.13	20.47	7.26	3.88	
Kaswa δ	55.73*	0.65*	24.86	52.65	161.6*	206.82	18.58	4.44	4.05	
Kaswa ε	40.58*	0.88*	23.57	30.18	98.97	324.11	17.66	7.13	3.16	
Kaswa λ	42.66*	0.91*	31.11	27.58	87.13	191.16	19.49	8.21	3.71	
UCC	17	0.102	14.4	43	18.98	59.94	2.56	0.86	7.00	
SQGs.rec.max	35	0.6	35.7	ND	123	ND	37.5	32	-	
% sample <sqg< td=""><td>100</td><td>100</td><td>0</td><td>-</td><td>16.67</td><td>-</td><td>0.00</td><td>0.00</td><td>-</td></sqg<>	100	100	0	-	16.67	-	0.00	0.00	-	

Legend: ND: Not Detected, UCC (Upper Continental Crust): pre-industrial world values (Wedepohl, 1995) SQGs.rec.max: Sediment quality guide recommendation for aquatic protection (CCME.EPC, 1999),

*Values marked with an asterisk indicate the concentration of toxic metals exceeding the recommended standards according to the sediment quality guide for the protection of aquatic life (SQGs).

Referring to global pre-industrial values (Upper Continental Crust), we note that the concentrations of all TMEs in these surface sediments are beyond the said values, this may also and/or reflect their enrichment of natural anthropogenic origin.

Furthermore, considering the guide recommendations for sediment quality for aquatic protection (SQGs standards), all samples (100%) displayed Pb and Cd concentrations above the maximum threshold considered, the average Pb concentration of the different sites being 43.22 ± 5.76 µg/g and that of Cd 0.83 ± 0.14 µg/g. However, 16.7% of samples, especially those from the Kaswa δ site (161.16±20.14 µg/g) showed Zn exceeding concentrations the standards recommended according to the sediment quality guide for the protection of aquatic life. On the other hand, the concentration of Zn in the other sites,

those of Fe, Mn, Cr and Ni were within safety standards, therefore did not present any danger.

Contamination of Sediments by Metallic Trace Elements

Geo-accumulation Index (Igeo)

The geo-accumulation index of the TMEs studied varies from one site to another. The minimum and maximum Igeo values for Cd are 2.12 (Kaswa) and 2.73 (Kaswa β) respectively. The thermal waters studied are thus moderately polluted in Cd (2<Igeo<3) in all the sites. The Igéo values for Pb, Cu and Zn oscillate between 0 and 1 in all sites, judging them from unpolluted to slightly polluted. Furthermore, Fe, Cr, Mn and Ni display negative Igeo values in all the sediments studied and are therefore not polluted in these metallic elements (Figure 2).



Figure 2: Geo-accumulation index in Kaswa/Mahagi thermal water sediments

CSJ 15(1): June, 2024 Enrichment Factor (EF)

Regarding the EF, we note that the Cd has undergone a serious enrichment, the EF oscillating between 11.24 and 19.86 (10 \leq EF \leq 25) observed at Kaswa δ and Kaswa β respectively. Pb, Cu and Zn are in the moderate enrichment range (3 \leq EF \leq 5) while Mn, Fe, Cr and Ni showed no enrichment (EF \leq 1) or minor enrichment in sediments (1 \leq EF \leq 3). Considering the classification suggested by Zhang *et al.*, (2014), we note that the Cd, Pb, Cu and Zn showed EF values>1.5 in the different sites, thus reflecting their anthropogenic source. On the other hand, Mn, Fe, Cr and Ni displayed EF values between 0 and 1.5, suggesting their geological Indeed, the enrichment of the thermal water sediments of Kaswa/Mahagi in TMEs can be justified by the influence of several factors including continental waters, the rise in the waters of Lake Albert sometimes reaching the beds of thermal waters, the waters runoff, rural activities through the use of fertilizers in the environment, intensive use of motorized machinery for fishing and others, illegal dumping, etc. These factors are possibly responsible for contamination and deterioration of the quality of these waters and their sediments.



Figure 3: Enrichment factor of metallic trace elements in sediments of Kaswa/Mahagi thermal waters

Contamination factor (CF) and degree of contamination (DC)

The contamination factor in TMEs shows that the sediments of the thermal waters of Kaswa/Mahagi are very highly contaminated with Cd (CF > 6), moderately contaminated with Pb, Cu, and Zn (1 < CF < 3), slightly contaminated with Fe, Mn, Cr and Ni (CF < 1) (Table 2).

For the degree of contamination, all metals traces considered, oscillated between 14.65 and 18.26 recorded at the Kaswa γ and Kaswa β sites respectively, qualifying them as sediments with considerable contamination (12 < DC < 24) (Table 2). We thus note that the contamination of these sediments is essentially influenced mainly by

the presence of cadmium which is then associated with other heavy metals studied.

Pollution Load Index (PLI)

The sediment pollutant load index (PLI) varied between 1.13 recorded at Kaswa γ and 1.29 recorded at Kaswa β . These values were greater than 1 (PLI > 1), indicating a progressive deterioration of sediment quality considering the classification used by Chaka and Munyaradzi (2022). These results are contrary to those obtained by Ouattara *et al.* (2024) about the waters of the N'zi River in Ivory Coast where progressive deterioration by trace metals was not observed.

Table 2: Contamination factor (CF), degree of contamination (DC) and pollution load index (PLI) of Kaswa/Mahagi thermal water sediments.

					CF				DC	PLI
	Pb	Cd	Cu	Fe	Zn	Mn	Cr	Ni		
Kaswa α	2.44	8.04	1.61	0.75	1.91	0.62	0.39	0.38	16.14	1.19
Kaswa β	2.24	10.1	1.58	0.67	1.97	0.56	0.72	0.42	18.26	1.29
Kaswa γ	2.39	6.57	2.24	0.6	1.52	0.36	0.59	0.38	14.65	1.13
Kaswa δ	3.28	6.37	1.78	1.23	3.11	0.39	0.53	0.23	16.92	1.27
Kaswa ε	2.39	8.63	1.68	0.7	1.9	0.62	0.51	0.38	16.81	1.24
Kaswa λ	2.51	8.92	2.22	0.64	1.68	0.36	0.56	0.43	17.32	1.21

CSJ 15(1): June, 2024 CONCLUSION

The present study made it possible to establish the distribution of trace metals and evaluate the level of the Kaswa/Mahagi thermal water sediments contamination by these metals. The study showed that the metal concentration varied from one trace element to another and also from one site to another, generally higher than preindustrial values. Cd and Pb showed values higher than the considered standards. Kaswa/Mahagi sediments moderately thermal water are contaminated, however with severe anthropogenic enrichment of cadmium. Other metallic trace elements were moderately or weakly involved in The sediment contamination. analysis of polymetallic toxicity showed considerable and worrying contamination influenced by Cd, which is secondarily associated with the other trace metals studied. These sediments are in progressive deterioration. The sediments of Kaswa/Mahagi thermal waters are therefore judged to be of poor quality. The contamination and pollution of these ecosystems are attributed to contributions of various origins, both natural and anthropogenic, of a diffuse or specific nature and still requires indepth study. In the future, it is essential to assess the real impact of the toxicity of these metallic elements on these ecosystems. Therefore, a speciation study of these heavy metals is desired. An integrated monitoring measure for these waters is also useful order to preserve these ecosystems and the health of the population. Thus, the basic data provided by this study will contribute to enriching the guiding information for the benefit of practitioners and researchers.

CONFLICT OF INTEREST

The authors of this work declare that they have no conflict of interest for both the data and the work as a whole.

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AUTHOR CONTRIBUTIONS

The corresponding author RB was responsible for the conception of this work and the writing of the manuscript. The authors YI, J-BD and TT contributed to the supervision of the work and the correction of the manuscript. The author CS provided, in addition to supervision, the supervision of the work as a whole and the correction of the manuscript. REFERENCES

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